Setting ARD Management Criteria for Mine Wastes with Low Sulfide and Negligible Carbonate Content

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ABSTRACT

Evaluation of ARD potential for rock with low (less than <1% by weight) sulfide content using conventional acid-base accounting criteria (e.g. net neutralization potential and neutralization potential ratio) can result in invalid classifications because neutralization potentials do not adequately represent the ability of acid-consuming silicate minerals to neutralize weak acidity. Rocks containing low sulfide concentrations generate acid at low rates that do not necessarily require fast-reacting carbonates to buffer pH to near neutral levels. Instead, meteoric weathering of silicate minerals by carbonic acid can deliver sufficient dissolved bicarbonate to offset acid generated and buffer pHs well above 7. Because silicate minerals dominate the mineralogy of many common rock types, bulk neutralization potential is effectively infinite compared to acid generation potential, and the determination of ARD potential depends on the rate of silicate weathering relative to sulfide oxidation rate. Furthermore, the bulk sulfide oxidation rate is typically correlated to sulfide content allowing sulfide content thresholds to be used as management criteria.

This paper will present an example of the use of this conceptual model to develop waste rock management criteria for the NorthMet Project in the nearly carbonate-absent Duluth Complex of northern Minnesota, USA. The method involved measurement of silicate weathering rates for rocks containing negligible sulfide and development of a relationship between sulfide content and oxidation rates. Interpretation of the data obtained provided an explanation for the lack of net acid generation in decades-long kinetic-testwork performed by the Minnesota Department of Natural Resources on samples containing less than 0.2% sulfur as pyrrhotite and chalcopyrite. The findings were used to develop waste rock management criteria for the proposed mine using sulfur content.

Keywords: silicate weathering, silicate alkalinity, Duluth Complex, low sulfide

INTRODUCTION

Conceptual Geochemical Model – Contact Water pH Modification By Silicate Minerals

The tendency for mine wastes to yield contact waters containing unacceptable concentrations of regulated contaminants largely hinges on weathering pH because most of the the contaminants are metals and solubility is in part a function of pH typically represented by reactions such as:

$$\mathrm{Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2 + 2H^+} \quad (1)$$

While higher pHs do not guarantee that concentrations will be below regulatory limits, the relationship between pH and metal concentrations indicates that concentrations will tend to be much higher at lower pHs. The trend is reversed when amphoteric behavior allows solubility to increase at higher pHs.

The weathering environment pH in mine wastes is commonly attributed to the balance between acid generating reactions represented by:

$$\mathrm{FeS_2 + {}^{15}\!/\!{}_4 O_2 + {}^{7}\!/\!{}_2 H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+} \quad (2)$$

and the consumption of acid (H^+) by carbonate minerals:

$$\mathrm{4Ca(CO)_3} + 4H^+ \rightarrow 4Ca^{2+} + \mathrm{4HCO_3^-} \quad (3)$$

The balance between these reactions is usually evaluated by analytical methods which are proxies for the iron sulfide and carbonate minerals (for example, acid-base accounting, ABA, Sobek et al., 1978; Lawrence & Wang, 1991 and net acid generation, NAG, AMIRA International, 2002).

This conventional theory and the analytical approaches used to quantify acid generating and acid consuming mine waste components fall short of correctly incorporating the role of silicates in modifying contact water pH because silicate minerals react much less rapidly than carbonate minerals and weathering rates are a function of pH. For example, neutralization potential (NP) determined as part of ABA is commonly observed to yield more apparent acid-consuming capacity than can be accounted for by the carbonate content (for example, Day, 2009) and this difference is assigned to acid consumption by silicate minerals. The aggressive low pH of the test conditions in the NP procedure (and similarly in the NAG procedure) result in acid neutralization by reactions such as:

$$\mathrm{CaAl_2Si_2O_8 + 8HCl \rightarrow Ca^{2+} + 2Al^{3+} + 2SiO_2 + 8Cl^- + 4H_2O} \quad (4)$$

Hydrolysis reactions for the resulting dissolved aluminum buffer pH in the range 4 to 5:

$$\mathrm{Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+} \quad (5)$$

Therefore, the low pH of the tests encourages silicate mineral dissolution, which buffers pHs through aluminum release (reaction (4)) at levels too low to usefully influence metal solubility relative to regulated limits. Furthermore, due to the slow weathering reaction kinetics of the consumption of acid by the above types of reactions and the method used to determine the amount of acid in the analytical procedures, the NP methods do not quantify the silicate mineral reservoir potentially available to neutralize acid.

