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TECHNICAL ARTICLE

Hydrogeochemistry and Contamination of Trace Elements in Cu-Porphyry Mine Tailings: A Case Study from the Sarcheshmeh Mine, SE Iran

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Abstract Geochemical and hydrochemical investigations were performed to understand the contamination potential of the Sarcheshmeh mine tailings. The geochemical mobility for the tailings is as follows: Cu > Cd > Co > Zn > Ni > Mn > S > Cr > Sn > As > Se > Fe = Bi > Sb = Pb = Mo. Highly mobile and contaminant elements (Cd, Cu, Zn, Mn, Co, Ni, S, and Cr), which significantly correlated with each other, were mainly concentrated in the surface evaporative layer of the old, weathered tailings, due to the high evaporation rate, which causes subsurface water to migrate upward via capillary action. The contamination potential associated with the tailings is controlled by: (1) dissolution of secondary evaporative soluble phases, especially after rainfall on the old weathered tailings, accompanied by low pH and high contamination loads of Al, Cd, Co, Mg, Cr, Cu, Mn, Ni, S, Se, and Zn; (2) processing of the Cu-porphyry ore under alkaline conditions, which is responsible for the high Mo (mean of 2.55 mg/L) and very low values of other contaminants in fresh tailings in the decantation pond; (3) low mobility of As, Fe, Pb, Sb, Mo, and Sn due to natural adsorption and co-precipitation in the tailings oxidizing zone. Speciation modeling showed that sulfate complexes (MSO_4^{+}, $M(SO_4)_{(aq)}$, $M(SO_4)_2^{-2}$, and $M(SO_4)_2^{-}$) and free metal species (M^{+2} and M^{+3}) are the dominant forms of dissolved cations in the acidic waters associated with the weathered tailings. In the alkaline and highly alkaline waters, trace element speciation was controlled by various hydroxide complexes, such as $M(OH)^{+}$, $M(OH)_3^{-}$, $M_3(OH)_4^{+2}$, $M_2(OH)_3^{+}$, $M(OH)_{2(aq)}$, $M(OH)_4^{-2}$, $Me(OH)_2^{+}$, $Me(OH)_4^{-}$, $Me(OH)_2^{+}$, $Me(OH)_{3(aq)}$, and $Me(OH)_4^{-}$ (where M represents bivalent and Me represents trivalent cations). The speciation pattern of As, Mo, and Se is mainly dominated by oxy-anion forms. The obtained results can be used as a basis for environmental management of the Cu-porphyry mine tailings.

Keywords Hydrogeochemical data · Speciation modeling

Introduction

Mining and processing of low-grade porphyry sulfide ores can produce huge volumes of solid and liquid waste materials (Khorasanipour et al. 2011b; Lottermoser 2003; Nordstrom and Alpers 1999). Among these, tailings pose major environmental challenges (Grangeia et al. 2011; McGregor and Blowes 2002; Sima et al. 2011). During the flotation of Cu porphyry copper ores, economically worthwhile minerals are extracted, while pyrite and other gangue minerals are disposed of as tailings waste. This waste is then discharged into a tailings impoundment. Associated challenges include: (1) During processing of low-grade metal ores, more than 99 % of the original material mined may be disposed of in tailings impoundments that consume large areas of land (Dold and Fontboté 2001; Saxena and Dhimole 2006); (2) The valuable minerals are never completely recovered and tailings always contain a small amount of these minerals, which have the

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potential for contamination (Dold and Fontboté 2001); (3) After deposition in the repository, tailings undergo chemical, physical and biological changes (Blowes et al. 1991; Coggans et al. 1999; Dold and Fontboté 2001; Johnson et al. 2000); (4) In addition to the primary mineralogy of the tailings and the efficiency of recovery processes, hydraulic sorting during deposition increases the heterogeneity of tailings waste (Lottermoser 2003); (5) 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).

Due to all of these factors, the hydrogeochemical characteristics of tailings and their environmental concerns, such as the nature and the size of associated risk, the feasibility of environmental management approaches, and mitigation options are site specific (Akcil and Koldas 2006; Dold and Fontboté 2001).

Several methods have been proposed for remediation and environmental management of tailings waste (Bjelkevik 2005; Jacob and Otte 2004; Lottermoser 2003; MiMi 2004). These methods are highly variable due to factors such as ore types and geochemistry, the procedures used for ore extraction, the quality of the process water, reagents used in process, the disposal techniques, and climate conditions.

The primary objective of this study was to investigate the hydrogeochemical behavior and contamination potential of hazardous trace elements in the Sarcheshmeh tailings impoundment. These data together with the site specific conditions can be used as a basis for remediation and environmental management of the tailings.

Site Descriptions

The Sarcheshmeh mine, 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. The location of the Sarcheshmeh porphyry copper mine and the geological structure around its tailings pond are presented in supplementary figures S-1a and b, respectively, which accompany the online version of this paper and can be downloaded for free by all subscribers. Mineralization in this porphyry district is similar to many other stockwork and vein-type deposits that are distributed in Eocene volcanics and Oligo-Miocene intrusives of quartz diorite, quartz monzonite and granodiorite composition (Atapour and Aftabi 2007).

The Sarcheshmeh area has a semi-arid climate with an annual temperature between −20 and 32 °C, a mean rainfall of 440 mm, and annual evaporation of about 1,170 mm. The geology of this region is primarily composed of Eocene basic-to-intermediate volcanic rocks including trachybasalt, trachyandesite, and/or andesite (Atapour and Aftabi 2007; Dimitrijevic 1973).

Nearly 1,215,000 t of tailings with an average Cu grade of 0.1 % and Mo grade of 0.009 % are produced annually in the Sarcheshmeh concentration plants (Khorasanipour et al. 2011b). The tailings impoundment is situated in a mountainous area, approximately 19 km north of the mine. The geology around the tailings pond is composed of trachybasalt, dolerite, sandstone, pebbly sandstone, and andesite-basaltic and trachyandesite rocks (Fig. S-1b).

The dam, which consists of several ponds, has been operating as a cross valley type since 1976, and has been filled gradually and sequentially. The annual output of roughly 11.4 million m^3 of tailings and its specific gravity of 1.28 t/m^3 was used to predict tailings dam volume. Figure 1 shows the main compartments of the Sarcheshmeh tailings impoundment. At present, the maximum depth of tailings is about 75 m and about 7.5 % of the tailings waste is pyrite (Khorasanipour et al. 2011b).

The Shour Sream receives natural and contaminated drainage from the Sarcheshmeh copper mine and its industrial complex. Part of this stream, especially after storm events in winter, eventually discharges into the tailings pond (Khorasanipour et al. 2011b). 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. The semi-arid climate and high evaporation rate are other significant factors that make most of the tailings impoundments dry quickly. Field indications of weathering reactions, including oxidation of sulfide minerals contained within the tailings and massive precipitation of secondary evaporative minerals are well represented in the oxidation zone of dried compartments of the tailings impoundment (Fig. 2). Field observations also indicate that the secondary evaporative minerals are highly water soluble and easily dissolve after heavy rains and wintertime storm events (Fig. 2c). The high solubility of efflorescent salts together with the high risk of human exposure to contaminants makes this a serious environmental problem (Bea et al. 2010; Dold and Fontboté 2001).

Methods of Investigation and Interpretation

Sampling and Analysis

Solid tailings and surface waters were sampled in order to investigate the geochemical and hydrochemical behaviors of potentially hazardous trace elements in the Sarcheshmeh mine tailings. Eighteen solid samples were collected from weathered and fresh tailings and also from evaporative

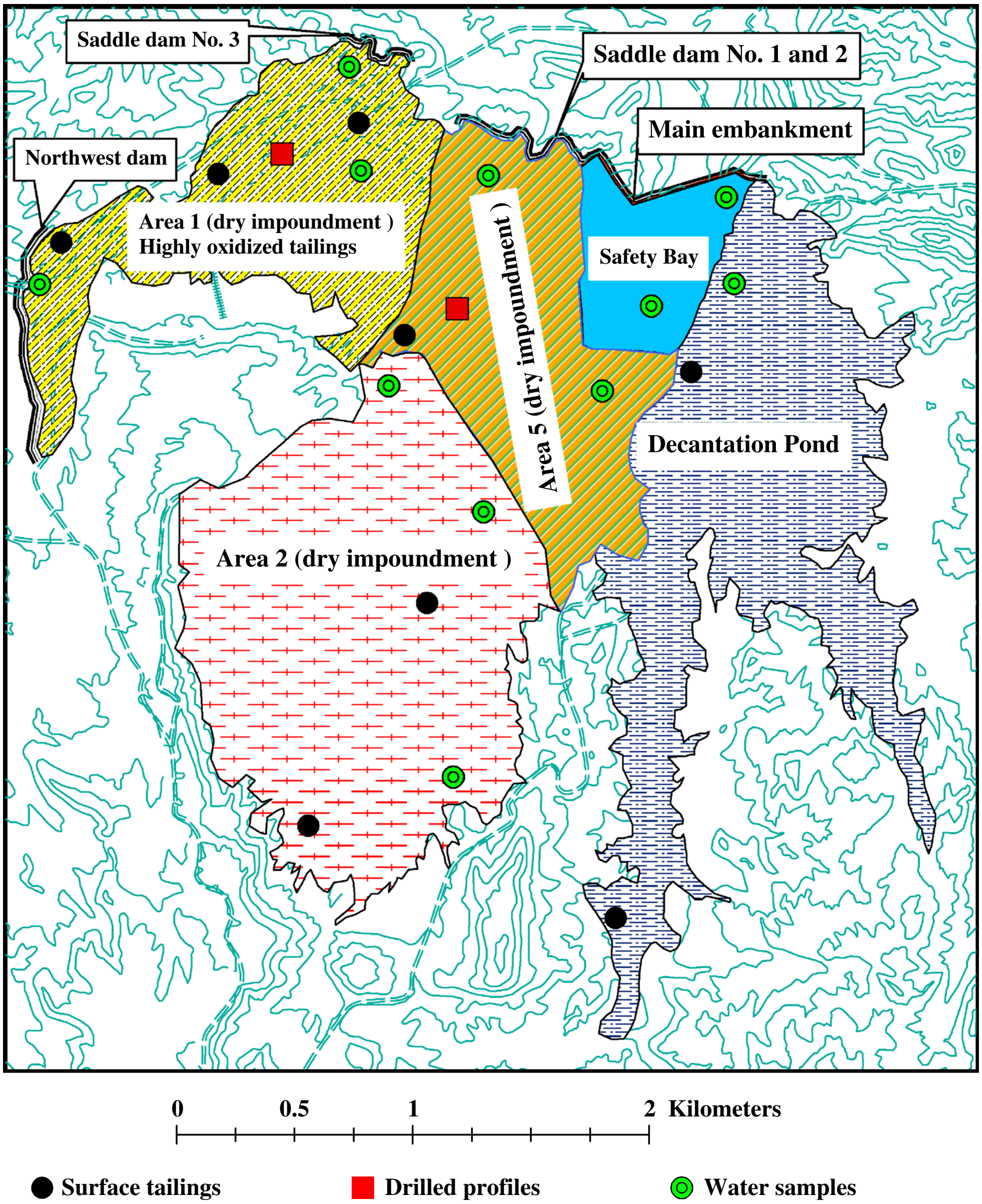

Fig. 1 The main compartments of the Sarcheshmeh dammed tailings pond

secondary minerals and efflorescent salts associated with the oxidation zone of dry impoundments. Detailed descriptions of the samples are given in Fig. 1 and Table 1. All solid samples were collected with a plastic device, stored in airtight plastic bags, and were transported to the laboratory immediately for oven drying. The total concentrations of metals and metalloids 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) after microwave multi-acid digestion at the Labwest Laboratory, Perth, Australia. The digestion procedure includes adding HCl + HNO_3 + HF into the sample, running it through the microwave under high temperature and pressure conditions, and finally adding boric acid solution to complex free fluoride and re-dissolving precipitates. This method yields near-total dissolution, and achieves good recoveries for the most resistive minerals.

