Sulfide Oxidation Kinetics in Low-Sulfide Tailings

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Abstract Oxidation kinetics of low sulfide tailings from two sources were measured in experimental tests in which surface areas of sulfide minerals determined by $N_{2(g)}$ adsorption. The surface areas were used to derive surface roughness factors based on particle size distributions. Using the surface area data, median rate constants ranged from $10^{-9.92}$ and $10^{-10.17}$ mol py/dm^2/s for the kinetic tests conducted on two different types of low sulfide tailings. These rate constants are in reasonably good agreement with the value of $10^{-10.19}$ mol py/dm^2/s reported by Williamson and Rimstidt (1994) for pyrite under water-saturated conditions.

Key words sulfide oxidation, kinetics, tailings, desulfurization

Introduction

Desulfurization technologies can reduce sulfide mineral contents in tailings to less than 1% and often less than 0.1-0.3%. This process produces a proportionately larger amount of low sulfide tailings and with the remainder of the sulfide content concentrated in a smaller amount of high sulfide tailings. While desulfurization can yield low sulfide contents, the potential still exists for acid generation for tailings with very low carbonate contents. Titratable acidities may be very low in leachates from low-sulfide tailings, but the potential exists for metal leaching. The purpose of this paper is to present data on the reactivity of desulfurized tailings in terms of oxidative dissolution rates using the form of the kinetic rate expression developed for pyrite oxidation by Williamson and Rimstidt (1994). The rate data and interpretation presented here are meant to provide information that is characteristic of low-sulfide tailings with little or no carbonate neutralization content. This information can be used in the development of models of tailings leachate chemistry and in the associated design of reclamation covers for desulfurized tailings.

Methods

Samples

Experimental tests were conducted with low-sulfide tailings from two sources. One source was the Aitik Mine operated by Boliden AB. The second source was pilot plant metallurgical tests conducted in 2009 and 2014 for the Resolution Copper (RC) project.

Acid Base Accounting and Mineralogy

Samples of tailings used in kinetic tests were analyzed for acid base accounting (ABA) parameters of: total S, sulfide-S, and neutralization potential. Carbonate neutralization potential (CaNP) was determined from total inorganic carbon.

Surface Area

Specific surface areas of four samples of high sulfide RC tailings were measured by $N_{2(g)}$ adsorption BET. The high sulfide tailings contained 20-25% sulfide-S. The specific surface areas measured for the high sulfide tailings are assumed to be representative of sulfide minerals in low sulfide tailings. Prior to BET measurement, the sulfide mineral contents were enriched by dispersing them in an aqueous solution of lithium meta-tungstate (density = 2.95 g/cm^3), followed by centrifugation to separate the float (silicates) and sink (sulfide) fractions. Total recoveries of the float and sink fractions were 92.3 to 99.9%.

The enriched fractions of the high sulfide tailings were analyzed for elemental contents. The total elemental contents averaged 97.5%. The remainder of 2.5% is thought to be mostly oxygen. The average elemental molar amounts for S and Fe, based on the weight % values were 1.56 and 0.77. These molar contents are equivalent to a ratio of S to Fe of 2.02:1.00, which is indicative of pyrite as the primary sulfide mineral in the samples.

Kinetic Testing

Laboratory Testing

Kinetic tests were conducted on low sulfide tailings samples from both RC and Aitik. These tests were conducted according to the humidity cell test (HCT) procedure described in ASTM 5744-96. The HCTs contained 0.5-1 kg of tailings and weekly application of 0.5-1 L of distilled water. The RC HCTs were run for 38-61 weeks. The Aitik HCTs were run for 96-199 weeks.

Leachates from humidity cell tests were analyzed for pH, acidity, alkalinity, conductivity, temperature, SO_4, and volume on a weekly basis. Full suites of analytes were determined for weekly leachates for the first five weeks and thereafter every fifth week.

Field Barrel Tests

Field barrel tests were conducted with three samples of low sulfide tailings. The three barrels contained 69.7, 78.6, and 95.6 kg of tailings. The barrels collected water from direct precipitation and were also irrigated on an approximate four-week cycle to generate sufficient leachate volumes for analyses.

Laboratory Oxygen Consumption Tests

Laboratory tests of oxidation consumption (“OxCon”) were conducted on six samples of RC tailings. Tailings samples with known moisture content were placed in sealed containers in which the decrease in O_2 in the container atmosphered was monitored over time (Bourgeot et al. 2011). The decreases in O_2 during were converted to sulfide oxidation rate, assuming that all O_2 loss was due to oxidation of pyrite and all iron produced by oxidation was re-precipitated as ferrihydrite.

Results and Discussion

Acid Base Accounting and Mineralogy

The ABA results show that all samples were low in sulfide-S (Table 1). The CaNP values were also very low, ranging from <0.4-10.5 kg $CaCO_3$/t.

