



# Potential of coal mine waste rock for generating acid mine drainage

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## ABSTRACT

Acid mine drainage (AMD) due to the oxidation of sulphide bearing waste rock (WR) is a common environmental problem associated with coal extraction. Therefore, WRs from the Lakhra coal field in Pakistan, were studied to i) perform a mineralogical and chemical characterisation, ii) determine the AMD generating potential and iii) estimate the leachability of elements. The chemical and mineralogical composition was studied using ICP, XRF, XRD and SEM. Acid base accounting and weathering cell test determined the acid producing potential of WRs. Besides organic material, the WRs were composed of quartz, pyrite, kaolinite, hematite and gypsum with varying amounts of calcite, lime, malladerite, spangolite, franklinite and birnessite. The major elements Si, Al, Ca and Fe were in the range (wt.%) of 8–12, 6–9, 0.3–3 and 1–10, respectively, with high S concentrations (19.4–113.3 g/kg). Trace elements were in the range (mg/kg) As (0.3–8), Cd (0.2–0.4), Co (15–75), Cr (67–111), Cu (25–101), Hg (0.1–0.2), Ni (50–107), Pb (8–20) and Zn (75–135). The AMD potential of WRs ranged from –70 to –492 kg CaCO<sub>3</sub>/tonne. During the test period of 192 days, the pH of leachates from very acidic WRs was maintained from 1 to 2.5, whereas, the less acidic WRs produced leachates of mildly acidic (2.7) to neutral (7.3) pH. The leachates from very acidic WRs ranged in the element concentrations of Fe, SO<sub>4</sub><sup>2-</sup> and Al from mg/L to g/L and As, B, Co, Cu, Mn, Ni and Zn from µg/L to mg/L. However, the leachates from less acidic WRs contained all major elements in mg/L and trace elements in µg/L concentrations except for B and Mn that ranged from µg/L to mg/L. The results show that the studied WRs have mild to strong acid producing potential and have the capacity to deteriorate natural water quality significantly. Therefore, necessary preventive or/and acid neutralising measures are strongly suggested.

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## 1. Introduction

Mining of minerals and metals has been a major industry, in terms of both economic importance and employment, since pre-historic times. It provides useful products, but also results in some unwanted and harmful by-products. Some of the most abundant and problematic of these by-products are mine waste rock and tailings. Both of these waste types are often sulphide-rich, principally due to high contents of iron sulphides such as pyrite (FeS<sub>2</sub>) and pyrrhotite (Fe<sub>1-x</sub>S). They also generally contain trace elements such as As, Si, Cu, Zn, Ni, Co, Mo and Cr. However, the structure and composition of mine wastes vary substantially, depending on the geology of the mine site and type of mineral or metal being extracted. Thus, contents of the minerals and elements present vary widely.

Coal mining raises particularly strong concerns, for several reasons. It is a very large-scale activity (according to WCA (2014) ca. 7.8 billion tonnes was extracted worldwide in 2012) and extraction levels are

increasing to meet increasing demands for electricity in many countries globally (IEA-CIAB, 2010). Its combustion releases noxious gases (such as CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub>) and Hg (US EPA, 2014) that are implicated in global climate change, and generates ashes containing ecologically harmful substances (including As, B, Cd, Cr, Cu, Pb, Se and Zn (ACCA, 2014)). Furthermore, coal mining generates WRs that are major potential sources of acid mine drainage (discharges carrying high loads of sulphide oxidation products and associated metals). For example, there are 41 coal mines in Korea that cumulatively release more than 141,000 m<sup>3</sup> AMD per day (Chon and Hwang, 2000). Nearly 19,300 km of streams and more than 180,000 acres of lakes and reservoirs in the USA have been contaminated by AMD (Kleinmann, 1989), and in Pennsylvania (for instance) coal mining is the biggest contributor to contamination of water bodies, being responsible for the pollution of over 2400 miles of streams (Mallo, 2011). Further details regarding quantities of AMD from coal mines and its impact on natural waters in various regions around the world have been reported by Bell et al. (2001), Black and Craw (2001), Cravotta et al. (2010), Equeenuddin et al. (2010), Lattuada et al. (2009), Nganje et al. (2010) and Sahoo et al. (2012).

Due to the scale and severe potential effects of its release, processes involved in AMD generation, associated problems and potential solutions have been increasingly intensively investigated in the last 50 years (Dold, 2010). The process is also known as acid rock drainage,

Abbreviations: ABA, Acid–base accounting; AMD, Acid mine drainage; AP, Acid producing potential; ARD, Acid rock drainage; CC, Continental crust; NP, Neutralisation potential; NNP, Net neutralisation potential; WR(s), Waste rock(s).

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but more frequently called AMD because it occurs mainly at mining sites. Its generation will begin (to some degree) as soon as mining operations start and may continue for centuries after mine closures (Johnson and Hallberg, 2005; Sheoran and Sheoran, 2006). It may be generated in mine tunnels and workings, open pits, WR piles and mill tailings (Blowes et al., 2003; Johnson and Hallberg, 2005). The amounts of AMD generated and the resulting environmental pollution are highly variable, but are increased by poor management of mining activities (Younger, 2000; Younger et al., 2002). The main sources of the sulphide oxidation products are iron sulphide minerals (mainly pyrite and pyrrhotite) present in metallic ores, coal beds or strata overlying and underlying the coal exposed to oxygen and water (INAP, 2009; Jennings et al., 2000; Lottermoser, 2007; Montero et al., 2005). The bacteria present in the system may also influence the process from minor to major extent by accelerating oxidation of sulphides of As, Cd, Co, Cu, Ga, Mo, Ni, Pb, Sb and Zn (Akcil and Koldas, 2006). The hydrology of the strata and site is also critical, because water is the transport medium.

AMD has low pH (by definition) and generally high dissolved metal contents (Akcil and Koldas, 2006; Macías et al., 2012; Younger, 2000). Notably, in the context of this study, coal mine waters may have particularly high iron concentrations (Robins, 1990). Once the acidic products have been produced by sulphide oxidation, they (and other associated contaminants) may be absorbed by buffering minerals present in the surrounding rocks (resulting in neutralisation of the drainage) (Akcil and Koldas, 2006). The produced AMD and its products (if not consumed by surrounding buffering minerals) may flush from the system either rapidly or potentially long in the future (Akcil and Koldas, 2006; Younger and Robins, 2002).

Although AMD generation occurs naturally, anthropogenic activities like mining greatly accelerate the process because they expose large surfaces of sulphide minerals to air, water, and microorganisms (Akcil and Koldas, 2006). According to Akcil and Koldas (2006) the main factors determining rates of AMD generation in wastes are: the content of Fe sulphides in the waste; pH; temperature; the oxygen content of the gas phase (if water saturation is less than 100%); the oxygen concentration in the aqueous phase; degree of water saturation; chemical activity of  $\text{Fe}^{3+}$ ; the area of surfaces of exposed metal sulphides; the chemical activation energy required to initiate the processes involved (notably oxidation of pyrite,  $\text{FeS}_2$ ); and bacterial activity. These factors highly vary among deposits. Therefore, it is highly important to elucidate the processes that generate AMD and possible strategies to prevent or treat it (CSIR, 2009; Zduin, 2001). In some cases AMD is of minor importance when a mine is in active production, because water pumping keeps the water tables low, but it may become severe in closed and abandoned mines due to the rebound of water tables (Johnson and Hallberg, 2005). Nevertheless, substantial amounts of AMD are often left untreated because most treatment technologies are either inadequate or expensive (Diz, 1997).

Pakistan has enormous coal reserves (amounting to about 186 Bt) and its utilisation is increasing every day (Shoab, 2012, 2013). The Lakhra coal field (one of the major coal fields in Pakistan) has been focused in this study. Since significant damage to natural water resources by AMD from coal mining has been reported around the world, AMD problems in the Lakhra coal mining area of Pakistan are also anticipated and the WRs from Lakhra have been insufficiently characterised. Therefore, the study presented here had three main objectives: first, to characterise coal mining wastes obtained from the Lakhra coal field in Pakistan to characterise their mineralogical and chemical composition, second, to evaluate the AMD-generating potential of four selected coal mine WR deposits and third, to evaluate the leachability of major and trace elements from these wastes in aqueous conditions with respect to time and physicochemical conditions (e.g. pH).

