

Determination of Elements Leachability from Sarcheshmeh Porphyry Copper Mine Tailings: Application of Toxicity Characteristic Leaching Procedure

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Abstract The Toxicity Characteristic Leaching Procedure (TCLP) was applied in order to determine the leachability and mobility of different trace metals and metalloids from the Sarcheshmeh Cu mine tailings. Twenty one solid samples were collected from weathered and fresh tailings and also from evaporative secondary minerals and efflorescence salts associated with the oxidation zone of dried tailings. According to the TCLP results, the most leachable and mobile trace elements are Ag, Al, Cd, Ni, S, Se, Co, Cr, Cu, Fe, Mn and Zn. These contaminant elements were concentrated in the surface evaporative layer formed on the top of old weathered tailings. Very high concentrations of Al (27,600 mgL⁻¹), Cu (56,900 mgL⁻¹), Mn (13,260 mgL⁻¹), S (151,800 mgL⁻¹), and Zn (3,935 mgL⁻¹) were observed in the TCLP results of the evaporative samples (mean values are presented). The results obtained from evaporative and efflorescence samples were higher than the regulatory levels for Al, Cu, Cd, Ni, Se, and Zn. The maximum leachability was found for Al and Cu, followed by Ni, Cd, Zn, and Se. The results of this study are useful for the prediction of contamination potential of trace elements and environmental management of mine tailings.

Keywords Sarcheshmeh mine tailings · TCLP experiment · Trace elements · Semiarid climate

1 Introduction

Mobility of toxic trace elements is an important factor for evaluating the short and long-term environmental impacts associated with the different mine wastes (Khorasanipour et al. 2011). During the recent decades, many single and sequential extraction methods have been developed in order to evaluate mobility, bio-availability, and speciation of hazardous trace elements in soil, sediment and solid wastes (Filgueiras et al. 2002; Gleyzes et al. 2002; Hlavay et al. 2004). Among these extraction methods, the Toxicity Characteristic Leaching Procedure

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(TCLP) was designed by the US EPA (1986; 1994) in order to ascertain the leachability potential of hazardous and toxic chemicals from solid waste under typical environmental conditions (Chang et al. 2001; US EPA 1994; Halim et al. 2005).

Sulfidic mine tailings are usually classified as potential hazardous waste. They are produced during the flotation of sulfide ores such as Cu porphyry or mixed sulfide ores and consist mainly of pyrite and other gangue minerals (Lottermoser 2003; Khorasanipour et al. 2011; Khorasanipour and Eslami 2014). The disposal of tailings and their subsequent hydro-geochemical changes are one of the great environmental problems of the scientific community (McGregor and Blowes 2002; Sima et al. 2011; Grangeia et al. 2011). Environmental aspects of mine tailings wastes were also investigated by several authors (e.g., Dold and Fontboté 2001; Saxena and Dhimole 2006; Blowes et al. 1991; Coggans et al. 1999). According to these studies, if sulfide mine wastes such as tailings are exposed to the atmospheric oxygen or dissolved oxygen in the vadose zone, the oxidation of sulfide minerals will occur with the combination of several processes such as acid producing, acid buffering reactions and secondary mineral formation. During the weathering and oxidation reactions of tailings many site specific conditions such as the primary mineralogy of the tailings, the efficiency of recovery processes and climatic conditions profoundly affect the geochemical behavior of trace metals (Dold and Fontboté 2001; Lottermoser 2003; Berger et al. 2008).

The environmental impacts of mine tailings in arid and semiarid climate conditions are enormous due to the continuous water and/or wind erosions (Redwan and Rammlmair 2012). Climate variations provide fundamental controls on many reactions, such as weathering intensity, secondary mineral formation, and the mobility of contaminant metals and metalloids from tailings (Berger et al. 2008; Dold and Fontboté 2001; Khorasanipour and Eslami 2014). In arid and semiarid areas, evaporative concentration causes secondary mineral precipitation at the surface or at a particular depth of tailings dams. These sulfate precipitates are commonly referred to as “efflorescences” or “evaporative salts”. Annual formation and dissolution of highly soluble sulfate salts can profoundly affect the hydro-geochemical of mine tailings (Olyphant et al. 1991; Bayless and Olyphant 1993; Hammarstrom et al. 2005).

The main object of this study is to identify the enrichment pattern of potentially hazardous trace elements including metals and metalloids in the Sarcheshmeh mine tailings. For this purpose, the TCL procedure was applied to the various solid samples including: fresh and weathered tailings, and secondary evaporative and efflorescence samples. These data are interesting and useful for prediction of contamination potential of tailings, because most of environmental concerns associated with these wastes are site specific and may vary from site to site considerably (Dold and Fontboté 2001; Lottermoser 2003; Akcil and Koldas 2006). Application of TCL procedure on the Sarcheshmeh mine tailings, as one of the world’s largest porphyry copper deposits located in semiarid climate conditions, is notable and exciting.

2 Site Description

The Sarcheshmeh mine, in one of the largest Oligo-Miocene porphyry copper deposits in the world, is located in the central Iranian volcano-plutonic copper belt, 160 km southwest of Kerman, Iran (Fig. 1a). Mineralization at the Sarcheshmeh copper deposits is occurring as many zones of stockwork and vein types that are equally distributed between Eocene volcanics and Oligo-Miocene of quartz diorite, quartz monzonite and granodiorite composition (Atapour and Aftabi 2007).