The actual role of silicates in controlling contact water pH is represented by weathering reactions between carbon dioxide and silicate minerals, such as:

$$CaAl_2Si_2O_8 + 2H_2O + 2H_2CO_3^0 \rightarrow Ca^{2+} + 2Al(OH)_3 + 2SiO_2 + 2HCO_3^- \quad (6)$$

This reaction is comparable to reaction (4) but involves carbonic acid (i.e. dissolved CO_2) rather than sulfuric acid and yields dissolved bicarbonate which can in turn be involved in buffering contact water pH in the near neutral pH range through reversible reactions such as:

$$Ca^{2+} + HCO_3^- \rightarrow CaCO_3 + H^+ \quad (7)$$

The potential role of silicates in modifying contact water pH at higher pHs is therefore limited to the delivery of alkalinity due to slow weathering resulting in exchange of protons with alkali and alkali earth cations in silicates. These reaction rates are very slow relative to dissolution of carbonate minerals and are therefore probably unimportant in carbonate-rich systems. They become much more important in carbonate-deficient systems containing low sulfide concentrations where the rate of acid generation can be balanced by the slow generation of alkalinity by silicate weathering. Furthermore, the silicate mineral reservoir is far greater than the acid that could be generated by sulfide oxidation resulting in an effectively perpetual source of alkalinity even when passivation of silicate mineral surfaces by secondary silicates occurs. In this setting, the rate of acid generation by sulfide oxidation therefore becomes the controlling variable rather than the actual quantity of silicate minerals.

This paper describes quantification of silicate weathering for a nearly carbonate-absent geological environment and the resulting definition of sulfide sulfur management criteria for waste rock management.

Study Area – Duluth Complex

The Duluth Complex in northern Minnesota is a layered gabbroic complex intruded approximately 1 billion years ago. The base of the complex contains copper and nickel sulfides, and platinum group elements formed from sulfide melts. The dominant minerals in the Duluth Complex are olivine and plagioclase, and carbonates were not formed as part of the original magmatic processes. Deuteric processes resulted in localized formation of secondary carbonates but at very low concentrations which are commonly undetectable.

The State of Minnesota recognized the benefits of economic recovery of metals from the Duluth Complex and initiated studies to support resource development (State of Minnesota 1979). Interest in large-scale open pit and underground mining accelerated in the 2000s and several projects are in various stages of economic and regulatory assessment. This includes PolyMet Mining Inc.'s NorthMet Project, which is the subject of this paper.

Previous Studies

The Lands and Mineral Division of the Minnesota Department of Natural Resources (MDNR-LAM) continues to conduct several test programs designed to evaluate the long term weathering of Duluth Complex rocks (e.g. Lapakko & Antonson, 2006). These have included chemical and mineralogical characterization, conventional humidity cells (ASTM, 2001) and other custom-designed laboratory kinetic tests, and monitoring of drainage from small field test piles and fullscale waste rock piles. The latter are stockpiles of Duluth Complex rocks resulting from stripping to access iron ore in the LTV Steel Mining Company's Dunka Pit.

The laboratory kinetic tests operated for over 18 years by MDNR-LAM (Lapakko & Antonson, 2006) have shown consistent leaching features including lack of pH depression in samples containing about 0.2% sulfur (Figure 1a), correlation of timing of pH depression and sulfur content (Figure 1b,c,d), recovery of pH following pH minimums (Figure 1b,c), and correlation of sulfide oxidation rates with sulfide content.

Program Design

The NorthMet Project would be an open pit mine with a proven and probable ore reserve of 275 million tonnes with a copper equivalent grade of 0.79% (Desautels & Zurowski, 2013). The sulfur block model for the deposit indicated that waste rock would contain sulfur concentrations ranging from 0.01% to greater than 1%. The majority of waste rock would contain less than 0.1%. A kinetic test program was designed in consultation with MDNR-LAM to develop waste management criteria. The detailed design evaluated the relationship between variables that could conceivably affect rock weathering behavior including sulfur content, rock type (variability between plagioclase- and olivine-rich troctolite end-members), sulfide mineralogy (iron versus copper and nickel sulfides as represented by samples of waste, low grade ore and ore), stratigraphic layer in the complex, and waste rock particle size. The influence of test protocol on outcomes was evaluated by parallel testing using conventional ASTM and MDNR-LAM-designed methods. The distribution of sulfur concentrations tested is shown in Figure 2. Several samples were selected containing 0.02% sulfur thereby indicating weathering chemistry for rock essentially containing no sulfide. Samples containing the highest sulfur concentrations in the test program were from the surrounding host rocks of the Duluth Complex rather than the intrusions themselves.

