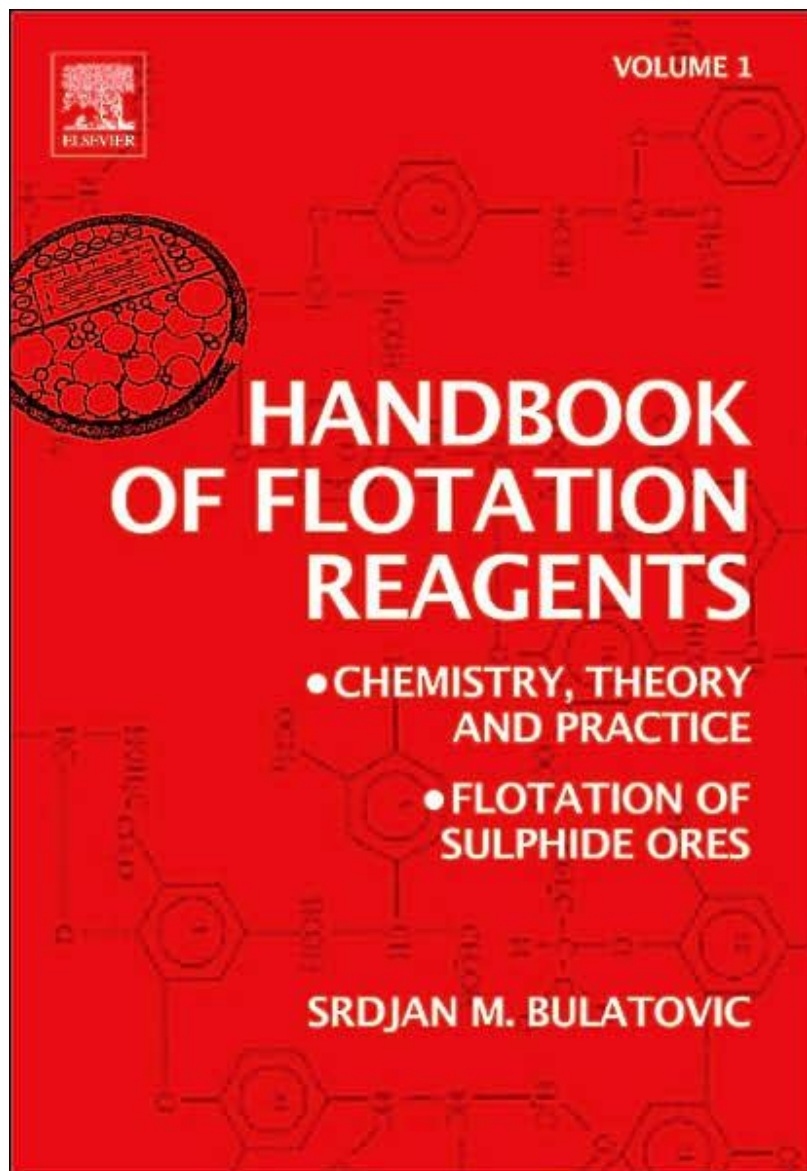# Handbook of Flotation Reagents

Chemistry, Theory and Practice: Flotation of Sulfide Ores

by *Srdjan M. Bulatovic*

- ISBN: 0444530290
- Publisher: Elsevier Science & Technology Books
- Pub. Date: April 2007

Contents

Introduction

Without reagents there would be no flotation, and without flotation the mining industry, as we know it today, would not exist. Reagents in mineral processing are therefore an inseparable part of the flotation process. Many books, articles and patents exist on development of reagents, reagent chemistry and reagent application. In spite of all this, researchers and those who work on the development of reagent schemes for the treatment of new ores or improvement in existing operations still rely heavily and almost exclusively on the advise of chemical companies and their technical services to select specific collectors or depressants for the plant. Unfortunately, the reagent schemes do not consist of only collectors and frothers. Pulp chemistry in an operating plant is a complex system involving the interaction of all additives, including collectors, depressants, activators, pH regulators, frothers and, most of all, soluble components of the ore and altered mineral surfaces.

In 1992, R. D. Crozier advocated that those who work on reagent scheme development must understand surface chemistry. This may be true for those dedicated to fundamental research using pure minerals, but not for those who are involved in applied research. Surface chemistry has been and will remain an important part of the flotation process, but even if we understand the surface chemistry of pure minerals, the same minerals in natural settings can be vastly different. What does this means in terms of reagent scheme development and development of new reagents? It means that we have to learn how to interpret the interactive effects of flotation reagents in a plant setting in order to develop or improve reagent schemes for given plant feeds. Would knowledge of flotation fundamentals help us solve these problems? Yes, to some degree, when we are dealing with a relatively simple ore. The real test arises when a particular reagent does not do what it is "supposed" to do; for example, if cyanide does not depress sphalerite or a particular collector is not as selective as described in the manufacturer's book, then one would say "the ore did not read the book."

A huge database exists on operating flotation plants, treating large quantities of sulfide ores such as porphyry copper ores and single or multiple base metal ores. When the matrix of the ore becomes complex by introduction of predominantly iron sulfides, these databases become statistics on production but not on treatment schemes.

This text is a condensed form of the fundamental knowledge of chemical reagents commonly used in flotation and is addressed to the researchers and plant metallurgists who employ these reagents. Flotation reagents are not only collectors and frothers, but include equally large groups of modifiers, regulators, depressants and activators. This latter group of flotation reagents is often neglected in basic research studies. It is not the intention of this text to prescribe recipes for particular ores, but is an attempt in some way to summarize the experience of many years of laboratory and plant studies of different reagent schemes.

Those who believe that flotation technology has evolved by "trial and error in operating mills, and that very little is based on fundamental research" may have forgotten that these operating plants also produce erroneous metallurgical results. It should be remembered that fundamental research has provided guidelines for those researchers and engineers involved in process design and development.

Confusion, however, arises from the fact those flotation properties of a given mineral often change when present in different ore matrices. This can be best illustrated by examining the flotation behavior of chalcopyrite found in porphyry ores, massive sulfide ores and mixed ores. Chalcopyrite from porphyry copper ore floats readily with any thiol collector with usually high recovery. However, the flotation property of chalcopyrite from a massive sulfide ore is vastly different and the floatability depends on the type of collector used, pH and modifier/depressant type. The floatability of chalcopyrite is further reduced in the presence of pyrrhotite.

Since all components in the ore have a pronounced effect on the flotation properties of a particular mineral, it is not possible to apply only basic research to develop a treatment process. The main purpose of applied research is to combine the fundamental knowledge of the chemical and physical aspects of flotation with the experience gained from plant operations to interpret the responses of an ore to conditions applied in the laboratory or the plant.

– 1 –

Classification of Flotation Reagents

Reagents are the most important part of the flotation process. In the early stage of the development of the flotation process, the major advances were due to better flotation reagents. In developing a treatment process, much time, energy and attention is spent on the selection of reagents to give the most effective separation and concentration results. In commercial plants, the control of reagent additions is the most important part of the flotation strategy.

Modern classification of the reagents is based on the function of a particular reagent. On this basis, reagents are divided into collectors, frothers, regulators and depressants. Several thousands of chemicals were either tested or suggested as flotation reagents. Nowadays, there are only a few hundred of these reagents that are extensively used in flotation.

Collectors are a fairly large group of organic chemical compounds, which differ in chemical composition and function. The basic purpose of the collector is to selectively form a hydrophobic layer on a given mineral surface in the flotation pulp and thus provide conditions for attachment of the hydrophobic particles to air bubbles and recovery of such particles in the froth product.

According to the ability of collectors to dissociate in water, they can be divided into distinct groups. *Ionizing collectors* consist of heteropolar organic molecules. Depending on the resulting charge, the collector assumes the character of a cation or anion. *Anionic* collectors are further classified into oxhydryl and sulfhydryl collectors on the basis of their solidophilic property.

Cationic collectors are chemical compounds in which the hydrocarbon radical is protonized. These reagents are amines from which the primary amines are the most important flotation collectors (i.e. R-NH$_2$).

Non-ionizing collectors are also divided into two groups. The members of the first group are the reagents containing bivalent sulfur. The second group contain non-polar hydrocarbon oils.

Frothers are heteropolar surface-active compounds that lower the surface tension of water and have the ability to adsorb on the air bubble–water interface. Their presence in the liquid phase increases the film strength of the air bubbles, thus providing better attachment of hydrophobic particles to the bubbles. Surface tension also affects the size of the air bubbles. The effectiveness of some of the frothers is very much dependent on pulp pH. Their performance is optimum when frother is in the molecular form.

For example, cresol at high pH is converted into an ionized compound, which does not act as a frother:
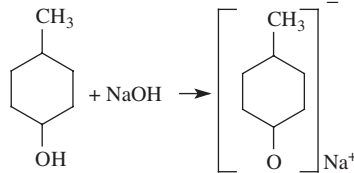
Quinoline in acid pH forms ions, which have poor frothing properties:
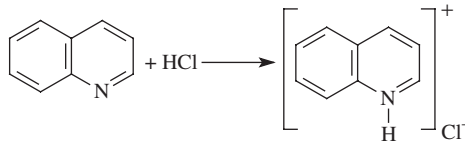
On the basis of the effectiveness of frothers at different pH values (i.e. the pH at which the frother is most effective), they can be divided into: *acidic,* when frothing ability is reduced with an increase in pH from acid to alkaline and *neutral,* when the performance of the frother does not depend on pH value of the pulp.

The acidic frothers are chemicals that belong to two basic groups: phenols (cresol, xylenol) and alkylsulfonates (surfactants).

The most important group of frothers is the neutral type of frothers. These frothers are divided into the following groups: cyclic alcohols, aliphatic alcohols, alkoxy paraffins and glycols.

Regulators: Activators, depressants and pH regulators are often referred to in the literature as modifiers or regulators of the flotation process. The main purpose of these reagents is to modify the action of the collector on mineral surfaces and as a consequence govern the selectivity of the flotation process. In the presence of regulators, the collector only adsorbs on particles that are targeted for recovery.

In some cases, a regulator reacts directly with the mineral surface (copper sulfate with sphalerite) and provides conditions for interaction of this mineral with the collector. These reagents are known as *activators*. Some regulators may reduce conditions for hydrophobization of a particular mineral with the collector, or they can make the surface hydrophilic. These reagents are called *depressants*. Both activators and depressants can be either inorganic or organic compounds.

The third group of modifiers is pH regulators. The purpose of these is to regulate the ionic composition of the pulp by changing the concentration of the hydrogen ion in the pulp. Consequently, this results in improvement in collector interaction with the selected mineral and reduces collector interaction with undesirable minerals. The pH regulators can also be depressants at the same time (e.g. lime and some organic acids).

This classification of regulators is very arbitrary. For example, regulators under certain conditions act as depressants and under other conditions as activators. Other important groups of reagents, which cannot be included in any group of regulators, are dispersants because of the multiplicity of functions that they can fulfill. Dispersants added to a pulp containing slimes or clay act as a cleansing medium and can improve the rate of flotation of particular minerals and reduce excessive collector consumption.

Flocculants are natural or synthetic polymers with different polar groups. Normally, they have molecular weights ranging from 20,000 to several millions, and they can be electrolytes and non-electrolytes. On the basis of the way they dissociate in water, flocculants can be loosely classified into the following groups:

(a)   Anionic polyelectrolytes dissociate in water into complex polymer anions and simple cations (Na^+, NH_4^+, K^+, etc).
(b)   Cationic polyelectrolytes dissociate into polymer cations and anions (Cl^-, SO_4^-, CH_3COO^-).
(c)   Amphoteric polyelectrolytes are polymers that contain both anionic and cationic groups.
(d)   Non-ionic polymers contain polar groups without attached an anion or cation.

– 2 –

Collectors

2.1 CLASSIFICATION

On a broad basis, collectors can be defined as organic chemical substances in which the molecular structure is divided into a non-polar and a polar group.

The non-polar portion of the collector molecule is a hydrocarbon radical, which does not react with water and is therefore water-repellent. In contrast to the non-polar part of the molecule, the polar part can react with water. A typical example of such a heteropolar molecular structure is sodium oleate (Figure 2.1).

The collector structure and composition determines its activity in relation to water dipoles. In the adsorption process of the collector on the mineral surface, the non-polar group of the collector is oriented toward the water phase and the polar parts toward the mineral surface. With this orientation, the mineral surface is rendered water-repellent (hydrophobic). Chemicals that are apolar hydrocarbon liquids (without a heteropolar structure) and that do not dissociate in water are also used as collectors.

Because the purpose of collectors is to render minerals water-repellent, these reagents are usually classified according to their ability to dissociate into ions in aqueous solution and having regard to which type of ions (anion or cation) gives the water-repelling effect [1].

When a collector dissociates into cation and anion, the one that is the direct cause of the water-repellent action, may be called the active repellent ion, and the other the non-active (non-repellent) ion. The repellent ion structure always includes a hydrocarbon radical, the presence of which ensures that the mineral is rendered water-repellent. These radicals cannot exist in the free state and do not directly attach themselves to the mineral surface. Therefore, the repellent radical includes another group of atoms attached to the carbon radical, which forms a connection between the radical and the mineral surface. This connector group is called a "solidophilic" group.

The water-repellent effect of the collector is directly related to the length and structure of the hydrocarbon radical, whereas the effect of the solidophil group depends on (a) the nature of the reaction with the mineral surface, (b) the strength of the collector attachment, and (c) selectivity, all of which are dependent on the solidophilic group's composition and structure. According to their ion dissociation
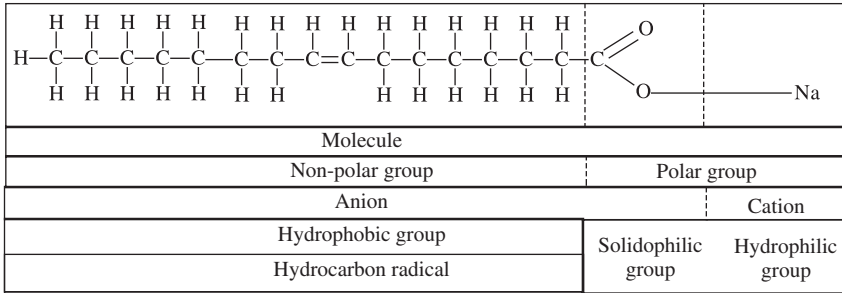
Figure 2.1 Molecular structure of sodium oleate.

properties, the mineral and solidophil group, Al. Glembocki and Plaksin [2] have classified collectors into the following two groups:

1. Ionizing compounds, which dissociate into ions in water.
2. Non-ionizing collectors, which are non-polar compounds, principally hydrocarbon compounds, insoluble in water. It is believed that these collectors render the mineral water-repellent by covering its surface with a thin film.

The larger group of collectors are ionizing, and are divided into the two following groups (Figure 2.2):

1. Anion collector, where the anion renders the mineral water-repellent.
2. Cation collector, where the cation renders the mineral surface water-repellent.

Anionic collectors are the group most widely used in flotation. These collectors are further subdivided based on the structure of the solidophilic group into oxhydryl collectors, when the solidophilic group is based on organic and sulfo-acid ions, and sulfhydryl collectors, when the solidophilic group contains bivalent sulfur.

The newest versions of anionic collectors are organic sulfides, *R*-S-*R*, containing an active sulfur atom but no other electron donors [3]. From this point of view, these collectors are something in between oxhydryl and sulfhydryl groups. What is not common to the above group of collectors is that the sulfur in the *R*-S-*R* position can share its lone pair of electrons for bond formation with metals on sulfide mineral surfaces. Because the sulfur is the only electron-donating atom, the effectiveness of these collectors is strictly related to pulp chemistry.

Groups that are not covered by this classification, are amphoteric compounds and chelating collectors.

2.2 OXHYDRYL COLLECTORS

Oxhydryl collectors are the largest group of anionic collectors, yet only a limited number of these reagents have found application in industrial practice. This is mainly due to the
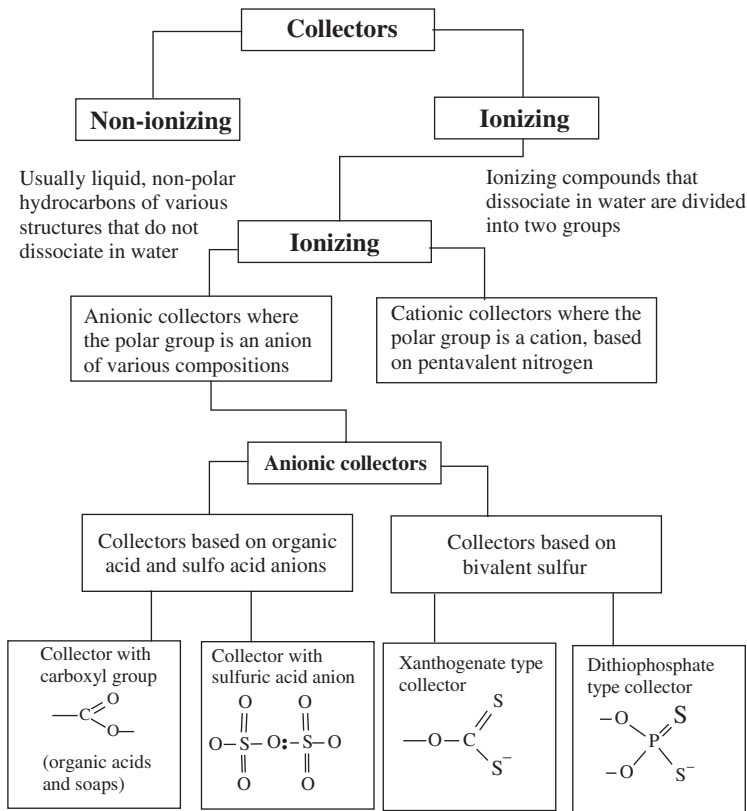
Figure 2.2 Classification of flotation collectors (reproduced with permission from Ref. [2]).

lack of applied research. In recent years, a fairly large number of new compounds have been developed, some of which are very important collectors for flotation of tantalite, niobium and titanium minerals and belong to a group of fatty alcohol ether sulfates and various phosphoric acid esters. Most of the basic research work conducted on oxhydryl collectors was devoted to sodium oleates and oleic acids [4–11], and to a lesser degree sulfo succinamates [12,13]. Oleic acid collectors therefore are the most widely used collectors in industrial mineral practice, not because they are more effective than other collectors, but because they are the most publicized through basic research. As compared to sulfhydryl collectors, the oxhydryl collectors are regarded as the least selective collectors and their performance is closely related to (a) the pulp preparation method and (b) type of modifier used and flotation pH value. Recent studies [14,15] have shown that by providing the right pulp chemistry, the oxhydryl collectors can be as selective as the sulfhydryl collectors.

On the basis of the composition and orientation of the solidophilic group, the oxhydryl collectors can be divided into nine subgroups. Table 2.1 shows the summary of various oxhydryl collectors.

Table 2.1

Summary of various oxhydryl collectors

Collector name	Substructural general formula	Related compounds
Carboxylate	$R-C{\Large{<}}^{O^-}_{O}$	
Alkyl sulfates	$R-O-\overset{\overset{S}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}-O^-$	Fatty alcohol ether sulfate
Sulfonates	$R-\overset{\overset{S}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}-O^-$	$R-\overset{\overset{H}{\|}}{\underset{\underset{R^1}{\|}}{C}}-\overset{\overset{S}{\|\|}}{\underset{\underset{O}{\|\|}}{S}}-O^-$ Alkene Sulfonate
Hydroxamate	$R-\overset{}{\underset{\underset{O}{\|\|}}{C}}-\overset{\overset{H}{\|}}{\underset{\underset{O^-}{\|}}{N}}$	
Sulfosuccinate	$R-O-\overset{\overset{O}{\|\|}}{C}-CH_2$ $Na-O-\overset{}{\underset{\underset{O}{\|\|}}{C}}-\overset{\overset{}{}}{\underset{\underset{H}{\|}}{C}}-O-S{\Large{<}}^{O}_{O-Na}$	
Sulfosuccinamate	$Na-O-\overset{\overset{O}{\|\|}}{C}-CH_2$ $R-\overset{}{\underset{\underset{H}{\|}}{N}}-\overset{}{\underset{\underset{O}{\|\|}}{C}}-\overset{}{\underset{\underset{H}{\|}}{C}}-O-S{\Large{<}}^{O}_{O-Na}$	**Alkyl sulfosuccinamate** $Na-O-\overset{\overset{O}{\|\|}}{C}-CH_2$ $R-\overset{}{\underset{\underset{R}{\|}}{N}}-\overset{}{\underset{\underset{O}{\|\|}}{C}}-\overset{}{\underset{\underset{H}{\|}}{C}}-O-S{\Large{<}}^{O}_{O-Na}$
Phosphonic acid	$R-P{\Large{<}}^{OH}_{OH}$ with $P=O$	Sodium, potassium salts of phosphonic acids. Ammonium salts of phosphonic acid.
Phosphoric acid esters	${RO\atop RO}{\Large{>}}P{\Large{<}}^{O}_{OH}$ \quad ${RO\atop HO}{\Large{>}}P{\Large{<}}^{O}_{OH}$	alkyl ether phosphate half ester

Oxhydryl collectors are principally used for flotation of oxidic minerals (silicates), carbonate materials, oxides and minerals containing sulfo group.

2.2.1 Carboxylates

Carboxylates are oxhydryl collectors that are most widely used in industrial practice in spite of the fact that selectivity of these collectors toward the gangue minerals is low. Selectivity largely depends on the method of pulp preparation, pH and the use of depressants. Typical members of this group are oleic acid, sodium oleate, synthetic fatty acids, tall oils and some oxidized petroleum derivatives.

Fatty acids of the formula C_nH_{2n+1} are saturated. Unsaturated fatty acids have a formula of C_nH_{2n-1}. Typical examples of saturated fatty acids are stearic acid, $C_{17}H_{35}COOH$, and palmitic acid, $C_{15}H_{31}COOH$. The example for an unsaturated fatty acid is oleic acid. From the flotation point of view, unsaturated fatty acids are much more important than saturated fatty acids. Unsaturated fatty acids are more selective than saturated fatty acids.

The structure and solubility of some more important fatty acids is shown in Table 2.2. Fatty acids are manufactured from either animal fats or vegetable oils, in the presence of an alkali, by the following reaction:

Fat   Glycerine   Fatty acid salt
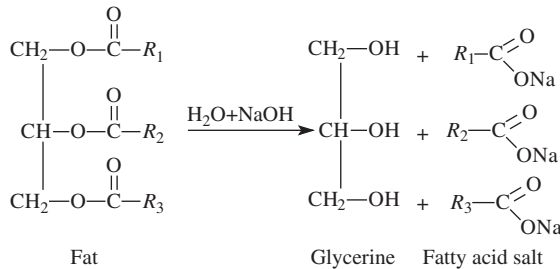
Fatty acid soaps are separated from glycerine and neutralized using mineral acids. The mixture is initially distilled or the acids are removed without distillation.

Different fatty acids used as collectors are mainly a mixture of oleic, linoleic, conjugated linoleic, palmitic and stearic acids. In the mineral industry, these fatty acids are known as tall oils. Actually, crude tall oils are converted by distillation into oils suitable as flotation collectors.

Most of the tall oils contain rosin acids ranging from several percent up to 50%. In most of the tall oils derived from either animal fat or vegetable oils, rosin acids are similar to those occurring in wood and gum rosins. The main constituent is abietic acid, which is usually in equilibrium with its isomer.

Depending on the manufacturer and the method of distillation, there are other rosin acids present in tall oils which differ from abietic acid either in the number or location of the double bonds or the structure of the side chain. Table 2.3 shows the types of rosin acids present in the tall oils.

Table 2.2

Structure and properties of some fatty acids

Fatty acid	General formula	Molecular weight	Solubility of undissociated molecule (mol/L, 20 °C)
Capric	$CH_3(CH_2)_8COOH$	198.25	3.0×10^{-4}
Lauric	$CH_3(CH_2)_{10}COOH$	200.32	1.2×10^{-5}
Myristic	$CH_3(CH_2)_{12}COOH$	228.38	1.0×10^{-6}
Palmitic	$CH_3(CH_2)_{14}COOH$	256.43	6.0×10^{-7}
Stearic	$CH_3(CH_2)_{16}COOH$	284.48	3.0×10^{-7}
Elaidic	$CH_3(CH_2)_7 CH{=}CH(CH_2)_7COOH$	283.33	–
Oleic	$CH_3(CH_2)_7CH {=}CH(CH_2)_7COOH$	282.47	–
Linoleic	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	280.45	–
Conjugated linoleic	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$	278.44	
Trans-oleic	$C_8H_{17}CH{-}CH{-}(CH_2)_7{-}COOH$	282.47	–

Studies carried out on different minerals, i.e. spodumene, Florida phosphates and silicates using tall oils with different rosin acid content [16] showed that the presence of rosin acid in the tall oil determines the power of the collector as well as the froth structure and selectivity. Another important feature of the tall oils with higher rosin acid is that dryness of froth and selectivity can be controlled by pre-mixing tall oil with non-polar hydrocarbons and oxidizing the mixture, which is not the case with either oleic acid or tall oil of low rosin content.

Fatty acids and tall oils are widely used for flotation of phosphates, lithium minerals (spodumene), silicates and rare-earth minerals (i.e. bastnaesite, monazite) where gravity separation is not possible because of the small size of the minerals. These collectors perform well on ores with simple gangue compositions and free from clay and slimes.

The flotation performance of fatty acids and tall oils is also dependent on the raw material from which they are manufactured. For example, fatty acids derived from vegetable oils are much better collectors than those derived from animal fats. The ratio of oleic and linoleic acid in tall oil plays an important role in the flotation. A sarcosine-based collector developed by Akzo-Nobel (Sweden) belongs to the carboxylate group, but does not resemble properties of either a fatty acid or tall oil. The hydrophobic radical is derived from either animal or vegetable fats and transformed using sarcosine-based compounds. In water, these reagents dissociate into ions where hydrocarbon ions become anions:

$$R\text{–}COOH + H_2O - R\text{–}COO^- + H^+{}_3O$$
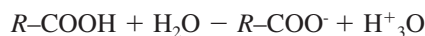
The dissociation constant is in the order of 10^{-4}–10^{-5}. Fifty percent of the compound is dissociated at a pH of approximately 9. They are weak acids. These collectors have different flotation properties than those of fatty acids, and in some cases they are more selective. They are successfully used for flotation of phosphates, monazite and heavy mineral sands.

Table 2.3

Rosin acid in tall oils

Abietic Acid

Neoabietic Acid

Palustric Acid

Dehydroabietic Acid

Dextropimaric acid

iso-Dextropimaric Acid
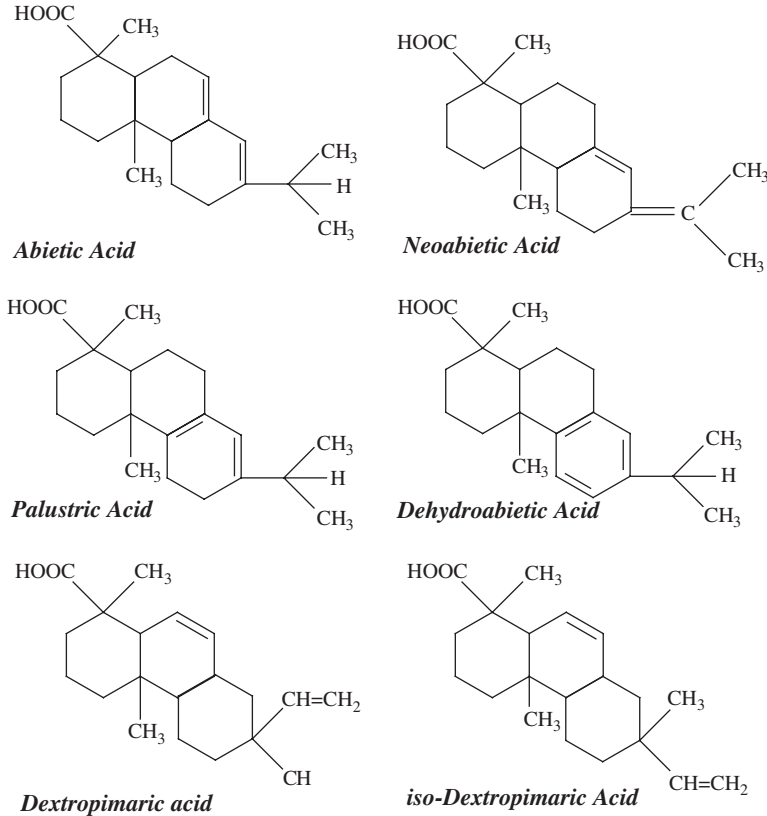
2.2.2   Alkyl sulfates

Alkyl sulfates are derivatives of sulfuric acid in which one hydrogen atom has been replaced by a hydrocarbon radical. If the remaining hydrogen is connected directly with the carbon radical, then these collectors are called sulfoacids and their salts sulfonates (R–CH_2–SO_3H). If the carbon radical is connected with sulfur by an oxygen bridge, the compounds are called alkyl sulfate salts. Sodium alkyl sulfates are generally used as flotation reagents. The newest modification of the same group of collectors is alkane sulfonate with the following formula:
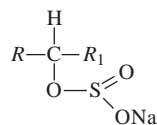
This collector is obtained by the sulfooxidation of *n*-paraffins with chain lengths of 14–17 carbons. The resultant secondary alkane sulfonates have the SO_3 group not in the terminal position but distributed statistically over the entire chain length. In some cases, alkyl sulfates are produced from aromatic compounds and have a formula

$$R$$
$$SO_3Na$$
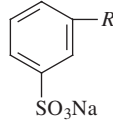
where the sulfo group is distributed over the aromatic molecule. Derivatives of sulfuric acid – alkyl sulfates and alkyl sulfonates – are produced by sulfuration of either straight-chain hydrocarbons or aromatic hydrocarbons and sulfuric acid or by anhydrous sulfuric acid. The alkyl sulfates are made by the following reaction:

$$R_1-CH=CH-R_2 \ + \ H_2SO_4 \longrightarrow R_1-CH_2-CH-R_2$$
$$OSO_3H$$
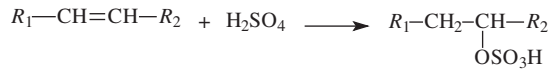
Using anhydrous sulfur and hydrocarbon sulfo acid, a compound is produced according to the following equation:

$$R-CH=CH_2 \xrightarrow{SO_3} R-CH-CH_2 \xrightarrow{H_2O} R-CH-CH_2$$
$$O-SO_2 \qquad OH \quad SO_3H$$

$$R-CH-CH_2 \xrightarrow{SO_3} R-CH-CH_2$$
$$O-SO_2 \qquad O \qquad SO_2$$
$$SO_2-O$$

$$R-CH-CH_2 \xrightarrow{H_2O} R-CH-CH_2 \xrightarrow{H_2O} R-CH_2-CH_2$$
$$O \quad SO_2 \qquad O \quad SO_3H \qquad SO_3H$$
$$SO_2-O \qquad SO_3H$$
$$+ \ H_2SO_4$$
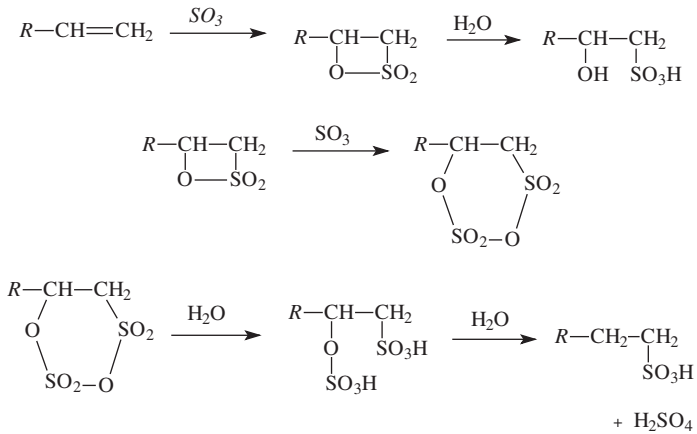
Alcohols with an excess of sulfuric acid react to form alkyl sulfates:

$$R–OH + H_2SO_4 \rightarrow ROSO_3H + H_2O$$
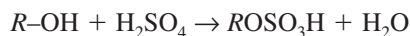
Alkyl sulfates are suitable for flotation of barite ($BaSO_4$) and other sulfur-containing minerals including celestite ($SrSO_4$), kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$). Because alkyl sulfates can act as emulsifiers, they are also used as a mixture with tall oil fatty acids to improve collecting power and, in some cases, reduce over frothing. Very little basic research has been carried out with these collectors and, therefore, the application of these collectors in industrial practice is limited.

2.2.3   Sulfonates

These collectors have a similar solidophilic group as alkyl sulfates, except that the hydro-carbon radical is directly connected to sulfur instead of through the oxygen bridge.

$$
R-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}-O^{\ominus}
$$
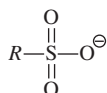
In practice, sulfonates are produced by treating petroleum fractions with sulfuric acid and removing the acid sludge formed during the reaction, followed by extraction of sulfonate and purification. Purification consists of removing inorganic salts. Petroleum fractions, however, are not the only raw material, unsaturated alcohols, unsaturated fatty acids and their esters are used as starting material. The products obtained are known as sulfonates. From the chemical point of view, almost nothing is known for certain about these reaction mixtures except that they are complex and variable in accordance with variations in the technique of preparation. In the available patent literature [17,18], several preparation methods relevant to flotation have been described. The most widely used reagents of sul-fonate type are the Cytec 800 series promoters.

2.2.4   Hydroxamates

Although the hydroxamates belong to a group of chelating collectors, they are classified as oxhydryl collectors [19]. Perhaps this is due to the fact that a cross-sectional area of the hydroxamate is equal to that of fatty acid ion (i.e. 22 Å^2). In solution, it also behaves as a fatty acid.

Hydroxamate-type collectors are obtained by the synthesis of alkylhydroxamic acid. There are three basic structures from which hydroxamates are synthesized. These are illustrated below:

$$
\underset{\underset{I}{R_3O \quad OR_2}}{R_1-C=N} \qquad \underset{\underset{II}{O \quad R_2}}{R_1-C-N-R_3} \qquad \underset{\underset{III}{HO \quad OR_2}}{R_1-C=N} \qquad \begin{array}{l} R_1 = C_nH_{2n+1} \\ R_2 = H, K, \text{ or Na} \\ R_3 = C_6 \text{ to } C_{12} \end{array}
$$
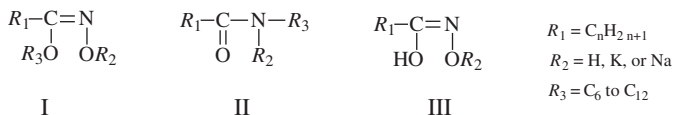
R_1 is usually an organic ligand (alkyl, acetyl and benzoyl) while R_2 and R_3 may be organic or inorganic. The alkyl hydroxamic acid shown in structure III is the most widely used for the synthesis of hydroxamates. These acids can be obtained as by-products during synthesis of higher homologs of carbonic acids, during oxidation of paraffins by oxygen. Typical hydroxamate structure is given below:

$$
R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{N}-H
$$
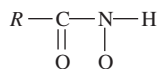
Although extensive research work has been carried out on the application of hydroxamates as flotation collectors for malachite [20,21], bastnaesite [22] and for flotation of titanates and pyrochlore [23], the only commercial application of hydroxamate has been achieved with Russian hydroxamate IM50 and similar compounds produced in China. From analyses of published data and reports on evaluations, three major factors emerged that limit the successful application of hydroxamates.

1.   *Differences in structure and floatability problems.* There is a striking difference between hydroxamates manufactured by Hoechst (Germany), Cytec (North America), the Russian IM50 and Chinese R801. The Russian IM50 collector contains a mixture of all three basic structures of hydroxamic acids with carbon-chain lengths between $R = C_7$ to C_9, where the amount of C_9 must not exceed 16% of the total mixture.

The hydroxamates manufactured by Hoechst have a carbon-chain length $R = C_7$ to C_{12}. Hydroxamates, initially manufactured by Ashland Chemicals (now Witco Chemicals) in North America, were alkyl methyl ammonium hydroxamates of the formula

$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{N}}$$
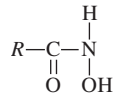
None of the hydroxamates with a chain length of $R = C_{12}$ are stable during prolonged storage.

2.   *The performance of hydroxamates* is directly proportional to the carbon-chain length. Reduced flotation performance was noted on carbon chains higher than C_9. A mixture of hydroxamates with a carbon-chain length between C_7 and C_9 were the most successful.

3.   *Recent studies on flotation of malachite* using the Russian hydroxamate IM50 and Hoechst dimethyl hydroxamate [24] showed that the performance of both collectors was sensitive to the slime content of the flotation pulp. In general, the hydroxamates are used for flotation of oxidic minerals (pyrochlore, cassiterite and ilmenite), rare-earth oxides and oxide copper minerals.

2.2.5   Sulfosuccinates and sulfosuccinamates

Sulfosuccinates are derived from carboxylates and succinic acids and are usually in the form of sodium salts. The most typical succinates used in flotation are tetra-sodium *N*-(1,2-dicarboxyethyl)-*N*-octodecyl-sulfosuccinate. Arbiter and Hin [12] first patented these collectors in 1967. The apparent differences between succinates used as surfactants and sulfosuccinates and sulfosuccinamates used as collectors is the sulfonation of the succinamate portion of the molecule.

There are marked differences in the performance of these collectors where sulfonation provides increased collecting power but reduced selectivity. Typical structure of the sulfo-succinamate collector is

$$C_{18}H_{37}-N-CH \begin{array}{l} CH_2COONa \\ COONa \end{array}$$
$$C=O$$
$$CH_2$$
$$CH-SO_3Na$$
$$COONa$$
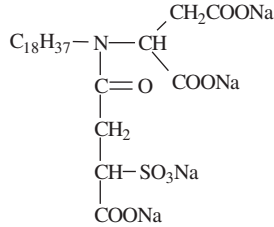
These collectors have found wide commercial use for flotation of cassiterite. Moreover, these collectors have also found application for flotation of heavy mineral sand and monazite when mixed with fatty acid.

2.2.6   Phosphonic acid

This collector was developed recently and was used primarily as specific collector for cassiterite from ores with complex gangue composition. A typical structure of styrene phosphonic acid is

$$CH=CH-P \begin{array}{l} OH \\ =O \\ OH \end{array}$$
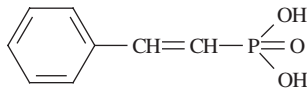
On the basis of the phosphonic acid, Albright and Wilson had developed a range of collectors mainly for flotation of oxidic minerals (i.e. cassiterite, ilmenite and pyrochlore). Very little is known about the performance of these collectors. Limited studies [24,25] conducted with cassiterite and rutile ores showed that some of these collectors produce voluminous froth but were very selective. Table 2.4 shows a list of phosphonic acids used in the mining industry (Albright & Wilson).

2.2.7   Phosphoric acid esters

The general formulas for phosphoric acid esters is as follows:

$$RO \diagdown \diagup O$$
$$P$$
$$RO \diagup \diagdown OH$$
and
$$RO \diagdown \diagup O$$
$$P$$
$$HO \diagup \diagdown OH$$

Dialkylphosphoric acid   *Alkylphosphoric acid*
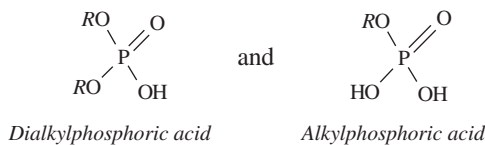
Table 2.4

List of some phosphonic acid–based reagents

Acid	"Briquest" name	Formula	Component	Molecular weight
(2-Hydroxyethyl) iminobis-(methylene phosphonic)	221-60A	$HOCH_2CH_2N(CH_2PO_3H_2)_2$	Acid	249
iso-Propyliminobis-(methylene phosphonic)	231-A	$i\text{-}PrN(CH_2PO_3H_2)_2$	Na salt	247
n-Propyliminobis-(methylene phosphonic)	2N31-A	$n\text{-}PrN(CH_2PO_3H_2)_2$	Na salt	247
n-Butyliminobis-(methylene phosphonic)	2N41-A	$n\text{-}BuN(CH_2PO_3H_2)_2$	Na salt	261
n-Hexyliminobis-(methylene phosphonic)	2N61-A	$n\text{-}HexylN(CH_2PO_3H2)_2$	Na salt	289
n-Heptyliminobis-(methylene phosphonic)	2N71-A	$n\text{-}HeptylN(CH_2PO_3H_2)_2$	Na salt	303
(2-Ethylhexyl)iminobis-(methylene phosphonic)	2N81-A	$(2\text{-}Ethylhexyl)N(CH_2PO_3H_2)_2$	Na salt	317
n-Octyliminobis-(methylene phosphonic)	2N81-A	$n\text{-}OctylN(CH_2PO_3H_2)_2$	Acid	317
iso-Nonyliminobis-(methylene phosphonic)	291-A	$iso\text{-}NonylN(CH_2PO_3H_2)_2$	Na salt	331
Dodecyliminobis-(methylene phosphonic)	2121-A	$DodecylN(CH_2PO_3H_2)_2$	Na salt	373
1-Hydroxyethane-1,1-diphosphonic	ADPA-60A	$CH_3C(OH)(PO_3H_2)_2$	Acid	206
Nitrilotris-(methylene phosphonic)	301-50A	$N[CH_2PO_3H_2]_3$	Na salt	299
Ethylenediaminetetrakis-(methylene phosphonic)	422-100A	$[CH_2N(CH_2PO_3H_2)_2]_2$	Na salt	436
Hexamethy lenediaminetetrakis-(methylene phosphonic)	462-A	$[C_3H_6N(CH_2PO_3H_2)_2]_2$	Na salt	492
Diethylenetriamine-pentakis-(methylene phosphonic)	543-45AS	$H_2O_3PCH_2N[C_2H_4N(CH_2PO_3H_2)_2]_2$	Acid	573
Triethylenetetramine-hexakis-(methylene phosphonic)	664-A	$C_{12}H_{36}N_4O_{18}P_6$	Na salt	710
Tetraethylenepentamine-heptakis-(methylenephonsphonic)	785-A	$C_{15}H_{44}N_5O_{21}P_7$	Na salt	847
Pentaethylenehexamine-octakis-(methylene phosphonic)	8106-A	$C_{18}H_{52}N_6O_{24}P_8$	Na salt	984

This group of collectors comprises a large number of products, which consist essentially of a mixture of mono and diesters of phosphoric acid. They differ in their non-polar hydrophobic radical that can be either aliphatic or aromatic. The non-polar group of the hydrocarbon radical is attached to the polar group via an oxygen bridge. Another group of these reagents is half esters, which were originally developed by Mechanobre [26] and used for flotation of apatite. They are regarded as strong collectors and can be used in either alkaline medium (flotation of apatite and scheelite) or in an acid medium for flotation of titanium minerals (ilmenite, rutile and perovskite). A similar group of collectors called "phosphoten" was also developed by Mechanobre and consists of 25% of pentavalent phosphorus and 75% naphthenic acid. The resulting reaction product is a powder with a specific gravity of 0.9 g/cm^3. This product is soluble in alcohol but not in water. This reagent was used for flotation of zircon, cassiterite and pyrochlore at pH values of 4–10.5.

2.2.8 Sulfhydryl collectors

Sulfhydryl collectors are called thiols. They are compounds containing the –SH group in combination with an organic radical. If the sulfhydride is connected to the carbon atom that is also part of the hydrocarbon chain, the thiol is usually called a mercaptan. However, the sulfhydride group may be connected to the hydrocarbon chain through a carbon atom that is not part of the hydrocarbon chain. If the connecting "key" carbon is attached to the hydrocarbon chain through oxygen or sulfur, *thiocarbonic acids* are obtained. If the connection is made between the key carbon atom and the chain through a nitrogen atom, the compounds are called *thiocarbamic acids* (one nitrogen) or *thioureas* (two nitrogen). If the key atom is phosphorus instead of carbon, the thiol is called *thiophosphoric acids*. The name "thiol" is adapted from the preparation of the fourth decimal index of chemical abstracts.

The relationship of thiols is shown in Table 2.5. The newest group of collectors are organic sulfides [27].

Mercaptans

Mercaptans are the simplest collectors from the thiol group and are derived from alcohols, ROH, in which the oxygen is replaced by sulfur, to yield RSH. They can be made by sulfidizing alcohols but usually other methods are used. The name "mercaptan" comes from their ability to form water-insoluble mercury compounds. One of the unusual characteristics of mercaptans is that a short-chain mercaptan has a skunk-like odor. Mercaptans, which are made from paraffin hydrocarbon, are only slightly soluble in water. One of the most important properties of mercaptans is that they can form water-insoluble metallic compounds. Mercaptans are easily oxidized to disulfides according to the reaction:

$$2R\text{SH} \rightarrow R\text{SS}R + 2\text{H}^+ + 2\text{e}$$

Disulfides of the alkyl mercaptans are pale yellow to colorless oils with characteristic skunk odour. Disulfides are water-insoluble unless they have a water-solubilizing group in their molecule.

Table 2.5

Classification of major thiol collectors

Name	Parent	Monothio	Dithio	Trithio
Mercaptans	R-OH (alcohol)	R-SH		
Thiocarboxylic acid	$R\!-\!C\!\!\diagup^{O}_{\diagdown OH}$	$R\!-\!C\!\!\diagup^{O}_{\diagdown SH}$	$R\!-\!C\!\!\diagup^{S}_{\diagdown SH}$	
Thiocarbanic acid	$R\!-\!O\!-\!C\!\!\diagup^{O}_{\diagdown OH}$	$R\!-\!O\!-\!C\!\!\diagup^{O}_{\diagdown SH}$	$R\!-\!O\!-\!C\!\!\diagup^{S}_{\diagdown SH}$	$R\!-\!S\!-\!C\!\!\diagup^{S}_{\diagdown SH}$
Thiocarbamic acid	$\overset{H}{\underset{H}{N}}\!-\!\overset{}{\underset{O}{C}}\!-\!OH$	$\overset{R}{\underset{H}{N}}\!-\!\overset{}{\underset{O}{C}}\!-\!SH$	$\overset{R}{\underset{H}{N}}\!-\!\overset{}{\underset{S}{C}}\!-\!SH$	
or		$\overset{R}{\underset{R_1}{N}}\!-\!\overset{}{\underset{O}{C}}\!-\!SH$	$\overset{R}{\underset{R_1}{N}}\!-\!\overset{}{\underset{S}{C}}\!-\!SH$	
Thiourea	$\overset{H_2N}{\underset{H_2N}{\diagup}}C\!=\!O$	$\overset{H_2N}{\underset{H_2N}{\diagup}}C\!=\!S$		
Phosphoric acid	$\overset{HO}{\underset{HO}{\diagup}}P\overset{O}{\underset{OH}{\diagdown}}$		$\overset{R_1O}{\underset{R_2O}{\diagup}}P\overset{S}{\underset{SH}{\diagdown}}$	
Mercapto-benzothiazole	(benzothiazole ring structure with S, C, N)			
Organic sulfides	$R^1\!-\!S\!-\!R^2$			

Although the chemistry of mercaptans has been studied in depth by Golikov [28] and others, their importance as flotation collectors has not been recognized. Some of the mercaptans are used as collectors for flotation of molybdenum, gold-bearing sulfides and enargite (Orfoms, Philips Petroleum).

2.2.9   Sulfur and nitrogen derivatives of carbonic acid

Sulfur and nitrogen derivatives of the carbonic acid are the most studied collectors and they represent important classes of collectors in sulfide mineral flotation.

Table 2.6

Classes of sulfur-nitrogen according to the distribution of bonds

Group	Distribution of bonds from key atom	Examples		
1	Four bonds to oxygen	Carbonic acid Carbon dioxide	$O{=}C\diagup^{OH}_{\diagdown OH}$ $O{=}C{=}O$	
2	Two two oxygen One to nitrogen	Carbamic acid	$H_2{-}N{-}C{\diagup^{O}_{\diagdown OH}}$	
3	Two to oxygen two to nitrogen	Isocyanic acid	$O{=}C{=}NH$	Urea $O{=}C{\diagup^{NH_2}_{\diagdown NH_2}}$
4	One to oxygen three to nitrogen	Cyanic acid	$H{-}O{-}C{\equiv}N$	$H{-}O{-}C{\diagup^{NH_2}_{\diagdown NH}}$
5	Four to nitrogen	Guanidine	$H{-}N{=}C{\diagup^{NH_2}_{\diagdown NH_2}}$	Cyanamid $N{\equiv}C{-}NH_2$
6	Three to oxygen one to sulfur	Monothiocarbonic acid	$H{-}S{-}C{\diagup^{O}_{\diagdown OH}}$ $S{=}C{\diagup^{OH}_{\diagdown OH}}$	
7	Two to oxygen two to sulfur			
8	One to oxygen three to sulfur	Dithiocarbonic acid Xantthic acid	$O{=}C{\diagup^{SH}_{\diagdown SH}}$ $S{=}C{\diagup^{OH}_{\diagdown SH}}$	
9	Four to sulfur	Carbon disulfide	$S{=}C{=}S$	Trithiocarbonic acid $S{=}C{\diagup^{SH}_{\diagdown SH}}$

Table 2.6 (*Continued*)

Group	Distribution of bonds from key atom	Examples
10	Three to sulfur one to nitrogen	Dithioarbamic acid
11	two to sulfur two to nitrogen	
12	one to sulfur three to nitrogen	Thiourea
13	Two to oxygen one to nitrogen one to sulfur	
14	one to oxygen one to nitrogen two to sulfur	Monothiocarbamic acid
15	one to oxygen two to nitrogen one to sulfur	

The sulfhydryl-sulfur can be connected to the carbonic acid radical in many different ways. Table 2.6 shows the different classes of connections according to the distribution of bonds from the key carbon through various stages. The hydrocarbon-chained derivatives are in turn obtained by replacing one or more hydrogen atoms by an alkyl or aryl group.

Xanthates and xanthic acids

Xanthates are the most important collectors for sulfide mineral flotation, as well as for oxides (i.e. oxide copper, lead and zinc minerals). Zeise first made xanthates in 1882, and they were first used in flotation in 1924.

Xanthates are a product of carbonic acid in which two oxygen atoms are replaced by sulfur and an alkyl group replaces one hydrogen atom.

Where Me = K^+, Na^+, or H^+

In the presence of moisture, xanthate hydrolyzes and forms unstable xanthic acids, which further decompose into carbon disulfide and the corresponding alcohol:

In solution, decomposition of xanthates increases with a reduction in the pH. Dissociation of xanthates in an acid medium also depends on the length of the carbon radical, where xanthates with longer carbon chains dissociate slower than xanthates with shorter hydrocarbon radical.

In an alkaline medium, xanthates are relatively stable as indicated in Table 2.7. At high alkaline solution, xanthates dissociate to form different compounds according to the following reactions:

$$R-O-C{\overset{S}{\underset{SK}{}}} + KOH \longrightarrow C{\overset{OK}{\underset{SK}{=}}}S + ROH$$

$$R-O-C{\overset{S}{\underset{SK}{}}} + KSH \longrightarrow C{\overset{SK}{\underset{SK}{=}}}S + ROH$$

$$R-O-C{\overset{S}{\underset{SK}{}}} + 5\ KSH \longrightarrow 2\ K_2S + K_2CO_3 + ROH + 2\ H_2O$$
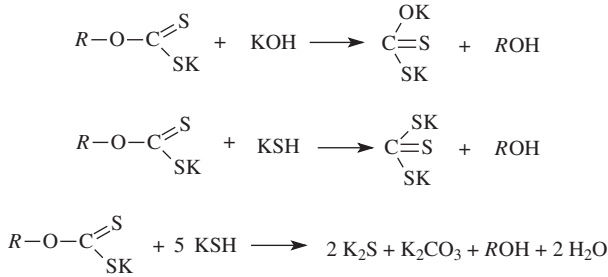
Xanthic acid can also be regarded as the acid ester of dithiocarbonic acid. Complete esterification may result in a rupture of the SH bond giving the neutral ester as ethyl-ethyl xanthate:

$$C_2H_5OC-(S)\ SC_2H_5$$
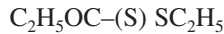
Diethyl xanthate has an ethereal odor reminiscent of leeks and can be distilled without decomposition at low pressure.

Alkyl esters of xanthic acid do not always involve the same hydrocarbon chain on both sides of the carbon atom; and it may also be possible that the atom that is double-bonded to the central carbon could be the oxygen (giving an ester) of sym-dithiocarbonic acid. Therefore, three isomers are possible for each composition.

$$1.\ ROC\underset{S}{\overset{\|}{S}}R_1 \qquad 2.\ R_1OC\underset{S}{\overset{\|}{S}}R \qquad 3.\ R_1OC\underset{O}{\overset{\|}{S}}R$$

Table 2.7

Changes in ethyl xanthate concentration as a function of time and pH [7]

pH	Initial concentration (g mol/L)	Concentration at time laps (h)			
		3	10	14	25
8	0.0104	0.0097	0.0098	0.0097	—
9	0.0107	0.0105	0.0103	0.0099	0.0100
10	0.0109	0.0104	0.0107	0.01107	0.0097
11	0.0105	0.0112	0.0114	0.0111	0.0109

These isomers, under suitable conditions, change from one form to another.

The preparation and composition relationship of thiocarbamates and thiourea are also related to xanthic acid or acid esters. These are the important flotation collectors while utilization of natural esters has not been established. New collectors developed by Cytec are also based on thiomines and thiourea. Neutralization of carbon disulfide, which can be regarded as the anhydride of dithiocarbonic acid, may be accomplished [29] by amines that have replaceable hydrogen. For example, by primary amine RNH$_2$ or secondary amines:

$$\begin{array}{c} R \\ R_1 \end{array}\!\!>\!\!N-H$$
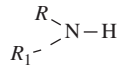
When the neutralization is carried out to the extent of tying up one of the acidic functions of dithiocarbonic acid, acid dithioamide is obtained, similar to the corresponding xanthic acid. However, when the neutralization is completed, the natural thioamide may be obtained. The examples of the neutralization reactions are as follows:

$$\begin{array}{c} R_1 \\ R \end{array}\!\!>\!\!NH + HOC\!\!-\!\!SH \ \longrightarrow \ \begin{array}{c} R_1 \\ R \end{array}\!\!>\!\!NC\!\!-\!\!SH \ + \ H_2O$$
$$\overset{\|}{S} \hspace{6.5cm} \overset{\|}{S}$$

$$\begin{array}{c} R_1 \\ R \end{array}\!\!>\!\!NC\!\!-\!\!SH \ + \ HN\!\!<\!\!\begin{array}{c} R_1 \\ R \end{array} \ \longrightarrow \ \begin{array}{c} R_1 \\ R \end{array}\!\!>\!\!N\!\!-\!\!C\!\!-\!\!N\!\!<\!\!\begin{array}{c} R_1 \\ R \end{array} \ + \ H_2S$$
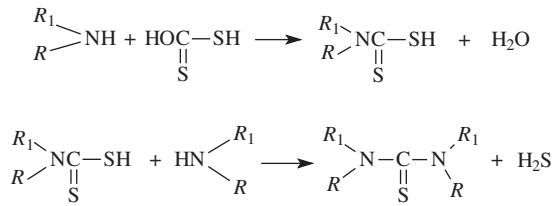
Carbon disulfide reacts exothermically with amines to produce either dithiocarbamic acid or thioureas [30] according to the proportion of the reactants.

Délépine and Marcel [31] have prepared dithiocarbamic acid in alkaline solution as this increases stability of the product. For example,

$$R\text{NH}_2 + \text{CS}_2 + \text{NaOH} \ \longrightarrow \ R\text{NHC}\!\!-\!\!\text{SNa} \ + \ \text{H}_2\text{O}$$
$$\overset{\|}{S}$$
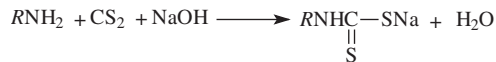
Since sodium or potassium can be replaced with ammonia, it is possible to also produce ammonium salt of dithiocarbamic acid:

$$R\text{NHC}\!\!-\!\!\text{SNH}_4$$
$$\overset{\|}{S}$$
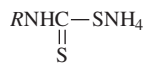
Because dithiocarbamic acids, thioureas and thiourethanes, as well as xanthic acids, can be regarded as formed by coupling dithiocarbamic acid with alcohols and amines where water (and hydrogen sulfide) is eliminated, it is possible that under suitable circumstances, the reaction may go in the reverse direction when water is present.

Xanthogen formates

The xanthogen formates were developed in the early 1960s, as collectors for flotation in an acid pulp. They are the reaction products of xanthate with ethyl chloroformates according to the reaction

$$ROC{\overset{S}{\underset{SK}{}}} + ROC{\overset{O}{\underset{Cl}{}}} \longrightarrow ROC\overset{S}{\overset{\|}{}}-S-\overset{O}{\overset{\|}{C}}-OR \ + \ KCl$$
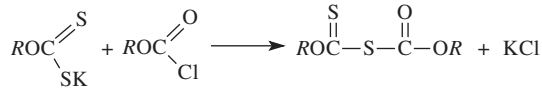
Usually they are produced from the lower carbon chain of xanthic acid (C_2–C_4).

These collectors hydrolyze in water relatively slowly, giving off COS. The collectors react readily with alkyl amines from which thionocarbamates are produced. Reaction of xanthogen formates and tertiary amines may produce quaternary ammonium salts according to the following reaction:

$$2\ CH_3HOCSOCH_2CH_3 + 2\ \underset{\underset{CH_2-CH_3}{|}}{N(CH_3)} \longrightarrow 2\ (CH_3)_3\overset{+}{N}-\overset{-}{S}-\overset{S}{\overset{\|}{C}}OCH_3 + (CH_3)_3\overset{+}{N}-\overset{-}{S}-\overset{S}{\overset{\|}{C}}-CH_3$$
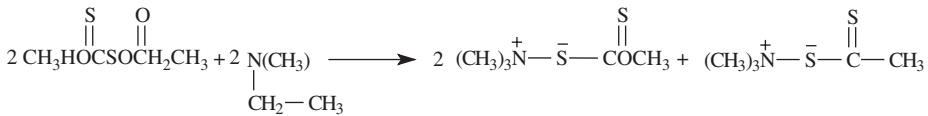
In general, there is limited data on the performance of these collectors except information used to recover copper in an acid circuit. Several porphyry copper operations use xanthogen formates for copper flotation as secondary collectors. Nowadays, attempts are being made to mix xanthogen formates with various frothers (Shell – Chile) to enhance the performance of these collectors.

Dialkyldixanthogenates

Dialkyldixanthogenates are similar to xanthogen formates and are the product of reacting xanthic acid (or oxidized xanthogenates) with an oxidant according to this reaction:

$$R-O-C{\overset{S}{\underset{SK}{}}} + \ J_2 \longrightarrow R-O-C{\overset{S}{\underset{S-S-\overset{S}{\overset{\|}{C}}-O-R}{}}} + \ KJ$$
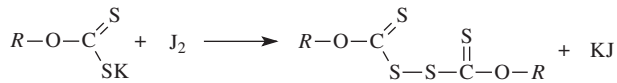
Oxidation occurs at relatively low temperature in water. These collectors are very stable in both acidic and alkaline solutions and virtually insoluble in water. Physical constants for dialkyldixanthogenates are shown in Table 2.8.

S-N-dialkyldithiocarbamates

These collectors were initially developed at Gincvetment (USSR) and described by C.N. Dudenko [32]. The starting material for synthesis of these reagents was the alkyl-trithio carbonic acid that is reacted with alkyl halides to form ester-alkyltrithiocarbamic

Table 2.8

Physical constants of dialkyldixanthogenates

Hydrocarbon radical	Melting temperature (°C)	Boiling temperature (°C)	Specific gravity (g/cm^3 at 20 °C)
CH_3	22.5–23	104–106	1.0136
C_2H_5	31.5	107–108	1.0766
n-C_4H_9	–	134–135	1.1518
n-C_6H_{13}	–	149–152	1.0897

Table 2.9

Physical characteristics of S-N-dialkyldithiocarbamates

R	R^1	Purity	Boiling point temperature (°C)	Specific gravity (20 °C, g/cm^3)
n-C_4H_9	C_2H_5	Pure	105–107	1.0810
n-C_6H_{13}	n-C_4H_9	Technical grade	–	0.9991
$C_{12}H_{25}$	n-C_4H_9	Technical grade	–	0.9717

acid. This acid is further reacted with primary amine to form *S-N*-dialkyl thiocarbamate according to the formula:
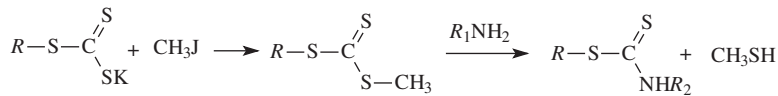
The physical characteristics of *S-N*-dialkyldithiocarbamates are shown in Table 2.9.

Dialkyldithiocarbamates are dark yellow liquids practically insoluble in water. They are stable in both alkaline and acid medium. In the presence of copper, zinc, lead or nickel cations, they form a white precipitate. These reagents are used as secondary collectors for flotation of copper, copper–molybdenum and copper–nickel ores. In North America, collector R-10 has a similar composition.

O-N-dialkylthionocarbamates

From the general formula of thionocarbamates (2), it can be seen that because of the coordination of solidophilic group (–O–[C=S]–NH–), they belong to the family of xanthates (1) and dialkyldithiocarbamates (3).
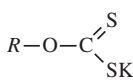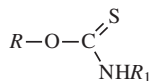
(1) Xanthate   (2) Dialkylthionocarbamate   (3) Dialkyldithiocarbamate
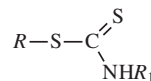
Dialkylthionocarbamates differ from the other two groups in distribution of bond from the key carbon. One of the first commercial *O-N*-dialkylthionocarbamates was Dow Z-200 that was an *O*-isopropyl-*N*-ethylthionocarbamate.

The synthesis of dialkylthionocarbamates is achieved by a number of different methods depending on the country where these reagents are produced. However, the principles are similar and two basic methods are described here. The first method is a two-stage reaction process, first reacting alkyl xanthate with alkyl halide to form ester of alkylxanthic acid as per the following reaction:

$$R-O-\underset{\underset{SK}{|}}{\overset{\overset{S}{||}}{C}} \;+\; CH_3(halide) \longrightarrow R-O-\underset{\underset{S-CH_3}{|}}{\overset{\overset{S}{||}}{C}} \;+\; K(halide)$$
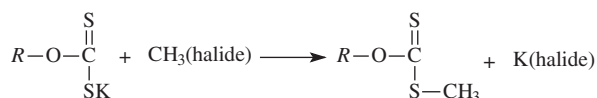
In the second stage, the ester from the first reaction is treated with a primary amine and methylmercaptan, which is the by-product, is removed.

$$R-O-\underset{\underset{S-R_1}{|}}{\overset{\overset{S}{||}}{C}} \;+\; R_2NH_2 \longrightarrow R-O-\underset{\underset{NH-R_1}{|}}{\overset{\overset{S}{||}}{C}} \;+\; R_2SH$$
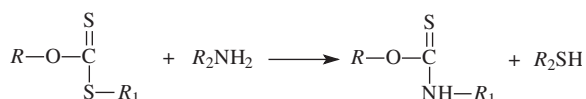
This is the method described by Harris [33].

The second method includes direct reaction of a xanthate with an alkyl amine in the presence of a catalyst (i.e. nickel or palladium salts). In this process methylmercaptan is not removed. The chemical reaction is as follows:

$$R-O-\overset{\overset{S}{||}}{C}-SK \;+\; NH_2\text{-}R_1 \xrightarrow{\text{catalyst}} R-O-\overset{\overset{S}{||}}{C}-NH-R_1 \;+\; KSH$$
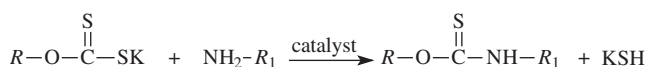
Table 2.10 shows the physical characteristics of different thionocarbamates.

Table 2.10

Thionocarbamate constants

R	R^1	Synthesis method	Weight (%)	Boiling temperature	Specific gravity at 20 °C (g/cm³)
C_2H_5	C_2H_5	I	35	56–57	1.0339
$n\text{-}C_4H_9$	$n\text{-}C_4H_9$	I	10	90–95	0.9579
C_2H_5	$n\text{-}C_4H_9$	I	13	94	0.9904
C_2H_5	$n\text{-}C_4H_9$	II	39	87	1.0054
$n\text{-}C_4H_9$	C_2H_5	I	11	103	0.9866
$n\text{-}C_4H_9$	C_2H_5	II	31	101	0.9916
$iso\text{-}C_8H_7$	C_2H_5	I	42	97	0.9958
$iso\text{-}C_8H_7$	CH_3	I	35	90–91	1.0290
$n\text{-}C_4H_9$	CH_3	II	66	104	1.0013

These reagents are insoluble liquids, colorless to dark brown in color. They can be dispersed in certain petroleum sulfonates forming a white milky liquid. They have been widely used in flotation of sulfide minerals, namely copper. They also have good collecting power for copper-activated sphalerites.

To a great extent, the performance of these collectors depends on the purity of the reagent. Dialkylthionocarbamates containing mercaptan or other impurities produce voluminous froth, and are non-selective.

Other collectors based on nitrogen derivatives and carbonic acid

Many of the collectors from this group were used sometimes in sulfide mineral flotation, but several have disappeared from the market. Collectors belonging to this group are thiocarbanilide, thiophenols, diphenyl thiocarbazide and some other compounds.

Thiocarbanilide (diphenyl thiourea) is a crystalline compound, only marginally soluble in water. In solution, it can assume a tautomeric form, typical of thiocarbanilide.
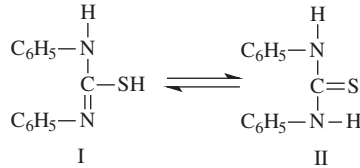
The first tautomer has acidic characteristics. The hydrogen can easily react with cations from the mineral surface and therefore can act as a collector. The second form (II) does not have collecting properties. Thiocarbanilide is a very effective and selective collector for galena. *Diphenylthiocarbazide* $(C_6H_5–NH–NH)_2–C=S$. This collector also appears in two forms; in the active form the hydrogen is connected to sulfur. This reagent can be both anionic and cationic. This collector can be utilized for flotation of nickel and cobalt minerals after treatment of the pulp with copper sulfate.

Mercaptobenzothiazoles

Heating a mixture of aniline, carbon disulfide and elemental sulfur in equal molar ratios according to the following formula in an autoclave obtains these collectors:
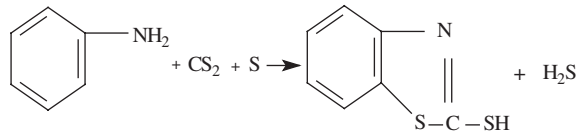
Mercaptobenzolthiozole is a yellowish, fine crystalline solid, insoluble in water but readily soluble in alkaline solutions. As a flotation reagent, this collector was the first used for flotation of lead carbonates and later for flotation of tarnished and oxidized copper minerals. Mercaptobenzolthiozole has been used in the chemical industry long before it was tried as a collector.

New collectors based on sulfur and nitrogen derivatives of carbonic acid

New development in sulfhydryl collectors was described by Avotins [3] and in various patents. These developments refer to the new Cytec and Dow Chemical collectors including modified thionocarbamates, dithiophosphinates, organic sulfides, trithiocarbamates and modified thiourea.

Modified Thiocarbamates

The *o*-isopropyl and *n*-ethyl thionocarbamates (Table 2.10) can be modified by substitution of an alkoxy carbonyl group on the N donors as per the following structure:

$$R-O-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{S}{\|}}{C}-OR_1$$
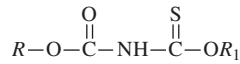
This modification provides additional active donor oxygen in the form of C=O attached to the alkoxy group. Functional groups of this kind are not restricted to thionocarbamates. They are much more complex groups [O–C–(=O)—NH–C(=S)–O] with different properties. The increased electron density on the C=O portion into which density is equally divided allows for the participation of oxygen in bonding with mineral surfaces.

The process for manufacturing modified thionocarbamates is described by Yun and Wang [34]. The reactions are:

$$C_2H_5O\underset{\underset{O}{\|}}{C}Cl + NaSCN \xrightarrow{\text{catalyst}} C_2H_5O\underset{\underset{O}{\|}}{C}CNS + NaCl$$

$$C_2H_5O\underset{\underset{O}{\|}}{C}CNS + ROH \xrightarrow{\text{catalyst}} C_2H_5O-\underset{\underset{O}{\|}}{C}-NH-\underset{\underset{S}{\|}}{C}-O-R$$
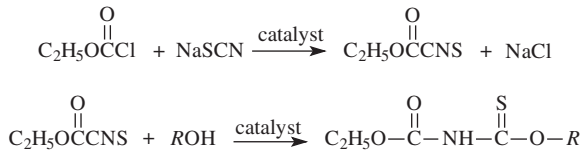
These reactions are unique since they are conducted in an aqueous medium and there are no sulfur-containing by-products.

Alkyl thionocarbamate (Cytec 5100 series) are produced by the following reaction:

$$NaSCN + CH_2=CH-CH_2Cl \xrightarrow{\text{catalyst}} CH_2=CH-CH_2\text{-}NCS + NaCl$$

$$CH_2=CH-CH_2\text{-}NCS + ROH \xrightarrow{\text{catalyst}} CH_2=CH-CH_2\text{-}NH-\underset{\underset{S}{\|}}{C}-O-R$$
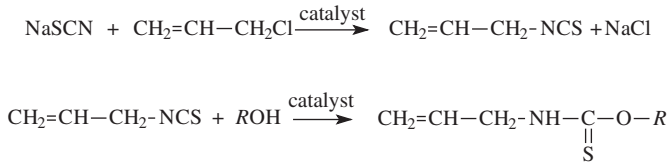
Another modification of alkyl thionocarbamate is obtained by incorporating an alkyl group on the N donor atom as shown below:

$$R-O-\underset{\underset{S}{\|}}{C}-\underset{\underset{H}{|}}{N}-\text{Allyl}$$

2.2.10   Dithiophosphinates

Dithiophosphinates are relatively new collectors for sulfide ore flotation. The difference between dithiophosphates and dithiophosphinates is that the hydrocarbon groups are linked directly to the phosphorus atom in the case of dithiophosphinates, as shown below.

$$
R-O\diagdown \overset{\overset{\displaystyle S}{\|}}{P}-S-Me^+ \qquad\qquad R\diagdown \overset{\overset{\displaystyle S}{\|}}{P}-S-Me^+
$$
$$
R_1-O\diagup \qquad\qquad\qquad\qquad R_1\diagup
$$

$$\text{Dithiophosphate} \qquad\qquad \text{Dithiophosphinate}$$

The representative of the dithiophosphinate group is Cytec's R3418A. Dithiophosphinates are produced by hydrolysis of elemental phosphorus to phosphine at high temperature. Phosphine is reacted with isobutylene to form a secondary phosphine intermediate. The product of this reaction is then reacted with sulfur in alkaline solution to give di-isobutyl dithiophosphinate. The process reactions are shown below:

I $8P + 12H_2O \longrightarrow 5\,PH_3 + 3\,H_3PO_4$

II $PH_3 + 2\,RCH{=}CH_2{-}PO_4 \xrightarrow{\text{catalyst}} (R{-}CH{=}CH_2)_2{-}\overset{\overset{\displaystyle S}{\|}}{P}{-}S{-}N\overset{\oplus}{a}$

III $(R{-}CH{=}CH_2)_2{-}\overset{\overset{\displaystyle S}{\|}}{P}{-}H + 2\,S \xrightarrow[\text{aqueous}]{\text{NaOH}} (R{-}CH{=}CH_2)_2{-}\overset{\overset{\displaystyle S}{\|}}{P}{-}S{-}N\overset{\oplus}{a}$

Other new modifications of the basic phosphorus group, $>P(=S)S$, are shown in the following structures:

$$
RO\diagdown \overset{\overset{\displaystyle S}{\|}}{P}-O-Na \qquad\qquad R\diagdown \overset{\overset{\displaystyle S}{\|}}{P}-O-Na
$$
$$
RO\diagup \qquad\qquad\qquad\qquad R\diagup
$$

$$\text{Monothiophosphate} \qquad\qquad \text{Monothiophosphinate}$$

Change in donor atom alters the collecting property because of changes in donor atom S and O [35].

2.2.11   Trithiocarbonates and substituted mercaptobenzothiozoles

The trithiocarbonates have a structure that contains three sulfur atoms as shown below:

$$R_1{-}S{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}S{-}R_2$$

All three sulfur atoms can participate in bonding to the mineral surfaces [36]. Philips Petroleum Company did most of the development of this class of collectors. Monoalkyl trithiocarbonate (Orfom 800 series) is used as a collector in flotation of copper and copper–lead ores.

These collectors are prepared by the reactions of mercaptans with carbon disulfide in aqueous medium. The chemical reactions are:

$$RSH \;+\; CS_2 \;\xrightarrow{\text{NaOH}}\; R-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-Na \;+\; H_2O$$

Further reaction with alkyl halide gives disubstituted trithiocarbonate.

$$R-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-Na \;+\; R_1Cl \;\longrightarrow\; R-S-\overset{\overset{\displaystyle S}{\|}}{C}-S-R_1 \;+\; NaCl$$

The other new collectors that are mentioned in the patent literature are substituted mercaptobenzothiozoles (MBTs) described in Section 2.3.

Organic Sulfide Collectors

Organic sulfides are collectors developed by Dow Chemical [37]. These collectors are based on the ring opening reaction of 2-ethyl oxazoline with a mercaptan. The following structures are reported in literature:

(1) $C_6H_{13}S(CH_2)_2\,NH_2$ = Dow Chemical designation F1

(2) $C_6H_{13}S(CH_2)_2\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-C_2H_5$ = Dow Chemical designation F2

(3) $C_6H_{13}\underset{\diagdown\;S\;\diagup}{CH-CH_2}$ = Dow Chemical designation S1

(4) $C_6H_{13}SCH_3$ = Dow Chemical designation S2

(5) $CH_3CH_2S(CH_2)_7CH_3$ = Dow Chemical designation S7
       Ethyl-n-octyl sulfide

The new collectors are much weaker than either dithiocarbamates or dithiophosphates. It was reported, however, that they are more selective than are other conventional collectors.

2.3 DITHIOPHOSPHATES

Alkyl and aryl dithiophosphoric acids and their alkali salts are widely used as sulfide collectors known as Aerofloat. The general formula for dithiophosphates is

$$\overset{\displaystyle RO}{\underset{\displaystyle RO}{}}\!\!\diagup\!\!P\!\!\diagdown\overset{\displaystyle S}{\underset{\displaystyle SMe}{}}$$
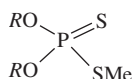
where *R* is an aromatic or aliphatic hydrocarbon radical and Me-hydrogen or an alkali metal.

In general, the phosphorus compounds used as flotation reagents represent a small number of known organic phosphorus compounds. The organic phosphorus compounds can be classified into two major groups: (a) compounds in which the phosphorus atom is directly connected to a hydrocarbon chain and (b) those in which a connection is made through another atom (i.e. oxygen). The alkyl and aryl dithiophosphates belong to the second class, paralleling the alkyl sulfuric acid and the xanthic acid but unlike the fatty acids or the amines in regard to the connection of hydrocarbons to the key atom.

Dialkyl dithiophosphoric acids are produced from the reaction of phosphorus pentasulfide (P_2S_5) with an alcohol in an inert medium. The reaction by-products include dialkyl sulfide, trialkyl dithiophates and sulfur. The acids are unstable and are converted into alkali metal salts for use as a collector.

Diaryl dithiophosphoric acids differ from dithiophosphates in that they are stable acids and insoluble in water. Diaryl dithiophosphates are based on benzene or cresol partially reacted with phosphorus pentasulfide.

In water, dithiophosphates dissociate according to the following formula:

$$(RO)_2 \, P \underset{SH}{\overset{S}{\diagup}} + 4H_2O \longrightarrow 2\,ROH + 2H_2S + H_3PO_4$$
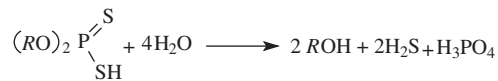
However, the above process, in a weak acid medium, is slow. Dithiophosphates can react with sulfuric acid as per the reaction given below:

$$2(RO)_2 \, P \underset{SH}{\overset{S}{\diagup}} + H_2SO_4 \longrightarrow (RO)_2PS_2S_2P(RO)_2 + H_2O + H_2SO_3$$
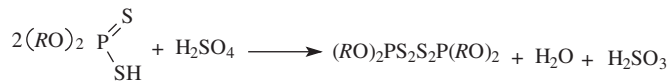
Decomposition of diaryl dithiophosphates increases with rising temperature, and at 60 °C, decomposition is relatively fast. Dithiophosphates react with other compounds in a manner similar to xanthic acid [38] as shown in the following reactions:

$$2(RO)_2 \, \overset{S}{\overset{\|}{P}}-SH \ + J_2 \longrightarrow (RO)_2 \, P-S-S-\overset{S}{\overset{\|}{P}}=(RO)_2 \ + HJ$$
$$\text{Bis(O,O-dialkyldithiophosphate)}$$
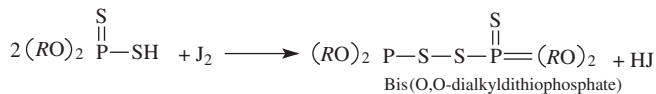
With chloroacetic acid, they form esters:

$$2(RO)_2 \, \overset{S}{\overset{\|}{P}}-SH + ClCO-OC_2H_5 \longrightarrow (RO)_2 \, \overset{S}{\overset{\|}{P}}-S-COOC_2O_5 + NaCl$$
$$\text{S-ethoxycarbonyl O,O-dialkyldithiophosphate}$$
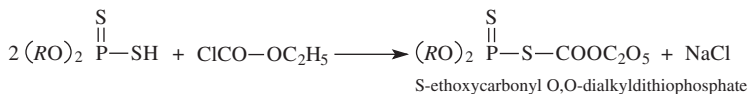
With chloramine, dithiophosphates produce a structure similar to thionocarbamates:

$$(RO)_2 \, \overset{S}{\overset{\|}{P}}-SH + ClNH_2 \longrightarrow (RO)_2 \, \overset{S}{\overset{\|}{P}}-S-NH_2 + HCl$$

Dithiophosphates can react with either NaCN or Na_2S according to the following reactions:

$$\begin{array}{c} RO \\ RO \end{array} \overset{S}{\underset{SH}{\overset{\|}{P}}} + \text{NaCN} \longrightarrow \begin{array}{c} RO \\ RO \end{array} \overset{S}{\underset{SNa}{\overset{\|}{P}}} + \text{HCN}$$

$$\begin{array}{c} RO \\ RO \end{array} \overset{S}{\underset{SH}{\overset{\|}{P}}} + Na_2S \longrightarrow \begin{array}{c} RO \\ RO \end{array} \overset{S}{\underset{SNa}{\overset{\|}{P}}} + H_2S$$
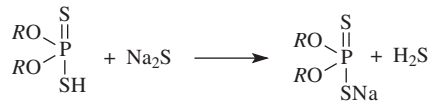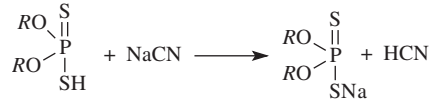
Dithiophosphoric acids react with heavy metal ions and can form hydrophobic insoluble precipitates.

Like xanthates, dithiophosphates are used exclusively as collectors in flotation of sulfide ore as a secondary collector with xanthates or alone.

2.3.1 Chelating reagents in mineral flotation

A chelate-forming reagent must have at least two atoms that can be coordinated by the metal at the same time. Such atoms are usually oxygen, nitrogen, sulfur and phosphorus. The coordination species that provide these donor atoms are known as a "ligands." When more than one atom of a single ligand molecule or ion interacts with a metal ion it may be presumed to bend itself pincer-like around the central atom to form a complex ring structure called a "chelate." An example of chelation of a diethyl dithiocarbamate reagent with nickel is shown as follows:

$$\begin{array}{ccccccc} H_5C_2 & & & S & S & & C_2H_5 \\ & N-C & & Ni & & C-N & \\ H_5C_2 & & & S & S & & C_2H_5 \end{array}$$
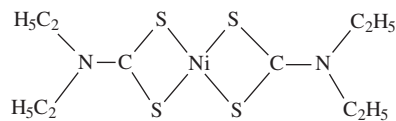
Development and evaluation of the chelating reagent as a flotation reagent was extensively studied for many years [39]. Some successful attempts have been reported [40,41]), but industrial application of these reagents has not been successful so far.

For the ideal flotation collector, the chelating functional groups should be part of a sufficiently long hydrocarbon chain (C_8–C_{18}) to impart adequate hydrophobicity to the mineral on adsorption. Hydrocarbon chain positioning [42] also affects the flotation properties of the chelating reagent.

There are three principal groups of reagents with chelating-type functional groups. These are (a) alkyl hydroxamates, (b) oximes and (c) mercapto compounds. The alkyl hydroxamates have already been discussed. Table 2.11 lists some of the chelating-type collectors based on oximes. Other chelating-type collectors that have been developed for commercial use include 1-tolyl arsonic acids, N-substituted sarcosine, 1-1diphosphoric

Table 2.11

Flotation collector with chelating-type functional group: oximes and
hydroxyquinoline (Prodip, 1988)

Reagent	Floated mineral
Dimethylglyoxime	Oxide nickel
Taurin, $NH_2(CH_2)_2SO_3H$	Oxidized lead ore
L-dioxime	Nickel ore
Hydroxy-oximes	Copper ore
Salicylaldehyde	cassiterite
8-Hydroxyquinoline	Copper oxide, Pyrochlore, Zinc oxides, Chalcopyrite
2,3-Alkyldione dioxime	Nickel ore
1-Nitroso-2-napthol	Cobalt arsenic ore

acid and alkane dicarboxylic acids, all of which were used for flotation of non-sulfide minerals. The mercapto compounds have been extensively studied by Borningo *et al*. [43].

From the mercapto compounds, the following reagents were evaluated as flotation collectors:

(a) MBT with the structure shown below:

$R \leq 12C$
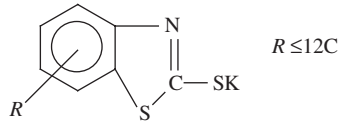
This collector was used for flotation of lead minerals.

(b) Amino thiophenol with alkyl and alkoxy hydrocarbon of the formula
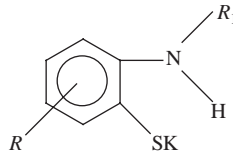
This collector was used for the flotation of lead and zinc minerals.

(c) Mercaptobenzoxazole (MBO) with a structure formula
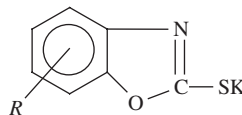
This collector has a mixed aliphatic–aromatic structure and contains a functional group, which forms chelates with copper.

2.4   CATIONIC COLLECTORS

Cationic collectors are organic compounds that have a positive charge when in an aqueous environment. The common element shared by all cationic collectors is a nitrogen group with unpaired electrons present, with a structure shown below:

$$\left[\ -\overset{|}{\underset{|}{N}}-\ \right]^{+}$$
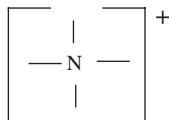
This covalent connection to nitrogen is usually a hydrogen atom and hydrocarbon group. A change in the number of hydrocarbon radicals connected to the nitrogen determines flotation characteristics of amines in general. Depending on the number of hydrocarbon radicals attached to the nitrogen bond, amines can be divided into primary (I), secondary (II) and tertiary (III). The fourth

$$
\begin{array}{ccc}
\overset{\displaystyle R}{\underset{\displaystyle H}{H-N}} &
\overset{\displaystyle R}{\underset{\displaystyle R}{H-N}} &
\overset{\displaystyle R}{\underset{\displaystyle R}{R-N}} \\
\textbf{(I)} & \textbf{(II)} & \textbf{(III)}
\end{array}
$$
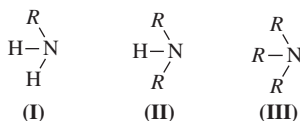
hydrogen can also be replaced by a hydrocarbon group, giving a quaternary ammonium base compound with the following structure:

$$\left[\ \begin{matrix} R_1 & & R_3 \\ & N & \\ R_2 & & R_4 \end{matrix}\ \right]^{+} \ \bar{A}$$
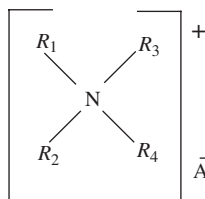
A is an anion, usually chloride or sulfate. Amines can also be classified into three groups according to the method by which they were obtained and the length of the hydrocarbon radical (Table 2.12).

Another classification of amines includes alkyl amines, aryl amines and alkyl-aryl amines according to whether the nitrogen atom is attached to a carbon atom of a chain or to a carbon atom of a cyclic structure or to both. Table 2.13 shows the structures of representative primary, secondary and tertiary amines.

2.4.1   Fatty amines

Fatty amines are normal aliphatic amines whose alkyl group contains 8–22 carbon atoms. They are the product of ammonolysis of natural fats. However, all high molecular-weight
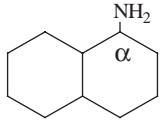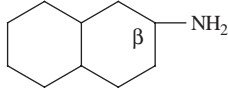
Table 2.12

Representative groups of amine collectors

Group	Structure	R	Form
Fatty amine	R–NH$_2$	C$_{12}$–C$_{24}$	Solid/paste
Fatty diamine	$\overset{\text{H}}{\underset{\|}{R\text{-N-C-C-C-NH}_2}}$	C$_{12}$–C$_{24}$	Solid/paste
Ether amine	R–O–C–C–C–NH$_2$	C$_6$–C$_{13}$	Liquid
Ether diamine	R–O–C–C–C–N–C–C–C–NH$_2$	C$_8$–C$_{13}$	Liquid
Condensates	R-C-N-C-C-N-C-C-N-C-R with H above and O (=O) below	C$_{18}$	Solid/paste

Table 2.13

Representative list of cationic reagents

Name	Structure	Type of compound
n-Amyl amine	C$_5$H$_{11}$NH$_2$	Primary aliphatic amine
n-Dodecyl amine	C$_{12}$H$_{25}$NH$_2$	Primary aliphatic amine
Di-n-amyl amine	(C$_5$H$_{11}$)$_2$NH	Secondary aliphatic amine
Tri-n-amyl amine	(C$_5$H$_{11}$)$_3$N	Tertiary aliphatic amine
Amyl amine hydrochloride	[C$_5$H$_{11}$NH$_3$]$^+$Cl$^-$	Salt of primary aliphatic amine
Tetramethyl ammonium chloride	[(CH$_3$)$_4$N]$^+$Cl$^-$	Salt of quaternary ammonium
Aniline	C$_6$H$_5$NH$_2$	Primary aromatic amine
p-Toluidine	CH$_3$C$_6$H$_4$NH$_2$	Primary aromatic amine
Benzyl amine	C$_6$H$_5$CH$_2$NH$_2$	Primary aromatic amine
Diphenyl amine	C$_6$H$_5$NC$_6$H$_5$ with $\|$ H below	Secondary aromatic amine
α-Naphthyl amine	(naphthalene structure with NH$_2$ at α position)	Primary aromatic amine
β-Naphthyl amine	(naphthalene structure with NH$_2$ at β position)	Primary aromatic amine
Pyridine	NC$_5$H$_5$	Nuclear nitrogen compound
r-Pikaline hydrochloride	[HCN$_3$H$_4$CH$_3$]$^+$Cl$^-$	Salt of nuclear nitrogen compound (benzene nucleus)
Quinoline hydrochloride	[HNC$_9$H$_7$]$^+$Cl$^-$	Salt of nuclear nitrogen compound (naphthalene nucleus)
Piperidine hydrochloride	[HNC$_5$H$_{10}$]$^+$Cl$^-$	Salt of nuclear nitrogen compound (hexahydrobenzene)

alkyl amines are not fatty amines. Typical examples are long-chain alkyl quaternary ammonium salts, which actually belong to the family of fatty amines even though they cannot exist as free amines. Like fatty acids, amines also have an unbranched carbon chain. Fatty amines may vary in the following three ways:

1. Length of the hydrocarbon chain
2. Degree of saturation of the alkyl groups
3. Number of alkyl groups attached to the amino-nitrogen, i.e. whether they are primary, secondary or tertiary amines

These characteristics were discussed previously.

Fatty amines are derived from fatty acids by conversion of the acids to nitrates followed by catalytic hydrogeneration of the nitriles to amines according to the following reactions:

$$
\text{(1)} \quad R-\overset{\overset{\textstyle O}{\|}}{C}-OH \ + \ NH_3 \ \longrightarrow \ R-\overset{\overset{\textstyle O}{\|}}{C}-O-NH_4
$$
$$
\qquad \underset{\text{Fatty acid}}{} \qquad \underset{\text{Ammonia}}{} \qquad\qquad \underset{\text{Ammonium soap}}{}
$$

$$
\text{(2)} \quad R-\overset{\overset{\textstyle O}{\|}}{C}-O-NH_4 \ \xrightarrow{\ \text{heat}\ } \ R-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \ + \ H_2O
$$
$$
\qquad \underset{\text{Ammonium soap}}{}
$$

$$
\text{(3)} \quad 2R-\overset{\overset{\textstyle O}{\|}}{C}-NH_2 \ \xrightarrow[\text{Catalyst}]{\ \text{heat}\ } \ R-\overset{\overset{\textstyle O}{\|}}{C}-O-NH_4 + RCN
$$
$$
\qquad \underset{\text{fatty acid amide}}{} \qquad\qquad\qquad \underset{\text{Ammonium soap}}{}
$$

$$
\text{(4)} \quad RCN \ + 2H_2 \ \xrightarrow{\ \text{catalyst}\ } \ R-CH_2 \cdot NH_2
$$
$$
\qquad \underset{\text{Nitrile}}{} \ \ \underset{\text{Hydrogen}}{} \qquad\qquad \underset{\text{Fatty amine}}{}
$$
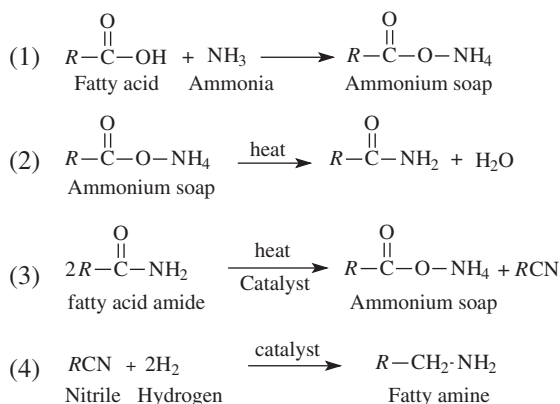
Reactions (1)–(3) are carried out simultaneously in a continuous operation, the ammonia soap from reaction (3) being again dehydrated to amide. Therefore, the only final product in this operation is nitrile. The nitriles are then hydrogenated to the amines – reaction (4) in a separate operation.

Reaction (4) shows the production of primary amines. The hydrogeneration of nitrile to a primary amine must be carried out at a temperature below 150 ºC and under alkaline conditions ([44]). Secondary fatty amines are obtained by hydrogeneration of nitriles at higher temperature [45]. Under these conditions, primary amines added to the alkylidene amines formed as an intermediate in the stepwise hydrogeneration of nitriles to yield secondary amines as per the following reactions:

$$
R-C\equiv N \ \xrightarrow{\ H_2\ } \ R-CH=NH \ \xrightarrow{\ H_2\ } \ R-CH_2-NH_2
$$
$$
\underset{\text{fatty acid nitrile}}{} \qquad \underset{\text{Alkylideneimine}}{} \qquad \underset{\text{primary alkylamine}}{}
$$

$$
R-CH=NH \ + \ R-CH_2-NH_2 \ \longrightarrow
$$
$$
\underset{\text{Alkylideneimine}}{} \qquad \underset{\text{primary alkylamine}}{}
$$

$$
\begin{array}{c} R-CH-NH_2 \\ | \\ NH \\ | \\ R-CH_2 \end{array} \ \xrightarrow{\ H_2\ } \ \begin{array}{c} R-H_2C \\ \diagdown \\ NH \ + \ NH_3 \\ \diagup \\ R-H_2C \end{array}
$$
$$
\qquad \underset{\text{intermediate}}{} \qquad\qquad \underset{\text{dialkylamine}}{}
$$
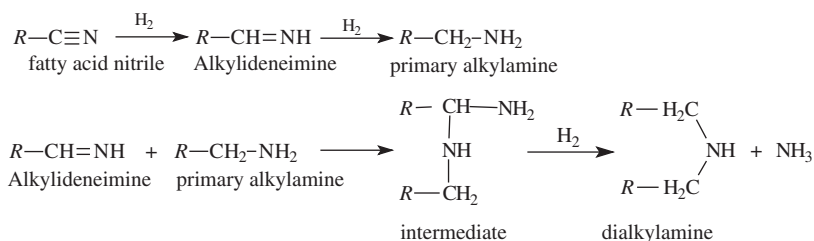
When the reaction is carried out at 200–250 ºC and the ammonia formed is continually removed from the converter, high yields of secondary amine are obtained.

Tertiary long-chain alkyl amines are prepared by the reaction of secondary amines with the corresponding 1-chloroalkane. The reaction is as follows:

$$
\begin{array}{c}
R \\
\diagdown \\
N-H \ + \ R-Cl \ \longrightarrow \ \left[R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{N}}-H \right]^{+} \ \left[Cl \right]^{-} \ \xrightarrow{\text{NaOH}} \ R-\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R}{|}}{N}} \ + \ NaCl \\
\diagup \\
R
\end{array}
$$

Dihexa-decylamine   1-Chloro-decane   Tertiary amine
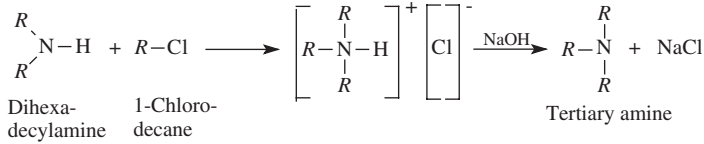
An important group of amines derived from the tertiary amines are quaternary ammonium salts, and they are produced from the additions of alkyl halides or sulfates to tertiary amines as per the following reactions:

(1) $R\text{NH}_2 \xrightarrow{R\text{-Cl}} R-\underset{\underset{\displaystyle H}{|}}{N}-R_1 \xrightarrow{R\text{-Cl}} R-\underset{\underset{\displaystyle R_2}{|}}{N}-R_1 \xrightarrow{R\text{-Cl}} \left[R-\overset{\overset{\displaystyle R_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{N}}-R_1 \right]^{+} \left[Cl \right]^{-}$

Alkylamine   Dialkylamine   Trialkylamine   Quaternary ammonium chloride

(2) $R\text{NH}_2 \xrightarrow{R_2\text{SO}_4} R-\underset{\underset{\displaystyle H}{|}}{N}-R_1 \xrightarrow{R_2\text{SO}_4} R-\underset{\underset{\displaystyle R_2}{|}}{N}-R_1 \xrightarrow{R_2\text{SO}_4} \left[R-\overset{\overset{\displaystyle R_3}{|}}{\underset{\underset{\displaystyle R_2}{|}}{N}}-R_1 \right]^{+} \left[OSO_3R_2 \right]^{-}$
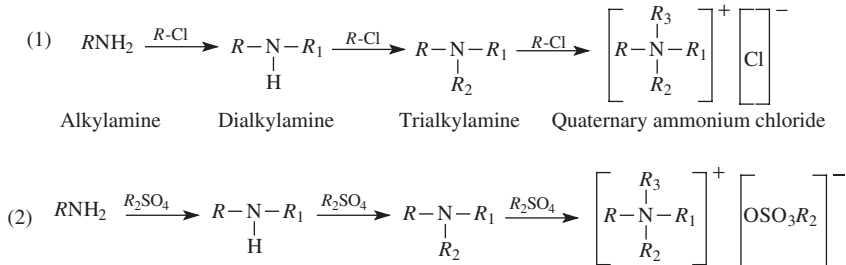
These collectors are selective in the flotation of some silicates.

2.4.2   Ether amines

When an alcohol is reacted with acrylonitrile and reduced, an amine is formed, which contains an oxygen atom in the chain that is separated from the nitrogen by three carbons. The presence of the oxygen atom (either linkage) imparts a hydrophilic character to the otherwise hydrophobic chain. Because of this kind of configuration, the ether amines are more soluble in water than fatty amines but they have a reduced collecting power.

Contacting the ether amine again with acrylonitrile would result in ether diamines. These products are usually liquid.

2.4.3   Condensates

The amine condensate is the reaction product of the polyamine with organic acid. The polyamines generally have short chain-length compounds with three or more nitrogen atoms in the chain. The organic acids are usually tall oil acids.

The condensates vary in the number of nitrogen groups present and in the total chain length depending on the starting materials and their relative mole ratios. The condensates

are in the form of solids or pastes at room temperature. Condensates are less important as flotation collectors, as are ether amines or fatty amines.

2.4.4   Cationic surface activity of amines

From the flotation perspective, it is very important to understand cationic surface activity of amines. The host of surface-active agents that consist of long hydrocarbon radicals and a hydrophobic group in the same molecule can be classified in the following four groups:

1. *Anion active agents*: The hydrophilic group is electronegative, and the hydrocarbon group is part of the negative component when the compound ionizes. For example, sodium lauryl sulfate, an anion active agent:

$$(CH_3–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–CH_2–O–SO_3)^-$$
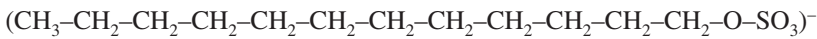
2. *Anionic*: The hydrophilic group is electrovalent and the hydrocarbon group is a part of the negative component when the compound ionizes, e.g. sodium lauryl sulfate:

$$Na^+[C_{12}H_{25}OSO_3]^-$$
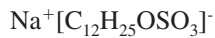
3. *Cationic*: The hydrophilic group is electronegative but the hydrocarbon group is part of the positive component when the compound ionizes. For example, laurylamine acetate:

$$[C_{12}H_{25}NH_3]^+[CH_3COO]^-$$
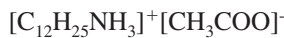
4. *Non-ionic*: The hydrophilic group is a covalent polar functional group that dissolves without ionization. For example, glyceryl monolaurate:

$$C_{12}H_{25}COOCH_2CHOHCH_2OH$$

5. *Amphoteric*: The hydrophilic group is electronegative but the hydrocarbon group acquires a positive charge in solution with acid pH and a negative charge at alkaline pH. The molecule is neutral at its isoelectric point.

It should be noted that a surface-active amine salt is cationic only when the long fatty alkyl/group is attached to the amino nitrogen that forms a positive ion. A common emulsifying agent triethanolamineoleate $[C_{17}H_{33}COO]^-[HN(CH_2CH_2OH)_3]^-$ is anionic because the long-chain hydrocarbon radical is part of a negative ion.

Amines are important chemicals in the mineral industry. The three most important applications of amines in the mineral industry are:

(a) Flotation collectors over a wide pH region (pH 1.5−11).
(b) Emulsifying agents for fatty acids to enhance the flotation performance.
(c) Raw material for the preparation of some anionic collectors.
(d) Depressants.

2.4.5   Amphoteric collectors

The amphoteric compounds are surface-active agents with the general formula

$$R_1\ X_1\ R_2\ X_2$$
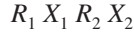
where
R_1 is a long alkyl chain, $8-18$ carbon atoms,
R_2 is one or more alkyl, aryl or cyclic hydrocarbon chains,
X_1 is one or more cationic functional groups,
X_2 is one or more anionic functional groups.
   The common types of collectors from this group are the long-chain amino acids with the formula
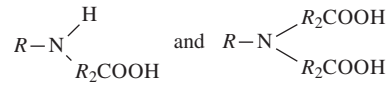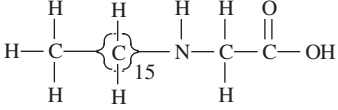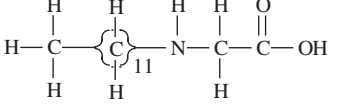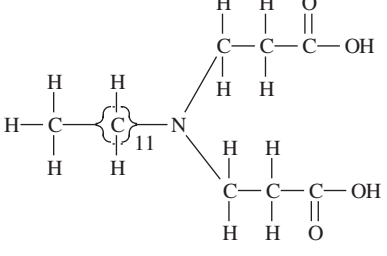
Typical examples of amphoteric flotation collectors are shown in Table 2.14.
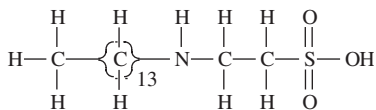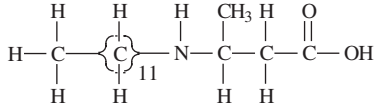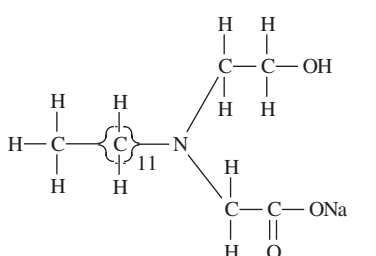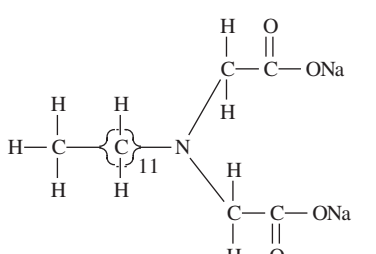
Table 2.14

Examples of amphoteric collectors

Name	Formula	Structure
Cetyl amino acetic acid	$C_{16}H_{33}NHCH_2COOH$	
N-lauryl-ρ-amino propionic acid	$C_{12}H_{25}NHCH_2COOH$	
N-lauryl-β iminodipropionic acid	$C_{12}H_{25}N(CH_2CH_2COOH)_2$	

(*Continued*)

Table 2.14   (*Continued*)

Name	Formula	Structure
N-myristyl taurine	$C_{14}H_{29}NHCH_2CH_2SO_3H$	
N-lauryl β aminobutyric acid	$C_{12}H_{25}NHCH(CH_3)CH_2COOH$	
Sodium hydroxyethyl-dodecylamino acetate	$C_{12}H_{25}N(C_2H_4OH)(CH_2COONa)$	
Sodium cetylamino diacetate	$C_{12}H_{25}N(C_2H_4OH)(CH_2COONa)$	

2.5   NON-IONIZING REAGENTS

Non-ionizing or non-polar reagents can be defined as chemical substances that cannot dissociate to form ions or are insoluble in water. They are hydrocarbon liquids obtained from crude oil (distillation, fractionation etc.) or from coal. The reagents from this group do not have a defined chemical composition because of differences in the characteristics of the crude oil or coal from which they are obtained. These reagents do not interact with water dipoles or mineral surfaces. Note that the molecules of the non-polar hydrocarbons have covalent bridging. Because non-polar reagents do not have a solidophilic group, they do not form orientated absorption layers on the mineral surface. It is believed that their adsorption on the mineral surface is imparted by adhesion. They readily adsorb on minerals that are naturally hydrophobic such as graphite, elemental sulfur and on some of the molybdenite found in vein deposits.

Apart from the use for flotation of naturally hydrophobic minerals, non-polar reagents have an application as froth modifiers during fatty acid and amine flotation. They are useful in modification of fatty acids [46] to improve selectivity of the collector.

The most widely used non-polar reagents are kerosene, transformer oil and synthetic hydrocarbon oils. Performance of the non-polar reagents is significantly improved when they are emulsified before use. It has been reported that use of the xanthate-fuel oil system [41] recovery of galena improved and also resulted in a reduction of xanthate consumption.

REFERENCES

1. Crozier, R.D., *Flotation Theory, Reagents and Ore Testing*, Pergamon Press, New York, 1992.
2. Glembocki, V.A., and Plaskin, I.N., *Flotation,* Gozgortexiizdat, 1961.
3. Avotins, P.T., Wang, S.S., and Nagaraj, D.R., Recent Advances in Sulphide Collector Development, In (P.S. Mulukutta ed.) *Reagents for Better Metallurgy*, SME, AIME General Meeting, 1994.
4. Fuerstenau, M.C., and Palmer, R.B., Anionic Flotation of Oxides and Silicates, *Flotation-Gaudin AM*, Memorial Volume, pp. 148–196, 1976.
5. Wyman, R.A., *The Floatability of Non-Metallic Minerals*, Canadian Department of Energy, Mines and Resources, TB108, TB186, 1976.
6. Glembocki, V.A., and Classen, V.I., *Theory of Flotation*, 2nd edn, Nedra, Moscow, 1963.
7. Mitrofanov, C.I., and Dudenko, C.B., *Theory and Practice of the Use of Flotation Reagents*, Nedra, Moscow, 1969.
8. Kakovskii, I.A., Anionic Flotation Collectors, *Tsvetnie Metaly* No. 2, 1950.
9. Plaksin, I.N., *Flotation Properties of Rare Minerals*, English Translation by Primary Sources, New York, 1967.
10. Grossman, L.I. et al., Flotation Separation of Calcium and Barium Minerals, *Tsvetnie Metaly* No. 1, 1955.
11. Bogdanov, V.I. et al., Study of the Reactions Between Beryl, Spodumene and Reagents Using Infra-red Spectroscopy, *Obogaschenie Rnd* No. 6, 1961.
12. Arbiter, N.B., and Hin, C.F., British Patent 1,110,643, 1967.
13. Lane, G., Acid Flotation Reagents for Oxidic Ore, PhD thesis, University of Tasmania, 1985.
14. Weiss, N.L., SME Mineral Processing Handbook, *SME/AIME*, New York, 1985.
15. Aplan, F.F., and Ennor, K.S., Fatty Acids in Flotation, In (R.W. Johnson and E. Frits eds) *Fatty Acid Industry*, Marcel Dekker, New York, 1989.
16. Bulatovic, S.M., and Salter, R., US Patent 4,772,382, September 2, 1988; US Patent 4,735,710, April 5, 1988.
17. Iwasaki, I., Iron Ore Flotation Theory and Practice, *Mining Engineering*, Vol. 35, 1983.
18. Norman, H., Sulphonate Type Flotation Reagents, In (D. Malhotra and W. Friggs eds) *Chemical Reagents in the Mineral Processing Industry*, SME Inc, Littleton, Colorado, 1986.
19. Fuerstenau, N.C., Chemistry of Collectors in Solution, In (R.P. King ed) Principles of Flotation, South African IMM, 1982.
20. Fuerstenau, D.W., and Pradip, C., The Adsorption of Hydroxamate on Semi-Soluble Minerals, Part 2, *Colloids and Surfaces*, No. 8, pp. 143–148, 1983.
21. Gayer, V., *Evaluation of Hoechst Hydroxamate on Flotation of Malachite from Dolomitic Ore at Kolwezi Concentrate*, Zaire, Report No. 1, 1981.
22. Fuerstenau, D.W., and Wie, J.M., An Alternative Reagent Scheme for the Flotation of the Mountain Pass Rare Earth Ore, *XIV International Mineral Processing Congress*, Vol. IV, Toronto, Canada, 1982.

23. Gorlovskeii, C.I. et al., Flotation of Titanium-Tantalum and Pyrochlore Using Hydroxamate (IM50 collector), Obogaschenie Rud No. 9, 1963.
24. Bulatovic, S.M., Bigg, A.C.T., and Yen, T., Improvement Studies for Flotation of Oxide Copper/Cobalt Ores from Gecamines Concentrators, Zaire, *LR-3150*, Vol. 6, 1981.
25. Bulatovic, S.M, Jessup, T., Process Development for Beneficiation of Mount Weld (Australia) Rare Earth Oxide Ore, *LR-3865*, Vol. 1, 1986.
26. Aleinikov, N.A. et al., US Patent 1,528,567, November 1987.
27. Klimpel, R.R., and Hansen, R.D., US Patent 4,676,890, June 1989.
28. Golikov, A.A. et al., Chemical Aspect of Adsorption of sulphydryl Collectors on the Mineral Surfaces, *Tsvetnie Metaly*, 1964.
29. Debus, H., Neutralization of Carbon Disulphide with Amines, *Liebig's Chemical Journal* (in German), Vol. 73, 1930.
30. Fry, H.S., New Methods for Preparing Thiocarbanilides, *Journal of the American Chemical Society*, Vol. 35, pp. 1539–1546, 1973.
31. Délépine, I., and Marcel, V., Metallic Salts of Dithiocarbamic Acid, *Comp. Rend*, Transaction vol. 85, Milling Method, pp. 144–165, 1925.
32. Dudenko, M., and Sobier, B.M., *Theory and Practice of Flotation Reagents, Nedra*, Moscow, 1969.
33. Harris, G., Alkyl Thionocarbamate Collector, US Patent 2,691,635, 1954.
34. Yun, L.F., and Wang, S.W., Collectors for Metal Sulphide Ores, UK Patent 2,163,068A, August 1986.
35. Fu, L.Y., and Wang, S.S., New Flotation Reagents, US Patent 4,802,915, February 1989.
36. Nagaraj, D.R. et al., The Chemistry and Structure Activity Relationships for New Sulphide Collectors, In (G.S. Dobby and S.R. Rao eds) *Processing of Complex Ores*, Pergamon, pp. 157–168, 1989.
37. Klimpel, R.K. and Hansen, R.D., Collector Composition for the Flotation of Mineral Value, US Patent 4,676,890, June 1987.
38. Oktawic, M., *Method for Production of Dithiophosphoric Acid*, Chemical Abstract 5212786, 1958.
39. Goetzev, G., and Davidtz, J., Sulphydryl Collectors in Bulk Flotation, *Rudodobiv Met* 1971(26) *2 Bulg*. IMM Vol. 89, No. 10, October 1989.
40. Marabini, A. et al., Chelating Reagents as Collectors and their Adsorption Mechanism (K.V.S. Sastry and M.C. Fuerstenau eds), *Challenges in Mineral Processing*, SME, 1989.
41. Gutzeit, G., *Chelate-Forming Organic Compounds as Flotation Reagents*, pp. 35–50, 1946.
42. Marabini, A.M. et al., A Calculation Method for Selection of Complexing Collectors Having Selective Action on a Cation, *Transactions of the Institute of Mining and Metallurgy Section C*, AIME Series V, Vol. 7, pp. 20–26, 1946.
43. Borningo, G., et al., Collecting Agents for Selective Flotation of Lead and Zinc Ores, US Patent 4,724,072, Transaction Institute of Mining and Metallurgy, February 1988.
44. Young, C., and Chrinstesen, P., Ether Amine Synthesis, US Patent 2,287,219, March 1932.
45. Armac Bulletin, No. 72–78.
46. Klassen, B.I., and Makrousou, B.A., *Principles and Theory of Flotation*, Gozgortexiizdat, (in Russian), 1959.

– 3 –

Frothers

3.1 DEFINITION AND PROPERTIES OF FROTHERS

Frothers are heteropolar surface-active compounds containing a polar group (OH, COOH, C=O, OSO_2 and SO_2OH) and a hydrocarbon radical, capable of adsorbing in the water–air interface. The frother molecules are arranged at the air–water interface such that the hydrophilic or polar groups are oriented into the water phase, and the hydrophobic or non-polar hydrocarbon chain in the air phase. In fact, the frother creates conditions for froth formation. The flotation froth is a three-phase system. The frother concentrates at the interface of water and air bubbles, forming an envelope around the bubbles, which prevents them from colliding or touching. Frothers also lower the surface tension of the water. The forces created around the air bubble in the presence of a frother prevent the bubbles from collapsing.

Many investigations have been carried out on froths and free liquid films [1–4] and extensive reviews are available on the theory of frothing and the stability of froths [5–8]. From the practical point of view, difficulties still remain in selecting an efficient frother for many operating plants. This is because the ionic composition of the pulp and the presence of various ultra-fine clay minerals have a dramatic effect on the frothing properties and froth stability in the flotation pulps.

Recent attempts to provide guidelines for frother selection [9] suggested that using technical concepts and extensive flotation cell experience can lead to the identification of frothers possessing a range of desirable performance characteristics. However, this may be too simplistic. Comparing plant and laboratory performance of frothers may lead to completely different results because of the changes of frothing properties under laboratory and plant conditions. One of the factors influencing of frothing properties, which has not been widely examined in basic research studies, is the relationship between the collecting power and frother properties. For example, when mineral particles tend to float fast after the addition of a collector with "high collecting power," the initial froth becomes over-crowded and very dry regardless of the type of frother used. When this initial dry froth is removed, the froth becomes persistent. This has been a common occurrence during flotation of porphyry-copper ores containing clay and during zinc flotation from massive sulfide ores.

3.2   THE EFFECT OF COLLECTOR ON FROTH PROPERTIES

The volume of froth generated in the flotation machine under standard operating conditions is often referred to as *froth power*. The froth power is influenced by the type of collector and frother used. For example, froth power normally increases with the number of carbon atoms in the hydrocarbon radical up to 6 or 7, and then drops dramatically when the hydrocarbon chain has more than 8 carbon atoms. A xanthate with less than 6 carbons in the alkyl group does not produce frothing alone, while octyl xanthate will produce froth on its own but will diminish froth if mixed with alcohol.

Mixing a longer chain xanthate (amyl) with a short chain alcohol increases the volume of the froth. The froth power increases strongly when amyl xanthate is combined with an alcohol containing 7–8 carbon atoms in the hydrocarbon radical. Xanthates with a shorter chain length (ethyl) decrease the froth power for alcohols with 5 or less carbon atoms.

In fatty acid flotation, certain alcohol-type frothers, such as pine oils, cresylic acid, etc. act as froth modifiers. For example, mixing tall oil fatty acid with a cyclic alcohol frother (pine oil) produces a froth that has improved loading properties and that collapses after discharge.

In cationic flotation with amines, addition of frother to the amine reduces collector consumption and improves the rate of flotation.

3.3   CLASSIFICATION OF FROTHERS

In the literature, there are several different classifications of frothers depending on their properties and behavior in solution. Dudenkov *et al*. [10] have classified the frothers depending on the frother behavior at different pH values. This classification is shown in Table 3.1. Another classification is based on the type of frother or compounds that act as collector and frother. Either classification is tentative because some of the compounds used as frother have been or still are proprietary products and their structures are seldom disclosed. These frothers will not be discussed in this section.

The acid frothers have been used extensively until the 1960s. Their application has been diminishing because of environmental considerations. Two types of acid frothers are common, namely, phenols and alkyl sulfonates. Neutral frothers are a much larger family of frothers and are more widely used. Frothers that have both collecting and frother properties have already been discussed. Froth modifiers are compounds different in nature from either acid or neutral frothers.

Table 3.1

Classification of frothers

Acidic	*Neutral*	*Basic*
Phenols	Aliphatic alcohols	Pyridine base
Alkyl sulfates	Cyclic alcohols	
	Alkoxy paraffins	
	Polypropylene glycol ethers	
	Polyglycol ethers	
	Polyglycol glycerol ethers	

3.4   ACIDIC FROTHERS

These frothers perform well only in acid pH. In an alkaline medium, their frothing properties are reduced. Typical examples of these reagents are phenols. These frothers are obtained as a by-product during gasification of coal tar and distillation of crude oil. The following two groups of frothers have been used in mineral processing plants, phenols and alkyl-lauryl sulfonates.

3.4.1   Phenols

Phenols are also known as aromatic alcohols. A typical frother from this group is cresol, consisting of a mixture of ortho (*o*) (35–40%), meta (*m*) (25–28%) and para (*p*) (35–40%) cresols. Cresols and close homologs of phenols are acidulation products of toluol. The general formulas of the main components of these cresols are:
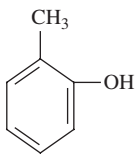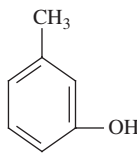
Orthocresol   *Metacresol*   *Paracresol*   *Phenol*
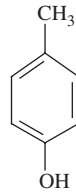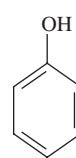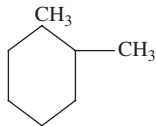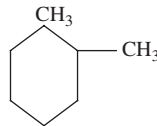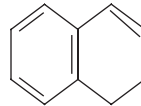
Orthoxylol   *Toluol*   *Naphthalin*

   The most effective frothers from this group are the *m*-cresol, *p*-cresol and *o*-cresol. Some physical properties of the tricresols are shown in Table 3.2.
   The main problem associated with the use of phenols as a frother is its variable composition, which depends on the source from which the frother is derived. *Xylenol* belongs to the aromatic alcohol type of frothers. In appearance, xylenol is a dark brown liquid similar to phenols with the same characteristic smell. Xylenol frother is a mixture of a higher molecular structure of phenol isomers. The chemical structure of xylenol is as follows:
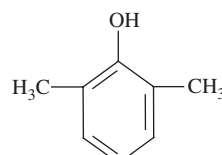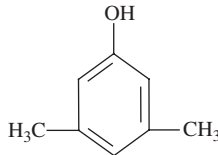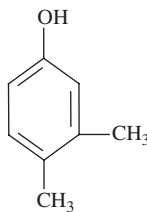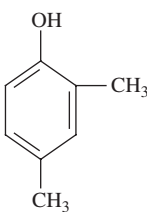
Table 3.2

Physical properties of the main components of tricresols [12]

Product	Formula	Freezing temperature (°C)	Boiling temperature (°C)
Phenol	C_6H_5OH	43.3	182.0
o-Cresol	$CH_3C_6H_4OH$	31.6	191.0
m-Cresol	$CH_3C_6H_4OH$	11.9	202.0
p-Cresol	$CH_3C_6H_4OH$	35.0	202.0
o-Xylol	$1,2\text{-}(CH_3)_2C_6H_4$	−28.0	144.0
m-Xylol	$1,3\text{-}(CH_3)_2C_6H_4$	−54.0	139.0
p-Xylol	$1,4\text{-}(CH_3)_2C_6H_4$	13.0	138.0
Toluol	$C_6H_5CH_3$	−93.0	110.6
Naphthalene	$C_{10}H_3$	80.0	218.0

The methyl groups can assume six different arrangements. The 3-4 position is the most abundant. These frothers are also obtained from coal by distillation. Similar to phenols, these frothers also have a variable composition.

Phenols and xylenol can be added to tall oil fatty acids to improve selectivity as well as power. A mixture of tall oil and cresol has been successfully used for flotation of spodumene and phenacite [11].

3.4.2 Alkylaryl sulfonates

Alkylaryl sulfonate can be described as an anionic frother with a structure that is composed of an aromatic hydrocarbon and an aliphatic radical:

$R =$ *aliphatic radical*
$Me =$ *metal*
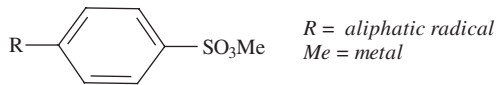
In spite of the fact that these frothers have good frothing properties, their application was limited, likely because most alkylaryl sulfonate frothers contain traces of sulfur, which interfere with flotation.

3.5 BASIC FROTHERS

These frothers are represented by pyridine and homologs, recovered as by-products from coal tar distillation. They are used for flotation of base-metal ores, mostly in the former Soviet Union. In Europe, a similar product was used to produce a collector used in the

flotation of oxide lead minerals (Hoechst). The following two structures are used as frothers:

pyridine
oxychloride

pyridin
sulfotrioxide
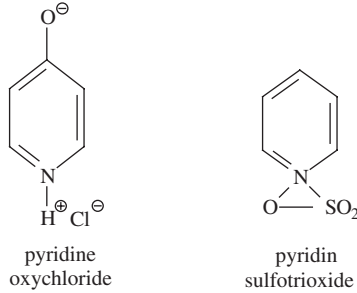
3.6   NEUTRAL FROTHERS

This is the most important group of frothers used widely in flotation of base-metal ores, oxidic minerals and industrial minerals. They are functional in both acidic and alkaline pulps. These frothers are divided into six sub-groups, with wide differences in chemical composition.

3.6.1   Aliphatic alcohols

These frothers are mixtures of alcohols containing 6–8 carbon atoms. They were at one time marketed by DuPont and they are tailored frothers for specific ore types. The best-known frother from this group is methyl isobutyl carbinol (MIBC) with the following formula:

$$H_3C-CH-CH_2-CH-CH_3$$
$$\qquad\ \ CH_3\qquad OH$$
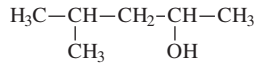
and 2-ethyl hexanol with the formula:

$$CH_3-CH_2-CH_2-CH-CH_2-OH$$
$$\qquad\qquad\qquad CH_2-CH_3$$
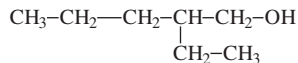
The properties of the more important aliphatic alcohol frothers are shown in Table 3.3.
Aliphatic alcohol frothers are used as mixtures of different carbon lengths and as a mixture of hydrocarbon oils. The following mixtures are common in mineral flotation:

• *Mixture of C6–C9 alcohols*: A specific gravity of 0.856 and viscosity of 5 cps (Brookfield). These frothers are regarded as highly selective.

Table 3.3

Properties of aliphatic alcohol frothers

Alcohol	Formula	Freezing point (°C)	Boiling point (°C)	Density (g/mL)	Solubility (g/L)
n-Pentanol	$CH_3(CH_2)_3CH_2OH$	−75	137.3	0.8144	23.0
Isoamyl alcohol	$(CH_3)_2CHCH_2CH_2OH$	−117	132	0.813	25.0
Hexanol	$CH_3(CH_2)_4CH_2OH$	−52	156.5	0.819	6.0
Heptanol	$CH_3(CH_2)_5CH_2OH$	−34	176	0.822	1.8
MIBC	$(CH_3)_2CHCH_2CHOHCH_3$	−90	132	0.808	17.0
Caprylic acid	$CH_3(CH_2)_5CHOHCH_3$	−38	179	0.822	12.0
4-Heptanol	$CH_3(CH_2)_2CHOH(CH_2)CH_3$	−41.2	161	0.8183	4.5

- *Mixture of C_4–C_7 alcohols + hydrocarbon oil*: A specific gravity of 0.82 and viscosity of 4.5 cps (Brookfield). These frothers are usually used during copper–molybdenum or molybdenum flotation.
- *Mixture of C_5–C_8 carbon alcohols*: A specific gravity of 0.81–0.83 and viscosity of 6.9 cps. These frothers gave less persistent froth than the other alcohol mixtures.

3.6.2   Cyclic alcohol (alpha terpineols)

These frothers were popular in the early days of flotation along with eucalyptus oils. These frothers are basically mixtures of different cyclic alcohols and they are produced as synthetic mixture or from the pine resins. The following are the basic structures of different components of cyclic alcohol frothers:
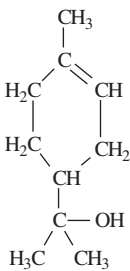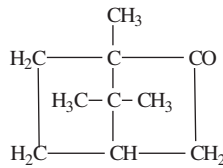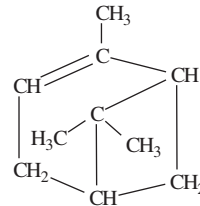
α-terpineol   α-camphor   α-pinene

The most abundant cyclic alcohols in the frother mixtures are terpineols (i.e. 90%) followed by borneol and pinene. The physical–chemical characteristics of cyclic alcohol frothers are shown in Table 3.4.

These frothers are less sensitive to the presence of clay minerals than other types of frothers and therefore they are extensively used in mixtures with aliphatic alcohol frothers for flotation of base metals and copper porphyry ores containing clay minerals. They are also used as additives to tall oil fatty acid in fatty acid flotation to improve froth stability. The major problem in the use of cyclic alcohol frothers derived from natural sources is that their composition is not always constant, and consequently frothing properties are variable.

Table 3.4

Physical chemical properties of cyclic alcohol frothers

Name	Chemical formula	Polar group	Solubility at 20 °C (g/L)	Density at 20 °C (g/mL)	Boiling point (°C)	Freezing point (°C)
α-Terpineol	$C_{10}H_{18}O$	−OH	2.2	0.919	219	−33
β-Terpineol	$C_{10}H_{18}O$	−OH	1.98	0.935	220	−35
γ-Terpineol	$C_{10}H_{18}O$	−OH	2.09	0.925	222	−36
Borneol	$C_{10}H_{18}O$	−OH	0.64	1.010	212	−210
Anetol	$C_{10}H_{12}O$	O−C	Insoluble	0.933	233	−
α-Camphor	$C_{10}H_{16}O$	C=O	1.60	0.912	201	−179
α-Pinene	$C_{10}H_{16}$	−	Insoluble	1.00	230	−65

3.6.3   Alkoxy paraffins

This group of frothers was developed in 1951 by Dr. Powell of South Africa. In recent years, a number of frothers were produced based on two main structures:

(a)   1,1,3-Triethoxybutane (TEB)

$$H_3C-CH-CH \begin{matrix} O-CH_2-CH_3 \\ \\ O-CH_2-CH_3 \end{matrix}$$

$$H_3C-H_2C-O$$
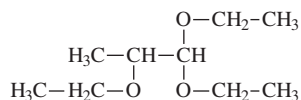
(b)   1,3,5-Trialkoxypropyl trioxane
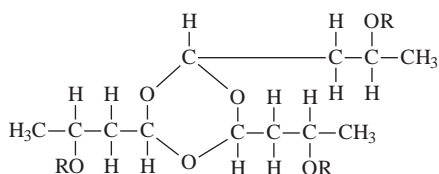
Only limited information is available on the chemistry and the properties of these frothers, although they are extensively used for flotation of base metals and oxidic mineral ores. Their frothing properties are much different from those of aliphatic and cyclic alcohols with respect to froth stability and sensitivity to the presence of clay minerals. However, they are selective and in many cases gave improved rates of flotation of copper and zinc minerals. They are highly effective during the flotation of oxide copper minerals using the sulfidization method.

3.6.4   Polyglycol ethers

Tueter of Dow Chemicals and Booth of Cyanamid first developed the polyglycol ether frother series in the early 1950s. These frothers are manufactured from synthetic brake

fluid and they are methoxy polypropylene glycols or polypropylene glycol methyl ethers with the formula

$$CH_3(OC_3H_6)_n-OH$$

There are several variations of polyglycol ethers produced by different manufacturers. Some of the more important frother structures are listed below:

(a) (a) $H-[O-C_3H_6]_n-OH$ $n = 4,5$

(b) (b) $R-[O-C_3H_6]_n-OH$

(c) (c) $R-[O-C_3H_6]_n-OH \star$ adduct
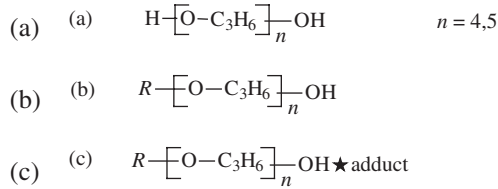
Some polyglycol ethers are also produced by condensation with butanol or ethylene oxide (structure (c)) or result as a reaction product of butanol and caustic soda.

The molecular weight and carbon length of polyglycol ether frothers determines its power and performance. A higher molecular-weight frother gave more persistent froth and less selective than a lower molecular-weight frother.

Unfortunately, the polyglycol ethers from different manufacturers behave differently. For example, Hoechst (Germany) polyglycol ether frothers (i.e. D13, D14 and D16) gave more selective froth than those produced by Dow (same general structure).

Polyglycol ethers produced from butanol and ethylene oxide are more selective and have a better carrying power than similar frothers produced from butanol and caustic soda.

3.6.5   Polypropylene glycol ethers

These frothers are partially soluble in water, and are a mixture of monomethyl ethers of polypropylene glycols with the following formula:

$$CH_3-[O-C_3H_6]_n-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \qquad n = 3,4,5,6$$
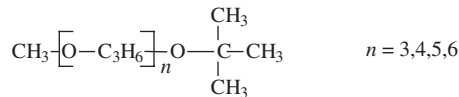
These frothers are normally used in base-metal flotation. They produce persistent froth and have relatively high carrying power.

3.6.6   Polyglycol glycerol ethers

Originally, these frothers were developed in the former Soviet Union under the trademark Frother E1, and in 1985 Dow Chemicals, under the trade names XK35004, XK35004.O1L

and XK35004.02L, produced similar frothers. The general formula of these frothers is as follows:

$$R-O-\left[\begin{array}{c} CH-CH_2-OH \\ | \\ CH_3 \end{array}\right]_n \qquad R = \quad \text{4 to 6 carbon atoms}$$
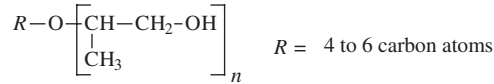
These frothers produced relatively strong froth with a fine texture.

REFERENCES

1. Klassen, V.I., and Mokrousov, V.A., *An Introduction to the Theory of Flotation*, Butterworth, London (English Translation), 1963.
2. Riggs, F.W., Frothers-An Operator's Guide, In (D. Malhorta and W.F. Riggs eds) *Chemical Reagents in the Mineral Processing Industry*, SME, 1986.
3. Harris, P.J., *Frothing Phenomena and Frother Principles of Flotation*, South African IMM, 1982.
4. Bansol, V.K., and Biswas, A.K., Collector-Frother Interactions in the Interfaces of a Flotation System, *Transactions of the Institution of Mining and Metallurgy Section C*, Vol. 84, p. 131, 1975.
5. Booth, R.B., and Freyberger, W.L., Froth and Frothing agents, In (D.W. Fuerstenau ed.) *Froth Flotation*, AIME, New York, p. 258, 1962.
6. Dudenkov, S.V., and Bakinov, K.G., Effect of the Structure of Frothing Agent Molecules on the Coalescence of Air Bubbles, *Tsvetnie Metaly*, 39, 1966.
7. Lekki, J., and Laskowski, J., A New Concept of Frothing in Flotation Systems and General Classification of Frother, *Transactions of the Institution of Mining and Metallurgy Section C*, Vol. 80, p. 174, 1975.
8. Livshitz, A.K., and Dudenkov, S.V., *Some Factors in Flotation Froth Stability*, Obogaschenie Rud, No. 3, 1963.
9. Klimpel, R.R., and Hansen, R.D., *Frothers Mineral Industry Reagents*, Marcel Dekker Inc., New York, Chapter 5, 1986.
10. Dudenkov, S.V., and Galikov, A.A., *Theory and Practice of Application of Flotation Reagents*, Nedra, Russia, 1969.
11. Bulatovic, S.M., Beryllium Flotation Process, US Patent 4,735,710, April 1988.
12. Sibbald, C.V., Chemistry of Cresols, *United States Bureau of Mines Bulletin*, No. 1136, 1969.

– 4 –

Modifying Reagents

4.1 CLASSIFICATION OF MODIFYING REAGENTS

Modifying reagents, commonly known as regulators, can be regarded as the most important chemicals in mineral processing, which control the interaction of collectors between individual minerals. With the use of modifying reagents, selective adsorption of collectors on specific minerals can be increased or can be decreased to achieve the separation of individual minerals. Because of the use of modifying reagents, it is possible to isolate individual mineral sulfides of lead, zinc and copper from complex sulfide ores. Similarly, it is possible to selectively separate calcium-containing minerals, such as fluorite, scheelite, and calcite from each other.

Regulating reagents, under different conditions, can show either activating or depressing action in flotation. Therefore, it is not possible to strictly classify regulating reagents into specific groups. A general classification of the modifying reagents is shown in Figure 4.1. The principal classes include inorganic modifying reagents and organic modifying reagents.

Acids, alkalis and metal salts represent inorganic modifying reagents. Organic modifiers are chemicals that contain polar groups, such as $-OH$, $-COOH$, $=CO$, $-NH_2$, $=NH$ and SO_3H. On the basis of the character of the polar group, which influences the action of the polymer, organic polymers can be divided into the following four subgroups:

1. Non-ionic polymers are chemicals that contain hydrolyzing polar groups: $-OH$, $=CO$, $-COOH$, but carry no electrical charge.
2. Anionic polymers contain polar groups: $-COOH$, $-SO_3H$, OSO_3H.
3. Cationic polymers contain polar groups: $-NH_2$, $=NH$.
4. Amphoteric polymers contain both cationic and anionic groups.

Reagents from the second, third and fourth group can also contain hydrating non-ionic polar groups. Because there are a large number of modifying reagents with single or multiple functions, for the purpose of understanding, only the important groups are discussed.
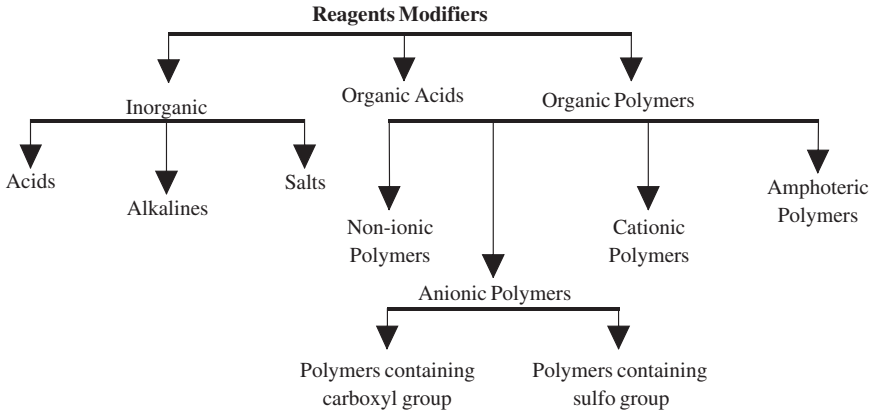
Figure 4.1 Classification of modifying reagents.

4.2   FUNCTIONS OF THE MODIFYING REAGENTS

Modifying reagents used in practice are numerous. Depending on its functional character, the modifying reagent reacts with mineral surfaces as well as with collectors and ions contained in the pulp. To provide selective collector adsorption, a modifying reagent must itself be selective. Let us examine a typical case for the use of modifying reagents: sodium cyanide and other water-soluble cyanides are used as modifying reagents for selective flotation of ores containing galena, sphalerite and gangue minerals. Xanthate interacts with all sulfides, including galena, sphalerite and pyrite and would not be a selective collector for specific sulfide minerals. Using only xanthate as a collector, it is possible to separate the bulk of sulfides from silica and other non-sulfide gangue minerals. In the presence of cyanide, conditions are created that allow the selective removal of galena with xanthate as the sole collector. Therefore, cyanide functions as a regulating agent during selective flotation of galena from sphalerite and pyrite.

Modifying reagents influence flotation in different ways, some of which include:

1.   Modifying reagents can react with mineral surfaces resulting in a change of the chemical composition of particular mineral surfaces. This can increase the adsorption of the collector on the mineral surface or can prevent collector adsorption entirely. For example, copper sulfate reacts with the surface of sphalerite resulting in increased collector adsorption and consequently, improved floatability. In contrast, sodium cyanide would dissolve copper from the sphalerite surface and prevent collector adsorption on sphalerite.

2.   Modifying reagents can also remove collector coatings from the mineral surface, causing depression of the mineral. For example, above a certain threshold concentration, sodium sulfide displaces the collector from galena, sphalerite and other sulfides resulting in depression of these minerals.

3.   Modifying reagents are capable of changing the floatability of particular minerals, regardless of their ability to react with collectors. Adsorption of modifying reagents

on mineral surfaces would create a hydrophilic mineral surface that cannot react with collectors.

4.   Modifying reagents can change the pH of the pulp. Since adsorption of collectors on the mineral surface in the majority of cases is pH related, these modifying reagents in fact control the adsorption of the collector on a mineral surface. For example, pyrite does not float in a highly alkaline pH environment, but reacts with xanthate and floats readily in a near neutral or acid pH range.

Changes in floatability of a mineral can also be achieved by interaction of modifying reagents with ions present in the flotation pulp. For example, heavy metal ions present in the pulp react with quartz and other silicates, thus enabling these minerals to adsorb the collector and become floatable. Prevention of the adsorption of heavy minerals on mineral surfaces is achieved with modifying reagents, for example, using lime or sodium sulfide:

$$CuSO_4 + Na_2S = CuS + Na_2SO_4;$$

$$3Ca(OH)_2 + Fe(SO_4)_3 = 2Fe(OH)_3 + 3CaSO_4$$
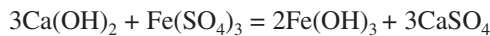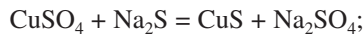
Heavy metals react with the collector in the pulp resulting in precipitation of an insoluble metal xanthate:

$$CuSO_4 + 2C_2H_5OCSSK = K_2SO_4 + Cu^+(C_2H_5OCSS) + \tfrac{1}{2}(C_2H_5OCSS)_2$$

4.3   INORGANIC MODIFIERS

4.3.1   Acids and alkalis

Acids and alkalis are modifiers that can have multiple functions. Mostly they are used as pH modifiers, but they can, at the same time, act as depressants and/or dispersants. In addition, certain reagents from this group [1] can induce flocculation particularly to fine particles. For example, alkalinity-control chemicals that contain a monovalent cation, such as Na^+ from caustic soda or K^+ from KOH, to act as dispersants. Divalent cations such as Ca^{2+} or Mg^{2+} can exhibit some flocculating behavior. A list of the most important acids and alkalis used in flotation practice are given in Table 4.1.

* *Sulfuric acid (H_2SO_4)* is the most widely used acid for pH control in mineral flotation. Sulfuric acid can be manufactured by several processes including the burning of pure sulfur, roasting of pyrite and from the recovery of SO_2 stack gas from a smelter operation. Sulfuric acid is a colorless to amber, slightly cloudy and oily liquid with a specific gravity of 1.84 at 95% strength.
  In mineral flotation, sulfuric acid is used in almost all applications involving acid pH control. It is also used as a pulp pretreatment chemical during flotation of oxidic and industrial minerals. Pulp pretreatment with sulfuric acid improves flotation of ilmenite, perovskite, phenacite, beryl and other minerals [2].

Table 4.1

Acids and alkaline used in mineral flotation

Chemical name	Chemical formula	Specific gravity	Freezing point at 1 atm (°C)
Sulfuric acid	H_2SO_4	1.84 (95% solution)	−40
Hydrochloric acid	HCl	1.17 (33% solution)	−40
Hydrofluoric acid	HF	1.01 (25% solution)	−30
Hydrofluorosilic acid	H_2SiF_6	1.02 (25% solution)	−30
Sulfurous acid	H_2SO_3	−	−20
Sodium carbonate	Na_2CO_3	2.5	−
Lime	CaO	2.13	−
Sodium hydroxide	NaOH	2.13	−
Ammonia	NH_4OH	0.68[a]	−78

[a]At boiling point.

- *Hydrochloric acid (HCl)* is a highly corrosive liquid, emitting a pungent odor and fumes in moist air. Concentrated hydrochloric acid is one of the strongest acids and thus any desired pH from 0 to 7 can be easily achieved with the required dosage. Hydrochloric acid is seldom used in mineral flotation. The largest use is in hydrometallurgical processes and the pickling of hot rolled steel. In some cases, hydrochloric acid is used for decoating iron-stained mineral surfaces before flotation.
- *Hydrofluoric acid (HF)* is a colorless liquid with a characteristic odor. It releases fumes when in contact with moist air. Hydrofluoric acid is manufactured from fluorite containing 96−97% CaF_2 by reacting it with concentrated sulfuric acid:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4$$
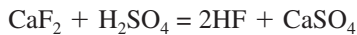
  The acid is sold as a 40% solution. The hydrofluoric acid is used as an activator and depressant, mostly during flotation of industrial minerals (i.e. columbite, tantalite, silica, feldspars).
- Hydrofluorosilicic acid *(H_2SiF_6)* is a colorless to light brown liquid. It is also manufactured from calcium fluoride or other fluoride-containing products. Hydrofluorosilic acid is a strong depressant for many silicates during flotation of a number of oxidic minerals. It is used for gangue depression during flotation of tin, columbite and tantalite.
- *Sulfurous acid (H_2SO_3)* is usually marketed as liquid SO_2. The bulk of SO_2 is produced from off-smelter gases. Although handling of SO_2 liquid requires special equipment, it is frequently used as a pH regulator and depressant, primarily during the treatment of complex sulfide ores. SO_2 is largely used in North American operations as a pyrite depressant and for the depression of galena during copper/lead separation.
- *Lime (CaO) and magnesium hydroxide (Mg(OH)_2).* Lime is the most widely used reagent in the mineral industry for flotation of sulfides and, in some cases, non-sulfide minerals. The word "lime" is a general term used to describe any kind of calcareous material or finely divided form of limestone and dolomite. In more strict chemical terms, lime is calcined limestone known as calcium oxide (CaO), quicklime or unslaked lime.

The slaked or hydrated lime $Ca(OH)_2$ is the form of lime primarily used in mineral flotation. Production of high-calcium lime is based on calcination of limestone at a temperature of 1100–1300 °C in kilns.

$$CaCO_3 + heat \rightleftharpoons CaO + CO_2$$
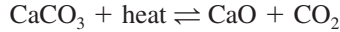
For high-magnesium (dolomitic) limestone, the calcination reaction (at 1000–1200 °C) is

$$CaCO_3 \cdot MgCO_3 \text{ (limestone)} + heat \rightleftharpoons CaOMgO \text{ (quicklime} - 2CO_2)$$
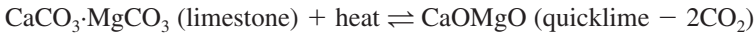
The high-calcium lime contains less than 5% MgO. In mineral processing practice, hydrated or slaked lime is usually used. The $Ca(OH)_2$ is obtained by adding water to the quicklime and then slaking it into a dry fine white powder.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 + heat$$
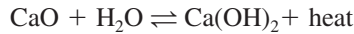
There are two types of lime used in mineral processing (see Table 4.2):

1. High-grade calcium quicklime (93–98% CaO).
2. Dolomitic quicklime (55–58% CaO and 37–41% MgO).

Dolomitic lime is more effective in total acid neutralization than the high-calcium lime. One of the unique characteristics of $Mg(OH)_2$ is its high pH buffering action with a pH of 10.5 being a practical upper limit that can be achieved.

- *Soda ash* is the name of various grades of sodium carbonate (Na_2CO_3). A large portion of soda ash is manufactured via the Solvay process, based on the following reaction:

$$NH_3 + CO_2 + H_2O \rightarrow NH_4HCO_3$$
$$NaCl + NH_4HCO_3 \rightarrow NaHCO_3 + NH_4Cl$$
$$2NaHCO_3 + heat \rightarrow Na_2CO_3 + CO_2 \text{ (recycled)}$$
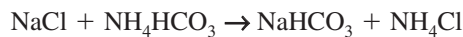
Soda ash is an off-white to white anhydrous powder or granular material. The quality of soda ash is usually characterized by the percent of sodium oxide (Na_2O) content.

