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TECHNICAL ARTICLE

Potential Release of Metals from Tailings and Soil at the Hamekasi Iron Mine, Hamadan, Iran

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Abstract This study focused on acid neutralization reactions and the effects of water composition on the release and mobility of metals from mine tailings. The aims of this study were to: investigate leaching of metals from neutral mine tailings, determine the factors responsible for metal leaching, and investigate potential metal filtering by the soil. Tailings and soil samples were collected from an iron mine and analyzed. Equilibrium thermodynamic data and metal fractionation were then used to predict precipitation/dissolution of minerals and ion adsorption/desorption. Three column experiments were designed. The first column was filled with tailings, while the second column contained tailings above a layer of soil; both were leached with distilled water as rainfall. The third column was packed with soil and percolated with synthetic groundwater. The results indicated that iron (Fe) and zinc (Zn) mobility are mainly controlled by precipitation–dissolution mechanisms, while sorption onto oxides and carbonates limit the mobility of copper (Cu) and nickel (Ni). Cadmium (Cd) and manganese (Mn) mobility are affected by both mechanisms. Water discharging from column 3 (soil washed with groundwater) contained high concentrations of dissolved metals, indicating that water composition played an important role in metal mobility. Buffering minerals like carbonates and hornblende, chlorite, and albite decreased acid generation.

Keywords Water composition · Acid neutralization potential · XRD analysis · PHREEQC · Leaching

Introduction

The contamination of soil and water resources is a major concern associated with mining. The incidence of potentially toxic contaminants (Norland and Veith 1995; Wong et al. 1998), the loss of essential nutrients (Wong 2003), and reduced or inhibited plant growth are often associated with tailings dumps. Waste properties, percolation rates, and oxygen availability greatly affect metal dissolution and acid formation (Doepker and Drake 1991). A comprehensive understanding of waste characteristics is required to predict the amount of contamination release. Mineralogical composition and reactivity of sulphides and neutralizing minerals all influence the magnitude and quality of acid mine drainage (AMD). Since tailings were discharged onto the soil surface and soil acts as a filter to protect water quality, soil characteristics, including physical and chemical properties such as cation exchange capacity (CEC), carbonate calcium, organic matter, oxide mineral contents, soil texture, and permeability, all affect the downward attenuation of metals from tailings. The fate of metals depends on the soil's chemical and physical properties, and especially on their speciation.

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Literature Review

Occurrence, abundance, and reactivity are three factors that affect the mobility of metals from tailings (Berner 1978; Maher 2010). Reactivity depends on the: inherent mobility of elements, pH of tailings pore water (Jurjovec et al. 2002; Pagnanelli et al. 2004), and water oxidation potential, temperature, and velocity. The primary mechanism of metal attenuation is neutralization (US EPA 2007), while factors that decrease interaction of dissolved metal ions with soil or solid surfaces increase metal mobility. Metal mobility is influenced by the acidification capacity of the tailings (Shu et al. 2001); an investigation of metal extractability in acidic and neutral mine tailings by Conesa et al. (2007) revealed that acidic tailings had a higher initial metal solubility, but that metal mobility can increase over long time periods in neutral tailings. Kim et al. (2014) reported that calcite buffered the pH, but that the surface charge of minerals, such as goethite and jarosite, were also important factors in controlling the chemical speciation of metals in the Samsanjeil Mine (Gosung, Korea).

Doepker and O'Connor (1991) suggested that metal mobility varied widely from waste to waste depending on the metallurgical process and the type of ore. Smuda et al. (2007) showed that precipitation of secondary minerals reduced metal leaching. According to Lapakko (1988), rapid acid consumption in Duluth waste rock was probably due to dissolution of plagioclase, olivine, and pyroxene. Weathering reactions are affected by variables such as the pH and concentrations of Aluminium (Al), calcium (Ca), magnesium (Mg), sodium (Na), and potassium (K), CO_2, and organic acids in the soil solution (Sverdrup and Warfvinge 1995).

Plante et al. (2010) investigated the role of sorption in controlling Nickel (Ni) concentrations in contaminated neutral drainage flowing from the waste rock piles of the Tio mine. El Adnani et al. (2015) focused on sorption phenomena (as a neutralization mechanism) to explain the low arsenic (As) concentrations in leachates despite significant As levels in the tailings. Laboratory studies using disturbed soil samples have indicated that soil characteristics correlate with metal mobility; however, the results vary due to different mineralogical and chemical soil characteristics and the selectivity of retention sites for each metal. Soil characteristics that positively correlated with cadmium (Cd) retention were pH (Christensen 1984; Tyler and McBride 1982), organic matter (OM) content, CEC (Sidle and Kardos 1977), and specific surface area (Korte et al. 1976), while free iron oxides were negatively correlated (Amacher et al. 1986). Zinc (Zn) retention was positively correlated with pH (Harter 1983), CEC (Sidle and Kardos 1977), and specific surface area (Korte et al. 1976). Positive correlations have also been found between copper (Cu) retention and pH (Tyler and McBride 1982), sum of bases, exchangeable Ca (Harter 1983), OM content (Hickey and Kittrick 1984), and CEC (Sidle and Kardos 1977).

Tyler and McBride (1982) showed that pH, CEC, and competitive cations in soils affect metal mobility. Exchangeable cations influence metal mobility, especially in neutral tailings (De Matos et al. 2001). In general, AMD has been more thoroughly studied, while neutral mine drainage is less well documented (Heikkinen et al. 2009; Kirby and Cravotta 2005). More attention has been paid to element mobility from neutral tailings with high silicates and low sulphide content in the last few decades (El Adnani et al. 2015; Heikkinen and Räisänen 2008, 2009; Plante et al. 2010). Tailings with high sulphide mineral content have also been investigated (Blowes and Jambor 1990; Jurjovec et al. 2002).

