Non-Ferrous Mine Waste Characterization Project Minnesota



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NON-FERROUS MINE WASTE CHARACTERIZATION PROJECT

Kim Lapakko

Minnesota Department of Natural Resources

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0. **EXECUTIVE SUMMARY**

Ten tailings samples from operating North American gold mines and two titanium tailings generated in pilot plant tests were characterized and subjected to dissolution testing to examine the relationship between the solid phase characteristics and drainage quality. The gold mine tailings were quite fine, with roughly 50 to 100% in the minus 270 mesh size fraction. These tailings contained 0.1% to 7.6% sulfur, most of which was associated with pyrite and pyrrhotite, and a total calcium carbonate and magnesium carbonate mineral content of 1.4% to 21%. The neutralization potentials determined by three different static tests generally approximated the content of these carbonate minerals fairly well. The static tests indicated that two of the samples were acid producers and that two samples had marginal potential for acid production.

None of the samples produced acidic drainage during the 52-week dissolution experiment, despite oxidation of iron sulfide minerals present in the tailings. This oxidation was reflected by sulfate concentrations observed in the drainage. Drainage quality data, in conjunction with mineralogic data, indicated that the acid produced by iron sulfide oxidation was being neutralized by the dissolution of the calcium carbonate and magnesium carbonate minerals in the tailings. Furthermore these data suggested that the additional dissolution of some samples may deplete their neutralization potential and ultimately produce acidic drainage. The comparison of sulfide oxidation rates with solid phase sulfur content indicates that the pyrite present in some samples was oxidizing more slowly than that present in others. Determining methods for quantifying the reactivity of pyrite was identified as an important issue in mine waste management.

Barium, zinc, arsenic, antimony, and molybedenum were the most commonly released trace metals. Barium concentrations in mine waste drainage in the field, where high sulfate concentrations are typical, would probably be controlled by the limited solubility of barium sulfate. Arsenic, antimony, and molybedenum, when occurring in elevated concentration as sulfide minerals, may present the greatest potential impact with neutral drainages. These metals are apparently released readily from sulfide minerals, and are fairly soluble in the circumneutral pH range.

Relative to the gold tailings, the titanium tailings were coarser and contained very few sulfide or carbonate minerals. They did contain elevated concentrations of chromium, copper, and nickel. The neutralization potentials determined by three static tests greatly overestimated the total calcium carbonate and magnesium carbonate content of these two samples. Although these tailings produced drainage of lower pH than the gold tailings, they present virtually no potential for acid production due to their minimal sulfide content. Copper, nickel, and zinc concentrations were elevated in these tailings and in the initial drainage. Concentrations subsequently decreased, suggesting that only a small fraction of the metals present in the solid phase were readily leachable under the conditions of this experiment. Additional solid phase examination is required to further examine this hypothesis.

1. **INTRODUCTION**

Exploration for gold, titanium, and other non-ferrous minerals is presently occurring in Minnesota. If an economic deposit is discovered, the mine wastes must be characterized and the mine waste drainage quality must be projected prior to mine development. This information will be used to identify the types of water quality control required to protect the water resources of the state. Since there is presently no mining of base or precious metals in Minnesota, there is little information available on the characteristics of and drainage quality from such mining wastes. The lack of such information will inhibit the effectiveness and efficiency of drainage quality projection, as well as the environmental review and permitting processes.

2. **OBJECTIVE**

The objective of this project is to determine the physical, chemical, and mineralogical characteristics, as well as the dissolution behavior, of a variety of rock samples which simulate potential mine wastes generated by future non-ferrous mineral development in Minnesota. The relationship between the solid phase composition and drainage quality will be examined to identify potential water quality impacts which may be produced by non-ferrous mining in Minnesota. Enumeration of these potential impacts will allow techniques for their abatement to be identified.

Furthermore, the information gathered will enhance the sparse data base presently available on the relationship between solid phase composition and drainage quality. Thus, the project intends to identify potential water quality impacts and aid interpretation of drainage quality prediction tests for non-ferrous mines proposed in Minnesota. This will allow development of non-ferrous mineral resources while minimizing adverse impacts on water resources in the state.

3. MINE WASTE DISSOLUTION

3.1. Introduction

Iron sulfide minerals, trace metal sulfide minerals, as well as calcium carbonate and magnesium carbonate minerals, play a dominant role in the release of acid and trace metals from mine wastes. The generation of acidic waters is the foremost concern for drainages from metallic mine wastes. In addition to high acidity, these drainages typically have elevated concentrations of the leachable trace metals present in the mine waste. Either condition can be toxic to aquatic organisms.

