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Environmental characterization of Sarcheshmeh Cu-smelting slag, Kerman, Iran: Application of geochemistry, mineralogy and single extraction methods

Mehdi Khorasanipour [a,*], Esmat Esmaeilzadeh [b]

[a] Department of Geology, Faculty of Sciences, Shahid Bahonar University of Kerman, Kerman, Iran
[b] Research and Development Division, Sarcheshmeh Copper Complex, Kerman, Iran

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ABSTRACT

Annually, more than 370,000 tons of slag waste is produced in Sarcheshmeh Copper Complex, the biggest Cu-producer in Iran. Geochemical, mineralogical and single extraction methods were used in order to evaluate the contamination potential of metal(loid)s associated with Sarcheshmeh smelting slags. Results showed that, like the other non-ferrous or base metal slags, Sarcheshmeh slags are considered as one of the metalliferous smelting wastes with the multi-elemental contamination potential of most of the potentially toxic elements. Mineralogical studies revealed that the mineral assemblage of the investigated samples is controlled by at least three main factors, including: (1) primary mineralogy of the ore concentrate (chalcocite, chalcopyrite, covellite ± pyrite); (2) smelting process (magnetite, fayalite, pyroxene); and (3) weathering reactions in arid to semiarid climate conditions [thenardite (Na_2SO_4), bonattite ($CuSO_4 \cdot 3H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$)]. Results obtained from the U.S. EPA toxicity characteristic leaching procedure (TCLP) and water soluble tests revealed that the order of leachability of target elements from the most to the least in the slag samples is as S ≫ Cu > > Zn > Fe > Mo > Pb > Ni > Mn > Co > As > Se > Sb > Cd > Cr = Sn = Ag = Bi. The maximum contamination potential, higher than the considered toxicity regulatory levels (one-hundred times the U.S. EPA maximum contamination level in drinking water), of As (9.35 mg/L), Mo (186.7 mg/L), Sb (3.50 mg/L) and Se (6.12 mg/L) was observed in the alkaline leached solutions (pH 9.67) of the sediments associated with the slag dump drainages, while the maximum concentrations of the other investigated elements such as Cu, Co, Cd, Fe, and Zn were measured in the acidic (pH < 5) leached solutions. Annually, about 18.7% of Sarcheshmeh reverberatory slags are used for other purposes such as sandblasting. Wind blowing slag particles, produced from the grinding and sieving facilities, are responsible for the enrichment of elements such as As, Cu, Mo, Pb, Sb, Sn, Zn, Cr, S and Fe in the topsoils around the slag preparation site. Based on the acid acetic (0.43 mol/L) and EDTA (0.05 mol/L) leaching tests, the solubility and thus the bioavailability of these potentially toxic elements also were increased in the surface contaminated soils, a subject that is very important from environmental point of view. Obtained results also emphasize on the need for the greater caution in the slag waste management.

1. Introduction

From the environmental point of view, pyrometallurgical slags are undesirable materials that must be considered as one of the anthropogenic threats to the natural environments due to the presence of high amounts of potentially toxic trace elements (metals and metalloids) such as Ag, As, Ba, Cd, Cu, Pb, Sb and Zn (Parsons et al., 2001; Ettler et al., 2005; Costagliola et al., 2008; Scheinert et al., 2009; Piatak and Seal, 2010; Kierczak et al., 2013; Lima and Bernardez, 2013; Dung et al., 2014; Jin et al., 2014; Potysz et al., 2015; Piatak et al., 2015). Several studies have investigated the role of slag particles in the soil (Sobanska et al., 2000; Sterckeman et al., 2000; Ettler, 2016), air (Sobanska et al., 1999) and river sediment contamination (Isaure et al., 2002; Vdovic et al., 2006). Traditionally, these wastes have been considered relatively inert in most of the weathering environments, based on the opinion that the potential contaminants are encapsulated in low soluble silicates, oxides, and glass compounds (Scales, 1986). Today, it is well understood that slag wastes can also contribute to the environmental contamination through the weathering and leaching processes (Manz and Castro, 1997; Parsons et al., 2001; Lottermoser, 2002; Piatak et al., 2004). For example, base-metal slag deposits at the Penn Mine in Calaveras County, California, are a source of environmental

* Corresponding author.
E-mail addresses: khorasani@uk.ac.ir, khorasani_283@yahoo.com (M. Khorasanipour).

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contamination through leaching of potentially toxic elements (Parsons et al., 2001).

Concentrating, roasting, and smelting are three critical steps in the processing of Cu porphyry sulfide ores. Slag waste is produced during smelting, converting, and some possible additional refining steps (Biswas and Davenport, 2002). A part of these wastes is recycled to the smelter because of their high metal content. Although, the amount of slag in comparison to the amount of metal produced varies based on the commodity (Piatak et al., 2015), it is estimated that the production of 1 ton of copper generates approximately 2.2–3 tons of copper slag (Shi et al., 2008). Based on the worldwide estimate, 2.2 tons of slag is produced per ton of Cu and about 24.6 million tons of slag is generated from the world copper production (Gorai et al., 2003). Dumping or disposal of such huge quantities of slag can cause environmental and space problems. These waste dumps have received a large amount of attention as potential pollutant sources (Kierczak et al., 2013). Recently, smelting slags are used as additives for several purposes including building and construction materials, concretes and abrasive materials (Shi et al., 2008; Potysz et al., 2015).

Characterization of slags according to the chemical, textural, and mineralogical studies is recommended as the first step of environmental investigations (Ettler et al., 2009a, 2009b; Piatak et al., 2015; Potysz et al., 2015). Mineralogical characteristics of the slag wastes have been well described by a number of studies (e.g. Parsons et al., 2001; Lottermoser, 2002; Piatak et al., 2004; Puziewicz et al., 2007; Ettler et al., 2009a, 2009b; Piatak and Seal, 2010). Although, each slag type usually contains a specific chemical, mineralogical and therefore the specific elemental assemblages that may be of environmental concern, generally non-ferrous slags such as Cu ore slag may have a higher potential to negatively impact the environment compared to the ferrous slags (Piatak et al., 2015). Today, due to the presence of high concentrations of potentially contaminant trace elements and the sulfide minerals, most studies emphasize on the mobilization potential of pollutants of the slag waste dumps (Vdovic et al., 2006; Shanmuganathan et al., 2008; Yang et al., 2010; Kierczak et al., 2013; Dung et al., 2014). Release of toxic metals from smelting slags is controlled by several factors including pH, metal content, texture, and geochemical/mineralogical composition of slags (Ettler et al., 2009a,b; Ash et al., 2013; Kierczak et al., 2013; Jin et al., 2014). Leaching tests are more common methods used to assess the environmental risk associated with the slag wastes (Potysz et al., 2015, 2016). For example, the leachability of potentially toxic trace elements from copper slags have been investigated by several studies (e.g. Lagos and Luraschi, 1997; Shanmuganathan et al., 2008; Yang et al., 2010; Kierczak et al., 2013; Dung et al., 2014). Most of these studies (Lagos and Luraschi, 1997; Parsons et al., 2001; Lim and Chu, 2006; Shanmuganathan et al., 2008; Ettler et al., 2009b; Piatak et al., 2015) have used the adopted U.S. EPA toxicity characteristic leaching procedure (TCLP) test for determining the leachability of trace toxic elements.

The Sarcheshmeh smelting plant is the biggest Cu producer in Iran, which produces about 2 tons of slag per ton of Cu. Annually, more than 370,000 tons of slag are produced and dumped around the smelting site in Sarcheshmeh industrial complex. This study was conducted in order to investigate the environmental characterization of Sarcheshmeh smelting slags. The main objectives are as follows:

1- Identifying the concentration, leachability and toxicity potential of the toxic trace elements in the smelting slags;
2- Identifying the mineralogical composition of Sarcheshmeh slag;
3- Determining the role of grinding and sieving facilities in the trace element contamination of the surrounding soils;
4- Predicting the leachability and thus the contaminant potential of metal(loid)s in the contaminated soils by using the single extraction methods.

2. Material and method

2.1. Site description

The Sarcheshmeh mine as one of the largest porphyry copper deposits in the world is located at 29°58′N and 55°51′E and about 160 km southwest of Kerman city. The geological map around this mine is shown in Fig. 1A. Several studies have been investigating the ore forming processes including alteration and mineralization in Sarcheshmeh porphyry copper mine (e.g. Hezarkhani, 2006; Shahabpour and Doorandish, 2007; Atapour and Aftabi, 2007; Aftabi and Atapour, 2010). Mineralization in the Sarcheshmeh mine is associated with a complex intrusive body, named Sarcheshmeh Stock, which intruded into a folded and faulted Early Tertiary volcano–sedimentary series comprising trachybasalt/trachyandesite and andesitic lavas, tuffs, ignimbrites, and agglomerates (Shahabpour and Kramers, 1987; Aftabi and Atapour, 2010). Eocene basic-to-intermediate volcanic rocks, including trachybasalt, trachyandesite, and/or andesite are the primary rocks in Sarcheshmeh area (Atapour and Aftabi, 2007; Dimitrijevic, 1973). The main host rocks around Sarcheshmeh porphyry copper deposit are Eocene trachybasalts intruded by Miocene quartz monzonite and granodiorite (Aftabi and Atapour, 2010). Sarcheshmeh Stock is exposed over an area of about 1.2 km by 2.2 km and contains 450 Mtons of ore with average grades of 1.13% Cu and 0.03% Mo and a cutoff grade of 0.4% Cu (Waterman and Hamilton, 1975). The copper–molybdenum mineralization/alteration zones occur both in the porphyry stock and the surrounded trachybasalt rocks (Aftabi and Atapour, 2010).

The Sarcheshmeh area has a semi-arid climate conditions with an annual temperature between −20 and 32 °C, a mean rainfall of 440 mm, and annual evaporation of about 1170 mm (Khorasanipour and Eslami, 2014). The wind speed, sometimes exceeds 100 km/h (Doulati Ardejani et al., 2008).

Approximately, 374,000 tons of reverberatory furnace smelter slag and 12,800 to 12,900 tons of converter smelter slag (with 3.5 to 4% of Cu) are produced in Sarcheshmeh industrial complex, annually. As noted earlier, most of the converter slag is recycled and recharged to the reverberatory furnace smelter. Therefore, the reverberatory slags are the most important smelting wastes in Sarcheshmeh Copper Industrial Complex. These wastes are dumped near the smelting plant (Fig. 1B). Annually, about 70,000 tons or 18.7% of the produced reverberatory slags are used for the other purposes such as sandblasting. The preparation site is located near the Sarcheshmeh Township, where large amount of reverberatory slags is dumped for the grinding and sieving processes (Fig. 1C). The older parts of the reverberatory slag dump were weathered and the signs of weathering products were observed in the slag dump drainages (Fig. 2).

2.2. Sampling and sample preparation

In this study, 8 samples of the reverberatory slags and 2 samples of the converter slags were sampled from the Sarcheshmeh slag wastes. Collected samples were from fresh slag, powder slags around the grinding and sieving facilities and also the sediments of the slag dump drainages (Fig. 2). For the geochemical investigations, slag samples were pulverized to <75 μm and stored in polyethylene bottles.