Twelve water samples were collected in the winter season from different water resources associated with the Sarcheshmeh tailings impoundment to evaluate the hydrochemical behavior of potential contaminants. These samples were from the decantation pond, safety bay, middle impoundments (areas 2 and 5), and accumulated water in the dry impoundments after rainfall. The Shour Stream was also sampled. Electrical conductivity (EC) and pH were measured in the field with a Toledo MP-120 multi-parameter device that was calibrated by standard solutions at pH values of 4 and 7. Collected samples were immediately filtered through 0.45 μm filters (ALBET, Nitrato Celulosa), acidified with concentrated HNO_3

Table 1 The total concentration of potentially hazardous trace elements in the solid samples

Sample	Description	Concentrations of metals and metalloids (mg/kg)																
		As	Bi	Cd	Co	Mo	Ni	Pb	Sb	Se	Sn	Zn	Zr	Cr	Mn	Cu (%)	S (%)	Fe (%)
	Detection limits (ppm)	0.5	0.1	0.05	0.2	0.1	2	0.2	0.1	0.05	0.2	0.2	1	2	2	0.2	50	100
T-1	Secondary evaporative phases	2.6	<0.1	8.48	450	1.9	406	0.9	0.1	6.10	10.2	8,847	1	37	19,766	3.41	13.25	0.19
T-2	Weathered tailings	28.2	0.8	<0.05	11	71.0	<2	71.0	5.5	6.06	7.3	57.5	6	24	62	0.03	1.32	3.97
T-3	Secondary evaporative phases	3.8	0.4	11.10	216	4.9	272	1.9	0.4	8.35	3.2	2,968	1	44	10,017	4.24	7.86	0.28
T-4	Secondary evaporative phases	4.4	<0.1	6.06	317	2.7	335	0.6	0.2	4.08	2.5	4,988	1	44	14,817	2.14	14.17	0.61
T-5	Surface efflorescence salts	22.1	0.3	2.04	136	30	142	12.5	1.8	3.42	2.0	1,450	4	64	3,228	1.30	8.91	3.47
T-6	Secondary evaporative phases	2.9	<0.1	28.20	403	2.7	489	0.6	0.2	13.18	10.2	6,515	1	78	19,420	6.49	13.81	0.43
T-7	Surface efflorescence salts	24.9	0.2	2.65	195	20	178	7.4	0.7	2.22	7.6	3,263	2	55	7,891	0.66	12.22	4.94
T-8	Weathered tailings	14.7	1.0	1.02	37.4	71.8	26	50.3	4.0	3.92	5.8	416	11	35	2,081	0.22	5.34	7.67
T-9	Weathered tailings	31.4	1.1	0.10	11.9	95.5	11	57.5	3.9	6.29	3.0	115	7	20	289	0.07	1.16	3.83
T-10	Weathered tailings	18.7	0.8	0.08	23.1	109	20	49.2	2.2	10.67	8.7	90	3	23	239	0.08	3.26	5.61
T-11	Fresh tailings	33.4	0.9	0.35	40.5	104	55	63.0	9.2	6.59	11.2	998	9	35	1,779	0.15	2.80	4.80
T-12	Surface efflorescence salts	6.0	<0.1	10.41	383	11	373	1.7	0.2	5.58	12.6	7,839	<1	60	16,680	2.61	15.40	0.34
T-13	Weathered tailings	16.5	0.7	1.50	45.2	58.1	36	93.4	5.3	4.62	19.0	576	6	34	1,734	0.29	3.68	3.61
T-14	Weathered tailings	19.0	1.2	0.20	27.3	44.3	30	48.6	6.3	5.54	17.4	238	5	38	486	0.17	2.15	5.70
T-15	Weathered tailings	13.7	0.7	0.37	19.0	114.7	31	54.7	2.7	4.39	11.1	167	5	41	457	0.09	1.29	3.23
T-16	Fresh tailings	13.8	0.8	0.46	28.0	82.3	28	53.6	3.1	5.49	8.9	158	11	39	726	0.18	2.14	4.20
T-17	Fresh tailings	22.9	1.4	0.46	18.4	153	20	37.3	3.7	4.93	2.6	168	4	27	679	0.09	1.29	3.28
T-18	Fresh tailings	21.6	0.8	0.56	42.3	202	46	45.4	4.9	9.00	3.2	119	8	47	562	0.17	4.77	6.7
Crustal abundance[a]	Upper continental crust	4.8	0.16	0.09	17.3	1.1	47	17	0.4	0.09	2.1	67	193	62	–	0.003	0.006	–
	Bulk continental crust	2.5	0.2	0.08	26.6	0.8	59	11	0.2	0.13	1.7	72	68	135	950[b]	0.003	0.04	5[b]

[a] Rudnick and Gao (2003), [b] Mason and Moore (1982)

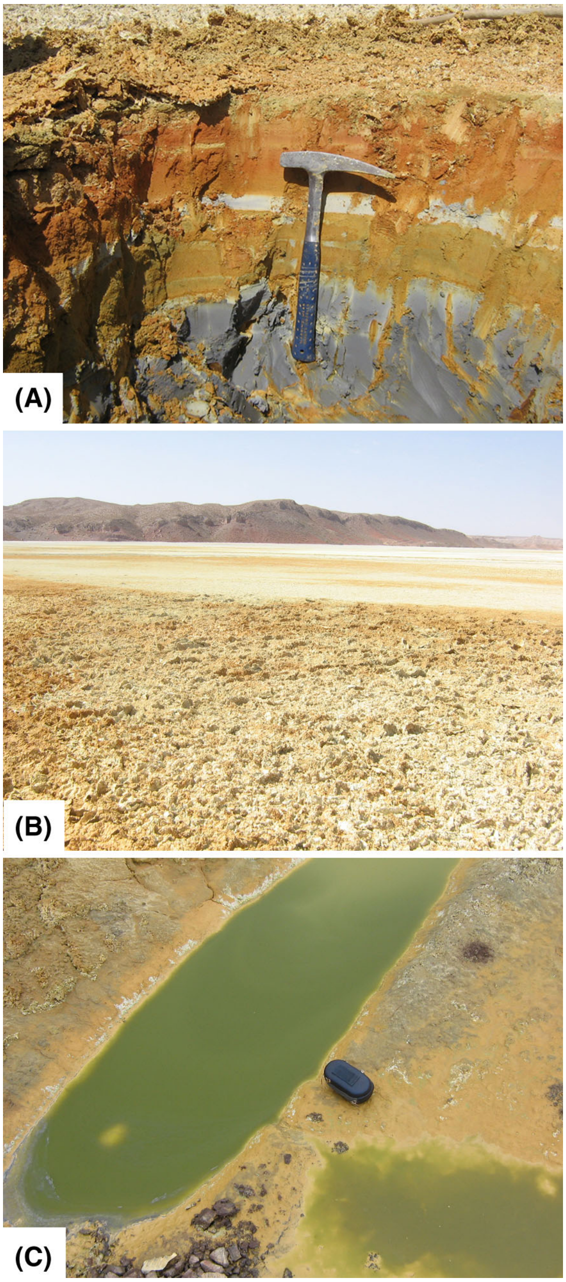

Fig. 2 **a** Field indicators of the hydrogeochemical changes of tailings waste in old dried impoundments; **b** massive precipitation of secondary evaporative minerals and efflorescent salts on the top of old weathered tailings; **c** acidic contaminated waters after dissolution of surface evaporative layer

(at pH <2), and stored at 4 °C until elemental analysis was performed. Filtered (0.45 µm filters) unacidified samples were also collected for anion analysis.

Major and trace element concentrations in water samples were determined using ICP-MS/OES at the Labwest Laboratory, Perth, Western Australia. Sulfate and Cl^- were determined by spectrophotometry and Mohr's method, respectively. For water samples, the limit of detection for investigated elements is 0.5 µg/L for As, Se and Zn; 0.05 µg/L for Cd, Mn, Sb, Ca, K, Mg, Na and Sn; 0.02 µg/L for Co; 0.2 µg/L for Cu and Ni; 10 µg/L for Fe; 0.1 µg/L for Mo and Pb; and 1 µg/L for Al and Cr.

The quality of analytical methods was verified for both solid and water samples by analyzing standards and multi-elemental certified reference materials (GSD-6, GSD-8, OREAS-90, and STD TMDA-70) and by duplicate samples in each series of analysis. The relative standard deviations (RSD) for most of the target metals were ±5 % for duplicated samples.

Multivariate Statistical Methods

Multivariate statistical methods, including principal components analysis (PCA), and cluster analysis (CA), were used to analyze the multivariate relationships between target elements (or variables) in both geochemical and hydrochemical data sets. These methods have been widely applied in environmental applications (e.g. Candeias et al. 2011; Chaparro et al. 2011; Khorasanipour et al. 2012; Loska and Wiechuła 2003). In this study, initial and varimax normalized rotated PCA were performed on the raw data sets using the correlation matrix because this method will correct for magnitude and scale differences (DelValls et al. 1998; Emmerson et al. 1997; Webster 2001). Significant principal components extracted from the variables were retained with eigenvalues >1.0, as suggested by Kaiser Criterion (Kaiser 1960). Factor loadings >0.6 were considered significant (DelValls et al. 1998) and excellent, if they were >0.71 (Yongming et al. 2006).

A hierarchical method was used for cluster analysis because, with 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 correlation as the criterion for forming clusters of elements (or variables). The multivariate statistical analyses were performed using SPSS v19 software.

