

Speciation and solubility relationships of Al, Cu and Fe in solutions associated with sulfuric acid leached mine waste rock

M. Shum · L. Lavkulich

Abstract Solutions from oxidized waste rock originating from an acid-leached waste dump were studied. The dissolution data suggest that after the majority of the soluble solid phases are removed, remaining solid phases continued to buffer the solutions in the acidic pH range. Incorporating the solution data into MINTEQA2 identified controls on the solubility of Al, Cu and Fe at pH values from about 2.5 to slightly over 5. Sulfate appears to play a significant role in the formation of solubility controlling solid phases for Al and Cu. This is not the case for Fe, and is suggested that Fe and Cu solubility may be controlled by cupric ferrite at low pH values.

Key words Mine water chemistry · Secondary mineral dissolution · Saturation indices · Waste rock solution

Introduction

Oxidation of sulfidic mine waste can lead to the discharge of high levels of total dissolved solids (particularly metals and SO_4^{2-}) and low pH waters which can be hazardous to the environment. High concentrations of Al and Fe are typical in acid sulfate waters (Bigham and others 1996). Under typical soil conditions, Al activity appears to be controlled by the solubility of gibbsite or kaolinite, while Fe activity is controlled by goethite or amorphous $\text{Fe}(\text{OH})_3$ (Nordstrom 1982; Stumm and Morgan 1981). However, in areas of sulfide oxidation, high

concentrations of sulfate modify the aqueous geochemistry of Al and Fe. In acid sulfate drainage waters and leachate solutions from mine waste tailings and soils, solubility appears to be controlled by a variety of basic Al/Fe oxides, oxyhydroxides, and sulfate phases (goethite, gibbsite, alunite, jurbanite; Karathanasis and others 1988; Monterroso and others 1994).

To manage effectively metals contaminated drainage from mine waste dumps it is important to understand the mechanisms controlling metal solubility. Leaching of mine materials for metal extraction (e.g. acid solutions for Cu, cyanide solutions for gold) may alter the types of secondary minerals formed because of changes in the geochemical environment caused by leaching solutions. At the Gibraltar mine site in central British Columbia, selected rock dumps are commercially leached with sulfuric acid to recover Cu in the on-site solvent extraction/electrowinning plant (Klohn Leonoff Consulting Engineers 1991).

Little is known about the effect commercial leaching will have on drainage water chemistry under post-operational (post-leaching) conditions. However, leaching of waste dumps for the recovery of metals may influence the phases controlling solubility and solution chemistry during post-operational conditions. The objective of this study was to examine the water chemistry, speciation and solubility control for Al, Cu, and Fe in solutions from oxidized waste rock collected from an acid-leached waste rock stockpile.

Site and sampling description

The Gibraltar site is an open pit Cu-Mo mine located in central British Columbia approximately 360 km north of Vancouver (Fig. 1). The Gibraltar property is located at elevations between 914–1231 m on the western flank of Granite Mountain, and receives 32.5 cm precipitation annually. The Gibraltar ore body is a large low-grade porphyry deposit with copper disseminated in fine grained igneous intrusions and adjacent host rock (Bysouth and Carpenter 1984). Chalcopyrite (CuFeS_2) is the primary Cu mineral mined with minor amounts of molybdenite (MoS_2). The mine has been in operation since 1972. The rock in the waste piles has a relatively uniform mineralogical composition of 50% saussuritized andesine

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Experimental and analytical methods

In the laboratory, samples were air-dried, then gently crushed with a wood rolling pin, and sieved to isolate the silt + clay (<0.05 mm) fraction. All analyses were performed on the silt + clay (<0.05 mm) fraction.

Duplicate 1.0-g samples of silt + clay sized waste rock material were placed in a 50-ml screw-cap centrifuge tube with 30 ml of distilled-deionized H₂O. Samples were allowed to react in the absence of light on a oscillating shaker for 153 days with 80% solution exchange/renewal at 1, 2, and 6 h, and 1, 3, 9, 20, 41, 100, and 153 days. At each sampling time, samples were centrifuged at 10000 g for 20 min, 80% (24 ml) of elutriate removed, and fresh extracting solution added. Aliquots were taken from each elutriate for measurements of pH (Orion 420 A meter, with Ag/AgCl internal reference and temperature calibration, calibrated at pH 2 and 7), Eh (Orion combination Pt/Ag-AgCl electrode), and EC (YSI conductivity bridge). The remaining solution was stored in high density polyethylene bottles in a refrigerator (4 °C) prior to further analysis. The shaker oscillated gently in approximately 0.5-cm-diameter circles at a rate of 150–180 oscillations per minute thus minimizing the effects of particle abrasion. Samples within the centrifuge tubes were resuspended and uncapped for 2–4 h daily to maintain oxic conditions in the solutions.

The redox potential (Eh) was used to calculate the activity of Fe²⁺ (aq) and Fe³⁺ (aq) in the solutions. The calculations were performed using the chemical equilibrium model MINTEQA2 (US EPA 1991). A limitation of the Pt electrode is its tendency to form oxides in aerated and oxidizing (pe + pH > 14.8) solutions causing errors in Eh measurement (Whitfield 1974). However, studies have shown that Eh measurements in acidic, iron-rich solutions are a valid indicator of redox status and can be used to calculate the activity of Fe²⁺ (aq) and Fe³⁺ (aq) (Levy and others 1997; Sung and Morgan 1980). Redox potential (pe + pH) measurements in the solutions in this