## 2. Materials and methods

### 2.1. Materials

Samples were collected from four WR deposits near three underground coal mines (designated M1, M2 and M3) in Lakhra coal field, located 45 km NW of Hyderabad, Sindh province, Pakistan (Fig. 1). The mines extract coal from the Lakhra coal field, which is estimated to contain reserves amounting to 1.3 Bt and covers about 1309 km<sup>2</sup> (GoS, 2012). The quality of coal in the Lakhra field varies from lignite to sub-bituminous (GoS, 2012). The WR samples were designated (Table 1) WR1 and WR2 (collected from M1), WR3 (collected from M2) and WR4 (collected from M3). Each WR sample was composed of nine different sub-samples. WR1 was piled for about two or three months (therefore, weathering is assumed to have started), while the others were fresh, a few days to a few weeks old. For comparative analysis, samples of grey rock (GR) collected from a stratum above the WR strata and a coal sample from M1 were also included. Another WR sample (WR5) was collected from M1, at a different depth, a year later to assess possible depth-related variations in its composition.

### 2.2. Methods

#### 2.2.1. Mineralogical characterisation

Initially samples were crushed and milled to a particle size of <0.125 mm, then examined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer (with  $\text{CuK}\alpha$  radiation at 45 kV and 40 mA, and scanning range in Bragg–Brentano geometry from 5° to 90°).

#### 2.2.2. Scanning electron microscope (SEM)

The SEM analyses were carried out on WR samples using a FEI Magellan 400 XHR SEM. The thin sections were prepared by Vancouver Petrographics Ltd., Vancouver, BC Canada. The SEM was equipped with an INCA Energy 450 system with an X-MAX80 EDS detector. The detectors used were through-lens detector (TLD) and Everhart–Thornley detector (ETD). The operating voltages were set to 10 kV.

#### 2.2.3. Total element composition

The percentage of total solid content (TS, %) of WR samples was determined by using Eq. (1) after drying the sample in a laboratory oven at about 105 °C for 24 h ± 15 min.

$$\text{TS (\%)} = \frac{\text{wt}_a - \text{wt}_b}{\text{wt}_a} \times 100 \quad (1)$$

where TS is the total solid content in percent,  $\text{wt}_a$  is the weight of material in gramme before drying, and  $\text{wt}_b$  is the weight of material in gramme after drying.

In addition, the contents of 29 major elements (Si, Al, Ca, Fe, K, Mg, Mn, Na, P, Ti) and trace elements (As, Ba, Be, Cd, Co, Cr, Cu, Hg, Nb, Ni, Pb, S, Sc, Sr, V, W, Y, Zn, Zr) of the WRs were determined, by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES; (Martin et al., 1991) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Long and Martin, 1991) at a SWEDAC-accredited laboratory (ALS Scandinavia, Luleå, Sweden). The ICP-AES analyses were performed using a Perkin Elmer Optima DV 5300 instrument following US EPA Method 200.7 (modified). The ICP-MS analyses were performed using a Thermo Scientific Element instrument following US EPA Method 200.8 (modified). Briefly, the samples were digested with  $\text{HNO}_3$  after drying at 50 °C and analysed for As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn. All other elements were analysed after fusion with lithium methaborate ( $\text{LiBO}_2$ ) and subsequent dissolution in  $\text{HNO}_3$ .

The determination of chemical composition of WRs was also realised by X-ray fluorescence (XRF) method using Olympus DELTA Premium Handheld XRF analyser to assess variation in composition within each

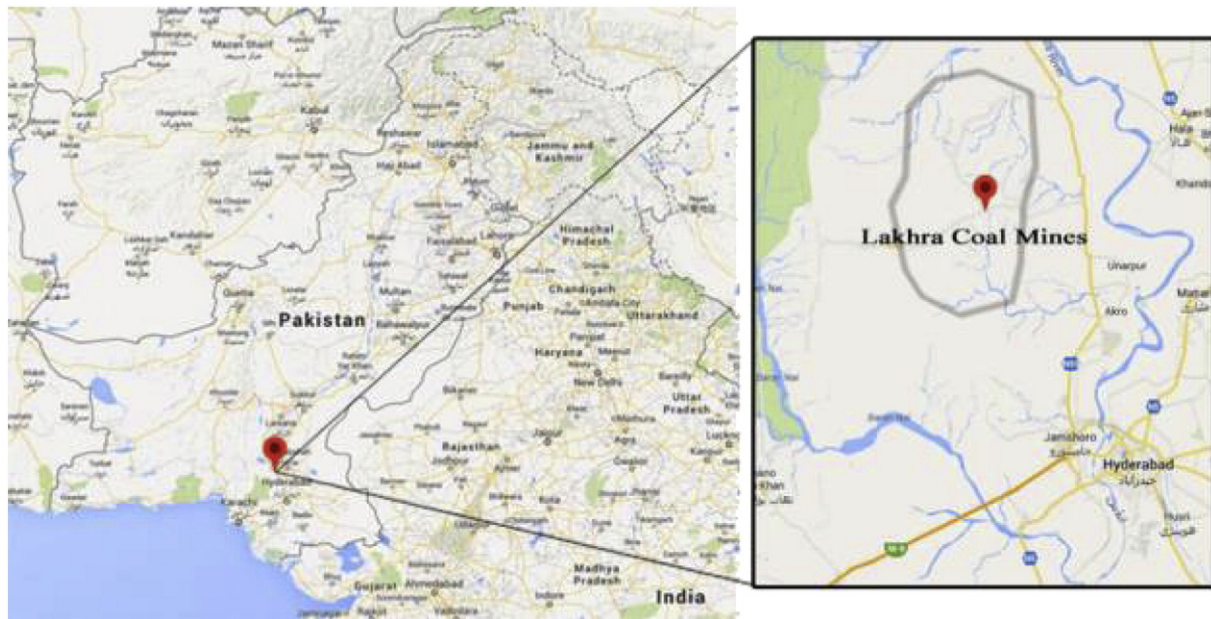


Fig. 1. Location of Lakhra Coal Field in Pakistan.  
Source: Google Maps.

WR deposit. ICP-AES and -MS analyses were performed on three sub-samples of each WR, whereas, XRF was performed on all WR samples.

#### 2.2.4. AMD-generating potential

2.2.4.1. *Static test (ABA)*. A modified procedure of the Swedish standard SS-EN 15875 (SIS, 2011) for acid base accounting analysis was applied to evaluate the WR samples' acidifying and neutralisation potentials.

WR samples ( $2.0 \pm 0.1$  g dry mass) of  $<0.125$  mm particle size were weighed into a 125 mL glass beaker. Deionised (MilliQ) water ( $90 \pm 0.5$  mL) was added and each suspension was stirred using a magnetic stirrer at room temperature for  $15 \pm 5$  min. The pH was then measured to check if it was  $>2-2.5$  (a criterion for the subsequent test protocol). Presumed amounts of 0.1 M HCl required to bring the pH to the 2–2.5 range were added, if necessary, and the samples were stirred again for  $22 \text{ h} \pm 15$  min, then the pH was re-measured. If the pH exceeded 2.5 a presumed amount of 0.1 M HCl required to bring the suspension to the target range was added and the samples were stirred for  $2 \text{ h} \pm 15$  min. Provided the pH was found to be within the required range, the sample was stirred again using a magnetic stirrer and simultaneously titrated with 0.1 M NaOH to reach a static pH of 8.3. The total volumes of HCl and NaOH added were noted and the acidifying and neutralisation potentials of the samples were calculated using Eqs. (2) and (3).

$$AP = 31.25 \times W_s \quad (2)$$

where AP is the acidifying potential of the sample in Kg  $\text{CaCO}_3$ /tonne and  $W_s$  is the weight of total sulphur as a mass fraction in percent.

$$NP = 50 \times \frac{C_A \times V_A - C_B \times V_B}{M_d} \quad (3)$$

where NP is the neutralisation potential of the sample in kg  $\text{CaCO}_3$ /tonne;  $C_A$  and  $C_B$  are the concentrations of HCl and NaOH used, respectively;  $V_A$  and  $V_B$  are the total volumes of HCl and NaOH added, respectively; and  $M_d$  is the dry mass of the test material in grammes.

The net neutralisation potential (NNP) was calculated by subtracting the AP value from the NP value. Materials with NNP values  $<-20$  kg  $\text{CaCO}_3$ /tonne and  $>20$  kg  $\text{CaCO}_3$ /tonne are usually regarding as acid-

producing and acid-consuming, respectively, and uncertain otherwise (Miller et al., 1991; SRK, 1989).

Another way to evaluate the AMD production potential from static test results is to determine the NP to AP ratio (neutralisation potential ratio, NPR). A material is typically considered non-acid producing if  $NP/AP > 2.5$ , uncertain if  $2.5 > NP/AP > 1$ , and acid-producing if  $NP/AP < 1$  (Adam et al., 1997).