Speciation Modeling

Metals and metalloids may be transported in mine water in various speciations; only inorganic speciations are reported in this study. The geochemical modeling program Visual MINTEQ version 3 (Gustafsson 2000) was used to calculate the equilibrium aqueous speciations. The code of this software, originally built on USEPA's MINTEQA2 software, has been maintained by Jon Petter Gustafsson at KTH, Sweden, since 2000.The Visual MINTEQ database contains thermodynamic data for most of the common aqueous species (free ions, complexes with carbonate, sulfate, fluoride, hydroxide, phosphate, and chloride ligands). Speciation calculations were performed for four pH ranges: acidic (pH 2.4–4.1), near-neutral (pH 6.8), near-alkaline (pH 8), and highly alkaline (pH 12). The speciation results for the target

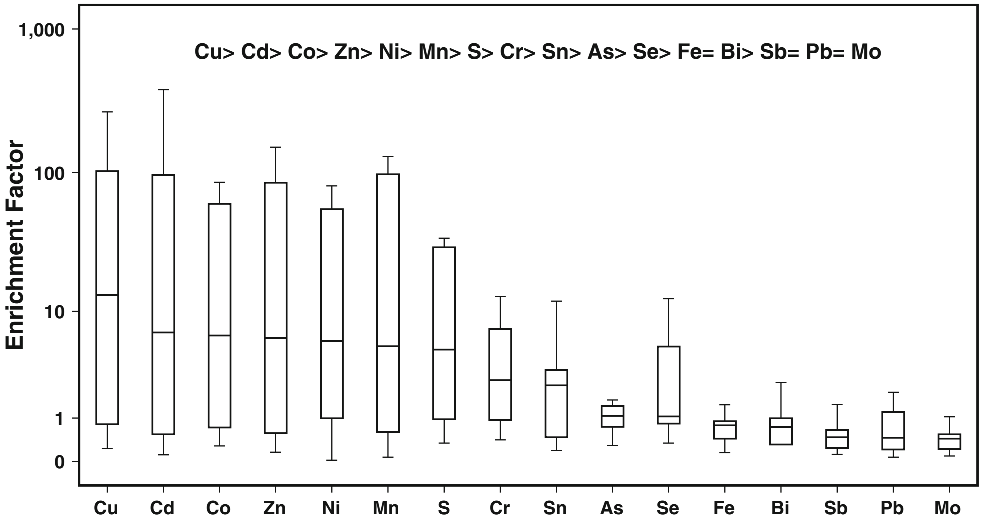

Fig. 3 A box plot showing the order of mobility for potentially hazardous trace elements subsequent to release by sulfide oxidation and weathering of fresh tailings

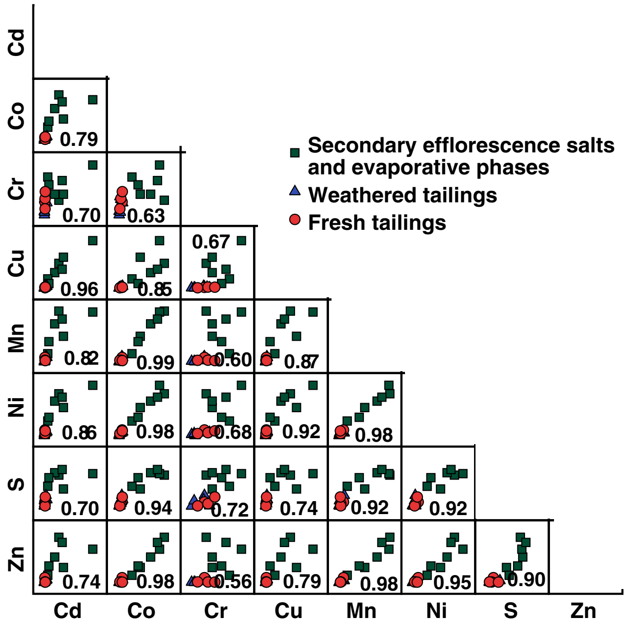

Fig. 4 The correlation matrix between total concentrations of highly mobile trace elements in the solid tailings samples

geochemical variables, including major anions, major and minor cations, metalloids, and oxy-anions, are presented in supplementary Tables S-1, S-2, and S-3, respectively.

Results and Discussion

Geochemical Investigations Based on the Total Concentration Data

As noted earlier, solid samples were collected from different areas of the tailings impoundment. Results indicate that the total concentration of potentially hazardous trace elements in the solid samples varies considerably (Table 1). These geochemical differences are consistent with the different geochemical processes that take place in tailings ponds. If we consider the fresh tailings as the principal contaminant source, the normalized enrichment or depletion factor for hazardous trace elements in weathered tailings or evaporative phases can be calculated according to Eq. 1.

$$\mathrm{EF/DF} = \frac{\frac{[M]}{[Zr]}\ \text{weathered tailings or evaporative phases}}{\frac{[M]}{[Zr]}\ \text{fresh tailings}} \qquad (1)$$

where: EF/DF is the normalized enrichment or depletion factor, [M] is the total concentration of target elements, and [Zr] is the concentration of Zr that was used as the normalizing element (Holmström et al. 2001). It is assumed that Zr is an immobile element and is resistant to low temperature weathering (Nickel 1973; Watson and Harrison 1983). From this calculation, the following order of trace elements mobility can be set up for solid tailings based on median enrichment values: Cu > Cd > Co > Zn > Ni > Mn > S > Cr > Sn > As > Se > Fe = Bi > Sb = Pb = Mo (Fig. 3). The mobility of these metals subsequent to release by sulfide oxidation and weathering reactions are controlled by processes such as precipitation-dissolution, co-precipitation, solid-solution substitutions and adsorption–desorption (Blowes et al. 1998; Lottermoser 2003).

Dold and Fontboté (2001) noted that climate is important in controlling the fate and movement of contaminant metals in tailings impoundments. Results showed that among the potential contaminant elements, Cd, Co, Cr, Cu,

Table 2 Component matrices and total variance explained by applying the PCA method to the total concentration data set of hazardous elements

Elements	Component matrix			Rotated component matrix			Communalities
	F1	F2	F3	F1	F2	F3	
As	−0.81			−0.72			0.67
Bi	−0.91			−0.93			0.9
Cd	0.83			0.68			0.91
Co	0.97			0.94			0.96
Cr	0.75			0.78			0.63
Cu	0.89			0.71			0.95
Fe	−0.84			−0.70			0.74
Mn	0.96			0.92			0.94
Mo	−0.88			−0.88			0.82
Ni	0.99			0.92			0.98
Pb	−0.90			−0.83			0.9
S	0.93			0.96			0.95
Sb	−0.82			−0.73			0.8
Se		0.88			0.96		0.94
Sn			0.90			0.96	0.94
Zn	0.92			0.92			0.88
Initial eigenvalues	11.3	1.46	1.20	9.9	2.481	1.58	
% of variance	70.63	9.13	7.52	61.87	15.50	9.92	
Cumulative %	70.63	79.7	87.3	61.87	77.37	87.3	

Factor loadings lower than 0.5 are removed. Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization; rotation converged in five iterations

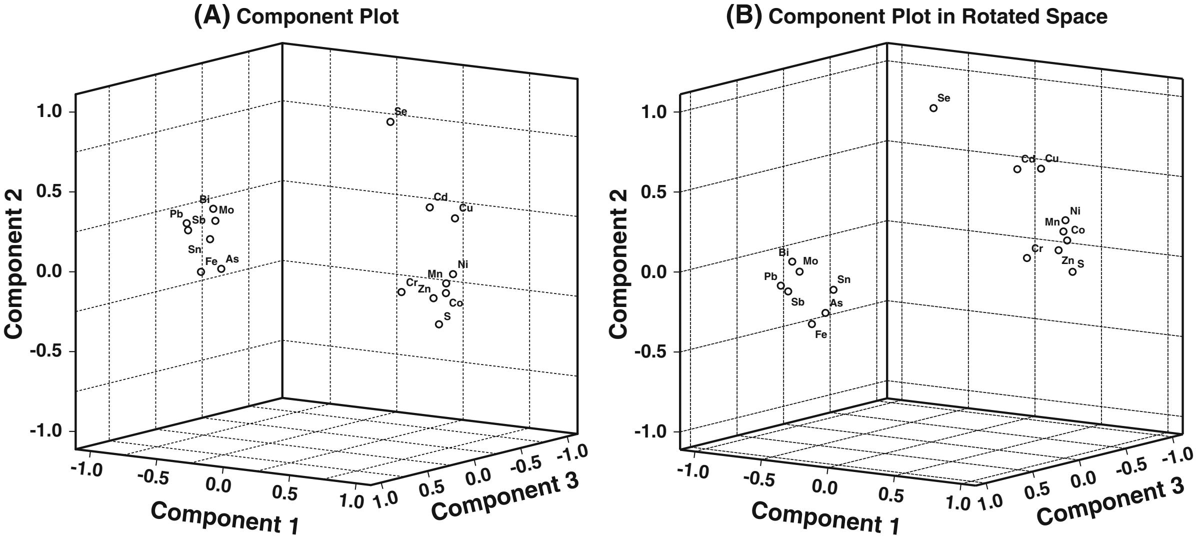

Fig. 5 PCA results in the three dimensional space: plots of loadings of the first three principal components of initial (**a**) and rotated (**b**) PCA results from total concentration data set

Mn, Ni, S, and Zn are highly mobile and were concentrated in the surface evaporative layer of tailings, whereas elements such as Mo, As, Pb, Se, and Sb have a lower concentration in the surface layer compared to the fresh and weathered tailings. High values of Cd (28.2 mg/kg), Co (449 mg/kg), Cu (6.45 %), Mn (1.2 %), Zn (8,847 mg/kg), and S (15.4 %) were observed in the surface evaporative layer of old, dry impoundments. Highly mobile contaminants (Cd, Cr, Co, Cu, Mn, Ni, S, and Zn) are positively correlated with each other and strongly concentrated in efflorescent salts and evaporative phases (Fig. 4).

The Sarcheshmeh tailings impoundment is located in a climate where evaporation exceeds precipitation. In these conditions, water flows upward via capillary forces and

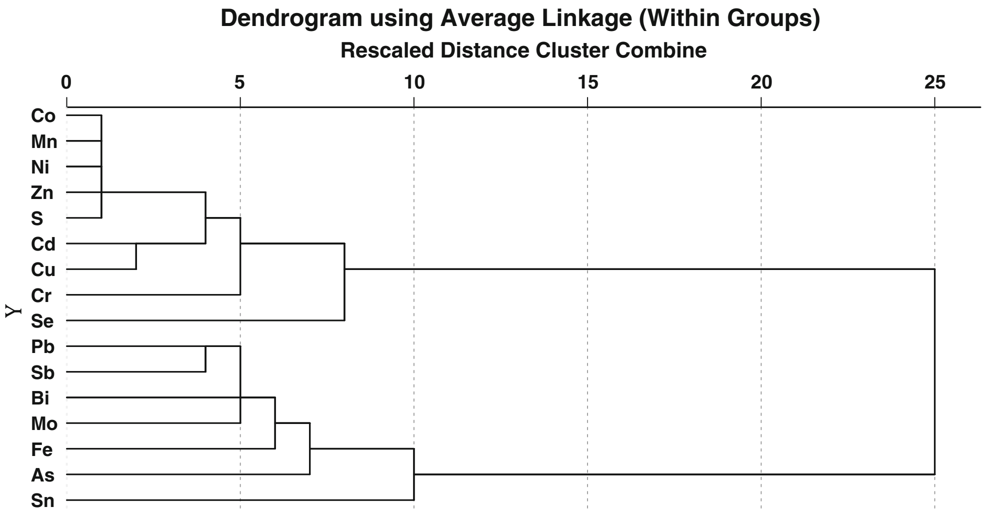

Fig. 6 Hierarchical cluster analysis results of geochemical data set by the use of the "within-groups linkage" method; similarities have been calculated from the Pearson correlation

mobilized elements are transported to the top of the tailings. This geochemical condition and behavior has also been observed at the El Teniente and El Salvador porphyry copper tailings (Dold and Fontboté 2001).

Initial and rotated varimax principal components analysis was performed on the total concentration data set by computing the eigenvectors (Table 2). Three factors have eigenvectors higher than the Kaiser (1960) and explain more than 87 % of the total variance of the geochemical data set. Other factors (eigenvectors <1) were not considered since they explain very low percentages of variance.