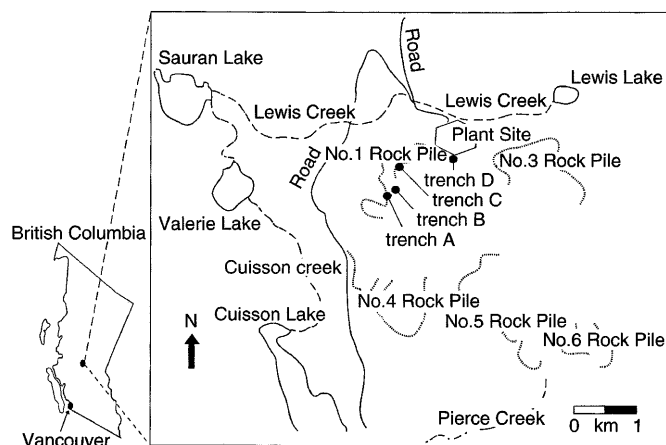


Fig. 1

Site and sampling locations at the Gibraltar mine site

plagioclase, 20% chlorite, and 30% quartz, with plagioclase altered to albite-epidote-zoisite and muscovite. Host rock may contain biotite and minor hornblende. Accessory minerals may include magnetite and rutile. Copper content in the rock dumps varies from 0.11–0.27%, and pyrite content may be as high as 6% (Bysouth and Carpenter 1984; Bysouth and others 1995). There are over 300 million tonnes of waste rock on the site (Feasby and Jones 1994). Chalcantite (CuSO₄ · 5H₂O) has been identified as a post-mining leach product (Bysouth and others 1995).

One dump was selected for study. Four trenches were excavated in this waste dump and samples collected and stored in plastic bags, then transferred to the laboratory for analysis. Eight samples (two from each trench) were selected based on color and particle-size to represent the heterogeneous nature of the waste and the various acid leaching regimes (Table 1).

Table 1
Characterization of morphologic features (color and particle size)

ID	Tench	Munsell color				Particle size analysis				
		Hue		Val Chr		Sieving %coarse (> 2 mm)	%fines (≤ 2 mm)	Hydrometer method		
								%sand	%silt	%clay
2	A	2.5	Y	8 / 4	Pale yellow	37	63	52	26	12
9	A	10	YR	7.5 / 8	yellow	69	31	60	27	13
11	B	2.5	Y	8 / 6	yellow	87	13	57	23	19
16	B	5	Y	8 / 2	white	80	20	60	23	15
22	C	2.5	Y	7 / 2	light gray	78	22	59	26	15
27	C	2.5	Y	6.5 / 6	yellow	79	21	72	18	10
31	D	2.5	Y	7 / 6	yellow	74	26	70	21	9
33	D	5	Y	7 / 4	Pale yellow	76	24	67	27	6

study were always < 14.8 , suggesting errors were minimal.

All solutions were analyzed for total dissolved SO_4^{2-} -S, Al, Ca, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Zn. Sulfate was determined by turbidimetry using a spectrometer (Rhoades 1982). Total dissolved elements, except K and Na, were determined using a Thermo Jarrel-Ash ICP-AES (Model AtomCop Series 1000–100). K and Na were determined by atomic absorption spectrometry on a Perkin-Elmer AAS model 306 instrument using an air-acetylene flame.

Data from deionized water extracts were entered into MINTEQA2 to obtain speciation, activities and saturation indices (SI) in order to examine mineral solubility, and examine possible changes in composition with time. Saturation index (SI) value for various solids was calculated by MINTEQA2 using the equation:

$$\text{SI} = \log(\text{IAP})/K_{\text{sp}}$$

where IAP is the ion activity product observed in solution, and K_{sp} is the theoretical solubility. Positive SI values indicate that a solution is oversaturated or supersaturated with respect to a given solid phase, while a negative SI value indicates undersaturation. A condition of oversaturation or supersaturation indicates that precipitation of the respective mineral phase is thermodynamically possible. When SI equals 0, the solution and the solid phase under consideration are in apparent equilibrium. Solutions unsaturated with respect to a given solid phase suggest that phase can dissolve as a reactant. In this study, apparent equilibrium is defined as when the SI value for a solid phase is between -1.0 and $+1.0$, thus allowing for inherent uncertainties in the analytical and thermodynamic data. Geochemical calculations performed using computer codes do not prove the presence or absence of a phase, but provide an indication of the tendency for a reaction to occur.

Other analytical data used in the program were pH, Eh, and ionic strength (IS). Electrical conductivity was converted to IS according to the following relationships (Alva and others 1991):

$$\text{EC} < 1 \text{ mScm}^{-1}: \text{IS}(\text{mM}) = 0.012 \text{ EC}(\text{mScm}^{-1}) - 0.0002$$

$$\text{EC} > 1 \text{ mScm}^{-1}: \text{IS}(\text{mM}) = 0.012 \text{ EC}(\text{mScm}^{-1}) - 0.0006$$

Result and discussion

Solution quality and chemistry

To simplify the presentation of the data, only selected data from the solutions are presented in Table 2. These data show an acidic solution forms from contact with the waste rock materials. Considering the data from all the solutions, the pH ranged from 3.3–5.2 ($\bar{X}1 = 4.0$) and redox potential varied from 360–520 mV ($\bar{X}1 = 400$). These variations reflect differences of the age of the waste, depth from surface, composition, and the acid leaching regime from the waste rock pile. Values for pH were relatively constant for each solution and generally varied within ± 0.5 pH units from the first pH measurement.

The relatively stable pH values suggest that after the soluble phases are leached, the remaining solid phases keep the system buffered in the low pH range. Electrical conductivity measurement decreased with increased reaction time during the initial day of the experiment, but reached a steady-state afterwards, as indicated by the stabilization of the electrical conductivity.

Solution chemistry (Table 2) indicates the dissolution of soluble secondary weathering products, such as Ca and Fe(II) sulfates (e.g. gypsum CaSO_4 and melanterite $\text{Fe}^{II}\text{SO}_4 \cdot 7\text{H}_2\text{O}$), occurs rapidly agreeing with the decreasing trend observed for the electrical conductivity. A variety of hydrated sulfate minerals are common during periods of dry weather in the vicinity of sulfide mineralization in undersaturated systems (Nordstrom 1982; Williams 1990). Release of Al and Cu begins to increase by day 20 indicating that after the initial leaching and removal of soluble and exchangeable elements, the dissolution of metastable secondary phases or primary minerals begins to control the water chemistry.

