

MASS BALANCE ASSESSMENT OF INITIAL WEATHERING PROCESSES DERIVED FROM OXYGEN CONSUMPTION RATES IN WASTE SULFIDE ORE¹

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Abstract: A stoichiometric model for initial weathering processes in fresh waste rock has been developed for Aitik ore. Based on element mass balances, solubility equilibrium, mineralogy of unreacted waste rock, and literature data, we identified the dominant geochemical processes and determined geochemical reaction rates for weathering of pyrite, chalcopyrite, calcite, plagioclase and biotite using fluxes derived from large experimental columns filled with waste rock. The oxidation rate of reduced Fe and S was based on O₂-consumption rates that were previously determined in the columns. In the fresh waste rock, acidity production from pyrite weathering and rapid consumption of acidity by calcite dissolution dominate the proton balance. At an acidity production rate of 7.8 meq. kg⁻¹ year⁻¹ of waste rock and a calcite alkalinity reservoir of 0-60 meq. kg⁻¹, we expect the waste rock leachate to remain near-neutral pH for 0-8 years. When calcite is consumed and pH drops, dissolution of previously precipitated copper on the order of 0-1.8 mmole copper kg⁻¹ of waste rock may temporarily increase the pollution load at the site.

Introduction

The release of heavy metals, sulfate, and acidity from mining waste exposed to the atmosphere is a potentially serious and long lasting environmental problem. Metal release rates depend critically on geochemical and transport processes that controls pH and redox buffer systems. Published data on chemistry of waste leachates (Wai et al. 1980, Sullivan and Yelton 1988) illustrate the correlation between trace metal concentrations and pH. At neutral pH, precipitation of (hydr)oxide metal precipitates or adsorption of free metal species on mineral surfaces can limit concentrations of trace metals. Acid leachates, however, often exhibit trace metal concentrations orders of magnitude higher (Karlsson et al. 1988) because of the higher solubility of secondary phases and the lack of adsorption at low pH. To predict pollution loads and implement efficient remediation strategies, processes controlling the pH buffer system need to be understood and predicted.

We have previously studied geochemical processes at the Aitik mining waste rock site in northern Sweden (Strömberg and Banwart 1994), using field data. Due to the low pH (3.5-4) of drainage waters from the waste rock heaps, thermodynamic solubility constraints suggest that copper released from sulfide weathering is essentially conserved in the aqueous phase. The low pH conditions are caused by the relatively rapid acidity

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generation from pyrite oxidation in comparison with the rate of alkalinity production from silicate mineral weathering. Contributions to the total alkalinity mass balance for the heaps indicated calcite dissolution was small. Trace amounts of calcite are found in the fresh waste rock, however, and are assumed to react rapidly to completion soon after dumping of the waste rock. The average age of these heaps is approximately 8 years old.

In this paper, we investigate geochemical processes in fresh waste rock from the same site, using large experimental columns (0.8 m diameter x 2 m) filled with waste rock. Here we propose that the dominating geochemical reactions are simultaneous dissolution of sulfide minerals and calcite. We follow these reactions using water chemistry analysis of leachate from the columns. Based on element mass balances, solubility equilibrium considerations, results from mineralogical investigations of unreacted waste rock, and literature data, we construct a stoichiometric model for leachate genesis in the columns.

Column Experiments

The column experiments are part of an environmental assessment program for the Aitik waste rock site, which has been in progress for 2 years. Six columns are in operation, each filled with approximately 1,500 kg of waste rock. Bennett et al. (1993) determined O₂-consumption within the columns as a measure of sulfide mineral dissolution rates. The columns are unsaturated with water and are operated under oxic conditions, open to the atmosphere both from the top and the bottom. Irrigation rate and temperature within the columns are maintained close to that at the site (irrigation rate: 0.7 m year⁻¹; temperature: 5 °C). These large-scale column experiments approach the complexity of the field scale such as a range of particle sizes, a complex mineralogy, and possibly heterogeneous flowpaths. In contrast to field studies, however, the column experiments retain the capacity to determine precise element mass balances and the possibility to manipulate hydrologic and chemical inputs.