Field studies showed a remarkable contamination layer of the wind-dispersed slag particles on the top of the soils around the grinding and sieving facilities of the preparation site close to Sarcheshmeh Township. Surface (0–5 cm) and subsurface (20–40 cm) soils were sampled in order to investigate the role of these slag particles in the contamination of the surrounding soils (Fig. 1C). The Sarcheshmeh slag dump, near Sarcheshmeh smelting plant, also has a remarkable effect on its surrounding soil through wind-dispersed slag particles. Surface soil (0–5 cm) around this

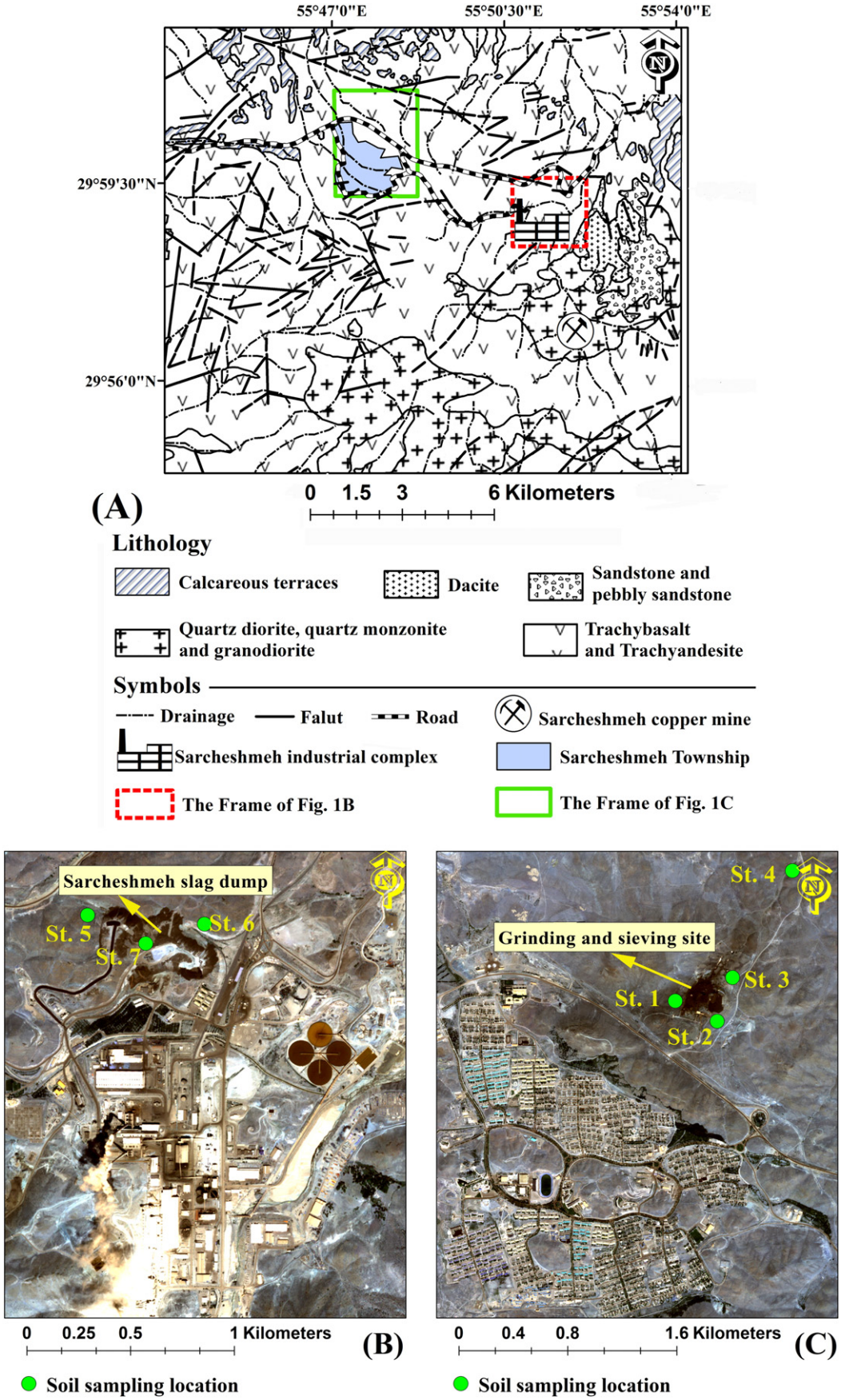

Fig. 1. (A) Geological map around the Sarcheshmeh Cu industrial complex; (B) the location of Sarcheshmeh slag sump; and (C) the location of the slag preparation sited in vicinity of the Sarcheshmeh Township. Location of soil samples are shown in B and C.

Fig. 2. Weathering products as white sediments associated with the slag dump drainages.

dump also was sampled for the geochemical analysis (Fig. 1B). All soil samples were sieved through a clean 2-mm stainless steel sieve. The fraction below 2-mm was used for the total concentration analysis and single extraction methods.

2.3. Total concentration analysis

The total concentration of the target elements was determined on pulverized slag samples using microwave multi-acid digestion at the Labwest Laboratory, Perth, Australia. The microwave technique for the digestion process was used as a sealed pressure vessel, effectively a bomb digestion, which enables the process to proceed at high pressures and temperatures.

Soil samples were air-dried in the laboratory to constant weight. An aliquot part of each sample was finely ground in an agate mortar and used for subsequent total concentration analyses in the Labwest Laboratory, Perth, Australia. The total contents of the target elements were determined using inductively coupled plasma optical emission spectrometry (ICP-OES; Fe, Mn, S, and Cr) and inductively coupled plasma-mass spectrometry (ICP-MS; Ag, As, Bi, Cd, Co, Cu, Mo, Ni, Pb, Sb, Se, Sn, and Zn).

For the total concentration data, the analytical and instrumental quality assurance and quality control (QA/QC) were evaluated using sample duplicates. The Relative Percent of Difference (RPD) of the results obtained from repeated samples was calculated using equation 1. The RPD defined as the difference between duplicate values divided by the average of the duplicate values and multiplied by 100.

$$\mathrm{RPD} = \frac{(\mathrm{A}-\mathrm{B})}{(\mathrm{A}+\mathrm{B})/2} \times 100 \qquad (1)$$

The estimated RPD for the target elements in the duplicated samples were in the range of 0.66 ± 0.96% (mean ± standard deviation).

The accuracy of the total concentration results was evaluated using multi-elemental certificated references materials at the Labwest laboratory, Perth, Australia.

2.4. Mineralogical studies

The mineralogy of the collected samples was qualitatively determined by a Philips Xpert pro X-ray diffraction system (XRD) in Iran Mineral Processing Research Centre (IMPRC), Karaj, Iran. This X-ray diffraction system uses cobalt radiation (Kα line with a mean wavelength of 1.789 Å, operated at 40 kV and 35 mA, scans were recorded from 4 to 85 2θ). Also, ore microscopy of prepared polished sections of slags was implemented in the Central Laboratory of Sarcheshmeh Copper Complex with a Leica DMLP Reflected/transmitted light polarizing microscope.

2.5. Single extraction methods

Single step leaching tests were performed in order to evaluate the leachability of the selected elements (Ag, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Se, Sn, and Zn) in the collected slags and soil samples. Three types of leaching tests were used to simulate different environmental conditions. The extraction methods were: (1) water soluble test; (2) the U.S. EPA toxicity characteristic leaching procedure (TCLP), and (3) the standard single extraction tests, based on the 0.05 mol/L ethylenediamine tetraacetic acid (EDTA) and 0.43 mol/L acetic acid solutions. TCLP and water soluble methods were applied only to the slag samples and surface soil sample around the Sarcheshmeh slag dump, while standard single extraction methods was applied only to the soil samples. Below is the detailed description of the extraction methods.

2.5.1. Water soluble test

Water soluble fraction, as an example of natural conditions, contains the most mobile or soluble forms of trace elements. Water soluble fraction was determined by placing 1 g of air dried solid sample into 50 c of deionized H_2O and shaking it for 2 h at the ambient temperature. The extracted phase was separated from the solid phase by centrifugation at 4500 rpm for 20 min and the supernatant was then filtered through a 0.45 μm filter (ALBET, Nitrato Celulosa model), kept in dark bottles, and stored at 4 °C until analysis. All extracts were analyzed using ICP MS/OES at the Labwest Laboratory, Perth, Australia.

2.5.2. TCLP test

Description of the U.S. Environmental Protection Agency protocols for leaching methods can be found in U.S. EPA (1994). TCLP extraction method was applied using one out of two different buffer acidic leaching solutions depending on the alkalinity and the buffering capacity of waste samples. These extraction solutions are “solution 1” with a pH of 4.93 ± 0.05 and “solution 2” with a pH of 2.99 ± 0.05 (Margui et al., 2004). The initial pH of samples was determined by adding 96.5 mL of deionized water to 5 g of each solid phase into borosilicate glass beaker, covered with a watch glass and stirred vigorously for 5 min using a magnetic stirrer. After extraction, the final pH of the solution was recorded using Toledo MP-120 pH meter model. This pH value is a key factor for the selection of the appropriate leaching solution. Except for the contaminated soil around the Sarcheshmeh slag dump, the initial pH values of all selected slag samples were higher than 5 (range from 5.85 to 9.77). In this condition, according to the U.S. EPA instruction (Method 1311; Lagos and Luraschi, 1997; Parsons et al., 2001) 3.5 mL 1 N HCl was added to the sample, covered with a watchglass and heated to 50 °C for 10 min. After cooling the pH of all samples were <5, and therefore, the extraction “solution 1” was used for all samples as specified by the U.S. EPA (1994). This extraction solution was prepared by adding 5.7 mL of glacial acetic acid and 64.3 mL of 1 N

NaOH to 500 mL of reagent water and then diluted to a volume of l L. TCLP was applied in the ambient conditions with Liquid to Solid (L/S) ratio equal to 20 L/kg for 18 ± 2 h. It is assumed that steady-state conditions were met after this period. Following the extraction period the liquid extracts were separated from the solid phase by centrifugation at 4500 rpm, and then filtration through 0.45 μm filter (ALBET, Nitrato Celulosa, model). All extracts were analyzed using ICP-MS/OES at the Labwest Laboratory, Perth, Australia.

2.5.3. EDTA and acid acetic leaching tests

The single extraction methods based on the 0.05 mol/L EDTA and 0.43 mol/L acetic acid leaching solutions are among the main procedures identified for the extraction of metals from a soil matrix (Dean, 2007). These extraction solutions were prepared according to the recommended standard method of Institute for Reference Materials and Measurements of the European Commission (Rauret et al., 2001). The detailed applied instructions for EDTA and acid acetic leaching procedures (modified after Dean, 2003) are as follows, respectively.

2.5.4. EDTA (0.05 mol/L) extraction method

I. 5 g of <2 mm dried soil sample was placed into the 250 mL borosilicate bottle.
II. 50 mL of EDTA leaching solution was added to the sample.
III. The sample container was shaken for 1 h in the ambient conditions at speed of 100 rpm.
IV. The sample was centrifuged at 4000 rpm for 20 min and then the supernatant was removed and filtered through 0.45 μm filter (ALBET, Nitrato Celulosa, model).
V. Leached solutions were kept in polyethylene bottles and stored at 4 °C prior to analysis.

2.5.5. Acid acetic (0.43 mol/L) extraction method

I. 5 g of dried soil sample was placed into the 250 mL borosilicate bottle.
II. 200 mL of acetic acid was added to the sample.
III. The sample container was shaken for 16 h in the ambient conditions with speed of 100 rpm.
IV. The sample was centrifuged at 4000 rpm for 20 min and then the supernatant was removed and filtered through 0.45 μm filter (ALBET, Nitrato Celulosa, model).
II. Leached solutions were kept in polyethylene bottles and stored at 4 °C prior to analysis.

All extracted solutions were analyzed using ICP-MS/OES at the Labwest Laboratory, Perth, Australia.

2.6. Quality control of the leaching procedures

Quality assurance of the leaching procedures was achieved thought analysis of the method blank (containing the extraction solution, but no solid phase), certificated reference material and also carrying out the leaching procedure in duplicate for a number of samples. RPD values of water soluble and TCLP extraction methods in the duplicated samples were in the range of 2.69 ± 4.9 and 0.47 ± 4.08%, respectively (mean ± standard deviation).

The qualifications of EDTA and acid acetic leaching procedure were evaluated through the analysis of BCR-700 Certified References Material (CRM). The extractable fraction of some of the trace elements (Cd, Cr, Cu, Ni, Pb, and Zn) is certificated by harmonized EDTA and acetic acid extraction procedures in BCR-700, an organic-rich soil. The results obtained from BCR-700 and the certificated values are shown in the Supplementary Table S1. As shown in this table, RPD values for the certificated trace elements range from 0.15 to 4.68% for Zn and Cr, respectively.