Solutions with the highest element loadings were characterized by low pH values, high electrical conductivity, and were collected in zones of oxidized Fe accumulation. These zones were clearly evident from their reddish (5YR–10YR) color in the field, and tended to have high amounts of soluble sulfate products likely derived from on-site acid leaching or pyrite oxidation.

Geochemical modeling

Ion activity, species distribution, and saturation index values were calculated using solution chemistry data entered into MINTEQA2 (US EPA 1991). These results show a wide range of variation but some trends are evident in the data.

Measured Eh values were used to calculate Fe^{3+} and Fe^{2+} activities in the MINTEQA2 program. Fe^{3+} activities ranged from 9×10^{-13} to 5×10^{-10} and Fe^{2+} activities ranged from 1×10^{-7} to 1×10^{-4} . Blowes and Jambor (1990) found similar results for pore water collected from the vadose zone of mine tailings though they determined Fe^{2+} analytically. The Fe^{3+} concentrations determined using Eh measurements were used to calculate the degree of saturation for ferric and ferrous oxyhydroxide and sulfate minerals. In the pH and Eh range measured in these solutions, ferrous iron concentrations were much higher than for ferric iron.

Metal species distribution reflected changes in either Eh-pH or SO_4^{2-} activity in the solutions. Generally, soluble Al, Cu, and Fe were found as the uncomplexed free metal (M^{n+}) ion or monomers bound to mono-sulfate (M-SO_4), except when SO_4^{2-} concentration exceeded 150 mg/L in solution, which resulted in metal di-sulfate species. Initial high SO_4^{2-} activity from the dissolution of soluble sulfate phases results in the presence of metal sulfate ($\text{M-(SO}_4)_n$ where n = the number of sulfate components) species in solution. As the reaction time increases, removal of soluble SO_4^{2-} phases from the solids then the solutions, leads to decreased SO_4^{2-} activity and an increase in the proportion of uncomplexed free metal

Table 2

Selected solution quality and chemical data of waste rock solutions (mean of duplicate samples)

Sample	Reaction time (days)	pH	Eh (mV)	EC (S/m)	Al	Ca	Cu	Fe	SO ₄ ²⁻
							(mg/l)		
9	0.04	3.3	483	0.23	6.86	570	8.16	4.41	1554
	0.08	3.6	464	0.21	2.64	507	1.70	1.05	1394
	0.25	3.6	463	0.15	1.27	354	0.59	0.66	998
	1	3.6	470	0.06	0.30	104	0.28	0.43	258
	3	3.5	468	0.03	0.14	24	0.14	0.36	77
	9	3.6	470	0.02	nd	13	0.14	0.12	27
	20	3.6	504	0.02	0.03	7	0.22	0.13	24
	41	3.8	456	0.01	0.01	5	0.16	0.04	14
	100	3.6	452	0.02	0.05	6	0.66	0.12	23
	153	3.5	437	0.01	0.07	5	0.67	0.03	17
11	0.04	3.4	473	0.23	15.40	568	12.75	1.70	1605
	0.08	3.8	440	0.21	3.49	484	2.38	0.22	1428
	0.25	3.9	430	0.18	1.43	472	0.83	0.38	1188
	1	3.8	464	0.01	0.54	260	0.44	0.03	675
	3	3.7	435	0.04	0.25	55	0.34	0.20	164
	9	3.6	418	0.03	0.19	23	0.44	0.11	55
	20	3.4	515	0.02	0.27	11	0.96	0.04	48
	41	3.5	483	0.02	0.25	9	1.57	0.02	37
	100	3.5	501	0.01	0.79	8	3.18	0.03	47
	153	3.6	479	0.02	0.55	4	1.78	0.03	27
22	0.04	4.3	411	0.20	4.93	458	55.14	0.07	1373
	0.08	4.6	384	0.27	1.13	162	13.07	0.00	439
	0.25	4.7	382	0.03	0.33	46	4.16	0.03	128
	1	4.5	439	0.01	0.07	14	1.66	nd	40
	3	4.2	417	0.01	0.02	8	1.40	nd	17
	9	4.5	392	0.00	0.02	6	1.66	0.03	10
	20	4.5	443	0.01	0.18	6	2.75	nd	3
	41	4.6	390	0.01	0.19	7	4.04	0.05	5
	100	4.3	420	0.01	1.15	8	11.22	0.03	3
	153	4.2	425	0.01	0.74	4	6.04	0.08	3

(Mⁿ⁺) ion and hydrolyzed species (Table 3 and 4). The predominant species in the most acid solutions were M-(SO₄²⁻)_n and the free metal ion species. In the pH range and high SO₄²⁻ activity of the solutions, Cu-OH species were not present. The proportion of M-(SO₄²⁻)_n species for a particular metal tended to be greater than 50%, and decreased rapidly with each solution sampling event and by day 3 reached less than 10% of the SO₄²⁻-S speciation. The predominance of Al-SO₄, Fe-SO₄, Al³⁺ and Fe³⁺ in surface waters and mine soils in mining regions has been shown by others (Alvarez and others 1993; Monterroso and others 1994).

As pH increased, the proportion of M-(OH)_n increased (except for Cu) and M-(SO₄)_n decreased in response to the competition between SO₄²⁻ and OH⁻ for free metal ion species (Fig. 2 and 3). The different Fe-(OH)_n and Al-(OH)_n species appear to be highly dependent on pH. Total Fe-(OH)_n and Al-(OH)_n species increased with acidity. Ferric iron speciation at values of pH > 3.5 is dominated by the di-hydroxylized Fe³⁺ species, while at lower pH values the dominant species is the mono-hydroxylized species. Levels of SO₄²⁻ were unaffected by pH.