The aims of this study were to: (1) investigate leaching of metals from neutral mine tailings, (2) identify factors responsible for metal leaching, and (3) investigate the role of soil in metal filtering. We studied the effect that water infiltration from mine tailings with an uncertain acid generation potential (containing quartz, hornblende, albite, and minor amounts of sulphides) might have on groundwater chemistry. Although disposal of neutral tailings on surface soil may pose much less environmental risk than acid-generating tailings, a general chemical imbalance in the soils can decrease biological activity, affect pH, and degrade organic and mineral sorption complexes, and release metals into groundwater.

Site Description

The Hamekasi (Baba Ali) iron mine is located in the northwestern part of Hamadan province, in western Iran. The site is about 10 km² in area and comprises rock units from the Palaeozoic, Mesozoic, and Cenozoic periods. The regional geology is dominated by diorite, schist, and granodiorite. Magnetite, hematite, and goethite are the main mineralogical components of the Baba Ali ore body, with minor amounts of sulfide minerals, such as chalcopyrite, pyrite, bornite, malachite, and chalcocite. The minerals present in the tailings are calcite and silicate minerals like chlorite, quartz, feldspar, pyroxene, epidote, amphibole, and garnet, as well as sulfide minerals. Exploitation of the confirmed reserves of iron up to 4×10^6 t began by open pit mining in 1994 at a rate of 10,000 t per year. The background concentrations of Cd, Zn, Cu, and Ni were 1.59, 82, 40, and 70 mg/kg (Krami et al. 2013). Tailings produced at the mine were deposited in a 10 ha area west of the mine site and 2.5 km west of the village of Baba Ali. The climate is semi-arid, with 325 mm of annual precipitation, and maximum and minimum temperatures of +40 and

−23.8 °C, respectively. The wet and dry seasons generally occur between November and May and between June and October, respectively.

The underlying rocks are andesite and basalt. The mineral assemblage in the andesite is typically dominated by plagioclase plus pyroxene and hornblende. Magnetite, zircon, apatite, ilmenite, biotite, and garnet are common accessory minerals. The depth to groundwater is low and some springs were observed around the tailing disposal area (Fig. 1).

Materials and Methods

Sample Collection and Analysis

About 5 kg of non-oxidized tailings and composite soil samples were collected from mined and agricultural land around the mine area in 2011 (Fig. 1). Soil samples were randomly collected from agricultural land and then mixed to prepare composite soil samples. The depth of sampling for soil and tailings was 0–30 and 0–10 cm, respectively. Samples were initially air-dried and crushed in the laboratory for physical and chemical analyses.

Column Experiments

The experiments were performed in 30 cm long columns with inner diameters of 2 cm. The columns were filled as follows: column 1 was packed with 50 g of crushed tailings with a particle size less than 10 mm to a depth of 10 cm; column 2 contained a 10 cm layer of soil covered by 5 cm of tailings; and column 3 was filled with the soil sample (on the basis of soil taxonomy, it was classified as xerept). The column experiments were carried out under unsaturated conditions in duplicates for 60 days. Columns 1 and 2 were washed with low mineralized water as rainfall while column 3 was leached with synthetic groundwater (Supplementary Table 1) (composition similar to the natural groundwater). The effluents were collected daily for 60 days and analyzed. The effluent volumes, pH, and electrical conductivity (EC) were immediately measured. Before cation analysis, leachates were filtered through a 0.45 µm filter and acidified by adding concentrated HNO_3. The concentrations of Ca and Mg were measured by

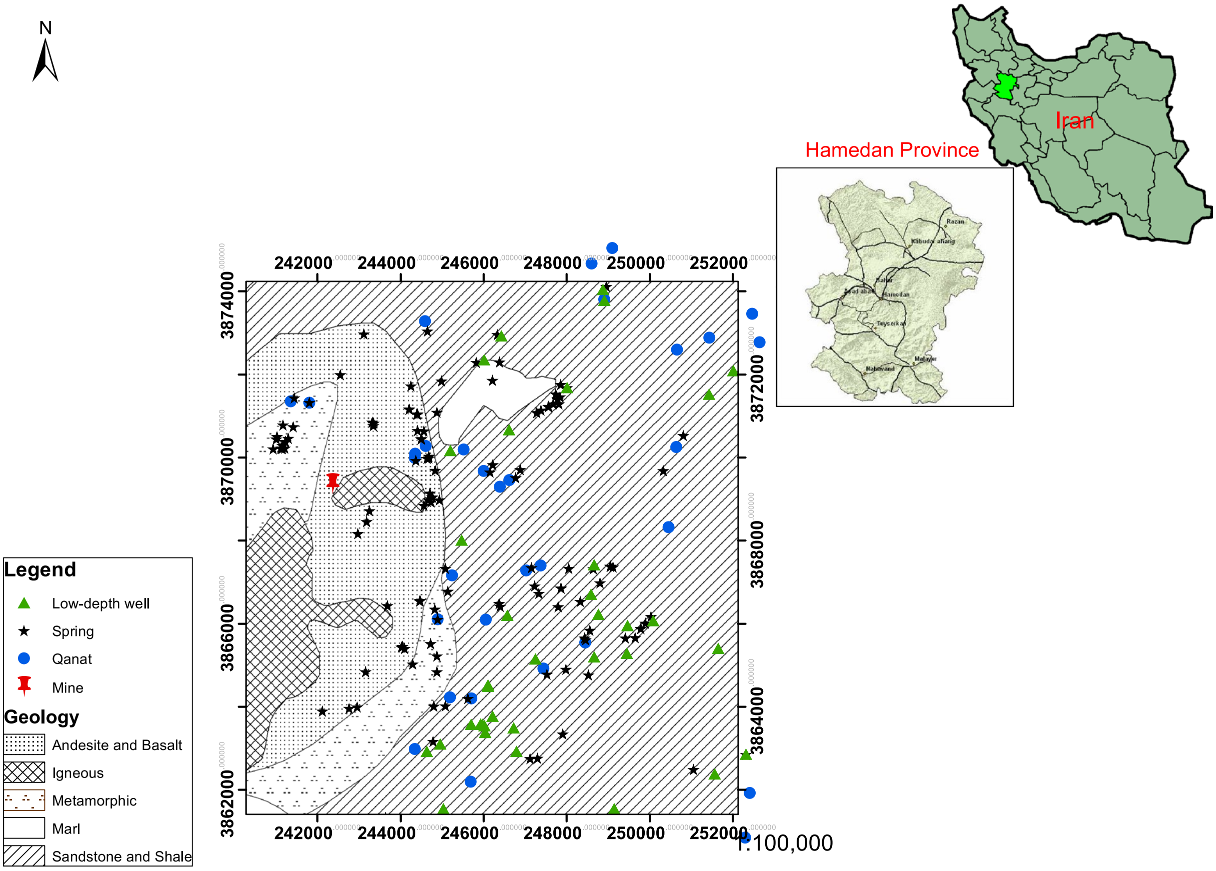

Fig. 1 Mine Location and geological units and low-depth well, springs and qanat in iron mine