Surface Area

Specific surfaces areas for the four samples of enriched high sulfide tailings are given in Table 2. Values ranged from 17.7 to 49.5 dm^2/g with an overall average of 34.7 dm^2/g.

The specific surface area (S_{geo}) in dm^2/g of non-porous mineral particles can be estimated from the following equation, assuming spherical geometry (White, 1995):

$$S_{geo} = \frac{6}{\rho D} \lambda \Big/ 100 \qquad (1)$$

In Eq. 3-1, ρ is the mineral density in g/cm^3, D is the particle diameter in cm, λ is the surface roughness factor, which is the ratio of the measured surface area (S_{meas}) to the geometric surface area ($\lambda = S_{meas}/S_{geo}$), and the factor of 100 is to convert areas from cm^2 to dm^2. Equation 1 can be applied to calculate λ, using the BET-measured surface areas, particle size distribution (PSD) data, an estimate of D from the geometric mean of the upper and lower sieve sizes for each size fraction used to determine PSDs, and ρ_{pyrite} of 5.01 g/cm^3.

Table 3 gives the results of the application of Eq. 1 for the PSDs of the high sulfide tailings used for BET surface area measurements. The average value of λ is 4.8. Roughness factors for unweathered silicates range from 2-10 and 100-1000s for weathered silicates (White, 1995). Given a lack of weathering experienced by fresh tailings, the range for λ of 3.1-7 is reasonable.

An estimate for λ provides a means to estimate specific surface areas for other tailings types given data on PSDs and Eq. 1. This approach was used to calculate surface areas for the RC and Aitik low sulfide tailings used in the kinetic tests.

Table 1 *Acid base accounting results for low sulfide tailings samples used in kinetic tests*

Sample Source	Number	Mean Total S (%)	Mean Sulfide-S (%)	Mean Sulfate-S (%)	Mean CaNP (kg $CaCO_3$/t)
RC	18	0.23	0.18	0.05	3.98
Aitik	11	0.46	0.43	0.04	4.20
RC Barrels	3	0.10	0.12	0.02	1.63
Oxcon	6	0.21	0.15	0.06	NA

Table 2 *BET Surface areas of enriched high sulfide tailings*

Sample	Duplicate #1 (dm^2/g)	Duplicate #2 (dm^2/g)	Average (dm^2/g)
24 MC-1	45.6	42.9	44.3
32 MC-5*	49.5	44.9	47.2
35 MC-1	30.9	26.3	28.6
37 MC-2	19.7	17.7	18.7

*Blind duplicate of 24 MC-1

Table 3 *Surface roughness factors for sulfide-enriched fractions of pyrite tailings*

Sample	Geometric Surface Area (S_{geo} for λ=1) (dm^2/g)	BET Surface Area (dm^2/g)	Roughness Factor λ (unit-less)
24 MC-1	6.4	44.2	7.0
32 MC-5	8.4	47.2	5.6
35 MC-1	7.8	28.6	3.7
37 MC-2	6.1	18.7	3.1
Averages	7.2	34.7	4.8

Kinetic Test Trends

Final average pH values from HCTs and barrel tests are shown in Fig. 1. Values for pH show scatter when plotted against initial CaNP but show a more discernible trend when plotted against the initial sulfide-S content. Samples with sulfide-S contents greater than about 0.2 to 0.3% typically produced acidic pH values (< 5.6).

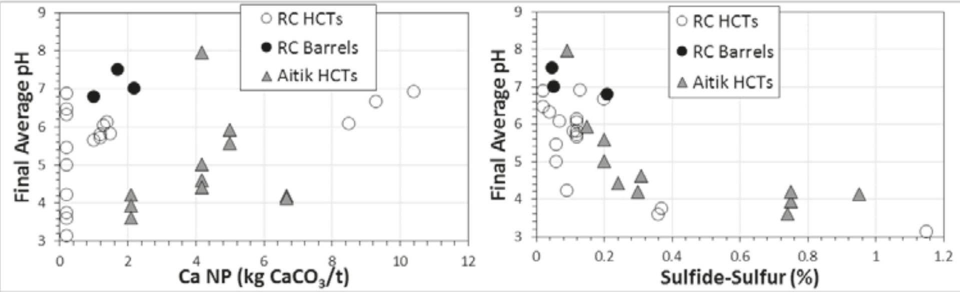

Figure 1 *Average final pH values as a function of initial CaNP and sulfide-sulfur*

Rate Expression

The approach for deriving a specific rate constant for from the kinetic tests involved converting data on sulfate production over time into the form of the rate expression developed for pyrite oxidation (r) by Williamson and Rimstidt (1994):

$$r\left(\frac{mol\ py}{dm^2 \cdot s}\right) = k\left(\frac{A}{V}\right)\frac{m_{DO2}^{0.5}}{m_{H+}^{0.11}} \quad \text{where } k = 10^{-10.19\pm0.10} \qquad (2)$$