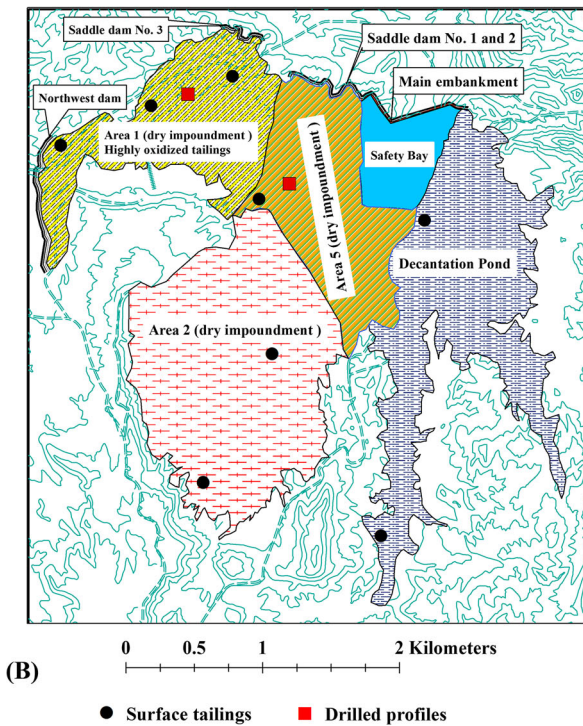
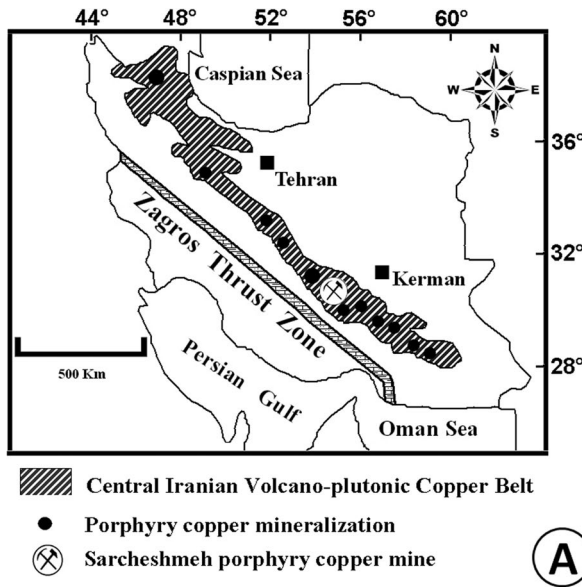


Fig. 1 a Central Iranian tectono-volcanic copper belt and the location of the Sarcheshmeh porphyry copper deposit (Modified after Shahabpour and Kramers 1987). b The main compartments of the Sarcheshmeh tailings sedimentation impoundment

The Sarcheshmeh area is located in semiarid climate conditions. The annual temperature of this area ranges from -20 to 32 °C, mean rainfall of 440 mm, and annual evaporation of about 1,170 mm (Khorasanipour et al. 2011). The main lithological structures around the Sarcheshmeh porphyry copper mine are Eocene basic-to-intermediate volcanic rocks (trachybasalt, trachyandesite, and/or andesite) (Dimitrijevic 1973; Atapour and Aftabi 2007).

The production of mine tailings in the Sarcheshmeh concentration plants is nearly 1,215,000 t per year (Khorasanipour et al. 2011). The mean content of pyrite as a main sulfide mineral is about 7.5 % in the Sarchshmeh mine tailings (Khorasanipour et al. 2011).

The tailings sedimentation impoundment of the Sarcheshmeh copper mine is located in a mountainous area, approximately 19 km north of the mine. The dam, which currently consists of several ponds, has been operating as a cross valley type since 1976, and has been filled gradually and sequentially (Khorasanipour and Eslami 2014). The annual output of roughly 11.4 million m^3 of tailings with specific gravity of $1.28 t/m^3$ was used as a basis for prediction of tailings dam volume. Figure 1b shows the main compartments of the Sarcheshmenh dammed tailings pond. At present, the maximum depth of tailings reaches about 75 m.

Most of the supernatant water from the decantation pond discharges into the safety bay and is then recycled to the Sarcheshmeh copper complex for further industrial use. Semiarid climate conditions and high evaporation rate are other significant factors that cause most of tailing impoundments to dry quickly. Field indications of the weathering reactions, including oxidation of sulfide minerals contained within the tailings and massive precipitation of secondary evaporative minerals are well observed in the oxidation zone of dried compartments of the Sarcheshmeh tailings impoundment. Some of the field indications of tailings weathering are presented in Fig. 2a and b.

3 Material and Methods

Twenty one solid samples were collected mainly from weathered and fresh tailings and also from evaporative secondary minerals and efflorescence salts associated with the oxidation zone of dry impoundments. Figure 3 shows the schematic representation of data acquisition. Samples were collected by plastic device and stored in air-tight plastic bags. After oven drying and microwave multi-acid digestion ($HCl+HNO_3+HF$ +boric acid solution), the total content of target trace elements were determined using ICP-MS (As, Cd, Co, Cu, Mo, Ni, Pb, Sb, Se, Sn, and Zn) and ICP-OES (Fe, Mn, Cr, and S) at the Labwest Laboratory, Perth, Australia.

3.1 Leaching Procedure

In this study, the US EPA TCLP (1994) 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 is a key factor for the selection of the appropriate leaching solution which is determined by the addition of 96.5 mL of deionized water to 5 g of each solid phase into borosilicate glass beaker. The beaker was covered with a watch glass and stirred vigorously for 5 min using a magnetic stirrer and then the pH of the solution was recorded using Toledo MP-120 pH meter model. The pH values of the samples range from 2.85 to 8.31 (Table 1).