METHODOLOGY

Sample Acquisition and Preparation

Samples were selected from drill core using logged characteristics and analytical data in the exploration database. Two sections of each core interval were retained for mineralogical characterization and the balance was crushed to meet the specifications of the various test methods.

Mineralogy

Mineralogy was described using optical methods on polished thin sections. For each mineral, the crystal shape, grain size and texture were described. Electron microprobe was used to determine concentrations of major element oxides, arsenic, cobalt, copper, iron, nickel, titanium and zinc in grains of all major silicates, oxides and sulfides.

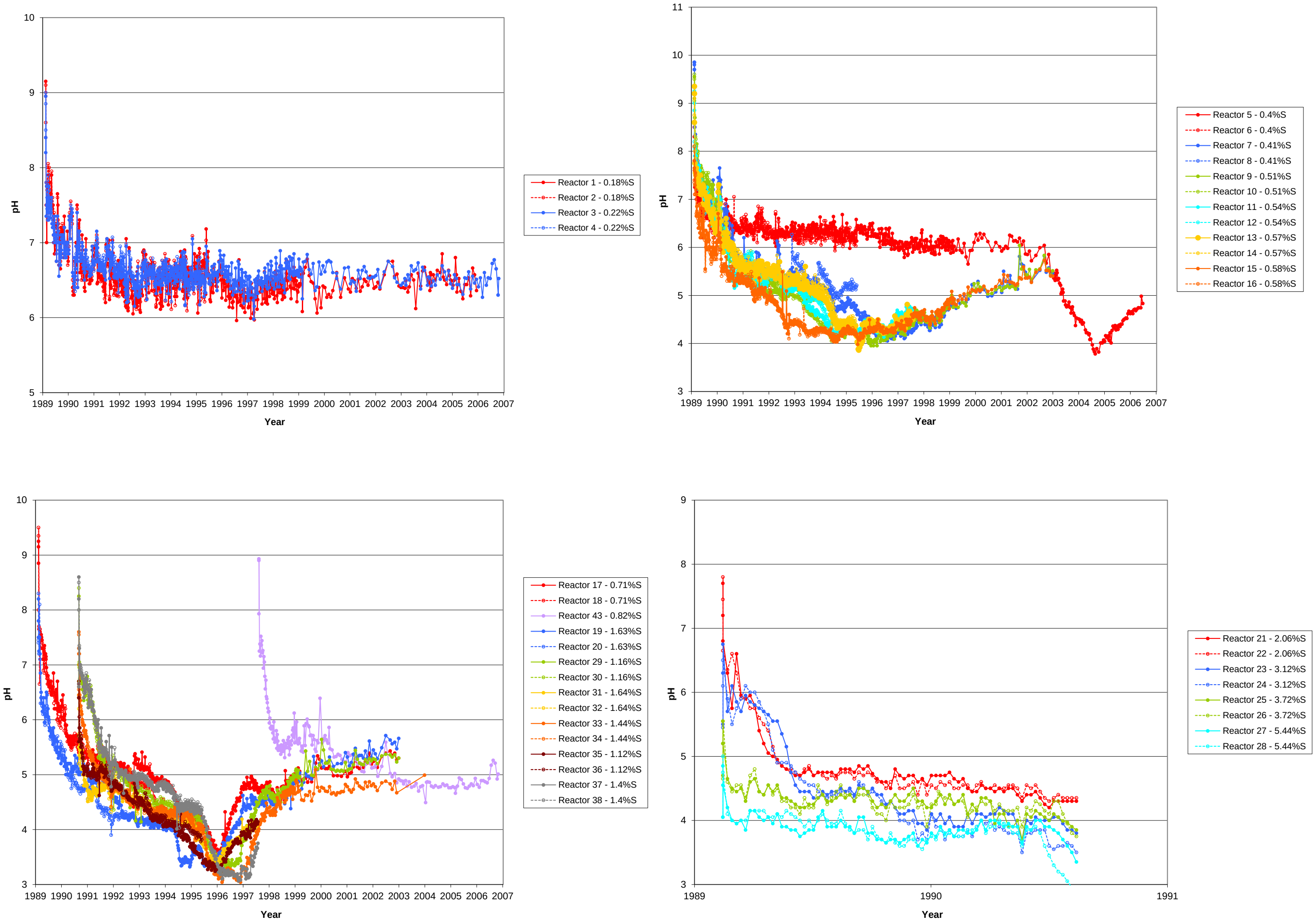

Figure 1 pH Trends for a selection of long term laboratory kinetic tests operated by MDNR-LAM

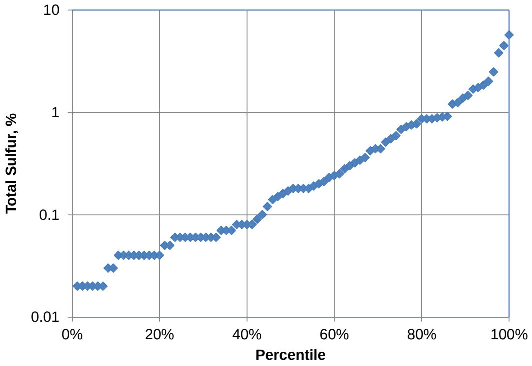

Figure 2 Distribution of sulfur concentrations in rock humidity cells for the NorthMet project. Each symbol is one test.

Humidity Cells

Humidity cells were performed using the ASTM (2001) methodology. The sample charge was 1 kg and the weekly leaching volume was 0.5 L. Leachate analysis included weekly pH, conductivity and ORP; sulfate, acidity, alkalinity, chloride and fluoride every two weeks, and an element scan every two weeks. For every fourth week, the element scan was performed using a low level ICP-MS method. ICP-OES was used for the intervening weeks. This approach recognized that the test work was expected to proceed for many years and therefore was selected to control costs. As the program proceeded, analytical frequency was further reduced. Some humidity cells have now been operating for over 10 years.

Quality Assurance and Quality Control