The accuracy and precision of results for non-certificated elements, as proposed by Zhang (2007), were verified by analyzing multi-elemental reference materials and duplicating same solutions, respectively.

3. Results and discussion

3.1. Total concentration results of the slag samples

Characterization of the bulk chemical composition of slag is essential to understanding its nature and environmental behavior. Table 1 shows the total concentrations of the target elements in eight samples of the reverberatory furnace smelter slags and two samples of the converter furnace smelter slags. Compared to the reverberatory slags, elements such as Cu, Ag, Co, and Pb showed higher concentrations in the converter slags (Sl-9 and Sl-10). The mean concentrations of Cu in the reverberatory and converter slags were 1.46 and 8.5%, respectively. High concentration of Cu in the converter furnace slags is the reason for the recycling and reusing of this type of smelting waste in Sarcheshmeh industrial complex.

Mineralization in the Sarcheshmeh porphyry copper mine is similar to many other stockwork and vein-type deposits distributed in Eocene volcanics and Oligo-Miocene intrusives of quartz diorite, quartz monzonite and granodiorite composition (Atapour and Aftabi, 2007). In this study, normalized enrichment factor (NEF, Khorasanipour and Eslami, 2014) was used to evaluate the geochemical enrichment of target elements in the slag samples. This enrichment factor was calculated on the basis of the normal content of each target element in the unmineralized granodiorite (Mason and Moore, 1982) (Eq. (2)).

$$\mathrm{NEF} = \frac{\frac{[\mathrm{M}]}{[\mathrm{Sc}]}\text{Slag samples}}{\frac{[\mathrm{M}]}{[\mathrm{Sc}]}\text{unmineralized granodiorite}} \tag{2}$$

where NEF is the normalized enrichment factor, [M] is the total content of target elements and [Sc] is the content of Sc used as the normalizing element. Scandium as an immobile and resistant element can be a substitute for Al^{3+}, Fe^{3+}, Y^{3+}, and Ti^{3+}, and has already been used for calculating trace element enrichments (Shotyk et al., 2000). From this calculation, the following order of trace elements enrichment can be set up for Sarcheshmeh slags based on the median enrichment values: Sb > Mo > Cu > As > Se > Zn > Pb > S > Sn > Ag > Cd > Co > Bi > Fe > Cr > Ni > Mn (Fig. 3). Very high NEF values of most of the potentially trace toxic elements, especially Sb, Mo, Cu, As, Se, Zn, Pb and S, suggest that Sarcheshmeh smelting slags must be considered as one of the metalliferous smelting wastes with the multi-elemental contamination potential. It is also notable that depending on the several factors such as the type of smelted ores, fluxes, and additives applied during the pyrometallurgical process the bulk chemical composition of Cu-slags varies from one smelting site to another (Gbor et al., 2000; Lottermoser, 2002, 2005; Mateus et al., 2011; Potysz et al., 2015).

3.2. Mineralogical composition of Sarcheshmeh slag

X-ray mineralogical results of the selected slag samples are shown in Table 2. In this study, magnetite, fayalite, pyroxene, chalcocite, chalcopyrite, thenardite and quartz are the main mineralogical phase identified by the XRD method in the selected slag samples. Also, according to XRD results, it is possible that Zn and Cu incorporated into the spinel type structure lines and substituting those of other major compounds in the fresh slags. Spinels are a class of minerals containing a face-centered cubic close-packed crystal structure with the standard structure of $A^{2+}B_2^{3+}O_4$. A represents a divalent cations, B represents a trivalent cation and O is generally oxygen (Myers and Foster, 2012). However, there exists substantial variation in the composition and structure of minerals

Table 1
Total concentration (mg/kg) results of target elements in the slag samples (S1 to S8 reverberatory furnace smelter slags; S9 and S10 converter smelter slags). The detection limits are shown in parentheses.

Sample no.	ICP-Ms													ICP-OES			
	Ag	As	Bi	Cd	Co	Mo	Ni	Pb	Sb	Se	Sn	Zn	Cu (%)	Fe (%)	S (%)	Cr	Mn
	(0.01)	(0.5)	(0.1)	(0.05)	(0.2)	(0.1)	(2)	(0.2)	(0.1)	(0.05)	(0.2)	(0.2)	(0.2)	(100)	(50)	(2)	(2)
Sl-1	1.15	806	1.20	3.69	100	1400	14	324	327	4.4	46.7	5042	0.99	29.43	1.07	212	273
Sl-2	0.52	345	0.70	3.12	140	1798	14	407	327	4.8	41.1	4651	0.59	34.43	1.17	130	269
Sl-3	1.82	687	1.40	4.41	89	1300	26	259	271	12.4	46.6	4367	1.53	23.36	4.06	158	207
Sl-4	1.98	754	1.60	4.82	85	1397	26	328	303	10.8	48.8	4652	1.57	24.80	2.77	184	248
Sl-5	0.94	707	1.80	3.04	103	1058	16	379	333	5.0	40.9	5680	0.93	29.13	1.07	152	309
Sl-6	0.75	814	1.00	3.89	99	1638	16	428	320	3.9	64.6	5140	0.79	30.66	0.97	321	296
Sl-7	4.88	549	1.70	3.58	216	1097	91	576	304	16.4	38.1	6038	4.38	33.27	1.96	229	271
Sl-8	0.96	812	1.10	4.31	106	1536	18	484	332	4.7	70.9	5274	0.96	29.49	1.09	219	292
Sl-9	6.20	42	1.00	0.17	580	240	230	1600	300	24.0	49.0	4690	8.09	50.06	2.39	81	110
Sl-10	6.90	42	1.10	0.12	580	240	250	1600	300	26.0	48.0	4740	9.00	48.02	2.85	80	109
Granodiorite[a]	0.07	2	0.10[b]	0.20	10	1	20	15	0.2	0.05[b]	2.0	60	0.003	5.00[c]	0.056[d]	20	1200

Sample description: Sl-1, Sl-2, Sl-5, Sl-6 and Sl-8, fresh slag; Sl-3 and Sl-4, slag drainage sediments; Sl-7, powder slags around the grinding and sieving facilities; Sl-9 and Sl-10, fresh converter furnace slags.
[a] Granodiorite, Levinson (1974).
[b] Granite, Levinson (1974).
[c] Bulk continental crust, Mason and Moore (1982).
[d] Upper continental crust, Rudnick and Gao (2003).

classified as spinels. This variation allows the incorporation of many metals into the spinel mineral (Myers and Foster, 2012). Therefore, the slag can contain complex spinel solid solutions, whose composition mainly depends on the bulk chemistry of the charge. According to the mineralogical results spinels in Sarcheshmeh slags are mainly rich in magnetite.

It is notable that, the diversity of the mineral phase in the slag waste depends on its cooling rates. Generally, the variety of the mineralogical phases is poorer in fast cooled slags compared to those cooled at the slower rates because slow cooling results in crystallization of phases closer to equilibrium and the formation of more phases (Kierczak and Pietranik, 2011; Potysz et al., 2015), whereas rapid cooling leads to the formation of the material with amorphous structures (e.g. Piatak et al., 2004; Kuo et al., 2008; Alvarez-Valero et al., 2009).

Quartz and thenardite (Na_2SO_4) were only found in X-ray mineralogical results of the white sediments of the slag dump drainages. Thenardite is an anhydrous sodium sulfate mineral, which occurs in arid evaporative environments. It seems that the source of Na is related to the processing process of Sarcheshmeh ore. As noted in Section 2.1 Sarcheshmeh mine is a Cu-Mo porphyry deposits. Separation and upgradation of the molybdenite of the bulk copper–molybdenite concentrate is one of the main steps in the processing process of Sarcheshmeh ore. This step is generally accomplished by selective molybdenite flotation following copper and iron sulfide depression. Sodium hydrosulphide (NaHS) is used during depressing the Cu from the Cu–Mo concentrate. Therefore, the Cu-concentrate is contaminated with sodium hydrosulphide compound.

Microscopic studies of the prepared polished section of the slags showed that minerals such as magnetite, chalcocite, chalcopyrite, as well as, covellite and thin layers of native copper (in chalcocite mineral) are present in a fayalitic and silicate glass matrix (Fig. 4A and B). These mineralogical results are similar to most commonly reported base-metal slags. For example, magnetite, a member of the spinel group minerals, is the most commonly reported phases in non-ferrous slags (Piatak et al., 2015). Silicates in the olivine, pyroxene, and melilite groups, as well as glass, spinels, and SiO_2 (i.e., quartz and other

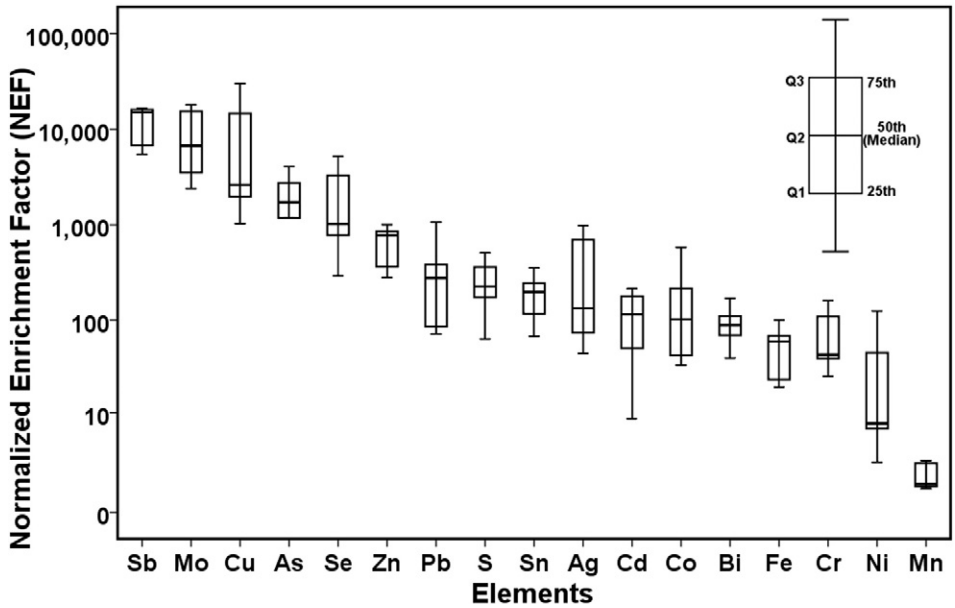

Fig. 3. Box plot showing the order of enrichment for target elements in the slag samples according to the normalized enrichment factor (NEF).

Table 2
The mineralogical composition of the selected slag samples and contaminated soil around the Sarcheshmeh slag dump.

Sample no.	Mineral composition
Sl-1	Magnetite, fayalite, pyroxene, chalcocite, chalcopyrite, Zn and Cu are possibly incorporated into spinel type structure lines
Sl-3	Magnetite, fayalite, pyroxene, chalcopyrite, quartz, thenardite
Sl-4	Magnetite, fayalite, pyroxene, chalcopyrite, quartz, thenardite
Sl-6	Magnetite, fayalite, pyroxene
Sl-7	Magnetite, fayalite, pyroxene
So-6	Quartz, albite, alkali feldspar, hematite, bonattite, pyrite, chalcopyrite, gypsum, chlorite, mica-illite

Sample description: Sl-1, and Sl-6, fresh slag; Sl-3 and Sl-4, sediments of the slag drainage; Sl-7, powder slags around the sizing and grinding facilities; So-6 contaminated soil around the slag dump.

polymorphs) are other commonly found minerals in non-ferrous slags (Piatak et al., 2015). Fayalite and silicate glass are the most identified silicate phases and represent volumetrically major compounds of the Cu-slags materials (Potysz et al., 2015).On the other hand, sulfides and intermetallic compounds are less abundant than the silicates and oxides (Piatak et al., 2015). Despite this fact that sulfides minerals such as bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), and chalcocite (Cu_2S) are volumetrically minor phases in Cu-slags, they are primary metal-carriers which makes them significant for environmental risk assessment (Potysz et al., 2015).