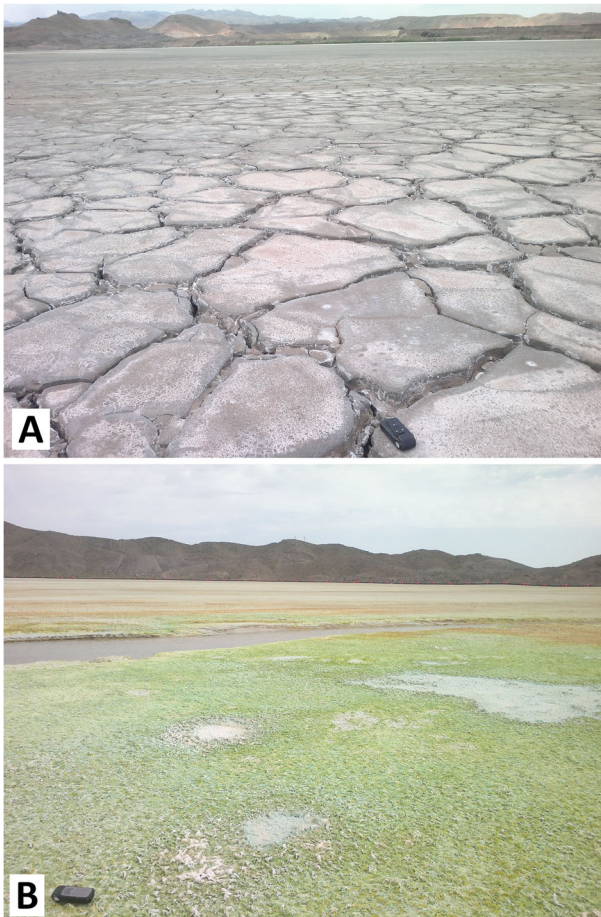


Fig. 2 a Dried fresh tailings due to the high evaporation rate and reuse of tailings water. b Massive precipitations of secondary evaporative minerals and efflorescence salts formed on the top of old weathered tailings

The acidic pH values were mainly associated with the weathered tailings and secondary evaporative phases. Based on the initial pH values, the extraction “solution 1” was used for all samples as specified by the US EPA (1994). This extraction solution is 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 1 liter.

TCLP involves leaching at ambient conditions and 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 3,500 rpm, and then filtration through 0.45 μm filter (ALBET, NitratoCelulosa, model). All extracts were acidified using nitric acid to pH < 2 and analyzed using ICP-MS/OES at the Labwest Laboratory, Perth, Australia. The limit of detection for target trace elements mostly ranges from 0.5 to 1 $\mu\text{g/L}$.

Quality assurance of the leaching procedure was achieved using analysis of method blank (containing the extraction solution but no solid phase) and also carrying out the leaching procedure in duplicate for a number of samples. The Relative Percent of Difference (RPD) of the results obtained from repeated samples was calculated using following Eq. (1). The RPD is

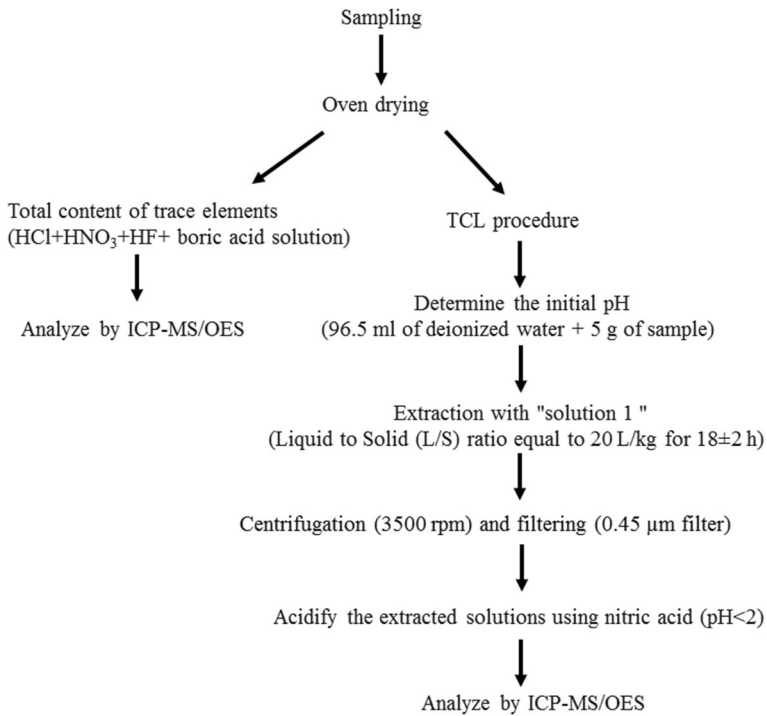


Fig. 3 Schematic representation of data acquisition

the difference between duplicate values divided by the average of the duplicate values and multiplied by 100.

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

The RPD values for target elements are mainly below $\pm 2\%$. The accuracy and precision of results, as proposed by Zhang (2007), were verified by analyzing multi-elemental reference materials and duplicating same solutions, respectively.

3.2 Statistical Methods

The multivariate relationships between elements (or variables) were investigated by using of principal components analysis (PCA), and cluster analysis (CA) methods. In order to correct the magnitude and scale differences, the varimax normalized rotation PCA was performed on the data sets using correlation matrix (DelValls et al. 1998; Emmerson et al. 1997; Webster 2001). Significant principal components (eigenvalues >1.0) were extracted from the variables based on the Kaiser Criterion (Kaiser 1960). The factor loadings were considered significant or excellent if they were >0.6 or >0.71 , respectively (DelValls et al. 1998; Yongming et al. 2006).