Saturation data were plotted to examine mineral solubility relationships responsible for the control of metal ion concentrations in the solutions. Solutions supersaturated (SI is +) with respect to a solid phase cannot dissolve the phase but can potentially be precipitated as a product under appropriate conditions. For some minerals, precipitation under surface temperatures and pressures is not likely or very slow because of kinetic constraints, which results in supersaturation with respect to those minerals. Undersaturated solutions can indicate the dissolution of a solid phase if it exists in the system.

Aluminum equilibria in acid mine waters has been studied extensively and a number of mineral phases have been identified as possible solubility controls (Karathanasis and others 1988; Monterroso and others 1994; Nordstrom 1982; Nordstrom and Ball 1986; Sullivan and others 1988). Mineral phases which were considered here for the control of Al solubility were: amorphous Al(OH)₃, basaluminite Al₄(OH)₁₀SO₄·5H₂O, jurbanite AlOHSO₄, alunite KAl₃(SO₄)₂(OH)₆, gibbsite Al(OH)₃, and diaspore AlO(OH).

The more acidic solutions were undersaturated with respect to alunite, basaluminite, amorphous Al(OH)₃, gibb-

Table 3

Distribution of selected aqueous species and saturation indices from selected samples after reaction time of 0.04 days, calculated using MINTEQA2 (US EPA 1991)

Parameter		9	11	22
<i>Distribution of aqueous species</i>				
Iron (III)	% Fe ³⁺	1	1	—
	% FeOH ²⁺	13	14	10
	% Fe(OH) ₂ ⁺	10	14	85
	% FeSO ₄ ⁺	62	58	5
	% Fe(SO ₄) ₂ ⁻	14	13	—
Iron (II)	% Fe ²⁺	46	46	47
	% FeSO ₄	54	54	53
Aluminium	% Al ³⁺	8	8	9
	% AlSO ₄ ⁺	59	59	59
	% Al(SO ₄) ₂ ⁻	33	32	31
	% AlOH ²⁺	—	—	2
	% Al(OH) ₂ ⁺	—	—	—
Copper	% Cu ²⁺	42	42	43
	% CuSO ₄ ⁰	59	58	57
Sulfate	% SO ₄ ²⁻	44	42	47
	% HSO ₄ ⁻	2	2	—
	% CuSO ₄ ⁰	—	—	4
	% AlSO ₄ ⁺	—	2	—
	% Al(SO ₄) ₂ ⁻	1	2	—
<i>Saturation indices for solid phases</i>				
Al(OH) ₃ (amorphous)		-5.3	-4.7	-2.4
Al(OH) ₃ (gibbsite)		-3.7	-3.1	-0.7
AlOHSO ₄ (jurbanite)		-0.3	0.2	0.6
KAl ₃ (SO ₄) ₂ (OH) ₆ (alunite)		-2.5	-1.6	3.9
CuO (tenorite)		-5.4	-5.0	-2.5
CuSO ₄ ·5H ₂ O (chalcantite)		-3.8	-3.6	-3.0
α-CuFe ₂ O ₄ (cupric ferrite)		-2.6	-2.8	0.4
FeSO ₄ ·7H ₂ O (melanterite)		-4.1	-4.5	-5.9
Fe(OH) ₃ (ferrihydrite)		-4.3	-4.6	-4.2
α-FeOOH (goethite)		0.0	-0.3	0.1
γ-FeOOH (lepidocrocite)		-0.8	-1.1	-0.7
α-Fe ₂ O ₃ (hematite)		5.0	4.4	5.1
KFe ₃ (SO ₄) ₂ (OH) ₆ (jarosite)		-3.2	-5.1	-5.4

Table 4

Distribution of selected aqueous species and saturation indices from selected samples after reaction time of 153 days, calculated using MINTEQA2 (US EPA 1991)

Parameter		9	11	22
<i>Distribution of aqueous species</i>				
Iron (III)	% Fe ³⁺	2	2	—
	% FeOH ²⁺	41	39	14
	% Fe(OH) ₂ ⁺	53	55	86
	% FeSO ₄ ⁺	3	4	—
	% Fe(SO ₄) ₂ ⁻	—	—	—
Iron (II)	% Fe ²⁺	97	96	100
	% FeSO ₄	3	4	—
Aluminium	% Al ³⁺	83	77	85
	% AlSO ₄ ⁺	14	20	3
	% Al(SO ₄) ₂ ⁻	—	—	—
	% AlOH ²⁺	2	2	11
	% Al(OH) ₂ ⁺	—	—	2
Copper	% Cu ²⁺	97	95	99
	% CuSO ₄ ⁰	3	5	—
Sulfate	% SO ₄ ²⁻	95	94	93
	% HSO ₄ ⁻	3	2	—
	% CuSO ₄ ⁰	—	—	2
	% AlSO ₄ ⁺	—	1.5	2
	% Al(SO ₄) ₂ ⁻	—	—	—
<i>Saturation indices for solid phases</i>				
Al(OH) ₃ (amorphous)		-5.7	-4.7	-2.7
Al(OH) ₃ (gibbsite)		-4.1	-3.1	-1.0
AlOHSO ₄ (jurbanite)		-2.7	-1.6	-1.8
KAl ₃ (SO ₄) ₂ (OH) ₆ (alunite)		-7.4	-3.4	-2.1
CuO (tenorite)		-5.7	-5.2	-3.4
CuSO ₄ ·5H ₂ O (chalcantite)		-6.1	-5.5	-5.9
α-CuFe ₂ O ₄ (cupric ferrite)		-6.9	-4.8	-0.1
FeSO ₄ ·7H ₂ O (melanterite)		-7.6	-7.4	-7.9
Fe(OH) ₃ (ferrihydrite)		-6.3	-5.5	-4.0
α-FeOOH (goethite)		-2.0	-1.2	0.2
γ-FeOOH (lepidocrocite)		-2.8	-1.9	-0.5
α-Fe ₂ O ₃ (hematite)		1.0	2.7	5.5
KFe ₃ (SO ₄) ₂ (OH) ₆ (jarosite)		-13.0	-9.4	-10.1

site, but as pH increased these phases approached equilibrium (Fig. 4). Solutions were slightly undersaturated or at equilibrium with, alunite, gibbsite, and diasporite from pH 3.7–5, and a jurbanite-type phase for the entire pH range of the samples. Solutions approached equilibrium with an amorphous form of Al(OH)₃ if the pH value is >5. The least stable phase was basaluminite which was significantly undersaturated for all pH values <4.5. Solutions collected at all reaction times were generally at equilibrium or slightly supersaturated with diasporite. Solutions collected during the first 6 hours of the experiment tended to be at equilibrium with respect to jurbanite.