Factor 1 accounts for 70.6 % of the total variance, with significant positive loadings of Cd, Co, Cr, Cu, Mn, Ni, S, and Zn, and negative loadings of As, Bi, Fe, Mo, Pb, and Sb, in the initial component matrix of PCA. This distinct separation clearly reflects the different geochemical behaviors of these contaminants. As noted earlier, elements with positive loadings (Cd, Co, Cr, Cu, Mn, Ni, S, and Zn) are highly mobile and concentrated in the surface evaporative layer of tailings, while the other elements (As, Bi, Fe, Mo, Pb, and Sb) have higher concentrations in the fresh or weathered tailings. This geochemical association was also found in the first component of the rotated PCA.

The second PCA factor in the initial and rotated matrices explains 9.3 and 15.5 % of the total data variance, respectively. Selenium is the only element that has a significant loading in this factor, and Sn is the only element that has a significant loading in the third factor of both the initial and rotated component matrices.

The geochemical relationships between different hazardous metals can be made easier to understand by mapping the variable loadings. Figure 5a, b show the three-dimensional plots of the initial and rotated component matrices of the total concentration data set, respectively. In these figures, a close relationship can be distinguished between elements with the same geochemical behavior. The distance of Se from the other two major groups is considerable in both 3-D PCA plots, which demonstrates its obvious geochemical differences.

Hierarchical cluster analysis (CA) was also used in this study in order to identify relatively homogeneous groups of variables and to examine the results obtained from PCA method. A dendrogram was constructed to evaluate the cohesiveness of the relationships between target hazardous elements. The corresponding CA of the relationship between target elements is shown in Fig. 6. The distance axis represents the degree of association between groups of variables (or elements), i.e. the lower the axis value, the more significant the association.

Two distinct groups of elements can be identified in the CA results. These two groups and the degree of association of the elements in each group can be summarized as: (1) $Co = Mn = Ni = Zn = S > Cd = Cu > Cr \gg Se$; and (2) $Pb = Sb > Bi = Mo > Fe > As \gg Sn$. The CA results are similar to the PCA, but it appears that due to high mobility, the geochemical association between Co, Mn, Ni, Zn, S, Cd, Cu, and Cr is stronger than the other factors. Also, despite the low mobility of Pb, Sb, Bi, Mo, Fe, As, and Sn, different mechanisms are responsible for their geochemical associations.

Pyrite is by far the most abundant sulfide mineral in the Sarcheshmeh tailings waste (Khorasanipour et al. 2011b). Geochemical association of most of the chalcophile elements is compatible with the presence of sulfide minerals, especially pyrite in the tailings. Pyrite may contain or coexist with other trace elements, like As, Bi, Cd, Co, Cu, Ga, In, Hg, Mo, Pb, Re, Sb, Se, Sn, Te, and Zn (Spears et al. 1994). Spears et al. (1994) stated that Cu, As, Fe, and

Table 3 The values of pH, EC, SO_4^{-2} and concentrations of measured elements in surface water samples

Sample	pH	EC (μs/cm)	Concentration (mg/L)												
			TDS	SO4	Ca	Mg	Na	K	Cl	Al	Cu	Fe	Mn	Mo	Zn
W-1	11.9	2,960	2,043	980	96	1.2	630	85.75	131	0.06	0.01	0.02	0.002	2.57	0.009
W-2	11.9	3,060	2,045	856	132	1.3	665	97.75	145	0.05	0.01	0.03	0.001	2.6	0.006
W-3	12	2,990	1,991	591	68.1	1	585	93.63	236	0.16	0.01	0.08	0.006	2.49	0.01
W-4	4.1	7,060	7,071	2,144	344	330	920	45	976	68.5	262	0.76	163	0.03	54
W-5	3.7	11,320	10,490	3,970	245	460	1,950	48.85	2,122	144	358	1.86	223	0.03	78.4
W-6	2.5	6,430	9,665	2,956	110	460	305	5.95	303	358	554	33	230	0	86.5
W-7	6.8	10,450	7,865	2,644	545	32	1,950	310	1,718	0	0.09	0.1	1.66	2.06	0.025
W-8	3	14,060	27,121	12,846	58	1,300	830	1.59	505	1,194	1,551	16	444	0.01	221.9
W-9	3.8	5,530	5,551	2,130	344	195	670	61.95	512	101	133	5.78	79	0.25	27.9
W-10	7.8	5,810	4,394	1,724	363	79	1,120	59	808	0.02	0.09	0.05	0.031	1.81	0.004
W-11	8	5,850	4,374	1,923	325	78	1,100	58.3	822	0.02	0.05	0.04	0.011	1.88	0.01
W-12	2.4	9,830	16,940	6,411	93	530	600	70.35	606	940	122	250	97	0.02	64.3
US EPA (2009)	6.5–9.5	–	500	500	–	–	200	–	250	0.05	1	0.3	0.05	–	5
WHO (2006)	6.5–8.8	–	500	250	–	–		–	250	0.2	0.2	–	–	–	0.3
WHO (2004)		–	–	–	–	–	–	–	–	–	–	–	0.4	0.07	–

	pH	EC	Concentration (μg/L)									
			As	Cd	Co	Bi	Cr	Ni	Pb	Sb	Se	Sn
W-1 (μs/cm)	9	3	0.27	BDL	2	1.2	0.5	4.75	43.3	0.03		
W-2			9.6	3	0.35	BDL	1	1.3	0.7	5.73	45.7	0.03
W-3	11.9	2,960	10	3	0.79	0.68	2	3.9	2.2	5.52	41.9	0.06
W-4	11.9	3,060	3	154	4,179	0.1	59	2,937	1.3	4.75	37.1	0.4
W-5	12	2,990	5	157	6,397	BDL	89	4,020	1.2	4.54	42	0.47
W-6	4.1	7,060	6	279	7,116	BDL	287	4,900	9.1	6.8	52.3	0.27
W-7	3.7	11,320	10	3	8.87	BDL	2	11.2	1	7.4	34.7	0.19
W-8	2.5	6,430	9	555	19,510	BDL	628	10,377	1.8	5.8	118	0.36
W-9	6.8	10,450	3	94	2,173	BDL	52	1,551	2	4.66	20.1	0.15
W-10	3	14,060	47	2	2.66	BDL	2	3.8	0.8	6	2	0.24
W-11	3.8	5,530	49	2	1.07	BDL	2	2.9	0.9	4.65	2.7	0.12
W-12	7.8	5,810	325	611	3,041	4.68	249	12,034	1,320	15	30.2	4.63
US EPA (2009)	8	5,850	10	3	–	–	–	20	10	18	10	–
WHO (2006)	2.4	9,830	10	5	–	–	–	70	10	6	50	–
WHO (2004)	6.5–9.5	–	–	–	–	–	50	–	–	–	–	–

BDL below detection limit. Sample descriptions: W-1 and W-2, safety bay; W-3, decantation pond; W-4, drainage channel in dry impoundment; W-5, W-6, W-8 and W-9, accumulated waters in dry impoundments after rainfalls; W-7, W-10 and W-11 middle impoundment; W-12 Shour river discharge

Mn may have a common origin in pyrite oxidation. Chalcopyrite is the most important ore mineral in Cu-porphyry deposits and can similarly contain elements 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). Despite their different geochemical behavior, elements like Cr can replace iron in pyrite and chalcopyrite (Boyle 1974).

If sulfide tailings are exposed to air for prolonged periods, evaporation of tailings water commonly leads to the formation of secondary evaporative sulfate-bearing minerals such as gypsum or jarosite (Dold and Fontboté 2001; Johnson et al. 2000; McGregor and Blowes 2002). Supersaturation results in the precipitation of secondary sulfates and strong enrichment of soluble trace elements at the top of the weathered tailings, as observed in the dried ponds of the tailings impoundment. Several studies have shown that the mobility of released elements depends on the composition of the fresh tailings, weathering intensity, chemical characteristics of each element, co-precipitation

Table 4 Component matrices and total variance explained by applying the PCA method to the hydrochemical variables

Variables	Component matrix				Rotated component matrix				Communalities
	F1	F2	F3	F4	F1	F2	F3	F4	
pH	−0.75				−0.53			−0.7	0.95
EC	0.78				0.78				0.99
SO4	0.94				0.95				0.95
TDS	0.97				0.92				0.98
Al	0.96				0.84				0.98
Cd	0.96				0.75				0.99
Co	0.88				0.97				0.99
Cr	0.95				0.94				0.97
Cu	0.85				0.97				0.99
Mn	0.87				0.92				0.98
Mg	0.96				0.95				0.99
Mo	−0.76				−0.54			−0.77	0.95
Ni	0.96				0.73				0.99
S	0.98				0.88				0.98
Se	0.69				0.9				0.92
Zn	0.93				0.96				0.99
As		0.91				0.98			0.97
Fe		0.86				0.98			0.99
Pb		0.89				0.99			0.99
Sb		0.85				0.97			0.96
Sn		0.85				0.98			0.98
Cl			0.94				0.94		0.91
Ca			0.79				0.81		0.82
Na			0.91				0.94		0.92
K			0.55	0.59			0.6	−0.64	0.87
Initial eigenvalues	14.2	5.24	3.36	1.32	12.02	6.49	3.4	2.21	
% of variance	56.81	20.95	13.45	5.27	48.09	25.96	13.61	8.83	
Cumulative %	56.81	77.77	91.21	96.49	48.09	74.05	87.66	96.49	

Factor loadings lower than 0.5 are removed. Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization. Rotation converged in five iterations

and adsorption–desorption reactions, and climatic conditions (Dold and Fontboté 2001; Khorasanipour et al. 2011b, 2012; Lottermoser 2003; McGregor and Blowes 2002). Elemental assemblage of liquids in the weathering zone also can affect the mobility of contaminant metals. For example, in mine waters with high Mn and low Fe concentrations, such as the waters of the Sarcheshmeh copper mine (Shahabpour and Doorandish 2007), the natural removal of Mn, Cd, and, in some cases, Zn, is limited by co-precipitation and adsorption reactions (Khorasanipour et al. 2011a; Skousen et al. 1990). Therefore, the precipitation of these elements as sediment phases is limited by the requirement of high pH or supersaturation.

Hydrochemical Investigations

As noted earlier, surface water samples were collected from various water resources associated with the tailings impoundment during winter. The hydrochemical characteristics of these samples are shown in Table 3. Their pH ranged between 2.4 and 12. This unusual pH range corresponds with the different processes that control the hydrochemical characteristics of water in the tailings ponds. Acidic waters are predominantly found in the Shour stream discharge and temporary accumulated water in dry impoundments after heavy storms. Highly alkaline pH values were found in the decantation pond and safety bay due to the use of alkaline materials during copper sulfide flotation. The Shour stream's low pH is mainly due to acidic mine drainage and effluents of a leaching plant that occasionally discharges into the stream during winter (Khorasanipour et al. 2011b).

Hydrochemical data show high values of EC (14,060 μs/cm), total dissolved solids (TDS, 14,060 mg/L), SO_4^{-2} (12,846.4 mg/L), Cl^- (2,121.9 mg/L), Al (1,194.8 mg/L), Cd (557.6 μg/L), Co (19.51 mg/L), Cr (287 μg/L), Cu (1,551 mg/L), Fe (32.83 mg/L), Mn (444.8 mg/L), Ni (10.4 mg/L), and Zn (221.8 mg/L) in the acidic waters accumulated in the old weathered tailings ponds (Table 3).