Hierarchical cluster analysis was used in this study. By using this method, the standardization of variables is performed automatically before computing proximities. Cluster analysis was applied to standardized data using the “Within-groups linkage” method, with Pearson

Table 1 Results obtained from the TCLP experiments

Sample No	Initial pH	Concentration (mg/L)																
		Ag	As	Bi	Cd	Co	Cr	Fe	Mo	Ni	Pb	Sb	Se	Zn	Al	Cu	Mn	S
T1	3.40	1.013	1.42	0.012	35.85	530	17.68	205.95	0.54	358.51	0.004	0.059	5.19	5663.6	32,000	27,650	16,000	164,200
T2	3.29	5.125	1.39	0.034	34.29	396	13.62	155.86	0.33	260.09	0.295	0.112	8.07	2543.0	18,200	46,810	10,400	108,500
T3	3.26	0.431	2.13	0.006	19.36	624	22.04	1771.0	0.69	316.26	0.029	0.079	4.54	4408.4	34,500	26,830	13,150	180,900
T4	3.06	0.008	8.53	0.010	5.06	237	29.69	9268.6	0.38	177.95	0.008	0.101	1.20	1141.9	28,200	13,700	3,010	116,100
T5	3.19	4.135	2.36	0.009	79.68	717	27.76	570.23	0.30	387.08	0.268	0.120	14.90	4437.2	23,400	79,500	16,970	155,800
T6	3.26	6.000	3.44	0.017	119.43	1,159	35.35	598.09	0.52	449.04	0.224	0.118	25.22	4834.3	26,200	135,100	18,530	164,100
T7	3.25	5.943	3.76	0.009	121.72	1,098	34.39	607.64	0.47	454.77	0.050	0.102	25.60	4853.4	26,600	132,400	19,870	172,900
T8	2.85	0.047	4.17	0.010	8.96	283.5	18.50	8735.8	0.40	211.26	0.270	0.114	1.22	2112.6	24,200	7,441	6,300	129,400
T9	3.70	0.678	4.30	0.014	50.22	924.1	22.15	177.58	3.67	322.70	0.034	0.118	8.86	5422.8	35,100	42,960	15,160	174,700
T10	3.71	0.006	0.06	0.009	0.35	5.50	0.17	4.39	0.05	3.53	0.172	0.057	0.08	49.30	400	278.9	164.3	4,833
T11	3.14	0.032	0.56	0.012	5.00	86.57	4.70	736.32	0.20	56.32	0.162	0.112	0.48	852.38	4,900	2,720	2,450	39,800
T12	3.24	0.003	0.13	0.012	0.26	6.48	0.06	8.17	0.02	4.31	0.015	0.074	0.09	67.27	100	91.97	177.8	3,819
T13	3.67	0.003	0.08	0.014	0.22	5.41	0.04	2.26	0.01	3.88	0.019	0.091	0.07	54.48	100	81.61	163.2	3,166
T14	3.46	0.010	0.19	0.007	5.39	84.69	2.55	26.83	0.18	54.24	0.006	0.093	0.58	561.42	2,500	3,045	159.4	27,780
T15	3.33	0.002	0.08	0.008	0.47	20.47	0.21	1.33	0.02	11.03	0.002	0.076	0.13	137.06	100	638.8	269.2	8,417
T16	3.40	0.003	0.06	0.010	0.78	18.83	0.44	0.77	0.00	12.19	0.050	0.068	0.11	117.29	200	437.9	326.0	6,751
T17	6.70	0.002	0.08	0.018	0.84	2.62	0.02	3.08	0.10	1.82	0.323	0.097	0.05	36.77	15.4	342.7	122.8	1,039
T18	6.67	0.008	0.09	0.013	0.68	6.80	0.27	44.53	0.04	4.70	3.058	0.283	0.11	155.77	131.4	245.2	157.4	2,331
T19	8.31	0.001	0.08	0.022	0.29	1.09	0.04	47.34	0.65	1.32	1.536	0.163	0.18	18.14	25.66	61.41	25.10	3,935
T20	5.46	0.000	0.19	0.011	1.46	18.72	0.25	12.42	0.01	9.68	1.864	0.085	0.07	263.58	62.28	414.5	874.8	4,335
T21	6.70	0.007	0.16	0.011	0.85	3.64	0.06	19.54	0.11	2.45	0.393	0.146	0.20	46.18	7.08	32,000	156.3	1,283
Regulatory level ^{A, B}	5	5	5	1	5	5	5	5	7	7	5	0.6	1	500	5	100	5	100

Sample descriptions: T1-T9 secondary evaporative and effluence samples; T10-T16 weathered tailings; and T17-T21 fresh un-weathered tailings

A: silver, As, Cd, Cr, Ni, Pb, and Se are regulated under National Interim Primary Drinking Water Standards, NIPDWS (Margui et al. 2004) B: Aluminum, Cu and Zn are regulated under a secondary water quality standards (U.S EPA 2009)

correlation as the criterion for forming clusters of elements (or variables). The SPSS software version 19 was used to perform the multivariate methods.

4 Results and Discussion

As noted earlier, samples were collected from different parts of the Sarcheshmeh tailings impoundment to evaluate elements leachability and mobility during the weathering of tailings. Table 1 shows the results obtained from TCLP experiments for target trace elements (Al, As, Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Se, and Zn). The mean concentrations of trace elements in the TCLP results were compared with the mean total concentration of these elements (multi-acid digestion, HCl+HNO₃+HF+boric acid solution). The results for three groups of samples including fresh and weathered tailings and also secondary evaporative and efflorescence phases are shown in Fig. 4. A remarkable difference is observed in the correlation between total and leachable fractions of trace elements in the different group of samples. The correlation coefficients $-R^2$ between TCLP results and total concentrations in the fresh tailings, weathered tailings and evaporative and efflorescence samples are 0.55, 0.67 and 0.95, respectively. The reasons for the different geochemical behavior of trace elements in different types of tailings are discussed in the following sections.