2.2.4.2. *Kinetic test*. To evaluate the sulphide reactivity, oxidation kinetics, metal solubility and overall leaching behaviour of the sampled materials they were subjected to kinetic testing using weathering cells and procedures similar to those described by Cruz et al. (2001). The main advantage of this weathering test is its rapidity (test durations range from 20 to 25 weeks) and the small volume of material required (Villeneuve et al., 2003). In each test a sample of material (as collected), weighing approximately 70 g (dry weight), was placed in a Buchner funnel with a  $0.45 \mu\text{m}$  nylon filter and exposed to 28, 7-day, cycles (192 days) consisting of exposure to ambient air for 2 days, leaching on the third day, followed by a further 3 days of exposure to air and a further leaching on the seventh day. In the leachings  $70 \pm 2$  mL of deionised water was added to the funnel for 3 h, and then the leachate was recovered by applying slight suction to the filter vessel. The pH, redox potential (Eh), and conductivity of each leachate were determined. In addition, following storage in a laboratory freezer below  $-18^\circ\text{C}$ , their element contents were determined using equipment and procedures described above, additionally, modified procedures of

Table 1  
Details of the WR samples.

Sample designation	Number of sub-samples	Source	Characteristics
WR1	09	M1	Two to three months old
WR2	09	M1	Less than a week old
WR3	09	M2	Less than a week old
WR4	09	M3	Less than a week old
GR	09	M1	Less than a week old, sampled from a stratum above the WR1 strata
Coal		M1	Fresh (24 h)
WR5	09	M1	Fresh (24 h), sampled at different depth after 1 year



CSN EN ISO 10304-1 and CSN EN ISO 10304-2 for Cl, F and  $\text{SO}_4^{2-}$  and CSN EN 1484 for DOC at ALS Scandinavia, Luleå, Sweden.

**2.2.4.3. Geochemical modelling.** Geochemical modelling was applied to investigate the possibilities that metals may have precipitated or secondary minerals may have formed during the weathering tests, by calculating saturation indices (SIs) using the geochemical equilibrium model PHREEQC (Parkhurst and Appelo, 2013) and MINTEQA2 database (Allison et al., 1991). A SI indicates the thermodynamic tendency of a given mineral to precipitate or dissolve in an aqueous solution, and is given by:

$$\text{SI} = \log(\text{IAP}/K_s) \quad (4)$$

where IAP is the relevant ion activity product, calculated from data acquired for the water sample, and  $K_s$  is the theoretical solubility product (both adjusted to the temperature of the sample). A negative SI indicates that the solution is not saturated with respect to a particular solid phase and that the solid phase would tend to dissolve if present, while a positive value indicates a tendency for the mineral to precipitate. A value close to zero suggests that the mineral is in equilibrium in the solution and may either precipitate or dissolve.

### 3. Results

#### 3.1. Mineralogy

Pyrite, quartz, and kaolinite were the major constituent minerals detected by XRD in WR3 and WR4, while in WR1 the main mineral was arsenopyrite, with variable pyrite contents. However, WR2 lacked pyrite and quartz and the main constituent minerals were hematite and gypsum. Variable contents of other minerals such as calcite, gypsum, spangolite and birnessite were also observed in WR replicates ( $n = 3$ ), as shown in Table 2.

The minerals detected by XRD were also confirmed by SEM. SEM analyses for all WRs are shown in Fig. 2. In WR1, section a contains the kaolinite surrounded by Fe-species (arsenopyrite and pyrite) and section b purely contains a mixture of kaolinite, gypsum and calcite. WR2 contains Fe-species (hematite) surrounded by kaolinite, quartz and gypsum in section a, whereas, section b contains hematite mainly. Section a in WR3 contains pyrite as major constituting mineral with irregular settlement of quartz and kaolinite particles, whereas, pyrite is surrounded by quartz and kaolinite in section b. However, the situation is different in WR4 than other WRs where section a is composed of pyrite only and section b contains a mixture of other minerals such as kaolinite, quartz and gypsum. The homogenous plain surfaced area is rich in C, indicating coal content in WRs, with irregular occurrence of other minerals such as quartz, kaolinite and gypsum.

#### 3.2. Chemical composition

The dry contents of the WR samples ranged from 77 to 90% by weight (wt.%), and those of the GR and coal samples were similar, 93 wt.% and 76 wt.%, respectively. The major and trace element composition data (Table 3) showed that GR had 5–6 and 3–4 times higher Si and Al contents, respectively, than the WR samples, showing that

silicate minerals are more abundant in it. In addition, WR5 had higher Si and Al contents than the WR1–WR4 samples. In WR1, the Ca content was about three times higher than in all of the other samples, but very similar to the average continental crust (CC) content. Iron content ranged from 3 to 10 wt.% across the samples, being highest in WR3 followed by WR4 (5 wt.%). Titanium was only found in WR5 and GR samples (in the 1–2 wt.% range). Contents of the other major elements (K, Mg, Mn, Na, P and Ti) were quite low (0.1–0.9 wt.%) in all samples.

The S content was 2–5 orders of magnitude higher, in all of the samples, than contents of the other trace elements. The heavy metal analyses showed that As contents ranged from 0.1–8 mg/kg, being highest in WR1 followed by WR3 and WR4 (3.88 and 2.06 mg/kg, respectively). Cadmium concentrations were similar in all of the samples, and were similar to its concentration in continental crust (0.2 mg/kg).

The data from XRF analysis is shown in Table 4. The only considerable difference in chemical composition determined by ICP and XRF was observed in the concentrations of Al, As, Cd, Co, Hg, S, Sr, V and W in all WRs. Additionally, Fe was detected 4% supplementary by XRF than ICP in WR1. Arsenic was not detected by XRF in any WR sample. Cadmium concentrations were 221 mg/kg in WR1, 75 mg/kg in WR2, 217 mg/kg in WR3 and 192 mg/kg in WR4 more than ICP. Similarly, Co concentrations in WR1, 2, 3 and 4 were 282, 132, 360 and 278 mg/kg higher, respectively, in XRF than ICP. Mercury was not detected in WR1 and WR3, while its concentrations were 3 and 5 mg/kg higher in WR2 and WR4, respectively, than ICP. Sulphur was measured about 2 times higher in WR2–4 by ICP than XRF.

#### 3.3. Acid mine drainage potential

The acid base accounting analysis indicated that all the WRs 1–4 have strong acid-generating potential, but WR3 and WR4 have the highest potential, followed by WR1 and WR2 (Table 5).

#### 3.4. Kinetic leaching test

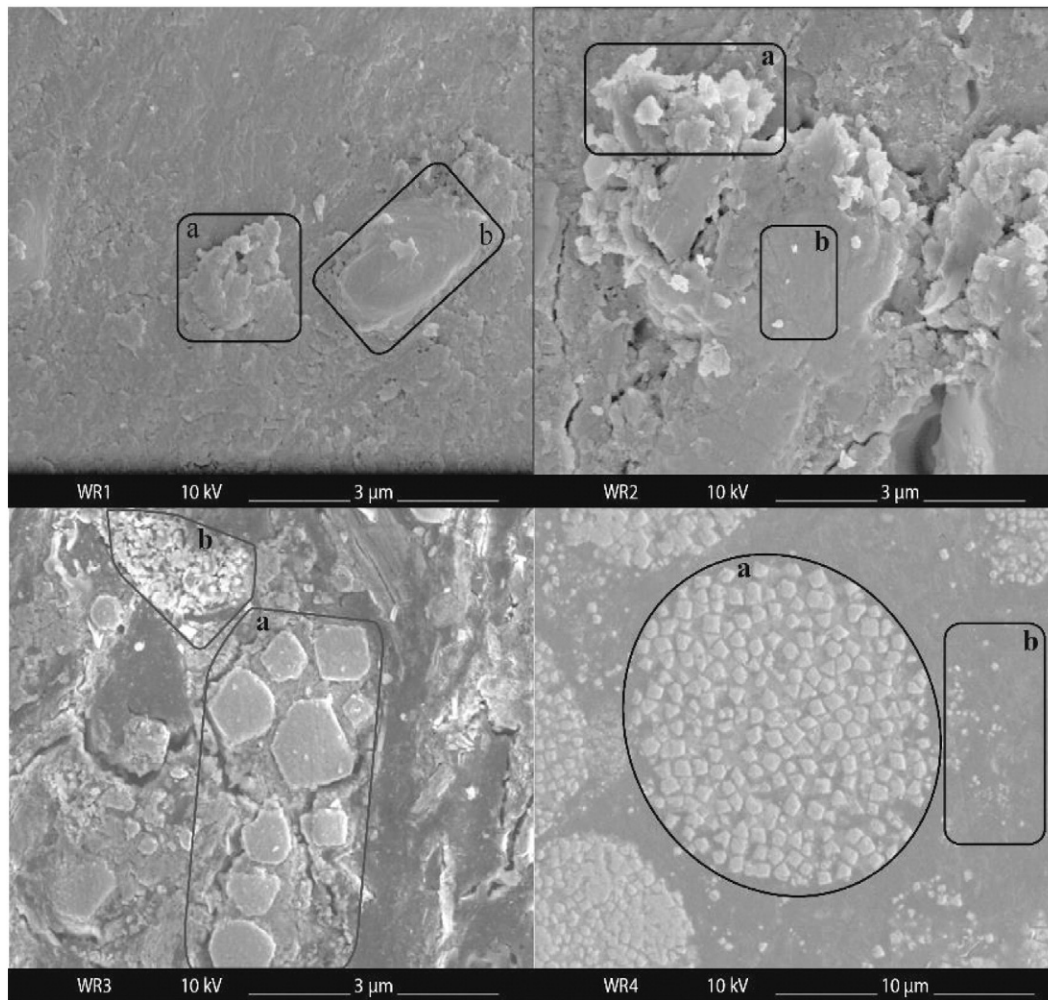
The minimum and maximum concentrations of selected elements in leachates obtained from the kinetic leaching tests with WR samples 1–4 are shown and compared with WHO (2011) drinking water standards in Table 6. The leaching patterns of selected elements are shown in Fig. 3.