titration. The sulfate (SO_4) concentration was determined by spectrophotometry at 420 nm. Metals were determined by atomic adsorption spectroscopy.

Soil and Tailings Characteristics

The physical and chemical properties of soil and tailings were analyzed before and after the leaching experiments. Particle size distribution of the soil and tailings samples was determined by the hydrometer method. The wet combustion method (Nelson et al. 1996) was used for organic carbon analysis. The calcium carbonate equivalent (CCE) was determined by neutralization with HCl. The pH and EC were measured in a 1:5 and 1:10 solid to water extract using pH and EC meters for the soil and tailings, respectively. For the tailings, 20 g of crushed sample and 200 mL of deionized water were placed in a 250 mL Erlenmeyer flask and the mixture was shaken for 24 h, after which the pH and EC were measured in the supernatant. The CEC of the soil and tailings was determined using the ammonium acetate method (Rowell 1994).

Mineralogical Analysis

The mineralogical composition of the soil and tailings samples before and after leaching was investigated by X-ray diffraction (XRD) on an APD 2000 instrument using Cu-kα radiation. Analysis of XRD data and mineral phase identification were done using Match software, databases such as Mindat (http://www.mindat.org/) and Webminerals (http://www.webminerals.com), and by comparison of the diffraction patterns to the PDF-2 database.

Sequential Extraction of Soil and Mine Tailings

Determination of the metal fractions provided information about the potential release of contaminants and metal migration. Sequential extraction is widely used to study element fractionation in soils and sediments (Hall et al. 1996; Tessier et al. 1979) and has been increasingly used to study the complex processes of sulphide oxidation and retention of mobilized elements by secondary phases via precipitation and sorption processes (El Adnani et al. 2015; McCarty et al. 1998; Plante et al. 2010; Ribet et al. 1995).

A method of Dold and Fontbote (2001) was used to extract metals from the sulphide fraction of the tailings. This method cannot extract metals bound to organic fractions. The amount of organic carbon in the tailings was negligible, while the organic carbon content in the soil was 1.3%, so it was decided to determine metal fractionation in the soil samples using sequential extraction (Salbu and Krekling 1998). Five fractions were identified, the: exchangeable fraction (extraction with 20 mL of 1 M ammonium acetate), carbonate-bound fraction (extraction using 20 mL of 1 M ammonium acetate at pH 5), Fe and Mn oxides-bound fraction (extraction with 0.04 M NH_2OH HCl in 25% acetic acid), organically bound fraction (extraction with 15 mL of 30% H_2O_2 at pH 2 at 80 °C and then with adding 5 mL of 3.2 M ammonium acetate in 20% HNO_3), and the residual fraction (1 mL of concentrated $HClO_4 + 5$ mL of concentrated HNO_3 at 60 °C).

Seven fractions were extracted using 1 g of tailings: soluble and exchangeable fraction—extraction with 50 mL of 1 M ammonium acetate at pH 7 for 2 h; carbonate bound fraction—extraction with 50 mL of 1 M ammonium acetate at pH 5, Mn-oxide bound fraction—extraction with 50 mL of 0.1 M NH_2OHHCl at pH 2 for 30 min; poorly crystallized Fe-oxides bound fraction—extraction with 50 mL of 0.2 M ammonium oxalate at pH 3.3 in the dark for 4 h; crystalline Fe-oxide bound fraction—extraction with 50 mL of 0.2 M ammonium oxalate at pH 3.3 and heating at 100 °C for 30 min; sulphide bound fraction—adding 750 mg $KClO_3 + 5$ mL of 12 M HCl, vortex, adding a further 10 mL of HCl 12 M, vortex, after 30 min, adding 15 mL of distilled water, and finally adding 10 mL of 4 M HNO_3 and shaking at 90 °C for 20 min; and residual fraction—extraction with 2 mL of 16 M HNO_3 heated at 200 °C until dryness, cooling and adding 2 mL of 12 M HCl and then heating again, adding 10 mL of $HF:HClO_4:HNO_3$ (5:3:2) and heating at 120 °C to dryness, and finally warming gently for 5–10 min (Dold and Fontbote 2001).

Partition Coefficient of Metals

The partition coefficient (K_d) of the metals was measured to describe the metal leachability. The K_d was calculated from isotherm data and indicated the distribution of metals between the solution and solid phases.

$$K_d = q/C$$

where q is the metal concentration in the solid phase (g/kg), C is the metal concentration in the soil solution (g/L), and K_d is the partition coefficient (L/kg). In the isotherm experiments, 2 g of soil were equilibrated with different concentrations of metals (0, 5, 10, 25, 35, and 50 mg/L) in the presence and absence of synthetic groundwater.

Acid Production Potential

The potential for acid production was evaluated by acid base accounting (ABA), using the Sobek procedure (Sobek et al. 1978).

Geochemical Modelling

The equilibrium geochemical speciation/mass transfer model (PHREEQC) and the WATEQ4F thermodynamic database was used (Parkhurst and Appelo 1999) for speciation, saturation index (SI) calculations, and inverse modelling. Speciation modelling is useful when mineral dissolution/precipitation needs to be known. It uses chemical analysis of water to calculate the distribution of aqueous species by using an ion-association aqueous model. The most important results of speciation calculations are SI values, which indicate whether a mineral should dissolve or precipitate. The input data, including the temperature, pH, major ions, and mineral phases, were selected based on the mineralogical analysis. However, a number of phases defined in PHREEQC, including amorphous and poorly crystalline minerals, were not detected by XRD analysis.