A total of 12 water samples were taken from the columns during experimental weeks 7 - 15. The samples were autoclaved (200 kPa for 30 min.) and acidified (10 ml concentrated HNO₃ to 40 ml sample) at the time of sampling and analysed within one week. Analyses on filtered (0.2 µm pore-diameter cellulose acetate membranefilteres) and unfiltered samples showed no measurable difference in composition. Total concentrations of dissolved metals were measured using inductively coupled plasma - atomic emission spectroscopy (ICP-AES, ARL-3580) and flame atomic adsorption spectroscopy (Perkin-Elmer 100B). Silicon was determined spectrophotometrically using molybdenum blue as chromogen. Anions were analysed using a Tecator 6200 ion chromatograph. Alkalinity was determined by volumetric titration of an unacidified aliquot of each sample by strong acid to the H₂O-CO₂ endpoint, and is reported as bicarbonate ion concentration. Proton activity was measured within one hour after sampling using a combined glass electrode - Ag/AgCl(s) and reference electrode system (Metrohm 691) calibrated with standard buffer solutions at pH 4 and 7, respectively.

Results and Discussion

Calculation of Aqueous Speciation

Table 1 gives the composition of column effluents. Speciation calculations for effluent composition from waste rock columns were carried out using the geochemical code PHREEQE (Parkhurst et al. 1980) with the original WATEQ thermodynamic data base (Truesdell and Jones 1974) revised by Nordstrom et al. (1991). Because the columns are maintained at oxic conditions with unsaturated water flow, we fixed p_e by assuming equilibrium with the atmospheric reservoir of $O_2(g)$. Table 2 summarizes the degree of saturation with respect to selected minerals. Calcite, previously identified in rock samples (Bergström 1981), is near saturation. The effluents are also near saturation with respect to gypsum, chalcedony, and amorphous aluminum hydroxide, as possible alteration products of the rock matrix. The apparent partial pressure of $CO_2(g)$ as calculated from aqueous speciation is $pCO_2 = 10^{-2.4}$ atm. Effluents are at or near saturation with respect to several possible secondary copper-bearing minerals (tenorite, azurite, brochantite). These copper minerals have been identified in natural bedrock where supergene enrichment occurred (Cook 1978).

Table 1. Composition of column effluents, Mean concentrations \pm 1 S.D.

[SO ₄ ²⁻]	19 \pm 2.0	mM	[Ca ²⁺]	16 \pm 2.7	mM	[Al ³⁺]	19 \pm 0.9	μ M
[HCO ₃ ⁻]	1.6 \pm 0.5	"	[Mg ²⁺]	2.5 \pm 0.7	"	[Fe]total	1.5 \pm 0.4	"
[Cl ⁻]	1.7 \pm 0.9	"	[K ⁺]	0.87 \pm 0.4	"	[Cu]total	5.5 \pm 3.2	"
[H ₄ SiO ₄]	0.28 \pm 0.1	"	[Na ⁺]	3.6 \pm 1.9	"	[Zn ²⁺]	29 \pm 33	"
pH	7.2 \pm 0.2	"	[Mn]total	0.11 \pm 0.02	"			

Table 2. Saturation index (S.I. \pm 1 S.D.) with respect to selected minerals¹.