The specific rate constant k = $10^{-10.19\pm0.10}$ is for the unit convention of surface area to volume (A/V) of 1 dm^2/dm^3 used in the PHREEQC geochemical model (Parkhurst and Appelo, 2013). The conversion of the experimental kinetic data over time into the form of Eq. (2) is based on:

$$FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3(s) + 2\ SO_4^{-2} + 4\ H^+ \qquad (3)$$

In converting kinetic data, we assumed there was no limitation of O_2 in the tests, that pH values were not low enough to allow Fe^{+3} to be an important oxidant, and pyrite is the predominant reactive sulfide. As pyrite is oxidized, its mass and surface area will decrease. The change in surface area (S) with time resulting from oxidation of the pyrite was estimated from:

$$S = S_0\left(\frac{m}{m_0}\right)^{0.67} \qquad (4)$$

In Eq. 4, S_o is the initial surface area and m and m_o are the remaining and initial pyrite amounts.

Oxidation Kinetics

Oxidation rates from literature studies where rates have been normalized to surface areas for pyrite are compared to rates for RC and Aitik tailings in Fig. 2. The surface areas for RC and Aitik tailings were 34.7 dm^2/g and 59.7 dm^2/g, respectively. The RC value is from the $N_{2(g)}$ BET measurement the Aitik value was from PSDs and average λ of 4.8 (Eq. 1). On Fig. 2, rates from the kinetic tests were aggregated into three groups based on the percentage of consumption of the initial sulfide-S contents: 10-40%, 40-60%, and 60-80%. The rate data were aggregated into these groups for two reasons. First, the rates are based on sulfate generation according to the stoichiometry of Eq. 3; hence, not using rates for times when <10% of the initial sulfide-S content had been consumed avoided the problem of initial washoff of sulfate from surface products created during storage. Second, the pH values in some tests decreased over time before reaching steady values. Aggregating rates for the ranges of sulfide-S consumption lumps together rates over narrower pH ranges, which allows better discrimination of the effects of pH on rate constants.

Also shown in Fig, 2 are rates reported by Williamson (2015) and Lapakko and Antonson (2006). The range from Williamson (2015) is for tests conducted on granular mixtures that were synthesized by mixing measured amounts of pyrite, quartz, and calcite to create mineral compositions with a high degree of characterization. The rates obtained by Williamson (2015) for these synthetic compositions overlap with many of those obtained from the low sulfide RC and Aitik tailings. The rates from Lapakko and Antonson (2006) were derived from tests on waste rock samples for which surface areas of the sulfide minerals were estimated. The majority of these rates are also in good agreement with the rates determined for the low sulfide tailings.

In general, the rates for the low sulfide RC and Aitik tailings range up to about 10 times higher than those calculated with the Williamson and Rimstidt (1994) rate expression for pH < ~6. At pH > 6, the rates for the RC and Aitik low sulfide tailings are in better agreement with the rate expression. Also shown in Fig. 3 are rates for oxidation by moist air from Jerz and Rimstidt (2004), Williamson (2013), and Williamson (2015). These rates overlap with those obtained from the OxCon tests on RC low sulfide tailings. The primary exceptions that deviate the other rates are those from the field barrel tests that are about 100 times slower than the laboratory tests. These slower rates are likely due to less access to O_2 because of the closed sides and bottoms, leaving diffusion in to the top surface as the only route for O_2 entry. Also, a high fraction of the leachate was observed to flow down the inside surfaces of the barrels rather than through the body of tailings thereby reducing probable contact with much of the sulfide mineral content.

The Williamson and Rimstidt (1994) rate expression is based on a statistical analysis of studies conducted in aqueous systems where pyrite grains were immersed in water with controlled dissolved O_2 concentrations. In contrast, the kinetic tests on low sulfide tailings were conducted within an unsaturated matrix of silicate minerals through which air is forced followed by periodic application of distilled water to rinse out reaction products. Considering the difference in experimental procedures, the differences in rates between the different testing procedures are not as large as might be expected.