It seems that, the mineral assemblage of Sarcheshmeh slag samples was controlled by at least three main factors, including: (1) the mineralogy of the ore concentrate; (2) the smelting processes, and (3) the weathering and environmental conditions of the slag waste dump. The mineralogy of the fresh slags is controlled by the two first factors, while the third factor controls the secondary mineral formation. For

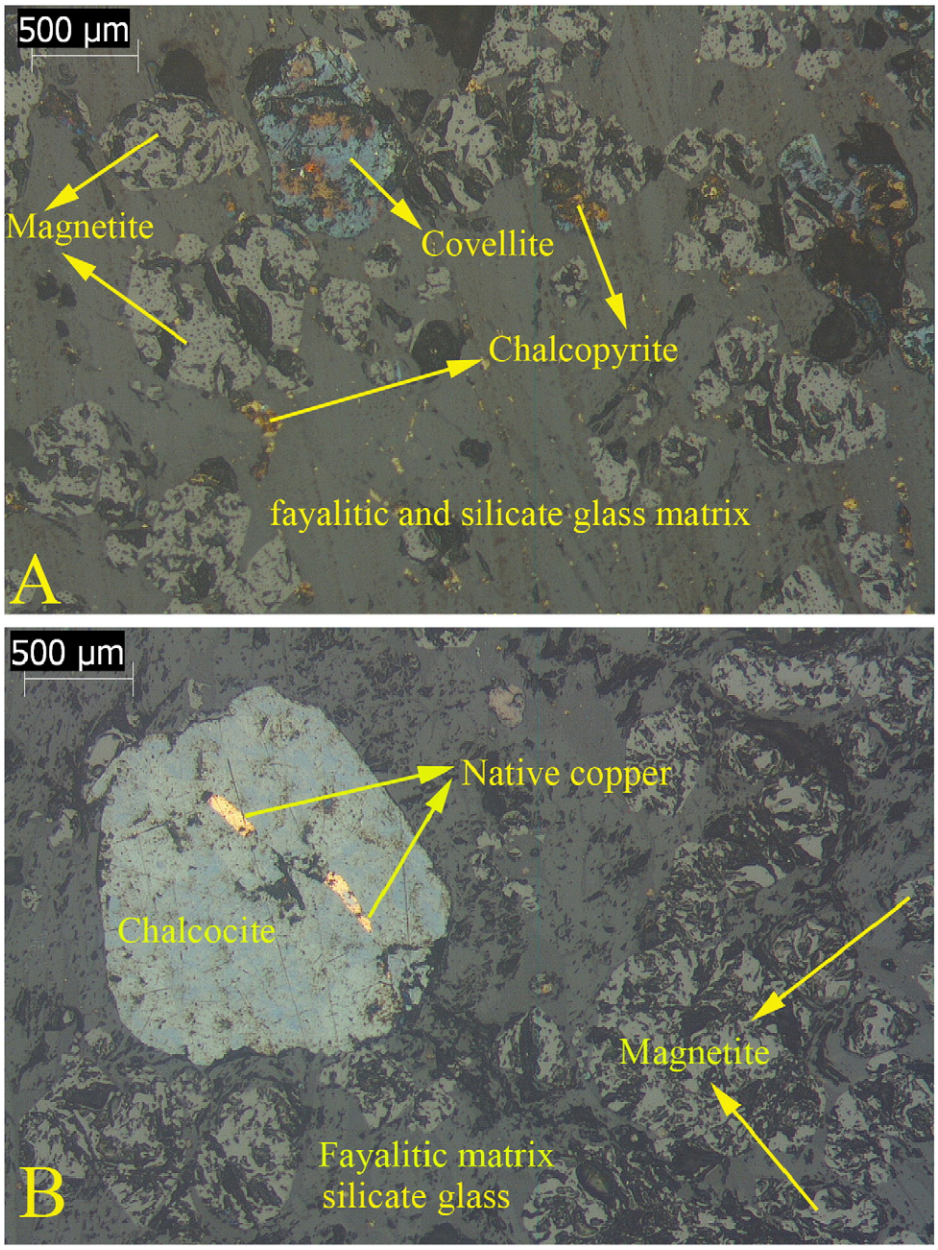

Fig. 4. Photomicrograph in plain reflected light showing the mineral assemblage of the slag samples. (A) chalcopyrite, covellite, and magnetite in the fayalitic matrix; (B) chalcocite, native copper, and magnetite in the fayalitic and silicate glass matrix.

example, chalcopyrite, chalcocite, and covellite are the most important ore minerals in Sarcheshmeh Cu-porphyry deposit which compose the ore concentrate mineralogy, while magnetite, fayalite, and pyroxene are formed from molted materials (ore concentrate + fluxes) during the smelting processes. On the other hand, the formation of thenardite is completely controlled by weathering and environmental conditions. During the smelting processes, sulfide minerals, an environmentally important component of the slag dump (Lasamis and Norman, 1997; Parsons et al., 2001; Piatak et al., 2015), can oxidize to iron oxide in the presence of silica to produce a crystalline fayalite (Fe_2SiO_4) (Li et al., 2009). It is reported that fayalite in non-ferrous slags such as Sarcheshmeh smelting slags, may contain trace elements such as Zn, Ni, and Pb (Parsons et al., 2001). Similar to olivine, several studies also have shown the trace element substitutions in the pyroxenes. For example, Zn substitutions (with concentrations reaching nearly 8 wt.% ZnO) in Zn slag from Poland (Puziewicz et al., 2007), Co in Cu–Co slag from Zambia that contains approximately 1 wt.% CoO (Vítková et al., 2010) and Pb–Ag medieval slag from the Czech Republic that contains up to 7 wt.% PbO (Ettler et al., 2009a).

As noted earlier, surface soil around the Sarcheshmeh slag dump contaminated through the wind-dispersed slag particles which produced from grinding and sieving processes. The mineralogy of this contaminated soil was composed of quartz, albite, alkali feldspar, hematite, bonattite, pyrite, chalcopyrite, gypsum, chlorite, and mica-illite. The presence of sulfide minerals and also secondary minerals like bonattite ($CuSO_4 \cdot 3H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) showed the role of slag dump and environmental conditions in the mineralogy of the surrounding soils. The two latest minerals, i.e. the product of the weathering reactions, also have been reported in the evaporative zone of the old weathered tailings in Sarcheshmeh tailings dam (Khorasanipour et al., 2011). The enrichment of potentially toxic elements such as Cd, Cr, and Pb in the secondary phases has been reported for both ferrous and non-ferrous slags (Piatak et al., 2015). During rainfall events, these secondary phases have a great potential for dissolving and releasing of trace elements into the surrounding environments.

3.3. The leachability of target elements in the slag samples

The results obtained from water soluble and TCLP leaching methods are shown in Tables 3 and 4, respectively. As noted earlier, these single extraction methods were applied to the selected slag samples and contaminated soil around the Sarcheshmeh slag dump. For both of water soluble and TCLP leaching methods the concentrations of Ag, Bi and Sn were below the detection values limit (0.05 μg/L for the three of them). In water soluble method, pH of water after the extraction time (2 h) ranged from 4.55 to 9.84. The contaminated soil around the Sarcheshmeh slag dump showed the most acidic pH value. pH of powder slag waste ranged from 5.82 to 6.55, while the mean pH values of samples associated with drainage sediments of the slag dump was 9.67. These ranges of pH showed the different geochemical characteristics of the collected samples. According to water soluble results, it is expected that the slag dump drainages have alkaline pH values. This is due to the (1) Limited reactivity of the sulfide minerals due to the encapsulation of these minerals in the slag waste; and (2) enrichment of the alkaline products of the weathering reactions due to the arid and semiarid climate conditions.

In order to evaluate the leachability potential of target elements in each of the collected samples, the percent of leachability was calculated according to the Eq. (3).

$$PL = \frac{\text{Leached Fraction}}{\text{Total Concentration}} \times 100 \quad (3)$$

where, PL is the percent of leachability for each of the target elements in each of the collected samples. The percent of leachability (PL) of the target elements in water soluble and TCLP leaching tests are shown for fresh slags, sediments of the slag dump drainages and the contaminated soil around the Sarcheshmeh slag dump are shown as scatter diagrams in Figs. 5, 6 and 7, respectively. The remarkable results are as follows:

1. In all slag samples, the maximum percent of leachability (PL) was observed for Ni, S, Cd, Cu, Co, and Zn, respectively (Fig. 5A to E). In these samples the minimum PL values were calculated for As, Cr, Fe, Mo, and Sb.
2. For sediments of the slag dump drainages (Sl-3 and Sl-4) maximum PL values were calculated for S, Se, Mo, and Cd, while elements such as Fe, Cr and Pb have the minimum PL values (Fig. 6A and B). Other elements (As, Sb, Mn, Ni, Cu, Co, and Zn) showed medium PL values (generally lower than 10%). The leachability of the target elements in these samples showed a remarkable difference with the slag samples. This is due to the different geochemical characteristics of these two groups of samples. For example, the maximum leachability or contamination potential of As (9.35 mg/L), Mo (186.7 mg/L), Sb (3.50 mg/L) and Se (6.12 mg/L) was observed in the leached

Table 3
The water soluble concentration of target elements (mg/L) in the slag samples and contaminated soil around the Sarcheshmeh slag dump. The detection values (μg/L) are shown in the parenthesis.

Sample no.	pH	Ag	As	Bi	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	S	Sb	Se	Sn	Zn
		(0.05)	(0.5)	(0.05)	(0.05)	(0.02)	(0.001)	(0.1)	(0.01)	(0.05)	(0.1)	(0.2)	(0.1)	(1.0)	(0.05)	(0.5)	(0.05)	(0.5)
Sl-1	5.82	BDL	0.18	BDL	0.27	2.05	BDL	209.79	14.50	2.95	0.12	3.09	0.32	1025	0.18	0.06	BDL	132.4
Sl-2	5.99	BDL	0.09	BDL	0.14	3.03	BDL	16.78	168.06	4.40	0.40	3.36	0.20	1102	0.02	0.07	BDL	130.0
Sl-3	9.84	BDL	10.42	BDL	0.33	0.10	0.03	4.49	BDL	0.42	331	0.13	0.05	67,000	2.96	8.32	BDL	1.8
Sl-4	9.51	BDL	5.76	BDL	0.19	0.03	0.03	33.69	2.11	0.37	156	0.05	0.04	43,400	1.94	4.60	BDL	1.0
Sl-5	6.13	BDL	0.18	BDL	0.23	2.26	BDL	78.40	13.03	6.49	0.29	3.28	0.23	1010	0.14	0.08	BDL	184.0
Sl-6	6.55	BDL	0.25	BDL	0.21	1.71	BDL	68.09	0.65	2.29	0.09	2.79	0.37	836	0.29	0.05	BDL	111.3
Sl-7	6.30	BDL	0.09	BDL	0.39	2.44	0.03	139.69	0.25	2.43	0.11	12.62	0.49	759	0.21	0.04	BDL	68.1
So-6	4.55	BDL	0.70	BDL	11.34	21.48	0.10	51,900	18.12	672	0.56	14.75	0.04	41,800	0.43	3.44	BDL	645.6
So-6 (Repeated)	4.55	BDL	0.86	BDL	11.46	21.26	0.13	50,800	20.66	689	0.12	14.64	0.23	41,900	0.48	3.53	BDL	629.8
Drinking water		0.1	0.01[a]	–	0.005[a]	–	0.1[a]	1.3[a]	0.3[a]	0.05[a]	0.04[b]	–	0.015	–	0.006[a]	0.05[a]	–	5[a]
standard			0.01[c]	–	0.003[c]	–	0.05[c]	2[c]	–	–	0.7[d]	0.07[c]	0.01[c]	–	0.02[c]	0.04[c]	–	–

Sample description: Sl-1, Sl-2, Sl-5 and Sl-6, fresh slag; Sl-3 and Sl-4, slag drainage sediments; Sl-7, powder slags around the grinding and sieving facilities and So-6, contaminated soil around the slag dump.
BDL: below detection limit.
[a] U.S. EPA Maximum Contamination Level (MCL), Available on http://www.epa.gov/your-drinking-water/table-regulated-drinking-water-contaminants#Inorganic.
[b] De Zuane (1997).
[c] World Health Organization (WHO) (2011).
[d] World Health Organization (WHO) (2004).