These results suggest Al³⁺ activity may be subjected to several possible control mechanisms depending on pH values. Al³⁺ activity seems to be controlled by jurbanite

and gibbsite (or diasporite) at pH <5 which agrees with results from other studies of acid mine systems (Karathanasis and others 1988; Monterroso and others 1994; Nordstrom and Ball 1986). Winland and others (1991) indicate activity of Al in acid mine solutions with pH <6 is consistent with the stoichiometry of jurbanite. Equilibrium with respect to alunite in the same solutions as jurbanite and gibbsite is likely possible allowing for some overlap in stability regions in naturally occurring environments. Nordstrom (1982) suggests alunite is stable between jurbanite and gibbsite (diasporite) in the pH range 3.3–5.7 for the range between 10⁻⁴ and 10⁻² M sulfate. Solutions approached equilibrium with amorphous Al(OH)₃ at pH 5 which agrees with other studies that determined amorphous Al(OH)₃ controls Al³⁺ at pH greater than 4.6–5 (Monterroso and others 1994; Nord-

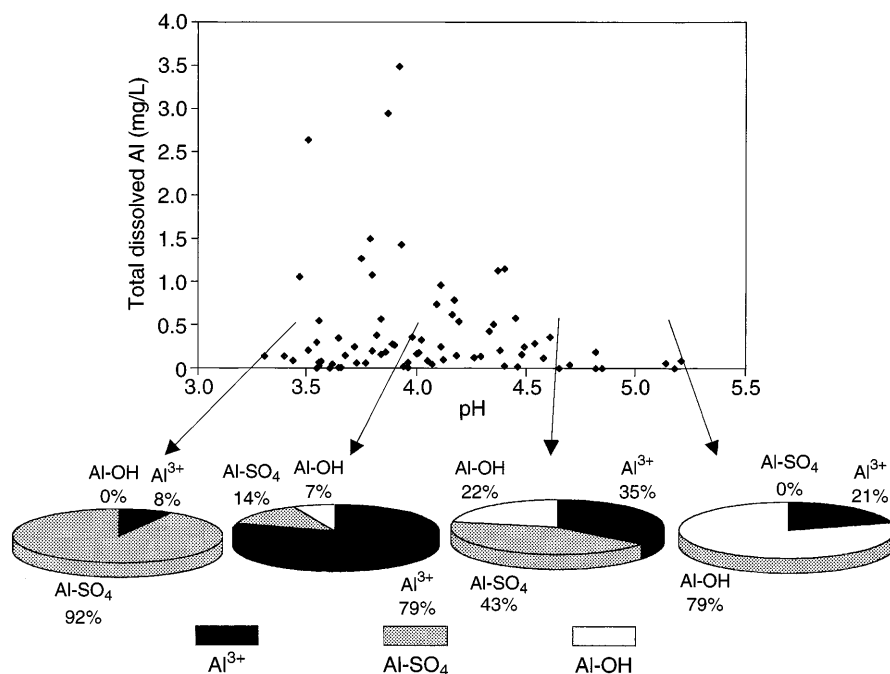


Fig. 2
Total soluble aluminium concentration (mg/l) determined in solutions and speciation vs. pH in solutions

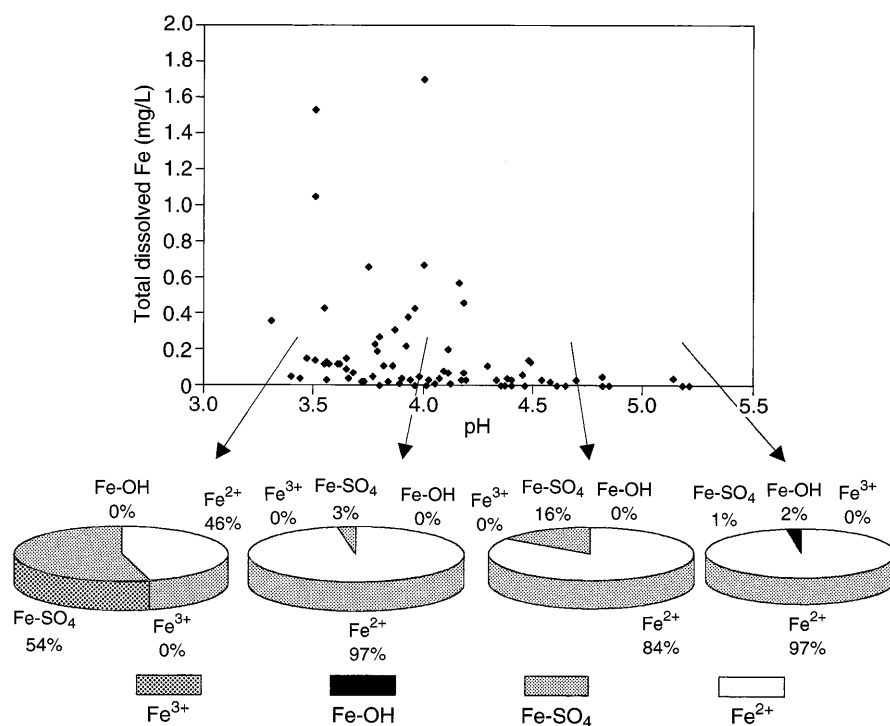


Fig. 3
Total soluble iron concentration (mg/l) determined in solutions and speciation vs. pH in solutions