Results and Discussion

Soil and Tailings Properties

The physical and chemical analyses of the soil and tailings samples are presented in Supplementary Table 2.

The pH and EC of Leachates

The leachates of the three columns all had slightly alkaline or alkaline pH values (Fig. 2a). According to XRD analysis, the tailings were dominated by quartz, albite, hornblende, chlorite, and calcite, while sulphide minerals like pyrite, arsenopyrite, chalcopyrite, bornite, malachite, and chalcocite were detected at low concentrations. However, as little as 0.2% sulphide in rocks can trigger acidic drainage, depending on site conditions. Additionally significant volumes of rock containing 1–5% sulfur as sulphide can indicate that AMD is likely to develop over the long term (Lapakko 2003; Morin and Hutt 1997). Although the static test results indicated that the tailings had an uncertain acid generation potential (Table 1), the high neutralization potential of the tailings and relatively low sulphide mineral content produced an alkaline effluent in column 1. The XRD results and calcium carbonate measurements confirmed the presence of calcite in the tailings (Supplementary Fig. 1; Table 2). Acidity released by sulphide mineral oxidation was neutralized by dissolution of carbonates. In addition, some acid buffering capacity was provided by silicate minerals like chlorite, hornblende, and albite. Supplementary Fig. 2 indicates that the height (intensity) of the chlorite peak decreased and that hornblende was not detected after leaching. Silicates have a higher neutralization potential than carbonates, but their dissolution rate is slower (Hakkou et al. 2008). Li and Bernier (1999) reported that the contribution of chlorite to alkalinity production (mainly Mg and Ca) was about 15–20%. Jurjovec et al. (2002) reported chlorite reduction during a leaching experiment of 60%. Hakkou et al. (2008) found that the acid neutralization potential of muscovite, albite, and chlorite was 0.14, 0.6, and 1.5 kg $CaCO_3$/t of minerals, respectively. The relatively high rate of weathering of these minerals may have been due to the particle size of the tailings (Strömberg and Banwart 1999), the type of chlorite and hornblende minerals (Ross 1975), laboratory conditions, and pH (Zazzi 2009). The particle size of the tailings was less than 2 mm and the chlorite and hornblende had a high Fe content.

The buffering role of the soil must be also considered in columns 2 and 3. The high CEC of the soil and the release of alkaline elements like Ca, Mg, K, and Na increased the pH of the leachates (Morin 1983; Smyth 1981). Silicates can buffer the pH at near-neutral levels when sulfide oxidation is slow and/or sulfide values are relatively low (Blowes et al. 2003; Plante et al. 2011).

The highest EC was measured in the first leachates in all of the columns, and EC decreased gradually over time. The leachates in column 3 had the highest EC values, presumably due to the composition of the synthetic groundwater. A sharp decrease was observed after the easily dissolved chemical species were released (Fig. 2b). The pH of the leachates and metal mobility would have been affected by the changing Ca and SO_4 concentrations (Flores and Sola 2010; Schuwirth and Hofmann 2006; Fig. 2c, d). In all three columns, Ca and SO_4 concentrations decreased during the leaching. The leachates had higher concentrations of Ca than SO_4 and the column 3 leachate had the highest Ca concentrations. Increased SO_4 concentrations were evidence of enhanced metal leaching, while the presence of Ca and other alkaline cations such as Na, K, and Mg decreased metal mobility. The Ca and SO_4 released in the leachate were principally due to dissolution of calcite, plagioclase, and sulphides, respectively (Blowes and Jambor 1990; Flores and Sola 2010; Hakkou et al. 2008; Kossoff et al. 2011, 2012).

Leaching of Metals

Different mechanisms affect the leaching of metals. The release of metals in the three columns was separately investigated using geochemical modeling and fractionation methods.