##### 3.4.1. Waste rock 1

The pH of leachates from WR1 consistently ranged from 5.6 to 7.3, showing that this waste has a neutral nature. Their conductivity steadily decreased during the 28 cycles from 10 to 1.2 mS/cm. Aluminium and Cr were only leached at the start of the tests, and their concentrations subsequently remained below detection limits. Copper was strongly leached in the first cycle and its concentration subsequently remained below 1 µg/L except in the 16th (105 days) and final (28th, 192 days) cycles. In marked contrast, the Pb concentration was low in the first cycle (0.4 µg/L), and subsequently remained <0.2 µg/L (with no significant change) until the final (28th, 192 days) cycle where it rose to 3.16 µg/L. Arsenic concentrations remained consistently below 1 µg/L and Hg was not detected in leachates in any of the test cycles. Boron concentrations steadily decreased from 12 mg/L to 422 µg/L. Co concentrations also steadily declined except during the final cycle, when it

**Table 2**  
Mineralogy of WRs as determined by XRD.

WR1	WR2	WR3	WR4
Dominated by quartz ( $\text{SiO}_2$ ), arsenopyrite ( $\text{FeAsS}$ ) and kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), with variable amounts of pyrite ( $\text{Fe}_2\text{S}$ ), calcite ( $\text{CaCO}_3$ ), lime (CaO) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )	Dominated by kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), Hematite ( $\text{Fe}_2\text{O}_3$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), with variable amounts of quartz ( $\text{SiO}_2$ )	Dominated by pyrite ( $\text{FeS}_2$ ), quartz ( $\text{SiO}_2$ ) and kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), with variable amounts of malladerite ( $\text{Na}_2\text{SiF}_6$ ), spangolite ( $\text{Cu}_6\text{Al}(\text{SO}_4)(\text{OH})_{12}\text{Cl} \cdot 3(\text{H}_2\text{O})$ ), franklinite ( $\text{ZnFe}_2\text{O}_4$ )	Dominated by pyrite ( $\text{FeS}_2$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), quartz ( $\text{SiO}_2$ ) and $\text{TiO}_2$ , with variable amounts of birnessite ( $(\text{Na}_{0.3}\text{Ca}_{0.1}\text{K}_{0.1})(\text{Mn}^{4+}, \text{Mn}^{3+})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )



**Fig. 2.** SEM images with EDS analyses of WRs. WR1: a) kaolinite and arsenopyrite/pyrite, b) kaolinite, gypsum and calcite. WR2: a) hematite, kaolinite, quartz and gypsum, b) hematite. WR3: a) mainly pyrite with quartz and kaolinite, b) pyrite, quartz and kaolinite. WR4: a) pyrite, b) kaolinite, quartz and gypsum.

rose, but remained within the ranges 6.7–3050  $\mu\text{g/L}$  (respectively). Concentrations of manganese and  $\text{SO}_4^{2-}$  were higher, and highest in the 1st cycle. The manganese concentration was 59.5 mg/L in the 1st cycle, dropped to 10.9 mg/L in the 2nd cycle then remained in the range 1.9–8 mg/L, while the  $\text{SO}_4^{2-}$  concentration decreased from 8.6 g/L in the 1st cycle to 2.9 g/L in the 2nd cycle then steadily declined to 0.7 g/L. Zinc, Fe, Mg, Na and Cl concentrations gradually decreased, and only Ca concentrations gradually increased, by ca. 50 mg/L per cycle.

#### 3.4.2. Waste rock 2

This WR was mildly to strongly acidic in nature, yielding leachates with pH ranging from 2.7 (in the 8th cycle, 52 days) to 4.9. The electrical conductivity of the leachates gradually declined from 11.18 to 0.4 mS/cm, except in the 8th cycle (52 days) when it rose to 2 mS/cm before declining again. However, this sudden dip in pH and spike in EC did not influence the leachability of any elements except Al, Cu and Zn. The most abundantly leached major elements and their leachate concentrations (in mg/L) were Ca (31–372), Mg (15.9–1380), Na (0.6 to 801), Cl (3.1 to 1130) and S (in the form  $\text{SO}_4^{2-}$ , 189–7240), while the most abundantly leached trace elements and their leachate concentrations (in  $\mu\text{g/L}$ ) were Al (58.7–2715), B (244–23000), Co (37–1050), Mn (305–8125), Ni (36–951) and Zn (44–1030). Leachate concentrations of Fe and K were in the ranges 0.3–4 and 8–26 mg/L, respectively, while those of As, Cd, Cr, Cu and Pb were in the ranges 0.5–1, 0.07–3.36, 2.36–42, 1–34 and 0.2–7.5  $\mu\text{g/L}$ , respectively.

#### 3.4.3. Waste rock 3

WR3 was the most acidic in nature of the WRs, yielding leachates with pH ranging from 0.94 to 2.3 throughout the test, and electrical conductivity declining from 58.2 to 3.5 mS/cm. The strong acidity of the leachates was reflected in high concentrations of all the major elements, which ranged for Ca, Fe, K, Mg, Na, Cl, and  $\text{SO}_4^{2-}$  from 2.6 to 469, 391 to 36,450, 1.25 to 20, 0.6 to 1255, 0.6 to 928, 2.3 to 524 and 985 to 101,940 mg/L, respectively. Among the trace elements, Al leached extremely strongly (concentrations declining from 1.5 g/L to 5.6 mg/L), while concentrations of Mn, Zn, Ni, Co, B, Cr, Cu, As, Cd and Pd ranged from ( $\mu\text{g/L}$  to mg/L) 355 to 54.4, 139 to 45.2, 133 to 33.1, 157 to 32.4, 280 to 15.8, 92 to 6.6, 89 to 2.6, 3 to 1, 0.6 to 233  $\mu\text{g/L}$  and 4 to 130  $\mu\text{g/L}$ , respectively. Mercury was not detected in any of the leachates.

#### 3.4.4. Waste rock 4

Like WR3, WR4 yielded leachates with extremely low pH (1.2 to 2.5) and high loads of major and trace elements, including environmentally detrimental metals (e.g. B, Co, Cu, Ni and Zn). Concentrations of the major elements Fe,  $\text{SO}_4^{2-}$ , Ca, K, Mg, Na and Cl ranged from 221 mg/L to 17.9 g/L, 548 mg/L to 91 g/L, 4.11 to 404, 0.7 to 13.7, 0.5 to 695.5, 0.7 to 336 and 1.5 to 136.5 mg/L, respectively. Of the trace elements Al leached most abundantly (concentrations ranging from 7.3 mg/L to 1.3 g/L), followed by Mn, Zn, Co, Ni, Cu, B and Cr, at concentrations ranging from 319  $\mu\text{g}$  to 75.7 mg, 148  $\mu\text{g}$  to 74.3 mg, 105  $\mu\text{g}$  to 57.7 mg, 182  $\mu\text{g}$

**Table 3**

Major and trace element composition of the samples from ICP-MS and -AES analyses.