strom and Ball 1986). Karathanasis and others (1988) suggest the change occurring between pH 4.5–5 is the boundary for Al³⁺ control between basic aluminum sulfates and aluminosilicates. Al³⁺ activity in solutions with pH < 5 seems to be controlled by jurbanite, alunite, and gibbsite (diaspore), depending on the SO₄²⁻-S activity in the solution. In solutions with pH > 5, an amorphous Al(OH)₃ controls the Al activity. Studies examining secondary Fe phases in acid mine waters have suggested the presence of the following Fe mi-

nerals in the system: FeOH₂SO₄ (Sullivan and others 1988), α-FeOOH [goethite] (Levy and others 1997), KFe₃(SO₄)₂(OH)₆ [K-jarosite] (Levy and others 1997), g-FeOOH [lepidocrocite] (Bigham 1994), Fe₅OH₈·4H₂O ferrihydrite (Bigham 1994), FeSO₄·7H₂O melanterite (Monterroso and others 1994). Mineral phases that were evaluated for saturation in these solutions were ferrihydrite, goethite, melanterite, lepidocrocite, K-jarosite, α-Fe₂O₃ hematite, FeO·Fe₂O₃ magnetite, and α-CuFe₂O₄ cupric ferrite. Bigham (1994) indicates schwertmannite