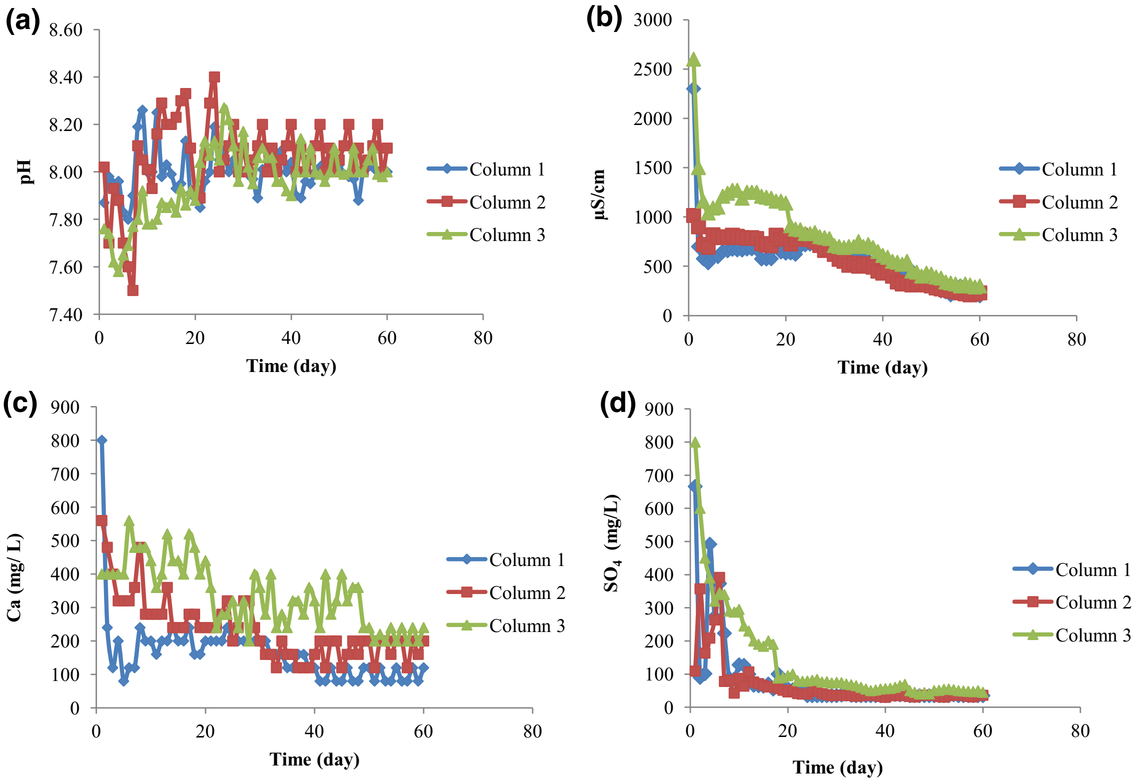

Fig. 2 Changes in pH, EC, Ca and SO_4 concentration during leaching experiments in three columns

Table 1 Potential of acid mine production

Sample	AP	NP	NPR	ARD-ML[a]
Fresh tailings	55	110	2.0	Uncertain
Leached tailings	45	70	1.5	Uncertain

AP acid potential (kg $CaCO_3$/ton of mineral), *NP* neutralization potential (kg $CaCO_3$/ton of mineral), *NPR* neutralization potential ratio (NP/AP)

[a] Screening criterion for identification of potentially ARD-ML generation (ASTM 1996; Morin and Hutt 1997): $NPR < 1$, likely acid generating; NPR 1–2, uncertain acid generation potential; $NPR > 2$, potentially non-acid generating

Fe

Changes in Fe concentration as a function of time are presented in Fig. 3a. The Fe was not significantly leached during the experiment and largely remained in the solid mass. Iron concentrations in the leachates were relatively constant during much of the experiment, with the first concentration peak appearing in pore volumes 12 and 13 in columns 1 and 2, respectively, while it was observed in pore volume 4 for column 3. The geochemical modeling, fractionation and XRD analysis were combined to determine the mechanisms controlling Fe mobility. Saturation index values calculated by geochemical modeling indicated that the effluents were undersaturated with respect to $FeCO_3$ (siderite), melanterite, and jarosite, while $Fe(OH)_3$ and goethite precipitated (Table 2). The release of Fe from weathering of sulphide minerals was not only controlled by the rate of sulphide oxidation, but also by the formation of Fe-oxides and hydroxides (Gunsinger et al. 2006; Jurjovec et al. 2002, 2004). Many researchers believe that the formation of insoluble Fe-hydroxides controls Fe concentrations in leachates (Bigham et al. 1996; Jambor et al. 2000). According to the PHREEQC2 program, the distribution of Fe species for the leachates showed the following order $Fe(OH)_3 > Fe(OH)_4^- > Fe(OH)_2^+ > Fe^{2+} > FeHCO_3^+ = FeCO_3$ (Supplementary Table 3). Leachates were dominated by $Fe(OH)_3$ species, and as pH increased, Fe speciation was controlled by the hydroxide complexes. The Fe enrichment in the oxide fraction was demonstrated by fractionation analysis; the Fe-oxide fraction increased after leaching (Supplementary Tables 4, 5). Oxidation modified element fractionation, resulting in a change in element mobility. Depending on the effects of oxidation during the extraction period, metals commonly associated with the sulphide phases are possibly redistributed into the acid-soluble, reducible, or residual fractions (Bacon and Davidson 2008; Tack and Verloo 1995). Comparing the Fe fractions in the leached and fresh tailings revealed the lower sulphide mineral content, which corresponded to the Fe precipitation.