Table 4
The TCLP leachable concentration of target elements (mg/L) in the slag samples and contaminated soil around the Sarcheshmeh slag dump. The detection values (μg/L) are shown in the parenthesis.

Sample no.	Ag	As	Bi	Cd	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	S	Sb	Se	Sn	Zn
	(0.05)	(0.5)	(0.05)	(0.05)	(0.02)	(0.001)	(0.1)	(0.01)	(0.05)	(0.1)	(0.2)	(0.1)	(1.0)	(0.05)	(0.5)	(0.05)	(0.5)
Sl-1	BDL	0.02	BDL	0.28	3.23	0.04	544	123.40	3.54	0.17	3.63	6.30	1211	0.02	0.08	BDL	136.4
Sl-2	BDL	0.06	BDL	0.12	4.49	BDL	47.51	223.90	5.25	0.87	3.56	2.55	1650	0.02	0.05	BDL	138.8
Sl-3	BDL	8.99	BDL	0.91	2.01	0.02	1484	46.81	4.83	164.75	2.34	0.50	53,030	4.98	7.09	BDL	77.6
Sl-4	BDL	12.26	BDL	0.94	1.25	0.02	1230	43.83	4.48	94.97	1.57	0.22	37,100	4.08	4.42	BDL	70.2
Sl-5	BDL	0.01	BDL	0.22	3.43	0.02	328	84.80	4.80	0.12	3.51	3.86	1330	0.01	0.09	BDL	202.5
Sl-6	BDL	0.08	BDL	0.23	2.93	0.04	287	124.60	3.02	1.08	3.54	6.49	1002	0.04	0.09	BDL	134.1
Sl-7	BDL	0.07	BDL	0.57	6.60	0.08	1690	186.60	4.15	0.34	31.26	42.83	1230	1.07	0.07	BDL	117.1
So-6	BDL	0.54	BDL	10.22	22.32	0.12	40,900	13.66	686	0.03	14.20	0.03	40,790	0.36	3.00	BDL	398.3
Regulatory level[a]	10	1	–	0.5	–	10	130	30	5	4	7	1.5	–	0.6	5	–	500

Sample description: Sl-1, Sl-2, Sl-5 and Sl-6, fresh slag; Sl-3 and Sl-4, slag drainage sediments; Sl-7, powder slags around the grinding and sieving facilities and So-6, contaminated soil around the slag dump. BDL: Below Detection Limit.
[a] All elements are regulated under US EPA maximum contamination level (MCL) in drinking water. Only Ni is regulated under WHO (2011).

solutions of the sediments associated with the slag dump drainages (SL-3 and SL-4), which have alkaline pH values (pH 9.67); the mean values of water soluble and TCLP leaching methods are presented. On the other hand, the maximum concentration of elements such as Ni, Cu, Co, Cd and Zn was measured in the near acidic leached solutions of the slag samples.

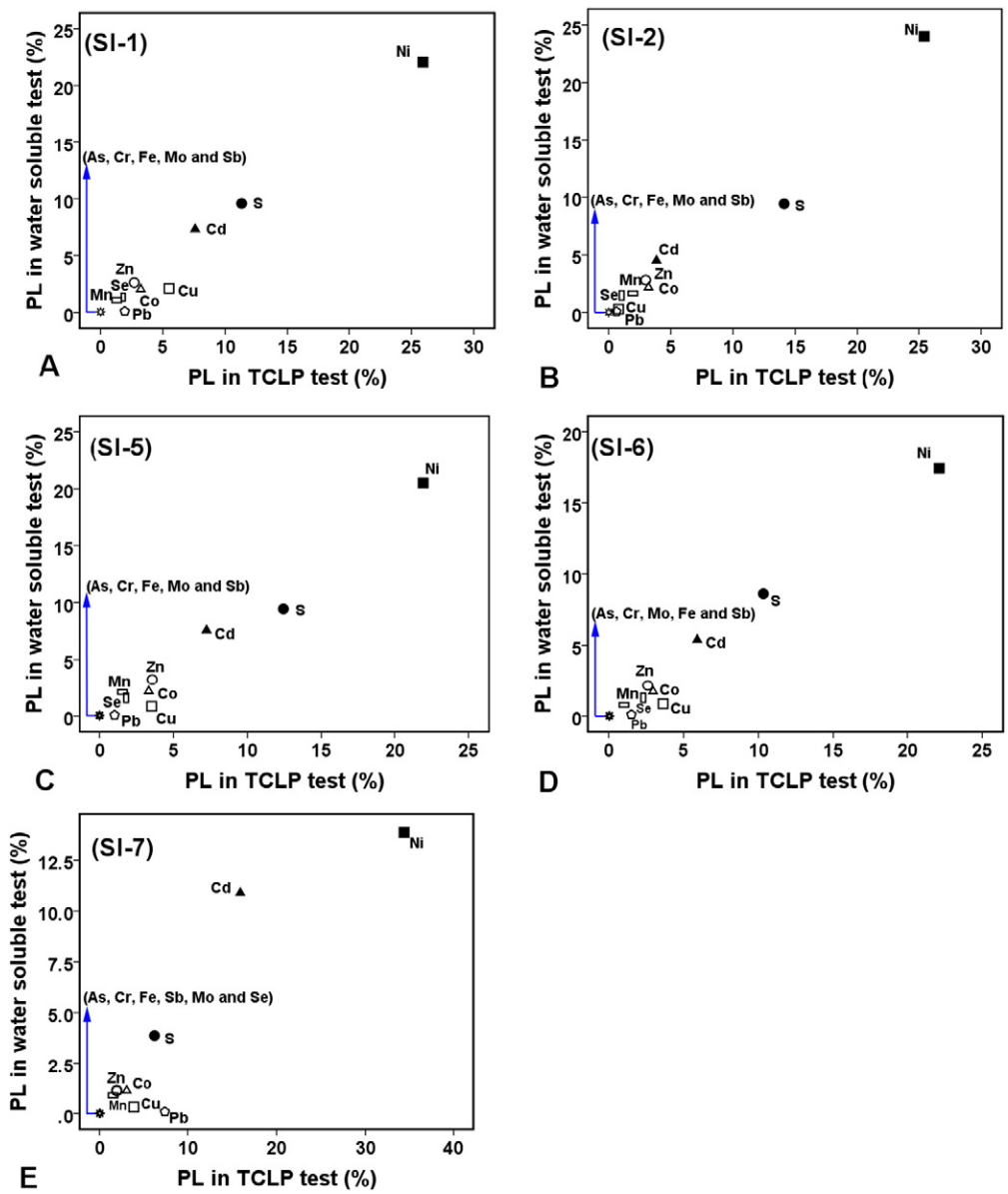

Fig. 5. (A to E) The percent of leachability (PL) for the target elements in the collected samples of the reverberatory slags.

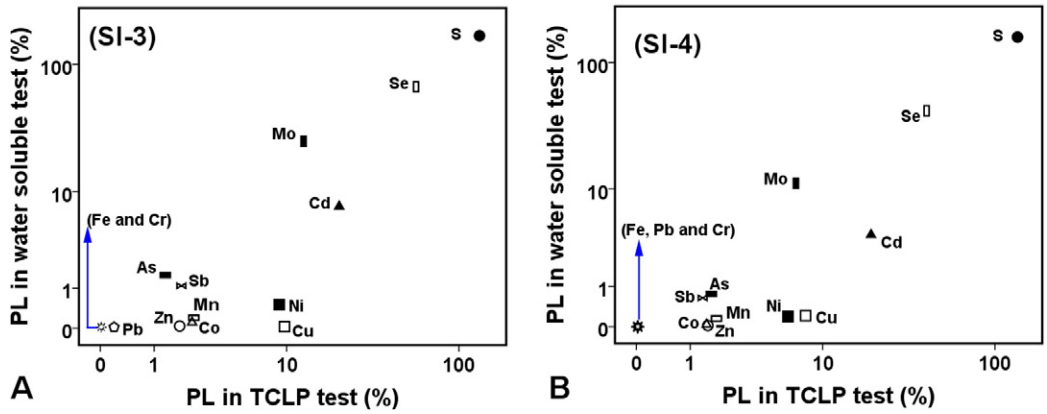

Fig. 6. (A and B) The percent of leachability (PL) for the target elements in the two collected samples of the slag dump drainages.

3. According to the PL values S, Cd, Mn, Cu, Co, Zn, Ni, and Se have the maximum leachability in the contaminated soil around the slag dump drainage (Fig. 7). In this sample the minimum leachability was observed for Fe, Pb, Mo, Sb, Cr and As. For both of the leaching methods the maximum leachability or contamination potential of target elements were observed in the contaminated soil around the Sarcheshmeh slag dump. For example, very high concentrations of Cd (11.34 mg/L), Co (21.4 mg/L), Cu (51,900 mg/L), Fe (18.12 mg/L), Ni (14.75 mg/L), S (41,800 mg/L), and Zn (645.6 mg/L) were readily water soluble in the contaminated soil around the Sarcheshmeh slag dump (Table 3). Therefore, the wind-dispersed slag particles can remarkably increase the reactivity and leachability potential of the contaminant trace elements in the contaminated soil around the grinding and sieving facilities.

Other studies also have been well demonstrated that metal(loid)s are mostly mobilized by the dissolution of primary slag phases and may contaminate the surrounding environment (Bril et al., 2008; Piatak and Seal, 2010). Different geochemical behavior of As, Mo, Sb, and Se in the contaminated mining areas also has been reported in other studies (Smuda et al., 2008; Khorasanipour et al., 2011; Khorasanipour and Eslami, 2014). These elements can form oxyanions which are more mobile at higher pH conditions. For example, Smuda et al. (2008) have shown that Mo is mobile (up to 3.9 mg/L) as MoO_4^{2-} in the alkaline conditions. Generally, the mobilization of heavy metals occurs primarily at low pH, oxidizing environments (Lottermoser, 2003), while elements such as As is relatively mobile over a wide range of pH (i.e. extremely acid to alkaline) and redox conditions (e.g. Masscheleyn et al., 1991; Roddick-Lanzilotta et al., 2002; Khorasanipour and Esmaeilzadeh, 2015). Adsorption onto and co-precipitation with ferric hydroxides are very effective removal mechanisms of As and Mo from contaminated mine waters (Manceau, 1995; Dold and Fontboté 2001; Roddick-Lanzilotta et al., 2002; Khorasanipour et al., 2011).

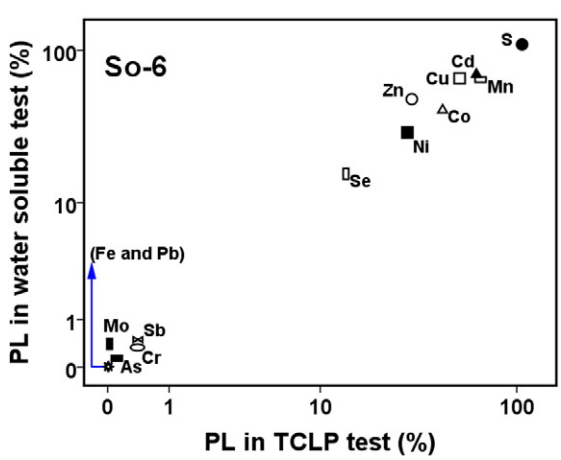

Fig. 7. The percent of leachability for the target elements in the contaminated soil around Sarcheshmeh slag dump.