ELEMENT	WR1 <sup>a</sup>	WR2 <sup>a</sup>	WR3 <sup>a</sup>	WR4 <sup>a</sup>	WR5 <sup>a</sup>	GR <sup>a</sup>	Coal <sup>a</sup>	CC <sup>b</sup>
Dry weight (%)	90.53 ± 5.38	77.33 ± 0.12	83.93 ± 0.23	80.73 ± 2.39	85.47 ± 2.54	93.67 ± 0.58	76.77 ± 0.15	<i>n.d.</i>
Si (% dw)	8.33 ± 5.79	11.14 ± 2.04	9.54 ± 3.97	12.47 ± 1.94	31.37 ± 3.59	44.4 ± 1.91	1.31 ± 1.1	27.72
Al (% dw)	6.84 ± 4.7	9.24 ± 1.72	6.26 ± 2.35	9.35 ± 1.13	20.03 ± 0.91	27.87 ± 0.92	0.84 ± 0.72	8.13
Ca (% dw)	3.69 ± 5.64	0.44 ± 0.1	0.36 ± 0.06	0.33 ± 0.03	0.45 ± 0.06	0.2 ± 0	0.75 ± 0.07	3.63
Fe (% dw)	3.9 ± 4.26	1.57 ± 0.42	10.07 ± 3.88	5.63 ± 2.91	3.21 ± 0.74	2.65 ± 0.1	1.61 ± 0.58	5
K (% dw)	0.4 ± 0.25	0.41 ± 0.11	0.33 ± 0.16	0.35 ± 0.03	0.81 ± 0.03	1.27 ± 0.07	0.1 ± 0	2.59
Mg (% dw)	0.51 ± 0.09	0.54 ± 0.01	0.28 ± 0.04	0.26 ± 0.01	0.88 ± 0.01	0.94 ± 0.06	0.56 ± 0.17	2.09
Mn (% dw)	0.05 ± 0.07	0 ± 0	0.01 ± 0	0.02 ± 0.01	0.01 ± 0	0.01 ± 0	0 ± 0	0.095
Na (% dw)	0.16 ± 0.09	0.21 ± 0.04	0.21 ± 0.02	0.14 ± 0.01	0.25 ± 0.01	0.23 ± 0.02	0.28 ± 0.01	2.83
P (% dw)	0.02 ± 0.01	0.02 ± 0	0.02 ± 0.01	0.03 ± 0	0.09 ± 0.01	0.11 ± 0	0.01 ± 0	0.11
Ti (% dw)	0.41 ± 0.31	0.57 ± 0.13	0.69 ± 0.34	0.87 ± 0.19	1.35 ± 0.12	1.96 ± 0.08	0.04 ± 0.03	0.44
LOI (% dw)	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	38.63 ± 4.21	15.83 ± 0.45	90.4 ± 4.04	<i>n.d.</i>
As (mg/kg dw)	8.15 ± 8.13	0.3 ± 0.08	3.88 ± 0.73	2.06 ± 0.41	0.29 ± 0.07	0.29 ± 0.12	0.1 ± 0	1.8
Ba (mg/kg dw)	98.53 ± 61.46	123 ± 22	83.33 ± 36.15	101 ± 18	165 ± 13	227 ± 10	19.11 ± 12	425
Be (mg/kg dw)	2.3 ± 1.48	3.48 ± 0.42	1.84 ± 0.32	2.01 ± 0.78	3.39 ± 0.21	2.89 ± 0.26	2.06 ± 1.01	2.8
Cd (mg/kg dw)	0.3 ± 0.04	0.22 ± 0.07	0.25 ± 0.12	0.45 ± 0.37	0.24 ± 0.02	0.29 ± 0.11	0.05 ± 0.06	0.2
Co (mg/kg dw)	40.23 ± 26.07	15.43 ± 4.55	43.5 ± 21.88	75.37 ± 35.54	24.47 ± 4.76	15 ± 6.24	5.88 ± 1.95	25
Cr (mg/kg dw)	67.63 ± 52.6	111 ± 20	101 ± 37	102 ± 38	133 ± 16	164 ± 12	12.37 ± 4.1	100
Cu (mg/kg dw)	73.43 ± 53.26	101 ± 30	24.97 ± 2.04	68.13 ± 24.55	90 ± 13.43	66.77 ± 12.81	11.46 ± 3.67	55
Hg (mg/kg dw)	0.22 ± 0.07	0.14 ± 0.02	0.1 ± 0.02	0.12 ± 0.05	0.1 ± 0.02	0.05 ± 0.01	0.09 ± 0.02	0.08
Nb (mg/kg dw)	14.6 ± 9.41	21.2 ± 4.19	21 ± 9.36	24.67 ± 6.5	28.07 ± 5.52	45.67 ± 1.19	5 ± 0	20
Ni (mg/kg dw)	87.83 ± 38.94	50.27 ± 14.26	61.1 ± 30.57	107 ± 28	40.17 ± 5.12	33.93 ± 13.25	8.55 ± 3.65	75
Pb (mg/kg dw)	14.54 ± 9.14	20.27 ± 5.02	8.88 ± 3.57	13.01 ± 3.69	12.63 ± 0.8	16.53 ± 5.8	1.45 ± 0.82	13
S (mg/kg dw)	107933 ± 120564	19400 ± 1473	113300 ± 47345	74433 ± 6757	21667 ± 2495	5503 ± 1821	31733 ± 8071	260
Sc (mg/kg dw)	18.23 ± 9.9	27.5 ± 1.01	12.47 ± 2.67	19.3 ± 3.95	25.4 ± 4.25	26.47 ± 1.26	1.95 ± 0.84	22
Sr (mg/kg dw)	302 ± 103	241 ± 10	126 ± 18	167 ± 34	238 ± 7	254 ± 11	160 ± 89	375
V (mg/kg dw)	178 ± 139	256 ± 38	139 ± 47	153 ± 38	259 ± 40	203 ± 7	12.03 ± 7.46	135
W (mg/kg dw)	1.18 ± 0.14	1.11 ± 0.18	1.03 ± 0.33	1.09 ± 0.25	1.72 ± 0.18	2.21 ± 0.1	0.4 ± 0	1.5
Y (mg/kg dw)	31.37 ± 12.72	41.97 ± 1.35	20.87 ± 3.07	30.17 ± 13.66	38.53 ± 2.44	35.17 ± 0.49	8.99 ± 6.25	33
Zn (mg/kg dw)	70.6 ± 7.6	50.1 ± 3.9	49.67 ± 15.15	105 ± 109	48.63 ± 7.05	48.1 ± 15.02	10.28 ± 8.47	70
Zr (mg/kg dw)	75.03 ± 56.56	119.7 ± 22	135 ± 50	135 ± 33	163 ± 30	215 ± 10	6.11 ± 4.95	165

dw = dry weight, *n.d.* = not determined.<sup>a</sup> Mean ± standard deviation (n = 3).<sup>b</sup> Continental crust after Krauskopf and Bird (1995).

to 57.1 mg, 137 µg to 26.7 mg, 186 µg to 10.5 mg and 247 µg to 4.4 mg per litre, respectively. The concentrations of As (1–708 µg/L), Cd (3.3–327 µg/L) and Pb (1.4–20 µg/L) were lower than those of the other measured elements. Mercury was only the monitored element that remained below the detection limit throughout the test.

### 3.5. Geochemical modelling

Patterns of saturation indices obtained from geochemical modelling based on the physicochemical analyses of the kinetic test leachates are shown in Fig. 4. The results show that most considered mineral phases

**Table 4**

Major and trace element composition of the samples from XRF analyses.