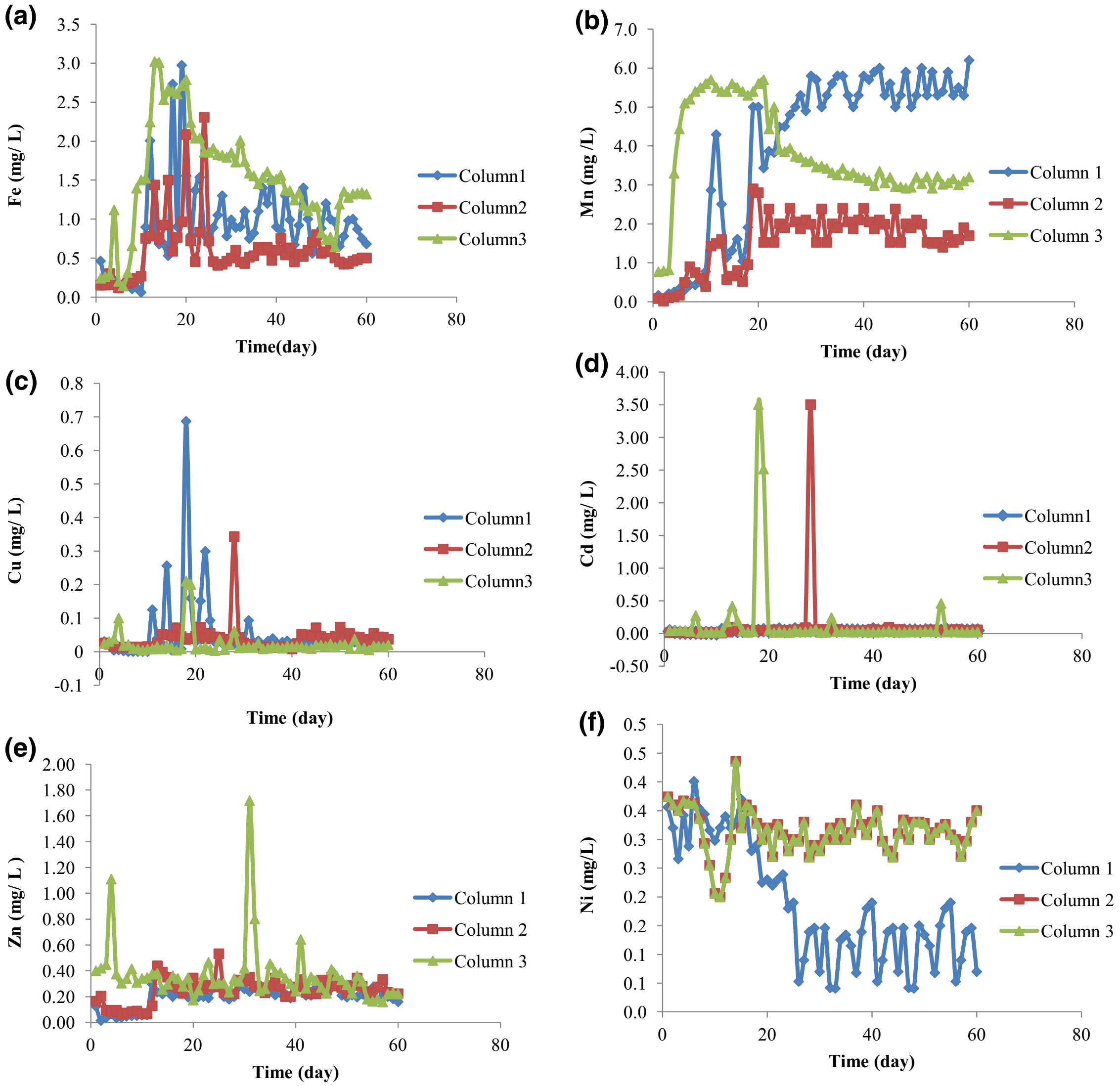

Fig. 3 Changes in metals concentration with time in three columns

Mn

An ascending trend in manganese (Mn) in the leachate was observed in column 1, while Mn leaching from columns 2 and 3 decreased after 22 pore volumes (Fig. 3b). The geochemical modeling indicated that the leachates were slightly supersaturated with respect to $MnCO_3$ and $MnHPO_4$ during leaching, while other Mn-bearing minerals were undersaturated. The leaching of Mn over time and the changes in $MnCO_3$ and $MnHPO_4$ SI values showed that Mn mobility was controlled by these minerals (Table 2).

In the tailings column (column 1), Mn mobility up to the 11th pore volume was controlled by $MnCO_3$; afterwards, it was controlled by both $MnCO_3$ and $MnHPO_4$. According to the speciation analysis, the main species were $MnCO_3 > Mn^{2+} > MnHCO_3^+$ (Supplementary Table 3). In addition, $MnCO_3$ was detected by XRD. Alkaline conditions favor the precipitation of secondary phases, especially $MnCO_3$ (Pareuil et al. 2011). The enrichment of Mn in the carbonate fraction demonstrates that Mn leaching may be limited by sorption mechanisms (Supplementary Table 4). Manganese sorption on carbonate and Fe-oxide and $MnCO_3$ precipitation were the main reactions controlling Mn release in the tailings leachates. A comparison of the leached and fresh tailings showed that the tailings were depleted in the Mn-oxide and sulphide fractions, while Mn was enriched in the oxide and exchangeable fractions.

In column 2 (which contained tailings and soil), Mn leaching was limited by $MnCO_3$ formation from the first pore volume up to pore volume 8; afterwards, $MnCO_3$ and $MnHPO_4$ were the controlling phases. Geochemical analysis showed that the precipitated phase was $MnCO_3$

Table 2 Calculated saturation index for leachates using PHREEQC program

	Formula units of minerals	Column 1	Column 2	Column 3
Albite	$AlNaSi_3O_8$	−10	−9.77	−9.5
Alunite	$KAl_3(SO_4)_2(OH)_6$	−6.28	−6.4	−6.25
Annite	$KFe_3^{2+}AlSi_3O_{12}H_2F_2$	−0.5	−0.1	*1.39*
Anorthite	$Ca_{0.716}Mn_{0.196}Na_{0.45}O_8Si_{2.089}$	−5.4	−5.3	−5.41
Biotite	$Al_{1.207}Fe_{0.4}K_{1.906}Mg_{0.512}Mn_{0.007}$	−7	−5.36	−5.5
Calcite	$CaCO_3$	*1.38*	*1.16*	*1.44*
Chlorite	$Fe_{3.2}Mg_{1.8}Al2Si_3H_8O_{18}$	−5	−4.76	−4.8
$CuCO_3$	$CuCO_3$	−3.89	−5.5	−4
$CdSiO_3$	$CdSiO_3$	−5.7	−5.7	−5.7
Diopside	$Ca_{0.87}Mg_{0.94}Mn_{0.19}Si_2O_2$	−4.9	−4.67	−4.8
Dolomite	$MgCaCO_3$	*1.35*	*2.9*	*1.44*
Ferrohornblende	$Ca_2Fe_4Al_2Si_7H_2O_{24}$	−4.5	−3.9	−3.1
$Fe(OH)_3$	$Fe(OH)_3$	*2.57*	*2.48*	*2.93*
Gaspeite	$NiCO_3$	−5.4	−5.4	−5.36
Goethite	FeOOH	*9*	*8.3*	*8.6*
Hematite	Fe_2O_3	*20*	*18.7*	*19.65*
Jarosite	$Fe_{2.85}H_{6.73}Na_{0.75}O_{14}S_2$	−4.2	−3.9	−2.57
Kaolinite	$Al_2Si_2O_9$	−0.65	−0.7	−0.66
Magnetite	Fe_3O_4	*19.5*	*19*	*20.7*
Magnesiohornblende	$Ca_2Mg_4Al_2Si_7H_2O_{24}$	−4	−4.2	−3
Melanterite	$FeSO_4 \cdot 7H_2O$	−8	−9.66	−8.55
Muscovite	$Al_3KSi_3HO_{12}$	*1.4*	*1.3*	*1.48*
Otavite	$CdCO_3$	*0.6*	*0.66*	*0.73*
Pyrolusite	MnO_2	−6.5	−6.8	−6.36
$MnHPO_4$	$MnHPO_4$	*1.25*	*0.62*	*1.47*
Quartz	SiO_2	−1.8	−1.8	−1.8
Rhodochrosite	$MnCO_3$	*1.5*	*1.1*	*1.77*
Siderite	$FeCO_3$	−1	−1.37	−0.66
$ZnCO_3$	$ZnCO_3$	−1	−1.05	−0.9
$ZnSiO_3$	$ZNSiO_3$	*0.5*	*0.44*	*0.63*

Italic numbers indicates that the solution is supersaturated with respect to the mineral phases

although it was not detected by XRD. The lack of mineralogical evidence may be attributed to the low accumulated masses in the solid sample. Chemical fractionation showed that Mn sorption onto the carbonate fraction was constant after leaching, but the enhancement of Mn sorbed on the oxide fraction was remarkable (Supplementary Table 5). Thus, sorption and $MnCO_3$ precipitation are the main mechanisms that limited Mn concentrations in column 2.