3.3.1. Comparison with the regulatory levels

In order to evaluate the toxicity potential of the target elements, their concentration in TCLP leached solutions was compared with the regulatory values. This comparison was made by using Eq. (4).

$$EF = \frac{\text{Concentration in TCLP leached solution}}{\text{Regulatory level}} \quad (4)$$

A solid waste exhibits the characteristic of toxicity if the concentration of any target contaminant in TCLP extract is greater than or equal to the respective recommended U.S. EPA regulatory limit value (Margui et al., 2004). The regulatory levels for the potentially toxic elements are typically based on 100 times the National Interim Primary Drinking Water Standards for metals, NIPDWS (Margui et al., 2004). These regulatory values are 5 mg/L for As, Pb, and Cr, 1 mg/L for Cd and Se, and 7 mg/L for Ni (Eckert and Guo, 1998). Given that TCLP regulatory limits do not exist for all target elements, in this study, one-hundred times the U.S. EPA maximum contamination level (MCL) of target elements, defined by the U.S. EPA (www.epa.gor), were used for evaluation of the TCLP results. These regulatory limits are 1 mg/L for As, 0.5 mg/L for Cd, 10 mg/L for Cr, 130 mg/L for Cu, 30 mg/L for Fe, 5 mg/L for Mn, 4 mg/L for Mo, 7 mg/L for Ni, 1.5 mg/L for Pb, 0.6 mg/L for Sb, 5 mg/L for Se and 500 mg/L for Zn.

Comparison of TCLP results with the considered regulatory levels demonstrated the outstanding role of the geochemical properties of each of the collected samples in their toxicity potential. Table 5 shows the enrichment factor values of the target elements calculated according to Eq. (4). These results showed that the concentrations of As, Cd, Cr, Mn, Mo, Sb, Se and Zn leached from slag samples after 18 h extraction period are mainly below the considered regulatory levels. In these samples the enrichment values of Cu, Fe, and Pb were higher than the regulatory levels.

Enrichment values showed that the concentrations of As, Cu, Mo, Sb and Se are higher than the regulatory levels in the leached solutions obtained from the sediments of the slag dump drainages (Sl-3 and Sl-4). Other elements were lower than the regulatory levels in these samples. It is also notable that TCLP concentrations of Cd, Cu, Mn and Ni were higher than the considered toxicity regulatory levels in the contaminated soil around the Sarcheshmeh slag dump. It seems that, a part of this contamination is associated with other sources, especially the smelting plant and air pollution, in the Sarcheshmeh industrial complex.

Table 5
The enrichment factor values of the target elements in the TCLP leached solutions compared with the considered regulatory values (one-hundred times U.S. EPA maximum concentration level in drinking water). The significant enrichments were highlighted.

Sample no.	As	Cd	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Sb	Se	Zn
Sl-1	0.02	0.56	0.00	**4.18**	**4.11**	0.71	0.04	0.52	**4.20**	0.03	0.02	0.27
Sl-2	0.06	0.24	0.00	0.37	**7.46**	1.05	0.22	0.51	1.70	0.03	0.01	0.28
Sl-3	**8.99**	1.82	0.00	**11.42**	1.56	0.97	**41.19**	0.33	0.33	**8.30**	**1.42**	0.16
Sl-4	**12.26**	1.88	0.00	**9.46**	1.46	0.90	**23.74**	0.22	0.15	**6.80**	0.88	0.14
Sl-5	0.01	0.44	0.00	2.52	**2.83**	0.96	0.03	0.50	**2.57**	0.02	0.02	0.41
Sl-6	0.08	0.46	0.00	2.21	**4.15**	0.60	0.27	0.51	**4.33**	0.07	0.02	0.27
Sl-7	0.07	1.14	0.01	**13.00**	**6.22**	0.83	0.09	**4.47**	**28.55**	1.78	0.01	0.23
So-6	0.54	**20.44**	0.01	**314.62**	0.46	**137.20**	0.01	**2.03**	0.02	0.60	0.60	0.80

Sample description: Sl-1, Sl-2, Sl-5 and Sl-6, fresh slag; Sl-3 and Sl-4, slag drainage sediments; Sl-7, powder slags around the grinding and sieving facilities; and So-6, contaminated soil around the slag dump.

3.4. Total concentration results of the soil samples

Table 6 shows the total concentration of the target elements in the collected soil samples. These samples were from soil profiles around the preparation site near the Sarcheshmeh Township (St. 1 to St. 4; Fig. 1C), and the soil samples around the Sarcheshmeh slag dump (St. 5 to St. 7; Fig. 1B). In order to evaluate the role of air-dispersed slag particles in the soil contamination, especially around the grinding and sieving facilities of the preparation site, soil samples were collected from the surface (0–5 cm) and subsurface (20–40 cm) depths. Total concentrations of some of the target elements, such as As, Cu, Mo, Pb, Sb, Sn, Zn, Cr, S and Fe, showed a remarkable difference between surface and subsurface soil samples. For example, the surface and subsurface concentrations of these elements in the soil profile in the vicinity of the grinding and sieving site near the Sarcheshmeh Township (St. 2 in Table 6) were respectively: 245 and 26 mg/kg for As, 4580 and 105 mg/kg for Cu, 421 and 1.9 mg/kg for Mo, 145 and 24 mg/kg for Pb, 98.7 and 1.1 mg/kg for Sb, 14.7 and 1.3 mg/kg for Sn, 240 and 98 mg/kg for Zn, 200 and 71 mg/kg for Cr, 5170 and 68 mg/kg for S, 14.4 and 5.95% for Fe. These differences between surface and subsurface soil samples were decreased by increasing the distance from the grinding and sieving site around the Sarcheshmeh Township (Fig. 1C). The soil profiles around the Sarcheshmeh slag dump (St.5 and St.6) also showed the enrichment of trace elements in the topsoil layer, although it seems that a part of this contamination arising from other sources, especially smelting plant and air pollution (Khorasanipour and Aftabi, 2011).

Total concentration of target elements in soil samples was also compared with the average world values in soil (As, Bi, Cd, Cu, Mo, Pb, Se, Zn and Cr from Kabata-Pendias and Mukherjee, 2007; Sb, Sn and S from McBride, 1994), mean world soil background values (Co, Ni, and Sc from Kabata-Pendias and Pendias, 2001) and typical concentration in soil (Fe from Agarwal, 2009). This comparison was made by using of the normalized enrichment factor (NEF, Eq. (5)).

$$\mathrm{NEF} = \frac{\frac{[\mathrm{M}]}{[\mathrm{Sc}]}\text{collected soil sample}}{\frac{[\mathrm{M}]}{[\mathrm{Sc}]}\text{average world or background values}} \tag{5}$$

where, M is the concentration of target element and Sc is the concentration of scandium, used as the normalizing element. An NEF < 1 indicates no enrichment and NEF > 10 represents anthropogenic source (Turner and Simmonds, 2006). To assess degree of metal contamination NEF ≤ 2 are considered as low enrichment, 2 < NEF ≤ 5 moderate enrichment, 5 < NEF ≤ 20 significant enrichment, 20 < NEF ≤ 40 very high enrichment and NEF > 40 represents extremely high enrichment (Lu et al.,

Table 6
Total concentration (mg/kg) of target elements in the collected soil samples.

Station no.	Sample description	ICP-MS														ICP-OES			
		Ag	As	Bi	Cd	Co	Cu	Mo	Ni	Mn	Pb	Sb	Se	Sn	Zn	Cr	Sc	S	Fe (%)
St. 1	0–5 cm	0.26	87.9	0.60	0.93	26.80	1340	98.9	44	1200	59.2	23.40	0.98	4.30	753	97	15	1310	7.59
	20–40 cm	0.10	25.8	0.20	0.21	20.90	96	1.2	44	1305	20.7	0.80	0.42	1.30	96	69	15	25	5.70
St. 2	0–5 cm	0.69	245	0.90	1.98	47.70	5280	421.0	53	1071	145.4	98.70	2.39	14.70	2410	200	12	5170	15.44
	20–40 cm	0.11	26.0	0.20	0.22	21.50	105	1.9	44	1304	24.0	1.10	0.41	1.30	98	71	16	68	5.95
St. 3	0–5 cm	0.57	285.4	1.00	1.97	45.20	4460	354.9	53	1091	132.5	87.10	2.28	11.60	2079	173	13	4250	13.52
	20–40 cm	0.09	108.5	0.10	0.17	25.10	115	1.4	49	1169	19.8	0.70	0.58	1.30	2080	89	20	25	5.90
St. 4	0–5 cm	0.22	114.9	0.60	0.80	22.20	780	58.9	45	975	50.6	15.60	0.60	3.40	454	87	14	751	7.03
	20–40 cm	0.11	97.5	0.20	0.17	17.40	92	1.3	39	859	19.9	1.10	0.47	1.20	95	57	17	90	5.10
St. 5	0–5 cm	0.85	224.7	4.90	6.09	28.10	3020	19.4	36	1265	195.9	19.90	3.22	4.80	374	43	22	1430	7.37
	20–40 cm	0.12	46.5	0.40	0.34	27.50	155	1.9	34	1205	34.3	2.30	0.70	1.30	172	34	19	25	5.65
St. 6	0–5 cm	3.57	516.9	11.20	12.49	25.80	12,100	67.4	41	818	419.6	55.40	8.59	9.30	638	44	14	5480	5.90
	20–40 cm	0.19	68.3	0.80	1.64	20.90	297	3.2	35	1052	38.6	4.10	0.83	1.80	129	41	15	82	4.97
St. 7	0–5 cm	10.70	497.5	27.20	16.21	52.20	78,600	138.6	50	1037	420.9	88.60	21.88	5.80	1330	30	16	38,400	8.17
World background ranges[a]	Mean	–	9	–	0.6	5.5	20	1.8	16	470	32	–	0.35	–	60	45	10	–	–
	Maximum	–	67	–	2	50	120	5.2	90	3900	140	–	1.3	–	480	150	20	–	–
Average world values[b]		–	5	0.2	0.5	–	20	1.8	–	437	25	–	0.33	–	63	54		–	–
Typical concentration in soil[c]		–	–	–	0.06	8	20	–	40	850	10	–	–	–	50	100		–	3.8
Average worldwide soil[d]		–	13.75	0.2	0.5	–	34	2	–	–	47	2	–	2	36			300	–

Sample descriptions: St.1 to St.4 are soil profiles around the grinding and sieving site near the Sarcheshmeh Township, St. 5 to St. 7 are collected soil samples around the Sarcheshmeh slag dump.

[a] Kabata-Pendias and Pendias (2001).
[b] Kabata-Pendias and Mukherjee (2007).
[c] Agarwal (2009).
[d] McBride (1994).

Table 7
Normalized enrichment factor (NEF) result of the target elements in soil samples compare with the average world values. Values higher than the moderate enrichment degree (NEF > 5) are highlighted.