4.1 Fresh Tailings

The results from TCLP experiments showed that the leachable fraction of most of trace elements such as Ag, Al, As, Bi, Co, Cr, Se, Sb, Mo, Zn, Mn, and Cu leached from the fresh tailings comprised a small percentage of their total concentrations (Fig. 4a). Fresh tailings are the primary source of trace elements. Sarcheshmeh tailings are mainly composed of quartz (42 %), albite (9 %), sericite (24 %), chlorite (11 %), orthoclase (8.3 %), and pyrite (7.5 %) (Khorasanipour et al. 2011). Generally, most of trace elements in sulfidic mine wastes tailings are associated with the sulfide minerals, especially pyrite. Pyrite is the most abundant sulfide mineral in the Sarcheshmeh mine tailings and comprise about 7.5 % of tailings (Khorasanipour et al. 2011). The iron sulfide, pyrite, is strongly associated with many trace metals like As, Bi, Cd, Co, Cu, Ga, In, Hg, Mo, Pb, Re, Sb, Se, Tn, Te, and Zn (Spears et al. 1994). Chalcopyrite, the most important ore mineral in Cu-porphyry deposits, also 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). Sulfide minerals in the fresh tailings samples are not oxidized, and therefore, their associated trace elements are mainly in the form of non-leachable fraction.

4.2 Weathered Tailings

The concentrations of Cd, Co, Cu, Mn, Ni, S, and Zn are increased in the TCLP results of weathered tailings (Fig. 4b). In spite of this fact, the concentration of Ag, Al, As, Bi, Cr, Fe, Mo, Pb, Sb, and Se in TCLP leachates still remains much lower than their total concentrations. Tailing wastes become chemically unstable when exposed to an oxidizing environment, but the geochemical behavior of trace elements during the weathering and oxidation reactions, and subsequent acidic conditions, are considerably different. For example, the divalent cations are usually mobile under acidic conditions, while oxy-anions like Mo (V, VI) and As (V) show increasing adsorption to Fe (III) oxy-hydroxides with decreasing pH (Dzombak and Morel 1990; Dold and Fontboté 2001; Khorasanipour et al. 2012). This relationship is reflected by

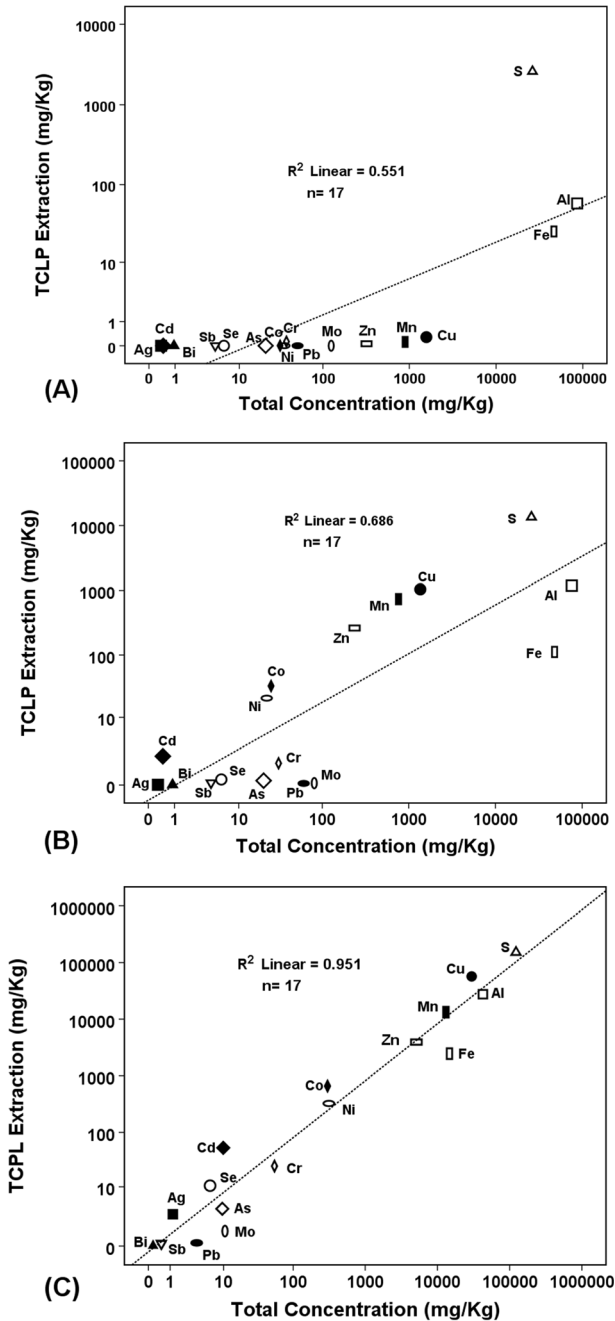


Fig. 4 The TCLP results versus the total concentrations of target trace elements in **a** fresh tailings, **b** weathered tailings and **c** evaporative and efflorescence samples

the increased As concentration in Fe (III) oxy-hydroxides fraction in the oxidation zone of tailings (Dold and Fontboté 2001). Kelepertzis et al. (2012) also noted that the low Pb level as

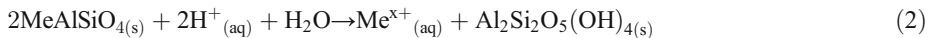
soluble fraction in the oxidation zone is related to the adsorption onto suspended and colloidal particles of hydrous ferric oxides. It is notable that, adsorption/desorption of trace elements is a selective process. For example, As and Pb are the most effectively adsorbed metal at acidic pH values, whereas Zn, Cd, and Ni are adsorbed at near neutral pH values (Plumlee 1999). By contrast, Mo is mobile up to 3.9 mg/L (Smuda et al. 2008) or up to 2.55 mg/L (Khorasanipour and Eslami 2014) in alkaline tailings waters.

The low concentration of Ag, Al, As, Bi, Cr, Fe, Mo, Pb, Sb, and Se in the TCLP results of weathered tailings is due to the one of the following reasons:

- 1- The natural adsorption by adsorptive agents such as Fe-oxy-hydroxides that retain trace elements such as As, Pb, Bi and Mo in the solid form;
- 2- The movement of the released trace elements (Ag, Al, Cr, Se and Sb) from weathering zone and concentrate in the surface evaporative layer.