ELEMENT	WR1 <sup>a</sup>	WR2 <sup>a</sup>	WR3 <sup>a</sup>	WR4 <sup>a</sup>	GR <sup>a</sup>
Al (%)	0.88 ± 0.05	0.58 ± 0	0.55 ± 0	0.68 ± 0	1.38 ± 0
Ca (%)	4.79 ± 0.05	0.5 ± 0	0.28 ± 0	0.23 ± 0	0.17 ± 0
Fe (%)	7.42 ± 0.02	1.44 ± 0	8.26 ± 0.02	6.24 ± 0.01	1.59 ± 0
K (%)	0.55 ± 0.01	0.59 ± 0	0.46 ± 0.01	0.48 ± 0.01	1.8 ± 0.01
Mg (%)	0.55 ± 0.23	0.65 ± 0.27	0.8 ± 0.33	0.95 ± 0.33	0.78 ± 0.32
Mn (%)	0.06 ± 0	0.01 ± 0	0.01 ± 0	0.02 ± 0	0.01 ± 0
P (%)	1.7 ± 0.36	<i>n.d.</i>	0.42 ± 0.12	<i>n.d.</i>	0.01 ± 0
Si (%)	2.04 ± 0.02	1.53 ± 0.02	1.37 ± 0.02	1.69 ± 0.02	3.82 ± 0.03
Ti (%)	0.38 ± 0	0.43 ± 0	0.52 ± 0.01	0.66 ± 0.01	0.87 ± 0.01
As (mg/kg)	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	2.4 ± 1
Cd (mg/kg)	221.83 ± 8.86	76.05 ± 5	217.11 ± 7.33	192.88 ± 7.22	183.5 ± 6
Co (mg/kg)	322.32 ± 35.09	153.56 ± 20.79	404.24 ± 38.73	353.89 ± 34.69	149.27 ± 23.53
Cr (mg/kg)	94.62 ± 14.53	112.59 ± 13.79	121.19 ± 15.79	172.83 ± 22.18	201.33 ± 24.29
Cu (mg/kg)	76.77 ± 5.1	82.5 ± 4.87	41.66 ± 4.38	78.17 ± 4.61	72.38 ± 4.5
Hg (mg/kg)	<i>n.d.</i>	3 ± 1.2	<i>n.d.</i>	5.7 ± 1.8	4.7 ± 1.3
Ni (mg/kg)	56.33 ± 9.66	46.31 ± 5.83	60.55 ± 9.77	85.12 ± 9.86	108.03 ± 8.96
Pb (mg/kg)	18.96 ± 2.29	22.97 ± 2.29	7.95 ± 2.14	12.18 ± 1.99	45.51 ± 2.82
S (mg/kg)	100617.05 ± 1481.55	9083.27 ± 202.83	59178.94 ± 770.44	32393.94 ± 523	2804.5 ± 104.66
Sr (mg/kg)	185.3 ± 3.15	171.25 ± 2.08	110.47 ± 1.93	148.61 ± 2.63	245.5 ± 3
V (mg/kg)	210.82 ± 32.58	284.5 ± 36.58	198.46 ± 36.95	261.65 ± 38.61	378.51 ± 50.59
W (mg/kg)	37.6 ± 5.13	15.3 ± 2.91	25.33 ± 5	35.73 ± 5.75	23.5 ± 4
Y (mg/kg)	17.06 ± 0.92	29.46 ± 0.82	11.67 ± 0.85	27.46 ± 1.13	34.1 ± 1.1
Zn (mg/kg)	72.95 ± 3.65	61.77 ± 3.04	64.44 ± 3.38	130.2 ± 4.38	98.88 ± 4.16
Zr (mg/kg)	77.52 ± 1.77	112.89 ± 1.62	117.97 ± 2.48	170.71 ± 2.96	250.37 ± 2.44

*n.d.* = not detected.<sup>a</sup> Mean ± standard deviation (n = 9).

**Table 5**  
AMD generation potential of the WRs (mean  $\pm$  standard deviation, n = 3).

Measured as kg CaCO <sub>3</sub> /tonne (except NPR)	WR1	WR2	WR3	WR4
AP	123 $\pm$ 93	61 $\pm$ 5	354 $\pm$ 148	245 $\pm$ 4
NP	-21 $\pm$ 19	-9 $\pm$ 3	-138 $\pm$ 30	-107 $\pm$ 1
NPR	-0.15 $\pm$ 0.03	-0.15 $\pm$ 0.05	-0.42 $\pm$ 0.11	-0.43 $\pm$ 0.01
NNP	-144 $\pm$ 112	-70 $\pm$ 6	-492 $\pm$ 178	-352 $\pm$ 5

were not likely to precipitate. Diaspore (AlOOH), goethite (FeOOH) and hematite (Fe<sub>2</sub>O<sub>3</sub>) were likely to dissolve in WR2, WR3 and WR4 leachates, but precipitate in WR1 leachates. Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) was likely to precipitate in WR3 and WR4 leachates obtained on the 7th day of the tests, but dissolve in all of the other leachates. Similarly, gibbsite (Al(OH)<sub>3</sub>) was likely to precipitate in WR1 leachates from the 7th day of the tests, but dissolve in all of the other leachates.

#### 4. Discussion

The metals in mining waste are usually associated with inorganic constituents due to the dominance of silicate and sulphide minerals (Sahoo et al., 2014). Similarly, in coal certain trace elements such as Zn, As, Cu, Pb, and possibly Se, are probably associated with sulphides, sulphates, and selenides (Dai et al., 2006; Hower et al., 2008; Riley et al., 2012; Seredin et al., 2013). However, coal is a complex substance, within which Cr may be associated with clay minerals (Hower et al., 1990, 2000; Hower and Bland, 1989; Zubovic, 1976, 1966) and organic matter (Dai et al., 2008). Mercury and As are mainly connected with pyrite or other sulphide species (Hower et al., 2008), although As may also be associated with clay minerals (Dai et al., 2012; Diehl et al., 2004, 2012; Kolker, 2012; Swaine, 1990). Similar associations are likely to be present in WR from coal mining.

According to the mineralogical characterisation, the WRs examined here were rich in pyrite (the main acid generator), hematite, quartz, calcite, lime, gypsum and kaolinite, in accordance with findings for coal mining wastes in South Africa (Bell et al., 2001; Equeenuddin et al., 2010). All of these minerals may make important contributions to the self-neutralisation potential of WRs. In addition, in WR1 As is bound to pyrite in arsenopyrite, as previously observed in a Kentucky coal (Hower et al., 2008). However, they may also participate in weathering

reactions, depending on the pH. Notably, sulphate minerals may participate in acid generation (Nordstrom, 1982), especially Fe<sup>II</sup> or Fe<sup>III</sup> sulphates, which hydrolyse Fe upon dissolution to form Fe(OH)<sub>3</sub> (Jennings et al., 2000).

The ABA tests showed that the WRs have strong acid generation potential, especially WR3 and WR4. However, WR1 and WR2 have mild to strongly acidic nature.

Significant portion of the metals, metalloids and other elements released during the process of sulphide oxidation are retained in wastes as secondary mineral precipitates (Lin, 1997; Lin and Herbert, 1997). The secondary minerals formed during the weathering of sulphides are relatively insoluble in natural waters and their precipitation and re-dissolution controls the pH and chemical composition of leachates (Lottermoser, 2007).

Leachates yielded by WR3 and WR4 had extremely low pH, in accordance with the ABA test results. Elements leached more strongly from WR3 and WR4 than from WRs 1 and 2, especially Fe, Al, some trace elements (As and Ni) and heavy metals (Cd, Co, Cr, Cu and Pb). The high concentrations together with saturation indices computed by PHREEQC indicate strong oxidation of sulphide-bearing minerals (especially pyrite). However, high Al concentrations were detected in leachates from WRs 2–4, which can be attributed to minerals (detected in mineralogy of WRs) including kaolinite (Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>) and spangolite (Cu<sub>6</sub>Al(SO<sub>4</sub>)(OH)<sub>12</sub>Cl·3(H<sub>2</sub>O)) and undersaturated conditions (in geochemical modelling) for Diaspore (AlOOH) and gibbsite (Al(OH)<sub>3</sub>). The dissolution of Al- and Fe-bearing minerals may generate Al<sup>3+</sup> and Fe<sup>3+</sup> which, upon raising pH conditions from acidic, may precipitate as gibbsite and ferrihydrite, respectively, and exacerbate acidity (Deutsch, 1997).

WR2 behaved differently from the other WRs in that its leachates from the kinetic tests varied from mildly to strongly acidic (Table 6). However, an unexpected dip in its pH and rise in EC was observed in the 8th cycle (52 days), accompanied by increases in concentrations of Al, Fe, Cu and Zn, together with minor reduction in Ca concentration (Fig. 3F). Since the Fe/S ratio also increased (Fig. 3N), these shifts may have been due to high reactivity of sulphide minerals, resulting in the pH reductions, that does not allow minerals to precipitate (as show in Fig. 4) and causes remobilisation of Al and Fe.

The near-neutral pH, relatively low Fe concentration, and relatively high concentrations of Ca and SO<sub>4</sub><sup>2-</sup> of leachates from WR1 indicate that it contains abundant available neutralising species. Their high Ca

**Table 6**  
Concentrations of selected elements in leachates from WRs 1–4 in the kinetic leaching tests compared to WHO (2011) drinking water standards.