Table 4.2

Properties of commercial lime products

Description	Quicklime		Hydrates	
	High calcium	Dolomitic	High calcium	Dolomitic
Primary constituents	CaO	CaO, MgO	$Ca(OH)_2$	$Ca(OH)_2$, $Mg(OH)_2$
Specific gravity	3.2–3.4	3.2–3.4	2.2–2.4	2.6–2.8
Bulk density (g/L)	885–950	885–950	410–550	510–550
Specific heat at 38 °C (cal/g/°C)	0.19	0.21	0.29	0.29
Heat of hydrate (cal/g)	–	–	270	210

The properties of soda ash used in the mineral processing industry are as follows (from soda ash manufacturers Product Manual (i.e. Nymoc 1986)):

Sodium carbonate anhydrous	99%
Sodium oxide equivalent	58%
Bulk density	560–1280 g/L

The most prominent characteristic of soda ash in solution is the high buffered pH response. For example, changing the sodium carbonate dosage from 0.03% to 30% only causes the solution pH to change from 10.5 to 11.7. Because of this, in mineral processing application, soda ash is used for pH control to a maximum value of 10.5.

- *Caustic soda (NaOH)* is regarded as the strongest alkaline pH regulator. Caustic soda is a very active substance and is highly corrosive. The bulk of caustic soda is manufactured by electrolysis of saturated brines (NaCl). Caustic soda has a very strong pH-regulating capability (i.e. from pH 7 to pH 14) at a relatively low dosage compared to other alkaline substances. Commercially, caustic soda is available in anhydrous form, but in most mining applications the caustic soda is supplied as a 50% solution. The properties of commercial caustic soda are as follows:

Sodium hydroxide	>98%
Sodium oxide equivalent	>76%
Specific gravity (beads)	2.13
Melting point	318 °C
Solubility at 20 °C	109 g/100 g water

In the mineral processing industry, sodium hydroxide is mostly used for alkalinity control during the processing of non-metallic minerals. In base metal flotation, the use of sodium hydroxide is rare.

- *Ammonia (NH$_3$)* is an alkaline gas with a sharp, penetrating odor. Reacting nitrogen and hydrogen under pressure, in the presence of a catalyst, produces ammonia. Gaseous ammonia is flammable in air at concentrations of 15–28% by volume. Anhydrous liquid ammonia is a colorless liquid with a strong odor. Ammonia, because of its unique chemical properties to metal ions, is primarily used in hydrometallurgical processing. In the mineral processing industry, ammonia is rarely used as a pH regulator. There was only one operating plant in the world [3] that used ammonia as a pH regulator in treatment of a copper/zinc ore.

4.3.2 Salts

This section includes a fairly large group of modifiers used in the mineral industry. They are used as depressants, activators and dispersants. The most commonly used salts are discussed in this section.

- *Copper sulfate (CuSO$_4$·5H$_2$O)* is widely used as an activator for sphalerite, pyrite, pyrrhotite and other sulfides during processing of base metal ores. During flotation of some silicate minerals, copper sulfate is used as depressant [4], e.g. zirconium.

In manufacturing copper sulfate, sulfuric acid and scrap copper metal are used. The process is based on the oxidation of metal and dissolution with H_2SO_4 according to the following reaction:

$$4Cu + O_2 = 2Cu_2O$$

$$Cu_2O + H_2SO_4 = CuSO_4 + H_2O$$

$$2Cu_2SO_4 + 2H_2SO_4 + O_2 = 4CuSO_4 + 2H_2O$$
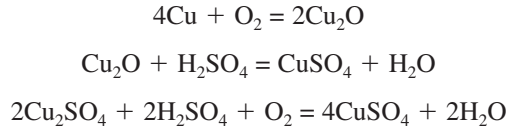
Usually, in mineral processing applications, copper sulfate is delivered in crystal form.

- *Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)* is a white powder, very soluble in water (i.e. 37% at 20 °C). Zinc sulfate is primarily used in base-metal flotation as a depressant for sphalerite. Zinc sulfate has been used to depress talc in by-product molybdenum circuit [5].
  $ZnSO_4$ is manufactured by reacting zinc metal or zinc oxide with sulfuric acid. The dissolution reaction is carried out at 80–100 °C as follows:

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O + 20.8 \text{ cal}$$

$$Zn + H_2SO_4 = ZnSO_4 + H_2 + 37.2 \text{ cal}$$
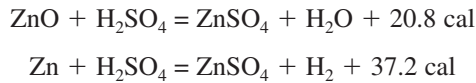
  In mineral processing, $ZnSO_4 \cdot 7H_2O$ is delivered in powder form and used as solution at 10–25%.
- *Ferro sulfate ($FeSO_4 \cdot 7H_2O$)* is a crystalline substance greenish in color, with a specific gravity of 1.899. Ferro sulfate is obtained from various solutions using a vacuum crystallization method. Ferro sulfate has been used as a depressant and co-depressant in the following applications: (a) depression of sphalerite together with cyanide [6], (b) depression of fine molybdenite also with cyanide, and (c) in copper/lead separation using a method, based on copper depression by cyanide.
- *Ferric chloride ($FeCl_3$)* is obtained by an iron chlorination method at a temperature of 600–700 °C. Very limited data are available on the use of ferric chloride in the mineral processing industry. Ferric chloride has a depressing effect on barite and can be used in barite–celestite separation. It was also evaluated as a depressant during niobium–zirconium separation. In general, ferric and ferrous compounds are not selective depressants and in many cases are detrimental for flotation of oxidic and industrial minerals as in the case of anionic flotation, fatty acid, iron complexes or oleate iron complexes.
- *Zincates, $Na[Zn(OH)_3]$ and $Na_2[Zn(OH)_4]$* are used as sphalerite depressants during copper–zinc and lead–zinc flotation. This reagent can be prepared by reacting $ZnSO_4$ with excess NaOH as per the following reactions:

$$ZnSO_4 + 3NaOH = Na[Zn(OH)_3] + Na_2SO_4$$

$$ZnSO_4 + 4NaOH = Na_2[Zn(OH)_4] + Na_2SO_4$$
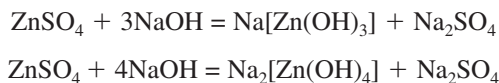
It has been reported [7] that zinc hydroxides are effective zinc depressants during flotation of copper–zinc ores.

- *Aluminum Sulfate ($Al_2(SO_4)_3 \cdot 12H_2O$)* is a white powder, highly soluble in water. Reacting kaolin or nepheline with sulfuric acid can obtain aluminum sulfate. Aluminum sulfate is primarily used in non-metallic flotation and in by-product molybdenum circuits. In molybdenum circuits, alum is used for depression of talc at pH 7. Also it can be used for talc depression during the treatment of talcous nickel ores together with carboxyl methyl cellulose. Aluminum salts have a depressing effect on calcite, dolomite and barite. It is used as co-depressant during fluoride flotation from the ores containing barite.
- *Aluminum chloride ($AlCl_3$)* can be obtained by reacting carbon dioxide and chlorine with kaolin at high temperatures. It is highly hygroscopic with a specific gravity of 2.3. It is highly soluble in water and in organic solvents. Similar to aluminum sulfate, aluminum chloride is used as a co-depressant for calcite, fluorite and dolomite.
- *Ammonium sulfate ($(NH_4)_2SO_4$)* is a white, crystalline salt obtained by reacting ammonia and sulfuric acid. This compound is used as a depressant for sphalerite during flotation of complex copper–lead–zinc ores. In plant practice, it is used in a number of concentrators in Mexico, specifically the San Martin operation, treating Cu–Pb–Zn ores containing pyrrhotite [8]. Ammonium sulfate also improves floatability of copper and lead using xanthate collector at pH 7.5–9.0.
- *Ammonium sulfide ($(NH_4)_2S$)* is a liquid with an obnoxious odor and because of this, it is not normally used in mineral processing. However, this is the most effective depressant for bornite and covellite. Essentially, $(NH_4)_2S$ dissolves excess sulfur from the mineral surface, that allows other depressants to adsorb onto the mineral surface. In copper–lead separation, from a bulk concentrate containing covellite and bornite, $(NH_4)_2S$ can effectively be used together with cyanide.
- *Barium chloride ($BaCl_2 \cdot 2H_2O$)* is a colorless, white powder highly soluble in water (25% at 10 °C). It is quite a toxic reagent. Barium chloride is used during borite flotation as an activator. Barium chloride also has a depressing effect on fluorite and cassiterite.
- *Sodium sulfide ($Na_2S \cdot 9H_2O$)* is a hygroscopic substance with a specific gravity of 1.864 and a melting temperature of 1180 °C. The reagent is soluble in water. The aqueous solution of sodium sulfide has a highly alkaline reaction resulting from its hydrolysis:

$$Na_2S + H_2O \rightleftharpoons NaOH + NaHS$$
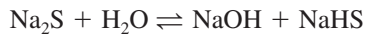
The 0.1 normal solution of Na_2S at 25 °C temperature has a degree of dissociation of 86.69%. In the presence of oxygen, sodium sulfide slowly oxidizes to form thiosulfate as per this reaction:

$$2Na_2SO + 2O_2 \rightleftharpoons Na_2S_2O_3 + 2NaOH$$

As a reagent, sodium sulfide is widely used in both sulfide and non-metallic mineral flotation. Some of the roles of sodium sulfide include:

1. A sulfidizing reagent for metallic copper, oxide copper, lead and zinc minerals.
2. A depressant during selective flotation of copper–lead–zinc and copper–zinc ores. Na_2S is a selective depressant when used in conjunction with other sulfur-containing depressants [9] (i.e. Na_2SO_3, $Na_2S_2O_5$).

3. For desorption of collectors during copper–lead and copper–molybdenum separation.
4. As a dispersant during flotation of ores containing ultra-fine slimes (i.e. <5 μm).

In non-metallic flotation, sodium sulfide is also used as a depressant and for collector desorption, in particular, fatty acids from monazite, pyrochlore, zircon and microcline. As a depressant for quartz, sodium sulfide is an excellent depressant for iron-activated quartz as well as non-activated quartz [10].

- *Sodium hydrosulfide (NaHS)* is stable only in solution. When in contact with oxygen (air), it slowly oxidizes. If a solution of NaHS is heated, it is converted into Na_2S and H_2S.

$$2BaHS \xrightarrow{\text{heat}} Na_2S + H_2S\uparrow$$

The solubility of NaHS in water at 20°C is 42%. Commercial quantities of NaHS are obtained by reaction of sodium sulfide with caustic soda or with H_2S gas.

$$Na_2S + NaOH = NaHS + H_2O$$

$$Na_2S + H_2S = 2NaHS$$
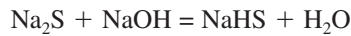
Sodium hydrosulfide can be used as a replacement for $Na_2S\cdot9H_2O$ during sulfidization of oxide minerals. Sodium hydrosulfide in solution has a much lower alkalinity than Na_2S.

Although the performance of NaHS is not the same as for Na_2S, it is used because of its cost-effectiveness.

Sulfur–oxygen compounds

In most of the important S–O compounds, sulfur appears as either S^{4-} or S^{6-}, as in SO_2 or SO_3. In the thiosulfuric acid, the two sulfur atoms have different valences, II and VI (Table 4.3).

Sodium sulfite (Na_2SO_3), thiosulfate ($Na_2S_2O_3$)

These represent an important group of flotation reagents. They are present naturally in almost all massive sulfide ores after grinding, as a result of partial oxidation.

Sulfites and thiosulfates have the capabilities of forming stable complexes with many metals and are strong reductants.

Sulfite ion (SO_3^{2-})
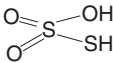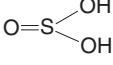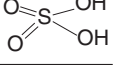
This forms complexes with Mn, Fe, Co, Ni, Pd, Cu, Ag, Au, Zn and Hg. The complexes can be bonded in different ways [11] through oxygen and sulfur as shown in Figure 4.2.

Thiosulfate ion ($S_2O_3^{2-}$)

This ion forms strong complexes with monovalent ions Cu^+, Ag^+ and Au^+; divalent Cu^{2+} is reduced to Cu^+ complex. Alkaline thiosulfate solution dissolves many insoluble salts of

Table 4.3

Oxides and acids of sulfur

Valency	Oxide	Formula	Acid	Formula
II	SO	H_2SO_2	Sulfuryl	$S{\scriptsize<}^{OH}_{OH}$
II,VI	S_2O_3	$H_2S_2O_3$	Thiosulfuric	$O{=}S{(=}O)^{OH}_{SH}$
IV	SO_2	H_2SO_3	Sulfurous	$O{=}S{<}^{OH}_{OH}$
VI	SO_3	H_2SO_4	Sulfuric	$O{=}S{(=}O)^{OH}_{OH}$
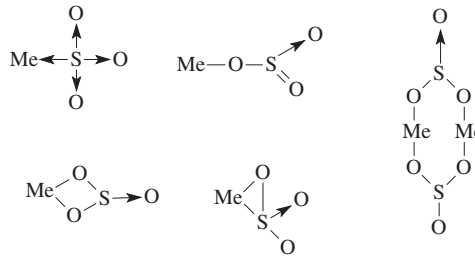
Figure 4.2 Different modes of Me (metal) bonding through O (oxygen) or S (sulfur) in complexes with sulfite ions [10].

Pb^{2+}, Hg^{2+}, Cu^+ and Ag^+. The monovalent complexes are mostly S-bonded, while the divalent ones may be S^- or O^- bonded. In mineral processing, sodium sulfite (Na_2SO_3) and metabisulfite ($Na_2S_2O_5$) are the most widely used compounds. Na_2SO_3 is used in conjunction with either lime or Na_2S for depression of pyrite during flotation of copper–zinc ores. The depressing effect of Na_2SO_3 is pH-related [12]. $Na_2S_2O_5$ is a depressant for pyrite and galena during selective flotation of Cu–Pb–Zn ores. It is used in many operating plants.

Lead nitrate ($Pb(NO_3)_2$)

This is a white to colorless fine crystalline compound, extremely soluble in water (34% at 20 °C). Commercial production is based on dissolution of lead metal or lead compounds in nitric acid (36–40% solution). Lead nitrate is considered to be an activator in mineral processing. Although lead may activate sphalerite, similar to $CuSO_4$, the use of $Pb(NO_3)_2$ is limited to the activation of stibnite during beneficiation of antimony ores. Lead nitrate is the most widely used chemical in cyanidation of precious metals as an accelerator.

Potassium permanganate ($KMnO_4$)

This is a crystalline substance with a deep purple color, extremely soluble in water (60 g/L). At a temperature above 200 °C, $KMnO_4$ decomposes according to the following reaction:

$$2KMnO_4 \overset{Heat}{\rightleftharpoons} K_2MnO_4 + MnO_2 + O_2$$

Reduction of $KMnO_4$ is rapid and is related to pH:

(a)   In acid medium,

$$5K_2SO_3 + 2KMnO_4 + 3H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 3H_2O$$

(b)   At neutral pH,

$$3K_2SO_3 + 2KMnO_4 + H_2O = 3K_2SO_4 + 2MnO_2 + 2KOH$$

(c)   In alkaline medium,

$$K_2SO_3 + 2KMnO_4 + 2KOH = K_2SO_4 + 2K_2MnO_4 + H_2O$$
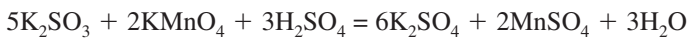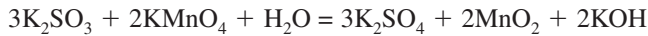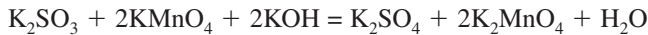
Potassium permanganate has a depressing effect on most sulfide minerals including sphalerite, pyrrhotite and chalcopyrite. It has been used to depress pyrrhotite and arsenopyrite in a pyrite flotation alkaline circuit. Studies were carried out on the depression of copper in copper–molybdenite separation with promising results. There is very little known about the depressing action of $KMnO_4$ in relation to pH.

Dichromate ($K_2Cr_2O_7$, $Na_2Cr_2O_7$)

This is an orange, crystalline substance with a specific gravity of 2.68. Solubility in water is 11.7% at 20 °C. Both potassium and sodium dichromate are used in mineral processing. Dichromate solutions have an acid reaction because $Cr_2O_7^{2-}$ ion reacts with water as follows:

$$H_2O + Cr_2O_7^{2-} \rightleftharpoons HCr_2O_4^- + H^+ + CrO_4^-$$

Salts of chromic acid in acid medium are oxidants (Cr^{4+} changes to Cr^{3+}). In principle, dichromates are used in selective separation of copper–lead bulk concentrates, usually in acid pH. A mixture of sodium dichromate and sodium silicate has shown to be an excellent lead depressant during copper flotation from a bulk copper–lead concentrate containing secondary copper minerals [13].

Cyanide compounds

Cyanides are compounds that contain a monovalent CN group as an active ion. In the mineral processing practice, NaCN, KCN and ferro cyanides are used. Most of the simple cyanide compounds have good solubility in water and give highly alkaline reaction.

Commercially, sodium cyanide is produced from calcium cyanamide, carbon and sodium chloride as per the following reactions:

$$Ca(CN)_2 + C + 2NaCl = 2NaCN + CaCl_2$$

$$Ca(CN)_2 + C + Na_2CO_3 = 2NaCN + CaO + CO_2$$
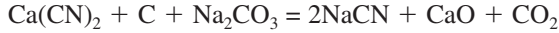
Ferro cyanide and *ferri cyanide* also belong to a group of cyanide compounds with limited application in mineral processing. These reagents are strong copper and iron sulfide depressants in the pH range 6.5–8.5. They are preferably used in separating copper from copper–lead concentrates when secondary copper minerals are present and for depression of iron sulfides during nickel–cobalt separation.

Sodium zinc cyanide complex [Na_2Zn(CN)_4] is produced by mixing ZnO with excess sodium cyanide. Cyanide (NaCN and KCN) is widely used in flotation of polymetallic sulfide ores as a depressant for sphalerite during copper–zinc, lead–zinc and copper–lead–zinc, and as depressant for copper during copper–lead separation. Cyanide is also used to depress pyrite and nickel during copper/nickel separation.

Sodium zinc cyanide complex is used for depression of copper in a copper–molybdenum separation. When chalcocite or covellite is present, the sodium zinc cyanide complex is used as a replacement for sodium cyanide. Secondary copper minerals are strong cyanide consumers but react slowly with $Na_2Zn(CN)_4$.

Sodium fluoride (NaF)

Sodium fluoride is a white to yellowish powder, poorly soluble in water. The NaF solubility in water is 3.85% at 15 °C and 4.21% at 25 °C. Commercially, NaF is obtained by reacting hydrofluoric acid with sodium hydroxide. This reaction is a by-product during the production of superphosphates from fluoro-apatite. Sodium fluoride is an important depressant used exclusively during beneficiation of non-sulfide minerals, as well as the rare-earth minerals as a depressant alone or in combination with other depressants. It is used together with starch as co-depressant for rutile and ilmenite during zirconium–titanium separation or during reverse silicate flotation from rutile and ilmenite with cationic collectors. Although it is believed that Na_2F is a silicate depressant, studies have shown that it does not depress silicate minerals [14]. In fact, it improves depression of oxides and silicates when used with other depressants.

Sodium and potassium fluorosilicate (Na_2SiF_6, K_2SiF_6)

Potassium fluorosilicate is a white to yellowish powder, poorly soluble in water (0.68% at 20 °C). Because of its poor solubility, it is not commonly used as a modifying reagent. Na_2SiF_6 is a white, isomorphous powder. Solubility in water is similar to that of NaF. In acid pH, solubility improves.

Commercially, Na_2SiF_6 is produced by treatment of fluorosilic acid with sodium chloride, as shown in the following reaction:

$$H_2SiF_6 + 2NaCl = Na_2SiF_6 + 2HCl$$
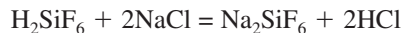
Dried Na_2SiF_6 contains 93–98% Na_2SiF_6. The Na_2SiF_6 is a depressant for silicates, specifically topaz, tourmaline and some aluminosilicates. It is used in the separation of

rutile from zircon, pyrochlore from zircon, cassiterite and tantalite and during flotation of cassiterite for depression of topaz, tourmaline and aegirine. In aqua solution, Na_2SiF_6 hydrolyzes as follows:

$$Na_2SiF_6 \rightleftharpoons 2Na^+ + SiF_6^{2-}$$

$$SiF_6^{2-} \rightleftharpoons SiF_4^- + 2F^-$$

$$SiF_4 + 3H_2O \rightleftharpoons H_2SiO_3 + 4HF$$
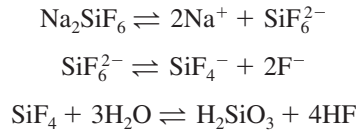
Sodium silicate

Sodium silicate (liquid silicate, metso or sodium silicate beads) has the general formula Na_2SiO_3. The liquid silicates ("O" and "N" brand) are clear, thick liquids, while silicate powder is a granular, white substance. Sodium silicate is a mixture of sodium or potassium salts. Sodium silicates are primarily used in mineral flotation practice. Sodium silicate generally consists of metasilicate (Na_2SiO_3), dimetasilicate ($Na_2Si_2O_5$) and orthosilicate (Na_4SiO_4). The chemical composition of sodium silicate can be expressed by the general formula mNa_2O $nSiO_2$. The ratio n/m is referred to as the modulus of sodium silicate and is very characteristic. Silicates whose modulus varies from 2.2 to 3.0 are frequently used in mineral flotation. Sodium silicates with lower modulus form a strongly alkaline pulp and have weak depressing effect, whereas the modulus of water-insoluble sodium silicates exceeds 3.0. Sodium orthosilicate, $2Na_2O \cdot SiO_2$, contains the maximum amount of Na_2O, while the amount of Na_2O decreases from metasilicate, $Na_2O \cdot SiO_2$, to sodium disilicate, $NaHSiO_2$ or Na_2SiO_5.

The dissolution process of sodium silicate is very complex. The dissolution process starts with the dissolution of Na_2O where only a small amount of silicate is dissolved and, subsequently, the residual swelled silica gel is dissolved with only a small amount of the remaining alkali. Therefore, the dissolution of silicate is actually comprised of hydration of sodium silicate with the formation of NaOH, followed by dissolution of sodium silicate and dissociation. At the end, the residual silicate is peptized by the strongly alkaline solution.

Sodium orthosilicate hydrolyzes in aqueous solution according to the formula:

$$Na_4SiO_4 + H_2O \rightarrow 2NaOH + Na_2SiO_3$$
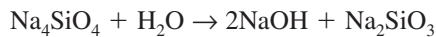
Sodium disilicate is less water-soluble than monosilicate and therefore hydrolyzes less. The hydrolytic dissociation is quite strong with sodium metasilicate:

$$Na_2SiO_3 + H_2O \rightleftharpoons NaHSiO_3 + NaOH$$
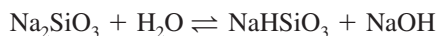
The concentration of OH^- ions increases considerably with dilution of sodium silicate. For this reason, the procedure for the preparation of sodium silicate for use in flotation should be standardized Usually, concentrations in the range 2–5% are recommended because at these concentrations, the sodium silicate solution is most stable.

The bulk of the silica in the aqueous solution of mono and disilicate exists in colloidal form. However, solutions of tri- and tetrasilicates contain complexes of mono and disilicates with an excess of SiO_2 or hydrated silica.

Sodium silicate is widely used in mineral flotation as depressant, dispersant and as controlling agent of some soluble ions For example, sodium silicate interacts with calcium ions in solution forming nearly insoluble calcium silicate [15]. For industrial and sulfate-type minerals (barite), sodium silicate is usually part of the reagent scheme. Sodium silicate is extensively used in base-metal flotation.

Salts of phosphoric and polyphosphorus acids

Different salts of phosphoric and polyphosphoric acids are used in flotation. From this fairly large family of reagents, sodium phosphate is the preferred species. Mono- and disodium phosphates are rarely used.

(a)   Trisodium phosphate, $Na_3PO_4 \cdot 12H_2O$, is a white, crystalline substance highly soluble in water. Neutralizing phosphoric acid with soda ash produces trisodium phosphate. The resulting disodium phosphate is treated with sodium hydroxide to produce trisodium phosphate as per the following reaction:

$$H_3PO_4 \xrightarrow{Na_2CO_3} Na_2HPO_4 \xrightarrow{NaOH} Na_3PO_4$$

During dehydration of sodium orthophosphate, metaphosphate and polyphosphate are produced. Metaphosphate has the general formula $Me_n(PO_3)_n$, where $n = 3$ or 4 (tri- and tetrametaphosphate). Metaphosphate has the characteristic branched structure as shown below:

Tetrametaphosphate
$P_4O_{12}^{-4}$

Hexametaphosphate
$P_6O_{18}^{-6}$
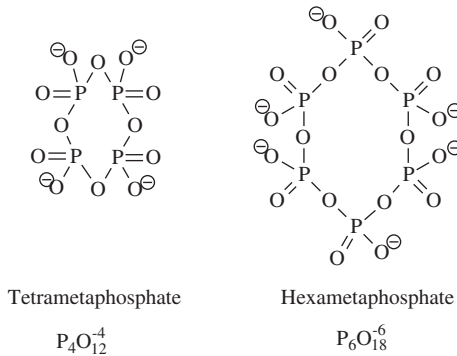
These two phosphates are the most important regulators. In solution, metaphosphates have a neutral reaction and they are relatively stable at room temperature. At an elevated temperature, around 60 °C, they hydrolyze to orthophosphate. In an alkaline solution, they decompose to polyphosphates.

(b)   Sodium trimetaphosphate, $Na_3[P_3O_9]$, is the most stable compound of this group of reagents. The hydrated form of sodium trimetaphosphate contains 6 or 10 molecules of water of crystallization. Commercial production is obtained by heating $NaPO_3$ at 525 °C. Sodium hexametaphosphate (SHMP) or water glass $Na_6P_6O_{18}$ is basically

the salt of metaphosphoric acid. SHMP is difficult to dissolve. By mixing SHMP for 1–3 h, a solution of 8–10% can be obtained. The pH of this solution is about 5. Because of a weak acid reaction, the SHMP reacts with cations of bivalent metals forming $Na_2MeP_6O_{18}$ or $Na_4MeP_6O_{18}$. In the presence of oxygen, SHMP slowly decomposes into pyrophosphate and orthophosphate.

Polyphosphates

These reagents have a general formula $Me_{n+2}P_nO_{3n+1}$ or $Me_nP_nO_{3n+1}$, where n can be between 1 and 10^6. The major characteristics of the reagents from this group are the negatively charged (PO_4^{3-}) ion and the connection with an oxygen bridge. For example, sodium tripolyphosphate $Na_5[P_3O_{10}]$ has the following configuration:

$$
\begin{array}{ccccccc}
& O & & O & & O & \\
& \| & & \| & & \| & \\
NaO- & P & -O- & P & -O- & P & -ONa \\
& | & & | & & | & \\
& ONa & & ONa & & ONa &
\end{array}
$$
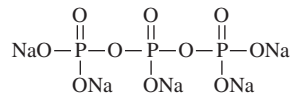
Representatives of the polyphosphate group are:

(a) Sodium pyrophosphate $Na_4P_2O_7$, obtained by degradation of disodium phosphate at a temperature of 350–400 °C.
(b) Acid sodium pyrophosphate $Na_2H_2P_2O_7$, obtained by degradation of monosodium phosphate at a temperature of 225–250 °C.
(c) Mono-ammonium phosphate $NH_4H_2PO_4$, a crystalline compound with specific gravity of 1.3. Commercially, $NH_4H_2PO_4$ is produced by reacting phosphoric acid with ammonia followed by centrifuging and drying.

Polyphosphates have a number of functions in mineral flotation practice, some of which include:

• Precipitation of heavy metal ions. Polyphosphates are used in the flotation of base-metal ores where control of heavy metals is required.
• Depressing of iron sulfides and alkaline earth minerals during flotation of copper–molybdenum ores. Some of the phosphate compounds are used as gangue depressants during pyrochlore flotation and also during flotation of phenacite and bertrandite.

4.4 ORGANIC MODIFIERS

Organic modifiers may be classified into two main groups: *organic polymers* and *organic acids*. The organic polymers are a fairly large group of organic compounds with complex structures, some of which have not yet been classified. They represent an important group of modifiers used in the flotation of both sulfide and non-sulfide minerals. Only a few of organic acids are used in mineral flotation. Some of these acids (i.e. lactic acid) are capable of forming soluble inner complexes and could therefore be classified as chelating modifiers.

4.4.1 Organic polymers

As mentioned earlier, organic polymers can be divided into four major groups according to the character of their polar group. The representatives of each of these four groups of polymers are listed in Table 4.4.

However, polymers can undergo many modifications, so the above classification can only be loosely applied. For example, modified starches can assume either non-ionic or cationic characteristics and by reacting quebracho with certain amines the polymer can become amphoteric.

The use of organic polymers in mineral flotation is closely related to the composition of the polymer. Certain polymers can be used as dispersants, flocculants and depressants. In contrast, starches can be used as depressants but some starches from the same group do not show any depressing ability.

A mixture of organic polymers has shown improved depressing action. A typical example Agent G4 (a mixture of quebracho, dextrin and surfactant) has been used for many years in the Mount Isa Hilton concentrator to perform as a modifier. Chemical composition and structure are very important properties.

Table 4.4

List of organic polymer representatives of the four major groups

Group	Polymer	Active polar group
Non-ionic	Starches, dextrins, gum arabic, tannin derivatives, oxycellulose, polyvinyl alcohol	$-OH$, $=CO$
Cationic polymers	Polyvinyl amine, polyamine substituted dithiocarbamate. Amino acids: γ-amino butyric acid, β-alamine, ethylene diamine, diethylene triamine, 2-(2-hydroxyethyl) piperazin	$-NH_2$, $=NH$
Anionic polymers	Carboxymethyl cellulose, alginic acids, cellulose gums, guar gums, polyacrylates, modified lignin sulfonates	$-COOH$ $-SO_3H$ $-OSO_3H$
Amphoteric	Animal glue, amine-treated quebracho	Anionic + cationic groups

Chemistry of the more important organic polymers used in mineral flotation

The chemistry of organic polymers is the most complex of all reagents used in flotation. Certain polymers such as starches, dextrins or modifications of lignin sulfonates and Quebracho are of undefined chemical composition. For example, about 75 different types of starches and over 120 dextrins exist and many have chemical structures that are highly questionable [16]. However, in working with polymers it is important to know at least the general chemistry of the particular polymer and the way the polymer was manufactured. The general chemistry of the most important polymers is described in the following section.

Nonionic polymers

The representatives of this group of polymers most widely used in flotation are starches, dextrins, tannic acid derivatives and oxycellulose. Ordinary starch consists largely of glucopyranose units formed by α-(1–4) linkages as shown in Figure 4.3 and can have a molecular weight of up to 150,000. The glucopyranose unit consists of two main fractions, the insoluble fraction, amylose, and soluble fraction, amylopectin. In general, amylopectin has a branched point structure and can differ according to the sources from which starch is obtained. In addition, the ratio of amylose and amylopectin is never constant. It is neither amylose nor amylopectin that determines whether the starch is usable in flotation but the various modifications introduced during manufacture, accidentally or intentionally. The aldehydic and alcoholic terminals in the starch structure are responsible for various modifications of starches. For example, the degree of starch oxidation [17] and type of oxidant determines the functionality of the starch.
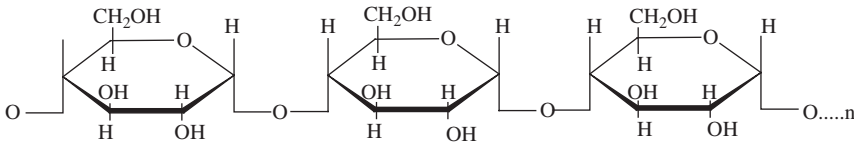
Figure 4.3 General structures of starch.

Dextrins are water-soluble polysaccharides. They are intermediate products resulting from the hydrolytic breakdown of the starch. Solubility in water depends on process parameters such as temperature, retention time and acidity. Structural changes that take place are difficult to determine but it is known that dextrins have a shorter chain length and branched molecules [18].

The most common tannic acid derivative widely used in flotation is Quebracho. The main phenolic nuclei present in Quebracho are resorcinol/phloroglucinol and catechol/pyrogallol of the structure shown in Figure 4.4.

where n = 1 to 200
and molecular weight
is 200 to 50,000
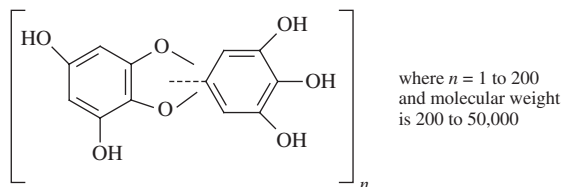
Figure 4.4 Quebracho structure.

Quebracho is commercially available in the following three forms: (a) standard Quebracho, a direct hot-water extract from the heart-wood with adjusted pH (Qu–O), (b) sulfited Quebracho, in which sulfonic acid groups have been introduced (Qu–S) and (c) aminated Quebracho (Qu–A), where amine groups are introduced to ordinary Quebracho, rendering the polymer amphoteric (iso-electric point at pH 7). Each of these types of Quebracho has a different depressing effect.

Oxycellulose is the reaction product of alkyl cellulose and ethylene oxide (Figure 4.5).

$$[C_6H_7O_2(OH)_2OCH_2CH_2OH]n$$
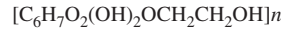
Figure 4.5 Oxycellulose structure.

The effectiveness of oxycellulose as depressant [19] depends on the degree of esterification and polymerization.

Anionic polymers

The most widely used polymers in mineral flotation from this group are carboxymethyl cellulose, cellulose gum and lignin sulfonates. Polyacrylates are the newest group of polymers, which have limited application. Carboxymethyl cellulose (Figure 4.6) is obtained by reaction of monochloroacetic acid or its sodium salts with alkali cellulose.
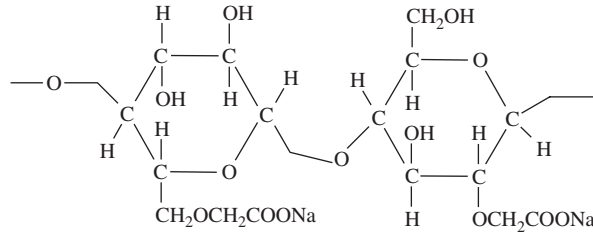
Figure 4.6 Carboxymethyl cellulose.

Carboxymethyl cellulose is manufactured with molecular weights ranging from 50,000 to 800,000. Several modifications are of interest to flotation because they display good depressing properties for highly floatable magnesium-bearing minerals. These include sodium salts of phenolphthalein ether cellulose (Figure 4.7) and ethanesulfo cellulose (Figure 4.8).
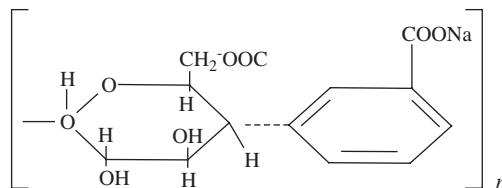
Figure 4.7 Phenolphthalein ether cellulose.
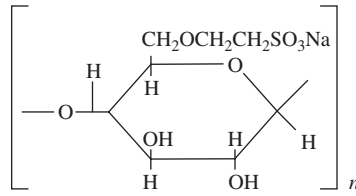
Figure 4.8 Ethanesulfo cellulose structure.

Guar gums are derived from corn starch in which hydroxyethyl groups have been chemically substituted for a very small number of hydroxyl groups (Figure 4.9). There is a series of these products available, all of which depend on the degree of substitution and type of starch used.
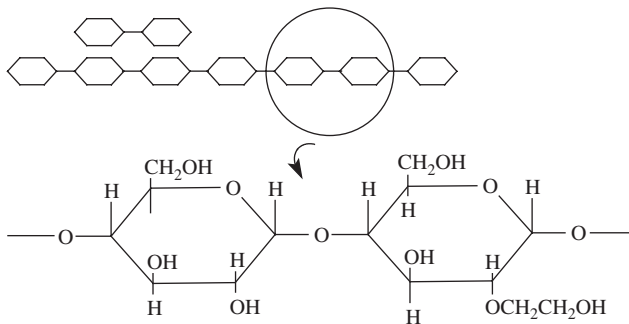
Figure 4.9 Typical structure of guar gum.

Alginic acids are another group of polymers that did not find application in sulfide mineral flotation because of poor solubility and unstable composition. There are reports, however, that alginic acid showed excellent depressing effect on hydrophobic calcium minerals. The molecule of polyalginic acid is shown in Figure 4.10.
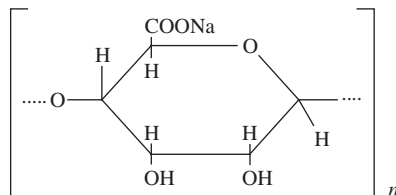
Figure 4.10 Polyalginic acid structure.

Another important anionic polymer is lignin sulfonate, which is used as dispersant, flocculant and depressant. Lignin is an amorphous polyphenolic compound derived from enzymatic polymerization of three phenylpropanoid monomers shown in Figure 4.11.
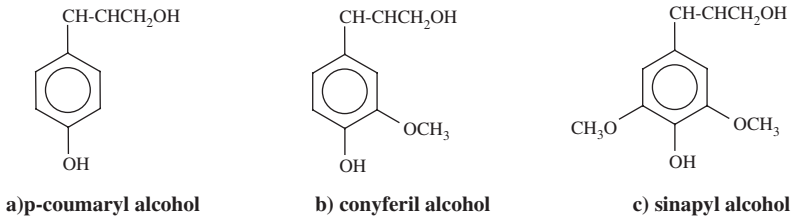
Figure 4.11 Monomers of lignin sulfonates: (a) p-coumaryl alcohol, (b) coniferyl alcohol and (c) sinapyl alcohol.
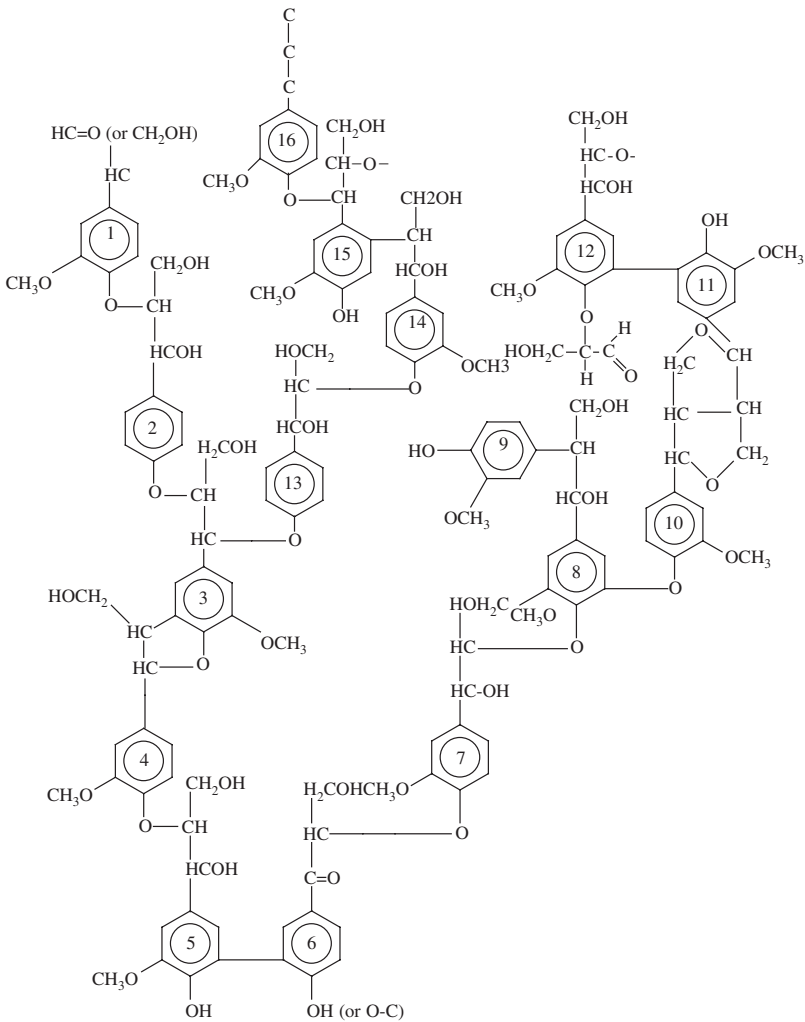
Figure 4.12 Structural model of lignin (short form).

The biosynthesis process, which consists essentially of radical coupling reactions, sometimes followed by additions of water, leads to the formation of three-dimensional polymers.

The simplest structural formula of lignin sulfonate is shown in Figure 4.12.

In practice, there are about 60 different types of lignins of interest; these are lignins with a molecular weight between 15,000 and 100,000 and are sugar free. The depressing effect of a specific lignin can be significantly improved when lignin is treated with a surfactant [20].

Low-molecular-weight acrylic acids and their derivatives are the newest polymers used in sulfide mineral flotation. These are mainly sodium salts of acrylic acid with a structural formula shown in Figure 4.13.

$$\cdots\!-\!CH_2\!-\!CH\!-\!CH_2\!-\!CH\!-\!CH_2\!-\!CH\!-\!\cdots$$

$$\underset{COONa}{|}\qquad\underset{COONa}{|}\qquad\underset{COONa}{|}$$
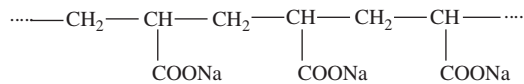
Figure 4.13 Sodium acrylate structure.

The newest member of the acrylic-based polymer is synthesized by Cytec [21] with the formula shown in Figure 4.14.

$$\left[\!-\!\left(CH_2\text{ - }CH\right)_{\!90}\!\left(CH_2\text{ - }CH\right)\!-\!\right]$$

$$\underset{C=O}{|}\qquad\qquad\underset{C=O}{|}$$
$$\underset{NH_2}{|}\qquad\qquad\underset{NH}{|}$$
$$\qquad\qquad\qquad\underset{CH_2}{|}$$
$$\qquad\qquad\qquad NH(CH_2)_2CH_3$$
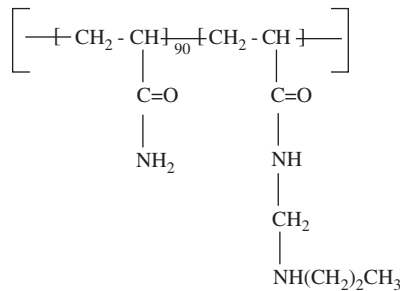
Figure 4.14 Structural formula of acrylic acid polymeric depressant.

This polymer was successfully used as pyrrhotite depressant during copper–nickel bulk flotation.

Cationic polymers

The most important groups of the cationic polymers that are used in mineral flotation include:

(a)   Ethylenediamine with the formula indicated in Figure 4.15.

$$H_2N\text{ - }C_2H_4\text{ - }NH_2$$

Figure 4.15 Ethylenediamine.

(b)   Diethylenetriamine (DETA; Figure 4.16)

$$H_2N - C_2H_4 - NH - C_2H_4 - NH_2$$
Figure 4.16 DETA.

(c)   Polyamines substituted dithiocarbamate with the formula shown in Figure 4.17.

$$\begin{array}{cc} R_2 & S \\ | & || \\ [R_1 - N - R_3 - NH - C - S]_X - M \end{array}$$
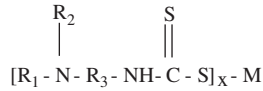
where R_1 and R_2 are amino ethyl group and R_3 hydrocarbon group

Figure 4.17 Polyamine substituted dithiocarbamate

(d)   Amino acids such as β-alamine; $NH_2-(CH_2)_3-COOH$ and γ-amino butyric acid; $NH_2-(CH_2)_2-COOH$.
The application of amino oxides as depressants for pyrite has also been investigated.

4.4.2   Organic acids − carboxylates

Organic acids have been used as gangue depressants during flotation of ores containing oxidic minerals. The most widely used organic acids are listed below:

a) Oxalic Acid
$$\begin{array}{c} COOH \\ | \\ COOH \end{array}$$

c) D-TartaricAcid
$$\begin{array}{c} HOCHCOOH \\ | \\ HOCHCOOH \end{array}$$

b) Citric Acid
$$\begin{array}{c} CH_2COOH \\ | \\ HO - C - COOH \\ | \\ CH_2COOH \end{array}$$
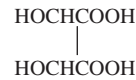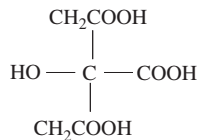
These acids have been used in the following applications:

•   During the flotation of niobium as a silica, dolomite depressant and as pH regulator (oxalic acid).

- During niobium/zirconium separation from bulk concentrate as a zirconium depressant (oxalic, citric acid)
- During flotation of rare-earth oxides (bastnaesite, monazite) as gangue depressant (citric, tartaric acid).

Oxalic acid has been tried as a pyrrhotite depressant. Other organic acids, which have shown good depressing action of different silicates and aluminosilicates but have not been industrially tested, are given below

a) Mucic Acid

$$HOCHCOOH$$
$$|$$
$$HO - C - H$$
$$|$$
$$HO - C - H$$
$$|$$
$$HO - CHCOOH$$

b) Succinic Acid

$$CH_2COOH$$
$$|$$
$$CH_2COOH$$

c) Glutaric Acid

$$CH_2COOH$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2COOH$$

d) Adipic Acid

$$CH_2COOH$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2$$
$$|$$
$$CH_2COOH$$
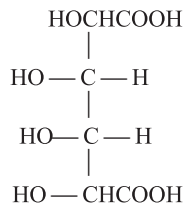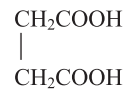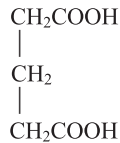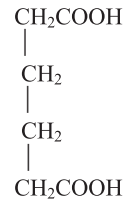
Organic acids that contain the $-OH$ group in the molecule (i.e. citric, tartaric and mucic acids) are good dispersants for some oxidic minerals such as cassiterite, tantalite and columbite [22]. Organic acid with $-OH$ groups have also shown good depressing effect on iron sulfides when used alone or in combination with ammonium salts [23].

4.5   CHELATING COMPOUNDS AS MODIFIERS/GANGUE DEPRESSANTS

Some chelating compounds are capable of complete bonding of the activating cations into undissociable, hydratable inner complexes. Such chelating reagents are capable of depressing some gangue minerals (i.e. silicates and aluminosilicates) [24].

It is believed that these chelates react with ions in solution pulp (i.e. calcium, magnesium iron) and form undissociated complexes that prevent activation of minerals. Their structure must embody two classes of functional groups resulting in a chelate ring closure by reaction with an ion.

Table 4.5

Organic compounds that form soluble or hydrophilic inner complexes [24]

Organic compound yielding soluble or hydrophobic chelate	Corresponding chelate (example)	Salt-forming group	Complex forming group	Reactive grouping feature	Hydrophilic group or
2 Aminoethanol					
H₂N–CH₂–CH₂–OH (structure)	structure with Ag	$-NH_2$	$-OH$	$N-C-C-OH$ (with H_2, H_2, OH)	Short carbon chain (2 C) one hydroxyl group intact
Sulfuric acid	structure (COOH, OH, HO₃S ring with Fe/₃)	$-COOH$	$-OH$	$O-C-C-C-OH$ (with OH, OH)	$-SO_3H$
Lactic acid	structure (H–C–H, H–C–OH, COOH with Fe/₃)	$-COOH$	$-OH$	$O=C-C-OH$ (with OH)	Short carbon chain, one hydroxyl group intact

Dilsonitroso acetate
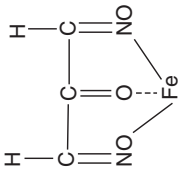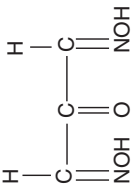
Quinolinic acid
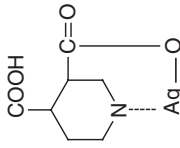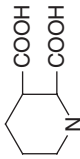
Guanylurea
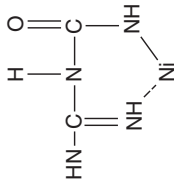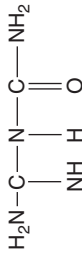
Short carbon chain, carbonyl group intact
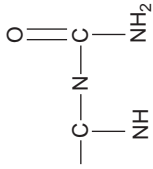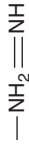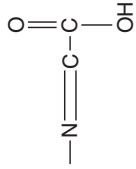
Typical examples of organic compounds forming soluble or hydrophilic inner complexes are shown in Table 4.5. The use of these reagents as depressants is not new. They have been examined in a number of studies [25,26] with positive results. For example, lactic acid showed good depressing effect on hornblende, pyroxene and biotite during flotation of hematite and ilmenite minerals. The use of quinolinic acid during flotation of hematite results in the adsorption of quinoline on hematite, allowing amine to selectively adsorb onto the hematite surface.

REFERENCES

1. Laskowski, J.S., and Pugh, R.J., Dispersion Stability and Dispersing Agents, *Colloid Chemistry in Mineral Processing*, Vol. 12, 1992.
2. Bulatovic, S.M., and Wyslouzil, D.M., *Process Development for Treatment of Complex Perovskite, Ilmenite and Rutile Ore*, Elsevier, 1998.
3. Polkin, C.A., *Beneficiation of Ores Containing Rare, Oxidic and Gold Containing Minerals*, 2nd edn., Nevada, 1987.
4. Shirley, J.F., Inorganic dispersant, In (D. Malhotra and W.F. Riggs eds) *Inorganic Depressants Chemical Reagents in Mineral Processing Industry*, SME 1986.
5. Draskic, D., Cyanide Depression of Naturally Floating Sphalerite in the Presence of Ferrous Ions, In (M.J. Jones ed) *Complex Sulphide Ores*, IMM, October 1980.
6. Konev, B.A., Separation of Copper-Zinc Sulphides, *Gornii Journal*, No. 11, pp. 66–73, 1973.
7. Bulatovic, S.M., *Plant Improvement Studies at San Martin Concentrator, Mexico*, Report of Investigation LR-4670, April 1996.
8. Shchekalva, R.N., and Podnek, A.K., Cyanide-Free Flotation of Copper-Zinc Ores from the Rarabash Deposit, *Tsvetnie Metaly*, No. 6, pp. 31–39, 1975.
9. Polkin, C.I., *Processing Practices of Non-metallic and Rare Earth Ores*, 2nd edn, Nedra, Moscow, 1987.
10. Leja, J., *Surface Chemistry of Froth Flotation*, Plenum Press, New York, 1982.
11. Veishinin, E.A., Cyanide-Free Flotation of Copper-Zinc Ore from the Uchalinsk Deposit, *Tsvetnie Metaly*, Vol. 10, pp. 120–125, 1969.
12. Bulatovic, S.M., New Copper-Lead Separation Process, US Patent 4,246,096, January 1981.
13. Eigeles, M.A., *Regulating Reagents in Mineral Processing*, Nedra, Moscow, 1977.
14. Basmanov, Y.A., Use of Sodium Silicate in Mineral Flotation, Concentration of Mineral Ores (Papers), *Goskhimizdat*, September 1950.
15. Radley, J.A., *Starches and Their Derivatives'*, 4th edn, Chapman & Hall, pp. 282–354, 1968.
16. Bulatovic, S.M., An Investigation of Different Starches as Iron Depressants During Amine Silica Flotation, Report of Investigation, 256pp., 1977.
17. A.E. Stately Manufacturing Company, Starches and Their Derivatives, Bullit. 217/423-44-11.
18. Gorlovskii, C.I., High Molecular Weight Organic Compounds as Flotation Depressants, *Obogashenie Rud*, No. 6, pp. 26–33, 1956.
19. Roberts, D., US Patent 3,844,412, October 1974.
20. Bulatovic, S.M., Wyslouzil, D.M., and Rawling, K.R., Laboratory and Plant Evaluation of New Organic Depressant DS20 for Treatment of Nanisivic Massive Lead-Zinc Sulphide Ore, Conference of Metallurgist, Ottawa, Canada, 1986.
21. Rothenberg, A.S., and Lip, D.W., Polymeric Sulphide Mineral Depressants, US Patent 4,744,893, pp. 346–366, May 1988.

22. Parsonage, P., and Marsden, A., The Influence of Structure of Reagents and Their Effectiveness as Dispersants for Cassiterite Suspension, *International Journal of Mineral Processing*, Vol. 20, pp. 161–192, 1987.

23. Bulatovic, S.M., and Salter, R.S., *Process Development for Treatment of Refractory Massive Sulphide Copper Ores*, Copper '91, Ottawa, Canada, August 18–21 1991.

24. Gutzeit, G., Chelate-Forming Organic Compounds as Flotation Reagents, *AIME*, February 1946.

25. Dho. H., and Iwasaki, I., Chelating Modifiers in the Cationic Silica Flotation of Magnetic Taconite Concentrate, *Minerals and Metallurgical Processing*, p. 65, May 1996.

26. Iwaski, I., Bridging Theory and Practice in Iron Ore Flotation, In (R.R. Klimpel and L.G. Chanders eds) *Advances in Coal and Mineral Processing Using Flotation*, pp. 177–190, 1985.

– 5 –

Flocculants

5.1 INTRODUCTION

Polymers of different chemical composition are used in the mineral processing industry as flocculants, coagulants and dispersants. The number of these polymers continues to grow and applications have expanded to include selective flocculation, anti-scaling agents and binders for dust control. All these chemicals are either organic polymers or inorganic substances. Because polymeric compounds can vary in electrical charge, molecular weight, three-dimensional structure and hydrophobicity, the range of compositions of functional polymers is virtually limitless.

The polymers used in the above applications can be broadly defined as large molecules made up of repeating units. In the case of long-chain synthetic polymers, a reactive monomer unit is polymerized with the same or other monomer units in a sequential fashion resulting in molecular strands. The number of linked units may vary anywhere from a few to as many as hundreds of thousands. This number reflects the molecular weight of the polymer.

The polymers used in flocculation, coagulation and dispersion, are either synthetic polymers (produced from polyacrylates) or natural polymers (starches, guar gums, etc.).

5.2 CLASSIFICATION OF FLOCCULANTS, COAGULANTS AND DISPERSANTS

The chemicals used for flocculation, coagulation and dispersion can be classified into two broad groups: inorganic and organic reagents. A different classification [1] is based on the action of the flocculant and is divided into the following categories:

- Polymers with flocculating action
- Polymers with dispersing actions
- Polymers with coagulating actions.

5.2.1 Inorganic flocculants

Inorganic flocculants are used in applications where the source of cationic charge is required. Typical inorganic flocculants include:

- Calcium salts; typically lime
- Aluminum salts; such as sulfates or soda alum
- Iron salts such as ferrous sulfate and ferric chloride.

Aluminum salts have been widely used in water treatment applications as well as in those in which coagulation is required. Ferro salts are used in applications where low pH is used, namely, in hydrometallurgical processes.

5.2.2 Organic flocculants

Organic flocculants can be divided into two main groups [2]: natural and synthetic flocculants.
Natural flocculants are derived from natural sources and have the general formula
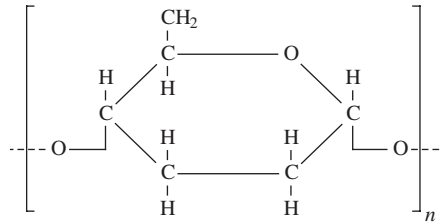
These flocculants can be derived from guar gums, hydrolyzed starch, modified polysaccharides and others. The use of these flocculants is less common for dewatering, but they are widely used for selective flocculation during the treatment of iron ores and other oxides.
Synthetic flocculants are commonly used in dewatering circuits. The number and varieties of these flocculants is very large. In principle, these flocculants can be divided into three distinct classes depending on the charge of the functional group.

Non-ionic polymers

These polymers are exclusively derived from acrylamides by polymerization. The molecular weight of these polymers ranges from 1 to 15 million. A typical structure of a non-ionic polyacrylamide is
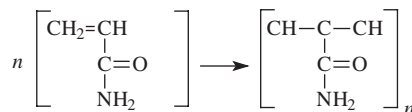
Other non-ionic polymers include

$$\left[-CH_2-CH-\atop\quad\ \ CN\right]_n \qquad \left[-OCH_2-CH_2-\right]_n$$

Polyacrylonitriles   and polyethylene oxide:
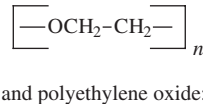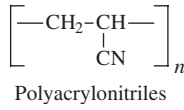
Polyelectrolytes

Polyelectrolytes, depending on their charge (i.e. positive or negative) can be anionic or cationic. The representatives of the anionic flocculant group are:
Co-polymers of acrylates–acrylamides:

$$\left[\left(-CH_2-CH-\atop{C=O\atop NH_2}\right)_x \left(-CH_2-CH-\atop{C=O\atop O-Na}\right)_y\right]_n$$
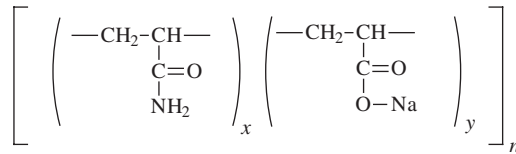
The y-component can vary between 10% and 30%.

Examples are the separan-type flocculant:
Separan NP10 $Y = 10\%$
Separan NP20 $Y = 20\%$
Separan NP30 $Y = 30\%$

$$\left[-CH_2-CH-\atop{C=O\atop O-Na}\right]_n \qquad \left[-CH_2-C-\atop{CH_3\ \ \atop{C=O\atop O-Na}}\right]_n$$

Polyacrylates   Polymethacrylates
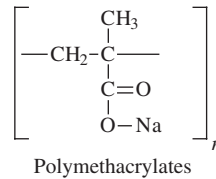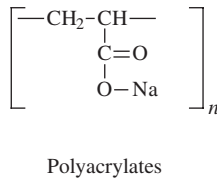
Aerofloc 548 and 552 flocculants belong to this group.

$$\left[H_2C-CH-\atop{\bigcirc\atop SO_3H}\right]_n \qquad \left[-CH_2-CH-\atop\qquad\ SO_3H\right]_n$$

Polystyrene - sulfonic acid   Polyvinyl - sulfonic acid
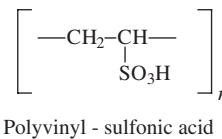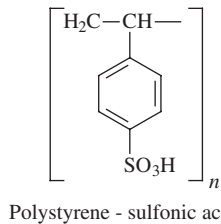
Examples of flocculants from this group are natural polymers produced from carboxymethylcellulose, Tylose CBR400 and methylcellulose Tylose MH200, manufactured by Clariant Chemicals (formerly Hoechst Chemicals).

Cationic polyelectrolytes are represented by polyethylene amines, polyvinyl amines and polyvinyl pyridines:

Polyethylene amines   Polyvinyl amines

Polyvinyl pyridines
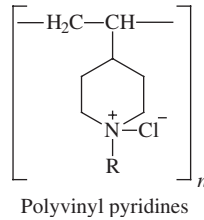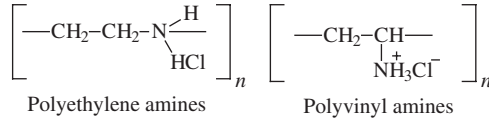
The reaction products of the polyacrylamide and primary amines are:

Co-polymers

Co-polymers are a reaction product of maleic acid and other compounds described by Wadsworth *et al.* [3], and include the following:
Co-polymer of styrene and maleic acid:

Co-polymer of acrylic acid and maleic acid

Co-polymer of vinylmethyl ether and maleic acid

5.3   GENERAL APPLICATION

Application of the reagents described under flocculants can be broadly categorized into three major groups. These include flocculants, coagulants and dispersants. Table 5.1 lists some of the most important polymers that belong to each category.

Polymeric and inorganic flocculants are employed in the mineral processing industry during the treatment of sulfides, oxides and silicates. Nowadays, they are used more and more in water treatment plants and also in waste treatment.

Coagulants are chemicals that reduce the repellent charge on solids, allowing them to collide and agglomerate. In the treatment of very fine particles, such as clay, hydrometallurgical leach residue, etc., coagulants are used together with flocculants to improve settling characteristics.

Dispersants in mineral processing have found a wide range of applications. In flotation of clay-containing ores, dispersants have been found to improve metallurgical results and

Table 5.1

List of the most important polymers presented in three categories

Category	Chemical/polymer	Class
Flocculants	1. Polyacrylamides	Non-ionic
	2. Acrylamide/sodium acrylate co-polymers	Anionic
	3. Sodium or ammonium polyacrylates	Anionic
	4. Acrylamide DMAEM[a] or DMEA[a] quat co-polymers	Cationic
	5. Acrylamide DADMAC co-polymers	Cationic
	6. Polyethylene oxide	Non-ionic
	7. Guar gum	−
	8. Hydrolyzed starch	−
	9. Acrylamide/sodium 2-amps co-polymers (sulfonate)	Anionic
	10. Modified polysaccharides	−
	11. Ferro salts	−
Coagulants	1. Poly DADMAC	−
	2. DADMAC/acrylamide co-polymers	−
	3. Epichlorohydrin/dimethylamine condensation polymers	−
	4. Poly aluminum chloride	−
	5. Amine/formaldehyde condensation reagents	−
Dispersants	1. Polyacrylic acid sodium or ammonium salts	Low molecular weight
	2. Methylacrylates/acrylic co-polymers	Low molecular weight
	3. Acrylate/2-amps co-polymers	Low molecular weight
	4. Polymaleic acid and sodium salts	Low molecular weight
	5. Methacrylate/acrylic co-polymers and salts	Low molecular weight

[a]Homopolymers of diallyl dimethyl ammonium chloride with the general formula:

reduce reagent consumptions. Dispersants are extensively used in selective flocculation. In maintaining the stability of slurry and controlling slurry viscosity, dispersants play an important role. Many regulating reagents described in Chapter 3 also have a dispersing effect.

REFERENCES

1. Mahoney, R.P., and Roe, J.W., Polymer Usage in Mineral Beneficiation, In (P.S. Mulukutta ed) *Reagents for Better Metallurgy*, SMME, 1994.
2. Blazy, P., Flocculation and Flocculants, *Industrie Minerale-Metallurgie,* Paris, France, 1973.
3. Wadsworth, H.E., and Cutler, I.B., Flocculation of Mineral Suspensions with Coprecipitated Polyelectrolytes, *Mining Engineering*, Vol.6, pp. 134–142, April 1956.

– 6 –

Summary of the Theoretical Aspects of Flotation

6.1 INTRODUCTION

In mineral processing, flotation can be defined as a technique used for concentration and/or purification of mineral value, which is governed by interfacial properties of the solid–liquid–gas system and changes in these properties by additions of various reagents to the system. Flotation is not in any way a chemical, physiochemical or physical process; it is a combination of chemical, physiochemical and physical phenomenas that govern the three-phase flotation system. In spite of dramatic progress in the past 90 years of mineral science on understanding the flotation process, the flotation phenomena is still unpredictable. For example, in chemistry it is possible to predict a chemical reaction and the end product can be defined. In physics, for example, motion obeys the law of physics, etc. In mineral flotation, even if we tend to think that flotation is governed by the law of flotation phenomena, which is predictable, this in fact is not true. If there are laws that govern flotation phenomena, which can be predicted similar to chemical reactions or physical law, then it would be possible to create a perfect flotation system.

The progress and achievements made in mineral science over the past 80 years is undoubtedly a breakthrough which makes development of a separation process much easier, even though the mechanism involved in flotation or non-flotation with various reagents is not yet fully established. It is believed that a flotation process is primarily the result of the tendency of certain surface-active species to concentrate at the liquid–gas interface and the tendency of some other species or particles to associate with or adsorb these surface-active species [1]. The techniques based on the ability and tendency of various species to associate with the different reagents are ion flotation for the separation of ions, micro-flotation for the separation of minerals that possess primarily polar surfaces and froth flotation for the separation of minerals that posses mostly polar surfaces.

It should be noted that flotation is not concerned with altering the chemical nature of the solid phase (mineral particles), but to alter or modify their surfaces [2]. In theory, freshly exposed mineral particles possess some level of surface energy. In practice, this may or may not be the case, because their surface energy, known in scientific terms, does not exist due to the fact that during milling and mining, the surface energy of the particulate mineral cannot be preserved and these surfaces are altered by either oxidation or contamination.

Therefore, the action of the collector on mineral surfaces or other modifiers is not the same as that of pure minerals used in scientific studies and the mode of adsorption of, say, a collector on a mineral surface is obviously different. It is, however, possible that surfaces of specific minerals can be restored by using surface modifiers, which may restore the natural surface. Therefore, modifiers and collectors play a decisive role in flotation or non-flotation of particular minerals. Unfortunately, only limited data exist on the contribution of modifiers to collector action on mineral surfaces. The exception is only a few modifiers such as pH modifiers, cyanides and sodium sulfate.

This chapter summarizes theoretical aspects of flotation. The intention is to help understand the basic principles of flotation from the practical point of view.

6.2 THE THREE-PHASE SYSTEM AND ITS IMPORTANCE IN FLOTATION

The three-phase system (i.e. particles–air–water) has been the subject of numerous studies since the early days of flotation. The interfacial phenomenon is considered to play a decisive role in flotation and represents the basic foundation of the theory of flotation. In reality, the three-phase system is so complex that theoretical consideration of the laws governing the system is merely hypothetical and is based on many approximations.

The mineral–water, mineral–air and water–air interfaces are considered to posses a surface energy that plays a decisive role in most of the aspects of the flotation phenomenon. Because the atoms and ions, which are part of the mineral surface, are subjected to different transformations due to the changes in the environment, the same can apply to the water and gaseous phases. It is considered that elemental particles, which may exist in the surface layer, possess a greater amount of energy than those inside the bulk phase. This excess of energy is known as surface energy.

In principle, there is evidence that solubility of minerals is related to surface energy. The surface energy is also responsible for adsorption and non-adsorption of reagents in the interfacial phases.

6.2.1 Mineral particle phase

In practice, the mineral particle phase is the most complex, not only because it consists of numerous different minerals, but also as the mineral particles undergo many changes. Because of this, they may also release different ions and cations, which migrate into the liquid phase, making the liquid phase also complex. In theory, the mineral phase represents a major problem in theoretical explanations and treatment of flotation processes. Regardless, the surface character of a mineral particle plays a major role in their interaction with reagents. It is important to mention some of the features of mineral surfaces related to the interaction with reagents.

The chemical composition of the mineral surface in natural ore is never the same as determined by the chemical formula of the particular mineral. The mineral particle may not be liberated or may contain inclusions of other minerals known as composite particles. The mineral particle defects (i.e. cracks) that occur during grinding or naturally in the crystals

are common. The cracks in the crystal are believed to form non-equilibrium forces of the particular mineral.

The physiochemical properties of the mineral surface of the same mineral species are considered to be variable, which means that the adsorption layer of the reagent on such a surface may also be variable. This phenomenon is referred to as the heterogeneity of a mineral surface. It is believed that heterogeneity of the mineral surface effects the interaction with different reagents. Numerous attempts have been made [3] to classify minerals according to their chemical and crystallographic properties. In such a classification, the crystals are differentiated according to the presence of strong inter-atomic or weak inter-molecular bonds. Gardner [4] has modified the above classification method by using criteria that include sharing of electrons by neighboring atoms or groups and the presence of a charge in atoms or groups. In 1950, Gardner [5] classified minerals, according to their flotation properties, into six major groups shown in Table 6.1.

These classifications, although intended to provide a scientific basis for understanding flotation phenomena; in reality the properties of crystals and minerals cannot be classified according to crystallographic, chemical or flotation properties. There are a number of major problems that cannot be incorporated in any of the classifications, some of which include the following:

- Although during size reduction crystals under impact break along crystallographic planes (i.e. "planes of cleavage"), they also undergo secondary fractures that definitely alter surface properties of the crystal, so the basic rules of crystal fractures do not exist in reality.

Table 6.1

Classification of minerals by Gardner [5]

Group	Minerals	Representatives
1	Sulfides of heavy and native metals	Copper, lead, zinc, bismuth, antimony and mercury
2	Non-polar, non-metallic minerals	Graphite, sulfur, coal and talc
3	Oxidized minerals of heavy metals	Carbonates, sulfates and silicates of copper, lead, zinc and other salts derived from oxygenated acids
4	Polar salt-type minerals that contain cations of calcium, magnesium, barium and strontium	Scheelite, apatite, fluorite, calcite, bornite, magnesite, dolomite and celestite.
5	Oxides, silicates and aluminosilicates	Silica, zircon, rutile, ilmenite, hematite, magnetite, feldspar, spodumene, mica, sericite, kaolinite, tourmaline, etc.
6	Soluble salts of alkyl and alkaline earth metals	Sylvite, langbeinite, kyanite, etc.

- The surface properties of the same crystal may vary considerably with the origin of formation. For example, zircon crystals found in heavy mineral sands, sedimentary and hard rock deposits all have different surface properties and crystal structure. Zircon found in hard rock deposits does not have a distinct crystal structure as the zircon found in heavy mineral sands. Accordingly, the flotation property of these two zircon mineral species is different. There are numerous examples of such differences for many minerals including oxides, silicates and sulfides.
- Classification of minerals according to flotation properties can be regarded as the most generalized form of classification, merely because, for example, the flotability of sulfides with xanthate collectors can be as good as the flotability of polar salt minerals with fatty acids.

In reality, the mineral particle phase is never one mineral phase, even in the case of the simplest ore, such as porphyry copper ore. It is a multi-mineral system, which is composed of a variety of different minerals with different crystallographic chemical and surface properties. The chemical interaction of ions from different minerals in the multi-mineral particle phase always occurs. For example, in the case of polymetallic ores containing copper and zinc, where copper minerals can be oxidized or altered, the sphalerite on its surface may contain copper cations rendering sphalerite flotable under conditions in which chalcopyrite is floated. Although it is shown that, for example, pyrochlore can be floated with fatty acid collectors and sodium oleate in real practice, this is never the case because separation of pyrochlore from the multi-mineral phase using fatty acids is impossible.

During size reduction, the complete liberation of the individual minerals and crystals may not be possible and, therefore, the composite particles always exist in solid phase. It is not always the case that properties of minerals depend chiefly on their composition and structure, but the properties of the minerals are also dependent on the interactions of the multi-mineral system. Although theory of flotation has provided an understanding of the individual mineral surface properties, this is not the case for most mineral systems where the surface properties of individual minerals may differ significant, especially chemical properties of mineral surfaces [6].

6.2.2   Liquid phase

The liquid (i.e. water) is the phase in which the separation of minerals by flotation takes place. All key processes are an attachment of minerals to air bubbles; the physiochemical properties of the surface of the particles and the reagents employed are in some way related to properties of water. The understanding of liquids and their structure is much more advanced than that of solids (i.e. mineral particles). The properties of water, however, have not received much emphasis in any analyses of the flotation phenomenon and it is rarely mentioned in studies of flotation fundamentals.

The structure of water molecules in the modern theory of liquids differs from the previous theories, which were based on the analogy between liquids and gases. The modern theory approximates the liquid phase to crystalline solids at temperatures close to a crystallization temperature. At normal temperature [7] and pressure, the molecules of water are packed in tetrahedra (Figure 6.1). At different temperatures, the structure of water changes.
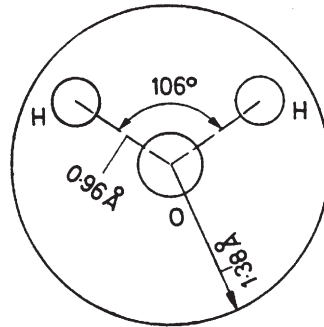
Figure 6.1 Structure of water [7].

Several important properties of water relevant to flotation are given below.

Hydration of ions

The pseudo-crystalline structure of water extends over a small distance containing a fairly large number of molecules that are considered unstable and undergo constant separation [8]. This state of water only exists when water is in the pure state. The presence of ions in water leads to the formation of condensed water ions around foreign ions, which is known as hydration of the ion. The formation of hydration sheaths means that the energy of the bond between the ion and water dipoles is much greater than the attraction between dipoles. The energy of hydration depends on the ion valency and other factors such as temperature, polarities, etc. From the point of view of flotation, with increasing orientation and stability of water dipoles, water loses its solubilizing properties. At the same time, the diffusion of ions in polarized water is more difficult; therefore, the solvent action of water is connected with the hydration of the dissolved ions.

Solubility of minerals in water

Most of the minerals in the water phase undergo dissolution, transferring ions or cations in solution. It is believed that ideally, dissolution occurs when the hydration energy exceeds lattice energy. The solubility determines, in fact, the ionic composition of water. Also, a reverse process of deposition back to the mineral may occur when the molecules of water are consumed for the formation of a hydrated layer surrounding the ions separated from the mineral surface. The rate of dissolution of the ions depends on many factors, some of which include temperature, particle size, vapor pressure in solution, surface tension, etc.

The ionic equilibrium and solubility are important characteristics of solutions for a chemical reaction to happen in water. It is believed that a chemical reaction in solution is possible only with the collision of ions; molecules are formed when forces of cohesion between atoms exceed the force of hydration. A necessary requirement for a chemical reaction in solution is the removal of ions from solution in the form of weakly dissociated molecules such as nearly insoluble substances or precipitates. Therefore, for the reaction to proceed in a particular direction, the solubility must decrease. Such conditions are normally utilized in determining the possibility of interaction between various reagent and mineral surfaces.

Impurities in water

The water used in mineral processing contains a fairly large amount of impurities. Water in contact with minerals dissolves ions and cations. Even the chemical composition of natural water is highly complex and variable. It is believed that the most important characteristic of water is water hardness. Hardness expresses the sum of multivalent cations and is usually measured as milligram equivalent. In particular, hardness of water is important during fatty acid and amine flotation.

It should be pointed out that the effect of water impurities on the flotation of a particular mineral is quite difficult to determine. In some cases cations do not affect floatability, while in other cases they have a negative effect. It is positively established from plant practice that the presence of organic and biological substances in water has a negative effect on flotability.

Dissolved gases

Perhaps the most important constituents of water are dissolved gases. These should not be mixed with air bubbles, which are used as hydrophobic mineral carriers. The gases in the flotation pulp play multiple roles during the flotation process. Gases may adsorb on the mineral surfaces causing oxidation, which in turn affects the solubility of minerals, and most importantly, in sulfide mineral flotation regulate flotability of minerals.

6.2.3   The air phase

The air phase has always been associated with aeration of flotation pulp and dissolved gases. The purpose of aeration, however, is not to create air bubbles as a carrier of hydrophobic minerals, but rather to provide sufficient dissolved oxygen necessary in some cases to achieve differential flotation. Bubbles or injected air in a flotation machine should be considered as the air phase, whose sole purpose is to provide air bubbles on which hydrophobic minerals are attached and transported to the froth phase. There have been extensive studies on the behavior of air bubbles in flotation pulps and the methods by which particles are attached on the bubbles.

6.3   THE FLOTATION THEORY

The flotation process is governed by a complex phenomenon occurring on the surface of mineral particles and air bubbles formed in the water phase. The research data on the properties of the interfaces generated over the past 100 years forms the basis of the present theory of flotation. Perhaps the most comprehensive account of the surface phenomenon of flotation in the early stage was given by Irving Langmuir   1919 [8], which became the basis for all research work conducted since. He wrote, "The tendency of the particles to attach themselves to the bubbles of the froth is measured by the contact angle formed between the oily surface of the bubble and the contaminated surface of the solid. The selective action by which substances, like galena, are separated from quartz is dependent upon the contact angle formed by the oiled surface rather than by any selective tendency for the oil to be taken up by some minerals more than by others."

Seventy years later, D.W. Fuerstenau [9] wrote, "An electrical double layer is a system in which, by definition, there exists a separation of electrical charge at an interface; that is, a layer of positive charge and a layer of negative charge, with the whole system being electrically neutral. Double layers can extend into one or both of the phases in the system, an example of the latter being oil–water or semi—conductor–water system."

Despite enormous progress in mineral flotation science since 1920, there is substantial disagreement on the point of view of surface phenomena and wetability in any mineral system.

For practitioners of the mineral engineering science, it would be appropriate to define various terms on which the theory of flotation and, most importantly, reagent adsorption is based. Moreover, the hydrophobicity is also explained by different interfacial phenomena. It is believed that one of the most important properties of the mineral surfaces is the electrical characteristics. The electrical properties of a mineral surface are determined by two potentials; namely, electrochemical and electrokinetic. In the water phase, the ions from the mineral surface interact with water or other constituents present in the water. During this process, some of the ions are transferred into solution, which causes changes in the electrical equilibrium on the mineral surface making the mineral surface electrically charged. It is believed that some of the ions transferred into the solution are concentrated by the action of the charge of the surface of the mineral near the surface where space separation of the surface occurs. This is called the *electrical double layer*. The electrical double layer theory plays a very important role in adsorption of reagents on the mineral surface.

The charges in the electrical double layer may occur when ions of the two layers separate during movement of particles in the liquid. When the ions of the diffused layer move away from the surface, the electroneutrality of the mineral surface is disturbed and the differences in the potential arise between the moving particles and the liquid. In mineral flotation science, this is called the *electrokinetic potential* or *zeta potential*. The zeta potential measurement is used to determine the action of collectors on the mineral surface. The relationship established between flotability and the changes in the electrokinetic potential forms the basis for determining the attachment of the reagent on the mineral surface. According to V.I. Klassen and V.A. Macrousor, "If the charge in the magnitude of the electrokinetic potential is not accompanied by the charge of its sign, then the action of the reagent concerns only the external diffused portion of the electrical double layer. However, if the sign of the potential changes as well, then the ion of the reagents are the potential-determining ion and can penetrate the inner layer of the electrical double layer."

Finally, the crystal structures of different minerals are different as well as the electronic structure of an atom in the structure, which means different types of bonding occurs in the electrical double layer. Some of the more important types of bonding include the following.

Ion bonding. In general, the ionic bond is formed between a positively and negatively charged ion and acts over a long distance, constituting long-range forces. In practice, depending on the electronic structure of an atom on a mineral surface or liquid phase, it can either give up its valence electrons to become a positive ion or accept electrons from any available source to become a negatively charged ion. For example, in an isolated pair of oppositely charged ions, the energy of the bond between these ions can be expressed as

a sum of an attractive or a repulsive contribution of the overall potential energy as per the following equations:

$$U \text{ ionic} = \underbrace{\frac{Z + Z^{-}e^{2}}{d}}_{\substack{\text{attractive} \\ \text{energy}}} + \underbrace{\frac{a\,e^{2}}{d^{n}}}_{\substack{\text{repulsive} \\ \text{energy}}}$$

where Z and Z^{-} are the numbers of positive or negative charges on the two ions,

e is the electronic charge expressed as 1.602×10^{-19} C,

d the distance between the centers of the ions,

a the constant for the given ionic compound and

n depends on the electronic configuration of the ions.

When an ionic particle is placed in a polar liquid, the attractive force between the ions becomes diminished, which in turn causes a breakdown in the crystal lattice producing the solute species.

Covalent bonding. The covalent bond is formed at a much shorter distance than the ionic bond and occurs whenever the two approaching atoms can share one or more pairs of electrons, each atom contributing one electron of each pair.

The charges in the energy levels of the atoms involved in covalent bonding formed as a result of electron sharing may be represented by either the valence bond theory or the resonance energy concept. These two methods of treating covalent bonding are believed to represent equivalent approximations; neither can be called correct or incorrect. Their utilities depend on the degree of clarity of bond representation and their ability to predict the behavior of molecules.

Hydrogen bonding. Hydrogen bonding occurs when the hydrogen is bonded to the electronegative elements (F, O, N, Cl) or electronegative groups such as $-CCl_3$ and $-CN$. Hydrogen bonding may occur in gases, liquids and also solids. Hydrogen bonding plays an important role in many interfacial phenomena such as systems involving oxides and oxidized solids, carbonates, silicates and water. The strength of hydrogen bonding is much lower than that of covalent bonding. It is sufficient to provide stable interactions. In studying hydrogen bonding, infrared and Raman spectroscopy are used. In scientific studies, the molecular orbital theory and the electrostatic approach have been used to explain hydrogen bond formation. When compared with the molecular orbital theory, the electrostatic approach is much simpler. A covalent bond between hydrogen and a strongly electronegative atom 'I' is highly polarized, where a large dipole is created, which tends to interact with any other electronegative atom 'K' by aligning the positive ends $I^{\ominus}$—$H^{\oplus}$....$K^{\ominus}$.... giving, in effect, a dipole–dipole interaction. The lone pair of electrons plays an important part in determining the strength and the direction of hydrogen bonds. In a number of cases, hydrogen bonds may also have a covalent character.

London dispersion forces – Van der Waals interaction. The aggregation of all covalently bonded non-polar molecules may occur depending on temperature and pressure. Such aggregation results from the action of dispersion forces. Basic information about these

forces is obtained from the constants *a* and *b* in the Van der Waals thermal equation of state of molecular behavior of gases;

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation gives qualitative description of the behavior of gases and liquids by choice of *a* and *b* for low pressure and high temperature. It cannot be made to fit the experimental data over any wide range of *P* and *T*. The term a/V^2 is a measure of inter-molecular forces causing departure from the ideal behavior of gases.

In all multi-phase systems, Van der Waals forces are present and exert a major influence on interactions. These interactions include adsorption and adhesion of polyatomic aggregates such as non-polar and polar molecules or aggregates (i.e. colloidal particles). The stability of colloidal dispersion, is, in fact, determined by the balance between attractive Van der Waals forces and the repulsive forces between the double layer of electrical charge surrounding each colloidal particle. The stability of the mineralized froth actually depends on the balance of these two types of forces (i.e. Van der Waals and electrical).

Metallic Bonding. The bond theory of solids is formed to explain flotation systems involving the separation of metallic phases such as flotation of native gold, native copper or cement copper.

Metals have many physical properties, different from those of other minerals. The most pronounced ones are high electrical conductance, high thermal conductance and high strength and density. These properties are due to the existence of a special type of bonding called metallic bonding, which is neither ionic nor covalent bonding. The metallic bonding theory is based on split energy levels and the existence of special, forbidden zones.

When two atoms approach each other, each energy state of those atoms splits into two states. When *a* atoms are coming together to form a lattice of solids, each energy state of the individual atoms splits into *a* states, some of which may be degenerate (i.e. have the same energy).

Since the splitting of energy states occurs as a result of one overlap between the electronic bonds of participating atoms, the electrons in the inner shells that are completely filled do not overlap and show no bond structure. In fact, the distance between the atoms' so-called lattice constant *n* for metallic solids plays a critical role in determining the differences between electron waves and the deviation of energy space into permitted and forbidden zones.

6.3.1   The electrical characteristics of interfaces, electrical double layer and zeta potential

The surface charge in establishing electrical characteristics of interfaces such as solid–liquid, liquid–gas and liquid–liquid are quite important in the theory of flotation practice. Whenever a new solid surface is formed in a gaseous or liquid environment, for example, during dry or wet grinding, it either becomes charged at the moment of rapture or picks up charges by subsequent adsorption of ions. Freshly ground solids remain uncharged only if

the cleavage exclusively raptures Van der Waals bonds, and when the underlying lattice points are occupied by covalently bonded molecules and in addition if there is no mobile charge in the system, such as electrons, ions or dipoles.

Whenever mobile electrons are present the interface becomes charged. The exceptions are the specific conditions that result in the mutual compensation of charges resulting in a point zero charge (P.I.), which leads to electrical potential differences.

The electrical potential at any given point is defined as the energy necessary to bring the unit charge from infinity to a certain point. In a material medium other than vacuum, such as phase b, the energy required to bring the charge through the medium depends on the interaction between medium b and the charged particles. This work energy is called *electrochemical potential* and is defined by $\overline{U}_a^\alpha = U_a^\alpha + Zae\varphi\rho\alpha$ where φ is the chemical potential and donates all non-electrostatic interaction of species with the medium α. Za denotes the charges carried out by a (Za is the valence, e the unit electronic charge). φa is known as the inner potential and is constant within the phase α and represents work done in transporting unit charge across the interface comprised of a layer of dipoles.

The inner potential φ^α is a sum of the so-called outer potential γ^α and the surface potential χ^α: $\varphi^\alpha = \gamma^\alpha + \chi^\alpha$. The outer potential γ^α represents the work done to bring the unit charge from infinity to a point just outside the interface.

The potential difference between the surface and the solution yields the total double layer potential. The schematic representation of the double layer and potential is shown in Figure 6.2.

During formation of the interface the rearrangement of species occurs, which results in establishing a layer of charges that has attracted a layer of counter charges. There are several models of the distribution of charges. The first was originated back in 1890 and 1913 by Gany and Chapman. They suggested that the charges form a diffuse continuum of ions in a
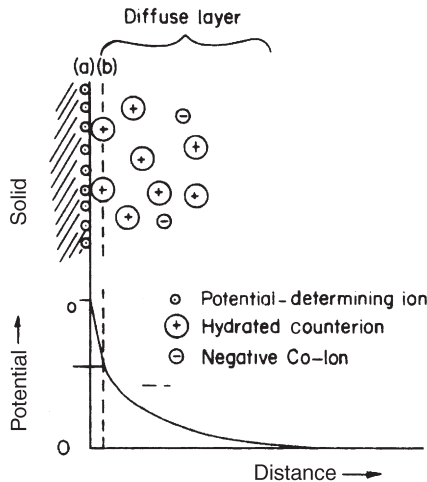
Figure 6.2 Schematic representation of the double layer and potential drop across the double layer; (a) surface charge, (b) stern layer and (c) diffuse layer and counter ion.

structureless dielectric. In 1924, Stern modified the Gany–Chapman model by replacing the point charges approximation with ions of finite size, which are capable of approaching the surface of the solids no closer than a minimum distance d. Later on, Stern combined the model of the diffuse layer with that of a condenser-like compact Helmholtz model, which formed a new Stern model consisting of two layers in series and is called a compound double layer or triple layer. In addition, Stern introduced the concept of specific adsorption of ions within the Helmholtz portion of the compound double layer at a distance β from the solid surface. The area of these adsorbed unhydrated ions (in layer) is called the inner Helmholtz plane (IHP), while that of the closest approach for the more weakly adsorbed hydrated ions at area d is called the outer Helmholtz plane (OHP). The above three stages of the model development are shown in Figure 6.3a, b and c.

According to the character of the specifically adsorbed ions in the IHP and the concentration of ions in the electrolyte solution, two modifications of the Stern compound layer may be encountered in addition to that shown in Figure 6.3.

These two modifications are shown in Figure 6.4. The first modification (a) is proposed to explain the occurrence of charge reversal within the compound layer. The second modification (b) shows the compound double layer in concentrated electrolyte solution when the diffuse layer disappears.

Within the thickness of the compact layer, the potential changes linearly from the inner potential of the metallic phase ϕm to some given level γd, which is determined by the excess charge qm in the vicinity of the compact layer. The potential within the diffuse layer is evaluated starting with Poisson's equation and applying Boltzman's exponential distribution law
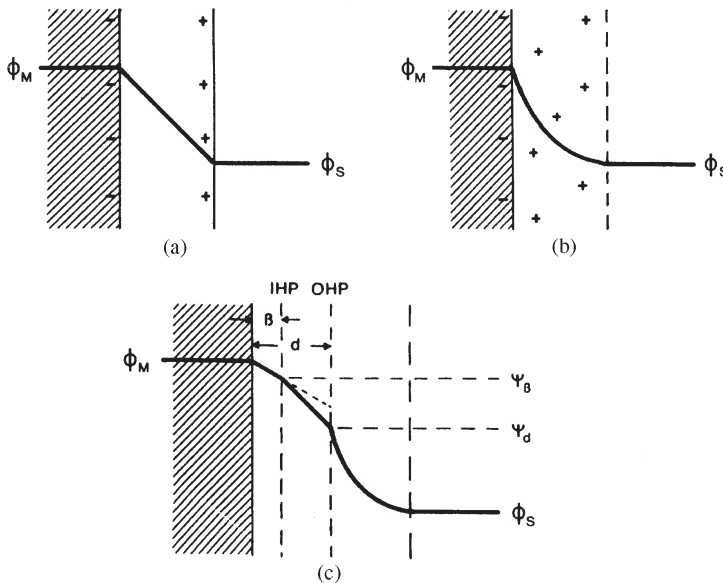
Figure 6.3 Three stages of development of the double layer: (a) Helmholtz–Perin compact layer, (b) Gany–Chapman diffuse layer and (c) Stern double layer

to the concentration of positive and negative ions within the diffuse layer. These are relatively complex relations as shown in the following equations:

(1)   The slope of the potential function

$$\frac{d\phi}{dx} = -\left(\frac{32TTCokT}{\in}\right)\frac{1}{2}\sin h\left(\frac{Ze\phi}{2KT}\right)$$

(2)   Equation for the potential drop within the diffuse layer:

$$\Phi x = \left(\frac{4kT}{Ze}\right)\tanh^{-1}[Zef(0)4kT]\exp\left(\frac{-x}{Ld}\right)$$

(3)   Equation for the potential at $x = 0$ ($x =$ distance from metallic surface):

$$\Phi(0) = \left(\frac{2kT}{Ze}\right)\sinh^{-1}\left(\frac{q}{2A}\right)$$

(4)   Equation for the charge q present on each side of the interface of equal value but opposite sign:

$$q = 2A\sinh\left(\frac{Ze\Phi(0)}{2kT}\right)$$

(5)   Equation for differential capacitance C_2:

$$C_2 = \left(\frac{AZe}{kT}\right)\cosh\frac{Ze\phi(o)}{2kT}$$

where Co is the concentration of ions in the bulk electrolyte, Z the valence, e the electronic unit change and ε the dielectric constant.
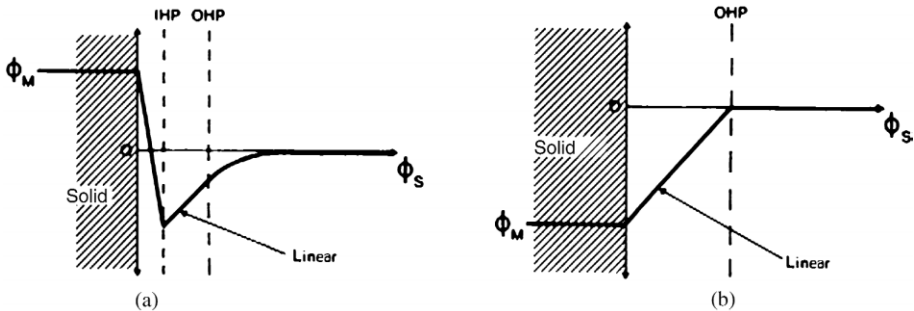
Figure 6.4 Two types of modification of the Stern compound layer.

The electrokinetic phenomena involving the inter-relation between mechanical and electrical effects of the moving interface are widely used in colloid and surface chemistry. These electrokinetic data are usually expressed in the zeta potential. The zeta potential arises at the slipping plane where the liquid is forced to move relative to the solid. Only those ions in the diffuse layer outside of the slipping plane are involved in the electrokinetic process. The zeta potential measurement is a basic tool in studying various reagent adsorptions.

6.3.2   The adsorption theories

Adsorption in general terms can be defined as a change in the chemical content of phases at an interface, most commonly the accumulation of the one component either from the solution or gaseous phase. This effect is detected as a change in concentration of that component in the bulk phase. For example, if one component of a solution is adsorbed, other components from the solution show an apparent increase in concentration and this is termed as negatively adsorbed. There are different cases of adsorption, some of which are purely physical in nature and others involve a chemical reaction, etc. In mineral science, it is very important to identify particular cases of adsorption, which are unfortunately not easy because the controlling laws are quite different.

Some of the most important adsorption theories used in mineral science are summarized below.

Physisorption is the phenomenon that is driven by the reduction in free energy of the surface. For example, the uptake of non-reactive vapors by charcoal can be considered a physical reaction. Another class of physisorption process may occur at the surface of the solution. For example, alcohol has a nature to adsorb on the surface of a solution. The adsorption is confirmed by a significant reduction of the surface tension and was verified by analyzing the foam produced by passing air through the solution. It was therefore concluded that accumulation of alcohol at the air–water interface is purely physical.

In 1878, Gibbs determined a thermodynamic relationship between the amount of adsorption G, per unit area and the reduction of surface tension αc. This reaction is as follows:

$$G = \frac{-cd\alpha c}{RTdc}$$

G can be determined from αc. G is the excess mass of solute per unit area of the interface. The Gibbs theory was checked later on by experimental work. This theory has run into difficulties in cases where electrolytes are involved. For example, electrolytic salts such as NaCl can raise the surface tension of the water. Organic electrolytes such as soaps are very strongly positively adsorbed, resulting in a decrease in surface tension significantly. It should be noted that where physical adsorption applies, the adsorption before and after adsorption cannot be measured. The reduction, however, can be deducted from measurements of the adsorption employing the Gibbs integrated form in a reversed, integrated form.

$$Lo - dp = RT \int_{o}^{p} Gd(\ln p)$$

From this equation, with the solid–gas interface, the αo, αp is known as surface pressure of the adsorbed gas. The adsorption can be evaluated from measurement of G, of vapors from pressure o to p.

In mineral processing, the measurement of the physical adsorption of gases is used to determine the specific surface area of finely divided solids such as porous minerals or clay.

Chemisorptions. In contrast to physisorption, there are numerous examples of adsorption where a chemical reaction is involved. In the earliest research by Langmuir (1916), he had discovered that various gases strongly attach to clean metal surfaces. Likewise, oxygen is held so strongly by tungsten that it can only be removed at high temperature. Many oxide minerals react with water; examples are SiO_2 and Fe_2O_3, which chemisorbs the water by the exposed surface group (i.e. from SiOH and FeOH groups). In the case of minerals that are strongly soluble, they are capable of reacting to precipitate a less soluble product when in contact with a given reagent [10]. As an example, a sodium oleate collector can react with calcite ($CaCO_3$) to precipitate calcium oleate with a low solubility product. It is believed that the uptake of oleate ions is simply governed by mass action.

The chemisorption phenomenon is used to explain the adsorption of certain reagents (i.e. carboxylates) on mostly oxide minerals such as the hematite–oleic acid system but is not limited to sulfides. The lead–xanthate system may also involve chemisorptions [11].

The chemisorptions and physical co-adsorption are related in some ways. The physical co-adsorption occurs during the change or increase in covalent bonding formed on adsorption relative to mostly covalent bond in the corresponding compound. An example is a concurrent physical co-adsorption of sodium oleate on fluorite and barite described by Peck and Wadsworth [12], where the chemisorptions occurs in alkaline pH and co-adsorption at acidic and neutral pH.

The *electrochemical theory of adsorption* is associated with semiconducting properties of minerals and involves sulfide minerals. In the case of sulfide minerals, the electrochemical model involves oxygen. A typical example of proposed electrochemical model is the xanthate–galena system involving the following reactions:

$$PbS + 2X^- \rightarrow PbX_2 + S^\circ + 2e \quad \text{anodic}$$

$$H_2O + \frac{1}{2}O_2 + 2e = 2OH^- \qquad \text{cathodic}$$
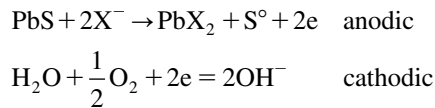
In this model, the role of oxygen is to oxidize the lattice sulfide ion to sulfur.

Electrostatic model of flotation. This model is relevant for silicate and oxide minerals and involves reagents that adsorb through physical interaction and function as counter-ions in the double layer. The phenomenon is strictly pH-related, which determines the sign of the mineral surface [13]. The example of the dependence of flotation can be found in the experimental work by Gaudin [14], where they studied the flotation behavior of geothite in the presence of two anionic collectors. Figure 6.5 shows the results obtained.

The electrostatic model is broadly used to explain the adsorption of collectors on oxides and silicate minerals using cationic reagents.
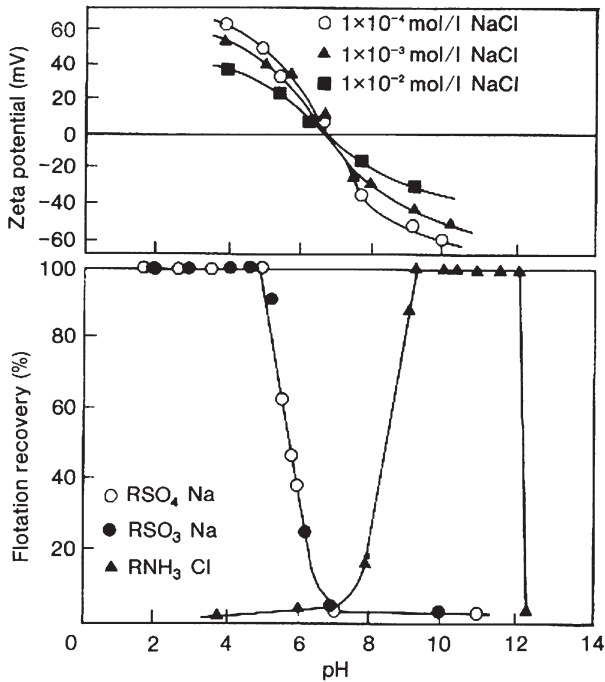
Figure 6.5 The dependence of the flotation of geothite FeO(OH) on surface changes. The upper curves show the zeta potential as a function of pH at different concentrations of NaCl, indicating PZC to be 6.7. The lower curves are the flotation recoveries in 10–3 mol/L solution of dodecyl ammonium chloride (Iwasaky et al., 1960).

6.3.3   Colloid chemistry and adsorption – the Heminicelle theory

The Heminicelle theory has been put forward by Gaudin and Fuerstenau [14]. It involves weak electrolyte-type collectors such as fatty acids and primary diphatic amines, which adsorb on mineral surfaces as a precipitate. These collector molecules form a colloidal precipitate, which subsequently interacts with mineral surfaces as a precipitate. The insoluble in water non-ions are emulsified in the flotation system and their flotation properties result mostly from the above fact. The properties of weak electrolyte-type collectors under the same conditions may resemble those of either strong electrolytes or non-ionics, which are responsible for heminicellation.

6.4   THE WETABILITY AND CONTACT ANGLE IN MINERAL PROCESSING

The interfacial wetability in mineral processing science is known as *hydrophilicity* and *hydrophobicity*. Hydrophilic solids are completely wetted by the bulk water phase or aqueous solution. Hydrophobicity is partial or incomplete wetability of a solid phase by the water phase. Wetting, therefore, signifies the adhesion of a liquid phase to another

phase (i.e. solid or liquid) such that the cohesion of the spreading (wetting) phase is extended. The wetability of mineral surfaces in the liquid phase is essentially determined by hydration of minerals and air bubbles. The formation of hydrated layers around ions, molecules and mineral surfaces is associated with specific characteristics of water due to its dipole structure and other properties of its molecules. The process of surface hydration is believed to be determined by the behavior of different substances existing in the water. It should be remembered there are two types of hydration: (a) hydration of solvent by water and (b) the chemical hydration in which water enters the bulk of the solids.

Klassen and Mocronsov [15] considered the hydrated layer, their structure and stability to be dependent on the nature of the minerals, reagents and composition of water and other factors determining the conditions under which flotation occurs. The process of hydration affects the solubility of minerals and reagents as well as interaction between minerals and reagents, attachment of minerals to bubbles, coalescence of bubbles and coagulation of mineral particles.

The hydration of different phases in the presence of reagents causes a particle to attach to an air bubble. The profile of attachment to the three-phase system is known as "angle" across the liquid phase. This angle is assumed to be directly related to the contact angle established by the same liquid on a flat surface of the same solids.

6.4.1   Wetability and contact angle relationships

It should be pointed out that the establishment of a relationship between wetability of mineral particles and their flotability was the major stage in the development of the modern theory of flotation. In this process, the wetability and the contact angle played an important role. In the early stages, Rehbinder and co-workers established the relationship between flotability of the minerals and the changes in the history of the contact angle, showing that the wetability of the mineral surfaces and the effect of the adsorption of the flotation reagents determines the main physiochemical aspects of all processes of flotation [16].

According to Rehbinder, the wetability phenomenon occurs at the boundaries separating flotation phases along the perimeter of their contact (i.e. perimeter of wetability). The forces acting along the triple phase of the perimeter of wetting are called by Rehbinder flotation forces as shown in Figure 6.6 [17]. This attachment of a bubble to a solid is a part of all textbooks dealing the theory of flotation since the 1930s.
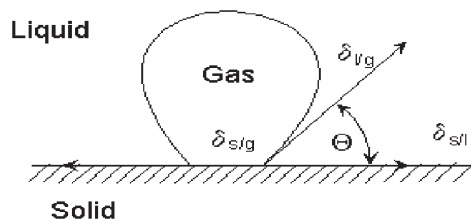
Figure 6.6   Contact angle by Rehbinder.

The Rehbinder equation for quantitative determination of magnitude of wetability is shown in the equation below:

$$V = \mathrm{Cos}\,\frac{\sigma\,5/g - \sigma\,5/l}{s\,l/g}$$

The magnitude of V depends on the sign of flotation forces in the above relation, and V describes the molecular nature of the solids surface with respect to the differences of the free surface energy on the boundary of the solid–gas and solid–liquid interfaces.

Earlier, it was indicated that wetting signifies an adhesion of a liquid phase to another phase, such as the cohesion of the spreading when the wetting phase is extended.

Theoretically, when the column of pure liquid is separated by direct pull to form two surfaces, the energy of the cohesion Wc of this liquid is converted to surface energy:

$$Wc = 2\wp o$$

where $\wp o$ = specific surface free energy of the liquid. Therefore, if such a liquid contains surface-active components, the work of creating new surfaces is equal to the changes in the surface free energy:

$$Wc = 2(\wp o + \mu iGi) = 2\wp$$

where $\wp$ is the surface tension and μi a constant .

In the case of two liquids a and b, which are insoluble in each other and spread along the interface, Dupré law defines the work of adhesion:

$$Wc = \wp a + \wp b - \wp ab$$

This equation indicates that two new surface tensions $\wp a$ and $\wp b$ are created, with a loss of the initially existing interfacial tensions $\wp ab$. The work done by Kitchener [18] extended this approach to the spreading of one insoluble liquid over another liquid or solid phase, known as the "spreading coefficient" defined as $S = Wa - Wc > 0$.

The relevance of the adhesion and cohesion is in that they are used to establish surface forces and the spreading coefficient to consequently evaluate the difference of two unknown surface quantities. The spreading coefficient, however, is assumed to be positive or negative, and a presumed negative spreading coefficient and the work of adhesion indicates non-wetting liquid on a solid.

6.4.2   Interpretations of contact angle

In the initial stage of the theory of flotation, the conditions leading to the formation of a contact angle on a flat solid were often considered to be synonymous with collector

adsorption and flotation conditions. The first textbook on flotation by Wark (1938) provides insight into evidence regarding the significance of contact angle studies in flotation research.

Extensive studies conducted during the past four decades on contact angle measurements [19–22] lead to the conclusion that equilibrium in a system involving contact angles is frequently not established. There are a number of problems that may influence contact angle measurements:

- The heterogeneity of the surface is opposed to the polished, ideal surface in a contact angle measurement and may be responsible for a discontinuous change in the contour of the three-phase contact often observed in the real system [23]. For flotation systems, the heterogeneity of the solid surface and the development of scattered patches of hydrophobic areas caused by such a surface, makes the model of contact angle derived from a polished flat surface highly unrealistic.
- In practice, the particle bubble attachments under agitation and aeration are dynamic processes that cannot be analyzed based on the contact angle value obtained at equilibrium [24]. In their studies, Leya and Poling [25] concluded that the contact angle is simply an indication of the extent by which the given solid–liquid–air system utilizes the free energy of interfaces in the bubble deformation system (Figure 6.7).
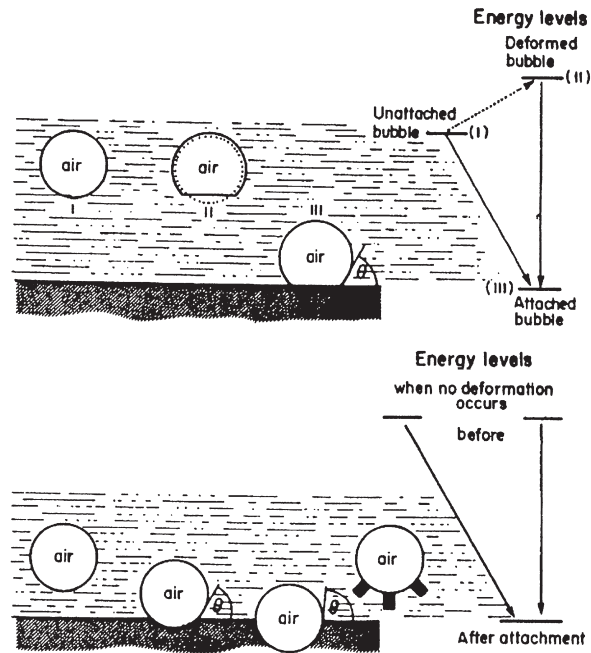
Figure 6.7 (a) Deformation of a bubble on attachment to a rigid flat surface and the relationship between respective energy levels before and after deformation and attachment. (b) Attachment of a bubble to solids without deformation of the air–liquid interface [30].

In spite of the problem with this interpretation of the contact angle measurement, the contact angle is considered a highly useful parameter reflecting the concluding remarks by Ralston [26]. In his interpretation of static and dynamic contact angles: "Our understanding of contact angle is extensive, but far from complete, and as new approaches and techniques focus on collectors, adsorption mechanisms, surfactant reorientation effects, improved models of dynamic contact angles and the like, extensive benefits to mineral processing are anticipated."

6.5 HYDROPHOBICITY AND BUBBLE MINERALIZATION

Flotation is often referred to as a carrier process in which air bubbles function as a carrier of hydrophobic mineral particles. Since the bubbles can only differentiate between hydrophobic and hydrophilic particles, the selective separation depends very much upon differences in hydrophobicity between separated mineral particles. The flotation systems, however, are not by any means perfect and can be in practice regarded as an unpredictable system often leading to separation problems which cannot be easily explained by any theory of flotation.

From the practical point of view, the hydrophobicity and bubble mineralization are perhaps the two most important factors in flotation and govern the system kinetics and selectivity of flotation.

As any of the numerous flotation theories, the aspects of hydrophobicity and bubble mineralization has been the subject of many studies and different interpretations.

6.5.1 Hydrophobicity

Hydrophobicity can be defined as the process of selectively converting the surfaces of particular minerals from a hydrophilic condition (provided that the mineral is not naturally hydrophobic) to a hydrophobic (water-repellant) condition , which creates a condition for attachment to air bubbles. This conversion of the mineral surface from hydrophilic to hydrophobic is different for different mineral groups, e.g. silicates, oxides, sulfides, etc.

In the case of silicate minerals, dispersion forces, hydration of non-polar sites and ionization play critical roles in the hydrophobicity. In their work with silicates, Laskowski and Kitchener have shown that surface hydration controls hydrophobicity; that is, the hydrophobicity arises from the exceptionally large cohesive energy of water, which is influenced exclusively by hydrogen bonding. The instability of water films of a specific thickness on hydrophobic solids is fundamentally due to a deficiency of hydrogen bonding in these films as compared to liquid water.

However, the conversion of mineral surfaces from hydrophilic to hydrophobic by using collectors (i.e. amines, sulfonates, etc.) is also considered to be due to electrostatic attraction between the polar head of collector [27] and the charged surface sites of the particular mineral. Because the electrostatic forces are not strong enough to maintain bonding, they are assisted by the associated interaction of collectors. The electrical nature of the particle–solution interface is the result of either preferential dissolution of lattice ions or the

hydrolysis of the surface species followed by pH-dependent dissociation of the surface hydroxyls as per the following reaction:

$$-M(H_2O)^+_{surface} \rightleftharpoons MOH_{surface} \overset{OH^-}{\rightleftharpoons} -MO^-_{surface} + H_2O$$

The surface ions are considered (surface) potential-determining ions where H^+ and OH^- are the corresponding ions of the oxide minerals.

The hydrophobicity of oxides is believed to be influenced, to a large extent, by the electrochemical nature of the oxide–solution interface. The hydrogen and hydroxyl ions, when adsorbed on the oxide surface, together constitute a polarizable hydration layer with a hydrogen-bonded structure.

The surface behavior of oxides and silicates is highly dependent on pH. According to this, the following three types of surface behavior can be distinguished:

1.   *Acidic*, which is when the pH range is above the ZPC. There is little or no dissociation and the activities of H^+ and OH^- in the hydration layer are significantly altered due to ion surface interactions.
2.   *Basic*, usually shows converse behavior of ions in solution.
3.   *Amphoteric*, usually considered a composite of (1) and (2) with or without specific adsorption of anions. Specific adsorption of ions on oxides can affect the hydrophobicity significantly.

Finally, chemisorptions may be responsible for the conversion of hydrophilic surfaces to hydrophobic. Such a case is the adsorption of amines and Na-oleate on hematite [28].

The sulfide minerals behave quite differently from those of silicates and oxides and therefore hydrophobicity is achieved by different interactions. First, it should be pointed out that there is a problem of uncertainty whether the sulfide minerals are naturally hydrophobic or hydrophilic. Some sulfide minerals (i.e. molybdenum, elemental sulfur, reagar, etc.) are naturally hydrophobic. Sulfide minerals, in general, are regarded as inherently non-flotable. The latest studies concerning collectorless flotation [29,30] strongly pointed out that chalcopyrite and galena are flotable without the use of a collector. This phenomenon has been explained by the chemical charges of the mineral surface, which are closely related to the interfacial electrochemical potential of the system, which strongly affects the nature of the sulfide mineral surface (i.e. formation of S^o species) and therefore controls its collectorless flotation.

In real practice, during the treatment of polar metallic ores containing copper–zinc–pyrite and lead–copper–zinc, pyrite–copper–nickel—pyrrhotite, in a number of cases it has been observed that the flotability of copper–zinc–pyrite or copper—nickel–pyrrhotite is the same with or without the use of a collector. To practitioners of mineral processing, this phenomenon called "preactivated mineral species," which hardly explains the real problem associated with hydrophobicity and the modern theory of flotation. What is really known from actual practice is that the problem in such cases lies in the selective conversion of hydrophobic surfaces to hydrophilic, not the other way around. It should

therefore be pointed out that all sulfide minerals in the polymetallic complex system may acquire a certain degree of hydrophobicity in one way or another. This may be influenced by (a) compositional and textural variation of sulfide minerals, (b) their origin of formation or (c) surface modification. Numerous research works carried out on various ores described in the preceding chapters strongly point out that some minerals (i.e. chalcopyrite, sphalerite) from various origins have vastly different responses to flotation. The "acquired" hydrophobicity of the sulfide minerals may also come as a result of mineral surface transformation influenced by soluble cations coupled with electronic transition, which may take place in the surface redox process. However, it should be noted that sulfide minerals cannot form hydrogen bonds on the surfaces unlike the oxygen-containing minerals and therefore they are not strongly hydrophilic. Because of this, any change in the surface properties of the sulfide minerals can result in "acquired" hydrophobicity, which means that the sulfide minerals cannot be classified as either hydrophilic or hydrophobic. The hydrophobicity of the sulfide mineral phenomenon was the subject of numerous studies and as a result there are numerous interpretations.

- *Hydrophobicity influenced by physical-chemical adsorption*. The physical-chemical adsorption proposed by Mellgren [31] involves surface oxidation, which causes the formation of metal oxides, carbonates and sulfates where after collector additions such as xanthate, the collector reacts in a metathetical ion-exchange reaction. Later studies with xanthates have shown that the chemical reaction that occurs involves metal xanthates.
- *Hydrophobicity influenced by electrochemical adsorption*. The basis for electrochemical adsorption is oxygen and the model in general considers that sulfide minerals are good electronic conductors and interact with collectors that involve simultaneous electrochemical reaction at the mineral surface, where the cathodic step usually involves the reaction of oxygen:

$$O_2 + 2H_2O + 4e^- = 4OH^-$$
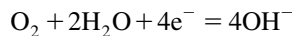
This is followed by an anodic step, involving oxidation of either the collector or the mineral [32].
- *Hydrophobicity influenced by elemental sulfur formation*. The response of the sulfide minerals to flotation without the use of collectors was first reported in 1932. However, more extensive studies have been carried out in 1970 and 1980 [33,34], indicating that flotability of the specific minerals is due to a sulfur-enriched surface.

Finkelstein *et al*. have extensively studied the hydrophobicity and the sulfur concentration at the mineral surface. Figure 6.8 shows the dependence of flotation recovery on the concentration of sulfur at the surface, indicating that there is no correlation between the amount of sulfur on the surface and the degree of flotability.
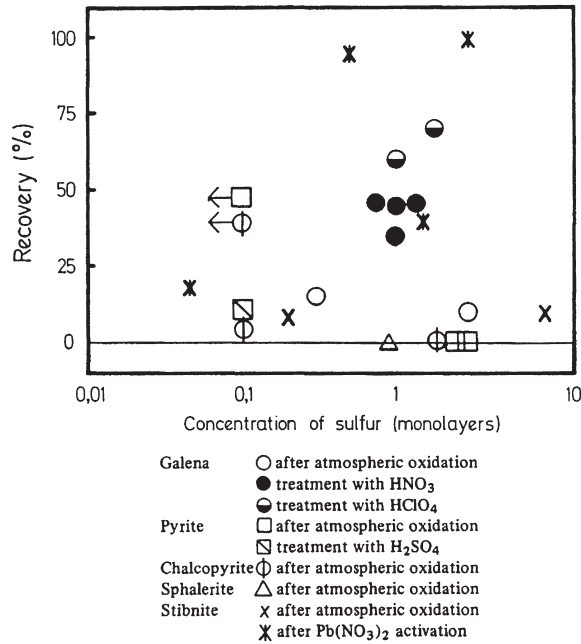
Figure 6.8 Dependence of flotation recovery on the concentration of sulfur at the surface [33].

This has been explained by the effect of hydrophobic oxidation of products whose presence would be favored by the conditions under which sulfur is formed.

6.5.2 Bubble mineralization

The mechanism of bubble mineralization and its transport of the froth phase is associated with a large number of physical, mechanical and chemical factors. As discussed in the previous section, the first and major prerequisite is the hydrophobicity of the particle. That is, the particle must be rendered hydrophobic to be able to attach to the air bubble. The physical factors that govern mineralization are numerous [35–37] and depend largely on the type of apparatus (i.e. flotation machine). This is perhaps the most controversial part associated with bubble mineralization.

In general, there are two main theories on bubble mineralization. These include (a) collision of hydrophobic mineral particles with air bubbles, in which the particle is attached to an air bubble, and (b) formation of air bubbles on the mineral particles as a result of precipitation of dissolved air gases in the water known in modern flotation theory as dissolved gas flotation.

The first process has been widely considered a principal theory of air bubble mineralization. The other process proposed in early stages of flotation development involved the initial precipitation of small bubbles that later collide with large air bubbles where coalescence occurs.

In the interpretation of the kinetics of bubble mineralization, two major principles must be clearly distinguished:

- Theoretical principles, where the study of bubble mineralization was carried out under conditions different than those used for industrial cells. With this also came empirical evaluation of bubble mineralization.
- Principles that reflect industrial equipment, i.e. flotation cells where the bubble mineralization kinetics are much different than those observed in a Whelan–Brown apparatus, where the collision of bubbles and particles are filmed [38].

The theoretical overview of bubble mineralization is summarized below:

Early studies by Taggart [37] are based on work with different apparatuses. It has been concluded that well-conditioned particles must collide several times with air bubbles before attachment occurs. Bogdanov *et al*. [39] postulated that the concentration of the floating minerals increases with the decrease in the depth of the pulp. In all of these studies, the importance of particle impact with bubbles was stressed. Studies conducted by Wrobel [40] showed that impact does not play any role in bubble mineralization.

The coalescence mechanism of bubble mineralization was proposed by Klassen [41] where the intermediate mechanism of attachment is involved. By this mechanism, large bubbles possessing sufficient buoying coalesce with micro-bubbles present on the mineral surface and are attached to those particles much faster than in the absence of micro-bubbles.

In the early 1950s, Mesheryakov [42] indicated in his studies on the activation of flotation by the nucleation of gas bubbles that the velocity of the process of attachment of mineral particles to micro-bubbles depends on quantity and quality of micro-bubbles at the solid–liquid interface.

Schulze [41] postulated that the attachment is governed by the following three processes

1.   Approach of the solid particle to the liquid–gaseous interface upon the formation of a thin film between phase boundaries.
2.   Formation of three-phase contact (TPC).
3.   Rupture of the particle out of the fluid interface.

This three-stage process is illustrated in Figure 6.9.

In the first step, a thin film is formed between the solid surface and the fluid interface influenced by electrostatic and Van der Waals forces. To destroy the film, work is required. This rupture is the prerequisite for the formation of TPC. The rupture process mainly plays a regulating role that is important for selectivity.

In the second step, the TPC is formed between the liquid, solid and gas phases with contact angle θ_i. The TPC must spread over the solid surface at a high speed to establish a particle in the gas–liquid interface.

The forces acting on the particles, such as its weight in the gravitational field, the heterostatic pressure, buoyancy, force of tension and turbulent field force on an impeller of a flotation machine have to be counter-balanced by the capillary force. For a particle to float,
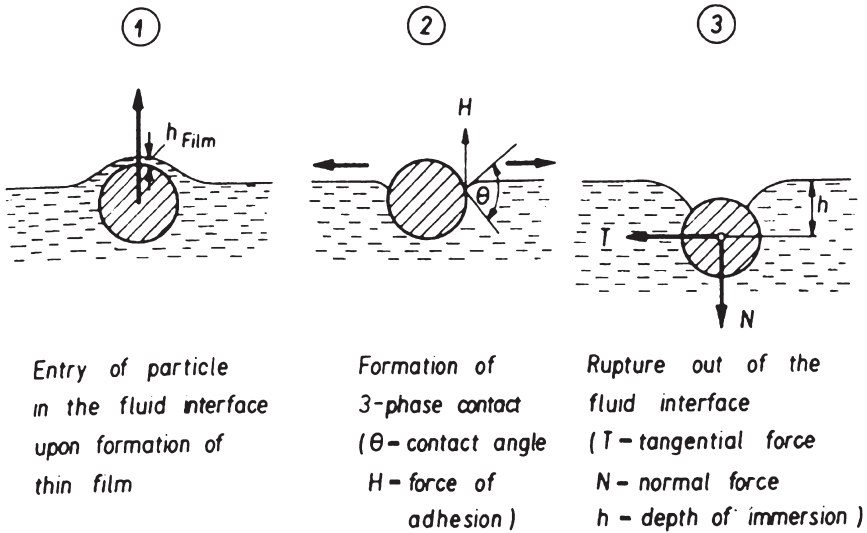
Figure 6.9 The three processes during the attachment of particles to bubbles [41].

the work required for rupturing the film of the phase boundary must be greater than its kinetic and potential energy.

In determining the surface energy of the solid particles in the air–liquid interface [43], the theory of contact angle (i.e. capillary force), stability of the bubble on the mineral surface (Figure 6.10) can be expressed by the following equation:

$$\cos \theta = \frac{\sigma t - \sigma z}{\sigma l} \tag{6.1}$$

where θ is the contact angle, σt the forces at the solid–gas interface, σz the forces at the solid–liquid interface and $\sigma \ell$ the forces at the liquid-gas interface.

The energy ΔW required for air bubbles to displace water per unit of surface can be expressed by the equation

$$\Delta W = \sigma_z + \sigma_z - \sigma t \tag{6.2}$$

From eqs. (6.1) and (6.2), the work required for attachment of air bubbles to solid particles can be expressed as

$$\Delta W = \sigma \ell (1 - \cos \theta) \tag{6.3}$$

The relation ΔW is the measure of the attachment of an air bubble to the hydrophobic particles. The detachment of particles from the air bubbles may occur if the detachment forces are
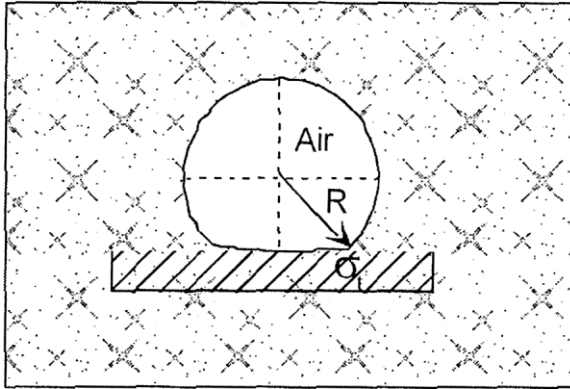
Figure 6.10 Graphic representation of the mineral bubble attachment.

greater than the capillary forces. For determining the capillary forces of an air bubble attachment to a flat mineral surface, Karbanov and Frimkin have proposed the following relations:

$$\underline{\Pi}a \sim Gz\sin\theta = Vg\wp + \frac{\Pi a^2(2\sigma - Hgc)}{4R} \qquad (6.4)$$

where a is the diameter of air bubble, Gz the surface force (dyn/cm), θ the contact angle, V the volume of air bubble (cm^3), g the gravitational forces (cm/sec^2), c the specific gravity of liquid phase, R the diameter of air bubble (cm) and H the height of air bubble.

Although this equation describes the behavior of particles on the attachment of air bubbles, it does not give a good correlation with experimental results.

Bogdanov *et al* have determined the probability of particle attachment to air bubbles through the probability of collision of a particle with an air bubble Wi and probability of attachment W_2.

The probability of particle collision with air bubbles is expressed as

$$Wi = \frac{3qLd}{2VD^2}\left(\frac{b_1 d}{b_2}\right) \qquad (6.5)$$

where q is the quantity of air in the flotation cell per unit time, L the trajectory of the air bubble in the pulp, d and D the average diameters of the particle and air bubble, respectively, b_1 and b_2 the coefficients of the rate of falling and rising of the particle and V the working area of flotation cell.

From the above equation, the probability of collision is proportional to the air volume and the trajectory of the bubble in the flotation cell.

The probability of attachment K is expressed as

$$W_2 = \frac{K}{Wi} \qquad (6.6)$$

The practical overview of bubble mineralization is quite different from the theoretical postulation. Since the theory of bubble mineralization was born, the concept of cell design has changed and, consequently, the hydrodynamic characteristics are dramatically altered in the large cells. Some of the new features of the larger size cells are (a) reduced power intake per unit volume by as much as 10 times, (b) geometric ratio between rotor/stator and a changed cell, (c) decreased air per unit volume of the cell and (d) the height of the pulp from the mixing zone (i.e. impeller stator) is increased six times in the large volume cells. Compared with the earlier theories of bubble mineralization, the present situation is very different.

Recently, Laplante *et al*. [44]studied the effect of airflow rate on the kinetics of flotation. They concluded that when the airflow rate increases, the size of the air bubble increases, resulting in a decrease in flotability. In contrast, Mahrota and Carup suggested that flotability increases with increase in airflow rate.

The studies conducted by Gorain *et al* [45] on the industrial 2.8-m³ flotation cell fitted with different impellers concluded that neither airflow rate nor the type of impeller used can be related to flotability. Instead, it is the bubble surface area flux *Sb* in the cell that is well correlated with the rate of flotation (Figure 6.11).

Assuming that the theories of bubble mineralization discussed earlier are correct, the dispersability of air bubbles together with the bubble diameter play a decisive role in the bubble particle mineralization from a practical point of view.

The mineralization of air bubbles is very much a kinetic process, which is expressed as the rate of flotation.

6.5.3   Kinetics of bubble mineralization

As discussed earlier, the theories of the bubble mineralization processare empirical. From the practical point of view, the process is highly complex and therefore the empirical
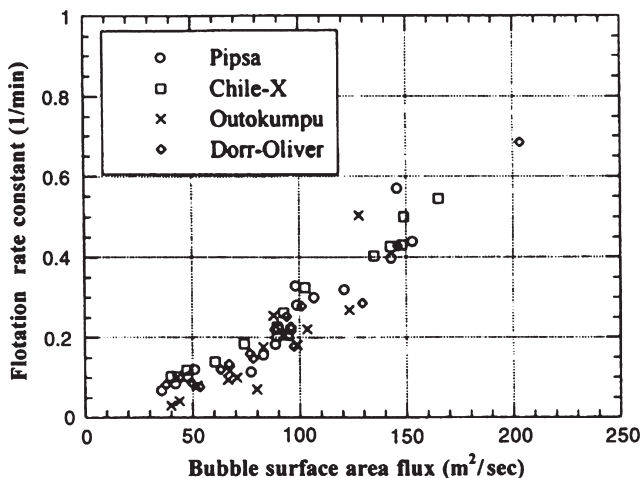
Figure 6.11 Variation in the flotation rate constant with bubble surface area flux for four different impellers and different operating conditions.

concept cannot be accurately applied in real practice. However, it is believed that an accurate evaluation of the kinetics of bubble mineralization can be facilitated by statistical analyses of the process.

Several aspects of the statistical evaluation of the probability of bubble mineralization are presented below.

The probability of flotation of a given mineral particle can be determined by the probabilities of the individual states. These states include

(a)   interaction of particles with reagents,
(b)   collision with bubbles and attachment to bubbles,
(c)   action of separating forces,
(d)   conditions and formation of airflow,
(e)   the process occurring in the froth layer, etc.

Table 6.2 shows some of the more important factors involved in the kinetics of bubble mineralization. The empirical calculation of the probability of bubble mineralization is given in eq. (6.5).

It should be noted that many attempts have been made to mathematically describe the kinetics of bubble mineralization, but no universal solution including all or most of the

Table 6.2

Principal factors determining probability of bubble mineralization [22][a]

Number	Probability of formation of mineralized bubbles	Interactions
1	Pulp density	
2	Action of separating forces	
3	Processes in froth layer	
4	Stability of attachment	
5	Form of mineral/bubble aggregates	
6	Bubble size	
7	Intensity of pulp agitation	
8	pulp climate	
9	Specific gravity of particles	
10	Shape of particles	
11	Hydration of particle surface	6, 15, 14, 13
12	Nature of particle surface	
13	Adsorption of gases	
14	Adsorbed reagents	
15	Presence of slime	
16	Precipitation of bubble from solution	
17	Quantities of bubbles	
18	Residence time of bubbles in pulp	
19	Aeration of pulp	17, 18, 6
20	Probability of collision of particles with bubbles	19, 7, 9
21	Probability of attachment or collectors	22, 10, 11
22	Modes of collision	

[a]An introduction of theories of flotation; Nedra, 1959.

variables has been found, which leads to the conclusion that the description of kinetics of bubble mineralization is purely empirical. From the standpoint of modern mineral processing science involving modeling of the flotation process, the empirical basis of the process has been a major obstacle. In relation to the bubble mineralization kinetics, the rate and intensity of flotation can best describe the flotation phenomenon in the real world.

6.5.4   Rate of flotation

The rate of flotation can be defined as a measure of the efficiency of flotation expressed per unit time. The rate of flotation accounts for the amount of floated particles with regard to time ($d\varepsilon/dt$). However, there are several problems related to the rate of flotation, some of which include (a) an experimental method determining the rate of flotation, (b) the effect of flotation variables and (c) equations denoting the rate of flotation. In spite of these, the rate of flotation is the most reliable source of describing the flotation kinetics. There are numerous methods by which the kinetics of flotation in determined. Some of the most prominent kinetic models are listed in Table 6.3.

Table 6.3

Description of different models

Author	Formula	Description
Grudera, Kaclur, model 1 (M1) component,	$\dfrac{dc}{dt} = KC^n \quad C = C_o \exp(-K_1 t)$ $r = R\infty(1 - \exp(-K_1 t))$ $A \xrightarrow{K_1} B$	Classical model. R is the recovery of component at times t, $R\infty$ the ultimate recovery of component, K_1 the first-order rate for component (min-1), n-order of reaction.
Klimpel, Huber Panu (Mayor Panu), (84), model 2 (M2) mate"	$r = R\infty\left[1 - \dfrac{1}{K_2 t}(1 - \exp(-K_2 t))\right]$	Rectangular distribution of flotability r is the recovery at time t, $R\infty$ the "ulti-recovery, K_2 the rate constant representing the largest allowed value of rectangular distribution
Mayer and Klimpel (84), model 3 (M3)	$r = \left(\dfrac{K_3}{K_3 - K_3}\right)(1 - \exp(-K_3^* t))$ $- \left(\dfrac{K_3}{K_3 - K_3^*}\right)(1 - \exp(-K_3 t))$ $A \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} B \xrightarrow{K_3^{*2}} \in$ A – concentration of component in the pulp B – concentration of component in the froth C – recovered component	First-order two-stage kinetic model. Similar to the model described by Harris and Rimmer [46.]. K_3 is much greater than K_3^*. K_3 – choose value (5000) to be sufficiently large for the model parameter solution.

Table 6.3   (*Continued*)

Author	Formula	Description
	K_3 – rate constant describing transfer from pulp to froth (min^{-1}) K_3^* – rate constant describing transfer from froth to concentrate (min^{-1}) K_{-3} – rate constant describing drainage from froth to pulp (min^{-1})	K_3 – large = $R\infty\,(1-\exp^{-}K_3t)$ taken as a limit which is the same as in M1. (The system that accounts for drainage from froth to pulp, but was neglected)
Mayer and Klimpel, model 4 (M4)	$$r = \frac{K_4 R\infty}{K_4 + K_{-4}}\left[1 - \exp(K_4 + K_{-4})t\right]$$ $A \underset{K_{-4}}{\overset{\overrightarrow{K^+}}{\leftarrow/}} B$ K_4 – rate constant describing transformation of pulp to frother (min^{-1}) K_{-4} – rate constant describing froth to drainage A – concentration of component of time t B – concentration of component in forth time t	First-order reversible kinetic model assumes constant flotability of particles. $K_4 \gg K_{-4}$ where K_{-4} is small. K_- $K_{-4} \to 0 = R^\infty[1-\exp(-K_4 t)]$
Imaizumi and Inoue, 1965, model 5 (M5)	$$\frac{W}{W_0} = \frac{1}{(1+Kt)^N}$$ rearranged into the recovery term when $\quad N = 1$ $$r = R\infty\left(1 - \frac{1}{1+t/K_5}\right)$$ W – weight of component in cell at time t W_0 – weight of component in cell at time $t = 0$ K – rate constant (min) N – number of cells in series	Fully mixed reactor model rate term K_5 is the denominator so that its units will be in terms of time instead time inverse. Note that for small K is the $R\infty$ most important parameter.
Meyer and Klimpel, model 6 (M6)	$$r = \frac{K_6 t}{(1+K_6 t)^m}$$ K_6 – rate constant at time t $$\text{Limit } t \to 0 \frac{K_6 t}{(1+K_6 t)^m} = K^6 t$$	Gas/solid kinetic adsorption model. Significance of this model is that it does not have ultimate recovery $R\infty$, instead includes a parameter that approximates ultimate recovery at reasonable flotation time. (m has value greater than 1)
Model 7 (M7), similar to Bull model	$$\frac{r}{r} = \frac{KC}{1+KC} 1$$	Improved gas/solid adsorption model. M6 is the same as the Langmui

Table 6.3 (*Continued*)

Author	Formula	Description
	r − adsorbtion density $r\infty$ − ultimate adsrobtion desedensity (monolayer) K − equilbrium constant C − concentration $$r = R\infty \left(\frac{K_7 t}{a + K_7 t} \right) 2$$ $$\frac{t}{r} = \frac{1}{K_7 R\infty} + \frac{t}{R\infty} 3$$ $$\frac{1}{R} = \left(\frac{1}{K_7 R\infty} \right)\frac{1}{t} + \frac{1}{R\infty} 4$$	adsorption model when $m = 1$. Substituting recovery for adsorption density, rate for equilibrium constant and time for concentration. $\lim K\dfrac{1}{s} = \dfrac{1}{K_5}$ (Model 5 than) $$r = R\infty \frac{(K\frac{1}{5}t)}{1 + K\frac{1}{s}t}$$ indicating that mathematical form of M5 and M7 is the same.
Arbiter, 1951, model 8 (M8)	$$r = \frac{R\infty 2 K_8 t}{1 + R\infty K_8 t}$$	Second-order kinetic model derived from first-order model by assuming $N = 2$ and integrating to obtain second-order expression (identical to M5 and M7). $R\infty$ becomes bigger when approaches 1
Klimpel, 1980, model 9 (M9)	$$r = R\infty \left\{ 1 - \frac{1}{K_9 t} [\ln(1 + K_9 t)] \right\}$$	Second-order kinetic model with rectangular distribution of flotabilities. As for Model 2, this model assumes that flotation components are rectangularly distributed.
Kellsal, model 10 (M10)	$$r = (1 - \phi)\left[1\exp\left(\frac{-K - t}{10t} \right) \right]$$ $$+ \phi \left[1 - \exp\left(\frac{-Kt}{105} \right) \right]$$ ϕ = fraction of flotation component with slow rate constant. Kt = fast rate constant (min^{-1}) 105 = slow rate constant (min^{-1})	Ultimate fractional recovery is assumed to be 1. Fits data better than 1, 3, 4

Table 6.3   (*Continued*)

Author	Formula	Description
Jowett, 1974, model 11 (M11)	$r = (R\infty - \phi)\,(1-\exp-\ Kaaft)$ $+\phi(1-\exp(-k115x6)]$	For parameters fast and slow floating compounds. Confidence are much less discrete and introduces gross parameter dilute which completely masked test differences.
Ene-Dano Loche, Huber Panu, 1976, model 12 (M12)	$r = R\infty\left(1 - \dfrac{\exp(K125-t)-\exp(K124t)}{(Ku124-Ku125)t}\right)$ $Ku125$ – rate constant for lower size of rectangular size distribution $K124$ – rate constant for upper size of rectangular conditional size distribution.	The parameter kinetic model with particle flotability proportional to the size distribution.

As can be seen from these data, it is not possible to develop a universal model that would describe the flotation process as a whole. In the mini-models listed, the authors have used simple ores (e.g. copper porphyry ores), which would correlate well with experimental data (e.g. Klimpel models). In the case of complex ores, such a model cannot be applied. In general, the approach in model selection would be the selection of criteria based on the process that has to be described (effect of reagents, pulp density, etc). Some criteria on the methodology in the determination of the rate of flotation is described below.

The most simple example of the process kinetics are the rate tf/h, concentrate production tc/h), recovery per given unit time, etc. As an example of how to use these criteria, let us examine the floatability of sphalerite as a function of aeration assuming that aeration had a positive effect on sphalerite flotation. It is of interest to analyze the kinetics of sphalerite flotation with and without aeration. These results are plotted in Figure 6.12, indicating that with aeration, flotation of zinc improves in the initial stage (i.e. first 4 min) and also produces improved selectivity. In practice, from this example, it may be possible to increase froth discharge rate, which would result in the improvement of overall circuit performance. Of more importance is the relationship between rate of flotation of floated minerals and gangue particles expressed as selectivity index L.

$$L = \frac{Km}{Kg} - \frac{\log(1-\varepsilon m)}{\log(1-\varepsilon g)}$$

In assessing the kinetics of flotation, two steps are usually followed. In the first step, using experimental data, recovery ε versus time t is plotted in increments $\Delta\varepsilon$, and in the second step, the rate of flotation determined using one of the formulas. The simplest kinetic formula is the so-called first-order chemical reaction.

$$\frac{\mathrm{d}\varepsilon}{\mathrm{d}t} = K(1-\varepsilon) \tag{6.7}$$
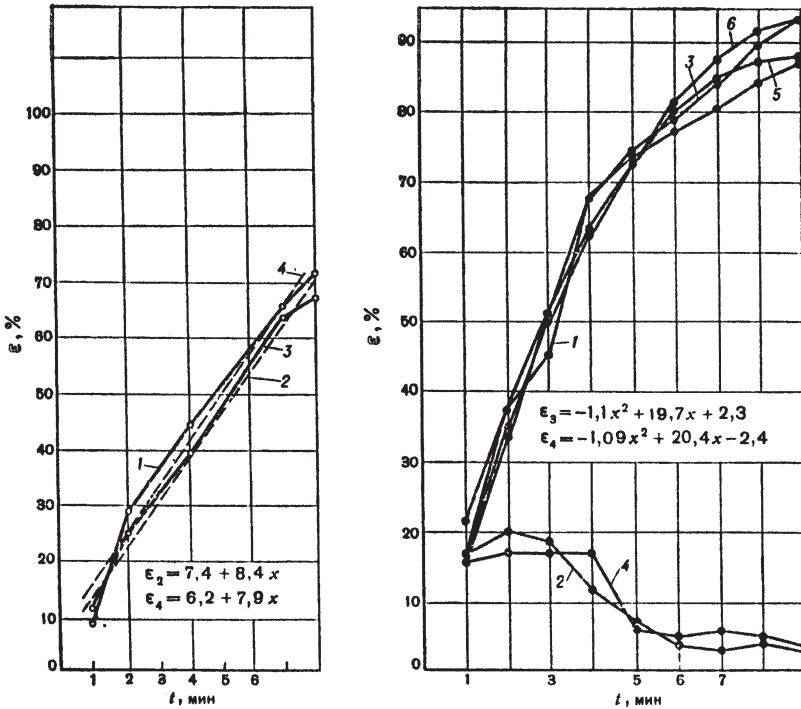
Figure 6.12 Flotation kinetics of sphalerite in a zinc–pyrite bulk flotation. Curves 1 and 4 with aeration, 2 and 3 without aeration. Curves 1 and 3 experimental, 2 and 4 calculated.

where ε is the recovery, t the time and K the rate constant.

Assuming that at $t = 0$, $\varepsilon = 0$:

$$\varepsilon(t) = 1 - e^{-Kt} \quad \text{or} \quad 1 - \varepsilon = e^{-Kt} \tag{6.8}$$

It should be noted that it cannot be assumed that experimental data will fit the theoretical curve. For example, curve $a\chi^{\delta}$ can be similar to curve $1 - e^{-Kt}$, in which case curve $\varepsilon(t)$ would satisfy the first order. This corresponds to flotability of slow floating fractions where recovery increase per unit time is small. Giving different values for K, it is possible to fit several curves that would satisfy eq. (6.8) and best fit experimental data that represent the kinetic constant. This method is considered to be inaccurate. A more simple and accurate way is the linear representation of the kinetic constant. The eq. (6.8) in logarithmic form is as follows:

$$\ln(1 - \varepsilon) = -Kt \quad \text{or} \quad \ln\left(\frac{1}{1 - \varepsilon}\right) = Kt \tag{6.9}$$

This equation satisfies the first order in coordinates and represents the strength line. The tangent of the slope angle is the kinetic constant. Expressing eq. (6.7) in logarithmic form:

$$\log \frac{d\varepsilon}{dt} = \log k + \log(1 - \varepsilon) \tag{6.10}$$

where the curve coordinates should also be a linear curve from which the kinetic constant can be graphically determined. The graphical method of determining the kinetic constant is not accurate and can be used only to give some idea of the kinetics of a process. For a more accurate determination of the kinetic constant, a statistical method is used and usually accounts for experimental errors, as shown in the example below:

Assuming that $\sigma(R)$ is the experimental error for recovery then the corrected recovery would be $E_{(c)} = E \pm \sigma_{(R)}$ including corrected recovery in the first-order equation, the kinetic constant is determined from the following relations:

$$K = \frac{1}{t} \ln \frac{1}{1-E} = \frac{\ln 10}{t} \lg \frac{1}{1-E_{(c)}} \quad \text{for In} 10 = 2{,}3026$$

$$K = \frac{E}{t}\left(1 + \frac{E^2}{3}\right) \text{ after revision of this equation}$$

$$\Delta K = \frac{1}{t}\left(E^2\sigma + E\sigma(1+5) + \sigma + \frac{\left(\dfrac{\sigma}{2+\sigma}\right)}{\left(\dfrac{3}{3+t\,\sigma/2}\right)} \right)(E^2 + E + 1)$$

$$= \frac{E^2\sigma + E\sigma(1+\sigma) + \sigma + \sigma/(2+\sigma^4/3)}{t} = \frac{\sigma}{2}(E^2 + E + 1)$$

If, for example, t = 0.05 during 6 min of flotation at a recovery of $E = 0.9$, then $K = 0.03$ or $\Delta K = 0.00225$ with a relative error of 3–5%.

This method would be sufficient for simple study case (i.e. simple copper ore). In more complex cases (ore), the flotability of minerals is not always uniform; so calculating the rate constant using recovery for short intervals of time usually gives higher rate constants and for longer intervals the rate constant is lower. To avoid this problem, the least squares method is used. For example,

$$Y = at \tag{6.11}$$

$$Y = a + x \tag{6.12}$$

In eq. 6.11,

$$y = \ln \frac{1}{1-E}; a = K$$

In eq. 6.12, y = log(de/dt); a = log k, x = log(1 − E).

Table 6.4

Kinetic constant calculation using least squares method

tic %	Ei%	y	TixYi	Ti²	at	e⁻ᵃᵗ	Ex
10	13.1	0.143	1.430	100	0.089	0.9148	8.5
20	21.1	0.237	4.760	400	0.178	0.8369	16.3
40	37.5	0.469	17.586	1600	0.356	0.7005	30.0
60	50.4	0.700	54.00	3600	0.534	0.5862	41.4
100	68.0	1.138	113.80	10000	0.890	0.4106	58.9
160	81.5	1.685	269.60	25600	1.424	0.2407	75.9
200	84.4	1.865	371.120	40000	1.780	0.1686	83.0
260	85.2	1.908	496.080	67600	2.314	0.0989	90.1

E1328.38E1.48.90a = K = (1328.35/148.900 = 0.0089)

For eq. 6.11, for n experiments,

$$Z = \sum_{r=1}^{n}(ya - at_1)^2$$

Calculating $\dfrac{dz}{de}$ at 0 flotation time: $\sum_{r=1}^{n} E_1(ya - ati) = 0$

From this equation, a is calculated as

$$a = \frac{\sum_{i-1}^{n} EiYi}{\sum_{i-1}^{n} E\frac{2}{1}}$$

From the example using copper flotation data, the calculation of the kinetic constant is shown in Table 6.4. The data approximate the curve

$$E(t) = 1 - \exp(-00089E)$$

Using the least squares method, eq. (6.12) becomes:

$$a = \frac{1}{n}\sum_{t=1}^{n}(Yi - xi)$$

In reality, kinetic curves derived from experimental data often do not fit values calculated from the first-order equation. This may be due to a number of factors, including differences in flotability. This is where different kinetic models come into play. The following example of fit model development illustrates the model development process to give some idea about

how various models from Table 6.3 are derived and what they mean. In the majority of model developments, it is assumed that there is a maximum value for recovery E_{max} such that

$$Et = E_{max}(1 - E^{-KT}) \tag{6.13}$$

If the flotation time is sufficiently long, then it can be assumed that E_{max} is equal to the recovery achieved in the experiment. On this basis, the rate constant calculation is derived from the following relations:

$$e^{-KT} = 1 - \frac{1}{E_{max}} \text{ from which } K_t = \ln\frac{1}{\Delta - \dfrac{E}{E_{max}}}$$

From eq. (6.13), the expression for kinetic constant is

$$Z = \sum_{i=1}^{n}\left[Yi - a(1 - e^{lt}i)\right]^2$$

If $Yi = E(Ti)$ and $a = E_{max}$, $b = K$; then

$$\sum_{i-1}^{n}\left[Yi - a(1 - e^{-lti})\right](1 - E^{-bti}) = 0$$

$$\sum_{i-1}^{n}\left[Yi - a(1 - e^{-lti})\right]tie^{-bti} = 0$$

The simpler but less accurate method of determining E_{max} is a graphical method where during the experiment two recovery values are determined at two time intervals:

$E(tr)$ and $E(tr - 1) = E_{r-1}$ representing $\Delta = tr - tr - 1$

From eq. (6.13),

$$Er - 1 = E_{max}(1 - e^{-Ktr-1})$$
$$Er = E_{max}(1 - e^{-K(tr-1\Delta)})$$

Substituting for $E_{max} - Er - 1$ and $E_{max} - Er$ in the following equation:

$$\frac{E_{max} - Er - 1}{E_{max} - Er} = e^{-K\Delta} \quad \text{or}$$

$$Er - 1 = Ere^{-K\Delta} + E_{max}(1 - e^{-K\Delta})$$

The above equation is a linear function of $Er - 1 = a + bEr$. To define this relationship, the experimental data can be approximated to obtain a curve that is near E_{max}. At relatively long flotation time, it is always assumed that recovery is maximum therefore Er and $Er - 1$ equal the maximum. The graphical determination of E_{max} involves determining curve intercepts from $Er - 1$ (Er) and curve $Er - 1 = Er$. By including the graphical value of E_{max} in eq. (6.13), the kinetic constant is calculated. The accuracy of this method depends on the accuracy of the curves and the angle of intercept. For smaller angles of intercept, the error is large.