Station no.	Sample depth	As	Bi	Cd	Co	Cu	Mo	Ni	Mn	Pb	Sb	Se	Sn	Zn	Cr	S	Fe
St. 1	0–5 cm	**11.7**	2.0	1.2	3.2	**44**	**37**	1.8	2.7	1.6	**7.8**	2.0	1.4	**8.0**	1.2	2.9	1.3
	20–40 cm	3.4	0.7	0.3	2.5	3.2	0.4	1.8	3.0	0.6	0.3	0.8	0.4	1.0	0.9	0.1	1.0
St. 2	0–5 cm	**40.8**	3.8	3.3	**7.2**	**220**	**195**	2.8	2.5	4.8	**41.1**	**6.0**	**6.1**	**31.9**	3.1	**14.4**	3.4
	20–40 cm	3.3	0.6	0.3	2.4	3.3	0.7	1.7	3.0	0.6	0.3	0.8	0.4	1.0	0.8	0.1	1.0
St. 3	0–5 cm	**43.9**	3.8	3.0	**6.3**	**171**	**152**	2.5	2.5	4.1	**33**	**5.3**	4.5	**25.4**	2.5	**10.9**	2.7
	20–40 cm	**10.9**	0.3	0.2	2.3	2.9	0.4	1.5	2.7	0.4	0.2	0.9	0.3	**16.5**	0.8	0.0	0.8
St. 4	0–5 cm	**16.4**	2.1	1.1	2.9	**28**	**23.4**	2.0	2.2	1.4	**5.6**	1.3	1.2	**5.1**	1.2	1.8	1.3
	20–40 cm	**11.5**	0.6	0.2	1.9	2.7	0.4	1.4	2.0	0.5	0.3	0.8	0.4	0.9	0.6	0.2	0.8
St. 5	0–5 cm	**20.4**	11.1	**5.5**	2.3	**69**	4.9	1.0	2.9	3.6	4.5	4.4	1.1	2.7	0.4	2.2	0.9
	20–40 cm	4.9	1.1	0.4	2.6	4.1	0.6	1.1	2.8	0.7	0.6	1.1	0.3	1.4	0.3	0.0	0.8
St. 6	0–5 cm	**73.8**	**40.0**	**17.8**	3.4	**432**	**26.7**	1.8	1.9	**12.0**	**19.8**	**18.6**	3.3	**7.2**	0.6	**13.0**	1.1
	20–40 cm	**9.1**	2.7	2.2	2.5	**9.9**	1.2	1.5	2.4	1.0	1.4	1.7	0.6	1.4	0.5	0.2	0.9
St. 7	0–5 cm	**62.2**	**85.0**	**20.3**	**5.9**	**2456**	**48**	2.0	2.4	**10.5**	**28**	**41**	1.8	**13.2**	0.3	**80**	1.3

Sample descriptions: St. 1 to St. 4 are soil profiles around the grinding and sieving site near the Sarcheshmeh Township, St. 5 to St. 7 are collected soil samples around the Sarcheshmeh slag dump.

2009). Table 7 shows NEF results calculated for the investigated soil samples. The remarkable results are as follows:

1. Surface and sub-surface enrichment values showed a remarkable difference in the investigated soil samples, especially for soil profiles in the vicinity of the grinding and sieving site (St. 1 to St. 4). In these samples, NEF values of As, Co, Mo, Sb, Se, Zn and S in surface samples were much higher than subsurface soils.
2. Arsenic was the only element that showed enrichments higher than its average world value (5 mg/kg) in nearly all samples, although the degree of enrichment in the surface samples were much higher than the subsurface samples. Geogenic arsenic contamination is one of the main environmental problems in Kerman Cenozoic Magmatic arc, where the most important porphyry copper deposits of Iran, such as Sarcheshmeh mine, are located (Khorasanipour and Esmaeilzadeh, 2015).
3. Among the investigated soil samples the maximum enrichment values, generally very high (20 < NEF ≤ 40, Cd, Sb and Se) and extremely high (NEF > 40, As, Bi, Cu, Mo and S) enrichments degrees, were observed for the surface soils around Sarcheshmeh slag dump (St. 6 and St. 7). It is obvious that a part of this contamination is associated with other contamination sources such as the smelting plant in Sarcheshmeh industrial complex.
4. Nearly all subsurface soil samples, showed low enrichment values of target elements (NEF ≤ 2).

3.5. The leachability of target elements in the soil samples

As noted earlier, the leachable fraction of the target elements in the collected soil samples was determined using EDTA (0.05 mol/L) and acid acetic (0.43 mol/L) leaching solutions. These single extraction methods are classified as "functionally defined speciation methods", in which the 'function' is plant or human availability (De Vivo et al., 2008). The results obtained from these two leaching tests are shown in the supplementary Tables S2 and S3, respectively. As a result of arid and semiarid climate conditions, development of the soil profiles is restricted in the Sarcheshmeh area, and most of the soils are classified as inceptisol or young immature soils with coarse-grained loamy sand to sandy loam texture (Khorasanipour and Aftabi, 2011). In order to evaluate the leachability potential of the target elements in each of the collected soil samples, the concentrations of these elements in the acid acetic and EDTA leaching methods were potted against each other (Fig. 8A to O). The remarkable results of the soil leaching tests are as follows:

1. For most of the target elements, especially As, Cu, Cd, Fe and Zn, the leached concentrations in surface soils are much higher than the subsurface samples. Manganese was the only element that showed the same surface and subsurface pattern in the leached solutions.
2. The maximum contamination potential was found in the soil stations around the Sarcheshmeh slag dump (St. 5 to St. 7). For example, a remarkable increase was observed in the leached concentration of some the elements such as S, Se, and Cu in the soil samples collected around the Sarcheshmeh slag dump. For these samples, the differences between surface and subsurface soils were also lower than the soil profiles around grinding and sieving site (St. 1 to St. 4). As note earlier, around the Sarcheshmeh industrial complex other contamination sources rather than the slag dump also have a considerable role in the soil contamination.
3. For some of the investigated elements such as Co, Cu, Fe, Mo, Ni, and Sb the leached concentration by 0.43 M acid acetic leaching solution was higher than EDTA method. Also, the differences between surface and subsurface values of these elements were sharper in the results of the acid acetic leaching test. This issue is related to this fact that the extraction methods such as EDTA, displaces metals from insoluble organic and organometallic complexes (Tlustos et al., 1994). The lower concentration of the target elements in EDTA results is associated with the soil characteristics in the Sarcheshmeh area, which is located in the arid and semiarid climate conditions with low content of organic matter. In this area, soil texture mainly ranges from coarse-grained loamy sand to sandy loam, the pH ranges 5.2–7.8 and the organic matter content is low (ranges between 0.08 and 1.4%) (Khorasanipour and Aftabi, 2011).
4. Around the slag grinding and sieving site a remarkable differences were observed between the leachable concentration of target elements in the surface and subsurface soil layers (St. 1 to St. 4). For example, the mean concentration of the target elements in the acid acetic leached solutions of the surface and subsurface soil layers in the vicinity of the grinding and sieving site (mean soluble concentration for St. 1 to St. 4) were respectively: 685 and 1.35 mg/L for Cu, 141.2 and 31.22 mg/L for S, 3320 and 9.4 mg/L for Fe, 156 and 20 mg/L for Zn, 24.3 and 2.7 mg/L for As. The other notable elements were Cd (4.9 and 0.04 mg/L), Pb (16.27 and 0.72 mg/L), Ni (11.2 and 1.85 mg/kg), Cr (4.6 and 0.13 mg/L) and Co (3.46 and 0.14 mg/L). These results demonstrated that, the wind-dispersed slag particles from the preparation site have a major role in increasing the contamination potential of metal(loid)s in the surface layer of the surrounding soils. Grinding and sieving processes, as the two main steps in the preparation process, are responsible for liberating and dispersing of sulfide minerals encapsulated in the fresh slag wastes. Weathering and oxidation of these minerals result in the releasing of acid (H^+) and most of the potential toxic trace elements during the natural soil forming processes. For example chalcopyrite, the most important ore mineral in Cu-porphyry deposits was found in Sarcheshmeh slag

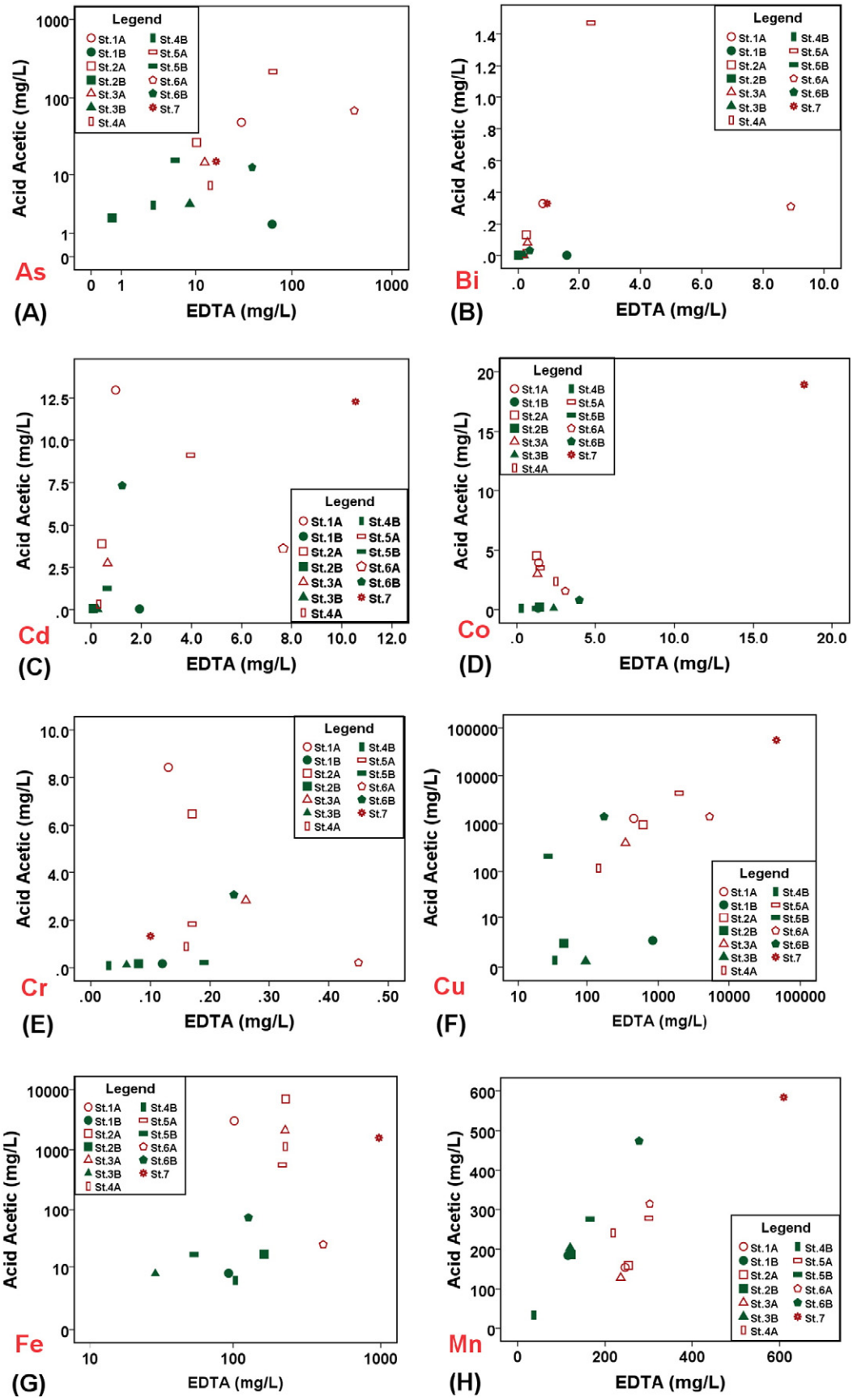

Fig. 8. Scatter plots showing the soluble or leach-able concentration of the target elements in the collected soil samples. For each of the elements, surface and subsurface soil samples are also identified in red and green colures, respectively.