Sorption and precipitation also controlled Mn concentrations in column 3. Although the involved mechanisms were similar in the two columns, Mn concentrations in column 3 were higher than in column 2. The high ionic strength of the leaching solution in column 3 resulted in an earlier peak. Mn sorption decreased in the presence of the major cations due to a low K_d value (Supplementary Table 6) and Mn mobility increased as a result of this low retardation factor (Supplementary Table 7). Increasing ionic strength generally reduces metal sorption due to its influence on both sorbate and sorbent properties (Naidu et al. 1997). The large amount of leached Mn at the beginning of the experiment in column 3 was due to an increased exchangeable fraction, while the formation of a Fe-oxide fraction caused Mn concentrations to decrease at the end of the experiment (Supplementary Table 5). The low K_d in the synthetic groundwater caused an increased Mn mobility at the beginning of the experiment while precipitation of the oxide fraction controlled the Mn concentrations in the leachates. Additionally, increased soil pH and carbonate buffering can allow the formation of metal–carbonate precipitates and secondary minerals (Chlopecka and Adriano 1996; McBride 1989).

Cu

In general, Cu concentrations in the leachates were negligible in all three columns (Fig. 3c). Geochemical modeling showed that leachates from the three columns were consistently undersaturated with respect to Cu-bearing minerals with the exception of cupric ferrite in column 1, which, however, was not detected by XRD. The dominant Cu species in the leachates were $Cu(OH)_2$ and $CuCO_3$ (Supplementary Table 3). The high sorption capacity and the slightly alkaline pH limited Cu mobility. The fractionation results indicated that in column 1, Cu was enriched in the oxide and residual fractions, while the carbonate fraction was constant after leaching (Supplementary Table 4). More Cu was bound to the oxide fraction in columns 2 and 3 (Supplementary Table 5). Moreover, Cu bound to the organic fraction increased in column 3. The highest K_d values and retardation factors were obtained for Cu (Supplementary Tables 6, 7), which were not affected by water composition, unlike the other elements. Surface sorption immobilizes Cu and decreased the dissolved Cu in the pore water (Lu et al. 2005; Morin et al. 1999).

Cd

In general, Cd concentrations were low in the leachates of the three columns, due to its low content in the mobile fraction and the high pH and sorption capacity of the soil and tailings (Fig. 3d). The calculated SI results indicated that the leachates was oversaturated with respect to otavite, and the fractionation results showed that Cd increased in the carbonate fractions. Thus, it likely that both precipitation and sorption control Cd leaching. The role of precipitation and interaction of Cd with calcite surfaces have been described as chemisorbed complexes and surface precipitates (Zachara et al. 1991). Rapid initial sorption of Cd on the calcite may be followed by a slower phase of dehydration and co-precipitation (Davis et al. 1987; Zachara et al. 1991).

The sorption of Cd on carbonate and Fe-oxide fractions increased after the leaching experiments (Supplementary Tables 4, 5). Metals sometimes re-adsorb or re-precipitate after an initial rapid release, so the low Cd concentration in the leachates might have been due this behavior at a leachate pH of 8 (Ho et al. 2012).

Zn

The Zn leaching pattern was similar in columns 1 and 2, while column 3 differed, mostly in the number and shape of the concentration peaks (Fig. 3e). Zinc leaching was negligible at the beginning of the experiment up to pore volume10 and then increased sharply in columns 1 and 2; in column 3, the first peak occurred in pore volume 4 followed by gradual fluctuations until the second peak was observed in pore volume 28, after which it stabilized. Generally, column 1 leachates had lower Zn concentrations than column 2 due to less exchangeable and carbonate fractions. According to the calculated SI, the leachates were oversaturated with respect to $ZnSiO_3$ (Table 2). The lack of changes in Zn sorbed onto the different fractions in the leached samples confirms that precipitation and dissolution controlled Zn mobility (Supplementary Tables 4, 5). In general, the low Zn concentrations in the leachates were due to the alkaline pH and its subsequent precipitation as $ZnSiO_3$. Zinc is mobilized when the ionic strength increases (Sauvé et al. 2000) and the pH decreases; for every unit increase in pH, Zn^{2+} concentration decreases 100-fold (Fonseca et al. 2010; Šcancar et al. 2000; Warwick et al. 1998).

Ni

The Ni leaching patterns are presented in Fig. 3f. The Ni concentrations in the column 1 leachates decreased over time. The Ni concentration was 0.35 mg/L at the beginning of leaching, but was negligible by the end of the experiment. Leachates from the three columns were consistently undersaturated with respect to Ni-bearing minerals (Table 2). The speciation results showed that the dominant species was $NiCO_3$ (Supplementary Table 3), even though, based on the geochemical modeling, Ni mobility should not be controlled by $NiCO_3$ (PHREEQC indicated that $NiCO_3$ should not be thermodynamically stable). Alpers et al. (1994) and Xue et al. (2001) reported that Ni mineral formation tends to be kinetically slow. The leaching of Ni was similar in columns 2 and 3 (Fig. 3f), with higher Ni concentrations in the column 3 leachates. Similar to the other metals, Ni mobility increased when synthetic groundwater was used due to the high ionic strength of the synthetic groundwater and its low K_d value (Supplementary Table 6). Comparison of the leached and original samples indicated that Ni increased in the carbonate and Fe-oxide/hydroxide fractions, and indeed, adsorption onto Fe-oxide and carbonate can effectively reduce Ni mobility. Rose and Ghazi (1998) observed that Ni can be sorbed onto the surface or incorporated into the structure of Fe-oxide.