REFERENCES

1. Somasundaran, P., Interfacial Chemistry of Particulate Flotation: Advances in Interfacial Phenomena of Particulate Solution/Gas Systems, *Application to Flotation Research*, AICE, New York, 1975.
2. Sutherland, H.L., and Wark, I.W., *Principles of Flotation*, Australian IMM, Melbourne, 1955.
3. Laskowski, J., Particle Bubble Attachment in Flotation, *Mineral Science*, Vol. 6, No. 4, pp. 66–71, 1974.
4. Gardner, J.R., and Woods, R., The Use of Particulate Bed Electrode for the Electrochemical Investigation of the Metal and Sulphide Flotation. *Australian Journal of Chemistry*, Vol. 27, pp. 21–33, 1973.
5. Gardner, J.R., and Woods, R., *An Electrochemical Investigation of Contact Angle and of Flotation in the Presence of Alkyl Xanthate*, 1974.
6. Arbiter, N., and Beebe, R.R., Mineral Processing Weeds – Erolution or Revolution, Challenging Status of Domestic Mining, In (M.C. Fuertenau and K.V.S. Sastry eds) *Challenges in Mineral Processing*, SME Inc, Littleton, Colorado, 1989.
7. Bernal, J.O., and Fowler, R., Structure of Water and Ionic Solutions. *Advanced Physical Science*, Moscow, No. 5, 1954.
8. Langmuir, I., The Mechanism of the Surface Phenomena of Flotation. *Transactions of the Faraday Society*, Vol. 20, pp. 138–144, 1920.
9. Fuerstenau, D.W., Mineral–Water Interfaces and the Electrical Double Layer Principles of Flotation, In (R.P. King ed) *IMME*, South African Institute of Mining & Metallurgy, Johannesburg, 1982.
10. Poling, G.W., Reaction between Thiol Reagents and Sulphide Minerals in Flotation, In (M.C. Fuerstenau ed) *A.M. Gaudin Memorial Volume*, AIME, New York, pp. 334–363, 1976.
11. Finkelstein, N.P., Quantitative Aspects of the Role of Oxygen in the Interaction between Xanthate and Galena, *Separation Science*, No. 5, pp. 277–295, 1970.
12. Peck, A.S., and Wadsworth, M.E., An infrared study of the flotation of Hematite with Oleic Acid and Sodium Oleate, *Trans. AIME*, pp.235–301, 1964.
13. Iwasaki, I., Cooke S.R.B., and Choi, H.S., Flotation Characteristics of Hematite, Goethite and Activated Quartz with 18-Carbon Aliphatic Acid and Related Compounds, *Transactions of AIME*, p. 217, 1960.
14. Gaudin, A.M., and Fuerstenau, D.W., Activation and Deactivation of Sphalerite with Ag and Cl ions, *Transactions of IME*, Vol. 208, p. 1365, 1957.
15. Klassen, V.I., and Mocrousor, V.A., An Introduction to the Theory of Flotation, Nedra, Moscow, pp. 39–70, 1959.
16. Harkins, D., *The Physical Chemistry of Surface Films*, Reinhold, New York, 1952.

17. Adam, N.K., and Livingston, H.K., Contact Angle and Work of Adhesion, *Nature*, Vol. 180, pp. 128–140, 1958.
18. Kitchener, J.A., Gravity, the Angle of Contact and Young's Equation. A Critical Review, *Proceedings of 3rd International Congress of Surface Active Cologne*, France Vol. 2, pp. 426–432, 1960.
19. Johnston, R.E., Dettre, R.H., and Brandreth, J.R., Dynamic Contact Angles and Contact Angle Hysteresis, *Journal of Colloid Interface Science*, Vol. 62, pp. 205–212, 1977.
20. Neumann, Q.W., and Good, R.J., Thermodynamics of Contact Angles 1, Heterogenous Solid Surfaces, *Journal of Colloid Interface Science*, Vol. 38, pp. 341–258, 1972.
21. Padday, J.F., Wetting, *Spreading and Adhesion*, Academic Press, London, 1978.
22. Klassen, V.I., and Macrousov, V.A., An Introduction to Theory of Flotation, Nedra, Moscow, 1958.
23. Leya, J., and Poling, G.W., On Interpretation of Contact Angle, V International Mineral Processing Congress, London, pp. 325–332, 1960.
24. Ralston, J., and Neuxcombe, G., Static and Dynamic Contact Angle, In (J.C. Laskowsky and J. Ralston eds) *Colloid Chemistry in Mineral Processing*, Elsevier 1992.
25. Laskowski, J., and Kitchener, J.A., The Hydrophilic–Hydrophobic Transition of Silica, *Journal of Colloid and Interface Science*, Vol. 29, No.4, pp. 670–679, 1969.
26. Somasundaran, P., Interfacial Chemistry of Particulate Flotation, In (P. Somasundaran and R. B. Grieves eds) *Advances in Interfacial Phenomena*, Vol. 71, pp. 11–21, 1975.
27. Heyes, G.W., and Trahar, W.J., The Natural Flotability of Chalcopyrite, *International Journal of Mineral Processing*, Vol. 7, pp. 317–344, 1977.
28. Lepetic, V.M., Flotation of Chalcopyrite without Collector after Dry Autogenous Grinding, *Canadian Institute of Metallurgy Bulletin*, pp. 71–77, 1974.
29. Taggart, A.F., Chemical Reactions in Flotation, *IMME*, No. 312, pp. 3–33, 1930.
30. Leya, J., and Schulman, J.H., Molecular Interaction between Frothers and Collectors, *Transactions of IMME*, Vol. 72, pp. 417–423, 1962.
31. Mellgren, O., Heat of Absorption and Surface Reactions of Potassium Ethyl Xanthate on Galena, *IMME*, Vol. 235, pp. 46–60, 1966.
32. Allison, S.A., Finkelstein N.P., *Transactions of AIME*, Vol. 3, p. 2613, 1972.
33. Finkelstein, N.P., and Allison, S.A., Natural and Induced Hydrophobicity in Sulphide Mineral Systems, *AICHE Symposium Series*, Vol. 71, No. 150, pp. 11–22, 1975.
34. Arbiter, H., and Harris, K., Modeling of Flotation Process using Hydrodynamic Criteria of Flotation Machine, *VIII International Mineral Processing Congress*, Moscow, 1968.
35. Arutyunan, B.S., Evaluation of the Air Distribution and Transport in Deep Air Lift Machines, *Experimental Information*, No. 6, 1960.
36. Whelan, P.R., and Brown, D.J., *Particle Bubble Attachment in Froth Flotation*. AICHE Symposium Series, Vol. 73, No. 180, 1977.
37. Taggart, A. (ed) *Handbook of Mineral Dressing*, Vol. 3, (GNTI), 1930.
38. Volkova, Z.V., Attachment of Mineral Particles in Air Bubble in Flotation, *Journal of Physical Chemistry*, Moscow, No. 14, 1950.
39. Klassen, V.I., Activation of Flotable Minerals by Air Precipitating from Solution, *Process Academy*, No. 5, pp. 6–21, 1949.
40. Wrobel, S., *Mine and Quarry*, No. 313, pp. 48–55, 1952.
41. Shulze, H.J., *New Theoretical and Experimental Investigation on Stability of Bubble/Particle Aggregates in Flotation: A Theory of Upper Particle Size on Flotability*, 1977.
42. Mesheryakov, N.F., *Flotation Machines*, Izdatelstro, Nedra, Moscow 1972.
43. Bogdanov, O.S., and Podnek, A.K., Basics of Theory and Technology of Flotation Process, *Transation Institute of Mechanobre, Leningrad, Russia*, p. 124, 1959.

44. Laplante, A.R., Finch, A.R., The Effect of Airflow Rate on the Kinetics of Flotation, Part I, The Transfer of Material from the Slurry to the Froth. *International Journal of Mineral Processing*, Vol. 11, p. 203, 1983.
45. Gorain, B.K., Studies of Impeller Type, Impeller Speed and Airflow Rate in the Industrial Scale Flotation Cell, Part 4, Effect of Bubble Surface Area Flux on Flotation Performance, *Mineral Engineering*, Vol. 96, pp. 148–156, 1996.
46. Harris, A., and Rimmer, H.W., Study of Two Phase Model of the Flotation Process, *Trans IMM*, Vol. 75, ppc 153–c162, 1966.

Adsorption Mechanism of Flotation Collectors

7.1 INTRODUCTION

The adsorption mechanism of flotation collectors on mineral surfaces is a highly complex phenomenon. Even with today's scientific approach to mineral processing, there remain unresolved aspects with respect to collector adsorption. This can be best illustrated through some passages from contributing investigators.

On xanthate adsorption: "Despite the large amount of studies that have been devoted to the reaction between sulfide minerals and xanthate collectors, it is still uncertain, which of the reaction products are responsible for rendering minerals hydrophobic" [1].

On starch adsorption: "The adsorption mechanism of starch-type polysaccharides on mineral surfaces are not well understood. While hydrogen bonding was considered the primary adsorption mechanism for starch, hydrophobic bonding was proposed for the adsorption of dextrin" [2].

On colloidal interfaces: "Despite many recent studies on wetting phenomena some fundamental surface chemical problems remain to be solved for a proper understanding of colloidal interactions and particularly of the mechanism of the froth flotation process for beneficiation of minerals" [3].

On the role of oxygen on xanthate adsorption: "The role of oxygen in xanthate adsorption has been the subject of considerable controversy over the years. Some investigators have stated that the presence of oxygen is absolutely necessary for xanthate adsorption on sulfides, while others have found the presence of quantities of oxygen at the mono-layer coverage to be deleterious to xanthate adsorption" [4].

Researchers concerned with the fundamentals of reagent adsorption may argue on these issues quite rightfully. In practical situations, there are many contributing factors.

For example, in a flotation pulp, a fairly large number of xanthate species may be present in various proportions such as xanthate ion, xanthic acid, dixanthogen, monothiocarbonate ion, and carbon disulfide. Because of the large variety of species present in any xanthate flotation system, it is very unlikely that only a single mechanism of adsorption is involved. Therefore, all mechanisms proposed in various studies may be correct for specific conditions.

Whether or not oxygen is involved in the xanthate adsorption, its presence when treating complex sulfide ores is highly important. This has been proven in practice many times.

Why is the mechanism of starch and dextrin adsorption on mineral surfaces not understood? The simple answer is the lack of understanding of the chemistry of starches and dextrins. In 220 references published on the use of polymers in flotation since the 1980s, i.e. starches and dextrins, only two papers have described the starches and dextrins available in the market today, the different chemical compositions and the effect of the methods of manufacturing.

In spite of such difficulties, the knowledge generated in these studies is extremely helpful in designing reagent schemes to solve difficult metallurgical problems. The importance of the adsorption mechanism cannot be judged as right or wrong or whether such a phenomenon is understood or not. The proposed mechanism can serve as a starting point for the selection of reagents and might lead to a better utilization of various reagents in mineral processing. The subsequent chapters on the reagent adsorption phenomenon are arranged in a way to help in the selection of specific reagent schemes rather than understanding the adsorption phenomenon. In reality, there are many phenomena that simply cannot be explained, as shown in this very unusual example.

In 1995, a pilot plant study on perovskite ore was conducted (i.e. titanium calcium minerals) using a modified phosphoric ester as the principal collector. During the pilot plant campaign, quantities of concentrate were produced and stored in plastic drums outside the building exposed to hot summers and cold winters. Four years later, a sample was taken, repulped and surprisingly the concentrate was flotable. Virtually all perovskite was floated. What kind of adsorption mechanism is involved that would render hydrophobicity after four years of storage? Modern science could not explain this phenomenon and the client is still searching for a solution to desorb the collector before it goes to hydrometallurgical treatment.

7.2   TECHNIQUES USED IN THE STUDIES

There are a fairly large number of techniques used to study the adsorption of reagents on mineral surfaces. In most of these studies, polished mineral surfaces or synthetic mixtures of minerals are used. The reason for this is quite obvious. Minerals that occur in natural ores would complicate these studies by introducing either contaminated mineral surfaces or a surface with inherited defects in the crystal structure.

Electrochemical techniques are used most widely, individually or along with other techniques. Table 7.1 lists some techniques applied to the study of adsorption phenomena.

Advantages and disadvantages of these techniques had been discussed at length [5–8]. The preference of using a specific technique appears to be at the discretion of the researchers who use these techniques.

The application field for electrochemical techniques is quite large. Table 7.2 contains a list of applications of electrochemical techniques employed specifically in sulfide mineral flotation. These techniques combined with those listed in Table 7.1 represent the basic techniques for the study of adsorption of reagents, characterization of mineral surfaces and interfacial phenomena. It should be noted that some of these electrochemical techniques may be directly applied in operating plants as a tool in optimizing the reagent schemes.

Table 7.1

Experimental techniques for studies in mineral processing

Tasks	Techniques	Type of information
Characterization of surface	1. Electron microscopy	Visual observation.
	2. Cathodic polarization	Indicate cracks and crystal defects
	3. Gas adsorption	Indicate cracks and micropores in surface
	4. Electron energy diffraction (LEED)	Surface atomic structure
	5. Electron spectroscopy (ESCA)	Surface chemical analyses
Surface/solution interaction	1. Surface reaction (indirect, analytical methods, pH, AA, O_2 electrodes, specific electrodes)	Collector concentration, interactions (xanthate, oxygen, etc).
	2. Calorimetry	Heat of reaction
	3. Infrared spectroscopy	Extraction & analyses of surface products
	4. Electron diffraction	Orientation of adsorbed species
	5. Electron spectroscopy (ESCA) and electron spin resonance (ESR)	Oxidation state of surface
	6. Micro autoradiography	Presence of foreign ions on mineral surface
	7. Electrochemical techniques	See Table 7.2.
	8. Zeta potential	Adsorption behavior of species
Surface wetability and hydrophobicity	1. Contact angle measurement	Wetability of surface
	2. Captive bubble + goniometer	Wetability of surface
	3. Halimond tube flotation	Wetability of surface
Particle/bubble Interaction	1. Cinematographic	Attachment of particle to bubble behavior of small particles in stabilizing or breaking Liquid film between air bubbles.
	2. High-speed photography	

Table 7-2

Electrochemical techniques used in sulfide mineral flotation

Electrochemical techniques	Other techniques	Type of information
Rest potentials		
(a) Galena electrode/xanthate solution	−	Electrochemical model of adsorption
(b) Several sulfide mineral. No reagent	−	Relative order of oxidation
(c) Platinum electrode/flotation pulp	−	ORP of solution
(d) Several sulfide/xanthate solutions	−	Correlation with product of oxidation
Thermodynamic Eh−pH diagram		
Calculation of thermodynamic diagrams in the present of flotation reagents	−	Prediction of stability domains of flotation/non-flotation

(*Continued*)

Table 7-2   (*Continued*)

Electrochemical techniques	Other techniques	Type of information
Polarization		
(a) Steady-state polarization	−	Oxidation of xanthate on mineral electrode
(b) Steady-state polarization	Reflection spectroscopy, x-ray diffraction	Identification of surface products
(c) Steady-state polarization	UV spectroscopy	Identification of solution species
(d) Potentiodynamic voltametry	−	Sulfide mineral collector reaction
(e) Potentiodynamic voltametry	Contact angle	Contact angle as function of potential
(f) Potentiodynamic voltametry	photo voltage	Indirect surface characterization
(g) Potentiodynamic voltametry	FTIR spectroscopy	Identification of surface species
(h) Potentiodynamic voltametry	XPS	Identification of surface species
(i) Galvanostatic polarization	Contact angle	Surface hydrophobicity
Transient methods		
(a) Chronoamperometry	−	Mechanism of xanthate adsorption
(b) Intermittent galvanostatic polarization	−	Indirect information of surface products
(c) Interfacial capacitance	−	Capacitance as a function of potentials
(d) AC impedance	−	Impedance as a function of potential

7.3   REQUIREMENTS FOR COLLECTOR ADSORPTION

The textbooks for mineral processing describe the criterion of partial wetting of the hydrophobic surface as "a resistance of surface displacement of the adsorbate at the line of contact between the three phases, solids–liquid–gas." This means that reagents that convert a hydrophilic to a hydrophobic surface must be adsorbed and become relatively immobilized. This immobilization increases the ability to withstand movement of the liquid along the shear plane adjacent to solid without displacement, thus preventing complete wetting of the solids. It is believed that the concept of relative immobilization of collector molecules proceeds in different stages, shown in Figure 7.1 [9]. Only states within the intermediate energy levels, e.g. within the range F, may be appropriate for flotation purposes. A very strong adsorption, chemisorbed state of $\theta \cong O$, may lead to excessive weakening or even a breakage of the residual bonds between the adsorption site and the solid. Some species that are physically adsorbed and within the range $0.8 \ Z \leq \theta \leq 1$ may be too weak to withstand external forces imposed during attachment to bubbles.

In view of the major differences in the properties of different reagents, the conditions leading to adsorption are different. In general, to achieve adsorption several requirements must be fulfilled. These include:

(a)   Relative immobilization of the collector species.
(b)   Development of sufficient hydrophobic character to withstand the mechanical and dynamic effects of the particular flotation system.
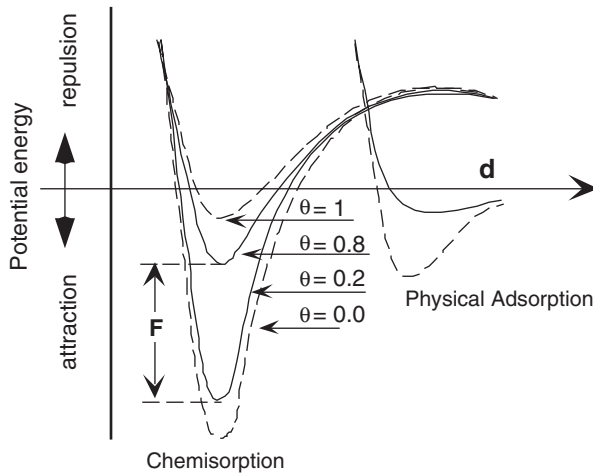
Figure 7.1 Schematic representation of the range of adsorption energies on chemisorption and physical adsorption of surfactants conducive to flotation.

(c)   Selection of a collector–modifier system that would permit control of adequate selectivity.

(d)   Suitable choice of a collector–frother system that would provide satisfactory separation kinetics of separation to be achieved.

In operating plants, it is not possible to check on the mode of adsorption of a collector on a mineral surface or to know the interaction of a vast number of collectors, modifiers and frothers. However, it is possible to exploit the general knowledge of collector adsorption to develop an effective reagent scheme for selective separation of different sulfide and non-sulfide ores. This is achieved through a combination of practical and theoretical knowledge of the action of reagents. This can be demonstrated through the following examples.

1.   The theoretical knowledge obtained from research on long-chain cationic collectors [9–11] provided a basis for the difficult sequential flotation of K feldspar from Na feldspar, two minerals with almost the same flotability. How? It has been established that if CF_3 and CF_2 groups from fluorochemical collectors are substituted for CH_3 and CH_2 groups, there is an acid strengthening effect of anionic groups and a base weakening on cationic groups. In the separation of K feldspar and Na feldspar, this can be highly advantageous because under high concentration of salts (i.e. NaCl and KCl) in the pulp, the collector with strengthened anionic groups would selectively adsorb a K feldspar and selective flotation is achieved.

2.   In the flotation of massive sulfide Cu–Pb–Zn ores, where the bulk Cu–Pb concentrate is floated and subsequently separated using, e.g. a collector depression method, the adsorption mechanism of xanthates can be advantageously utilized for desorption of collector from galena. For example, when copper–lead is floated in slightly acidic conditions, xanthic acid (*R*OCSSH) is formed, which can be effectively removed from the galena surface in the presence of a specific dextrin allowing sequential flotation.

3.   The knowledge accumulated on the pentlandite–pyrrhotite–pyrite system is now utilized to advantage for effectively depressing hexagonal and monoclinic pyrrhotite. These are a few examples out of many where theoretical aspects of reagent adsorption can form the basis for designing a reagent scheme for any particular ore.

7.4   MECHANISM OF SULFHYDRYL COLLECTOR ADSORPTION

7.4.1   Properties of sulfhydryl collectors in solution

The representation of sulfhydryl collectors that has been extensively studied are xanthates, although dithiocarbamates, mercaptans (thiols) and dithiophosphates are equally important.

Xanthates

Alkyl xanthates with short hydrocarbon chains are readily soluble in water and the solubility decreases with the increase in chain length. Table 7.3 shows the solubility products of heavy metal salts. The stability of xanthates in aqueous solutions under varying conditions has been the subject of numerous investigations. A large number of xanthate species could be identified in the flotation pulp including xanthate ion ($ROCS_2$), monothiocarbonate ($ROCOS^-$), xanthic acid ($ROCS_2H$), carbon disulfide (CS_2), and dixanthogen ($ROCS_2S_2COR$).

From the numerous reactions describing the decomposition process, there are six reactions that are relevant to the flotation system. These are:

Reaction 1 – Hydrolysis of xanthate ion:

$$K^+ + ROCS_2^- + H_2O \underset{K2}{\overset{K1}{\rightleftharpoons}} K^+ + OH^- + ROCS_2H \quad \text{(xanthic acid)}$$
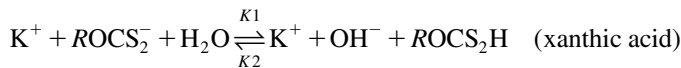
Table 7.3

Solubility products of heavy metal xanthates [12]

Xanthogen	Zn	Cd	Hg	Au	Ag	Cu
Ethyl	4.9×10^{-9}	2.6×10^{-14}	1.7×10^{-38}	6.0×10^{-30}	5.0×10^{-19}	5.2×10^{-20}
Propyl	3.4×10^{-10}	–	1.1×10^{-39}	–	1.4×10^{-19}	–
Butyl	3.7×10^{-11}	2.10×10^{-16}	1.2×10^{-40}	4.8×10^{-31}	3.6×10^{-20}	4.7×10^{-21}
Amyl	1.55×10^{-12}	8.50×10^{-19}	–	1.0×10^{-31}	1.5×10^{-20}	–
Hexyl	1.25×10^{-13}	9.40×10^{-20}	–	3.5×10^{-32}	2.4×10^{-21}	–
Heptyl	1.35×10^{-14}	9.20×10^{-22}	–	1.0×10^{-32}	–	–
Octyl	1.50×10^{-16}	7.20	–	–	1.4×10^{-22}	8.8×10^{-24}
Iso-propyl	2.20×10^{-10}	–	–	–	1.0×10^{-19}	–
Iso-butyl	2.75×10^{-11}	–	–	–	1.6×10^{-20}	–
Iso-amyl	3.10×10^{-12}	1.6×10^{-17}	1.0×10^{-41}	–	$5.4 - 10^{-21}$	–

Reaction 2 – Decomposition of xantic acid:

$$ROCS_2H \xrightarrow{\text{K3}} ROH + CS_2$$
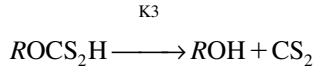
Reaction 3 – Hydrolytic decomposition:

$$6ROCS_2 + 3H_2O \rightarrow 6ROH + CO_3^{2-} + 3CS_2 + 2CS_3^{2-}$$

Reaction 4 – Oxidation to dixanthogen:

(a) $2ROCS_2^- \rightleftharpoons (ROCS_2)_2 + 2e$

(b) $2ROCS_2^- + \dfrac{1}{2}O_2 + H_2O \rightleftharpoons (ROCS_2)_2 + 2OH^-$
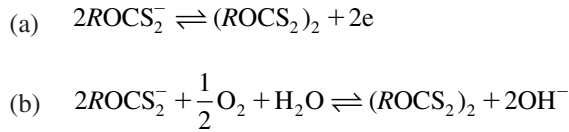
Reaction 5 – Oxidation to monothiocarbonate:
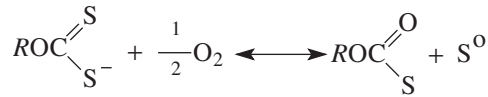
Reaction 6 – Oxidation to perxanthate:
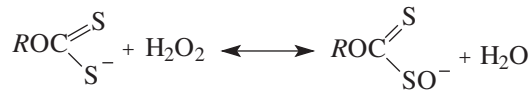
Reactions 1 and 2 are the main reactions of decomposition in acidic solution [13], where $K1$, $K2$ and $K3$ are the rate constants of the decomposition.

Reaction 3 occurs in highly alkaline pulps, under which condition the decomposition reactions yield stable products [14]. For flotation, the importance is placed on the reactions occurring in a pH region between 6 and 12, such as Reaction 4 [15]. Oxidation of xanthate ions can be accomplished by a number of oxidizing chemicals [16] including oxygen (Reaction 5) and hydrogen peroxide (Reaction 6) [17].

Dithiocarbamates

These collectors are extensively used in base-metal flotation, alone or in combination with xanthates. They are more selective than xanthates, especially toward iron sulfides. With the exception of alkali and alkaline-earth metals, all other metallic salts of dithiocarbamate are

insoluble. It is believed that the stability of dithiocarbamate in solutions of various pH is similar to that of xanthate. In acid solution, dithiocarbamate decomposes into amine and CS_2, following a first-order reaction rate.

Dithiophosphates

Dithiophosphates are the most widely used collectors after xanthates. They are used alone or in combination with xanthates for virtually all sulfides, precious metals and platinum group minerals. As with xanthates, dithiophosphates form metal dithiophosphates [18]. Aqueous solutions of Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+} and Ga^{3+} do not form precipitates with diethyl dithiophosphate ions. Table 7.4 shows the solubility products of some dithiophosphates. Dialkyl dithiophosphoric acids are stronger acids than xanthate (with pK ~ 0) and they do not decompose in an acid solution. The dithiophosphates of heavy metals dissolve in water much more readily than the corresponding xanthates (comparison in Tables 7.3 and 7.4).

7.4.2   Adsorption mechanism

There are several mechanisms involved in the adsorption of sulfhydryl collectors on mineral surfaces. These include chemisorption at metal ion sites on a surface and physical adsorption. These are accepted adsorption mechanisms. The most troublesome question for researchers remains the role of oxygen on adsorption and the role of metal xanthate or metal dithiophosphate.

Collector adsorption in the absence of oxygen was studied by a number of researchers [19223] with the following conclusions:

- Adsorption of various xanthates on sphalerite as a function of pH is shown in Figure 7.2, indicating that adsorption is not possible above pH 6.6 with heptyl xanthate and above pH 7.4 with octyl xanthate. The mechanism of adsorption appears to be chemisorption. In such a system, monolayer coverage occurs at 1.6×10^{-5} mol xanthate per gram of sphalerite.

Table 7.4

Solubility products of some alkyl and aryl dithiophosphates [12]

Dithio-phosphates	Pb	Cd	Zn	Ag	Cu	Ti
Methyl	5×10^{-11}	–	–	4.2×10^{-16}	8×10^{-16}	–
Ethyl	7.5×10^{-12}	1.5×10^{-10}	1.5×10^{-2}	1.2×10^{-16}	1.4×10^{-16}	1.2×10^{-5}
Propyl	6.0×10^{-14}	4.0×10^{-11}	–	–	–	–
Butyl	6.1×10^{-16}	3.8×10^{-13}	–	5.0×10^{-19}	2.2×10^{-18}	–
Iso-amyl	4.2×10^{-18}	–	$1.0–10^{-8}$	4.0×10^{-20}	–	–
Phenyl	6.8×10^{-16}	1.5×10^{-11}	–	7.4×10^{-19}	–	–
O-Cresyl	1.8×10^{-17}	1.5×10^{-13}	–	3.8×10^{-19}	7×10^{-18}	3.1×10^{-9}
P-Cresyl	7.7×10^{-18}	6.8×10^{-14}	–	5.0×10^{-20}	2.0×10^{-19}	2.9×10^{-10}
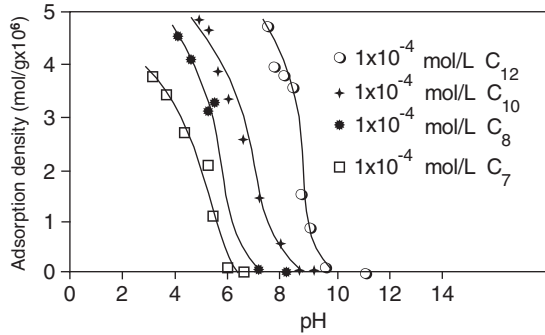
Figure 7.2 Adsorption density of various xanthates on sphalerite as a function of pH in virtual absence of oxygen (Fuerstenau and Mishra).

- In the case of pyrite, adsorption of short-chain xanthates does not occur above pH 8 in the absence of oxygen and adsorption is below the monolayer coverage. Xanthate chemisorbs on pyrite under these conditions. It has been postulated that in the absence of oxygen in the system, the oxidized form of xanthate, dixanthogen, when added in sufficient quantities can fulfill the role of initial adsorption at the surface. Physical adsorption is then possible on this layer. This means that in the absence of oxygen, the adsorption mechanism involves chemisorption and physical co-adsorption.
- The adsorption of xanthate in the presence of oxygen is explained as follows. Xanthates react with many metal ions and since metal xanthates or dixanthogens are necessary to establish hydrophobicity, oxygen is required to provide the metal ions for metal xanthate formation. Metal ions are formed by reacting with oxygen in the presence of a suitable electron acceptor. In other terms, the oxygen allows a charge transfer to take place on the sulfide surface. Along this line, it has been established that as a result of sulfide surface oxidation, the surface becomes hydrophobic and the mineral may be floatable without collector. This hydrophobic state of minerals (chalcopyrite, sphalerite) may be generated by either an appropriate combination of M–S–O atoms on the surface or by the formation of polymerized elemental sulfur on the mineral surface. The latter is used to explain the collectorless flotation phenomenon.
- From the relevant adsorption studies conducted on xanthate adsorption on mineral surfaces, it can be concluded that in the case of chemisorption of xanthate into mineral surfaces, oxygen may or may not be required. This likely depends on the type of species available (i.e. ionic xanthate or non-ionized dixanthogen) and the type of sulfide minerals. To establish the required degree of hydrophobicity on the initially hydrophilic surface, a definite oxidation level is required whenever an ionic xanthate species is present. How is this viewed from a practical point of view? A good example would be the bulk flotation of copper–lead from a massive sulfide ore with xanthates, followed by selective separation. In practice, the bulk flotation is usually performed in an alkaline or slightly acid circuit (i.e. pH 6.8–10.8). The separation of copper from lead is often carried out in an acid pH (3.5–4.5) in the presence of galena depressant. The decomposition to xanthic acid takes place at this pH. In the alkaline pulp, metal
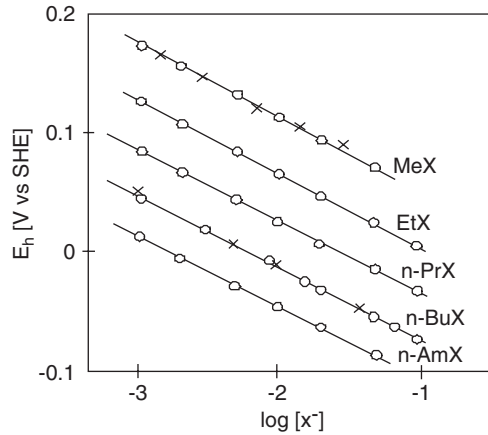
Figure 7.3 Redox potentials of the alkyl xanthate−dialkyl dixanthogen couples for methyl- to *n*-amyl xanthates [22].

xanthate is responsible for the hydrophobicity, whereas in the acid pH range the metal xanthate does not exist but chalcopyrite is still floatable. What this means is that the flotation behavior of certain minerals from different ores does not fit a single adsorption theory.

- The electrochemical theory of adsorption involves electrochemical oxidation of thiol collectors to dimers (i.e. dixanthogen) at the surface of certain sulfide minerals. This oxidation is explained as follows. In solution a mineral develops a potential difference, which is called "rest potential." During xanthate oxidation, it also creates a reversible potential (i.e. Reaction 4, Section 7.4.1). When the rest potential is larger than the reversible potential (i.e. Nernst potential), oxidation of xanthate to dixanthogen occurs. Dixanthogen has been found on the various mineral surfaces with the rest potential greater than +0.13 V. When the rest potential is cathodic or lower than the reversible potential (i.e. xanthate/dixanthogen), oxidation of metal xanthate cannot occur, and then metal xanthate is adsorbed on the sulfide surface. Studies carried out on this subject have shown that flotation of gold metal or galena is not induced until the potential at the solid−liquid interface is above that for PbX_2 formation (in the case of galena flotation) or above the reversible potential for oxidation of xanthate ions to dixanthogen as shown in Figure 7.3.

7.4.3　Sulfide mineral surface under flotation conditions

From the previous discussions (Section 7.4.2), it is evident that collector adsorption on mineral surfaces is either a chemical reaction or the result from electrochemical oxidation of collector on the mineral surfaces.

In actual practice, the solid phase is usually represented by a multi-mineral system and in the liquid phase, in addition to collector, different modifiers are present. In such a system, the adsorption of collector on the mineral surface can be significantly altered, which

is actually the objective of the selective flotation of individual minerals. Such alteration cannot be determined with a high degree of certainty, but consideration of the flotation of sulfides in terms of adsorption may provide a means of exploring ways in which flotation can be modified to achieve sequential flotation of individual minerals. Therefore, it is appropriate to summarize the findings on the conditions of the sulfide surfaces under which certain minerals are floatable.

Galena

In the presence of xanthate (i.e. 1×10^{-5} mol/L), galena is floatable in a pH range between 2 and 10. Under galena flotation conditions, xanthate is present in the following two forms [24]: (a) xanthate chemisorbed at the monolayer coverage and (b) lead xanthate adsorbed at multi-layer coverage. The multi-layer of lead xanthate is believed to be held together by Van der Waals bonding of hydrocarbon chains of the xanthate. The coverage of the collector on galena (i.e. xanthate) as a function of potential was extensively studied ([25,26]. It was determined that the potential dependence on flotation is a function of the mode of pretreatment of the mineral as shown in Figure 7.4. The solid curve marked as current is a voltammogram for galena in an ethyl xanthate solution and exhibits an anodic peak at ~0 V as a result of xanthate chemisorption. It is therefore evident that galena floats in a chemisorption region (i.e. solid curve). In the case when galena is ground under oxidizing conditions, flotation occurs at a much lower potential (i.e. dashed curve).

For a charged species such as the xanthate ion to chemisorb without transfer of charge, an ion of similar charge must be replaced on the surface. Hydroxyl ions may be adsorbed under the above conditions and could be replaced readily by xanthate ions in a slightly basic medium. In the case of an oxygen deficiency system, only a monolayer of xanthate
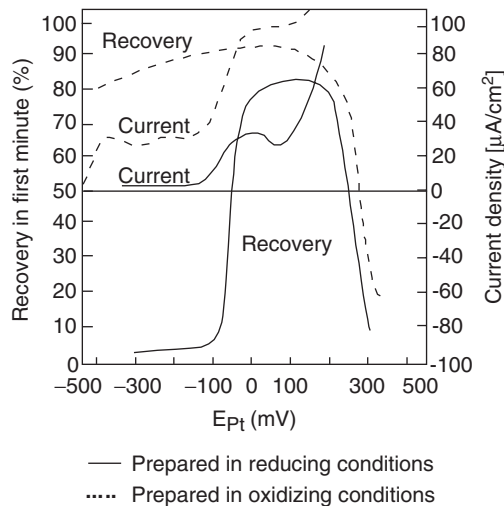
Figure 7.4 Anodic current and flotation response of galena as a function of potential in the presence of ethyl xanthate after preparation in oxidizing and reducing environments [26].

coverage is present on the galena. When the system is exposed to air, a multi-layer coverage occurs which may be attributed to the following three sequences [27]:

1.   Oxidation of a sulfide surface to thiosulfate, in the presence of oxygen: galena is oxidized to sulfate as per the following equation:

$$PbS(s) + 2O_2(g) \rightleftharpoons PbSO_4(s), K = 10^{126}$$
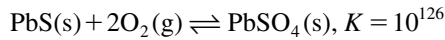
2.   A metathetic replacement of surface thiosulfate and sulfate by carbonate, according to the following reaction:

$$PbSO_4(s) + CO_3^{2-} \rightleftharpoons PbCO_3(s) + SO_4^{2-}$$
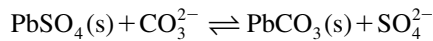
3.   Metathetic replacement of lead carbonate, sulfate or thiosulfate by xanthate.

   Therefore, the adsorption of xanthate on galena occurs in two stages: the first stage being a chemisorption of one xanthate ion on each lead surface ion, during which the exchange of xanthate for hydroxyl ion takes place, and in the second stage, the adsorption of bulk precipitated lead ethyl xanthate formed by metathetic replacement of sulfur oxygen species as well as carbonate on the surface.

Chalcocite

As for galena, xanthate adsorption on chalcocite is also believed to be a two-stage process. First in the presence of an insoluble xanthate species, a chemisorbed layer is formed followed by the formation of multi-layers of cuprous xanthate. The formation of cuprous xanthate was found to occur [28] by two different reactions, including direct anodic oxidation and ion exchange. The second reaction occurs via the oxidation of the surface of a mineral to form a species such as copper hydroxide that can react when xanthate is added. Ion exchange experiments [29] using a chalcocite amyl xanthate system showed that approximately half the ions exchanged upon xanthate adsorption are hydroxyl and the balance is principally carbonate and some sulfate (Table 7.5). The equivalence between xanthate adsorbed and anions released is not as close as that of the galena–xanthate system. In the case where a large amount of insoluble xanthate is taken into account, the amount of xanthate adsorbed is close to that of the amount of anions emitted into the solution.

   In the dithiophosphate–chalcocite system, it has been demonstrated [30] that copper diethyldithiophosphate is formed on the surface of chalcocite, which indicates a chemisorption reaction.

Sphalerite

Xanthate adsorption on activated sphalerite appears to be similar to that of chalcocite. In the presence of oxygen, zinc xanthate may also be formed. There has been evidence [31] that in the presence of oxygen, a weak acid species of sulfhydryl collector is chemisorbed.

Table 7.5

Effect of grinding on formation of products from chalcocite: 50 g chalcocite treated with 10 mL of potassium *n*-amyl xanthate [29]

Substance[a]	Grinding time (h)		
	1.25	2.50	5.0
	Product leached from surface (mg)		
Cuprous xanthate	1,670	1,524	1,224
Compounds A, A$_1$, B	0	171	246
Compound C	0	0	177
	Product in filtrate (mmol)		
OH$^-$	5.30	3.43	3.48
CO$_3^{2-}$	2.39	3.86	3.95
SO$_4^{2-}$	0.51	0.65	0.93
Reducing ions	0.00	0.18	0.16
Residual X$^-$	1.77	0.30	0.00
Total anions	9.97	8.41	8.52
Potassium cation	9.73	8.49	6.63
pH	11.8	12.0	12.0

[a]Cuprous xanthate − Cu$_2$[SC(S)OC$_5$H$_{11}$]$_2$; compound A − Cu$_2$S·Cu$_2$[SC(S)OC$_5$H$_{11}$]$_2$; compound A$_1$ − Cu$_2$S·Cu$_2$[SC(O)OC$_5$H$_{11}$]$_2$; compound B − 2Cu$_2$S·Cu$_2$[SC(S)OC$_5$H$_{11}$]$_2$; compound C − 3Cu$_2$S·Cu$_2$[SC(S)OC$_5$H$_{11}$]$_2$.

Pyrite

In the case of pyrite, the dixanthogen species are responsible for its flotation. Dixanthogen on a pyrite surface is formed by oxidation of xanthate coupled with cathodic reduction of adsorbed oxygen [32] as per the reaction

$$2X^- \rightleftharpoons X_2 + 2e \qquad \text{anodic}$$

$$\frac{1}{2}O_2(ads) + H_2O + 2e \rightleftharpoons 2OH^- \qquad \text{cathodic,}$$
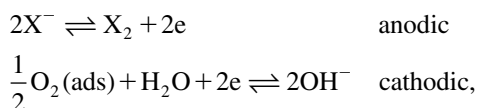
where X^- is xanthate and X_2 dixanthogen.
Because the sulfides are electric conductors, the overall reaction by be written as follows:

$$2X^- + \frac{1}{2}O_2(ads) + H_2O \rightleftharpoons X_2 + 2OH^-$$
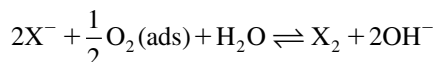
In such a case, flotation of pyrite is only possible at a pH below 11 with short-chain xanthates. However, it has been found that flotation of pyrite is possible at the potential value above the reversible value for dixanthogen formation. It is postulated that in this region, the hydrophobic entity is an iron xanthate species. Due to anodic oxidation of pyrite to iron oxide [33] that occurs in aqueous solution, iron oxide can form on pyrite exposed to air. Ion exchange could then take place between the oxide and xanthate without any additional

exchange of charge. The presence of iron hydroxy xanthate has been suggested [34] to account for the appearance of monothiocarbonate in the pyrite–xanthate system.

Chalcopyrite

Chalcopyrite is highly floatable with xanthate in a pH region between 2 and 12 [35]. Because of this, it is believed that both electrochemical oxidation of xanthate to dixanthogen as well as a chemisorption of xanthate on chalcopyrite is responsible for flotation. This is because the dixanthogen is not stable above pH 11.0.

7.5   MECHANISM OF ADSORPTION OF NON-THIO COLLECTORS

7.5.1   Properties of non-thiol collectors in solution

Oxhydryl: collectors (see Chapter 3) include carboxylates, sulfonates and alkyl sulfates. These collectors have a much longer carbon chain than thiol collectors, $C_{10}-C_{18}$ (thiols C_4-C_{12}). The long carbon chain of these collectors makes them insoluble in water solution.

Carboxylates (i.e. fatty acids) dissociate into negatively charged carboxylate anions as per the equation

$$R\text{COOH} \rightleftharpoons \text{H}^+ + R\text{COO}^-$$
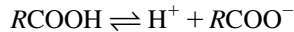
Table 2.2 (Chapter 2) shows the solubility of various fatty acids. The solubility of the fatty acids containing double bonds in their hydrocarbon chains, such as oleic acid, is greater than those of the saturated varieties, such as stearic acid. Because the double bond is polar, the polar water molecules are attracted to them. It should be noted, however, that the solubility of carboxylates increases greatly when they are in a saponified form.

Sulfonates and alkyl sulfates possess a high degree of solubility in water, as shown below:

* Hexadecyl sulfate $- 9 \times 10^{-4}$ mol/L
* Tetradecyl sulfate $- 1 \times 10^{-1}$ mol/L
* Dodecyl sulfate $- 5$ mol/L

It is believed that the dissolved species is $R\text{SO}_4^-$, since alkyl sulfates are essentially salts of strong acids. All three groups of carboxylate collectors form micelles. Critical micellation values for various chain lengths are listed in Table 7.6.

The oxhydryl collectors are capable of forming polyvalent metal collector salts. The solubility of these salts is a function of the several features of the collector including the inorganic component of the collector molecule and the hydrocarbon chain length. Solubility products of calcium carboxylates and calcium sulfonates are listed in Table 7.7.

Table 7.6

Critical micelle concentration of various oxyhydryl collectors as a function of chain length [36]

Chain length	Micelle concentration (mol/L)		
	Carboxylate	Sulfonate	Alkyl sulfate
C_{12}	2.6×10^{-2}	9.8×10^{-3}	8.2×10^{-3}
C_{14}	6.9×10^{-3}	2.5×10^{-3}	2.0×10^{-3}
C_{16}	2.1×10^{-3}	7.0×10^{-4}	2.1×10^{-4}
C_{18}	1.8×10^{-3}	7.5×10^{-4}	3.0×10^{-4}

Table 7.7

Solubility products of calcium carboxylates and sulfonates [37]

Carbon atoms in molecule	Solubility product	
	$Ca(RCOO)_2$	$Ca(RSO_3)_2$
8	2.69×10^{-7}	–
10	3.80×10^{-10}	8.51×10^{-9}
12	7.94×10^{-13}	4.68×10^{-11}
14	1.100×10^{-15}	2.88×10^{-14}
16	3.80×10^{-18}	1.58×10^{-16}

Dissolved cations can complex with oxyhydryl collectors leading to precipitation, especially in the presence of partially soluble minerals (e.g. calcite, dolomite). When ion concentration in solution is high enough to exceed the solubility product of the soap, it results in precipitation of the collector and possible adsorption on the surface. Under these conditions, the adsorption of collector is non-specific. The type of ions present in solution would determine the interactions in the system.

Cationic collectors (i.e. amines) ionize in aqueous solution as follows:

$$RNH_2(aq) + H_2O \rightleftharpoons RNH_3^+ + OH^-$$
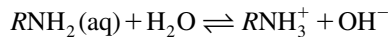
In a saturated system,

$$RNH_2(s) \rightleftharpoons RNH_2(aq)$$
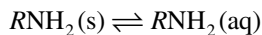
The primary, secondary and tertiary amines are weak bases, whereas quaternary amines are strong bases. Quaternary amines are completely ionized at all pH values, while ionization of primary, secondary and tertiary amines is very much pH-dependent. It should be noted that depending on the pH, the predominance of certain species can be represented by the logarithmic concentration diagram shown in Figure 7.5.
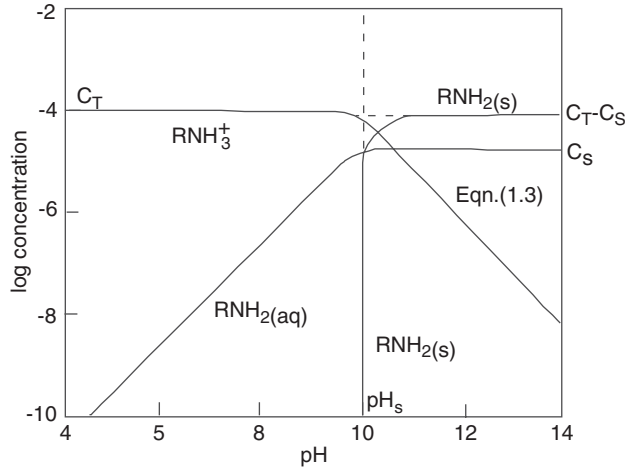
Figure 7.5 Logarithmic concentration diagram for 1×10^{-4} mol/L total dodecyl amine [38].

The dependence of the solubility on the pH is clearly demonstrated in the figure. At these above pHs, the concentration of $R\mathrm{NH_2(aq)}$ is constant, C_S at a given temperature. In such a case, the equilibrium is

$$\log[R\mathrm{NH_3^+}] = 14 - \mathrm{p}K - \mathrm{pH} + \log C_s \qquad (7.1)$$

which gives a straight line of slope -1 on the plot. The line (7.1) intersects the abscissa pHs at the point where the concentration of $R\mathrm{NH^+_3}$ is just equal to the differences between the total concentration of amine originally added, C_T and the solubility C_S. The critical pH is then given as

$$\mathrm{pHs} = 14 - \mathrm{p}K + \log Cs - \log(C_T - C_S) \qquad (7.2)$$

where C_T is the total concentration of amine in any of the forms $R\mathrm{NH^+_3}$, $R\mathrm{NH_2}$ and $R\mathrm{NH_2}$ (s). At very high pH, ionization is completely suppressed, so that $[\mathrm{RNH^+3}] \cong \mathrm{O}$ and

$$R\mathrm{NH_2}(s) = C_T - C_S \qquad (7.3)$$

When the pH is lower than pHs, $R\mathrm{NH_2(S)} = 0$, so the other concentrations are governed by

$$\log[R\mathrm{NH_3^+}] - \log[RH_2] = 14 - \mathrm{p}K - \mathrm{pH} \qquad (7.4)$$

and $$[R\mathrm{NH_3^+}] + [R\mathrm{NH_2}] = C_T \qquad (7.5)$$

Solutions of eqs. (7.4) and (7.5) does not produce straight lines on the graph, but they form a straight line assemblage at a very low pH,

$$[RNH^+{}_3] = C_T \tag{7.6}$$

and
$$\log[RNH_2] = pH + pK - 14 - \log C_T \tag{7.7}$$

which is a straight line of slope 1, which intersects the abscissa pHs at a concentration $C_S C_T/(C_T - C_S)$. A particularly significant point is obtained when pH = 14 − pK; then,

$$\log([RNH^+{}_3]/[RNH_2]) = 0$$

and
$$[RNH^+{}_3] = [RNH_2]$$

$$RNH^+{}_3 = 0.5 C_T$$

In this case, 50% of the amine is ionized. The log concentration diagram for various amines is shown in Figure 7.6.
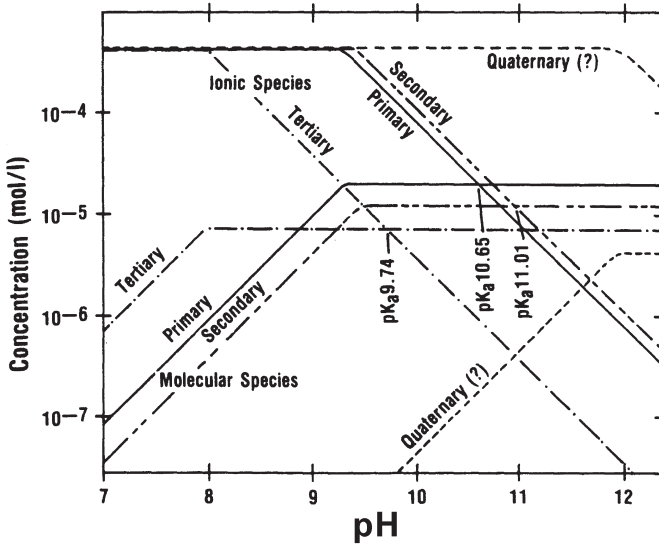
Figure 7.6 Log concentration diagram for 4×10^{-4} mol solution of C_{12} chain. Primary, secondary, tertiary and quaternary amines. Solid species were present but not shown [39].

There are two characteristics of cationic collectors that are important to the adsorption phenomenon. These are critical micelle concentration (CMC) at the KRAFT point. Micelles are aggregates of collector ions of colloidal size that are formed by Van der Waals bonding between hydrocarbon chains of the collector. They are formed because the hydro-carbon chain is non-ionic in nature and a mutual incompatibility between polar water molecules and non-polar hydrocarbon chain exists. When a certain concentration of col-lector ions is reached in solution, it is called critical micelle concentration (CMC). There is a limit to the number of collector ions that can be contained within a micelle owing to the electrostatic repulsion between charged heads. Inorganic salts, which produce ions of opposite charge, or natural organic molecules, such as long-chain alcohols, may reduce the repulsive force between the charged heads and hence lower the CMC. The CMC is depend-ent on a number of factors, including:

- The number of ionic groups in the collector molecule. The CMC becomes larger with the replacement of the hydrogen atom by an ionic group.
- If the surface-active substance contains two large hydrocarbon chains, the second chain may lower the CMC. This is the case for quaternary ammonium bromides.
- The presence of a double bond in the chain of a collector may result in an increase in CMC by several times.
- For collectors, such as *n*-alkyl amines that are weak bases, the CMC should be a func-tion of pH.

The KRAFT point is another important characteristic of the collector in solution at certain temperatures. Figure 7.7 shows the relationship between solubility, the CMC and temperature for a typical surfactant salt.

The importance of the CMC in flotation relates to the manner in which a long-chain sur-factant active substance adsorbs on the mineral surface. However, concentrations of cationic collectors, used in actual practice, are substantially below their CMC.

The KRAFT point for ionic collectors may influence the manner of adsorption. Below the KRAFT point, stable micelles do not form and the collector adsorption is different.
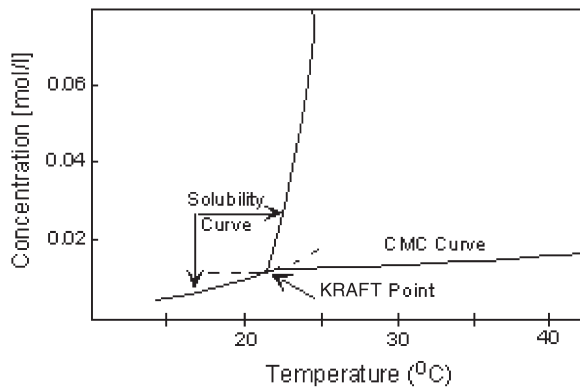
Figure 7.7 Phase diagram for a surfactant salt near the KRAFT point.

At a temperature above the KRAFT point, micelles and also hemimicelles should form, resulting in a liquid film with substantial mobility on mineral surfaces.

7.5.2 Adsorption mechanism of surfactants

In the adsorption of non-thiol collectors on mineral surfaces, three mechanisms are involved. These are (1) chemisorption, (2) specific adsorption in the inner layer without charge transfer and (3) electrostatic adsorption over a network of laterally bonded complex counter-ions.

Chemisorption followed by physical co-adsorption

Surfactants such as fatty acids, alkyl sulfates, amines and alkyl hydroxamate [40−42] have been proposed to adsorb by means of chemical interactions on a variety of minerals. Also, hydrogen bond formation between the mineral surface and surfactants containing hydroxyl, phenolic, carboxylic and amine groups have been proposed.

In addition, a concurrent physical co-adsorption of Na-oleate on fluorite and barite was found to occur at an alkaline pH [43] while the co-adsorption of oleic acid occurs at acidic and neutral pH. In such a system, there is a strong dependence on the type of the solid-inorganic anions combined as shown in Figure 7.8. The anions added appear to compete in their adsorption with the oleate ion to a different extent at fluorite surfaces and at barite surfaces; the lattice constituent anions, F^- and SO_4^{2-} respectively, lower the proportion of chemisorbed oleate to a much greater extent than other anions.
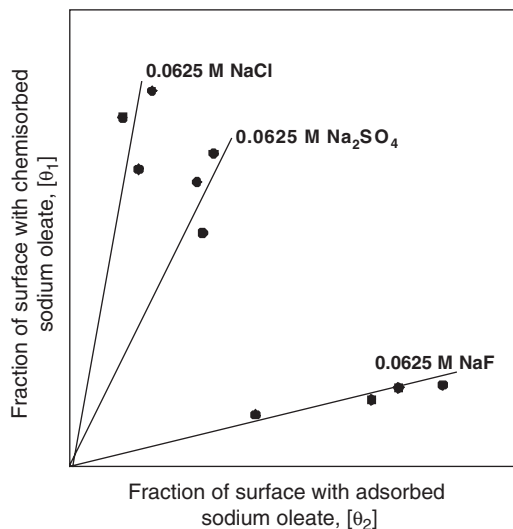
Figure 7.8 The effect of different inorganic salts present in 0.0625 M concentration on the relative proportion of chemisorbed and physically co-adsorbed oleate species at pH 9.5 [43].

It is possible that physical adsorption of non-ionized carboxylic acid may be responsible for an increase in the overall hydrophobicity of the adsorbed layer. However, a physical co-adsorption of an excess of ionized carboxylic species should, in general, have a negative effect on hydrophobization. If the species, which is chemisorbed, forms a diffuse monolayer covering the surface, then the physically adsorbing species may associate with a pre-adsorbed molecule, either in parallel mode such as hydrocarbon group interacting by Van der Waals forces or in an inverted mode, where representative hydrocarbons interact with each other. This may occur in a case where the polar group of the physically co-adsorbed species is electrostatically repelled from the site that it would otherwise occupy. If adsorption continues, the diffuse monolayer of the chemisorbed species becomes more condensed; consequently, in solution, on approaching CMC the limiting arrangements of the inverted mode of adsorption is reached regardless of the initial mode of co-adsorption. The second layer is adsorbed through Van der Waals bonds in the terminal CH_3 groups of the respective hydrocarbon chain and the polar groups are in the opposite direction.

From the practical point of view, for the surfactant to adsorb by chemisorption, it must form ion complexes. The solubility of these complexes is dependent on the number of CH_3 groups in the collector chain; therefore, the length of the hydrocarbon chain influences chemisorption. Even with the use of new techniques, there is no means available to determine the arrangements of molecules adsorbed at the interfaces.

Specific adsorption of ionized collectors in the IHP

Various studies [44,45] of the zeta potential of quartz, goethite, etc. in the presence of inorganic electrolytes, as well as in the presence of surfactants, have shown a direct correlation between the zeta potential and the adsorption of oppositely charged surfactants. This is demonstrated in Figure 7.9.

This indicates that the basic adsorption of the collector is electrostatic and involves the ionized form of collector.

When electrostatic forces play a major role in the adsorption process, the presence of inert ions may influence adsorption due to competition between different counter-ions for the surface. Collectors with longer alkyl chains are capable of crossing the electrostatic barrier and, in the case of flotation, into a positive zeta potential region.

The adsorption in the IHP always precedes chemisorption when the charge transfer does not take place, which may indicate that the system either does not possess sufficient energy of activation or does not possess appropriate acceptors or donors under the given conditions. The evidence of the adsorption in the IHP in some metal oxides − ionized collector systems, is provided in literature [46,47].

Electrical interaction

In aqueous solution, most of the solid particles possess some degree of surface charge that may be dependent on either the pH or chemical composition of the solution. These charges may be formed from preferential dissolution or hydrolysis of surface groups, and the selective adsorption of potential determining ions. The surface charge, therefore, results in an electrochemical potential near the solid surface. The oppositely charged collector then can
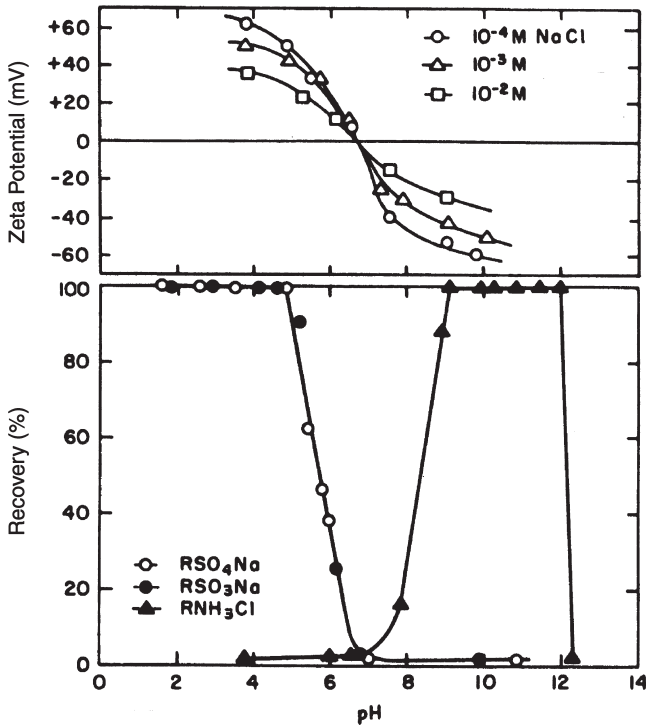
Figure 7.9 The dependence of flotation recovery of goethite on the zeta potential of the solid2liquid interface and the charge of polar group of collector: NaCl concentration 1024, 1023 and 1022 molar. Recovery curves were obtained for 1023 M dodecyl ammonium chloride (RNH3Cl), sodium dodecyl sulfate (RSO4Na) and sodium dodecyl sulfonate (RSO3Na).

adsorb on such mineral surfaces, which are termed electrical interaction. It is believed that the electrical interaction between the adsorbate and the substrate is one of the major factors influencing the adsorption process. The electrostatic interaction usually includes coulombic and dipole terms. The dipole term arises from the exchange between surfactant and water dipoles upon adsorption of surfactant on the mineral surface. For the coulombic term, the collector ion and the mineral surface must exhibit opposite signs to promote adsorption.

In several studies of the oxide–surfactant system [48,49], it has been concluded that colombic interaction plays a dominant role in the adsorption process. However, in other studies [50] it has been postulated that the electrokinetic charges are very small (i.e. 0.1% of the total charges), therefore the effect of the electrokinetic potential on surfactant adsorption is very small as well.

Furthermore, the case of electrostatic interaction appears to be an exception rather than the rule for surfactant adsorption. Several systems seem to respond to the theory of electrostatic adsorption.

Lateral chain interaction

Almost all adsorption isotherms derived from experimental work are of the shape shown in Figure 7.10, and are characterized by several regions. At low concentration, adsorption increases linearly with concentration in area I. The adsorption in this region is attributed to ion exchange between the surfactant and other ions in the double layer. At certain collector concentrations a sharp increase in the slope of adsorption results, which appears to be characteristic to many collector−mineral systems. This actually means that increasing the surface coverage increases the affinity of collector to adsorb more. Usually, the adsorption in region II is accompanied by a sharp increase in the electrokinetic potential. It is believed that the above facts have been attributed to *lateral association* of the collector species in the adsorbed monolayer to form hemimicelles due to the removal of alkyl chains from the aqueous environment in a process similar to the formation of micelles in a bulk solution.

The lateral-chain interaction between pre-adsorbed collector and other species of surfactants may also influence the overall degree of hydrophobicity. This association extends the degree of hydrophobic character by lateral bonds along the surface without contributing an equal degree of change to adsorption bonds with the solid in the direction perpendicular to the solid surface.

Adsorption of non-ionic surfactants

It is known that flotation collectors such as fatty acids and long-chain aliphatic amines under certain pH are non-ionic in nature. The adsorption isotherm of non-ionic collectors is reversible with usually small hysteresis. Because of this, it is believed that non-ionic collectors are adsorbed physically rather than chemically except for possible hydrogen bonding with hydroxyl groups on the surface. Most non-ionic collectors contain polar groups that can form hydrogen bonds with surface hydroxyls rendering the surface hydrophobic.
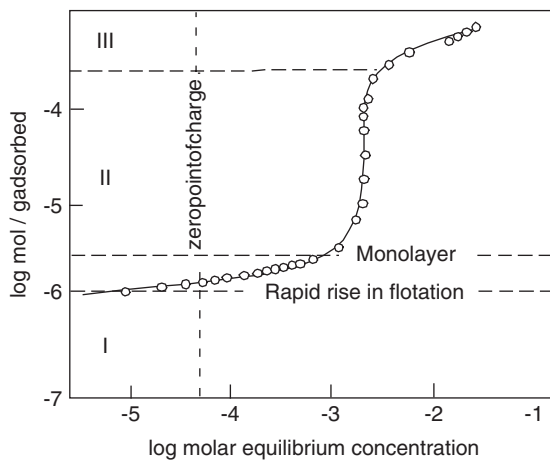
Figure 7.10 Adsorption isotherm for the adsorption of dodecylpyridinium ions on silver iodide suspended in 1024 M KI solution [51].

Generally, the affinity of non-ionic surfactants for most minerals is lower than that of the ionic collector because the bonding energy between the hydrophilic species and the solid is weak. In the case of minerals with low polarity, adsorption may result mainly from the interaction between surface and the hydrophobic species of the surfactant. The maximum amount adsorbed depends on the strength of interaction between the surface and the polar group of the surfactant. There are three kinds of polar group interactions. These are:

- *Weak polar head–surface interaction*, where collector molecules adsorb lying flat on the solid surface until the surface becomes saturated. In a case where the collector concentration is near the CMC, the adsorption increases with the adsorbed molecules oriented perpendicular to the surface and the polar head pointing toward the bulk solution.
- *Intermediate polar head–surface interaction* is similar to a weak polar surface interaction. When a solid surface becomes saturated with a monolayer of surfactant, the interaction of the polar head with the surface is too to allow orientation and consequently to allow adsorption of additional molecules with the polar head pointed towards the bulk solution. The polar head–surface interaction, however, is not strong enough to displace the hydrocarbon chain from the surface and monolayer of vertically oriented molecules.
- *Strong polar head–surface interaction* refers to a progressive increase in adsorption of vertically oriented molecules with increased collector concentration, in which case the polar heads interact with the surface. In this particular case, the formation of a double layer of adsorbed molecules is possible so that the maximum amount of adsorbed collector is much higher than that of the first two cases.

7.5.3   Some factors affecting surfactant adsorption and their relevance to flotation

Many oxide and silicate minerals have similar flotation behavior under a set of conditions (e.g. pH, collector concentration, etc.). The surface chemistry of a large number of oxides and silicates is also similar. In base-metal flotation, very often additions of collector and pH modifiers are required to achieve good flotation of a particular mineral. This is not the case with the separation of complex oxide–silicate systems, where much more complex reagent schemes are required. Moreover, in the case of many oxide ores and silicates, there are a number of different methods by which separation can be accomplished. For example, there are about four different methods by which titanium minerals can be recovered from the associated gangue minerals. In the case of hematite and iron oxides, six different separation procedures have been developed. Adsorption of collector for each separation system may be different along with the conditions used. Several important parameters that affect adsorption of collectors are discussed in this section.

The polymerized counter-ion complexes and adsorption of collector on these complexes is highly important for selective flotation of minerals involving surfactants. The mechanism involves polymerization of oppositely charged complex ions by hydrogen bonding to form a network of adsorption sites. It has been demonstrated [52] that conditions under such interaction correlate well with flotation of minerals, which can release ions required

for the complexing counter-ions. The polymerizing ionic complexes established at the solid–liquid interface are entirely new solidified substances. This new substance may represent a three-dimensional layer of bonded complexes formed with the original Gouy–Chapman layer of solids or it may be a two-dimensional film formed at the original OHP (as discussed earlier). It should be pointed out that the presence of collectors is not in any way a prerequisite for formation of the solidified network of polymerized complexes. Under certain conditions (hydrogen bonding), a polymerized network of such complexes can be created regardless of the presence or absence of collectors in the solution phase. The adsorption of collectors resulting from such a network is usually unselective unless some kind of regulating chemical is present to control the formation of such complexes. For this reason, pulp pre-treatment, slime removal, etc. may be essential before additions of collectors.

The length of hydrocarbon chain of a collector is quite important because it controls the interaction of the collector with water molecules; so the collector chain length has a pronounced effect on the adsorption of the particular collector at the solid–water and air–water interfaces. Along with CMC, the collector chain length is an important part of the reagent scheme development for separation involving non-thiol collectors.

The neutral molecule formation is related to pH and hydrolysis of a collector. Some minerals (i.e. silicates) become more hydrophobic when certain collector ions hydrolyze, as the pH becomes alkaline. For example, primary amine salts hydrolyze in alkaline solution to yield amines as per the following reaction:

$$R\mathrm{NH_2(aq)} + \mathrm{H_2O} \rightleftharpoons R\mathrm{NH_3^+} + \mathrm{OH^-}$$
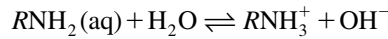
At a certain pH, the neutral amines reach a point where they cannot adsorb alone. The important role of a neutral amine molecule is actually to increase the contact angle to a maximum at a certain pH.

Another way of creating neutral molecules in the flotation system is the addition of frothers [53].

In practical terms, in flotation using this phenomenon, it is possible to selectively remove quartz from titanium minerals (i.e. rutile, ilmenite) by reverse quartz flotation at a pH between 10.5 and 11.5 using amine (C_{18} + starch). This is one of many examples where such a separation occurs in actual practice.

Inorganic ions play a very important role in any separation system with non-thiol collectors. Inorganic ions can cause depression or activation of minerals.

(a)   In the depression process, the multi-valent ions are charged similar to the collector. Because collector ions function as counter-ions in the double layer, their adsorption density depends on the competition with other counter-ions in solution. Therefore, the presence of extensive amounts of dissolved salts can inhibit flotation of a particular mineral. For example, the concentration of 0.03 mol/L of NaCl results in depression of goethite using a quaternary amine salt as collector [54]. This phenomenon can also be utilized for selective separation of lithium minerals from feldspars using quaternary

amines. For example, petalite can be selectively floated from a mixture of Na and K feldspars in the presence of a mixture of NaCl + KCl up to 0.8 mol/L and a quaternary ammonium salt as collector.

It is believed that at low collector concentration, inorganic ions depress flotation through ionic competition for sites in the double layer; but at elevated collector concentration or at CMC, the specific adsorption potential is high due to association at the surface. Inorganic ions have little effect on flotation.

(b) The activation process with inorganic ions involves the adsorption of inorganic ions on mineral surfaces and they function as a link between surface and collector, which are charged similarly. This is called activation in flotation. For example, at a very low pH (i.e. 1−2), controlled by sulfuric acid, hydrochloric acid or hydrofluoric acid, both rutile and ilmenite respond well to flotation when using a modified phosphoric acid ester collector, while at a higher pH (i.e. 4−6) selectivity is completely lost.

Regardless of the type of collector, in the adsorption phenomenon there are two very critical factors involved in the flotation of oxides, silicates and carbonates. These are the presence of ultra-fine slimes and the surface properties of the minerals.

In any flotation system involving surfactants, the presence of slimes can either completely inhibit flotation of particular minerals or cause non-specific adsorption of the collector on mineral surfaces resulting in non-selective flotation. Normally, slimes can be removed from the flotation system but not completely, and therefore slimes are always present in the system to some degree. There are no data available in the literature which provide information on the mode of collector adsorption when slimes are present in the system. From a practical point of view, the harmful effect of slime can be controlled in several ways, including the use of specific chelating agents, and the use of a dispersant (i.e. usually polymers).

The effect of these chemicals is discussed in the preceding chapters, but it should be pointed out that the future of development of an effective separation system lies not in the understanding of surface chemistry but in the understanding of the interaction phenomenon of much more complex systems such as slimes and surface interaction in more complex environments.

The surface properties of minerals from natural ores composed of multi-mineral systems are substantially different from the systems used in the studies of adsorption of surfactants. It is often the case that the crystal structure contains defects, the surface is covered by multi-valent ions or ultra-fine slimes or altered by weathering or other mineralogical changes. Several possibilities exist to improve adsorption of collectors on such surfaces, some of which include pulp pretreatment with acid or alkalis and the use of modified surfactants.

The effect of pulp pretreatment is discussed in the following chapters. The use of modified collectors had a significant effect on flotation of specific minerals from very complex ores. These collector modifications (i.e. fatty acids) were found to provide excellent selectivity and high recovery for many oxides and silicates.

Perhaps more detailed studies of such collector modifications may provide valuable information for the design of more effective reagent schemes.

REFERENCES

1. Finkelstein, N.P., and Allison, S.A., Natural and Induced Hydrophobicity in Sulphide Mineral Systems, *AICLHE Symposium series*, Vol. 71, No. 150, pp. 165–175, 1976.

2. Liu, Q., and Laskowski, J.S., The Role of Metal Hydroxides at Mineral Surface in Dextrin Adsorption, *Studies on Modified Quartz Samples*, Mineral Science and Engineering 6, University of British Columbia, p. 223, 1974.

3. Kitchener, J.A., and Laskowski, J.S., The Hydrophylic–Hydrophobic Transition on Silica, *Journal of Colloid and Interface Science*, Vol. 29, pp. 670–679, 1968.

4. Fuerstenau, M.C., Thiol Collector Adsorption Processes. The Physical Chemistry of Mineral Reagent Interaction in Sulphide Flotation, *Symposium Series*, April 6, 1978.

5. Allison, S.A., Experimental Techniques for the Study of Surface and Flotation, In (R.P. King ed) *Principles of Flotation*, SAMME, pp. 227–237, 1982.

6. Castro, S.H., and Laskowski, J.S., Application of the Dodecylamine Ion Surfactant Selective Electrode in Oxide Flotation Research, In (S.H. Castro and J. Alvares eds) *Froth Flotation*, Vol. 9, pp. 44–50, 1988.

7. Chander, S., and Gebhardt, J.G., Application of Electrochemical Techniques in Sulphide Mineral Flotation In (K.V.S. Sastry and M.C. Fuerstenau eds) *Challenges in Mineral Processing*, SMME, SME Inc, Littleton, Colorado, 1989.

8. Natarajan, K.A., and Iwasaki, I., Practical Implications of Eh Measurements in Sulphide Flotation Circuits, *Transactions of SME-AIME*, Vol. 254, pp. 323–328, 1975.

9. Smith, R.W., Structure Function Relationships of Long Chain Collectors, In (K.V.S. Sastry and M.C. Fuerstenau eds) *Challenges in Mineral Processing*, SMME, SME Inc, Littleton, Colorado, pp. 51–90, 1989.

10. Cooke, S.R., and Talbot, E.L., Fluorochemical Collectors in Flotation, *Transactions of SME-AIME*, Vol. 202, pp. 145–153, 1955.

11. Greenstein, J.P., and Winitz, M., Amino Acids as Dipolar Ions, In (J.P. Greenstein ed) *Chemistry of Amino Acids*, New York, pp. 435–522, 1961.

12. Kakovsky, I.A., Physiochemical Properties of Some Flotation Reagents and their Salts with Ions of Heavy Non-ferrous Metals, *Second International Congress of Surface Activity*, Vol. IV, pp. 225–237, 1957.

13. Iwasaki, I., and Cooke, S.R., The Decomposition of Xanthate in Acid Solution, *Journal of the American Chemical Society*, No. 80, pp. 285–288, 1958.

14. Philip, B., and Fichte, C., Kinetic Studies on the Decomposition of Xanthate, *Faserforsch Textilt.*, Vol. 11, pp. 118–124, 1960.

15. Finkelstin, N.P., Kinetic and Thermodynamic Aspects of the Interaction between Potassium Ethyl Xanthate on Oxygen in Aqueous Solution, *Transactions of IMM*, Vol. 76, pp. C51–C59, 1967.

16. Tipman, R.N., and Leja, J., Reactivity of Xanthate and Dixantogen Solution of Different pH, *Colloid and Polymers Science*, Vol. 253, pp. 4–10, 1975.

17. Jones, M.H., and Woodcock, J.T., Perxanthates – A New Factor in the Theory and Practice of Flotation, *International Journal of Mineral Processing*, No. 5, pp. 285–296, 1978.

18. Busev, A.I., and Ivanyutin, M.I., Dialkyl and Diaryl Dithiophosphate Acids as flotation Agents, *Analytical Chemistry*, Vol. 13 (Chem Abstract 53,5954), Mascow, 1959.

19. Fuerstenau, M.C., and Kuhn, M.C., Xanthate Adsorption on Selected Sulphides in the Presence of Oxygen, *International Journal of Mineral Processing*, Vol. 17, pp. 148–156, 1980.

20. Heyes, G.W., and Trahar, W.J., The Natural Flotability of Chalcopyrite, *International Journal of Mineral Processing*, No. 4, pp. 317–344, 1977.

21. Gardner, J.R., and Woods, R., The Use of Particulate Bed Electrode for the Electrochemical Investigation of Metal and Sulphide Flotation, *Australian Journal of Chemistry*, No. 26, pp. 1635–1644, 1973.

22. Majima, H., and Takeda, M., Electrochemical Studies of the Xanthate–Dixantogen System on Pyrite, *Transactions of AIME*, Vol. 241, pp. 431–436, 1968.

23. Leja, J., Xanthate Adsorption Studies Using Infrared Spectroscopy, Part II Evaporated Lead Sulfide, Galena and Metallic Lead Substances, *Transactions of IMM*, Vol. 72, p. 414, 1963.

24. Yamasaki, T., and Usui, S., Infrared Spectroscopic Studies of Xanthate Adsorbed on Zinc Sulfide, *Transactions of AIME*, Vol. 235, p. 36, 1965.

25. Guy, P.J., and Trahar, W.J., Electrochemistry of Sulfide Flotation, *International Journal of Mineral Processing*, Vol. 15, pp. 167–174, 1984.

26. Guy, P.J., and Trahar, W.J., Flotation of Sulphide Minerals, In (K.S.E. Frossberg ed) *Developments in Mineral Processing*, No. 6, Elsevier, pp. 63–71, 1985.

27. Fuerstenau, M.C., Adsorption of Sulphydril Collectors, In (P. King ed) *Principles of Flotation*, IMM, Johannesburg, p. 91, 1982.

28. Richardson, P.E., Studies of Xanthate Adsorption on Minerals, *International Mineral Processing Journal*, No. 12, p. 73, 1984.

29. Dewey, F., *Reaction of Sulphur Collecting Agents with Certain Copper Minerals*, Masters Thesis, Montana College of Mineral Science, 1933.

30. Chander, S., and Fuerstenau, D.W., Effect of Potassium Diethyldithiophosphates, *Transactions of the Institute of Mining and Metallurgy Section* 3, Vol. 84, No. 814, pp. 325–331, 1974.

31. Steininger, J., Collector Ionization in Sphalerite Flotation with Sulphydril Compounds, *Transactions of AIME*, Vol. 238, p. 251, 1967.

32. Woods, R., Flotation, In (M.C. Fuerstenau ed) *A.M. Gaudin Memorial Volume*, AIME, New York, p. 298, 1976.

33. Usul, A.H., and Tolun, R., Electrochemical Study of Pyrite Oxygen–Pyrite System, *International Journal of Mineral Processing*, Vol. 1, p. 135, 1974.

34. Hamilton, I.C., and Woods, S.R., Mechanism of Mineral Flotation, *Journal of Analytical Chemistry*, Vol. 118, p. 327, 1981.

35. Kakovsky, I.A., Physiochemical Properties of Some Flotation Reagents, *Second International Congress of Surface Activity*, London, 1957.

36. Mukerjee, P., and Mysels, K.J., Critical Micelle Concentrations of Aqueous Surfactant Systems, *National Bureau of Standards*, NSRDS-NBS36, 1971.

37. Al Ahar, A.A., and Beck, W., Thermodynamic Solubility Products of Long-Chain Normal Fatty Acids and their Alkaline Earth and Lanthanum Salts in Water, *Journal of Electrochemistry*, No. 27, p. 59, 1970.

38. Fuerstenau, M.C., Chemistry of Collectors in Solution, In (R.P. King ed) *Principles of Flotation*, South Africa, IMM, pp. 1–16, 1982.

39. Smith, R.W., Cationic and Amphoteric Collectors, In (P. Somasundran and B.M. Mondgil eds) *Reagents in Mineral Technology*, Marcel Dekker Inc., New York, 1987.

40. French, R.O., and Wadsworth, M.E., *Physical Chemistry*, Vol. 58, p. 805, 1954.

41. Peck, A.S., and Wadsworth, M.E., An Infrared Study of the Flotation of Hematite with Oleic Acid and Sodium Oleate, *Seventh International Mineral Processing Congress*, New York, p. 259, 1965.

42. Peck, A.S., and Raby, L.H., An Infrared Study of the Flotation of Hematite with Oleic Acid and Sodium Oleate, *Transactions of AIME*, Vol. 235, pp. 301–306, 1966.

43. Peck, A.S., and Wadsworth, M.E., Infrared Study of the Depression Effect of Fluoride, Sulphate and Chloride on Chemisorption of Oleate on Fluorite and Barite, *Transactions of AIME*, Vol. 156, pp. 174–185, 1965.

44. Iwasaki, I., and Cook, S.R.B., *Flotation Characteristics of Goethite*, Report of Investigation 5593, U.S. Bureau of Mines, 1960.

45. Fuerstenau, M.C., Elgillani, D.A., and Miller, J.D., Adsorption Mechanism in Non-metallic Activation System, *Transactions of AIME*, Vol. 241, pp. 11–14, 1970.

46. Coelho, E.M., Flotation of Oxidized Copper Minerals: An Infrared Spectroscopic Study, PhD, Thesis, UBC, Vancouver, 1972.
47. Modi, H.J., and Fuerstenau, D.W., Flotation of Corundum – An Electrochemical Interpretation, *Transactions of AIME*, Vol. 217, pp. 381–387, 1960.
48. Chander, P., and Somasundian, P. J., *Colloid Interface Science*, Vol. 75, p. 171, 1980.
49. Shanis, S.A., Flotation System New Concept, *Transactions of AIME*, No. 258, p. 176, 1975.
50. Cook, M.A., Studies of Activation of Quartz with Calcium Ion, *Journal of Colloid Interface Science*, No. 28, 1968.
51. Jaycock, M.J., and Ottewill, R.H., Adsorption of Surface Active Agents by Charged Solids, Bulletin No. 677, *Transactions of IMM*, Vol. 72, pp. 497–506, 1973.
52. Schulman, J.H., and Smith, T.D., *Selective Flotation of Metals and Minerals in Recent Development of Mineral Processing*, First IMPC, IMM, London, 1952.
53. Leja, J., and Schulman, J.H., Flotation Theory: Molecular Interaction between Frothers and Collectors at Solid/Liquid/Air Interfaces, *Transactions of AIME*, Vol. 199, p. 221, 1954.
54. Iwasaki, I. Cook, S.R.B., Harraway, D.H., and Choi, H.S., Flotation Characteristics of Hematite, Goethite and Activated Quartz with 18-Carbon Aliphatic Acid and Related Compounds, *Transactions of AIME*, Vol. 217, p. 237, 1960.

– 8 –

Interaction of Inorganic Regulating Reagents

8.1   INTRODUCTION

In any flotation system, the use of the collector alone is very rare and may be sufficient for selective flotation if the minerals differ sharply in their flotation properties. In practice, such a case does not exist and these differences in flotation properties are achieved by the use of regulating reagents. The regulating reagents are used for increasing selectivity and/or recovery of floated minerals.

Regulating reagents are also capable of controlling the adsorption of collectors on mineral surfaces. Therefore, the introduction of regulating reagents in the practice of flotation enables flotation separation of complex sulfide ores, silicates, oxides, calcium-containing minerals, etc.

The regulating reagents, under different conditions, can act as activator, depressant, dispersant, etc. For this reason, classification of the regulating reagents into different groups according to their interaction cannot be made and would be grossly inappropriate.

On a number of occasions, in the previous chapters, the importance of understanding the surface chemistry and action of collectors has been stressed. However, understanding the action of regulating reagents is a different matter. Perhaps the biggest weakness of the mineral flotation science is the lack of understanding of the action of regulating reagents. It is safe to say that the importance of these reagents in mineral flotation is grossly underestimated. Some of the problems can best be illustrated through several examples from practice. Sodium cyanide is a classic example of a regulating reagent that is widely used as a depressant in sulfide flotation, i.e. for depression of iron sulfides (e.g. pyrite, marcasite, sphalerite, etc.), pre-activated sphalerite and in large concentrations as depressant for chalcopyrite in separation of copper–lead from bulk concentrate. It has been demonstrated that in the case of some lead–zinc ores, the lead does not float without the presence of cyanide. Figure 8.1 shows the relationship between cyanide additions and lead recovery. It is obvious from the example that cyanide is responsible for the alteration of the surface properties of galena and the promotion of collector adsorption.

Another common depressant used in practice is the zinc sulfate ($ZnSO_4 \cdot 7H_2O$), which is employed for depression of sphalerite.
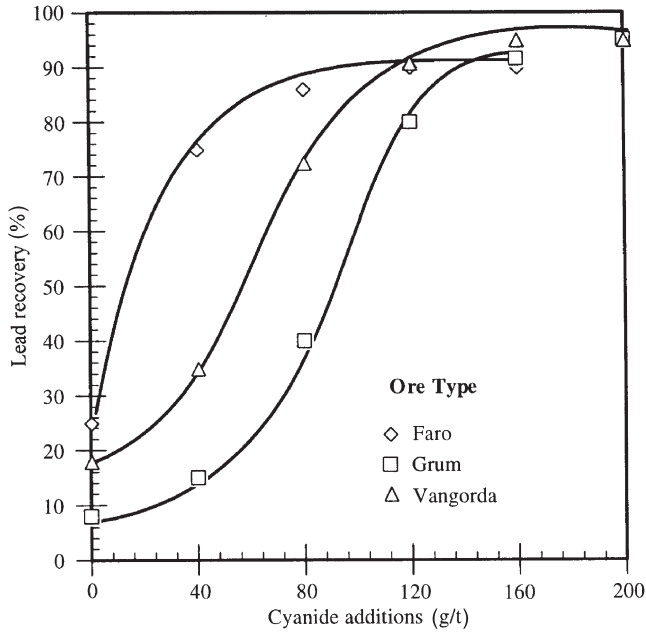
Figure 8.1 Effect of cyanide additions on lead flotation from various faro ores [1].
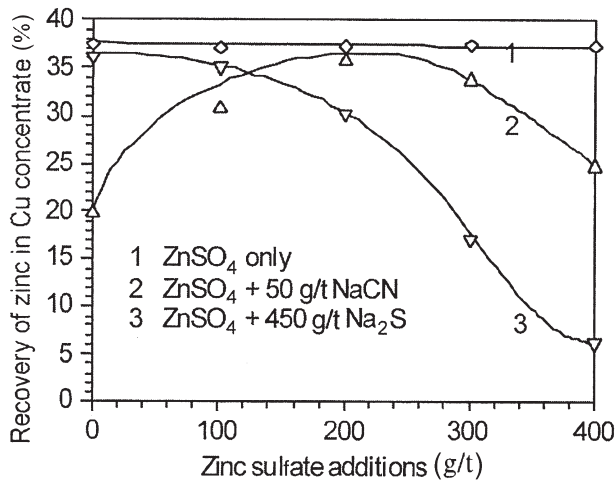
Figure 8.2 Effect of ZnSO4 on Zn depression during Cu flotation from Cu/Zn ore.

In some of the ores, $ZnSO_4 \cdot 7H_2O$ does not show any depressing action, even if it is used with cyanide. However, when used in conjunction with Na_2S, good sphalerite depression is achieved. Figure 8.2 shows the depressing effect of $ZnSO_4 \cdot 7H_2O$ on sphalerite in the presence of different regulating reagents.

From the practical point of view the action of regulating reagents depends very much on the nature and type of mineral present in the ore, as well as the ionic composition of the pulp. Specific or selective adsorption of regulating reagents depends also on the particle size of the mineral present in the pulp.

At finer sizes, selective depression or activation of individual minerals is much more difficult to achieve.

8.2   INTERACTION OF REGULATING REAGENTS IN SULFIDE FLOTATION

8.2.1   Activating action of regulating reagents

Regulating reagents used as activators increase the difference in the hydration of separate minerals, lowering the hydration of floated particles, which in turn activate their flotation. Activation of a specific mineral is also associated with the changes in composition of the liquid phase, which in a way influences the dynamic character of a liquid–solid interface. Some activating reagents are capable of interacting not only on water–mineral interfaces, but also on water–air interfaces. The interacting effects of activators are associated with several forces of interactions. These forms are discussed below.

Chemical cleaning of the mineral surface

Oxidation of mineral surfaces of different minerals always occurs in natural ores and the degree of oxidation depends on the nature and formation of the ore body. Regulating reagents can be used as mineral-surface cleaning agents. Acid treatment of many sulfide minerals can improve its flotability. Acid treatment of pyritic ore with hydrochloric acid and subsequent washing can greatly improve its flotability. Chalcopyrite coated with limonite is normally not amenable for selective flotation. After pre-treatment with the oxalic acid and subsequent washing its flotability can be restored. *In situ* pre-activated sphalerite with heavy metal cations usually represents a problem in selective separation. Pretreatment of the pulp with $Na_2S \cdot 9H_2O$ at a pH of 10.5–11.5 would remove most of the cations from the sphalerite surfaces.

Ionic exchange and ionic adsorption

On contact with water, different minerals can release ions resulting in the creation of electrical potential. In such cases, certain ions can also adsorb onto mineral surfaces. Chalcopyrite, sphalerite and pyrite can be floated without collector when these minerals are pretreated with 1% solution HS and then washed with hydrochloric acid.

Sulfide ions can adsorb onto the surfaces of galena, sphalerite, pyrite and chalcopyrite. Figure 8.3 shows the adsorption of sulfur on mineral surfaces as a function of contact time.

Adsorption of cations on the mineral surfaces is explained by cation exchange. For example, zinc cations can be displaced by other cations forming less soluble compounds with available sulfur ions (e.g. copper, lead, silver, etc.). Because the copper, lead and silver xanthogen are less soluble than zinc xantogen, these cations are activators for
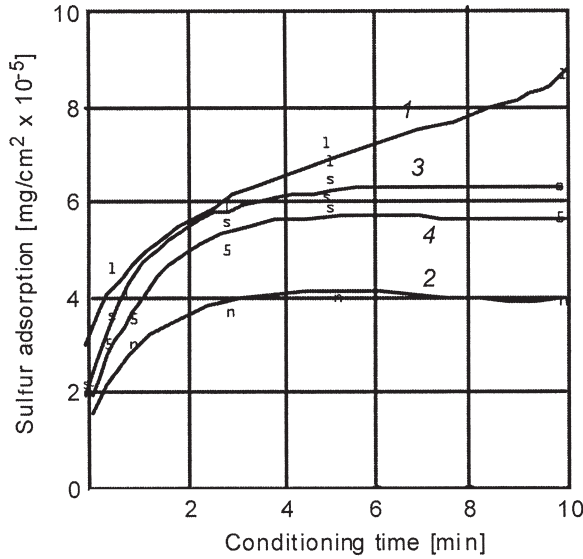
Figure 8.3 Adsorption kinetics of sulfur (Rad Act S^{35}) on sulfide minerals. Curve 1 - galena, curve 2 - chalcopyrite, curve 3 - pyrite, curve 4 - sphalerite.

sphalerite. The activation of sphalerite by copper cations was discovered in 1911 by Bradford showing the following stoichiometric reaction:

$$ZnS + Cu^{2+} \rightarrow CuS + Zn^{2+}$$
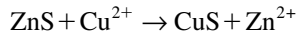
where the amount of adsorbed copper is equal to the amount of desorbed zinc cations. It has been demonstrated [2] that the maximum adsorption of copper cations on sphalerite occurring at a pH of about 5.5. The adsorption kinetics were expressed by the equation

$$A = a + b \log t$$
$$\frac{dA}{dt} = K^{cs}$$

where c is the concentration of copper ion in solution, s the adsorption surface, A the amount of adsorbed copper in time t and K the rate constant (3.5 at pH 5.5 and 1.5×10^6 at pH 10) .

   On this basis, it was concluded that activation of sphalerite with copper ions in alkaline pH is not only a chemical process but also adsorption of colloidal copper hydroxide without ion exchange. In case of dissociation of copper ammonium complexes [3] the dissociation constant is relatively small and is equal to 4.7×10^{-15}, which indicates that the ration of free copper ions and copper ions in complex forms are relatively large.

$$[Cu(NH_3)_4{}^{2+} \rightarrow Cu^{2+} + 4NH_3(aq)]$$
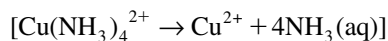
In contrast, silver is rapidly adsorbed by sphalerite [4]. The silver activation of sphalerite is controlled by the following reaction:

$$ZnS(s) + 2Ag^+ = Ag_2S(s) + Zn^{2+}$$
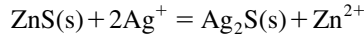
$$K = [Zn^{2+}/Ag]^2 \approx 0.5 \times 10^{26}$$

Lead sulfide is only slightly less soluble than zinc sulfides and, therefore, the reaction of activation would be:

$$ZnS + Pb^{2+} = Pbs + Zn^{2+}$$
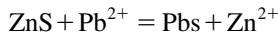
The uptake of lead by sphalerite is low and generally in the monolayer range, which follows a logarithmic relation.

The adsorption of Cu^{2+} and Pb^{2+} on pyrite [5] does not involve cation exchange with the mineral lattice, but the hydroxides are involved. The activation products [6] were CuS_2 or $(CuFe)S_2$ together with surface cupric hydroxide, which interacts with the ferric hydroxides resulting from the oxidation of the surface. The adsorbed cupric hydroxides dissolve readily in water. The adsorption in the cuprous form is dependent on the pH, whereas that of the cupric form rises sharply to a peak of about pH 9. The adsorption of hydroxide has an induction stage: Cu(II) is adsorbed on the surface only after it has been exposed to the activation solution for about 15 min, but it takes only 2 min for Cu(I) to reach maximum density at the surface at pH 5. However, it takes much longer at higher pH (10). It is believed that at pH 10, Cu(I) forms two adsorption stages, the second of which starts once the adsorption of the hydroxide commences. It appears that activation involves ionic exchange and ionic adsorption simultaneously. This adsorption of ions on pyrite surfaces is also associated with collector adsorption.

Catalytic oxidation

Studies with copper-activated galena [7] using spectroscopy (XPS) and scanning electron microscopy have indicated the formation of Cu_2S rather than CuS. Similar studies conducted on galena and pyrrhotite [8] showed that pyrrhotite and galena have a rest potential close to that of covellite, indicating formation of covellite on the galena and pyrrhotite surface. In contrast to the above, the potential of copper-activated pyrite was greater than that of covellite. This indicates that the action of Cu(II) leads to catalytic oxidation of the pyrite surface to elemental sulfur, which is responsible for the surface to become hydrophobic.

Formation of hydroxydes at the surface

This formation plays an important role in the activation process. Metal cations (mono- and divalent) exist in aqueous solution as complexes of H_2O molecules or OH^- ions, where the oxidation state of the metal cations is tri- and tetravalent, in addition to hydroxyl complexes, some oxo complexes containing O^{2-} as a ligand in the pH region between 4 and 10. Because of the limited pH range of the aqueous solution, not all of the

possible metal complexes can exist as anionic hydroxyl or oxo complexes. Polymerization of the species may result in the formation of multi-molecular complexes such as dimers, trimers, etc. and in the formation of colloidal hydroxyl polymers. These molecular species are bonded through OH bridges resulting in the formation of olation or through O bridges resulting in oxolation. For example,

$$[(H_2O)_4Fe] \quad \left\langle \frac{OH}{OH} \right\rangle \quad [Fe(H_2O)_4]^{4+}$$
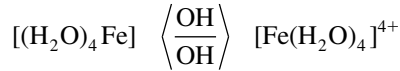
Dimers are usually expressed as $Fe_2(OH_2)^{4+}$. It should be noted that very strongly acidic or basic species do not polymerized. Polymerization is possible for the weak acid and base. It has been shown [9] that multi-molecular hydrolysis products of metallic cations are of almost universal occurrence in aqueous solution. Table 8.1 shows the examples of complex hydroxyl species.

The adsorption of metal hydroxides on mineral surfaces has been examined in a number of studies [10,11]. It was postulated that some processes occur at metallic sulfides and that the properties of the resulting surfaces are determined by the cation and its hydrolysis products rather than the particular solid substate, leading to surfaces covered with positively charged hydroxides in the intermediate pH range and with uncharged hydroxide complexes at a pH range greater than 9. Some studies showed evidence [12] that there is a marked increase in abstraction of activating species at the pH value close to zero zeta potential (OZP). Therefore, the process involved in the abstraction of the cations and their

Table 8.1

Example of hydrolysis species [9]

Be^{3+}	$Be(OH)$, Be_2OH^{3+}, $Be(OH)$
Mg^{2+}	$MgOH$
Sc^{3+}	$Sc[Sc(OH)_2]_n^{(3 + \frac{n)+}{2})\,4+}$, $n = 1,2,3,\ldots$
Cr^{3+}	$CrOH^{2+}$, $Cr(OH)_2^{4+}$, $Cr(OH)_2^{6+}$, $Cr(OH)_2^-$
UO_3^{2+}	$(UO_2)_2OH^{3+}$, $(UO_2)(OH)_2^{3+}$, $(UO_2)_3(OH)_5^+$, $(UO_3)_3(OH)_4^{2+}$, $(UO_2)_4(OH)_6^{2+}$
Mn^{2+}	$Mn(OH)^+$, $Mn(OH)$
Fe^{2+}	$Fe(OH)^+$, $Fe(OH)_3^-$
Fe^{3+}	$Fe(OH)^{2+}$, $Fe(OH)_2^{4+}$, $Fe(OH)_2^+$, $Fe(OH)_2^-$, and multi-nuclear intermediates in precipitation of colloidal $Fe(OH)_3$
Cu^{2+}	$Cu(OH)^+$, $Cu_2(OH)_2^{2+}$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$
Ag^+	$AgOH$, Ag_2OH^+, $Ag_2(OH)_2$, $Ag(OH)$
Hg^{2+}	$HgOH^+$, Hg_2OH^{3+}, $Hg2(OH)$
Al^{3+}	$Al_3(OH)_{20}^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al(OH)_4^-$
Pb^{2+}	$Pb_4(OH)_4^{4+}$, $Pb_6(OH)_8^{4+}$, $Pb_{13}(OH)_4^{2+}$, $Pb(OH)_3^-$
Si^{4+}	$SiO(OH)_3^-$, $SiO_2(OH)_2^{2-}$, $Si_4O_6(OH)_6^{2-}$

hydrolysis is not random coagulation, but rather involves a specific surface of chemical forces. The abstraction of activators in the form of neutral hydroxides results in an exchange ratio that exceeds unity, particularly at high pH values. However, there is a conflicting theory whether hydrolyzed forms of cations at the metallic sulfides are effective activators or if they react with collectors.

Some investigations [13] have stated that flotation requires that hydrolyzed products be converted to the sulfide form as per the following reaction:

$$ZnS + Cu(OH)_x^{(2-x)+} \Leftrightarrow CuS + Zn(OH)_x^{(2-x)+}$$
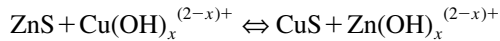
Therefore, only the sulfide form of the activator at the surface accounts for the selectivity of the flotation of different minerals. Because the conversion process is relatively slow, effective flotation at alkaline pH value requires extended conditioning. Other studies [13] on the activation of sphalerite by lead nitrate showed lead activation and flotation with ethyl xanthate as a collector at a pH value between 4 and 9. EDTA, which dissolves lead hydroxides but not lead sulfides, depressed flotation under alkaline conditions even after extended conditioning time, indicating that adsorbed hydrolyzed lead species are effective activators.

From a practical point of view, it should be remembered that there are three major factors that govern the extent of hydrolysis. These are

- pH value
- Concentration of metallic ions involved in the hydrolysis
- The presence of interfering ions in solution.

The role of other ions in solution on the hydrolysis and activation was never considered in any studies. For example, oxy ions $S_2O_3^{2-}$, SO_3^{2-} and $S_nO_n^{2-}$ are capable of acting as activators for many sulfides.

Figure 8.4 shows the effect of aeration of pulp on the concentration of $Na_2S_2O_3$ in the solution.

In these experiments, de-ionized water was used and the filtrate of the pulp contained 2.4 mg/L Zn, 1.8 mg/L Cu and 80 mg/L Fe. Oxidation in the presence of oxy ions can prevent the formation of ion hydroxides on mineral surfaces. Also, the presence of oxygen in the pulp can change the adsorption mechanism on mineral surfaces. Therefore, the importance of the formation of hydroxyl ions or metal sulfides on mineral surfaces is only a theory and the real mechanism of the activation by metal ions is not known. It is likely that the adsorption mechanism of activation by heavy metal ions is very different from that reported in the literature.

In practice, there are numerous examples that pyrite readily floats at a pH above 11 or that sphalerite is readily flotable at a pH between 6.5 and 8.5 without activation. These occurrences are very common when a high concentration of cations and $S_nO_m^{2-}$ ions are present in the mineral pulp. In the presence of oxygen, the pulp containing polymetallic ore almost always sulfite ions SO_3^{2-}; thiosulfate ions $S_2O_3^{2-}$ are present in the pulp. Almost all sulfide minerals (e.g. galena, pyrite, pyrrhotite, etc.) release thio compounds as the principal soluble product of their oxidation. Sulfite and thiosulfite ions are capable of forming complexes with
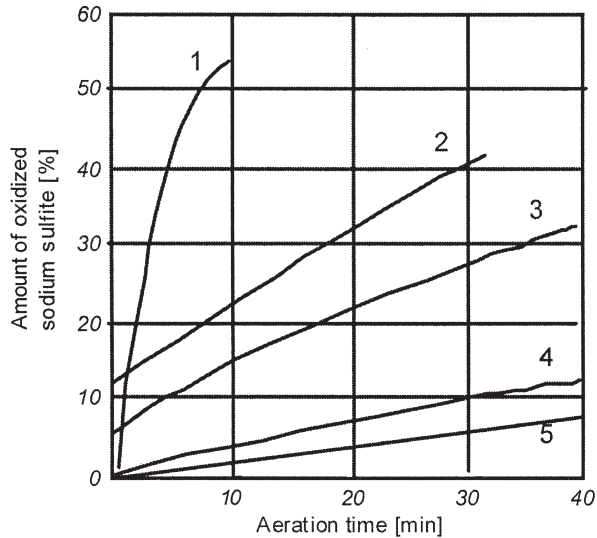
Figure 8.4 Stability of sodium sulfite aeration at different concentrations of Na2S2O3. Curve 1 - no Na$_2$S$_2$O$_3$, curve 2 - 2-20 mg/L Na$_2$S$_2$O$_3$, curve 3 - 40 mg/L Na$_2$S$_2$O$_3$, curve 4 - 60 mg/L Na$_2$S$_2$O$_3$, curve 5 - 136 mg/L Na$_2$S$_2$O$_3$.

many cations. The adsorption of these complexes on the mineral surfaces may be very different from that of the metal ion itself.

8.2.2 Depressing action of regulating reagents

In general, the regulating reagents used as depressants have an action opposite to that of the regulators used as activators. For example, the activators provide improved adsorption of the collector on a particular mineral, while depressants either desorb the collector or activator from a mineral surface or prevent the adsorption of the collector on a particular mineral. Depending on the function of a particular depressant, there are several mechanisms of the action of depressants, some of which include:

- Desorption of the collector adsorbed on mineral surfaces as a result of chemical reaction, forming with desorbed collector-insoluble compounds that are not capable of re-adsorbing on the mineral surfaces.
- Interaction of the depressant regulator with the activator on mineral surfaces on which the activator is adsorbed, causing desorption of activator (NaCN–CuS on sphalerite).
- Interaction of the depressant regulator with cations present in the pulp, preventing adsorption of such cations on mineral surfaces and causing activation.
- Adsorption of the depressants on the mineral surfaces mainly in the monolayer, thus preventing adsorption of collector.

Because a large number of regulators/depressants are electrolytes, the first step of interaction involves electrostatic forces. In case of adsorption of depressants on the mineral surfaces, chemosorption is also involved.

The reagents containing divalent sulfur (Na₂S·9H₂O)

$Na_2S\cdot9H_2O$ and other related compounds (NaHS) are used as depressant, activator and collector desorbing agents. In addition, Na_2S has a dispersing effect on clay-containing pulp. This section discusses the depressing effect of sodium sulfide. Because of the multiple actions of Na_2S and the fact that different sulfide minerals have a different tolerance toward the level of additions of Na_2S, this reagent is not commonly used as a depressant in spite of its effectiveness. Also, owing to the difficulties in reliable techniques for determining various forms of sulfur oxidation species present on the surface of different sulfide minerals and in solution, the true role of $Na_2S\cdot9H_2O$ as a depressant is not well understood. The presence of elemental sulfur and thiosulfates on the surface of sulfides and in solution has been documented but it is not known with certainty whether the presence of $Na_2S\cdot9H_2O$ (NaHS) prevents or destroys the hydrophobic character on individual sulfides by forming thio-anions or other compounds. From a practical point of view, achieving selective depression of individual minerals during flotation of a complex ore requires different sets of necessary parameters. For example, depression of pre-activated sphalerite from a scarn-type ore during flotation of copper concentrate by Na_2S occurs in a very narrow pH region, while in the case of copper–zinc ores containing secondary copper minerals, sphalerite depression is accomplished at a much higher pH. Figure 8.5 shows the effect of $Na_2S\cdot9H_2O$ on sphalerite depression as a function of pH from different ore types.

The performance of Na_2S as a pyrite/sphalerite depressant can greatly improve when used in combination with Na_2SO_3.
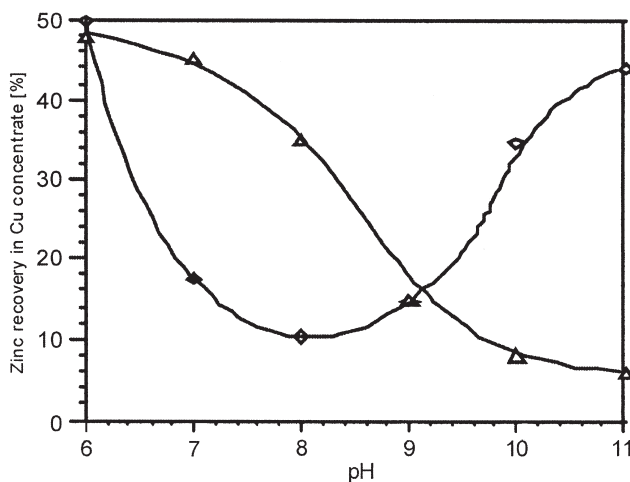
Figure 8.5 Effect of pH on sphalerite depression during copper flotation using 900 g/t $Na_2S\cdot9H_2O$ + 500 g/t $ZnSO_4$. (a) Scarn ore and (b) Cu/Zn ore with secondary copper minerals present [14].
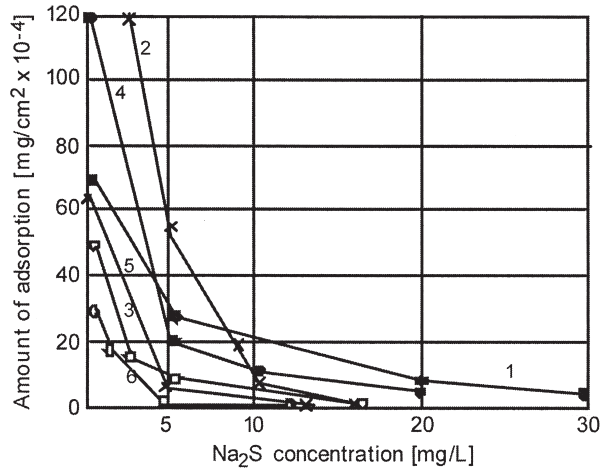
Figure 8.6 Relationship between butyl xanthate adsorption and $Na_2S \cdot 9H_2O$ concentration on different sulfides without Na_2S treatment: curve 1 - galena, curve 2 - chalcopyrite, curve 3 - sphalerite. Pretreated with Na_2S for a 24-h period: curve 4 - galena, curve 5 - chalcopyrite, curve 6 - sphalerite [15].
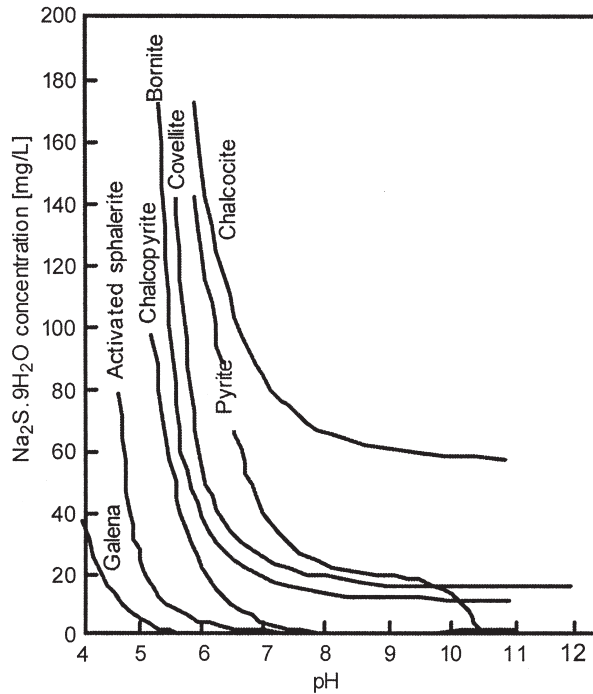
Figure 8.7 Contact curves for several sulfide minerals. Potassium ethyl xanthate concentration 25 mg/L [16].

The presence of Na_2S in the liquid phase can prevent the adsorption of xanthate on mineral surfaces. Figure 8.6 shows the relationship between butyl xanthate adsorption on different minerals as a function of $Na_2S \cdot 9H_2O$ concentration, indicating that collector adsorption on galena increased after treatment with $Na_2S \cdot 9H_2O$.

In other studies [16], it was concluded (Figure 8.7) that of all sulfides involved in the studies, galena exhibits the greatest sensitivity to sulfide ion, and that $Na_2S \cdot 9H_2O$ is an effective galena depressant. In plant operations treating Cu/Pb/Zn ores where Na_2S + Na_2SO_3 was used as a replacement for cyanide [17], the use of Na_2S improved flotability of both galena and chalcopyrite. These differences arise from the problems discussed at the beginning of this section.

Zinc sulfate ($ZnSO_4 \cdot 7H_2O$)

Zinc sulfate is used as a principal depressant for sphalerite during flotation of lead–zinc, copper–zinc and copper–lead–zinc ores. The studies carried out by a number of researchers [18] have shown that zinc sulfate alone does not depress sphalerite (i.e. neither pure sphalerite nor copper-activated sphalerite). The depressing action of zinc sulfate occurs only in the presence of hydroxyl ions where it is due to zinc hydroxide adsorbing on the surface of sphalerite and preventing adsorption of xanthate. The effect of zinc sulfate on the adsorption of xanthate was studied using a mixture of chalcopyrite, pyrite and sphalerite [19]. The results showed that the adsorption of the collector in the presence of $ZnSO_4$ decreased with increased pH (Figure 8.8).

In actual practice, zinc sulfate is used in conjunction with cyanide. In cases where the copper–zinc ore contains secondary or altered copper minerals, $NaZn(CN)_4$ complex is used. This complex is also effectively used for the depression of marcasite at a pH between 4.5 and 6.5 in some operating plants during the flotation of Cu–Pb bulk concentrate from Cu–Pb–Zn ores. Some operating plants use a colloidal mixture consisting of $ZnSO_4$–NaCN–Ca(OH)$_2$ in a ratio 1:2:2. Though nothing is known about these depressants from the literature, their depressing action is known practically. It is interesting to note that these depressants are often more effective than either $ZnSO_4 \cdot 7H_2O$ or a combination of $ZnSO_4 \cdot 7H_2O$ and cyanide.

Cyanide compounds

Cyanides and ferrocyanates have long been used in base-mineral flotation in the selective depression of a number of sulfides (e.g. pyrite, pyrrhotite, sphalerite, marcasite, etc.). The mechanism by which the cyanide ion acts as a depressant for various sulfide minerals has been the subject of many investigations and reviews. Some authorities have suggested that the depressing effect is due to the competition between cyanide and xanthate ions for the mineral surface [3]. In some cases [20], the depressing action of cyanide is due to the removal of adsorbed copper ions from the mineral surface into solution. In the case of pyrite, the proposed mechanism of depression is the formation of a reaction product between the ferric ion and the pyrite surface and cyanide (ferrocyanide) ions derived from solution, which is in fact an electrochemical reaction [21].

Regardless of the postulation and conflicting conclusions, it should be remembered that cyanide in solution can form (a) numerous complexes with transition metals, (b) organic
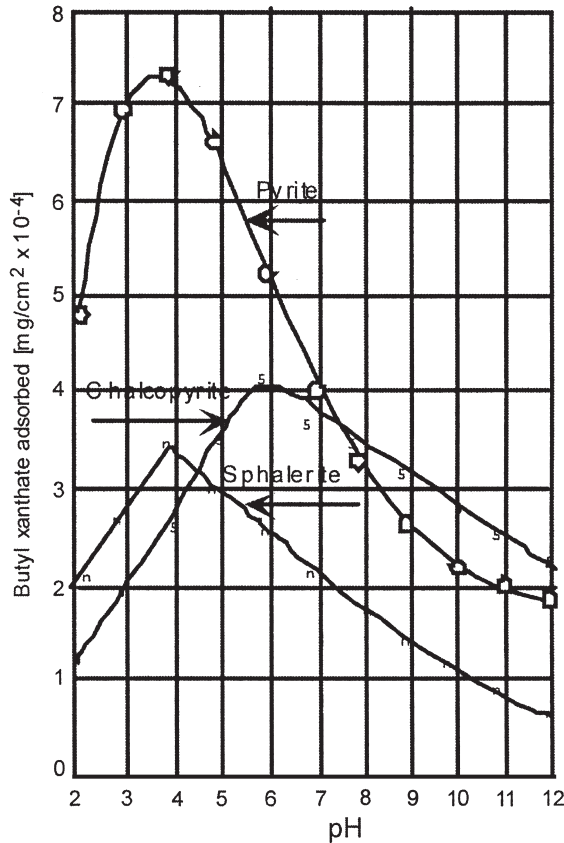
Figure 8.8 Effect of zinc sulfate on the adsorption of butyl xanthate by sulfide minerals at various pH values.

compounds (collectors), (c) other regulating reagents present in the pulp, etc. Considering these facts, the action of cyanides in mineral pulp is highly complex and this fact has been ignored in many studies. Some of the cyanide complexes relevant to flotation are discussed below.

- *Iron*. Divalent (Fe^{2+}; $K_4Fe(CN)_6 \cdot 3H_2O$) ferrocyanide is strongly hydrated. A solution of $Fe(CN)_6^{4-}$ does not respond to reagents for either Fe^{2+} or CN^-. Trivalent (Fe^{3+}; $K_3Fe(CN)_6$) ferricyanide is weakly hydrated and is not as stable as $Fe(CN)_6^{4-}$. The solubility products of ferrocyanide can vary considerably. The insoluble metallic ferrocyanides are amorphous. A fairly large number of double salts of ferrocyanides are known and can form when cyanide is present in mineral pulp.
- *Copper*. Cuprous cyanide complexes include $CuCN$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. When KCN is added to a solution containing Cu^{2+}, fine $Cu(CN)_2$ is precipitated but rapidly decomposes into $CuCN$ and cyanogen $(CN)_2$.
- *Zinc*. A solution containing Zn^{2+} and CN^- yields $Zn(CN)_2$, which in excess of cyanide produces complex ions $Zn(CN)^{3-}$ and $Zn(CN)_4^{2-}$, which are insoluble in water.

- *Lead*. Pb^{2+} forms an insoluble complex in water, $Pb(NO)_2$, which decomposes by acid.
- *Cyanide*. This reacts with many sulfur-containing regulators, e.g. H_2S giving thio-cyanoformanide: $N{=}CCNH_2$ or dithia oxamide: $H_2NC{-}CNH_2$. With thiosulfates, it forms thiocyanidate: $CN^- + S_2O_3^{2-} \rightarrow CNS^- + SO_3^{2-}$.
- The thiocyanate ion forms complexes with most transition metals. There are several possible ways of coordination, including:

  1. $M{-}S{-}C{=}N$
  2. $M{-}N{=}C{=}S$
  3. $M{-}S^-{-}C{=}N^+{-}M$
  4. $M{-}S{-}M$

- *Dixanthogen* reacts with CN^- forming at first an alkyl thiocyanate as an intermediate product, which is unstable and decomposes to dialkyl monosulfide and thiocyanate

$$[ROCSS]_2 + KCN(ROCS)_2S + KSCN$$

Each of the above compounds may in one way or another affect flotation (i.e. depression or deactivation) of particular minerals.

The practice of mineral flotation has found several applications for cyanide, some of which are not even reported in the literature and are lost in various mill files. Some of these applications are listed below:

- Cyanide and its iron complexes are used for deactivation of *in situ* pre-activated sulfides such as sphalerite, pyrite and chalcopyrite, which in turn renders the sphalerite surface hydrophilic. Some of the most elegant methods of separation of complex Cu–Pb–Zn ores from scarn ore involve deactivation of the bulk Cu–Pb–Zn concentrate. The selective flotation by deactivation is very much related to the (a) type of collector used, (b) pH and (c) contact time with cyanide.
- In most cases of depression of iron sulfides during flotation of copper–zinc, copper–lead–zinc, lead–zinc, etc., cyanide is used in combination with other depressants mainly to counteract the frothing nature of cyanide. From plant practice, it is known that at a pH above 9, a voluminous froth is produced. Nothing is known regarding how cyanide influences changes in frothing properties.
- Cyanide can act as an activator under different circumstances. This is explained [22] by the fact that cyanide is a complexing agent for many ions of heavy metals, which in turn can form collector complexes that serve as activator. In the presence of secondary and oxidized minerals, cyanide shows a strong activating effect on sphalerite [23].

It can be concluded that although cyanide is a widely used depressant, its depressing action is highly complex and dependent on the nature of the mineral used, the ionic composition of the pulp, the pH and the type of collector used.

Sulfo-oxy compounds

Na_2SO_3, sulfur dioxide and other thiosulfate compounds have long been used as depressants during flotation of complex massive sulfide ores. Since the introduction of sodium sulfite

for pyrite and sphalerite depression in 1919 at the Midvale Mill in Utah [24], other similar compounds of different thiosulfates and sulfur dioxides were tested and introduced in various plants around the world. Some of these compounds were used to replace cyanide in a number of plants [25].

From actual practice, it is known that whenever sulfide minerals are present in the pulp, sulfur-containing compounds play an important role. The metallic ions usually have preference for sulfur ligands rather than oxygen ligands. It is known that there are two sequences of compounds, one consisting of hydrogen oxide, alcohols and esters and the other hydrogen sulfides, thiols and thio-esters. These two sequences show the following features:

(a)   The permanent dipole decreases in the oxygen sequence $\mu H_2O > \mu ROH > \mu R_2O$ but increases for analogous sulfur compounds $\mu H_2S < \mu RSH < \mu R_2S$.
b)   The polarizability is decreased slightly in going from H_2S to R_2S and a significant decrease occurs in going from H_2O to R_2O.

Sulfides obtained by precipitation from aqueous solution are frequently almost amorphous, nucleation being much faster than the subsequent growth of crystallites. Sulfides of cations with an s^2p^6 electronic configuration and low charges do not form thio-anions because they are hydrolyzed by water. Cations with s^2p^6 configuration and high positive charges form almost insoluble sulfides. However, these are soluble in ammonium or potassium sulfide, giving thio-anions that are stable in solution.

Sulfite ion (SO_3^{2-}) forms complexes with Mn, Co, Ni, Pd, Cu, Ag, Au, Zn, Cd and Hg. In these complexes, the ligand can be bonded in a number of ways through O or S.

The thiosulfate ion ($S_2O_3^{2-}$) forms strong complexes with monovalent ions Cu^+, Ag^+ and $Au+$; divalent Cu^{2+} is reduced to Cu^+ complex. Alkaline thiosulfate solution dissolves many insoluble salts of Pb^{2+}, Hg^{2+}, Cu^+ and Ag^+.

Sulfur dioxide (SO_2) is dissolved in water forming sulfurous acid, which is a weak acid with the following dissociation constant:

$$K_1 = \frac{[H_2SO_3^-][H^+]}{[H_2SO_3]} = 2.10^{-2} \text{ and } K_2 = \frac{[H^+][SO_3^{2-}]}{[H^+][SO_3^{2-}]} = 6.10^{-8}$$

Therefore, when SO_2 is dissolved in aqueous solution it forms the following molecules and ions: SO_2, H_2SO_3, H^+, HSO_3^- and SO_3^{2-}.

The effect of pH on the formation of molecules and ions is illustrated in Table 8.2.

Some data in the literature [26] has indicated that the principal ion responsible for depression is HSO_3^-.

The mechanism of the depressing action of sulfide ions in alkaline solution appears to be associated with several phenomena, some of which include:

(a)   The sulfide ion reduces Eh and thus prevents collector adsorption on mineral surfaces. This is a result of oxidizing reaction of the following type:

$$2X^- = X_2 + 2e^-, MS + X^- = MX + S^o + e^-$$
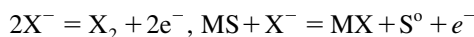
Table 8.2

Effect of pH on dissociation of SO_2 in water [26]

pH	H_2SO_3 (mg/L)	HSO_3^- (mg/L)	SO_3^{2-} (mg/L)
		SO_2 dissociation	
1	1.06	0.21	1.24×10^{-7}
2	4.26×10^{-1}	0.84	4.96×10^{-6}
3	6.10×10^{-2}	1.20	0.71×10^{-5}
4	6.40×10^{-3}	1.26	7.48×10^{-4}
5	6.40×10^{-4}	1.26	7.48×10^{-3}
6	6.0×10^{-5}	1.19	7.05×10^{-2}
7	4.0×10^{-6}	0.64	4.67×10^{-1}
8	9.1×10^{-8}	0.17	1.06
9	1.06×10^{-9}	2.1×10^{-2}	1.25
10	1.06×10^{-11}	2.1×10^{-3}	1.25
11	1.06×10^{-13}	2.1×10^{-4}	1.25
12	1.06×10^{-15}	2.1×10^{-5}	1.25
13	1.06×10^{-17}	2.1×10^{-6}	1.25
14	1.06×10^{-19}	2.1×10^{-7}	1.25

which involves the formation of a hydrophobic species responsible for flotation. Reagents that create reducing conditions would prevent the formation of hydrophobic species such as X_2 and MX and in a sense, would act as a depressant.

(b) Specific adsorption postulates that the sulfite ion [27] adsorbs on pyrite surface sites preventing the adsorption of molecular oxygen, which is a prerequisite for the adsorption of xanthate on pyrite surface, resulting in depression.
(c) Desorption of xanthate by sulfide ions specifically from pyrite was studied in a pH region between 5 and 11 [28]. It was concluded that decomposition of xanthate by sulfite ions occurs as per the following reaction:

$$2C_2H_5OC(S)SK + 2K_2SO_3 + 2KHSO_3 + 2O_2$$
$$\rightarrow 2C_2H_5OC(S)SOK \rightarrow 2C_2H_5OH + 4K_2S_2O_3 + 2CO_2$$
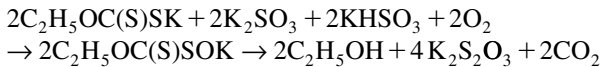
Although sulfur and thiosulfide are good depressants for pyrite and other iron sulfides and galena during sequential flotation of copper, both of these reagents have a depressing effect on precious metals. With the cations of precious metals, both sulfide and thiosulfide form stable complexes. Thiosulfate ion with silver complex is much more stable than sulfide ion complex, as can be seen from Table 8.3.

Another reason for reduction in the floatability of precious metals in the presence of sulfide and thiosulfides is that these reagents are capable of reducing oxygen and also have an oxidizing effect on silver and gold.

Iron salts

There is very little known about the depressing effect of iron salts during flotation of sulfide ore although it is known that ferro sulfate is used as a depressant for pyrite. In the San

Table 8.3

Dissociation constant of sulfide and thiosulfide complexes

Reaction	K	Complex dissociation constant
$AgC_2H_5\,OCSS + 2SO_3^{2-} = Ag(SO_3)_2^{3-} + C_2H_5OCSS^-$	2.2×10^{-10}	3.8×10^{-9}
$AgC_2H_5OCSS + 2S_2O_3^{2-} = Ag(S_2O_3)_2^{3-} + C_2H_5OCSS^-$	2.0×10^{-5}	4.2×10^{-14}
$CuC_2H_5OCSS + 2S_2O_3^{2-} = Cu(S_2O_3)_2 + C_2H_5OCSS^-$	1.0×10^{-6}	$5 - 10^{-14}$
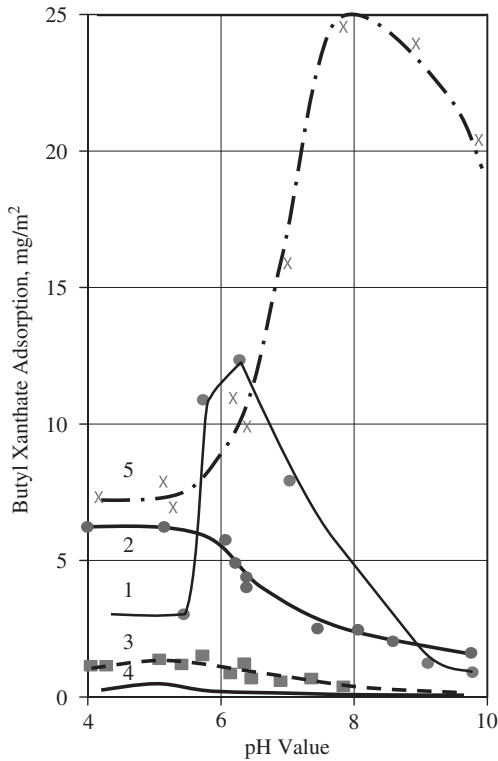
Figure 8.9 Effect of pH on butyl xanthate adsorption in the presence of iron sulfate (1000 mg/t). 1 - galena, 2 - chalcopyrite, 3 - sphalerite, 4 - pyrite, 5 - chalcosine [29].

Francisco plant (Mexico), iron sulfate together with starch, zinc hydrosulfate and sulfuric acid is used for galena depression during copper flotation. At elevated additions and weakly acid medium, ferro sulfate has shown a depressing effect on galena, sphalerite and, to a lesser degree, on chalcopyrite. Figure 8.9 shows the effect of xanthate adsorption on different minerals in the presence of ferro sulfate indicating that in an acid pH, xanthate adsorption on chalcopyrite is higher than on galena. In this pH region, selective separation of chalcopyrite from galena may be possible. The depressing action of iron salts was also explained by the fact that ferro sulfate uptakes oxygen and creates an oxygen deficiency.

Since oxygen is required for collector adsorption, in the presence of a ferro sulfate collector the adsorption ability may be reduced. Research work has been carried out using a mixture of ferro sulfate an sodium sulfite as a depressant [30]. The results of these studies showed that at pH 6, a precipitate of iron hydroxide is formed. This compound is believed to adsorb on galena surface causing depression. Another study [31] showed that iron sulfate and sodium sulfite in acid pH form ferric sulfate $[FeSO_3 \cdot SO_4]^{2-}$ and at higher concentrations they form ferric disulfite $[Fe(SO_3)_2]^2$. The pH region where the galena depression occurs corresponds to the pH region of ferric sulfate–sulfate formation. Adsorption of ferric disulfite on galenite, pyrite and sphalerite corresponds to the flotation activity of these minerals. Chalcopyrite retains its flotability in the pH region where ferric disulfite is formed while pyrite, galena and sphalerite remain depressed.

Chromium ($K_2Cr_2O_7$, $Na_2Cr_2O_7$ and K_2CrO_4)

These are depressants with relatively limited application. In sulfide ore flotation, they are used for galena depression during copper flotation from copper–lead bulk concentrates. The depressing action of chromite is associated with the adsorption of $HCrO_4^-$ and CrO_4^{2-} on a particular mineral. At a pH above 8, the adsorption of CrO_4^{2-} ion is much higher on galena than on pyrite, chalcopyrite and sphalerite.

Adsorption of chromium ions on galena increases with increase in temperature and the concentration of chromium ions.

A mixture of sodium silicate and sodium dichromate (a yellow viscous liquid) has shown improved selectivity in copper–lead than chromium alone [32]. This mixture (i.e. $Na_2SiO_3:Na_2Cr_2O_7 = 1:1$) has been successfully used in Cu–Pb separation circuits in a number of operating plants.

Phosphate compounds

Sodium phosphate and other phosphate compounds are normally used in non-metallic flotation as a depressant and dispersant. Phosphates are strong complexing agents for many polyvalent cations, forming insoluble complexes that prevent adsorption of these cations on mineral surfaces, thus preventing activation.

In the sulfide mineral flotation, some studies were carried out with galena. It has been demonstrated that sodium phosphates are capable of desorbing the collector from the galena, resulting in complete galena depression at higher additions (Figure 8.10).

It is believed that this mechanism is a chemosorption process. Studies conducted on galena and other sulfides with sodium phosphate and polyphosphates [34] indicated the following:

- With the use of polyphosphate, it is possible to achieve selective separation of galena and chalcopyrite from the bulk concentrate. The most efficient depression of galena occurs at pH 10. At this pH, hydrophilization of galena is due to the formation of lead phosphate $Pb_3(PO_4)_2$ and also hydroxyl ion formed as a result of hydrolyzing of sodium phosphate. At a lower pH value, the concentration of PO_4^{3-} ion sharply decreases, whereas the concentration of HPO_4^{2-} increases, in which case a more soluble salt of $PbHPO_4$ may form. Therefore, the depressing effect of phosphates on galena is greatly reduced.
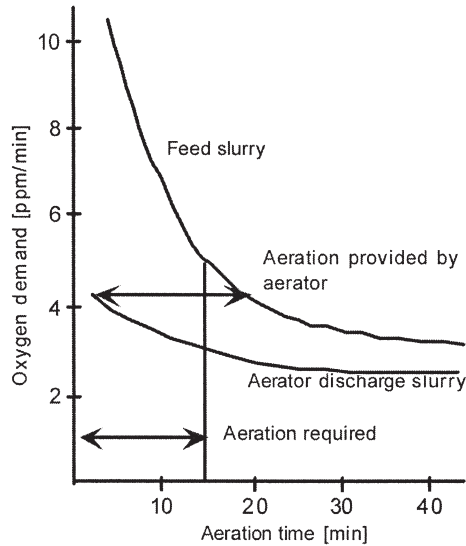
Figure 8.10 Recovery in flotation (1) of galena and (2) sorption of ethyl xanthate versus amount of Na3PO4 added [33].

- Chalcopyrite, bornite and chalcosine adsorbs a negligible amount of phosphate ions, therefore phosphates do not depress these minerals.
- The use of phosphates in combination with $Na_2S·9H_2O$ as a copper depressant during molybdenum flotation from the bulk concentrate usually results in improved depression of copper minerals and a reduction in $Na_2S·9H_2O$ additions is achieved. As a result, a NoKs reagent was developed, which is a product of the reaction of pentavalent phosphorus with $Na_2S·9H_2O$. The NoKs reagent is used in many operating plants for copper depression during molybdenum flotation.

Calcium-containing compounds CaO and CaCl$_2$

Chlorinated lime, although is not commonly used as a depressant, but in specific cases has shown a depressing effect on chalcopyrite during copper–lead separation from a bulk concentrate. The formation of ferrohydroxide and copper hydroxide on the chalcopyrite surfaces is responsible for the depression. In the separation of copper–molybdenum, $CaCl_2$ improves the depression of NaHS or $Na_2S·9H_2O$.

   Lime is normally used as a pH regulator exclusively in sulfide mineral flotation. However, it is also the principal depressant for iron sulfides (pyrite, pyrrhotite, marcasite, etc.). The depression mechanism of lime was extensively studied mainly because of its wide application.

   There is conflicting data on the mechanism responsible for depression using lime. Some investigators [35] have postulated that the depression of sulfides by lime is a result of increased hydroxyl ion concentration in the same way as the action of sodium hydroxide. In this case, pyrite in an alkaline solution forms colloidal hydrated iron oxide FeO(OH) or Fe(OH)$_3$ on the pyrite surface, thus preventing collector adsorption. However, the depressing effect of lime is vastly different from that of other alkalines (i.e. NaOH) [36]. Some

other authors considered the depression of lime to be due to formation of films of sulfate and dithiosulfate salts. Detailed evaluation of the depressing effect of lime by Plaksin *et al.* [37] led to the conclusion that the depression by lime in the flotation of pyrite was related to the formation of a mixed film of $Fe(OH)_3$, $FeO(OH)$, $CaSO_4$ and $CaCO_3$ on the surface of the pyrite. The depressing action of lime on arsenopyrite is the result of the formation of a layer of finely dispersed particles of lime on the surface of the mineral because the oxidation of arsenopyrite is hindered by its crystallographic structure. Such a view cannot be correct because the separation of pyrite and arsenopyrite is commercially done at pH 12 or relatively high concentration of lime, so the depression of arsenopyrite does not occur even at a very high concentrations of lime.

Other specific depressants

In recent years, significant progress has been achieved in the effectiveness of inorganic and organic depressants by mixing and modifying specific depressants. Although the effect is documented, the mechanism of the depressing action is not known. Some of these mixtures (or modified depressants) have found application in various operating plants. Some of these reagents are described below.

Depressant P82. This depressant has been successfully used for the deactivation of activated sphalerite [38] as well as for depression of iron sulfide. This depressant is composed of the following reagents:

$$
\begin{array}{ll}
Na_2S_2O_3 & 35\% \\
NaHSO_3 + Na_2S_2O_5 & 60\% \\
ZnSO_4 \cdot 7H_2O & 5\%
\end{array}
$$

Depressant A3-3 was found to be effective for altered and oxidized pyrite, marcasite and hexagonal pyrrhotite. The depressant also improves the rate of copper flotation and does not affect flotability of lead [39]. The composition of the depressant is as follows:

$$
\begin{array}{ll}
Na_2SiO_3 & 40\% \\
Na_2S_2O_5 & 40\% \\
Al_2(SO_3)_3 & 20\%
\end{array}
$$

Depressant OS3 has been developed for the depression of pre-activated sphalerite and oxidized pyrite. It is basically a replacement for SO_2, but with much more effectiveness. This depressant was successfully tested in a copper–zinc plant [40], and is composed of the following reagents:

$$
\begin{array}{ll}
Na_2S_2O_5 & 80\% \\
Oxalic\ Acid & 20\%
\end{array}
$$

Agent G4 cyanide complex. Agent G4 has been used for quite a long time for the depression of carbonaceous pyrite and is a mixture of organic compounds consisting of dextrin (50%), quebracho (40%) and surfactant (10%). When this complex is pre-mixed with cyanide in a ratio 60:40, it provides an excellent depressant for sphalerite and pyrite.

Depressant SHQ was recently developed as a co-depressant for carbonaceous pyrite, pyrrhotite and marcasite. When pre-mixed with cyanide, it provides an excellent depression of pre-activated sphalerite. This depressant is composed of the following:

$$Na_2SiO_3 \qquad 40\%$$
$$Na_3PO_4 \qquad 40\%$$
$$Quebracho \quad 20\%$$

These are several examples of many effective depressant mixtures developed for selective flotation.

8.2.3   Hydroxyl and hydrogen ions

The pH in flotation systems is a measure of the activity of OH^- and H^+ ions. The amount of acid or alkali needed to achieve a specific pH or depression is usually controlled by the pH value in flotation pulps. As discussed in previous chapters, the pH of the liquid phase determines adsorption of the collector on a specific mineral or the activity of the modifying reagents. In almost all flotation systems, the pH determines the interaction and behavior of the majority of species in the liquid phase including reagents. There are no prescribed rules for the optimum pH value for a given flotation system, but there is a pH region in which specific collectors and regulators perform the best. Apart from conventional pulp modifiers such as lime (CaO), soda ash (Na_2CO_3), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4), a fairly large number of other modifiers can change the pH of the flotation system. Some of these include $Na_2S \cdot 9H_2O$, sodium silicate, organic acids, etc.

Although it is believed that almost all minerals can be suppressed by sufficient additions of H^+ or OH^- ions [41], these ions are not in any way depressants. It is the pH and the other types of interaction from hydrolyses of modifiers containing H^+ and OH^- groups which create the depressing or activating conditions of particular minerals. The basic role of H^+ and OH^- ions is not to act as depressant but rather to provide (a) the desired pH of a flotation system and (b) regulate the adsorption behavior of collectors, depressants and modifiers. The exceptions are modifiers with H^+ and OH^- groups, which are designated as depressants (i.e. $Ca(OH)_2$, H_2SO_4, HSO_3, etc.).

Behavior of hydroxyl and hydrogen ions in flotation pulp

There are a number of factors that influence the flotation behavior of minerals in the presence of H^+ and OH^- ions. These factors are more pronounced in the flotation of oxides and silicates than sulfides. Some of these factors are discussed below.

Mineral oxidation. The sulfide minerals in aqueous solution almost always tend to oxidize and the pH of the solution is an important parameter that determines the degree of oxidation and the nature of the oxidation products. A product of oxidation, whether soluble, weakly soluble or insoluble, such as oxides, hydrolydes or sulfates, can significantly influence the interaction of various reagents with the mineral surface.

The degree of oxidation of the individual mineral in the presence of H^+ or OH^- ions cannot be predicted, although such attempts have been made [41]. This is because the oxidation of individual sulfide minerals depends very much upon the nature of the mineral itself and the origin of the formation.

Mineral solubility. All sulfide minerals have some degree of solubility in aqueous solution. Among a number of other factors discussed earlier, the pH of the solution influences the amount of soluble specimens in solution. However, the degree of solubility of certain minerals determines the amount of alkali or acid to achieve the desired pH value. For example, too much acid-soluble species in solution (SO_4) would require high additions of lime. In such flotation systems, very high alkaline addition requirement is most often highly detrimental to selective flotation. Therefore, compromise pH values have to be found or another approach has to be followed.

The existence of high amounts of soluble species that influence the consumption of a particular pH regulator is also a sign of the presence of a degree of alteration. This is discussed in Chapters 11 to 16.

Reaction of H^+ and OH^- ions with dissolved ions from the mineral lattice is common, especially when multi-valent ions are present in solution. These ions may react with H^+ or OH^- ions to form complexes that may exhibit high surface activity. Hydrolysis of this type of transition metal through this kind of reaction is expressed as

$$M^{2+} + OH^- \rightarrow MOH^+; K = \frac{[MOH+]}{[M^{2+}][OH^-]}$$
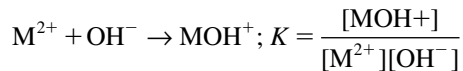
The importance of hydrolysis on activation has been discussed in earlier chapters.

Hydroxyl ion as a depressant. As stated earlier, a number of investigations define hydroxyl ions as depressants [42], defining a critical pH value above which the mineral will not float. The relationship between the critical collector concentration and pH is often referred to as a critical curve. This is applicable for some cases, but very often in real practice, the theory of critical collector concentration and pH does not work.

In some operating plants [43], galena flotation is carried out at pH 4–5 with xanthate collector where the concentration of the collector on galena is supposed to be 0. A similar situation is found for other minerals, such as pyrite, chalcopyrite and sphalerite. The reason for such behavior is not known and has never been examined. It is therefore evident that hydroxyl ions in sulfide flotation do not act directly as depressants, but through interaction can indirectly cause depression. In spite of this, it is worth mentioning several theories that various researchers used to explain the depressing action of hydroxyl ions. These are:

(a) Competition between hydroxyl and collector ions. Gaudin [3] considers the collector adsorption–desorption process to be one of ion exchange involving hydroxyl ions:

$$X^-(ads) + OH^-(aq) \rightleftharpoons OH^-(ads) + X^-(aq)$$
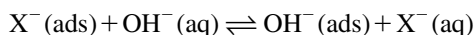
For the conditions that govern flotation or non-flotation, the above equation can be expressed as

$$X^-(ads) = \text{constant}$$

For a given collector–mineral system, the equation can be expressed as

$$[OX^-(ads)]$$

(b)   Chemical metathesis theory postulates [44] that all dissolved reagents in flotation pulps, either by action on the to-be-floated or on the not-to-be floated particles affect their flotability, function by reason of chemical reactions of well recognized types between the reagent and theaffected particle .

(c)   Kinetic theory basically implies that the effect of increasing the solution pH on oxidation rate can be counter-acted by an increase in xanthate concentrate, where [45]

$$[X^-][OH]^{0.8} = \text{constant}$$

which is a modified version of the Bovsky equation.

Requirements of acid/alkali for pH regulation

The amount of pH regulator needed to adjust the pH of a slurry may be calculated through *buffer capacity*. The buffer capacity b_c is defined as the amount of acid or alkali needed to make an incremental change in the pH:

$$b_c = dC_A = \frac{dC_B}{d\,pH}$$

where C_A and C_B are the amount of acid or alkali in units required for change in pH (e.g. kg/t of ore). Generally, C_A and C_B are functions of natural pH of slurry and the density of the slurry. A buffer capacity of the slurry can also be a measurement of the resistance of the slurry to changes in pH. In some cases, a buffer capacity of the ore is defined as a weighed average of the buffer capacity of constituent minerals:

$$b_c(\text{ore}) = \sum f_i b_{ci}$$

where f_i is the weight fraction and b_{ci} is the buffer capacity of mineral i. The value of b_c (ore) for slurries of pure minerals can be determined thermodynamically, but in natural ores experimental measurements are required.

The calculation of buffer capacity from thermodynamic data requires a knowledge of the manner in which H^+ and OH^- ions are consumed when acid and alkali are added to

the pulp. It is believed that H$^+$ or OH$^-$ ions are consumed by (a) the changing of the electrical double layer and (b) by the extent of dissolution and oxidation of the mineral mixture. Very often, a high b_c value means that the oxidation state of a particular mineral is also high.

8.2.4   Oxygen as a regulating agent in sulfide mineral flotation

The role of oxygen in the adsorption of collectors has been discussed in previous chapters. However, the induction of oxygen to flotation study through aeration for the purpose of depression–activation has been practiced in many operating plants for over 40 years. The investigations into aeration [46] led to the finding that the rate of the oxygen consumption of a slurry or oxygen demand was primarily a function of the susceptibility of the mineral surface to oxidation. By measuring the oxygen demand during aeration (i.e. oxygen probe), it is possible to determine the amount of oxygen required to obtain good selectivity in flotation. Figure 8.11 shows the oxygen demand as a function of aeration time, obtained in an operating plant. The data for this figure is interpreted such that the point of maximum curvature corresponds roughly to the aeration time required (amount of oxygen consumed) to obtain optimum metallurgical results.

In this particular case, "depression" of pyrite by oxygen and "activation" of chalcopyrite occurs after the oxygen demand (i.e. consumption reaches a certain point).

Experimental work conducted on various sulfide ores [47] shows that the flotation of chalcopyrites increased up to a certain maximum by increasing oxidation by air, after
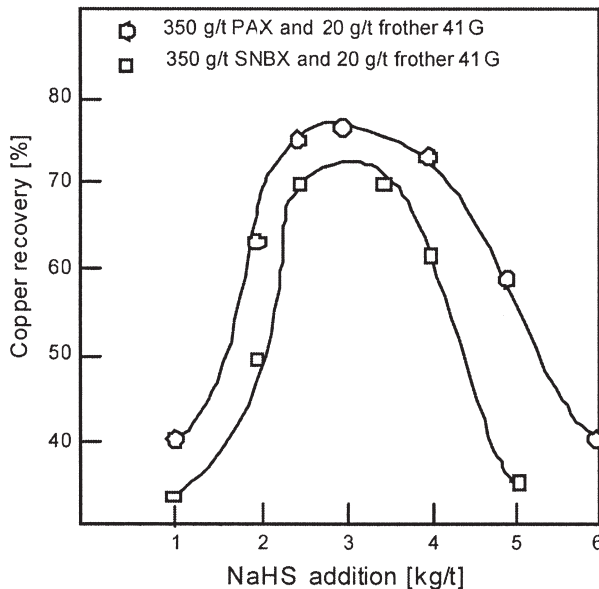
Figure 8.11 Oxygen demand versus aeration time [46].

which further oxidation had no marked influence on the flotation properties. In contrast, galena required very little to no oxidation for flotation and flotability rapidly increased thereby. For iron sulfides, flotation properties become very different with increasing oxidation. Some investigations [48] conducted on sulfide ores showed that flotation of pyrrhotite increases with an increased degree of oxidation up to a certain limit. The degree of oxidation of particular ores depend on the mineral composition of the ore. Copper–pyrrhotite ore requires extensive aeration to obtain maximum flotation rate for chalcopyrite as pyrrhotite is rapid consumer of oxygen. Extensive aeration of pyrrhotite-containing ores is also beneficial in preventing activation of pyrrhotite by copper ions. Plant experience has shown that during zinc flotation from the ore containing pyrrhotite [49], aeration during copper activation of sphalerite improves selectivity dramatically.