3.2. Acid Production

The stoichiometry of iron sulfide oxidation expresses the relative amounts of reactants required and products yielded in the oxidation of one mole of iron sulfide. Although there are numerous physical, chemical, and biological complexities to be considered, the basic reactions presented represent the fundamental process of acid generation as an oxidation

of iron sulfide minerals to an assumed equilibrium state. Intermediate stages of the reaction are not considered, nor is the influence of other solid or dissolved components which may be present in a complex reaction environment.

The dissolution of iron sulfide minerals leads to the majority of acid production by mine wastes. Although there are numerous different iron sulfide minerals, the oxidation of a simple iron sulfide mineral is represented by reaction 1 (Nelson, 1978). The overall reaction

$$FeS(s) + (3/2)H_2O + (9/4)O_2(g) = FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq)$$
[1]

of FeS with water and oxygen releases two moles of acid and one mole of sulfate. The two moles of acid produced are the net result of the oxidation of ferrous iron and the subsequent precipitation of ferric iron, as lepidocrocite, in this example (Nelson, 1978; Sung and Morgan, 1980). The oxidation of sulfide to sulfate does not produce acid.

$$S^{2}(aq) + 2O_{2}(g) = SO_{4}^{2}(aq)$$
 [2]

The most common iron sulfide associated with mine wastes is pyrite (FeS₂). The stoichiometry of pyrite oxidation is presented in reaction 3 (Stumm and Morgan, 1981). As in reaction 1, two moles of acid are produced by the oxidation and subsequent precipitation

$$FeS_{2}(s) + (5/2)H_{2}O + (15/4)O_{2}(g) = FeOOH(s) + 4H^{+}(aq) + 2SO_{4}^{2}(aq)$$
[3]

of iron. An additional two moles of acid are produced by the oxidation of the two moles of sulfur, which have an average oxidation state of -1, to sulfate.

$$S^{-1} + (1/2) H_2O + (7/4)O_2(g) = SO_4^{2-}(aq) + H^+(aq)$$
 [4]

Two points regarding the stoichiometry of these reactions are of particular interest to the prediction of acid mine drainage. First, the oxidation of iron sulfide minerals yields two moles of acid for each mole of sulfur present in the iron sulfide. This is one of the fundamentals upon which static tests are based. Second, the molar ratio of sulfate release to acid release is 2:1, which can facilitate interpretation of water quality data generated by mine waste dissolution.

This interpretation can be complicated by the dissolution of sulfate minerals which yield other sulfate to acid ratios. Calcium sulfate dissolution will yield sulfate to solution but no acid (reaction 5). Jarosite dissolution may result in a molar ratio of sulfate release to acid release of 1.5:1 (reaction 6). The molar ratio of sulfate to acid released to solution may also

$$CaSO_4(s) = Ca^{2+}(aq) + SO_4^{2-}(aq)$$
 [5]

$$KFe_{3}(SO_{4})_{2}(OH)_{6}(s) = K^{+} + 3FeOOH(s) + 2SO_{4}^{2}(aq) + 3H^{+}(aq)$$
[6]

be altered by the precipitation of calcium sulfate. This would occur if the calcium and sulfate concentrations increased to the point where the calcium sulfate solubility product

were exceeded.

The rate of iron sulfide oxidation is influenced by the pH in the immediate vicinity of the mineral surface. Kleinmann et al. (1980) described three pH dependent phases of this oxidation. The oxidation is slow in the neutral to mildly acidic (~pH 4.5) range. As pH decreases the environment becomes more favorable to *Thiobacillus ferrooxidans* bacteria, which accelerate the rate of sulfide oxidation and consequent acid production. As the pH in the microenvironment around the sulfide mineral decreases below about 3, the aqueous concentration ferric iron reaches a level at which it oxidizes the iron sulfide at a more rapid rate. This reaction sequence is also bacterially mediated.

The sulfide mineral composition may affect acid production in at least three ways. First, the oxidation rates and, therefore, acid production rates vary among iron sulfide minerals. Second, galvanic interaction among minerals can affect sulfide mineral oxidation rates (Natarajan and Iwasaki, 1983). Finally, trace metals released by one sulfide mineral may accelerate dissolution of others by catalyzing sulfide oxidation (Nelson, 1978).

The rate of oxidation varies among iron sulfide minerals and even among different forms of pyrite. For example, marcasite (FeS₂) is also reported to be more reactive than pyrrhotite (Fe_{n-1}S_n, Reimers and Hjelmstad, 1987). Marcasite and pyrite have the same chemical formula but a different mineral structure. For minerals separated from Texas lignite, the order of reaction rate was reported as marcasite > framboidal pyrite > crystalline pyrite (Pugh et al., 1984). For pyrite occurring with coal, framboidal pyrite has been observed to oxidize twice as fast as crystalline pyrite of the same particle size (Caruccio, 1990).