The Sarcheshmeh tailings impoundment is located in a climate where evaporation exceeds the precipitation. In this climate regime, the water-flow direction changes to upward migration via the capillary force, and therefore, mobilized elements are transported to the top of the weathered tailings. This geochemical condition is same as the El Teniente and El Salvador porphyry copper tailings (Dold and Fontboté 2001).

The primary mineral assemblage was subjected to weathering and oxidation reactions in the upper oxidation zone of the tailings. In addition to the well-established pyrite oxidation reactions, chemical weathering of silicate minerals, such as albite and orthoclase, can consume hydrogen ions and release their elements (Ca, Na, K, Mg, Mn, or Fe) through incongruent (Eq. 2) or congruent weathering (Eq. 3) (Lottermoser 2003).



where Me = Ca, Na, K, Mg, Mn, or Fe.

4.3 Secondary Evaporative and Efflorescence Phases

The TCLP results show that most of hazardous trace elements such as Ag, Al, As, Cd, Ni, S, Se, Co, Cr, Cu, Fe, Mn and Zn are concentrated as leachable fraction in the surface evaporative minerals and efflorescence phases. The maximum correlation between TCLP results with the total concentration data was observed in this group of samples. Bismuth, Mo, Sb, and Pb are the only elements that have minimum concentration in the TCLP solutions of evaporative samples (Fig. 4c). Very high concentrations of Al (27,600 mg L⁻¹), Cu (56,900 mg L⁻¹), Mn (13,260 mg L⁻¹), S (151,800 mg L⁻¹), and Zn (3,935 mg L⁻¹) were observed in the TCLP results of the evaporative samples (mean values are presented). Evaporation of tailings water, especially from weathering zone, commonly leads to super-saturation, which controls the precipitation of mainly water soluble secondary sulfate minerals (Johnson et al. 2000; Dold and Fontboté 2001; McGregor and Blowes 2002). As suggested by other authors (e.g., Cravotta 1994; Lin 1997; Khorasanipour and Eslami 2014), formation and dissolution of secondary minerals, especially simple hydrous metal sulfates, can release metals, acidity, and sulfate into the water. This process is responsible for the low pH (from 2.5 to 4.1) and high

concentrations of contaminants in the water samples associated with the highly weathered tailings (Khorasanipour and Eslami 2014).

According to Khorasanipour and Eslami (2014), dissolution of soluble secondary mineral phases, which are formed at and near the surface of the old weathered tailings, is responsible for the development of highly contaminated waters in short periods of time in the dry impoundment of the Sarchshmeleh mine tailings. Fine grain size increases the water retention capacity and capillarity force of the tailings, resulting in higher mobilization of water to the surface and enrichment of bivalent cations, Cl^- , and SO_4^{2-} in water soluble phases. Significant upward mobilization of Al, Na, Cl, Cd, Co, Cr, Cu, Mg, Mn, Ni, Se, SO_4^{2-} , and Zn takes place during the dry seasons in the Sarchshmeleh mine tailings (Khorasanipour and Eslami 2014). Upward migration is later superimposed on the general trend of downward mobilization during the rainy season. These hydro-geochemical and environmental important processes are similar to those has been reported in previous studies (Dold and Fontboté 2001; Wu et al. 2009; Zhao et al. 2012).

4.4 Multivariate Statistical Descriptions

Principal component analysis (PCA) and cluster analysis (CA), as the most important multivariate statistical methods, have been widely used to interpret the geochemical, hydro-geochemical and environmental data sets (Khorasanipour et al. 2012). These methods provide a further insight about the latent relationship between variables and/or samples.

According to the Varimax rotated principal components analysis, four factors have eigenvectors higher than Kaiser Criterion (1960) (Table 2). The 90 % of the total variance of the TCLP data is explained by these four principal components. Factor 1, with about 50 % of the total variance, has significant positive loadings of Al, Cd, Cr, Cu, Mn, Mo, Ni, S, Se, and Zn. According to the TCLP results, these elements (except Mo) were highly mobile and concentrated in the surface evaporative layer of tailings. In the TCLP results, the leachable fraction of Mo was also increased from fresh tailings to the weathered tailings and surface evaporative samples as same as other elements such as Cu, S and Zn, but in all cases the leachable fraction of Mo comprised very small fraction of its total concentration.

The second factor of PCA contains 17 % of the total variance of data. Iron, As and Sn are elements that have significant loadings in this factor. The role of iron in the adsorption of hazardous trace elements, like As, especially in weathered tailings, is obvious. Component 3 that accounted for 12.7 % of the variance in the rotated PCA matrix is characterized by high loadings of Ag and Bi. Also, Pb and Sb are situated in the component 4 of PCA that accounted for 10.7 % of the total variance. Except of Ag, which was increased in the TCLP results of evaporative samples, in other cases elements in these two latest factors of PCA have low concentration in the TCLP experiments. The relationships between different trace elements can be made easier to understand by mapping the variable loadings. Figure 5 represents the three-dimensional plots of the rotated component matrices of the TCLP data set. In this figure, a clear distinction is observed between elements with the same geochemical behavior. The most leachable trace elements (Al, Cd, Cr, Cu, Mn, Mo, Ni, S, Se, and Zn) are well separated from trace elements with low leachability in the 3-D PCA plot.