It can therefore be concluded that oxygen in the flotation pulp plays the role of depressant and activator.

8.3   INTERACTION OF REGULATING REAGENTS IN NON-METALLIC FLOTATION

The interaction of regulating reagents in non-metallic flotation is quite different from that of sulfide flotation. Many regulating reagents used in non-metallic flotation are not used in sulfide flotation and likewise the regulating reagents used in sulfide flotation are not used in non-metallic flotation. There are only a few exceptions (e.g. Na_2S, silicates, phosphates) that are used in both sulfide and non-sulfide flotation. Polymeric regulating reagents, however, are used in both sulfide and non-sulfide mineral flotation. Most of the regulating reagents used in non-metallic flotation are closely related to collector adsorption. This is mainly dictated by the nature of the collector used (i.e. cationic or anionic flotation).

It should be noted that many regulating reagents used in non-metallic flotation have not been studied and very little is known about the interaction of such modifiers.

One of the main problems in defining the role of regulating reagents in non-metallic flotation is that many regulating reagents can be activators for some minerals and depressants for others; therefore classifying such reagents as activator or depressant would be impossible. Therefore, the regulating reagents in this section are discussed according to their role under particular conditions.

8.3.1   Regulating reagents containing divalent sulfur

The most common representative of this group of reagents is sodium sulfide ($Na_2S \cdot 9H_2O$), whose role as depressant in sulfide mineral flotation has already been discussed. $Na_2S \cdot 9H_2O$ and NaHS are more widely used in oxide mineral flotation as an activator for oxide copper, lead and zinc minerals. In addition, the Na_2S has found application as a depressant in non-metallic flotation, where fatty acid collectors are used. Its function is mainly to desorb the collector from the particular mineral surfaces.

Sodium sulfide is a salt with a strong base and weak aging. In aqueous solution, it hydrolyzes as follows:

$$Na_2S + 2H_2O \rightarrow 2NaOh + H_2S$$

$$NaOH \rightarrow Na^+ + OH^-$$

$$H_2S \rightarrow H^+ + HS^-$$
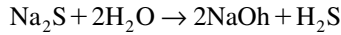
Because the dissociation constant of SH^- and H_2S is relatively small, while the dissociation constant of NaOH is much higher, Na_2S always has an alkaline reaction. In the aqueous solution containing Na_2S, the ions Na^+, OH^-, SH^-, S^{2-} and molecules H_2S are always present. These ions may have a significant effect on the surface properties of many minerals. It is believed that SH^- and S^{2-} ions have the strongest affinity to mineral surfaces. For example, when malachite is contacted with Na_2S, it results in a sharp increase in its hydrophobicity. Hydrophobicity of oxide minerals with Na_2S is sometimes so strong that when, for example, contacting cerusite with Na_2S for 5 min the cerusite becomes flotable without collector addition.

It is believed that in the sulfidization process [50], sulfur ions S^{2-} react with the mineral surface, in which process the sulfate or carbonate ions are displaced with S^{2-} forming corresponding sulfides amenable to flotation with a xanthate collector. With a relatively high concentration of Na_2S, the layer of sulfide forms on the mineral surface in a relatively short period of time. In the case of cerusite, the following reactions may occur:

$$Na_2S + H_2O \rightleftharpoons Na_2SH + NaOH; \ PbCO_3 + 3NaOH \rightarrow H_2O + Na_2CO_3 + NaHPbO_2;$$

$$NaHS + NaHPbO_2 = 2NaOH + PbS$$

$$or \ Na_2S + PbCO_3 = Na_2CO_3 + PbS$$
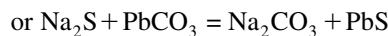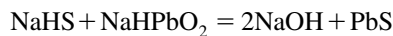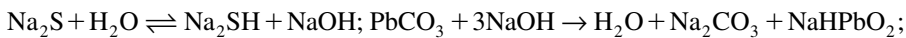
The layer of sulfides formed on the surfaces of cerusite and malachite are easily visible under a microscope because they rapidly change color.

In some cases, the sulfidization of minerals that do not sulfidize under normal conditions (i.e. silicates) can be accomplished by thermal treatment with elemental sulfur [51].

In the presence of oxygen (i.e. air), a sulfidized layer on the surface of the mineral may oxidize and prevent the sulfidizing action of S^{2-}, SH^- ions, where under these conditions, it results in non-flotation or use of excessive amounts of sulfidizer. In experimental studies carried out with Na_2S solution in the presence of oxygen, the Na_2S initially oxidizes to SO_4^{2-} [52] followed by oxidation of minerals. It is believed that as sulfide minerals require some oxygen for the collector to be adsorbed onto the mineral surface, minerals cannot
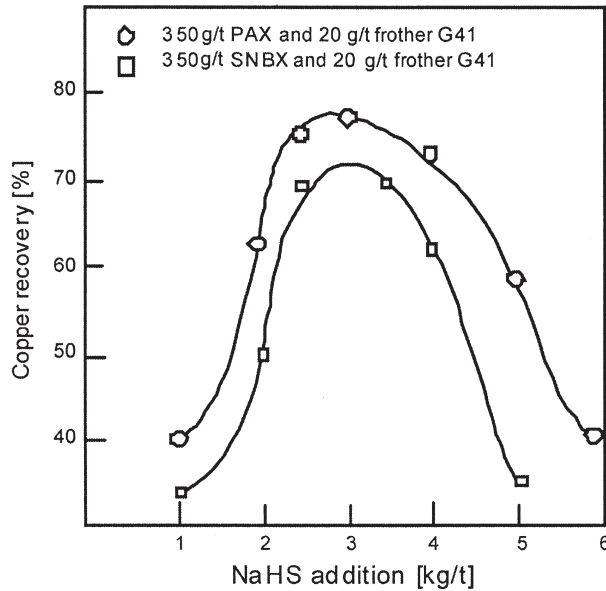
Figure 8.12 Effect of level of sulfidizer on malachite recovery [53].

adsorb a collector and float in the presence of free S^{2-} and HS^- ions on the sulfidized oxide.

Studies conducted on malachite ores [53] have shown that the level of sulfidizer plays an important role in the flotability of sulfidized malachite. Figure 8.12 shows the effect of sulfidizer additions on malachite recovery.

Studies conducted on cerusite, malachite and chryssocola [54] have shown that the rate of sulfidization increases with increase in the initial rate of sulfidizer additions. The sulfidization rate of cerusite, however, is affected by the presence of hydrogen ions; therefore, the maximum rate of sulfidization occurs at a pH 9.5–10. The rate of sulfidization of malachite is not sensitive to pH and a relatively constant rate of sulfidization occurs at a pH between 8 and 11.

An increase in temperature usually results in an increase in the rate of sulfidization. The maximum rate of sulfidization occurs at a temperature of 60°C.

The major setback in the sulfidization flotation of natural ores is the presence of ultra-fine slimes in the ore. Almost all operating plants treating oxide copper ore (Zambia, Former Republic of Zaire) contain fine slimes. The presence of fine slimes in the flotation pulp may cause (a) increased collector and sulfidizer requirements and (b) reduced selectivity and reduced recovery. There is little to no data in the available literature that deal with this subject.

8.3.2   Sodium silicate

Sodium silicate is a widely used regulating reagent in the flotation of non-sulfide minerals. Sodium silicate is used as depressant and activator and is a universal peptizing agent

effective when slimes are present in the pulp. In addition, in many cases it influences froth-ing properties, rendering froth more brittle. The composition of sodium silicate is dis-cussed in Chapter 4.

The dissolution process of sodium silicate is relatively complex and consists of its hydration with the formation of NaOH, followed by dissolution of silica, its subsequent dissociation and finally peptization of the residual silica by the strongly alkaline solution.

Sodium ortho silicate hydrolyzes according to the equation:

$$Na_4SiO_4 + H_2O \rightarrow 2NaOH + Na_2SiO_3$$
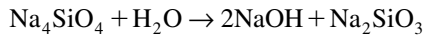
Sodium silicate is less soluble in water than monosilicate and is also less hydrolyzable. The hydrolytic dissociation is particularly strong with sodium metasilicate:

$$2Na_2SiO_3 + H_2O \rightarrow Na_2Si_2O_5 + 2NaOH$$
$$Na_2SiO_3 + H_2O \rightarrow NaHSiO_3 + NaOH$$
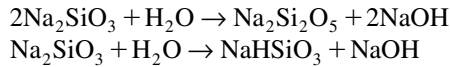
Hydrolysis and concentration of OH^- ions increases with reduced concentration and increase in temperature.

Sodium silicate reacts ions in solution; e.g. calcium forming nearly insoluble calcium silicates. Sodium silicate also interacts with mineral surfaces [55], preventing collector adsorption. Therefore, the depression by sodium silicate involves blocking of collector adsorption.

The activating action of sodium silicate (i.e. cerusite, fluoride, apatite) is explained by three actions [56]: (a) improvement in frothing characteristics, (b) peptization of slimes and (c) completion of certain ions responsible for interaction with collectors, thus making them less active.

The selective depression of silicate can be significantly improved. Several of these methods are reported in the literature:

- Introducing or pre-mixing of sodium silicate with polyvalent cations (i.e. salts of alu-minum). $Al(NO_3)_3 \cdot 9H_2O$, $Al_2(SO_4)_3 \cdot 18H_3$ and $AlCl_3$ were used to improve depression of calcite during flotation of fluoride. Aluminum and other polyvalent salts together with silicate were used in the flotation of scheelite and apatite from carbonaceous gangue.
- The mixture of polyvalent metal salts and acidified silicate [57] were used as an effec-tive depressant for silicate gangue during the flotation of hematite.

The sodium metasilicate is used for the separation of monazite from zircon and rutile. Figure 8.13 shows the effect of the level of sodium metasilicate on flotability of monazite, zircon and rutile.

Data on this figure showed the strong depressing effect of sodium metasilicate on zir-con and rutile.

The mechanism of the depressing action of silicates is not well understood, but it is believed that in most cases, the hydrated micelles of silica acid are responsible for the
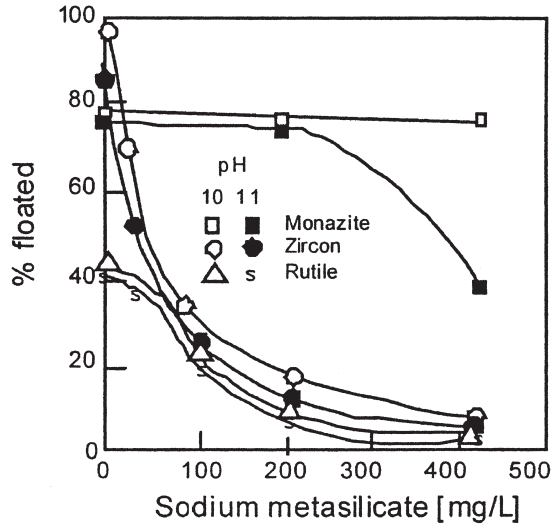
Figure 8.13 Flotability of monazite, zircon and rutile as a function of sodium metasilicate concentration using hydroxamate collector [58].

depression. These micelles may adsorb on mineral surfaces under certain conditions. Physical adsorption is often mentioned in the literature [59].

8.3.3   Fluorides

Fluorides in the form of NaF, HF, H_2SiF_6 and Na_2SiF_6 have been widely used in the flotation of silicates and oxides as modifying reagents. These compounds have both an activating and depressing effect on a wide group of silicate minerals. Fluoride ions (NaF, HF) have an activating effect on zircon, feldspar and beryl when used in small quantities. However, when used in larger quantities together with organic acids, fluorides have a depressing effect on zircon and are used in the separation of columbite/tantalite from zircon. Fluorides have a strong depressing effect on silica, spodumene and petalite in acid pH. There are several mechanisms proposed for fluoride activation, some of which include:

- Fluoride can charge alumina sites on mineral surfaces by forming alumina–fluoride complexes where a cationic collector [60] adsorbs on these sites.
- The activation process may result from the adsorption of the fluorosilicate on the surface of an alumina site, where the ore is exposed as a result of fluoride attack [61]. This results in the formation of negatively charged sites which attract collector. The depressing action of fluoride on a number of silicates including silica, topaz, spodumene, foresterite, pollucite, etc. is not well understood. It is believed that during flotation with fatty acids, the fluorides form colloidal precipitates of H_2SiO_3 on mineral surfaces.

The effect of fluoride on certain minerals may also be associated with the crystal structure of particular minerals. For example, fluoride depresses minerals with chain and ortho structures, while activating minerals with framework and sheet structure.

8.3.4 Metal ions

Metal ions can profoundly affect the flotation of both oxide and silicate minerals. This depends largely on the type of collector used (i.e. anionic, cationic, amphoteric). In most cases, metal ions are highly detrimental during flotation of most oxide minerals. The activation of silicates by metallic cations impairs the selectivity of the separation of oxides and silicates or individual silicates themselves, such as beryllium minerals (beryl, phenacite) from quartz [62]. In the activation of silicates by ferric and lead cations, it was postulated that hydroxy complexes are responsible for activation ($FeOH^{2+}$, $PbOH^+$, etc.). In the case of complex silicate minerals containing iron oxides, it is possible that auto-activation may occur through selective dissolution of iron species that form hydroxy complexes in solution and re-adsorb on mineral surfaces. This re-adsorbed hydroxy complex may function as an activator in the presence of an anionic collector.

In the flotation of quartz, it is known that heavy-metal cations (Cu, Pb, Fe) act as activators for quartz. Likewise, the use of small quantities of $CuSO_4$ in the flotation of zircon with a cationic collector improves flotability of zircon. It is believed that chemosorption of high molecular-weight collectors on oxide and silicate minerals occurs at a pH range in which metal ions, present in aqueous solution, have hydrolyzed to hydroxy complexes [63]. The flotation of pyrolusite with fatty acid, for example, occurs in a pH region above 8 (i.e. where hydroxy complexes are formed).

From a practical point of view, flotation separation of silicates or oxides from silicates by removal of heavy-metal anions is desirable for achieving good selectivity using either anionic or cationic flotation technique. This is essentially accomplished by acid pre-treatment and de-sliming before flotation.

8.3.5 Role of inorganic ions

The organic ions in solution during the anionic and cationic flotation of silicates and oxides have both a depressing and activating role.

Owing to the fact that collector ions function as counter-ions in the double layer, their adsorption density depends on competition with other counter-ions in solution. Therefore, the presence of excessive amounts of dissolved salts can reduce flotability of particular minerals, in which case inorganic ions act as depressants. For example [64], the flotation of goethite with quaternary amine salts at a pH of 11 is reduced to about 5% in the presence of 0.03 mol/L NaCl, where the reduction in flotation results from competition from Na^+ ions. In other studies [65], it was shown that Ba^{2+} and Na^+ ions inhibited flotation of quartz using low dosages of ammonium acetate collector, where the effect was much greater with divalent salts. For multi-valent ions to act as depressants, they have to be charged similar to a collector. An example is the flotation of alumina with sodium dodecyl sulfate in the presence of Cl^- and SO_4^{2-} ions, where these ions completely inhibit flotation of alumina.

The activating effect of ions on the flotation of oxides is pH-dependent. For example, the flotation of ilmenite with ammonium acetate at pH 5.2 when using HCl and H_2SO_4 decreases [66]. However, the flotation increases sharply when the pH is lowered to about 3.2 because SO_4^{2-} acts as an ilmenite activator. Some of the inorganic ions (i.e. $MgSO_4$, $MgCl_2$, NaCl, etc.) have a positive effect on the flotation of naturally hydrophobic minerals. This is explained by the change in the electrochemical potential resulting from the adsorption of ions, which in turn improves the adsorption of hydrocarbon on mineral surfaces.

REFERENCES

1. Bulatovic, S.M., and Wyslouzil, D.M., Development and Application of New Technology for Treatment of Complex Massive Sulphide Ore, *Minerals Engineering*, Vol. 12, No. 2, pp. 85–92, 1999.
2. Bazanova, N.M., and Mitrofanov, S.I., Kinetics of Adsorption of Copper on Sphalerite, *Obogashchenie Rud*, No. 6, 1961.
3. Gaudin, A.M., *Flotation*, 2nd Edition, McGraw-Hill, New York, 1957.
4. Gaudin, A.M., and Fuerstenau, D.W., Activation and Deactivation of Sphalerite with Ag Ions and CN, *Minerals Engineering*, Vol. 9, pp. 28–35, 1957.
5. Fuerstenau, D.W., Activation in Flotation of Sulphide Minerals, In (R.P. King ed) *Principles of Flotation*, IMME, Johannesburg, pp. 183–199, 1982.
6. Gircys, J., and Laskowski, J., Copper Activation Studies with Sphalerite, *Canadian Metallurgical Quarterly*, II, pp. 73–78, 1972.
7. Leppinen, J., Laajalehto, K., Kartio, I., and Suoninen, E., FTR and XPS of Surface Chemistry of Pyrite in Flotation, *XIX International Mineral Processing Congress*, San Francisco, 1995.
8. Nicol, M.J., *An Electrochemical Study of the Interaction of Copper (II) Ion with Sulphide Minerals*, Electrochemistry Society, Pennington, pp. 152–168, 1984.
9. Sillen, L.G., Quantitative Studies of Hydrolytic Equilibriums, *Quarterly Reviews*, Vol. 13, 1959.
10. Salatic, D., and Manojlovic, M., Influence of Copper and Zinc Salts on the Surface Phenomena of Galena, Chalcopyrite and Sphalerite, *XI International Mineral Processing Congress* (Special Edition), 1975.
11. Wang, X., The Aqueous Surface Chemistry of Activation in the Flotation of Sulphide Minerals – A Review, *Mineral Processing Extractive Metallurgy*, No. 4, pp. c144–c151, 1989.
12. Ralston, J., and Healy, T.W., Activation of Zinc Sulphide with Cu(II) Cd(II) and Pb(II), Activation in Neutral and Weakly Acidic Media, *International Journal of Mineral Processing*, No. 7, pp. 203–217, 1980.
13. Trahar, W.J., and Warren, L.J., The Activation of Sphalerite by Lead – A Flotation Perspective, *International Journal of Mineral Processing*, No. 49, pp. 121–148, 1977.
14. Bulatovic, S.M., *Process Development for Treatment of Refractory Cu/Pb/Zn Ores*, Report of Investigation, LR-5397, 1998.
15. Bogdanov, O.C., and Haiman, B.J., *Introduction in Theory and Practice of Flotation*, L. IZD. Mechanobr (Russia), 1959.
16. Wark, I.W., and Cox, A.B., Principal of Flotation III – An experimental study on the influence of cyanide alkalis and copper sulphate on effect of sulphur-bearing collectors at the mineral surface, *Transactions of AIME*, Vol. B4, 1939.
17. Sobrez, B.M., Evaluation of NaHS as a Replacement for Na_2Sx9H_2O, *Bulletin of the Institute of Information on Mineral Processing*, No. 10(39), Russia, 1954.

18. Bogdanov, O.C., Investigation of the Action of Modifying Reagents in Flotation, *International Mineral Processing Congress*, Stockholm, p. 419, 1957.
19. Mitrofanov, S.I., Solution of Some Problems Concerning Theory and Practice of Selective Flotation, *International Mineral Processing Congress*, p. 441, Stockholm, 1957.
20. Paterson, J.G., and Salman, R., Use of Cyanides as Depressants, *Canadian Mining and Metallurgical Bulletin*, No. 61, p. 74, 1968.
21. Elgillani, D.A., and Fuerstenau, D.W., Mechanism invloved in cyanide depression of pyrite, *Transactions of AIME*, No. 241, p. 437, 1968.
22. Plaksin, I.N., Activating Action of Cyanide During Flotation of Complex Sulphide Ores, *Rudi Srednei Azil*, pp. 60–70 (Russia), 1970.
23. Bulatovic, S.M., *Process Development for Treatment of Pinos Altos (New Mexico) Copper Zinc Ore*, Report of Investigation, LR-3360, Vol. 2, 1979.
24. Pallanch, R.A., *Flotation Practice*, American Institute of Mining and Engineering, New York, 1982.
25. Bhubov, L.I., Mitrofanoi, S.I., and Dudenkov, S.V., Present Trends in the Use of Flotation Reagents and New Approaches, *Tsvetnie Metaly*, UDC622.765.06, 1969.
26. Korshebaev, K.T., and Sokolov, M.A., The Effect of SO_2 on Flotation of Sulphide Minerals, *Vestnik Akademii Nank. KOZ*, Vol. 21, pp. 66–67, 1965.
27. Miller, J.D., Pyrite Depression by Reduction of Solution Oxidation Potential, *US Water Pollution Control Research Series*, 12010DIM 08/70, 1971.
28. Yamamoto, T., Flotation of Kuroco ore Japan, In (M.J. Jones ed) *Complex Sulphide Ore*, IMM, London p. 7, 1980.
29. Dudenkov, C.B., and Polkin, I.N., *Principles of Theory and Practice in the Use of Flotation Reagents*, Nedra, p. 184, 1969.
30. Plaskin, I.N., and Shafeeve, R.S., Effect of Some Polyelectrolytes on Xanthate Adsorption on Galena, *DAN SSSR*, Vol. 2, pp. 82–87, 1960.
31. Belograzov, K.F., The Behaviour of Flotation Processes, *Metalurgizdat*, 1947.
32. Bulatovic, S.M., New Copper–Lead Separation Process, US Patent 4,246,096, January 20, 1981.
33. Konev, A.S., and Debrivnaia, L.B., Flotation Separation of Bulk Sulphide Concentrates, *Mechanobre Institute Bulletin*, No. 5, 1957.
34. Plaksin, I.N., and Mokronsov, R.N., An Investigation of the Adsorption of Sulphydryl Collectors in the Presence of Depressing Reagents, *Mining Institute and Academy of Sciences*, USSR, No. 2, 1955.
35. Plaksin, I.N., and Miasnrkova, G.A., Some Data on Depression of Pyrite by Lime, *Academy of Sciience SSSR*, No. 4, 1956.
36. Bulatovic, S.M., Report of Investigation, May 2001 (Report LR 10136 pp. 33–36)
37. Plaksin, I.N., and Kursakova, G.M., Flotation Concentration of Arsenopyritic Ores, *Academy of Science SSSR*, No. 6, 1955.
38. Krogh, S.R., Natural Activation of Sphalerite and Possible Deactivation with Thiosulphate and Sulphite, *IMM*, pp. C44–C50, March 1979.
39. Bulatovic, S.M., New Pyrite Depressant, US Patent, 1989.
40. Bulatovic, S.M., and Barjaktar, H., Lahanos Copper–Zinc Concentrator; An Innovative Way to Improve Plant Performance – Challenge Scopes in Mineral Processing, In (M. Kemal et al. eds) *6th International Mineral Processing Symposium*, 1996.
41. Chander, S., *Electrochemistry in Mineral and Metal Processing*, In (P.E. Richardson et al. eds) Electrochemical Society, London, p. 14, 1984.
42. Wark, I.W., and Cox, A.B., Principal of flotation 2 – Flotation of sulphide ores, *Transactions of AIME*, Vol. 112, p. 189, 1934.
43. Salatic, V., and Bulatovic, S.M., Treating Complex Lead–Zinc Ore in the Caribou Mill, New Brunswick, Canada, *3rd Balkan Conference in Mineral Processing*, October 1999.

44. Taggart, A.F., Taylor, T.C., and Knoll, A.F., Experiments with flotation reagents, *Transactions of AIME*, Vol. 87, p. 217, 1930.

45. Janelski, N.D., and Kim, J., *International Journal of Mineral Processing*, No. 4, p. 227, 1977.

46. Konigsmann, K.V., Effect of aeration on flotation, In (A.D. Zunkel, R.S. Boorman, A.E. Morris, and R.J. Vesely eds) *Flotation Techniques for Complex Ores, Complex Sulphides*, IME, pp. 333–342, 1985.

47. Plaksin, I.N., Interaction of Minerals with Gasses and Reagents in Flotation, *Mining Engineering*, March 1959.

48. Holmsen, T.W., Influence of Oxidation on the Flotation of Cu/Zn Iron Sulphides Ores, *Mining Magazine*, Vol. 17, No. 2, 1967.

49. Bulatovic, S.M., *Improvement in Plant Metallurgical Results at San Martin Concentrator Mexico*, Report of Investigation, LR4876, 1997.

50. Shorsher, I.N., Flotation of Carbonate Minerals (Cerusite and Malachite), *Gostopekhizdad*, 1959.

51. Cizicov, D.M., and Tjurnikova, V.I., Processing of Oxide Ores, *Tsvetnaja Metallurgia*, No. 8, 1941.

52. Mitrofanov, S.I., and Klassen, V.I., Study of the Sulphidization Reaction on Oxide Minerals, Vol. 10, *Metallurgizedat*, 1955.

53. Bulatovic, S.M., Ferron, C.J., and Yen, W.T., Development and Plant Appplication of New Collector for Oxide Copper/Cobalt Ore Flotation for Gecamines, Zaire Flotation Plants, *Copper 92*, Ottawa, August 2–6, 1992.

54. Rey, M., Flotation of Oxidized Ores of Lead, Copper and Zinc, *Transactions of IMM*, Vol. 63, pp. 423–431, 1953.

55. Klassen, Y.I., and Mokrousov, V.A., *Introduction to Theory of Flotation*, Butterworth, London, 1963.

56. Petrov, N.E., *New Method for Flotation of Low Grade Sheelite Ores*, ONTI, 1940.

57. Yang, D.C., Polyvalent Metal Salts and Alkali Metal Silicates, US patent 4,132,635, January 2, 1979.

58. Parez, O., and Perez, E.C., Effect of Sodium Metalsilicate and Sodium Sulphide on Flotation of Monazite, Zircon and Rutile with Oleate and Hydroxamate, *Minerals Engineering*, Vol. 6, No. 1, pp. 186–190, 1993.

59. Glembockii, B.A., Klassen, B.I., and Plaksin, I.N., *Flotation*, Gosgortexizdat, 1961.

60. Warren, L.J., and Kitchener, J.A., Role of Fluoride in flotation of Feldspar, Adsorption of Quartz, Corundum and Potassium Feldspar, *Transactions of IMM*, Vol. 81, p. C137, 1972.

61. Joj, A.S., Flotation of Silicates, 2. Adsorption of Ions on feldspar in Relation to Flotation Response, *Transactions of IMM*, No. 75, p. C82, 1966.

62. Fuerstenau, M.C., and Miller, J.D., Metal Ion Hydrolysis and Surface Charge in Beryl Flotation, *Transactions of IMM*, No. 74, p. C381, 1965.

63. Smolik, J.J., and Trivedi, N., Surface Characteristics and Flotation Behaviour of Alumosilicates, *Transactions of IMM*, Vol. 256, p. 69, 1966.

64. Iwaski, I., Cooke, S.R.B., and Choi, H.S., Flotation Characteristics of Hematite, Geothite and Activated Quartz with 18-Carbon Chain Aliphate Acid and Related Compounds, *Transactions of AIME*, Vol. 217, p. 76, 1960.

65. Fuerstenau, M.C., Role of Metal Ions Hydrolysis on Oxide and Silicate Flotation Systems, *AICLHE Symposium Series*, No. 150, p. 71, 1975.

66. Nakatsuka, K., and Matsuoka, I., Flotation of Ilmenite from Magnetic Sand, *9th International Mineral Processing Congress*, Prague, p. 251, 1970.

Interaction of Organic Regulating Reagents

9.1 INTRODUCTION

As discussed in Chapter 4, polymer molecules consist of many segments that usually have considerable degrees of freedom. In solution, they behave different from other surfactants having more or less random coils. When such coils adsorb on the surface, the conformation of the molecules changes, depending on the balance between entropy and energy. For a low concentration of polymer in solution, it is believed that the adsorbed chain lies flat on the surface, but in a solution of finite concentration the adsorbed layer may have considerable thickness with parts of each chain extending into solution. Therefore, the models used to explain adsorption of low molecular-weight substances (i.e. Langmuir model) has no meaning for adsorption of polymers. Normally, any adsorption theory for polymers should account for its specific characteristics. Because the polymers are hetero-dispersed with a wide molecular-weight distribution, the characterization of the adsorption layer is rather difficult. In spite of the fairly large amount of data in the literature, much of this material cannot be interpreted because the relevant variables are not controlled or are simply unknown.

In many studies, the hetero-dispersed polymers are compared with homo-dispersed polymers with the same average molecular-weight distribution in the real sample. Such an assumption breaks down completely for adsorption measurements since as a result of strong preferential adsorption of long chains, the average molecular weight of the adsorbed material is very different from that in the solution. These implications have been included in interpretations of the experimental data.

Theoretical aspects of the adsorption of a polyelectrolyte class of polymers are believed to be much more complicated than the uncharged macromolecules because of the presence of long-range electrostatic interactions. Therefore, the theory of the adsorption of the polyelectrolyte class of polymers is still in the early stages of development.

Although extensively studied, no conclusive adsorption model has been proposed for the effect of polymers on colloidal stability.

The action of polymers as depressants, flocculants, coagulants or dispersants depends very much on the chemical characteristics of the polymers, some of which include

• polymer type of functionality,
• steric configuration of the functional group,

- charge density and
- molecular weight.

These are only a few of the important requirements of polymers used in mineral processing.

9.2 SUMMARY OF THEORETICAL ASPECTS OF POLYMER ADSORPTION

9.2.1 The theoretical models

There are several models proposed for the adsorption of polymers, some of which include

- free-energy contribution,
- Scheufjens and Fleer theory and
- scaling concepts.

With respect to free-energy contributions, which play a role in the flexible chain molecular adsorption on the surface, there are several theories including the following:

- *The adsorption energy* due to the contacts of the segments with the surface. In this case, adsorption takes place only if the energy of the segment surface contact is lower than that of the solvent surface contact. The measure of this exchange energy is the dimensional parameter φ_s. It defines the net effect of exchange of a solvent molecule of the surface and the segment of bulk solution as $-\varphi_s kT$. On the basis of this definition, φ_s is positive for the adsorbed polymer, showing that the total adsorption energy is proportional to the number of adsorbed segments.
- *The conformational entropy* of the chain. This represents entropy loss occurring upon adsorption and accounts for the reduction in the internal degrees of freedom within the chain when adsorbed. An estimate of this effect is obtained by determining the ratio of the possible position of each bond in the surface layer and in the bulk of solution. If P_a and P_c are the coordination numbers of the two-dimensional surface layers and the three-dimensional solution, then the conformational energy can be approximated by $K \ln P_a/P_c$ per bond or for a long chain per adsorbed segment.
- *The entropy of mixing of chain and solvent* is related more to the configurational entropy loss occurring when the homogenous polymer solution is separated in a polymer-rich surface "phase" and the solution becomes enriched by solvent. The energy of mixing of chain and solvent has two terms: one for the chain and one for the solvent. If the polymer volume fraction is k_a in the adsorbed layer and k_b in the solution, the entropy loss for the polymer is described as $P \ln k_a^\phi/k_b^\phi$ per solvent molecule.
- *The polymer–solvent nearest neighbor interaction* is described as a consequence of the mutual interaction between segments and solvent molecules. Poor solvent segments attract each other, promoting adsorption.
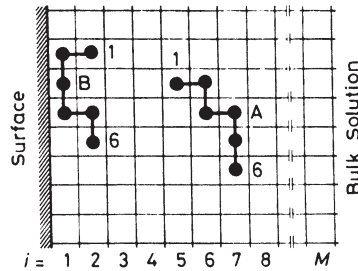
Figure 9.1 Schematic illustration of the lattice model with two possible conformations for a hexamer [1].

9.2.2   The Scheutjens and Fleer lattice model

This model arose from the need to count all possible conformations through the use of a lattice model, where the lattice layers are parallel to the surface as shown in Figure 9.1.

In this case, the layer number i runs from $i = 1$ (surface layer) to M, a layer in the homogenous bulk solution. Each site of the lattice has z immediate neighbors; $\lambda_0 Z$ in the same layer and $\lambda_0 Z$ in each of the two adjacent layers, where $\lambda_0 + 2\lambda_1 = 1$. In the simple cubic lattice, $\lambda_0 = 4/6$ and in a hexagonal lattice, $\lambda_0 = 6/12$. In terms of λ_1, the critical adsorption energy parameter Xs can be expressed as

$$Xs = \ln(1 - \lambda_1)$$

which is 0.288 in a hexagonal lattice. Usually, chain conformation in the lattice is defined by specifying the layer numbers where each of the segments of the chain is found. In Figure 9.1, as an example, two conformations of a hexamer are indicated, one non-adsorbed (A) with segments in layers 5,6,6,7,7,7 and one adsorbed (B) with segments 2,1,1,2,2. It should be noted that conformations defined in this way do not specify in which particular lattice site each segment is found and may contain many different sub-conformations with specific layer sites. The conformation distribution and free-energy distribution can be defined by mathematical calculations, which are not a subject of this discussion.

9.2.3   Scaling concept theory

This theory is based on a number of predictions. For example, for polymers in dilute solution, the scaling theory [2] predicts that under good solvency conditions, the molecules consisting of the "r" segments do not behave as gansin chains with dimensions proportional to $r^{0.5}$, but due to self-avoidancy, the functionability is $r^{0.6}$. In semi-dilute solutions, the chains begin to overlap and the system can be considered a transient network with a mesh size "e", the so-called correlation length. The correlation length decreases with increasing concentration. In a concentrated solution, the segments of a chain will meet mainly segments of other chains, and the behavior is more ideal.

The scaling concept has been applied by other investigators [3] with slightly different assumptions. The adsorption layer is assumed to be divided into the following three regions: (a) the "proximal" regime, where the segment surface interactions dominate, (b) the "central" regime, where the network has a correlation length "e" that depends on the local segment concentration and (c) the "distant" regime, where the segment density is supposed to decay exponentially to the bulk solution values. In the central regime, the segment concentration is predicted to drop as $x^{-4/3}$ where x is the distance from the surface. This exponent is derived from the so-called self-similarity condition, since in solution the correlation length decreases as $e \sim \varphi^{-4/3}$.

It is believed that the present state of the scaling theory is not sufficient for a quantitative comparison with experimental data.

This short summary of the theoretical aspects of polymer adsorption on surfaces is given to show that polymer adsorption on mineral surfaces is very different from collector adsorption or adsorption of inorganic modifiers. Mineral science largely ignores these difficulties and uses hydrophobic bonding, hydrogen bonding, free energy and chemical adsorption theories to explain polymer adsorption on mineral surfaces. These aspects will be discussed later.

9.3   EFFECT OF THE PROPERTIES OF POLYMERS ON ITS PERFORMANCE AS DEPRESSANTS

9.3.1   Polymeric versus monomeric speciens

Water-soluble polymers containing bearing groups such as starch and dextrin import strong hydrophilicity as well as good affinity to gangue minerals such as some sulfides. These polymers are not nearly as surface-active as most charged collector functionalities and therefore compete less effectively for active sites on the mineral surfaces. Monomeric polyhydroxyl polymers such as ethylene glycol, glycerine and glucose are not effective depressants, although adsorption and desorption of functional groups on the mineral surfaces exists. It is believed that water molecules compete strongly with the mineral surface for the hydroxyl groups.

Because of the limited number of available functional groups, monomeric polymers are not capable of establishing or maintaining adequate association with the mineral particles. Polymers such as starch and other polysaccharides have a large number of hydroxyl groups with which they can maintain dynamic adsorption equilibrium. It should be pointed out, however, that polymers with high molecular weight are not effective depressants. It should be noted that the configuration of functional groups in the polymers plays an important role in the depressing action of polymers.

9.3.2   Effect of type of functional groups

Broadly, organic polymers usually determine the interaction mechanism with mineral surfaces based on the character of their functional groups. They also determine the

strength of the attraction force, which also depends on the type of interaction, surface properties of minerals and the chemical properties of aqueous medium of the system [4]. Functional groups of polymers can be non-ionic functional groups such as $-OH$, $=CO$ and $-COOH$, anionic functional groups such as $-COOH$, $-SO_3H$ and $-OSO_3H$, cationic functional groups containing cations $-NH_z$ and $=NH$ and amphoteric functional groups containing both anionic and cationic groups. Since each of these functional groups exhibits a varying degree of affinity to different minerals, the depressing action of various polymers is specific to certain groups of minerals. The selection of organic polymers as depressants for particular minerals can be similar to that of collectors.

For example, fatty acids, which contain a carboxylate functioning with a hydrocarbon chain, are good collectors for calcite, dolomite, apatite and hematite [5]. Similarly, carboxylated polymers (i.e. carboxyl cellulose) are good depressants for the same minerals. For most silicate minerals, cationic flotation with amine is used. Polymers based on cationically modified polysaccharides have been found to be very effective as depressants for silicate minerals. In the practice of non-metallic mineral flotation, where polymers are widely used as depressants in the selective separation of oxides, carbonates, etc., from silicates, there is a general route for the selection of an appropriate polymer as depressant. For a collector that floats a particular mineral, a depressant with a functionality similar to the collector is selected, the difference being that the polymer has a hydrophilic character.

9.3.3   The effect of stearic configuration of the functional groups and stearic stabilization

Polymers are unique in that they possess a large number of functional groups. It is believed that stearic arrangements have an appreciable influence on the effectiveness of a polymer as depressant. For example, Figure 9.2 shows three polymers with different stearic configurations of the OH group. The two neighboring OH groups in glactomaman have a cis configuration compared to those of starch, which has a trans configuration. The neighboring OH groups of those polymers are attached to the rigid ring structure of the repeating glucose units, so they remain fixed to the structure where the two neighboring OH groups on dihydroxy propyl cellulose are not directly attached to the ring structure and basically can be exchanged. The dihydroxy propyl cellulose OH groups may assume either a cis- or trans-type configuration. In some cases, a cis-hydroxyl group is much more effective as a depressant because the two OH groups can adsorb simultaneously on the mineral surface. This, however, would depend largely on the crystal structure of the particular mineral.

9.3.4   Charge density

Polymers based on ionic functional groups such as carboxylates, sulfonates and amines can be designed with a different charge density. This is particularly true with sulfonates and amines.
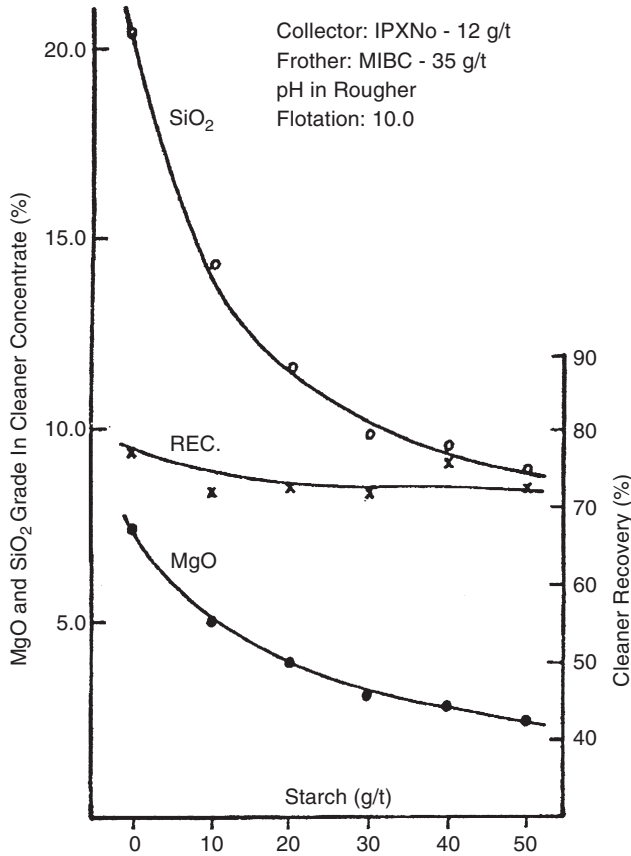
Figure 9.2 Copper recovery, MgO and SiO_2 content in the cleaner flotation as a function of starch additions [7].

Cationic depressants with strong cationic characters are not good depressants [6] because they can act as activators of minerals that are intended to be depressed. The depressing action of polymers also depends on the carboxyl functionality. Polymers with an excessive carboxylate charge density, in some cases, are good depressants for activated silica.

9.4   ACTION OF POLYMERS AS DEPRESSANTS

Compared with collectors and other chemicals used in mineral flotation, polymers are the most complex chemicals and therefore their action as depressants is not very well understood. The use of polymers in metallic and non-metallic flotation, however, is quite extensive but the number of polymers is rather limited. As mentioned before, the action when using polymers depends on the nature of its active polar groups; therefore, the discussion on the action of polymers is along these lines.

9.4.1   Action of non-ionic polymers

Representatives from this group consist of starches, dextrins, gum arabic, tanin derivatives, oxycellulose and polyrimil alcohol. The non-ionic polymers are widely used in both non-metallic and metallic flotation as depressants.

Starches and dextrins

In general, starch contains an abundance of hydroxyl groups, where each anhydro-glucose unit contains secondary hydroxyls and a large majority contains primary hydroxyls. These hydroxyls can potentially react with any chemical capable of reacting with alcoholic hydroxyls including ions in solution and collectors. Because of the behavior of starches and dextrins, a three-phase flotation system is highly complex. There are conflicting data on the adsorption mechanism as well as the action of both starches and dextrins.

In studies conducted on copper sulfide ores using low molecular weights, use of corn starch [7] for the depression of pre-activated Mg_2SiO_3 and aluminosilicate indicated that good depression of these minerals was achieved using a relatively low dosage of starch (Figure 9.2). In this case, enstalite (Mg_2SiO_3) was pre-activated with Fe^{2+} ions.

The effect of starch derivatives as iron depressants during anionic and cationic flotation of silica has been extensively studied. In the studies conducted with different corn starches [8], different viscosity adjustments were by homogenization. The results obtained showed that there is an optimum molecular size for starch (Figure 9.3) that acts most effectively as depressant and that extensive reduction in molecular size is not an advantage. When the results of waxy sorghum, corn and amylomaize starches are compared with the relative contents of amylose and amylopectin, it is apparent that the latter component is affected most by the mechanical shearing action.

Chemical modification of starches, such as degree of substitution (DS), was shown to improve the depressing action of starch on oxides. It was speculated that this change [9] resulted in the conformation of starch molecules at the mineral surfaces being more stretched out due to the presence of charged functional groups within the structure, thus making starch more effective as depressant. Studies carried out on titanium depression during calcite flotation using anionic collector [10] confirmed that chemically altered corn starch out-performed dextrin and guar gum as a perovskite depressant (Figure 9.4).

The adsorption of starch on iron oxides has been shown to be strongly dependent on the presence of calcium ions [11]. Adsorption of starch in the presence of calcium ions improved with the increase in pH. The role of the metal ion on dextrin adsorption was also extensively examined [12], indicating that the adsorption of dextrin on lead-coated starch is much higher than on uncoated quartz.

From these studies, it appears that the presence of ions in solution or mineral surfaces influences the adsorption of starch and dextrin significantly.

In sulfide mineral flotation, starch and dextrin are used for depression of iron sulfides. A fairly large number of operations, wherein copper–lead separation galena depression is involved, use starches and dextrins. In such separations, depression of galena depends on a number of factors including pH, collector concentration and type of starch and dextrin used [13].
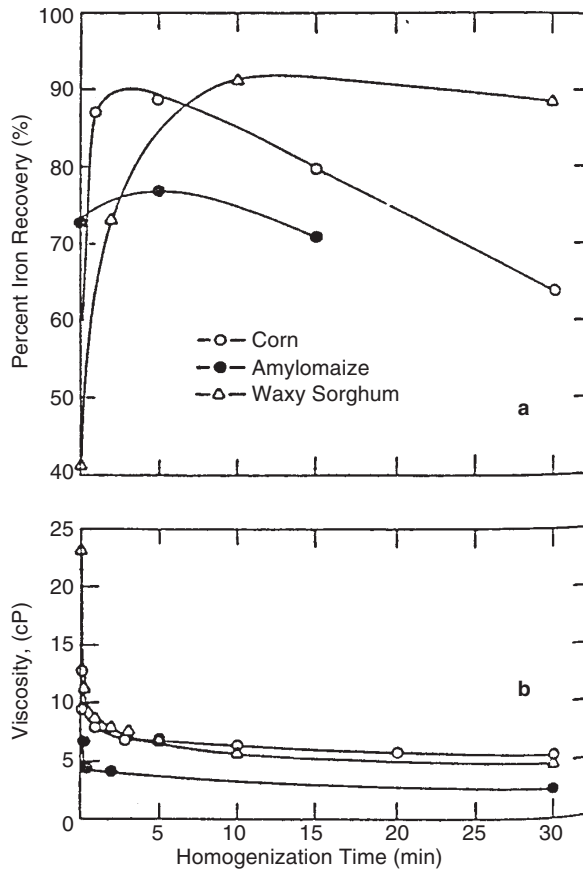
Figure 9.3 Time versus viscosity graph illustrating effect of homogenization.

Dextrins are commercially used for the depression of carbonaceous pyrite at the Mount Isa copper concentrator. For this purpose, cross-linked low molecular-weight dextrin (D101) is used [14].

In spite of the potential for the application of starches and dextrins in sulfide mineral flotation, research work in this area is rather limited.

Gum arabic

Gum arabic is a polysaccharide that contains 36.6% unhydrogalactose and highly hydrated polar groups of –OH, –COOH and –CHO. The importance of this depressant is that it is highly effective for calcite and dolomite in the presence of a sarcosine-type of collector. Studies conducted on the apatite–calcite–dolomite system [15] showed that for gum arabic to act as a depressant, a certain level of calcium ion is required. It was postulated that calcium ions are involved in a bridging mechanism between the polymeric molecule and the mineral surface. The suggested mechanism
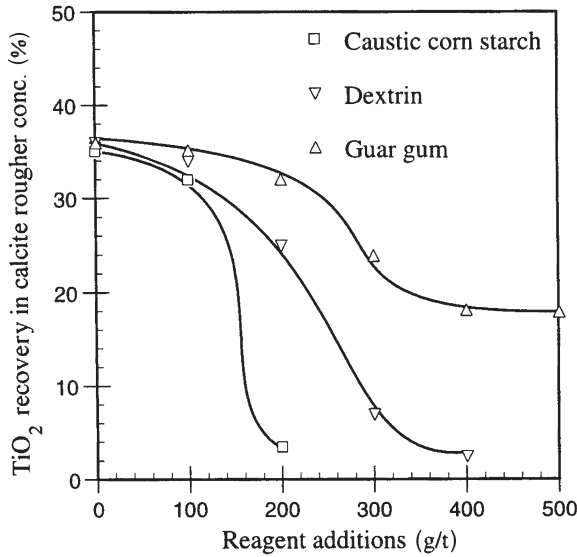
Figure 9.4 Effect of different polymers on perovskite depression during calcite flotation using tall oil fatty acids [10].

of adsorption by chemical interaction and electrostatic adsorption was not supported by experimental work.

Tanin derivatives

The most widely used depressant from this group is quebracho. Its chemical composition and structure is highly complex and contains varieties of polyphenols and tannic acid. The components of quebracho have molecular weights ranging from 200 to 50,000. The relevant importance of each of the molecular-weight groups present in the quebracho structure to its depression action has not been determined, but it is believed that tannin with a molecular weight between 10,000 and 20,000 is responsible for the depression of particular gangue minerals. Quebracho itself also contains a quinic acid derivative in addition to many monomers of polyphenols (C15). A detailed investigation showed that all the fractions representing quebracho accelerate to a common level of acetyl, 39%, and is in agreement with the fact that quebracho has high molecular-weight components.

From the depressing action point of view, these high molecular-weight components play an important role. The application of quebracho (and tanin) in mineral processing is three-fold. It can be used as (a) depressant, (b) dispersant and (c) flocculant. Both quebracho "O" and "S" have been used as specific depressants for calcite, borite and other gangue mineral flotations. Quebracho is used as a depressant in the separation of hematite from calcite, uranium oxide from gangue and manganese oxide from gangue.

It is believed that the depressing action of quebracho is due to the fact that it displaces the collector from the mineral surfaces. In specific cases, calcite depression results from

the adsorption of quebracho into the calcite by the formation of calcite complex Ca^{2+} ions and the OH groups of quebracho catechol/pyrogallol B ring.

Quebracho also acts as a depressant in the separation of sulfide minerals with xanthate. In this case, there is no displacement of the collectors and it is believed that quebracho depresses those minerals onto which the H bond can attach and thus makes them hydrophilic. This is because unlike other sulfide mineral depressants, which are used in highly alkaline pH, quebracho exerts its effects at much lower pH (i.e. 6–8), whereas at high pH it does not show any depressant effect. The effect of quebracho on pyrite depression is shown in Figure 9.5. The depressing effect of quebracho on pyrite occurs in a relatively narrow pH region (i.e. 6–8). The depressing effect of quebracho on sulfides depends largely on the type of quebracho used and the flotation pH.

Quebracho as a dispersant of clay

In alkaline pH, both forms of quebracho (O and S) act very efficiently as dispersants of clay when added to aqueous suspension; one of the earlier applications being the use of quebracho in preparing DAG colloidal graphite. The main industrial application has been the use of quebracho to maintain low viscosity and low thixotropy in the bentenitic clay used in the drilling and paper industry.

In recent studies where quebracho was examined in the flotation of porphyry copper ore containing kaolin and ilite clays, it was shown that quebracho significantly reduced pulp viscosity and increases copper recovery (Table 9.1) [16].

The nature of quebracho's action on clay minerals is not known. The dispersion of clay minerals depends on the particle charge, and to some extent, particle hydration. It is speculated that quebracho polyphenols adsorb onto the clay surfaces resulting in changes in the attraction forces, thus preventing aggregation of the particles.

Figure 9.5 Effect of pH and type of quebracho in the depression of floated pyrite. Quebracho in Mineral Processing, Quebracho Institute 1979, Figure 276.

Table 9.1

Effect of quebracho S and sodium silicate on pulp viscosity and copper recovery
from clay-containing porphyry copper ore [16].

Reagent used	Additions (g/t)	Pulp viscosity (cP) (Brukfield)	Flotation pH	Copper recovery (%)
Quebracho 'S'	0	295	9.0	75
Quebracho 'S'	200	180	9.0	82
Quebracho 'S'	400	160	9.0	89
Quebracho 'S'	600	140	9.0	89
Silicate 'O'	200	260	9.0	76
Silicate 'O'	400	200	9.0	77
Silicate 'O'	600	190	9.0	80

It should be noted that quebracho reacts with oxygen, causing an oxygen deficiency, which is a setback for the use of quebracho in flotation of base-metal ores where oxygen is required for flotation.

Quebracho as a flocculant

Quebracho can also be converted into a highly effective flocculant. By treating quebracho with a primary amine [17], quebracho can be converted into an amphoteric compound having positively charged groups in the molecule. This is achieved by the Mannich reaction, by using formaldehyde to polymerize the reaction product to a molecular weight of 30,000–40,000. The addition of amine results in a reaction at 6–8 position of quebracho resorcinol/phloroglucinol type A ring as per the following reaction:

$$Q - H + NH_2R \xrightarrow{HCHO} Q - CH_2 - NH.R$$
$$Q - H + Q - CH_2 - NH.R \xrightarrow{HCHO} Q - CH_2 - N.R$$
$$\underset{CH_2 - Q}{\overset{1}{|}}$$

The amphoteric quebracho is the most effective flocculant and is attained at the iso-electric point of the molecules, close to neutral.

Other depressants based on quebracho chemistry

Quebracho can react with dextrins in the presence of surfactants. On the basis of such a reaction, Bayer has produced a depressant under the trade name "Agent G4." This was used for many years as a depressant for carbonaceous gangue at the Mount Isa Hilton Concentrator (Australia). This depressant is composed of 55% dextrin, 40% quebracho and 5% surfactant [18]. Agent G4 was also examined as a mixture with inorganic depressant [19] where good depression of (a) pyrite and (b) pre-activated sphalerite is achieved.

A mixture of sodium silicate–sodium phosphate and quebracho in a ratio of 40/40/20 provides good clay dispersant and pyrite depressant at pH >11.0. This mixture is known as the QHS depressant [20].

In all cases, depression of iron sulfides and sphalerite is significantly enhanced by the mixture described above.

9.4.2   Anionic polymers

The representatives of these polymers are listed below:

- Carboxymethyl cellulose
- Carboxyethyl cellulose
- Alginic acids
- Cellulose gums
- Guar gum
- Polyacrylates
- Modified lignin sulfonates

Non-ionic polymers are used for the depression of naturally hydrophobic gangue (talc) and silicates, namely, aluminosilicates, chlorites, etc., and also preactivated quartz.

A typical example of the effect of guar (Acrol F2) on the depression of pre-activated aluminosilicates during flotation of copper–gold ore is illustrated in Figure 9.6 [21].

Carboxymethyl cellulose, cellulose gums and polyacrylates are widely used for the depression of activated silicates with cations.

Studies carried out on talcose mineral depression using CMC [22] showed that the depression of talc with CMC was greatly influenced by the ionic strength and pH of the solution. Talc
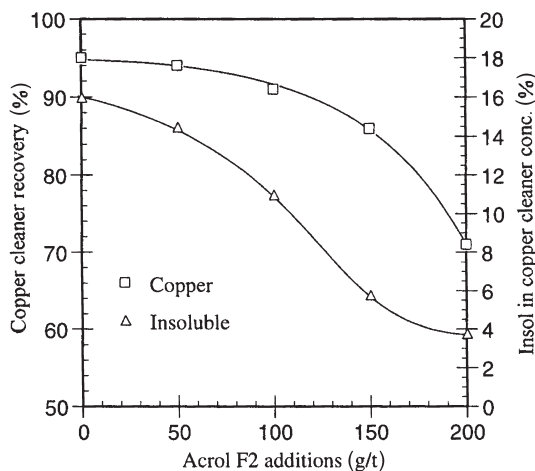
Figure 9.6 Effect of Acrol F2 guar on insol content of the copper concentrate recovery (flotation pH 11.0).

depression improved by either an increased ionic strength of CMC or reduced pH of flotation. The presence of magnesium ions with CMC also improved talc depression considerably.

In another study [23], CMC was investigated as a depressant for activated minerals. These studies have shown that the effectiveness of CMC as a depressant increased when the molecular structure of CMC was altered. Improved depression was achieved when carboxymethyl groups were substituted in clusters rather than distributed evenly along the chain. The use of CMC for floatable gangue depression during sulfide flotation has been widely accepted and CMC is used in many operating plants for depression of talc, activated silicates and magnesium-bearing minerals.

Studies conducted on potash ores containing clay minerals [24] using an aliphatic amine as collector showed substantial improvement in the silvanite recovery in the presence of 500 g/t CMC. It has been postulated that CMC adsorbs on the clay mineral surfaces, thus increasing amount of collector available for adsorption on silvanite.

Cellulose gum and guar gum have been extensively used for the depression of activated gangue during auriferous gold flotation and flotation of platinum group minerals. Particularly, guar gums are effective for depression of aluminosilicates, prophyllite, chlorites and calcite. Because guar gum is normally used as a flocculant for fines, the guar gum used as a dispersant is actually modified. The modification of guar gum for use as a depressant involves two steps: (1) substitution of certain anionic or non-ionic groups in place of some OH groups in the guar gum structure and (2) depolymerization of the guar gum structure by breaking the 1–4 linkage in the structure. Depolymerization [25] usually results in the introduction of anionic COO groups in the guar gum structure. These modified guar gums are successfully used in most PGM operating plants in South Africa, for hydrophobic gangue depression and in flotation of auriferous pyrite [26] from cyanide leaching dumps. It has been shown that when using guar gum, the concentrate grade and recovery improve substantially. Figure 9.7 shows the effect of the level of guar gum on gold-bearing sulfide flotation at pH values of 6.5 and 8.0.
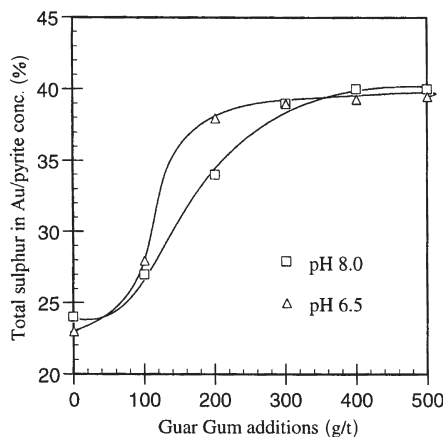
Figure 9.7 Effect of guar gum and pH on auriferous pyrite flotation.

Lignin sulfonate derivatives are used as depressants and dispersants. They are used as depressants in both sulfide and non-metallic flotation. In sulfide flotation, lignin sulfonates are effective only when they are modified with other polymers (e.g. dextrins) in the presence of inorganic compounds [27]. These depressants are commercially used in several operating plants treating lead–zinc ore, primarily for depression of carbonaceous pyrite [28]. Their actions are similar to those of Agent G4, discussed previously. However, very little is known about the mechanics of lignin sulfonate as a depressant in massive sulfide flotation. In non-metallic flotation, a modified lignin sulfonate, with a molecular weight of 20,000–25,000, was used as a depressant for calcite and borite during flotation of bastnaesite [29]. The modification of lignin sulfonate was achieved with surfactant.

From the limited literature available, it appears that the depressing effect of lignin sulfonate on both iron sulfides and non-metallic gangue depends on the degree of type of modification. In the flotation of sulfide ores, modification with dextrin plus inorganic ions gives a component, which effectively depresses iron sulfides, and in particular, carbonaceous pyrite. In non-metallic flotation, lignin sulfonate modified with surfactant is an effective depressant for calcite, barite and celestite.

It should be pointed out that unmodified lignin sulfonate is not an effective depressant.

Lignin sulfonates are also used as dispersing agents. Studies carried out on lignin sulfonate as a dispersant for titanium oxides [30] showed that the adsorption of lignin on rutile increased the stability of suspension. The results also indicated that dispersion power correlated approximately with sulfur content. Strongly anionic lignin sulfonates were also shown to adsorb onto negatively charged polystyrene latex particles and the lignin with the lowest degree of sulfonization gave the highest adsorption [31].

9.4.3   Cationic polymers

Cationic polymers have only recently been introduced in the flotation of sulfide minerals as a depressant for iron sulfides and as a collector adsorption-assisting agent. Diethylene triamine and similar compounds containing the –N–C–C–N– structure have shown good depressing action on pyrrhotite and pyrite. In contrast, amino acid compounds such as f-amino butyric acid [CH_2–$(CH_2)_3$–$COOH$] and β-aminovaleric acid [NH_2–$(CH_2)_4$–$COOH$] are used as collector-promoting agents. There is only limited information on the mechanism of the action of cationic polymers. Some relevant research data, however, is presented in this section.

The studies conducted with amino acids [32] on sulfide and non-sulfide minerals showed that amino acid plays the role of collection-promoting agent in sulfide flotation with xanthate as a collector. Another study [33], also with sulfides (i.e. galena) and oxides (malachite), showed that co-adsorption of xanthate with amino acids takes place at the mineral–water interface. It has been postulated that the mutual interaction among amino acids and xanthate is due to columbic forces, different from those of Van der Waals forces. The galena and oxide copper minerals have shown improved flotability when using xanthate with amino acids than when using xanthate alone in the pH range where amino acids exist as dipolar ions. This pH region is usually between 5 and 7. However, the optimum amount of amino acid must be

added to obtain maximum xanthate adsorption depending on the solution pH, concentration and chain length of co-existing xanthate.

The depressing action of diethylene triamine (DETA) was evaluated in both the laboratory and plant. Several independent studies, using different approaches, have come to different conclusions. Extensive studies by Inco [34] with DETA and EDA have shown several important trends:

- The DETA has a maximum depressing effect on pyrite and pyrrhotite under oxidizing conditions or in the presence of an oxidizing agent. It was also established that pH plays a significant role in the depression action of DETA on both pyrite and pyrrhotite. Figure 9.8 shows the effect of pH on pyrrhotite depression with and without DETA.
- It was suggested that the depressing effect of DETA is associated with chelation with metal ions on the mineral surface. This may not be the case because the cationic compounds at different pH usually change polar groups, which may be responsible for adsorption.

In other studies [35], it has been demonstrated that the effectiveness of cationic polymers largely depends on the presence of sulfoxy compounds in the pulp. For example, using DETA with Na_2SO_3, SO_2 or even Na_2S makes it an effective pyrrhotite and pyrite depressant. The mechanism of pyrrhotite depression with DETA, however, has not been explained as yet in any studies.
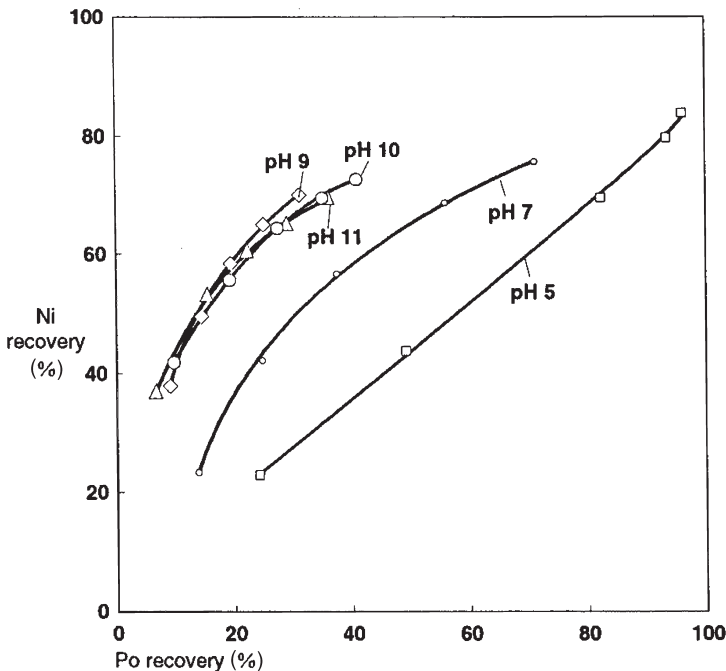
Figure 9.8 Effect of pH on pyrrhotite depression with and without the use of DETA.

9.5   CONCLUDING REMARKS

Although the use of organic polymers in the flotation of polymetallic and non-metallic ores is quite extensive with only limited numbers of polymers being used, their action and adsorption mechanism is very complex and so far it is only postulation.

The mode of starch adsorption at a solid–solution interface was studied by a number of researchers [36–38]. It has been indicated that the adsorption of starch on oxides (hematite) and silicates (quartz) is dependent on pH, where adsorption decreases with an increase in the pH, as shown in Figure 9.9.

The conclusion of this work was that starch is more strongly adsorbed on electronegative hematite than quartz. The interaction of the starch and hematite–quartz system was considered to be chemical in nature. The chemical nature of the adsorption of dextrin was also postulated in research with sulfide and in the separation of sphalerite from galena. It is, however, known that all operating plants that use dextrin in separation of galena–chalcopyrite require the use of sulfur oxide as a co-depressant or the agent that governs adsorption of dextrin on galena surfaces.

If this is the case, according to the earlier discussion, the adsorption of starches and dextrin is governed by electrostatic forces through intermediate ions with opposite charges.

In the case of many anionic, non-ionic polymers, the adsorption of polymers on mineral surfaces decreases with an increase in pH. In contrast, in the case of cationic polymers, the adsorption increases with an increase in pH. This indicates that a number of adsorption mechanisms are involved.

It should be pointed out that the chemistry of polymeric depressants plays a decisive role in their depressing action on both sulfide and non-sulfide minerals. For example, the chemistry of dextrin, starches and their derivatives also determines whether these compounds can
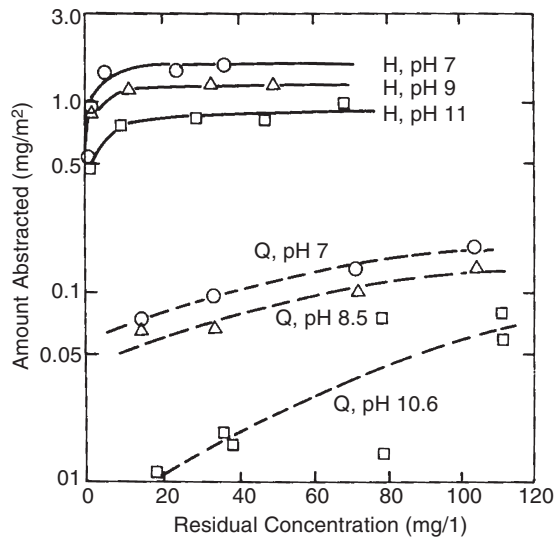
Figure 9.9 Adsorption of corn starch on hematite (H) and quartz (Q) as a function of pH [39].

be used as flocculants, dispersants or depressants. Starches and dextrins used in selective flocculation have different chemical compositions and molecular weights from those used as depressants for either sulfides or non-sulfides.

Guar gums that are used commercially as flocculants, dispersants and depressants have modified structures to serve these purposes.

The adsorption mechanism of these polymers is explained in the same way as for collectors. However, the polymer behavior in solution, discussed earlier, cannot support such a theory.

REFERENCES

1. Fleer, G.J., and Scheutjens, J.M.H., Insoluble Mondayers at Liquid Gas Interface, *Advances in Colloid Interface Science*, No. 36, p. 341, 1882.
2. DeGennes, P.G., *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca, NY, 1979.
3. DeGennes, P.G., *Macromolecules*, Vol. 14, 1937; *Comptes Rendus Academy of Science Paris*, Vol. 11, p. 294, 1982.
4. Fuerstenau, D.W., *Froth Flotation*, 50th Anniversary Volume, AIMME, New York, p. 59, 1962.
5. Kitchener, J.A., and Pugh, R.J., Colloid Chemistry in mineral Processing, *Colloidal Interface Science*, No. 35, p. 656, 1971.
6. Lee, L.T., and Somasundran, P., Polymer–Surfactant Interaction in Flotation of Quartz, 111th AIME Meeting, February 1982.
7. Dudenkov, C.B., and Mitrofanov, C.I., *Theory and Practice in the Use of Chemical Reagents*, Izd, Nedra, Moscow, 1969.
8. Iwasaki, I., and Choi, H., Use of Starches and Starch Derivatives as Depressants and Flocculants in Iron Ore Beneficiation, *Transactions of AIME*, Vol. 244, March 1969.
9. Verwey, E.J.W., *The Role of Electric Double Layer in the Behavior of Lyophobic Colloids*, Physical Chemistry of Surface Film, New York, 1952.
10. Bulatovic, S.M., and Wyslouzil, D.M., *Process Development for Treatment of Ilmenite, Perovskite and Rutile Ore*, Unpublished paper, 1999.
11. Hanna, H.S., Adsorption of Some Starches on Particles of Spar Minerals, In (A. Bishay ed) *Recent Advances in Science and Technology Minerals*, Vol. 1, p. 365, 1973.
12. Liu, Q.I., and Laskowski, J., The Role of Metal Hydroxides on Mineral Surfaces in Dextrin Adsorption Studies of Modified Quartz Samples, *International Journal of Mineral Processing*, No. 26, pp. 33–37, 1989.
13. Bulatovic, S.M., Use of Organic Polymers in the Flotation of Polymetallic Ores – A Review, *International Journal of Mineral Processing*, No. 46, pp. 69–72, 1999.
14. Grano, S.R., and Prod, U., Treatment of Naturally Hydrophobic Minerals at the Copper Concentrator of Mt. Isa Mines Ltd., *Forth Mill Operators Conference*, Burnie, Tasmania, South Africa, March 1991.
15. Parsonage, P., Depressant Junction of Calcite, Dolomite and Apatite Reagents in the Mineral Industry, In (M.J. Jones and R. Oblatt eds) *IMM*, Annual Conference of Metallurgist, Denver, Colorado, September 1984.
16. Bulatovic, S.M., *Flotation of Clay-Containing Copper/Molybdenum Ores*, R&D Report of Investigation, LR019, March 1988.
17. White, R., Watkins, M.C., Knowles, B., and Hastings, C., British Patent 899721, March 1962.
18. Bulatovic, S.M., Private communication, June 1982.
19. Bulatovic, S.M., and Bigg, A.C.T., *An Investigation of the Recovery of Copper and Zinc from Kutcho Creek Orebody*, Report of Investigation LR3215, Canada, 1986.

20. Bulatovic, S.M., and Jessup, T., *Effect of Depressant QHS on Pyrrhotite/Pyrite Depression at St. Martin Concentrator (Mexico)*, Report of Investigation LR4251, 1996.

21. Bulatovic, S.M., *An Investigation of the Recovery of Copper and Gold from Batu Hijau (Indonesia) Ore Samples*, Report of Investigation LR4440, 1995.

22. Rho, M.K., The Effect of Physical Variables of Carboxymethyl Cellulose Reagents on the Depression of Magnesia-Bearing Minerals in Western Australia Nickel Sulphide Ore, *13th International Mineral Processing Congress*, Warsaw, pp. 346–366, 1981.

23. Mashanyare, A.E., *The Problem of Talc and Other Gangue Minerals in the Flotation of Nickel and Copper Sulphides*, Masters Thesis, University of Zimbabwe, Harare, 1982.

24. Arsentev, V.A., and Gorlovskii, C.I., *Organic Modifiers for Flotation of Clay Containing Ores*, Tsvetnie Metaly, No. 6, p. 9, 1977.

25. Appleton, A.E., *Flocculation of Aqueous Quartz Suspension with Natural and Cationic Polymers in the Presence of Co(II), Ca(II) and Fe(III)*, CSIRO Special Report, CFENG004, 1982.

26. Technical Bulletin No. 2, *Acrol Gangue Depressants in Base Metal Sulphide and Oxide Flotation*, Johannesburg, South Africa, 1986.

27. Bulatovic, S.M., *Development and Application of Depressant DS26 for Depression of Carbonaceous Pyrite during Flotation of Lead/Zinc from Tara Ore (Ireland)*, Report of Investigation LR3218, 1981.

28. Bulatovic, S.M., Some Aspects of Recent Improvement in Treatment and Separation of Refractory Polymetallic Ore, *SME Annual Meeting*, February 1990.

29. Bulatovic, S.M., *Evaluation of Modified Polymers for Depression of Calcite and Barite during Flotation of Bastnaesite from Mountain Pass Ore*, Report of Investigation, LR4852.

30. Rezanowich, J.E., et al., *Pulp & Paper Magazine*, No. 62, Canada, January 1961.

31. Sadowski, A., *Mineral Metal Processing*, Canada, p. 217, 1985.

32. Takahashi, K., and Wakamatsu, T., The Role of Amino Acids on the Xanthate Adsorption at the Water/Mineral Interface, *International Journal of Mineral Processing*, Vol. 12, No. 1–3, pp. 125–132, 1984.

33. Mukai, S., and Wakamatsu, T., Copper Silicate Mineral Flotation by Activation with Organic Copper Avid Reagent, *Prospectors 11th International Mineral Process Congress*, p. 671, Calgary, 1975.

34. Maricovena, A.M., and Eggar, R., Inco Develops a New Pyrrhotite Depressant, In (T. Yalcin ed) *Innovation in Mineral Processing*, Sudbury, Canada, pp. 330–335, 1994.

35. Booth, R.B., Depression of Gangue During Flotation, US Patent 2,211,686, 1940.

36. Haung, H., and Todo, N., Adsorption Reactions in the Depression of Coal by Organic Colloids, *Recent Developments in Separation Science*, CRC Press, U.S.A, 1978.

37. Lim, S.K., Crosslinked Starches as Depressants in Mineral Ore Flotation, US Patent 4,339,331, U.S.A, 1982.

38. Balajee, S.R., and Iwasaki, T., Adsorption Mechanism of Starches in Flotation and Flocculation of Iron Ores, *Transactions of AIME*, U.S.A, Vol. 244, pp. 126–135, 1973.

39. Bulatovic S.M., and Wyslouzil, D.M., *Selection of Reagent Scheme to Treat Massive Sulphide Complex Ores*, In (R. Zunkel ed) CIM, Montreal, Canada, 1985.

– 10 –

Action of Flotation Frothers

10.1   INTRODUCTION

Froth information is usually described as one of the most important aspects in flotation and also in other industrial fields. The investigation of frothing properties and its physico-chemical characteristics dates back to 1920.

The presence of a frothing agent, either as a neutral frother or in multiple functions as both collector and frother, is vital to every flotation process. In addition to the formation of froth, a frother has a significant effect on the increase in air dispersion in the flotation machine, reduction in coalescence of individual bubbles in the pulp and decrease in the rate at which the bubbles rise to the surface. Frothers increase the strength of the bubbles and the stability of the froth that is formed as a result of the rise of mineralized air bubbles to the surface of the pulp.

The frothing ability of their aqueous solution is believed to be connected with a decrease in the surface tension and froth studies were therefore associated with measuring the surface tension and the foam volume or stability. In fact, it should be remembered that the best foaming agents are not necessarily the best flotation frothers and the importance of the interaction of frothers and collectors in particle bubble attachment cannot be neglected.

In general, the flotation selectivity of surface-active frothers is not high, which makes frother selection in flotation practice quite difficult, especially when a fairly large number of factors influence the action of frother and froth stability in general. From a practical point of view, the requirements for optimum frother selection can be summarized as follows:

*   The froth structure in the froth zone must be such that it allows free flow of mineralized bubbles and must not produce "dry" froth, which is difficult to remove, even with the aid of froth pedals. The froth must not be persistent in the upgrading stages. Perhaps the best frother for this particular ore is that which retains the same structure from roughing to final cleaning operation.
*   The frother must be sufficiently selective. Similar to collectors, frothers can pass a certain degree of selectivity and the selectivity of the frother can be measured by the degree of entrainment of the gangue particles.
*   In general, the frother determines the rate of flotation in almost every flotation system and the selection of the frother must always be tied with flotation kinetics.

- Froth breakage is an important requirement. However, froth breakage characteristics are also associated with fineness of grind, presence of fines and most of all, the presence of clay minerals. In these cases, there is a trade between froth breakage and good frothing properties.
- The important requirement of low sensitivity of the frother to changes in pH and ionic composition of the pulp is the most difficult to fulfill. In spite of the fact that there is a large group of frothers, discussed in Chapter 4, used over a wide pH region, the froth structure and foaming characteristics change dramatically with changes in pH. In many flotation systems, the pH is changed from one unit operation to another (i.e. roughing–cleaning) and with the pH change, frothing also changes.
- The frother also must have low sensitivity to particular modifiers. It is often the case that in the presence of specific modifiers (e.g. depressant, regulator, etc.), the frothing properties of a specific frother changes significantly. Therefore, it should be remembered there is a synergy between frothing properties in the presence of modifiers.

10.2   THEORY OF THE ACTION OF FROTHERS

Over the past several decades, extensive research has been carried out on frothers and free liquid films [1–4]. Some of the conclusions drawn from these studies were that pure liquids do not froth and the presence of surface-active agents is required to induce frothing. When the surface agent is added to the liquid, the surface tension of the solution decreases as a result of the heteropolar nature of the molecules, which leads to preferential adsorption of these molecules at the air–water interface. These molecules are arranged in such a way that the hydrophilic polar group is oriented in the water phase and the hydrophobic (non-polar) hydrocarbon chain in the air phase. The adsorption of the surface-active agent at the interface is related to the decrease in surface tension and can be described by the Gibbs adsorption reaction (10.1):

$$\Gamma = \frac{-a}{RT} \frac{d\rho}{d\alpha} \qquad (10.1)$$

where Γ is the surface excess concentration of the surface-active agent, ρ the surface tension and α the activity of solute.

In the case of dilute solution, which is normally employed in flotation, the activity can be replaced by the concentration of the surface-active agent. In this case, the surface tension of a solution is an indication of the surface activity of the solutes.

The dynamic froth is a complex physico-chemical system, which cannot be explained by one theory suitable for all types of froths under different conditions. The actual properties of froths depend on a fairly large number of variables. There is no sharp transition from a weakly frothing solution to a strongly frothing one, or between an unstable or persistent froth. The extreme types, however, can be visually distinguished as unstable or transient and persistent froths. It should be noted that in some cases, the froth tends to collapse. This occurs when the froth acquires a higher surface energy than the segregated gas and liquid where the froth tends to collapse spontaneously.

A typical unstable froth breaks down as the liquid drains between bubbles. In such a case, the bubbles remain spherical but collapse when they touch. The surface force, which opposes coalescence in these froths, is too weak to stop coalescence but reduces it to some extent.

It is believed that in the case of metastable froths, the drainage of the liquid from between bubbles may occur to some extent, which becomes almost planar lamellas of uniform thickness. Without vibration, evaporation or other disturbances, these films can last indefinitely. In the case of this type of froth, there is a slow diffusion of gas from the smaller bubbles into larger ones as a result of pressure differences. The rate of diffusion is inversely proportional to the radius of the bubble and may cause the froth to break down.

In experimental work [5,6] another explanation for froth stability has been proposed, i.e. that the positive value of disjoining pressure inhibits the thinning of the lamellae. According to the Gibbs theory [7], during stretching of foam lamellae a local rise in surface tension occurs in thin layers as a result of surfactant depletion by adsorption into the stretched portion producing a change in surface elasticity. Gibbs defined the coefficient of static surface elasticity E as the stress divided by strain per unit area. For an area A of a two-face lamella, when the surface tension rises to $y + dy$ the thickness of the lamellae decreases to $h - dh$, where the surface elasticity is given as:

$$E = \frac{2dj}{dA/A} = \frac{2dj}{d \ln A} = \frac{2dj}{\ln h}$$

(10.2)

If a thin film of a solution of a surface-active agent is subjected to local thinning, the surface tension of that part increases because any increase in surface area of the thin film lends to a decrease of solute molecule concentration in the film and, consequently, to a rise in equilibrium surface tension. This theory, however, applies only to a static system and specifically to thin lamellae, where there are insufficient surface-active molecules in the body of the film to diffuse to the surface and lower the surface tension again.

Under dynamic conditions, the surface tension in a froth film is higher during extension [8] and lower during compression than the equilibrium value. This is known as the Marangony effect and operates on an expanding or contracting surface carrying an adsorbed layer, irrespective of the thickness of the underlying liquid and provides a restoring force that tends to protect the film against local thinning. Marangony [9] in fact explained the foam stability as due to the ability of a frothing solution to withstand a variation in its surface tension within 0.1–0.001 s. There is no clear-cut technique to measure magnitude of the Marangony effect and the theoretical treatment is still incomplete.

In a dilute solution, there is a lag in attainment of local surface tension equilibrium, which mainly arises from the time required for the surface-active molecules to diffuse from the interior of the liquid into the newly formed surface or, conversely, the diffusion away from the compressed surface. The other factors that may affect the rate at which the solute arrives at the surface are the convective transport of surface-active molecules, possible electrical repulsion or stearic hindrance to the entrance of large molecules into an already packed monolayer.

The surface transport theory, proposed by Ewers and Sutherland [10] was regarded as an extension of the Marangony theory with the only difference being the specification of the mechanism for the movement of solution once the gradient of the surface tension leads first to a surface flow, which in turn may cause the adjoining liquid layers to move into the thinned section. This does not imply any special viscosity of the film or adjoining water layer and arises solely from the viscous drag of the contracting monolayer.

The rate at which the surface-active molecules arrive at the interface is critical and the time for which the surface elasticity must come into play has been shown to be in the region of 10^{-1}–10^{-3} s. This effect accounts for the fact that optimum concentration for maximum frothing is usually found.

Another important factor, which was shown to affect the stability of the froth, is the viscosity or plasticity of the adsorbed layer to surface-active minerals. Some researchers [11] differentiate the following three types of froth stability:

1.   Transient foams form in concentrations for which the initial black-film formation occurs – the values of the critical thickness.
2.   Highly persistent froth is obtained from solutions of higher concentrations whose rupture is assumed to be due to surface fluctuation (under mechanical stimuli).
3.   Froths of intermediate stability form when the frother concentration is of low value with a sharp transition region from low to high stability; both the process of thinning and black-spot formation play a part in these froths.

10.3   THE MECHANISM OF FROTHER ACTION

Apart from the ability of frothers to form froth, they have other important roles including:

• Creating finer bubbles, whereby the dispersion of air in the flotation cell also improves.
• Reducing coalescence of individual air bubbles.
• Reducing the rate of bubble rise from the mixing zone to the froth zone.
• Increasing the strength of the bubbles and stability of froth.

These effects are discussed in the following section.

10.3.1   Frother and dispersion of bubbles in the flotation pulp

It has been established by experimental work that the size of bubbles in the flotation mechanism in the presence of frothing agents can decrease significantly [12]. This may result from two interrelated actions: (a) improvement in air dispersion and (b) deterioration in the coalescence of air bubbles in the pulp. Both actions affect froth formation and bubble transport to the froth zone. Even in the absence of surface-active agents on the bubble surface, the coalescence of bubbles takes place instantaneously. In the presence of a frother, however, the coalescence of bubbles occurs at a much shorter distance than in the absence of frother. Molecules of the frother usually adsorb on air bubbles, thus increasing the stability

of the hydrated layer surrounding the bubble. The hydrophilic groups of adsorbed frothers are directed to the liquid phase and actively interact with molecules of water. This in fact leads to an increase in the mechanical strength of the envelope surrounding the bubbles and prevents destruction or collision with other bubbles.

It is believed that the concentration of froth in the pulp determines the coalescence of air bubbles [13], where higher concentration increases coalescence. It has been determined that a frother may prevent coalescence only when the air bubbles do not differ appreciably in their size. The coalescence of bubbles possessing large differences in diameter is highly pronounced.

10.3.2   Frother and rate of rise of bubbles in the pulp

Experimental work carried out by Frumkin *et al.* [14] demonstrated that molecules of surface-active agents, which adsorb on the surface of bubbles, are shifted to the bottom portion of the air bubble during their upward movement in the liquid or pulp. This results in lowering the surface tension in this region, creating difference in the surface tension between the upper and lower region of the bubble. Along the surface of the air bubble, a force is created which attempts to equalize the surface tension to prevent further shifting of frother molecules to the lower portion of the bubble. These forces hinder the motion of the molecules on the surface of the air bubbles, thus lowering the mobility of bubbles. This decrease in mobility makes the bubbles behave like solid spheres. The decrease in the velocity of the air bubble due to the surface-active agent is pronounced. The increased coverage of the lower surface of the bubble is proportional to the amount of frother concentration in the pulp. It also depends on the size of the air bubbles, increasing significantly for larger bubbles.

10.4.   TWO-PHASE FROTHS

In reality, froth systems are thermodynamically unstable, because of the presence of a fairly large amount of free energy. Therefore, most of the processes that occur in the froth are directed toward froth breakage. It is considered that a stable system can only be accomplished in the case of complete separation of the system into two phases (i.e. liquid and gas). Some researchers [15] consider that froth stability cannot be studied from the point of view of thermodynamic potential. The correct analyses of froth stability must be based on kinetics of the process itself. The kinetics of froth destruction, according to Talmud and Bresler [16] occurs as follows. At the moment of froth formation, the air bubbles are separated by a thick film of liquid. The thickness of this liquid film is in the order of 1 μm. The film is bonded on both sides by solvated envelopes possessing properties different from those of the intermediate water layer from which the water drains at the bottom of the froth. The froth is trimmed to such a degree that the boundary-hydrated layers are brought into contact with each other. The second stage involves removal of liquid in the two contacting boundary layers. The thinned film becomes thermodynamically unstable and very wet. Any external action may spontaneously disrupt such a film, leading to coalescence of the adjacent bubbles in the froth.

The drainage of water from froth occurs in the initial minutes in the case of unstable froth. The water is drained under the influence of gravity, although other factors (e.g. pressure and difference in capillary pressure) are also important. The thickness of the solvated water envelopes also strongly affects the drainage of water. The greater the hydration of the capillaries, the more slowly the water drains.

The drainage of liquid from planar boundaries in a fine bubble froth is low. This is due to the fact that a small air bubble in the froth has more uniform surface curvature and, consequently, the difference in local film pressure is smaller. Very small bubbles remain spherical and the froth retains a lot of water, even with the densest packing. According to this, for a froth to have maximum stability, there has to be optimum size of air bubbles.

Frothers play the role of stabilizing the film around the bubbles. Some researchers [16] classify all reagents stabilizing water envelopes in the froth into the following groups:

- Substances soluble in water, which form the molecular solution. Such substances are low- and medium-chain-length alcohols.
- Surface-active agents forming colloidal or polycolloidal solution in water. When concentrated in the adsorbed layer, these substances form special gel-like structures, which approximate solid bodies.
- Surface-active substances, which are practically insoluble in water.

It is believed that the formation of a reagent film around air bubbles plays an important role in the prevention of film thinning due to its higher mechanical strength. The first group of reagents does not exhibit beneficial mechanical properties. The reagents of the second group, which tend to concentrate in the adsorbed layer, impart higher mechanical strength. The reagents of the third group act differently on films and their action depends on their structure and the presence of other reagents.

In the case of the two-phase froth, for maximum stability the adsorbed layers must be mechanically strong and of sufficient mobility to re-establish the initial concentration in the stretched portion of the film. It should be noted that most of the frothers used in the practice of flotation belong to the first group. Their stabilizing effect on froth is explained as follows.

The heteropolar frother molecules orient themselves in the adsorbed layer with their polar groups directed toward the liquid phase. The polar group undergoes strong hydration and forms a base of thick hydrated layer on the water surface. Hydration of the polar group is affected by the composition of water and distance of frother molecules. The hydrated layer of uniformly oriented molecules exhibits strong resistance to destruction. The hydrated layer of the surface films in the froth plays an important role, not only in the attachment of mineral particles to bubble, but also in determining the stability of the froth.

There is an optimum concentration of frother at which the most stable froth is obtained. Excess of frother from the first group leads to a decrease in froth stability and may even suppress the froth completely. This is explained by the fact that high frother concentration strongly decreases the surface tension of the solution; thus the conditions for the formation of a sufficiently stable hydrated layer deteriorates.

Frothers of the second group, which forms polycolloidal and colloidal solutions such as soaps and saponines, have a different effect on froth stability with increased concentration. In excess, they do not reduce froth stability as much as the frothers from the first group due to the formation of colloidal film with a much higher mechanical strength. These froths are usually very persistent and difficult to break.

For each heteropolar surface-active agent, the optimum conditions for the stability of hydrated layers occur at a definite concentration of electrolyte and depend on the valence of the electrolyte cations. It has been suggested that a combination of several surface-active agents is quite effective in controlling and regulating froth properties. The stability of the two-phase froth also depends on the characteristic size of the air bubbles. It has been confirmed that the stability of the froth is decreased if the adjoining bubbles differ in size. This is due to a large difference in their capillary pressure.

10.5   THREE-PHASE FROTHS

The basic principle established for the two-phase froth is applicable to the three-phase froth. However, the presence of solids in the froth greatly alters its characteristics. The presence of solids in the froth may improve the stability of the froth or may have a negative effect. In the most general terms [17], the effect of solid particles on froth can be described as follows:

- In the presence of solid particles, the stability of the flotation froth and the strength of the bonding between the bubbles sharply increase, especially with the increased tendency of attachment of mineral particles to the air bubbles.
- There is an optimum particle size, which acts as a froth stabilizer. Very large particles and very fine slimes show smaller effects than particles of intermediate size. Certain clay slimes may even have a destabilizing effect on froth.
- The shape of mineral particles plays an important role in increasing froth stability. Lamellar particles in general yield the most stable profile.
- When frothers and flotation regulating agents do not alter the attachment of the mineral particles to air bubbles, they affect the stability of the three-phase froth in the same way as they affect the two-phase froth. The exception is if these chemicals change the tendency of attachment of mineral particles in the froth considerably, they have a decisive effect on froth stability.

In some instances, very unstable or flat froths are also obtained in the presence of solids. Some researchers [18] have found that well-dispersed hydrophobic particles can break froths, presumably by accelerating the coalescence of bubbles in the pulp as well as in the froth. They suggested that fine hydrophobic particles, which form by the reaction of the collector with metal ions in solution, destabilize the froth. These very small particles (i.e. 0.2–0.5 μm) with a contact angle greater than 90° rupture the thin film between the bubbles. The conditions of attachment of bigger hydrophobic particles to the surface of the

bubbles floating in the pulp and to air bubbles residing in the froth are never identical, and are dependent on the following factors:

- Coalescence of bubbles in the froth, which leads to a sharp decrease in their surface, may result in a high degree of mineralization. The surface of the bubble may be completely covered by mineral particles.
- The time of contact between particles and bubbles in the froth is estimated to be 10–50 times greater than that between particles and bubbles in the pulp, which increases the possibility of firm attachment of particles with bubbles, thus eliminating hysteresis of contact angle.
- Forces tending to dislodge the mineral particles from bubbles are mainly forces of gravity. It is believed that the separation of mineral particles from air bubbles takes place mainly during coalescence of the bubbles. Therefore, conditions in the froth are more favorable than those in the pulp, for support of hydrophobic particles by air bubbles.

According to Gibb's theory of froth distraction, the presence of mineral particles strongly affects the kinetics of froth collapse. The drainage of water from mineralized froth is hindered as a result of constrictions in the passages, caused by increase in the roughness of bubble walls and the bridges of gangue particles not attached to air bubbles. Thinning of the water film is limited to the distance determined by contacting mineral particles.

The flocculation of particles in the froth layer can greatly increase froth stability according to the work of Kehbinder and Lubman [19]. Likewise, the attached mineral particles in the froth increase the structural mechanical properties of the liquid film in the froth. As a result of this, a very stable froth can be produced. In actual practice, however, a flocculated froth is less selective and is often difficult to remove.

The relationship between particle size and froth stabilization was extensively studied [20,21] using high-speed photography. It has been demonstrated that the position of particles in the interface is dependent on the contact angle. With a contact angle of 74°, as soon as the particle touches the lower interface, the equilibrium contact angle at the lower end of the particle is established without disrupting the film. As the film thins further, the particle moves away from its thinnest section, and the film finally breaks when it reaches its natural rupture thickness. With a higher contact angle (i.e. $\theta = 102°$), the particle ruptures the film within milliseconds of contacting the lower interface. The larger particles, if they have a high enough contact angle, will destabilize the froth. For example, galena particles at a contact angle of 90° can destabilize froth. This is attributed to the cleavage characteristics of galena, which forms very smooth, regular particles along whose surfaces the movement of the three-phase boundary can occur with a very low driving force.

The thickness of the individual films in a froth that are ruptured by these types of particles can be related to the hydrophobicity, size and shape of the particles since these factors govern the degree of penetration of the particles in the film. Therefore, for constant particle hydrophobicity and shape, the rate of the film rupture and, consequently, the froth stability can be related to the size and number of particles present in the froth.

If the rate of thinning of froth film is governed by the equation

$$\delta^2 = \frac{4\eta z}{\rho g t}$$

<div align="right">(10.3)</div>

Where ϑ = density, δ = film thickness at distance z, t = time the film became parabolic, η = viscosity of solution.

Table 10.1 shows that for hydrophobic quartz particles (θ = 102°), the relationship holds for particles diameters 400–5 µm. Below 5 µm, the efficiency of the hydrophobic particles decreases owing to visible flocculation of fine particles. This means that very hydrophobic particles of all sizes can destroy froth and unless the surface of the particles is modified by the frother, the destabilizing effect is almost independent of the frother used.

In contrast, stabilization of the froth film requires more than one particle, so the stabilization of the film with particles of low hydrophobicity occurs only when a close-packed monolayer of particles is formed in the froth.

Therefore, the types, conditions and size of particles in the flotation system can have a significant effect on the stability of the froth, and in many systems the froth stability may be controlled more easily by modifying hydrophobicity or the degree of froth flocculation

Table 10.1

Destablization of froth with hydrophobic quartz particlesas a function of particle size [21]

Average particle size α (µm)	Mass required[a] (mg)	Number of particles (χ)	$\alpha^2\chi \times 100$
1.5	0.63	96,500,000	217.0
3.0	0.26	4,980,000	45.0
5.0	0.16	662,000	16.5
7.0	0.14	211,000	10.3
9.0	0.15	106,000	8.6
12.5	0.21	55,600	8.7
20.0	0.48	31,000	12.4
31.0	0.73	12,700	12.2
48.5	0.91	4,120	9.7
81.0	1.45	1,410	9.3
115.0	2.15	731	9.7
163.0	3.23	385	10.2
230.0	4.60	195	10.0
326.0	6.20	92	10.0
388.0	8.80	78	12.0
460.0	13.80	73	16.0
544.0	18.80	60	18.0

[a]Mass of hydrophobic quartz required to reduce intermediate froth volume to 1.0 cm^3.

of the particles, rather than by changing the type of frother. The exception is when clay is present in the ore, in which case, the type of frother plays an important role.

10.6   ACTION OF FROTHERS IN THE PRESENCE OF COLLECTOR

The association of frothers and collectors has been proven to strongly influence some flotation parameters while leaving the others unaffected. The following examples illustrate these effects:

- As long as the frother molecules form a gaseous type of monolayer at the air–water interface, the magnitude of the contact angle established by the adsorbed collector is unaffected. However, when the frother molecules tend to form a condensed film, the contact angle can be altered.
- The increase and decrease in the adsorption of the collector at the solid–liquid interface may or may not take place, depending on the relative proportion of the frother and collector and their relative extent of interaction at the interfaces and in the bulk of the solution.
- There is an indication that the zeta potential of a solid in both xanthate and amine systems undergoes a change on adsorption of frother molecules.
- In a number of cases, the increase in the level of addition of frother results in an increase in recovery. This is common when treating a slimy ore, and ores that contain clay minerals.

REFERENCES

1. Sutherland, K.L., and Wark, I.W., *Principles of Flotation*, Australian Institute of Mining and Metallurgy, Melbourne, 1955.
2. De Vries, A.J., *Foam Stability, Rubber Stitching*, Delf, New York, 1957.
3. Harris, P.J., Frothing Phenomena and Frothers, In (R.P. King ed) *Principles of Flotation*, South African IMM, pp. 237–263, 1982.
4. Kitchener, J.A., and Cooper, C.F., Current Concepts in the Theory of Foaming, *Quarterly Review*, London, No. 13, pp. 71–79, 1959.
5. Derjaguin, B.V., The Elastic Properties of Froth, *Journal of Physical Chemistry*, No. 6, pp. 11–16, 1931.
6. Eigels, M.A., and Mocronsov, V.A., A Method in Destroying Mineralized Froth, In *Rationalization of Processes and Mechanisms in Mineral Dressing*, BTI Mintsvetmet, 1948.
7. Mysel, J., *Soap Films – Studies of their Thinning*, Pergamon Press, London, 1959.
8. Derjaguin, B.V., and Titijevskaya, A.S., Static and Dynamic Stability of Free Films and Froths, *Proceedings of the 2nd International Congress of Surface Activity*, London, Vol. 11, pp. 211–219, 1957.
9. Sutherland, K.L., The Change of Surface and Interfacial Tensions of Solution with Time, *Reviews of Pure and Applied Chemistry*, Australia, pp. 35–50, 1951.
10. Ewers, W.E., and Sutherland, K.L., The Role of Surface Transport in the Stability and Breakdown of Foams, *Australian Journal of Science Research*, Vol. A5, pp. 697–710, 1952.

11. Miles, G.D., Ross, J., and Shedlosky, L., Foam Drainage, *Journal of Physical Chemistry*, Moscow, No. 40, pp. 93–107, 1945.

12. Klassen, V.I., *Problem in the Theory of Aeration and Flotation*, Goskhimisdat, Moscow, 1949.

13. Frumkin, A.N., and Levich, V.G., The Effect of Surface Active Agents on Motion at the Boundary of the Liquid Medium, *Journal of Physical Chemistry*, Moscow, No. 21, 1947.

14. Bogdanov, O.S., and Barskii, L.A., Effect of Frother on the Content of Air in a Flotation Pulp, *Bulletin of the Academy of Science*, USSR, No. 3, 1959.

15. Rehbinder, P.A., *The Problems of Emulsions and Froths in the Food Industry, Colloids in the Food Industry*, Pishchepromizdat, Moscow, 1950.

16. Shkodin, A.M., and Tikhomivova, G.P., Frothing in Mixtures of Surface-Active Colloids, *Colloid Journal*, Moscow, No. 13, 1951.

17. Livshitz, A.K., and Dudenkov, S.V., Some Factors in Flotation Froth Stability, *Proceedings of the 7th International Mineral Processing* Congress, p. 367, New York, 1965.

18. Klassen, V.I., and Mucrousov, V.A., *An Introduction to the Theory of Flotation*, Butterworths, London, 1963.

19. Dudenkov, S.V., and Shafeev, E.S., Effect of Structure of Frothing Agent Molecules on the Coalescence of Air Bubbles, *Tsvetnie Metally*, No. 39, pp. 12–15, 1966.

20. Hansen, D.M., Diagnosis of Froth and Emulsion Problems in Flotation and Froth Extraction Units, *Canadian Metallurgical Quarterly*, No. 13, pp. 659–668, 1974.

21. Dippenar, A., *The Effect of Particles on the Stability of Flotation Froths*, Report No. 1988, National Institute for Metallurgy, Johannesburg, 1978.

– 11 –

Dispersion, Coagulation and Flocculation

11.1   INTRODUCTION

Dispersion, selective coagulation and flocculation are the major accessories of the mineral engineering field. The organic and inorganic chemicals used in these functions belong to a group of modifiers. A number of chemicals used as dispersants are also used as depressants and activators. The organic polymers used as depressants are also used as flocculants, when their chemical structure is altered. In a number of applications, dispersants and flocculants are used together where selective flocculation is required.

The dispersing modifiers are used to prevent fine particle from aggregating, and in many cases, to reduce pulp viscosity. Aggregation or the slime coating phenomenon is common where slimes are present in the pulp, and has a negative effect on flotation. Dispersion is also used in various hydrometallurgical processes as well as in selective flocculation where gangue minerals are dispersed while valuable minerals are flocculated.

The action of dispersing agents in mineral processing is therefore to (a) improve flotability of the mineral by preventing slime coating on the mineral particles and (b) disperse fines or gangue minerals during selective flocculation.

The flocculation process is opposite to dispersion. In a dispersed system, particles of all species can be aggregated into larger structures by several mechanisms. Aggregation, based on reducing inter-particle repulsion forces, is known as coagulation and the aggregates are called coagula. If coagulation is induced by a polymer-bridging action, the process is called flocculation and the aggregates are called flocs. When aggregation is achieved as a result of the action of an immersible bridging liquid, such as oil, the process is called agglomeration and the aggregates are referred to as agglomerates. The mechanisms include both those in coagulation (i.e. action of electrolytes) and bridging flocculation by either inorganic polymers or by precipitating metal hydroxides. The latter is known as sweep flocculation [1].

The flocculation process using polymers is usually classified according to the action of polymers on the particles. If the polymer adsorbs on several particles simultaneously resulting in formation of molecular bridges between the adjoining particles in the floc, it is called bridging flocculation. In the case where polymer molecules are branched, or as an alternative if two or more types of interacting polymer molecules of a linear type are used so that there is a three-dimensional gel-type network enmeshing the particles into a floc, the gel flocculating process is termed network flocculation. Under carefully controlled polymer

additions as well as hydrodynamic conditions, a compact strong pellet-like floc can be produced, which is called pelleting flocculation [2].

The action of cationic polymers on a negatively charged particle is somewhat similar to the action of coagulation where the charge neutralization can be a predominant mechanism over that of polymer bridging. Flocculation by "non-adsorbing" free polymers is known as depletion flocculation, which may result from high concentration of polymer in solution. This phenomenon is explained [3] as follows. When the distance between approaching particles is smaller than the size of the polymer molecules, none of these molecules can enter the region between these particles, which is then composed of only the solvent. The solutions outside the particle retain their bulk polymer concentration and therefore exert an inward force arising from osmotic pressure. This inward force causes the particles to flocculate. This theory assumes that polymer molecules have a rigid configuration in solution, where particles are treated as semi-permeable membranes and does not consider the free energy charge involved in bridging the particles to close approach.

Bridging flocculation, by linear polymer molecules, is the main flocculation mechanism in mineral engineering practice.

The selective flocculation technique is very different from flocculation itself. Selective flocculation utilizes the differences between physical and chemical properties of the various mineral components in mixed suspension. It is based on preferential adsorption of the flocculant on a specific mineral to be flocculated, leaving the remaining particles in suspension. Very often, in selective flocculation the dispersion of particles that would remain in solution is required; so in this case, dispersion flocculation is essential for achieving the goal of separation. Selective dispersion, like selective flocculation, utilizes the differences in the chemical and physical properties of minerals, and is based on the preferential adsorption of selective dispersants on specific particles.

11.2   DISPERSING REAGENTS

Dispersing reagents are basically modifiers, which are discussed in Chapter 4, and most of these dispersing modifiers are also either depressants or activators. In short, they have multiple functions. Dispersing reagents are inorganic compounds and organic polymers, which are specifically designed for such a function.

Representatives of inorganic dispersants are sodium silicate and sodium polyphosphates. These dispersants are also used as depressants and activators and have been described in previous chapters.

Representatives of organic dispersants are starches, dextrins, guars, quebracho, lignin sulfonates and polyglycol ether. All these polymers are also used as depressants in the same form and molecular structure as they are used as dispersants. Therefore, most dispersants are also depressants and it can be said that they have a dual function. The polymers that have a flocculating effect are those with altered molecular structures. For example, quebracho can have a flocculating effect after it is treated with amine. The polymerized guar gum is a flocculant, but after alteration and de-polymerization it acts as a dispersant and depressant.

11.2.1   Action of dispersing reagents

In Chapters 8 and 9, the interaction of inorganic and organic modifiers has been discussed extensively, in which different actions of these reagents were concluded by different studies. For example, it was postulated that the depressing effect of both silicates and phosphates are due to some sort of chemical interaction on the mineral surface. However, dispersant action is quite different from that of depressing action because the purpose of a dispersant is to prevent aggregation of fine and clay particles. One can expect that the mechanism of dispersion is somewhat different in the sense that the function of a dispersant is to control the charge density at the solid–liquid interface or the electrical charges of ultrafine particles.

Inorganic dispersants

The action of sodium silicate as a dispersant is mainly associated with disassociated polysilicic acid, which is partly ionized in aqueous solution. Its adsorption must lead to an increased negative charge of the solid and, consequently, has to stabilize mineral systems against aggregation. Some investigators [4] postulate that polymeric sodium silicate adsorbs by multiple weak bonds to form hydrated layers at the mineral surface. As a result, dispersion is due to both increased negative zeta potential values and hydrated layers.

In contrast, polyphosphates are good complexing agents, which exhibit a high adsorption affinity on specific mineral surfaces. Adsorption may be influenced by electrostatic forces, hydrogen bonding, or forming a strong covalent bond with a number of metallic cations.

In studies of polyphosphates as dispersants, it was determined [5] that amino polyphosphates and polyphosphates are the most effective dispersants.

Organic dispersants

The theory behind the action of polymers as dispersants is somewhat similar to that of the action as depressants. The mechanism of interaction of polymers with mineral surfaces is summarized as follows.

In the case of starches and dextrins, it is postulated that coulombic forces acting between the mineral surface and starch molecules hinder adsorption and that adsorption is caused by non-ionic interactions. In this and other cases of starch adsorption, hydrogen bonding is responsible for adsorption. This conclusion is based on adsorption studies of starches on hematite and quartz [6]. In other studies [7,8] using a quartz dextrin system where pure, methylated and lead-activated quartz were reacted with dextrin, it was concluded that for adsorption of dextrin on mineral surfaces, the chemical interaction and some type of hydrophobic bonding is responsible for adsorption. Figure 11.1 shows the effect of pH on the adsorption of dextrin on quartz. In actual practice, dextrin is used to depress iron oxides, titanium oxides, etc. during the flotation of quartz, zircon and other silicates.

Studies carried out with polyethylene oxide [9] have indicated that a combination of hydrogen bonding and hydrophobic interaction is responsible for the adsorption on the mineral surface. It is believed that [10] that alcoholic groups (–OH) do not confer dispersant properties on a molecule; however, if hydroxybenzene has –OH groups on adjacent
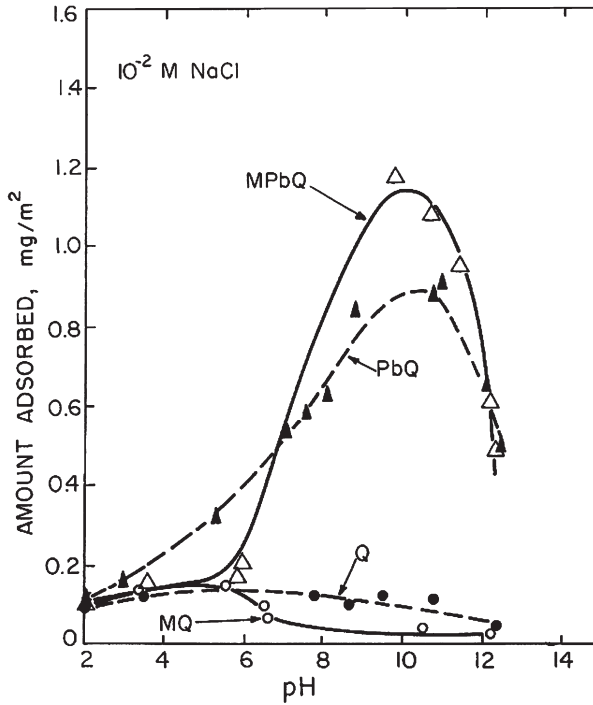
Figure 11.1 Effect of pH on adsorption of dextrin on pure quartz (Q), methylated quartz (MQ), lead-coated quartz (PbQ) and methylated lead-coated quartz (MPbQ). Dextrin concentration of 50 ppm [7].

carbon atoms (quebracho constituents), then these groups disassociate when adsorbing on positive sites, increasing the solid net negative charge.

In the case of tannin derivatives [11], it was postulated that tannins become chemisorbed through Ca^{2+} ions either on the surface of the mineral lattice or as Ca^{2+} adsorbed on it from the solution.

The practical perspective

It should be understood that dispersion is intended to (a) prevent aggregation of ultra-fine particles and (b) prevent slime coatings on the mineral particles. From a flotation point of view, the presence of ultra-fine slime and clay may inhibit flotation of many minerals through slime coating or adsorption of reagents on clay particles.

The ultra-fine slimes, as well as clay minerals, have different surface properties in comparison with larger particles with respect to surface energy and behavior. In a number of investigations [12,13], it was demonstrated that electrostatic forces are involved in slime-clay adsorption on the mineral surfaces, where oppositely charged mineral and slime particles are attracted to each other. It is obvious that slime coatings are less likely to form a dispersed system. Dispersion in the slime mineral system and hence the electrostatic attachment of fines to the mineral surface depends on the fines (both edges and faces) surface charge in various environments.

Some researchers [14] indicate that clay particles may be flocculated or aggregated in several ways: face-to-face, age-to-age, face-to-age or in combinations. These associations may be affected by changing the charge on the clay. While the iso-electric point of kaolinite occurs at pH 3.3 and bentonite at pH < 3, the faces [15] of clays are always negatively charged, while the clay edges exhibit an iso-electric point at about a natural pH. It is found that the presence of inorganic salts and alkaline substances affects the flocculation and flocculation–dispersion behavior of ultra-fine particles significantly.

Some investigators [16] have proposed three ways of clay dispersion that may occur: (a) removal of positive charges by proton transfer or additions of NaOH, (b) neutralization of positively charged anion adsorption (i.e. Cl^-) and (c) addition of a clay mineral with opposite charges. Some other investigators working with coal [17,18] have found that if the sign of the charge on coal is controlled by rendering it with the same charge as that of the clay, then a clay coating on the coal surface may be prevented.

Therefore, the dispersing action of polymers is not by any means associated with the polymer adsorption on larger particles (i.e. quartz, oxides, etc.). Actually, these polymers provide the conditions under which clay or ultra-fine particles are maintained in a dispersed state. If the slime coating is a result of electrostatic forces, as stated earlier, then the polymer action on a dispersant is different from that of a depressing action, and the adsorption mechanism is different. In practice, modified starches are good dispersants for silicate slimes but are not effective for the dispersion of kaolinite–illite clays. The sodium sulfonate of the formaldehyde naphthalene condensation product is a good dispersant for calcite fines, but not for silicate fines. Quebracho is a good dispersant for kaolinite and illite clays, but not for either calcite or silicate slimes. Therefore, it can be concluded that the interaction of the polymeric dispersant with ultra-fine slimes is electrostatic.

11.3   SELECTIVE COAGULATION

11.3.1   Introduction

Coagulation or selective coagulation occurs in an initially dispersed mixed colloidal system, where differences in the slow rates of coagulation of various species are of sufficient magnitude that one species may separate out, leaving the other in suspension after a certain period of time. To avoid rapid mutual coagulation of the different components, all particles must carry the same sign of charge. The separation process can be somewhat controlled by careful adjustment of the surface potential, so that one component is reduced to a point where slow coagulation occurs without mutual coagulation.

From the DLVO theory, the collision of the fast coagulation process resulting from such an interaction may be dependent on the initial particle concentration and sizes. However, in a slow coagulation process, the potential energy barrier makes a major contribution to the stability of the system. The DLVO theory is a theory of interaction potential between colloidal particles, which has been put together by Derjaguin, Landann, Verwey and Overbeek [19,20] and is intended to analyze colloidal particles using electrostatic repulsion forces together with the Van der Waals force between

spherical particles. Although the DLVO theory is also used to explain selective coagulation, there are certain restrictions of the theory when applied to colloidal mineral mixtures, some of which include the following. The actual DLVO theory is limited to coagulation and dispersion of particles of identical size and nature, and symmetrical double-layer interactions in the electrolyte solution. In the mineral particle system, neither identical nor spherical particles exist. The theory has never been confirmed by experiments in any colloidal model.

11.3.2 Application of DLVO theory to selective coagulation

In accordance to the classical DLVO theory, the overall potential energy of the interaction (Y_t) between two particles is defined by

$$Y_t = V_e + V_a \tag{11.1}$$

where V_e is the electrostatic double-layer repulsive potential and V_a the Van der Waals attraction. Some investigators [21] have considered a case of spherical particles with diameters a_1 and a_2 with low surface potential p_1 and p_2 ($ep/Kt < 1$) and a thin double layer ($ak > 1$) where the relationship between V_e and V_a and the distance Ho between surfaces can be described as follows:

$$V_e = \frac{F_e}{4} f(p_1, p_2 < H_0) \tag{11.2}$$

$$V_a = F \frac{A}{6H_0} \tag{11.3}$$

where F is a size factor $(a_1 a_2)/(a_1 + a_2)$ and A is the rate constant.

In the case of selective coagulation, the rate of coagulation is an important factor for the various combinations of particles present in mixed suspension. Because the rate of coagulation is a function of the concentration of particles and their size, it is not sufficient to adopt a simple energy criterion to distinguish rates in a mixture.

From the DLVO theory, the coagulation time $t_{1/2}$ is related to a stability coefficient W, which provides a quantitative measure of the stability of the dispersion and the initial concentration N_0 of the particles by the equation:

$$t_{1/2} = \frac{3\eta W}{4k_B T N_0} \tag{11.4}$$

where t is the rate factor and η is the size.

This is a generic equation and appropriate values of W, $N_{0(1)}$ and $N_{0(2)}$ must be provided for the collision of unlike particles. In case the colloids are not monodisperse, a range of coagulation times can be obtained for the various possible combinations of size. For each

combination, W_{12} can be calculated by an extension of the Fuchs theory for spheres unequal size (cf) [21] where:

$$W_{12} \approx 2a^- \int\limits_{2a^-}^{\infty} \exp\left(\frac{V_{12}}{KbT}\right)\frac{dR}{R^2}$$

(11.5)

where $R = (a_1 + a_2 + H_0)$. In this case, W_{12} is the interaction energy between particles 1 and 2 and a^- is the mean of a_1 and a_2. For the purpose of an exploratory survey, a range of W_{12} values can be expressed as

$$W_{12} \approx \frac{1}{2K(a^-)}\exp\frac{V_{max}}{KbT}$$

(11.6)
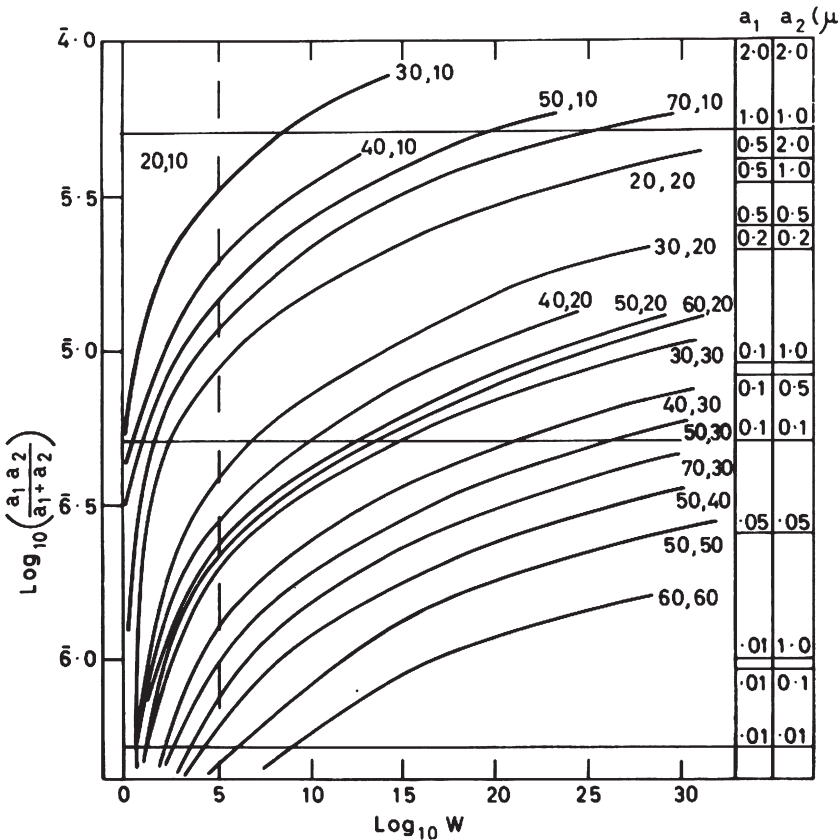
Figure 11.2 Stability curves: constant potential; $A = 3 \times 10^{-20}$.

Using the above equation, some investigators [22] have provided a series of stability curves relating W_{12} to the radii a_1 and a_2 and the surface potential p_1 and p_2. These relations are shown in Figure 11.2.

11.3.3   Application of selective coagulation to binary mineral mixtures

Selective coagulation is normally achievable on a uniformly micron-sized particle. In fact, to achieve clear-cut selective coagulation, it is desirable to choose two components having spherical or at least spheroidal particles of a narrow size range, which should be below 1 μm in radius to avoid an instability problem. Selective coagulation is achieved by exploiting the difference in the coagulation rates of the two mineral components following adjustment in pH and/or strength of the medium. Therefore, optimal conditions have to be chosen such that the two colloids carry the same sign of surface charge and, based on the proposed theory of selective coagulation, a fairly large difference in surface potential exists. The following are several examples of selective coagulation of different systems examined by various authors.

- Experimental work with the quartz–rutile system [23] has shown (Table 11.1) that selective coagulation of the mixture occurs at about pH 5.6. Both quartz and rutile components in this case carry a negative surface charge at this pH, but at this point quartz sol remained stable while rutile undergoes rapid coagulation. In a higher pH region (i.e. pH 7–10), both rutile and quartz remain stable and the coagulation of rutile occurs in the presence of electrolyte NaCl. These experiments were conducted on particles with sizes ranging between 0.05 and 0.2 μm radius.
- In the case of a quartz–hematite system [24], it has been confirmed that selective coagulation of hematite from quartz occurs in slightly alkaline conditions when only a low concentration of electrolyte is present in solution. In this region, quartz retains a high negative surface potential, thus remaining stable while hematite is reduced to a low negative value where it coagulates. This is in accordance with the DLVO theory. The stability region for a quartz–hematite mixture is illustrated in Figure 11.3. The data in this figure indicate that hematite has a pH of about 6.0. In the presence of electrolytes, selective coagulation of the quartz–hematite system occurs between 0.015 and 0.1 M

Table 11.1

Separation and selective coagulation in analyses of the silica–rutile system [23]

pH	Electrolyte (NaCl) concentration (M)	Supernatant liquid assays (%)		Sediment analyses (%)	
		SiO_2	TiO_2	SiO_2	TiO_2
5.6	–	98	2	7	93
9.5	0.020	95	5	4	96
9.5	0.023	89	11	13	87
9.5	0.027	87	13	1	90
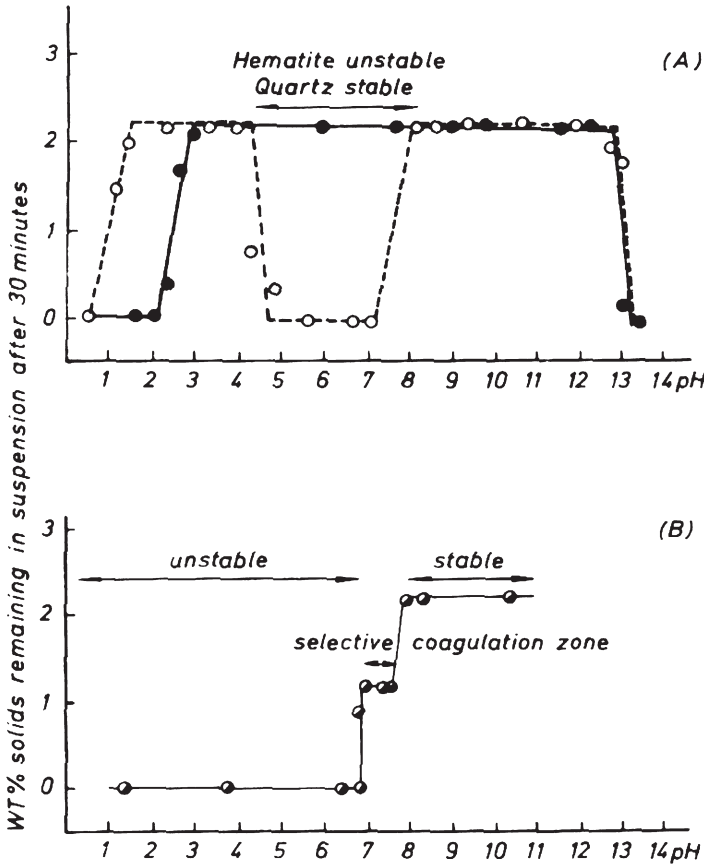
Figure 11.3 The stability region of A (●) hematite and (○) quartz and B suspension, the hematite + quartz mixed suspension [24].

of NaCl. In this region, quartz remains stable and the hematite coagulates while both components retain a negative surface potential.

- In mixtures of colloidal clays with different charges or particle size, possibilities exist of selective coagulation occurring in dilute electrolyte solution. Studies were carried out [25] with model clay colloids consisting of sodium smectites, which are composed of negatively charged silicate layers about 1 μm thick. Experiments were conducted with low- and high-charge systems. It was determined from these experiments that critical coagulation concentration (ccc) corresponds to the lowest concentration of electrolyte in the case of face-to-face coagulation of the separate smectite system. To prevent age-to-face coagulation occurring in these systems, it was necessary to add diphosphate (which adsorbs on positively charged edges) to increase negative charges on the sites.

It should be noted that in industry, no attempts have been made to apply selective coagulation in the separation of individual minerals.

11.4 FLOCCULATION

11.4.1 Action of flocculants

Polymer adsorption and particle flocculation can be considered transport processes [25]. The rates of these transport processes depend on diffusion and induced velocity gradient. In fact, the velocity gradient affects polymer–particle collision, leading to adsorption, and particle–particle collision, resulting in flocculation. In the absence of induced velocity gradients, Brownian motion diffusion is the main mechanism for particle collision and polymer adsorption.

Some researchers have postulated that the kinetics of polymer adsorption can be assumed to be transport-limited; thus the adsorption depends on the rate of arrival (or collision) of the polymer molecules at the particle surface. This may be valid only at low surface coverage as the adsorption rate usually decreases when the surface becomes more fully covered by the adsorbed polymer. Because flocculation does not require high or complete surface coverage, transport-limited coverage may be sufficient. The number of particle–polymer collisions in unit volume per unit time, J_{12}, for a suspension containing n_1 number of particles and n_2 polymer molecules can be expressed as

$$J_{12} = K_{12} n_1 n_2 \dots \tag{11.7}$$

where K_{12} is the rate constant usually determined from the following relations:

$$K_{12} = \left(2K \frac{T}{3\mu} \right) \left(\frac{a_1 + a_2}{a_1 a_2} \right)^2 \tag{11.8}$$

or
$$K_{12} = (413) D (a_1 + a_2)^2 \tag{11.9}$$

where T is the absolute temperature, μ the viscosity and D the velocity gradient or shear rate (s^{-1}), and a_1 and a_2 the radii of the particle and polymer, respectively. Eq. (11.8) is applicable for diffusion controlled adsorption in the absence of induced velocity gradient, while eq. (11.9) is used when agitation is used.

The flocculation rate can be described by eq. (11.7), in terms of collision rate between polymer loaded particles when $\eta_1 = \eta_2$, and

$$j = \frac{d\eta_F}{dt} = K\eta_2 \tag{11.10}$$

where η_F is the number concentration of flocs. Because not all the collisions are effective in producing flocculation, a collision efficiency factor E is introduced into eq. (11.10), which was estimated [26] as

$$E = Q1a \tag{11.11}$$

Accordingly, the rate of formation of binary particle flocs in the beginning of flocculation can be determined by the LaMer formula:

$$\frac{d\eta_F}{dt} = A\eta_1^2\,\theta(1-\theta). \tag{11.12}$$

where η_1 and η_F are the number concentration of primary and binary particles (flocs), θ the fraction of surface covered by the polymer and A the flocculation rate constant. The rate of flocculation from eq. (11.12) is equal to the product of particle collision frequency and a collision efficiency factor

$$E : \frac{d\eta_F}{da} = A\eta_1^2 E \tag{11.13}$$

The above equations contain a number of simplifying assumptions such as the polymer configuration in solution the same as on the particle, which is not the case; also the particle–polymer–particle collision and subsequent breakage was not considered.

Other researchers [27] proposed a model allowing for a minimum distance between two particles H_{min}, which is determined by a balance of surface forces acting on those particles. Attempts to account for non-adsorbed segments of the polymer molecular bridge in solution (loops), which extend some distance h into the liquid from the particle surface, have been made. According to this, the binary collision bridging efficiency is expressed by the equation

$$E = 1 - [1 - 2\varnothing(1 - \varnothing\partial)]^N \tag{11.14}$$

where N is the number of interacting pairs ($N = n_1 n_j$; Hoggs model). The value for N is calculated from the following equations:

$$N = \frac{r(h - H_{min})}{h^2} \qquad \text{equal size separation} \tag{11.15}$$

$$N = \frac{2rj}{h^2} \cdot \frac{2ri(h - H_{min}) - (h - H_{min})^2}{2[ri + rj - (h - H_{min})]} \qquad \text{unequal size separation} \tag{11.16}$$

where j is the smaller particle, i the larger one and r is the particle diameter. In this model, it is also assumed that the polymer adsorption rate is not a limiting factor and no re-orientation of multiple bridges is allowed between the adjoining particles. Also, deterioration of N for non-spherical particles, floc–floc or floc–particles is very difficult. Therefore, in all these models simultaneous adsorption of polymer molecules on several particles is not included.

11.4.2   Rate of floc growth, breakage and hydrodynamic effect of flocculation

The rate of floc growth, breakage and hydrodynamic effect of flocculation are the major factors that influence flocculation and the selection of flocculant in the actual practice.

- Floc growth usually occurs by a random process, which involves floc–floc collision as well as floc–particle collision and produces irregular structures. The approximate expression for floc growth rate [28] based on theoretical analysis of agitated suspensions is

$$\frac{d_X^1}{dt} = KED\phi_X \tag{11.17}$$

where X is the floc size at time t, D the shear rate due to agitation, ϕ the volume fraction of solids in suspension, E the collision efficiency factor and K a constant (~1). Since E can be assumed to be constant with time, after integration, eq. (11.17) assumes the following form:

$$\frac{\ell\eta_X^1}{X_0} = KED\phi t \tag{11.18}$$

where X_0 is the initial floc size.
- Rate of floc breakage, unlike floc growth, may not be characterized by breakage mode functions because the dissipation rate of the parent floc size, as multiple levels of aggregation structures, yields disintegration at different degrees of severity. Some insight into floc breakage can be found in the literature [29]. Such cases where eddies are responsible for floc disintegration can be characterized by rough equality between floc yield stress Ty and dynamic pressure:

$$Ty \approx \psi\rho v^2 \tag{11.19}$$

where $\psi\rho$ is the fluid density and V the fluid velocity.

$$Vc = \sqrt{\frac{2T_v}{\rho}} \tag{11.20}$$

where Vc is the critical velocity.
Velocities higher than Vc would result in floc breakage. But floc yield stress must be independently determined before the above equations can be used. Other researchers [29,30]

have proposed a model by which maximum stable floc size (d_{max}) can be determined in a flocculation process using agitation:

$$d_{max} = \left(\frac{F_H^{1/2}}{\rho_1} \right)(\upsilon\varepsilon)^{-1/4} \tag{11.21}$$

where F_H is the average adhesion force between particles, ρ_1 the fluid density, υ the kinematic viscosity and ε the energy dissipation rate. A population balance model developed for size reduction was used to describe the floc degradation process where re-agglomeration of floc fragments was assumed to be negligible. A mass balance on flocs in some size interval can be expressed by the following equation:

$$\frac{dW_i}{dt} = \sum_{j=1}^{i=1} b_{ij} \; S/W, -S_i W_i \tag{11.22}$$

where w_i is the mass fraction of floc in size interval (i) at time (t), S_i the specific rate of breakage of flocs, and b_{ij} the mass function of fragments produced by breakage of floc size (j) which fall into class (i).

- A hydrodynamic effect is the third major factor that effects flocculation. Hydrodynamic forces in suspension affect the flocculation process in many ways, including by (a) dispersion of polymer molecules, (b) polymer adsorption, (c) floc formation, (d) floc break up and (e) floc growth. The effect of hydrodynamic forces on the various flocculation functions (eqs. (11.7)–(11.21)) have been represented by the mean shear rate as expressed by the velocity gradient D (s^{-1}). The usual method of calculating D is through the following equation:

$$D = \left(\frac{P}{\mu\gamma} \right)^{1/2} \tag{11.23}$$

where P is the power transmitted to the fluid, μ the viscosity of fluid and γ the fluid volume. For an inline mixing system, the power dissipated is given by the following relationship:

$$P = \rho Q F \tag{11.24}$$

where F is the head loss due to friction, Q the volumetric flow rate, and ρ the fluid density. The head loss due to friction is calculated from the following equation:

$$F = \frac{4fLU^2}{2dgc} \tag{11.25}$$

where F is the head friction factor, L the length of tube, μ the fluid velocity, d the tube diameter, and gc the dimensional constant. From the eqs (11.23) and (11.25), the equation for the velocity gradient in an in-line, plug-flow mixing is obtained:

$$D = \left(\frac{2\rho}{gc\mu}\right)^{1/2}\left(\frac{f}{c}\right)\frac{1/2}{X}\,\upsilon 3/2 \qquad (11.26)$$

The validity of the mean velocity gradient D as an expression of shear rate acting on individual particle or floc in a turbulent regime under inhomogeneous and anisotropic conditions, usually encountered in flocculation processes, is questionable. In spite of this, D has been commonly used because of the difficulty in determining the actual shear rate acting on the individual particles or flocs. It should be noted, however, that much of the literature in the field of water treatment describes guideline values for good flocculation as $D = 50$ s^{-1} for $t = 20$ min, so that $Dt = 10^4$ or 10^5 [30]. It is a known fact that the energy dispersion rate per unit mass $(2) = E\ E_{local}/E_{mean} = E_{lock}/E_{min}$ is much higher near the impeller than some distance away from it, where $E_{local}/E_{mean} = 100$ in some cases. Floc breakage is also a consequence of local micro-turbulence, not mean flow conditions. The intensity and structure of the micro-turbulence depends, however, on the energy dispersion rate E and kinematic viscosity μ. The mean energy dispersion rate E_m in a tank containing M mass of fluid and power input P is expressed as

$$E_m = \frac{P}{M} \qquad (11.27)$$

The local dissipation rate E varies with the distance X downstream as follows:

$$E \approx 5.0 \times 10^4 \exp(-0.14X) \qquad (11.28)$$

It is believed that prevailing hydrodynamic conditions affect the efficiency of the polymer mixing process as well as floc formation and growth processes. For example, the gentle, low-shear conditions (close to laminar regime) favor good floc formation and result in both high floc recovery and grade.

11.4.3 The use of flocculation in mineral processing

The application of polymeric flocculation in mineral processing is quite wide and also variable. Almost every mineral processing plant uses polymeric flocculants in one way or another, and can be viewed in terms of the application of a flocculant relevant to a specific unit process, such as flocculation thickening, filtration and centrifugation. Flocculants are also used in selective flocculation, dispersion and flotation. However, it should be remembered that only specific polymers are used in dispersion and flotation as a depressant.

These have already been discussed. Some of the essential applications of polymer flocculants are described below:

- *Flocculation/settling*. Perhaps the earliest application of polymers was in the clarification of various effluents in wastewater treatment or clarification of effluent for re-use in mineral processing plants. Fine particles contained in the effluent are settled using flocculant polymers.
- *Filtration*. The polymeric flocculants used in filtration applications have several objectives, including to (a) reduce size of settling equipment (thickeners), (b) improve clarity of the thickener effluent and (c) improve filterability of the filtered material. The use of flocculants in the filtration process is also designed to obtain slurry that forms a filter cake with an open structure of high permeability with a reduced amount of free fines that tend to block or "blind" the filter medium.

  In these applications, large, loose flocs are most effective in causing rapid settling. However, they trap water in the floc structure and can be unsuitable for filtration because they can induce high moisture content. In practical applications, flocs that are small, strong and equi-sized are good for filtration and provide low cake moisture. It is therefore very important to select the proper flocculant for a specific material that is to be de-watered.
- *Centrifugation*. Polymeric flocculants are also used in de-watering slurry by centrifugation. On an industrial scale, centrifugation techniques are primarily used in the clay industry. A limitation that was recognized earlier regarding the use of flocculants in centrifuges was the lack of adequate resistance of the polymers to very high local shear forces that exist at the point where the suspension (slurry) enters the bowl via the axial feed and accelerates the bowl speed. To avoid this problem, a special high-shear-resistant flocculant has been developed for this purpose.

11.5   SELECTIVE FLOCCULATION

11.5.1   Introduction

Selective flocculation is the newest process primarily developed for fine-particle processing. This process is designed to separate valuable minerals from waste minerals using a selective flocculation method. Selective flocculation is also used in fine-particle colloid separation in several other applications other than minerals (e.g. cholesterol separation and the pulp and paper industry).

Selective flocculation, like flotation, utilizes the differences in the physical–chemical properties of various fine mineral components in the three-phase system. It is based on the preferential adsorption of the flocculant on a particular mineral to be flocculated, leaving the remaining particles in suspension.

In some applications, the reverse of selective flocculation, being selective dispersion of a particular mineral, is desirable as in the purification of kaolin or coal. Selective dispersion, which also utilizes the properties of the mineral surface, is based on selective adsorption of

the specific dispersant on the particles intended to be dispersed, leaving the remaining suspension particles to be flocculated by a general type of flocculant.

The selective flocculation process involves several steps including (a) general dispersion of mineral particles in which all the particles are stable and uniformly distributed in the suspension, (b) selective adsorption of flocculant and floc formation and (c) floc conditioning, which aims at obtaining flocs with desirable properties for their subsequent separation and with minimum entrainment of dispersed particles and separation of flocculated particles from dispersed particles.

11.5.2   Mechanisms of selective adsorption of polymers

It is believed that that the forces involved in the adsorption of polymeric flocculants on mineral surfaces can be physical or chemical or both. The forces that are considered to be physical, which do not form chemical bonding and usually result in physisorption regardless of the chemical nature of the interface, are as follows:

(a)   Electrostatic (coulombic) forces, which result in the adsorption of polyelectrolytes onto any surface with the opposite charge, regardless of their chemical nature.
(b)   London–Van der Waals forces, in which neutral molecules or atoms constitute systems of oscillating charges producing synchronized dipoles that attract each other [31].
(c)   Dipole attraction forces are suggested [32] to explain the flocculation of ionic-type crystals (fluorite) by a non-ionic polyacrylamide-type flocculant.
(d)   Hydrophobic association has been characterized by the tendency of non-polar molecular groups to escape from an aqueous environment, which results from chemical forces and includes chemical bonding, coordination bonding and hydrogen bonding. Chemical bonding is believed to be a reaction of polymer groups with metallic sites on a solid surface, which results in the formation of insoluble compounds by covalent or ionic bonding. In contrast, coordination bonding involves chelating or complex formation, resulting in polymer attachment on the surface. Hydrogen bonding occurs when a hydrogen atom from the organic compound is combined with a strongly electronegative atom (such as O, S and N) in which a hydrogen atom is able to accept electrons from atoms on a solid surface, such as from the –OH groups of the hydrated surface of an oxide mineral, resulting in the formation of a hydrogen bond.

On the basis of the action and requirement for selective flocculation, the design or selection of a specific polymer for a particular mineral surface is actually based on the action of polymers. Therefore, the following examples of polymer chemistry should be mentioned.

•   *Selective polymers based on chemosorption* [33] are polymers commonly used for selective flocculation of sulfide and oxidic minerals. Representative flocculants are those from the polyxanthate group, which are used for selective flocculation of sulfide and oxide copper minerals. The chelating or complexing polymer, polyacrylamide-glycol-bis-2-hydroxyanie (PAMG), was designed for selective flocculation of copper

minerals from natural ore. Other examples of chemisorbing selective polymers are poly-oximes, which are designed for separation of cassiterite from quartz and tourmaline [34]. The chemisorbing or chelating polymers used for achieving selective flocculation so far are considered to have the most practical and promising mechanism.

- *Selective polymers based on their stereo-selective effect.* These flocculants have not yet been designed as such, or used in selective flocculation, although there is a potential [35] for development in the future. The design of this type of flocculant involves the geo-metrical arrangement of the flocculant group, so as to match the geometric structure of the binding ionic (or atomic) sites on a certain mineral surface, where selective adsorp-tion occurs. The structural effect, such as sterite-hindrance ring strain and specific size fit could be employed to produce selective flocculation based on stearic effect.

- *Selective polymers based on hydrophobic effect.* Hydrophobic or partially hydrophobic polymers appear to have the greatest potential for selective flocculation of hydropho-bic solids (with natural or induced hydrophobicity) in mixed suspension with hydrophilic solids. Such flocculants have been tested [36] on hydrophobisized copper minerals, using polyethylene oxide.

11.5.3   Application of selective flocculation in mineral processing

Selective flocculation is extensively studied on both laboratory and pilot plant scale. Selective flocculation has been successfully applied at an industrial scale in treating iron ore. Progress in the application of selective flocculation has been made and in the near future will expand to the industrial scale as a means of pre-concentrating mineral value in a more cost-effective manner. The following are some examples of recent research and development on selective flocculation.

- *Selective flocculation of copper ores* was extensively examined [37]. In these studies, several copper minerals were included and a number of high molecular-weight poly-mers incorporating sulfhydryl (SH) or other groups were tested. These polymers have the ability to selectively complex or chelate copper ions. In the study, evidence of selec-tivity of flocculation with synthetic mixtures of finely divided minerals was obtained. For example, xanthate-containing polymers, such as cellulose, cellulose derivatives and PVA xanthates, showed marked selectivity toward minerals such as galena, pyrite, chalcopyrite and chrysoccola, while they had little or no flocculating effect on calcite, quartz, feldspar and kaolinite. These polyxanthates almost fulfill the ideal case of yes-or-no adsorption. With these specifically adsorbed polymers, selective flocculation of chrysoccola from quartz and galena from calcite was achieved. It was pointed out that soluble Cu^{2+} ions can activate gangue minerals, which makes polyxanthate flocculants unselective. The addition of $Na_2S \cdot 9H_2O$ as a masking agent eliminates harmful effects of cations. A chelating flocculant, such as PAMG, was found to readily flocculate cop-per minerals from the gangue, including calcite, quartz, feldspar and dolomite in the presence of polyphosphates and/or polyacrylates. Quantitative flocculation tests (colour of flocs) at pH 10 showed that chrysoccola was readily separated from calcite and quartz. Table 11.2 shows the experimental results obtained on disseminated copper

Table 11.2

Selective flocculation results obtained on copper oxide ore [38]. Feed – 5.4% Cu. <16 μm,
dispersants – calgon – dispex N40, flocculant – PAMG

Conditions	Product	Assays % Cu	% Distribution Cu
25% solids, distilled water	Rougher concentrate	22.5	69.0
	Scavenger concentrate	7.3	17.0
	Tailings	1.1	14.0
5% solids, distilled water	Rougher concentrate	23.5	64.0
	Scavenger concentrate	3.8	23.0
	Tailings	1.5	13.0
10% solids, tap water	Rougher concentrate	19.6	62.0
	Scavenger concentrate	5.3	12.0
	Tailings	2.0	26.0
30% solids, tap water	Rougher concentrate	18.2	62.0
	Scavenger concentrate	3.0	2.0
	Tailings	2.0	36.0

ore [38]. There is an indication that refractory ores can be upgraded by selective floc-
culation and may be adopted for industrial applications.

- *Selective flocculation of iron ores* has already been applied to commercial use [39]. In
  this case, selective flocculation of iron oxides is achieved using starch and is separated
  from fine silica using a thickener, and caustic soda at pH 10.5 is used as silica dispersant.
- *Selective flocculation of sylrinite ores*. The literature [40] describes the development
  and commercial application of selective flocculation–flotation process for upgrading
  sylrinite ore. The ore contains sylrinite (KCl + NaCl) and gangue, dolomite, hematite,
  quartz, kaolinite, illite, chlorite and anhydrite. In this case, a non-ionic polyacrylamide
  flocculant is used at natural pH. The flocculated gangues were floated using a sul-
  fonate-type collector.

REFERENCES

1. O'Melia, C.R., Flocculation, Sedimentation and Consolidation, In (B.M. Mondgil and P. Somasundran eds) *Engineering Foundation*, Permagan Press, New York, pp. 159-169, 1986.
2. Yusa, M., In (Y.A. Ahia ed) *Flocculation in Biotechnology and Separation Systems*, Elsevier, pp. 755–764, 1987.
3. Asakura, S., and Oosawa, F., *Chemical Physics*, Vol. 22, p. 1255, 1954.
4. Leja, J., *Surface Chemistry of Froth Flotation*, Plenum Press, 1982.
5. Parsonage, P., and Marsden, A., *International Journal of Mineral Processing*, Vol. 10, p. 219, 1988.
6. Balajee, S.R., and Iwasaki, I., *Transactions of AIME*, Vol. 244, p. 401, 1969.
7. Liu, Q., and Laskowski, J.S., *Colloid Interface Science*, Vol. 101, p. 130, 1989.

8. Liu, Q., and Laskowski, J.S., *International Journal of Mineral Processing*, No. 26, p. 297, 1989.

9. Rubio, J., *Colloids Surface*, No. 3, p. 79, 1981.

10. Parsonage, P., and Marsden, A., *International Journal of Mineral Processing*, No. 20, p. 161, 1987.

11. Schulze, J.H., Hanna, H.S., and Freiberg, R., *Forschungsh A*, No. 33, p. 476, 1970.

12. Jewet, A., and Pearse, M.J., *Fuel*, No. 35, pp. 303–309, 1956.

13. Plaskin, I.N., and Ocolowich, A.M., Publ. Nanka, Moscow, 1965.

14. Del Guidice, G.R.M., A Study of Slime Coating in Flotation, *Transactions of AIME*, Vol. 112, pp. 398–409, 1934.

15. Dovenfeld, A.C., Slime Coatings, How to Explain and Control Them, *Engineering and Mining Journal*, Vol. 154, pp. 87–91, 1953.

16. Bankoff, S.G., Experiments with Slime Coatings, *Transactions of AIME*, Vol. 153, pp. 473–478, 1943.

17. Sun, S.C., The Mechanism of Slime Coatings in Flotation, *Transactions of AIME*, Vol. 153, pp. 479–491, 1943.

18. Fuerstenau, D.W., and Atak, S., Iron Oxide Slime Coating in Flotation, *Transactions of AIME*, Vol. 211, pp. 792–794, 1958.

19. Derjaguin, B.V., and Kussakov, L.Y., *Acta Physicochim*, No. 10, p. 153, 1939.

20. Verwey, E.J., and Overbeek, J.T., *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948.

21. Hogg, R., Kimpel, R.C., and Ray, T.D., *Transactions of the Faraday Society*, No. 62, p. 1638, 1966.

22. Pugh, R.J., and Kitchener, J.A., *Journal of Colloid Interface Science*, No. 32, p. 161, 1971.

23. Pugh, R.J., and Kitchener, J.A., *Journal of Colloid Interface Science*, No. 38, p. 167, 1972.

24. Pugh R.J., *Colloid Polymer Science*, No. 252, p. 400, 1972.

25. Pugh, R.J., Selective Coagulation of Colloidal Mineral Particles, In (J.S. Laskowski and J. Ralston eds) *Colloid Chemistry in Mineral Processing*, Elsevier, Vol. 12, 1992.

26. Gregory, J., In (Y.A. Attia ed) *Flocculation in Biotechnology and Separation Systems*, Elsevier, 1987.

27. Deason, D.M., In (Y.A. Attia ed) Flocculation in Biotechnology and Separation Systems, Elsevier, pp. 21–30, 1982.

28. Smellie, R.H., and LaMer, V.K., *Colloid Science*, Vol. 23, p. 589, 1958.

29. Glasgow, L.A., *Chemical Engineering Progress*, Vol. 16, pp. 51–55, 1989.

30. Hogg, R., Moudgil, B.M., and Sheiner, B.J., Flocculation, Sedimentation and Consolidation, *Engineering Foundation*, Vol. 29, pp. 217–228, 1986.

31. Attia, Y.A., *Separation Science and Technology*, No. 17, p. 485, 1982.

32. Slater, W.R., Clark, J.P., and Kitchener, J.A., *Proceedings of the British Ceramics Society*, Vol. 13, pp. 146–150, 1969.