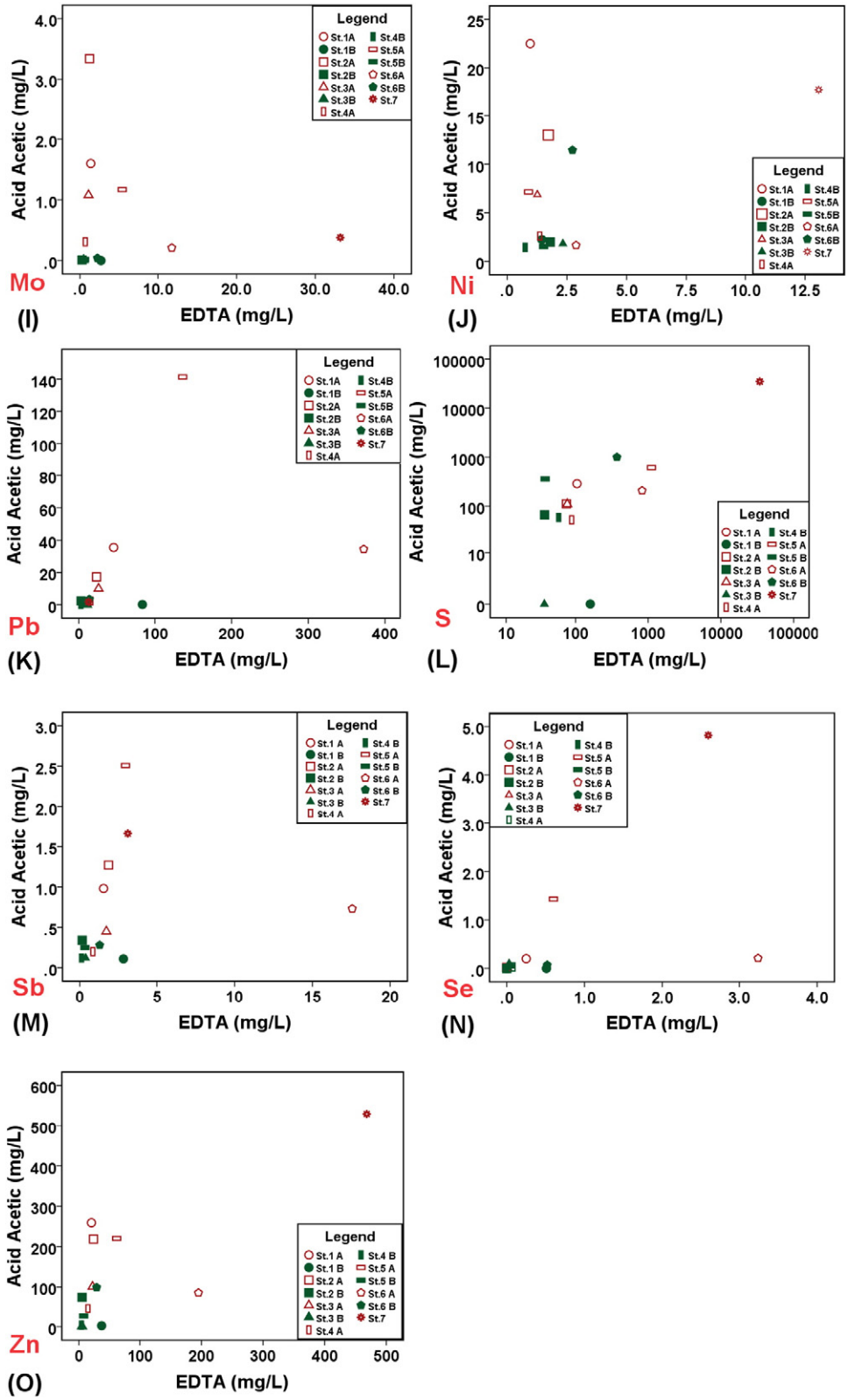

Fig. 8 (*continued*).

waste, can host minor and trace metals, such as Ag, As, Bi, Cd, Co, Cr, In, Mn, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, and Zn in the form of cation substitutions (Vaughan and Craig, 1978).

It is notable that physical, chemical, and biological factors govern the mechanisms of transformations, speciation, dynamics, bioavailability, toxicity, and fate of metals and metalloids in the soil environment (Huang and Gobran, 2005). Soil leaching tests such as acid acetic and EDTA methods will not necessarily measure plant-available contents but rather, the labile or mobile species contents. They can best be indicated as potentially plant-available contents rather than actual contents (Violante et al., 2008). According to the total concentration results it

was obvious that soils around Sarcheshmeh slag dump and slag preparation site were contaminated mainly as a result of the wind-dispersed slag particles. Other studies has also been shown that direct deposition of the slag particles from the slag dumps can result in the contamination of the surrounding soils (Ettler, 2016). For more than three decades, soil around Sarcheshmeh industrial complex is faced with various contamination sources, while soil contamination around the slag preparation site has been related to the grinding and sieving facilities since 15 years ago. Single extraction results of the acid acetic and EDTA methods revealed that the soluble fraction of the most of the contaminant elements also was increased in the contaminated topsoils. The soluble fraction for most of the investigated elements such As, Cd, Cu, Co, Mo, Sb and Pb were much higher than the natural conditions. More discussion for some of these elements is given in the following.

Arsenic is the only element that has both geogenic and anthropogenic contamination sources in the investigated soil samples. The mean soluble concentrations of this element in surface and subsurface soil samples were 69.2 and 13.2 mg/L, respectively. Several important factors such as clay minerals, oxy-hydroxides of Fe and Mn, as well as the organic compounds control the geochemical behavior of As in soil environment (Bhattacharya et al., 2002), but the concentration of this element in soils and soil solutions is generally controlled by ferric hydroxide (Kabata-Pendias and Mukherjee, 2007).

Cadmium concentration in the un-contaminated soil solutions varies from 0.0002 to 0.3 mg/L, depending on techniques used for obtaining solution (Kabata-Pendias and Mukherjee, 2007). The soluble concentrations of this element in the investigated surface and subsurface soil samples were 4.96 and 1.08 mg/L, respectively.

The mean soluble concentrations of Co in the investigated surface and subsurface soil samples were 4.79 and 1.01 mg/L, respectively. Iron and Mn oxy-hydroxides have the greatest importance in the Co distribution in soils (Kabata-Pendias and Mukherjee, 2007). Acetic acid-soluble and EDTA extractable Co usually correspond to the readily available pool of this metal. Like cobalt, Ni is also strongly associated with the soil Fe and Mn oxy-hydroxides. Other soil properties, such the content of clay and organic matter and pH, also control Ni behavior, and its phyto-availability (Kabata-Pendias and Mukherjee, 2007). The mean soluble concentration of this element in the surface and sub-surface investigated soil samples were 6.69 and 2.58 mg/L, respectively.

Concentration of Cu in soil solution ranges from 0.0005 to 0.135 mg/L (Kabata-Pendias and Mukherjee, 2007). The soluble concentration of Cu in the investigated soil samples was much higher than these values. The mean soluble concentration of Cu in surface and subsurface soil samples were 8550 and 235 mg/L, respectively. In uncontaminated soils, only about 1% of the total amount of Cu in soil is present in the soil solution (Ponizovsky et al., 2006). The mobility and thus bioavailability of this element is especially affected by the natural sorption agents such as oxy-hydroxide particles of Al, Mn, Fe, and organic matter, pH, Eh, organic matter, soil texture, mineral composition, temperature, and water regime (Kabata-Pendias and Mukherjee, 2007).

In this study, the mean soluble concentrations of Fe in surface and subsurface soil samples were 1270 and 58 mg/L, respectively. Generally, the contents of easily soluble and exchangeable fractions of Fe in soil are very low in comparison to its total concentration and ranges from 0.03 to 0.55 mg/L in soil solution in common soil pH, but in highly acidic soils it can exceed more than 2 mg/L (Kabata-Pendias and Wiacek, 1985).

The mobility of Mn in soils is highly dependent on the pH and redox potential (Kabata-Pendias and Mukherjee, 2007). The mean soluble concentration of this element in the leached solution of the surface and subsurface investigated soil samples were 309 and 193 mg/L, respectively. Concentrations of Mn in natural soil solutions range from 0.025 to 2 mg/L, depending on the soil kinds and techniques used for obtaining solutions (Kabata-Pendias and Pendias, 2001).

The geochemical behavior of Mo in soils differs greatly from that of other trace metals, and it is slightly mobile in acid soils (pH < 4–5) and readily mobilized in alkaline soils (pH > 6.5) (Kabata-Pendias and Mukherjee, 2007). Soluble concentration of this element in the surface and sub-surface investigated soil samples were 4.48 and 0.53 mg/L, respectively. Soils in arid and semiarid regions, such as Sarcheshmeh area, usually contain relatively high amounts of Mo (Kabata-Pendias and Mukherjee, 2007).

Pb concentrations in soil solution are relatively low (<0.0001 to 0.06 mg/L) (Kabata-Pendias and Mukherjee, 2007) and about only 0.005–0.13% of Pb in the soil solution is available to plants (Davies, 1995). The mean soluble concentration of this element in the surface and subsurface investigated soil samples were 62.4 and 10.5 mg/L, respectively.

The mean Sb concentrations in the investigated surface and subsurface soil samples were 2.67 and 0.57 mg/L, respectively. Antimony is slightly mobile in soils because it is attached strongly to particles that contain Fe, Mn, and Al oxy-hydroxides (Kabata-Pendias and Mukherjee, 2007). Like the results obtained in this study, Sb showed quite high concentration in surface layers of the contaminated soils near other industrial sites, especially around the Cu-smelters such as East of Tacoma (ranges between 65 and 109 mg/L) and Maury Island (ranges 49–204 mg/L) in the USA (Flynn et al., 2003). The soluble concentration of this element ranges from 0.007 to 0.03 mg/kg in the contaminated soils around Sb smelters and Sb mining (Li and Thornton, 1993).

The mean soluble concentrations of Se in the surface and subsurface soil samples were 0.96 and 0.11 mg/L, respectively. Generally, Eh and pH are the two main factors that control Se forms and its behavior in soils, however several other parameters like organic ligands, clays, and hydroxides also play very significant roles (Kabata-Pendias and Mukherjee, 2007). High mobility and phyto-availability of Se can be expected in soils of high pH and Eh (most commonly in arid and semi-arid regions), and conversely low mobility can be assumed in soils with high contents of natural sorptive materials such as hydroxides, organic matter and granulometric clay fractions. The maximum adsorption of this element occurs between pH 3 and pH 5 and decreases as pH rises (Kabata-Pendias and Mukherjee, 2007).

The soluble concentration of Zn in natural soil is 35 (13–72) mg/L (Tyler and Olsson, 2002). However, depending on techniques used for obtaining soil solution its concentrations vary between 0.021 and 0.57 mg/L (Kabata-Pendias and Pendias, 2001). In this study, the mean soluble concentrations of Zn in the surface and subsurface soil samples were 161 and 24 mg/L, respectively.

Bismuth, S and Sn also showed higher soluble concentration in the surface soil samples. The mean soluble concentrations for these elements in the surface and sub-surface soil samples were respectively: 1.18 and 0.19 mg/L for Bi, 5200 and 182 mg/L for S, and 0.32 and 0.05 mg/L for Sn.

4. Conclusion

The results of this study provide insights into the contamination potential and environmental impacts of the Sarcheshmeh Cu-slags. According to the geochemical results multi-elemental contamination potential was observed in the Sarcheshmeh slags, corresponded to the presence of various metal(loid)s such as Cu, Mo, S, As, Ag, Sb, Se, Pb, Cd, Co and Zn in this waste. The mineralogical composition of the slag samples was the same as other metalliferous base metal slags and controlled by the primary mineralogy of the ore concentrate, the smelting process and the weathering reactions in the semiarid climate conditions. Leaching studies showed that the type and the leachability potential of contaminant elements were different among the investigated samples, remarkably. The leached concentrations of several elements such as As, Mo, Co, Cu, Fe and Se in TCLP test were exceeded from the considered regulatory guidelines for the toxicity.

Wind-dispersed slag particles, produced from the slag grinding and sieving facilities, are responsible for the contamination of topsoil layer around the slag preparation site. This contamination source increased

the total leachable (bio-available) concentrations of most of the target elements in the surface layer of the soil profiles. Obtained results demonstrated that the Sarcheshmeh Cu slags can pose an environmental risk through the natural weathering of the slag dump (As, Mo, Sb and Se) and the wind-dispersed slag particles in the contaminated soils (Cu, S, Mn, Fe, Zn, Pb, and As). Although, the contamination potential was local and highly concentrated around the slag waste dump and slag preparation site, the obtained results underscore the critical role of environmental considerations in the management of slag wastes.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gexplo.2016.03.015.

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