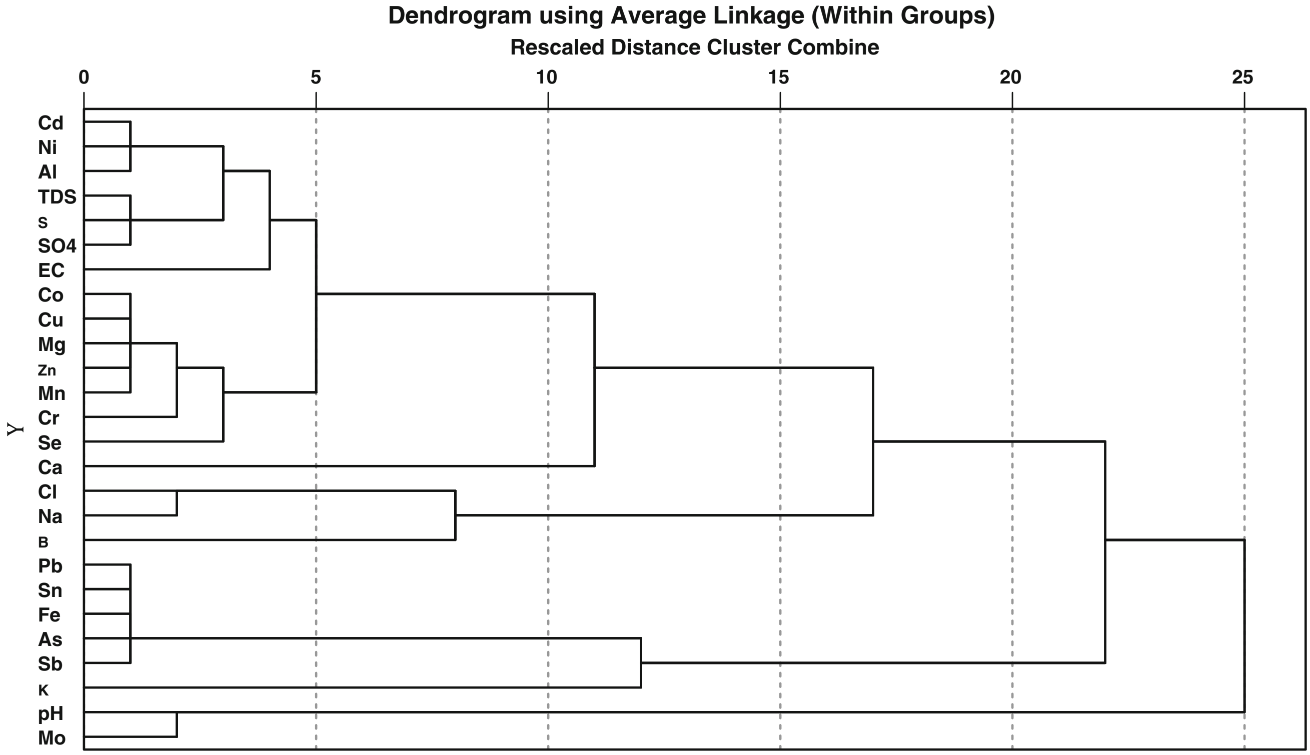

Fig. 7 Dendrogram resulting from the hydrochemical data set by the use of "Within-groups linkage" method of hierarchical cluster analysis; the similarities are calculated from the Pearson correlation

In these samples (W4, W5, W6 and W8), the As, Mo, Pb, Sb, Bi, and Sn concentrations were below recommended drinking water threshold limits (U.S. EPA 2009; WHO 2004, 2006) or even below detection value (Bi). The hydrochemistry of the Shour Stream water (W12) resemble the acidic water in the dry impoundments except that the concentrations of As (324.8 µg/L), Bi (4.68 µg/L), Pb (1,320.5 µg/L), Sb (14.97 µg/L), and Sn (4.63 µg/L) are increased. It seems that occasional discharges of industrially-contaminated waters, especially the leaching plant effluents, are responsible for the high contaminant load of the Shour Stream. High values of Al (940 mg/L), Fe (250 mg/L), Mn (96.6 mg/L), Cu (122 mg/L), Ni (12.04 mg/L), and Zn (66.3 mg/L) also were measured in this stream.

Molybdenum is the only element that has a very high concentration in the alkaline decantation pond and safety bay (mean value 2.55 mg/L) water, while other potential contaminants are well below recommended drinking water values. Previous studies (Smuda et al. 2008) have also shown that Mo is mobile (up to 3.9 mg/L) as MoO_4^{2-} in the alkaline tailings waters. The high pH used in the flotation process mobilized Mo by desorption of MoO_4^{2-} from Fe oxyhydroxides and clays (Goldberg et al. 1996), and by dissolution of secondary Mo phases like ferrimolybdite (Sarafian and Furbish 1965).

Assessment of the hydrochemical data set using the PCA method indicates that four significant components (eigenvectors higher than 1) account for 96.48 % of the total variance (Table 4). Component 1 accounts for 56.8 and 48 % of initial and rotated PCA, respectively. This component is mainly associated with significant positive loadings of EC, SO_4^{-2}, TDS, Al, Cd, Co, Mg, Cr, Cu, Mn, Ni, S, Se, and Zn and significant negative loading of pH and Mo in the initial PCA method. This hydrochemical relationship between variables corresponds with the release and transport of soluble contaminants during low pH acid-oxidation conditions.

The second component of the PCA has significant positive loadings for As, Fe, Pb, Sb, and Sn. This factor accounted for about 20.9 and 25.95 % of total variance in the initial and rotated PCA, respectively. The elements in this factor have very low concentration in water samples compared with variables in the first PCA component. Component 3 that accounted for 13.5 % of the variance in both initial and rotated matrices is characterized by high loadings of Cl, Ca, and Na. Component 4 that accounted for only 5.3 and 8.8 % of total variances of initial and rotated matrices, respectively, has a significant loading for K. Elements in these two last factors, especially Cl and Na are highly concentrated in the water samples, but their hydrochemical behavior is different from variables in the first component of the PCA, remarkably.

Cluster analysis was used to assess the relationships between hydrochemical variables. The corresponding CA of the hydrochemical data set in the form of a dendrogram is shown in Fig. 7. Results show that according to the common hydrochemical associations and similar behaviors, the variables can be categorized into four main groups and several sub-clusters:

1. Cd, Ni, Al, TDS, S, SO_4^{-2}, Co, Cu, Mg, Zn, Mn, Cr, EC, and Se: This group of variables is the same as the first component of the PCA, but according to the CA results, it is possible to distinguish more homogenous subgroups. On the basis of the first level of associations, the following relationships can be defined among the hydrochemical variable in the first group:

   - Cd, Ni, and Al;
   - TDS, S, and SO_4;
   - Co, Cu, Mg, Zn, Mn, and Cr;

The EC and Se are related to the above-mentioned subgroups in the higher orders of the association.

2. Strong correlation of Pb, Sn, Fe, As, and Sb in the first order CA result; this hydrochemical relationship is also endorsed by both PCA and CA methods.
3. The correlation between pH and Mo, corresponding with the high Mo concentrations in the alkaline waters of the decantation pond and safety bay.
4. Cl = Na > Ca ≫ K; Cl and Na are mobile under most conditions over a wide pH range, in contrast to the soluble group 1 trace elements (Langmuir 1997).

According to the above-mentioned results, several factors, such as the tailings mineralogy, weathering reactions, the method of copper sulfide processing, management of the surface water effluents, and climatic conditions profoundly affect the characteristics of water in the Sarcheshmeh tailings. It is often assumed that tailings contain minerals similar to those of the ore, only with a much smaller grain size and more pyrite (Lottermoser 2003). The Sarcheshmeh Stock is a complex intrusive body, which is exposed over an area of about 1.2 by 2.2 km. The diorite-to-granodiorite groundmass is fine-grained, and consists mainly of quartz, plagioclase and k-feldspar, with lesser biotite and amphibole (Hezarkhani 2006). The mineralogy of the Sarcheshmeh tailings is mainly composed of quartz (42 %), albite (9 %), sericite (24 %), chlorite (11 %), orthoclase (8.3 %), and pyrite (7.5 %) (Khorasanipour et al. 2011b). This 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 through congruent (Eq. 2) or incongruent weathering (Eq. 3) (Lottermoser 2003).

$$2MeAlSiO_{4(s)} + 2H^+_{(aq)} + H_2O \rightarrow Me^{x+}_{(aq)} + Al_2Si_2O_5(OH)_{4(s)} \quad (2)$$

$$MeAlSiO_{4(s)} + H^+_{(aq)} + 3H_2O \rightarrow Me^{x+}_{(aq)} + Al^{3+}_{(aq)} + H_4SiO_{4(aq)} + 3OH^-_{(aq)} \quad (3)$$

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

Incongruent destruction of plagioclase and orthoclase minerals is responsible for the release of Na, Ca, and K from the tailings. Other elements, such as Mg, Mn, Fe, and Al can also be released during the weathering of silicate minerals. For example, the by-products of feldspar and chlorite weathering are Na^+, K^+, Ca^{2+}, silicic acid (H_4SiO_4), and clay minerals. Further dissolution of clay minerals such as kaolinite can consume hydrogen ions and release dissolved Al^{3+} (Eq. 4, Lottermoser 2003).

$$Al_2Si_2O_5(OH)_{4(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+} + 2H_4SiO_{4(aq)} + H_2O \quad (4)$$

Chloride as a lithophile and highly mobile element is a minor constituent of various minerals, like amphiboles, micas, and clay minerals, and goes into solution as Cl^- ions as a result of such weathering reactions.

Although the oxidation of sulfide minerals, especially pyrite, is the prime source of AMD associated with the Sarcheshmeh tailings, the current characteristics of the AMD in the old, weathered tailings is directly related to the secondary minerals. Prolonged precipitation of secondary minerals may occur at the surface or at depth in tailings and waste rock piles (Holmström and Ohlander 1999; McSweeney and Madison 1988). These secondary minerals form in response to a combination of processes, such as oxidation of sulfide minerals, capillary forces, evaporation, hydrolysis, and neutralization reactions (Lottermoser 2003). As suggested by others (e.g. Cravotta 1994; Lin 1997), formation and dissolution of secondary minerals, especially simple hydrous metal sulfates, can release metals, acidity, and sulfate into the water. This is responsible for the low pH (from 2.5 to 4.1) and high contaminant concentrations in the water samples associated with the highly weathered tailings. It is well understood that precipitation of some secondary minerals can also influence pH. For example, the formation of Fe^{3+} and Al^{3+} hydroxides generates acidity, whereas the precipitation of some Fe^{2+}, Mn^{2+}, Fe^{3+}, and Al^{3+} sulfate salts consumes acid (Lottermoser 2003).