33. Attia, Y.A., and Kitchener, J.A., *Proceedings of the 11th International Mineral Processing Congress*, University of Calgliari Press, Calgliary, Italy, 1975.

34. Attia, Y.A., *International Journal of Mineral Processing*, No. 4, p. 209, 1977.

35. Rubio, J., and Kitchener, J.A., *Transactions of the Institute of Mining and Metallurgy*, Vol. 86, p. 97, 1978.

36. Sresty, G.C., Raja, A., and Somasundran, P., *Recent Advances in Separation Science*, Vol. IV, CRC Press, pp. 72–80, 1978.

37. Krishnans, V., and Attia, Y.A., *Selective Flocculation Technology*, Group Program, USA, 1983.

38. Drzymala, J., and Fuerstenau, D.W., *International Journal of Mineral Processing*, No. 8, p. 265, 1988.

39. Sisselman, R., *Engineering and Mining Journal*, Vol. 176, p. 52, 1975.

40. Banks, A.F., In (P. Somasundran and N. Arbiter eds) *Beneficiation of Mineral Slimes*, NSF Workshop Report, 1979.

– 12 –

Flotation of Copper Sulfide Ores

12.1   COPPER ORES AND MINERALS

More than 170 copper-containing minerals are known and only 10–15 of these minerals have any economic value. The most important economic copper minerals are chalcopyrite, chalcocite, bornite and covellite. Table 12.1 lists the copper minerals of economic value.

From a processing point of view, copper ores could be divided into:

- Copper sulfide ores, where the pyrite content can vary from 10% to 90%. The predominant sulfide mineral in this ore is pyrite, but may also contain pyrrhotite and marcasite. Some copper sulfide ores also contain significant quantities of gold and silver. According to the mineral compositions, these ores can be sub-divided into three main groups including (a) copper–gold ore, (b) copper sulfide ore with moderate pyrite content and (c) massive sulfide copper ores.
- Copper porphyry ores are the most abundant copper ores; more than 60% of the world's copper production is from these ores. They most often contain molybdenum, which is recovered as a by-product. There are several major areas in the world where

Table 12.1

Copper sulfide minerals with economic value

Mineral	Chemical formula	Copper content (%)	Specific gravity (g/cm^3)
Native copper	Cu	100.0	8.8
Bornite	Cu_5FeS_4	63.3	5.0
Chalcocite	Cu_2S	79.8	5.7
Chalcopyrite	$CuFeS_2$	34.6	4.2
Covellite	CuS	66.4	4.6
Digenite	Cu_2S	79.8	5.7
Enargite	Cu_3AsS_4	48.3	4.4
Tennatite	$3Cu_2S \cdot As_2S_3$	57.5	4.4
Tetrahedrite	$3Cu_2S \cdot Sb_2S_3$	52.1	4.8

235

copper mineralization occurs, known as copper belts. Some of the most important copper resources are listed below.

- Chilean porphyry region including Peru
- Zambian copper belt
- Pacific rim region
- Congo copper belt
- North American copper region located in Arizona (USA) and British Columbia (Canada)
- Eastern Europe copper region
- Australian copper regions

12.2 GENERAL OVERVIEW OF GEOLOGICAL AND MINERALOGICAL COMPOSITIONS

12.2.1 Porphyry copper and copper–molybdenum ores

Although it seems that porphyry copper deposits are relatively simple, the geology of porphyry copper ores is relatively complex and varies significantly within the ore body.

Most of the South American copper deposits are largely related to upper Mesozoic and Cenozoic calc, alkaline magnetic activity, which extends through most of the Andean Range [1]. The geological history of most of South American porphyry during the Mesozoic age can be roughly outlined as a succession of moraine sedimentation and continental declination in a precratonic slope. The formation of porphyry deposits has been interpreted as a culmination of volcanic episodes in most of the Andean range [2].

Most of these deposits are affected by the typical alteration of hypogene mineralization assemblages. These alterations and supergene enrichments play an important role in most South American porphyry deposits. This enrichment of an alteration–mineralization process in a porphyry deposit can be generalized as sub-volcanic magmatic developments of a metal-rich magma, where residual fluids mixed with metallic matter during the late stage of its cooling, displacing supergene mineralization. This occurrence is very important from an ore-processing point of view.

The geology of North American porphyry deposits is quite different from those of the South American deposits. The Canadian porphyry (i.e. British Columbia region) is dominated by granitic and lesser metamorphic rock of the cost crystalline belt, which borders Mesozoic, volcanic and sedimentary rock of the mountain belt.

The age of Mesozoic, volcanic and sedimentary rocks range from the late Triassic to early Cretaceous. Swarms of porphyry dykes and associated small stocks are common to the mineralized areas. Some of the ore bodies are sheet-like formations of granodiorite, which based on its texture is related to the late Triassic formations. The mineralized zones occur not only in breccia, but also in closely fractured zones along and adjacent to the guichon quartz, diorite and granodiorite contact. In some parts of these mineralized zones,

the mineralization is closely allied to but post-dates a quartz monzonite porphyry stock that appears to be an offshoot from the quartz monzonite. A large part of sulfide mineralization occurs within the dyke swarm.

Porphyry copper deposits in the American southwest [2] lie in a cratonic setting along a continental margin that was subjected to the stresses of laramide subfraction. These deposits formed in and above a Proterozoic basement that resulted from widespread intrusions of magmas of crystal derivation. Convective cooling of magmas resulted in the development of zoned sulfide mineralization in a number of large districts (Arizona, New Mexico, etc.). These zoned deposits have copper–molybdenum–silver and gold in their core.

The Pacific Rim porphyry ores are known to contain significant quantities of gold and can be regarded as a copper–gold ore. These deposits are placed in a variety of subduction-related settings, especially around the Pacific Rim [3], and they are underlined by both oceanic and cratonic crusts in either extensional or compressional tectonic regimes. The deposits are associated with composite porphyry stocks of steep cylindrical form that commonly intrude coeval volcanic piles. Stocks and associated volcanic rocks range in composition from low-potassium calc alkalic through high-potassium calc-alkalic to potassic alcolic. Much of the sulfides along with precious metals were introduced during potassium–silicate alteration ($\pm$ amphibole and other calcic minerals), which may be partially overprinted by intermediate argillic (sericite–clay–chlorite) assemblages. Hydrothermal magnetite is abundant in many, but not all, rich potassium–silicate alteration zones. Advanced argillic alteration is widespread in shallow parts of the system, whereas underlying sericitic alteration is typically minor. Gold and copper contents vary sympathetically and the silver–gold ratio is low.

The most complex deposits of porphyry are in the African region (Zambian belt), along with the Congo region. These deposits range from porphyry sulfide deposits to mixed oxides–sulfides to oxides. These deposits are discussed in the preceding chapters.

Although there is a geological similarity of the ores from different regions, the mineral composition is highly variable even within the ore body itself. A typical example of the mineral composition of major Chilean deposits is shown in Table 12.2.

12.2.2 Sulfide copper and copper–gold ores

From a processing point of view, the sulfide copper and copper–gold ores can be divided into two major groups including ores with moderate pyrite content (e.g. 5–15% of the total ore) and massive sulfide ores where pyrite content can be up to 95% of the ore.

- Ores with moderate pyrite content can be regarded as transition ores between porphyry and massive sulfide. One of the common copper sulfide ores with moderate pyrite content is known as copper and copper–gold scarns. Most copper or copper–gold scarns form in close proximity to the contacts of stock with relatively oxidized scarn mineralogy dominated by andvaderic garnet. Other phases include diopsidic pyroxene, vesuvianite, rellastonite, actinalite and epidote. Hematite and magnetite are common in most of these types of deposits and the presence of dolomitic wall rocks coincides with massive magnetic leads (e.g. Polahara, Africa and Antamina, Peru).

Table 12.2

Mineral compositions of major Chilean deposits [4]

Description	El Salvador	Disputada	Chucquicamata	El Teniente
Formation	Volcanogenic	Volcanic	Three-stage formation	Sedimentary volcanic
Gangue minerals	Andesitic sediments Andesite Chlorites Quartz Biotite Violites Tourmaline K feldspar Quartz-sericite	Quartz Diorite Grandorite K silicates	Quartz Sericite K silicates Na silicates Andesite Breccia	Breccia Andesite Quartz Diorite Potassic feldspar K silicates
Clay minerals	Alunite Cadinite Kaolinite	Brammallite Chlinochlore I Chamosite	Illite Kaolinite Chamosite	Hydrobiotite Illite Alunite
Alteration	Supergene blanket	Secondary alteration oxidized zones	Phyllic alteration, secondary enrichment of hypogene zones	Secondary alteration oxidized zone
Sulfides	Chalcopyrite Chalcosine Enargite Pyrite Covellite Molybdenite	Chalcosine Chalcopyrite Pyrite Molybdenite[a]	Chalcosine Chalcopyrite Bornite Enargite Pyrite Molybdenite	Chalcopyrite Bornite Molybdenite Lindenite
Oxides	Malachite, supergene alteration of chalcocite	Supergene chalcocite	Malachite Bronchantite Atacamite	Supergene alteration

[a]Molybdenum mineralogy is more complex [8] and varies from one ore body to another.

Sulfide mineralogy and metal ratio may be systematically zoned relative to the conservative fluton. In general, pyrite and chalcopyrite are the most abundant near the fluton with chalcopyrite increasing away from the fluton and finally bornite occurring in wollastonite zones near the marble zone.

In copper scarn containing nonticellite (Mid Erin, Canada; Irian Jaya, Indonesia; etc.), bornite–chalcopyrite are dominant sulfides rather than pyrite chalcopyrite. In the porphyry copper deposits, the transition zones between supergene and hypogene mineralization can be regarded as pyritic copper ores with a pyrite content of up to 20% (e.g. Spence, Mansa Mina, Chile and South Kemesis, Canada). These ores, in addition to pyrite and chalcopyrite, contain some enargite as well as mineralized pockets of sphalerite and galena.

From a processing point of view, the copper sulfides and copper–gold sulfides with moderate pyrite content are considered to be relatively easy to treat, the exceptions being ores with clay content and transition ores. In the case of transition ores, at times separation of chalcopyrite from pyrite may become a significant problem.

- Massive copper sulfide deposits constitute a specific class of strata-bound mineral deposits that occur in [5] thick sequences of clastic sedimentary rock and intercalated basalt. These ore deposits are found throughout the world in rocks from the early Proterozoic to early Tertiary age. These deposits typically form stratiform lenses and sheet-like accumulations of semi-massive to massive sulfides. Footwall feeder zones are present in several deposits. The minerals are predominately pyrite and/or pyrrhotite with variable amounts of chalcopyrite and a trace of sphalerite and galena, arsenopyrite and gold. Some of these types of deposits have significant cobalt, mainly in cobaltiferous pyrite and high cobalt/nickel ratios. A typical mineral composition of massive copper ores and their characteristics are given in Table 12.3.

Processing features of these ores vary significantly. Some ores, normally coarse-grained ores, can be easily processed. Fine-grained ores that contain pyrrhotite or secondary copper

Table 12.3

Summary features of massive sulfide copper ores [6]

Features	Description
Definition	Massive strata-bound cupriferous pyrite (or pyrrhotite) deposits hosted by a mixture of clastic sedimentary rocks and minor tholeiitic basalt
Age	Protezoic to early Tertiary (mainly late Proterozoic) to Mesozoic
Geologic setting	Riff basins containing clastic sedimentary rocks and generally minor tholeiitic basalt (mainly as flows, tuffs and sils) commonly with associated strata-bound alteration zones and/or chemical sediments
Host rocks	Pelitic schist, metagrey rocks, quartzite, chlorite-rich schist, muscovite-rich schist, local metachert magnetite iron formation, caticule, albitite and tourmaline
Structure and texture	Laminated banded or massive fine-grained sulfides; highly deformed deposits characterized by breccia or locally some deposits have footwall stringer zones
Sulfides and related minerals	Pyrite, pyrrhotite, chalcopyrite, magnetite, $\pm$galena, $\pm$arsenopyrite, $\pm$cobaltite, $\pm$tetrahedrite, $\pm$cubanite, $\pm$gold, $\pm$molybdenite
Gangue minerals	Quartz, muscovite, carbonate, albite, chlorite, amphibole and tourmaline
Examples	Besshi, Japan; Windy Craggy, Canada; Matchless, Namibia; Linu, China; Crandon (stringer ore), USA; Basin Bor, Yugoslavia; Black Sea, Turkey; Neves Corvo, Portugal
Typical grade	1.1−2.5% Cu commonly with significant amounts of silver and some gold

minerals are difficult to treat and, in some cases, require a special treatment process (i.e. reagent scheme) to produce commercial grade concentrates.

12.3   FLOTATION PROPERTIES OF INDIVIDUAL COPPER MINERALS AND ASSOCIATED SULFIDES

Flotation properties of individual copper minerals and associated sulfides from natural ores differ significantly. The mineralogy of the ore mineral impurities in a crystal structure, variation in crystal structure, other interfering gangue minerals and the liberation characteristics of individual minerals in a particular ore are some of the factors that influence flotation properties of an individual mineral. One may expect that floatability of a particular mineral would be similar to that quoted in the literature; however, this has never been the case and the flotation and separation of individual minerals from each ore is a separate case in itself. Flotation properties of individual minerals described here are based on the study of many natural ores in the laboratory as well as pilot plants.

Chalcopyrite, CuFeS$_2$ (Cu, 34.56%; Fe, 30.52%; hardness, 3–4 and specific gravity, 4.2). Chalcopyrite together with chalcosine is one of the most important minerals for the production of copper. In most copper sulfide deposits, chalcopyrite is the primary copper mineral, while in a large majority of porphyry copper ores, chalcopyrite is a secondary copper mineral. In some cases, chalcopyrite is also present with bornite and covellite.

Chalcopyrite from coarse-grained sulfide ores floats readily with xanthate collector in a pH region 5–11.5. Chalcopyrite, without any impurities present in the crystal structure, is a stable mineral and does not oxidize readily. It has been postulated that chalcopyrite oxidizes in a weak acid (pH 6) and acid medium where, in the solution, appears as H$^+$, Cu^{2+}, Fe^{2+} and SO [7]. During oxidation, iron hydroxide may form on the mineral surfaces.

Chalcopyrite from massive and finely disseminated sulfide ores has different flotation properties. The floatability of chalcopyrite is highly dependent on oxygen present in the ore (i.e. aeration), pH of the pulp and the type of collector. From this ore type, chalcopyrite floats much better with dithiophosphate and thionocarbamate collector than with xanthate. Figure 12.1 shows the effect of aeration on the rate of chalcopyrite flotation from massive sulfide ores [8].

Aeration also has a positive effect on selectivity toward other sulfides (pyrite, pyrrhotite). During flotation of chalcopyrite from pyrrhotite, pH plays an important role in the floatability of chalcopyrite. When using Na$_2$SO$_3$ or other sulfur-containing compounds, good flotation of chalcopyrite is achieved at a pH of 8.5–10. When Na$_2$SO$_3$ or Na$_2$S$_2$O$_5$ does not depress pyrrhotite, chalcopyrite can be floated at a pH over 12 in the presence of ammoniacal compounds.

Sulfates, dichromates, hydrosulfates (small quantities) and some starches do not depress chalcopyrite, except at relatively high additions. Sodium cyanide is a good chalcopyrite depressant at higher additions (i.e. >100 g/t) and a pH between 8 and 11. Large quantities of hydrosulfide (NaHS) or Na$_2$S depress chalcopyrite. This phenomenon is utilized for separation of molybdenum from chalcopyrite.

Bornite, Cu$_3$FeS$_3$ (Cu, 55.5%; Fe, 16.4%; S, 28.1%; hardness, 3; specific gravity, 5.1). Most often in ores, bornite is represented as a secondary copper mineral, together with
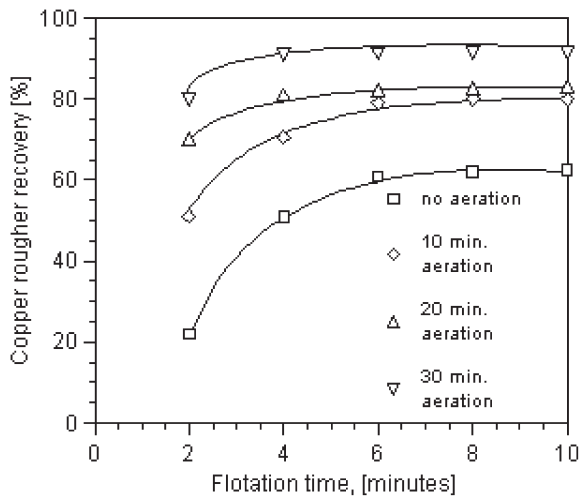
Figure 12.1 Effect of aeration on the rate of copper flotation.

chalcopyrite and chalcosine, mainly in porphyry copper–molybdenum and copper–gold ores. Bornite is relatively stable and does not oxidize. Its floatability depends very much on the size. Fine bornite (<20 μm) does not float readily and this may represent a significant problem during beneficiation of disseminated sulfides where the bornite is present. Floatability of bornite is also pH related, where at a pH >10 its floatability improves greatly. Mercaptobenothiozoles and trithiocarbonates, together with xanthates with higher carbon, are good bornite collector combinations.

Covellite, CuS (Cu, 64.44%; S, 35.56%; hardness, 1–2; specific gravity, 4.5). Covellite is a secondary copper mineral often present in copper–gold porphyry (Batu Hijau, Indonesia), copper scarns (Antamina, Peru) and massive copper ores from volcanogenic formation (Basin Bor, Yugoslavia). Covellite is a brittle mineral and tends to slime during grinding operations. When present in massive sulfides, it represents a significant separation problem. Thionocarbamate in combination with xanthate floats bornite well in alkaline pH (i.e. >11.0). The use of cresol-type reagents may be beneficial for flotation of covellite. Cresol was used for many years as a co-collector in the Basin Bor concentrator (Yugoslavia).

Additions of small quantities of Na_2S, (i.e. 200–400 g/t) improves the floatability of bornite. Tannic acid derivatives (quebracho) and lignin sulfonates do not depress covellite; therefore, in the treatment of massive sulfide ores that contain covellite, these reagents were used for the depression of pyrite at high pH (>11.5).

Chalcosine, Cu₂S (Cu, 79.83%; S, 20.17%; hardness, 2–3; specific gravity, 5.5). In many porphyry copper and copper–molybdenum ores, chalcosine is a primary mineral. Chalcopyrite, bornite and covellite in these deposits are the secondary copper minerals. Chalcosine may also be a secondary mineral with chalcopyrite and bornite depending on the way it is formed. The chalcosine in hydrothermal and volcanogenic deposits is formed by a reaction of copper sulfate and pyrite:

$$5FeS_2 + 14CuSO_4 + 12H_2O \rightarrow 7Cu_2S + 5FeSO_4 + 12H_2SO_4$$
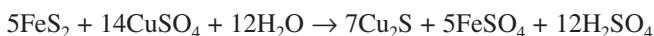
This reaction is characteristic of the secondary zones of formation of a copper ore body. Chalcosine may partially or completely transform into malachite, azurite, chalcocite, etc. and therefore in many porphyry deposits, zones of oxide copper are present.

As a covellite, chalcosine tends to slime during grinding, which is one of the main problems associated with the treatment of ores that contain chalcosine as the primary copper mineral. Chalcosine floats well with xanthate collector with dithiophosphate or thionocarbamate as secondary collector. Almost all operations treating porphyry ores that contain chalcosine use secondary collectors together with xanthate. Cyanide is a poor chalcosine depressant and even at high addition rates does not depress chalcosine. Sulfur-containing reagents, such as NaHS and Na_2S are good chalcosine depressants. At relatively low pH (i.e. 4–6) chalcosine can be depressed with some organic acids.

Enargite, Cu_3AsS_4; tennantite, $3CuS_2S \cdot As_2S_3$ and tetrahedrite, $3C_2S \cdot Sb_2S_3$ as individual minerals do not have significant economic value, although a fairly large deposit of the ores that contain enargite are known (Cerro Depasco, Peru). The enargite deposits that contain gold (El Indio, Chile) have been in operation for 15 years. High selenium enargite was mined in the 1980s in Copper Bor, Yugoslavia. Enargite, tennantite and tetrahedrite are usually secondary minerals to other copper sulfides. Flotation properties of these minerals are not well understood due to the fact that these properties were not studied.

From laboratory and plant data, enargite has flotation properties similar to chalcosine. Tennantite and tetrahedrite do not respond well to flotation using xanthate collector. Tetrahedrite floats well with aerophine and mercaptan collectors at pH between 8 and 10. Gold-containing enargite was successfully floated with xanthate + dithiophosphate (El Indio, Chile) at a pH between 8 and 10. Enargite also floats well with thionocarbamate and mercaptans at low pH (i.e. 5–7).

Native copper (Cu, 100%). Native copper appears in a number of copper–gold sulfide ores (Chemex, South Canada; Igarape Bahia, Brazil; Nephton, Canada; Kamoto Mine, Zaire) as a secondary mineral or as primary copper mineral (White Pine, USA). Depending on the grinding method used, native copper can assume many different shapes (wire, plates, balls, etc.). In a number of operations, a portion of native copper is recovered by screening (Afton, Canada; White Pine, USA) and the finer fractions are floated. Floatability of native copper depends on the shape of the mineral after grinding. The wire shape is the least floatable, while the flakes respond well to xanthate flotation at a pH of 9–11. A pH <9 has a negative effect on the floatability of native copper. The use of Na_2S has a positive effect on native copper flotation and it is known that additions of 100–500 g/t improved native copper significantly.

Pyrite, FeS_2 (Fe, 46.6%; S, 53.4%; hardness, 6; specific gravity, 5) is the most abundant sulfide in virtually all types of ores. This is one of the most studied minerals and yet the most problematic, interfering mineral – not only in flotation of copper ores but also in the flotation of virtually all sulfide ores. In many ores, pyrite can appear in many varieties, some of which are crystalline pyrite, isomorphous pyrite, altered, oxidized, pre-activated, etc. Pre-activated pyrite comes from the impurities in the pyrite crystal structure or as micron-sized impurity of silver minerals, copper, cobalt, nickel, etc.

Pyrite is readily oxidized, which is associated with pyrite crystallography and its crystal structure. Thus, the sulfur ions in a pyrite structure are usually paved and form $[S_2]^{2-}$; with large distance as compared with iron cations. As a result, it is often the

case that pyrite may contain elemental sulfur on its surfaces, which forms according to the reaction:

$$FeS_2 \rightarrow FeS + S$$
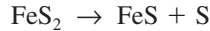
Elemental sulfur on pyrite surfaces makes pyrite highly floatable. During the grinding of natural ores, pyrite uptakes oxygen, which reacts with pyrite surfaces forming different sulfur-containing compounds depending on the pulp pH. In alkaline pH, it forms SO_4 ions, which in an acid pH form S_2O_3.

Pyrite belongs to a group of highly floatable minerals and can be effectively floated in the presence of a frother only. However, it should be pointed out that the floatability of pyrite, as well as hydrophobicity (depression), largely depends on the temperature under which pyrite is formed. For example, pyrite formed under low temperature (i.e. well crystalline pyrite) is less floatable than pyrite formed at a higher temperature. In the case of porphyry copper ores and low pyrite sulfide ores, the pyrite mainly contains impurities consisting of copper, gold and silver. Rejection of this pyrite is achieved at high alkaline pH (i.e. >11.5). In general, the depression of pyrite and selection of depressants largely depends on the type of ore treated. Some of the depressant systems for pyrite will be discussed in the following chapters.

One of the very important characteristics of pyrite is that in an alkaline pH, pyrite is well depressed and in an acid pH, the floatability of pyrite improves significantly. In an alkaline pH, secondary depressants such as organic compounds, sulfates and cyanide are quite effective. Successful pyrite depression is very much dependent on the ability of the pyrite to oxidize quickly. As a result of this oxidation, the iron hydroxide $Fe(OH)_3$ is formed on the surface of the pyrite, which increases hydration of the minerals and reduces adsorption of the collector.

Pyrrhotite, Fe_nS_{n+1} (Fe, 60%; S, 40%; hardness, 3.5; specific gravity, 4.5). There are two types of pyrrhotite commonly present in massive copper sulfide ores. These are (a) hexagonal pyrrhotite, which in flotation behaves similar to altered pyrite and (b) monoclinic pyrrhotite, which is highly reactive and extremely difficult to reject during flotation of copper minerals. Most often, pyrrhotite contains nickel, cobalt, copper and platinum, which replace iron. Pyrrhotite is a highly reactive mineral. It oxidizes rapidly forming sulfur anion in solution.

Pyrrhotite also uptakes oxygen rapidly and during flotation of copper from pyrrhotite-containing ores, does not float until the pyrrhotite completely oxidizes and free oxygen appears in the pulp. Figure 12.2 shows the effect of aeration on copper flotation from two pyrrhotite ores.

Pyrrhotite can be easily activated by copper cations and when soluble copper is present in the ore pyrrhotite, depression becomes very difficult. Activated pyrrhotite with copper ions floats without the addition of collector. Deactivation of pyrrhotite, activated with copper ions, can be achieved at a pH of about 4.5. At this pH, floatability of pyrrhotite is significantly reduced.

Marcasite has the same chemical composition as pyrite, but different crystal structure (rhomboidal) with a specific gravity of 4.8. Marcasite is usually found in hydrothermal sulfide copper ores and is formed at a much lower temperature than pyrite. Marcasite contains
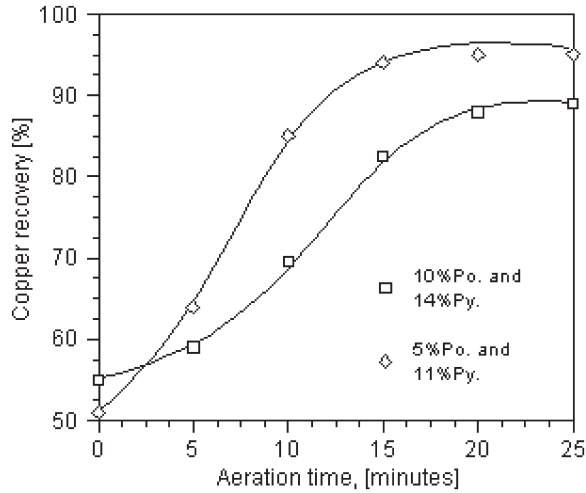
Figure 12.2 Effect of aeration on copper flotation from copper–pyrrhotite ores [9].

impurities such as thallium, arsenic and antimony. Marcasite has a greater floatability than pyrite and depression with cyanide in alkaline pH is quite difficult, even at higher cyanide additions. The floatability of marcasite is reduced at a pH between 4.5 and 6.5 and depression in this pH region is effectively achieved using ZnO/NaCN complex [10].

12.4 FLOTATION PRACTICE IN BENEFICIATION OF COPPER AND COPPER–MOLYBDENUM ORES

The selection of reagent scheme and flowsheet used in actual plant practice is usually dictated by the nature and mineralogy of the ore, type of minerals present, flotation behavior of gangue minerals, amount and occurrence of pyrite in the ore and the presence of clay minerals in the ore.

Some regions where porphyry copper deposits are located (Chile; Arizona, USA) have very similar operating practices regardless of the differences in ore characteristics. For example, there is a striking similarity in operating practices of a number of Chilean plants where few changes in the reagent scheme have been made in the past two decades [4], in spite of the fact that the ore mineralogy has changed, resulting in a decline in metallurgy. Changes in metallurgy due to change in mineralogy have been evident in many operating plants around the world, especially with a decline in ore grade. In many instances, the metallurgy in these plants has not been corrected. There are two principal reasons for this:

- Research laboratories of many corporations are either closed or reduced to a minimum as cost-saving measures; so plant support laboratories do not exist or are not capable of providing solutions for the decline in plant metallurgy.
- In modern mineral processing practice, emphasis is placed on the development and application of new, large equipment such as columns, large flotation equipment and

large grinding equipment. Large flotation cells (or other equipment) are not designed to improve metallurgy, but rather to reduce capital and operating costs. In fact, it has not yet been positively established what effect large ($100~m^3$) cells have on floatability. So far, it is known that in the case of large-scale equipment, the concentrate pulling rate per square meter is several times lower than that of the smaller flotation cells.

Development of new reagents, however, has advanced at a much slower pace than that of equipment. Therefore, there is a wide gap between progress in the development of mineral processing equipment and mining chemicals.

It should be noted that most operating plants treating porphyry copper and copper molybdenum ores are very large, treating between 20,000 and 150,000 tpd of ore where the emphasis is placed on coarser grinding regardless of the fine-grinding requirement. There is no collector designed for coarse middling particles. However, the conditions for such a goal can be created, with combinations of reagents and operating conditions. It is well established that in actual plant practice, the proper selection of modifier, collector, frother, as well as operating parameters (i.e. pH, pulp density, etc.) are the key in providing an efficient treatment process.

12.4.1   Effect of grinding on metallurgy

In a large number of the older operating plants that use conventional rod mill/ball mill grinding, there is a tendency to convert the conventional grinding circuits into an SAG mill/ball mill grinding configuration. All the new plants are using the SAG mill/ball mill circuit. A typical SAG mill/ball mill circuit is shown in Figure 12.3. Some plants have an SAG mill grinding circuit configuration somewhat different from that shown in the flowsheet in Figure 12.3. The design of the grinding circuit flowsheet is dictated by the hardness of the ore, and the ore treated using the flowsheet in Figure 12.4 has a relatively high SAG mill work index. The design of this type of flowsheet results in reduced power consumption, but difficulties in maintaining a constant.
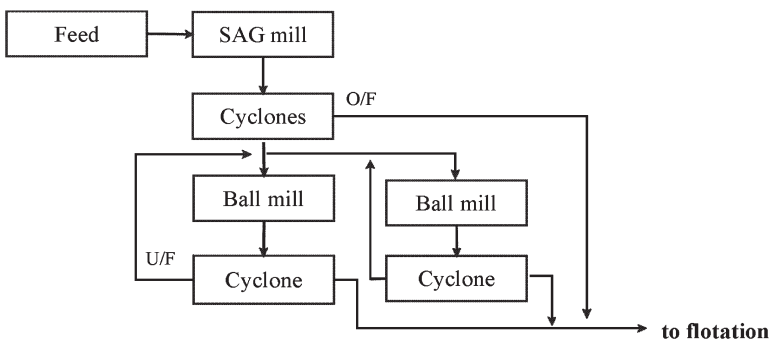
Figure 12.3 Typical porphyry copper ore grinding circuit.

Figure 12.4   Flowsheet used for the treatment of hard ore with a work index of 14–18.

Table 12.4

Grinding circuit data from selected plants.

Concentrator	Type of grinding circuit	Operating work index range, metric	Grinding	
			% <74 μm	K_{80} (μτm)
El Salvador, Chile	Ball mill/rod mill	12.5–14	48	214
Chuquicamata, Chile	Ball mill/rod mill (old)	12–14	38	320
	SAG mill/ball mill (new)	13–16	40	300
El Teniente, Chile				
Colon	SAG mill/ball mill	13–14	46	180
Sewell	SAG mill/ball mill	12–13	48	175
Disputada, Chile	SAG mill/ball mill	12 –13	52	160
El Cobre, Chile	SAG mill/rod mill/ball mill	14–16	55	140
Escondida, Chile	SAG mill/ball mill	12–16	50	160
Bouganville				
Papua New Guinea	Ball mill/ball mill	11–13	44	175
Mount Isa, Australia	Rod mill/ball mill	12–13	50	160
Acadia Hill, Australia	SAG mill/ball mill	13–14	52	140
Toquepala, Peru	Sag mill/ball mill	12–16	40	300
Rokano, Zambia	Rod mill/ball mill	11–13	65	120
Batu Hijau, Indonesia	SAG mill/ball mill	12–13	48	180

In most porphyry deposits, the hardness of the ore varies considerably and the work index of porphyry ores is much higher than that of sulfide ores. Therefore, the tendency is to grind coarser in spite of the fact that a coarser grind contains an appreciable amount of middling particles. Some grinding circuit data is shown in Table 12.4.

In many operations, the fineness of grind is not stable and this instability is influenced by the following factors:

- Variation in hardness of ore within the ore body.
- High pulp viscosity caused by the presence of clay minerals, which reduces both grindability and flotation efficiency.
- Insufficient circuit control.

It is obvious that the grinding performance significantly affects metallurgical results. Perhaps the most influential factor is the preferential grinding of different copper minerals according to their hardness. In spite of the fact that the average grind size may be relatively coarse, according to the plant data shown in Table 12.4, between 40% and 60% of the total copper in the feed is frequently in the <44-µm fraction. This is due to the fact that the heavier minerals of the copper concentrate are found in the cyclone underflow and consequently are over ground. The rate of copper flotation is reduced at smaller size fractions. Some copper is also contained in the coarser fraction where copper recovery from these fractions averages less than 50%. The copper recovery in the size fraction from selected concentrates is shown in Figure 12.5.

A similar trend can be found in many operating plants. Copper distribution in flotation feed from some concentrators is shown in Table 12.5. The table also gives the liberation profile of copper in the individual size fractions. The copper losses in the flotation tailings of many plants are even distributed between the coarse fractions (>200 µm) and the fine fractions (<20 µm).
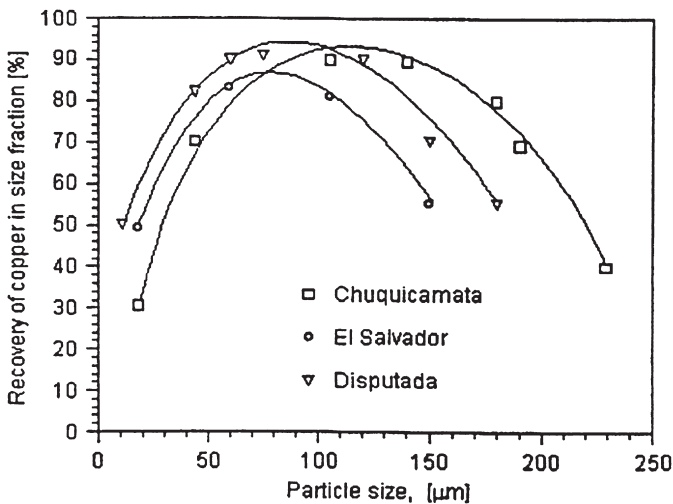
Figure 12.5 Copper recovery in size fraction from different concentrators.

Table 12.5

Copper distribution by size fraction and copper liberation profile in the Chuquicamata and
El Teniente flotation feed (Chile)

Chuquicamata flotation feed				El Teniente Sewell flotation feed			
Particle size	Assay % Cu	% Distri- bution Cu	% Cu liberated	Particle size	Assay % Cu	% Distri- bution Cu	% Cu liberated
(μm)				(μm)			
+48	0.44	6.60	11	+48	0.52	5.37	14
+65–48	0.48	10.30	22	+65	0.61	7.44	28
+100–65	0.66	13.30	40	+100	0.75	8.06	49
+150–100	0.80	7.14	75	+150	1.00	9.61	77
+200–150	1.38	6.50	82	+200	1.52	8.16	86
+270–200	2.01	5.70	84	+270	1.95	5.58	88
+325–270	1.99	5.61	90	+325	2.05	4.34	89
−325	1.33	44.85	93	−325	1.42	51.44	92
Total	1.18	100.00	—	Total	1.27	100.00	—

12.4.2 Reagent schemes in flotation of porphyry copper and copper–molybdenum ores

Reagent schemes used for the treatment of porphyry copper and copper–molybdenum ores are relatively simple and usually involve lime as a modifier, xanthate as the primary collector and a secondary collector. The secondary collector type varies from operation to operation and is selected from a variety of collectors including dithiophosphates, mercaptans, thionocarbamates, xanthogen formates, etc.

The choice of secondary collector depends on a relatively large number of factors, some of which include (a) type of copper minerals present in the ore (i.e. single copper mineral or varieties), (b) composition of gangue minerals in the ore, (c) the presence and type of clay minerals and (d) type of frother used.

There is a wide variation in the selection of the type of frother, and in many operating plants a mixture of two or more frothers are used. The main reason for this is interference from clay minerals, which in some cases tend to produce a dry froth and therefore difficult to remove. A mixture of frothers may solve this problem. In some cases, an alcohol-type of frother may give a brittle froth, which is also difficult to remove from the cell.

Choice of modifiers and their effect on flotation

In most operating plants, lime is used as a pH modifier as well as for the depression of pyrite during the cleaning operation. Only in a small number of plants, an alternative pyrite depressant is used. The flotation pH in the majority of plants is above 10 and most often over 11. The relatively high pH used in operating plants is not designed to depress pyrite,
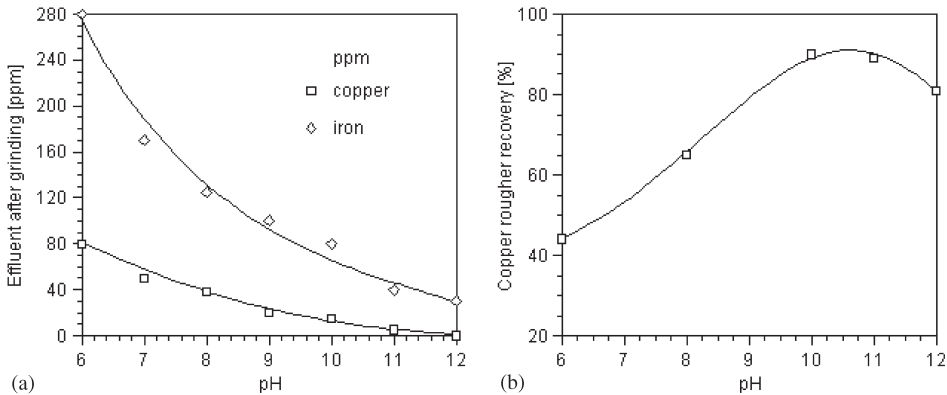
Figure 12.6 Effect of pH on copper rougher recovery.

but rather as a frother modifier. In reality, the higher pH produces a stable froth with better carrying power than at a lower pH, for the majority of porphyry copper ores.

In other instances where soluble cations (i.e. Cu^{2+}, Fe^{2+}) are present in the pulp, they are precipitated at a high pH, which may result in improved collector adsorption. Figure 12.6a shows copper and iron concentrations in the flotation pulp and copper recovery as a function of pH.

These results were achieved with xanthate + dithiophosphate collectors.

Experimental test work conducted at a number of plant laboratories, as well as plant trials at different pH [11,12,13] has pointed out two major factors that dictate the amount of lime used:

- The floatability of copper at different pH is related to the type of frother used. With certain frothers, copper recovery can be significantly increased at a lower pH range, while some frothers require a higher pH to retain a more lasting frothing power.
- The floatability of middling particles (i.e. >200 μm) improves with increased pH. Table 12.6 shows copper recovery in the plus 150 μm fraction as a function of pH.

This indicates that middling and coarse particles improved floatability at a higher pH region. This is true in the case where copper is represented by chalcosine as the major copper mineral. In the case of chalcopyrite ore, a lower pH is more desirable (i.e. 8.5–9.5) because at a higher pH, the floatability of chalcopyrite is reduced, especially the coarser particles.

Lime is also used as a pyrite depressant during copper cleaning operations. In the majority of plants, most of the pyrite reports to the rougher concentrate mainly because a portion of the copper is associated with pyrite at a coarser size or the pyrite is pre-activated with copper cations.

Depression of pyrite in the case of porphyry ores containing chalcosine occurs at a relatively high pH (i.e. >11.5), while in the case of chalcopyrite, the pH is maintained at about 10.5–11. Lime is not always effective as a pyrite depressant and in many operations,

Table 12.6

Effect of pH on recovery of copper in >150 μm fractions and overall copper rougher recovery
(Chuquicamata mill feed ore)

pH	Lime	Feed		>150 μm fraction		Total rougher concentrate	
	additions (g/t)	Assay % Cu	Grind K_{80} (μm)	Assay % Cu	% Recovered Cu	Assay % Cu	% Recovered Cu
8	150	1.12	305	11.5	20.2	14.2	70.5
9	480	1.14	302	10.1	33.5	13.1	75.2
10	800	1.14	305	9.2	38.3	12.2	88.0
11	1200	1.13	303	8.5	55.4	10.0	92.1

□   CaO 900 g/t, HQS nil, pH 10.5   ▽   CaO nil, HQS 200 g/t, pH 8.8
○   CaO 1300 g/t, HQS nil, pH 11.5   ç   CaO nil, HQS 400 g/t, pH8.8
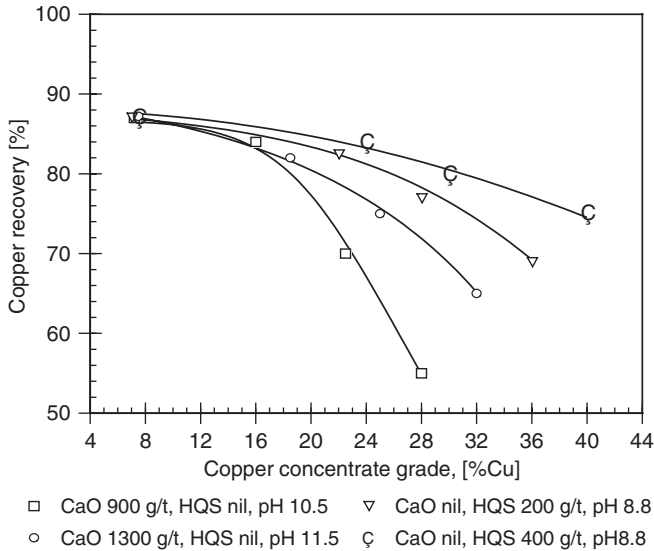
Figure 12.7 Effect of lime and HQS depressant on copper cleaning.

treating chalcosine ore does not exceed 29% Cu. One of the reasons for this lower grade
may be insufficient liberation during re-grind, but most often the problem lies with effi-
cient depression of pyrite.

There are a number of alternative depressants, which have been proven effective in the
depression of pyrite [14,15], some of which include oxidized starches and HQS mixture.
This depressant is a mixture of sodium silicate (Na_2SiO_3), sodium phosphate mono-basic
(NaH_2PO_4) and quebracho in a ratio of 40:40:20. The effectiveness of this depressant is
examined on the El Salvador ore (Chile), which contains preactivated pyrite. Figure 12.7
shows the effect of HQS on copper cleaning. Only small quantities of this depressant can
result in a significant increase in concentrate grade.

Oxidized starches and dextrins are also effective pyrite depressants during upgradation of the rougher concentrate. Oxidized starches are also used in operating plants for pyrite depression. The starch or dextrin is usually added to the re-grinding and during the cleaning operations.

Choice of collector

In most porphyry copper and copper molybdenum operations, xanthate is used as the primary collector, while a variety of secondary collectors are used including dithiophosphates, xanthogen formates, thionocarbamates, xanthic esters and mercaptobenzothiazole. In some cases, only dithiophosphate collectors are used. There is no general rule by which secondary collectors are selected. There are, however, several factors that influence the selection of this collector. These include:

- *The presence of clay minerals in the ore*. When clay minerals are present, mercaptans or dithiophosphates are beneficial for recovery of both copper and molybdenum.
- *The type of copper minerals*. If a mixture of two or more copper minerals is present in the ore (i.e. chalcocite, covellite, chalcopyrite), then thionocarbamate, together with xanthate, is the most effective collector combination. Thionocarbamate, however, is a poor collector for molybdenite and in this case, a small amount of fuel oil is added to the grinding stage to aid molybdenum recovery.
- *The presence of middlings*. One of the most effective collectors [16] for the flotation of middling particles is a combination of xanthogen formate and mercaptan. Xanthogen formate is used as a primary collector and is usually added to the grinding mills.
- *The type of frother used* also plays an important role in selection of a collector. Many porphyry copper plants have a frothing problem and because of this, the usual tendency is to use collectors with frothing properties. Table 12.7 lists reagent schemes according to the type of copper minerals and ore gangue compositions.

Since in actual practice, relatively coarse grinds are used, the proper selection of collector combinations is extremely important for the flotation of coarse and middling

Table 12.7

Reagent schemes for porphyry copper and copper molybdenum ores based on ore composition

Collector combinations	Copper minerals	Ore composition
1. PAX, thionocarbamate, fuel oil	Cp, Mo	Arkose, silicate, limestone
2. KEX, dithiophosphate	Cp, Bo	Quartz, feldspar, magnetite
3. PAX, mercaptan	Cp, Bo	Quartz, calcite, chlorite
4. KAX, SIPX, fuel oil	Cp, Mo	Quartz, diorite, feldspar, biotite
5. PAX, xanthogen formate	Cc, Cp, Bo	Quartz, complex aluminosilicates
6. Thionocarbamate, dithiophosphate	Cp, Bo, Cov	Feldspars, silicates
7. PIBX, dithiophosphate	Bo, Cc	Silicates
8. PAX, fuel oil, thionocarbamate	Cc, Mo, Cp	Andesite, diorite
9. Dithiophosphate, mercaptan, fuel oil	Cc, Mo	

particles. Even with a coarse grind, fine copper is also created because of the tendency of heavy sulfides to concentrate in the cyclone underflow and, consequently, over grind. In many operating plants, about 50% of the total copper is lost in the tailing in the form of fine copper (i.e. <20 μm size).

Frothers

One of the most difficult tasks is the selection of a proper frother. Its importance has not always been recognized, despite the fact that many operating plants treating porphyry copper ores use two or more frothers. Frequently, a frother is not powerful enough to recover coarse middlings or is not selective enough to float fine copper. In the literature [17], seven basic requirements for a good flotation frother have been listed, which also include low sensitivity to changes in pH and dissolved salt content. However, very often in porphyry copper flotation, the frothing is generally controlled by pH. The presence of clay in the ore is the main reason for unstable froths and reduced frothing power.

It has been demonstrated that destabilization of frother occurs in the presence of ultrafine particles; thus the reduction in flotation may occur [18]. It is common practice that during flotation of porphyry copper ores containing clay minerals, the copper froth becomes highly flocculated after xanthate collector additions, resulting in dry froth that is difficult to remove. To prevent froth dryness, a collector with frothing properties in combination with two or more frothers is used.

Recent studies [19] have indicated that the stability of the froth may be more effectively controlled by modifying or preventing flocculation of hydrophobic particles. The reagents that control frothing properties in the lower pH region are certain amine oxides, which if added to an alcohol or alkoxy paraffin frother, are able to reduce the detrimental effect of ultra-fine clay minerals on froth stability. These frother mixtures are known as the HP series of frothers [20]. Studies have shown that the use of these frother mixtures can result in a significant improvement in the rate of copper flotation. Figure 12.8 shows the effect of the HP frothers on the rate of copper flotation from ores containing illite clay minerals.

Table 12.8 lists some of the frothers typically used in the flotation of porphyry copper and copper molybdenum ores. The data shown in Table 12.8 are composed from plant data.
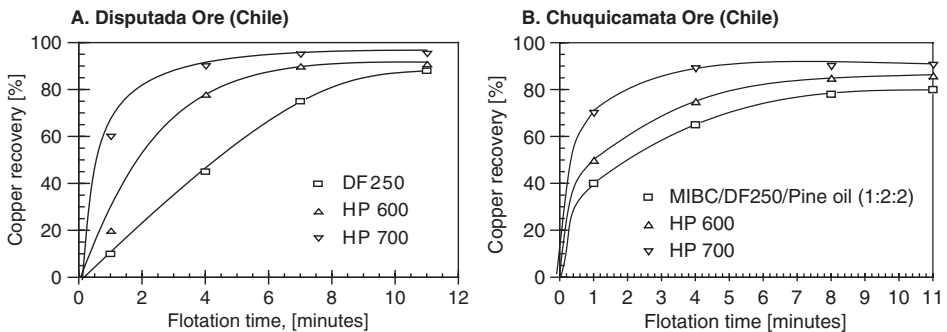
Figure 12.8 Effect of different frothers on the rate of copper flotation from an illite clay-containing ore.

Table 12.8

Frother combinations used in clay-containing porphyry copper ores

Type of clay, rock ID	Frother used	Flotation pH
Kaolin, quartz porphyry	Pine Oil:MIBC:Dow 250 = 2:1:2	9.5–10.0
Illite, kaolin	Dow 250:MIBC = 2:1 or HP700	9.0–10.0
Quartz/andesite	MIBC:TEB = 1:2	
Montmorilonite, illite	Pine Oil:TEB:MIBC = 2:2:1	7.5–8.5
Andesite, supergene	HP700 or HP600	
Charmosite, illite	Dow 250:MIBC	8.5–9.5
Andesite	Dow 1012:41G:MIBC = 1:2:1	
Bramollite, kaolinite	TEB:41G:MIBC = 1:1:2	9.0–10.0
Quartz/andesite	Dow 1012:MIBC = 1:2	

Note: TEB, 41G = alkoxy paraffin, pine oil, MIBC = alcohols, Dow 250, Dow 1012 = glycols, HP700, HP600 = alcohols in amine oxide.

It should be remembered that in may cases when certain clay types are present in the ore, the frothing properties, as well as floatability of different particle sizes, is pH-dependent. Certain types of clay at higher pH would increase pulp viscosity dramatically, which in turn reduces frothing properties and increases the transfer of fine particles into the froth, and in such cases, low pH flotation is desirable and therefore an appropriate frother has to be selected.

12.4.3   Molybdenum flotation and separation from porphyry copper molybdenum ores

Approximately 50% of the world's molybdenum production comes from copper–molybdenum ore as a by-product. The floatability of molybdenum during copper flotation also depends on many factors, including type of collector, type of frother, flotation pH and type of hydrocarbon oil used. During the flotation of copper molybdenum ores, fuel oil or kerosene is added to the grinding to enhance molybdenum recovery. In some cases, both kerosene and fuel oil interferes with frothing and very often addition of hydrocarbon is usually avoided. Instead, the hydrocarbon oils are usually added to the copper–molybdenum separation stage.

The effect of various hydrocarbon oils was extensively studied in both copper–moly bulk flotation and co pper–moly separation [21–23]. From these studies, several important conclusions can be drawn:

- The high viscosity oils, such as Cornea 21, Sunray DX Vapor oil and Texaco No. 539, gave high molybdenum recovery with slightly lower MoS_2 recovery than those obtained with low-viscosity oils. In contrast, low-viscosity oils gave lower recoveries than the high viscosity oils but at a somewhat higher concentrate grade. Table 12.9 shows the effect of the type of oil on molybdenum rougher concentrate grade and recovery.

Table 12.9

Effect of type of oil on molybdenum rougher concentrate grade and recovery – oil additions 80 g/t of concentrate

Oil type	Viscosity C St. at 35 °C	% Assays MoS_2	% Recovery MoS_2
Kerosene	1.32	14.1	81
Store oil	1.85	10.2	84
Royalite flotation oil	1.85	11.3	84
E407 solvent	1.87	11.0	83
Dieseline	2.23	12.8	83
Light furnace oil	3.39	11.0	84
Untreated CCLGO	3.39	10.8	85
Pella 911	7.23	11.4	86
Ondina 17	16.70	8.8	89
Carnea 21	22.00	10.1	87
Sunray DX vapor oil	22.00	11.3	86
Texaco No. 539	22.20	11.1	86
100/100 motor stock	22.30	11.0	86
100/100 HVI pale	22.90	9.8	87
50:50 light furnace oil	17.50	10.3	87
90/210 pale oil	17.90	10.5	88
50/50 light furnace oil mix	18.80	9.1	86
L50/210 HVI bight stock	24.90	8.4	91

- Molybdenum recovery, in both bulk Cu–Mo concentrate and the MoS_2 separation, depends very much on the type of frother used. Operating plant data, as well as laboratory studies, have indicated that aromatic alcohols (i.e. pine oil) and alkoxy paraffin gave better MoS_2 recovery than straight alcohol (MIBC) or glycol.

During copper–molybdenum separation, using straight oil creates a dry, collapsing froth. The use of emulsifier improved molybdenum recovery significantly. An emulsifier such as sulfated coconut oil (Artic Sintex L) with the following formula:

$$H–C–O–C–C_{11}H_{23}$$
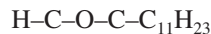
has been used extensively in a number of operating plants. Other suitable emulsifiers are different lauryl sulfates ($C_{12}–H_{23}–SO_4–Me$). The advantage of Syntex as an emulsifier is that it does not react with pulp ions like the lauryl sulfates, which makes it more stable and usually results in improved molybdenum recovery during Cu–MoS_2 separation.

Copper–molybdenum separation may be considered as a relatively complex process and usually depends on the nature and composition of the bulk Cu–MoS_2 concentrates. Some of the major parameters that affect selection of Cu–MoS_2 bulk separation techniques include the following:

- *Type of collector used in Cu/MoS$_2$ bulk flotation*. If xanthate is used, only as a Cu–MoS_2 bulk collector, then desorption of the collector from the mineral surface is achieved with

either Na_2S or NaHS. This is not the case if dithiophosphate or thionocarbamate collectors are used. Desorption of those collectors using Na_2S or NaHS cannot be accomplished and, consequently, an alternative $Cu–MoS_2$ separation technique is used.

- *Type of copper minerals present in the bulk concentrate*. In case chalcopyrite is present as a primary copper mineral, the separation method involves the Na_2S or NaHS method. If the copper concentrate is chalcocite or other minerals such as bornite, covellite, digenite, etc., then another available separation method is used.
- *Impurities content of the bulk concentrate* also plays an important role in the selection of Co/MoS_2 separation method. The bulk concentrate may contain impurities such as gold, silver, zinc and floatable non-sulfide gangue. To reject these impurities, different depressants are used.

There are a number of $Cu–MoS_2$ separation methods available and have been practiced in operating plants for a number of years. Table 12.10 lists some of the most important separation methods that are practiced extensively in industrial practice.

Table 12.10

Copper–molybdenum separation methods

| Method	Description
Roasting method	Oxidizing roasting of $Cu–MoS_2$ bulk concentrate at temperatures of 250–450 °C. The roasted concentrate is repulped and the molybdenum floated using oil + frother. In some cases, the siliceous gangue is floated ahead of the molybdenum using a cationic collector. This is also known as the "Utah Process"
Steam treatment	The $Cu–MoS_2$ is thickened to 45–65% solids. The thickened pulp is conditioned with lime to a pH of 11–11.5 for about 30 min–1 h, followed by steam treatment for between 1 and 4 h. The pulp temperature is maintained near boiling. After heating, the pulp is further aerated (cooling stage) until the temperature reaches 30–35 °C. After aeration, the pulp is diluted to 15–25% solids and the molybdenum is floated using frother and oil and cleaned to grade. Another variation of this procedure is that the MoS_2 rougher concentrate is dried and roasted to 300–400 °C and then the MoS_2 is refloated
Ferrocyanide method, $Na_4Fe(CN)_6$	There are several varieties of this method, which have evolved from the basic method and have been adopted for various plants. The basic method involves dewatering the concentrate, conditioning with oxidizing reagents followed by additions of ferrocyanide and flotation of MoS_2. The NaCN may also be added late in the cleaning stages. Other variations of the basic method include • Sodium hypochlorite or H_2O_2 + $Na_4Fe(CN)_6$ Sulfuric acid is also used for pH control. Exfoam 636 (polyglycol modified kerosene), fuel oil and frother are part of this reagent scheme

(Continued)

Table 12.10   (*Continued*)

Method	Description
	• Dichromate – $NH_4Fe(CN)_6$. In this case, H_2O_2 is replaced with $Na_2Cr_2O_7$ at acid pH. Zinc cyanide complex is part of the reagent scheme • $Na_4Fe(CN)_6$ + $(NH_4)_2S$ is used in cases where secondary copper minerals are present
Nokes method	1. Phosphate ORLR 744 – is a product of the reaction of P_2S_5 with NaOH. The bulk concentrate is dewatered before conditioning with LR744. Sometimes $(NH_4)_2S$ is used in the preconditioning. Sodium cyanide in the final cleaning stages is also used. In some cases, it is used with NaHS 2. Arsenic Nokes – is a reaction product of As_2O_3 and Na_2S. This depressant is used alone or in combination with NaCN or $K_4Fe(CN)_6$
Sulfide method	This method is the most widely used and involves dewatering of the concentrate before conditioning with Na_2S or NaHS. Other combinations used with this depressant include: • NaHS : $(NH_4)_2S$ = 80:20 or 85:15 • NaHS + $Na_2Cr_2O_7$ • NaHS + $NaZn(CN)_4$, NaCN • Steam + NaHS • Steam + Na_2S

The sulfide Cu–Mo separation process is primarily used in the case where chalcopyrite is the primary copper mineral. In some cases, on a mixture of chalcopyrite–bornite, Na_2S is used rather than NaHS.

The Nokes reagents are only used in a few plants and are now being replaced by other methods. The phosphate Nokes is produced by reacting P_2S_5 with NaOH:

$$P_2S_5 + 10NaOH \rightarrow Na_3PO_3S + 2Na_2S + 5H_2O$$
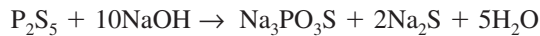
It is easily prepared, but involves a very dangerous operation as Na_2S gas is evolved and can be evolved copiously if the reaction runs away.

Arsenic Nokes (Anamol D) is prepared by reacting arsenic trioxide with Na_2S as per the following reaction:

$$As_2O_3 + 3NaS + 2H_2O \rightarrow Na_3AsO_2S_2 + NaAsO_3 + H^+$$

or
$$As_2O_3 + 3NaS + 2H_2O \rightarrow Na_3AsO_4 + Na_3AsOS_3 + H^+$$

It is believed that the depressant species are HS^-, sodium arsenate and a mixture of mono-di- and tri-thioarsenate. With Anamol D, the HS^- ions are more important as a

depressant than arsenic compounds, which may function only as an oxidation inhibitor. In the phosphate Nokes, there is little HS^- ion concentration, suggesting that the phosphorus compounds are responsible for the depression of sulfides.

In the literature, several other depressants are used during copper–molybdenum separation, some of which are worth mentioning. These are:

- The use of thioglycerol [24]. The thioglycerol $HSCH_2CH(OH)CH_2OH$ is used alone or in combination with other depressants.
- The use of chlorine xanthate with the formula $R_3N^+–CH_2–CH_2–O–C–S^-$ is described in reference [25]. This depressant has been used in several plants for a short period of time.

Other auxiliary processes also used in molybdenum upgrading and the removal of non-sulfide gangue involve MoS_2 depression and flotation of gangue using a cationic collector. Some of these depressants used include ammonium lignin sulfonate [26], or dextrin. Selective depression of MoS_2 is also accomplished with methylene blue [27].

In the separation of copper–molybdenum, conditioning time, pulp density and point of reagent additions are very important, and during the development of separation techniques these variables must always be taken into account.

12.4.4   Plant reagent scheme data and factors influencing plant metallurgy

The plant reagent data have changed significantly over the years as the ore grade and mineralogy have changed. Most of these changes were attributed to the use of different secondary collectors and frothers in the copper roughing and cleaning operation. In the molybdenum circuits, some changes in the use of separation techniques occurred over the past several years. Recently, new plants have been built and reagent schemes in some of these plants have already been changed.

Reagent scheme in the copper and copper–molybdenum bulk flotation

Table 12.11 shows plant operating conditions and reagent schemes for the most important porphyry copper and copper–molybdenum ores. The data for these plants were collected over the past several years (1995–1999). During this period, different types and lower grade ores have been treated and consequently the reagent schemes changed.

Some operating plants, during the treatment of supergene ore types as well as transition ore zones, use small quantities of $Na_2S \cdot 9H_2O$ or NaHS. This reagent is occasionally used. Almost all operations employ re-grinding of the rougher concentrate before cleaning. Lime is exclusively used as a pyrite depressant, and only a few plants use small quantities of cyanide in addition to lime, but only when chalcopyrite is present. Some plants use small quantities of starch or guar where the insol is a problem in the copper concentrate.

The most effective work conducted in an operating plant was by a chemical manufacturer, where various collectors and frothers were examined. These data are not available to the public and cannot be accessed.

Table 12.11a

Plant operating data

Plant	Major Cu minerals capacity (tpd)	Head assay %		Concentration assay %		% Recovery		Grind	
		Cu	MoS$_2$	Cu	MoS$_2$	Cu	MoS$_2$	% <200 mesh	K_{80} µm
Canada									
Gibraltar	60,000 Cp,Bo	0.28	0.01	30.0	85	80	35	60	145
Lornex	90,000 Cp,Bo	0.35	0.01	33.0	85	84	60	50	160
Gaspe	35,000 Cp,Cc,Cov	0.66	0.02	30.0	90	89	55	55	148
Island Copper	35,000 Cp	0.50	0.02	25.0	90	85	66	65	138
Brenda	24,000 Cp	0.20	0.03	25.0	90	78	82	40	220
Granisle Copper	18,000 Cp,Bo	0.43	–	25.0	–	85	–	60	150
USA									
Utah Copper	180,000 Cp,Bo,Cov	0.40	0.02	28	90	87	56	55	152
Sierrita	105,000 Cp	0.30	0.02	25	87	84	70	50	166
San Manuel	75,000 Cp,Cc	0.45	0.01	31	87	89	60	60	152
Morency	60,000 Cc,Bo	0.50	0.01	25	–	85	–	52	163
Butte	60,000 Cp,Cc	0.60	–	26	–	80	–	50	170
Pima	55,000 Cp,Cc	0.40	0.02	27	64	80	40	60	148
Pinto Valley	50,000 Cp	0.38	0.01	25	–	82	–	48	180
Twin Butte	30,000 Cp	0.50	0.02	28	73	76	35	52	165
Mineral Park	200,000 Cp,Cc	0.35	0.02	22	90	75	62	61	158
Baghdad	10,000 Cc	0.65	0.03	33	90	86	65	40	225
Peru (P) & Chile (C)									
South Copper (P)	80,000 Cp,Cc	1.1	0.02	30	87	85	38	55	170
El Salvador (C)	25,000 Cc	0.79	0.02	29	95	78	60	65	139
Escondida (C)	120,000 Cc	1.90	–	44	–	88	–	50	160
Disputada (C)	40,000 Cc,Cp	0.80	0.01	29	80	84	40	65	140
El Cobre (C)	18,000 Cc,Cp	1.70	0.05	28	–	85	–	60	148
El Teniente (C)									
Sewell & Colon	60,000 Cc,Cp	1.10	0.02	29	95	80	42	65	144
Andina	20,000 Cp	1.15	0.015	28	–	85	–	70	125
Chaluahuasi (C)	60,000 Cc	1.20	–	35	–	88	–	50	180
Pacific Rim Australia									
Acadia Hills	60,000 Cp	0.60	–	30	–	88	–	60	145
Mount Isa Copper	65,000 Cp	1.02	–	25	–	90	–	55	172
Dos Altos[a]	35,000 Cp	0.42	–	28	–	82	–	50	1.82
Philex[a]	30,000 Cp,Bo	0.35	–	25	–	90	–	55	158
Lepanto[a]	10,000 Cp	1.50	–	30	–	92	–	60	142
Stonino[a]	15,000 Cp	0.40	–	24	–	85	–	–	–
Mar Copper[a]	18,000 Cp	0.75	–	25	–	85	–	80	101

(*Continued*)

Table 12.11a   (*Continued*)

Plant	Major Cu minerals capacity (tpd)	Head assay %		Concen- tration assay %		% Recovery		Grind	
		Cu	MoS$_2$	Cu	MoS$_2$	Cu	MoS$_2$	% <200 µm mesh	K_{80} µm
Russia									
Balkhashi	40,000 Cp,Bo	0.40	0.015	24.0	85	85	40	60	143
Bozchshakul	18,000 Cp	0.58	0.020	18.0	75	78	56	50	178
Almalyk	50,000 Cp	0.50	0.01	19	85	77	40	45	190
Kadzharan	20,000 Cp	1.25	0.05	17	79	80	68	61	144
Agarak	12,000 Cp	1.50	0.02	18	81	79	75	70	118
Koundarskoie	30,000 Cp	1.10	0.015	18	83	88	66	66	138
Europe									
Majdanpek, Yug	15,000 Cp	0.77	0.005	26.5	–	85	–	50	169
Krivelj Bor	25,000 Cp	0.35	–	28	–	78	–	40	220
Medez Bulgaria	28,000 Cp	0.35	0.011	15	65	81	30	55	155
Africa									
Mufulira ZCCM	18,000 Bo,Cov	2.45	–	46.0	–	88	–	45	210
Palabora SA	80,000 Cp,Bo	0.55	–	32.5	–	83	–	52	170
Komoto, Congo Sulfide circuit	15,000 Cc,Bo	4.60	–	48.0	–	82	–	65	139

[a]Philippines.

Table 12.11b

Plant reagent scheme

Plant	Collectors	Frother	pH	
			Ro	Cl
Canada				
Gibraltar	Dithiophosphate, PAX	MIBC	10.5	11.1
Lornex	PAX, dithiophosphate, Fuel oil	Pine Oil	9.5	11.5
Gaspe	PAX, xanthogen formulate, Fuel oil	Pine Oil	10.0	10.5
Island Copper	SIBX	Dow 1012	10.5	11.2
Brenda	SIBX, xanthic ester	MIBC	8.0	8.5
Granisle Copper	PAX, xanthic ester	Dow 250	10.0	10.5
USA				
Utah Copper	Dithiophosphate, Fuel oil	Dow 250/MIBC	8.5	9.5
Sierrita	SIPX, xanthic ester, Fuel Oil	MIBC	11.0	11.5
San Manuel	Xanthogen formulate, thionocarbamate	MIBC	10.5	11.0
Morency	Thionocarbamate	Dow 250/MIBC	10.5	10.5

Table 12.11b   (*Continued*)

Plant	Collectors	Frother	pH	
			Ro	Cl
Butte	Thionocarbamate	Pine oil/MIBC	10.5	11.0
Pima	SAX, Fuel oil	MIBC/Dow 1012	11.5	11.5
Pinto Valley	NIBX, dithiophosphate	MIBC	11.5	11.5
Twin Butte	NIBX, dithiophosphate	X31/MIBC	11.0	11.5
Mineral Park	Thionocarbamate, xanthic ester	MIBC	11.5	11.5
Bagdad	PAX, Fuel oil	Pine oil/MIBC	11.5	11.5
Peru and Chile				
South Copper (P)	SIPX, dithiophosphate	Pine oil	11.5	11.8
El Salvador (C)	PAX, thionocarbamate	Teefroth TB/Pine oil	10.8	11.5
Escondida (C)	SIPX, mercaptan, xanthic ester	MIBC/Pine oil/Dow 1020	10.5	10.8
Disputada (C)	Dithiophosphate	Dow 250	10.0	10.5
El Cobre (C)	Dithiophosphate, mercaptan, PAX	MIBC/Dow 250	10.0	10.0
El Teniente (C)				
Sewell	Xanthogen formulate, Fuel oil	Dow 250	4.0	11.5
Colon	Xanthic ester, Fuel oil	Dow 250	11.0	11.5
Andina (C)	Thionocarbamate, Fuel oil	MIBC/Dow 250	9.0	9.5
Chaluahuasi (C)	SIPX, thionocarbamate	Pine oil/MIBC	10.5	10.5
Pacific Rim, Australia				
Acadia Hills	PAX, dithiophosphate	MIBC	10.0	10.5
Mount Isa Copper	PAX, dithiophosphate	MIBC	10.0	11.2
Dos Altos	KEX, dithiophosphate	41G	9.0	9.5
Philex	PAX, dithiophosphate, thionocarbamate	MIBC	8.5	9.0
Lepanto	Dithiophosphate, xanthogen formulate	MIBC	5.6	10.0
Stonino	NIBX	MIBC	8.5	10.5
Mar Copper	NIBX, thionocarbamate	MIBC	9.0	10.5
Russia				
Balkashi	SIPX, Fuel oil	Equivalent to Dow 250 or Dow 1012	11.5	12.0
Bozchshakul	SIPX, Fuel oil	MIBC	11.5	12.0
Almalyk	KEX, PAX mixture, Fuel oil emulsified	Pine oil	9.5	10.5
Kadzharan	KEX/PAX mixture, Fuel oil	Pine Oil	10.0	10.5
Agarak	PAX	Equivalent to Dow 250 or Dow 1012	9.0	10.0
Koundorskoie	KEX, xanthogen formulate	Equivalent to Dow 250 or Dow 1012	12.0	12.0
Europe				
Majdaupek, Yug.	PAX, dithiophosphate	MIBC	10.5	11.5
Krivelj Bor, Yug.	KEX, thionocarbamate, kresol	Dow 250	11.0	12.0
Medet, Bulgaria	KEX/SIPX mixture, Fuel oil	Pine Oil	10.0	10.5

(*Continued*)

Table 12.11b   (*Continued*)

Plant	Collectors	Frother	pH	
			Ro	Cl
Africa				
Mufulira ZCCM	SSBX, mercaptan	Sencol 1200	10.8	10.8
Palabora, SA	SIBX, thionocarbamate	TEB	7.5	8.0
Kamoto, Congo	SNBX, dithiophosphate	TEB	7.5	7.5
Sulfide circuit				

Reagent scheme used in the copper–molybdenum separation related to the presence and type of copper minerals

Table 12.12 shows the plant reagent scheme used in copper–molybdenum separation. The reagent scheme for Cu–Mo separation largely depends on (a) the type of copper minerals present, (b) type of reagent scheme used and (c) the presence of other impurities in the concentrate (i.e. insol, lead, zinc, precious metals, etc.). In operating plants where chalcocite is the predominant mineral, either ferrocyanide or Nokes reagents are used. In the case of chalcopyrite, either NaHS or Na_2S is practiced. Ferrocyanide or cyanide is also added in the later cleaning stages.

Most plants use leaching of the final MoS_2 concentrate. Leaching is conducted with cyanide or acid in the presence of ferrochloride.

Factors affecting reagent scheme selection

There are a number of factors that influence reagent scheme selection and also the performance of operating plants, some of which are summarized below:
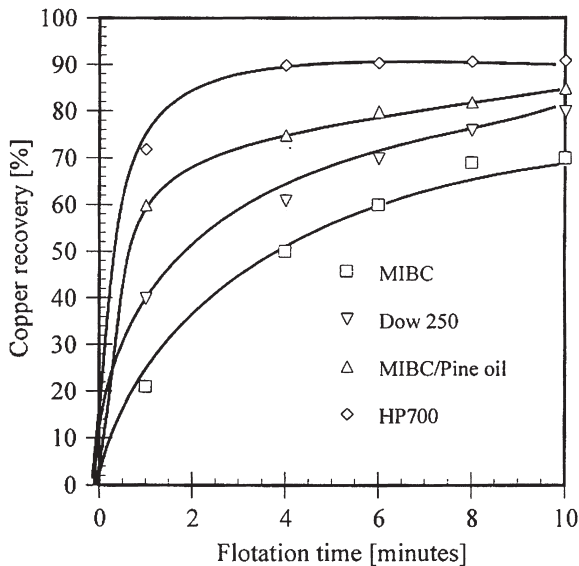
- Ore mineralogy and gangue composition play a decisive role in the selection of the reagent scheme and operating parameters in a plant. Ores, either normal or supergene-altered, that contain chalcocite require collector combinations different from hypogene ores that contain only chalcopyrite. Ores with mixed copper minerals (i.e. chalcopyrite, pyrite, bornite, etc.) would sometimes require the use of three collectors to obtain optimum metallurgy.
- The most detrimental factor for flotation is the presence of clay in the ore. The presence of clay in porphyry ores causes a loss in recovery, possibly due to the presence of slime coatings on mineral surfaces or on air bubbles. Clay increases reagent consumption and can create serious frothing (or non-frothing) problems. As a result, large quantities of slime are transferred into the concentrate during the roughing or scavenging stages. There are several possible ways of reducing the detrimental effect of clay slimes on flotation [28], some of which include (a) use of an alternative flowsheet, (b) flotation at reduced pulp density, (c) use of special frothers and (d) use of alternative modifiers.
- Depression of pyrite may also represent a significant problem in operating plants as well as in developing a reagent scheme research. In most plants, pyrite is depressed with lime at high pH. However, there are also a number of alternative depressants that

Table 12.12

Copper–molybdenum reagent scheme

Plant	Copper minerals	Thermal treatment	Primary depressant	Secondary depressant	Leach of concentrate
Canada					
Brenda	Cp	–	NaHS	–	Yes
Gaspe	Cp,Cov,Cc	Steam	NaHS	$Na_2(CrO_4)$	Yes
Iland Copper	Cp	–	NaHS	$Na_2Zn(CN)_4$, NaCN	Yes
Lornex	Cp,Bo	–	NaHS	–	Yes
Gibraltar	Cp,Bo	–	Na_2S	–	No
USA					
Utah	Bo,Co	Roasting	Utah process	NaCN, Nokes	Yes
Ray	Cp	Steam	$Na_4Fe(CN)_6$	Nokes	Yes
Chino	Cp	Steam, roasting	NaHS	Nokes	Yes
McGill	Cp	Steam	$Na_4Fe(CN)_6$	NaCN	Yes
Sierrita	Cp	Steam	Nokes	–	Yes
Mineral Park	Cp	–	$Na_4Fe(CN)_6$, NaOCl	–	Yes
Esperanza	Cp	Pressure oxidization	$Na_4Fe(CN)_6$	–	Yes
San Manuel	Cp/Cc	–	$Na_4Fe(CN)_6$, H_2O_2	$Na_2Zn(CN)_4$, H_2O_2	Yes
Mission	Cp	–	Na_2S/NaHS (80:20)	NaCN	Yes
Silver Bell	Cp,Co	Roasting	Utah process	–	Yes
Pima	Cp,Cc	–	NaHS, $(NH_4)_2S$	roast for talc	Yes
Bagdad	Cc,Cp	Cooking	Nokes	–	Yes
Morency	Cp,Cc	Roasting	$Na_4Fe(CN)_6$	$Na_2Zn(CN_4)$, H_2O_2	Yes
Twin Butte	Cp	–	NaHS	–	Yes
Inspiration	Cc,Cov	Autoclave steaming	Nokes	–	Yes
Miami	Cp,Cov	–	Nokes	$(NH_4)_2S$	Yes
Chile					
Chuquicamata	Cc	–	arsenic Nokes	NaCN	Yes
El Teniente	Cc,Cp	–	Nokes	NaCN	Yes
El Salvador	Cc	–	arsenic Nokes	$K_4Fe(CN)_6$	Yes
Andina	Cp	–	NaHS	–	
Peru					
Southern Copper	Cc,Cp	–	$Na_4Fe(CN)_6$, $Na(ClO_4)$	–	Yes
Russia					
Balkhashi	Cp	–	Na_2S	–	Yes
Almalyk	Cp	–	Na_2S	–	Yes
Kadzharan	Cp	–	Na_2S	–	Yes
Europe					
Medet, Bulgaria	Cp	Steaming	Na2S	–	Yes

Figure 12.9 Effect of frother type on copper flotation from clay-containing porphyry copper ore [28].

can be used. The usual problems experienced in plants with rejection of pyrite include (a) insufficient re-grind, (b) very high lime additions that create voluminous froth in the cleaning when using glycol-type frother, together with mineral oil for MoS_2 recovery, such that the circuit becomes difficult to control and (c) improper selection of collector–frother combination.

- During the development stage of a treatment process of a new ore, attention should be given to the development of the correct re-grind requirement and determining the effect of reagents used in the roughing and subsequent cleaning operations.
- Differences occur in grinding size between laboratory and plant grinding. In the case of a porphyry ore, a float grind is very difficult to impossible to reproduce. The major reason for this is that a porphyry copper ore contains a large portion of light gangue (i.e. specific gravity 2.6–2.7) and during cyclone classification, heavy sulfides tend to concentrate in the cyclone underflow and, consequently, a portion is over ground. Some plant survey data [29] have shown as high as 80% copper in the ore in the recirculation loads in the ball mill grinding circuit. As a result, about 50% of copper losses in the tailing of operating plants is contained in the <20-μm fraction in spite of the fact that most of the plants use a coarse grind. When developing a reagent scheme for new ore or evaluating the mill feed ore in the laboratory, this factor is never taken into account and as a result, usually an inadequate reagent scheme is developed.

Frother selection in the laboratory testwork in a number of cases is a key factor, especially when clay minerals are present in the ore. Perhaps the most detrimental clay minerals in an ore are montomorillonite and chamosite. Experimental work conducted with

different frothers on ores containing montomorillonite and illite clay showed that the frother type had a significant effect on the rate of copper flotation and recovery. This effect is illustrated in Figure 12.9. The HP700 frother gave the best results. This frother contains amine oxide.

12.4.5   Flowsheet used in flotation of porphyry copper ores and copper–molybdenum separation

Flowsheets used in the flotation of porphyry copper ores are relatively simple compared with the flowsheets used in the flotation of massive sulfide ores. The most typical flowsheet is shown in Figure 12.10. There is some deviation in the flowsheet shown in Figure 12-11, used by El Salvador (Chile), which utilizes cascade flotation of the tailing. This cascade flotation plant increased the plants copper recovery by about 2%.

Some operating plants use copper scalp and copper retreat circuits. An example of such a flowsheet is shown in Figure 12.12.

Other variations in this flowsheet include separate treatment for rougher and scavenger concentrates. Such a flowsheet is practiced at the El Cobre Concentrator (Chile) and is shown in Figure 12.13.

Several plants practice a sand-slime separation and a separate flotation of sand and slimes. Such a flowsheet is used by the San Marcelina plant in the Philippines.

The copper–molybdenum separation flowsheets are relatively complex and vary widely, especially where the concentrate is subjected to thermal treatment before separation or where the Utah process is used (roasting–flotation). A typical flotation flowsheet used in a Cu–Mo separation is shown in Figure 12.14.

Nowadays, the number of cleaning stages is substantially reduced by using column flotation.
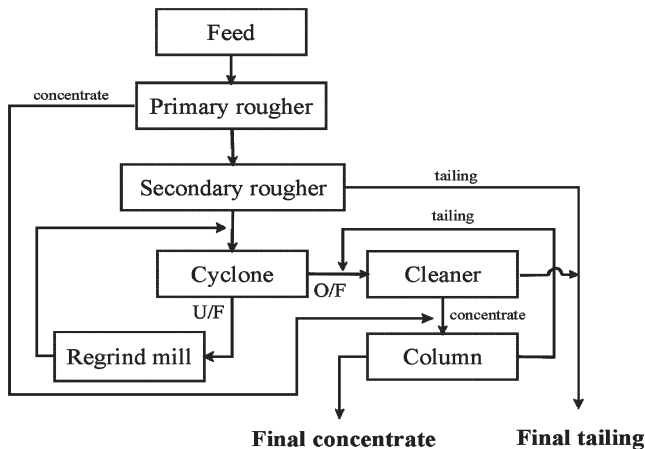
Figure 12.10 A typical flowsheet used in the flotation of porphyry copper ores.
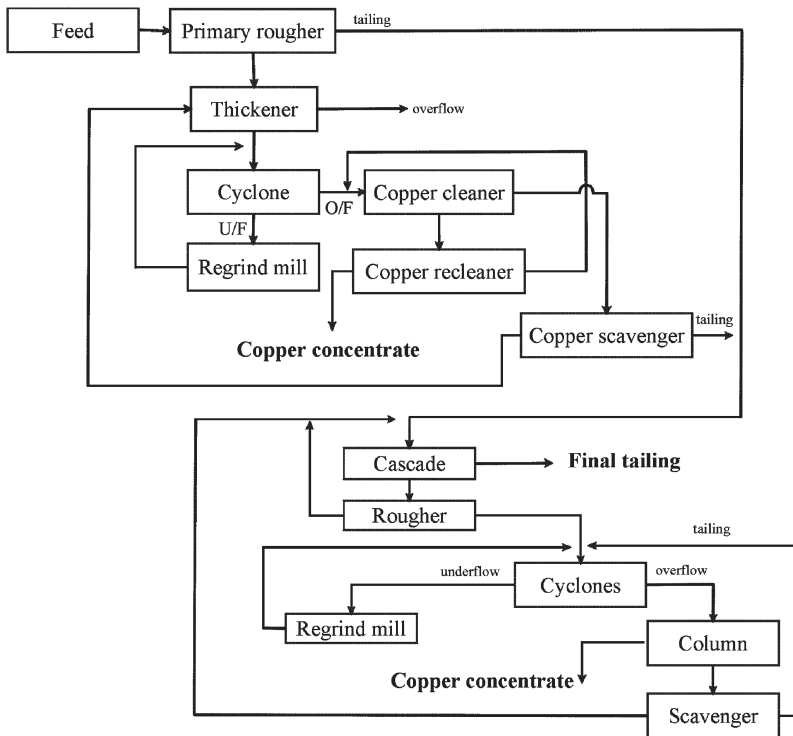
Figure 12.11 The El Salvador (Chile) plant flowsheet.

12.5   FLOTATION PRACTICE IN BENEFICIATION OF SULFIDE COPPER AND COPPER–GOLD ORES

Copper sulfide ores with medium pyrite content contain up to 50% sulfides, the average sulfide content is about 15% Fe_2S. Some of these ores may underline porphyry copper deposits known as a high-pyrite hypogene ore type. In other cases, they appear as copper scarns (Antamina–Peru copper ore) or stringer ores, which sometimes are pockets or lenses of massive sulfides (e.g. Crandon, USA and Woodlawn, Australia). The stringer ores usually contain small quantities of zinc or both lead and zinc (i.e. 0.2–0.4% Zn and 0.1–0.2% Pb).

Primary copper–gold ores may contain between 6% and 50% pyrite and primarily contain chalcopyrite. In some cases, bornite and covellite may be present in the lower portion of the ore body (Batu Hijau, Indonesia) or enargite (El Indio, Chile). In other sulfides, these ores contain pyrite and sometimes arsenopyrite and pyrrhotite. The gold in these ores is represented by electrum or as copper auride. In most of these ores, a portion of gold is contained in pyrite.

Ores with an elevated amount of arsenopyrite belong to a group of arsenical copper–gold ores. The characteristics of these ores is that the gold is encapsulated in all sulfides (e.g. arsenopyrite, pyrite and chalcopyrite) and sometimes also in quartz.
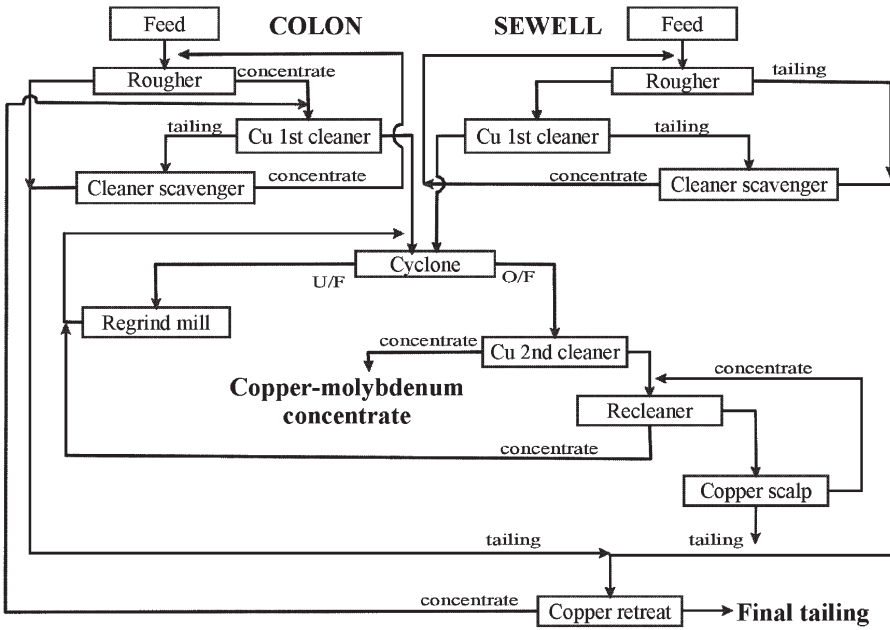
Figure 12.12 The El Teniente plant flowsheet.
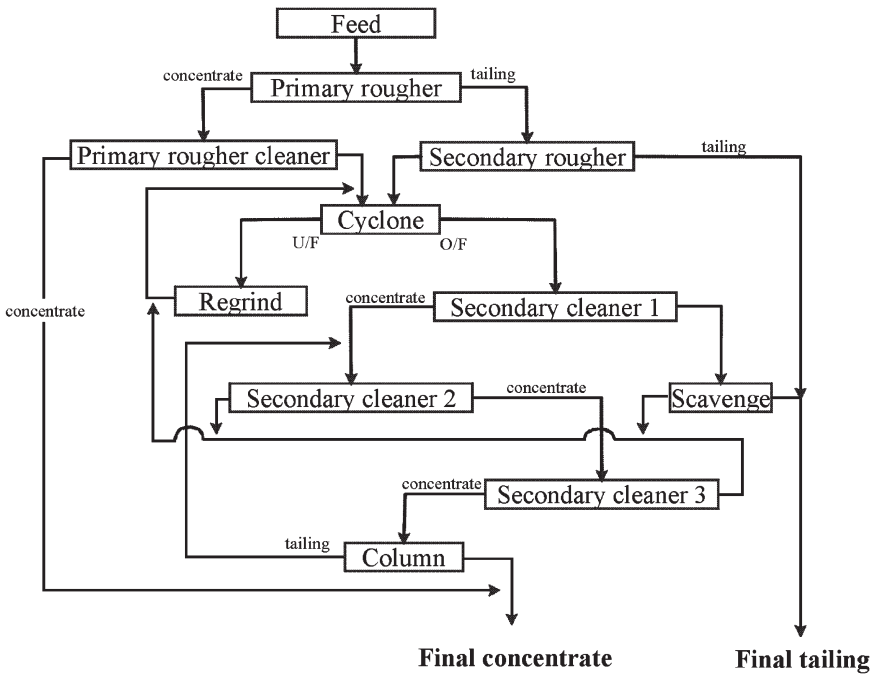
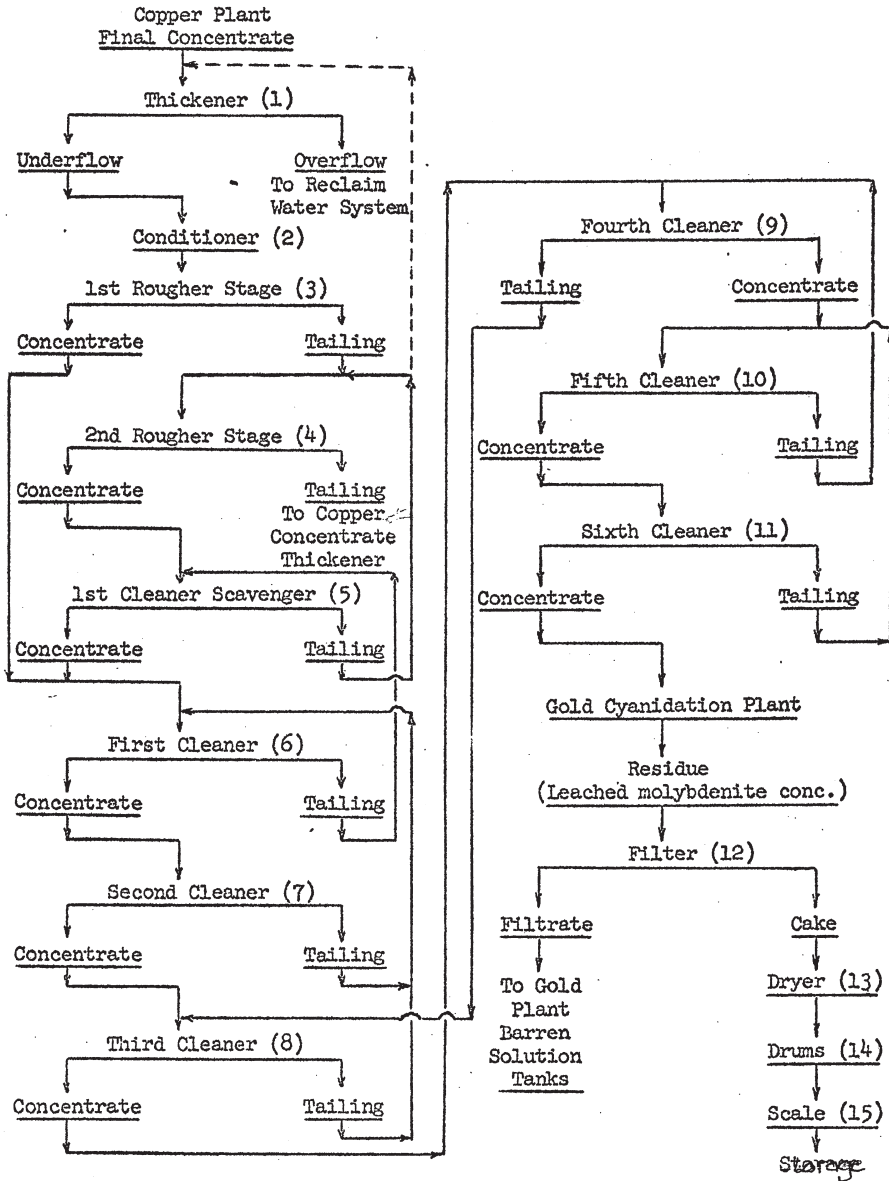**Figure 12.13** The El Corbre plant flowsheet.

Figure 12.14 San Manuel's (Arizona) copper–molybdenum flowsheet.

Partially oxidized copper–gold ores, such as those from Red Dome (Australia), belong to a group of refractory ores and also contain high clay. The gold in these ores is also found in iron hydroxides and oxide copper.

12.5.1   Flotation of sulfide copper ores

Sulfide copper ores are considered easy to treat provided that the main copper mineral is chalcopyrite. In case the ore contains secondary copper minerals, such as chalcocite, bornite and covellite, depression of pyrite may be a problem because the pyrite can be activated by copper ions generated during the grinding operation. Some copper sulfide ores can be partially oxidized, also influencing the selection of a reagent scheme, with the exception being a hypogene sulfide copper ore. Copper sulfide ores are normally finer grained than porphyry copper ores and require finer grinding (i.e. 70–80% <200 mesh).

Flotation characteristics and treatment options

The flotation processing characteristics of sulfide copper ores are different from that of porphyry copper ores in several ways, some of which include:

• The pyrite in these ores is more active than in the porphyry copper ores, so the depression of pyrite is more difficult. Some ores contain pyrrhotite and marcasite, which in many cases contaminates the concentrate. In the ores where pyrrhotite is present, copper concentrate can be as low as 16–20% Cu.
• Copper sulfide ores are disseminated and in some cases, would require fine re-grinding of the rougher concentrate (~25 μm). Fine copper minerals have a low rate of flotation, which may result in losses in recovery.
• The presence of clay minerals in these ores has a pronounced negative effect on copper metallurgy.
• In general, there are three options practiced in the treatment of these ores. These are (1) sequential copper flotation from pyrite and other sulfides, the most common practice in the treatment of sulfides ores and (2) bulk or semi-bulk flotation followed by copper–pyrite separation after re-grinding of the bulk concentrate. This method is used in the case where copper is finely disseminated with pyrite or with ore that contains clay minerals (of acidic nature), which interferes with copper flotation. Several plants in central copper plants use this method.
• Slime sand separation method is used when the ore contains slime and clay minerals, which interferes with flotation. The slime and sand fractions are then separately floated.

Reagent scheme used for flotation of sulfide copper ores

Unlike porphyry copper ore, where the reagent schemes are similar for most operations, the reagent schemes used for the treatment of sulfide copper ores are much more diverse and are designed to cope with specific problems associated with processing the ore.

When treating hypogene sulfide copper ores, the reagent scheme is relatively simple. It uses xanthate as a collector in alkaline pH (11.0–11.5). In some cases, dithiophosphate is used as a secondary collector when secondary copper minerals are present in the ore. In the case of stringer ore and copper ores in which the pyrite is active, the reagent scheme is more complex and involves different depressant combinations. Several of the most common depressant combinations are discussed below.

- Aeration has been practiced in a number of operations in North America and is highly effective when the ore contains pyrrhotite. It is interesting to note that in the presence of pyrrhotite during grinding, because of reactivity of pyrrhotite, oxygen is depleted and the floatability of copper is significantly reduced. The effect of aeration [30,31] has been extensively studied. Figure 12.15 shows the effect of aeration on the rate of copper flotation from a pyrrhotite-containing copper ore.

- The use of Na_2S and Na_2SO_3 depressants, together with lime, can be effective for the flotation of slow-floating chalcopyrite and/or when treating partially oxidized or
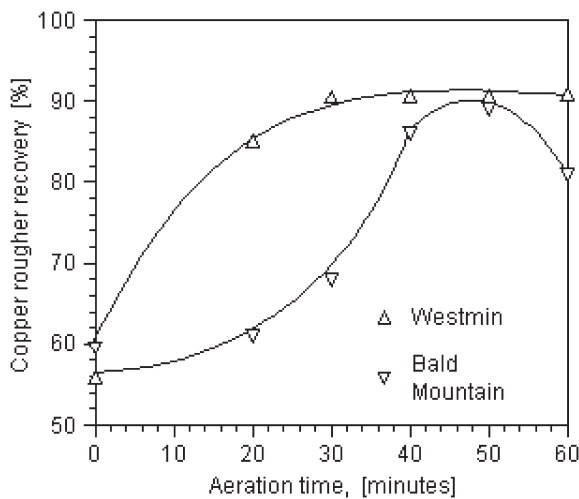
Figure 12.15 Effect of aeration on copper rougher scavenger flotation from a pyrrhotite-containing copper ore. Airflow is 5 L/min.

Table 12.13

Effect of Na_2S and Na_2SO_3 on copper flotation from altered ore using potassium amyl xanthate as collector

Depressant used	pH		Cu Ro Concentration		Cu Cl Concentration	
	Ro	Cl	Assay % Cu	Reco-very % Cu	Assay % Cu	Reco-very % Cu
CaO, NaCN = 50 g/t	10.5	10.5	4.5	85	18.3	66.5
CaO, Na_2S = 100 g/t	10.5	10.5	8.3	86	22.0	70.0
CaO, Na_2S = 300 g/t	10.4	10.5	8.8	90	24	73.5
CaO, Na_2SO_3 = 300 g/t	10.5	10.5	7.4	89	23	75.0
CaO, Na_2SO_3 = 300 g/t, Na_2S = 250 g/t	10.5	10.5	12.4	94	28	82.3

tarnished copper ores. Na_2S is used with lime or in combination with Na_2SO_3. The Na_2SO_3 can also be used in combination with lime. Table 12.13 shows the metallurgical results obtained with Na_2S and Na_2SO_3 depressants on a stringer-altered copper sulfide ore. Both Na_2S and Na_2SO_3 had a beneficial effect on copper concentrate grade and recovery over that of cyanide.

- The use of sodium silicate is practiced with ores that contain non-sulfide slime. Sodium silicate can also be used as a mixture with carboxyl methyl cellulose in the ratio Na_2SiO_3:CMC = 3:1. This combination is highly effective for depressing chlorite-containing ores.

- Complexed cyanide, depressant DDS4, is a new depressant that is highly effective in the depression of pre-activated pyrite and marcasite. This depressant was developed as a result of extensive studies [32] in both laboratory and pilot plant. The effectiveness of this depressant is illustrated in Figure 12.16. The DDS4 depressant is prepared from quebracho branched yellow dextrin in the following ratio: dextrin:quebracho:NaCN = 2:1:2.

- The choice of collector also depends on the nature and occurrence of copper and associated sulfides. In most cases, xanthate collectors are used alone or in combination with dithiophosphates or thionocarbamates. Dithiophosphates and thionocarbamates are normally used when secondary copper minerals are present in the ore or when the copper flotation is carried out at lower pH. Good metallurgical results are obtained with thionocarbamate during the flotation of clay-containing sulfide copper ore.

- A mixture of xanthates (i.e. ethyl-butyl, ethyl-isopropyl) has been successfully used in a number of Russian operations [33. Table 12.14 shows the effect of xanthate mixtures on copper recovery from chalcopyrite copper sulfide ores. Both selectivity and recovery were improved when using a mixture of two xanthates.
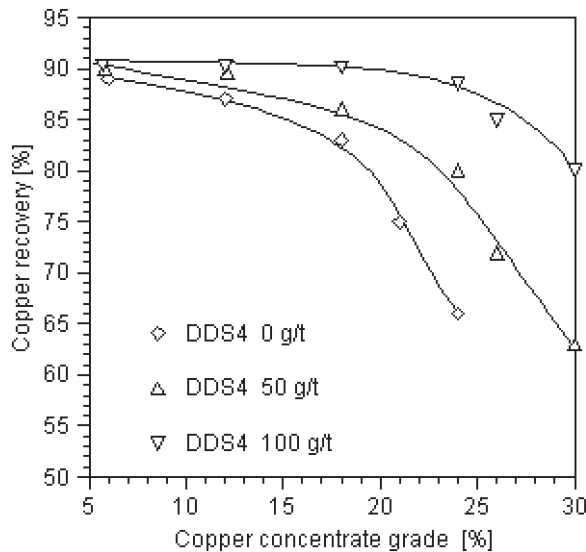
Figure 12.16 Effect of depressant DDS4 on copper concentrate grade flotation and upgrading.

Table 12.14

Effect of different xanthates and xanthate mixtures on copper flotation and upgrading

Collector Used	pH		Cu Ro concentrate		Cu Cl concentrate	
	Ro	Cl	Assay % Cu	Recovery % Cu	Assay % Cu	Recovery % Cu
Sodium ethyl xanthate	9.5	10.0	12.1	85.8	28.1	74.5
Sodium isopropyl xanthate	9.5	10.0	9.3	90.1	24.3	81.0
Potassium amyl xanthate	9.5	10.0	7.2	95.3	23.2	85.5
Sodium ethyl/sodium isopropyl xanthate (1:1)	9.5	10.0	13.4	92.4	29.6	87.0
Sodium ethyl/potassium amyl xanthate (1:1)	9.5	10.0	14.6	93.3	30.1	88.0
Sodium isopropyl/potassium amyl xanthate (1:1)	9.5	10.0	14.5	96.8	31.3	89.6

Table 12.15

Examples of reagent schemes used in the treatment of copper sulfide ores

| Ore type major gangue minerals	Depressants and modifiers	Collectors and frothers	Other	pH Ro	Cl
Hypogene ore with a pyrite content of 30%, coarse to fine grained	Lime NaCN	Xanthate + dithiophosphate	–	10.5	11–11.5
Medium- to fine-grained ores. Chalcopyrite, pyrite and pyrrhotite	Lime, Na_2SO_3 or lime + $Na_2S_2O_5$	Xanthate + dithiophosphate or thionocarbamate	DDS4 aeration	9.5	9.5
Stringer, partially oxidized ore. Chalcopyrite, pyrite. Activated pyrite.	Soda ash + SO_2 or lime + DDS4	Dithiophosphate, alkoxy thiono-carbamate	$Na_2S + Na_2SO_3$ or NaCN to cleaners	10.5	11.0
High-clay sulfides, chalcopyrite + covellite, bornite, pyrite 8–15% andesite rock + clay	Na_2S, lime sodium silicate	Xanthate + phosphine	Dextrin	Natural	11.0
Scarn sulfide copper alumino silicate, dolomite quartz pyrite 10–15% chalcopyrite	Lime or NaCN to cleaners	Xanthate + dithiophosphate or thiono-carbamate	Na_2SiO_3	11.0	11.8
Disseminated secondary copper ore with chlorites, volcanic tuff, alumino silicate, pyrite 5–10%	Dextrin, Na_2S or lime, dextrin	Higher xanthate, isobutyl, dithiophosphate	Pre-condition before cleaning	Natural	Natural
Stringer ore with floatable gangue (talc chlorites) pyrite 10–20%	Lime, guar or lime/CMC	Xanthate or xanthate mixture	Modified starch, lime	Natural	11.0
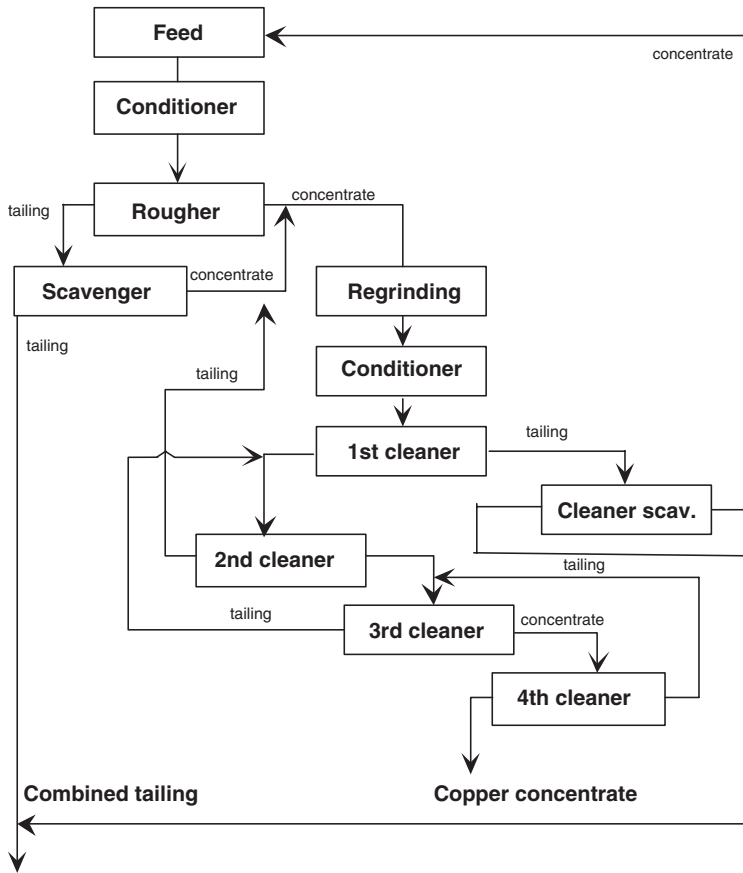
Figure 12.17 Sequential copper pyrite flowsheet.

- Frother choice varies from one ore type to the other. Most commonly, an alcohol-type frother is used. The exception is when clay slimes are present in the ore; then a mixture of two frothers or a glycol-type frother is employed.

In Table 12.15, the reagent schemes employed for the treatment of sulfide copper ores are listed. These reagent schemes were developed for treatment of sulfide copper ores in both the laboratory and the pilot plant, and some have been transferred into actual operation. The use of small quantities of starches has been practiced in several Brazilian plants. At the Mount Isa copper concentrator (Australia), dextrin (D110) was used to control the flotation of hydrophobic gangue. Some copper ores are high in chlorite-type gangue, which is difficult to control (Olympic Dam, Australia; Selobas, Brazil). In recent years, modified starches have been shown to have a beneficial effect on fluorine and chlorine gangue rejection. The ester and succinate-modified starches gave positive results.
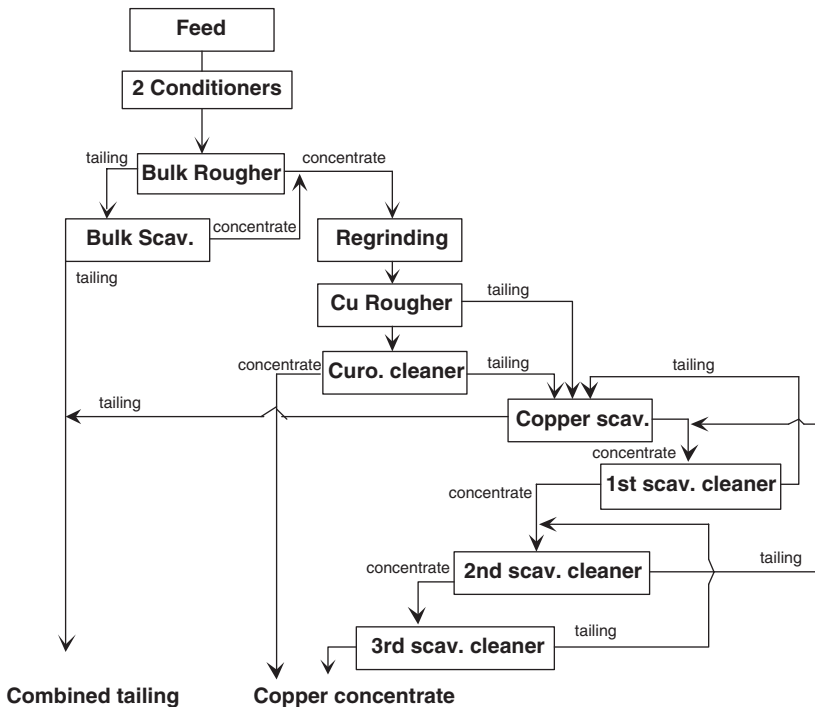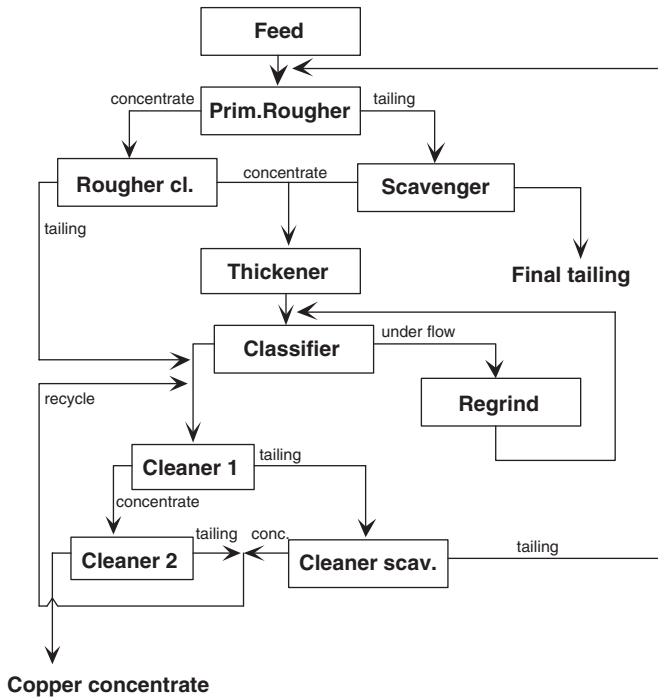
Figure 12.18 Bulk flotation flowsheet.

Flowsheets used for the treatment of sulfide copper ores

There are several basic types of flowsheets employed in the treatment of sulfide ores, some of which include:

(a) Sequential copper pyrite flotation flowsheet, shown in Figure 12.17. This type of flowsheet is employed in a number of North American operations.
(b) Bulk flotation flowsheet that is normally used in cases where the ore is acidic and pyrite does not exceed 15% by weight. It is used in the treatment of altered copper sulfide ores (Figure 12.18). An alternative flowsheet is a semi-bulk flowsheet, which is used in some operations in Australia.

   When the ore contains secondary copper minerals in addition to chalcopyrite, then a two-stage grinding flotation flowsheet is used. This flowsheet is designed to avoid sliming of bornite and covellite minerals. A similar flowsheet (Figure 12.19) is used where only portions of concentrate are re-ground.
   Other flowsheets employed include sand–slime separation and separate flotation of the sand and slime. Such a flowsheet is rarely used and has never been proven in actual practice to be advantageous over the conventional sequential flowsheets. In cases where the

Figure 12.19 The Balhashkoi plant (Russia) flowsheet.

pyrite chalcopyrite is finely disseminated, a two-stage re-grind may be incorporated into the flowsheets.

12.5.2 Flotation of copper–gold ores

The literature classifies copper–gold ore as a porphyry copper ore [34]. Although some porphyry copper ores contain gold (San Manuel, USA) from a processing point of view, these ores cannot be classified as porphyry copper ores because they do not respond to flotation in the same way as porphyry copper ores. In addition, the mineralogy of these ores is different from that of porphyry copper ores.

Gold mineralogy and its effect on flotation

Over 80% of the gold found in copper–gold ores is metallic gold with variable size and association. Gold with transition elements, such as silver (gold–silver alloy), copper (copper aurides) and iron are common in most of the hypogene and altered copper–gold ores (i.e. supergene). The distribution of gold in an ore plays an important role in the selection of the type of flotation process that can be applied to recover the gold [34]. Usually, gold is contained in low concentration, as minute particles. New mineralogical techniques are available that make it possible to give an accurate account of the association of gold in the principal host minerals, sulfides and gangue. However, the evaluation of many flotation

products would be time-consuming and hence impractical for process control. Since floatability data from actual gold minerals are virtually non-existent, they have to be derived from systematic development work. From the combined efforts of flotation studies and mineralogical examinations, some pertinent information on the floatability of gold can be elucidated.

The flotation of properties of elemental gold and gold–silver alloys depend strongly on the deformation and final shape of the particles after primary grinding and re-grinding. Because of its high density, gold particles can form platelets that are difficult to float. Small particles <20 μm are readily recovered by flotation.

The surfaces of gold particles can become coated with precipitates of iron compounds or other heavy metals, either naturally or during the process of grinding. Flotation of these coated particles, even with high dosages of collector, is weak and erratic.

Gold minerals, such as aurocupride ($AuCu_3$), usually float readily in the primary copper circuit. If cyanide or $Na_2S_2O_5$ is present as depressant, gold recovery deteriorates.

Gold tellurides present in the copper ores float readily, but recovery can be compromised by the presence of soluble, heavy-metal salts [35]. Gold pyrite middlings (i.e. auropyrite) can only be selectively concentrated with the appropriate flowsheet adjustments and the use of selectivity-assisting agents.

During the recovery of copper from copper–gold ores, the emphasis is usually placed on producing a marketable copper concentrate. Gold recovery, although important, is often difficult to consider when optimizing the copper circuit. The need to reject gangue (insol) and iron sulfides, during cleaning of the copper concentrate, invariably leads to losses of gold. Some depressants, such as lime and cyanide, which are part of the reagent scheme during the treatment of copper–gold ores, have a negative effect on flotation. This can often be overcome by changing the flowsheet and using a more selective collector.

Ore types and processing characteristics

The processing characteristics of a copper–gold ore can vary from ore to ore and are closely related to the mineralogical composition of the ore. On the basis of its processing characteristics, the copper–gold ore can be classified into three distinct groups. These are:

- *Copper–gold ores with moderate to high pyrite* (e.g. Alumbrera, Freeport, OK-Tedy). In these ores, gold occurs as elemental gold, some of which can be associated with pyrite ore in the copper minerals. Chalcopyrite is the predominant copper mineral, but can also contain pyrrhotite (Noranda and Campbell in Canada). The reagent scheme used in the treatment of these ores varies considerably, along with the treatment flowsheets.
- *Copper–gold ores with low pyrite content* (i.e. <5% Fe_2S). These deposits range from easy-to-treat ores to highly complex mineralogical matrix. The clay may be present in high concentration and with a wide range of composition (e.g. Minas Conga, Cerro Corona, Peru; South Kemess, Canada). The copper in these ores may be present as chalcopyrite or chalcopyrite–bornite–covellite. Some of these deposits consist of several ore types including (a) oxide blankets, (b) supergene altered zones and (c) transition ore zones with high pyrite.

- *Altered supergene copper–gold ore*. These ores belong to a group of difficult-to-treat ores (Red Dome, Australia; Brazil). In these ores, a large portion of the gold (up to 50%) may be associated with gangue (Red Dome), in which case the combination of flotation and cyanidation is used.

Invariably, these ores have high iron hydrohydes and goethite slimes present, which is the principal problem in the processing of this ore.

Reagent schemes and the effect of individual reagents on flotation of copper and gold

The choice of reagent schemes for the treatment of copper–gold ores is based in principle on the nature of the ore and gold association in the contained minerals. Some operating plants, such as OK-Tedy [36], Freeport, Indonesia [37], and Tintaya, Peru [38] use a lime circuit with selective collectors. This choice is based on the presence of variable amounts of pyrite in the deposit and the emphasis on maintaining high-grade copper concentrates. The recovery of gold is not optimum under these conditions. Recent research work [39] has shown that the overall gold recovery is not entirely dependent on the collector used, but could be enhanced by the use of modifying reagents or changes in the configuration of the flowsheet. These factors have not been considered as yet in the design of new plants.

Selection of collectors

Most operating plants treating porphyry copper–gold ores use various types of xanthate as a primary collector, in combination with phosphine or dithiophosphate as a secondary collector. In most instances, these combinations gave satisfactory results with respect to concentrate grade and copper–gold recoveries.

During the treatment of ores with elevated levels of pyrite, dithiophosphates are employed with little or no xanthate added to the scavenger flotation stage. Use of xanthate with ores containing clay creates a dry froth that requires additions of specific frothers or a blend of different frothers similar to those used in porphyry copper–molybdenum ore flotation.

Laboratory studies on a number of copper–gold ores [40] containing pyrite have shown that gold recovery in rougher–scavenger flotation is a function of pyrite recovery in the copper concentrate. Figure 12.20 shows the relationship between gold and pyrite recoveries using xanthate and dithiophosphate, alone or in combination. In these experiments, total collector additions were 40 g/t.

When treating ores with low pyrite content and mixed copper minerals, the gold recovery in the copper concentrate is strongly related to the type of xanthate used. Figure 12.21 shows the effect of the type of xanthate used on gold recovery from the Batu Hijau (Indonesia) copper–gold ore.

The collector choice for oxidized copper–gold ores [41] is somewhat different than that normally employed using sulfide copper–gold ore. As mentioned earlier, one of the major obstacles in the treatment of these ores is the presence of iron oxides (goethite) and iron hydroxide slimes, which interfere with flotation of copper and gold.

Studies carried out at Red Dome (Australia) with new collectors manufactured by Senmin, South Africa showed that copper and gold recoveries can be substantially improved by using the new collectors SN127 and PM230. Figure 12.22 shows the effect of these collectors on copper–gold flotation from Red Dome oxide ore.
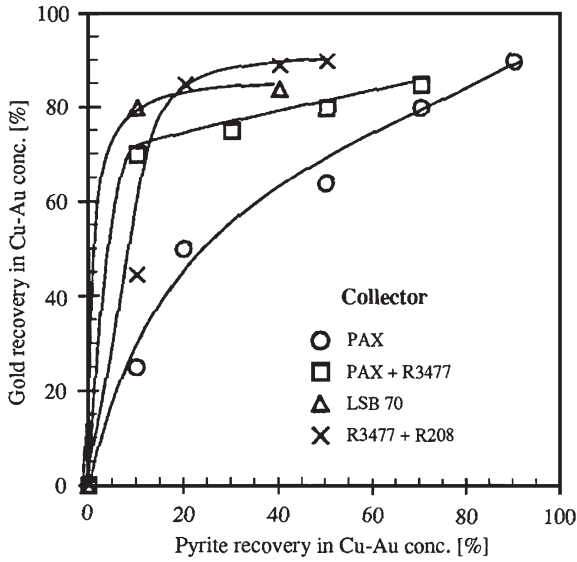
Figure 12.20 Relationship between copper and pyrite recoveries in the copper–gold rougher–scavenger concentrates.
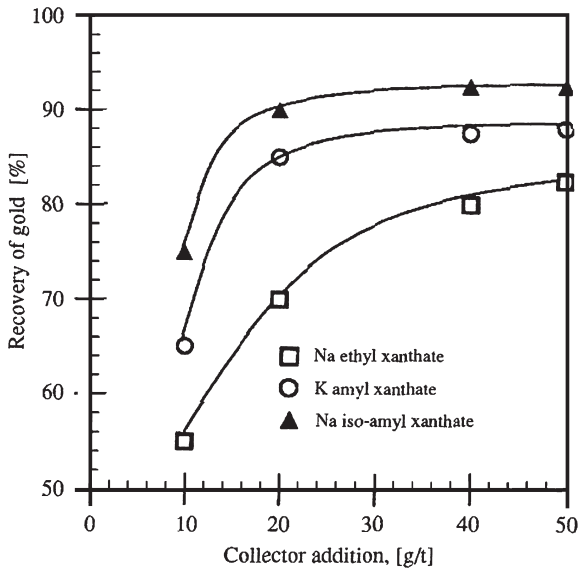
Figure 12.21 Effect of the type of xanthate on gold recovery from the Batu Hijau (Indonesia) copper–gold ore.
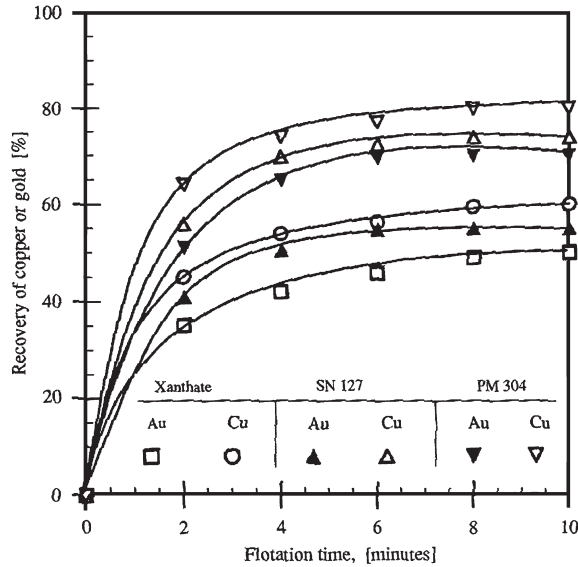
Figure 12.22 Effect of the type of collector on copper and gold flotation from Red Dome (Australia) oxide ore.

Collector SN127 is a succinic acid–modified dithiophosphate, while collector PM230 is an esterified xanthate.

The Igarape Bahia oxide copper–gold ore is quite unique in that it consists of several ore bodies, including a malachite, cuprite and sulfide zone. The cuprite zone also contains an appreciable amount of native copper. The reagent scheme developed for the treatment of this ore is quite unique and gives good metallurgical results. The iron oxide and hydroxide slimes were depressed with polyacrylimide-modified starch while the copper flotation was accomplished using phosphoric acid ester–modified xanthate with sulfidization. The effect of depressant and collector on copper–gold recoveries is shown in Table 12.16.

The data in Table 12.16 show that significant improvement in copper and gold recoveries is achieved with the use of collector PM230 plus acrylic acid–modified starch. Xanthate or xanthate and dithiophosphate gave poor metallurgical results.

The type of modifier and selectivity-assisting agents play an important role in beneficiation of copper–gold ores; therefore, important consideration must be given to the choice of depressant and modifiers when selecting the reagent scheme for a particular ore. In most operating plants, lime is used for pH control. Lime is satisfactory with ores that have higher pyrite content, but cannot be used with ores that contain clay or those with an acidic natural pH.

In the case of a clay ore, lime increases pulp viscosity, which in turn retards the rate of flotation of gold. Acidic natural pH may increase lime consumption dramatically (i.e. up to 10 kg/t) resulting in complete depression of both copper and gold. Sodium hydroxide gives better results than lime for this ore type.

The effect of different modifiers on gold recovery from a high clay ore is illustrated in Figure 12.23. The use of sodium hydroxide gave the highest rate of copper flotation. Soda

Table 12.16

Effect of type of collector and iron oxide depressant on copper–gold flotation from Igarape Bahia (Brazil) oxide gold ore [42]

Ore type	Collector type	Sulfi dizer	Depressant	Concentration Assays		% Distri- bution	
				%Cu	%Au	Cu	Au
Malachite ore	PAX	Na$_2$S	Na$_2$SiO$_3$	22	13.8	60	55
3.5% Cu	PAX+3477[a]	Na$_2$S	Na$_2$SiO$_3$	25	17.1	62	54
2.4 g/t Au	PM230[b]	Na$_2$S	Na$_2$SiO$_3$	25	16.3	84	80
	PM230	Na$_2$S	Caustic starch	26	16.8	86	81
	PM230	Na$_2$S	Acrylic acid modified starch	38	25.1	88	85
Cuprite ore	PAX	Na$_2$S	Na$_2$SiO$_3$	35	32.4	66	48
2.75% Cu	PAX+3477[a]	Na$_2$S	Na$_2$SiO$_3$	38	36.1	67	50
3.5 g/t Au	PM230	Na$_2$S	Na$_2$SiO$_3$	45	55.9	80	78
	PM230	Na$_2$S	Caustic starch	50	62.8	82	81
	PM230	Na$_2$S	Acrylic acid modified starch	56	69.6	86	84

[a]Dithiophosphate.
[b]Phosphine ester–modified xanthate.
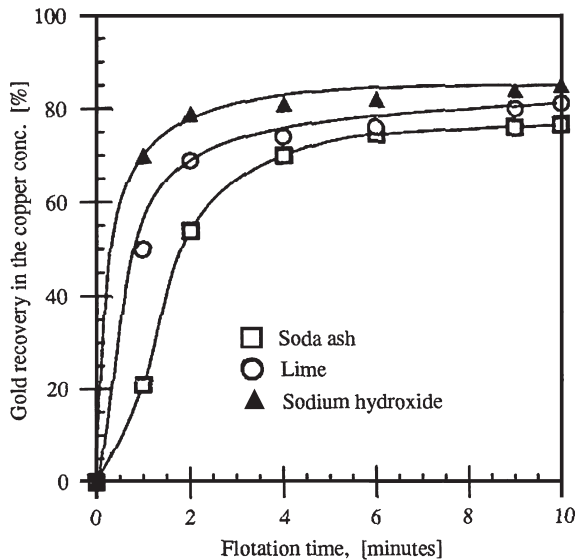
Figure 12.23 Effect of the type of modifier on the rate of gold flotation at pH 9.2.

ash and NaOH are suitable for low-pyrite copper–gold ores, but not for copper–gold ores with high pyrite content.

Ore with high pyrite content requires higher lime additions for pyrite depression and sometimes NaCN is also used. This flotation is not favorable for gold, as both cyanide and high lime have negative effects on gold recovery, and gold recovery is usually compromised for production of a marketable grade copper–gold ore. Recent research work [42] carried out with different organic acids has indicated that in the presence of high lime, gold recovery can be enhanced by adding small quantities of organic acid. Figure 12.24 shows the effect of oxalic and citric acid on the recovery of gold in the presence of high lime (pH 11.5).

The presence of insol during the treatment of copper–gold sulfide ores may be a problem due to the fact that these ores contain highly floatable gangue minerals (e.g. aluminosilicates, fluorite gangue, etc.), which usually contaminate copper concentrate. Maintenance of high copper concentrate grade requires that gangue depressant be used. Silicates, carboxyl methyl cellulose and guars are common depressants used. The effect of these depressants on the insol content of a copper–gold concentrate is illustrated in Figure 12.25. The results obtained in Figure 12.25a show depression of aluminosilicate gangue, while Figure 12.25b shows the effect of depression of chloritic gangue.

Flowsheets

Together with reagent schemes, the flowsheet configuration plays an important role in the recovery of gold from a copper–gold ore. The most common flowsheet used in the
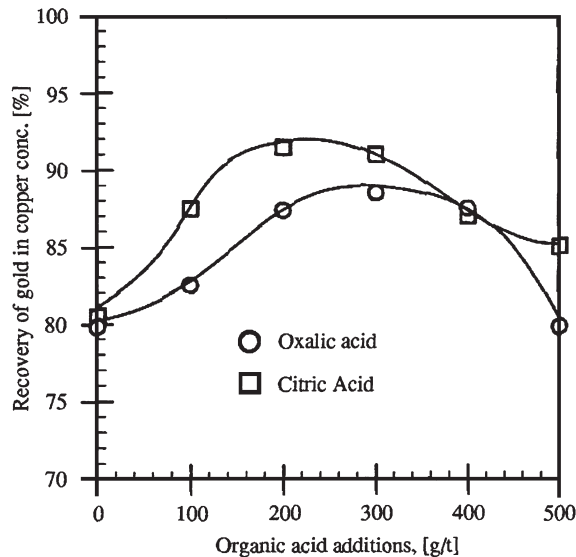
Figure 12.24 Effect of different organic acids on gold recovery in the copper concentrate using lime−cyanide pyrite depressant (pH 11.5, NaCN additions 50 g/t ore).
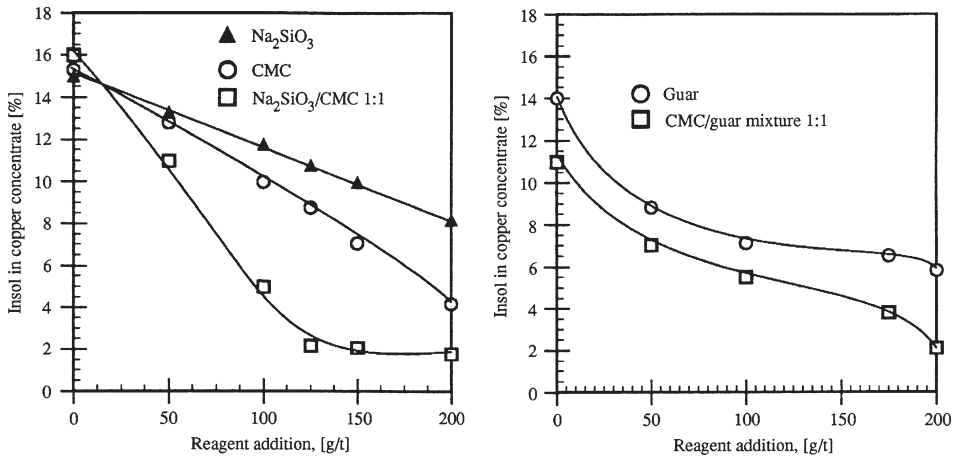
Figure 12.25 Effect of different depressants on the insol content of the copper concentrate.

treatment of copper–gold ores is shown in Figure 12.26. This flowsheet is used in a number of operating plants, such as OK-Tedy, Freeport (Indonesia), Tintaya (Peru), etc.

Modification of this flowsheet could include column flotation of the rougher concentrate (Freeport). Since the emphasis when using this flowsheet is usually on the recovery of copper at high grade, pyrite in this case is rejected through the scavenger tailing together with an appreciable amount of gold. The alternative flowsheet to this is bulk flotation of all sulfides followed by sequential flotation of copper–gold from a bulk concentrate. This flowsheet is shown in Figure 12.27. The effectiveness of this flowsheet is studied on the OK-Tedy ore (Papua, New Guinea) and on the Cerro Corona (Peru) ore. These results are compared in Table 12.17.

The bulk flowsheet gave superior gold recovery to that of the conventional selective flotation flowsheet. The applicability of the bulk flowsheet depends on the amount of pyrite present in the ore. In the case of high-pyrite copper–gold ore, the bulk flotation flowsheet does not work as well.

The complexity of the copper–gold ore rapidly increases when several copper minerals are present in the ore and differences in liberation size increases. For example, bornite and covellite are brittle and tend to slime during grinding and re-grinding of the bulk concentrate. In this case, a split-circuit flowsheet has been proposed, which is shown in Figure 12.28.

Table 12.18 shows the metallurgical results obtained using a conventional flowsheet (Figure 12.26) and a split-circuit flowsheet (Figure 12.28) on the Batu Hijau ore (Indonesia).

Different reagent schemes are used in operating plants according to the ore type treated. The flowsheet varies accordingly. Table 12.19 shows the reagent scheme developed for the treatment of different ore types.

New technology available nowadays has an appreciable advantage in the improvement of gold metallurgy in operating plants. This technology, although already developed at the laboratory and pilot-plant scale, has not been applied at an industrial scale yet. Some of
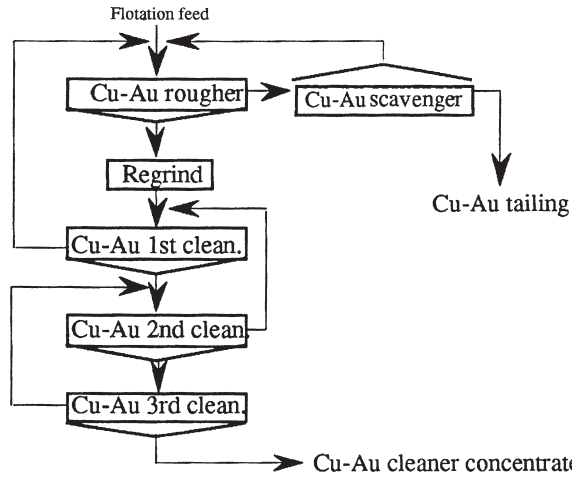
Figure 12.26 Conventional copper–gold flotation flowsheet.
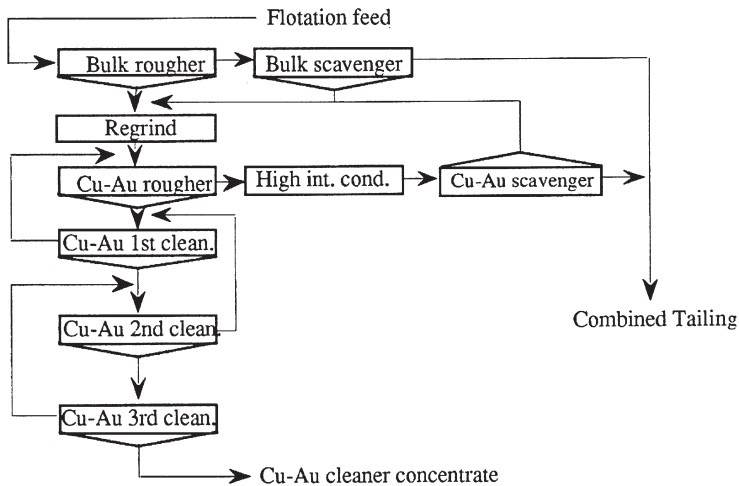
Figure 12.27 Bulk copper=gold flotation flowsheet.

the large ore bodies are still in the development stage, while some operating plants are slow in implementing new technology.

12.5.3   Flotation of massive sulfide copper ores

Complex massive sulfide copper ores are finely disseminated ores containing chalcopyrite ($CuFS_2$), pyrite (FeS_2), pyrrhotite (Fe_xSn) and other varieties of iron-bearing minerals.

Table 12.17

Effect of flowsheet configuration on Cu/Au flotation from different ores [44]

| Ore	Flowsheet used	Product	Weight %	Assays % (g/t)		% Distribution	
				Cu	Au	Cu	Au
OK-Tedy	Conventional	Cu/Au Cl concentration	1.62	42.6	58.3	88.4	80.7
mill feed	Figure 12.27	Cu/Au total tail	98.38	0.091	0.23	11.6	19.3
		Head (calc)	100.00	0.78	1.17	100.0	100.0
OK-Tedy	Bulk	Cu/Au Cl concentration	1.73	41.8	58.7	93.8	87.6
Mill feed	Figure 12.28	Cu/Au total tail	98.27	0.049	0.13	6.2	12.4
		Head (calc)	100.00	0.77	1.10	100.0	100.0
Cerro	Conventional	Cu/Au Cl concentration	2.28	27.6	33.0	95.4	76.7
Corona	Figure 12.27	Cu/Au total tail	97.72	0.031	0.23	4.6	23.3
		Head (calc)	100.00	0.66	0.98	100.0	100.0
Cerro	Bulk	Cu/Au Cl concentration	2.32	27.1	36.9	95.2	85.8
Corona	Figure 12.28	Cu/Au total tail	97.68	0.032	0.14	4.8	14.2
		Head (calc)	100.00	0.66	0.96	100.0	100.0
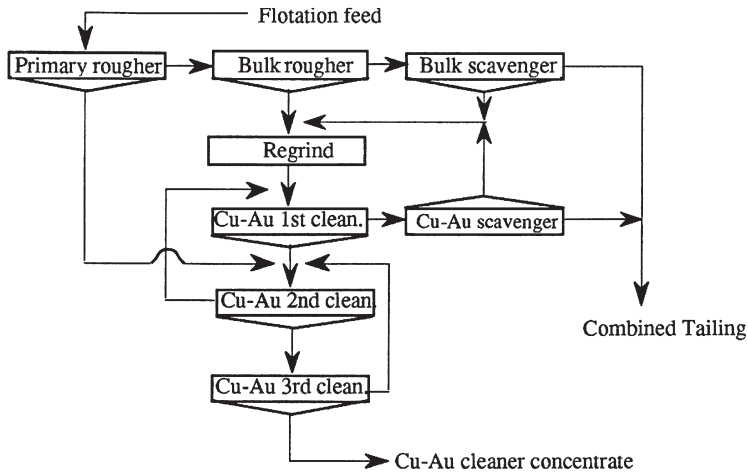
Figure 12.28 Split-circuit flowsheet.

They represent important resources of copper in a number of areas of North America and Europe (Iberian Pyrite Belt). Because of their complex nature and fine textures, they represent specific and difficult metallurgical problems during all steps of beneficiation, including tailing and other waste disposal. Using conventional flotation techniques, the metallurgy is usually unsatisfactory, which renders the ore to be classified as refractory.

The major problem associated with the treatment of these ores is the low flotation recovery and poor selectivity between all sulfides. The selectivity problem arises from

Table 12.18

Effect of split-circuit flowsheet on Cu/Au flotation from Batu Hijau ore (pilot plant results)

Flowsheet	Product	Weight	Assays % (g/t)		% Distribution	
		%	Cu	Au	Cu	Au
Conventional	Cu/Au Cl concentration	1.48	36.6	26.6	93.5	80.4
Figure 12.27	Cu/Au comb tail	98.52	0.038	0.097	6.5	19.6
	Head (calc)	100.00	0.58	0.47	100.0	100.0
Split circuit	Cu/Au Cl concentration	1.36	40.2	30.1	94.0	83.5
Figure 12.29	Cu/Au comb tail	98.64	0.035	0.08	6.0	16.5
	Head (calc)	100.00	0.58	0.49	100.0	100.0

Table 12.19

Reagent schemes and metallurgical results obtained on different ore types

Ore type treated and concentrator	Flowsheet and reagent scheme	Concentration assays		% Distribution	
		% Cu	Au (g/t)	Cu	Au

Campbell, Canada
 	
Copper–gold ore
    with moderate pyrite
	Conventional flowsheet
	    with re-treatment
	of tailing by gravity
	    concentration xanthate–lime
	    circuit
		24.5	38.1	93	70

Mount Morgan, Australia
Copper–gold pyrite with
    chalcopyrite as the main
    copper mineral
	Conventional Cu/Au flowsheet
	    with the use of dithiophosphate
	    collector in alkaline media
		23.8	124	81.0	82.0

El Indio, Chile
Cu/Au with pyrite and
    highly acidic pH of the
    ore (i.e. 3–4). Enargite
    as the main gold mineral
	Wash the ore before flotation.
	    Use of xanthate + modified
	    thionocarbamate collector
	    (two-stage flotation flowsheet)
		35	150	88	75

Minas Conga, Peru
High clay ore with
    different content of
    pyrite and ore types.
    Natural acid pH
	Bulk flotation of all sulfides
	    followed by sequential Cu/Au
	    flotation from the bulk
	    concentrate using lime + SHQ
	    depressant, collector PAX
	    + xanthic ester.
		31.5	35	90.1	80.1

Batu Hijau, Indonesia
Andesite type with
    chalcopyrite, covellite
    and bornite
	Bulk flotation of all sulfides
	    followed by sequential
	    flotation of Cu/Au using
	    xanthate + dithiophosphate
	    collector in a soda ash medium.
		33.5	38	93	85.5

Table 12.19   (*Continued*)

Ore type treated and concentrator	Flowsheet and reagent scheme	Concentration assays		% Distribution	
		% Cu	Au (g/t)	Cu	Au
OK-Tedy, Indonesia Chalcopyrite, pyrite ore with quartz and alumino-silicate gangue	Sequential copper flotation using dithio-phosphate collector in a lime circuit.	42	58	88	80
Freeport, Indonesia Mixed copper ore with variable pyrite content	Sequential flotation using modified dithiophosphate collector + xanthate in an alkaline medium.	28	33	83	78

Table 12.20

Solubility results on the Cayeli Riz (Turkey) copper ore (yellow ore)

Element (mg/L)	Assays				
	pH 6.0	pH 8.0	pH 10.0	pH 11.0	pH 12.0
Copper, Cu	8.5	6.3	4.3	1.5	<0.5
Iron, Fe	400	300	210	105	<0.5
Sulfur, SO	850	620	360	180	30

the similarity in flotation properties of all sulfides, which is attributed to the following factors:

- When these ores are ground to their liberation size (i.e. 15–30 µm), the floatability of the individual mineral species is not only reduced but losses in selectivity may occur. At a fine size, the mineral properties undergo many surface changes, and therefore it is quite difficult to control selectivity between individual minerals.
- The weathering of iron sulfides causes accelerated weathering of copper sulfides [43]. Actual corrosion of minerals as a result of weathering can be found at contacts between different minerals, both in the exposed ore and in a ground ore. This may result in salt formation or dissolution of heavy metals and consequently adsorption of foreign ions, which may further reduce differential in floatability between chalcopyrite and iron sulfides. A typical example of the formation of cations and other ions during grinding of a massive sulfide copper ore is illustrated in Table 12.20. These data were obtained from the Cayeli Riz (Turkey) yellow ore. The formation of ions in solution decreases with an increase in pH. The results shown were obtained by grinding 1000 g of ore with de-mineralized water at 45% solids.
- Some massive sulfide copper ores contain secondary copper minerals, which can be attributed to pre-activation of pyrite, either *in situ* or during the grinding operation.

The massive sulfide copper ores in Western Europe are concentrated in the Black Sea region (Turkey), the Iberian Belt (Neves Corvo, Portugal), Canada (Windy Craggy) and Eastern USA (Bald Mountain). The copper grade of these ores may range from 1.5% Cu (Bald Mountain) to 8% Cu (Neves Corvo). Some of these ores, such as the Neves Corvo ore, contain sulfosalts, bismuth and some zinc. Rejection of these impurities may also represent a significant problem.

Processing characteristics of a massive sulfide ore

When using a conventional flotation reagent scheme and flowsheet, only a few of these ores respond (i.e. lime + NaCN + collector), giving extremely poor metallurgical results. The majority of these ores require a specific treatment process to achieve satisfactory metallurgical results. Each ore type also responds differently to flotation under similar reagent schemes, which is not the case when treating porphyry copper ores. Therefore, each individual ore deposit and operating plant uses a different reagent scheme, which may indicate that for each ore, the reagent scheme has to be tailored through extensive laboratory and pilot plant work.

The use of a specific depressant system for the depression of iron sulfides is a key to the solution of the metallurgical problem during the processing of massive sulfide copper ores. This is actually dictated by the nature of the ore and its mineralogy.

The presence of various impurity elements on the mineral surface may also have significant consequences. New mineralogical techniques (i.e. electron probe microscopy) have indicated the presence of a copper layer on pyrite mineral surfaces or contamination of chalcopyrite with sulfosalts or bismuth. Precise knowledge of the mineral surface state is very important in developing an efficient reagent scheme.

It is very difficult to generalize the performance of different collectors or modifiers in the flotation of massive sulfide ores because both collectors and modifiers perform differently for different ore types.

Reagent scheme used in treatment of massive sulfide and refractory copper ore

In the treatment of porphyry copper ores, the emphasis is always placed on the selection of collector–frother to achieve good metallurgical results. This approach never works in the treatment of massive sulfide copper ores. Although collectors are important, they are not critical in achieving good metallurgy. The depressants and modifying reagents are in fact the most critical reagents in the treatment of massive sulfide ores. In the case of this ore, there is much synergy between functioning of the depressant systems and the collector used.

Choice of depressants

The most common depressants used in the treatment of massive sulfide ores, such as lime and cyanide, are not effective on finely disseminated massive sulfide ores. Lime is used as co-depressant with another auxiliary depressant. In operating plants, lime with Na_2SO_3, $Na_2S_2O_5$ or SO_2 is normally used [47]. When the ore contains soluble ions, the ore is ground with high lime and conditioned with SO_2 to slightly acidic pH (i.e. 6.8–8.5),
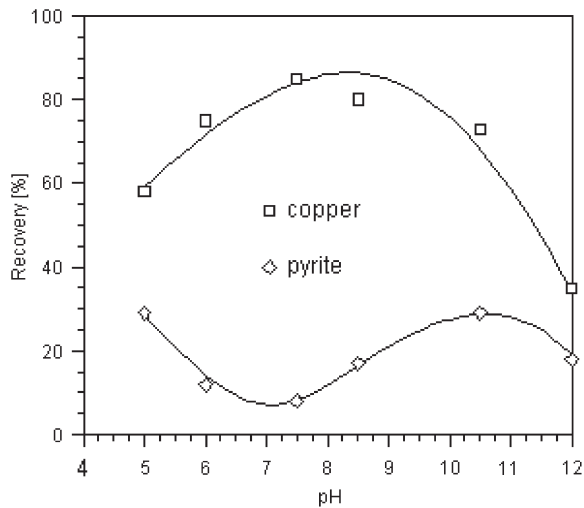
Figure 12.29 Effect of pH adjusted with SO_2 on copper flotation from the Cayeli Riz Yellow ore (lime added to the grind, 10 kg/t).

followed by copper flotation. The effect of the lime–SO_2 depressant system on the Cayeli Riz Yellow ore is shown in Figure 12.29.

Optimum copper recovery was obtained at a pH of 8.0–6.8. In some cases, Na_2S may be added to the grind as a supplementary depressant.

The Na_2SO_3–lime or $Na_2S_2O_5$–lime combination was used with massive sulfide ores at a pH region between 10.0 and 11.0. Neither Na_2SO_3 nor $Na_2S_2O_5$ is an effective depressant at a pH >11.

In recent years, a new line of effective depressants for massive sulfides has been discovered, some of which include depressant A3-3 , organic acid mixture with ammonium compound and modified starches depressant SD series [44,45].

The A3-3 depressant is a mixture of Na_2SiO_3:$Na_2S_2O_5$:$Al_2(SO_3)_3$ in the ratio of 40:40:20. When the mixture is prepared, it slowly releases SO_2, which may be the major contributing factor to its depressing ability.

The oxalic acid–NH_4Cl (1:1) mixture has found application in the treatment of massive sulfide copper ores with high pyrrhotite content. Depressants from the SD series, when pre-mixed with small quantities of cyanide, are excellent depressants for both pyrrhotite and carbonaceous pyrite.

The effect of depressant A3-3 on copper flotation from Bald Mountain's (USA) massive sulfide ore is shown in Table 12-21. Significant improvement in the concentrate grade and recovery was achieved with the use of A3-3.

The depressant oxalic acid–NH_4Cl mixture was a part of the reagent scheme for treatment of Windy Craggy massive sulfide pyrrhotite ore (B.C. Canada). This depressant was particularly effective at high pH (i.e. >12) and appears to improve the rate of copper flotation significantly. The effect of this mixture was studied in the pilot plant. Table 12.22

Table 12.21

Effect of depressant A3-3 on copper flotation from Bald Mountain copper ore (USA).
Lime added to the grind

Depressant A3-3 Additions (g/t)	Collector Used	pH	Assay % Cu	% Distribution
Cu				
0	PAX R3501[a]	10.4	3.5	66.2
200	PAX R3501	10.3	6.1	69.3
400	PAX R3501	10.4	7.4	75.8
600	PAX R3501	10.3	8.1	78.4
800	PAX R3501	10.3	9.1	85.5
1000	PAX R3501	10.3	9.5	90.3

[a]Dithiophosphate

Table 12.22

Effect of oxalic acid/ammonium chloride mixture on copper flotation from Windy Craggy ore –
pilot plant results (flotation pH >12)

Oxalic acid/NH_4Cl (1:1) additions (g/t)	Product %	Weight % Cu	Assay Cu	% Distribution
0	Cu concentrate	8.01	20.6	75.0
	Cu final tailing	91.99	0.59	25.0
	Feed	100.00	2.20	100.0
400	Cu concentrate	6.75	28.2	86.6
	Cu final tailing	93.25	0.31	13.4
	Feed	100.00	2.21	100.0

shows the results obtained in the pilot plant with and without additions of oxalic
acid–NH_4Cl mixture.