Routine quality assurance measures included analysis of 10% of solids and leachates in duplicate. In addition, 10% of all kinetic tests were operated in duplicate and blank kinetic tests.

RESULTS AND DISCUSSION

Mineralogical Characteristics

The dominant minerals in all Duluth Complex samples were plagioclase and olivine. Clinopyroxene and orthopyroxene were present in minor quantities with chlorite and serpentine as alteration products. Using microprobe data, plagioclase was determined to be of approximate labradorite composition being calcium enriched and the average composition of olivine was 57% forsterite (Mg_2SiO_4) and 43% fayalite (Fe_2SiO_4).

Dominant sulfide minerals determined from thin sections were pyrrhotite ($Fe_{1-x}S$) and chalcopyrite ($CuFeS_2$). Chalcopyrite was dominant when sulfur concentrations were very low (<0.05%) and in low grade and ore grade samples. Otherwise pyrrhotite dominated. The dominant nickel sulfide was pentlandite ($(Fe,Ni)_9S_8$) and cubanite ($CuFe_2S_3$) tended to be present in comparable amounts to pentlandite. Trace levels of various cobalt, copper, lead, nickel, iron and zinc sulfides and arsenides were identified. Calcite was very rarely identified.

Humidity Cell Results

Leachate Chemistry

Leachate pH trends for two groups of waste rock cells are shown in Figure 3. Samples containing less than or equal to 0.05% sulfur have consistently yielded pHs near 7 following initial decline in pH which lasted approximately 1 year. There has been a slight overall tendency for pH to increase over time in the long term testwork. Samples with more than 0.05% sulfur have also mostly yielded pHs between 6 and 7 with only three samples containing sulfur concentreations exceeding 0.4% showing lower pHs. Alkalinity concentrations have been consistently detected above 1 mg $CaCO_3$/L and tend to be less than 10 mg $CaCO_3$/L.