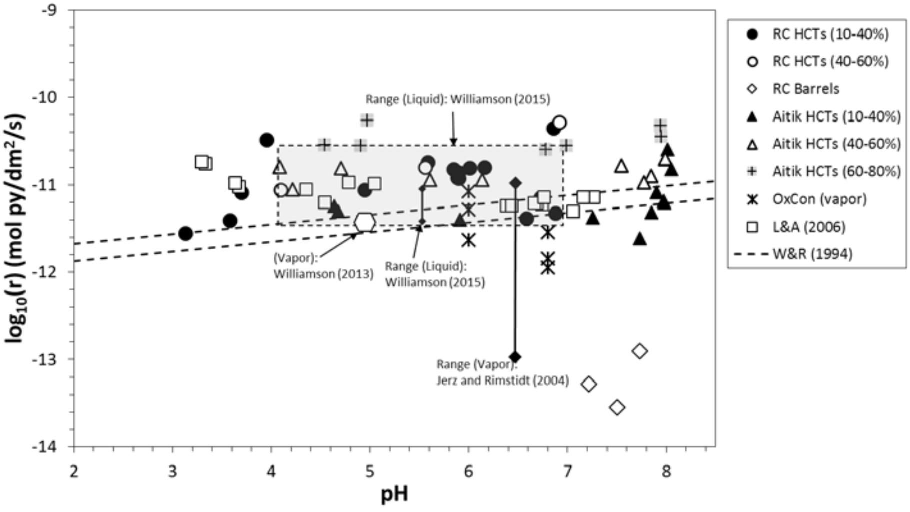

Figure 2 *Comparison of sulfide oxidation rates*

Specific Rate Constant

The rate expression from Williamson and Rimstidt (1994) in Eq. 2 can be rearranged to solve for the specific rate constant (k):

$$k = r \Big/ \left(\frac{A}{V} \frac{m_{DO2}^{0.5}}{m_{H^+}^{0.11}} \right) \qquad (5)$$

Application of Eq. 5 to calculate specific rate constants from the kinetic tests is shown in Fig. 3. The specific rate constants align approximately along a single trend that is relatively independent of the initial sulfide-S as would be expected for a representative rate constant. Table 4 gives a summary of the rate constants obtained from the kinetic tests.

Table 4 *Specific rate constants for sulfide oxidation by dissolved O2 for low sulfide tailings*

Humidity Cells (10-40% Pyrite Consumed)	**Humidity Cells (40-60% Pyrite Consumed)**	**Humidity Cells (60-80% Pyrite Consumed)**	**Barrels**	**OxCon**		**Williamson and Rimstidt (1994)**
log$_{10}$ (k) (mol py/ dm^2/s)	**log$_{10}$ (k) (mol py/ dm^2/s)**	**log$_{10}$ (k) (mol py/dm^2/s**	**log$_{10}$ (k) (mol py/ dm^2/s)**	**Gravimetric Moisture Content**	**log$_{10}$ (k) (mol py/ dm^2/s)**	**log$_{10}$ (k) (mol py/ dm^2/s)**
Mean = -9.78	Mean = -9.66	Mean = -9.21	Mean = -12.19	5%	Mean† = -10.64	-10.19±0.10
Median = -9.98	Median = -9.77	Median = -9.34	Median = -12.27	20%	Mean† = -10.35	
10th% = -10.34	10th% = -9.93	10th% = -9.52	**	24-26%	Mean† = -10.13	
90th% = -9.62	90th% = -9.46	90th% = -8.97	**			

Notes: *Only three HCTs had measureable rates for pyrite consumption > 40%, so percentiles were not calculated; **Only three barrel tests were conducted, negating calculation of additional statistics; †Mean of two experiments at each moisture content

Conclusions

Low sulfide tailings can produce acidic leachates even when sulfide-S contents are very low when neutralization capacities are also very low. Measurements of PSDs and specific surface areas provide a means to refine kinetic testing data into the form of the rate expression developed by Williamson and Rimstidt (1994) for pyrite oxidation. This rate expression is easily incorporated into geochemical models to facilitate simulation of sulfide oxidation processes.

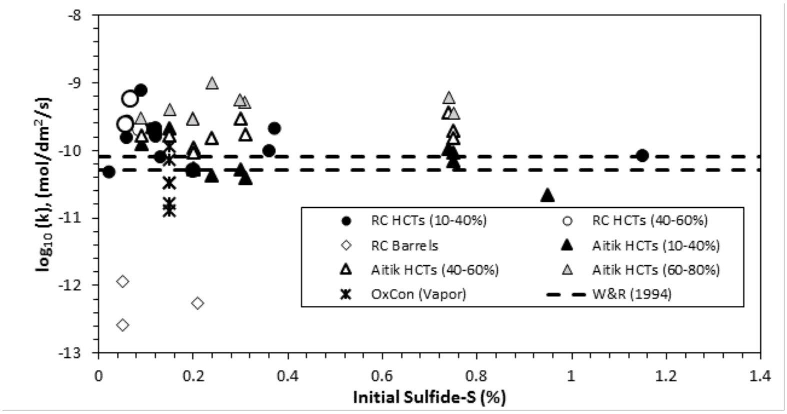

Figure 3 *Specific rate constants as a function of initial sulfide-S content*

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