Dissolution of soluble Fe^{2+}, Mn^{2+}, Fe^{3+}, and Al^{3+} sulfate salts, such as jarosite, alunite, halotrichite, and coquimbite, releases H^+ ions (Lottermoser 2003). It is clear that dissolution of soluble secondary mineral phases that form at and near the surface of the weathered tailings in the dry impoundment is responsible for the rapid development of highly contaminated waters. 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 dissolved bivalent cations, Cl^-, and SO_4^{-2}. Significant upward mobilization of Al, Na, Cl, Cd, Co, Cr, Cu, Mg, Mn, Ni, Se, $SO_4{}^{-2}$, and Zn occurs during the dry seasons. Upward migration is later superimposed on the general trend of downward mobilization during the rainy season. These hydrochemical and environmental important processes are similar to what has previously been reported (Dold and Fontboté 2001; Wu et al. 2009; Zhao et al. 2012).

Mobilization of contaminants is controlled by pH and Eh, but adsorption onto and co-precipitation with Fe^{3+} hydroxides are very effective removal mechanisms that can explain the hydrochemical relationship of As, Sb, Pb, Mo, and Sn in the oxidation zone.

Speciation Results of Major Anions

Sulfate, chloride, and carbonate ions were the most important anions measured. Speciation modeling showed that SO_4^{-2} is the dominant form of sulfate ions at all pH ranges, and its proportion increased from acidic to highly alkaline waters. In acidic water, others sulfate species, such as $Al(SO_4)^{-2}$, $MgSO_{4(aq)}$, $AlSO_4{}^+$, $NaSO_4$, $CaSO_{4(aq)}$, $HSO_4{}^-$, $CuSO_{4(aq)}$, $Fe(SO_4)^{2-}$, $MnSO_{4(aq)}$, and $FeSO_4{}^+$ can also play an important role (Table S-1). At elevated pH, only three sulfate species, $MgSO_{4(aq)}$, $NaSO_4{}^-$, and $CaSO_{4(aq)}$, were significant, relative to SO_4^{-2}. The proportions of these species also increased from near-neutral to highly alkaline waters.

Chloride was the dominant form of Cl at all pH ranges, including acidic (97.6 %), near-neutral (97.1 %), near-alkaline (98 %), and highly alkaline waters (98.9 %). The speciation pattern of carbonate ion, which was only measured in the highly alkaline waters of the decantation impoundment and safety bay, was as CO_3^{-2} (62.4 %), $CaCO_{3(aq)}$ (19.6 %), $NaCO_3{}^-$ (16.7 %), and $HCO_3{}^-$ (1.0 %).

Speciation Results of Cations

The speciation results of major and trace cations are shown in Table S-2. In most cases, the highest aqueous concentrations were associated with oxidizing, acid conditions. Generally, as pH increases, aqueous metal species are inclined to precipitate as hydroxide, oxy-hydroxide, or hydroxy-sulfate phases (Berger et al. 2008). Speciation modeling for the collected samples in the four pH ranges (acidic, near-neutral, near-alkaline, and highly alkaline) show that sulfate complexes ($MSO_4{}^+$, $M(SO_4)_{(aq)}$, $M(SO_4)_2^{-2}$, and $M(SO_4)_2^-$) and free metal species (M^{+2} and M^{+3}) are the primary forms of dissolved trace cations in the acidic waters associated with the old, weathered tailings. Considerable amounts of some trace elements, such as Cu, Mn, Zn, Cd, Co, Ni, Pb, and sulfate, remain in solution at near-alkaline pH values. The free metal species in solution decrease as the importance of hydroxide complexes increases. As pH increases, the speciation of trace elements is controlled by hydroxide complexes and adsorption processes. Adsorption of metals is a selective process, and chemical composition of the water changes as pH increases (Lottermoser 2003). For example, As and Pb are the most effectively adsorbed metals at acidic pH values, whereas Zn, Cd, and Ni are adsorbed at near-neutral pH (Plumlee et al. 1999). Various hydroxide species, such as $M(OH)^+$, $M(OH)_3^-$, $M_3(OH)_4^{+2}$, $M_2(OH)_3^+$, $M(OH)_{2(aq)}$, $M(OH)_4^{-2}$ (where M represents bivalent cations like Cu, Zn, and Cd) and $Me(OH)_2^+$, $Me(OH)_4^-$, $Me(OH)_2{}^+$, $Me(OH)_{3(aq)}$, and $Me(OH)_4^-$ (where Me represents trivalent cations like Al, Fe, and Cr) are mainly formed at near-alkaline to highly alkaline pH. Among these hydroxide species, the $M(OH)_{2(aq)}$, $M(OH)_3^-$, $Me(OH)_{3(aq)}$, and $Me(OH)_4^-$, are the dominant aqueous species.

The proportion of dissolved trace elements present as other inorganic complexes were predicted to be negligible (<1 %), with very little influence on trace element speciation. It is worth noting that although Cl^- content in the water samples is high (Table 3), in most cases (except for Cd, Cu, Zn, and Sn), the proportion of chloride complexes of trace elements was generally less than 1 %. A description of the cation speciation follows:

Major Cations (Ca, Mg, Na, and K)

Speciation modeling predicts that, among the major cations (Ca, Mg, Na, and K), the dominant dissolved inorganic species are sulfate complexes ($M(SO_4)_{(aq)}$ and $M(SO_4)^-$) and free ions (M^{+2} and M^+). These species are dominant in all pH ranges, from acid to highly alkaline conditions. Other species, such as $CaOH^+$ (2.0 %), $CaCO_{3(aq)}$ (3.0 %), $MgOH^+$ (29.7 %), and $MgCO_{3(aq)}$ (1.2 %) are only formed in highly alkaline water.

Aluminum

Dissolved aluminum concentrations are strongly pH dependent, and the formation of secondary aluminum minerals, colloids, and amorphous substances controls aqueous aluminum concentrations (Nordstrom and Alpers 1999). Speciation modeling predicts that sulfate complexes (48.4 % as $Al(SO_4)_2^-$ and 47.7 % as $AlSO_4{}^+$) and free ions (3.9 % as Al^{3+}) are the important Al species in the acidic waters. Most Al species, including $Al(SO_4)_2^-$ (21.2 %),

$AlSO_4^+$ (24.9 %), Al^{3+} (2.2 %), $Al(OH)_2^+$ (19.2 %), $Al(OH)_4^-$ (16.2 %), $AlOH^{+2}$ (8.2 %), and $Al(OH)_{3(aq)}$ (8.1 %), were predicted to form at near-neutral pH. On the other hand, $Al(OH)_4^-$, is the only dominant form of Al at near alkaline (97.7 %) and highly alkaline (≈ 100 %) pH. Nordstrom and Alpers (1999) also reported that Al is present in several forms in mine waters, including Al^{3+}, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(SO_4)^+$, and $Al(SO_4)_2^-$.

Copper

In surface waters, Cu is likely to occur as Cu^{2+}, $Cu(OH)^+$, $CuCO_3$, and $CuSO_4$ (Witczak and Adamczyk 1995). Speciation results showed that, in acidic to near-neutral waters, $CuSO_{4(aq)}$ and Cu^{2+} are the dominant forms of Cu, respectively. These Cu species, together with $CuOH^+$ (24.4 %), are also present in near-alkaline waters, while $Cu(OH)_3^-$ is the dominant form (98.2 %) of Cu in highly alkaline water. Other Cu species, such as $CuCl^+$, $CuOH^+$, and $Cu_3(OH)_4^{+2}$, also occur (≈1 %) in the investigated samples.

Iron

Most Fe speciation in the acidic waters is in the form of sulfate complexes (55.8 % as $FeSO_4^+$ and 22.5 % as $Fe(SO4)_2^-$), hydroxide complexes (12.3 % as $FeOH^{+2}$ and 7.1 % as $Fe(OH)_2^+$), and free ions (1.9 % as Fe^{3+}). The dominant form of Fe in the near-neutral to near-alkaline water samples is $(OH)_2{}^+$, while in highly alkaline water, it is mainly $Fe(OH)_4^-$ (99.9 %). Ferris et al. (2000) reported that most Fe compounds are easily soluble in water at pH <7; however, under oxidizing conditions, they are precipitated as oxides. Also, iron can be present in mine waters in several forms, such as Fe^{2+}, Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(SO_4)^+$, and $Fe(SO_4)_2^-$. Dissolved iron concentrations and its speciation (i.e. Fe^{2+} or Fe^{3+}) are strongly Eh and pH dependent (Lottermoser 2003).

Manganese

In various surface water conditions, several Mn species are likely to occur, such as: Mn^{2+}, $MnOH^+$, $MnCl^+$, $MnHCO_3{}^+$, $Mn(OH)_3^-$, and $MnSO4^0$ (Witczak and Adamczyk 1995). Speciation modeling showed that sulfate ($MnSO_{4(aq)}$) and free ions (Mn^{2+}) are the prevalent forms of Mn at acidic and near-alkaline pH values. The hydroxide forms of this element, $Mn_2(OH)_3^+$ (92.3 %) and $MnOH^+$ (4.2 %), and its carbonate form (1.8 % as $MnCO_{3(aq)}$) are only formed in highly alkaline waters. Laboratory and field treatment tests of the acid mine water using lime also indicated that Mn remains in solution at relatively high pH levels; generally, a pH of ≈ 10 is required to decrease the concentration of dissolved Mn to acceptable levels (Khorasanipour et al. 2011a).

Zinc

Speciation modeling predicted that the dominant dissolved Zn inorganic species at acidic to near-alkaline pH are $ZnSO_{4(aq)}$, $Zn(SO_4)_2^{-2}$, and Zn^{+2}, while the hydroxides species of this element, $Zn(OH)_3^-$ (64.36 %), $Zn(OH)_{2(aq)}$ (18.8 %), and $Zn(OH)_4^{-2}$ (16.8 %), are mainly formed in highly alkaline water. Witczak and Adamczyk (1995) showed that: between pH 4 and 7, Zn exists in freshwater as aqua ion; at pH 7, the dominant forms of Zn are the free ion (98 %) and ZnSO4 (2 %); and at pH 9, the main Zn species are the monohydrooxide ion (78 %), $ZnCO_3$ (16 %), and the free ion (6 %).

Cadmium

The speciation pattern of Cd in acidic to near-alkaline water is dominated by sulfate species ($Cd(SO_4)_2^{-2}$, $CdSO_{4(aq)}$), free ions (Cd^{2+}), and chloride species ($CdCl^+$ and $CdCl_{2(aq)}$). Like Zn, the hydroxide species, $Cd(OH)_{2(aq)}$ (89.2 %) and $Cd(OH)_3^-$ (9.5 %), are the dominant Cd forms in highly alkaline waters. During weathering, Cd forms simple compounds, such as CdO, $Cd(OH)_2$, $CdCl_2$, and CdF_2, which are easily mobilized and follow Zn, especially in sedimentation processes (Kabata-Pendias and Mukherjee 2007). In fresh water, Cd is present as Cd^{2+}, $Cd(OH)^+$, and $CdCO3^0$, and also as inorganic compounds and organic complexes (NTP 1991).

Cobalt and Nickel

The speciation pattern of Co and Ni is very similar; more than 99 % consists of sulfate complexes ($CoSO_{4(aq)}$ and $NiSO_{4(aq)}$) and free ion species (Co^{+2} and Ni^+). Hydroxide species of Co and Ni, $Co(OH)_{2(aq)}$ (82 %), $Co(OH)_3^-$ (17.8 %), $Ni(OH)_3{}^-$ (91.5 %), and $Ni(OH)_{2(aq)}$ (8.4 %), are only formed in highly alkaline water. In the natural environment, Co and Ni do not remain long in aquatic environments since soluble species are easily adsorbed by suspended organic matter and by Fe–Mn oxy-hydroxides (Kabata-Pendias and Mukherjee 2007).