Figure 6 shows the results of the hierarchical cluster analysis (CA). Three distinct groups of elements were identified according to the cluster analysis. The main results are as follows:

- 1- Elements with high leachability and mobility: According to the degree of association, this group of elements is divided into the several subgroups including:

Table 2 Component matrices and total variance explained by applying the Varimax rotated PCA method to the TCLP results. Factor loadings lower than 0.5 are removed

Variables	Rotated component matrix				Communalities
	F1	F2	F3	F4	
Al	0.87				0.99
Cd	0.87				0.98
Co	0.98				0.98
Cr	0.78				0.99
Cu	0.83				0.98
Mn	0.97				0.97
Mo	0.69				0.98
Ni	0.93				0.98
S	0.91				0.97
Se	0.85				0.98
Zn	0.98				0.97
As		0.87			0.97
Fe		0.95			0.75
Sn		0.80			0.95
Ag			0.85		0.95
Bi			0.71		0.87
Pb				0.90	0.92
Sb				0.95	0.89
Initial Eigenvalues	9.00	3.05	2.29	1.93	
Percent of variance	49.99	16.94	12.73	10.73	
Cumulative percent	49.99	66.93	79.66	90.39	

Factor loadings lower than 0.5 are removed

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in five iterations

- I. Cu=Se=Cd>Ag
 - II. Mn=Zn=Ni=Co
 - III. Al=S>Co
- 2- As=Fe>>Sn. This elemental association is same as the second component of the PCA.
 - 3- Pb and Sb have a strong association in this group similar to the fourth component of PCA. The association of Bi with Pb and Sb is also very weak in the higher order of cluster analysis.

According to the cluster analysis method, it is possible to classify target trace elements in more homogenous groups of elemental associations. These results strongly confirm PCA results.

4.5 Comparison With the Regulatory Levels

A solid waste exhibits the characteristic of toxicity if the concentration of any target contaminant in the TCLP extract is greater than or equal to the respective recommended US EPA

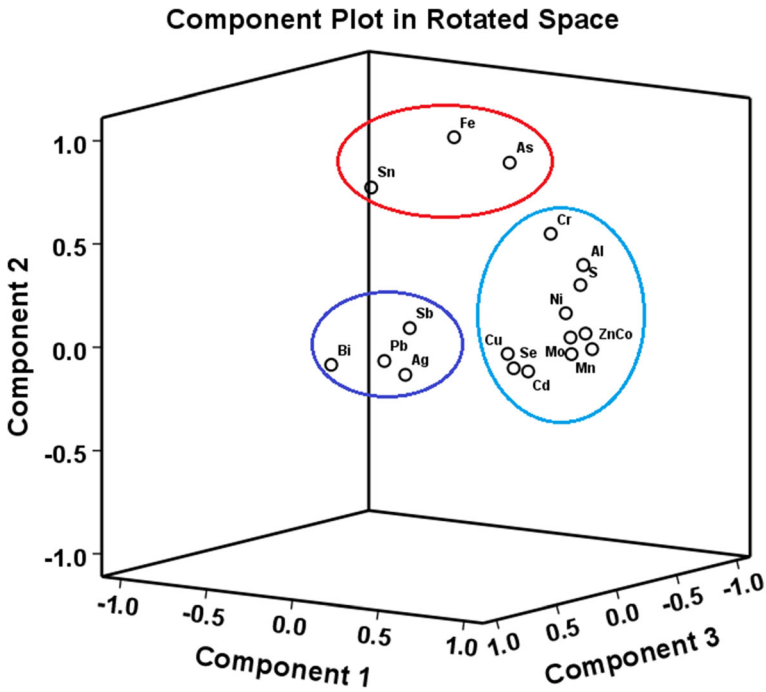


Fig. 5 The PCA results in the three dimensional space: plot of loadings of the first three principal components of varimax rotated PCA

regulatory limit value (Margui et al. 2004). The regulatory levels or standard values typically are 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, Ag and Cr, 1 mg/L for Cd and Se, and 7 mg/L for Ni (Eckert and Guo 1998). Given that TCLP regulatory

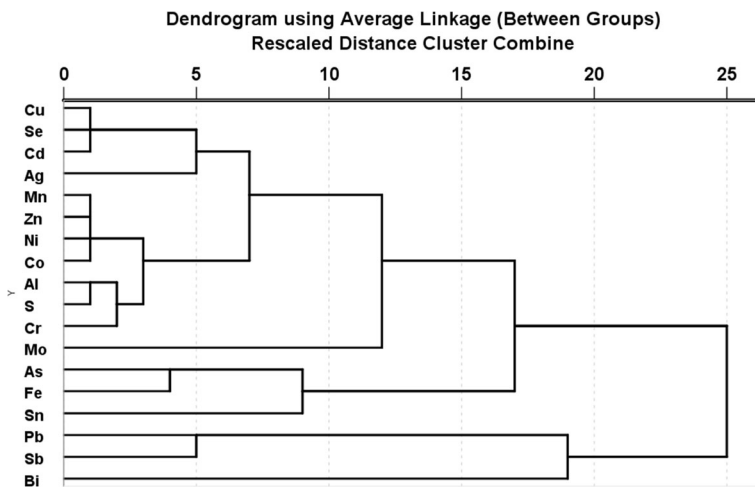


Fig. 6 Hierarchical cluster analysis results of TCLP data set by the use of “Between-groups linkage” method. Similarities have been calculated from the Pearson correlation

limits exist for only nine metals, in this study, one-hundred times the secondary drinking water standards of Cu, Al, Sb and Zn, defined by the US EPA (2009), were also used for evaluation of TCLP results. These values are 100 mg/L for Cu, 5 mg/L for Al, 0.6 mg/L for Sb, and 500 mg/L for Zn. The TCLP results were compared to the regulatory levels by using the following Eq. (4):