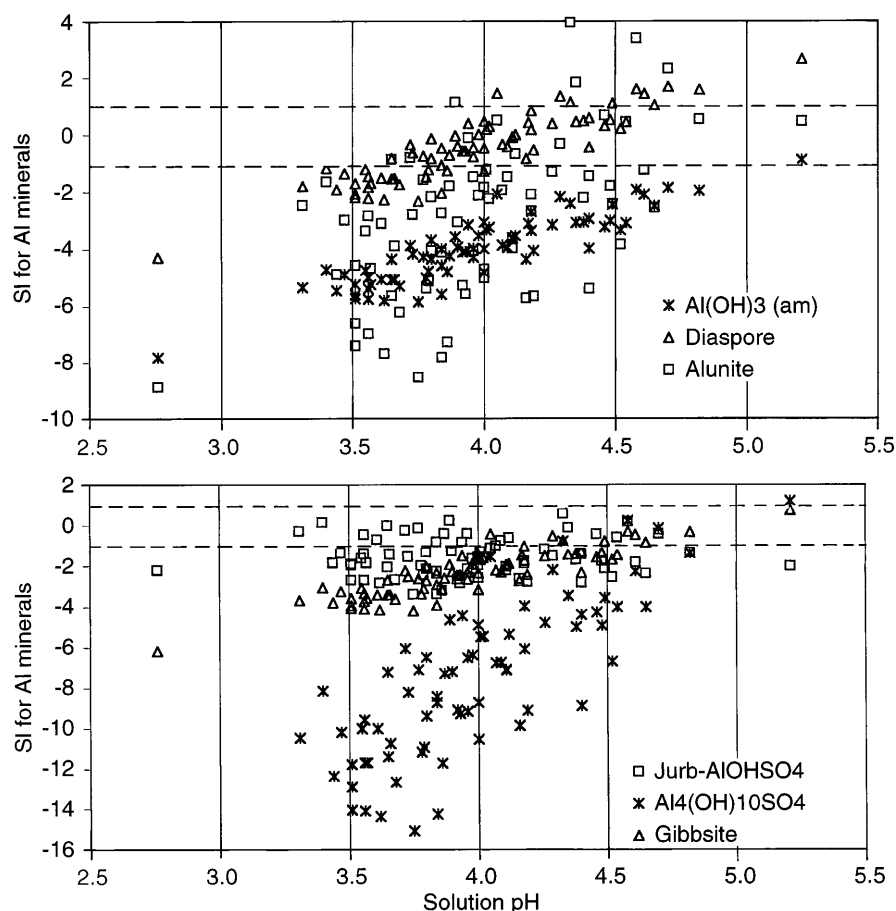


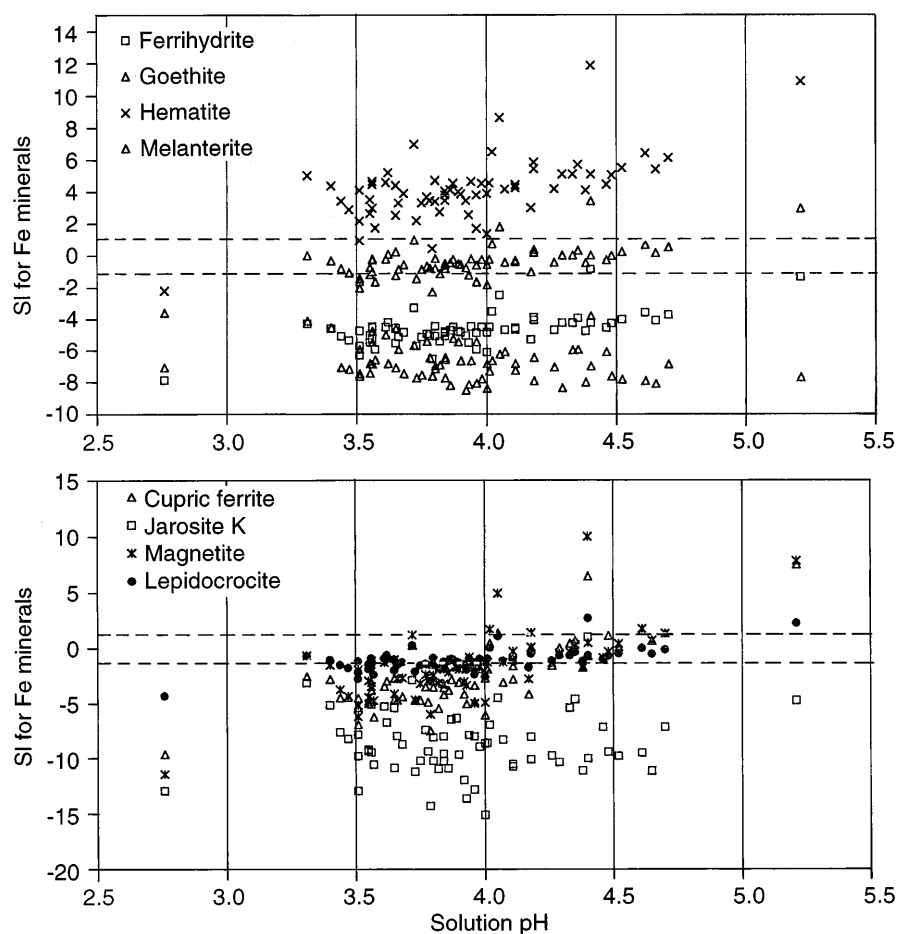
Fig. 4

Saturation indices vs. pH for different Al mineral phases based on thermodynamic data from the geochemical model MINTEQA2 (US EPA 1991). Mineral phases in equilibrium are located between the two dashed lines

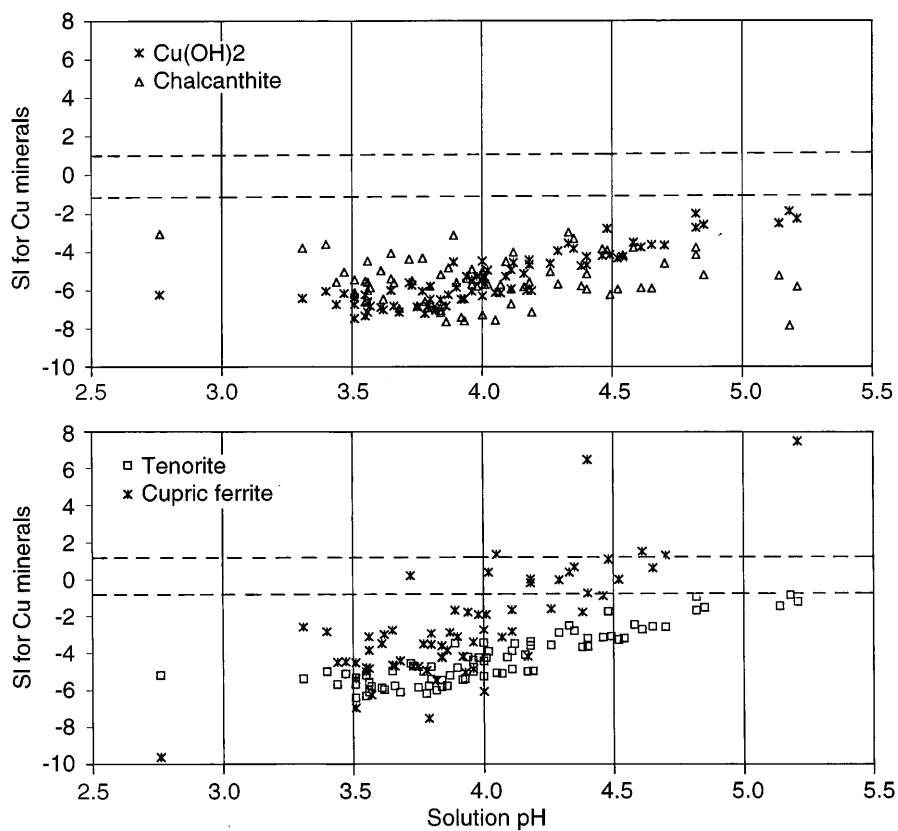
$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ is the most common mineral associated with ochreous precipitates in acidic mine drainage, but it could not be incorporated into the MINTEQA2 model due to the lack of thermodynamic data.

Dissolved Fe in leachates were at equilibrium with goethite, lepidocrocite, cupric ferrite, and magnetite (Fig. 5). The most stable phase in these solutions tended to be hematite. Solutions collected were generally unsaturated with respect to ferrihydrite, melanterite, K-jarosite, and many other $\text{Fe}(\text{II})-(\text{SO}_4)_n \cdot m\text{H}_2\text{O}$ phases for all samples. Solutions were saturated and in apparent equilibrium with goethite and lepidocrocite for solution pH values up to 4.7, and with cupric ferrite and magnetite for solutions with values of pH 4–4.7. Solutions with pH > 4.7 appear to be at equilibrium with ferrihydrite, although there were few data points. Langmuir and Whittemore (1971) have suggested $\text{Fe}(\text{OH})_3$ and poorly crystalline goethite are the first ferric phases to precipitate in streams impacted by acid mine waters, but will transform with time into the more stable phases, crystalline goethite and lepidocrocite. Goethite usually accompanies lepidocrocite (Langmuir and Whittemore 1971) and has been found in, at or near equilibrium in pore waters from mine tailings (Blowes and Jambor 1990). Lepidocrocite is the major initial product of the oxidation and precipitation of ferrous iron bearing solutions, although the presence of other metal ions plays a role in determining crystallinity and stability towards goethite (Williams 1990). Transforma-

tion from lepidocrocite to goethite in surface environments occurs on a pedogenic time scale (i.e. 10^3 years; Schwertmann and Fitzpatrick 1992). Goethite and hematite have similar solubility (K_{sp} hematite $\approx 10^{-43}$ – 10^{-42} , K_{sp} goethite $\approx 10^{-44}$ – 10^{-43}) and stability, but slow kinetic rates, due to either slow dissolution of the metastable form or hampered nucleation of the stable phase by contaminating compounds. This leads to the formation of poorly crystalline, metastable phases such as ferrihydrite, lepidocrocite and microcrystalline goethite at surficial temperatures (Bigham 1994; Schwertmann and Fitzpatrick 1992; Schwertmann and Taylor 1989). Ferrihydrite is likely to form in slightly acid to alkaline solutions with high levels of dissolved Fe (Bigham 1994). Bigham and others (1996) identified mixtures of schwertmannite and goethite in precipitates collected from water with pH 2.8–4.5. Dissolved Fe activity in these solutions appears to be controlled by a mixture of goethite, hematite, and lepidocrocite, and at values of pH > 4 with higher Cu^{2+} activity, possibly cupric ferrite. The coexistence of goethite and hematite is widely observed in many subtropical and tropical soils and reflects their similar thermodynamic stability (Schwertmann and Taylor 1989). If pH increases above 5, ferrihydrite may play a role. Ferrihydrite is likely formed by rapid oxidation and hydrolysis of Fe^{2+} in the presence of silicate and is widespread and characteristic of young Fe-oxide accumulations (Schwertmann and Taylor 1989).