Chromium

The speciation pattern of Cr in the investigated samples is remarkably varied. In acidic waters, $CrSO_4{}^+$ (72.3 %) and Cr^{+3} (23.0 %) were the dominant Cr species. Speciation modeling predicted that at increased pH, the dominant Cr species are mainly hydroxide forms: $CrOH^{+2}$, $Cr(OH)_{3(aq)}$, $Cr(OH)_2^{+1}$, $Cr(OH)_2^{+1}$, and $Cr(OH)_4^-$. The dominant hydroxide species of Cr at near-alkaline and highly alkaline pH are $Cr(OH)_{3(aq)}$ (95.7 %) and $Cr(OH)_4^-$ (78.9 %), respectively. Under natural conditions, aqua/hydroxo complexes of Cr^{3+} dominated, although various complexes with organic matter are likely (Kabata-Pendias and Mukherjee 2007). Witczak and Adamczyk (1995) also reported that Cr may occur in surface water as ions, e.g. CrO_4^{2-}, $Cr_2O_7^{2-}$, $CrOH^{2+}$, and Cr^{3+}.

Lead

The speciation of Pb from acidic to near-alkaline pH is mainly $PbSO_{4(aq)}$, $Pb(SO_4)_2^{-2}$, Pb^{+2}, and $PbCl^+$, respectively. The hydroxide forms of this element, $Pb(OH)_3^-$ (91.5 %) and $Pb(OH)_{2(aq)}$ (8.4 %), were predicted to form in highly alkaline waters. In most aquatic environments, Pb forms one of the less mobile species, which eventually precipitates on the bottom sediment. Surface waters are generally neutral or alkaline, which results in Pb being associated with less mobile forms (Laxen and Harrison 1983). Moreover, Pb is known for preferential adsorption onto suspended and colloidal particles of hydrous ferric oxides, resulting in relatively low dissolved Pb levels (Kelepertzis et al. 2012). In surface and ground waters, its species are: Pb^{2+}, $PbOH^+$, $PbHCO_3^+$, and $PbSO_4^0$ (Witczak and Adamczyk 1995).

Tin

Speciation modeling predict a verity of species for Sn, including Sn^{+2} (51.6 %), $SnOH^+$ (17.7 %), $Sn(OH)_2$ (17.2 %), and $SnCl^+$ (12.4 %) in water samples with acidic pH. The hydroxide forms, $Sn(OH)_2$ and $Sn(OH)_3^-$, dominate at near-neutral to highly alkaline pH.

Speciation Results of Metalloids and Oxy-Anions

The speciation results of metalloids and oxy-anions are shown in Table S-3 and are described as follows:

Arsenic

In all aquatic environments, As generally occurs as pentavalent arsenate ($HnAsO_4$ n–3) under oxidizing conditions, whereas trivalent arsenite ($HnAsO_3$ n^{-3}) predominates under reducing conditions (Pokrovski et al. 1996). According to speciation modeling, different oxy-anions species of As were determined in the investigated samples. The proportion of As species at different pH values are: $H_2AsO_4^-$ (86.9 %) and H_3AsO_4 (13 %) in acidic water; $H2AsO_4^-$ (57.3 %) and $HAsO_4^{-2}$ (42.7 %) at near-neutral pH; $HAsO_4^{-2}$ (94.4 %) at near-alkaline pH; and AsO_4^{-3} (75.5 %) and $HAsO_4^{-2}$ (24.5 %) at highly alkaline pH. In contrast to the bivalent cations, which are mobile under acidic conditions, oxy-anions like Mo (V, VI) and As (V) show increasing adsorption to the Fe(III) oxy-hydroxides with decreasing pH (Dzombak and Morel 1990; Khorasanipour et al. 2012). This relationship is reflected by increased As concentrations in the Fe(III) oxy-hydroxides fraction in the oxidation zone of tailings (Dold and Fontboté 2001). Adsorption onto and co-precipitation with Fe^{3+} hydroxides are very efficient removal mechanisms for arsenic in mine waters (Roddick-Lanzilotta et al. 2002).

Molybdenum

Hydrochemical data (Table 2) clearly show that Mo concentrations increased at alkaline pH. According to the speciation results, various Mo species were predicted to form in the acidic waters, including: $MoO_3(H_2O)_{3(aq)}$ (66.2 %), MoO_4^{-2} (12.7 %), $HMoO_4^-$ (10.8), $MgMoO_{4(aq)}$ (8.6 %), and $CaMoO_{4(aq)}$ (2.5 %). Most of these species are also present at near-neutral to near-alkaline pH, but at increased pH, the dominant specie of Mo is MoO_4^{-2}. Molybdenum exhibits unusual geochemical behavior since it is likely to form oxyanions in most environmental compartments; however, under reducing conditions, it has a high affinity for sulfur (Kabata-Pendias and Mukherjee 2007). Dold and Fontboté (2001) proposed that Mo is possibly associated with the Fe(III) oxy-hydroxide and Fe(III) oxide fractions because it is adsorbed to schwertmannite and jarosite. According to Anbar (2004), speciation of Mo in waters is affected by the pH-Eh regime; the MoO_4^{2-} ion predominates at $pH > 5$, whereas $HMoO_4^-$ occurs at pH <5, and species such as $Mo_7O_{26}^{4-}$ or $Mo_8O_{24}^{6-}$ predominate at $pH < 6$, at high Mo concentrations.

Antimony

Antimony displays both metallic and nonmetallic characteristics. The dominant specie of Sb is $Sb(OH)_6^{-1}$ at acidic to near-alkaline pH, while $Sb(OH)_{5(aq)}$ is the dominant form of this element in highly alkaline water samples. Bodek et al. (1988) showed that simple antimony cations (i.e. Sb^{+3} and Sb^{+5}) do not occur in solution, but that hydrolyzed forms (e.g. $Sb(OH)_6^-$) are found. The dominant species in the pH range typical of natural environments are $Sb(OH)_3$, in the case of trivalent antimony, and $Sb(OH)_6^-$ for pentavalent antimony. In oxidizing environments, $Sb(OH)_6^-$, is the dominant species at pH >3, whereas $Sb(OH)_3$ dominates in relatively reducing conditions (Kabata-Pendias and Mukherjee 2007).

Selenium

Speciation results showed that SeO_4^{-2} was the prevalent form of Se at all pH ranges in the investigated samples. Other inorganic complexes of this element, such as $MnSeO_{4(aq)}$, $HSeO_4^{-1}$ (in acidic waters), and $CaSeO_{4(aq)}$ (at all pH ranges), were predicted to have very little influence on Se speciation. Commonly occurring species (Se^{4+} and Se^{6+}) do not form stable compounds and are preferably absorbed by minerals, particularly clay minerals and Fe and Mn oxy-hydroxides (Kabata-Pendias and Mukherjee 2007).

Conclusions

The Sarcheshmeh tailings impoundment is situated in a semi-arid environment with high evaporation rates during the dry seasons. Geochemical and hydrochemical investigations were performed to identify the contamination potential and environmental concerns associated with the potentially hazardous trace elements in the Sarcheshmeh tailings. The significant results follow:

1. Oxidation of sulfide minerals contained within the tailings and massive precipitation of secondary evaporative mineral and efflorescent salts are well developed in the oxidation zone of the dry ponds. The geochemical behaviors of potential contaminants during the weathering reactions diff considerably. The orders of mobility for contaminants subject to release by sulfide oxidation and weathering are: Cu > Cd > Co > Zn > Ni > Mn > S > Cr > Sn > As > Se > Fe = Bi > Sb = Pb = Mo.
2. Due to capillary forces and the high evaporation rate, a 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, while As, Mo, Pb, Sb, Bi, and Sn have very low mobility.
3. The formation and dissolution of secondary minerals are responsible for low pH (from 2.5 to 4.1) and high values of EC, TDS, SO_4^{-2}, Cl^-, Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, and Zn after heavy rainfall and storm events in winter.
4. Most of the tailings water is recovered from the safety bay and is reused for industrial purposes. Geochemical reactions are responsible for the unexpected hydrochemical changes, such as significant mobilization of toxic hazardous elements. High values of corrosive ions like chlorine in highly acidic fluids can promote corrosion of pipes and pumps in water recycling systems and diminish its value for further use.
5. According to the speciation calculations, various species of trace elements form in the investigated samples, depending on pH, which controls the hydrochemical characteristics of the investigated water samples. The speciation pattern of cationic forms (M^{+2} and M^{3+}) is mainly controlled by the presence of high sulfate values in the acidic, weathered tailings. In these acidic waters, sulfate complexes (MSO_4^+, $M(SO_4)_{(aq)}$, $M(SO_4)_2^{-2}$, and $M(SO_4)_2^-$) and free metal species (M^{+2} and M^{+3}) were the dominant forms. The free metal species in solution decreased as the importance of the hydroxide complexes increases. Various hydroxide species of trace elements such as $M(OH)^+$, $M(OH)_3^-$, $M_3(OH)_4^{+2}$, $M_2(OH)_3^+$, $M(OH)_{2(aq)}$, $M(OH)_4^{-2}$ (where M represents bivalent cations like Cu, Zn, and Cd) and $Me(OH)_2^+$, $Me(OH)_4^-$, $Me(OH)_2^+$, $Me(OH)_{3(aq)}$, and $Me(OH)_4^-$ (where Me represents trivalent cations like Al, Fe, and Cr) are mainly formed in near-alkaline to highly alkaline pH conditions.
6. Speciation results also indicate that oxy-anion species are the prevalent forms of As, Mo, and Se at approximately all pH ranges.
7. Considering hydrochemical results together with site-specific conditions can be a valuable basis for environmental management of tailings.