Hammack (1985) found that pyrite samples with "coatings of sulfate salts and iron oxides" were less reactive than uncoated samples. The surface properties and surface reactivities of coal pyrites are also reported to differ from those of "mineral" pyrite (Lai et al., 1989). Their results indicated that at 88% humidity and 21% oxygen, the abiotic oxidation rate in air of coal pyrite was almost four times that of mineral pyrite. Under the same reaction conditions, Hammack et al. (1988) found oxidation rates to increase in the order sedimentary/hydrothermal pyrite < hydrothermal pyrite < hydrothermal pyrite /marcasite < sedimentary pyrite. The rates determined were based on the sulfate/sulfide ratios at the mineral surface which neglect the influence of mass transfer.

3.3. Trace Metal Sulfide Oxidation

The oxidation of trace metal sulfide minerals releases trace metals but does not contribute acid (reaction 7). Concentrations of trace metals tend to increase exponentially as solution

$$CuS(s) + 2O_2(g) = Cu^{2+}(aq) + SO_4^{2-}(aq)$$
 [7]

pH decreases, therefore acidic drainages often contain elevated trace metal concentrations. However, circumneutral drainages can contain elevated concentrations of trace metals such as nickel (Eger and Lapakko, 1985) and molybdenum (Brown, 1989) which, compared to other trace metals, are relatively soluble in this pH range.

3.4. Acid Consumption

The balance between the rates of acid production by iron sulfide oxidation and host rock buffering will determine the acidity of mine waste drainage. Calcium carbonate is the most effective mineral for neutralizing the acid produced by the oxidation of iron sulfides, and can be used to mitigate acid release. Reaction 8 is the dominant reaction above about pH 6.3, while reaction 9 is dominant at lower pH. Magnesium carbonate can also neutralize

$$CaCO_{3}(s) + H^{+}(aq) = HCO_{3}(aq) + Ca^{2+}(aq)$$
 [8]

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq)$$
[9]

acid, but its rate of dissolution is reported to be slower than that of calcium carbonate (Rauch and White, 1977). Carbonates of iron and manganese will provide no net neutralization.

3.5. Available Reactive Sulfide Surface Area

The available sulfide mineral surface area will influence the quality of mining waste drainage. The oxidation rate of individual metal sulfide minerals has been reported to be directly proportional to the reactive sulfide mineral surface area available (Sato, 1960a, 1960b; Sato and Mooney, 1960; Nelson, 1978; Lapakko, 1980). The reactive sulfide mineral surface area present is a function of the sulfide grain size, the roughness of the grain surface, and the mode of mineral occurrence within the rock matrix. As particle size decreases, the specific surface area (surface area per unit mass) increases. Thus, a kilogram of small iron sulfide particles will oxidize more rapidly than a kilogram of larger particles, since the small particles have a larger surface area. Similarly, a rough particle will have a greater surface area than a smooth particle of the same diameter and mass.

The mode of occurrence of sulfide minerals within the host rock will influence the availability of the mineral surface for reaction. Sulfides which are liberated (free from the matrix of the rock and its other minerals) will have their entire surface area available for reaction. Sulfides which are included within other minerals will not be available for reaction with atmospheric oxygen and water. As particle size decreases the extent of sulfide liberation increases. In larger rocks sulfide minerals are more likely to occur within the rock matrix, as inclusions within other minerals or between other minerals (interstitially). Over time these minerals may be liberated by physical and/or chemical weathering of the encapsulating rock or mineral.

4. **BACKGROUND ON PREDICTIVE TESTING**

4.1. Introduction

Sources of information relevant to predicting the release of acid from mine waste include (modified from Ferguson and Erickson, 1987):

- previous experience with the mine waste;
- chemical, mineralogical, and physical analyses of the waste;
- static tests designed to quantify the content of acid producing and acid consuming minerals;
- kinetic tests which examine rates of dissolution;
- field dissolution tests; and
- mathematical models.

The most accurate method of determining the quality of a waste is to expose operational scale waste to environmental weathering for decades. Since this is typically impractical within the time frame for permitting a proposed mine, numerous tests have been developed to estimate drainage quality more rapidly. Static tests applied to mine wastes focus on quantification of total capacity to produce acid (e.g. iron sulfide content) and to consume acid (e.g. calcium carbonate and magnesium carbonate content). These solid phase characteristics are dominant influences on the release of acid and trace metals. Kinetic tests generate information on dissolution of mine wastes in laboratory tests.

The objective of static tests is to quantify the capacity of a mine waste to produce acid and its capacity to consume acid. These capacities are typically based on analysis of solid phase characteristics such as sulfur content and a neutralization capacity typically determined by some form of titration. Comparison of these potentials by difference (Sobek et al., 1978) or ratio (Caruccio et al., 1980) typically is used to determine if a waste will generate acid.

Kinetic tests address the rates of acid production and consumption, and are typically more expensive and time consuming than static tests. In these tests mine waste samples are allowed to oxidize under prescribed conditions. The resultant drainage quality is then assumed to represent that which would be generated by the actual mine waste under field conditions.