	WR1	WR2	WR3	WR4	WHO
	Min–max	Min–max	Min–max	Min–max	
Al (µg/L)	2–1145	58.7–2715	5600–1,525,000	7285–1,310,000	900
As (µg/L)	0.5–1	0.5–1	2.9–1009.5	1.08–708	10
B (µg/L)	422–12,250	244–23,000	280–15,750	186–10,450	2400
Cd (µg/L)	0.05–6.9	0.07–3.36	0.6–233	3.25–327.5	3
Co (µg/L)	6.7–3050	37.35–1050	157–32,350	105–57,700	Not specified
Cr (µg/L)	0.5–1.3	2.36–42	92.5–6590	247.5–4425	50
Cu (µg/L)	1–17.3	1–34.4	89.3–2640	137–26,750	2000
Mn (µg/L)	1,980–59,550	305–8125	355–54,350	319–75,700	400 <sup>P</sup>
Ni (µg/L)	6.36–3040	36.2–951.5	133–33,050	182–57,150	70
Pb (µg/L)	0.2–3.16	0.2–7.5	4–130	1.41–20	10
Zn (µg/L)	6.87–2500	44.3–1030	139–45,150	148–74,350	10–50
Ca (mg/L)	346–513	31.85–372	2.68–469.5	4.11–404	Not specified
Fe (mg/L)	0.004–140	0.3–4.8	391.5–36,450	221–17,900	0.5–50
K (mg/L)	6.7–32.4	8.83–26.8	1.25–20	0.7–13.7	Not specified
Mg (mg/L)	9.14–1370	15.9–1380	0.6–1255	0.5–695.5	Not specified
Na (mg/L)	2.27–556	0.6–801	0.6–928	0.7–336	<20
Cl (mg/L)	3.88–1030	3.1–1130	2.3–524.5	1.5–136.5	5
SO <sub>4</sub> <sup>2-</sup> (mg/L)	777–8625	189–7,240	985–101,940	548–91,510	500 <sup>P</sup>
pH	5.6–7.3	2.7–4.9	0.945–2.3	1.2–2.5	Not specified
EC (mS/cm)	1.2–10	0.4–11.18	3.5–58.2	1.8–34.85	Not specified

<sup>P</sup> Preliminary.



and S contents (Table 3) can be attributed to the presence of calcite, lime and gypsum (Table 2), and their low concentrations of metals (except Mn) indicate that sulphide dissolution was very slow in WR1 (Table 6). The secondary sulphate minerals in coal are usually hydrous Ca, Mn, Na, and K sulphates, but hydrous metal sulphates with divalent cations ( $Me^{2+} \cdot SO_4 \cdot nH_2O$ ) may also be present (Jambor et al., 2000a, 2000b). These hydrous metal sulphates can re-dissolve in water and release ions back into solution (Lottermoser, 2007). Therefore, the anomalously high concentrations of Mn in the leachates can be

attributed to the dissolution of secondary minerals (Lottermoser, 2007) such as Pyrochroite ( $Mn(OH)_2$ ), Manganite ( $MnOOH$ ),  $MnSO_4$ , Bixbyite ( $Mn_2O_3$ ), Hausmannite ( $Mn_3O_4$ ) and Birnessite ( $MnO_2$ ).

The ABA results showed that WR1 has strong acid generation potential. The neutral nature of WR1 is presumably dependant on the content of Ca-bearing species and pH conditions of the aqueous solution with which it reacts. When the available calcite is exhausted, the pH will drop and concentrations will increase due to sulphide oxidation. Since acid is used to simulate acid-producing reactions in the ABA test,

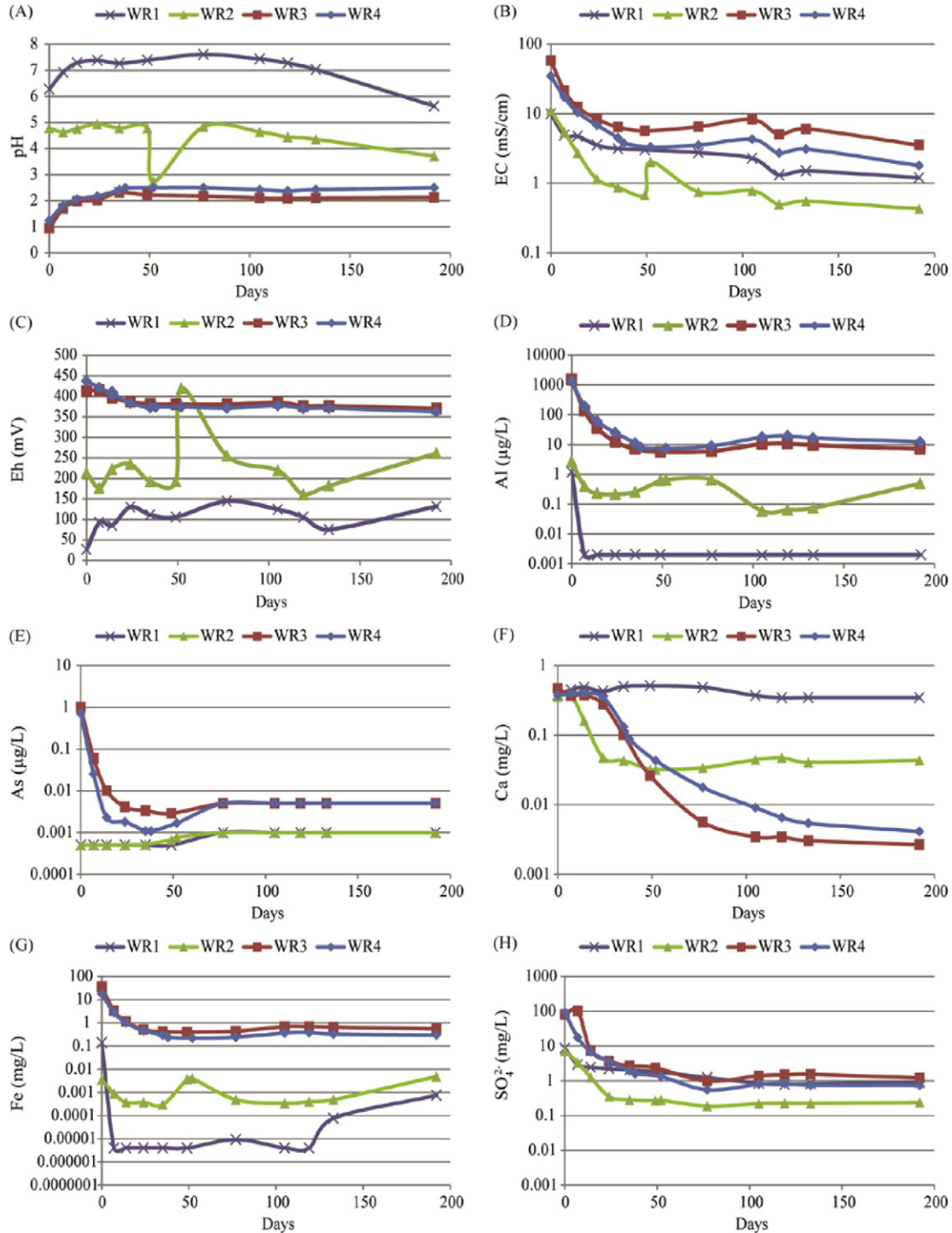


Fig. 3. Physicochemical characteristics of leachates obtained in the kinetic tests: (A) pH; (B) EC; (C) Eh; concentrations of (D) Al, (E) As, (F) Ca, (G) Fe, (H)  $SO_4^{2-}$ , (I) Cu, (J) Cd, (K) Mn, (L) Ni, (M) Zn; and (N) Fe to S ratio.