References

Akcil A, Koldas S (2006) Acid mine drainage (AMD): causes, treatment and case studies. J Clean Prod 14:1139–1145

Anbar AD (2004) Molybdenum stable isotopes: observations, interpretations and directions. Rev Miner Geochem 55:429–454

Atapour H, Aftabi A (2007) The geochemistry of gossans associated with Sarcheshmeh porphyry copper deposit, Rafsanjan, Kerman, Iran: implications for exploration and the environment. J Geochem Explor 93:47–65

Bea SA, Ayora C, Carrera J, Saaltink MW, Dold B (2010) Geochemical and environmental controls on the genesis of soluble efflorescent salts in coastal mine tailings deposits: a discussion based on reactive transport modeling. J Contam Hydrol 111:65–82

Berger BR, Ayuso RA, Wynn JC, Seal RR (2008) Preliminary model of porphyry copper deposits. USGS Open-File Report 1321, Washington, USA

Bjelkevik A (2005) Water cover closure design for tailings dams. State of the art report. Dept of Civil and Environmental Eng, Luleå Univ of Technology, Sweden

Blowes DW, Reardon EJ, Cherry JA, Jambor JL (1991) The formation and potential importance of cemented layers in inactive sulfide mine tailings. Geochim Cosmochim Acta 55:965–978

Blowes DW, Lortie Gould WD, Jambor JL, Hanton-Fong CJ (1998) Geochemical, mineralogical and microbiological characterization of sulfide-bearing carbonate-rich gold-mine tailings impoundents, Joutel, Quebec. Appl Geochem 13:387–705

Bodek I, Lyman WJ, Reehl RF, Rosenblatt DH (1988) Environmental inorganic chemistry properties, processes and estimation methods. Pergamon Press, New York, pp 7.1-1–7.1-5

Boyle RW (1974) The use of major elemental ratios in detailed geochemical prospecting utilizing primary halos. J Geochem Explor 3:345–369

Candeias C, Ferreira da Silva E, Salgueiro ar, Pereira HG, Reis AP, Patinha C, Matos jx, Avila PH (2011) The use of multivariate statistical analysis of geochemical data for assessing the spatial distribution of soil contamination by potentially toxic elements in the Aljustrel mining area (Iberian Pyrite Belt, Portugal). Environ Earth Sci 62:1461–1479

Chaparro MAE, Chaparro MAE, Rajkumar P, Ramasamy V, Sinito AM (2011) Magnetic parameters, trace elements, and multivariate statistical studies of river sediments from southeastern India: a case study from the Vellar River. Environ Earth Sci 63:297–310

Coggans CL, Blowes DW, Robertson WD, Jambor JL (1999) The hydrogeochemistry of nickel-mine tailing impoundments—Copper Cliff, Ontario. In: Filipek LH, Plumlee GS (eds), Environmental geochemistry of mineral deposits. Rev Econ Geol Soc 6B:447–456

Cravotta CA (1994) Secondary iron-sulfate minerals as sources of sulfate and acidity. In: Alpers CN, Blowes DW (eds) Environmental geochemistry of sulfide oxidation. Am Chem Soc Symp Ser 550:345–364

DelValls TA, Forja JM, Gonzalez-Mazo E, Gomez-Parra A (1998) Determining contamination sources in marine sediments using multivariate analysis. Trends Anal Chem 17:181–192

Dimitrijevic MD (1973) Geology of the Kerman Region. Institute for geological and mining exploration and investigation of nuclear and other mineral raw material. Iran Geol Survey Rept Yu/52, Beograd, Yugoslavia

Dold B, Fontboté L (2001) Element cycling and secondary mineralogy in porphyry copper tailings as function of climate, primary mineralogy, and mineral processing. J Geochem Explor 74:2–55

Dzombak DA, Morel FMM (1990) Surface complexation modeling: hydrous ferric oxides. Wiley, New York City

Emmerson RHC, O'Reilly-Wiese SB, Macleod CL, Lester JN (1997) A multivariate assessment of metal distribution in inter-tidal sediments of the Blackwater Estuary, UK. Mar Pollut Bull 34:960–968

Ferris FG, Hallberg RO, Lyven B, Pedersen K (2000) Retention of strontium, cesium, lead and uranium by bacterial iron oxides from a subterranean environment. Appl Geochem 15:1035–1042

Goldberg S, Forster HS, Godfrey CL (1996) Molybdenum adsorption on oxides, clay minerals, and soils. Soil Sci Soc Am J 60(2):425–432

Grangeia C, Ávila P, Matias M, Ferreira da Silva E (2011) Mine tailings integrated investigations: the case of Rio tailings (Panasqueira Mine, Central Portugal). Eng Geol 123:359–372

Gustafsson JP (2000) Visual MINTEQ version 3. Land and water resources engineering. Teknikringen KTH (Royal Inst of Technology), Stockholm

Hezarkhani H (2006) Hydrothermal evolution of the Sar-Cheshmeh porphyry Cu–Mo deposit, Iran: evidence from fluid inclusions. J Asian Earth Sci 28:409–422

Holmström H, Ohlander B (1999) Oxygen penetration and subsequent reactions in flooded sulphidic mine tailings: a study at Stekenjokk, northern Sweden. Appl Geochem 14:747–759

Holmström H, Salmon UJ, Carlsson E, Petrov P, Öhlander B (2001) Geochemical investigations of sulfide-bearing tailings at Kristineberg, northern Sweden, a few years after remediation. Sci Total Environ 273:111–133

Jacob DL, Otte ML (2004) Long-term effects of submergence and wetland vegetation on metals in a 90-year old abandoned Pb-Zn mine tailings pond. Environ Pollut 130:337–345

Johnson RH, Blowes DW, Robertson WD, Jambor JL (2000) The hydrogeochemistry of the Nickel Rim mine tailings impoundment, Sudbury, Ontario. J Contam Hydro l41:49–80

Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, Berlin

Kaiser HF (1960) The application of electronic computers to factor analysis. Educ Psychol Meas 20:141–151

Kelepertzis E, Argyraki A, Daftsis E (2012) Geochemical signature of surface water and stream sediments of a mineralized drainage basin at NE Chalkidiki, Greece: a pre-mining survey. J Geochem Explor 114:70–81

Khorasanipour M, Moore F, Naseh R (2011a) Lime treatment of mine drainage at the Sarcheshmeh porphyry copper mine, Iran. Mine Water Environ 30:216–230

Khorasanipour M, Tangestani MH, Naseh R, Hajmohammadi H (2011b) Hydrochemistry, mineralogy and chemical fractionation of mine and processing wastes associated with porphyry copper mines: a case study from the Sarcheshmeh mine, SE Iran. Appl Geochem 26:714–730

Khorasanipour M, Tangestani MH, Naseh R (2012) Application of multivariate statistical methods to indicate the origin and geochemical behavior of potentially hazardous elements in sediment around the Sarcheshmeh copper mine, SE Iran. Environ Earth Sci 66:589–605

Langmuir D (1997) Aqueous environmental geochemistry. Prentice-Hall Inc, New York City, ISBN 10:0023674121

Laxen DPH, Harrison RM (1983) The physio-chemical speciation of selected metals in the treated effluent of a lead-acid battery manufacturer and its effect on metal speciation in the receiving water. Water Res 17:71–80

Lin Z (1997) Mineralogical and chemical characterization of wastes from the Sulfuric acid industry in Falun, Sweden. Environ Geol 39:152–162

Loska K, Wiechuła D (2003) Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemosphere 51:723–733

Lottermoser BG (2003) Mine waste: characterization, treatment and environmental impacts. Springer, Berlin

Mason B, Moore CB (1982) Principles of geochemistry, 4th edn. Wiley, NewYork city

McGregor RG, Blowes DW (2002) The physical, chemical and mineralogical properties of three cemented layers within sulfide-bearing mine tailings. J Geochem Explor 76:195–207

McSweeney K, Madison FW (1988) Formation of a cemented surface horizon in sulfidic mine waste. J Environ Qual 17:256–262

MiMi (2004) Mitigation of the environmental impact from mining waste. In: Höglund LO, Herbert R (eds) MiMi-performance assessment main report. MiMi, Luleå, Sweden, MiMi 2003:3, ISSN 1403-9478. www.mistra.org/mimi

Nickel E (1973) Experimental dissolution of light and heavy minerals in comparison with weathering and intrastitial solution. Contrib Sedimentol 1:1–68

Nordstrom DK, Alpers CN (1999) Geochemistry of acid mine waters. Environ Geochem Miner Depos 6A:133–160

NTP (National Toxicology Program) (1991) Cadmium and certain cadmium compounds. In: 7th annual report on carcinogens, summary. US Public Health Service, Dept of Health and Human Services, Washington, DC, USA, pp 114–121

Plumlee GS, Smith KS, Montour MR, Fichlin WH, Mosier EL (1999) Geologic control on the composition of natural waters and mine waters drainage diverse minerals-deposit types. In: Filipek LH, Plumlee GS (eds) Environmental geochemistry of mineral deposits. Rev Econ Geol 6B:373–432

Pokrovski G, Gout R, Schott J, Zotov A, Harrichoury JC (1996) Thermodynamic properties and stoichiometry of As (III) hydroxide complexes at hydrothermal conditions. Geochim Cosmochim Acta 60:737–749

Roddick-Lanzilotta AJ, McQuillan AJ, Craw D (2002) Infrared spectroscopic characterization of arsenate (V) ion adsorption from mine waters, Macreas mine, New Zealand. Appl Geochem 17:445–454

Rudnick RL, Gao S (2003) Treatise on geochemistry, vol 3. Elsevier, Netherlands, pp 1–64

Sarafian PG, Furbish WJ (1965) Solubilities of natural and synthetic ferrimolybdite. Am Mineral 50:223–226

Saxena M, Dhimole LK (2006) Utilization and value addition of copper tailing as an extender for development of paints. J Hazard Mater 129:50–57

Shahabpour J, Doorandish M (2007) Mine drainage water from the Sar Cheshmeh porphyry copper mine, Kerman, IR Iran. Environ Monit Assess 141:105–120

Shahabpour J, Kramers JD (1987) Lead isotope data from the Sarcheshmeh porphyry copper deposit, Iran. Miner Deposita 22:275–281

Sima M, Dold B, Frei L, Senila M, Balteanu D, Zobrist J (2011) Sulfide oxidation and acid mine drainage formation within two active tailings impoundments in the Golden Quadrangle of the Apuseni Mountains, Romania. J Hazard Mater 189:624–639

Skousen J, Politan K, Hilton T, Meek A (1990) Acid mine drainage treatment systems: chemicals and coasts. Green Lands 20(4): 31–37

Smuda J, Dold B, Spangenberg JA, Pfeifer HR (2008) Geochemistry and stable isotope composition of fresh alkaline porphyry copper tailings: implications on sources and mobility of elements during transport and early stages of deposition. Chem Geol 256:62–76

Spears DA, Tarazona MRM, Lee S (1994) Pyrite in UK coals: its environmental significance. Fuel 37:1051–1055

US EPA (US Environmental Protection Agency) (2009) National primary and secondary regulations. http://www.epa.gov/safewater

Vaughan DJ, Craig JR (1978) Mineral chemistry of metal sulfides. Cambridge earth science series. Cambridge University Press, Cambridge

Watson EB, Harrison TM (1983) Zircon saturation revised: temperature and composition effects in a variety of crystal magma types. Earth Planet Sci Lett 64:295–304

Webster R (2001) Statistics to support soil research and their presentation. Eur J Soil Sci 52:331–340

WHO (2006) Guidelines for drinking-water quality. 1st addendum to 3rd edn, vol 1. World Health Organization Geneva

WHO (World Health Organization) (2004) Guidelines for drinking-water quality, 3rd edn, vol 1. World Health Organization, Geneva, pp 488–496

Witczak S, Adamczyk A (1995) Catalog of selected physical and chemical indicies for ground water contamination, and analytical methods. Bibl Monitor Þrodowiska, Warszawa (in Polish) In: Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, Berlin

Wu P, Tang CY, Liu CQ, Zhu LJ, Pei TQ, Feng LJ (2009) Geochemical distribution and removal of As, Fe, Mn and Al in a surface water system affected by acid mine drainage at a coalfield in southwestern China. Environ Geol 57(7):1457–1467

Yongming H, Peixuan D, Junji C, Posmentier ES (2006) Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci Total Environ 355:176–186

Zhao H, Xia B, Qin J, Zhang J (2012) Hydrogeochemical and mineralogical characteristics related to heavy metal attenuation in a stream polluted by acid mine drainage: a case study in Dabaoshan Mine, China. J Environ Sci 24(6):979–989