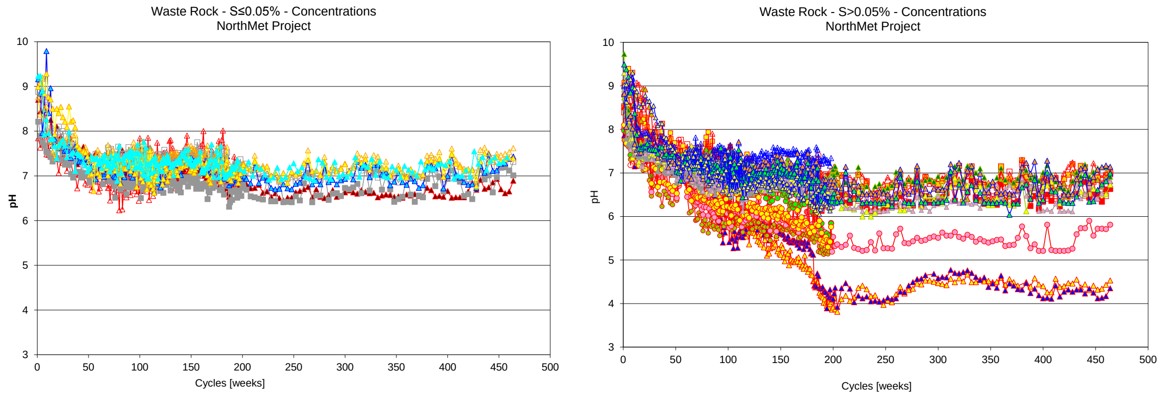

Figure 3 Selected humidity cell results for Duluth Complex samples from the NorthMet project grouped according to sulfide content

Interpretation of Sulfide Threshold for Acid Generation

Method

Long term test work on Duluth Complex samples performed by both MDNR-LAM and PolyMet Mining Inc. shows that samples with 0.4% and greater initial sulfur content generate acidic leachates under laboratory conditions. In this instance, acid generation is defined as a pH of 5.5 which is consistently below that of the deionized water used to leach the samples. MDNR-LAM's long term test work also shows that samples containing about 0.2% sulfide do not generate acid after 20 years of weathering. A sample containing 0.2% sulfur in the NorthMet program has shown pH near 5.5 (Figure 3) but detectable alkalinity (> 1 mg $CaCO_3$/L) is also released. These test data imply that a sulfur criterion for segregation of waste rock should be between 0.2% and 0.4%; however, a residual concern is that any of the MDNR-LAM or NorthMet Project tests with 0.2% sulfur could start to generate acid in the future. The NorthMet data were therefore interpreted to evaluate what the potential threshold of alkalinity release from weathering of silicates could be in order to offset acid generation from sulfide oxidation. The interpretation method used was as follows:

- Leachate from samples containing lowest sulfur concentrations were interpreted to determine if the chemistry was consistent with the silicate minerals that appear to be weathering, and were then used to establish alkalinity generation rates in the near absence of sulfide minerals.
- The correlation between oxidation rates and sulfur content was evaluated.
- Acid generation rates were compared to alkalinity generation rates to determine if a threshold sulfur concentration could be identified and used as a waste managemetn criterion.

Mineralogical Interpretation of Leachates

Selected typical leachates from six humidity cells containing 0.02% sulfur and carbonate content at or below the detection limit of 0.2% CO_2 were modeled using Geochemist's Workbench® to evaluate if leachate composition was consistent with the mineralogy of the samples. Three samples were described as troctolite and three as anorthosite. The latter contains a relatively greater proportion of plagioclase compared to olivine. The minerals assumed to be reacting were chalcopyrite ($CuFeS_2$, reacting amount calculated from sulfate concentrations), anorthite ($CaAl_2Si_2O_8$, reacting amount calculated from calcium), albite ($NaAlSi_3O_8$, reacting amount calculated from sodium), forsterite (Mg_2SiO_4, reacting amount calculated from magnesium) and fayalite (Fe_2SiO_4. reacting amount calculated from magnesium and the composition of olivine indicated by microprobe). The reaction was assumed to occur at 20^oC (laboratory temperature) in the presence of fixed atmospheric oxygen (fugacity of 0.2) and carbon dioxide (fugacity of $10^{-3.4}$). Controlling secondary minerals were assumed to be amorphous ferric hydroxide ($Fe(OH)_3$), malachite ($Cu_2CO_3(OH)_2$), gibbsite ($Al(OH)_3$), kaolinite ($Al_2Si_2O_5(OH)_4$) and amorphous silica (SiO_2).