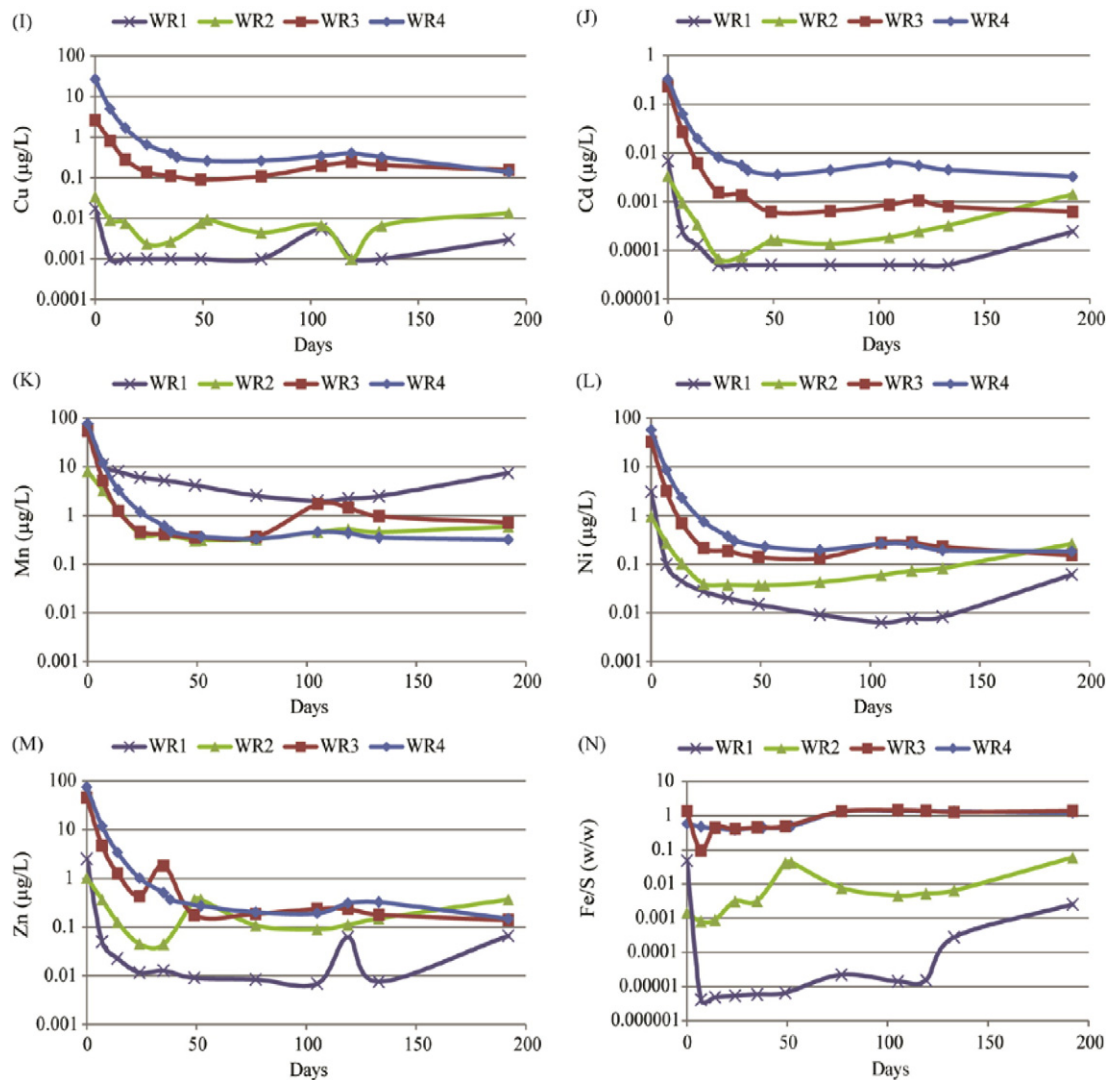


Fig. 3 (continued).

therefore the test results may have been over-estimated than the actual case. However, decreasing pattern of pH and increasing concentration of Fe indicate that the available neutralising species (such as Ca) are exhausting with time and failing to neutralise acidity. Another contributor to the relatively low reactivity of WR1 may be the formation of Fe-oxihydroxy precipitates (Goethite) on the mineral surfaces due to the presence of dissolved Fe and close to neutral pH (Cruz et al., 2001). Precipitation of Goethite along with Hematite, Diaspore and Magnesioferrite suggested by PHREEQC in WR1 has significantly influenced the chemical composition of leachates by binding elements and keeping pH conditions near neutral.

## 5. Conclusions

Mining WRs from the Lakhra coal field were characterised and their element leachability (reflecting their potential impact on natural water resources) was studied. Chemical characterisation showed that the WRs had high Si, Al and Fe contents, ranging from 8 to 12, 6 to 9 and 3 to 6 wt.%, respectively, and sulphur contents ranging from 74 to 107 g/kg. Contents of the trace elements As, Cd, Co, Cr, Cu, Pb and Zn were in the ranges of 0.3–8, 0.2–0.4, 15–75, 67–111, 73–101, 8–20 and 49–105 mg/kg, respectively. NNP values obtained (–70 to –492 kg CaCO<sub>3</sub>/tonne) indicate that all of the WRs have strong AMD-generation potential. In kinetic tests, the pH of leachates obtained

from WR1 was close to neutral, indicating that the lime and neutralising agents were abundantly available to consume the acids generated by oxidation, that slowly exhaust as shown by decreasing pH pattern. Additionally, the precipitation of Goethite, Hematite, Diaspore and Magnesioferrite in WR1 consumed acidity and controlled trace element mobility. However, leachates from WR2, WR3 and WR4 had significant concentrations of both major and trace elements with acidic pH and constantly undersaturated conditions for all selected minerals. Interestingly, in leachates from WR2 the pH dipped and the Fe/S ratio rose in the 8th (52 days) cycle, probably due to an increase in sulphide oxidation that was clearly observed with decrease in saturation levels of almost all minerals in geochemical modelling of leachates. Overall, the results clearly show that the WRs have significant AMD-generation potential and may significantly impair the quality of natural waters by leaching excessive quantities of major and trace elements compared to WHO drinking water standards.

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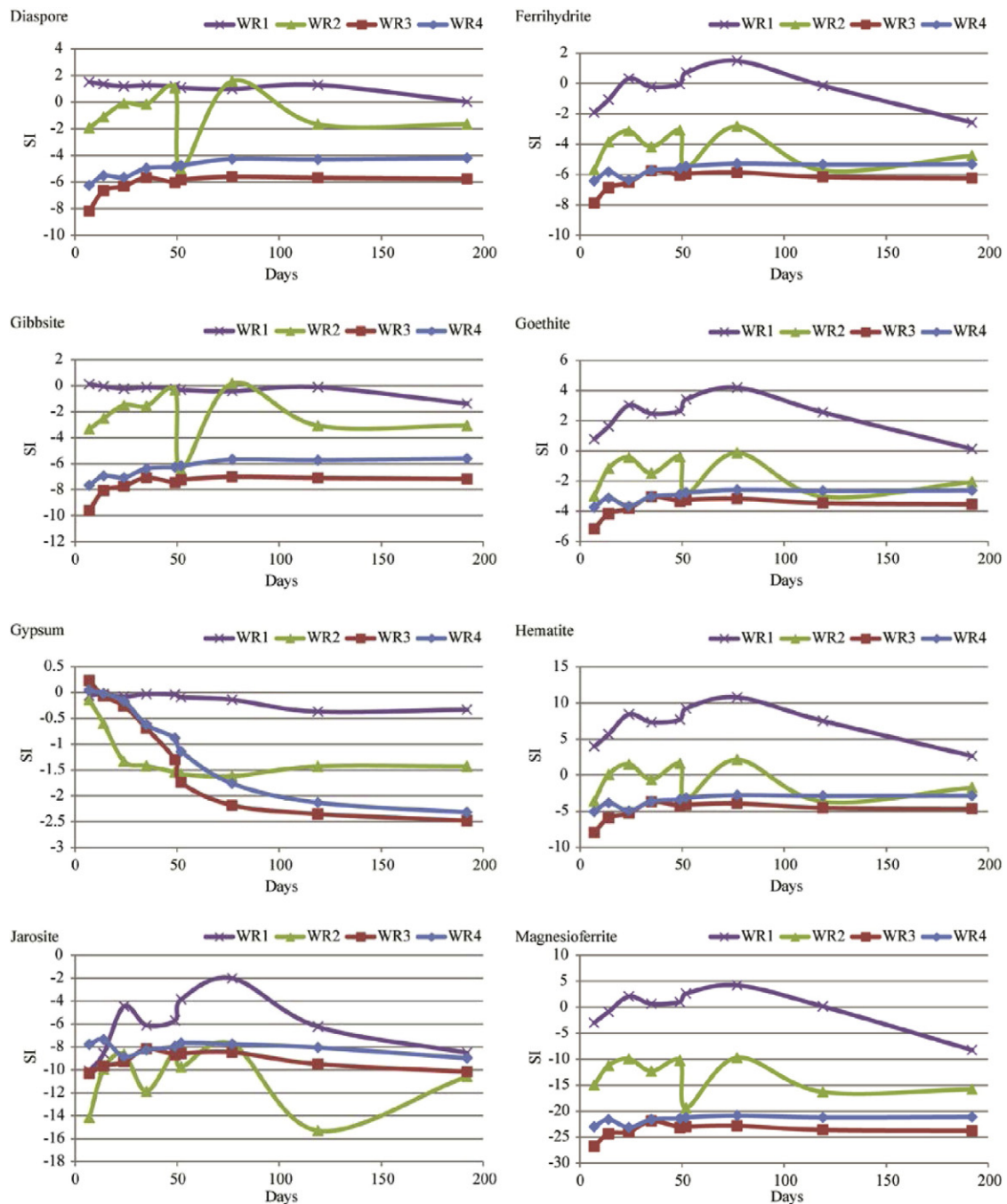


Fig. 4. Saturation Index (SI) of selected minerals as computed by PHREEQC based on the physicochemical analyses of the kinetic test leachates.

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