Calcite (CaCO ₃)	-0.26 \pm 0.4	Cu(OH) ₂ (am)	-1.4 \pm 0.22 ²
Gypsum (CaSO ₄ *2H ₂ O)	0.10 \pm 0.1	Antlerite (Cu ₃ SO ₄ (OH) ₄)	-1.2 \pm 0.72 ²
Chalcedony (SiO ₂)	0.23 \pm 0.1	Brochantite (Cu ₄ SO ₄ (OH) ₆)	0.40 \pm 0.92 ²
Al(OH) ₃ (am)	0.66 \pm 0.1	Malachite (Cu ₂ CO ₃ (OH) ₂)	-0.57 \pm 0.42 ²
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	9.3 \pm 0.4	Azurite (Cu ₃ (CO ₃) ₂ (OH) ₂)	-0.09 \pm 0.72 ²
Fe(OH) ₃ (am)	2.9 \pm 0.3	Tenorite (CuO)	-0.35 \pm 0.22 ²
Manganite (MnOOH)	6.0 \pm 0.3	Cupric ferrite (CuFe ₂ O ₄)	16 \pm 0.52 ²
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	8.2 \pm 1.0	Smithsonite (ZnCO ₃)	-1.6 \pm 0.33 ³
Jarosite (KFe ₃ (SO ₄) ₂ (OH) ₆)	1.8 \pm 0.4	Franklinite (ZnFe ₂ O ₄)	15 \pm 0.83 ³

¹Saturation index = log (IAP/ K_g'), where IAP is the ion activity product and K_g' is the conditional solubility product at experimental temperature, pressure and ionic strength.

²thermodyn. data Vieillard (1988).

³thermodyn. data Lindsay (1979).

Stoichiometric Model

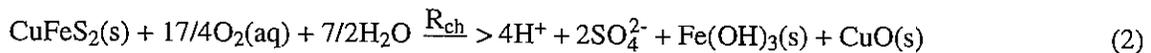
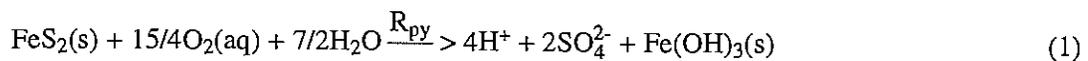
Sulfide minerals are far from equilibrium in oxic environments, and weathering is constrained only by reaction kinetics or transport of molecular oxygen. Sulfide content in the Aitik waste rock is dominated by pyrite with smaller quantities of chalcopyrite, pyrrhotite, and sphalerite, as shown by examination of thin sections (table 3). Elemental analysis determined total sulfur and metal content of the rock, although pyrite and pyrrhotite cannot be distinguished from each other by this method.

Table 3. Mineral Composition of unreacted waste rock¹.

Plagioclase (oligoclase, Ab. 70%, An. 30%)		10-30 vol.%
Albite	NaAlSi ₃ O ₈	
Anorthite	CaAl ₂ Si ₂ O ₈	
K-feldspar	KAlSi ₃ O ₈	10-30 vol.%
Biotite	K(Fe _{1.5} Mg _{1.5})AlSi ₃ O ₁₀ (OH) ₂	10-20 vol.%
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	1-34 vol.%
Quartz	SiO ₂	20-30 vol.%
Pyrite and pyrrhotite	FeS ₂ and FeS	0.4-1.7 vol.%
Chalcopyrite	CuFeS ₂	0.1-0.4 vol.%
Sphalerite	ZnS	0.01-0.06 vol.%
Calcite	CaCO ₃	0-0.3 vol.%

¹Sulfide content is estimated from elemental analysis of sulfur (Leco) and metals (powder XRF; Philips 1600). Distribution of rock forming minerals was estimated by examination of 50 thin sections (Bergström, 1981).

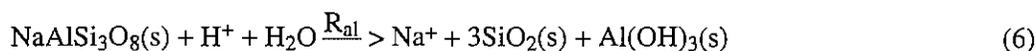
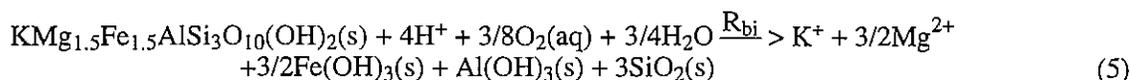
We consider oxidative weathering of pyrite by equation 1 and chalcopyrite by equation 2, as dominating sulfide phases. In defining the stoichiometry of equations 1 and 2, iron and copper are assumed to be conserved in solid phases. We reach this conclusion by noting that the fluxes of Fe(total) and copper from the columns are at least three orders of magnitude less than sulfate fluxes and oxygen consumption rates. The R and subscript denotes net forward reaction rate.