Measured and modelled leachate pHs were strongly correlated though the model over-predicted leachate pH in all six cases (Figure 4). Over-prediction was greater for the troctolite samples. Modelled alkalinity was very close to measured alkalinity for all six samples (Figure 4). Average modeled silicon concentrations were 1.9 mg/L compared to average measured concentrations of 1.2 mg/L. This modeling demonstrates that measured alkalinity generation can originate from meteoric weathering of the dominant silicate minerals confirming the conceptual model and indicating silicate weathering is a long term source of alkalinity. Stability of long term trends (approaching 10 years for this dataset and 20 years for the MDNR's dataset, Figure 1) has provided sufficient time for stripping of carbonate minerals even if present at the detection limit.

Based on this finding, longer term stable data from humidity cells were used to calculate an average alkalinity generation rate of 3.3 ± 0.4 mg $CaCO_3$/kg/week. The 5th to 95th percentile range for the rates was 2.1 to 5.3 mg$CaCO_3$/kg/week. For subsequent calculations and comparison to acid generation rates, 2.9 mg$CaCO_3$/kg/week as the lower confidence limit (at α=0.05) on the mean was selected to represent long-term base-level alkalinity generation by weathering of silicate minerals. Because the humidity cell tests were operated by leaching with 0.5 L of deionized water, the rate used corresponds to a concentration of about 5.8 mg$CaCO_3$/L

Relationships Between Sulfide Concentrations and Sulfate Release

Average sulfate release rates (calculated after an initial flush of sulfate from the humidity cells had completed at the start of the tests) were compared to sulfide concentrations (Figure 5). The correlation was very strong for sulfur concentrations below 0.1% but was weaker at higher sulfur concentrations where it appeared that some samples yielded distinctively lower sulfate release for a given sulfur content, whereas others showed higher sulfate release at the same sulfur concentration. Correlations of sulfate release and sulfide content have also been reported by MDNR-LAM researchers (Lapakko and Antonson, 2006).

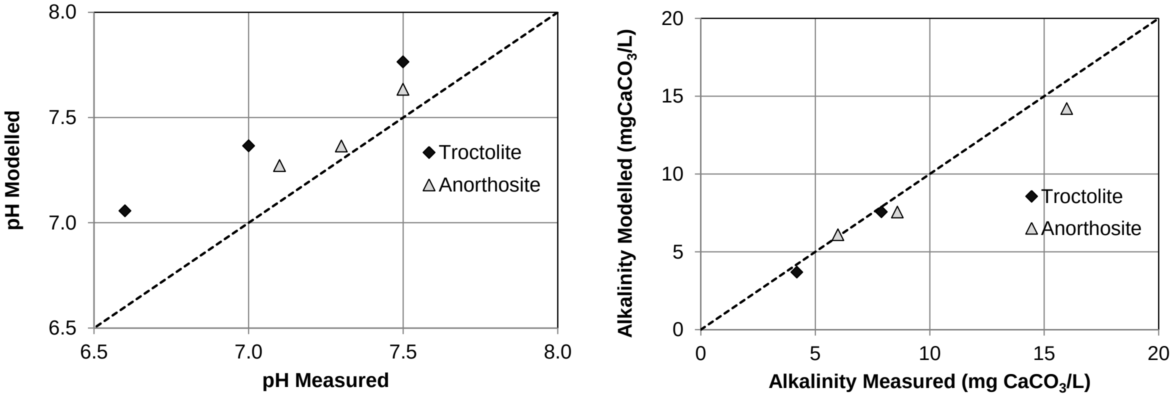

Figure 4. Comparison of measured and modeled humidity cell leachate pH and alkalinity for low sulfur samples. The dashed line indicates parity.

Grouping of samples according to Cu/S weight (mg/mg) ratios (i.e. reflecting the relative amounts of pyrrhotite and chalcopyrite) showed that samples with higher ratios (chalcopyrite enriched) yielded higher sulfate release rates whereas those with lower ratios (pyrrhotite enriched) yielded lower sulfate release. This finding applied across the range of sulfur concentrations including those with low sulfur content (Figure 5). Broadly, the ratio grouping correlates with the economic classification into low grade ore and waste. Three samples classified as lean ore but with lower ratios did not group with the waste rock samples but their sulfate release rates were unstable at the time of the interpretation and subsequently yielded low release rates.