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

where EF is the enrichment factor. The results showed that the concentrations of Ag, As, Pb, and Sb leached from different samples after 18 h extraction period are mainly below the recommended regulatory levels. On the other hand, the concentrations of Al, Cu, Cd, Cr, Ni, Se and Zn in TCLP results are much higher than the regulatory levels. Among the investigated toxic metals the maximum enrichments were observed for Al and Cu, followed by Ni>Cd>Zn>Se>Cr. Figure 7 shows the order of trace elements enrichment based on the median values. The enrichment values for trace elements in the three groups of investigated samples (fresh and weathered tailings and evaporative phases) are remarkably different. For example, the concentration of Al, Cu, Cd, Ni, Se, and Zn in the TCLP results of fresh and weathered tailings are lower than their recommended regulatory levels. On the contrary, the results obtained for these elements in evaporative and the efflorescence samples exceed the criteria of 100 times the US EPA regulatory levels. These results clearly show how a very hazardous waste material is made from non-hazardous fresh tailings. The weathering and associated processes together with the semiarid climate conditions are responsible for the release and transport of hazardous trace elements from fresh tailings to the surface evaporative layer on the top of old weathered tailings. The correlation matrix between enrichment values also shows that the most leachable and potentially contaminant trace elements (Al, Cu, Ni, Cd, Zn, Se, and Cr) are positively correlated with each other and strongly concentrated in the efflorescence salts and secondary evaporative minerals (Fig. 8).

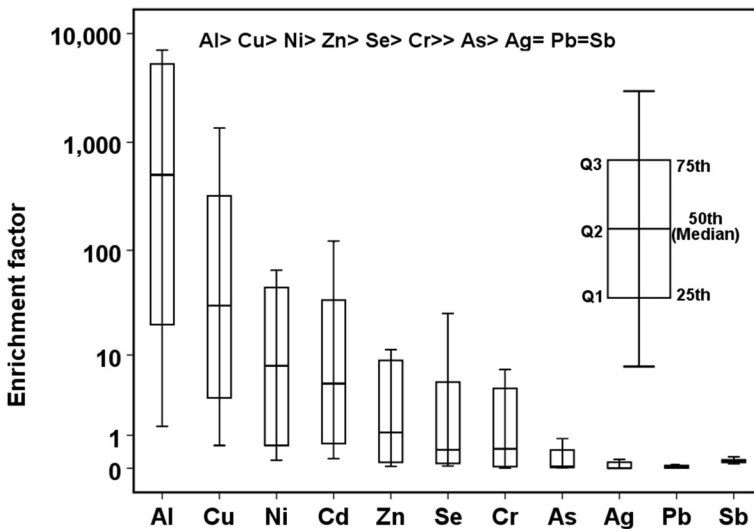


Fig. 7 Box plot showing the order of enrichment for Cu, Cd, Se, Al, Ni, As and Ag in the TCLP results compared with the U.S. EPA regulatory levels

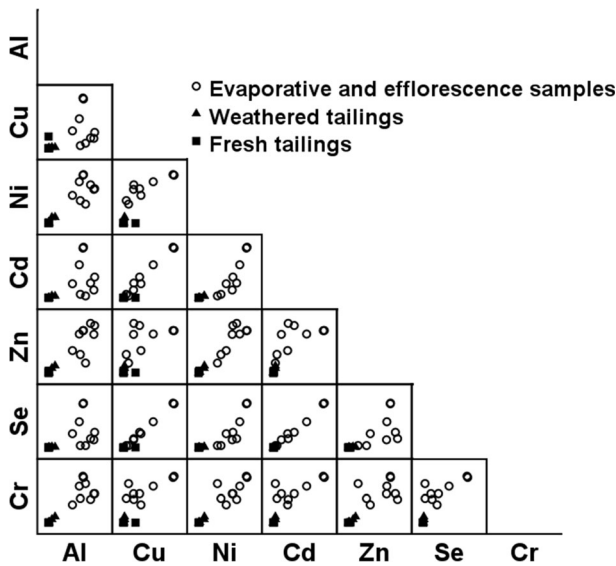


Fig. 8 The correlation matrix between enrichment values of most of leachable and highly mobile trace elements

Weathering and oxidation of fresh tailings lead to the trace metal contamination in the Sarcheshmeh tailings impoundment. Environmental management of mine tailings for short and long periods of times must be done taking into consideration the several site specific conditions such as: (1) tailings impoundment is situated in semiarid climatic condition with high evaporation rates of water in dry seasons; (2) due to the fine grain size of tailings uncovered tailings are susceptible to severe water and wind erosion, which creates pollution for air, soil and water; (3) multi-elemental contamination is observed in tailings waste; (4) the dam is not at the final stage and in the future the old weathered tailings will be covered by new fresh tailings; (5) most of tailings water is recycled from the tailings impoundment to the Sarcheshmeh copper complex for further industrial use.

5 Conclusions

Sarcheshmeh mine tailings are dried quickly and exposed to the weathering and oxidation reactions due to the semiarid climate conditions. The supernatant waters are recycled and reused for further industrial purposes. According to the TCLP experiments, remarkable differences were observed between the leachability and mobility potential of different trace elements during the weathering and oxidation of fresh tailings. The leachable fraction of potentially hazardous trace elements was increased from weathered tailings to the evaporative and efflorescence phases. A remarkable increase was observed in the leachable fraction of Ag, Al, As, Cd, Ni, S, Se, Co, Cr, Cu, Mn and Zn in the surface evaporative layer of old weathered tailings.

The concentrations of Al, Cu, Cd, Ni, Se and Zn in the TCLP results of the evaporative and efflorescence samples are much higher than the recommended regulatory levels and must be classified as hazardous materials. These hazardous waste materials are formed as a result of weathering and oxidation of fresh tailings. High evaporation rate together with the capillary forces are responsible for the movement of released elements

to the surface and formation of secondary evaporative phases on the top of weathered tailing in dried impoundments. The contamination potential of trace elements in the Sarcheshmeh mine tailings is controlled by geochemical and climatological conditions. Both of these factors are of crucial importance for environmental management and remediation actions of tailings.

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