   Both copper recovery and concentrate grade improved with the use of depressant.

Choice of collector

The choice of collector depends very much on the type of depressant system used. If the
flotation is conducted in alkaline pH, then xanthate is used as primary collector with dithio-
phosphate, thionocarbamate or phosphine as secondary collector. If flotation is conducted at
slightly acidic circuit, then dithiophosphate, thionocarbamate or phosphine are used as pri-
mary collector, while xanthate is used as secondary collector, usually added to the scavenger
stage. The effect of the collector type using acid pH flotation is compared in Table 12.23.
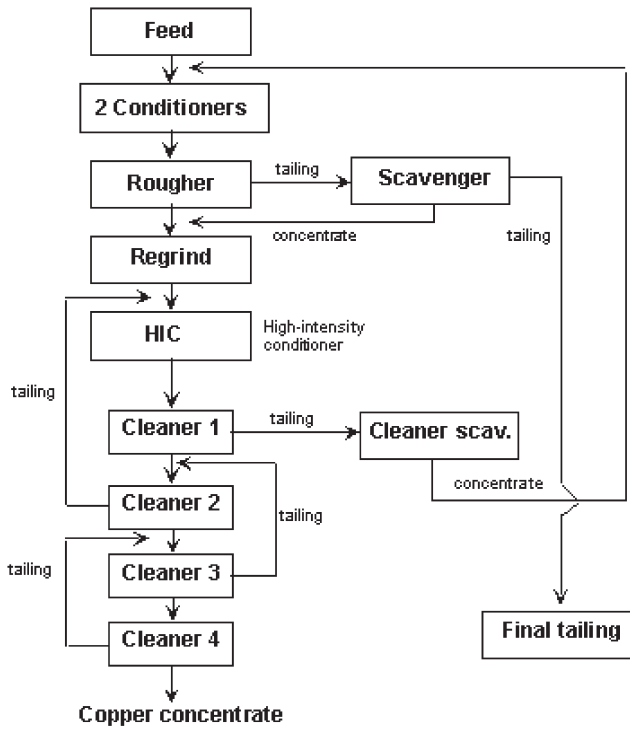
Figure 12.30 Flowsheet used in the treatment of massive sulfide copper ores.

Table 12.23

Effect of type of collector on copper flotation from Neves Corvo (Portugal) massive sulfide ore.
Lime–$Na_2S_2O_5$ depressant system. Flotation at pH 6.8 [44]

Collector type	Rougher		Cleaner	
	Assay % Cu	% Dist Cu	Assay % Cu	% Dist Cu
Na isobutyl xanthate	14.3	93.3	21.5	85.1
Dithiophosphate (LSB)	18.6	92.5	25.2	80.2
Thionocarbamate (X-23)	22.2	85.5	30.1	75.2
Phosphine (3418A)	17.4	93.1	28.5	83.1
Phosphine + dithiophosphate	18.4	95.2	30.3	86.6

Table 12.24

Different reagent schemes used in various plants on massive sulfide copper ores

| Type	Ore Description	Depressants used	Collector type	Pretreatment
1	Massive sulfide ore with moderate dissemination, pyrite 70–90%, copper 1.6–3% Primary grind $K_{80} =$ 65–75 µm Re–grind $K_{80} = 35$–25 µm	1. Lime–Na_2SO_3 2. Lime–$Na_2S_2O_5$ 3. Lime, NaCN, Na_2SO_3	Xanthate + dithio-phosphate dithiophosphate phosphinate	Conditioning with dithiophosphate + collector
2	Disseminated massive sulfide ore with soluble ions + cations present in the ore (SO, Cu^{2+}, Fe^{2+}, etc.). Grind $K_{80} = 55$–40 µm Re-grind $K_{80} = 30$–20 µm Cayeli Riz Black Sea copper	Lime to pH 12–19 SO_2 to pH 6.8–8.5 in conditioning auxiliary depressants Na_2S or NaCN	Dithiophosphate + phosphinate	SO_2 condi- tioning HIC after re-grind
3	Weathered massive sulfide copper ore with tarnished chalcopyrite, signs of pyrite oxidation. Varieties of pyrite present. May contain impurities such as arsenopyrite, sulfo–salts, bismuth, etc. Sulfides >90% Grind $K_{80} = 50$–60 µm Re–grind $K_{80} = 30$–20 µm	1. Lime–A3–3 2. Lime–SD200/NaCN (3:1 ratio) Lime–A3–3/SD200 3. A3–3, SD200/NaCN (3:1 ratio)	Dithiophosphate + xanthate mixture Dithiophosphate + phosphinate	HIC after re-grind
4	Massive sulfides with pyrite + pyrrhotite, 20% pyrite + 60% pyrrhotite. Finely disseminated ore Grind $K_{80} = 30$–40 µm Re–grind $K_{80} = $<20 µm	1. High lime+oxalic acid/NH_4Cl 2. Lime/DS200/NaCN 3:1 + oxalic acid/NH_4Cl (1:1 ratio)	Xanthate + dithio-phosphate Phosphinate + xanthate	Extensive condi tioning, HIC after re–grind
5	Massive sulfide ore with carbonaceous pyrite. Sometimes may contain Arsenopyrite & marcasite Grind $K_{80} = 45$–70 µm Re–grind $K_{80} = 25$–30 µm	Na_2SO_3 + modified Dextrin (DSS20) Lime/A3–3 Modified dextrin Na_2S, A3–3	Phosphinate + dithiophosphate Phosphinate − xanthate	

Flowsheet configuration'

The flowsheet used in the treatment of massive sulfide ores is relatively simple (Figure 12.30) and usually uses open-circuit first cleaner.

Some of the most important features of this flowsheet are preconditioning with reagents and high-intensity conditioning (HIC) used after re-grind. Particularly, high-intensity con- ditioning is extremely effective when a re-grind of the rougher concentrate to <20 µm is
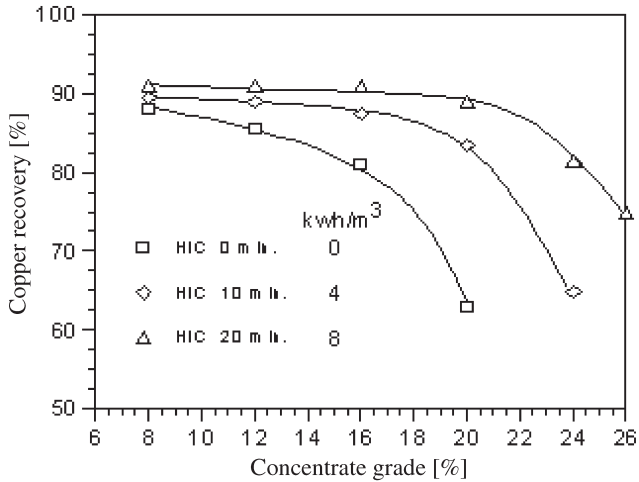
Figure 12.31 Effect of high-intensity conditioning on copper grade/recovery relationship (Cayeli Riz yellow ore).

required. Reagents are usually used in the high-intensity conditioning stage to enhance selective aggregation of fine particles [46]. The effect of high-intensity conditioning on the copper grade/recovery relationship is shown in Figure 12.31.

A summary of different reagent schemes for the treatment of massive sulfide copper ores is given in Table 12.24. These reagent schemes were either developed throughout research work (laboratory and pilot plant) or are in use in various plants. Some of the reagent combinations are new technology, which is applicable to a fairly large number of massive sulfide ores.

REFERENCES

1. Meyer, C., and Hemley R., Wall Rock Alteration, In *Geochemistry of Hydrothermal Ore Deposits*, Pergamon Press, New York, Chapter 6, p. 296, 1967.
2. Titley, S.R., Characteristics of Porphyry Copper Occurrence in the American South West, In (R.V. Kirkham and W.D. Sinclair eds) *Mineral Deposits Modelling*, Geological Association of Canada, Canada, pp. 265–270, 1997.
3. Mutschler, F.E., and Mooney, T.C., Precious Metal Deposits Related to Alkalic Igneous Rock: Provisional Classification Grade-Tonnage Data and Exploration Frontiers, In (R.V. Kirkham and W.D. Sinclair eds) *Mineral Deposits Modelling*, Geological Association of Canada, Canada, pp. 320–333, 1997.
4. Bulatovic, S.M., and Wyslouzil, D.M., Operating Practices in the Beneficiation of Major Porphyry Copper/Molybdenum Plants from Chile: Innovated Technology and Opportunities – A Review, *Mineral Engineering*, Vol. 11, No. 4, pp. 313–331, 1998.
5. Graig, J.R., Compositional and Textural Variations of the Major Iron and Base Metal Sulphide Minerals. In (P.M.J. Gray and J.F. Castle eds) *Sulphide Deposits, Their Origin and Processing*, IMM, South Africa, Johannesburg pp. 1–15, 1990.

6. Titley, S.R., Characteristics of High Temperature Massive Sulphide Ores in the United States, Mexico and Peru, In (R.V. Kirkham and W.D. Sinclair eds) *Mineral Deposit Modelling*, Geological Association of Canada, Canada, pp. 585–592, 1993.

7. Bogdanov, O.C., Theory and Practice of Flotation, *Metalurgizdat*, pp. 215–230, 1965.

8. Spira, V.K., *Oxygen Demand in Noranda Operating Plants*, Interim Report No. 12, Noranda Research Center, 1974.

9. Stone, K., *Flotation of Pyrrhotite using SO$_2$*, Doctorate Dissertation, Queens University, Kingston, Ontario 1974.

10. Bulatovic, S.M., *New Process for Depression of Marcasite during Copper–Lead Cleaning has been Introduced in the Viburnum Mill, USA*, Internal Technical Note No. 4, 1984.

11. Bulatovic, S.M., *Evaluation of New Reagent Scheme for Mansa Mina Chile Ore*, Report of Investigation 43824, January 1996.

12. Daniel, H., and Bulatovic, S.M., *Evaluation of New Collectors for Treatment of Porphyry Copper Ore, Senmin, South Africa*, Report of Investigation LR074, January 1995.

13. Munoz, F.J.C., *Evaluation of Disputada High Clay Ore*, Report of Investigation, LR Chile 2017, June 1993.

14. Bulatovic, S.M., Jessup, T., and Jackson, J.F., US Patent No. 5,049,612, Sept. 17, 1991.

15. Bulatovic, S.M., *Separation of Polymetallic Sulphides by Froth Flotation*, US Patent No. 4,880,529, Nov. 14, 1989.

16. Crozier, R.D., *Flotation, Theory Reagents and Ore Testing*, Pergamon Press, New York, 1992.

17. Harris, P.J., Frothing Phenomena and Frothers, In (R.P. King ed) *Principles of Flotation Froth*, IMM, South Africa, pp. 237–250, 1989.

18. Dippenaar, A., *The Effect of Particles on the Stability of Flotation Froth*, Report No. 81, IMM, South Africa, 1988.

19. Bulatovic, S.M., *Evaluation of New HP Frothers from Senmin on Escondida Plant Pulp, Chile*, Report of Investigation, LR-5435, May 1999.

20. Bulatovic, S.M., Evaluation of Different Frothers on Chucquicamata and Disputada Plant and Pulp, Private communication, 1996.

21. Von Hahn, H.E.A., Flotation of Molybdenite with Various Oil Refinery Fractions, *Conference of Metallurgists*, CIMM, Vancouver BC, August 25–28, 1968.

22. Glembotskii, V.A., Klassen, V.I., and Plaskin, I.N., *Flotation*, Nedra, Moscow, 1958.

23. Hernlund, R.W., Flotation of porphyry copper ore, *Quarterly Colorado School of Mines*, Report 56, No. 3, p. 177, 1961.

24. US Patent 3,785,488, January 15, 1974.

25. US Patent 3,788,467, January 29, 1974.

26. US Patent 3,912,623, October 14, 1975.

27. US Patent 2,095,967, January 1936.

28. Bulatovic, S.M., and Wyslouzil, D.M., Effect of Clay Slime on Flotation, *Copper '99*, Phoenix, October 1999.

29. Milos Sepilvoda, L.C., *Audit of Grinding Circuit of El Salvador Concentrator*, Monthly Lab Report No. 22, April 1995.

30. Konigsmann, K.V., Flotation Techniques for Complex Ores, In (A. Zunkel ed) *Complex Sulphides*, The Metallurgical Society, San Francisco, 1985.

31. Spira, P., and Roseblum, P., Application of Oxygen Demand, Measurement to Aeration Design, *10th Annual Meeting of the Canadian Mineral Processors*, pp. 484–550, Ottawa, 1978.

32. Bulatovic, S.M., Wyslouzil, D.M., and Rawling, K.A., Laboratory and Plant Evaluation of New Organic Depressant for Treatment of Nanisivik Massive Sulphide Lead–Zinc Ore, *18th Annual Meeting of Canadian Mineral Processors*, Ottawa, 1986.

33. Dudenkov, C.B., and Janis, N.A., *Principles of Theory and Practice of Flotation Reagents*, IZD Nedra, Moscow, 1969.
34. Bulatovic, S.M., Flotation Behaviour of Gold During Processing of Copper–Gold Ores and Refractory Gold-Bearing Sulphides, *Minerals Engineering*, Vol. 10, No. 9, pp. 895–905, 1997.
35. Martins, V., Dunne, R.C., and Gelfi, P., *Treatment of Partially Refractory Gold Ores*, Randol Gold Forum, Australia, 1991.
36. Lloyd, A., OK-Tedy Starts Up Copper–Gold Concentrator and New Gold Plant, *Engineering and Mining Journal*, Vol. 12, pp. 48–53, November 1987.
37. McCulloch, W.E., Flash Flotation for Improved Gold Recovery at Freeport, Indonesia, *Minerals and Metallurgical Processing*, Vol. 7, pp. 144–148, 1990.
38. Bulatovic, S.M., *Possible Improvement in Tintaya, Peru, Precious Metals Metallurgy*, Report of Investigation, LR-5341, 1996.
39. Bulatovic, S.M., *Evaluation of New HD Collector in Flotation of Copper–Gold Ore from Northern Ontario*, Report of Investigation, LR-029, 1991.
40. Allison, S.A., and Dunne, R.C., *The Flotation of Gold from South African Fold Mine Residues*, *14th IMPC*, Toronto, pp. II-9–II-18, 1982.
41. Bulatovic, S.M., *An Investigation of the Recovery of Gold and Copper from Igarape Bahia Oxide Copper–Gold Ore*, Report of Investigation, LR-5354, prepared for CVRD Brazil, 1997.
42. Bulatovic, S.M., *Effect of Organic Acid on Gold Flotation from Copper–Gold Ore*, Report of Investigation, LR-029 No. 4, 1992.
43. Plante, C., Effect of Oxidation on Sulphide Minerals on their Flotation Properties, *Transactions of AIME*, Vol. 285, 1963, Private Communication.
44. Bulatovic, S.M., and Salter, R.S., Process Development for Treatment of Refractory Massive Sulphide Copper Ores, *Copper 91*, Ottawa, August 1991.
45. Bulatovic, S.M., *New SD22 Depressant Improves Plant Metallurgy at Tara Concentrator, Ireland*, Lakefield Research Technical Note No. 6, 1983.
46. Bulatovic, S.M., *Review of Neves Corvo, Portugal Concentrator and Possible Improvement in Plant Metallurgy*, Prepared for RTZ, Report of Investigation, LR-4682, August 1991.
47. Bulatovic, S.M., and Wyslouzil, D.M., Research and Development in Selective Froth Flotation of Mineral Fines from Polymetallic Refractory Sulphide Ores, *Indonesian Mineral Processing Conference*, September 1991.

– 13 –

Flotation of Copper–Zinc Ores

13.1 SOME GEOLOGICAL AND MINERALOGICAL FEATURES OF COPPER–ZINC ORES RELEVANT TO FLOTATION

The geology and mineralogy of copper–zinc ores is similar to that of copper–lead–zinc ores, and in most cases, these ores are grouped together with copper–lead–zinc ores. There are several geological formations of massive sulfide copper–zinc deposits. These include:

(a)   Ores related to volcanic formation
(b)   Ores related to marine mafic extrusive rocks – Breccia type massive sulfide ores
(c)   Ores related to marine felsic ore, mafic extrusive rocks – epithermal ores
(d)   Copper–zinc scarns

The copper–zinc ores of volcanic formation occur in two principal formations: (a) areas dominated by mafic volcanic rock and (b) areas containing sub-equal amounts of mafic volcanic rock and sedimentary strata. These deposits are characterized [1] by significant variation in the mineralogical compositions and the alteration associated with the depth of the deposit. Deposits that are formed at a depth of more than 500 m are associated with a sequence of primary mafic flows. Typical deposits from this group are the Noranda district, Matagami Lake district and Flin Flon district (Canada).

Deposits that are shallow (i.e. 300–1500 m) are formed by mafic and felsic rock. The volcanogenic deposits contain up to 80% pyrite, sphalerite, chalcopyrite and often pyrrhotite. The ratio of copper and zinc varies widely. The complexity of the ore is also highly variable. With respect to processing characteristics, these ores can be regarded as complex massive sulfide ores and their floatability is related to the degree of alteration. There are two distinct types of alteration of these deposits. These include: (a) alteration pipes occurring directly below massive sulfide zones which have extremely complex mineralization and (b) lower semi-conformable alteration zones occurring several hundred meters below the sulfide zone. They may represent, in part, a reservoir zone where the sulfur and metal are leached. Some of the alteration pipes have a chloritic core and contain talc.

Breccia-type massive sulfide copper–zinc ores are a specific class of strata-bound mineral deposits that occur in thick sequence of clastic sedimentary rock and intercalated

basalt. Originally, noted by metamorphic belt of Shikolu, Japan, these deposit types are recognized throughout the world (Africa, Canada, USA, etc.) in rocks from the Early Protozoic to Tertiary age. These deposits typically form stratiform lenses and sheet-like accumulation of semi-massive to massive sulfides. Ore minerals are dominantly pyrite and/or pyrrhotite with variable amounts of chalcopyrite and sphalerite and minor to trace amounts of galena. These deposits contain significant amounts of precious metals (gold and silver). These deposits are different from those of the massive sulfide lead-rich deposits commonly associated with rhyolites. The ores from these deposits can form simple-to-treat to highly refractory ores (Goldstream, Canada).

Another kind of breccia-type massive sulfide copper–zinc ore is the deposits from the Outokumpu Mining district. These deposits are hosted by chemogenic quartzite and calcareous–silicate rock. The uniqueness of these deposits is they are high in cobalt and nickel. From a processing point of view, these deposits can be classified as difficult-to-treat to relatively simple ores. The largest deposits of this type are Kerelly, Petllilahti and Kylylahti.

The copper–zinc, or simply zinc, scarns occur in continental settings, associated with either subduction or rifting. The copper–zinc scarns are rare due to the fact that they are more common as lead–zinc ores with significant amounts of silver and gold. The largest copper–zinc scarn deposit is the Antamina deposit in Peru.

In most of the copper–zinc deposits, the valuable minerals are chalcopyrite and sphalerite. In some deposits, bornite, covellite and other porphyry copper minerals are present. The presence of secondary copper minerals in the copper–zinc ores represent a significant problem, specifically related to selectivity between copper and zinc minerals.

Sphalerite is the most important mineral which appears in many lead–zinc and copper–lead–zinc ores. There are several varieties of sphalerite including: marmatite – black variety with high iron, clesofen – colorless and preshibamit – high cadmium sphalerite.

The composition of sphalerite is highly variable and depends on the impurities contained in sphalerite. These impurities are either replacements of zinc in the crystal structure of sphalerite or the formation of emulsions in the mineral itself, as micron inclusions or 'disease' in sphalerite. The most common impurities in sphalerite are iron, cadmium, copper, indium, gallium, tin and other elements. Iron content of sphalerite can vary from 1 to 25%, cadmium can be as high as 1.5%. The copper can vary from traces to 20%. These impurities in the sphalerite are critical for determining reagent schemes suitable for the treatment of copper–zinc ore.

Copper–zinc ores also contain gold in the form of electrum or copper–aurid and silver, mostly as sulfosalts, and to a lesser degree, argentite.

13.2   FLOTATION PROPERTIES OF COPPER–ZINC ORES

In the flotation of copper–zinc massive sulfide ores, the flotation properties of copper and zinc are determined by the nature and composition of the ore. Selectivity between chalcopyrite and sphalerite, in principle, is determined by the type of copper minerals present in the ore. The simplest separation was achieved when only chalcopyrite is present in the ore. The presence of secondary copper minerals (i.e. bornite, covellite and digenite)

represents a significant problem in the separation of copper from sphalerite. This is because the secondary copper minerals are soluble and during grinding, or *in situ*, they release copper ions, which activate sphalerite. It is quite common that copper–zinc ores that contain secondary copper minerals have a covellite layer on the sphalerite surface.

Apart from the copper activation of sphalerite, the presence of silver, arsenic or other ions, which come from sulfosalts, may activate sphalerite and create a problem in the selective separation of copper and sphalerite. Although literature and textbooks contain vast references on flotation, activation and de-activation of sphalerite [2–4], little to nothing is known regarding the flotation behavior of sphalerite that contains impurities, even though it is the mineral that has been studied the most. In actual practice, the separation of sphalerite from copper can be very difficult on one hand, or flotation of sphalerite from pyrite and/or pyrrhotite can be relatively easy, on the other hand.

The flotation properties of sphalerite are also very much related to the iron content of the sphalerite. It has been established that adsorption of collector on sphalerite decreases with an increase of iron content of sphalerite [5], also the activation of sphalerite at higher pH decreases with an increase in iron content. For example, the optimum pH for activation of marmatite from massive sulfide ore is between 10 and 10.5, while with a higher pH, recovery of marmatite decreases.

In some deposits where weathering of the ore is dominant, or in the case of supergene alteration, sphalerite can be rich in copper giving rise to a chalcopyrite disease of sphalerite, in which case the sphalerite can be floated without activation with copper ions and, in a number of cases, may contaminate the copper concentrate.

The flotation behavior of chalcopyrite, found in copper–zinc ores, is similar to that of chalcopyrite from a massive sulfide ore. However, because during selective flotation of copper–zinc ores, different zinc depressants are used which may create different flotation environment, sometimes favorable for chalcopyrite flotation. The presence of pyrrhotite in copper–zinc ores, which is quite common, also affects the flotation of chalcopyrite in a way that pyrrhotite consumes oxygen that is required for chalcopyrite flotation resulting in decreased floatability. Therefore, the influence of oxygen in flotation of complex copper–zinc ores cannot be neglected. For example, a copper–zinc ore containing pyrrhotite needs extensive oxidation to promote chalcopyrite flotation [6]. Therefore, aeration is practiced in many operating plants that treat copper–zinc ores that contain pyrrhotite.

Copper–zinc massive sulfide ores are regarded as the most complex ores and consequently most difficult to treat. As a result, reagent schemes used in the various operating plants are very different. Based on the processing characteristics and mineral composition, the copper–zinc can be divided into the following four groups:

(a)   Low and medium sulfide copper–zinc ores, where chalcopyrite is the only copper mineral. These ores can be characterized as easy-to-treat ore. The sulfide content in this ore varies between 30 and 60%.

(b)   Copper–zinc massive sulfide ores, where the sulfide content of the ore ranges from 60 to 80% and the principal copper mineral in the ore is chalcopyrite. Pyrrhotite in the ore varies from 6 to 40%. The selectivity between copper and zinc does not represent a problem, but rejection of pyrite and pyrrhotite during zinc flotation can be difficult.

(c) Refractory massive sulfide ores, partially to highly altered, where the relatively high solubility of sulfide during grinding is common. These ores are usually finely disseminated and liberation occurs below 30 μm. Ores from the Black Sea region and Iberian Pyrite Belt are examples of these ores. The sulfide content of the ore is over 90%.

(d) Copper–zinc ores with mixed copper minerals (i.e. chalcopyrite, covellite, bornite and digenite) with moderate to high iron content, selective flotation of copper and zinc from these ores is extremely difficult and usually requires a special flowsheet and reagent scheme.

13.3   REAGENT PRACTICE IN FLOTATION OF LOW AND MEDIUM IRON SULFIDE CONTENT COPPER–ZINC ORES

These ores, in principle, are of volcanic origin with iron sulfide content ranging from 5 to 60%. The majority of these ores contain pyrrhotite, ranging from 3 to 15%. They are also characterized by low solubility of sulfides and therefore the ion content of the pulp is relatively low. The scarn ore also belongs to this group. Typically, most of these ores contain significant amounts of gold and silver and, consequently, the reagent scheme has been tailored to maximize precious metal recovery in the copper concentrate. These ores are concentrated in North America (i.e. Canada and USA), where the reagent scheme for treatment of these ores differs significantly from that used for concentrates from other parts of the world. In fact, it is called 'Canadian technology.' Most of these plants use aeration as a principal tool in controlling the rate of copper flotation, and thus, copper recovery.

13.3.1   Reagent schemes – modifiers and depressants

In the 1960s and 1970s, the reagent schemes used for treatment of copper–zinc ores were designed to maximize recovery of gold and silver.

Although cyanide was extensively used, the dosages were minimal because of the adverse effect on silver recovery. The effect of NaCN additions on silver and gold flotation from East Malartic (Canada) ore is illustrated in Figure 13.1 [7]. Higher additions of cyanide also had a negative effect on the rate of copper flotation, therefore the NaCN was used at a lower pH region (i.e. 8.5–9.0), where it was shown to be the most effective for depression of both pyrite and pyrrhotite.

In the ores where precious metals are present, the use of zinc sulfate ($ZnSO_4 \cdot 7H_2O$) was avoided and only a few plants are using small quantities of $ZnSO_4$ to aid zinc depression during copper flotation. In the presence of $ZnSO_4$, the recovery of both gold and silver in the copper concentrate is significantly reduced. Figure 13.2 shows the effect of $ZnSO_4$ on gold, silver and zinc recovery in the copper concentrate. Zinc rejection in the copper concentrate was reduced, but at higher $ZnSO_4$ additions, dramatic deterioration of gold and silver recoveries occur.

It is not known what causes deterioration of gold and silver in the presence of $ZnSO_4$. No literature data exist regarding the effect of $ZnSO_4$ on the floatability of individual
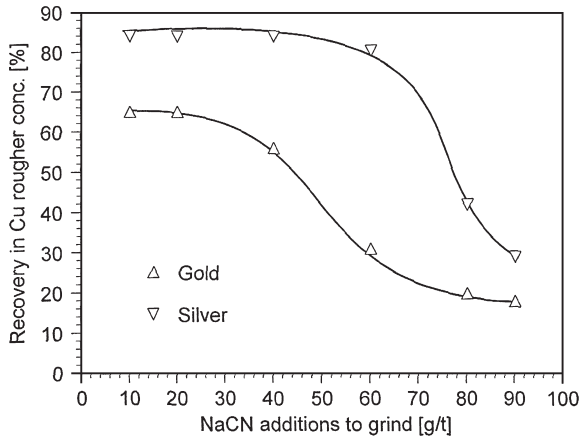
Figure 13.1 Effect of NaCN addition on gold and silver recovery in the copper rougher concentrate.
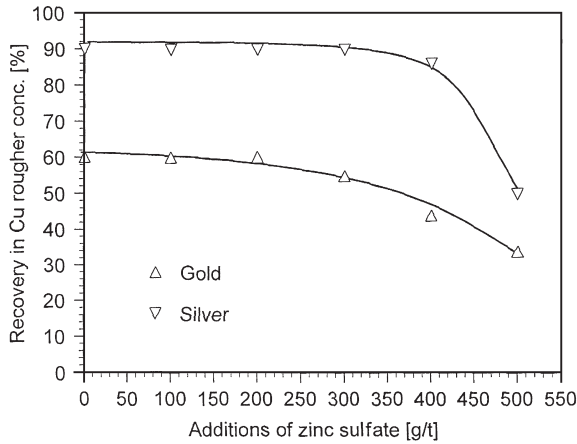
Figure 13.2 Effect of $ZnSO_4 \cdot 7H_2O$ additions on zinc, gold and silver recovery in the copper concentrate [8].

minerals. Plant data have also shown that high additions of $ZnSO_4$ have a negative effect on subsequent zinc flotation. This was most pronounced during flotation of lead–zinc ores. This phenomenon is discussed in more detail in Chapter 14. The effectiveness of $ZnSO_4$ as depressant decreases at a lower pH region (i.e. <9.0).

Depressant $(NH_4)_2SO_4$ was used in several plants that treat Cu–Zn ores containing pyrrhotite. In the presence of soda ash, $(NH_4)_2SO_4$ has shown a depressing effect on pyrrhotite. Studies have shown that the effectiveness of $(NH_4)_2SO_4$ as a depressant is related to pH. Figure 13.3 shows the effect of $(NH_4)_2SO_4$ on zinc concentrate grade at different pH levels. The results appear that ammonium sulfate was most effective at a pH between 9.5 and 10.5.
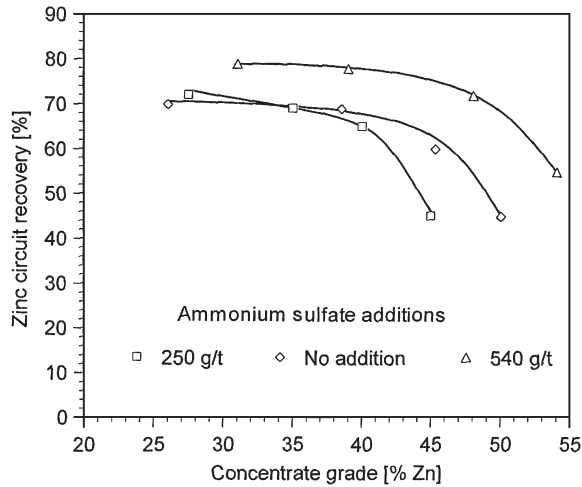
Figure 13.3 Effect of $(NH_4)_2SO_4$ on zinc concentrate upgrading from gold stream Cu/Zn pyrrhotite ore [9].

At the Geco plant, SO_2 gas was bubbled into a solution of NH_4OH and feed to the rod mill as a mixture which may produce $(NH_4)_2SO_4$.

The use of organic polymers, namely dextrin, was practiced in several plants as a pyrite/pyrrhotite depressant during both copper and zinc flotation. Small quantities of yellow dextrin were effective as pyrrhotite and pyrite depressant during both copper and zinc flotation. Some copper–zinc ores contain hydrophobic gangue (talc, chlorite). Depression of talc during copper flotation was effectively achieved with the use of carboxymethylcellulose (CMC).

Sodium sulfite (Na_2SO_3) is a part of the depressant system, together with lime, during the treatment of copper–zinc ore with elevated pyrrhotite content. It has been observed from plant practice that Na_2SO_3 is most effective at a pH region between 10 and 10.5. Other sulfur-containing compounds such as SO_2 and $Na_2S_2O_5$ have also been part of reagent schemes during the treatment of copper–zinc ores. $Na_2S_2O_5$ shows a depressing effect on both pyrite and pyrrhotite and also slows flotation of pre-activated sphalerite. The effect of level of $Na_2S_2O_5$ on copper flotation from Goldstream Ore is shown in Table 13.1.

These results were obtained in laboratory batch tests. Other depressants used were $ZnO/NaCN$ (1:3) and dithiophosphate collector. In the early 1990s, the Goldstream plant adopted $Na_2S_2O_5$ as their standard pyrrhotite depressant.

A new line of organic-based depressants, the 'SD' series and the 'HQS' series [10] were found to be highly effective pyrite/pyrrhotite depressants, and are used in several operating plants.

The principal pH modifier used in many plants that treat copper–zinc ore with precious metals is soda ash, mainly due to the fact that in the presence of lime, gold and silver recoveries are significantly reduced. Plant tests using lime were conducted at the East Sullivan Mines in the early 1970s where they normally used soda ash. The results obtained with soda ash and lime are compared in Table 13.2.

Table 13.1

Effect of $Na_2S_2O_5$ on copper flotation from Goldstream pyrrhotite ore

$Na_2S_2O_5$ additions (g/t)	pH	Copper rougher conc				Copper cleaner conc			
		Assays (%)		Dist (%)		Assays (%)		Dist (%)	
		Cu	Zn	Cu	Zn	Cu	Zn	Cu	Zn
0	6.5	4.3	3.2	85.1	45.6	14.1	2.2	71.3	25.2
300	6.7	6.5	3.1	88.8	38.3	16.3	2.1	74.4	20.1
600	6.6	7.4	2.6	89.6	28.2	18.5	2.0	80.1	18.1
900	6.5	8.1	2.3	92.2	25.3	22.4	1.6	83.1	11.4
1500	6.4	11.3	2.4	94.3	20.6	28.4	1.4	85.5	8.2
2000	6.3	12.2	2.2	95.1	18.5	30.3	1.4	86.1	7.1

Table 13.2

Effect of lime and soda ash on gold and silver recovery from the East Sullivan mine (Quebec)

Modifier (g/t)	Used pH	Product	Assays (%, g/t)				Distribution (%)			
			Cu	Zn	Au	Ag	Cu	Zn	Au	Ag
Na_2CO_3 = 400	9.1	Copper conc	21.3	3.24	7.1	150	91.7	13.7	82.5	70.0
		Cu circ tail	0.08	0.83	0.06	2.4	8.3	86.3	17.5	30.0
		Head	0.92	0.93	0.30	8.1	100.0	100.0	100.0	100.0
CaO = 280	9.5	Copper conc	20.8	4.1	5.2	130	90.0	15.2	72.2	65.0
		Cu Circ Tail	0.09	0.77	0.08	3.8	10.0	84.8	27.8	35.0
		Head	0.91	0.92	0.30	2.5	100.0	100.0	100.0	100.0

The absence of soda ash from the circuit also resulted in an increase in zinc content of the copper concentrate. In several operating plants, it has been observed [11] that the presence of soda ash in the copper circuit had a beneficial effect on subsequent zinc flotation. Lime is used in some operating plants, where precious metals are not present. Lime is proven to be a poor pyrrhotite depressant, especially at lower pH values.

Copper sulfate ($CuSO_4$) is a principal zinc activator used in the zinc circuit. The addition of $CuSO_4$ depends on the type of sphalerite present in the ore. Low iron sphalerite usually requires higher additions of $CuSO_4$ (i.e. between 100 and 150 g) per percent of zinc contained in the ore. Higher iron content of sphalerite requires lower dosages of $CuSO_4$. In many North American operating plants, the established plant consumption of $CuSO_4$ ranges from 60 to 80 g per percent of zinc in the ore. An overdose of $CuSO_4$ reduces zinc recovery and selectivity toward iron sulfides. This observation was made from plant data [12]. This phenomenon cannot be confirmed readily at a laboratory scale.

13.3.2   Reagent schemes – collectors and frothers

The type of collector used in selective flotation of copper–zinc ores depends on the following factors:

(a)   Presence of gold in the ore
(b)   Ratio of pyrite and pyrrhotite
(c)   Type of sphalerite present
(d)   Depressant system used

During the treatment of copper–zinc ores that contain precious metals, several collectors in the copper circuit were used, especially in the early days (i.e. from 1960s to 1980s). These collectors were AF242, AF35 and R208 (i.e. diaryl dithiophosphate and alkyl dithiophosphate). Xanthates were used as secondary collectors.

Xanthates in copper flotation are used as primary collectors with ores that do not contain precious metals and where the circuit pH is maintained above 9.5 (i.e. 10–10.5). When the amount of pyrrhotite in the ore is relatively high, alkyl dithiophosphate collectors are used as primary collectors and xanthates as secondary collectors.

In the 1980s, operating plants, which treat ore with precious metals, replaced dithiophosphates with a phosphine-based collector. This collector gave superior precious metal recoveries compared to dithiophosphate.

When the sulfur-containing depressants, such as SO_2, Na_2SO_3 and $Na_2S_2O_5$, were used as acid the preferred collectors are dithiophosphates or thionocarbamates.

In the zinc circuit, the principal collector used is xanthate. Few plants that treat ore with high pyrrhotite ore use modified thionocarbamate collectors. One operating plant (Flin Flon Operation) used xantogen formate as the principal zinc collector, which was later replaced by ethyl thionocarbamate.

The principal frother in a copper circuit is methyl isobutyl carbinol (MIBC) or other aliphatic alcohols. In some plants, pine oil is used. In zinc circuits, glycol-type frothers are used in the majority of cases. The exception being, where ores with elevated pyrrhotite content and the use of MIBC as the standard frother exists.

13.3.3   Operating plant reagent schemes

Table 13.3 shows the reagent schemes used in major operating plants that treat low and medium iron sulfide copper–zinc ores. Some of these plants have recently been closed as the deposit has been depleted, but the uniqueness of some of the reagent schemes is worth mentioning.

The presence of pyrrhotite in a number of operating plants represented a problem in pyrrhotite depression. Various plants adopted different techniques for rejection of pyrrhotite, which are worth describing. The following are different techniques used in various plants.

(a)   The Geco Concentrator uses extensive aeration in the copper circuit (i.e. about 15 min). Collector is also added in the aerators. In the zinc circuit, ammonia is used for

Table 13.3

Reagent schemes used in major operating plants

Concentrator and type of ore treated	Reagent additions		pH		Pretreatment
	Copper Circuit (g/t)	Zinc Circuit (g/t)	Cu	Zn	
Winston Lake, Canada Pyrite, pyrrhotite ore with	$Ca(OH)_2$ 400–800	$Ca(OH)_2$ 600	9.0–9.5	10.0	Long zinc feed conditioning with lime $CuSO_4$ + collector
~20% monoclinic pyrrhotite present in the ore	Na_2SO_3 500–600 DS200 50–100 R3477 10–150 SIPX 5–10	$CuSO_4$ 800–1500 SIPX 10 R3894[a] 10 MIBC 10			
BHP, Les Mines Selbaie Pyrite between 5 and 15% tarnished copper in weathered parts of the ore body	Na_2S 250 Na_2CO_3 600 R208 5–10 3418A 10–15 SO_2 to cleaners MIBC 0–10	$Ca(OH)_2$ 700–1000 $CuSO_4$ 250 R3894 5 SIPX 5–10 DF1012 5–10	9.2	10.5–11.5	Zinc cleaner feed conditioning
East Sullivan, Canada Ore consists essentially of pyrite, chalcopyrite, pyrrhotite and localized sphalerite. Total sulfur content 10%, Au/Ag present	Na_2CO_3 450 NaCN 12 Na_2SO_3 300 PAX 8 R108 14 R242 20 MIBC	$CuSO_4$ 250 R208 18 NaCN 12	9.2	9.0	Aeration = 12 min
Geco Mines, Canada Sedimentary deposit in amphibole–feldspar rock. Sulfides pyrite, pyrrhotite, chalcopyrite, sphalerite. Ore contains Ag	Na_2CO_3 400 NH_4OH 150 SO_2 200 NaEX 15 4.5 NaCN 12 PAX 15 R208 10	NH_4OH 480 $CuSO_4$ 320	8.5 clean	10.2	Aeration

(*Continued*)

Table 13.3   (*Continued*)

Concentrator and type of ore treated	Reagent additions		pH		Pretreatment
	Copper Circuit (g/t)	Zinc Circuit (g/t)	Cu	Zn	
Britannia Concentrator, Canada feeds Chalcopyrite, sphalerite, pyrite, gold + silver in a quartz chlorite–sericite schist, 16% total sulfide	$Ca(OH)_2$ 150 NaCN 80 $ZnSO_4$ 100 Na_2CO_3 100 PNBX 18 Pine oil 10	$Ca(OH)_2$ 400 $CuSO_4$ 250 PNBX 30 Pine oil 30	9.5	11.4	Conditioning copper and zinc
Kidd Creek, Canada Chalcopyrite, sphalerite, pyrite, marcasite in quartz–gabbro matrix. Total sulfide content 30–60%	$Ca(OH)_2$ 300 NaCN 20 SO_2 200–300 SIPX 15 R208 10 MIBC 15	$Ca(OH)_2$ 900 $CuSO_4$ 400 SIPX 15 Reverse flotation SO_2 = pH 4.5 Heat = 65 °C NaEX = 5 g/t	8.5–6.8	11.2	Aeration. Reverse pyrite marcasite flotation from zinc concentrate
Matagami Lake, Canada Chalcopyrite, sphalerite, pyrite in a sedimentary rock. Ore contained hydrophobic gangue	$Ca(OH)_2$ 300–600 $ZnSO_4$ 450 NaCN 50 CMC 120 SIPX 20 R3477 10	CaO 800 $CuSO_4$ 350 SIPX 30 Dow 1012 10	9.5	11.0	Aeration
East Malartic Mines, Canada Chalcopyrite, sphalerite, pyrite in a volcanogenic-rock. Significant quan-tities of gold present in the ore	Na_2CO_3 600 $ZnSO_4$ 550 R3477 10 PAX 5 3418A 10 MIBC 20 NaCN 70	CaO 1000 $CuSO_4$ 400 PAX 20 MIC 15	9.8	10.5	Preconditioning

(*Continued*)

Table 13.3   (*Continued*)

| Concentrator and type of ore treated	Reagent additions		pH		Pretreatment
	Copper Circuit (g/t)	Zinc Circuit (g/t)	Cu	Zn	
Pinos Altos, USA Chalcopyrite, sphalerite, secondary copper minerals in a sedimentary rock	Na_2S 400 Na_2SO_3 450 R208 20 PAX 5 MIBC 10	$Ca(OH)_2$ 400 $CuSO_4$ 380 PAX 10 R3894 10	8.5	10.0	
Twin J Mines, Canada Weint-type deposit with chalcopyrite, pyrite, sphalerite, gold and silver. Also containing clay minerals	Na_2CO_3 900 $ZnSO_4$ 300 NaCN 12 AF31 10 R208 25	$Ca(OH)_2$ 400 Na_2SiO_3 200 $CuSO_4$ 600 MIBC 20	8.8	10.5	Conditioning
Lake Dufault, Canada Chalcopyrite, pyrite, pyrrhotite, sphalerite in a sedimentary rock	Na_2CO_3 1500 Na_2SO_3 800 NaCN 15 $ZnSO_4$ 500 R404 40 PAX 20	$Ca(OH)_2$ 800 $CuSO_4$ 350 R3477 25 PAX 10	9.0	9.5	Copper skim flotation
Kevetty, Finland Chalcopyrite, pyrite, sphalerite in a volcano-genic rock	$Ca(OH)_2$ 800 SO_2 1500 SIPX/PAX 100 MIBC 20	$Ca(OH)_2$ 700 $CuSO_4$ 450 $Fe(SO_4)_2$ 500 MIBC 20	6.8 PAX 50	10.5	Lime–SO_2 conditioning in stages

[a] dithiocarbamate Cytec

pH control. It is believed that ammonia prevents activation of pyrrhotite in the presence of copper sulfate. Several attempts have been made through plant trials to replace ammonia with lime, but without success. When lime is added as pH modifier, the zinc concentrate grade drops from 51 to 47%.

(b) The Winston Lake Concentrator adopted quite a unique technique. In the copper circuit in the presence of Na_2SO_3 at pH 9.0, the pyrrhotite was well depressed. A long conditioning time with lime–$CuSO_4$-collector was also used in the zinc circuit. The $CuSO_4$ conditioner is a high-intensity conditioner (8'×8') equipped with a 150 HP motor. With the introduction of this conditioning technique, the zinc concentrate

Table 13.4

Metallurgical results obtained in the plants

Concentrators	Assays (%, g/t)			Assays (%, g/t)			Recovery (%)		
	Feed			Cu conc		Zn conc	Cu	Au	Zn
	Cu	Au	Zn	Cu	Au	Zn			
Winston Lake	0.7	0.3	13.5	27.2	8.4	54.5	76.0	40.5	94.0
Les Mines Selbaie	1.1	0.6	3.5	25.5	11.8	52.0	85.0	50.5	80.0
East Sullivan	0.9	0.3	0.9	21.5	6.8	52.9	91.0	82.0	81.8
Geco Mine	2.0	–	5.1	26.0	–	51.0	94.0	–	77.5
Britannia Mine	1.0	0.6	0.7	31.0	15.5	59.0	99.5	77.0	65.0
Kidd Creek	2.2	–	4.2	25.0	–	51.1	95.0	–	75.0
Matagami Lake	1.5	–	5.5	27.0	–	55.0	90.1	–	85.0
East Malartic	1.35	2.10	3.6	25.1	31.5	52.0	92.2	85.1	80.0
Pinos Altos	1.20	–	4.5	33.1	–	58.5	90.0	–	85.5
Twin J Mine	1.22	1.7	5.2	19.5	24.0	49.5	88.0	68.5	82.0
Lake Dufault	3.3	–	8.5	22.5	–	51.5	95.6	–	82.2
Kevetty	3.5	–	1.0	20.3	–	48.0	97.5	–	41.0
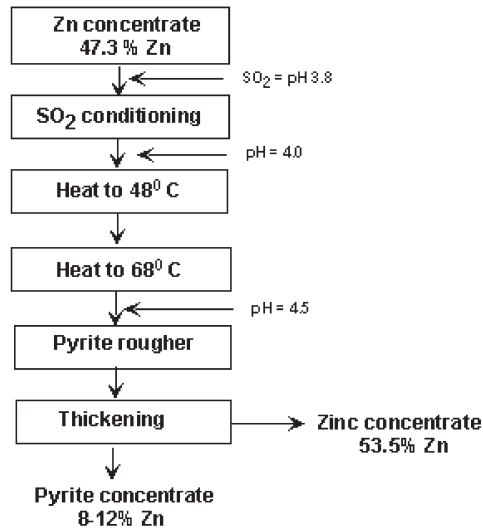
Figure 13.4 Schematic outline of reverse marcasite flotation circuit [13].

grade improved from 49% (start up of concentrator) to 54.5% Zn. Another important parameter in the zinc circuit flotation is pH control. In the roughing operation, pH was strictly controlled at 10.0 and in the cleaners at 9.5. The higher pH had a negative effect on zinc concentrate grade. It is believed that at higher pH, pyrrhotite tends to flocculate and reports to the zinc concentrate as an entrapment.

(c)   Some ores contained marcasite, which is readily floatable in the zinc concentrate. Kidd Creek Concentrator adopted a reverse flotation technique where the marcasite was floated away from the zinc using SO_2-heat method for sphalerite depression. Figure 13.4 shows a schematic outline of a reverse flotation method.

The most important parameter in this process is pH. The pH is strictly controlled at about 4.5. At a lower pH, the marcasite is depressed and will not float while at a higher pH, selectivity between marcasite and sphalerite deteriorates. By using this technique, the zinc concentrate was upgraded from 47.5 to 53% Zn with a 2% loss in overall zinc recovery.

13.4   REAGENT PRACTICE IN FLOTATION OF MASSIVE SULFIDE COPPER–ZINC ORES

This ore is common in many parts of the world, including North America, Russia, Europe (i.e. Turkey, Scandinavia, Spain and Portugal), Australia, South Africa and Japan. Some of these deposits are extremely complex and are considered as difficult-to-treat ore. Most of these ores are fine grained and require relatively fine grinding to achieve reasonable liberation. Sometimes grinding below 40 μm is required. Some deposits contain secondary copper minerals, which usually result in pre-activation of zinc minerals either *in situ* or during the grinding operation, where the separation of copper from zinc becomes very difficult and requires the use of a special reagent scheme and flowsheet.

The solubility of the ore, in some cases, represents a significant problem in sequential flotation of copper–zinc minerals. The ore that contains soluble metals (Cu^{2+}, Fe^{2+} and Ag^{2+}) often require special pretreatment to restore selectivity between copper and zinc minerals.

13.4.1   Processing Options

Unlike the treatment of copper–zinc ore, where sequential flotation of copper–zinc is usually used in the treatment of massive sulfide ores, a much more complex flowsheet and reagent scheme are employed. Including sequential flotation with special pre-treatment, a bulk copper–zinc flotation method followed by copper–zinc separation from the bulk concentrate and a special two-stage flotation method. The following are descriptions of some of the special techniques used in the treatment of massive sulfide copper–zinc ore.

Bulk flotation method

This method has been used in a number of Russian operating plants, where the ore contains secondary copper minerals and the selectivity between copper and zinc is poor when using the sequential flotation method. It is also used in some of the African plants. A typical flowsheet used in the bulk flotation method is shown in Figure 13.5.

When using this flowsheet, bulk copper–zinc flotation was performed in a lime circuit (pH = 10.5–11.5) with or without additions of $CuSO_4$. The bulk concentrate, after cleaning, was subjected to desorption usually with $Na_2S·7H_2O$ followed by copper flotation
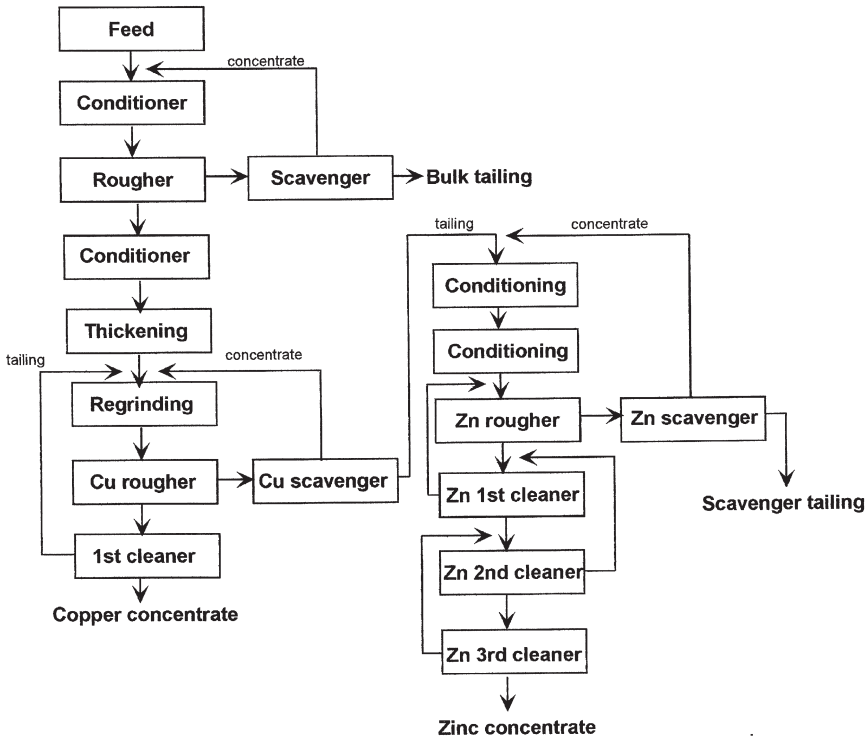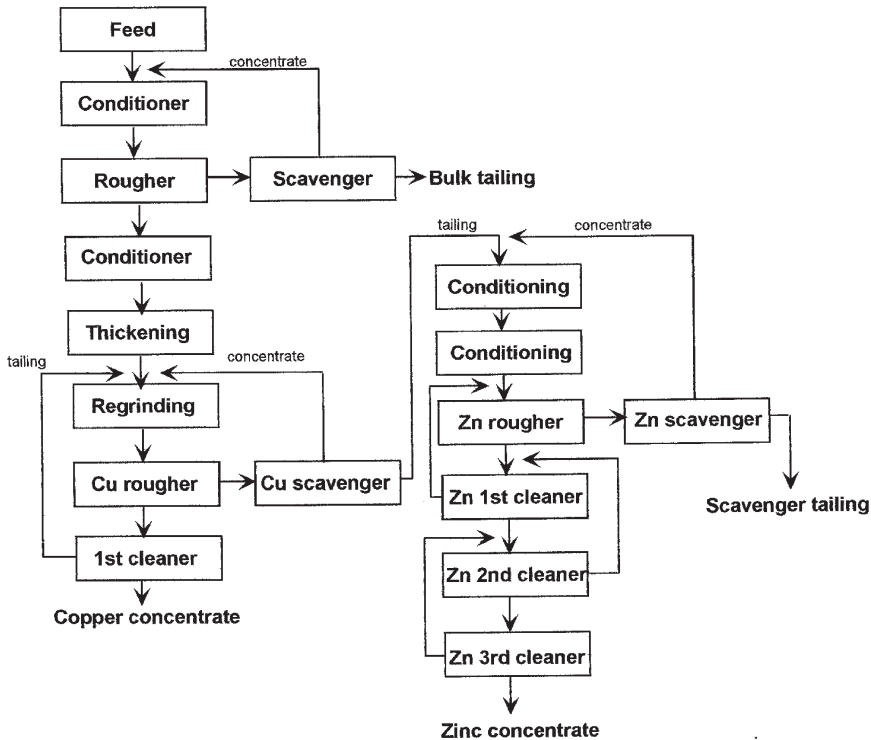
Figure 13.5   Bulk flotation flowsheet used for the treatment of copper–zinc ores using a zinc depression method.

using either a $ZnSO_4$–NaCN depressant system or a ferrosulfate–zinc hydroxide complex. Another version of copper–zinc separation from the bulk Cu–Zn bulk concentrate includes copper depression and zinc flotation. This is the case where the copper is mostly represented by secondary copper minerals (i.e. bornite, covellite and digenite). A schematic outline of the flowsheet and reagent scheme used in copper–zinc separation, where the copper depression is used, is shown in Figure 13.6. In this particular case, chalcopyrite is first sequentially floated followed by Cu–Zn bulk flotation of the secondary copper minerals. In the Cu–Zn separation, ferrocyanide was used. Such a flotation method was practiced in Lubumbashi (Kongo) copper–zinc plant. It is interesting to note that the sphalerite in this ore was high in cadmium.

Two-stage flotation process

This process is described in literature [14] and was developed as an alternative to a sequential flotation method. This method also utilizes bulk flotation of copper–zinc, while depressing pyrite. The bulk concentrate is treated with cyanide as a disorbing agent. Desorption-flotation was carried out in two stages. Figure 13.7 shows a schematic outline of the process, with levels and points of reagent addition. This method has been examined on the Priska (South Africa), the Pyhasalmi and Vihanti ores (Finland) with good metallurgical results.

Figure 13.6 Copper–zinc bulk flotation flowsheet followed by copper–zinc separation using copper depression method.

The level of cyanide in the desorption stage varies from 120 to 1000 g/t (Priska Mine). Conditioning with NaCN (i.e. desorption) is also an important variable of the process and ranges from 20 to 80 min.

This method has been developed at a laboratory scale and tested at a pilot plant scale, but has not found a commercial application yet.

Sequential flotation technique

The sequential flotation of copper–zinc from massive sulfide ore, usually involves a relatively complex flowsheet and reagent scheme. The choice of reagent scheme depends on the nature of the ore, liberation characteristics and degree of zinc activation.

In the case of finely disseminated ores, where pyrite depression is a major problem, a lime–SO_2 depressant system at pH between 6.8 and 8.0 gave reasonable separation. When the ore contains soluble cations (i.e. Cu, Zn, Fe etc.), the grinding is conducted at a high pH in the presence of either Na_2S or NaCN. The ground pulp is then conditioned at a lower pH, followed by copper flotation. In the zinc flotation circuit, the standard lime-$CuSO_4$ is used.

In most cases, in the treatment of massive sulfide ores the depressant system is emphasized due to the fact that success of selective flotation of copper–zinc from massive sulfide ores depends on the proper selection of depressant system.
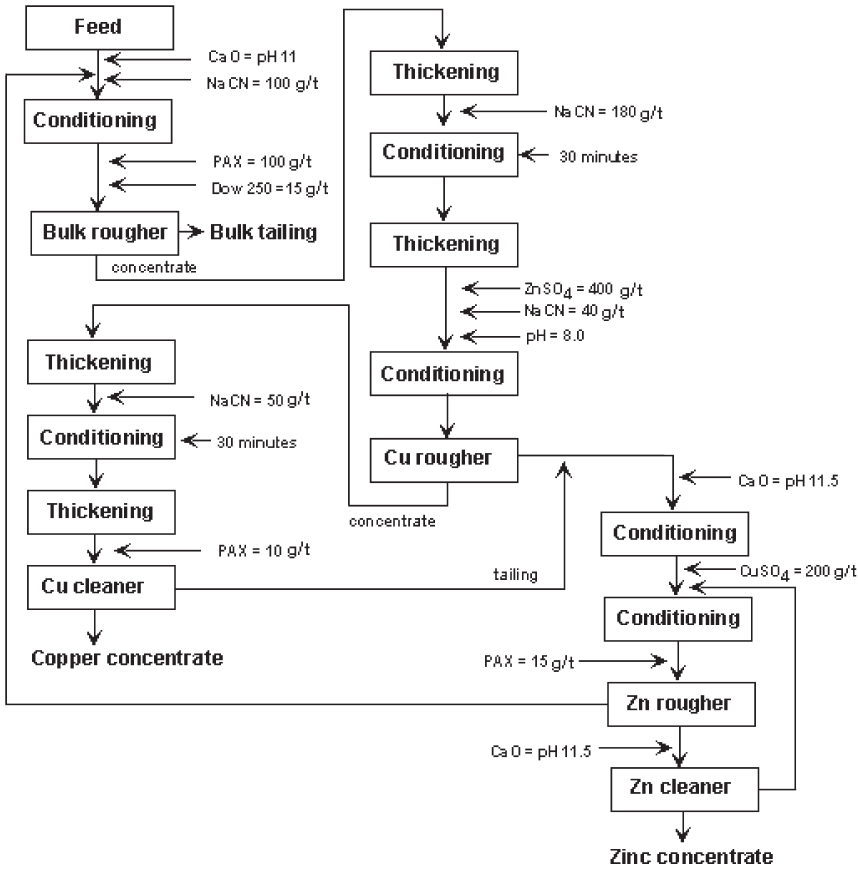
Figure 13.7 Two-stage copper—zinc separation process.

13.4.2   Reagent scheme and metallurgical results of the operating plants that treat massive sulfide copper–zinc ores

In the treatment of massive sulfide copper–zinc ores, the reagent scheme and flowsheet varies by region, where in various plants around the world different techniques are developed. For example, in Russian operations, a bulk flotation method is practiced. However selection of reagent scheme and flowsheet largely depends on the nature of the ore. In North American plants, a sequential flotation method has been used. Table 13.5 shows the reagent schemes of the most important plants that treat copper–zinc massive sulfide ores.

   The Flin Flon ore (Canada) contains an appreciable amount of pyrrhotite and marcasite, which represents a major problem in the treatment of ore in both the copper and zinc circuits. The pyrrhotite is very reactive and depletes the oxygen, resulting in very slow copper flotation. Aeration is used to improve the floatability of copper. In the zinc circuit, pyrrhotite is easily activated by $CuSO_4$, which is used for activation of sphalerite. To prevent flotation of pyrrhotite in the zinc circuit, a specific collector was used.

Table 13.5

Ore characteristics – flowsheet and reagent scheme used in the treatment of massive sulfide copper–zinc ores

Concentrator	Description of Ore and Treatment Process
Flin Flon, Canada	*Ore*: Massive sulfide mixed pyrite, pyrrhotite with some marcasite Contains about 65–80% sulfides. The principal copper mineral is chalcopyrite and the zinc mineral is sphalerite with an elevated iron content (9–12% Fe). Pyrrhotite present in the ore is monoclinic *Grind* = K_{80} of 78 μm *Reagents*: In the copper circuit, the reagents used include lime (pH 9.5), $ZnSO_4$ = 480 g/t, SO_2 = 80 g/t, NaCN = 25 g/t, R3477 = 15 g/t, PAX = 45 g/t. In the zinc circuit, the following reagents are used: lime (pH 10.5), $CuSO_4$ = 400–600 g/t, CA825 (thiono-carbamate) = 20 g/t Aeration was used in the copper circuit
Goldstream, Canada	*Ore*: Massive sulfide with predominantly monoclinic + hexagonal pyrrhotite (50%), pyrite (25%), with minor amount of alumino silicate. Copper is present as chalcopyrite. The high iron sphalerite was present. The ore contains significant quantities of gold (3 g/t) and silver (80 g/t) *Grind* = K_{80} of 65 μm *Reagents*: Copper circuit – $Na_2S_2O_5$ = 2000 g/t, CaO (pH 7.5), HQS = 800 g/t, $ZnSO_4$ = 400 g/t, 3418A = 20 g/t, PAX = 10 g/t Zinc circuit – $CuSO_4$ = 450 g/t, CaO = pH 10.5, SIPX = 25 g/t, MIBC = 15 g/t *Flowsheet*: Sequential Cu–Zn flotation with regrind of zinc concentrate before cleaning. Aeration in the copper circuit
Lynn Lake, Canada	*Ore*: Massive sulfides with predominantly pyrite (65–70%), granite, aluminosilicate and other gangue minerals. Chalcopyrite and sphalerite are principal valuable minerals *Grind* = K_{80} of 110 mm *Reagents*: Copper circuit – Lime = pH 10.5, $ZnSO_4$ = 400 g/t, NaCN = 15 g/t, SIPX = 20 g/t, R208 = 10 g/t Zinc circuit – CuSO4 = 450 g/t, CaO = pH 10.5, SIPX = 25 g/t, MIBC = 15 g/t *Flowsheet*: Sequential Cu–Zn flotation with regrind of the zinc concentrate before cleaning
City Services, USA	*Ore*: Massive sulfide pyrrhotite ore (about 66% sulfides) with some pyrite. Chalcopyrite and sphalerite are major valuable minerals *Reagents*: Copper circuit – CaO = pH 10.5 to grind, $ZnSO_4$ = 250 g/t, SO_2 = pH 6.8 conditioner, R3501 = 15 g/t, R208 = 10 g/t, cleaning pH = 6.5, MIBC = 10 g/t Zinc circuit – $CuSO_4$ = 200 g/t, CaO = pH 9.0, yellow dextrin = 200 g/t, SIPX = 10 g/t, R208 = 5 g/t, Dow = 250 g/t
Priska Mine, South Africa	*Ore*: A texturally zoned massive sulfide ore composed mainly of pyrite, chalcopyrite and sphalerite with minor quantities of pyrrhotite, arsenopyrite and galena. Zinc in this ore is pre-activated *Grind* = K80 of 63 mm *Reagents*: Copper circuit – NaCN = 230 g/t, H_2SO_4 = 750 g/t, $ZnSO_4$ = 880 g/t, R3477 = 30 g/t, MIBC = 20 g/t

(Continued)

Table 13.5   (*Continued*)

Concentrator	Description of Ore and Treatment Process
	Zinc circuit – CuSO4 = 300 g/t, CaO = pH 11.5, SIPX = 30 g/t, Dow250 = 10 g/t
	Flowsheet: Sequential
Cayeli Riz, Turkey	*Ore*: Massive sulfide copper–zinc ore consisting predominantly of pyrite (80%) with minor arsenopyrite and marcasite. The ore is partially oxidized and contains soluble? metal. It is also known as a black ore. The liberation occurs in between 12 and 20 mm
	Primary grind = K_{80} of 40 μm
	Regrind = K_{80} of 15 μm
	Reagents: Copper circuit – CaO = pH 11.5, NaCN = 100 g/t, Na2S = 200 g/t, SO2 = pH 8.5 conditioner, 3418A = 25 g/t, PAX = 10 g/t, cleaning SO2 = 4.5
	Zinc circuit: CaO = pH 11.8, CuSO4 = 1500 g/t, PAX = 100 g/t, 3894 = 10 g/t
	Flowsheet: Sequential with fine regrind
Bald Mountain, USA	*Ore*: Massive sulfide ore (95% sulfide) finely disseminated with chalcopyrite and sphalerite as the principal copper mineral. Liberation occurs at <15 μm
	Grind = K_{80} of 27 μm
	Regrind = K_{80} of 12 μm
	Reagents: Copper circuit – lime pH = 12.0, NH4Cl/Oxalic acid = 250 g/t, R3418A = 20 g/t, SO_2 pH 6.5, roughing and 4.5 cleaning
	Zinc circuit – pH 10.5, $CuSO_4$ = 280 g/t, SIPX = 30 g/t
	Flowsheet: Sequential
Tennessee Copper Corp.	*Ore*: Consists of pyrite, pyrrhotite (about 65% combined) in a sedimentary sulfide zone. Chalcopyrite and sphalerite are the principal valuable minerals. The non-sulfide gangues are carbonates
	Reagents: Bulk flotation – H2SO4 = pH 6.5, PAX = 150 g/t, MIBC = 15 g/t
	Copper circuit – $Ca(OH)_2$ = pH 9.5, NaCN = 300 g/t, R208 = 150 g/t
	Zinc circuit – $Ca(OH)_2$ = pH 11.5, CuSO4 = 450 g/t, SIPX = 10 g/t
	Flowsheet: Bulk sulfide flotation followed by Cu–Pb separation
Lahanos, Turkey	Ore: Massive sulfide ore of volcanogenic origin. This ore contains about 85% sulfides and some kaolinite clay minerals. It is finely disseminated with a liberation that occurs at about 15 mm
	Grind: K_{80} of 22 μm
	Reagents: Copper circuit – $Ca(OH)_2$ = pH 9.5, $Na_2S_2O_5$/Oxalic acid (4:1) = 1000 g/t, 3418A = 20 g/t, R3477 = 15 g/t, cleaning at pH 6.5
	Zinc circuit – $Ca(OH)_2$ = pH 12, $CuSO_4$ = 300 g/t, 3894 = 20 g/t
	Flowsheet: Sequential with the use of high intensity conditioners in the copper circuit
Rio Tinto Alfredo Deposit, Spain	*Ore*: Sedimentary finely disseminated massive sulfide ore with over 90% sulfides, where pyrite is the predominant mineral. Copper is represented by chalcopyrite. Zinc is a high iron. Sphalerite (10–12% Fe)
	Grind = K80 of 65 mm
	Regrind = K80 of 20–13 μm

Table 13.5   (*Continued*)

Concentrator	Description of Ore and Treatment Process
	Reagents: Copper circuit – $Ca(OH)_2$ = 800 g/t, A3–3* = 600 g/t, $Zn(SO4)_2$** = 600 g/t, PAX = 15 g/t, R208 = 10 g/t. Flotation pH 9.5, cleaning pH 6.8
	Zinc circuit – $Ca(OH)_2$ = pH 11.5, $CuSO_4$ = 350 g/t, Na_2SiO_3 = 150 g/t
	Flowsheet: Sequential with regrinding of the rougher concentrate. Conditioning with $Zn(SO4)2$
	*A3–3 = $Na_2S_2O_5$:Na_2SiO_3:$Al_2(SO_4)_2$ = 2:2:1
	**$Zn(SO_4)_2$ is a product of a reaction between $ZnSO_4$ and SO_2
Krasnouralskaia, Russia	*Ore*: The ore is of volcanogenic origin, consisting of chalcopyrite, sphalerite and pyrite (65%). The gangue minerals, quartz, sericite, chlorites. A portion of the sphalerite is in situ preactivated and floats with copper. The ore contains gold and silver
	Reagents: Semi-bulk circuit – Na_2CO_3 = 500 g/t, PAX = 40 g/t. Cu–Zn separation circuit: activated carbon = 200 g/t, NaCN = 160 g/t, $ZnSO_4$ = 1000 g/t, $Ca(OH)_2$ = 300 g/t
	Zinc circuit – $Ca(OH)_2$ = pH 11.5, $CuSO_4$ = 200 g/t, PAX = 35 g/t
	Flowsheet: Semi-bulk flowsheet with regrinding of the bulk concentrate followed by copper–zinc separation
Kirvograd, Russia	*Ore*: Impregnated massive sulfide ore with different ore types, ranging from scattered impregnated sulfides to massive sulfides. The major copper minerals include chalcopyrite and covellite with sphalerite as the major zinc mineral. The copper–zinc ore?? The copper–zinc ore contains an appreciable amount of iron hydroxide slimes
	Reagents: Cu–Zn bulk flotation – $Ca(OH)_2$ = pH 9.5, SIPX = 150 g/t, Cu–Zn separation – Na_2S = 500 g/t, activated carbon = 100 g/t, KCN (complex) = 200 g/t, $ZnSO_4$ = 800 g/t, sodium aeroflot = 10 g/t
	Zinc circuit – $Ca(OH)_2$ = 800 g/t, $CuSO_4$ = 300 g/t, PAX = 60 g/t, MIBC = 20 g/t
	Flowsheet: Bulk
Skedneuralsk, Russia	*Ore*: The ore treated comes from two deposits (Degfryarsk and Uchalisk) representing massive sulfides with an average sulfide content of 80%. Copper minerals are chalcopyrite, covellite and chalcosine. The zinc minerals are sphalerite with high iron content
	Reagents: Bulk – Na_2S = 300 g/t, PAX = 40 g/t, CaO = 8000 g/t; Cu–Zn separation – Na_2S = 1000 g/t, activated carbon = 100 g/t, KCN = 680 g/t, ZnSO4 = 1800 g/t, isobutyl Aeroflot = 20 g/t; Zinc circuit – $Ca(OH)_2$ = pH 11.5, $CuSO_4$ = 200 g/t, PAX = 15 g/t
	Flowsheet: Bulk with pretreatment of bulk concentrate with Na2S 2 activated carbon followed by dewatering before copper flotation
Karabash, Russia	*Ore*: Two ore types are treated at the Karabash plant (copper and copper2zinc ore). The copper−zinc ore consists of disseminated massive sulfides with 70285% pyrite content. The copper is represented by chalcopyrite, tennantite, bornite and covellite. Sphalerite is the main zinc mineral

Table 13.5   (*Continued*)

Concentrator	Description of Ore and Treatment Process
	Reagents: Bulk circuit − NaHS = 300 g/t, Ca(OH)$_2$ = pH 11.5, PAX = 45 g/t, sodium Aeroflot = ?; Cu$_2$Zn separation − Na$_2$S = 1000 g/t, activated carbon = 200 g/t, NaCN = 600 g/t, Zn(OH)$_2$ = 2000 g/t, pine oil = 5 g/t; zinc circuit − Ca(OH)$_2$ = pH 10.5, CuSO$_4$ = 250 g/t, PAX = 15 g/t, mineral spirit = 10 g/t
Ioshino, Japan	*Ore*: Sulfide ore with moderate pyrite content. The ore is partially oxidized and contains relatively high amounts of soluble salts, mainly created during the grinding operation. The ore contains chalcopyrite and chalcosine as the major copper minerals with sphalerite as the main mineral
	Grinding fineness = K$_{80}$ of 35 μm
	Reagents: Copper circuit − Ca(OH)$_2$ = pH 10.5, NaCN = 50 g/t, SO$_2$ = pH 5.2, R208 MIBC; zinc circuit − Ca(OH)$_2$ = pH >12, CuSO$_4$ = 300 g/t, SIPX = 15 g/t, MIBC
	Flowsheet: Sequential copper−zinc flotation
Adjustral, Portugal	*Ore*: The massive sulfides from the Iberian Pyrite Belt, specifically those from Adjustral (Portugal), are refractory, finely disseminated massive sulfide ores with a sulfide content of about 98%. The liberation of the individual minerals occurs at a range <15 mm
	Grind = K80 of 27 μm
	Regrind = K$_{80}$ of <12 mm
	Reagents: Copper circuit − Ca(OH)$_2$ = pH 11.8, DDS4* = 100 g/t, SO$_2$ = pH 8.0 rougher and 5.2 cleaners, PAX = 20 g/t, R3477 = 15 g/t, MIBC; zinc circuit − Ca(OH)$_2$ = pH 12.1, CuSO$_4$ = 400 g/t, 3894 = 15 g/t
	Flowsheet: Sequential with extended conditioning
	*DDS4 5 Dextrin:Quebracho:NaCN 1 3:1:3

In the early 1970s, the zinc collector used was modified xantogen formate (i.e. Minerec 748), while in the 1980s and 1990s, this collector was replaced with CA825 (ethyl thionocarbamate). Another operating plant treating high pyrrhotite ore is Goldstream, originally developed by Noranda and later operated by Bethlehem Copper. The initial process developed for treatment of this ore involved a lime–SO$_2$ system in the copper flotation and reverse pyrrhotite flotation from the zinc circuit using SO$_2$ at pH 4.0 [15]. This process did not work in actual plant operation and was later redesigned where Na$_2$S$_2$O$_5$–HQS was used as the depressant system in the copper circuit (Table 13.5). The HQS is a modified dextrin. The control of pyrrhotite flotation during the treatment of massive sulfide ores is much more difficult than that from low sulfide massive ores. The presence of soluble cations in the ore is always a problem using conventional flotation techniques. Soluble cations activate pyrite minerals, increasing collector consumption and very often activating sphalerite. In several operating plants (Cayeli Riz and Ioshina), the control of soluble cations is accomplished using a lime–SO$_2$ system. The ore is ground in the presence of high lime additions with either Na$_2$S or NaCN and then the pH is reduced to between 5.5 and 8.2 in

the conditioning stage before copper flotation. The level of lime is quite critical in achieving selective copper–zinc flotation and sometimes the lime requirement is in the range of 10 kg/t of the ore. The Lahanos concentrator uses a unique mixture of $Na_2S_2O_5$/Oxalic acid, also designed to control the soluble cations [15]. There is very little literature available regarding the mechanism of action of this mixture.

The presence of a secondary copper in the ore, like those from Russia, represent a special problem, specifically in selectivity between pyrite copper minerals and sphalerite. Most of these ores are treated using either a semi-bulk or bulk flotation flowsheet. Using this flowsheet, the copper and zinc are floated from the pyrite in alkaline pH. The bulk concentrate is then treated with Na_2S and activated carbon followed by selective copper–zinc flotation. In the majority of cases, $ZnSO_4$–NaCN is used. However, sometimes complexed cyanide and $Zn(OH)_2$ gave good separation.

The metallurgy from plant to plant varies considerably. Table 13.6 shows metallurgical results obtained in different operating plants that treat massive sulfide copper–zinc ores. Low copper concentrate grades were usually achieved when treating massive sulfide ores that contain secondary copper minerals. In the past decades, significant progress has been made in the improvement of selectivity toward copper–zinc and pyrite during the treatment of massive sulfide copper–zinc ores. This new technology is slowly being applied to the various operating plants, specifically the treatment of newly discovered ores.

Table 13.6

Metallurgical results obtained in operating plants treating massive sulfide copper−zinc ores

Concentrator	Assays (%)						Recovery (%)	
	Feed		Cu conc		Zn conc		Cu conc	Zn zonc
	Cu	Zn	Cu	Zn	Cu	Zn		
Flin Flon, Canada	2.5	4.5	25.5	4.3	0.9	52.2	95.5	75.3
Goldstream, Canada	3.1	3.3	27.1	3.8	1.1	47.5	92.4	60.3
Lynn Lake, Canada	1.8	4.6	24.8	4.6	1.2	54.5	89.3	80.5
City Services, USA	1.4	6.0	22.4	3.1	1.1	50.5	85.5	70.2
Priska, South Africa	1.6	1.7	25.5	3.95	2.10	50.1	85.5	70.4
Cayeli Riz, Turkey	3.3	11.5	22.5	8.60	3.10	49.1	80.3	65.6
Bald Mountain[a], USA	2.1	3.8	27.6	4.4	0.5	54.4	85.4	77.3
Tennessee Copper, USA	1.6	5.7	28.6	3.2	0.6	55.1	88.3	75.4
Lahanos, Turkey	4.2	2.6	22.5	6.1	0.9	50.5	80.1	66.2
Alfredo[a], Spain	2.1	2.0	25.5	3.1	0.9	52.2	85.5	58.2
Krasnouralskaia, Russia	1.8	2.0	16.6	3.8	0.8	50.0	82.2	68.3
Kirovograd, Russia	1.2	3.3	17.5	2.77	0.42	53.2	89.5	74.5
Sredneuralsk, Russia	1.4	4.0	16.0	8.60	1.80	47.6	75.6	33.2
Karabash, Russia	1.5	2.1	19.1	7.50	0.80	49.5	81.2	55.6
Ioshina, Japan	0.72	2.4	22.8	9.24	1.39	52.4	81.6	83.2
Adjustral[a], Portugal	1.20	4.40	23.5	5.60	0.89	50.6	75.5	80.2

[a]Pilot plant data.

13.5   REFRACTORY COPPER–ZINC ORES

Refractory copper–zinc ores are ores where the separation of individual copper–zinc minerals is not possible using conventional flotation techniques. The copper in these ores is represented by chalcopyrite (in lesser amounts), bornite, covellite, digenite and water-soluble sulfosalts. The sphalerite in the ore is preactivated by copper and/or silver minerals. A portion of the sphalerite contains micron inclusions of a variety of copper minerals. Pyrite in the ore can be partially oxidized and/or preactivated with heavy metal salts. These ores are regarded as the most difficult to treat with the exception of a few lead-zinc deposits. Out of several deposits scattered around the world, only two have been in production for some time. Several other deposits are in the development stage and the treatment process has been developed up to the pilot plant stage. The processes developed for treatment of these ores are quite unique and each process is described separately due to its uniqueness.

13.5.1   Lubumashi (Kongo) copper–zinc concentrate

The ore treated at this concentrator is 4.5% copper and 11.5% zinc. The copper minerals were represented by chalcopyrite, bornite and some covellite. The main zinc mineral is high in iron sphalerite. The gangue minerals consist mostly of dolomite with minor amounts of pyrite. This operation was the principal source of germanium ore for a period of 40 years. Figure 13.8 shows the treatment flowsheet with type and points of reagent addition.

The germanium and chalcopyrite were recovered in a prefloat circuit followed by copper–germanium separation using a magnetic separation method operated at about 1800 G. The primary and secondary copper concentrates assayed 22% copper and 12% zinc at about 70% copper recovery. The zinc concentrate contained 1.85% copper, 59.2% zinc at 71.5% zinc recovery.

13.5.2   Hanaoka (Japan) copper–zinc concentrator

This concentrator employed a unique separation method involving bulk flotation of the copper–zinc concentrate followed by thickening and filtration of the concentrate. The concentrate was aged for approximately 5 days followed by repulping in hot water and sequential copper–zinc flotation. The ore was volcanogenic with chalcopyrite and digenite as the main copper minerals. The ore contained 1.5% copper, 2.1% zinc and about 2.1% pyrite.

Bulk flotation was performed at an alkaline pH (i.e. 11.5) using xanthate collector. Zinc was recovered in a bulk concentrate without activation. The bulk concentrate assayed 15% copper and 21% zinc with a copper recovery of 78% and a zinc recovery of 76%. The filtered bulk concentrate after aging was repulped with hot water to about 40% solids and the copper was floated at 60 ºC with the addition of frother only, at pH 7.4. The copper tailing was stage conditioned with lime (pH 10.5) and copper sulfate, followed by zinc flotation and cleaning using collector R208. A copper concentrate, assaying 16.5% copper
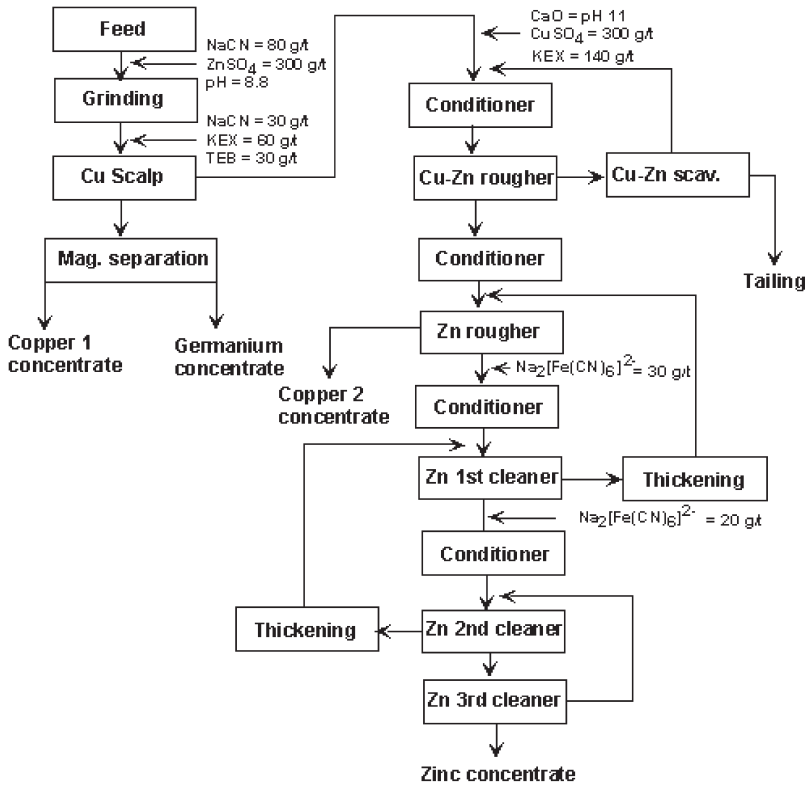
Figure 13.8 Lubumashi concentrator flowsheet and reagent additions.

and 5.6% zinc with 63% recovery, was produced. The zinc concentrate assayed 57% zinc at 70% zinc recovery.

13.5.3 Kutcho Creek ore deposit

The Kutcho Creek ore is relatively complex with chalcopyrite, bornite and covellite as the copper minerals and low iron sphalerite as the zinc mineral. The ore contained an appreciable amount of gold and silver. The silver minerals appear in the form of sulfosalts. The sphalerite is preactivated and is readily floatable without activation. After several years of extensive studies, a unique separation process was developed and was tested at pilot plant scale [16]. The schematic outline of this flowsheet and reagent scheme are illustrated in Figure 13.9.

In the copper–zinc bulk flotation circuit, lime xanthate was used where copper and zinc were recovered in a bulk concentrate assaying 12% Cu and 18% Zn. In this circuit, sphalerite was readily floatable without preactivation. In the copper–zinc separation circuit, the most critical parameter was conditioning time with alkaline and pH. With reduced conditioning
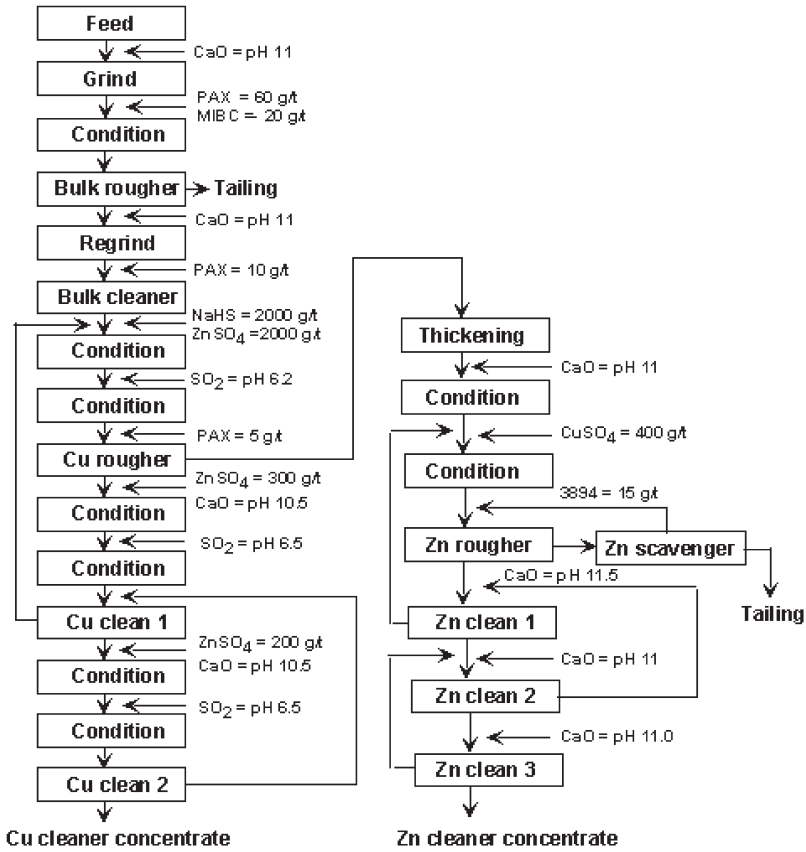
Figure 13.9 Flowsheet and reagent scheme developed for the treatment of Kutcho Creek ore.
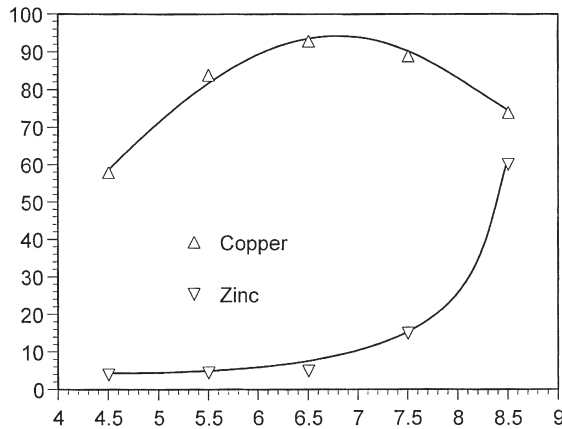
Figure 13.10 Effect of pH on copper−zinc separation from bulk cleaner concentrate.

time, with alkaline the selectivity between copper and zinc deteriorated. The pH above 6.5 gave poor Cu/Zn separation. Figure 3.10 shows the effect of pH on copper–zinc separation.

At a lower pH value, the recovery of copper was reduced. Using this separation method, a copper concentrate assaying 30% copper and 3.5% zinc was achieved with about 85% recovery. The zinc concentrate assayed 60% zinc at 78% recovery.

13.5.5   Maranda LCV copper–zinc deposit – South Africa

This is a highly refractory copper–zinc ore with supergene alteration. In addition, it contains talc and chlorites, which interfere with flotation of copper and zinc. The principal

Figure 13.11 Flowsheet and reagent scheme developed for the treatment of LCV copper−zinc ore.
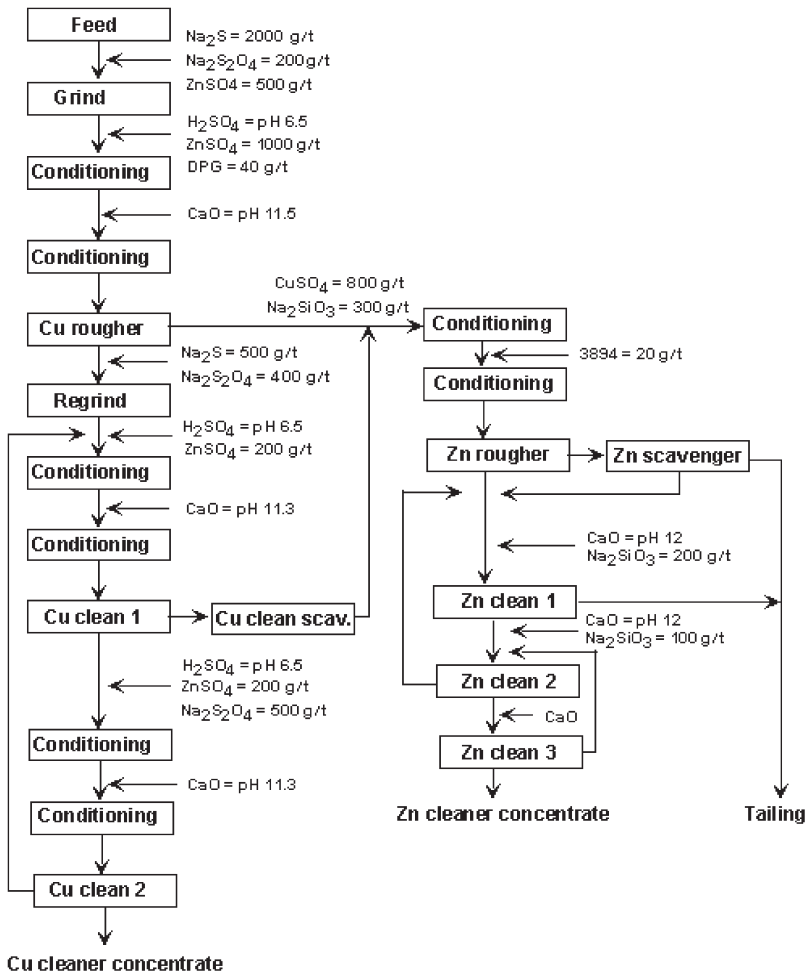
copper minerals in the ore are digenite (60%) and chalcopyrite (30%) with bornite and covellite. The zinc is represented by both sphalerite and marmatite with theoretical grade of about 54% zinc. The reagent scheme developed for treatment of this ore involves sequential flotation of copper and zinc using quite an unusual reagent scheme. The average ore grade was 1.9% copper and 12.5% zinc. The ore contains about 45% pyrite. The principal non-sulfide gangue minerals included talc, chlorites and aluminosilicates.

The reagent scheme and treatment flowsheet are illustrated in Figure 13.11.

The collector selected for copper flotation was diethyl-guanidine (DPG) dissolved in citric acid. This collector was highly selective toward sphalerite and marmatite and was capable of floating digenite, sphalerite middlings. The use of DPG dissolved in alcohol gave poor copper recovery.

None of the conventional collectors examined (i.e. xanthates and dithiophosphates) was selective. The successful zinc flotation from the copper tailing was achieved with dithiocarbamate collector (3894) without activation of sphalerite. Using this process, copper concentrate assaying 28% copper and 10.5% zinc was produced at about 75% copper recovery. The zinc cleaner concentrate assayed 52% zinc, 2.2% copper at 81.5% zinc recovery.
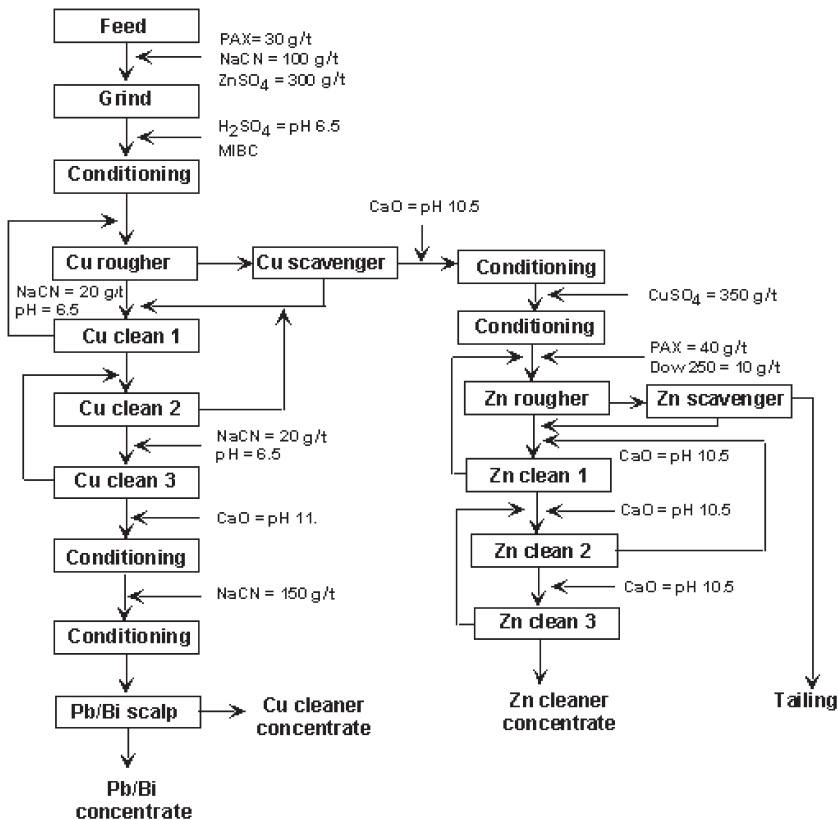

Figure 13.12 Flowsheet and reagent scheme used in treatment of Antamina ore.

13.6   FLOTATION OF COPPER–ZINC SCARNS

There are only a few copper–zinc scarn deposits, mainly located in the South American region. Some of the copper–zinc scarn can be refractory and would only respond to flotation using the processes described in the 'treatment of refractory copper–zinc ore' (i.e. Minas Conga scarns, Peru). Typically these ores contain chalcopyrite, bornite and covellite as the principal copper minerals. They also contain impurities such as bismuth, galena and various sulfosalts. The Antamina (Peru) deposit is the largest copper–zinc scarn deposit discovered to date. The ore also contains chalcopyrite and bornite as the principal copper minerals. The bornite is contaminated with bismuth in some parts of the ore body. The ore responds well to a more conventional treatment process. Figure 13.12 shows the flowsheet and reagent scheme developed for treatment of Antamina copper–zinc scarn ore. The ore types that contain bismuth associated with galena. A copper bismuth separation is introduced in the circuit and consists of depression of copper using cyanide and lead bismuth flotation without collector additions.

REFERENCES

1. Franklin, J.M., Volcanic Associated Massive Sulphide Deposits, In (R.V. Kirkham ed) *Mineral Deposit Modeling*, IMM, Johannesburg, South Africa, pp. 315–341, 1997.
2. Finkelstein, N.P., and Allison, S.A., The Chemistry of Activation Deactivation and Depression in the Flotation of Zinc Sulphides – A Review, In (M.C. Fuerstenau ed) *Flotation A.M. Gandin Memorial Volume*, MIM, Society of Mining Engineers Inc. Littleton, Colorado, Vol. 1, pp. 414–460A, 1976.
3. Clifford, K.L., Mechanism of Flotation of Natural Sphalerite with Xanthates, PhD Thesis University of Utah, 1971.
4. Goold, L.A., and Finkelstein, N.P., The Reaction of Sulphide Minerals with Thiol Compounds, NIMM, Johannesburg, South Africa, Report No. 1439, 1972.
5. Girczys, J.L., Copper Activation Studies with Sphalerite, Canadian Metallurgical Quarterly, Vol. 11, pp. 553–558, 1972.
6. Spira, P., and Rosenblurn, F., The Oxygen Demand of Flotation Pulps Canadian Mineral Processors Conference, Ottawa, Ontario, pp. 331–340, January 22–24, 1974.
7. Bulatovic, S.M., The Recovery of Copper–Zinc Gold and Silver from Kutcha Creek Ore, Report of Investigations, LR3361, 1979.
8. Fishman, M.A., and Soboev, D.C., *Flotation Practice in Treatment of Sulphides and Precious Metals*, Vol. 5, Metallurgizdat, Moscow, 1957.
9. Bulatovic, S.M., An Investigation of the Recovery of Copper, Zinc, Gold and Silver from Gold Stream Massive Sulphide Ore, Report of Investigations LR2968, 1984 (Prepared for Bethlehem Copper).
10. Bulatovic, S.M., and Jessup, T., Depressant for Flotation Separation of Polymetallic Ores, US Patent 4,877,517, October 31, 1989.
11. Shenstone, D.A., The Milling of Canadian Ores, In (J. Convey ed) 6th Commonwealth Mining and Metallurgical Congress, 1957.
12. Bulatovic, S.M., Plant Trial of the Level of CuSou at Geco Plant, Noranda Mines, *Geco Division Monthly Report*, May 1975.
13. Matienco, O., New Reverse Pyrite Marcasite Flotation from Zinc Circuit from Bore at Kidd Creek Concentrator, *Metallurgical Group Quarterly Report*, No. 3, June 1986.

14. Bushell, L.A., Lewis, J.M., and Lund, B.A., Two-Stage Process for the Recovery of Flotation Concentrates from Copper–Zinc Ores, NIMM, Johannesburg, South Africa, Report No. 1268, June 1971.
15. Stowe, K., Depression and Flotation of Pyrrhotite, PhD Thesis, Queens University, Kingston, Canada, 1975.
16. Sarbutt, K.W., and Bigg, A.C.T., Pilot Plant Evaluation of Kutcho Creek Ore, Sumitono Mining Co., LR 3671, 1984.

– 14 –

Flotation of Lead–Zinc Ores

14.1 INTRODUCTION

Lead–zinc ores are the most abundant ores in the world and they are found in everywhere, such as North America, South America, Balkan Peninsula, Europe, Russia, Australia and Africa. There is a fairly large variety of ores, ranging from carbonatite ores that are relatively easy to treat to refractory ores, where a treatment process has yet to be fully developed. Special ore types, which are regarded as silver ores are actually lead–zinc ores which are specifically treated for silver recovery. Most of the lead–zinc ore contains silver and to a lesser degree, gold. Almost 85% of the silver production in the world comes from lead–zinc ores.

Silver recovery in a large number of ores, specifically from South America, is emphasized, and some of these circuits were in fact designed to provide the highest possible silver recovery. The reagent scheme used in the treatment of lead–zinc ores varies considerably and depends on the nature and mineralogy of the ore. In most cases, $NaCN$–$ZnSO_4$ depressant system is used with xanthate + dithiophosphate collectors. These reagent schemes are normally employed for treatment of carbonatite and coarse-grained massive sulfides. However, for treatment of disseminated massive sulfide ores, a much more complex reagent scheme is used. In a number of cases, de-zincing of the lead concentrate or removal of arsenopyrite from the zinc concentrate is required. This adds to the complexity of the treatment process.

The type of reagent schemes also varies by regions, where the application of new technology (i.e. new collectors and depressants) in some regions is very slow and the operating plants rely on the old conventional processes and technology.

As for copper–zinc ores, some of the lead–zinc ores are treated using bulk flotation followed by lead–zinc separation. This method is basically used in cases where zinc is pre-activated *in situ* or during grinding. It is also used for the treatment of ores containing soluble cations and ores with acidic natural pH.

14.2 GENERAL GEOLOGICAL AND MINERALOGICAL FEATURES OF LEAD–ZINC ORES

One of the most important deposits from an economical point of view is that of hydrothermal and sedimentary origin. Other deposits of economic values include deposits related to

felsic intrusive rock (lead–zinc scarn), ores in clastic sedimentary rock (sandstone-hosted lead–zinc ores) and ores in carbonate rock.

The sedimentary lead–zinc deposits are important sources of lead and zinc and amount to about 50% of the world's lead–zinc production. Because many sedimentary deposits are formed in half-gabbro [1] basins, they are asymmetrically zoned, ranging in formation mound shafted vent, complexes to flanking, interbedded and epiclastic sediments. These deposits occur within basinal sediments that cap thick continental syn-rift sequences of coarse-grained clastic and are formed from the discharge of hydrothermal fluid into the sea floor. The main characteristic features of these deposits are described as follows:

The bulk of the ore is contained in a stratiform sulfide body with several lenses, some of which can have extremely variable mineralogy.

The stratiforms are mostly composed of sulfides, carbonates, chert, barite and carbonaceous matter. In most of these deposits pyrite is predominant sulfide mineral although some deposits (e.g. Sullivan and Mount Isa) pyrrhotite is predominant mineral. The main economic minerals are sphalerite and galena.

Some deposits contain significant quantities of silver. These deposits can occur in different shapes and forms including distal sedimentary facies, vent complex and feeder pipes, also with highly variable mineralogy. Table 14.1 shows the most important sedimentary deposits with general characteristics. From a processing point of view, these ores vary significantly in flotation characteristics and can be regarded as difficult to treat ore, to refractory massive sulfide. Sphalerite and galena in majority of the ores is finely disseminated and requires relatively fine grinding to achieve liberation. In addition, some of the deposits (Grum, Canada; Lady Loretta, Australia) contain secondary copper minerals, which cause problems in selectivity between sphalerite and galena.

The presence of carbonaceous pyrite, where pyrite is contaminated with either graphitic or organic carbon, influences selectivity between galena, sphalerite and pyrite species. Such deposits are Cirque (Canada), Mount Isa (Australia) and Elura (Australia). These ores also contain arsenopyrite and other trace impurities, which influence flotation properties of both lead and zinc. The silver recovery from these ores often does not exceed 60%.

The Dolstone (dolomite) deposits, or so called Mississippi Valley deposit type (MVT), are a varied family of epigenetic ores occurring predominantly in dolstate in which galena and sphalerite are the major minerals of economic value. Although these deposit are distributed throughout the world, the major districts occur in the United States and Canada. These deposits occur in districts covering several hundred square kilometers and they display remarkable similarity in mineral assemblage.

The majority of the MVT deposits have simple mineral compositions (i.e. lead, zinc and iron sulfides). Cadmium, germanium, gallium and indium are also present in some deposits and have been recovered with lead and zinc [2]. The silver content in the majority of these deposits is low and does not exceed 40 g/t. The main gangue minerals include carbonates, dolomite, borite and fluorite. Barite and fluorite are recovered from the ores with high borite and fluorite content.

In general, ores from these deposits are easy to treat and in operating plants, high lead and zinc concentrate grade are readily obtained using relatively simple reagent schemes.

Table 14.1

Ore grade and reserves of the most important lead–zinc sedimentary deposits

Deposit	Tonnage (m/t)	Assays (%, g/t)				Host gangue
		Pb	Zn	Ag	Cu	
Likak, USA	22	3.0	8.8	55	–	Carbonaceous shale or chert
Red Dog, USA	87	5.0	16.5	72	–	Carbonaceous shale
Cirque, Canada	33	2.0	8.0	57	–	Carbonaceous shale, chert
Faro DY, Canada	20	5.7	7.0	87	0.1	Carbonaceous shale
Faro Grum, Canada	40	4.0	7.0	65	0.1	Carbonaceous shale
Faro Vangorda, Canada	8	3.0	5.0	56	0.1	Carbonaceous shale
Sullivan, Canada	170	5.8	55	59	–	Carbonaceous shale
Navan, Ireland	70	2.6	10	33	–	Carbonate
Tara Mines, Ireland	60	3.0	8.0	66	–	Carbonate
Meggen, Germany	60	1.3	10	1.5	0.2	Carbonaceous shale
El Aguilar, Argentina	50	6.5	8.5	150	0.1	Shale, schist
Bleikvassali, Norway	8	2.5	42	–	0.2	Gneiss
Koushk, Iran	10	6.0	12.0	–	–	Carbonaceous shale
Broken Hill, S.Africa	87	3.6	1.8	48	–	Carbonaceous shale
HYC, Australia	190	4.1	9.5	40	–	Gneiss
Dugal River, Australia	40	2.0	12.0	37	–	Carbonate
Mount Isa, Australia	90	7.0	6.0	160	–	Carbonaceous shale
Lady Loretta, Australia	40	8.0	14.0	110	–	Carbonaceous shale
Hilton, Australia	40	8.0	10.0	180	–	Carbonaceous shale

Table 14.2

Ore grade and reserves of the most important MVT deposits

Deposit	Tonnage (m/t)	Assays (%, g/t)			Host gangue
		Pb	Zn	Ag	
West Fork, USA	15	6.2	3.3	8.0	Carbonate, borite
Sweet Water, USA	10	3.1	4.4	5.8	Carbonate, fluorite
Pine Point, Canada	20	3.5	8.8	6.5	Breccia
Jefferson City, USA	15	8.3	2.2	8.3	Breccia, dolomite, sediment
Pomorzony, Poland	11	1.5	3.6	12.2	Dolomite, calcite
N.F. Zinc Mine, Canada	15	2.5	9.9	11.8	Dolomite
Monte Cristo, USA	8	6.1	2.5	6.9	Organic sediment, calcite
Polaris Mine, Canada	20	3.6	12.2	8.9	Dolomite, calcite
Leadville, USA	8	4.4	12.6	15.5	Dolomite, calcite

In only several operating plants the MgO content of the zinc concentrate may be a problem where use of magnesium-bearing mineral depressants is required. Table 14.2 lists some of the major MVT deposits.

Although volcanic-associated massive sulfide deposits are commonly copper–zinc and copper–zinc–lead deposits, several major districts in South America of lead–zinc–silver

deposits are of volcanic-associated massive sulfides. The major districts of such mine-ralization are Cerro de Pasco region, Peru; Kajamarca region, Northern Peru and El Toki, Chile. Some Bolivian lead–zinc ores (Porco, Bolivar) are also of volcanogenic origin. The Iberian Pyrite belt also consists of volcanic origin.

The flotation properties of these ores vary considerably and ranges from easy-to-treat to refractory ore types. In some deposits, when alteration takes place, the ore that contains clay minerals, mainly iron hydroxides and illite. Some of these ores contain acidic gangue giving a natural pH of the ore of below 5.0. These ores usually contain high amount of sol-uble salts, where conventional depressants and collectors become ineffective for the treat-ment of these ores. One of the methods used in the treatment of acidic ores is a bulk flotation method of all sulfides followed by separation of the bulk concentrate.

14.3   FLOTATION PROPERTIES OF LEAD–ZINC ORES AND CLASSIFICATION OF THE ORE ACCORDING TO TREATABILITY

Because of the different types and varieties of lead–zinc ores scattered throughout the world, their flotation properties vary significantly, not only from one ore deposit to another, but also within deposits. A typical example can be found in the treatment of ores from the Faro region (Canada), where the ore from this region is represented by about eight different ore types, all of which respond differently to flotation [3]. During processing of these ores, different reagent schemes need to be employed. The most prominent characteristic of these ores is that galena does not float without the presence of cyanide. Figure 14.1 shows the effect of cyanide on galena flotation from different ore types.

During the treatment of some ores, the type of pH modifier is critical in flotation of galena where galena responds well to flotation only in the presence of soda ash. On the
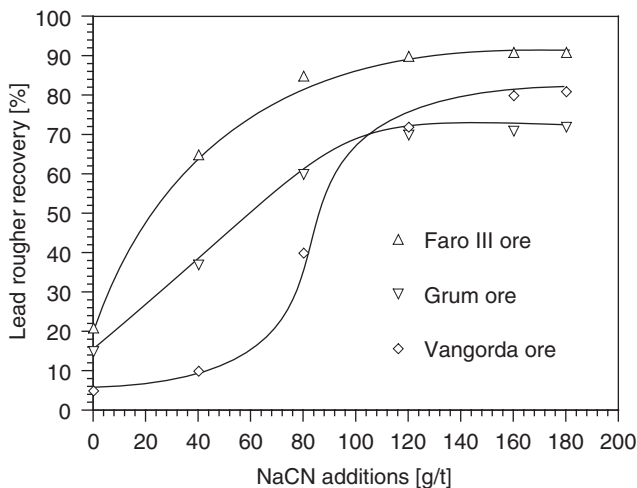
Figure 14.1 Effect of level of cyanide on the galena flotation from different faro ore types.

other hand, in the case of Tara Mines (Ireland), bolder ores galena floats only in the presence of high lime (pH >11.5). This shows that the function of alkali and depressants in differential flotation of lead–zinc is, in fact, to reduce deleterious effects of surface oxidation of minerals and presence of soluble salts in the ores.

The ores low in pyrite respond well to flotation and excellent metallurgical results can be achieved using a relatively simple reagent scheme.

A large variety of lead–zinc ores and consequent enormous differences in flotation properties from one ore to another have been recognized long ago [4] and an attempt has been made to classify the lead–zinc ores according to its flotation properties. Emphasis in this classification has been placed on the degree of oxidation, where the ore types are divided into (a) unoxidized and (b) oxidized-acid gangue and ore containing copper minerals. This classification, although useful, covers only 20% of the ore types, which are being treated nowadays. This classification is also based only on flotation properties of the ore and does not include mineralogical nature of the ores, related to flotation. Based on the data from about 230 operating plants around the world, the lead–zinc ores can be classified into the following six groups.

(a)   Coarse-grained lead–zinc ores with low to medium iron sulfide content typically dolstone (Mississippi Valley) type deposits. These ores have relatively simple mineralogy where galena and sphalerite are liberated at relatively coarse grind (i.e. K_{80} = 110–160 μm). The reagent scheme used in the treatment of these ores is simple and excellent grade and recoveries were achieved in almost all operating plants.

(b)   Massive sulfide ores with relatively coarse-grained pyrite, galena and sphalerite, normally volcanic-associated sulfides. These ores typically are unoxidized and the sphalerite is represented by mixed high iron sphalerite and marmatite ratio of sphalerite to marmatite varies (i.e. Milpo, Peru; Parko, Bolivia; Bolivar, Bolivia; Broken Hill, USA and Dariba, India).

(c)   Finely disseminated massive sulfide ores with or without carbonaceous gangue. These ores have relatively complex mineralogy where the iron sulfide content varies between 15% and 60% FeS_2. In addition to pyrite, the ore contains barite and slimes. The iron sulfides are represented by either pyrite or both pyrite and pyrrhotite (Faro II, Yukon; Huallanca, Peru; Meggen, Germany; Sullivan, Canada and Mount Isa, Australia).

(d)   Refractory lead–zinc ores are finely disseminated lead–zinc ores where liberation of the individual minerals occurs at K_{80} <10 μm. The iron sulfide content of the ore ranges from 10% (McArthur River, Century, Australia) to 90% (Caribou Mine, Canada). These ores, until recently, were considered untreatable, but with new technology processing of this ore is now possible with some success.

(e)   Oxidized and altered lead–zinc ores are characterized by the presence of acid gangue and the natural pH is acid (i.e. pH = 4.0–5.0). They cannot be processed and the use of cyanide is restricted because of the presence of soluble ions. Bulk flotation of galena, sphalerite or ore washing before grinding and flotation has been a standard practice in the treatment of these ores.

(f)   Lead–zinc–silver ores are the varieties of ores where silver minerals are predominant and the ore is in principal processes for recovery of silver. The silver in the ore ranges

from 150 to about 500 g/t. Some of the ores also contain gold in addition to silver. There are several quite complex deposits that treat lead–zinc–silver ores, some of which contain manganese sulfides (alabandite) which is difficult to remove (Uchucchaqua, Peru).

14.4 FLOWSHEET AND REAGENT SCHEME FOR THE TREATMENT OF LEAD–ZINC ORES

Because of the abundance of lead–zinc ores and the differences in processing characteristics, the reagent schemes and flowsheets vary widely from one ore type to another. The reagent scheme can be very simple or highly complex, depending on the ore type treated.

In many operating plants that treat massive sulfide ores, there is a requirement for de-zincing the lead concentrate or removal of pyrite or arsenic from the zinc concentrate. Such processes have been developed and successfully employed in many operating plants.

In a number of plants, the production of bulk lead–zinc concentrate (Mount Isa, Greens Creek) was practiced because of the problems involving sequential flotation of lead–zinc. However, a new technology exists where production of bulk concentrate can be eliminated and sequential lead–zinc flotation can be used. A typical example of such a conversion from bulk flotation to sequential flotation is the Calcquirique (El Brocal, Peru) plant [5], where after many years of bulk flotation, the plant is now converted into sequential lead–zinc–silver flotation. This conversion was made in early 1996.

14.4.1 Treatment of coarse-grained lead–zinc ores

The treatment of coarse-grained lead–zinc ores is the simplest case. These ores have a very simple gangue composition. They are unoxidized and do not contain any soluble salts. In these ores, sphalerite is not preactivated and in some cases the ore can be treated without any depressant additions. This clearly shows that the function of alkalis and depressants used in the treatment of massive sulfide lead–zinc ores is in principal to (a) modify surface properties of floated minerals, which have been altered during orebody formation and (b) correct deleterious influence of soluble salts on all minerals present in the ore.

In principle, the flotation of coarse-grained low sulfide lead–zinc ore is the textbook case of flotation of galena and sphalerite, which has been studied extensively.

The flowsheet used in operating plants treating these ores is shown in Figure 14.2.

From the operating plant, only New Jersey operating plant recovers lead using the gravity method ahead of the zinc flotation. This is due to the fact that the ore contains very little lead and high-grade lead concentrate has been obtained using gravity circuit. Typical reagent schemes used in the major operating plants treating coarse-grained lead–zinc ores are shown in Table 14.3.

As can be seen from the table, all the operating plants are using similar reagent schemes with the only differences being the levels of reagent additions. The Sweetwater and West Fork concentrators are using a mixture of xanthate and dithiophosphate in the zinc circuit. It is believed that this mixture improved the floatability of sphalerite. Depressant $ZnSO_4$ is
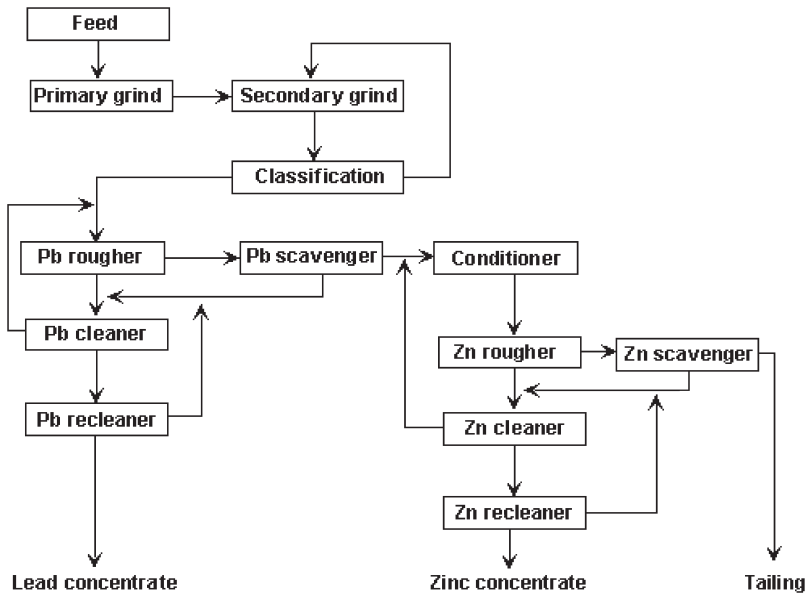
Figure 14.2 Typical flowsheet for the treatment of coarse-grained low sulfide lead–zinc ores.

Table 14.3

Reagent schemes used in the major lead–zinc plants treating coarse-grained lead–zinc ores

Concentrator	Reagent type, additions		pH	
	Lead circuit (g/t)	Zinc circuit	Pb	Zn
New Jersey Zinc, USA	−	$CuSO_4 = 600$ $AF211 = 48$ $AF65 = 25$	−	9.5
Pend Orielle, USA	$NaCN = 20$ $ZnSO_4 = 100$ $Na_2SiO_3 = 300$ $R242 = 15$ $PAX = 10$ $MIBC = 8$	$CaO = 200$ $CuSO_4 = 350$ $Na_2SiO_3 = 200$ $PAX = 25$ $Dow250 = 8$	8.5	10.0
Buick, USA	$ZnSO_4 = 600$ $PAX = 30$ $NaCN = 4$ $MIBC = 6$	$CuSO_4 = 60$ $PAX = 10$ $MIBC = 25$	8.5	8.5
Fletcher, USA	$ZnSO_4 = 725$ $NaCN = 4$ $PAX = 36$ $MIBC = 8$	$CuSO_4 = 95$ $R3477 = 5$ $MIBC = 3$	9.0	9.2
West Fork, USA	$ZnSO_4 = 920$ $NaCN = 4$ $SIPX = 36$ $AF70 = 9$	$CuSO_4 = 270$ $SIPX/3477 (1:1) = 6$ $AF70 = 9$	9.1	9.0

(Continued)

Table 14.3   (*Continued*)

Concentrator	Reagent type, additions		pH	
	Lead circuit (g/t)	Zinc circuit	Pb	Zn
Sweetwater, USA	$ZnSO_4 = 900$ $NaCN = 5$ $SIPX = 35$ $MIBC = 8$	$CuSO_4 = 180$ $SIPX/3477\ (1:1) = 8$ $AF70 = 10$	9.2	9.1
Polaris, Canada	$ZnSO_4 = 600$ $SIPX = 40$ $MIBC = 7$	$CuSO_4 = 300$ $SIPX = 25$ $Dow250 = 16$	8.8	8.9
Newfoundland Zinc, Canada	$ZnSO_4 = 600$ $NaCN = 10$ $PAX = 20$ $R242 = 7$	$CuSO_4 = 500$ $PAX = 6$ $DF250 = 1$	9.4	9.1
Gays River, Canada	$ZnSO_4 = 150$ $NaCN = 5$ $Na_2SiO_3 = 150$ $PAX = 10$ $R242 + 10$	$CuSO_4 = 200$ $SIPX = 15$ $Dow\ 1012 = 10$	9.1	9.3

Table 14.4

Metallurgical results obtained in the operating plants

	Assays (%)						Recovery (%)	
	Head		Pb conc		Zn conc			
	Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn
New Jersey Zinc	0.2	12.2	77.1	0.6	0.2	60.6	88.0	94.0
Buick	6.6	2.5	78.0	0.8	2.0	59.0	96.1	88.0
Fletcher	6.1	1.8	78.0	0.7	1.8	59.0	96.0	80.0
West Fork	6.2	3.3	78.0	1.0	1.6	59.0	98.0	80.0
Sweetwater	3.1	4.4	77.0	2.1	1.0	59.0	98.0	83.1
Polaris	3.3	8.6	76.7	1.9	0.4	63.0	95.0	94.0
Newfoundland Zinc	2.4	9.8	78.7	2.2	0.4	60.1	94.0	89.0
Gays River	2.5	8.5	73.2	3.6	0.2	63.3	90.0	93.1
Pend Oreille	3.5	6.5	73.2	2.8	0.6	58.8	92.0	93.3

usually added to the primary grind with a portion of the collector, while the NaCN is added to the cleaners only. Collectors are added to the secondary grind in the lead circuit.

The copper sulfate and zinc collector were normally added to the zinc conditioners. Both galena and sphalerite are floated in natural pH without any alkaline additions.

In virtually all plants, excellent metallurgical results are obtained (Table 14.4). The only problem experienced in a few of these plants was the elevated content of magnesium in the zinc concentrate (i.e. Gays River, Polaris). The Gays River uses sulfuric acid to leach magnesium occasionally.

14.4.2 Treatment of coarse-grained lead–zinc sulfide ores

These ores are either of sedimentary or volcanogenic origin. The mineralogy of these ores varies significantly and ranges from relatively simple ores (Nanisivic, Canada; Broken Hill, USA) to relatively complex sulfides (Emerald, Mexico; Mogul, Ireland). Accordingly, the metallurgy of these ores varies significantly and ranges from excellent to satisfactory.

As compared to coarse-grained low sulfide lead–zinc ores, in the treatment of these ores the level of depressants used is much higher and the alkaline is used for pH control, especially in the zinc circuit, where the flotation pH varies from 10.5 to 11.8, respectively. The sphalerite in these ores is higher in iron than the sphalerite found in the low iron coarse-grained lead–zinc ore and in some cases, the ore contains both sphalerite and marmatite, which may represent a problem during the processing of such ore. Some of the difficulties associated with processing of the ores containing marmatite can be described as follows:

The flotation kinetics of marmatite is much lower than that of sphalerite (Figure 14.3).

Experimental results shown in Figure 14.3 are conducted on two ore types (i.e. sphalerite and marmatite ore) from the Milpo Mine in Peru under the same flotation conditions.

The marmatite tends to drop during the cleaning operation, which usually results in a build up of recirculation load within the cleaning circuit. Figure 14.4 shows the grade-recovery relationship [7] between marmatite and sphalerite ore obtained under laboratory flotation conditions.

In flotation of ore containing marmatite the consumption of activator ($CuSO_4$) is much higher than that normally used for flotation of low iron sphalerite. Surveys from about 30 operating plants that treat varieties of sphalerite have indicated that the consumption of $CuSO_4$ required to activate sphalerite is proportional to the amount of iron present in the sphalerite. Figure 14.5 shows this relationship.
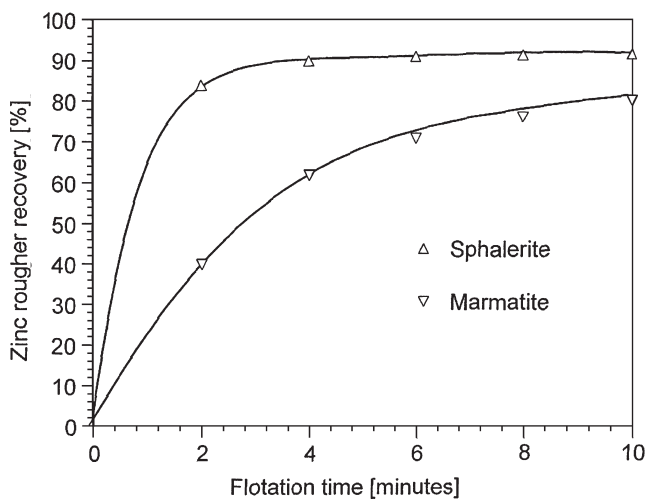
Figure 14.3 Effect of type of sphalerite on rate of flotation (Milpo, Peru sphalerite and marmatite ore) [6].
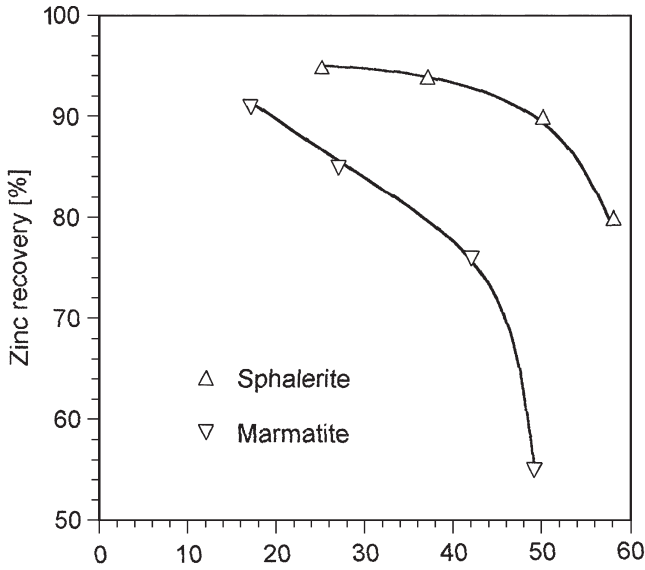
Figure 14.4 Grade-recovery relationship using marmatite and sphalerite rich ore.
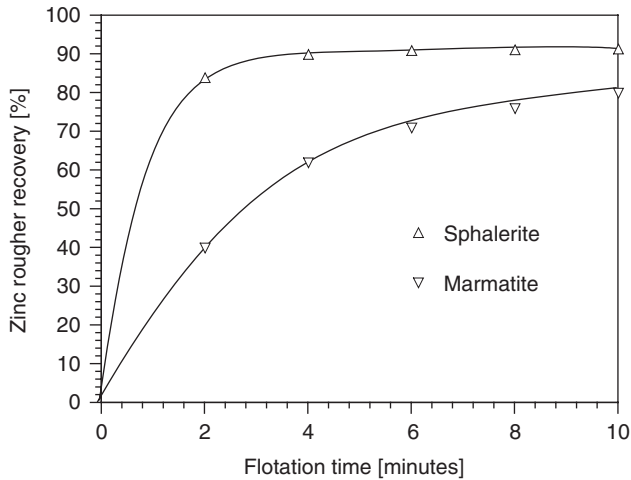
Figure 14.5 Effect of iron content in the sphalerite on $CuSO_4$ requirement – operating plant data [8].

The research data and the operating plant data have indicated that in order to success-
fully recover marmatitic zinc, higher additions of $CuSO_4$ are required. When using high
additions of $CuSO_4$, the collector choice should be xanthate as the primary collector and
thionocarbamate as the secondary collector.
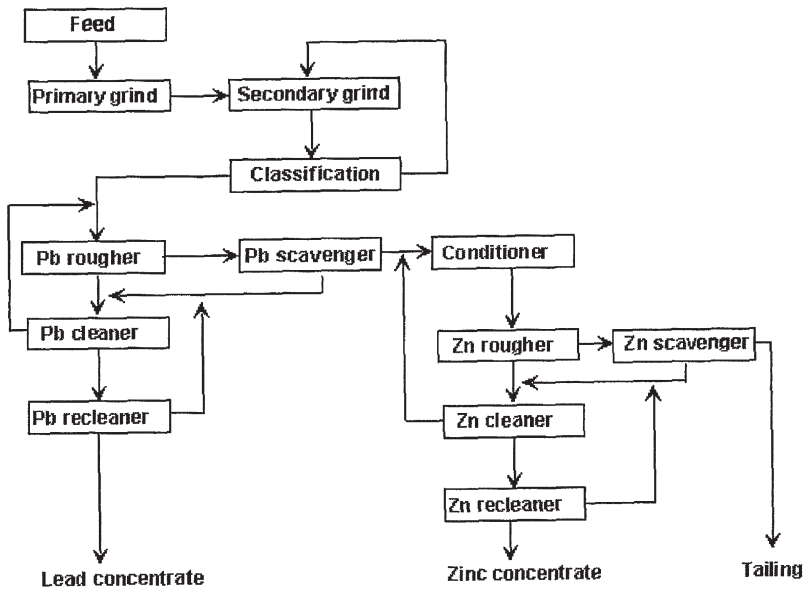
Figure 14.6 Flowsheet used in the treatment of coarse-grained lead–zinc sulfide ores.

Flowsheets used in the treatment of coarse-grained lead–zinc ores

The choice of flowsheet for treatment of coarse-grained lead–zinc sulfide ores can be simple as the one shown in Figure 14.2 or to slightly complex as that shown in Figure 14.6. In recent years, a number of operating plants have introduced flash flotation in the lead circuit where fairly large portion of lead is recovered in the grinding circuit. The objective of lead prefloat is to avoid sliming of the lead during grinding and in some cases to improve recovery of native silver if present in the ore. In some operating plants where the flash flotation is used, the lead recovery improved significantly. Regrind of the intermediate products in the zinc circuit have also been practices in a number of plants.

An alternative flowsheet practiced in several operating plants is the bulk flowsheet, shown in Figure 14.7 (i.e. El Mochito, Porko, Bolivia). This flowsheet is advantageous when the selectivity between lead and sphalerite has deteriorated after using the sequential flotation method.

Reagent scheme used in the treatment of coarse-grained lead–zinc sulfide ores

The reagent scheme used in the treatment of these ores is more complex than the reagent scheme used for treating low sulfide lead–zinc ores. Table 14.5 shows the reagent schemes used in major operating plants that employ bulk flowsheet. In Porko and Bolivar concentrators, the lead–zinc separation tailing is the final zinc concentrate while in the case of El Mochito, the zinc from the lead–zinc separation tailing is further upgraded using small quantities of $CuSO_4$ and lime at pH 11.5. The lime consumption at the Porko plant is relatively high because of the acid nature of the ore. The natural pH of this ore ranges from 5 to 5.5.
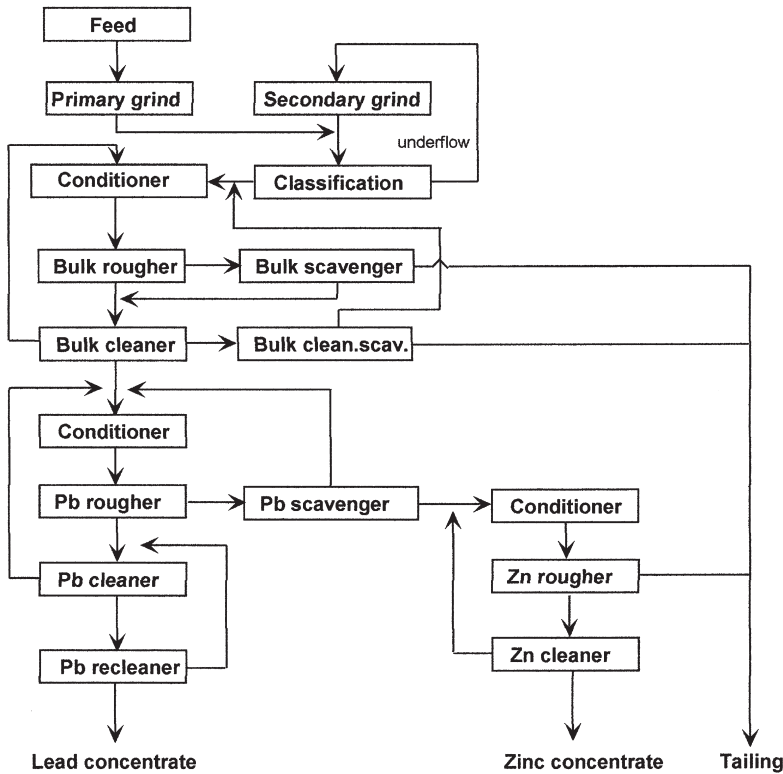
Figure 14.7 Bulk flotation flowsheet concept used in some operating plants.

The Bolivar plant contains marmatitic zinc resulting in a relatively high consumption of $CuSO_4$ used in the zinc circuit.

In general, the reagent consumptions in all three operating plants were relatively high. The average plant metallurgy is shown in Table 14.6.

Reagent schemes used in operating plants that employ the sequential lead–zinc flow-sheet are shown in Table 14.7.

The alkaline of choice in the lead circuit is either lime or soda ash. Soda ash is used in lead circuits where lime has a negative effect on flotation of lead. Lime, however, is used in the majority of operating plants as a pH modifier in both lead and zinc circuits for such differences in floatability between two alkaline is not known, and there is no literature data which may explain such a phenomenon.

In actual practice however, the differences are obvious. Some operating plants, where the natural pH of the ore exceeds 8.0, do not use any alkaline in the lead circuit.

The level of cyanide and $ZnSO_4$ also varies significantly from one plant to another. In some plants, higher level of cyanide improves the rate of lead flotation, although cyanide requirements for depression of pyrite and sphalerite are somewhat lower.

Depressants alkaline and portion of collector are usually added to the grinding stage where most of the collector is added to the rougher flotation feed of the corresponding

Table 14.5

Reagent scheme used in the operating plants using bulk flotation method

Concentrator	Reagent Additions (g/t)		
	Pb–Zn Bulk flot	Pb–Zn separation	Zn upgrading
Porko (Bolivia)	CaO = 10,800 (pH 10) CuSO$_4$ = 450 R242 = 5 SIPX = 80	ZnSO$_4$/NaCN = 214 MIBC = 10	–
Bolivar (Bolivia)	CaO = 3,000 AF242 = 70 SIPX = 200 MIBC = 59 CuSO$_4$ = 1,250	NaCN = 1,200 ZnSO$_4$ = 1,250	CaO = 200 CuSO$_4$ = 350 SIPX = 10 DF1012 = 6
El Mochito 11.8	CaO = 1,200	NaCN = 150	CaO = pH
	CuSO$_4$ = 400 AF3477 = 20 PAX = 30	ZnSO$_4$ = 280	CuSO$_4$ = 200 SIPX = 10 DF250 = 5
MIBC = 10 gr/t			

Table 14.6

Plant metallurgical results obtained using bulk flotation method

Concentrator	Assays (%, g/t)										
	Feed			Pb conc			Zn conc		Recovery (%)		
	Pb	Zn	Ag	Pb	Zn	Ag	Pb	Zn	Pb	Ag	Zn
Porko	0.82	8.57	95	59.0	9.7	3295	0.71	52.2	70.0	33.6	93.0
Bolivar	0.75	12.7	89	33.3	7.3	6800	2.04	49.1	60.1	61.2	91.5
El Mochito	2.60	11.5	60	63.0	5.4	1500	0.60	55.6	78.0	45.0	90.0

Table 14.7

Plant reagent schemes used during sequential lead–zinc flotation

Concentrator	Reagent type, additions (g/t)		pH	
	Lead circuit	Zinc circuit	Pb	Zn
DY Yukon, Canada	NaCN = 100 Na$_2$CO$_3$ = 800 R3477 = 10 MIBC = 20 SIPX = 25	CuSO$_4$ = 700 CaO = 1800 DF1012 = 60	9.0	11.0

(Continued)

Table 14.7   (*Continued*)

Concentrator	Reagent type, additions (g/t)		pH	
	Lead circuit	Zinc circuit	Pb	Zn
Nanisivic, Canada	CaO = 600 R242 = 6 PAX = 10 NaCN = 20 MIBC = 10	CaO = 1600 $CuSO_4$ = 800 PAX = 70 Dow 250 = 20	10.5	10.8
El Toki, Chile	CaO = 400 SIPX = 40 R407 = 15 MIBC = 20	CaO = 900 $CuSO_4$ = 400 SIPX = 30 Dow 250 = 15	9.5	10.6
San Cristobal, Peru	NaCN = 30 $ZnSO_4$ = 300 R242 = 20 R404 = 15 MIBC = 10	CaO = 600 $CuSO_4$ = 550 SIPX = 30 Dow 250 = 10	8.1	10.9
Milpo Mine, Peru	NaCN = 20 $ZnSO_4$ = 250 R3477 = 30 R400 = 10 PAX = 5 MIBC = 10	CaO = 1250 $CuSO_4$ = 880 PAX = 25 R242 = 20 AF70 = 15	7.8	10.5
Laisval, Sweden	NaCN = 10 Na_2CO_3 = 600 PAX = 10 AF31 = 5	CaO = 800 $CuSO_4$ = 250 PAX = 30 Dow 250 = 15	9.0	11.0
Mogul, Ireland	NaCN = 195 CaO = 800 PAX = 95 MIBC = 80	$CuSO_4$ = 1000 CaO = 2500 SIPX = 110 PAX = 40	Ro–9.7 Cl–11	Ro–10.0 Cl–11
Casandra, Greece	NaCN = 100 $ZnSO_4$ = 500 CaO = 600 R242 = 10 PAX = 60 MIBC = 25	CaO = 1200 $CuSO_4$ = 600 PAX = 45 Dow 250 = 10	9.6	11.2
Olympias, Greece	NaCN = 120 $ZnSO_4$ = 400 CaO = 350 PAX = 20 R208 = 10 MIBC = 10	CaO = 950 $CuSO_4$ = 400 SIPX = 20 MIBC = 15	9.0	11.0
Leadville, USA	Na_2CO_3 = 500 NaCN = 120 PAX = 45 R208 = 15	CaO = 600 $CuSO_4$ = 750 PAX = 60 MIBC = 25	9.0	10.5
Broken Hill, Australia	Na_2SO_3 = 150 KEX = 40 MIBC = 15	$CuSO_4$ = 422 CaO = 120 KEX = 40	8.2	9.5

(*Continued*)

Table 14.7   (*Continued*)

Concentrator	Reagent type, additions (g/t)		pH	
	Lead circuit	Zinc circuit	Pb	Zn
Grund, Germany	NaCN = 40 P82[a] = 10 H_2SO_4 = 400 KEX = 80	$CuSO_4$ = 282 CaO = 400 KEX = 50 Flotol B = 6 Flotol[b] B = 20	7.5	10.5
Emerald, Mexico	NaCN = 50 $ZnSO_4$ = 200 Na_2CO_3 = 300 Sod. aeroflot = 76	$CuSO_4$ = 500 CaO = 400 Aeroflot 31 = 25 Sod. aeroflot = 20	9.0	10.5
Reocin, Spain	Na_2CO_3 = 2500 NaCN = 90 AF25 = 12 SIBX = 130 MIBC = 10	$CuSO_4$ = 550 CaO = 900 SIBX = 20 Pine oil = 10	9.9	11.0
Sikhote-Alin, Russia	NaCN = 193 $ZnSO_4$ = 250 SIBX/KEX (2:1) = 170 Cresol = 90 Reagent Type, Additions g/t	CaO = 250 $CuSO_4$ = 380 SIBX/KEX (2:1) = 50 Pine oil = 10 PH	8.1	9.8
Salair, Russia	Na_2S = 200 NaCN = 50 Dithiophosphate = 20 KEX = 20	Na_2SiO_3 = 500 CaO = 500 CuSO4 = 420 KEX = 80 Pine oil = 20	8.5	10.0

[a]Low molecular weight polyacrylamide-based depressant.
[b]Pine oil.

circuits. As a rule, the alkaline and $CuSO_4$ in the zinc circuit are usually added to the conditioners before collector additions.

The metallurgical results obtained in the operating plants are shown in Table 14.8.

Treatment of disseminated massive sulfide ore with and without carbonaceous gangue minerals

These ores are considered to be complex massive sulfide ores and consequently, the treatment process for recovery of lead and zinc is also complex. Still these ores are treated using, more or less, conventional flotation techniques with some of the added features to either flowsheet and/or reagent schemes. Some operating plants, in addition to production of lead and zinc concentrates, also produce bulk lead–zinc concentrates as the third product. Such circuits are primarily designed to maximize recoveries of lead and zinc from treated ores. The bulk concentrate is often rich in precious metals (i.e. silver and gold), which represents an added value to the bulk concentrates.

In general, these ores are finely disseminated and liberation of individual minerals occurs in the range of K_{80} 15 μm to 40 μm. In a vast majority of operating plants, the primary grind is usually considerably coarser than the liberation size, and the rougher

Table 14.8

Plant metallurgical results obtained in operating plants

Concentrator	Assays (%, g/^{t})										
	Feed			Pb conc			Zn conc		Recovery (%)		
	Pb	Zn	Ag	Pb	Zn	Ag	Pb	Zn	Pb	Ag	Zn
DY, Canada	3.3	6.8	60.0	66.6	4.0	45.0	0.8	55.5	85	46	82
Nanisivic, Canada	0.2	8.8	–	48.0	3.5	–	0.2	58.0	40	–	93
El Toki, Chile	1.6	4.8	120	58.1	4.6	1300	0.5	52.0	70	62	78
San Cristobal	3.2	9.1	60	64.2	3.6	800	0.4	58.0	90	62	92.1
Milpo, Peru	1.8	8.7	100	70.2	1.6	1100	0.8	55.1	91	58	85.5
Las Vall, Sweden	3.1	4.6	–	76.0	1.4	–	1.5	58.1	92	–	75
Mogul, Ireland	2.2	7.0	–	56.0	2.5	–	2.2	52	66	–	86
Casandra, Greece	6.6	9.5	60	74	1.1	–	1.5	52.5	90.1	–	82
Olympias, Greece	2.4	4.6	110	55	3.0	–	1.1	52	75	–	78
Leadville, USA	3.6	8.5	120	60	1.5	1100	1.1	50.5	85	55.5	80
Broken Hill, Australia	7.6	11.5	84	76.8	4.0	450	1.2	52	96.9	83	90.1
Grund, Germany	6.2	2.3	133	71.3	2.8	1495	0.85	58.2	93.3	90	84
Emerald, Mexico	2.0	4.5	–	64.5	10.1	–	3.2	51.7	80	–	90.5
Reacin, Spain	0.7	12.0	–	77.9	2.80	–	2.8	58.4	–	66	94
Sikhote-Alin, Russia	2.6	8.4	–	66	1.50	–	2.1	55	–	88	74
Salair, Russia	6.1	5.4	–	68	2.2	–	3.3	54	–	92	85.5

concentrates are normally a bulk concentrate, which are upgraded after regrinding to liberation size. Another important features of these ores are (a) altered surface properties and crystal structure of the individual minerals, (b) contamination of the mineral surfaces with trace elements (i.e. Cu, Bi, Cd, etc.) and (c) the presence of carbonaceous gangue minerals, either impregnated with a particular mineral (i.e. pyrite, non-sulfide gangue) or as an individual mineral (graphitic carbon).

Processing options

In spite of the fact that the basic treatment process is sequential lead–zinc flotation, in a number of operating plants several alternatives are used. The most commonly used alternative added circuits include:

(a)   De-leading of the zinc concentrate
(b)   Reverse flotation of iron sulfides from the lead concentrate
(c)   Reverse iron sulfide flotation from the zinc concentrate, a method similar to that described in Chapter 13 during the treatment of copper–zinc ores
(d)   Bulk flotation technique, followed by lead–zinc separation.

De-leading of the zinc concentrate

The de-leading of the zinc concentrate is an operation that was added to the flowsheet with the objective of reducing the lead content of the zinc concentrate in cases where when using sequential lead–zinc flotation, contamination of zinc with lead cannot be avoided.

This occurs with ores in which, a portion of the lead minerals are either altered or the surfaces are contaminated with trace elements. De-leading of the zinc concentrate is usually accomplished by one of the following methods:

Depression of the zinc minerals and flotation of galena. As a zinc depressant, using this method, $ZnSO_4$ and cyanide are used at a pH between 8.5 and 9.0.

Depression of galena and flotation of sphalerite, dichromate is used as a lead depressant and sphalerite is floated in the froth product.

De-leading of the zinc concentrate has shown good results in a number of operating plants. The metallurgical results obtained at the Santa Barbara concentrator (Mexico) using a de-leading method are shown in Table 14.9.

The flowsheet and reagent scheme used in the Santa Barbara operating plant are shown in Figure 14.8.

A similar method was used extensively in several Canadian plants (Keno Hill, Golden Manitou) treating lead–zinc–silver ores.

The de-leading of zinc concentrate, using lead depression method, was practiced in the Sullivan concentrator (Canada). Initially $Na_2Cr_2O_7$ was used for lead depression (1960–1970)

Table 14.9

Metallurgical results obtained on the Santa Barbara (Mexico) de-leading circuit

Product	Assays (%, g/t)					
	Pb	Zn	Fe	Ag	Au	Cu
Zn conc (de-leading feed)	5.4	50.2	7.5	294	1.2	1.6
Zn de-leaded conc	1.1	54.5	7.2	171	0.8	1.1
Pb conc (froth product)	42.6	12.9	10.2	1364	4.6	6.0
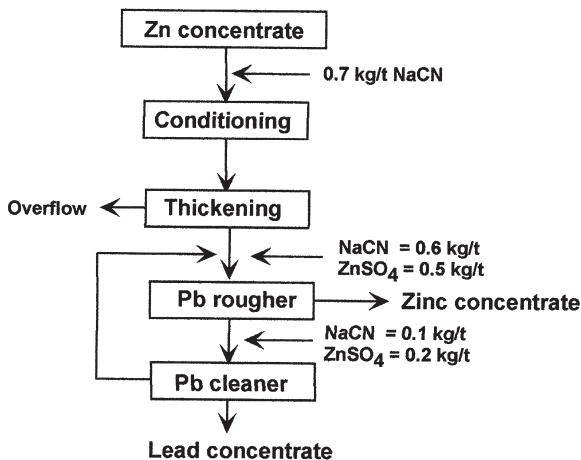
Figure 14.8 Santa Barbara de-leading of zinc concentrate flowsheet.

and more recently, dichromate was replaced by pulp thermal treatment. The pulp is heated to 60 °C using steam and the zinc is floated away from the lead using frother only.

**Reverse flotation of iron sulfides from the zinc concentrate**

There are several methods by which reverse flotation of iron sulfides can be accomplished, some of which have been successfully used in operating plants. The two most successful methods developed so far are described below:

(a)   Desorption method [9] used in the Dzesagstan concentrator (Russia) uses the flowsheet and reagent scheme shown in Figure 14.9. The zinc concentrate is first

Table 14.10

Metallurgical results obtained during reverse pyrite flotation using the desorption method

Product	Wt		Assays (%)				Distribution (%)		
	(%)	Zn	Pb	Fe	Cu	Zn	Pb	Fe	Cu
Zn cleaner conc (reverse flot feed)	100	47.6	3.50	8.86	2.82	100	100	100	100
Pyrite cleaner conc	30.5	11.7	9.86	26.6	8.85	7.3	85.4	90.0	90.0
Pyrite Ro tail (Zn conc)	69.5	63.3	0.73	1.20	0.20	92.5	14.6	10.0	10.0
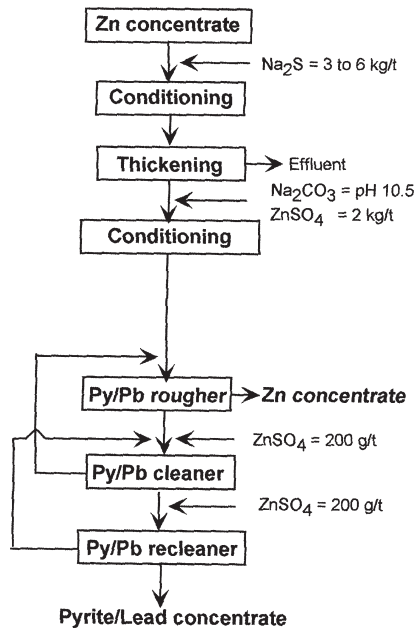
Figure 14.9 Flowsheet and reagent scheme used for reverse pyrite-galena flotation from the zinc cleaner concentrate – desorption method.

conditioned with Na_2S in diluted pulp (20% solids) followed by thickening and repulping zinc concentrate with fresh water. The concentrate is conditioned with Na_2CO_3 (pH 10.2) and $ZnSO_4$ followed by pyrite-galenite flotation using PAX and frother, pine oil. The metallurgical results obtained using this method are shown in Table 14.10.