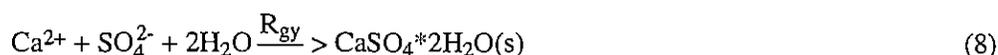
Calcite dissolution is an important source of alkalinity over the time scale of these experiments. Calcite content is low, however, even in fresh samples of unreacted rock (0-0.3 vol.%, Bergström 1981). The dissolution rate can be characterized as fast (e.g., Plummer et al. 1978) compared to the rate of acidity input and water flow rates in natural systems (Langmuir 1971). We calculate degassing of CO₂ by evaluating the mass balance for inorganic carbon.



An additional source of alkalinity is irreversible dissolution of primary minerals such as feldspars and micas. Table 3 lists dominant rock-forming minerals identified in samples from the site. We consider weathering of biotite by equation 5 and plagioclase by equations 6 and 7. Using mass balance considerations similar to those for iron and copper, we assume aluminum and silicon to be conserved in solid phases as weathering products. We neglect the weathering of K-feldspar and muscovite as sources of K⁺ because fluxes of Mg²⁺ and K⁺ as tracers for biotite weathering alone agree within a factor of two.



We also consider possible immobilization of calcium and sulfate as gypsum (equation 8).



Element Mass Balances for Waste Rock Columns

To estimate the reaction rates for the geochemical processes described in the previous section, we carry out a mass balance calculation for the waste rock columns. The mass balance for molecular oxygen includes a measured rate of oxygen consumption, J_{O_2} (mole O₂ kg⁻¹ s⁻¹), and rates of the oxygen-consuming reactions R_{py} , R_{ch} , and R_{bi} (mole kg⁻¹ s⁻¹). The consumption of molecular oxygen was previously determined for these columns to be on average $(2.4 \pm 0.8) \times 10^{-10}$ moles kg⁻¹ s⁻¹ for the waste rock matrix (Bennett et al. 1993).

$$J_{\text{O}_2} = 15/4R_{\text{py}} + 17/4R_{\text{ch}} + 3/8R_{\text{bi}} \quad (9)$$

A relationship between pyrite and chalcopyrite weathering is required, we therefore introduce a linear dependence between mineral reaction rate, R , mineral volume abundance, V , and relative reactivity. The dependence on mineral abundance can be expected for a reaction where accessibility to surface area is critical (surface controlled kinetic reaction). Steger and Desjardins (1978) showed with weathering experiments that the relative reactivity of chalcopyrite is approximately one-half that of pyrite.

$$R_{\text{ch}} = 1/2 \frac{V_{\text{ch}}}{V_{\text{py}}} R_{\text{py}} \quad (10)$$

The dissolution rates for biotite (R_{bi} , equation 5) and albite (R_{al} , equation 6) are given by using effluent concentrations, C (mole dm⁻³), of Mg²⁺ and Na⁺ as tracers for the respective reactions. The flow rate through the columns, Q , was 9.3×10^{-6} dm³ s⁻¹ and M , total mass of waste rock within the columns, is approximately 1,500 kg.

$$R_{\text{bi}} = 2/3 C_{\text{Mg}} Q/M \quad (12)$$

$$R_{al} = C_{Na} Q/M \quad (13)$$

Dissolution of anorthite, R_{an} (equation 7), is given by assuming a stoichiometric dissolution with respect to the end member composition of plagioclase (table 3). In any case, we expect the contribution of calcium from anorthite dissolution to be small in comparison with that from calcite dissolution. Laboratory studies at neutral pH show dissolution rates of anorthite and albite to be within one order of magnitude (Amrhein and Suarez 1988, Knauss and Wolery 1986). Calcite dissolution rate at neutral pH and atmospheric pCO_2 , however, is at least 5 orders of magnitude faster (Plummer et al. 1978).

$$R_{an} = 3/7 R_{al} \quad (13)$$

A mass balance for sulfate (equation 14) gives the rate of gypsum precipitation, R_{gy} (equation 8).