Weathering reactions can potentially sequester metals into neo-formed clay minerals, sulfate solids, and oxyhydroxides of Fe, Mn, and Al (Hudson-Edwards et al. 1997; Jambor et al. 2000).

Inverse Modeling

Inverse modeling was used to evaluate mole transfer of reactants in the column experiments. Hydrogeochemical analysis of the first and final pore volumes were used to evaluate possible mass-transfer in the three columns. Mineral phases in the inverse modeling were selected based on the calculated SI values derived from PHREEQC and mineralogical analysis of the tailings and soil. Albite,

Table 3 Models and mole transfers of reactants calculated by PHREEQC

Minerals	Column 1		Column 2		Column 3	
	Model 1	Model 2	Model 1	Model 2	Model 1	Model 2
Albite	1.20E−03	1.20E−03	2.20E−03	1.20E−03	3.13E−03	1.38E−03
Calcite	−2.07E−03	−2.80E−03	−1.07E−03	−1.80E−03	1.52E+00	0.00E+00
$Fe(OH)_3$(a)	−7.16E+00	0.00E+00	−8.16E+00	0.00E+00	−9.16E+00	−1.68E+01
Gibbsite	0.00E+00	−1.32E−03	0.00E+00	−1.32E−03	−3.04E−03	2.72E−03
Goethite	0.00E+00	1.68E+01	1.50E+00	0.00E+00	0.00E+00	1.68E+01
Pyrite	8.63E−01	2.20E−04	6.63E−01	1.20E−04	7.63E−01	2.20E−04
Pyrolusite	0.00E+00	9.92E+00	8.92E+00	0.00E+00	9.92E+00	0.00E+00
Anorthite	−7.29E−04	0.00E+00	−4.29E−04	0.00E+00	0.00E+00	−2.00E−03
Gypsum	0.00E+00	0.00E+00	0.00E+00	0.00E+00	−1.53E+00	−5.47E−04
Illite	0.00E+00	0.00E+00	0.00E+00	4.66E−05	−4.14E−05	−4.14E−05
Quartz	−2.53E−03	−3.78E−03	−2.53E−03	0.00E+00	−9.26E−03	0.00E+00
Siderite	1.02E+01	0.00E+00	8.20E+00	9.20E+00	8.39E+00	−3.30E−03
Smithsonite	1.53E−06	1.53E−06	1.50E−06	3.14E−06	2.14E−06	2.14E−06
Otavite	−3.56E−07	−3.56E−07	−3.56E−07	−3.56E−07	−3.57E−07	−3.57E−07
Rhodochrosite	0.00E+00	0.00E+00	−9.20E+00	0.00E+00	−9.92E+00	4.66E−05
$NiCO_3$	3.44E−06	2.44E−06	3.44E−06	2.44E−06	5.44E−06	4.44E−06
$CuCO_3$	1.53E−06	0.00E+00	0.00E+00	3.14E−06	0.00E+00	2.14E−06
Chlorite(14 A)	3.29E−04	7.09E−05	1.19E−04	5.09E−05	1.29E−04	6.09E−05
$ZnSiO_3$	−3.56E−06	−2.53E−06	2.14E−06	3.14E−06	5.44E−06	2.14E−06

Negative values indicate precipitation and positive values indicate dissolution

anorthite, illite, quartz, calcite, gypsum, gibbsite, halite, rhodochrosite, otavite, siderite, smithsonite, $CuCO_3$, $NiCO_3$, $Fe(OH)_3$, and CO_2 were considered as potential reactants for the three soil columns. Exchange reactions, including NaX, KX, CaX_2, and MgX_2 were only specified to be the potential reactants for columns 2 and 3. The inverse modeling results showed that albite and chlorite dissolved during leaching, which agrees with the XRD analyses. $Fe(OH)_3$ precipitated while siderite dissolution was predicted by the model. According to Table 3, Mn and Cd removal may have been due to precipitation of rhodochrosite and otavite, respectively. Dissolution of $CuCO_3$ was indicated by inverse modeling, which also suggested that Cu mobility is limited by sorption on oxides, carbonates, and aluminosilicates. The behavior of Ni was similar to Cu, although mineralogical analysis confirmed the occurrence of $NiCO_3$ in the leached samples.

Conclusion

Buffering minerals, like carbonates and silicate minerals (hornblende, chlorite, and albite) decrease acid generation in the dumped tailings of the Hamekasi (Baba Ali) mine. Sorption, sequential extraction, and XRD analysis, combined with geochemical modelling allowed us to describe and predict the leaching dynamics of Fe, Mn, Cd, Cu, Zn, and Ni. The release of metals from tailings and soil was influenced by water composition, pH, and the mineralogical composition of the tailings. Leaching with synthetic groundwater increased metal release due to the low K_d value of the water and the retardation factor in column 3 (soil leached with synthetic groundwater), except for Cu, possibly due to the formation of inner-sphere complexes. In columns 1 (tailings leached with distilled water) and 2 (soil and tailings leached with distilled water), metal immobilization was most likely due to the increased pH caused by calcite and silicate dissolution. The main mechanisms that limited metal mobility depended on the element. Solubility and precipitation reactions controlled Fe and Zn release, while Cu and Ni were principally controlled by sorption. The mobility of Cd and Mn were affected by both mechanisms. Sequential extractions of fresh and leached soil and tailings showed evidence of adsorption and remineralization. Changes in metal fractions after leaching affected metal concentrations in the leachates. Sorption of some metals (Cu, Ni, and Cd) onto Fe, Mn-oxides, and precipitation of some metals (Zn) in residual fractions may also explain the removal of these metals from the leachates.

The main limitations of this study were the small number of tailings samples and the short duration of the leaching tests. Future research should concentrate on samples of neutral tailings with various mineralogical compositions and conduct leaching experiments of longer duration.

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