Note that depressant (i.e. Na_2CO_3 + $ZnSO_4$) conditioning time varies between 10 and 15 min, respectively.

(b)   Thermal treatment method involves preheating the zinc concentrate with H_2SO_4 to pH 4.5, followed by pyrite flotation at 65 °C using pint oil or glycol as a frother. This method is described in Chapter 13.

Reverse flotation of iron sulfides from galena concentrate

There are two main methods used for reverse flotation of iron sulfides from a lead concentrate. The selection of a method depends on the nature of impurities present in the concentrate. In a case where carbonaceous pyrite and zinc are present in the concentrate, the reverse pyrite sphalerite flotation is accomplished by using the following procedure. The lead concentrate is stage conditioned with lime to a pH near 12.0 and a small quantity of $CuSO_4$, where the $CuSO_4$ is activator for both pyrite and sphalerite. The pyrite sphalerite is then floated using small quantities of xanthate and an alcohol-type frother. Such a reverse flotation method has been used at the Mount Isa Hilton lead–zinc concentrator [10]. The pyrite sphalerite concentrate produced in this circuit is a part of the feed for the bulk flotation circuit.

The hot separation method is the second method that has been commercially used. This method is somewhat different from the method of reverse iron sulfide flotation from zinc concentrate. When using this method, the concentrate is heated to 85 °C at a pH of about 4.5–5.0. The temperature of 85 °C was maintained for 10 min [11] and the pulp is then cooled to 60 °C, followed by iron sulfide flotation using frother only. Using this method, the zinc that is contained in the lead concentrate does not float with the pyrite.

Bulk lead–zinc flotation method

The application of this method is limited to ores where the liberation of the individual minerals occurs at a coarser size. This method has been successfully used with the lead–zinc ores that contain secondary copper minerals, which results in preactivation of sphalerite and selective lead–zinc flotation becomes very difficult.

Two basic methods have been practiced in operating plants. These methods are described below.

A sodium sulfide bulk concentrate desorption method, which is employed at the Loninogorsk concentrator [12] in Russia. The bulk lead–zinc concentrate is floated using a xanthate lime circuit without the use of zinc activator. The bulk lead concentrate is conditioned with Na_2S followed by thickening and washing the concentrate before separation. The washed concentrate is conditioned with Na_2CO_3 and $ZnSO_4$ followed by lead flotation using small quantities of collector. The flowsheet and reagent scheme used are shown in Figure 14.10. An alternative depressant combination also included Na_2SO_3 + $ZnSO_4$ or $ZnO/NaCN–Na_2CO_3$. The choice of depressants depends on the grade of the bulk concentrate and the amount of secondary copper present in the concentrate. In the presence of
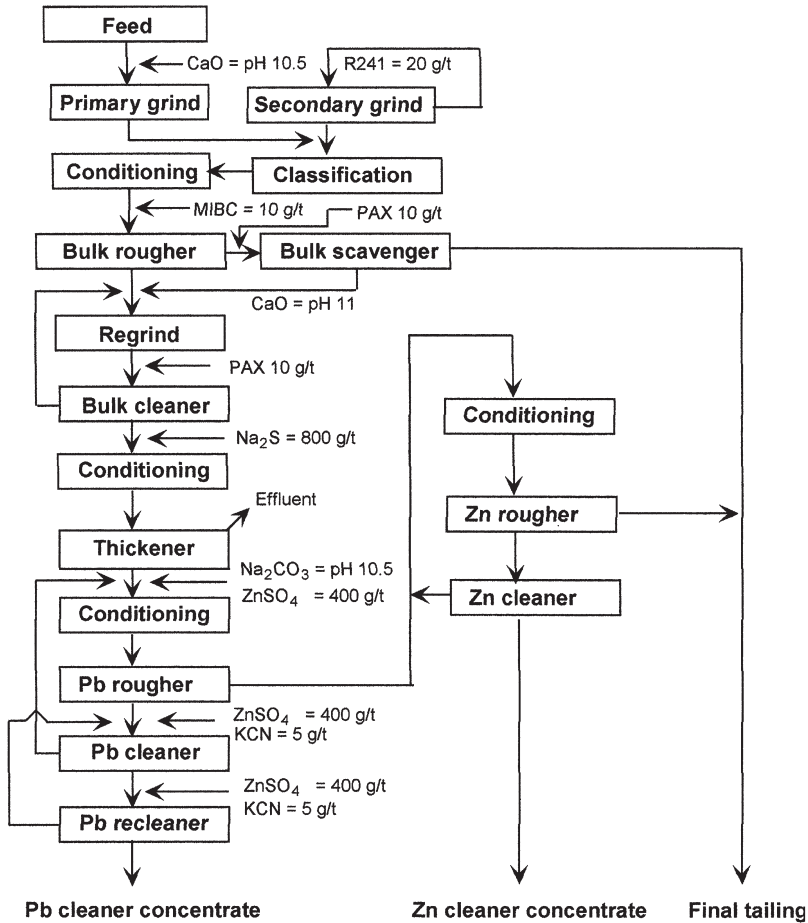
Figure 14.10 Bulk flotation followed by Na$_2$S desorption and separation flowsheet and reagent scheme.

secondary copper minerals, the use of cyanide should be avoided. In most cases, Na$_2$SO$_3$ is used as an alternative pyrite depressant.

The second method involves bulk flotation of lead–zinc concentrate followed by deactivation of sphalerite using NaCN without desorption of collector followed by lead flotation using lime-cyanide as depressant. This method has been developed for treatment of altered lead–zinc ores that contain acidic gangue minerals. A typical flowsheet and reagent scheme using the cyanide desorption method is shown in Figure 14.11.

Alternative depressant system in flotation of disseminated lead–zinc massive sulfide ores

In recent years, significant progress has been made in the development of new depressants, which in combination with conventional depressants, provide significant improvement in the metallurgical results. Some of these new depressants have been successfully employed
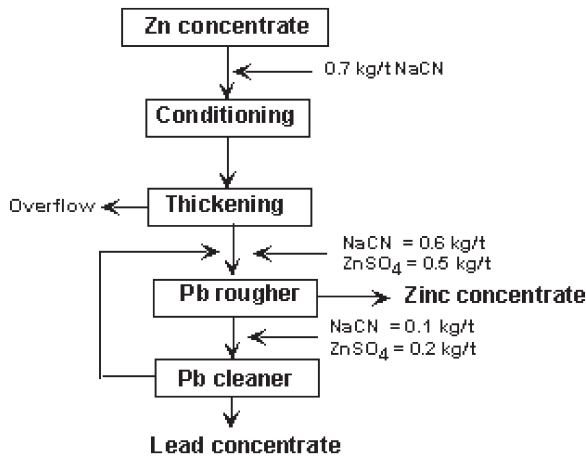
Figure 14.11 Bulk flotation flowsheet and reagent scheme using cyanide desorption method.

in operating plants [13]. There are several depressant systems identified to be quite effective for specific ore types and are described as follows:

Lime–NaCN/HQS mixture – SO$_2$ system

This depressant system was developed for treatment of lead–zinc ores that contain pyrrhotite and carbonaceous pyrite. The HQS is a modified dextrin, developed and marketed by Huntsman Chemicals, Canada. The ore is ground with lime and NaCN/HQS mixture + xanthate collector. The ground ore is conditioned with SO$_2$ to pH 6.8–8.8, depending on the ore type being treated, followed by lead flotation. During cleaning, NaCN/HQS + SO$_2$ is used. The lead cleaning pH is maintained at around 6.5. In the zinc circuit, CuSO$_4$/lime and depressant HQS are used. This system was tested on Mount Isa Hilton lead–zinc ore in continuous batch tests. Metallurgical results using the standard reagent scheme and the above reagent scheme are compared in Table 14.11. The results obtained using the new depressant system were superior to those using the standard plant reagent scheme.

Complexed cyanide

The complexed cyanide or cyanide mixture with organic depressants [15] was originally designed for depression of pyrite and pyrrhotite during different lead–zinc ores where the use of cyanide as depressant is either limited or reduced. The limitations of cyanide, used as a depressant, are associated with the following:

(a)   When the ore contains soluble ions, which reacts with cyanide therefore reducing its effectiveness.
(b)   When the ore contains secondary copper minerals, such as bornite, covellite and copper associated with sulfosalts, the cyanide dissolves the copper, which in turn, results in reduced or lost selectivity between lead and zinc minerals.

Table 14.11

Effect of lime NaCN/HQS–SO$_2$ depressant system on lead–zinc flotation from Mount Isa lead–zinc Hilton ore [14]

Depressants	Products	Wt (%)	Assays %		Distribution (%)	
			Pb	Zn	Pb	Zn
Standard plant	Pb cleaner conc	11.16	45.4	7.8	75.0	8.9
CaO,NaCN,D110[a]	Zn cleaner conc	15.92	3.6	48.0	8.5	78.0
Sodium ethyl xanthate	Zn comb tail	72.92	1.51	1.76	16.5	13.1
3418A	Feed	100.00	6.7	9.8	100.0	100.0
New	Pb cleaner conc	8.63	66.4	3.7	86.8	3.2
Lime NaCN/HQS	Zn cleaner conc	16.56	1.4	53.1	3.5	88.8
SO$_2$	Zn comb tail	74.81	0.87	1.05	9.7	8.0
	Feed	100.00	6.6	9.9	100.0	100.0

[a]Dextrin

Table 14.12

Effect of complexed cyanide on lead flotation from the Tara mine and Nanisivik Area 14 ore

Concentrator	Depressant type/additions (g/t)	Assays (%)		Assays (%)		Distribution (%)	
		Feed		Pb conc		Pb conc	
		Pb	Zn	Pb	Zn	Pb	Zn
Tara Mine	NaCN = 100	3.6	9.5	46.3	7.9	77.2	6.5
Bolder Ore	NaCN = 150	3.4	9.5	48.6	14.2	79.1	
10.9							
	DS25 = 100	3.5	9.2	55.4	5.8	82.4	4.4
	DDS4 = 200	3.6	9.5	62.2	3.3	85.2	2.1
Nanisivik	NaCN = 50	0.6	14.3	40.1	5.5	55.3	0.8
Aera 14 Ore	DDS22 = 50	0.6	14.2	55.5	2.8	66.6	0.3

In cases where the ore contains gold and silver, complexing of cyanide can be accomplished in several ways, including (a) adding cyanide to dextrin–quebracho mixture treated with surfactant and (b) adding cyanide to a mixture of lignin sulfonate and starch, previously treated with surfactant, followed by thermal treatment of the solution at a temperature of 55 °C.

The complexed cyanide with other organic depressant mixtures was found to be highly effective in the depression of oxidized pyrite and carbonaceous pyrite. The complexed cyanide was successfully used at the Tara Mine (Ireland) for depression of oxidized pyrite [16] and at the Nanisivik concentrator (Canada) for depression of carbonaceous pyrite [17]. These depressants are used under the trade name DS22 and DS25.

The lead metallurgy obtained with cyanide and complexed cyanide is shown in Table 14.12.

With the use of complexed cyanide, both pyrite and zinc depressions improved significantly.

Modified starches and dextrins

These are a new line of organic depressants specifically designed for depression of altered pyrite and pyrrhotite [18]. There are two groups of these depressants, the first group being a product of reaction of starches with monoamines and low molecular weight lignosulfonates. These depressants are manufactured under the trade name DS200. The second group is a product from a reaction between dextrin–quebracho mixture with high molecular weight polymer + Na_2S and they are produced under the trade name DS–HQS. Depressants from both groups have been successfully used in a number of operating plants [19]. These depressants have been successfully used in combination with Na_2CO_3 + $ZnSO_4$ or lime Na_2SO_3 as depressant systems.

During zinc flotation from lead tailings, pyrite depression may also represent a significant problem since any excess of $CuSO_4$ in the pulp may result in activation of pyrite. The excess of $CuSO_4$ in solution during zinc flotation is controlled by the following two ways:

(a)   The use of small quantities of Na_2S after copper conditioning: At Belonsovskii plant (Russia), Na_2S (35–50 g/t) was added after $CuSO_4$ conditioning just before xanthate additions. The use of Na_2S resulted in an improvement in frothing properties and improvement in zinc metallurgical results.
(b)   The use of ferro cyanide, also after $CuSO_4$ conditioning, has been proven beneficial for depression of pyrite. In this case, the pulp is stage conditioned with lime and copper sulfate (pH 10.5–11.0) followed by ferro cyanide additions (20–30 g/t) in a short conditioning stage, just before collector additions. In some operating plants the NaCN is used in place of $K_2Fe(CN)_6$.

The order of reagent additions in the conditioning and the conditioning intensity before zinc flotation are two very important factors in the efficient flotation of sphalerite. In a case where the ores contain marmatite or high iron sphalerite, the pulp is first conditioned with $CuSO_4$ at lower pH than in the second conditioner, lime is added to adjust pH (i.e. 10.5–11.5). The optimization of the order of reagent additions is best determined in a plant, not in a laboratory.

Flowsheet used in the treatment of disseminated massive sulfide ores

There are a variety of flowsheets used in the treatment of disseminated lead–zinc ores and they have been adapted for the treatment of specific ore types. The most usual is the sequential flowsheet, which is shown in Figure 14.12.

This flowsheet incorporates primary stage grinding and regrinding of both lead and zinc rougher concentrate. When the regrinding requirement is below K_{80} = 20 μm, then the stage regrind circuits are used (i.e. usually 2-regrind stages). The flowsheet that uses pyrite or graphite prefloat is shown in Figure 14.13.

This flowsheet was used at the Mount Isa Hilton lead–zinc concentrate from 1976 to 1985. Since then the Mount Isa flowsheet has changed to incorporate (a) reverse pyrite flotation from lead concentrate and (b) production of bulk concentrate. A typical flowsheet, which incorporates the production of a bulk lead–zinc concentrate is shown in Figure 14.14.
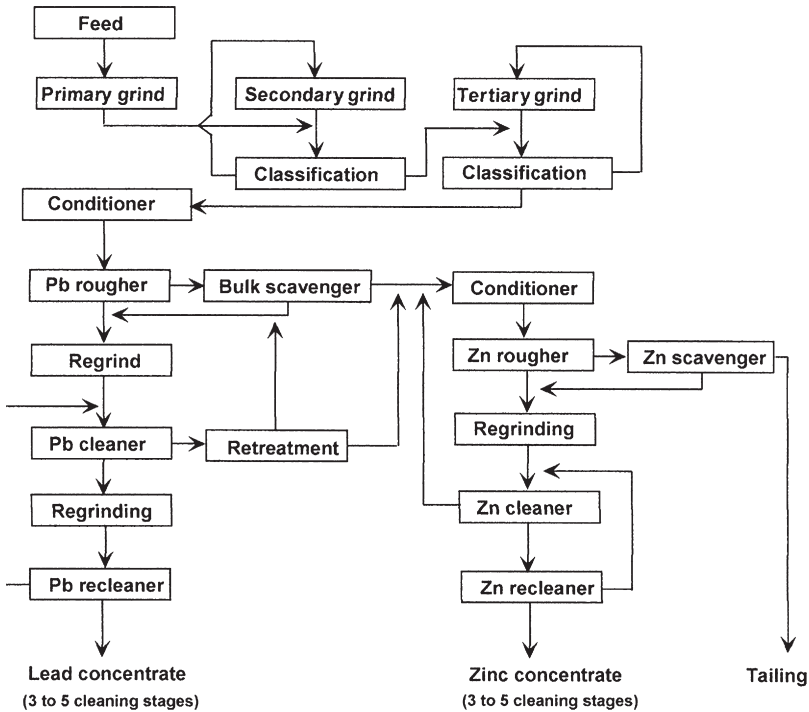
Figure 14.12 Sequential lead–zinc flowsheet.

This flowsheet has been used at the Greens Creek concentrator, which treats lead–zinc–gold–silver carbonaceous ore and at the Faro concentrator (Canada) during the treatment of the Faro 3 ore (1966–1975).

Other varieties of flowsheet include additions of de-leading of zinc concentrate, and reverse flotation of sulfides from the lead concentrate, described earlier.

Bulk flotation flowsheets are used in several operations in China and Russia.

Reagent schemes and metallurgical results

The reagent schemes used in the treatment of disseminated massive sulfide ores are not as uniform as those used for the treatment of coarse-grained low sulfide and medium sulfide ores, and these reagent schemes are highly variable with respect to the use of both collectors and depressants.

These reagent schemes, in principal, are based on laboratory research and plant experience where adjustment in the reagent scheme is made through extensive plant trials. There are numerous examples, where over the years, reagent schemes have changed several times. Typical examples of such changes are the Faro concentrator (Canada), the Mount Isa concentrator (Australia) and the Megan concentrator (Germany).

The reagent schemes used in the major operating plants that treat massive disseminated lead–zinc ores are shown in Table 14.13.
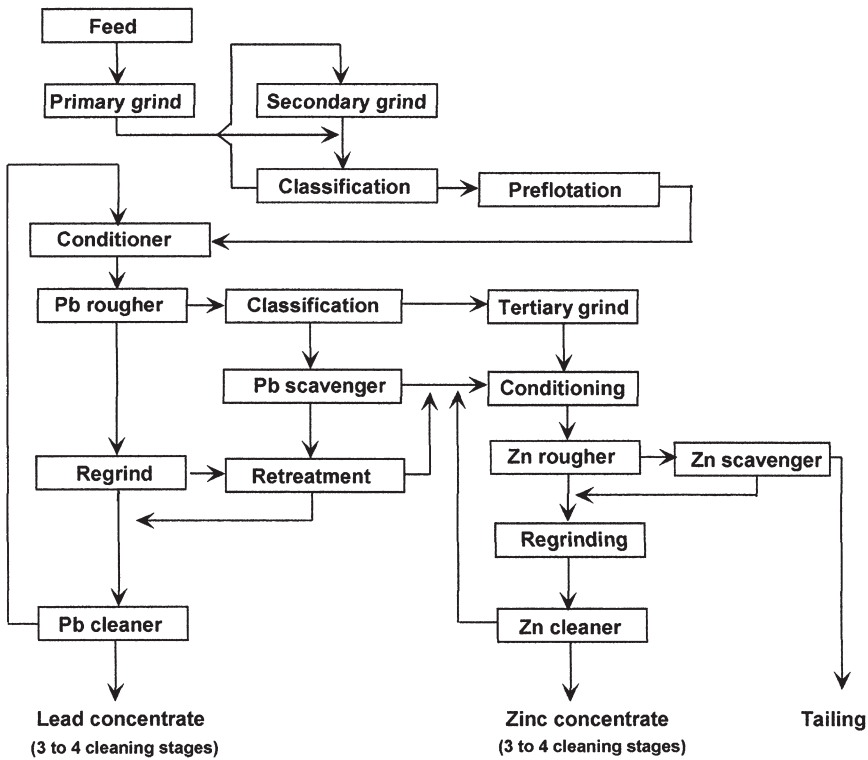
Figure 14.13 Flowsheet with a pyrite or graphite prefloat.

It should be noted that a reagent scheme also varies from one region to another. For example, the Russian operating plants have adopted different reagent schemes than those commonly used in North America and Europe. In South America, the reagent schemes are adopted to cope with the high elevation, namely because of the problem of thin air where the frothing properties are dramatically altered due to the problems arising with the selection of the right flotation equipment. Most of these operating plants are between 4200 and 4600 m elevation. In such cases, collectors with frothing properties are used.

The concentrators listed in Table 14.13 are but a few of about 40 concentrators treating similar ores, most of which have been shut down for sometime.

From the data shown in Table 14.13, one can appreciate the complexity of the problems involved in treatment of complex massive sulfide lead–zinc ores. The Greens Creek and Kamioka mine uses a 100 recycle water due to environmental restraints. A similar situation occurs at the Red Dog mine located in Alaska (Arctic), where certain reagents, such as lime are kept at a minimum to control cost, and the use of cyanide is also limited. This may contribute to the non-optimum reagent scheme of some operating plants located in environmentally sensitive areas.

The metallurgical results obtained in the plants listed in Table 14.13 are shown in Table 14.14. The data shown in this table does not include data on the production of bulk

Figure 14.14 Flowsheet used in the production of a bulk lead–zinc and lead–zinc concentrates.

concentrate due to the fact that operating plants do not report bulk flotation data. In most operating plants that produce bulk concentrate, the concentrate assays 9–15% Pb and 40–43% Zn and does not exceed 15% in recovery.

14.4.3   Treatment of oxidized and altered lead–zinc ores

Ores that have undergone partial or strong oxidation during formation of the orebody belong to this group. These ores usually have an acid character due to the presence of pyrrhotite and marcasite, as well as the presence of acid gangue. There are several problems associated in processing these ores. This includes the following:

The acidic nature of the ore, where the natural pH of the ore is between 5.5 and 6.5, restricts the use of conventional depressants such as cyanide, and in some cases, the consumption of alkali is extremely high to obtain an alkaline pH. The use of an excessive amount of alkali may also result in a reduction in the floatability of galena. Typical examples of such ores are the Laurium Mine in Greece and the Carthagena Mine in Spain.

Table 14.13

Reagent schemes used in treatment of disseminated massive sulfide ores

Concentrator	Ore type and reagent used
Faro I, II, Canada	*Ore*: Disseminated lead–zinc ore containing some secondary copper minerals + silver sulfo-salts. Pyrite with some pyrrhotite is also present in the ore *Grind* = K_{80} 65 μm *Flowsheet*: Semi-bulk flowsheet with production of a bulk Pb–Zn conc by combining Pb 3rd and Zn 3rd cleaner tails. The ore contained bornite *Reagents*: Pb circuit – Na_2CO_3 = 1800 g/t, NaCN = 200 g/t, Na_2SO_3 = 300 g/t, CaO = 300 g/t (Pb cleaners), SIPX = 80 g/t, R242 = 8 g/t, MIBC = 60 g/t, Zn circuit – CaO = 2000 g/t, $CuSO_4$ = 450 g/t, SIBX = 40 g/t, Dow 250 = 80 g/t *Other*: pH – Pb Ro = 9.0, Pb cleaner = 11.0 (with lime). Zn Ro = 10.5, Zn cleaner = 11.0. Regrind of Pb and Zn concentrate before cleaning
Faro, Grum & Vangorda, Canada	*Ore*: Impregnated massive sulfide ore with seven different ore types ranging from massive sulfide (>90% sulfide) to carbonaceous pyrite with cloritic gangue and fine slimes *Grind* = K_{80} 48 μm *Flowsheet*: Sequential with two-stage lead and zinc regrind *Regrind* = K_{80} 13 μm Pb and K_{80} 18 μm Zn *Reagents*: Pb circuit – CaO = 800 g/t, NaCN/HQS (1:1) = 280 g/t, SIPX = 100 g/t, 3418A = 15 g/t, MIBC = 6 g/t, Zn circuit – CaO = 1500 g/t, HQS = 300 g/t, $CuSO_4$ = 300 g/t, SIPX = 100 g/t, DF1012 = 110 g/t *Other*: pH – Pb circuit 8.8 to 9.9 Ro, 9.0 to 9.5 cleaner; Zn circuit – 10.5 to 10.8 Ro, 10.8 to 11.0 cleaner. Three-stage conditioning in the zinc circuit. High intensity conditioning in the zinc cleaners
Cirque, BC Canada	*Ore*: Finely disseminated massive sulfide containing several varieties of pyrite ranging from crystaline, isomorphic to carbonaceous, galena and sphalerite as the major valuable minerals with some silver *Grind* = K_{80} 45 μm *Regrind* = K_{80} 16 μm for lead and K_{80} 20 μm for zinc *Flowsheet*: Sequential *Reagents*: Pb circuit – CaO = 700 g/t, DDS200/NaCN (1:1) = 150 g/t, SO_2 = 450 g/t, PAX = 60 g/t, 3477 = 10 g/t, MIBC = 80 g/t. Zn circuit – $CuSO_4$ = 600 g/t, CaO = 200 g/t, PAX = 60 g/t, MIBC = 20 g/t *Other*: pH – grind 10.8, Pb Ro 8.8, Pb Cl 6.8, Zn Ro 10.5, Zn Cl 11.5
Sullivan, Canada	*Ore*: Disseminated ore containing mixed pyrite and pyrrhotite. Non-sulfide gangue are carbonates and schists. Galena and sphalerite are the major valuable minerals

Table 14.13   (*Continued*)

Concentrator	Ore type and reagent used
	Grind = K_{80} 70 µm
	Regrind = K_{80} 30 µm
	Flowsheet: Heavy media separation sequential lead–zinc flotation with de-zincing of lead concentrate
	Reagents: Pb circuit – NaCN = 90 g/t, CaO = 350 g/t, PAX = 130 g/t, MIBC = 180 g/t, Zn circuit – $CuSO_4$ 500 g/t, CaO = 400 g/t, PAX = 70 g/t, Dow250 = 110 g/t, De-zincing circuit – CaO = 300 g/t, $CuSO_4$ = 200 g/t, $Na_2Cr_2O_7$ = 100 g/t
	Other: pH – Pb Ro 8.4, Pb cleaner 8.0; Zn Ro 9.0, Zn cleaner 10.5, de-zincing temp = 65 °C
Red Dog, USA	*Ore*: Finely disseminated sulfides with carbonaceous gangue and a large amount of soluble salts. Pyrite content variable
	Grind = K_{80} 65 µm
	Flowsheet: Sequential with discard of the lead scavenger concentrate
	Reagents: Pb circuit – $ZnSO_4$ = 300 g/t, NaCN = 50 g/t, CaO = 300 g/t, PAX = 40 g/t, R208 = 20 g/t, Zn circuit – $CuSO_4$ = 2000–4000 g/t, PAX = 150 g/t, Na_2SiO_3 = 300 g/t, CaO = 450 g/t
	Other: pH – Pb flot 7.5, Zn flot 7.0, Tower mills and tank cells used in these circuits
Greens Creek, USA	*Ore*: Carbonaceous massive sulfide lead–zinc–gold–silver ore with appreciable amounts of graphitic and organic carbon. This ore, although belongs to the lead–zinc–silver ore, is grouped in the massive sulfide group due to its refractory nature
	Grind = K_{80} 54 µm, Pb regrind = K_{80} 25 µm, Zn regrind = K_{80} 28 µm
	Flowsheet: Semi-bulk with production of a bulk lead–zinc–silver concentrate plus carbon prefloat. The ore contains galena, sphalerite, a variety of silver minerals and native gold
	Reagents: Carbon prefloat – MIBC = 40 g/t, Pb circuit – H_2SO_4 = 400 g/t, $ZnSO_4$/NaCn (2:2) = 100 g/t, DS200 = 200 g/t, 3418A = 20 g/t, PAX = 60 g/t, Zn circuit – $CuSO_4$ = 800 g/t, CaO = 1200 g/t, PAX = 60 g/t, Dow250 = 60 g/t, Bulk circuit – CaO = 100 g/t, PAX = 20 g/t, R208 = 10 g/t
	Other: pH – Pb 8.5, Zn 10.5. H_2SO_4 added to lower recycle water pH (100% recycle water used). Regrind in tower mills. Column cleaning
Rozberg, Australia	*Ore*: Sulfide ore with varieties of pyrite and elevated amount of soluble cations
	Grind = K_{80} 82 µm, regrind = K_{80} 38 µm
	Reagents: Pb circuit – Na_2SO_3 = 300 g/t, $ZnSO_4$ = 800 g/t, NaCN = 50 g/t, CaO = 400 g/t, Na-ethyl xanthate = 150 g/t, MIBC = 20 g/t, Zn circuit – CaO = 2000 g/t, $CuSO_4$ = 900 g/t

Table 14.13 (*Continued*)

Concentrator	Ore type and reagent used
	Other: pH – Pb 9.0, Zn 10.1
	Mount Isa Hilton *Ore*: Disseminated lead-zinc ore with carbonaceous pyrite and pyrrhotite present. The principal valuable minerals include galena, sphalerite and silver sulfosalts
	Grind = K_{80} 75 μm, Regrind = K_{80} 25 μm
	Flowsheet: Sequential
	Reagents: Prefloat – MIBC = 60 g/t, PAX = 5 g/t, Pb circuit – NaCN = 210 g/t, Agent[a] G = 200 g/t, Na-ethyl xanthate = 190 g/t, 3418A = 10 g/t, MIBC = 26 g/t. Zn circuit – CaO = 300 g/t, $CuSO_4$ = 680 g/t, PAX = 75 g/t, Reverse pyrite flotation – CaO = 300 g/t
	Other: pH – Pb flot 8.0, Zn flot 10.0, Tower Mills, columns
Elura Mine, Australia	*Ore*: Fine disseminated sulfide ore with varieties of pyrite. The ore also contains significant quantities of arsenopyrite
	Grind = K_{80} 65 μm. Regrind = K_{80} 28 μm
	Flowsheet: Sequential with an added arsenic removal stage from the zinc concentrate
	Reagents: Pb circuit – NaCN = 190 g/t, CaO = 380 g/t, $ZnSO_4$ = 400 g/t, Na_2SO_3 = 450 g/t, Na-ethyl xanthate = 100 g/t, MIBC = 20 g/t. Zn circuit – CaO = 1200 g/t, $CuSO_4$ = 900 g/t, PAX = 25 g/t, sod aeroflot = 5 g/t, MIBC = 30 g/t. Arsenic circuit – CaO = 300 g/t, $ZnSO_4$ = 250 g/t
	Other: pH – Pb 9.0, Zn 10.5–11.5, arsenic reverse flotation from the zinc concentrate uses heat to 65 °C
Lady Loretta, Australia	*Ore*: Similar to the Mount Isa ore but without the presence of pyrrhotite
	Flowsheet: Sequential
	Reagents: Pb circuit – CaO = 250 g/t, NaCN = 250 g/t, $ZnSO_4$ = 300 g/t, PAX = 120 g/t, R208 = 10 g/t, MIBC = 30 g/t. Zn circuit – CaO = 1380 g/t, $CuSO_4$ = 1500 g/t, PAX = 65 g/t, Dow 250 = 25 g/t
	Other: pH – Pb circuit 10.5, Zn circuit 11.8. Aeration used in the lead circuit
Megan, Germany	*Ore*: Disseminated massive sulfide ore with about 72% sulfides. The remaining gangue are calcite, siderite and clays. The ore also contains marcasite in some portion of the orebody. Galena and sphalerite are disseminated in pyrite and each other
	Grind = K_{80} 65 μm
	Flowsheet: Bulk flotation without separation
	Reagents: Bulk – CaO = 4000 g/t, $CuSO_4$ = 2200 g/t, KAX = 730 g/t, Pine oil = 25 g/t
	Other: pH – 11.8 to >12, also includes a desliming circuit. The concentrate is thickened before upgrading
Tara Mine, Ireland	*Ore*: Several ore types ranging from medium pyrite content to massive sulfides (Bolder ore). The ore also contains gangue slimes (i.e. chlorites and calcite)

(*Continued*)

Table 14.13   (*Continued*)

Concentrator	Ore type and reagent used
	Grind = K_{80} 65 μm, regrind = K_{80} 25 μm
	Flowsheet: Sequential
	Reagents: Pb circuit – Na_2CO_3 = 850 g/t, DS25/NaCN = 130 g/t, PAX = 35 g/t, R208 = 15 g/t, MIBC = 15 g/t, zinc circuit – CaO = 1200 g/t, $CuSO_4$ = 980 g/t, Na_2SiO_3 = 300 g/t, PAX = 40 g/t, MIBC = 35 g/t
	Other: pH – Pb circuit 9.0 normal ore, uses lime when treating Bolder ore at pH 11.5. Zn circuit 10.5 open circuit 1st cleaner
Hualluanca, Peru	*Ore*: Massive pyrrhotite/pyrite ore with about 80% sulfide content. The ratio of pyrite to pyrrhotite is variable. Zinc is represented by 60% marmatite and 40% sphalerite
	Flowsheet: Sequential
	Reagents: Pb circuit – $ZnSO_4$/NaCN = 120 g/t, R242 = 15 g/t, 3418A = 18 g/t, PAX = 6.0. Zn circuit – SHQ = 50 g/t, CaO = 880 g/t, $CuSO_4$ = 680 g/t, PAX = 30 g/t, 3894 = 10 g/t, MIBC = 20 g/t
	Other: pH – Pb circuit 7.8, Zn circuit 10.5, SHQ = quebracho:Na_2SiO_3:$NaHPO_4$ = 20:40:40 ratio
Kamioka, Japan	*Ore*: Massive sulfide black ore with varieties of pyrite present. The ore contains slime and clay minerals
	Flowsheet: Bulk flotation, sequential Pb–Zn flotation through bulk concentrate
	Reagents: Bulk Pb–Zn circuit – Na_2CO_3 = 200 g/t, $CuSO_4$ = 320 g/t, NaCN = 20 g/t, NaEX = 36 g/t, MIBC = 80 g/t. Pb circuit – $ZnSO_4$ = 300 g/t, NaCN = 200 g/t. Zn upgrading circuit – $CuSO_4$ = 150 g/t, CaO = 1000 g/t, NaEX = 10 g/t, MIBC = 10 g/t
	Other: Bulk concentrate pretreated with NaCN, thickened and repulped before separation

[a]Dextrin:quebracho:surfactant (80:15:5) pyrrhotite depressant recently replaced by dextrin D110

The highly acidic ores (natural pH 5.0–5.5) contain a high amount of soluble salts, which interfere with flotation. In this case, the pyrite is extremely active and was difficult to depress.

Ores with strongly activated sphalerite, either by lead cations or by copper, which comes from the secondary copper minerals such as bornite, digenite and covellite, may contain iron hydroxides, slimes and clay minerals. A typical example is the San Gregorio Mine and the El Brocal (Tajo Norte) orebodies, both located in the Cerro de Pasko province of Peru.

Processing options

There are several methods by which these ores can be processed to some degree of success. The selection of treatment method depends on the degree of oxidation and amount of soluble cations present in the ore. Some of these options are described as follows:

(a)   When treating acidic ore with low level of soluble cations, a semi-bulk flotation method can be used. The reagent scheme and flowsheet for the treatment of these

Table 14.14

Plant metallurgical results obtained in various plants treating disseminated massive sulfide ores

| Concentrator | Assays (%, g/t) | | | | | | | | Recovery (%) | | |
| | Feed | | | Pb conc | | | Zn conc | | Pb conc | | Zn conc |
	Pb	Zn	Ag	Pb	Zn	Ag	Pb	Zn	Pb	Ag	
Faro I & II	3.3	6.2	66	63.5	6.8	750	1.6	49.2	70.0	46.0	77.0
Faro Grum & Vang	3.7	5.6	75	61.5	7.1	950	2.2	51.0	80.0	58.5	84.4
Cirque	2.8	8.9	40	69.1	4.4	–	1.5	57.0	81.0	–	88.5
Rozberg	6.4	11.2	–	58.9	16.2	–	2.5	56.5	64.3	–	86.4
Mount Isa	7.0	6.5	148	47.6	6.9	1206	2.9	50.0	82.4	80.5	71.8
Elura	4.6	7.5	–	45.5	7.7	–	2.2	51.0	75.5	–	78.2
Lady Loretta	2.7	14.6	–	52.2	6.7	–	3.4	56.0	77.1	–	85.0
Megan	1.3	10.0	15.0	–	–	–	–	–	–	–	–
Tara Mines	3.2	8.0	66.0	58.2	4.4	–	1.6	58.3	78.5	–	86.8
Huallanca	1.5	10.4	180.5	68.3	2.2	2700	0.8	50.0	80.2	66.5	90.0
Kamioka	2.8	6.6	–	56.6	3.4	–	5.4	51.0	70.2	–	75.5
Sullivan	5.8	5.5	59.0	55.0	8.8	–	1.8	52.5	75.0	–	80.1
Red Dog	5.4	17.8	–	51.0	9.1	–	2.2	55.6	35.1	–	75.3
Greens Creek	3.2	9.1	360	55.0	6.8	4800	2.3	55.0	66.0	55.5	64.0

Table 14.15

Lead–zinc metallurgical results obtained using $Na_2S_2O_5$–Na_2CO_3 depressant system – Infanta Mine, Spain [17]

| Product | Weight (%) | Assays (%) | | Distribution (%) | |
		Pb	Zn	Pb	Zn
Pb cleaner conc	6.68	58.71	6.60	85.2	4.6
ZN cleaner conc	13.94	2.40	57.30	7.3	84.1
Final tail	79.38	0.44	1.35	7.5	11.3
Feed	100.00	4.6	9.50	100.0	100.0

ores is illustrated in Figure 14.14. The Na_2SO_3 or $Na_2S_2O_5$ is good pyrite depressant and can be used individually or in combination. Dithiophosphates are usually the choice of collector for the lead circuit. In the zinc flotation circuit, a conventional lime−$CuSO_4$ circuit can be used.

Typical metallurgical results obtained using this method are shown in Table 14.15. It should be noted that aeration of the pulp prior to lead flotation increases floatability of lead, but does not necessarily improve depression of pyrite, although in some cases may help pyrite depression (Figure 14.15).
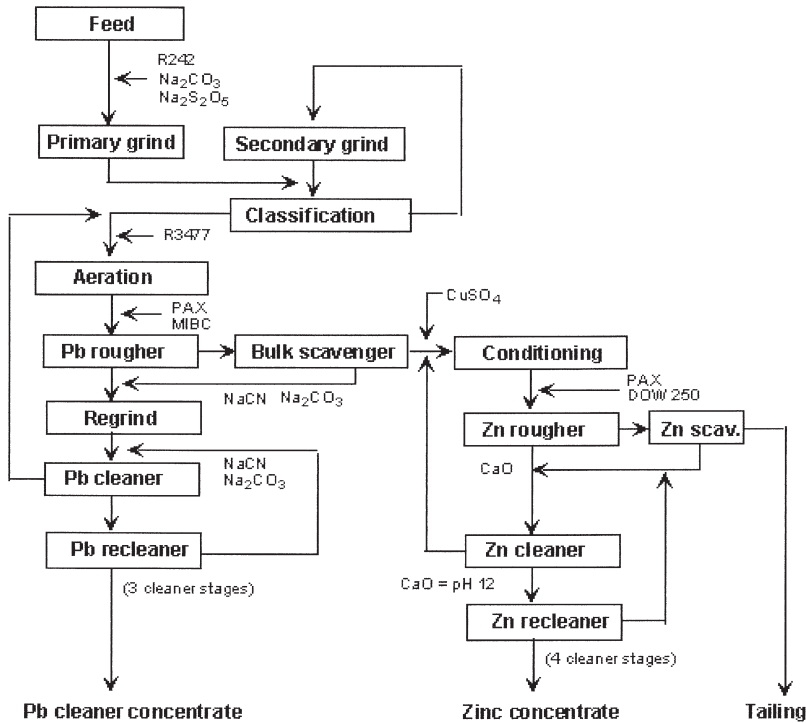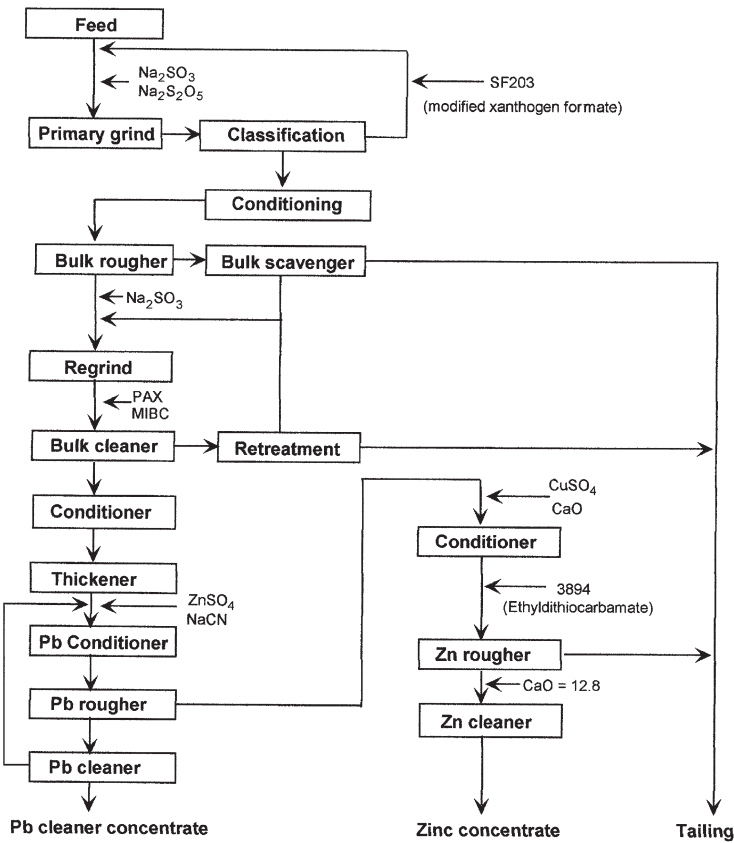
Figure 14.15 Flowsheet and reagent scheme used in the treatment of weakly acidic lead–zinc-ores.

The highly acid ores can be treated in the same way as acidic ores, except that an ore washing stage is added to the circuit. The Tajo Norte (Peru) altered ore is highly acidic and contained a high amount of soluble ions. No selectivity between lead and zinc was achieved on the ore as is, but after the washing of the ore, the selectivity was completely restored.

(b)   The ore with strongly activated sphalerite ore, normally altered ores and the selectivity using sequential lead–zinc flotation is extremely difficult. In addition, the ore may contain soluble ions as well as clay minerals. These ores can be successfully treated using bulk flotation scheme similar to that described in Figure 14.10, but somewhat different reagent combinations. In the bulk flotation, for example, dispersants are used to cope with clay together with Na_2S. In most cases, no collector desorption is required and zinc in the separation is effectively depressed with cyanide at high pH (i.e. 11.5–11.8). The flowsheet and reagent scheme examined on the San Gregorio ore is shown in Figure 14.16.

The results obtained using bulk and sequential flotation methods are shown in Table 14.16. The results obtained using the bulk flotation method were superior to those obtained when using the sequential flotation method.

Feed

Na₂SO₃
Na₂S₂O₅

SF203
(modified xanthogen formate)

Primary grind → Classification

Conditioning

Bulk rougher → Bulk scavenger

Na₂SO₃

Regrind

PAX
MIBC

Bulk cleaner → Retreatment

CuSO₄
CaO

Conditioner

Conditioner

3894
(Ethyldithiocarbamate)

Thickener

ZnSO₄
NaCN

Pb Conditioner

Zn rougher

CaO = 12.8

Pb rougher

Zn cleaner

Pb cleaner

Pb cleaner concentrate   Zinc concentrate   Tailing

Figure 14.16 Flowsheet and reagent scheme used for the treatment of ores with strongly activated sphalerite.

Table 14.16

Comparison of results obtained using bulk and sequential flotation methods

| Flotation method | San Gregorio Ore Zone | Assays (%) | | | | | | Distribution (%) | | | |
| | | Feed | | Pb conc | | Zn conc | | Pb conc | | Zn conc | |
		Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn
Bulk	West	2.2	8.6	58.1	4.8	0.4	53.2	70.1	1.1	3.3	85.6
Sequential	West	2.2	8.8	35.4	20.0	1.1	52.2	33.3	25.6	10.8	66.0
Bulk	South	3.4	9.9	60.1	3.3	0.8	55.5	80.3	2.2	4.1	86.1
Sequential	South	3.3	9.8	48.1	18.3	1.9	52.2	64.1	15.6	8.9	58.3

Operating plants

There are only a few operating plants that treat acidic ores which contain preactivated sphalerite. No detailed plant data are available, but the general operating conditions are described below:

Monterecchio lead–zinc ore (Sardinia) is treated using semi-bulk pyrite galena flotation with $Na_2S_2O_5$ and collector AF35. The pyrite is rejected during the cleaning at alkaline pH (9.5) with the use of cyanide.

Laurium Mine (Greece) was processing highly acidic ore. The ore was washed before grinding to remove soluble ions and then the lime is added to the grind with Na_2SO_3. Lead was floated with dithiophosphate collector.

El Brocal concentrator (Peru) uses an ore washing plant before secondary crushing to remove soluble ions and clay. In the lead circuit $ZnSO_4$, complexed cyanide and Na_2SO_3 are used with good metallurgy. Zinc is floated using a conventional $CuSO_4$–lime circuit.

14.4.4   Treatment of refractory lead–zinc ore

Refractory lead–zinc ores are defined as finely disseminated, with pyrite a content ranging from 10% (McArthur River, Australia) to 98% (Caribou Mine, Canada), where the liberation of the individual minerals occurs below K_{80} 10 μm, and where a commercial grade lead–zinc concentrate cannot be obtained using a conventional flotation technique. These ores, until recently, were considered as untreatable. The high pyrite (Caribou-type) refractory ore responds differently to flotation than the ore with a lower pyrite content (McArthur River) and therefore, two new treatment processes were developed. The reagent scheme and flowsheet developed for treatment of Caribou ore is illustrated in Figure 14.17. The most critical parameters for plant operations were regrind fineness for lead and zinc (i.e. K_{80} 110 μm) and the lead cleaning pH. The average plant metallurgical results obtained in late 1997 are shown in Table 14.17.

The McArthur River ore was treated using a bulk flotation method followed by stage regrinding and lead–zinc separation using quite a unique reagent scheme. In the Pb–Zn separation, depressant Na_2SO_3, silicate and complexed cyanide were used. The <7 μm galena was floated using aminated xanthate. The flowsheet and reagent scheme for the treatment of McArthur River ore is illustrated in Figure 14.18.

The metallurgical results obtained under laboratory conditions are shown in Table 14.18.

Currently, the McArthur River concentrate produces a bulk concentrate, which is further processed using a hydrometallurgical method.

14.4.5   Treatment of lead–zinc–silver ores

Most of ore types described in this chapter contain some silver or silver and gold, which is recovered in either lead or in both lead and zinc concentrates, in which case the precious metals are considered as a by-product for extra revenue. Emphasis in the treatment of these ores is placed on recovery of lead and zinc and the recovery of precious metals is usually
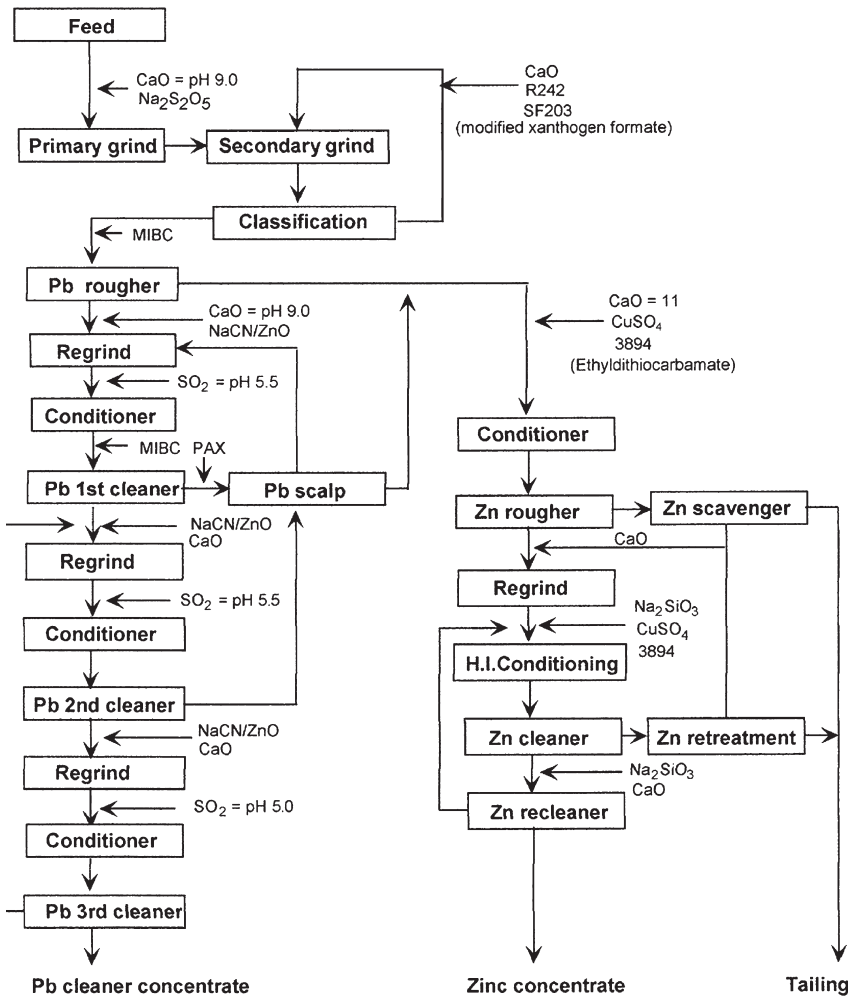
Figure 14.17 Caribou mine flowsheet and reagent scheme used in the 1997 plant operation.

Table 14.17

Plant metallurgical results obtained between July and October, 1997

Product	Weight (%)	Assays (%, g/t)			Distribution (%)		
		Pb	Zn	Ag	Pb	Zn	Ag
Feed	100.00	3.10	6.7	110.0	100.0	100.0	100.0
Pb concentrate	4.49	48.3	3.3	110.2	70.0	2.2	45.0
Zn concentrate	10.66	1.80	50.3	65.0	6.2	80.0	6.3
Zn combined tail	84.85	0.87	1.40	63.1	23.8	17.8	48.7
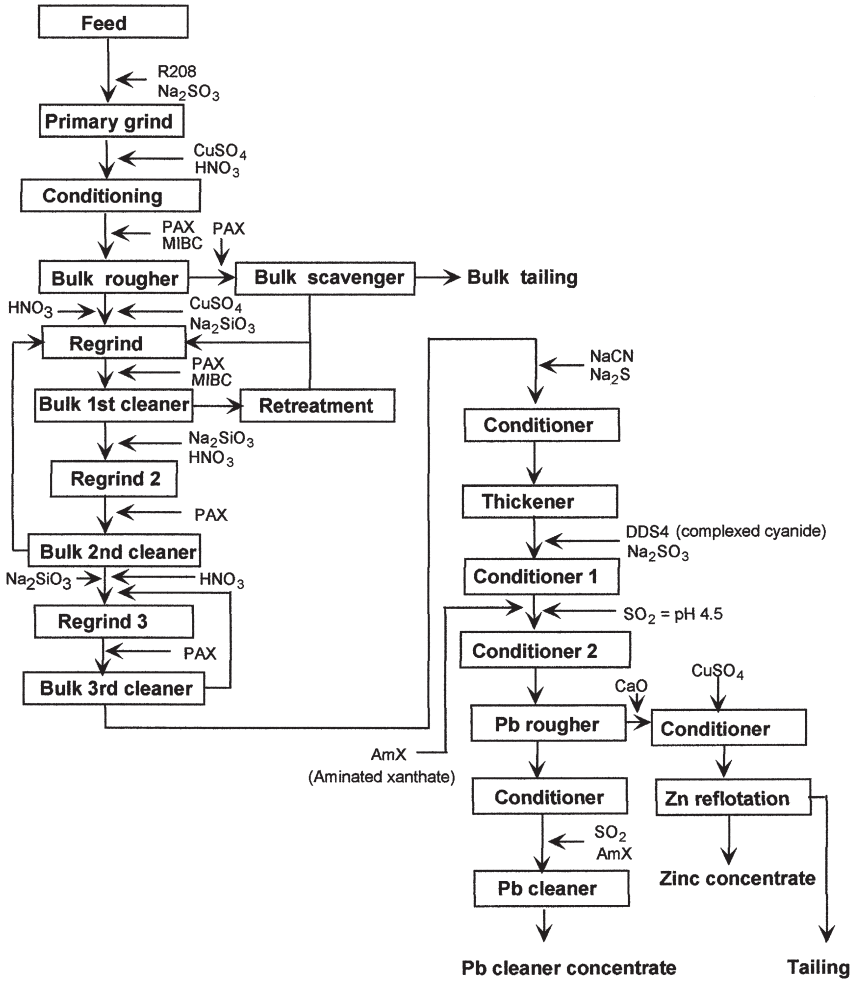
Figure 14.18 McArthur River flowsheet and reagent scheme.

Table 14.18

Metallurgical results obtained on McArthur River ore in a laboratory locked cycle test

Product	Weight (%)	Assays (%)		Distribution (%)	
		Pb	Zn	Pb	Zn
Feed	100.00	7.2	11.8	100.0	100.0
Pb concentrate	11.09	52.6	5.5	81.2	5.2
Zn concentrate	20.37	3.9	50.1	11.0	86.5
Bulk + Zn tails	68.54	0.83	1.43	7.8	8.3

not emphasized for a number of reasons, some of which include: (a) metallurgical problems with lead and zinc need to be solved, (b) lack of research data on the flotation of silver minerals and (c) some silver minerals (i.e. tetrahedrite, polybasite) are capable of releasing cations, Ag^{2+}, Cu^{2+}, which causes reduced selectivity between lead and zinc. Restoring selectivity between lead and zinc in such cases also reduces recovery of silver. The lead–zinc ores that contain a silver value or silver + gold value equal or higher than the value of the lead + zinc in the ore, are considered as lead–zinc–silver ores. During treatment of these ores, emphasis is placed on maximizing the recovery of silver, preferably in the lead concentrate.

Nature and occurrence of silver minerals in the lead–zinc–silver ores

So far, more than 200 silver minerals have been discovered in various sulfide ores, including platinum group minerals. Only about 25–30 of these minerals are of economic value, of which about 20 silver minerals are commonly found in lead–zinc–silver ores. Table 14.19 lists the major silver minerals occurring in the lead–zinc–silver ores.

Tetrahedrite, freibergite and andite are the most unstable silver minerals and because of the stability problem, these minerals are the source of soluble ions in a number of lead–zinc–silver ore, consequently preactivation of gangue minerals and sphalerite. Commonly, the lead–zinc–silver ore contains three or more silver minerals. In some cases (Ucucchacua, Peru), ore contains up to 10 different silver minerals. The presence of multiple silver minerals in the ore, also represent a problem in optimization of silver recovery.

Table 14.19

Silver carrying minerals in the lead–zinc–silver ores

Mineral	Formula	Ag content (wt %)[a]
Native silver	Ag	100.0
Pyrargirite	Ag_3SbS_3	59.8
Diaphorite	$Pb_2Ag_3Sb_3S_8$	23.8
Freibergite	$(AgCu,Fe)_{12}(SbAs)_4S_{13}$	25.0
Argentite (acanthite)	Ag_2S	87.1
Proustite	Ag_2AsS_3	65.0
Andorite	$PbAgSbS_6$	12.6
Miargirite	$AgSbS_2$	36.7
Jalpaite	Ag_3CuS_2	71.6
Stephanite	Ag_5SbS_4	68.3
Pyrostilpnite	Ag_3SbS_3	59.8
Owsheeite	$Pb_5Ag_2Sb_6S_{15}$	8.8
Tetrahedrite	$(Cu,Ag,Fe,Zn)_{12}Sb_3S_{14}$	1.0–34.0
Ag-bearing galena	PbS	0–0.6
Agularite	Ag_4SeS	10–18
Pearcite	$Ag_3As_2S_2$	20–25
Antimonpearcite	$(AgCu)_{16}(SbAs)_2S_{11}$	10–14
Polybasite	$(AgCu)_{16}Sb_2S_{11}$	8–18

[a]May vary from ore to ore

Flotation properties of major silver minerals

Very little is known regarding flotation of different silver minerals, and the literature available is scarce. Some information relevant to the flotation of silver minerals [20] gave an account of the influence of different reagents on the recovery of silver and also indicated that floatability of silver minerals depends on the amount of silver, in particular, silver-rich minerals, for example tetrahedrite floats much more effectively than tetrahedrite with a low silver content. In recent years, extensive laboratory and in-plant studies have been carried out [21–23], on a number of lead–zinc–silver ores with different silver minerals.

In general, the flotation of silver depends on a number of variables. These include:

(a)   Type and level of depressant additions
(b)   Flotation pH
(c)   Type of collector
(d)   Type of silver minerals present in the ore.

Effect of depressants and modifiers on flotation of silver minerals

Some of the conventional depressants normally used during lead–zinc flotation have a negative effect on flotation of a number of silver minerals. Cyanide has a depressing effect on a number of the silver minerals, including argentite, pyrargyrite, pronstite and tetrahedrite. Argentite and pyrargyrite are also soluble in cyanide. Experimental work conducted on Greens Creek ore, which contains tetrahedrite and argentite as major silver minerals indicated that the silver recovery in the lead concentrate was highly sensitive to the level of NaCN additions. Table 14.20 shows the effect of NaCN on silver recovery in the lead concentrate from Area 11 ore.

With the increase in level of NaCN, the lead grade increased slightly, but silver recovery in both rougher and cleaning was significantly reduced.

Alternative depressants used during the treatment of lead–zinc ores were Na_2S, Na_2SO_3 or complex cyanide.

The Na_2S was evaluated at Uchucchacua concentrator (Peru), where the standard cyanide depressant was replaced with Na_2S in the latter part of 1999. The results obtained

Table 14.20

Effect of level of cyanide on silver recovery in the lead concentrate from Area 11 ore [21]

NaCN additions (g/t)		Lead rougher conc				Lead cleaner conc			
		Assays (%, g/t)		Dist (%)		Assays (%, g/t)		Dist (%)	
Grind	Cleaners	Pb	Zn	Pb	Zn	Pb	Zn	Pb	Zn
25	5	13.6	3670	72	77	40.0	11,600	62	69
35	10	14.4	3890	72	74	42.1	11,700	61	66
45	15	15.5	4200	71.8	70	43.2	11,500	60.6	60
55	20	15.4	3400	70.9	55	44.1	9850	60.1	48

Table 14.21

Uchucchacua, Peru plant metallurgical results obtained with cyanide and Na$_2$S

Month 1999	Depressant type, add (g/t)	Feed Assays (%, g/t)			Lead final conc Assays (%, g/t)			Lead conc Recovery (%)		
		Pb	Zn	Ag	Pb	Zn	Ag	Pb	Zn	Ag
July	NaCN = 90	1.1	1.3	480	18.0	4.8	8060	88.0	16.0	65.5
August	NaCN = 85	0.9	1.2	470	16.5	4.6	7500	87.8	15.9	65.7
November	Na$_2$S = 360	1.1	1.3	478	17.0	4.1	8120	89.1	19.2	69.3
December	Na$_2$S = 400	1.1	1.2	460	17.2	4.6	7360	87.5	18.4	70.5

in the plant with NaCN and Na$_2$S are compared in Table 14.21. The use of Na$_2$S results is significant improvement in silver recovery.

The use of the combination of Na$_2$S and Na$_2$S$_2$O$_5$ has been studied on the United Keno Hill (Yukon) ore as a replacement for NaCN and ZnSO$_4$. The ore contained about five principal silver minerals, including native silver, pyrargirite, tetrahedrite, etc.

The use of ZnSO$_4$ did not show any negative effect.

The pH and type of pH modifier play an important role in the recovery of silver minerals. Most of the silver minerals do not favor lime as a pH modifier, because the floatability of the silver minerals is reduced in the presence of lime. The majority of Canadian operations use soda ash as the pH modifier, while South America operations float lead–silver at natural pH. Laboratory testwork results obtained on Keno Hill lead–zinc–silver ore show that when lime is used, the silver recovery is reduced significantly. When soda ash was used the silver recovery improved at a pH between 8 and 9.

Good silver recovery was obtained at natural pH (i.e. 7.5–8.0). Normally, the omission of a pH modifier from the lead–silver flotation, when low pyrite ore is treated, is common. In some cases, where small changes in pH are required, NaOH was used in place of lime.

Effect of collector on flotation of silver minerals

In the majority of operating plants that treat silver-bearing lead–zinc ores, two or more collectors are used for the flotation of silver-bearing minerals, where xanthate was used as the secondary collector. In the 1970s, the main silver collector was dithiophosphates with aromatic radical (R31, R25, Cytec) or ammonium salts (R241, R242). With the development of new groups of collectors, such as aerophines, modified trithionocarbamates and mercaptobenzothiozoles have found application as good silver collectors. Table 14.22 lists the usual collector combinations used for the treatment of lead–zinc–silver ores.

Higher carbon chain xanthates are usually favored for flotation of silver-bearing minerals. In selection of dithiophosphate collectors, attention should be paid to the type of silver minerals present in the ore.

Dithiophosphates with aromatic radicals (R25, R31) or ammonium salts are good collectors for the tetrahedrite and other silver minerals with low silver content. Mercaptan + dithiophosphate combinations float native silver well. The ethyl + secondary butyl dithiophosphate is a better collector for native silver than iso amyl or iso butyl dithiophosphates.

Table 14.22

Collector combinations used for treatment of lead–zinc–silver ores

Collector	Point of addition	Major silver minerals
Dithiophosphates (R25, R31)	Grinding	Tetrahedrite, Ag-bearing
Potassium amyl xanthate	Scavenging	galeodiaphorite
Mercaptan (R400)	Primary grind	Native silver, andorite
Dithiophosphate (R208)	Secondary grind	pyrargirite, argentite
Xanthate (PAX)	Scavenging	
Thionocarbamate/dithiophosphate mixture (R4037) pyrargirite, argentite	Secondary grinding	Native silver, andorite
Aerophone (3418A)	Secondary grinding	
Xanthate (Secc 1BX)	Rougher – scavenger	
Modified mercaptan (Orfan CA800) silver, polybasite, jalpaite, tetrahedrite	Primary grind	Silver/gold alloy, native
Dithionocarbamate (X-3)	Primary grind	
Xanthate (iso amyl xanthate)	Rougher/scavenger	
Ammonia dithiophosphate (R241) pyrostipnite	Primary grind	Tetrahedrite, proustite,
Aerophine (3418A)	Secondary grind	
Xanthate (SIPX)	Flotation	
Xantogen formate (SF203) andorite, native silver	Primary grind	Native gold, agularite
Mercaptan (R404)	Secondary grind	
Xanthate	Flotation	

The iso amyl and iso butyl dithiophosphates float silver minerals that contain copper and bismuth well.

The lead–zinc–silver ore that contains gold, a dymethyl dithiocarbamate collector, gave better metallurgy than dithiophosphate. It also provided improved selectivity towards sphalerite.

Plant reagent scheme and metallurgy

The lead–zinc–silver operating plants are relatively small operations with capacities ranging from 500 to about 3000 tpd. In some operating plants, where gold is present, pyrite concentrate is floated, which is later treated in a separate cyanidation circuit. Reagent scheme used in more important operating plants are listed in Table 14.23.

The United Keno Hill mine contains a variety of silver minerals (i.e. about 8 minerals) including native silver. In the early 1980s, detailed studies were performed to examine a number of different silver collector combinations. From the results obtained (Table 14.24), it appears that the most effective collector combinations were dithiophosphate, thionocarbamate and phosphinate, with no xanthate additions. The importance of the multiple collector

Table 14.23

Reagent schemes used in the treatment of lead–zinc–silver ores

Concentrator	Reagent type and additions (g/t)		pH	
	Lead circuit	Zinc circuit	Pb	Zn
Krasnorecheski, Russia	$Na_2CO_3 = 720$ $ZnSO_4 = 2500$ DMC (diethyl dithiocarbamate) = 30 SIPX = 10	$CaO = 600$ $CuSO_4 = 550$ SIPX = 30 Pine oil = 10	9.0	10.5
Sherlova Gora, Russia	$CaO = 350$ $ZnSO_4 = 400$ PAI (dithiophosphate) = 15 Pine oil = 10	$CaO = 1200$ $CuSO_4 = 300$ PAX = 20 SIPX = 35 MIBC = 15	9.5	11.5
Salmo Mine, Canada	$ZnSO_4 = 200$ NaCN = 60 AF25 = 65 PAX = 10 MIBC = 10	$CaO = 550$ NaCN = 5 $CuSO_4 = 350$ SIPX = 35 MIBC = 15	8.5	9.8
Grant Mascot, Canada	NaCN = 10 $ZnSO_4 = 100$ SNBX = 5 KEX = 10 Cresylic acid = 10	Lime = 200 $CuSO_4 = 200$ KEX = 15	8.3	8.5
Wilson Silver Mine, Canada	$Na_2SiO_3 = 150$ $Na_2SO_3 = 240$ Thiocarbanilide = 40 R3477 = 40 Pine oil = 5	–	8.9	–
United Keno Hill, Canada	NaCN = 30 $Na_2SO_3 = 300$ $CaO = 20$ Aeroflot 31 = 40 Mercaptan R404 = 30 SIPX = 30 Cresylic acid = 20	Lime = 250 $CuSO_4 = 320$ SIPX = 30	7.0	7.1
Undaychaqua-Volcan, Peru	NaCN = 50 $ZnSO_4 = 350$ AF31 = 20 R400 = 50 SIPX = 30 MIBC = 10	Lime = 40 $CuSO_4 = 380$ SIPX = 40 AF70 = 10	7.2	10.0
Mahr Tunnel-Volcan, Peru	NaCN = 20 $ZnSO_4 = 350$ AF241 = 35 R3477 = 50 MIBC = 25 PA = 20	Lime = 750 $CuSO_4 = 380$ SIPX = 40 MIBC = 20	7.7	9.5
Uchucchacua	NaHS = 400	$CaO = 1800$	7.3	11.5

(Continued)

Table 14.23   (*Continued*

Concentrator	Reagent type and additions (g/t)		pH	
	Lead circuit	Zinc circuit	Pb	Zn
Buenaventura-Peru	$ZnSO_4 = 500$ AF3047 = 50 3418A = 20 PAX = 60 MIBC = 30	$CuSO_4 = 400$ PAX = 40		

Table 14.24

Effect of different collector combinations on silver recovery from the United Keno Hill (Elsa) ore

Collector used, type	Lead-silver rougher conc			
	Assays (%, g/t)		Distribution (%)	
	Pb	Ag	Pb	Ag
SIPX = 100 g/t	18.0	3800	80.0	65.0
PAX = 100 g/t	16.0	3600	83.0	68.0
ORFOM 540[a] = 20 g/t, PAX = 80 g/t	19.6	4200	86.0	71.2
AF31 = 30g/t, AF208 = 30 g/t, PAX = 40 g/t	21.1	4600	88.0	82.3
AF241 = 30 g/t, AF3501 = 30 g/t, PAX = 40 g/t	20.2	4100	87.0	80.1
AF208 = 30 g/t, Z200 = 30 g/t, Aerophine 3418A = 15 g/t	25.5	5780	92.2	94.1
AF3477 = 30 g/t, Z200 = 30, PAX = 40	20.1	4900	89.1	85.0

[a] Philips Petroleum

combinations, where a number of silver minerals are present in the ore, has been demonstrated.

The Uchucchacua (Peru) ore has a unique character with respect to the presence of albandite (MnS_2), which floats with the lead–silver concentrate. In 1985, a concentrate leach plant was installed to remove alabandite by leaching.

In 1998, the silver recovery deteriorated and dropped from 69% Ag to 65% Ag. Extensive laboratory testwork, conducted in early 1999, resulted in the development of new reagent schemes [24], which resulted in depression of alabandite and improved silver recovery from 65% to 72% Ag.

The new reagent scheme (Table 14.23) consisted of Na_2S, which replaced NaCN and the introduction of alabandite depressant A3–3. This depressant is a mixture of $Na_2SiO_3:Al_2(SO_3)_4:Na_2S_2O_5 = 29:29:42$. The effect of depressant A3–3 on manganese content of the lead concentrate is shown in Figure 14.19.

Typical metallurgical results obtained in lead–zinc–silver ores in the operating plants listed in Table 14.23 are summarized in Table 14.25.
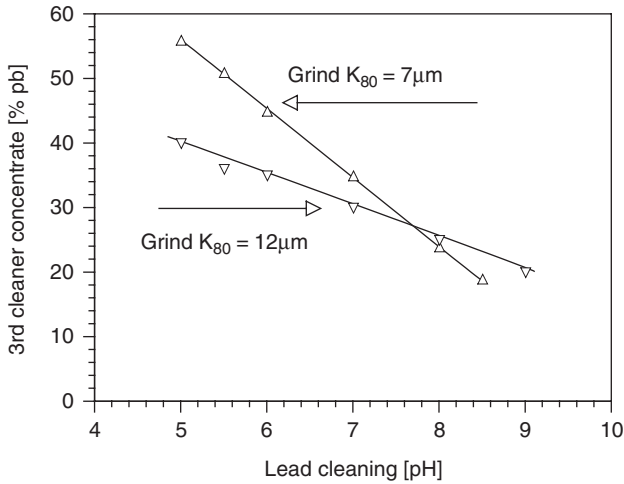
Figure 14.19 Effect of depressant A3–3 on alabandite content of the lead–silver concentrate.

Table 14.25

Plant metallurgical results obtained on lead–zinc–silver ores

| Concentrator | Assays (%, g/t) | | | | | | | | Recovery (%) | | | |
| | Feed | | | Pb/Ag conc | | | Zn conc | | Pb conc | | Zn conc | |
	Pb	Zn	Ag	Pb	Zn	Ag	Zn	Ag	Pb	Ag	Zn	Ag
Krasnorechensky	1.1	3.6	250	47.4	4.5	3980	47.8	250	88.8	79.3	84.1	6.7
Sherlova Gora	1.9	2.6	210	77.9	1.7	5170	41.5	220	80.4	71.9	60.3	5.2
Salmo Mine	1.5	4.4	180	70.8	6.9	1900	58.2	110	85.5	73.1	89.8	2.8
Giant Mascot	4.4	0.3	250	69.9	3.2	2800	50.9	120	94.9	65.5	50.9	3.3
Wilson Silver	4.5	8.6	1364	52.0	12.0	15360	55.0	1023	92.0	87.0	85.0	10.2
United Keno Hill	8.6	8.6	1229	71.3	3.6	9696	56.3	384	93.3	89.0	88.2	6.5
Undaychaqua	1.2	7.1	279	37.0	4.5	8100	56.8	440	89.0	69.5	89.0	4.5
Mahr	0.8	6.3	155	55.5	6.6	6020	58.5	3300	66.5	70.2	85.2	3.6
Uchucchacua	1.1	1.4	450	17.0	3.9	8800	44.0	1100	88.0	71.2	63.0	4.5

REFERENCES

1. Goodfellow, W.D., and Nowak, J., In (R.V. Kirkham, W.D. Sinclair, R.I. Thorpe, and S.M. Duke eds) Geology and Genesis of Stratiform Sediment Hosted (Sedex) Lead-Zinc Silver Sulphide Deposits: Mineral Deposits Modeling, CIMM, Chile, pp. 201– 252, 1997.
2. Leach, D.L., and Sangster, D.F., Mississippi Valley Lead Zinc Deposits, In (R.V. Kirkham, W.D. Sinclair, R.I. Thorpe, and S.M. Duke eds) *Mississippi Valley Lead–Zinc Deposits: Mineral Deposits Modeling*, Permagan Press, New York, pp. 289–312, 1997.

3. Carson, D.T.S., Geological and Mineralogical Investigation of the Favo and Green Orebodies, Interim Report Noranda Exploration Company Limited, 23 March 1977.

4. Rey, M., Differential Flotation of Lead–Zinc Ores – A Tentative Classification of the Ores and of Flotation Techniques, Progress in Mineral Dressing, IMPC, Stockholm, pp. 525–536, 1957.

5. Bulatovic, S.M., Development and Plant Application of the Sequential Lead–Zinc Flotation of Taho Norte El Brocal Ore Report of Investigation LR 4455, November 1996.

6. Bulatovic, S.M., Milpo Plant Improvement Studies LR 5438, March 1997.

7. Bulatovic, S.M., Effect of Ammoniacal Copper Sulphate on Flotability of Sphalerite and Marmatite, Interim R & D Report LR 029–5, June 1986.

8. Bulatovic, S.M., Flotation of Different Varieties of Sphalerite Plant Practice, Private Communication, 1983.

9. Konev, A.S., and Debriynaja, L.S., Separation of Bulk Sulphide Concentrate by Flotation, Progress in Mineral Dressing, IMPC Stockholm, pp. 555–561, 1957.

10 Johnson, N.S., and Grano, S.L., Xanthate and Diisobutyldithiophosphinate Collectors for Lead Roughing of the Mount Isa Hilton Concentrator, Fourth Extractive Metallurgy Conference, Aus. Ins. M., p. 203–210, 1991.

11. McTavish, S., Improvement in Zinc Metallurgy of Brunswick Mining and Smelting Concentrator, Research Report No.6, June 1977.

12. Wyslouzil, D.M., and Bulatovic, S.M., Selection of Reagent Scheme to Treat Massive Sulphide Ores. Complex Sulphides, In (A.D. Zunkel, and S.R. Rao eds) *SIMM*, November 1985.

13. Bulatovic, S.M., and Dan, L., Evaluation of New Reagent Scheme for Treatment of Mount Isa Lead Zinc Ores, Report of Investigation LR 5375, July 1996.

14. Bulatovic, S.M., Process Development of Cirque Lead–Zinc Ore, Report of Investigation LR 5416, September 1995.

15. Bulatovic, S.M., Wyslouzil, D., and Rawling, K.R., Laboratory and Plant Evaluation of Organic DS20 Depressant for Treatment of Nowasivik Massive Sulphide Lead Zinc Ore, Canadian Mineral Processors Conference, Ottawa, Canada, January 21–23, 1986.

16. Bulatovic, S.M., and Jessup, T., Depressant for Flotation Separation of Polymetallic Ores, US Patent 4,877,517. October 31, 1989.

17. McDonald, S., Application of New Organic Depressant in Treatment of Porco and Bolivar Lead Zinc Ore, Hansman Corporation of Canada Interim Report No.15, October 5, 1997.

18. Fishman, M.A., and Sobolev, D.C., Operating Practice in Treatment of Sulphide and Non-Metallic Ores, *Metallurgizdat*, Vol. 1, 1957.

19. Bulatovic, S.M., Process Development for Treatment of Greens Creek Lead–Zinc Silver Ore, Report of Investigation LR 3268, November 1982.

20. Bulatovic, S.M., and Lang, D., Plant Improvement Studies of Silver Lead and Zinc. Recoveries at Huollanca Concentrator Peru, Report of Investigation LR 5529, June 1999.

21. Glembotsky, A.V., and Kolemanova, A.E., The Replacement of Cyanide by New Organic Depressant in Selective Flotation of Polymetallic Lead Zinc Silver Ores, XIX International Mineral Processing Congress, San Francisco, Vol. 3, pp. 205–208, November 1995.

22. Bulatovic, S.M., Process Development for Silver Flotation From United Kano Hill Tailing, Interim Report LR 029, May 1982.

23. Bulatovic, S.M., and Jessup, T., Development and Plant Application of New Reagent Scheme for Treatment of Ucuccaqua Peru. Lead Zinc Ore, Report LR 5468, June 1993.

24. Bulatovic, S.M., Development of New Alabandite Depressant, Report of Investigation, LR1033.

– 15 –

Flotation of Copper–Lead–Zinc Ores

15.1 GENERAL OVERVIEW OF THE ORIGIN OF COPPER–LEAD–ZINC ORES

The copper–lead–zinc ores have an origin similar to copper–zinc and lead–zinc ores, the exception being those ores that contain copper, lead and zinc as the principal economic minerals. In addition, some of these ores contain significant amounts of precious metals and, more rarely, cobalt and nickel.

Similar to copper–zinc and lead–zinc ores, copper–lead–zinc ores have several major geological formations, of which the most important are:

- Deposits that occur in hydrothermal vein fillings and replacement (usually of limestone) bodies, often associated with intermediate to acid intrusions. These ores contain silver and gold in addition to copper, lead and zinc. Such deposits are found in North America, Cordillera, Zacatecas (Mexico), Transbaikalia (erstwhile Soviet Union) and Caspalca –(Peru).
- Massive sulfide deposits of volcanogenic origin, similar to those found in New Brunswick (Canada), Aznalcollar (Spain), Iberian Pyrite Belt (Turkey), Kuroko (Japan) and Hellyer (Tasmania). In this group, massive strata-bound deposits can be included.
- Sedimentary deposits are mostly found in the Viburnum trend.

15.1.1 Hydrothermal vein deposits

The copper—lead–zinc vein deposits are usually characterized by coarse-grained banded to massive aggregates of pyrite, galena, sphalerite and chalcopyrite. The bulk mineralogy is quite similar to that of strata-bound sulfide deposits, except that galena tends to be much more abundant in the vein deposit. Pyrite, sphalerite and gangue minerals, such as quartz, calcite and fluorite, often tend to be euhedral with the development of well-formed faces.

These deposits are formed as a result of the circulation of hydrothermal fluids that extract, transport and then precipitate sulfide minerals as open-space fillings and replacements. Often, near surface portions of these ores, it is revealed that there are moderate to extensive alterations by meteoric water. The oxidation of pyrite causes the formation of sulfuric acid and ferrous sulfate, which results in the breakdown of other

sulfides. The end result is that the uppermost parts of the veins consist of a boxwork gossan of iron oxides and hydroxides, and at the lower levels secondary covellite, chalcocite, galena and sometimes silver have been re-precipitated to form secondary carbonates, sulfates and silicates of copper, lead and zinc (Chalcivites, Mexico). Many ores of this type exhibit complex paragenesis in which multiple episodes of deposition, leaching and replacement are evident leading to the formation of covellite or chalcocite along fractures in chalcopyrite. In general, bands of iron-rich sphalerite appear as distinct bands. Sphalerite in these deposits frequently contains crystallographically oriented rows of chalcopyrite blebs, which have been referred to as "chalcopyrite disease" [1].

The treatment of these ores varies from simple to extremely difficult, especially the ores with secondary enrichment of copper.

15.1.2   Sedimentary deposits

Unlike the lead–zinc deposits from the Mississippi Valley, which are the simplest ore, the sedimentary copper–lead–zinc ores (e.g. the Viburnum trend) contain a diverse assemblage of minerals uncommon in most Mississippi Valley–type ore deposits [2]. These include siegenite, bravorite, gerstorfirite, carallite, digenite, covellite, pyrrhotite and marcasite. The valuable ore minerals exhibit a variety of open space and replacement textures. The chalcopyrite, galena and sphalerite are coarse-grained and adequate liberations occurs at about 55–65% <200 mesh.

A portion of this ore however is fine-grained or intricately inter-grown and represents varieties of recovery concentrate grade and deleterious constituent problem. Beneficiation problems that arise from the character of this ore texture include displacement of zinc in the lead concentrate, lead in the copper concentrate and lead, zinc and copper in the tailing.

The principal sulfide minerals in the most sedimentary ores are galena, sphalerite, chalcopyrite, marcasite and pyrite. All the sulfide minerals were repetitively deposited and occur in a variety of forms. Galena occurs as a massive replacement of the host rock dolomite, as replacements of the earlier deposited sulfide minerals and as euhedral crystals deposited in vugs. Sphalerite occurs dominantly as relatively fine-grain replacements of host rock dolomite, but small subsequently deposited vug-lined crystals are also present. Chalcopyrite occurs commonly as massive to colloform replacement masses, but also as subhedral crystals disseminated in host rock dolomite and as euhedral crystals in vugs.

The main gangue minerals, in addition to marcasite and pyrite are dolomite, quartz and calcite. The host rock Cambrian Bouneterre limestone has been dolomitized nearly all areas where it contains ore deposit.

Cobalt and nickel are present in significant quantities in some area of the Viburnum trend deposits (e.g. 0.3% Co and 0.5% Ni). Cobalt primarily occurs as seigenite; nickel is present mainly in bravoite and to a lesser degree, in seigenite.

Ores that contain cobalt and nickel also contain a substantial amount of clay minerals (illite, kaolinite group). Only recently, efforts have been put in place to the development of a process for the recovery of cobalt and nickel from these ores.

15.1.3   Massive sulfide deposits

Much like the lead–zinc massive sulfide deposits, the Cu–Pb–Zn massive sulfide ores are highly variable and can range from coarse-grained ore (Golden Grove, Australia) to finely disseminated massive sulfides (New Brunswick, Canada), refractory massive sulfides (Kuroco Hellyer), etc., altered massive sulfides (Tsumeb, Africa) and exclusively pyrrhotite ores (San Martin, Mexico).

The mineralogy and texture of these ores varies significantly and the processing characteristics also vary widely, and usually the treatment processes for beneficiation of these ores is highly complex. Some of the major characteristics of the massive sulfide deposits relevant to the processing characteristics are described as follows:

- *Coarse-grained massive sulfide ores* are somewhat different in mineralogy than the coarse-grained massive sulfide lead–zinc ores. They usually contain alteration bands and partially oxidized sulfides. The principal minerals are chalcopyrite, galena and sphalerite with widely variable ratios, but in most cases sphalerite is the most abundant followed by galena and chalcopyrite. Pyrite occurs in different forms and varieties ranging from crystalline to sugar-like altered pyrite. Marcasite may be present only in the ore with a high amount of silver (Kidd Creek C ore, Canada). Chalcopyrite in some ores may be tarnished and partially oxidized (Thalanga Mine, Australia). The processing characteristics of these ores vary widely and range from easy-to-treat to difficult-to-treat ores.
- *Disseminated massive sulfide deposits* are usually a strata-bound deposits of so-called "cupriferrous pyroclastic nature." The orebodies usually occur [3] within the lower carboniferouus volcango-sedimentary units, in which volcanic rocks account for most of the sequences of formation. The ore mineralogy is mostly formed by massive recrystallized pyrite. A wide variety of ore textures are common, such as annealed, euhedral, zoned, brecciated, framboidal and colloform. Other textural features include the enveloping of pyrite by sphalerite, galena, chalcopyrite or bournonite. Chalcopyrite usually infills cavities and fractures in pyrite. Sphalerite occurs as thin-film coatings, mineralized fractures and bands. Lead is represented by galena, bournonite and/or menenghinite. All these minerals infill cavities in pyrite or occur in close association to sphalerite. The liberation of the individual minerals varies widely and ranges from 50 to <10 μm. Treatment of these ores can be very difficult.
- *Refractory massive sulfide ores* are used as a term in a wide variety of contexts and there is no universally accepted definition. The term refractory massive sulfide ores is used to distinguish these ores from other massive sulfides, where the treatment process is extremely complex (New Brunswick and Kuroco). In the majority of cases, these ores are usually compared to Kuroco (Japan) and New Brunswick (Canada) ore types. The broad-scale features of these ores arise from the volcanogenic sedimentary origin where remobilization and recrystallization of the various minerals such as galena, sphalerite, chalcopyrite and tetrahedrite include possible sedimentary load structure in fine-grained pyrite.

  Sphalerite in a number of deposits forms coarse patches, commonly full of very small (<20 μm) inclusions of the other sulfides. Galena also forms coarse patches and veins, but these ores comparatively free from other sulfides that occur as

complex intergrowths with pyrite and sphalerite and as minute disseminated grains. Chalcopyrite may occur as coarse patches (100 μm) or as very small (<5 μm) inclusions in sphalerite.

Other sulfides that may occur in various orebodies include arsenopyrite, pyrrhotite and a variety of silver sulfosalts. The liberation profile varies significantly and ranges from 30 to 5 μm, respectively.

Kuroko black ore also belongs to this ore type. Kuroko black ore is a general term for the complex fine-grained sulfide ores [4], which are closely related to the host volcanic rocks of the Miocene age. The deposits of this type are usually massive and irregular in form and consist mainly of the following three distinct ore types: black, yellow and siliceous. Black ore is found on the top of the deposit and contains sphalerite, galena, chalcopyrite, tetrahedrite, barite and pyrite. The yellow ore occurs below the black ore and consists mainly of chalcopyrite with minor amounts of sphalerite, galena, barite and other copper minerals. Siliceous ores have the original structure of volcanic tuff or breccia impregnated with pyrite and chalcopyrite. These ores contain a considerable amount of clay minerals such as sericite, chlorites, and montmorillonite that cause considerable problems in flotation.

- *Oxidized and altered massive sulfide ores* are similar to coarse-grained sulfides, but these are either partially oxidized or contain supergene alteration. Major economic minerals are sphalerite, galena and chalcopyrite with significant quantities of secondary copper minerals. Oxidation and the secondary copper minerals are the principal problems in the treatment of these ore types. Some deposits in the Soviet Union and South-West Africa belong to this ore type.
- *Pyrrhotite copper–lead–zinc ore*, mostly situated in the Province of Zacatecas in Mexico, is unique in a way that it represents a significant mineral processing challenge, mainly in the separation of marmatite from sphalerite. The zinc in these ores is marmatitic and has flotation behavior similar to pyrrhotite, so the sequential flotation of marmatite represents a considerable problem.

15.2   TREATMENT OF COPPER–LEAD–ZINC ORES AND THE FACTORS THAT AFFECT THE SELECTION OF A TREATMENT METHOD

The treatment processes for the beneficiation of copper–lead–zinc ores are the most complex of all ores processed. The flotation behavior of the individual minerals is different from that of either lead–zinc or copper–zinc ore and therefore the treatment process is tailored based on the processing characteristics of the individual ore types. In general, there are three basic processing techniques commonly used in the treatment of copper–lead–zinc ore. These include

- A sequential copper–lead–zinc flotation method where the copper, lead and zinc are sequentially floated to produce separate copper, lead and zinc concentrates.
- The bulk copper–lead flotation method, followed by zinc flotation from the bulk tailing. The copper–lead separation is performed on the upgraded bulk concentrate. This method is the most commonly used in the treatment of copper–lead–zinc ores.

- Bulk copper–lead–zinc flotation followed by copper–lead–zinc separation from the bulk concentrate. This method is rarely used and is effective on the ores where the principal copper minerals are bornite, covellite and other secondary copper sulfides. Ores that contain clay minerals are also using the bulk flotation of all sulfide method.

There is no general rule by which a treatment method is selected and these rules cannot be prescribed. In some operating plants that use a sequential flotation method, the same ore also responds well to bulk copper–lead flotation [5]. There are, however, factors that influence the selection of a flotation method. These factors are described as follows:

- Some copper–lead–zinc ores that contain precious metals respond better to sequential copper–lead–zinc flotation than to bulk copper–lead flotation, specifically with respect to the recovery of gold and silver in the copper and lead concentrate. A typical example of such a case is the Silver Queen Mine in British Columbia (Canada) represented by copper–lead–zinc–silver–gold. Table 15.1 compares pilot-plant metallurgical results using sequential and bulk flotation methods [6].
- The sequential flotation method gave better precious metal recovery along with better selectivity than the copper–lead bulk flotation method.
- In some cases, when using Cu–Pb bulk flotation, the separation of copper and lead from the bulk concentrate is either very difficult or impossible. An example of such a case is the Black Mountain (South Africa) ore [7], which uses a sequential Cu–Zn separation method because of the above reasons.
- For some finely disseminated massive sulfide ores that require fine primary grinding and regrinding of the concentrate (i.e. <20 μm), sequential copper–lead flotation method performs much better than copper–lead bulk flotation method (Hellyer, Tasmania).
- For ores that contain pre-activated sphalerite (*in situ* or during grinding) copper–lead sequential flotation is a preferred flotation technique. An example of such is the Rozberg Concentrator in Australia [8].

The bulk copper–lead flotation method is the most economic and is used whenever possible. Using such a method, the copper–lead bulk concentrate is floated, followed by Cu–Pb upgrading and separation. Usually, the Cu–Pb separation tailing is the final lead or copper concentrate depending on the separation method used. However, there are cases where the upgrading of lead concentrate after separation is required and this makes the treatment process more complicated.

The reagent schemes used in sequential copper–lead–zinc flotation and bulk copper–lead flotation differ significantly and these two flotation techniques are presented in separate sections. It should be remembered that the selection of a reagent scheme using either technique depends on the origin of the ore and its mineralogy. The characteristics of an ore deposit have a controlled influence on the selection of reagent scheme using either flotation technique.

Table 15.1

Effect of sequential and bulk flotation methods for the treatment of the silver queen ore [7]

Flotation method	Product	Wt %	Assays % (g/t)					% Distribution				
			Cu	Pb	Zn	Au	Ag	Cu	Pb	Zn	Au	Ag
Sequential Cu–Pb–Zn	Cu concentration	3.5	27.7	1.91	5.93	7.53	6271	82.8	5.7	2.0	15.5	51.1
	Pb concentration	1.7	0.94	51.7	7.31	33.1	5675	1.4	73.6	1.2	32.5	22.7
	Zn concentration	16.1	0.46	0.44	60.2	0.87	232	6.3	5.9	93.1	8.3	8.8
	Zn comb tail	78.7	0.14	0.22	0.50	0.95	93.5	9.5	14.8	3.7	43.7	17.4
	Feed	100.0	1.18	1.19	10.4	1.72	423	100.0	100.0	100.0	100.0	100.0
Bulk Cu–Pb	Cu concentration	3.68	25.4	3.30	6.50	4.72	5103	78.5	10.1	2.3	10.1	44.4
	Pb concentration	1.64	2.60	50.4	8.90	32.0	6756	3.6	68.9	1.4	30.3	25.5
	Zn concentration	15.8	0.8	1.1	58.8	0.61	212	10.6	14.5	88.3	5.6	8.4
	Zn comb tail	78.9	0.11	0.10	1.00	1.17	119	7.3	6.5	8.0	54.0	21.7
	Feed	100.0	1.19	1.20	10.5	1.72	423	100.0	100.0	100.0	100.0	100.0

15.3   REAGENT PRACTICE USING SEQUENTIAL COPPER–LEAD–ZINC FLOTATION TECHNIQUE

The sequential copper–lead–zinc flotation practice utilizes several major reagent combinations in sequential copper–lead flotation, which include:

➢ Bisulfide method
➢ Starch/lime method
➢ Soda Ash/SO_2 or lime/SO_2 method.

The generalized flowsheet used in sequential flotation is shown in Figure 15.1.

15.3.1   Bisulfide sequential copper–lead–zinc flotation method

Using this method, the principal lead depressant during copper flotation is sodium bisulfide ($Na_2S_2O_5$). $Na_2S_2O_5$ is usually added to the grinding stage with or without $ZnSO_4$ for sphalerite depression. The copper is then floated using dithiophosphate (R208), dithiocarbamate (X-31), ethyl xanthate or combinations of xanthate and dithiophosphate. The level of $Na_2S_2O_5$ varies considerably and ranges from 2000 to 5000 g/t. Plant data [9] (Australia)
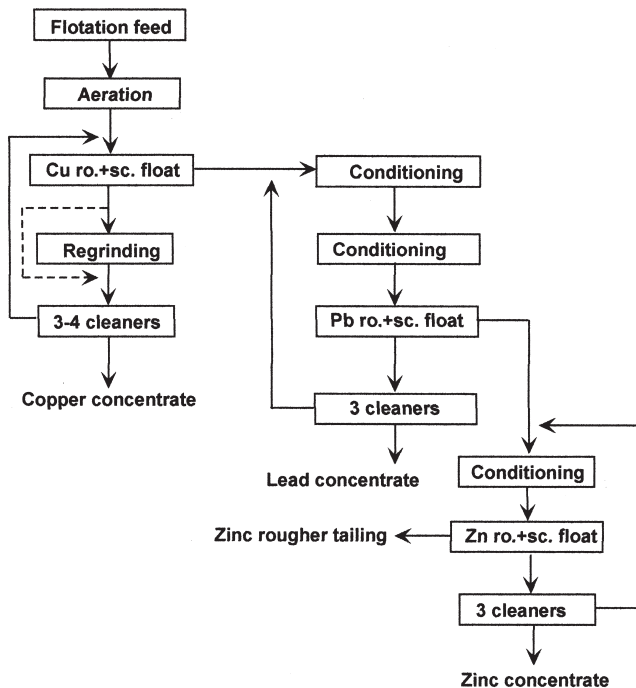
Figure 15.1 Flowsheet used in sequential copper–lead–zinc flotation.
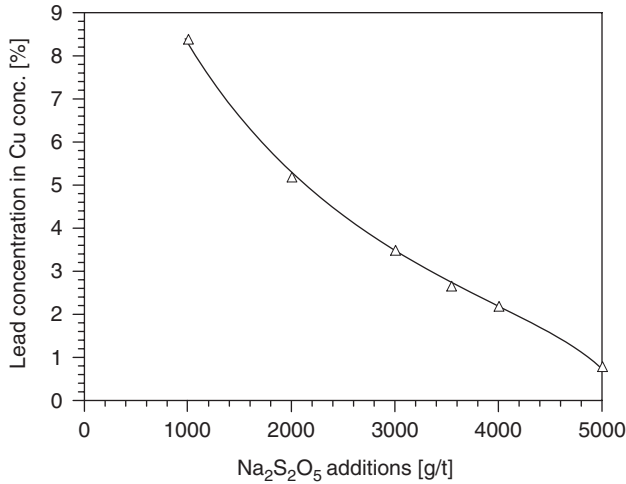
Figure 15.2 Effect of the level of $Na_2S_2O_5$ on lead assays of the copper concentrate.

showed that selectivity between copper–lead depends very much on the level of $Na_2S_2O_5$ used. Figure 15.2 shows the relationship between level of $Na_2S_2O_5$ additions and lead content of the copper concentrate. The optimum $Na_2S_2O_5$ addition was at about 5000 g/t. The Thalanga plant operates with additions of $Na_2S_2O_5$ at about 5000–5500 g/t. The usual pH in the copper flotation circuit is between 6.2 and 6.5. It appears from these plant operating data that at a higher pH the selectivity between copper and lead is reduced.

   The use of $Na_2S_2O_5$ in the copper circuit has some advantages in the subsequent lead flotation. Some of these advantages are described as follows:

(a)   Lead is re-activated more easily than when starch is used. With an increase in pH, lead re-activation occurs without any addition of modifying reagent.
(b)   The cyanide consumption for sphalerite depression is reduced since $Na_2S_2O_5$ retains its depressing effect on sphalerite during lead flotation.

In the lead circuit, most of the time soda ash and cyanide are used as the principal modifiers with dithiophosphate collector. When the pyrite depression is no problem, then small quantities of xanthate are used. The usual pH in the lead flotation circuit is between 9.0 and 9.5. Sphalerite is recovered using a conventional lime–$CuSO_4$ circuit with xanthate collector.

15.3.2   Soda ash–sulfurous acid Cu–Pb–Zn sequential flotation method

This method is usually accompanied by aeration with collector for copper flotation. The ore is ground with soda ash followed by conditioning by SO_2 to a pH between 4.5 and 6.0. The conditioned pulp is then passed to an aerator where the collector is added.
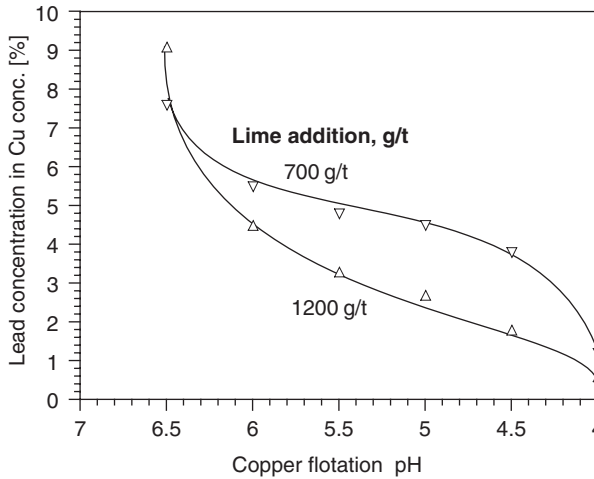
Figure 15.3 Effect of copper flotation pH on lead content of the copper concentrate using two levels of lime [10].

The collector choice depends on flotation pH selected and the nature of the ore. The Black Mountain plant (South Africa) uses thionocarbamate at pH 4.5, while at Rozberg, dithiophosphate (R25) is used at a flotation pH of about 5.8. Dithiophosphate at the Rozberg Concentrator gave better precious-metals recovery.

The flotation pH, using the SO_2/soda ash method, is quite important in maintaining good selectivity between copper and lead. The effect of flotation pH at different levels of alkali addition was studied in the Black Mountain ore (South Africa). Figure 15.3 shows the effect of pH on lead content of the copper concentrate. In this particular case, lime was used in the grinding circuit instead of soda ash.

The higher lime additions resulted in higher SO_2 additions and consequently improved lead depression.

The flotation of lead and zinc is performed in the same way as when $Na_2S_2O_5$ is used as a lead depressant.

15.3.3 The lime–starch–SO_2 depressant system in sequential Cu–Pb–Zn flotation

This method has been applied in the treatment of ores that contain significant quantities of precious metals, specifically silver minerals in the form of sulfosalts and ores where sphalerite is pre-activated.

The ore is ground with lime and starch to pH 10.5–11.2, followed by conditioning with SO_2 to a pH 5.5–4.5. The conditioning time is adjusted to provide stable and constant pH in the copper flotation. The collectors used in copper flotation using a lime-SO_2 depressant system are ethyldithiocarbamate and dithiophosphates. Xanthate, however, is not suitable using the above depressant system.

Using this flotation method, the successful depression of lead during copper flotation depends very much on the type of starch used. The research work conducted on Silver Queen ore has shown that oxidized starch was used effectively for the depression of galena [11]. Table 15.2 shows the effect of different starches on copper concentrate grade and lead displacement in the copper concentrate.

Dextrins, branched or modified, did not perform well when using this method. The use of ammonium Persulfate as a co-depressant for galena and sphalerite showed a substantial improvement in the selectivity between copper and lead–zinc. Figure 15.4 shows the effect of ammonium persulfate on lead and zinc depression during copper flotation. It is believed that ammonium persulfate has a complexing ability toward heavy metals and consequently improves selectivity. Similar effect was observed with the use of hexametaphosphate. With the use of hexametaphosphate, however, subsequent re-activation of galena is more difficult.

Lead flotation from the copper tailing is performed in a soda ash circuit using ZnO/NaCN as a zinc depressant. The lead flotation pH is about 7.0–7.5. A lower pH

Table 15.2

Effect of type of starch on copper concentrate grade and lead content of the copper concentrate

Type of starch	Assays % (g/t)					% Distribution				
	Cu	Pb	Zn	Au	Ag	Cu	Pb	Zn	Au	Ag
Oxidized starch (TJ)	27.2	1.4	4.2	9.3	6080	78.2	2.8	1.2	20.3	65.5
Corn gelatinized	25.0	3.3	5.1	8.3	5060	73.3	6.8	1.8	19.0	55.4
Potato caustic starch	24.1	6.3	5.5	7.5	4660	70.1	9.3	2.2	18.6	54.4
Pearl caustic starch	22.8	8.0	5.5	7.4	4680	71.1	15.1	3.0	17.7	55.2
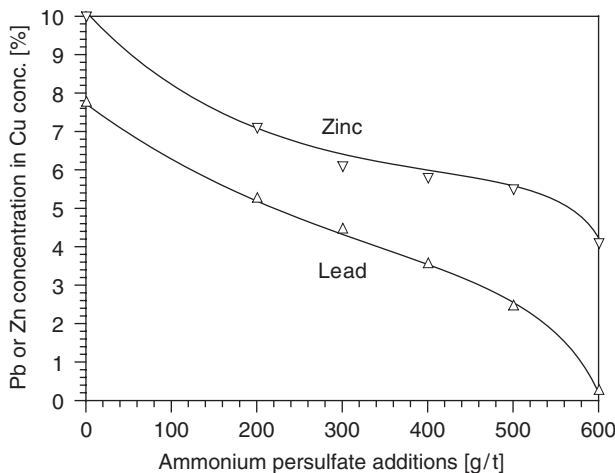
Figure 15.4 Effect of ammonium persulfate on lead and zinc depression during copper flotation.

appears to improve selectivity toward the zinc. Collectors used in the lead circuit are normally a combination of dithiophosphate and xanthate. In the zinc circuit, conventional lime $CuSO_4$ is used. The zinc flotation pH varies from 10.5 to 11 depending on the amount of pyrite present in the ore. Collector choice varies from xanthate to single thionocarbamate. Thionocarbamate gives greater selectivity than xanthates.

15.3.4 The operating plants using sequential copper–lead–zinc flotation

A number of operating plants that use sequential flotation of Cu–Pb–Zn are about 10% of all operating plants that process copper–lead–zinc ore. This is due to the fact that bulk copper–lead flotation is a much more cost-effective treatment route. However, the operating plants sequentially float Cu–Pb–Zn when either treating gold–silver-containing copper–lead–zinc ores where sequential flotation gives better precious metals recovery or when the bulk copper–lead flotation method does not work.

The ore characteristics and reagent scheme of the operating plant that uses sequential Cu–Pb–Zn flotation methods are shown in Table 15.3. The metallurgical results obtained are shown in Table 15.4. The Lake George plant is included in this section although it is

Table 15.3

Ore characteristics and reagent scheme used in sequential flotation of Cu–Pb–Zn ores

Concentrator	Description
Rozberg, Tasmania	*Ore*: The orebody is of strata-bound massive sulfide origin, associated with silicic and sedimentary rock. The principal sulfide minerals are pyrite, sphalerite, galena and chalcopyrite with a significant amount of tetrahedrite and gold-bearing minerals. *Grind*: $K_{80} = 75$ μm *Reagents*: Cu circuit – soda ash = 350 g/t, SO_2 = 250 g/t, sodium aerofroth = 716 g/t, AF25 = 3 g/t, cresylic acid = 15 g/t, pH = 6.8, aeration = 12 min. Lead circuit – soda ash = 530 g/t (pH 9.0), NaCN = 35 g/t, AF25 = 18 g/t. Zinc circuit – CaO = 530 g/t (pH 9.0), $CuSO_4$ = 950 g/t, sodium aerofroth = 40 g/t, thionocarbamate = 60 g/t.
Thalanga mine pancontinental resources, Australia	*Ore*: The orebody is of semi-massive sedimentary origin, contains goethite slime. The principal economic minerals are chalcopyrite, galena, sphalerite. The main gangue minerals are pyrite, quartz, dolomite and sericite. *Reagents*: Copper circuit – $Na_2S_2O_5$ = 5500 g/t, $ZnSO_4$ = 350 g/t, KEX = 50 g/t, MIBC = 15 g/t, pH = 6.6. Lead circuit – CaO = 350 g/t (pH 9.0), NaCN = 50 g/t, KEX = 60 g/t, R3477 = 10 g/t. Zinc circuit – CaO = 400 g/t (pH 11.0), $CuSO_4$ = 700 g/t, SIPX = 30 g/t, Dow 250 = 10 g/t.

(Continued)

Table 15.3   (*Continued*)

Concentrator	Description
Lake George, Australia	*Ore*: Massive sulfide finely disseminated ore of volcanogenic origin. The main minerals chalcopyrite, galena and sphalerite. *Reagents*: Copper circuit – CaO = 320 g/t, SO_2 = 600 g/t (pH 4.5), KEX = 20 g/t, AF25 = 10 g/t, pine oil = 5 g/t. Lead circuit – Na_2CO_3 = 700 g/t, NaCN = 40 g/t, AF25 = 30 g/t (pH 9.5). Zinc circuit – CaO = 1200 g/t (pH 10.8), $CuSO_4$ = 360 g/t, thionocarbamate = 20 g/t, KEX = 15 g/t.
Hellyer, Aberfoyle	*Ore*: Massive sulfide finely disseminated copper–lead–zinc ore, of volcanogenic origin. The principal economic minerals are chalcopyrite, galena, sphalerite, and tetrahedrite. The gangue minerals consist of 80% pyrite with minor quartz, calcite, sericite and arsenopyrite. Liberation 12–35 µm. *Reagents*: Copper circuit – $Na_2S_2O_5$ = 1500 g/t, $ZnSO_4$ = 300 g/t, R208 = 20 g/t, KEX = 10 g/t, aeration = 10 min. Lead circuit – Na_2CO_3 = 250 g/t (pH 9.5), NaCN = 100 g/t, R242 = 50 g/t, PAX = 15 g/t, MIBC = 10 g/t. Zinc circuit – CaO = 600 g/t, $CuSO_4$ = 1200 g/t, PAX = 80 g/t, Dow 1012 = 20 g/t. Bulk circuit – CaO = 300 g/t, R3477 = 10 g/t.
Black Mountain, S. Africa	*Ore*: Massive sulfide, strata-bound origin associated with sedimentary rock. The ore is partially oxidized. Chalcopyrite, galena and sphalerite are the principal economic minerals. *Grind*: K_{80} = 80 µm *Reagents*: Copper circuit – CaO = 400 g/t, SO_2 = 800 g/t (pH 4.5), thionocarbamate = 20 g/t, MIBC = 10 g/t. Lead circuit – Na_2CO_3 = 800 g/t, NaCN = 100 g/t, $ZnSO_4$ = 300 g/t, R241 = 20 g/t, PAX = 10 g/t (pH 9.4). Zinc circuit – CaO = 600 g/t (pH 10.5), $CuSO_4$ = 700 g/t, PAX = 25 g/t, pine oil = 10 g/t.
Silver Queen, BC Canada	*Ore*: Typical hydrothermal vein deposits, highly complex in mineral composition. The main copper minerals are chalcopyrite, tennantite, copper tetrahedrite. Galena and sphalerite are the other main economic minerals. Gold and silver are also present in the ore. *Reagents*: Copper circuit – CaO = 1200 g/t, oxidized starch = 200 g/t, SO_2 = 200 g/t (pH = 5.5), thionocarbamate = 15 g/t, MIB = 10 g/t. Lead circuit – ZnO/NaCN = 120 g/t, Na_2CO_3 = 1000 g/t (pH 7.5), R242 = 6 g/t, PAX = 6 g/t. Zinc circuit – CaO = 2000 g/t, $CuSO_4$ = 500 g/t, Na_2SiO_3 = 300 g/t, thionocarbamate = 15 g/t, MIBC = 6 g/t.

no longer in operation, because this was the first operating plant that selected the sequential copper–lead–zinc flotation method.

According to the literature, the low-grade copper concentrate that was produced at Rozberg was due to a requirement for maintaining a high gold recovery. It has been

Table 15.4

Metallurgical results obtained in the operating plants that use sequential Cu–Pb–Zn method

Concentrator	Product	Assays % (g/t)					% Distribution				
		Cu	Pb	Zn	Au	Ag	Cu	Pb	Zn	Au	Ag
Rozberg,	Feed	0.65	5.00	14.5	3.25	180	100	100	100	100	100
Australia	Cu concentration	13.0	23.6	13.6	61.5	296	65.5	15.4	3.1	62.0	53.8
	Pb concentration	0.25	70.0	5.60	4.77	690	1.9	56.5	5.6	7.2	18.4
	Zn concentration	0.35	3.42	53.5	1.10	35.9	12.6	16.0	86.2	6.6	14.1
Thalanga,	Feed	3.5	3.3	11.0	–	–	100	100	100	–	–
Australia	Cu concentration	28.3	2.1	4.4	–	–	85.8	4.0	2.1	–	–
	Pb concentration	0.65	60.2	8.3	–	–	2.6	78.3	4.0	–	–
	Zn concentration	0.55	3.3	58.5	–	–	4.5	7.7	90.0	–	–
Lake George,	Feed	0.50	5.8	10.4	–	–	100	100	100	–	–
Australia	Cu concentration	20.7	6.2	6.4	–	–	81.0	1.1	0.8	–	–
	Pb concentration	0.2	61.4	11.0	–	–	4.6	81.7	5.6	–	–
	Zn concentration	0.2	2.5	57.5	–	–	6.9	5.8	78.7	–	–
Hellyer,	Feed	0.35	7.5	13.5	3.3	160	100	100	100	100	100
Tasmania	Cu concentration	18.4	6.3	5.6	10.0	5000	25.0	0.2	0.3	10.0	20.0
	Pb concentration	0.2	60.0	4.8	–	600	20.0	60.0	0.8	–	20.0
	Zn concentration	0.2	3.3	50.5	–	200	15.0	10.1	63.3	–	–
Black Mountain,	Feed	0.40	3.6	12.5	–	–	100	100	100	–	–
South Africa	Cu concentration	25.3	2.6	3.3	–	–	70.1	0.4	0.5	–	–
	Pb concentration	0.12	60.3	8.5	–	–	10.4	75.5	1.8	–	–
	Zn concentration	0.20	3.2	55.5	–	–	8.6	9.5	80.8	–	–
Silver Queen,	Feed	1.18	1.19	10.4	2.33	423	100	100	100	100	100
BC Canada	Cu concentration	27.7	1.91	5.93	9.60	6360	82.8	5.7	2.0	25.1	66.6
	Pb concentration	0.9	51.7	7.31	33.3	5720	1.4	73.6	1.2	40.0	20.1
	Zn concentration	0.46	0.44	60.2	0.80	232	6.3	5.9	93.1	8.3	8.1

observed that when the copper concentrate increases to over 20% copper, gold recovery was reduced to about 45%.

In general, in most of the concentrators reasonably good metallurgical results were obtained, the exception being the Hellyer concentrator, which treats a very complex ore. This concentrator, in addition to producing copper, lead and zinc concentrates, also produces a lead–zinc concentrate.

15.4   REAGENT PRACTICE USING A BULK COPPER–LEAD FLOTATION METHOD

The bulk copper–lead flotation with depression of zinc followed by copper–lead separation and re-flotation of zinc is the most common practice in the treatment of copper–lead–zinc ores. About 90% of operating plants use this method. Separation of

copper and lead from the bulk concentrate is usually accomplished by two methods: (1) copper depression and lead flotation (the cyanide method) and (2) lead depression and copper flotation. There are a variety of reagent schemes for copper–lead bulk flotation depending on a fairly large number of factors, some of which include (a) the nature of the ore, (b) mineralogy and (c) head grade and degree of oxidation. The reagent scheme can be simple to extremely complex.

15.4.1   Flowsheet used in the treatment of copper–lead–zinc ores using a copper–lead bulk flotation method

There are several types of flowsheet used in copper–lead bulk flotation. The type of flowsheet is dictated by the complexity of the ore, as well as the copper–lead separation being used. The flowsheet that treats complex copper–lead–zinc ore is shown in Figure 15.5. This is a typical flowsheet used at New Brunswick Mining and Smelting and it is also used in some Russian operations. The flowsheet that uses lead depression and copper flotation in copper–lead separation is shown in Figure 15.6. There are several variations of this flowsheet, mainly in the copper–lead separation circuit combination. These variations are dictated by the separation method used. Conditioning capacities, number of cleaning stages or re-flotation of lead when required are the major variations in this flowsheet.

A final lead concentrate is not always obtained after copper–lead separation, and the upgrading of lead from the copper–lead separation tailing is required.
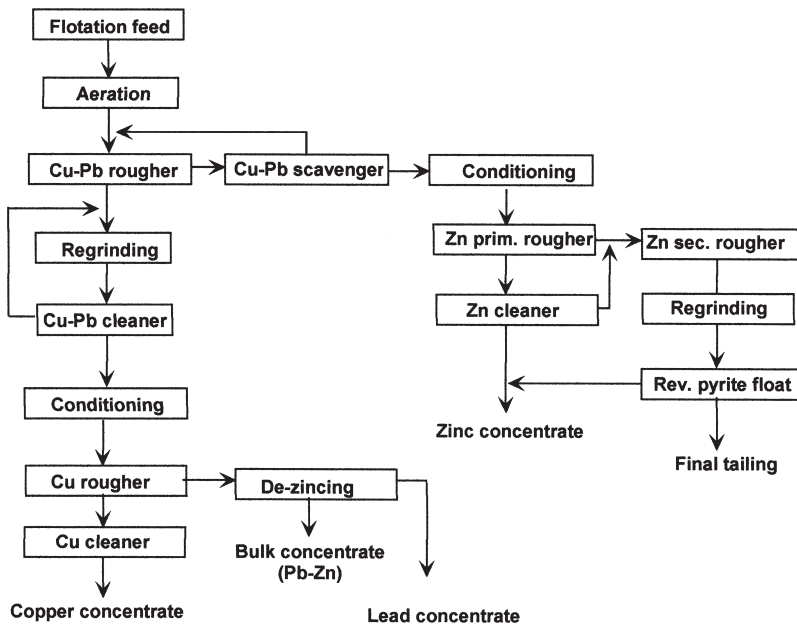
Figure 15.5 Flowsheet used in the treatment of complex massive sulfide Cu–Pb–Zn ores.
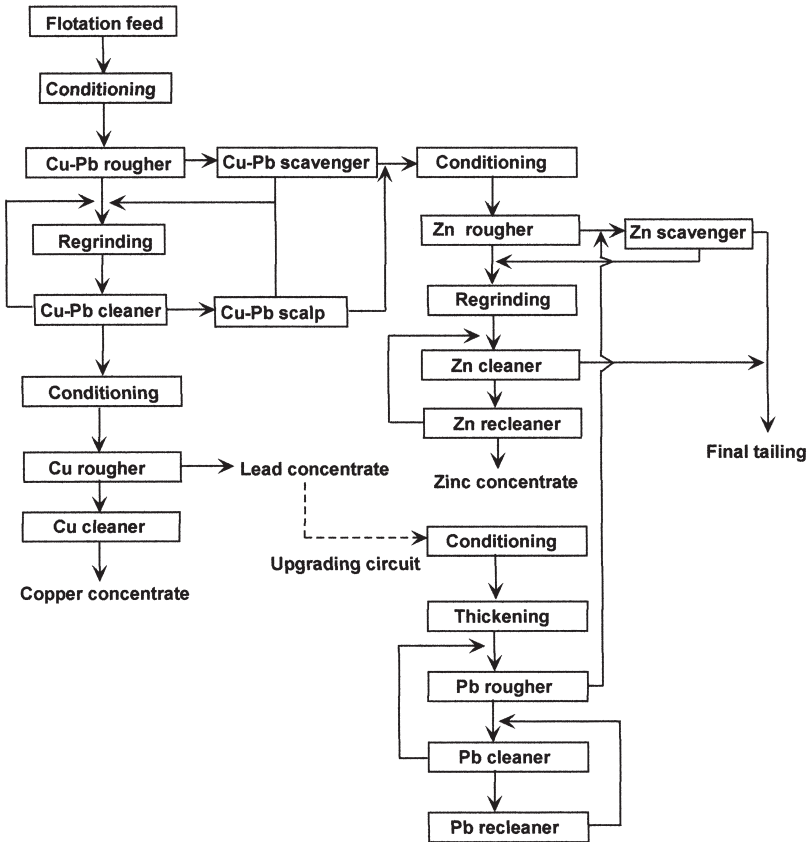
Figure 15.6 Flowsheet used in the treatment of copper–lead–zinc ores where a lead depressant is used in the copper–lead separation.

The flowsheet used in the case where copper depression is used in the copper–lead separation is shown in Figure 15.7.

These flowsheets are generalized and there are slight variations in the flowsheet configuration from one plant to the other.

15.4.2   General overview of the reagents used in the copper–lead bulk and zinc flotation

The reagent schemes used in copper–lead bulk flotation differ from those used either in the copper circuit during treatment of copper–zinc ores, or the lead circuit during the treatment of lead–zinc ores, specifically in the selection and use of collectors. Depressant combinations may be similar in a number of cases, but with lower additions of cyanide where cyanide is used. The modifiers used in the operating plants also vary widely. A soda ash–SO_2 combination is used in some circuits, and where the ore is partially oxidized, a
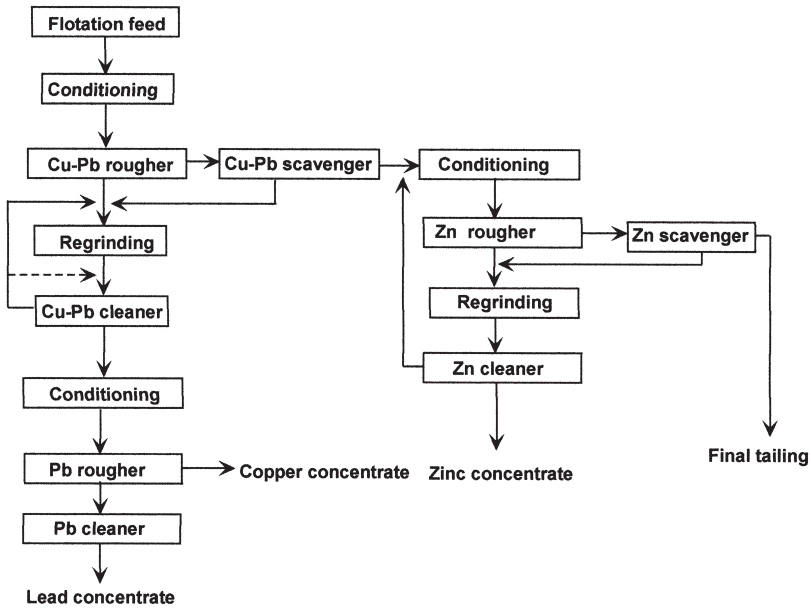
Figure 15.7 Flowsheet used in the treatment of copper–lead–zinc ores where copper depression is used in the copper–lead separation.

lime–SO_2 system is used. Lime without the addition of SO_2 is practiced when bulk Cu–Pb flotation is conducted in the alkaline circuit. The type of modifier used also depends on the type of depressant selected. Lime is usually added when Na_2SO_3 or Na_2S is used as the principal depressant during copper–lead bulk flotation. Soda ash is used together with NaCN and $ZnSO_4$, where bulk flotation pH does not exceed 9.0. From a survey conducted on about forty operating plants that treat copper–lead–zinc ores, the following trends have been established:

- In the treatment of finely disseminated ores, soda ash–SO_2 or lime–SO_2 with or without cyanide is used. The $ZnSO_4$ may also be used as a part of the depressant system.
- During the treatment of copper–lead–zinc ores that contain precious metals, neither lime nor $ZnSO_4$ is used, since these two reagents have a negative effect on precious-metal recovery. Soda ash and small quantities of cyanide are used.
- In the case of partially altered ores, where copper is tarnished, lime/SO_2–$ZnSO_4$/NaCN complex is used. The flotation pH is slightly acidic (i.e. 6.8).
- Depressant combinations in the treatment of copper–lead–zinc ores that contain pyrrhotite are quite unique in several plants. For example, in the San Martin concentrator (Mexico) depressants used in the copper–lead bulk flotation included NaCN, ammonium sulfate and zinc sulfate at natural pH. It is not known what role ammonium sulfate plays in this circuit, but it is observed that in the presence of ammonium sulfate copper flotation improves significantly.

The principal collector used in the copper–lead flotation is xanthate with secondary collectors such as dithiophosphates, thionocarbamates and mercaptans. The choice of collector also depends on the type of copper–lead separation method used. Usually, collectors with frothing properties should be avoided since desorption of these collectors from the mineral surfaces during copper–lead separation is quite difficult. In the past, popular collectors were phenol dithiophosphate and ammonia-based dithiophosphates (R25, R15 or R242). Butyl dithiophosphates are used with xanthates as secondary collectors.

Zinc flotation is conducted using the conventional lime–CuSO4 method with varieties of collectors, including xanthates, thionocarbamates and dithiophosphates. Combinations of xanthate and dithiophosphates are used in some cases.

15.4.3   Copper–lead separation methods

In general, there are two basic copper–lead separation methods commonly used during the treatment of copper–lead–zinc ores. These are described in the following sections.

Copper–lead separation method involving copper depression and lead flotation

This method is known as the cyanide method. It is used when the amount of chalcopyrite in the Cu–Pb bulk concentrate is much greater than the amount of galena (i.e. ratio over 2:1). Other pre-requisites of the successful use of the cyanide method include:

(a)   The concentrate must not contain secondary copper minerals.
(b)   The bulk concentrate must be sufficiently clean, so that after copper–lead separation, a marketable-grade copper concentrate is obtained. This is because the re-treatment of the copper concentrate for further upgrading after cyanide depression may not be either possible or economical. The disadvantage of this method is two-fold:
   •   The cyanide consumption is relatively high and amounts up to 300 g/t of ore in some cases.
   •   If native gold is present in the concentrate, cyanide dissolves free gold and substantial losses of gold may occur.

To avoid gold losses during Cu–Pb separation using the cyanide method, a complexed cyanide is used. The cyanide can be complexed by $ZnSO_4$ in the presence of alkali. The usual ratio of this complex is $ZnSO_4$:NaCN:Alkali = 2:1:2. The second method involves a complex of ZnO and NaCN in the ratio 1:3. The separation of copper and lead using the cyanide method can be substantially improved by the desorption of collector from the chalcopyrite surfaces, before adding cyanide. This can be accomplished by the use of activated carbon plus small dosages of cyanide [12]. The bulk concentrate is first pre-conditioned with activated carbon and small amounts of cyanide (20% of total cyanide addition) followed by additions of full amounts of cyanide and lead flotation. This method is illustrated in Figure 15.8.

There are several reagent combinations using cyanide separation method that have been practiced in operating plants. Table 15.5 shows various reagent combinations using the cyanide separation method.
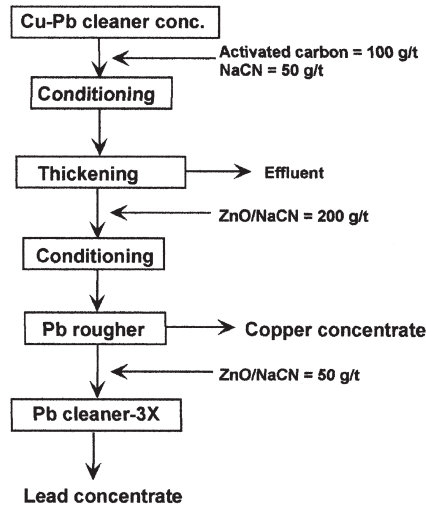
Figure 15.8 Cu–Pb separation flowsheet using activated carbon–cyanide collector desorption method.

Table 15.5

Reagent combinations using the cyanide separation method

Copper–lead bulk concentration composition	Combination	Dosage (g/t) concentration
Chalcopyrite, galena, low sphalerite coarse-grained	NaCN or KCN	500–3000
Chalcopyrite, galena with fine-grained minerals, <100 μm	NaCN or KCN Na_2SiO_3	500–6000 700–1800
Chalcopyrite, galena contaminated with sphalerite	NaCN or KCN Na_2S	600–7000 300–500
Chalcopyrite, galena with gold and silver present	NaCN/ZnSO$_4$/NaOH (1:2:2 ratio) Na_2SO_3	900–8000 400–1500
Chalcopyrite, galena with traces of secondary copper + silver sulfosalts	NaCN/ZnO (3:1 ratio) Activated carbon Na_2S	600–7000 50–200 100–600

The alkaline used for the $NaCN/ZnSO_4$ complex can also be lime and soda ash. Small quantities of Na_2S or Na_2SO_3 more or less act as froth modifiers. This is due to the fact that in the presence of large quantities of cyanide, the froth becomes voluminous (isopy-like) and when using either Na_2S or Na_2SO_3, the frothing properties are improved significantly.

Copper–lead separation method involving lead depression and copper flotation

This is the most widely used method in copper–lead separation and is normally employed when the amount of lead in the bulk concentrate is greater than copper or when the bulk concentrate is not sufficiently clean to produce a final copper and lead concentrate after separation, so that upgrading of the lead concentrate after copper–lead separation is required. Over the past several decades, numerous copper–lead separation methods have been examined [13–15] but only a few of these have found industrial application. There are three major sub-groups of copper–lead separation methods commonly used:

(a) Use of oxidizing reagents (i.e. bichromates, hypochlorites, etc.).
(b) Use of sulfoxy compounds with or without oxidants, or with starch derivatives.
(c) Use of SO_2/starch with or without heating (i.e. thermal treatment).

Each of these methods is specifically tailored to fit the nature and composition of the bulk concentrate involved in the separation. Table 15.6 lists some of the methods commonly employed in operating plants.

Dichromates are normally used in the separation of chalcopyrite and galena at a pH between 5.0 and 8.5. A lower pH is used to improve desorption of the collector from galena where dithiophosphates are used as primary collectors during bulk flotation. Dichromates can also be used together with starch or activated carbon. In some operating

Table 15.6

Reagent combinations employed for Cu–Pb separation using lead depression method

Sub–method	Reagents used	Dosage (g/t) concentration
Oxidizing reagents	$K_2Cr_2O_7$ or $Na_2Cr_2O_7$	250–2000
	H_2O_2	500–3000
	$KMnO_4$, H_2O_2	300–800, 300–500
	$CaCl(OCl)$, $Na_2Cr_2O_7$	200–500, 1000–2000
	Activated carbon, RB[a], CMC	100–200, 500–1000, 20–60
Sulfoxy compounds	Na_2SO_3, $FeSO_4 \cdot 7H_2O$	700–2000, 1200–1500
	$Na_2S_2O_3$, ferrosalts	700–200, 1000–2000
	$Na_2S_2O_3$, $(NH_4)_2S_2O_8$	600–1500, 300–600
SO_2 organic polymers	SO_2, starch	pH 3.5–5.5, 200–300
	SO_2, starch RB	pH 4.5, 200–300, 200
	SO_2, tannin	pH 3.5, 300–600
	SO_2, starch, heat 45–85 °C	pH 3.5–4.5, 100–300
	SO_2, dextrin, heat 45–85 °C	pH 3.5–5.0, 100–400
Phosphate compounds	H_3PO_4, H_2O_2	700–1500, 300–700
	NaH_2PO_4, H_2O_2	700–1500, 300–600
	$Ca(H_2PO_4)_2$, $CaCl(OCl)$	700–1500, 200–800

[a]$Na_2Cr_2O_7$:Na_2SiO_3 = 1:1.

plants (Bela Union, Peru) dichromate with $Na_2S_2O_5$ is used. This method is effective when secondary collectors are present in the ore. The separation pH is maintained at 6.5–7.5. The disadvantage of using dichromate is that when large quantities of $Na_2Cr_2O_7$ are used, depression of copper may occur, resulting in poor separation efficiency. To avoid depression of copper when using dichromate, reagent RB is a solution. The dichromate silicate complex is much more effective than dichromate alone, since it does not effect floatability of copper. This reagent is also used as a secondary depressant when using a starch–SO_2 separation method. When the upgrading of lead after copper–lead separation, the use of dichromate at low pH should be avoided since re-flotation of lead after dichromate depression is quite difficult.

Sulfoxy compounds, together with sulfosalts have been used in some Russian plants for the separation of low-grade Cu–Pb concentrate, where lead upgrading or de-zincing of the lead concentrate is required (Lenningradskaja). It is not known, however, whether this method is applicable to high-grade Cu–Pb bulk concentrate.

The SO_2–starch method is quite effective in copper–lead separation from low-grade Cu–Pb bulk concentrates where subsequent upgrading of the lead concentrate is required. This method is used in the treatment of disseminated massive sulfide copper–lead–zinc ores (New Brunswick, Canada; San Nicolas, Mexico). Pulp pre-heating using this method is also common. The procedure involves preconditioning the pulp with starch or dextrin at elevated temperature (65–85 °C), cooling the pulp in the presence of SO_2 to a pH of 5.0–5.5, followed by copper flotation. Kuroko (Japan) ore types use pulp pre-heating with SO_2–starch before copper flotation.

The use of phosphate compounds is rare but they can be effective lead depressants when secondary copper minerals are present in the ore. Sodium hypochlorite is also used for the de-leading of a copper concentrate after Cu–Pb separation using other separation methods.

In the separation of copper–lead bulk concentrate, the conditioning time and other pre-treatment methods are quite important.

When using dichromate in the Cu–Pb separation, the conditioning time is highly important and ranges from 10 min to about 4 h. For example, the Kasapalka plant (Peru) uses a dichromate method where the conditioning time with $Na_2Cr_2O_7$ is about 4 h. In some cases, treatment of the bulk concentrate with desorbing reagents (activated carbon or Na_2S) and thickening is practiced.

Other copper–lead separation method

In copper–lead separation practice, there are several other separation methods used, which are not common. These methods are used in cases where neither a cyanide method nor a lead depression method is effective. Such methods involve (a) cyanide–dichromate method and (b) SO_2–lime separation method. The combination of cyanide and dichromate method was developed at the Altigicvetment Institute (Russia) and was used in some operating plants [16]. The flowsheet used is shown in Figure 15.9.

The metallurgical results obtained using a two-stage process are shown in Table 15.7. This method is suitable when galena in the Cu–Pb bulk concentrate is relatively fine (i.e. $K_{80} < 30$ μm).

Most of the zinc was retained in the lead concentrate. An unusual copper–lead separation method, involving lead depression and copper flotation, was practiced at the San
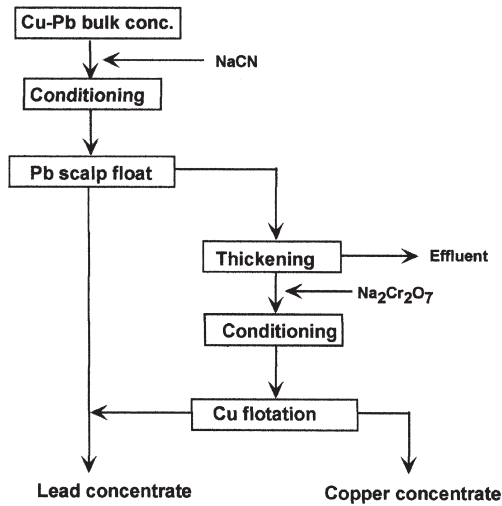
Figure 15.9 Flowsheet and reagent scheme using a combination of cyanide and dichromate methods.

Table 15.7

Copper–lead separation results obtained using two-stage separation method

Product	Assays %			% Distribution		
	Cu	Pb	Zn	Cu	Pb	Zn
Bulk concentrate	6.6	46.3	9.2	100	100	100
Lead concentrate	2.2	56.6	8.9	27.3	95.5	75.9
Copper concentrate	21.8	9.6	10.0	72.7	4.5	24.1

Francisco (Mexico) plant. The separation flowsheet with the point of reagent additions is shown in Figure 15.10.

The metallurgical results obtained in the concentrator are shown in Table 15.8. At the present time, the ore has changed and a cyanide copper–lead separation method is used.

During the development of a treatment process for the beneficiation of copper–lead–zinc ores, emphasis was usually placed on the development of an effective copper–lead separation method. This requires a very detailed evaluation of the number of separation methods suitable for a particular ore. Often, variables other than the reagent scheme are very important. These include pH, conditioning time, concentrate pre-treatment method, etc. Each of these parameters is an important part of the copper–lead separation method.
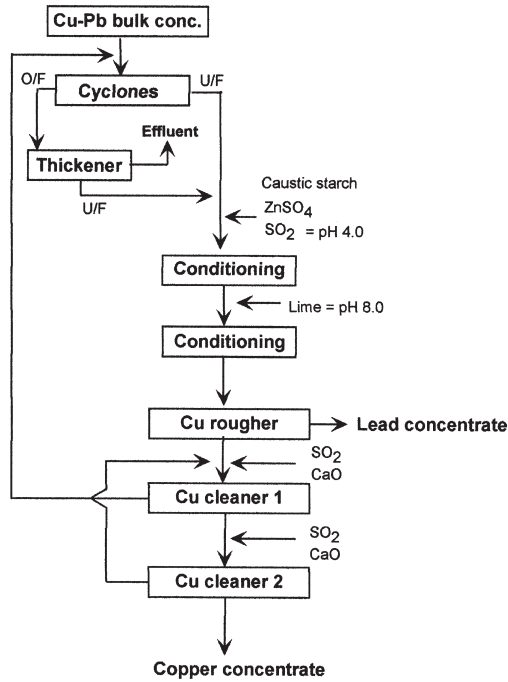
Figure 15.10 San Francisco (Mexico) copper–lead separation method.

Table 15.8

Metallurgical results obtained in San Francisco concentrator (1965–1975)

Product	Assays % (g/t)					% Distribution				
	Cu	Pb	Zn	Au	Ag	Cu	Pb	Zn	Au	Ag
Feed	0.80	6.65	9.43	0.91	176.1	100	100	100	100	100
Lead concentrate	1.92	61.0	9.87	4.3	1236.0	8.3	92.1	4.0	36.6	70.2
Copper concentrate	25.2	6.85	6.3	2.9	1069.3	72.2	1.3	0.8	10.5	15.1
Zinc concentrate	0.90	2.0	55.1	0.8	180.1	7.8	2.2	85.5	3.3	6.8

15.5   BULK COPPER–LEAD–ZINC FLOTATION METHOD AND SEPARATION OF COPPER, LEAD AND ZINC FROM BULK CONCENTRATE

This method is used when copper is represented by secondary copper minerals, namely, tennantite, chalcocite, bornite and covellite. In this case, the sphalerite is pre-activated and cannot be selectively depressed during copper–lead bulk flotation. The high-clay ores also employ the bulk flotation method because in the presence of clay, the depressants are not effective.

A typical example of copper–lead–zinc flotation in industrial practice is the Tsumeb concentrator (South Africa). Over the years, Tsumeb has done extensive work on the separation of copper–lead–zinc separation of the bulk sulfide concentrate [17].

An interesting feature of the Tsumeb metallurgical practice was the development of a method for the separation of copper and lead from zinc using a two-stage separation technique. The reagent scheme and flowsheet are illustrated in Figure 15.11.

Using this method, tennantite is selectively floated from the bulk concentrate followed by zinc flotation and lead depression using dichromate and Cytec's depressant R610. The R610 depressant is a complexed ammonium cyanide with zinc sulfate. Another method of copper–lead–zinc separation from the bulk sulfide concentrate involves the copper–lead–zinc scarn ore with high clay content [18]. In this particular ore, zinc was pre-activated and the use of depressants was not effective because of clay interference. The bulk copper–lead–zinc concentrate was floated using a collector only with some sodium silicate as dispersant. The separation is accomplished using the cyanide method for copper–zinc depression in the lead flotation circuit, and $ZnSO_4$ with H_2SO_4 for copper flotation from zinc concentrate. The flowsheet and reagent scheme is illustrated in Figure 15.12. The metallurgical results obtained are shown in Table 15.9.

These metallurgical results were obtained in a continuous laboratory locked cycle test. The bulk flotation method may be an effective method for treatment of low-grade refractory copper–lead–zinc ores.

15.6   UPGRADING OF LEAD CONCENTRATE FROM THE COPPER–LEAD SEPARATION TAILING

During the flotation of massive sulfide copper–lead–zinc ores, a low-grade copper–lead bulk concentrate is produced where, after copper–lead separation, a final lead concentrate
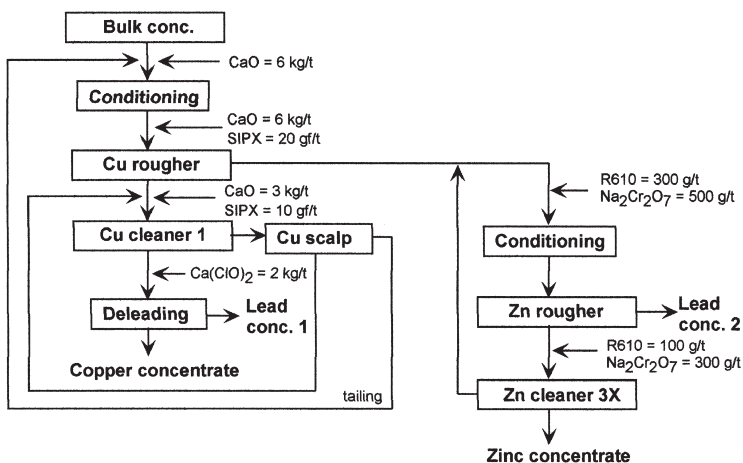
Figure 15.11 Flowsheet and reagent scheme used for separation of copper–lead–zinc concentrate at Tsumeb concentrator.
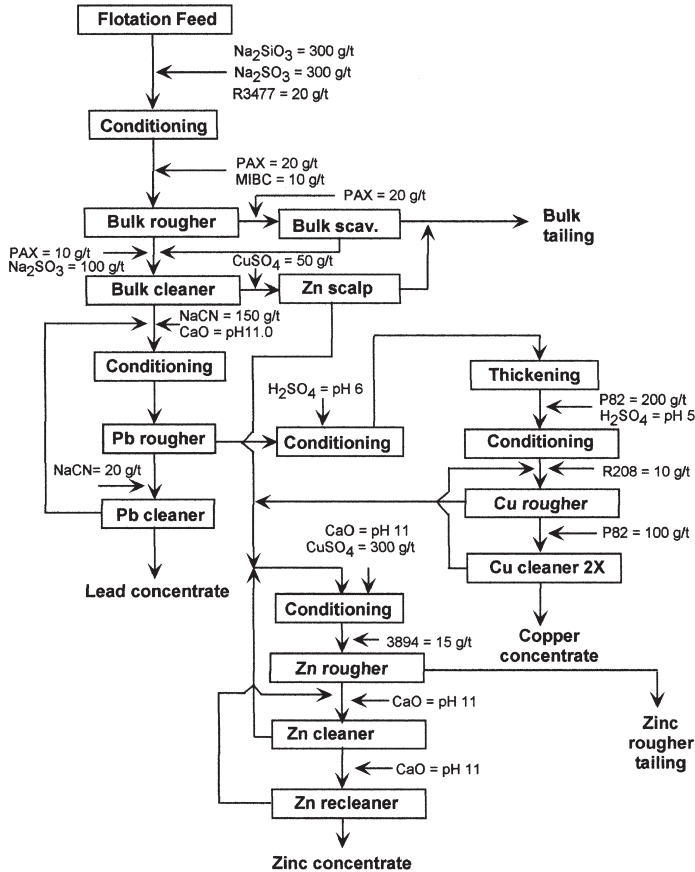
Figure 15.12 Flowsheet and reagent scheme developed for treatment of Minas Conga (Peru) scarn ore.

cannot be produced. The bulk concentrate is usually contaminated with pyrite and zinc. Therefore, upgrading of the lead concentrate after copper–lead flotation is usually required. The upgrading of the lead concentrate is accomplished by one of the following two methods:

- Direct flotation of impurities from the Cu–Pb separation tailing, a practice adopted by Brunswick Mining and Smelting operation.
- Lead flotation from the Cu–Pb separation tailing, a process developed for the treatment of Vermillion (Canada), Woodlawn Mine (Australia) and Crandon (USA) ores.

15.6.1   Direct flotation of impurities from the copper–lead separation tailing

This method is similar to the method developed for de-zincing of the lead concentrate, discussed in Chapter 14 with slightly different reagent combinations. A typical example is the

Table 15.9

Metallurgical results obtained on Perol (Peru) scarn copper–lead–zinc ore

	Product Assays % (g/t)					% Distribution				
	Cu	Pb	Zn	Au	Ag	Cu	Pb	Zn	Au	Ag
Feed	0.3	0.8	4.2	0.6	85	100	100	100	100	100
Copper concentrate	28.3	1.5	3.3	38.6	250	65.0	1.0	0.5	45.0	20.0
Lead concentrate	1.1	68.6	2.5	10.4	2200	4.8	85.5	0.6	10.1	60.2
Zinc concentrate	0.2	0.3	56.6	0.6	42	3.6	4.1	86.5	2.2	6.3

plant practice employed at the New Brunswick mining plant [19]. The lead upgrading flowsheet is shown in Figure 15.13.

The bulk flotation concentrate contained lead and zinc and is sold as a bulk Cu–Pb concentrate. The lead concentrate averages 42–48% at about 70% lead recovery.

15.6.2   Lead flotation from the copper–lead separation tailing

This method is used when pyrite is the main contaminant of the Cu–Pb bulk concentrate. Selection of a lead upgrading method depends on the copper–lead separation method used. If a starch–SO_2 separation method is used, re-flotation of the lead is achieved by adjusting the pH with soda ash and pre-conditioning with zinc cyanide complex. The lead is floated with dithiophosphate and xanthate collector. The lead flotation tailing is usually recycled to the zinc circuit since it contains an appreciable amount of zinc.

If the copper–lead separation involves dichromate, then removal of dichromate is required before the lead is floated. This method usually involves pre-conditioning the Cu–Pb separation tailing with acid, followed by thickening and re-pulping of the thickened tailing with fresh water. The lead is then floated with dithiophosphate in the presence of soda ash and cyanide in slightly acidic pH (i.e. 6.8) or alkaline pH (8.5–9.0). A schematic outline of the flowsheet and reagent scheme is shown in Figure 15.14.

The lead concentrate grade using this method is somewhat higher than that obtained using the reverse flotation method. Using this method, the lead tailing is also recycled to the subsequent zinc circuit together with Cu–Pb bulk flotation tailing.

15.7   REAGENT PRACTICE IN OPERATING PLANTS USING A COPPER–LEAD BULK FLOTATION METHOD

The reagent schemes of operating plants that use copper–lead bulk flotation method vary considerably, especially in the selection of copper–lead separation technique. The reagent scheme used depends primarily on the origin of the ore and the ore mineralogy. However, there are regional variations, which means that in some regions, the reagent schemes are different although the ores are similar. For example, the majority of Russian plants use different reagent schemes than South African plants treating similar ores. Some of the operating plants have used the most unusual reagent scheme where, for some modifiers used,
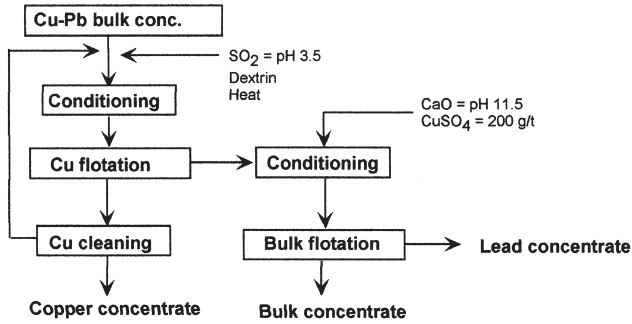
Figure 15.13 Flowsheet and reagent scheme employed for upgrading of lead concentrate from copper–lead separation tailing.
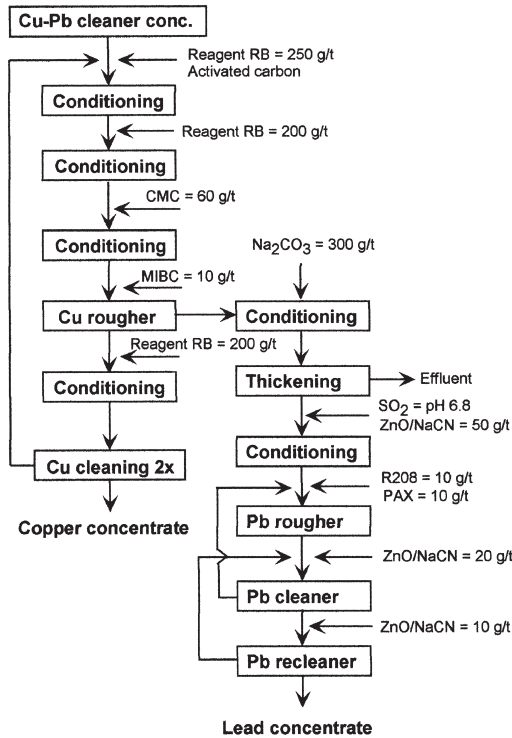
Figure 15.14 Lead flotation from Cu–Pb separation tailing flowsheet and reagent scheme.

the real function is not fully understood. Table 15.10 shows the reagent schemes of some of the most important operating plants around the world.