$$R_{gy} + C_{SO4} Q/M = 2R_{py} + 2R_{ch} \quad (14)$$

A mass balance for Ca (equation 15) gives the rate of calcite dissolution, R_{ca} (equation 3). Comparing the rate of calcite dissolution with the total proton balance (equation 16) gives a mass balance for inorganic carbon and thus CO_2 degassing, R_{dg} (equation 4).

$$R_{ca} + R_{an} = R_{gy} + C_{Ca} Q/M \quad (15)$$

$$4R_{py} + 4R_{ch} = R_{ca} + 4R_{bi} + R_{al} + 2R_{an} + R_{dg} \quad (16)$$

Geochemical Reaction Rates

Table 4 lists reaction rates for processes 1 - 8, obtained by solving equations 9 through 16. Acidity input from pyrite weathering and rapid acidity consumption by calcite dissolution dominate the proton balance.

Because speciation calculations indicate equilibrium with respect to calcite, the net rate of dissolution is apparently controlled by relatively slow acidity input from sulfide weathering with rapid reaction kinetics for calcite dissolution. The slightly elevated partial pressure of CO_2 as calculated from aqueous speciation indicates slow mass transfer for CO_2 between aqueous and gaseous phases. Because the carbonate system is open to the atmosphere, most of the inorganic carbon dissolved from calcite is released as carbon dioxide gas.

As opposed to rapid calcite dissolution, primary silicate mineral weathering is kinetically controlled and dissolution rates are not directly coupled with acidity input from sulfide weathering. Silicate weathering also contributes slightly to oxygen consumption due to the release of ferrous iron. Biotite and plagioclase weathering have previously been identified as dominant alkalinity sources in large-scale natural systems (Giovanoli et al. 1988). In the initial weathering of waste rock studied here, the relatively small reservoir of calcite dominates alkalinity generation due to fast dissolution kinetics.

We estimate the capacity of the calcite alkalinity reservoir to be 0 - 60 meq. kg^{-1} of waste rock based on the calcite content (table 3). The acidity production rate is 7.8 meq. $kg^{-1} year^{-1}$ of waste rock (table 4, equations 1

and 2). We therefore expect the waste rock leachate to remain pH neutral for 0-8 years. When calcite is depleted, the remaining slow silicate weathering will be insufficient to consume all acidity inputs from sulfide weathering, and leachate pH will consequently drop. This is in agreement with pH measurements of drainage water from older waste rock at the Aitik site. The reaction rates from these calculations are therefore only valid during the relatively short period of calcite buffering when waste rock is initially deposited at the Aitik site. Weathering rates on geologic timescales, or on the lifetime of the Aitik waste deposit, may depend on hydrologic and climatic conditions, formation of inhibiting secondary phases, and depletion of the sulfide minerals (Strömberg and Banwart, 1994).

The effluent data and the calculations show an accumulation of copper in secondary phases during calcite pH buffering. At an accumulation rate of 0.22 mmole kg⁻¹ year⁻¹ (equation 2), we can expect to have a reservoir of precipitated copper on the order 0-1.8 mmole kg⁻¹ of waste rock when all calcite has been consumed. Subsequent dissolution of this reservoir due to decrease in pH after calcite is consumed may temporarily increase the pollution load at the site.

Table 4. Geochemical reaction rates in mole kg⁻¹ s⁻¹ of waste rock.

Equation 1	Rpy (Pyrite diss.)	5.5 * 10 ⁻¹¹	Equation 5	Rbi (Biotite diss.)	1.0 * 10 ⁻¹¹
Equation 2	Rch (Chalcopyrite diss.)	6.9 * 10 ⁻¹²	Equation 6	Ral (Albite diss.)	2.2 * 10 ⁻¹¹
Equation 3	Rca (Calcite dis.)	9.6 * 10 ⁻¹¹	Equation 7	Ran (Anorthite diss.)	9.6 * 10 ⁻¹²
Equation 4	Rdg (CO2 deg.)	7.1 * 10 ⁻¹¹	Equation 8	Rgy (Gypsum precip.)	6.4 * 10 ⁻¹²

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