**Fig. 5**

Saturation indices vs. pH for different Fe mineral phases based on thermodynamic data from the geochemical model MINTEQA2 (US EPA 1991). Mineral phases in equilibrium are located between the two *dashed lines*

**Fig. 6**

Saturation indices vs. pH for different Cu mineral phases based on thermodynamic data from the geochemical model MINTEQA2 (US EPA 1991). Mineral phases in equilibrium are located between the two *dashed lines*

Secondary copper phases in waste rock and Cu equilibria have not been the subject of extensive study like Al or Fe. Secondary Cu phases identified in waste sulfide ore, mine drainage ochres, and natural bedrock where supergene enrichment has occurred include: CuO [tenorite], $\text{Cu}_3\text{SO}_4(\text{OH})_4$ [antlerite], $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ [azurite], $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ [brochantite], $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ [langite], $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$ [chalcantite], and $\text{Cu}_4(\text{SO}_4)(\text{OH})_6 \cdot \text{H}_2\text{O}$ posnjakite (Bigham 1994; Strömberg and others 1994; Williams 1990). Secondary copper phases considered here were: $\text{Cu}(\text{OH})_2$, tenorite, chalcantite, cupric ferrite, brochantite, langite, and antlerite. Results are presented in the bottom portion of Fig. 6. Data points for brochantite, langite, and antlerite were omitted to prevent clutter, but they fall on or near values for chalcantite. Chalcantite has been identified as a post-mine leaching product of the ores at Gibraltar (Bysouth and others 1995).

Cu solubility appears to be in apparent equilibrium with cupric ferrite for values of pH 4–4.7, and slightly unsaturated to saturated with tenorite for pH > 4.7 (Fig. 6).

$\text{Cu}(\text{OH})_2$ and all other basic Cu-sulfate phases approached equilibrium as pH increased and Cu solubility decreases. Langite was the least stable phase in these solutions. Of the simple Cu-sulfates, chalcantite is the most stable phase under acidic pHs, and as pH increases, the stable phases change from antlerite (metastable), brochantite, and under the least acidic conditions, tenorite (Williams 1990). This seems to contradict the results shown in Fig. 6 but in the gossan-forming environment, incorporation of Fe(III) into basic Cu sulfate compounds can lower their solubility (Thornber and Wildman 1984). Strömberg and others (1994) obtained effluents near saturation with respect to a suite of Cu-sulfate and Cu-OH minerals, including tenorite ($\text{SI} = -0.35 \pm 0.22$). Although site-specific, mine waste leachates tend to be oversaturated with respect to cupric ferrite (Lin 1996; Strömberg and others 1994).

The phases discussed have been previously suggested as possible controls for Al and Fe solubility, except for Cu. This may be due to the abundant literature on Al and Fe solubility in acid mine waters. Lindsay (1979) states that the minerals governing the solubility of Cu^{2+} in soils are not known, but suggests that soil-Cu may be cupric ferrite. Cupric ferrite has a solubility product ($K_{\text{sp}} = 10^{-50.12}$; Ball and Nordstrom 1991) much lower than for the Cu phases mentioned above.

The control of Al, Cu, and Fe speciation and solubility appears to change with the acidity in the system. This suggests that long term modelling of water chemistry in mine seepage is an iterative process. Changes in the geochemical environment caused by materials re-handling, liming, site rehabilitation, etc. are likely to result in non-equilibrium or metastable equilibrium conditions and changes in water quality characteristics. If the water flow is slow enough, equilibrium may be established, and the aqueous chemistry will be controlled by the dissolution/precipitation reactions, can be predicted through geochemical modeling.

Conclusion

Mine waste material from an acid-leached rock dump was collected from several trenches based on morphological features. The <0.05-mm fraction was placed in contact with H_2O for 153 days. Speciation and solubility were determined in sampled solutions.

Metal dissolution from the waste rock samples was rapid and near complete for most samples by day 3. Extremely high levels of soluble SO_4^{2-} -S suggest most metals were retained in sulfate forms. Geochemical modeling indicates several phases may be controlling metal levels in solutions. Dissolved Al^{3+} activity in solutions may have at least three possible control mechanisms, depending on solution acidity and SO_4^{2-} -S activity. Al control mechanisms for pH less than 5 seem to be controlled by jurbanite, alunite, and gibbsite (diaspore), depending on the SO_4^{2-} -S activity in the solution and an amorphous $\text{Al}(\text{OH})_3$ in solutions with pH > 5. Dissolved Fe activity appeared to be controlled by a mixture of goethite, hematite, and lepidocrocite, and at values of pH > 4 with higher Cu^{2+} activity, possibly cupric ferrite. For pH above 5, ferrihydrite may play a role. Cu solubility appeared to be controlled by two mineral phases depending on solution pH. In acidic solutions (pH 4–4.7), the only mineral phase in apparent equilibrium was cupric ferrite. As pH increased above 4.7, control corresponded to chalcantite or tenorite, depending on SO_4^{2-} -S activity. Other metals were not at equilibrium with any discrete phases likely to control their concentrations in solution. The acid leaching environment appears to be very similar in geochemical terms, to other mine waste environments. Similar phases were found to be at or near equilibrium suggesting they acted as solubility controls.

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