For a number of these plants, the exact mineralogical composition is not reported in the literature. In a fairly large portion of these plants, the bulk copper–zinc flotation does not vary much. Most of the differences are associated with the choice of the copper–lead separation method used in the various plants. The plant metallurgical results obtained in these operating plants are shown in Table 15.11. The concentrate quality varies from plant to plant but the overall metal recoveries are reasonably good.

In general, the gold and silver recoveries in these plants are somewhat lower than those achieved during the treatment of copper–zinc or lead–zinc ore. One of the reasons for this

Table 15.10

Ore characteristics and reagent schemes used in major operating plants using the copper–lead bulk flotation method

Plant	Ore and reagent scheme
Golden Grove, Australia	*Ore:* Massive sulfide ore with partially oxidized sulfides. Contains chalcopyrite, galena and sphalerite as the major economic minerals. Liberation occurs at <70 μm. Total sulfides content is about 70% with some floatable non-opaque gangue. *Reagents*: Cu–Pb bulk – CaO = 700 g/t, Na_2SO_3 = 800 g/t, CMC = 50 g/t, KEX/PAX (1:1) = 30 g/t, R3477 20 g/t, MIBC = 20 g/t. Cu–Pb separation – Reagent B = 350 g/t, starch = 50 g/t. Pb upgrading – $ZnSO_4$/NaCN = 150 g/t, CaO = 500 g/t, KEX = 30 g/t. Zn circuit – CaO = 2000 g/t, $CuSO_4$ = 500 g/t, PAX = 20 g/t, Z200 = 10 g/t.

Woodlawn Mine[a] Australia	*Ore*: Massive sulfide, finely disseminated ore. Contains
	    talc and naturally floatable aluminosilicates. Galena, chalcopyrite and sphalerite are the main valuable minerals. Liberation size is <20 μm.
	Reagents:
	Talc prefloat – MIBC/Fuel oil = 20 g/t.
	Cu–Pb bulk flotation – $ZnSO_4$/NaCN = 100 g/t, Na_2SO_3 = 300 g/t, Na_2CO_3 = 400 g/t, KEX = 30 g/t, R400 = 15 g/t.
	Cu–Pb separation – Reagent B = 300 g/t, SO_2 (pH 6.5), KEX = 10 g/t.
	Pb upgrading – $ZnSO_4$/NaCN = 150 g/t, Na_2S = 200 g/t, R208 = 20 g/t.
	Zinc circuit – $CuSO_4$ = 800 g/t, CaO = 800 g/t (pH 9.5), SIBX = 50 g/t, MIBC = 20 g/t.
	Talc – MIBC = 20 g/t.
	Copper – Na_2S = 400 g/t, SO_2 = 400 g/t (pH 6.0), CMC = 150 g/t, R404 = 80 g/t,
	    MIBC = 10 g/t, $NaHSO_3$ = 1000 g/t (cleaners).
	    Lead – CaO = 800 g/t (pH 7.5), SIPX = 20 g/t.
	Reverse gangue flotation – $NaHSO_3$ = 1500 g/t.
	Zinc – CaO = 1200 g/t (pH 10.0), $CuSO_4$ = 500 g/t, CMC = 50 g/t, SIBX = 80 g/t,
	MIBC = 15 g/t.

(*Continued*)

Table 15.10   (*Continued*)

Plant	Ore and reagent scheme
Western Mine Myra Lake Canada	*Ore*: Is a typical hydrothermal vein deposit with altered chalcopyrite and some secondary copper minerals. The ore contains significant quantities of silver in the form of sulfosalts and gold. Grind 70% <200 mesh. *Reagents*: Cu–Pb bulk flotation – Na_2SO_3 = 2000 g/t, $ZnSO_4$ = 800 g/t, NaCN = 200 g/t, R208 = 102 g/t, PAX = 8 g/t, Z200 = 15 g/t. Cu–Pb separation – NaCN = 300 g/t. Cu upgrading – Chlorine followed by thickening and regrinding. CaO = 900 g/t (pH 11.8), $ZnSO_4$ = 300 g/t, Na_2SO_3 = 300 g/t, R208 = 15 g/t, PAX = 10 g/t. Zinc circuit – $CuSO_4$ = 600 g/t, CaO = 800 g/t (pH 11.5), R208 = 20 g/t, PAX = 20 g/t.
Brunswick Mining and Smelting Canada	*Ore*: Finely disseminated massive sulfide ore with approximately 85% sulfides with the remaining 15% consisting of quartz, calcite and aluminosilicates. Pyrite is predominant with sphalerite, galena, chalcopyrite and tetrahedrite being the economic minerals. Carbon and pyrrhotite are also present in the ore. Grind = 37 μm. *Reagents*: Cu–Pb circuit – Na_2CO_3 = 700 g/t, SO_2 = 250 g/t (aeration), $ZnSO_4$ = 200 g/t, SIBX = 70 g/t, MIBC = 15 g/t. Cu–Pb separation – Guar = 150 g/t, SO_2 = 600 g/t (pH 3.5), SEX = 10 g/t. Pb concentre de-zincing – CaO = 400 g/t, $CuSO_4$ = 50 g/t, SIBX = 5 g/t. Zn circuit – CaO = 600 g/t, PAX = 20 g/t, MIBC = 10 g/t.
Sturgeon Lake Canada	*Ore*: Semi-massive Cu–Pb–Zn–Ag–Au ore with relatively coarse-grained pyrite. Chalcopyrite, galena, sphalerite and tetrahedrite as the main economic minerals. Gold is associated with chalcopyrite. *Reagents*: Cu–Pb bulk – Na_2SO_3 = 300 g/t, Na_2CO_3 = 650 g/t, $ZnSO_4$/NaCN = 150 g/t, PAX = 50 g/t, R208 = 20 g/t, MIBC = 10 g/t. Cu–Pb separation – heat 65 °C, Guar = 200 g/t, SO_2 (pH 4.5) Pb upgrading – CaO = 400 g/t, NaCN = 100 g/t, R208 = 20 g/t Zn circuit – CaO = 800 g/t, $CuSO_4$ = 800 g/t, SIPX = 50 g/t, MIBC = 10 g/t.
Buchans Mine Canada	*Ore*: Finely disseminated ore containing sphalerite, galena, chalcopyrite with bornite and tetrahedrite and gold. The non-opaque gangue was bornite, calcite and silicates. *Reagents*: Cu–Pb flotation – H_2SO_3 = 180 g/t, NaCN = 120 g/t, $ZnSO_4$ = 100 g/t, R301 = 100 g/t, thiocarbinol = 15 g/t Cu–Pb separation – SO_2 = 500 g/t, $Na_2Cr_2O_7$ = 600 g/t, MIBC = 5 g/t De-leading of copper concentrate – NaCN = 200 g/t, CaO = 250 g/t (pH 11.2) Zn circuit – CaO = 1200 g/t, $CuSO_4$ = 450 g/t, SIPX = 20 g/t, Dow 250 = 10 g/t.

(*Continued*)

Table 15.10   (*Continued*)

Plant	Ore and reagent scheme
San Martin Mexico	*Ore*: Massive sulfide ore with high pyrrhotite content (30%) and pyrite (10%). The principal valuable minerals are chalcopyrite, galena, marmatite and tetrahedrite. Liberation at about K_{80} = 120 μm. *Reagents*: Cu–Pb circuit – ammonium sulfate = 500 g/t, NaCN = 50 g/t, $ZnSO_4$ = 350 g/t, PAX = 10 g/t, R208 = 20 g/t. Cu–Pb separation – NaCN = 150 g/t, Na_2CO_3 = 100 g/t. Zn circuit – $CuSO_4$ = 400 g/t, CaO = 380 g/t (pH 9.5), HQS = 700 g/t, PAX = 15 g/t.
San Francisco Mexico	*Ore*: Massive sulfide with mixed pyrite, pyrrhotite. The ratio of pyrite to pyrrhotite is variable. Chalcopyrite, galena and marmatitic sphalerite are the principal economic minerals. Liberation at K_{80} = 85 μm. *Reagents*: Cu–Pb circuit – ammonium sulfate = 300 g/t, NaCN = 50 g/t, $ZnSO_4$ = 300 g/t, R241 = 10 g/t, PAX = 15 g/t, MIBC = 8 g/t. Cu–Pb separation – caustic starch = 120 g/t. Zn circuit – $CuSO_4$ = 500 g/t, CaO = 400 g/t, PAX = 30 g/t, MIBC = 25 g/t.
Morococha Peru	*Ore*: This ore is of volcanogenic origin. It is a semi-massive sulfide ore. Chalcopyrite, galena and mixed sphalerite, marmatite are major economic minerals. Tetrahedrite and freibergite are the principal silver minerals. *Reagents*: Cu–Pb circuit – $ZnSO_4$ = 300 g/t, NaCN = 30 g/t, SIPX = 30 g/t, R242 = 4 g/t, AF70 = 26 g/t. Cu–Pb separation – $Na_2S_2O_5$ = 100 g/t, $Na_2Cr_2O_7$ = 20 g/t (conditioning 120 min). Zn circuit – CaO = 2400 g/t, $CuSO_4$ = 340 g/t, SIPX = 62 g/t, AF70 = 20 g/t.
Cerro DePasco Peru	*Ore*: Massive sulfide with partially oxidized pyrite. Some ores contain clay minerals. The ore to plant feed is quite variable. *Reagents*: Cu–Pb circuit – CaO = 400 g/t, $ZnSO_4$ = 350 g/t, NaCN = 20 g/t, R241 = 20 g/t, PAX = 10 g/t, AF70 = 8 g/t. Cu–Pb separation – high copper ore $NaCN/ZnSO_4$ (pH 11) = 150 g/t, high lead ore $Na_2Cr_2O_7$ (pH 8.5) = 450 g/t. Zn circuit – CaO = 2000 g/t, $CuSO_4$ = 350 g/t, PAX = 40 g/t.
Casapalca Peru	*Ore*: Semi-massive sulfide ore with galena, sphalerite, chalcopyrite and tetrahedrite as the major valuable minerals. This ore also contains enargite, tennantite and covellite. Grind to 60% <200 mesh Cu:Pb:Zn = 1:5:8. *Reagents*: Cu–Pb circuit – $ZnSO_4$ = 420 g/t, NaCN = 40 g/t, AF31 = 16 g/t, SIPX = 36 g/t, AF70 = 15 g/t. Cu–Pb separation – $Na_2Cr_2O_7$ = 1200 g/t (pH 8). Zn circuit – CaO = 2000 g/t, $CuSO_4$ = 400 g/t, SIPX = 45 g/t, AF70 = 10 g/t.

(*Continued*)

Table 15.10   (*Continued*)

Plant	Ore and reagent scheme
San Cristobal Mahr Tunnel Peru	*Ore*: Semi-massive sulfide ore with about 45% sulfides. Non-opaque gangue minerals are quartz, Dolomite and aluminosilicates. Chalcopyrite is the predominant copper mineral with minor chalcocite, tennantite and bornite. Cu:Pb:Zn = 1:3:8. *Reagents*: Cu–Pb circuit – $ZnSO_4$ = 400 g/t, NaCN = 25 g/t, R241 = 15 g/t, PAX = 25 g/t. Cu–Pb separation – NaCN = 600 g/t (pH 11) Zn circuit – CaO = 1500 g/t, $CuSO_4$ = 660 g/t, PAX = 48 g/t, AF70/pine oil (2:1) = 20 g/t.
Leningradskara Russia	*Ore*: Massive sulfide ore with different ore types. The valuable minerals are represented by chalcopyrite, galena and sphalerite. Secondary copper minerals are also present in this ore. *Reagents*[b]: Cu–Pb circuit – Na_2S, Na_2CO_3, NaCN, PAX, Sodium Aeroflot. Cu–Pb separation – Na_2S, NaCN. Zn circuit – $CuSO_4$, CaO (pH 11.5), pine oil.
Zolotushinskaia Russia	*Ore*: Massive sulfide ore with a highly variable composition Pyrite, sphalerite, chalcopyrite and galena are the main sulfide minerals. Chlorite-sericite and quartz are the main non-opaque gangues. Grind = 75% <200 mesh. *Reagents*: Cu–Pb flotation – NaCN = 90 g/t, $ZnSO_4$ = 400 g/t, xanthogen formate = 18 g/t, xanthate = 20 g/t, pine oil = 10 g/t. Cu–Pb separation – activated carbon = 50 g/t, NaCN = 400 g/t, xanthate = 6 g/t. Zn circuit – CaO = 10,000 g/t, $CuSO_4$ = 400 g/t, xanthate = 120 g/t, Pine Oil = 10 g/t. De-coppering of zinc ore – conditioner #2 Na_2S = 1000 g/t (washing) Na_2CO_3 = 100 g/t, $ZnSO_4$ = 900 g/t, xanthate = 10 g/t, pine oil = 10 g/t.
Berozovskaia Russia	*Ore*: Partially oxidized massive sulfide ore containing chalcopyrite, galena and sphalerite. This ore contains oxidized copper and lead minerals. Grind = 75% <200 mesh. *Reagents*: Cu–Pb circuit – Na_2CO_3 = 300 g/t, Na_2S = 100 g/t, $ZnSO_4$ = 900 g/t, PAX = 100 g/t, cresylic acid = 10 g/t. Cu–Pb separation – NaCN = 1700 g/t, activated carbon = 100 g/t. Zn circuit – $CuSO_4$ = 450 g/t, CaO = 2000 g/t, Na-aeroflot = 20 g/t, PAX = 20 g/t.
Mizursk, Russia	*Ore*: This plant treats two kinds of ores: (1) disseminated massive sulfide ore and (2) impregnated massive sulfides. These two ore types are treated in two separate sections, using similar reagent schemes. *Reagents*: Cu–Pb circuit – Na_2SO_3 = 600 g/t, NaCN = 300 g/t, $ZnSO_4$ = 200 g/t, SIBX = 100 g/t, pine oil = 16 g/t. Cu–Pb separation – pre-treat concentrate with 600 g/t Na_2S, followed by thickening and re-pulping.

Table 15.10 (*Continued*)

Plant	Ore and reagent scheme
	Pb flotation – $ZnSO_4$ = 300 g/t, NaCN = 780 g/t.
	Zn circuit – $CuSO_4$ = 400 g/t, CaO = 3000 g/t, SIBX = 20 g/t, pine oil = 10 g/t.
Uchinotai Japan Kosakamin	*Ore*: Specific massive sulfide ore found only in Northern Japan. Known as a "black ore," or Kosaka ore as the other deposits contain copper, lead, zinc, gold and silver as the main valuable sulfide minerals. This ore contains significant quantities of borite and gypsum, which is also recoverable. The deposits are bedded and occur in acidic pyroclastics of Miocene age.
	Grind = 88% <200 mesh.
	Reagents:
	Cu–Pb circuit – $ZnSO_4$ = 400 g/t, AF208 = 100 g/t (pH 3.8–5.5, natural).
	Cu–Pb separation – dextrin = 80 g/t, SO_2 = pH 3.5, Heat 75 °C.
	Secondary Pb flotation – AF208 = 60 g/t, PAX = 10 g/t, NaCN = 300 g/t.
	Zn circuit – $CuSO_4$ = 460 g/t, CaO = 7000 g/t, AF208 = 35 g/t, KEX = 10 g/t.
	Flotation circuit includes separate slime/sand flotation.
Doyashiki, Japan	*Ore*: Similar to the Uchinotai ore, but with somewhat coarser-grained mill.
	Grind = 75% <200 mesh.
	Reagents:
	Bulk Cu–Pb–Zn flotation – CaO = 3000 g/t, KEX = 200 g/t, MIBC = 20 g/t.
	Pb circuit – $ZnSO_4$/NaCN = 400 g/t.
	Pb tailing filtered and stockpiled for about 5 days, then re-pulped with hot water (60 °C).
	Zn flotation – with frother only.
	Zn tailing – is copper concentrate.
Federal, USA	*Ore*: Massive sulfide with medium liberation size. Chalcopyrite, galena and sphalerite are the major valuable minerals. Dolomite, calcite and aluminosilicates are non-opaque gangue minerals. Some ore types contain marcasite and pyrrhotite.
	Reagents:
	Cu–Pb circuit – $ZnSO_4$ = 800 g/t, Na_2CO_3 = 600 g/t (pH 9.5), Na_2SO_3 = 300 g/t,
	R242 = 10 g/t, PAX = 15 g/t, MIBC = 15 g/t, R404 = 8 g/t.
	Cu–Pb separation – SO_2 = 1260 g/t (pH 4.2), $Na_2Cr_2O_7$ = 200 g/t, starch = 560 g/t.
	Zn circuit – CaO = 880 g/t (pH 11.3), $CuSO_4$ = 420 g/t, PAX = 25 g/t, AF10 = 10 g/t.
Pandora, USA	*Ore*: Semi-massive sulfide ore with relatively coarse grain. Chalcopyrite, galena and sphalerite are the main copper minerals in carbonate gangue.
	Reagents:
	Cu–Pb bulk flotation – Na_2SO_3 = 350 g/t, CaO = 350 g/t (pH 8.5), NaCN = 10 g/t,
	R404 = 10 g/t, SIPX = 15 g/t, AF65 = 10 g/t.
	Cu–Pb separation – NaCN/$ZnSO_4$ (3:2) = 220 g/t, KEX = 3 g/t.
	Zn circuit – CaO = 600 g/t (pH 10.5), $CuSO_4$ = 280 g/t, SIPX = 15 g/t, AF65 = 15 g/t.
Viburnum #27 Ore USA	*Ore*: Dolomitic ore with galena, chalcopyrite and sphalerit as the major valuable minerals. Marcasite is present at about 10% of the ore.

Table 15.10 (*Continued*)

Plant	Ore and reagent scheme
Reagents:	
	Cu–Pb circuit – NaCN = 20 g/t, PAX = 25 g/t, R208 = 20 g/t.
	Cu–Pb cleaning (marcasite rejection stage) – ZnO/NaCN = 50 g/t, SO$_2$ = 350 g/t (pH 5.5),
	MIBC = 10 g/t.
	Cu–Pb separation – SO$_2$ (pH 4.5), starch = 250 g/t, reagent RB = 200 g/t.
	Zn circuit – CuSO$_4$ = 200 g/t, PAX = 10 g/t, DF250 = 10 g/t.
Boliden, Sweden	*Ore*: Massive sulfide ore with chalcopyrite, galena and sphalerite as the valuable minerals. The ore contains about 65% sulfides.
	Reagents:
	Cu–Pb circuit – CaO = 800 g/t, Na$_2$SO$_3$ = 600 g/t, NaCN = 30 g/t, R3477 = 20 g/t, KEX = 15 g/t, MIBC = 10 g/t.
	Cu–Pb separation – Na$_2$Cr$_2$O$_7$ = 400 g/t.
	Zn circuit – CaO = 2000 g/t (pH 11.6), CuSO$_4$ = 400 g/t, PAX = 15 g/t, MIBC = 15 g/t.
Bihanti, Finland	*Ore*: No data available.
	Reagents:
	Cu–Pb circuit – ZnSO$_4$ = 600 g/t, Na$_2$CO$_3$ = 380 g/t, NaCN = 20 g/t, SEX = 20 g/t.
	Cu–Pb separation – Na$_2$Cr$_2$O$_7$ = 400 g/t.
	Zn circuit – CaO = 2500 g/t (pH 10.5), CuSO$_4$ = 440 g/t, SIPX = 35 g/t, DF250 = 20 g/t.

[a]Sequential flotation updated after 1985.
[b]The levels of these reagents are highly variable.

Table 15.11

Summary of plant metallurgical results

Concentrator	Assays %												% Recovery[a]		
	Head			Cu concentrate			Pb concentrate			Zn concentrate					
	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn
Golden Grove	1.0	0.7	10.9	29.2	2.1	2.3	0.18	40.9	3.4	0.24	0.16	58.6	87	74	93
Woodlawn	1.5	3.8	11.2	19.0	3.3	8.5	4.6	32.7	10.5	2.5	6.1	48.0	50.5	44	70
Myra Lake	1.4	1.2	7.5	28.0	3.0	9.5	3.0	42.2	15.1	0.6	0.9	52.0	78	81	82.5
Brunswick Min	0.3	3.5	8.8	21.0	6.0	3.5	0.4	32.0	5.4	0.2	1.9	52	54	55	75.5
Sturgeon Lake	2.2	3.4	10.5	22.5	4.1	10.5	1.0	50.0	10.2	1.0	1.5	52.0	65.5	62	78.3
Buchans	1.0	7.2	12.4	27.5	5.9	6.2	2.2	60.8	12.1	0.6	2.3	59.4	64	90	83
San Martin	1.3	2.4	5.5	22.5	4.2	5.5	1.0	50.0	6.5	0.2	0.8	47.2	70	68.5	65.5
San Francisco	0.6	1.2	8.3	23.3	3.5	4.5	0.3	49.5	5.5	0.1	0.6	48.0	60	66.5	75.5
Morococha	0.3	2.5	5.6	20.0	7.5	8.1	6.0	60.0	4.5	0.2	2.1	55.5	80	65	85
Cerro DePasco	0.4	2.2	6.1	22.2	4.5	7.6	2.0	60.1	5.8	0.3	1.6	52.2	70	68.4	80.2
Casapalca	0.4	2.8	5.6	26.0	8.2	5.0	1.1	55.0	4.8	0.3	0.8	53.5	65	69.4	81.2
Mahr Tunnel	0.6	2.1	7.4	21.2	7.5	3.8	1.0	58.0	4.4	0.2	1.9	55.5	75.5	70	82
Leningradskaia	1.2	3.1	6.5	28.7	5.0	3.8	1.5	52.4	11.4	0.7	1.3	56.9	62.4	84.5	81.2
Zolotushinskaia	1.4	2.8	8.8	19.4	2.3	9.5	3.9	48.4	11.7	1.8	1.2	55.0	80.3	83.2	79.3

(*Continued*)

Table 15.11 (*Continued*)

Concentrator	Assays %												% Recovery[a]		
	Head			Cu concentrate			Pb concentrate			Zn concentrate					
	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn	Cu	Pb	Zn
Berozovskia	1.5	4.1	9.2	28.8	2.7	4.5	1.0	53.2	15.2	1.5	0.3	51.0	83.0	82.0	87.1
Mizursk	1.4	2.9	8.8	25.2	4.8	6.8	1.6	73.0	5.0	0.5	1.4	57	75.3	86.1	88.2
Uchinotai	2.5	2.0	4.8	20.0	5.0	5.5	4.2	54.0	9.0	1.2	1.7	54	86	58	78
Doyashiki	1.2	0.3	1.4	16.5	1.4	6.0	6.0	53.0	7.0	2.0	1.0	60	82	63	63
Federal	0.2	1.9	12.1	27.4	2.2	4.1	1.0	68.1	4.2	0.1	0.8	55.5	62.4	94	88.3
Pandora	0.7	2.6	3.5	27.3	2.9	4.5	2.8	67.1	2.9	0.9	0.5	58	78	93	78.1
Viburnum #27	1.1	4.6	1.0	29.2	2.1	1.5	0.2	73.3	0.8	0.1	2.2	55.1	75.0	94.1	66.2
Boliden	1.0	2.0	8.0	19.2	3.3	5.6	2.8	43.3	5.5	0.9	1.2	50	54	66	80.2
Bihonti	0.8	0.5	10.2	25.3	1.7	5.5	1.1	50.9	4.4	0.3	0.1	54.6	80.5	70.3	93.9

[a]Exclude bulk concentrate

is that some of the gold–silver collectors (aerophines, modified mercaptans) cannot be used because they interfere with the copper–lead separation when using a specific copper–lead separation method. In some ores, gold is enclosed in pyrite at micron size, where the possibility of recovering the gold in a copper or lead concentrate is remote. In plant practice, most of the gold recovered reports in a copper concentrate.

In a large majority of plants, the copper and lead recoveries in corresponding plants are lower than those obtained treating copper–zinc ore (copper) and lead–zinc ores (lead).

REFERENCES

1. Craig, J.R., *Ore Microscopy and Ore Petrography*, Wiley, pp. 108–196, 1976.
2. Hagni, R.D., Mineralogy and Petrography of the Lead Zinc Copper Sulphide Ores of The Viburnum Trend, Southeast Missouri Sulphide Deposits – Their Origin and Processing, In (P.M.J. Gray ed), IMM pp. 73–84, 1990.
3. Cox, P.P., and Singer, D.A., Mineral Deposit Models, *US Geological Survey*, Professional Paper No. 1693, 1987.
4. Mineral Engineering Japan Visit, Black Ore District of Hokoroku, *Mining Engineering*, vol. 16, pp. 60–69, 1969.
5. Bulatovic, S.M., *Treatment Options of Thalanga Ore,* Report of Investigation, LR049, prepared for Pancontinental Resources, May 1993.
6. Bulatovic, S.M., et al., *The Recovery of Copper Lead Zinc Gold and Silver from Silver Queen Mine*, Report of Investigation, LR3373, prepared for Houston Metal Corporation, January 18, 1988.
7. Wyslouzil, D.M., *The Recovery of Copper Lead and Zinc from Bald Mountain Ore*, Report of Investigation, LR2260, prepared for Phelps Dodge Mining Company, January 1976.
8. Dixon, J.P., Operating Practice at Rozberg Concentrator, *Milling of Australian Ore Conference*, pp. 125–135, 1982.
9. Stewart, A.R., *Plant Monthly Report*, August 3, 1993, Private Communication (plant data).
10. Carson, V.M., South African IMM Interim Report No. 196, 1977.

11. Bulatovic, S.M., A *Laboratory Investigation of The Recovery of Copper Lead Zinc Gold and Silver from Silver Queen Mine*, Report of Investigation, LR3398, June 1989.
12. Bulatovic, S.M., and Wyslouzil, D.M., Selection of Reagent Scheme to Treat Massive Sulphide Ores, In (A.D. Zunkel ed) *Complex Sulphides*, AIME Publication, pp. 101–135, 1985.
13. McQuiston, F.W., Flotation of Complex Copper–Lead Zinc Ores, *Progress in Mineral Dressing IMPC*, vol. 3, pp. 511–519, Stockholm 1957.
14. *Milling Practice in Canada*, Canadian Institute of Mining Metallurgy, Collection of Plant Data, IMM, 1978.
15. Roberts, A.N., *Metallurgical Development of Woodlawn Mines Complex Sulphide Ores*, Processing of Complex Sulphide Ores, Rome, pp. 128–136, 1980.
16. Glembotzkii, R.V., and Urusova, S.M., *Improvement in Selective Flotation of Ozhezkazgan Ore*, Tsvetnie and Urusova, S.M., Metaly, No. 10, pp. 127–134, 1980.
17. Smith, T.S., *Evaluation of Different Cu–Pb Separation Methods at Tsumeab Mine*, Internal Report, 1976.
18. Bulatovic, S.M., *An Investigation of the Recovery of Copper–Lead and Zinc from Minas Conga Scarn Ores*, Report of Investigation, LR5433, prepared for CEDIMIN S.A., May 1999.
19. Hendriks, D., and Ounpuu, M.A., Modification of the Zinc Flotation Circuit of Brunswick Mining & Smelting Corp. Limited, In (A.D. Zunkel ed) *Complex Sulphides*, AIME Publication, pp. 366–371, 1985.

– 16 –

Flotation of Nickel and Nickel–Copper Ores

16.1   ORE TYPES AND MINERALOGY

There are more than 45 different nickel minerals, but only a few are of economic importance. Table 16.1 lists some of the most important nickel minerals. Nickel, in various ores can also be found in other minerals, such as pyrrhotite and various cobalt minerals as an exsolution in isomorphic phases. Nickel minerals can be divided into three major groups, including nickel sulfides, nickel arsenides and nickel antimonides, normally the minerals of magmatic and hydrothermal origin, nickel silicates and other similar compounds. From the sulfide minerals, the most abundant are pentlandite, rloanlit and nickelin. From the silicates, garnierite is the most abundant.

Millerite is a relatively rare mineral, more often found in hydrothermal deposits as a replacement for pentlandite. Pentlandite is the most abundant sulfide mineral and is the main nickel mineral in almost all nickel sulfide deposits.

In general, there are three basic types of nickel-containing ore deposits [1]. These include:

• Hydrothermal deposits formed as a result of nickel deposition from hydrothermal solution.
• Magmatic mafic deposits with two subtypes: (a) massive sulfide deposits and (b) impregnated deposits.
• Siliceous ore deposits containing mostly nickel silicates.

Magmatic nickel deposits are the most important nickel deposits and are concentrated in Australia (Mt. Windarra), North America (Sudbury region, Voisey Bay), and Northern Russia (Novilsk). Usually, these ores are massive sulfides, brecciated or disseminated ores. The most important minerals in these ores are chalcopyrite, pentlandite and pyrrhotite. However, these deposits may contain a fairly large number of other minerals containing silver, gold, cobalt and platinum group metals. This is due to the fact that they are formed from sulfide melts, which after separation from the parent silicate magma, coalesced into the base of the intrusion through gravitational setting.

The geological setting of nickel and copper–nickel deposits is variable, but in a generalized form the intrusion consists of upper layer of granophire, a middle layer of quartz gabbro and the lower layer of quartz-rich narite. The massive sulfide veins or lenses may appear at the lower margin of dykes intrusions.

Table 16.1

List of some important nickel minerals

Mineral	Chemical formula	Content % Ni	Hardness	Specific gravity
Millerite		NiS	3–4	5.2–5.6
Pentlandite	$(Fe,Ni)_9S_8$	21–30	3–4	4.6–5.0
Gersdorffite	NiAsS	35.4	5.5	5.6–6.2
Rloanlit	$NiAs_{2–3}$	14.5–21.2	5.0	6.3–7.0
Nickelin	NiAs	43.9	5.5	7.3–7.7
Annabergite	$Ni_3(AsO_4)_2 \cdot 8H_2O$	37.5	2.5–3.0	3.0
Garnierite	$Ni_4(Si_4O_{10})(OH)_4 \cdot 4H_2O$	0–45	–	–
Reevesite	$(CO_3)(OH)_{16} \cdot 4H_2O$	1–15	–	–

Unlike the North American deposits, the copper–nickel and nickel deposits found in Australia have different geology and mineralogical composition. Some of the deposits [2] are found in Archaean rocks. Predominate rocks are granite associated with "greenstones," which comprise banded iron, acid and basic volcanics, the ultramafic and minor sediments.

In the majority of nickel and copper–nickel deposits, the most abundant mineral is pyrrhotite (Fe_8S_9), chalcopyrite, pentlandite, magnetite and pyrite. Of these, the first three minerals are the most important from a processing point of view. The mineralogy of pyrrhotite perhaps plays the most important role in the treatment of nickel and copper–nickel ores. Pyrrhotite in these ores may occur in several crystallographic phases, two of which the most common are: (a) monoclinic pyrrhotite (Fe < 0.875), which is ferromagnetic or the so-called magnetic pyrrhotite, (b) hexagonal pyrrhotite (Fe > 0.875S), the less abundant phase is paramagnetic or "non–magnetic pyrrhotite." Both phases of pyrrhotite contain between 0.4% and 1.4% nickel, which may be present both in solid solution and as a micron-size exsolution called "flames" of pentlandite.

As mentioned earlier, a number of other minerals are present in the nickel and copper–nickel ores in various amounts. These include cobalt, selenium, platinum group metals and precious metals. Cobalt may occur in solid solution with pentlandite and pyrrhotite or, in some cases, as a cobalt mineral (bravoite). Selenium also occurs in solid solution with all sulfides. Silver may be found as an argentian pentlandite – $Ag(NiF3)_8S_8$, while gold occurs as an electrum and gold–bearing froodite, $AuPdBi_2$.

Platinum group metals occur in a variety of minerals including sperilite ($PtAs_{21}$), michenerite (PdBiTe), monocheite ($PtTe_2$), rhodium, ruthenium, iridium and osmium. Arsenopyrite, although rare, may be part of the nickel mineralization (KNO, Australia).

From the non–opaque gangue, very often the ore contains olivine, pyroxene, plagioclase and in some ores, talc, chlorite, actinolite, quartz and carbonates.

16.2   GENERAL OVERVIEW OF THE METHODS USED IN THE BENEFICIATION OF NICKEL AND COPPER–NICKEL ORES

At present, only sulfide ores are treated using a flotation method or a combination of magnetic separation/flotation or reduction roasting flotation. The nickel silicates are treated

using either pyrometallurgical or hydrometallurgical methods. There are three main districts where most of the nickel-bearing ores are found and are treated; these include North America (Canada), Australia and the Soviet Union (Russia). Ore treated in the Australian district differs significantly from that treated in North America and Russia. These ores contain naturally hydrophobic gangue, in addition to magnesia and calcite minerals. Some ores contain arsenopyrite (KNO).

One of the main characteristics of the nickel ore is that the final nickel concentrate is of low grade and does not exceed 18% Ni. Usually, the concentrate grade is between 6% and 11% Ni and in some cases, does not exceed 4%. This is due to the fact that in many ores, the nickel is contained in various inclusions, primarily pyrrhotite and other sulfides as well, which results in low-grade nickel concentrate.

Apart from the flotation, magnetic separation is a part of the treatment flowsheet and is used in a number of operating plants in Canada (e.g. Inco, Falconbridge) and Russia (Novilsk). Magnetic separation is used before or after flotation stages. In the treatment of copper–nickel ores, two main methods are used, which include sequential copper–nickel flotation, when the copper in the ore is much higher than the nickel, and a bulk copper–nickel flotation method, followed by copper–nickel separation using nickel depression and copper flotation.

16.3   FLOTATION PROCESSING CHARACTERISTICS OF NICKEL AND NICKEL–COPPER ORES

Flotation properties of nickel minerals have not been examined to the extent that other minerals have (i.e. galena, sphalerite, chalcopyrite), and therefore very little is known about the floatability of nickel minerals. Most of the research work on flotation of nickel minerals from natural ore has been carried out by (a) laboratories of large nickel producers (Inco, Falconbridge, WMC), and (b) by researchers in Russia on the ore from Russian deposits. Only limited data have been published, mainly in the past 10 years. Another problem associated with floatability of individual nickel minerals is that these minerals contain impurities of other minerals and therefore the surface properties of the individual minerals may vary from one deposit to another. Consequently, the flotation properties are variable. The type of gangue minerals plays an important role in the floatability of nickel and copper–nickel minerals. Some Australian nickel-bearing ores (Yakabindie) contain magnesium-bearing gangue and associated slimes. Flotation of nickel from this ore [3] is quite difficult and requires very high collector additions. In contrast, nickel flotation from massive ores, such as Voisey Bay (Canada) requires very little collector [4] due to the fact that nickel-bearing minerals are relatively floatable. On the basis of the literature [5], it has been stated that pentlandite, as well as other nickel minerals, float the best with higher xanthate (butyl and amyl). This is not necessarily true because in recent studies [6,7], it has been demonstrated that mercaptans and dithiophosphates are highly effective collectors for pentlandite and also highly selective toward pyrrhotite. Mercaptan R407 with xanthate has been used for flotation of Mt. Windarra ore from Australia.

When naturally floatable gangue is present in the ore, dithiophosphates or mercaptans are better collector choices than xanthates because in the presence of gangue depressants such as carboxymethylcellulose, these collectors perform better than xanthate.

Millerite, gersdorffite and nickelin have similar flotation properties as pentlandite. These three minerals, however, are known to oxidize relatively fast in the presence of oxygen. In general, nickel minerals are depressed with lime at a pH >9.5, the exception being millerite, where depression occurs at pH >10.0. This flotation property of millerite is beneficial in view that it can be separated from pyrite with the use of alkaline. Pentlandite has a tendency to oxidize relatively fast during aeration, resulting in the formation of a layer of iron oxides or iron hydroxides, which result in pentlandite depression. In an alkaline pulp, the formation of this oxidized layer does not occur. Pyrrhotite oxidizes faster than pentlandite and in the presence of alkaline, pyrrhotite depression does not improve although oxidation occurs.

Pentlandite along with pyrrhotite is activated by the use of copper sulfate. Floatability of pentlandite after depression with lime can be restored with the use of $CuSO_4$. This is not possible when cyanide is used as a pentlandite depressant. The $CuSO_4$ is used when sequential copper–nickel flotation method is utilized, where copper is selectively floated from pentlandite at high pH (10.5–11.0), followed by pentlandite reactivation with $CuSO_4$ and flotation with xanthate collector.

The flotation of copper during the treatment of copper–nickel ores does not represent any problem and copper recovery in the bulk Cu–Ni usually exceeds 90% Cu. Bulk flotation of copper and nickel is standard practice in many operating plants treating copper–nickel ore. The exception is when the copper to nickel ratio in the ore exceeds 2:1 or greater, in which case a sequential copper–nickel flotation method is used.

16.4   REAGENT PRACTICES IN FLOTATION OF NICKEL AND COPPER–NICKEL ORES

The reagent practice in the flotation of nickel and copper–nickel ores depends on three basic factors: (1) mineralogy of the ore, (2) flowsheet employed in the treatment of a specific ore and (3) degree of liberation.

From a mineralogical point of view, an ore that contains naturally floatable gangue has a different reagent scheme from that used for the treatment of massive sulfide ores. In the treatment of massive sulfide ores, the occurrence of pyrrhotite and the amount of nickel present in the pyrrhotite plays a decisive role in the selection of a reagent scheme. Pyrrhotite present in the copper–nickel ore can appear in a number of forms with different flotation responses. The main differences are in the ratio of iron to sulfur in the pyrrhotite. The atomic ratio of sulfur to iron changes from 1.0 to 1.25. The other reason for variation in floatability is the change in surface properties related to the amount of iron atoms in the crystal structure of the pyrrhotite.

The iron content of pyrrhotite varies from 58.2% to 63.5%, in which about 63% is divalent and 29.1% trivalent iron. The presence of trivalent iron in the pyrrhotite structure may result in improved collector adsorption on the mineral surface and consequently [8] improvement in floatability. The presence of hexagonal pyrrhotite in the ore represents a challenge in depression of this type of pyrrhotite because its flotation properties are very similar to that of pentlandite.

There are several different treatment flowsheets employed in treatment of nickel and copper–nickel ores. The type of flowsheet plays an important role in the selection of the

reagent scheme. As an example, a sequential copper–nickel flowsheet uses a different reagent scheme than when using a bulk Cu–Ni flowsheet. A case where magnetic pyrrhotite removed by magnetic separation ahead of flotation uses a different reagent combination than when using reagents where pyrrhotite is removed after flotation by magnetic separation.

16.4.1   Bulk sulfide flotation of nickel ore

The nickel ores without the presence of copper are mainly concentrated in Australia and to a lesser degree in North America. Some of these ores contain a substantial amount of hydrophobic gangue (talc), magnesium-bearing minerals some of which contain a fairly large amount of soluble ions (Mt. Keith, Australia). The flotation properties of nickel-bearing minerals from these ores are different from that of nickel minerals of massive sulfide ores. The pyrrhotite and pyrite content of these ores are relatively low and do not represent a problem in flotation unless the pyrrhotite contains a significant quantity of nickel. This is due to the fact that pyrrhotite from this ore type does not usually float as well as from the massive ores.

Collector and frother choice

The principal collectors used in the bulk flotation of nickel from nickel ores are xanthate and, to a lesser degree, dithiophosphates and mercaptans. In some operations, higher xanthate levels are used while in cases where clay slimes are present, low-carbon-chain xanthates are used. Studies carried out on the Yakabindie and Mt. Keith ores [9] from Australia with site water that contains very large amounts of soluble ions (i.e. >20,000 mg/t TDS) indicated that sodium ethyl at lower additions gave better nickel recovery than potassium amyl or isobutyl xanthate. Table 16.2 shows the effect of type and level of xanthate on the Yakabindie ore. It was also observed that high additions of ethyl xanthate gave the highest nickel recovery. Similar nickel flotation results were obtained on the Mt. Keith ore, which has the same gangue composition as the Yakabindie ore. The principal characteristics of ores from Western Australia are high magnesium content (magnesite, serpentine) and the water used is high in soluble ions.

Table 16.2

Effect of type and level of xanthate on flotation of Yakabindie ore [9]

Xanthate		Rougher concentrate			Ro + scavenger concentrate			Tail
Type	Addition (g/t)	Wt %	Assay % Ni	Recovery % Ni	Wt %	Assay % Ni	Recovery % Ni	Assays % Ni
SEX	150	9.5	1.4	28.0	23.2	1.55	76.1	0.145
PAX	300	9.8	1.1	21.8	25.4	1.31	70.9	0.183
SIBX	300	12.6	1.48	43.3	28.8	1.10	73.2	0.162
SIPX	300	9.0	1.50	29.5	28.2	1.09	74.4	0.159
SEX	500	9.5	2.02	41.6	27.3	1.34	80.5	0.122

Therefore, the collector consumptions are relatively high. Results of experimental work conducted on Mt. Keith ore [10] indicated that the use of mercaptans together with lower-chain xanthate gave better nickel recovery than xanthate alone. Table 16.3 shows metallurgical results obtained on Mt. Keith ore with different collector combinations.

The combination of sodium ethyl xanthate and mercaptan R407 gave improved nickel rougher and overall nickel recovery.

Extensive experimental work was carried out on Mt. Windarra ore (Poseidon, Australia) before plant design [11]. The nickel minerals in the Windarra ore are represented by both pentlandite (lower levels) and violarite, Ni_2FeSn (upper level). The nickel content of pyrrhotite is about 0.35% Ni. The effect of different collector types is shown in Table 16.4. Mercaptan collectors showed good selectivity and good nickel recovery. Xanthate alone gave high nickel recovery, but at low concentrate grade. The best metallurgical results were obtained using a combination of Na ethyl xanthate and mercaptan in a ratio of 50:50.

In the treatment of ores with predominant violarite and millerite, a combination of mercaptans and dithiophosphates perform better than xanthate. Experimental work conducted on the ore from British Columbia (Canada), where nickel is represented by violarite (70%)

Table 16.3

Effect of different collector combinations on nickel flotation from Mt. Keith ore [10]

Xanthate		Rougher concentrate			Ro + scavenger concentrate			Tail
Type	Addition (g/t)	Wt %	Assay % Ni	Recovery % Ni	Wt %	Assay % Ni	Recovery % Ni	Assays % Ni
SEX	250	6.33	2.8	30.1	18.4	2.01	77.4	0.150
PAX	250	7.20	2.0	22.3	21.1	1.62	74.3	0.175
SEX, R400	150+40	6.05	3.2	36.1	22.0	2.00	79.4	0.131
SEX, R407	150+40	7.40	2.95	41.1	23.3	2.36	81.1	0.110
SEX, R407	300+60	8.22	2.88	48.5	24.5	2.26	80.9	0.118
PAX, R407	150+60	7.77	2.50	34.5	21.5	2.15	78.7	0.130

Table 16.4

Effect of collector types on nickel flotation and upgrading from the Mt. Windarra ore (Australia)

Collector type	Ro + scavenger concentrate		Final concentrate	
	Assay % Ni	Recovery % Ni	Assay % Ni	Recovery % Ni
R407:IBX (80:20 ratio)	4.4	90.1	13.6	87.3
R407	5.6	89.9	12.5	86.3
R412	5.1	88.2	12.7	85.4
R3477	4.8	88.0	12.3	86.5
Thionocarbamate (1798)	5.9	66.0	8.1	43.7
IBX	2.6	95.0	5.0	93.8
SEX:R407 (50:50 ratio)	5.5	92.0	12.8	89.1

Table 16.5

Effect of different collectors on flotation of violarite and millerite [12]

Collector type	Rougher concentrate			Ro + scav concentrate			Assays
	Wt %	Assay % Ni	Recovery % Ni	Wt %	Assay % Ni	Recovery % Ni	% Ni
SIPX	4.1	5.8	21.1	20.8	3.1	68.5	0.39
PAX	5.6	4.9	25.5	22.0	3.3	69.8	0.30
R407	6.1	6.2	38.5	19.4	4.3	75.5	0.20
R3477	6.8	5.2	35.7	16.8	4.6	72.6	0.26
R407:R3477 (60:4))	5.9	6.8	41.0	21.2	5.5	86.5	0.12
R400	4.4	6.2	28.6	16.9	5.1	77.5	0.18
PAX:R407 (50:50)	6.1	4.9	26.6	20.2	4.9	79.5	0.14

and millerite (30%) indicated that a combination of mercaptan (60%) and dithiophosphates gave the highest nickel recovery. Table 16.5 shows the effect of various collectors on violarite/millerite flotation.

The choice of frother in the bulk flotation of a nickel ore also depends on the occurrence and nature of the ore as well as on the gangue slime present. In general, an alcohol-type frother, such as methyl-isopropyl carbonol (MIBC) has been commercially used. Where clay slime is present in the ore, a cyclic alcohol (pine oil) in a mixture with a glycol-type frother gave good metallurgical results. Glycol-type frothers are usually used in cases where a frothing problem caused by high pulp viscosity, exists.

There is no basic literature/data available on the effect of frothers on nickel flotation. The above data were taken from operating plants treating nickel ore.

Depression of hydrophobic gangue

Hydrophobic gangue minerals are present in the majority of nickel ores and in a number of copper–nickel ores. The presence of hydrophobic gangue represents a major problem in treatment of both nickel and copper–nickel ores. Normally, there are two distinct gangue types present in nickel ores. These include (a) talc chlorite in a serpentine rock and (b) magnesite dolomite in a carbonate rock. Talc chlorite is the most common hydrophobic mineral of the nickel ores. Magnesite dolomite is present in some of the Western Australian ores.

For the depression of hydrophobic gangue organics, the depressants most commonly used include starches, guars, dextrins and carboxymethylcellulose (CMC). Extensive studies of these depressants have been carried out over the years[13–15] on various nickel and copper–nickel ores and it has been established that CMC is the best depressant for talc. For chlorides, magnesite and dolomite, guars and dextrins have shown a good depressing effect. For depression of actinolite–talc, hexametaphosphate and sodium silicate, in acid pH, have been used.

The effectiveness of carboxymethylcellulose very much depends on the degree of substitution, the amount of sodium glycolite in the CMC and the molecular weight. The general characteristics of different CMCs commonly used in the flotation of nickel ores are shown in Table 16.6.

Table 16.6

General characteristics of different carboxymethylcellulose commonly used in the depression of talc chlorite gangue

Description	Bulk density (g/cm^3)	Actual density (g/cm^3)	Moisture (%)	NaCl (%)	Na glycolate (%)	Na CMC (%)	Total %
CMC 6CTL	0.72	1.675	6.3	17.1	13.1	62.4	98.9
CMC 6CTLI	0.70	1.656	7.1	17.3	13.4	61.6	99.4
Cellulose gum 7LT	0.69	1.420	11.2	1.6	1.0	87.1	100.9
Cellogen MG	0.76	1.903	9.4	2.2	1.2	88.5	100.2
Finnfix 30 230D	0.74	1.556	14.6	1.4	1.0	84.0	101.0
Finnfix 300 lot 772B/E	0.98	1.694	7.6	19.0	10.6	60.2	97.4
Finnfix BDA	0.79	1.715	9.5	12.9	7.6	70.2	100.2
Depramin-12	0.59	1.676	9.1	18.4	8.5	66.4	100.4
Depramin-19	0.46	1.640	8.5	13.8	5.5	71.8	99.6
Depramin-23	0.65	1.760	8.0	31.5	8.0	52.9	100.4
Depramin-25	0.65	1.714	7.7	29.7	8.4	53.9	99.7
Depramin-40	0.74	1.740	7.7	20.2	12.6	53.4	93.9
Depramin-75	0.68	1.761	7.2	32.5	7.3	53.4	100.4

Table 16.7

Effect of different types of CMC on nickel concentrate grade and recovery

CMC additions Type	Ni Ro + scavenger concentrate		Ni cleaner concentrate		Recovery % Ni
	Add (g/t)	Assay % Ni	Recovery % Ni	Assay % Ni	
CMC 6CTL	320	5.61	90.9	13.1	86.1
CMC 7LT	320	6.55	92.2	16.6	87.2
Cellogen MG	320	4.10	88.3	12.2	84.4
Depramin-12	320	5.10	89.2	11.8	85.5
Depramin-75	302	5.80	90.0	12.1	84.8

Different CMCs have been examined on a number of ores, including Mt. Windarra ore (Australia), Lynn Lake ore (Canada) and Thompson ore (Canada). The results obtained on the Windarra ore (Table 16.7) showed that a high molecular-weight CMC with the lowest sodium glycolite content gave the best talc depression and the highest concentrate grade. High molecular-weight CMC also has a depressing effect on the pyrrhotite present in the ore. The depressing effect of CMC was dependent on the pH used in flotation.

In these experiments, SO_2 and soda ash were used as pH modifiers. Data from Figure 16.1 indicated that at a higher pH (i.e. 8–9), the depressing effect of CMC improved considerably.

In the case of ores that contain magnesite–dolomitic gangue, guars show the most depressing effect on MgO and associated gangue. Table 16.8 shows the effect of different depressants during the flotation of Mt. Keith ore.

Table 16.8

Effect of different organic depressants on flotation of nickel from Mt. Keith ore

Depressant Type	Addition (g/t)	Ni Ro concentrate			Ni Ro + scavenger concentrate		
		Wt %	Assay % Ni	Recovery % Ni	Wt %	Assay % Ni	Recovery % Ni
CMC 7LT	150	9.5	1.40	28.0	23.2	1.55	76.1
Dextrin (Disper)	150	15.5	0.71	24.8	30.3	1.16	79.1
Guar	150	9.7	2.02	45.0	18.5	1.80	76.6
Starch (wheat)	150	18.3	0.61	25.5	38.7	1.02	78.7
Guar gum	150	9.0	2.10	40.6	19.1	1.79	78.2
Caustic starch	150	9.5	2.09	48.5	18.3	1.95	74.6

Table 16.9

Effect of different guar modifications on nickel flotation and upgrading from Thompson pipe ore

Guar type modification	Ro + scavenger concentrate		Cleaner concentrate	
	Assay % Ni	Recovery % Ni	Assay % Ni	Recovery % Ni
Guatec	1.2	86.5	3.5	75.0
Acrol (F20)	1.5	88.0	4.1	76.2
Acrol/Arquad 2HT (95:5)	2.0	89.1	5.5	80.0
Acrol/Arquad 2HT (90:10)	2.2	92.5	9.5	84.1
Guartec/Arquad 2HT (90:10)	2.4	94.4	10.2	85.5

The behavior of organic depressants on ores that contains serpentinized peridotite ($MgSiO_4$) with different talc varieties such as pyroaurite is different from that on ores that contain talc in granite and a greenstone setting. Examples are the pipe ore from the Thompson concentrator (Canada) and Mt. Keith ore (Australia). Floatable gangue depression is accomplished by extremely high pulp viscosity, which comes from magnesium-bearing minerals. The pulp viscosity is so high that pulp density is above 16% solids and air-bubble penetration through the pulp is not possible.

Extensive research carried out with these ores [16,17] indicated that specific guars, in conjunction with quaternary ammonium antistatic reagents (C_{25}–C_{50}), gave improved grade and recovery of the nickel concentrate. Table 16.9 shows the effect of different guars treated with quaternary ammonium chlorides (Arquad 2HT) on nickel concentrate grade and recovery from the Thompson pipe ore.

The more pronounced effect of quaternary ammonium chloride was achieved on the Mt. Keith ore. Figure 16.1 shows the effect of guar modified with quaternary ammonium chloride on the nickel grade and recovery relationship.

Data from Figure 16.1 showed substantial improvement in nickel grade and recovery with the use of quaternary ammonium chloride–modified guar.
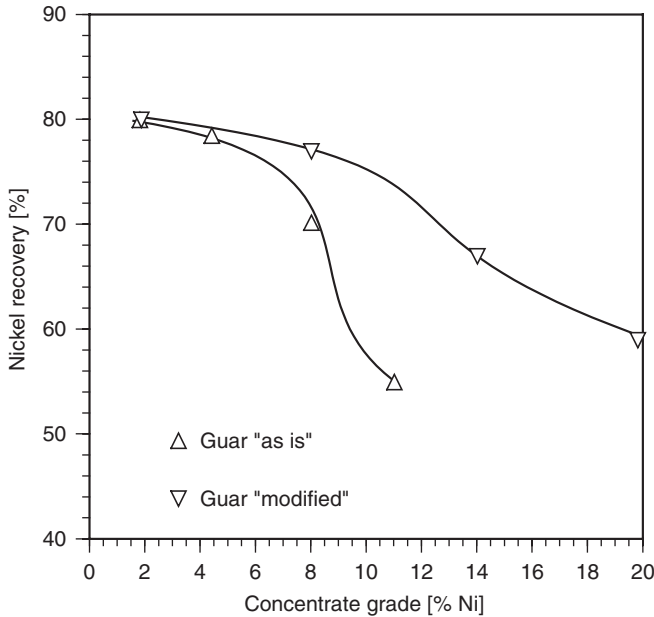
Figure 16.1 Effect of guar modified with quaternary ammonium chloride on nickel grade/recovery relationship – Mt. Keith ore.

Recent studies [18] have shown that a depressing effect of carboxymethyl cellulose can be substantially improved in the presence of aluminum chloride. It is postulated that improved depression of talc is due to the formation of Al(OH) on the mineral surfaces.

Effect of conditioning with reagents

In the flotation of nickel and copper–nickel ores that contain hydrophobic gangue, conditioning with reagents is essential in improving nickel recovery. The conditioning time was extensively examined on the Yakabindie and Mt. Keith ores. The effect of conditioning time and conditioning power is illustrated in Figure 16.2 for the Yakabindie ore.

When increasing conditioning power, there is a maximum nickel recovery where after prolonged conditioning, nickel recovery was reduced. A similar effect was observed in the Mt. Keith ore.

16.4.2   Flotation of copper–nickel ores

As stated earlier, the type of pyrrhotite present in the ore and flowsheet play an important role in selecting reagents for copper–nickel flotation. There are two basic flowsheets practiced in treatment of massive sulfide copper–nickel ores. These include (a) removal of monoclinic (magnetic) pyrrhotite by magnetic separation ahead of flotation and separate flotation of copper–nickel from magnetic pyrrhotite and from the pyrrhotite fraction and non-magnetic fraction and (b) bulk flotation of all sulfides followed by magnetic separation of
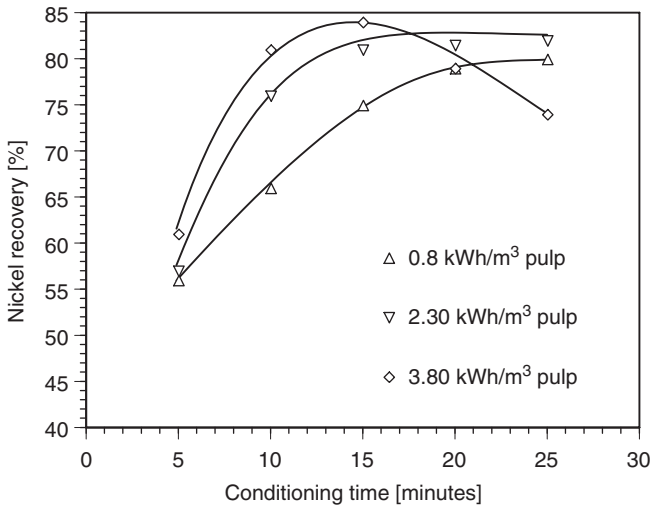
Figure 16.2 Effect of conditioning time and power on nickel flotation from Yakabindie ore.

pyrrhotite from bulk concentrate followed by upgrading of nickel from magnetic and non-magnetic fractions in separate circuits. The reagent suite for each of these circuits differs considerably.

Collectors in flotation of copper–nickel ores

The principal collectors in the flotation of copper–nickel ore are xanthates. Some research work conducted at different research facilities indicated that a higher carbon-chain xanthate gave higher nickel recovery than the lower-chain xanthates. Table 16.10 shows the effect of different xanthates on nickel recovery in the bulk concentrate from the Severonickel ore [19].

Experimental work carried out on the Voisey Bay ore (Canada) showed that the best nickel recovery was achieved by using sodium isopropyl xanthate. Figure 16.3 shows the effect of different xanthates on the rate of nickel flotation.

The Voisey Bay ore responded well to potassium amyl xanthate. Note that the Voisey Bay ore is a massive sulfide ore containing about 95% sulfides, most of which are hexagonal pyrrhotite.

In recent years, extensive studies have been conducted on various nickel ores to examine the effect of secondary collectors, mainly for the recovery of platinum group minerals [20]. It has been discovered that with the use of mercaptans (R400, SN50) and thionocarbamates (3894, X-31), significant improvement was made not only in platinum group metals (PGM) and cobalt recovery but also in nickel recovery and selectivity towards pyrrhotite. Table 16.11 shows the effect of secondary collectors on flotation of Clarabelle Inco (Canada) ores.

By using mercaptan in conjunction with thionocarbamate, it was possible to completely replace xanthate with significantly better metallurgy. Similar testwork was conducted on the Strathcona ore (Falconbridge) where xanthate was replaced by mercaptan and thionocarbamate in the primary rougher circuit. The effect of different collectors on copper–nickel

Table 16.10

Effect of different xanthates on nickel recovery from Severonickel (Russia) ore

Collector used		Ni rougher concentrate		Ni Ro + scavenger concentrate	
Type	Addition (g/t)	Assay % Ni	Recovery % Ni	Assay % Ni	Recovery % Ni
SEX	100	4.1	40.0	3.3	75.2
SIPX	90	5.2	51.5	3.6	78.2
SIBX	85	6.0	66.2	3.7	82.2
PAX	90	6.1	69.3	3.9	86.8
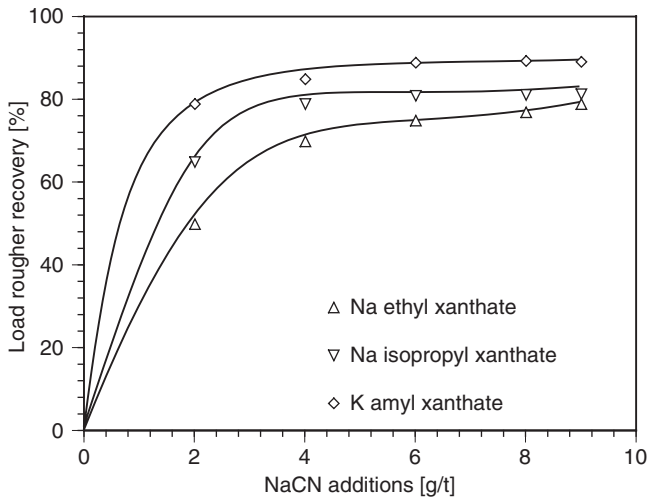
Figure 16.3 Effect of different xanthates on flotation of Voisey Bay ore.

Table 16.11

Effect of secondary collectors on flotation of copper, nickel and PGM from Clarabelle ore
containing hexagonal pyrrhotite

Collector type	Cu–Ni rougher concentrate					Cu–Ni rougher + scavenger conc				
	Assays %		% Distribution			Assays %		% Distribution		
	Cu	Ni	Cu	Ni	PGM	Cu	Ni	Cu	Ni	PGM
SIPX	1.46	12.4	48.9	42.6	20.5	0.76	6.98	78.0	73.9	65.1
SIPX, R400	1.95	10.6	70.3	38.7	30.5	0.85	7.17	89.6	86.3	69.5
SIPX, R407	1.98	11.0	72.5	39.9	31.6	0.85	8.22	90.0	87.0	69.9
SIPX, 3894	2.00	12.2	78.5	40.4	38.3	0.90	8.86	91.2	86.9	70.0
R407, 3894	3.30	16.8	73.5	40.0	40.0	1.20	9.33	92.8	87.7	73.3

Table 16.12

Effect of different collectors on copper–nickel flotation from Strathcona ore

Collector type	Cu–Ni primary rougher concentrate				Scavenger bulk concentrate			
	Assays %		% Recovery		Assays %		% Recovery	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
PAX	7.5	6.6	85.2	38.9	0.8	1.4	7.3	52.1
SIPX	8.1	7.2	86.1	40.2	0.7	1.5	7.9	51.0
SIPX, R400	9.0	8.5	87.1	46.4	0.7	1.6	7.0	48.2
SIPX, X–31	8.9	8.4	87.0	43.1	0.9	1.7	6.8	50.0
R400	12.5	11.8	90.0	46.0	0.5	1.8	6.0	45.5
R400, X–31	16.4	15.2	91.2	52.6	0.2	1.2	5.0	41.0

flotation on the Strathcona ore is shown in Table 16.12. By replacing xanthate with mercaptan and thionocarbamate, concentrate grade and nickel recovery in the primary rougher circuit improved significantly. In these experiments, sodium isopropyl xanthate was used in the scavenger bulk flotation where pyrrhotite and the remaining nickel floated. Since most of the research on nickel flotation was usually carried out by large nickel-producing companies, (e.g. Inco, Falconbridge and Western Mining), the focus was always been on the depression of pyrrhotite and maximizing nickel recovery. So very little to no studies were conducted on collector selection and evaluation, although recent research work [21] has shown that the collector type plays an important role in nickel flotation.

Choice of frother

In a number of operating plants where hydrophobic gangue was not present, strong frothers (i.e. glycol) were used mainly because of the following two reasons: (1) the copper–nickel ores usually contain slimes and when using alcohol-type frothers, the froth is not sufficiently stable and does not have carrying power and (2) recovery of coarse and middling particles during bulk flotation requires the use of stronger frothers. Research work on evaluating different frothers has been carried out at Roy Gordon (Inco) Laboratories [22] and by Falconbridge Limited at an industrial scale [23].

The results obtained on the Clarabelle ore are shown in Figure 16.4. The research data indicated that the highest pentlandite recovery was obtained using glycol-type frothers. Similarly, plant trials with different frothers at the Strathcona plant showed that a glycol-type frother gave the highest nickel recovery. These frothers, however, are less selective compared with alcohol-type frothers.

Depression of pyrrhotite

Pyrrhotite depression during copper–nickel flotation has been the focus of many studies [24–26] over the past 20 years, mainly to reduce sulfur emission during smelting of low-grade nickel concentrates. Most of the research work was directed to finding a suitable depressant combination that would effectively reject pyrrhotite while maintaining a high nickel recovery. The effectiveness of various new depressants is discussed below.
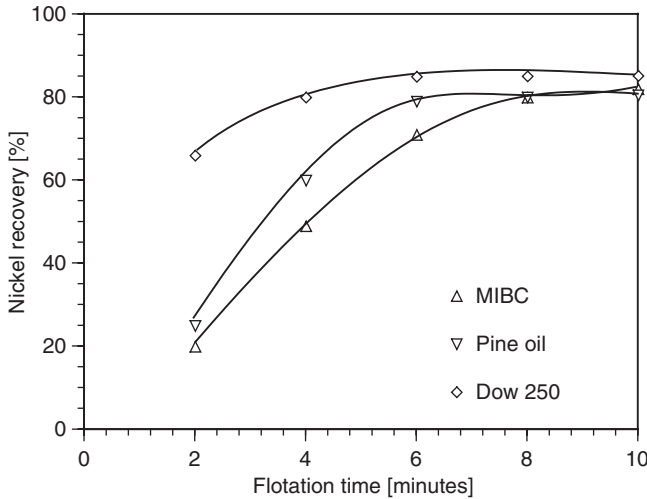
Figure 16.4 Effect of different frothers on nickel flotation using xanthate as collector.

- The soda ash–organic depressant system has been found application in a number of concentrators treating copper–nickel ores that contain hydrophobic gangue minerals such as talc and other aluminosilicates. Soda ash CMC or soda ash–dextrin were found to have a depressing effect on pyrrhotite. This was first noticed in development testwork carried out on the Mt. Windarra ore, where soda ash was used together with CMC. Along with rejection of talc, about 70% of the pyrrhotite was reported in the tailing. A beneficial effect of soda ash added together with CMC was observed in the treatment of the Thompson pipe ore and Shebandowan ore (Canada). When soda ash was introduced in the Thompson plant, the concentrate grade increased from 5% to 11% Ni [27].
- Organic depressants based on polyacrylic acid were developed and extensively tested by Cytec Chemical Company, primarily on the copper–nickel Sudbury ore for the recovery of copper and nickel from magnetic pyrrhotite. The effect of depressants S6339 and S5832 on the Strathcona Falconbridge ore is illustrated in Figure 16.5. Although good pyrrhotite depression was achieved, pentlandite was also depressed.
- Water-soluble polyamines were extensively tested as potential depressants for pyrrhotite. Experiments with polyamine-substituted dithiocarbamate were first carried out in the 1980s, by Phillips Petroleum, as a depressant for copper during copper–moly reparation. This research resulted in the development of a new depressant, [28] commercially available as ORFOM D8. This depressant is a reaction product of polyamine and carbon disulfide, and has shown good pyrrhotite depression when used together with soda ash in relatively small quantities. The nickel grade/recovery relationship, using different levels of ORFOM D8, is shown in Figure 16.6.

    In 1985, extensive research was conducted with polyamine-modified starches resulting in the development of a highly effective organic-based pyrrhotite depressant [29]. The effect of this depressant on pentlandite flotation and pyrrhotite depression is shown in Table 16.13.
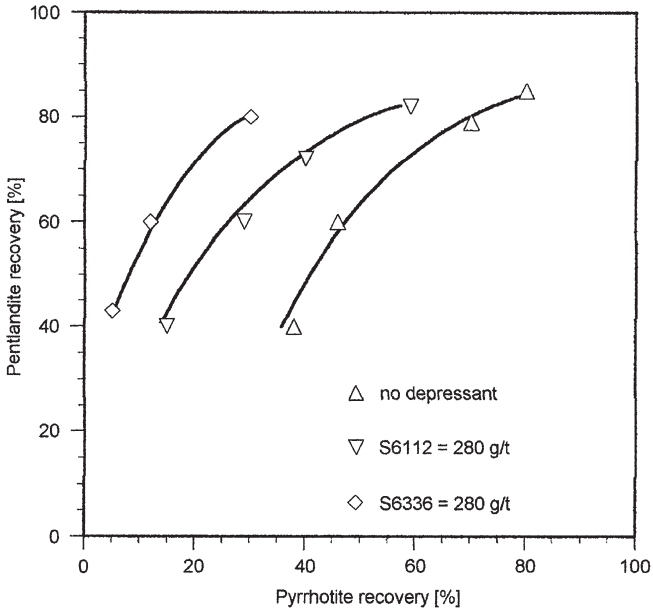
Figure 16.5 Effect of Cytec's organic depressants on nickel flotation from magnetic fraction.
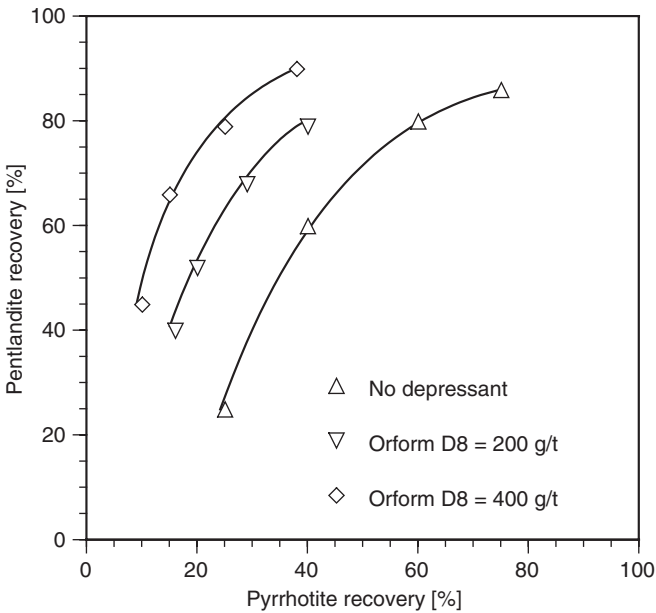
Figure 16.6 Effect of ORFOM D8 on pyrrhotite depression from Strathcona magnetic fractions.

Table 16.13

Effect of PKM depressant on nickel flotation from Strathcona magnetic fractions

Depressant PKM addition (g/t)	Product	Wt %	Assays %				% Distribution			
			Cu	Ni	Pn[a]	Po[b]	Cu	Ni	Pn	Po
0	Cu–Ni concentrate	58.0	0.32	1.45	2.40	87.7	79.7	61.2	89.4	62.5
	Cu–Ni tail	42.0	0.06	0.61	0.40	72.6	20.3	38.8	10.6	37.5
	Feed (magnetics)	100.0	0.21	1.10	1.59	81.3	100.0	100.0	100.0	100.0
250	Cu–Ni concentrate	23.2	0.59	2.16	4.5	84.0	71.9	43.5	68.9	18.2
	Cu–Ni tail	76.8	0.07	0.71	0.5	81.6	28.1	52.1	27.8	76.3
	Feed (magnetics)	100.0	0.19	1.05	1.4	82.1	100.0	100.0	100.0	100.0
450	Cu–Ni concentrate	8.0	1.63	4.73	11.9	62.4	70.2	36.3	66.2	6.2
	Cu–Ni tail	92.0	0.06	0.72	0.50	82.6	29.8	63.7	33.8	93.8
	Feed (magnetics)	100.0	0.19	1.04	1.4	80.0	100.0	100.0	100.0	100.0
800	Cu–Ni concentrate	2.7	3.73	8.96	24.1	28.1	51.1	23.2	45.0	1.2
	Cu–Ni tail	97.3	0.10	0.83	0.8	83.0	48.9	76.8	55.0	98.8
	Feed (magnetics)	100.0	0.20	1.05	1.5	81.7	100.0	100.0	100.0	100.0

[a]Pentlandite.
[b]Pyrrhotite.

Excellent pyrrhotite depression was achieved using amine-modified starch.

The use of polyamines alone as a pyrrhotite depressant was extensively tested [30] on the Clarabelle ore. It was found that ethylenediamine (EDA), diethylene-tetramine (DETA) and 2-(2-amino ethyl amino) ethanol (AEAE) showed a depressing effect on pyrrhotite. The effect of polyamines on pyrrhotite depression is illustrated in Figure 16.7. The DETA was introduced to Inco's Sudbury plant with partial success because the effectiveness of this depressant is relative to the amount of collector used in the main circuit.

Further research with sulfur-containing depressants (Na_2SO_3, SO_2) plus polyamines resulted in the development of a new depressant system [31] consisting of DETA and SO_2. This depressant system was also tested on the Strathcona ore. The results obtained are shown in Table 16.14. The function of SO_2 or Na_2SO_3 when used in conjunction with DETA is not known, but it may result in improved depressant adsorption on pyrrhotite.

Depressants from the P200 series were developed for the depression of marcasite during flotation of copper–zinc ores. In recent studies with various nickel ores, it was found that depressants from the P200 series are excellent depressants for both monoclinic and hexagonal pyrrhotite. Depressants from the P200 series are a mixture of $Na_2S_2O_5$, $NaHSO_3$, and $Na_2S_2O_3$ in various ratios, treated with either penta-amine or EDTA.

The effect of depressant P200 on the Strathcona magnetic fraction is shown in Figure 16.8.

Depressant P200 was superior to EDTA at 500 g/t additions. Depressant P200 was also evaluated on the Clarabelle (Sudbury) ore that primarily contained hexagonal pyrrhotite. The results obtained are shown in Figure 16.9. These results showed significant improvement in both nickel grade and recovery when using P200.
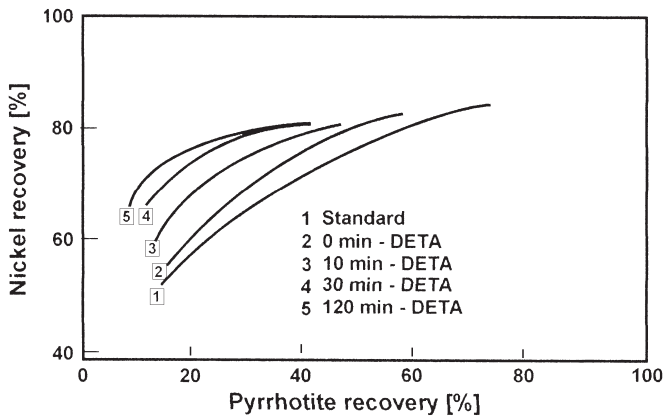
Figure 16.7 Effect of polyamines on pyrrhotite depression during the treatment of Clarabelle ore.

Table 16.14

Effect of EDTA–SO$_2$ depressant system on pentlandite flotation from Strathcona magnetic fraction

Reagent used (kg/t)	Product	Wt %	Assays %				% Distribution			
			Cu	Ni	S	Po	Cu	Ni	Pn	Po
None	Concentrate	39.5	0.43	1.99	33.7	80.1	62.5	73.4	70.7	46.9
	Tail	60.5	0.10	0.71	24.0	59.1	37.5	26.6	29.3	33.1
	Feed (magnetics)	100.0	0.23	1.24	27.8	67.4	100.0	100.0	100.0	100.0
DETA = 0.5	Concentrate	52.6	0.31	1.72	29.3	69.9	72.5	83.2	79.6	57.9
	Tail	47.4	0.07	0.72	22.8	56.3	27.5	16.8	20.4	42.1
	Feed (magnetics)	100.0	0.19	1.21	29.5	63.5	100.0	100.0	100.0	100.0
DETA = 0.25	Concentrate	18.8	0.76	3.16	26.2	57.4	49.3	74.7	70.8	14.9
SO$_2$ = 2.90	Tail	81.2	0.06	0.73	30.5	75.8	50.7	25.3	29.2	85.1
	Feed (magnetics)	100.0	0.20	1.21	29.2	72.3	100.0	100.0	100.0	100.0
DETA = 0.50	Concentrate	14.6	1.24	5.35	24.9	47.8	53.8	72.5	72.9	10.1
SO$_2$ = 2.9	Tail	85.5	0.08	0.78	29.1	72.2	46.2	27.5	27.1	89.9
	Feed (magnetics)	100.0	0.25	1.44	28.5	68.7	100.0	100.0	100.0	100.0
DETA = 0.5	Concentrate	14.6	1.20	3.15	31.1	68.8	41.6	71.9	72.9	14.3
SO$_2$ = 2.6	Tail	85.5	0.08	0.75	28.4	70.5	58.4	28.1	27.1	85.7
	Feed (magnetics)	100.0	0.24	1.10	28.8	70.2	100.0	100.0	100.0	100.0
DETA = 0.5	Concentrate	4.8	2.15	5.78	30.9	59.8	28.5	68.0	58.6	3.5
SO$_2$ = 2.6	Tail	95.2	0.05	0.72	33.4	83.3	71.5	32.0	41.4	96.5
	Feed (magnetics)	100.0	0.15	0.96	33.3	82.2	100.0	100.0	100.0	100.0

Choice of modifiers

In the flotation of copper–nickel ores, the following modifiers have been used:

- Sulfuric acid (H$_2$SO$_4$), acid flotation, pH4.5–6.5
- Sulfurous acid(SO$_2$), acid flotation, pH 5.5–6.5
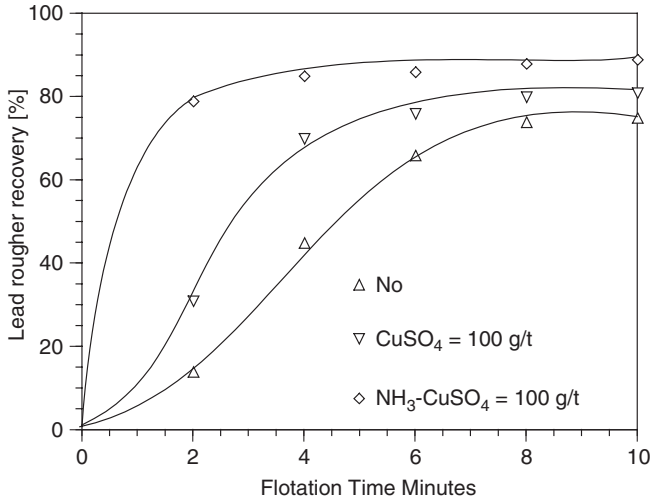
Figure 16.8 Effect of depressants P200 and DETA on pentlandite flotation from Strathcona magnetic fraction.
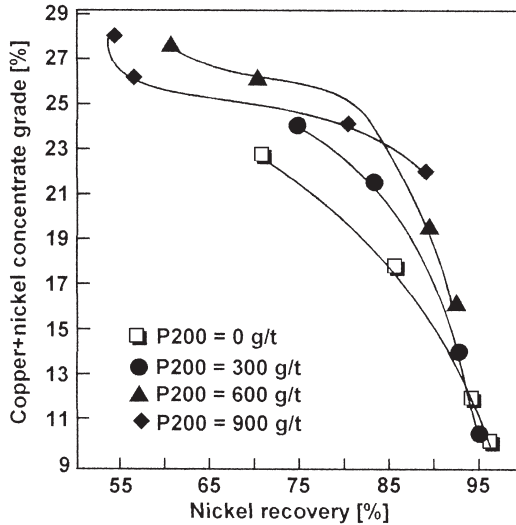
Figure 16.9 Effect of depressants P200 and DETA on nickel flotation from hexagonal ore (Clarabelle, Inco North Zone).

- Soda ash (Na_2CO_3), alkaline flotation, pH 7.5–8.5
- Lime (CaO), alkaline flotation, pH 9.0–10.0.

The choice of modifier mainly depends on the nature of the ore being treated, specifically gangue composition and the amount of sulfides present in the ore.

The Kotalahti (Finland) copper–nickel concentrator treats a mixture of disseminated and breccia ore associated with basic and ultra-basic rock. As a pH modifier, Kotalahti uses sulfuric acid, up to 9.5 kg/t. Using sulfuric acid allows high nickel recovery, up to 92%. Similarly, Hitura (Finland) plant also uses H_2SO_4 for pH control. The Hitura ore is serpentine intrusions and mica gneiss.

The Kamalda Blanka (Western Australia) plant treats ore consisting of pyrrhotite, pentlandite, and violarite in a serpentine rock. This concentrator uses SO_2 (1.5 kg) to obtain flotation pH of 5.5. It has been reported [31] that when using SO_2, both nickel concentrate grade and recovery improved significantly.

Soda ash is often used in the flotation of nickel and copper–nickel ores, where hydrophobic gangue is present in the ore. The Pechenga nickel (Russia) plant, Thompson mill (Canada), Shebandowon (Canada) and Mt. Windarra (Australia) plants use soda ash together with organic talc depressant. Some of the beneficial effects of soda ash include use as dispersant and improved depression of talc with CMC and prevention of slime coatings on the mineral surface.

Lime is used in the flotation of massive sulfide copper–nickel ores (Voisey Bay) and during the flotation of sulfide ore when it contains hexagonal pyrrhotite. A combination of lime and sulfuric acid is used in semi-bulk flotation where the lime is added to the primary rougher to float most of the copper with high-grade pentlandite. In the secondary flotation, where pyrrhotite and nickel middlings occur, H_2SO_4 and $CuSO_4$ are added to a pH of about 8.0–8.5.

Activation of pentlandite

In many operating plants, $CuSO_4$ is used as a pentlandite activator. The consumption of $CuSO_4$ ranges from 50 up to 800 g/t, mainly in cases where bulk nickel pyrrhotite
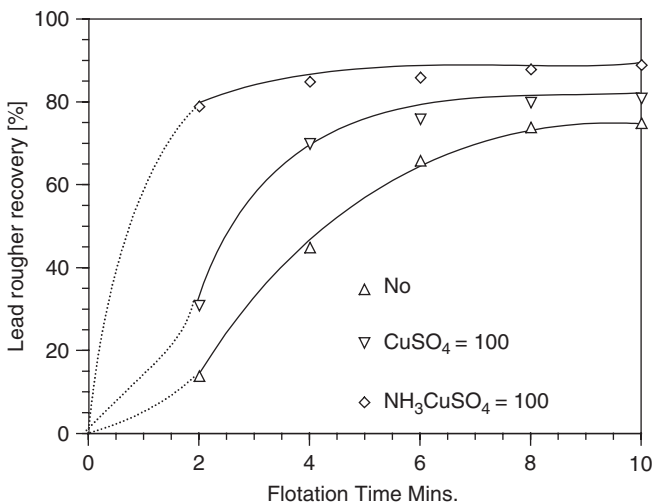
Figure 16.10 Effect of ammoniacal copper sulfate on nickel recovery of KNO ore [33].
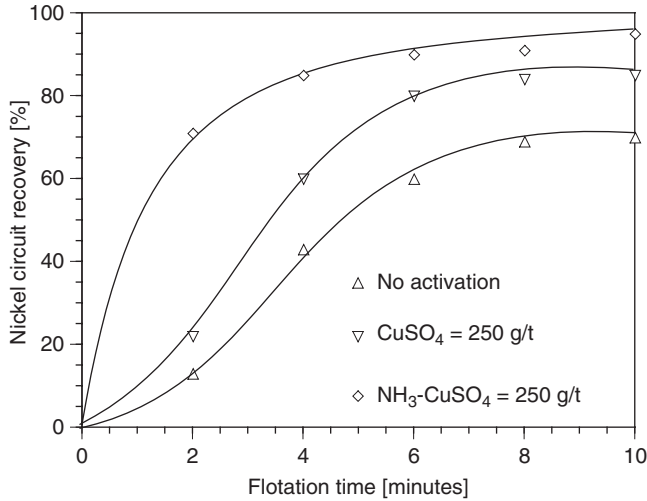
Figure 16.11 Effect of ammoniacal copper sulfate on nickel flotation in the secondary circuit of Strathcona ore.

concentrate is floated. There are no plant or laboratory data available to confirm the effectiveness of $CuSO_4$. Copper sulfate is also a good pyrrhotite activator and it is possible that it improves floatability of nickel pyrrhotite rather than pentlandite. $Pb(NO_3)_2$ was also tried as a substitute for $CuSO_4$ [32] but without success.

In recent studies [33], it has been demonstrated that the use of ammoniacal $CuSO_4$ substantially improved floatability of pentlandite and violarite.

The effect of ammoniacal $CuSO_4$ was evaluated on the Kamolda Blanka ore (Australia) and the Strathcona ore (Canada). The effect of ammoniacal $CuSO_4$ on the Kamolda Blanka ore is illustrated in Figure 16.10. The results indicated that when using only 100 g/t of ammoniacal $CuSO_4$, the rate of nickel flotation and recovery improved significantly.

The results obtained on the Strathcona ore indicated faster nickel flotation and better recovery (Figure 16.11).

16.4.3   Sequential flotation of copper–nickel ores

Numerous studies have been carried out [34,35] in which sequential copper–nickel flotation was examined. An example of sequential versus bulk flotation, followed by Cu–Ni separation is shown in Table 16.15. These experiments were carried out on copper–nickel ore from the Iskut River orebody in British Columbia, Canada. The flowsheet and reagent scheme used in the sequential flotation is shown in Figure 16.12.

When using a sequential flotation method, the nickel content of the copper concentrate was much lower than when using the bulk flotation followed by separation.

Sequential flotation in industrial practice is used in cases where the copper in the head is much greater than nickel (4–5 times). Sequential flotation was used at the Falconbridge Strathcona plant to treat dip zone copper–nickel ore assaying about 5.5%

Table 16.15

Results of Cu–Ni selective and bulk flotation followed by Cu–Ni separation from bulk cleaner concentrate

Flowsheet	Product	Assays %			% Distribution	
		Cu	Ni	Insol	Cu	Ni
Sequential Cu–Ni	Cu concentrate	26.2	0.40	10.4	70.1	2.6
flotation	Ni concentrate	1.46	6.30	11.6	16.0	70.2
	Ni Tail	0.12	0.30	–	13.9	27.2
	Feed	0.72	0.93	–	100.0	100.0
Bulk Cu/Ni flotation						
followed by Cu/Ni separation	Cu concentrate	27.2	2.5	9.8	75.0	6.6
Separation tail (Ni concentrate)	0.90	6.40	10.0	8.2	71.5	
Bulk Tail	0.12	0.28	–	16.8	21.9	
Feed	0.69	0.85	–	100.0	100.0	
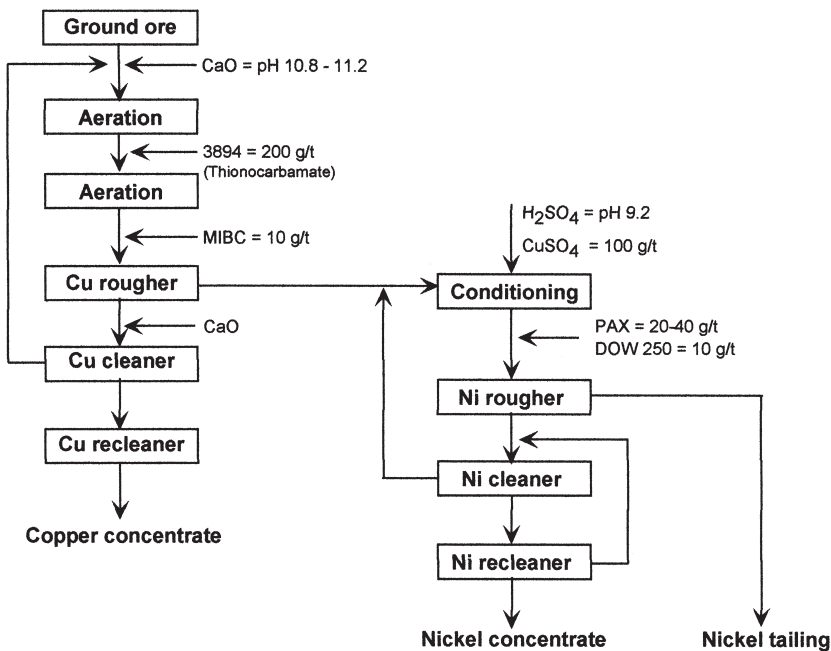
Figure 16.12 Sequential Cu–Ni flotation flowsheet and reagent scheme used in the treatment of Iskut River ore.

Cu and 0.4–0.6% Ni. The ore was high in platinum group metals. The reagent scheme used was similar to that shown in Figure 16.12, except that aeration was not used and collector was dithiophosphates. The metallurgical results obtained in this plant are shown in Table 16.16.

Table 16.16

Plant metallurgical results obtained on Strathcona dip zone Cu–Ni ore using a sequential flotation method [36]

Product	Assays %		% Distribution	
	Cu	Ni	Cu	Ni
Copper concentrate	26.0	0.2	95.5	7.6
Nickel concentrate	1.6	6.0	0.8	65.6
Nickel tail	0.2	0.15	3.7	26.8
Feed	5.20	0.47	100.0	100.0

16.4.4   Copper–nickel separation

Copper–nickel separation is the most common practice in the treatment of copper–nickel ores. Comprehensive research has been carried out by various organizations to develop a more efficient copper–nickel separation method. Some of the research work is discussed in the following sections.

Desorption of collector

In many operations, it was observed that if the collector level in the solution is reduced or a portion of the collector is desorbed from the mineral surfaces, then copper–nickel separation improves significantly. There are several methods used in the desorption and removal of collector. These include:

- Pre-treatment with NaHS and thickening of the bulk concentrate before separation.
- Stage aeration with SO_2 and lime, followed by copper flotation. This method is effectively used when pyrrhotite is not present in the bulk concentrate. The effect of oxidation on the xanthate level and selectivity index is shown in Figure 16.13.
- The use of other oxidants such as hypochloride (NaOCl) was also examined in the same studies. The effect of NaOCl on copper–nickel separation is shown in Figure 16.14. Comparing the data from Figures 16.15 and 16.16, it appears that both air oxidation and NaOCl gave a similar selectivity index.
- Pyrrhotite depression in the presence of cyanide and oxidation allowed pyrrhotite removal from the copper concentrate. The phenomenon of cyanide desorption of the collector during copper–lead separation is discussed in Chapter 15. It is likely that cyanide in the presence of air oxidation desorbs the collector from pyrrhotite resulting in gold pyrrhotite depression in an alkaline circuit. Figure 16.15 shows the effect of the level of cyanide on pyrrhotite depression with and without oxidation. Data in Figure 16.15 show that oxidation in the presence of 0.4 kg/t cyanide results in complete depression of pyrrhotite.

Reagent schemes used in copper–nickel separation

Collector desorption in copper–nickel separation is practiced when (a) excessive addition of collector is used in copper–nickel bulk flotation and (b) in a case where elevated
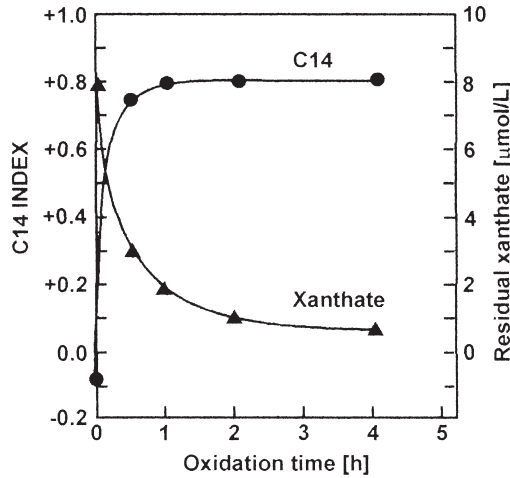
Figure 16.13 Effect of air oxidation on xanthate level and selectivity (C14) during copper–lead separation.
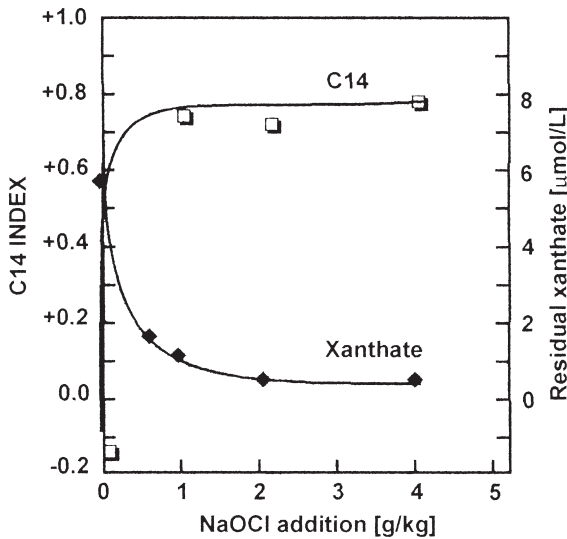
Figure 16.14 Effect of NaOCl on copper–nickel separation.

amounts of pyrrhotite is present in the bulk concentrate. The choice of copper–nickel separation methods is also governed by the amount of insol present in the bulk concentrate, in which case the use of cyanide is avoided because when cyanide is present, gangue becomes a separation interfering constituent of the bulk concentrate. A typical example is the Thompson plant, where in the presence of cyanide [36] the chalcopyrite was completely depressed. Some of the most commonly used copper–nickel separation methods are listed in Table 16.17.
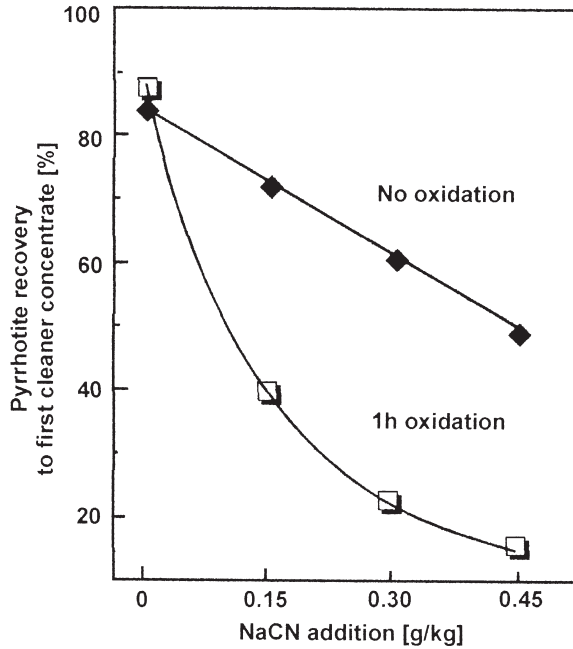
Figure 16.15 Effect of level of cyanide and oxidation on pyrrhotite depression during copper–nickel separation.

Table 16.17

Commonly used copper–nickel separation methods

Nickel concentrate quality	Reagent	PH	Pre-treatment
Bulk concentrate with no pyrrhotite present	Lime	11.5	None
	Lime, dextrin	11.0	None
	Lime, oxidized starch	11.0	None
Bulk concentrate with moderate to low amount of pyrrhotite	Lime, cyanide	10.5	none
	NaOCl, lime, cyanide	10.0	Pre-conditioning
	Activated carbon, lime, NaCN	10.5	Pre-conditioning
Bulk concentrate with high pyrrhotite content	Lime, SO$_2$, NaCN	11.0	Aeration
	Lime, NaCN	11.0	Collector desorption
	Lime, dextrin, NaCN	11.0	Aeration
Bulk concentrate where copper is much higher than nickel content	Lime, SO$_2$, starch	5.5	Stage conditioning with lime (pH 10.5) and SO$_2$ (pH 5.5)

The flowsheet practiced at the Inco (Sudbury) plant in the copper–nickel separation circuit is illustrated in Figure 16.16. Using this flowsheet, two nickel-type concentrates are produced including low- and high-grade concentrates. Metallurgical results obtained using this method are shown in Table 16.18.
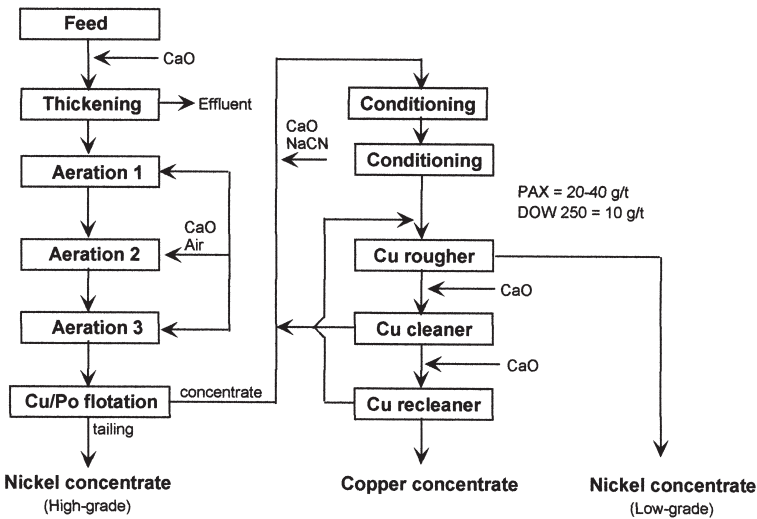
Figure 16.16 Copper–nickel separation flowsheet used at Inco-Sudbury concentrator.

Table 16.18

Metallurgical results obtained using two–stage separation

Product	Assays %			% Distribution		
	Cu	Ni	Po[a]	Cu	Ni	Po
Copper concentrate	30.4	0.67	3.6	96.2	2.2	5.1
High-grade Ni concentrate	0.09	30.5	4.4	0.2	86.4	5.5
Low-grade Ni concentrate	1.3	4.28	76.4	3.5	11.5	89.5
Feed	11.7	11.4	26.2	100.0	100.0	100.0

[a]Po – pyrrhotite.

The efficiency of separation was a function of level of cyanide and lime additions. Figure 16.17 shows the copper concentrate grade as a function of level of lime and cyanide.

16.4.5 Other processes involved in treatment of copper–nickel and nickel ores

Some of the processes that are used in the flotation of copper–nickel and nickel ores have been developed recently and are currently in use in a number of operating plants. Two of the quite interesting processes are described in this section. These are (a) nitrogen flotation and (b) the application of high-intensity conditioning (HIC).
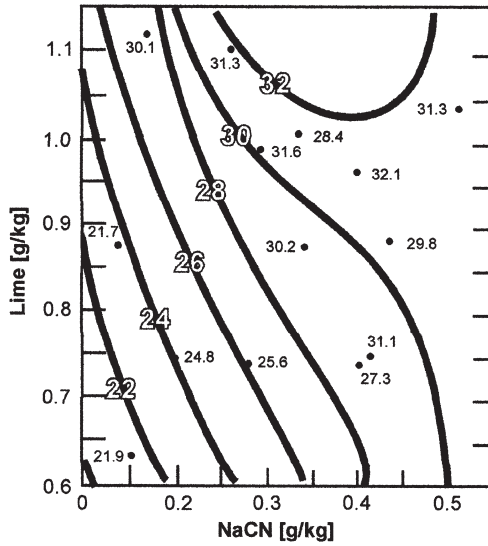
Figure 16.17 Copper concentrate grade as a function of lime and NaCN additions [37].
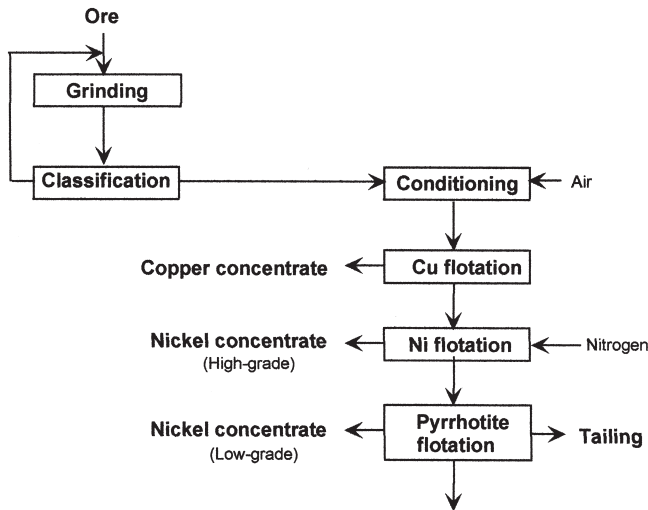
Figure 16.18 Flowsheet used in the Norilsk nickel complex in treatment of high-pyrrhotite ore.

Use of nitrogen in flotation

The use of nitrogen in the flotation of different ores has been extensively tested in the past two decades [38–40] and it was established that in the presence of nitrogen, (a) in some cases, floatability of certain minerals improves (gold sulfides) and (b) depression of certain minerals improved (pyrrhotite and copper in copper–moly separation). As a result

of these studies, nitrogen has found application in the mineral processing industry. Use of nitrogen in pentlandite–pyrrhotite separation was also extensively tested. As a result of these studies, nitrogen was introduced into the Norilsk concentrator in the nickel flotation circuit from pyrrhotite magnetic fraction. The flowsheet used at the Norilsk plant is shown in Figure 16.18. Using this flowsheet, the depression of pyrrhotite was significantly improved and a relatively high-grade nickel concentrate produced.

Effect of high-intensity conditioning

HIC was extensively tested specifically for the improvement of (a) rate of fine pentlandite flotation, (b) selectivity between pyrrhotite and pentlandite and (c) selectivity between gangue minerals and pentlandite [41].
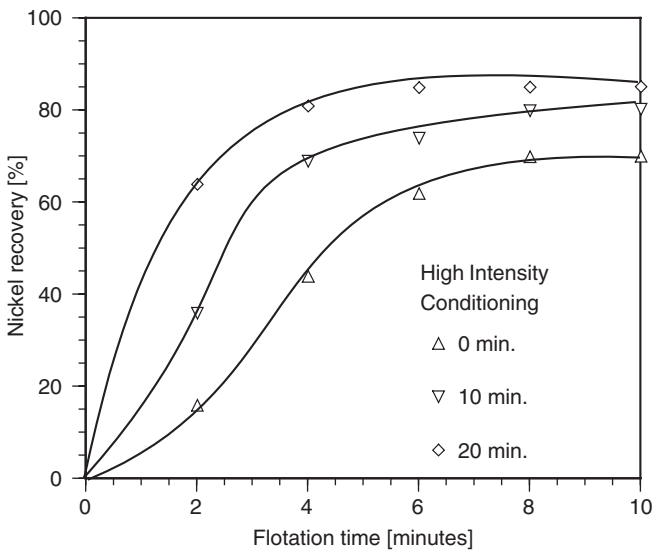
Figure 16.19 Effect of HIC on the rate of pentlandite flotation from Strathcona (Canada) non-magnetic fraction.

Table 16.19

Effect of HIC on concentrate grade and recovery obtained on Strathcona non-magnetic fraction

HIC Time (min)	Reagents used in HIC	Assays %		% Distribution	
		Ni	Cu	Ni	Cu
0	MIBC, 3894[a]	5.3	1.0	70.0	50.5
5	MIBC, 3894	7.0	1.4	72.5	55.6
10	MIBC, 3894	8.9	1.6	73.3	58.5
15	MIBC, 3894	10.3	2.2	75.5	61.0
20	MIBC, 3894	10.8	2.4	82.3	66.6

[a]Frother, thionocarbamate (Cytec).

The rate of fine pentlandite flotation can be enhanced significantly with HIC. Figure 16.19 shows the effect of HIC on the rate of nickel flotation from Strathcona (Canada) non-magnetic fraction.

It is postulated that in the presence of certain reagents, HIC enhances selective aggregation of fine pentlandite. During a pilot-plant trial, it was observed that HIC produces flocs rich in pentlandite.

Pilot-plant test work on non-magnetic fractions of the same plant indicated that with HIC, nickel concentrate grade and recovery from non-magnetic fractions can be substantially improved. Table 16.19 shows the effect of HIC on concentrate grade and recovery.

The effectiveness of HIC is usually determined by the amount and type of frother–collector added.

16.5   MATTE FLOTATION

Copper–nickel matte is a product obtained during the smelting of copper–nickel concentrate and ores. Until the 1940s, separation of matte was accomplished by a smelting method, where molten metals were separate. Such a process had a number of problems where separation was not efficient.

The first flotation method was developed at Mechanobre, Russia in 1942 [42] and later the International Nickel Company (Inco) patented a similar flotation process in 1945 [43].

In this development stage, it was established that during slow cooling of the matte, Cu_2S and Ni_3S_2 are formed in relatively coarse crystals. The major matte impurity is iron.

The main purpose of the flotation of matte is to produce selective copper and nickel concentrates. Copper–nickel matte has to be produced using a reverse sulfidizing method, where the matte is converted into copper–nickel sulfides. There are two basic methods for producing sulfide matte. These are:

- Bessemer matte, which is a sulfur-deficient matte. This type of matte allows precious metals and PGMs to be collected in metallic phase and later removed by magnetic separation. This method is practiced by Inco (Canada).
- Sulfur-rich matte is treated in the Novilsk and Severonickel plants in Russia. This type of matte is much more difficult to grind than sulfur-depleted matte.

The presence of iron in the matte represents a detrimental constituent for copper–nickel separation. According to the literature, the detrimental effect of iron in matte is seen through the following:

- Iron in the matte makes a complex intergrowth and crystallization of individual Cu, Ni sulfides is not sharp. The hardness of the matte also increases.
- Iron in the matte often converts into pyrrhotite, which complicates the copper–nickel separation and iron content of the matte of >1% Fe sharply reduces separation efficiency. Figure 16.20a,b shows the effect of iron on copper–nickel separation.

At Inco, during matte separation, the iron content of the matte does not exceed 1% Fe. However, a method was also developed where successful matte separation is achieved with
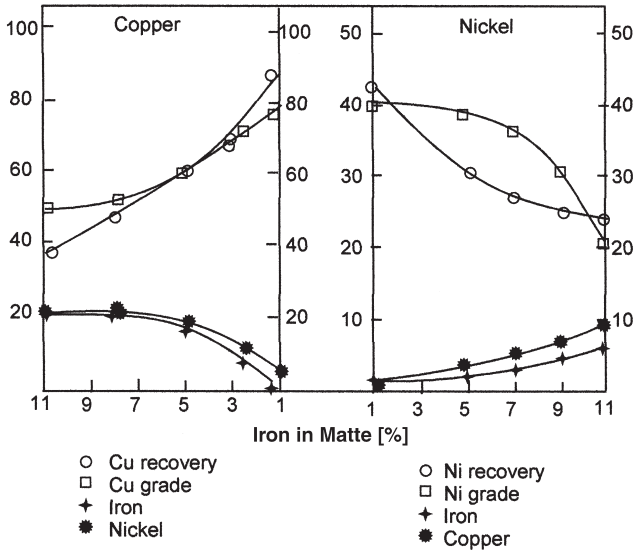
Figure 16.20 Effect of iron in the matte on copper–nickel separation.

higher iron content. This is achieved by slow cooling of the matte, from 800 °C to 200 °C, before grinding. In this case, regardless of the higher iron content, crystallization of sulfides is well formed, which allows good matte separation. Experimental data has shown that the matte cooling rate is related to the iron content as follows:

Iron content of the matte, % Fe	1	4	11
Cooling rate, °C/h	50	20	10

The matte cooling is done in such a way that the matte is covered with sand in different layers to maintain the desired cooling rate.

16.5.1 Reagents and flowsheets used in matte separation – Bessemer matte

Matte separation is practiced in only a few plants outside Russia, including Inco (Canada) and several plants in Russia, all of which use different separation techniques as well as different cooling methods.

The so-called Inco method was introduced in 1944 based on the separation of Bessemer matte. The only reagent used up to present was diphenylgianidine (DPG) and only recently efforts have been made to replace toxic DPG with a water-soluble collector. The generalized Inco matte separation flowsheet is shown in Figure 16.21, where the DPG is fed to each grinding mill.

In fact, DPG is soluble in alcohol and organic acids (citric acid) and only slightly water-soluble. The Cu–Ni matte separation retains good selectivity toward nickel. In detailed studies conducted on various mattes from Inco plants, it was demonstrated that the method of dissolution of DPG has a significant effect on floatability of copper

Figure 16.21   Simplified matte separation flowsheet.

Table 16.20

Effect of DPG dissolved in alcohol and citric acid on matte separation

| Type of DPG used | Cu rougher concentrate | | | Cu cleaner concentrate | | |
| | Assays % | | % Recovery | Assays % | | % Recovery |
	Cu	Ni	Cu	Cu	Ni	Cu
Dry DPG (as is)	48	30	94.2	69.2	6.0	89.1
DPG dissolved in alcohol	58	17	95.4	70.0	5.2	90.0
DPG dissolved in citric acid	66.2	14.3	96.6	74.0	2.2	91.0

minerals. The effect of DPG, used as is, dissolved in alcohol and in citric acid, on copper flotation is shown in Table 16.20. The best metallurgical results were obtained with DPG dissolved in citric acid.

Extensive studies conducted with different collectors have shown that DPG can be replaced by mercaptan collector with very similar separation efficiency. Studies were conducted in the early 1900s [44] to examine the effect of the xanthate–dextrin system on matte separation.

In these experiments, about 200 g/t of potassium ethyl xanthate was used. The optimum dosage of dextrin 12 (i.e. partially branched dextrin) was about 350 g/t.

16.5.2   Reagent and flowsheet used in matte separation – sulfur-rich matte

The so-called Inco method treats sulfur-depleted matte, while in Russian operations, sulfur-rich matte is treated in a separation circuit. In Russian operations, two major

flowsheets were developed and used at the Norlisk and Severonickel plants. The first
flowsheet involves production of copper–nickel bulk "melt" in addition to copper–nickel
concentrate. This flowsheet is shown in Figure 16.22.

Using this flowsheet, the matte is ground to 100% <44 μm and conditioned with NaOH
to pH 12.2–12.5, followed by copper flotation with additions of 1000–1300 g/t potassium
butyl xanthate. The metallurgical results obtained are shown in Table 16.21. The matte
with a higher iron content was treated with NaOH to pH 11.8, which is slightly lower than
that used in the treatment of low-iron matte.

The other flowsheet used at the Norilsk plant incorporates magnetic separation on the
nickel concentrate. This flowsheet is similar to that of the Severonickel plant, except that
the copper tailing is re-ground before magnetic separation.

The reagent scheme used is similar to that of the Severonickel plant, except that the
flotation pH is slightly lower.
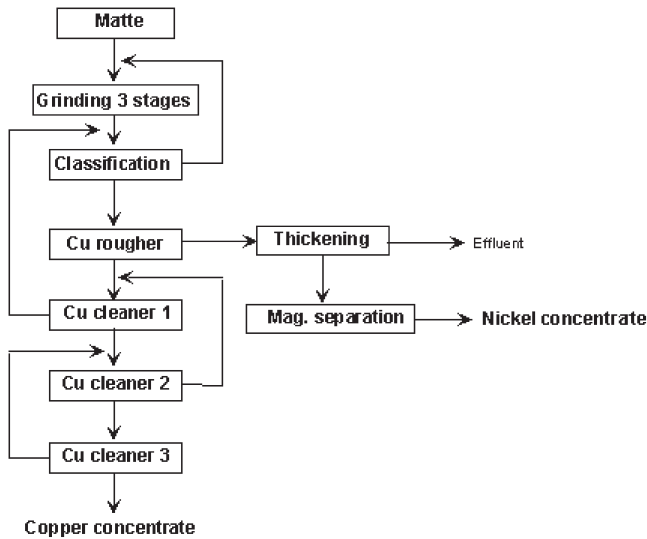
Figure 16.22 Flowsheet for matte separation used in the Severonickel plant, Russia.

Table 16.21

Metallurgical results obtained at the Severonickel matte separation plant

Product	Assays %			% Distribution		
	Cu	Ni	Co	Cu	Ni	Co
Copper concentrate	69.0	4.4	0.1	87.9	4.5	7.5
Nickel concentrate	3.5	68.0	0.9	5.6	89.1	86.0
Cu/Ni concentrate	30.1	36.0	0.5	6.5	6.4	6.5
Feed	32.6	39.7	0.55	100.0	100.0	100.0

16.6 PLANT PRACTICE IN TREATMENT OF NICKEL ORES

In contrast to the copper–nickel treatment flowsheets that are quite complex, flowsheets for the treatment of nickel ores are relatively simple, although the reagent schemes are somewhat similar. In some operating plants that treat highly viscous dolomitic ores (Mt. Keith), slime–sand separation is practiced.

16.6.1 Flowsheets

The most typical flowsheet used in nickel flotation is shown in Figure 16.23.

In some operations, re-grinding is not required. The slime–sand separation flowsheet is shown in Figure 16.24. This flowsheet is practiced at the Mt. Keith operation in Australia. The prominent feature of these flowsheets is the conditioning. Conditioning with reagents was found to be beneficial in two ways:

- Prolonged conditioning improves selectivity between nickel and gangue minerals.
- Conditioning with reagents results in an improved rate of nickel flotation and consequently improves overall nickel recovery.

16.6.2 Reagent schemes of the major operating plants

The reagent schemes used in nickel operating plants vary somewhat from one plant to the next. Analyses of data from the operating plants showed that reagent schemes are
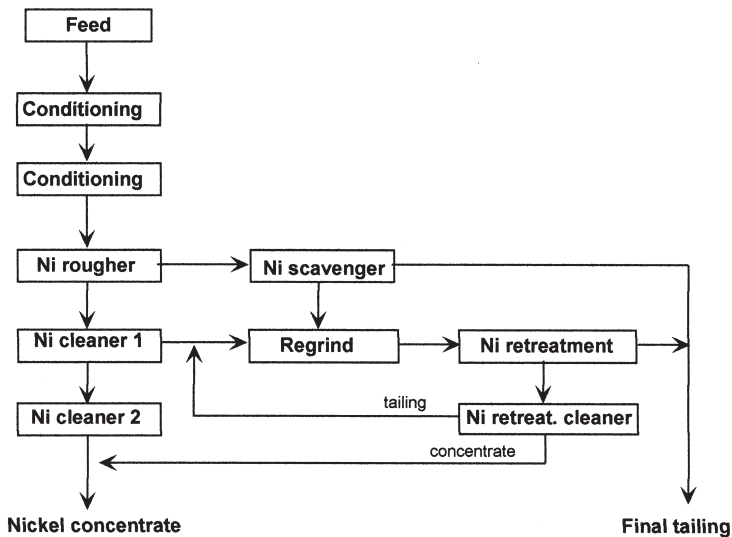
Figure 16.23 Typical flowsheet used in nickel flotation.
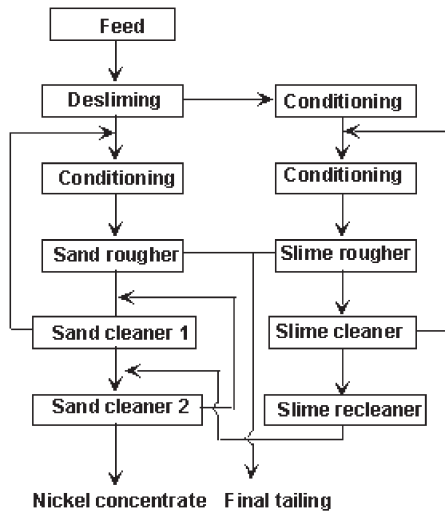
Figure 16.24 Slime–sand separation flowsheet (Mt Keith, Australia).

Table 16.22

Summary of reagent schemes used in operating nickel plants

Concentrator	Type of ore and reagent scheme
Mt Windarra (Poseidon Limited), Australia	*Ore*: Major sulfide minerals, pentlandite, and pyrrhotite with less pyrite iron oxides, serpentine, lantigorite, talc chlorite magnesite and carbonates. In some parts of the orebody, violarite is a major nickel mineral. *Grind*: K_{80} = 105 μm *Reagents*: Na_2CO_3 = pH 9.5–10.3, CMC = 200–300 g/t, R407 = 20 g/t, butyl xanthate = 400 g/t, MIBC = 0–10 g/t.
Yakabindie, Australia	*Ore*: The major valuable mineral is pentlandite in carbonate and dolomitic gangue minerals. The average MgO content of the ore is about 40% MgO. Minor amount of pyrrhotite is also present in the ore. *Grind*: K_{80} = 89 μm *Reagents*: Guar = 300 g/t, sodium ethyl xanthate = 600 g/t, TEB frother = 50 g/t, pH 9.0. *Other*: Long conditioning time is employed with collector (i.e. 30 min).
Mt Keith, Australia	*Ore*: This ore contains pentlandite as a major sulfide mineral with small amounts of pentlandite. The principal gangue minerals are dolomite and magnesite with calcite. The ore contains an appreciable amount of dolomite–magnesite slimes, which makes the pulp very viscous. The mine site water used in flotation is very high in ions such as MgO, CaO and Cl. *Grind*: K_{80} = 95 μm *Reagents*: Dextrin = 0–100 g/t, sodium ethyl xanthate = 400 g/t, Dow 250 = 50–100 g/t.

(*Continued*)

Table 16.22 (*Continued*)

Concentrator	Type of ore and reagent scheme
KNO, Australia	*Other*: Utilizes slime–sand separation flowsheet with prolonged conditioning time (20–30 min). *Ore*: The KNO ore is relatively complex and contains, in addition to pentlandite, hloanite and nikelin in serpentine matrix. Talc is also present in the ore. In some parts of the orebody, arsenopyrite is present. *Grind*: $K_{80} = 85$ μm *Reagents*: Na_2CO_3 = pH 9.5, Dextrin = 100–150 g/t, R407 = 20 g/t, SIPX = 10–20 g/t, MIBC = 15 g/t.

Table 16.23

Plant metallurgical results obtained in treatment of nickel ores

Concentrator	Head assays % Ni	Concentrate assays % Ni	Distribution % Ni
Mt. Windarra	1.75	18.4	85.9
Yakanbidie	0.56	19.9	68.3
Mt. Keith	0.50	16.5	72.0
KNO	1.95	12.6	84.3

mainly determined by the mineralogy of the ore, specifically the nature of gangue minerals present in the ore. The majority of these ores contain hydrophobic gangue minerals, such as talc and chlorites, and some of the ores contain other floatable gangue minerals, such as dolomite and calcite, which often are pre-activated and report to the nickel concentrate.

The reagent schemes used in major operating plants are shown in Table 16.22. Note that most of the current nickel operations are located in Australia and a few in South Africa. Several small operations (200–800 tpd) were operated in Canada, mainly in Northern Ontario and British Columbia.

Note that a large number of operations use a large quantity of xanthate. This is due to the fact that the plant water used in flotation contains fairly large amounts of soluble ions. In some operations, the pulp viscosity is very high, which also attributes to high collector consumptions.

16.6.3 Metallurgical results

The metallurgical results obtained in operating plants are shown in Table 16.23. Although in some plants reasonably good grade concentrate was obtained, the nickel recovery was relatively low mainly due to the complexity of the ore.

16.7   PLANT PRACTICE IN TREATMENT OF COPPER–NICKEL ORES

About 85% of the total world nickel production comes from copper–nickel ores. These ores are also important sources of production of cobalt and platinum group minerals. The largest copper–nickel operations are located in Canada and Russia. In other parts of the world, such as Africa, Scandinavian countries and Europe, there are only a few operating plants.

16.7.1   Flowsheets used in treatment of copper–nickel ores

The flowsheets used in the treatment of massive sulfide copper–nickel ores are relatively complex and most often involve magnetic separation where the monoclinic pyrrhotite is
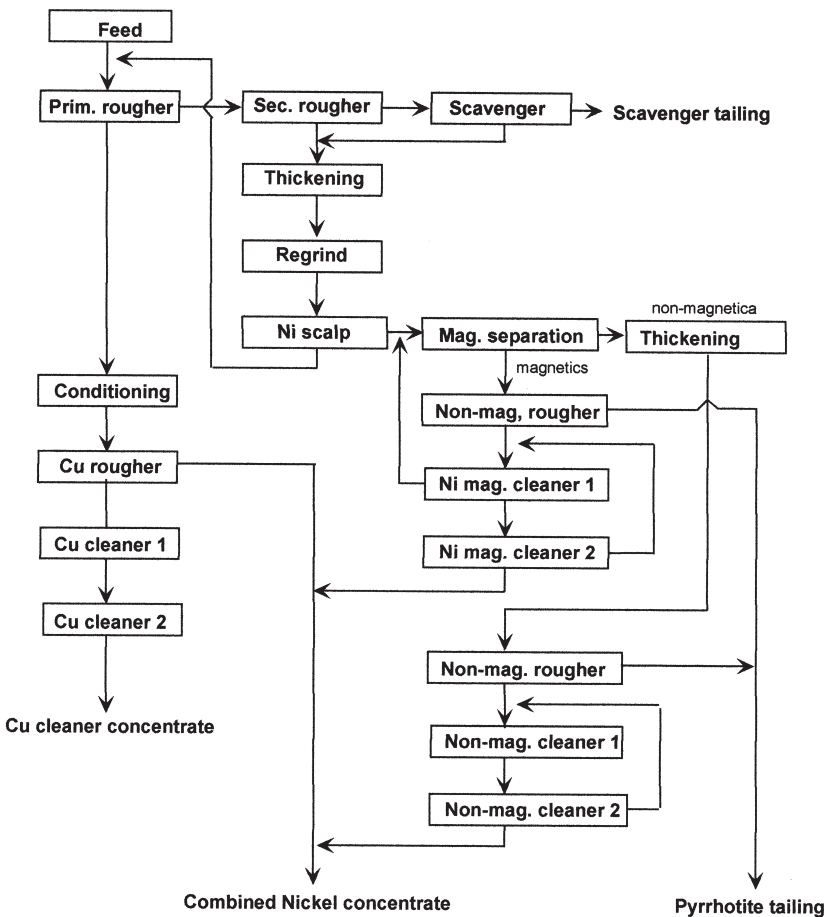
Figure 16.25 Generalized flowsheet used in the treatment of copper–nickel massive sulfide ores.
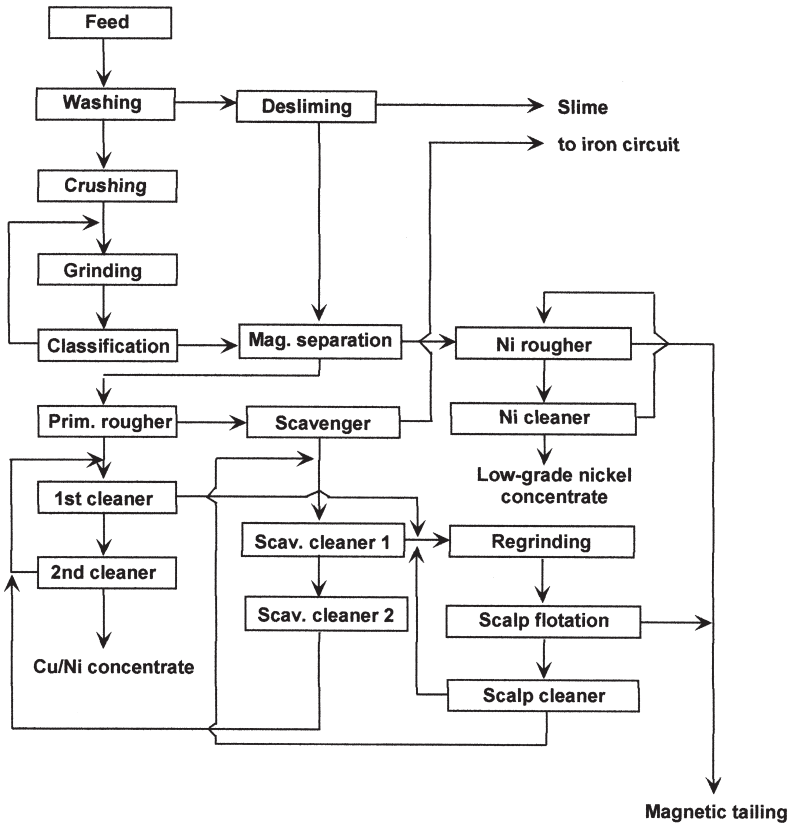
Figure 16.26 Flowsheet used in the treatment of semi-massive and massive Cu–Ni ores in Russian operation

present in the ore. Very often the configuration of these flowsheets changes. For example, at the Falconbridge Strathcona plant (Canada) between 1968 and 1995, about 20 different flowsheets have been evaluated. These changes have been mainly directed toward improvement in pyrrhotite rejection.

In the treatment of semi-massive and low pyrrhotite ores, the flowsheets are simpler, except when a copper–nickel separation circuit is added. In general terms, there are three types of flowsheets used in copper–nickel flotation. These include:

• The flowsheet used in the treatment of massive sulfide copper–nickel ores in Canadian operations. The generalized flowsheet is shown in Figure 16.25. There are variations of this flowsheet, which are mainly related to positioning of the magnetic separation and the method used in Cu–Ni separation. For example, Inco operations include magnetic separation ahead of flotation and also uses Cu–Ni separation method involving desorption.
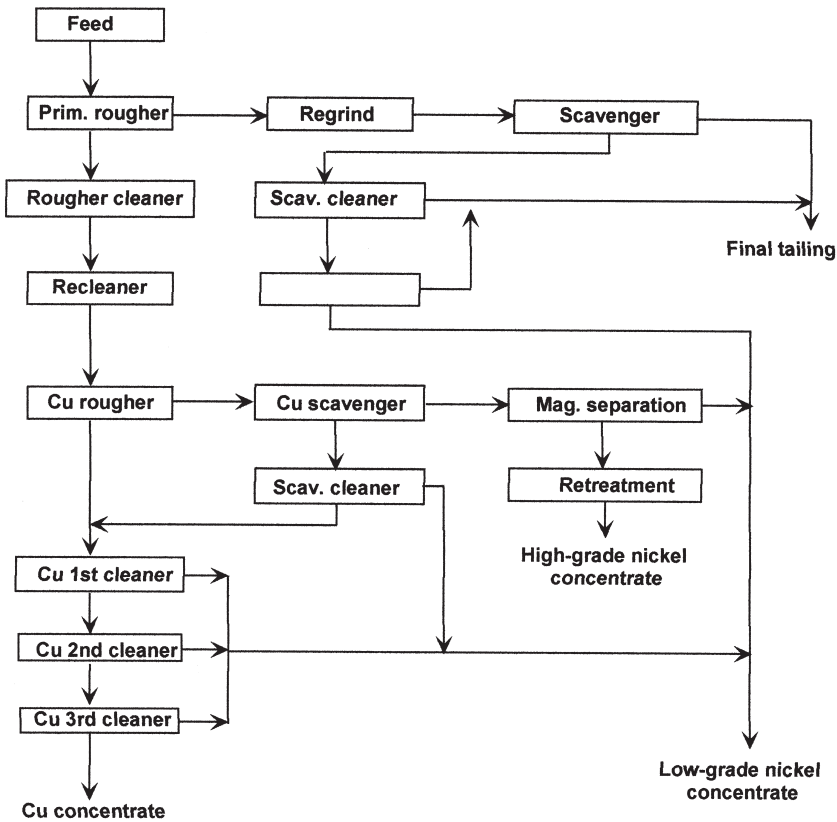
Figure 16.27 Flowsheet used in the treatment of low sulfide Cu–Ni ores.

- The flowsheet used in treatment of semi-massive copper–nickel ores found in Russia. These are perhaps the most complex flowsheets and are intended for treatment of disseminated copper–nickel ores. A typical example of such a flowsheet is shown in Figure 16.26. This type of flowsheet is used in the Severonickel and Penchengan nickel plants.
- The flowsheet used for low sulfide copper–nickel ores is shown in Figure 16.27. These are usually used in the treatment of ores that contain hydrophobic gangue minerals (e.g. talc, chlorites). The alteration of this flowsheet includes talc pre-float before copper–nickel flotation, but this case is quite rare.

16.7.2   Reagent schemes used in the treatment of copper–nickel ores

The reagent scheme used in the treatment of copper–nickel ores varies considerably, especially the use of modifiers and depressants. A wide variation in the use of various

depressants is related to the ore mineralogy. In many operating plants, copper sulfide is also used as activator. Table 16.24 lists the ore characteristics and reagent schemes used in major operating plants.

The ores described in Table 16.24 cover a variety of deposits with different mineralogy. Consequently, the reagent schemes used vary considerably from one operation to another. The operations in Finland use relatively high amounts of sulfuric acid, which is unusual, due to the fact that this ore does not contain clay minerals. In the Falconbridge operation, the

Table 16.24

Ore characteristics and reagent schemes used in major operating plants

Concentrator	Ore treated and reagent scheme
Pechenganickel, Russia	*Ore*: The ore treated belongs to the Kaul deposit and is composed of a mixture of sulfides in transformed serpentine rock. The major sulfide minerals are pentlandite, chalcopyrite and pyrrhotite. *Grind*: K_{80} = 74 µm *Re-grind*: 90% <44 µm *Reagents*: Na_2CO_3 = 3000 g/t (pH 10.2), butyl xanthate = 180 g/t, sodium Aeroflot = 200 g/t, cresylic acid = 250 g/t, $CuSO_4$ = 50–100 g/t, KT&M[a] depressant = 500 g/t.
Severonickel, Russia	*Ore*: This ore is a finely disseminated ore with pentlandite, chalcopyrite, pyrrhotite and magnetite. The major gangue minerals include olivine, pyroxene and chlorite. The ore contains significant quantities of cobalt, which is contained in pentlandite as an isomorphous mixture. *Grind*: K_{80} = 45 µm *Reagents*: $CuSO_4$ = 20–60 g/t, Na_2CO_3 = 2700 g/t (pH 9.2–9.4), NaBX = 180 g/t, sodium Aeroflot = 110 g/t, CMC = 400 g/t.
Norilsk, Russia	*Ore*: Massive sulfide ore with pentlandite, chalcopyrite and pyrrhotite. The ore contains about 60% sulfides with some pyroxene and silicates. *Grind*: K_{80} = 110 µm *Reagents*: Cu/Ni Flotation – NaOH = pH 9.5–10.0, PAX = 100 g/t,isopropyl Aeroflot = 50 g/t, cresylic acid = 20–50 g/t, $CuSO_4$ = 100 g/t. Cu–Ni separation – CaO, aeration, nitrogen copper flotation
Falconbridge–Strathcona Canada	*Ore*: Massive sulfide ore with chalcopyrite and pentlandite as the major valuable minerals with some PGM present in the pentlandite. The major gangue mineral is pyrrhotite, which contains nickel enclosed in a pyrrhotite crystal structure. The average nickel content of the pyrrhotite is 0.7–0.8% Ni. Other gangue minerals include pyroxene and silicates. *Reagents*: Cu–Ni bulk flotation – $CuSO_4$ = 50–100 g/t, CaO = pH 10.0 (primary rougher), SIPX = 150 g/t, Dow 250 = 60–80 g/t, H_2SO_4 = 650 g/t (secondary rougher). Cu–Ni separation – CaO = pH 11.5, NaCN = 20 g/t.

<div align="right">(Continued)</div>

Table 16.24   (*Continued*)

Concentrator	Ore treated and reagent scheme
International Inco Co. Clarabelle Mill, Canada	*Ore*: The Inco, Sudbury Basin ore contains a variety of ores (i.e. several ore types). The valuable minerals include chalcopyrite, pentlandite, gold and PGM minerals. Pyrrhotite appears in the following two forms: monoclinic and hexagonal pyrrhotite, both of which contain 0.6–1.2% Ni in solid solution as micron-sized exsolution "flames." The monoclinic phase accounts for 70% of the pyrrhotite in the ore, which is ferromagnetic, while hexagonal pyrrhotite is paramagnetic. The non-opaque minerals are quartz, serpentine and aluminosilicates. *Reagents*: CaO = pH 9.0–9.5, SIPX = 80 g/t, $CuSO_4$ = 100 g/t, DF250 = 60 g/t, DITA = 100 g/t. Cu–Ni separation – conditioning, aeration, CaO, NaCN (variable).
Thompson Mill, Canada	*Ore*: The two types of mineralization exist in the pipe deposit. A disseminated variety, which consists of fine-grained pentlandite with minor pyrrhotite and massive sulfide varieties of pentlandite and pyrrhotite. The host rock of nickel mineralization is serpentinized peridote, an ultrabasic rock rich in exsolved magnetite. *Grind*: K_{80} = 85 µm *Reagents*: $CuSO_4$ = 100–200 g/t, Na_2CO_3 = 300 g/t, SIPX = 50 g/t, MIBC = 50–80 g/t. Cu–Ni separation – CaO/SO_2 system
Shebandowan, Canada	*Ore*: The principal valuable minerals in the ore are chalcopyrite and pentlandite. The gangue constituents are tremolite, falite, magnesite and talc. *Reagents*: Na_2CO_3 = 1500 g/t, CMC = 200 g/t, SIPX = 30 g/t, MIBC = 10 g/t. Cu–Ni separation – CaO = pH 11.5, NaCN = 30 g/t.
Langmuir Plant, Canada	*Ore*: The ore consists of a massive pyrite and pyrrhotite zone within the andesite rock. Talc and serpentine alterations are common within the orebody. *Reagents*: Guartec = 650 g/t, $CuSO_4$ = 200 g/t, SIPX = 150 g/t, MIBC = 30 g/t.
Rankin Nickel, Canada	*Ore*: The main valuable minerals in the ore are pentlandite and chalcopyrite. The main gangue minerals are pyrrhotite and silicates. *Reagents*: Na_2CO_3 = 800 g/t (pH 9.5), starch = 300 g/t, PAX = 10 g/t, R3477 = 30 g/t, MIBC = 25 g/t.
Lynn Lake, Canada	*Ore*: Chalcopyrite and pentlandite are the major valuable minerals. Pyrrhotite and pyrite, to a lesser degree, are present in the ore. Talc and chlorite are also present. *Reagents*: Na_2CO_3 = 1800 g/t, Dextrin = 200 g/t, SIPX = 50 g/t, MIBC = 10 g/t, $CuSO_4$ = 20 g/t. Iskut River, Canada
Silver Standard Mine	*Ore*: This ore is a finely disseminated, semi massive sulfide and contains chalcopyrite and pentlandite with minor amounts of secondary nickel sulfides, as well as covellite and pyrite. The major gangue minerals are altered feldspars, pyroxenes and amphiboles.

(*Continued*)

Table 16.24   (*Continued*)

Concentrator	Ore treated and reagent scheme
	Grind: 75% >200 mesh
	Reagents: Cu–Ni flotation – caustic starch = 300 g/t,
	$CuSO_4$ = 100 g/t, PAX = 60 g/t, MIBC = 15 g/t. Cu–Ni separation – CaO = pH 11.2, NaCN = 20 g/t.
Union Mine, USA	*Ore*: Semi-massive sulfide ore with chalcopyrite and pentlandite present in the ore in a serpentine gangue matrix.
	Reagents: $CuSO_4$ = 100 g/t, Dextrin = 200 g/t, R407 = 20 g/t, PAX = 20 g/t, MIBC = 20 g/t.
Kotalahti, Finland	*Ore*: Two ore types are treated including disseminated ore and breccia-type ore. These two ore types are mixed together for processing.
	Reagents: H_2SO_4 = 9500 g/t, K-ethyl xanthate = 60 g/t, pine oil = 200 g/t, pH 4.5. Cu–Ni separation – CaO = 4800 g/t, dextrin = 30 g/t, pH 12.0
Hitura, Finland	*Ore*: A serpentine intrusion with mica gneiss ore with pentlandite and chalcopyrite as the major valuable minerals. These minerals are disseminated with silicates and magnetite requiring fine grind (i.e. K_{80} = 40 μm).
	Reagents: H_2SO_4 = 3000 g/t, PAX = 210 g/t, Pine Oil = 82 g/t, CMC = 100 g/t, Na_2CO_3 = 300 g/t, pH 3.5

[a]A mixture of CMC and quebracho.

Table 16.25

Metallurgical results obtained in the various plants

Concentrator	Feed Assays %		Bulk Cu–Ni concentrate Assays %		% Distribution		Cu concentrate % Distribution	
	Cu	Ni	Cu	Ni	Cu	Ni	Cu	Ni
Pechenganickel	1.22	1.85	4.20	6.65	93.5	86.2	22.5	1.50
Severonickel[a]	0.95	1.35	3.60	5.58	93.3	88.2	–	–
Norilsk	1.2	1.66	4.60	6.60	94.5	79.5	19.7	2.12
Strathcona, Falconbridge	1.32	1.40	6.80	7.10	96.0	83.0	27.5	0.90
Inco Limited	0.92	1.42	13.3	9.20	93.2	80.1	26.5	1.10
Thompson Mill	0.6	1.30	2.2	6.3	92.2	78.0	25.5	1.10
Shebandowan	1.2	1.30	8.8	9.80	92.5	80.1	26.1	0.90
Langmir	0.7	2.1	4.0	14.6	90.2	78.5	–	–
Rankin	0.8	3.3	3.25	13.6	84.1	75.5	–	–
Lynn Lake	0.36	1.15	–	8.3	84.0	88.5	–	–
Iskut River	0.72	0.90	5.58	5.69	83.6	722	20.0	1.81
Union Mine	0.43	0.72	4.2	6.60	93.2	78.5	–	–
Kotalahti	0.31	0.78	3.2	5.80	90.1	93.3	28.6	0.8
Hitura	0.30	0.40	0.10	40.1	81.0	81.2	30.0	–

[a]Siberia, Russia.

copper with pentlandite is initially floated at higher pH followed by nickel pyrrhotite flotation with reduced pH (i.e. 6.8) and addition of $CuSO_4$. Although the ores from the Sudbury area are similar, both the Inco and Falconbridge operations use different reagent schemes. The metallurgical results obtained at these various plants are shown in Table 16.25.

REFERENCES

1. Craig, J.R., and Vaughan, D.J., *Ore Microscopy and Ore Petrography*, Wiley, New York, pp. 108–140, 1982.

2. Congress Collection, *Plant Practice in Treatment of Non-Ferrous, Rare and Precious Metals in Soviet Union*, Nedra, Moscow, pp. 139–200, 1964.

3. Ryan, M.W., *Development of Reagent Scheme for Treatment of Yakabindie Ore*, Interim Report, No. 3, March 1991.

4. Ounpuu, M.A., *An Investigation of the Recovery of Copper and Nickel from Voisey Bay Ore*, Report of Investigation, LR3645, May 1993.

5. Fishman, M.A., and Sobolev, D.C., *Practices in Treatment of Sulphides and Precious Metals*, Vol. 3, Nedra, Moscow, 1961.

6. Raadshooven, C., *Plant Test in the Hardy Concentrator with Different Collectors*, Report of Investigation, Report 22, pp. 15–45, October 21, 1964.

7. Draper, N., and Eggar, G.E., The Development of Metallurgical Practice for Poseidon Limited Nickel Ores, *The Australian IMM*, May 1973.

8. Iwasaki, I., and Malisci, A.S., Use of Ozone in the Differential Flotation of Bulk Copper–Nickel Sulphide Concentrates, *SME-AIME Annual Meeting*, New York, February 24–28, 1985.

9. Bulatovic, S.M., *Development of Reagent Scheme for Treatment of Low Grade Nickel Ore*, Report of Investigation, LR029, December 15, 1989.

10. Bulatovic S.M., *An Investigation of the Recovery of Nickel from Mt. Keith Ore*, Report of Investigation, LR3480, October 20th, 1992.

11. MacHunter, M.W., *Processing of Windarra Ore in the Pilot Plant*, Amdel Report of Investigation, No. 2, January 1970.

12. Bulatovic, S.M., *Process Development for Treatment of Nickel Ore Containing Violarite and Millerite*, Report of Investigation, LR2010, May 1979.

13. Vaneev, I.I., Utilization of CMC in Flotation of Copper Nickel Ores, *Tsvetnie Metaly*, No. 11, pp. 77–83, 1957.

14. Vaneev, I.I., and Petrov, V., Application of High Molecular Organic Depressants in Treatment of Copper Nickel Ore, *Obogashenie Rud*, No. 2, 1961.

15. Zashikhin, N.V., Concentration of Copper Nickel Ores from Kola Peninsula, *Concentration and Agglomeration*, Vol. 3, 1957.

16. Claridge, P.G., and Tenbergen, P.A., Pipe Ore Processing Development in the Thompson Mill, *Canadian Mining Journal*, Vol. 6, pp. 96–101, June 1975.

17. Bulatovic, S.M., *Evaluation of Different Amines in Flotation of Nickel Ores, Report of Investigation*, LR029, June 1992.

18. Bogdanov, O.S., and Podnek, A.K., *Introduction of Theory and Practice in Flotation*, L. Izd. Mexanobr, 1959.

19. Poznayakov, V.Y., Development of Processing Technology for Sulphide Copper Nickel Ores at the Severonickel Combine, *Tsvetnie Metaly*, No. 9, 1966.

20. Van Raadshooven, W.H., *Five Year R&D Mineral Processing Plan at Strathcona Mill*, Literature Search Prepared for Falconbridge Limited, November 4, 1986.

21. Bulatovic, S.M., *Evaluation of New Collector for Nickel Flotation, R&D Report of Investigation*, LR029, January 1987.
22. Soindvik, K., *Evaluation of Different Frothers on Sudbury Copper Nickel Ore*, Report of Investigation, No. 38, April 20, 1971.
23. Doyle, R., *Plant Test with Different Reagents at Strathcona Mill*, May 13, 1974.
24. Marticorena, M.A., and Eggar, G.E., Inco Develops New Pyrrhotite Depressant, In (T. Yalcin ed) *Innovations in Mineral Processing*, vol.3, pp. 15–33, June 6–8, 1994.
25. Agar, G.E., *Flotation Separation of Pentlandite from Pyrrhotite Using Sulphur Dioxide*, – Air Conditioning Canadian Patent # 1,238,430, May 1992.
26. Bulatovic, S.M., and Jessup. T., *Depressant for Flotation Separation of Polymetallic Sulphide Ores*, US Patent # 5,049,612, Sept. 17, 1991.
27. Agar, G.E., Flotation of Chalcopyrite, Pentlandite, Pyrrhotite Ores, In (K.S.E. Forssberg ed) *Flotation of Sulphide Minerals*, , Elsevier, Stockholm, Sweden, pp. 1–21, 1990.
28. Bulatovic, S.M., *Evaluation of Various Depressants During Flotation of Copper, Nickel Pyrrhotite Ore*, Report of Investigation, LR029, December 1983.
29. Bulatovic, S.M., and Jessup, T., *Evaluation of PKM Base of Organic Depressant for Nickel Flotation from Strathcona Magnetic Fraction*, Report of Investigation, LR3380, June 1986.
30. Wells, P.F., Agar, G.E., and Reynolds, K.O., *Selective Flotation of Nickel Sulphide Ores*, Canadian Patent # 1,156,380, 1981.
31. Kelebek, S., and Wells, P.F., *Selective Flotation Process for Separation of Sulphide Minerals*, US Patent #5,411,148, May 2, 1995.
32. Lisovski, D.I., Activation of Oxidized Nickel Minerals During Treatment of the Ore, *Tsvetnie Metaly*, No. 7, 1958.
33. Bulatovic, S.M., *An Investigation of the Improvement in Nickel Recovery from KNO Ore (Australia)*, Report of Investigation, LR3920, May 1994.
34. Shelton, J., *Flotation Studies on Copper Nickel Sulphide Ores from Deposit Near Rockport Mine*, Bureau of Mines Report of Investigation, 5793, 1961.
35. Bulatovic, S.M., *An Investigation of Sequential Copper Nickel Flotation from Strathcona Dip Zone*, Report of Investigation, LR3368, October 1983.
36. Tipman, N.R., and Richardson, A.H., *The Thompson Mill Milling Practice in Canada*, CIM, Montreal, Quebec, pp. 139–142, 1978.
37. Kerr, A.N., and Kipkie, W.B., Recent Developments in Inco's Copper Cliff Mining Complex, In (A.D. Zunkel ed) *Complex Sulphides*, AIME, San Francisco, pp. 525–548, October 1985.
38. Rybas, V., Volkov, V., and Iranov, V.A., Ecological Outlook for New Technology of Copper Nickel Beneficiation Based on Flotation with Nitrogen, *XVIII IMPC Congress*, Sydney Australia, pp. 997–999, May 23–28, 1993.
39. Rybas, V., and Iranov, V.A., The Industrial Scale Nitrogen Flotation of Copper Nickel Ore at Norilsk, *Non-Ferrous Metals*, Vol. 9, pp. 93–95, 1981.
40. Finch, V., *Column Flotation with Nitrogen of Strathcona Non-Magnetic Thickener Underflow*, University of Montreal Interim Report, December 1986.
41. Bulatovic, S.M., and Salter, R.S., High Intensity Conditioning – A New Approach to Improving Flotation of Mineral Slimes Processing of Complex Ores, In (G.S. Dobby and S.R. Rao eds), *Flotation of Massive Sulphide Ores*, 28th Annual Conference of Metallurgist of CIM.
42. Zakharov, M.I., Improvement in Separation of Converted Copper–Nickel Matte, *Tsvetnie Metaly*, No. 6, July 1965.
43. Agar, G.E., Mc Laughlan, J.D., and Robertson, G.E., Choosing a Water Soluble Collector for Matte Separation, *XVIII IMPC*, Sydney Australia, pp. 989–991, May 23–28, 1993.
44. Nyamekye, G.A., and Laskowski, J.S., Differential Flotation of Inco Matte with the Use of Polysaccharides, *Copper '91*, Vol. 1, August 18–21, pp. 336–342, 1991.

Index