The finding that chalcopyrite appears to oxidize faster than pyrrhotite was counter-intuitive because pyrrhotite is usually considered to be more reactive than chalcopyrite. It was expected that the difference in reactivity could be attribited to differences in mineralogical occurrence (e.g. grain size or crystallinity) but no satisfactory explanation was developed.

DEVELOPMENT OF SULFUR CRITERIA FOR ACID GENERATION POTENTIAL

The conclusion that sulfate release is correlated with sulfide content when Cu/S ratios are considered, was then used to propose sulfur criteria for acid generation potential because a direct link exists between sulfur content and the alkalinity required to offset acid generation. The data in Figure 5 were used to define the two regression equations shown:

$$\text{For Cu/S<0.3: Total S (\%)} = 0.40\ R_{SO4}\,\text{(mg/kg/week)} - 0.70\ (n=15,\ r=0.98) \tag{8}$$

$$\text{For Cu/S>0.3: Total S (\%)} = 0.046\ R_{SO4}\,\text{(mg/kg/week)} - 0.01\ (n=37,\ r=0.93) \tag{9}$$

The alkalinity generation rate (2.9 mg CaCO$_3$/kg/week) was used to calculate a balancing acid generation rate in sulfate equivalents of 2.9 mg SO$_4$/kg/week which was then used to calculate threshold sulfur concentrations by the two regression equations. Due to the need to incorporate conservatism in the estimates for waste management, prediction envelopes were calculated for the regression equations based on a significance level of α=0.05.

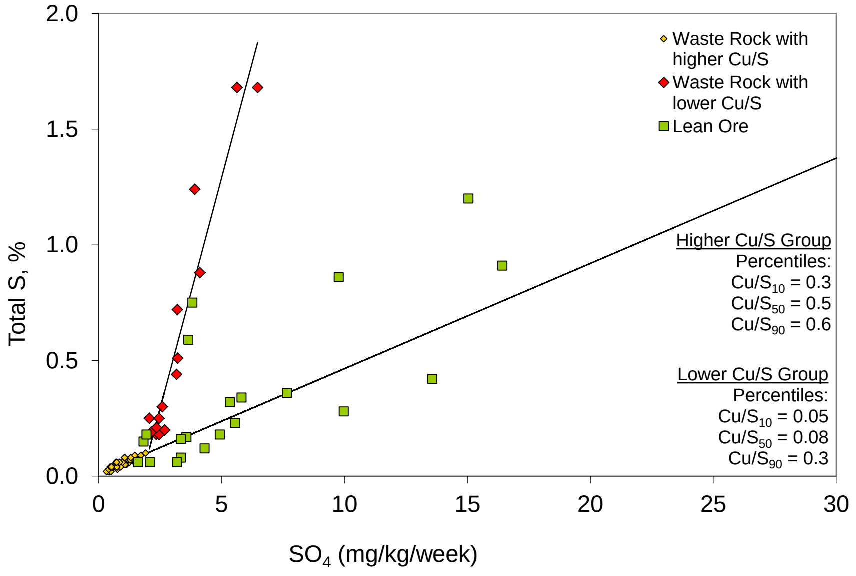

Figure 5 Relationships between average sulfate release and sulfur content

The resulting proposed sulfur criteria were 0.12% for higher Cu/S ratios and 0.31% for lower Cu/S ratios. Both criteria are consistent with the long term testwork performed by MDNR-LAM which showed acid generation occurred for samples with sulfur content greater than 0.4% and a smilar study by Campbell et al. (2012).

For the purpose of waste management, the project proceeded based on a single sulfur criterion of 0.12% due to the lack of an explanation for the difference in sulfide reactivity that resulted in the higher criterion of 0.31%.

CONCLUSIONS

Long term kinetic testwork performed on rocks from the Duluth Complex in northern Minnesota shows that alkalinity generated by weathering of silicate minerals provides a plausible explanation for the lack of acid generation in samples containing low sulfide concentrations. It is concluded that steady alkalinity generation offsets low levels of acid generation. Due to the overwhelming abundance of silicate minerals compared to acid generating sulfide minerals, waste segregation for acid geneation potential is appropriately based on sulfide content rather than coventional acid-base accounting methods. For the NorthMet Project, a site-specific sulfur criterion of 0.12% was adopted.

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NOMENCLATURE

ABA	Acid base accounting
MDNR-LAM	Minnesota Department of Natural Resources Lands and Minerals
NAG	Net acid generation
NP	Neutralization Potential

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