Each of the tests presents information which is to some degree relevant to the drainage quality generated by the mine waste in the field. However, at present there is no one test which can produce all the information necessary to evaluate all mine wastes under all conditions of disposal. As stated by Lawrence et al. (1989), who reviewed several tests for predicting mine waste drainage quality, "It is more likely that a combination of two or more tests will provide a more confident assessment but even then, for some samples, prediction might be uncertain." Furthermore, the testing process is complex. "Considerable skill and experience is required to conduct some tests and interpret results for accurate forecasts of mine drainage quality" (Ferguson and Erickson, 1987).

4.2. Static Tests

The objective of static tests is to quantify the capacity of a mine waste to produce acid and its capacity to consume acid. These tests do not take much time, are fairly inexpensive and simple, and are useful in predicting acid mine drainage "when the difference between acid producing and neutralizing mineral content is wide" (Ferguson and Erickson, 1987). They have been proposed as an initial screen for the acid drainage potential of mine wastes (Ferguson and Erickson, 1987; Lawrence et al., 1989). One shortcoming of the static tests is that they measure only the capacities for acid production and consumption, and do not consider the relative dissolution rates of acid producing and acid consuming minerals. Secondly, they assume all of the acid producing and acid consuming material present will react.

To accurately determine the capacity for acid production (or consumption), it is necessary to measure those and only those components which lead to acid production (or acid neutralization). Thus, the capacity for acid production should be calculated based on sulfur associated with iron sulfide minerals (reaction 1), some organically bound sulfur (Dollhopf, 1984), and sulfate associated with jarosite (Dollhopf, 1989). Sulfate minerals such as gypsum (CaSO₄) will not generate acid. Similarly, the capacity for acid consumption should measure the content of calcium carbonate, magnesium carbonate, and other buffering minerals. Typical techniques involve acid addition to the waste sample. The extent of reaction can be determined by either titration with base to determine the amount of acid consumed or measurement of the amount of carbon dioxide evolved (Evangelou et al., 1985; Morin, 1989).

Acid-Base Accounting, or ABA, was designed to evaluate the acid producing capacity of coal mine wastes. It was developed by Smith et al. (1974) and, subsequently, modified by Sobek et al. (1978). One of the early applications was presented by Caruccio et al. (1980). The test determines the acid producing potential (APP) and acid neutralizing potential (NP) of a mine waste. Whether or not a waste will produce acid is determined by the Net Neutralization Potential, which is the difference between these values (NP - APP = NP). The APP is determined based on the total sulfur content, and assumes that two moles of acid will be produced for each mole of sulfur present (reactions 1, 3). The sulfur content in percent is multiplied by 31.25 to yield the APP in units of tons acidity per 1000 tons rock (or equivalently, kg acidity per metric ton rock).

The APP calculation assumes that two moles of acid will be produced for every mole of sulfur present. If sulfur compounds which do not produce acid (including sulfate minerals such as gypsum, $CaSO_4$, and many forms of organic sulfur) are present in significant quantities, the use of total sulfur will overestimate the acid production potential. The sulfur present with gypsum will contribute to the total sulfur, but will not produce acid (reaction 5). An example of this shortcoming was presented by Lawrence et al. (1989).

To correct for the presence of sulfate minerals which do not produce acid, the APP can be based on the sulfide sulfur content (Lawrence et al., 1989). This procedure may underestimate the APP if acid producing sulfate minerals (e.g., jarosite) are present. Another procedure considers the potential contribution of both sulfides and acid-producing sulfate minerals (Reclamation Research Unit, Schafer and Associates, 1987). The oxidation of trace metal sulfides also release sulfate, as well as the associated trace metal, but does not contribute acid (reaction 7).

The ABA neutralization potential is determined by adding hydrochloric acid (the volume and strength of which is determined by the "fizz" test) to the sample, boiling, and then titrating with sodium hydroxide to determine the amount of acid consumed by the rock. The neutralization potentials calculated assume each mole of calcium carbonate or magnesium carbonate present will consume two moles of acid (reactions 9, 10). While these

$$MgCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Mg^{2+}(aq)$$
 [10]

reactions most likely contribute to acid consumption, it is possible that the stoichiometry is not precise. Above approximately pH 6.3, it seems likely that some fraction of the calcium carbonate and magnesium carbonate dissolution involves only one mole of acid per mole of carbonate mineral dissolved (reactions 8, 11).

$$MgCO_3(s) + H^+(aq) = HCO_3(aq) + Mg^{2+}(aq)$$
 [11]

Sobek et al. (1978) indicated that waste would produce acid if and only if Net NP (Net NP = NP - APP) was less than -5 kg CaCO₃/t, and results presented by Lawrence et al. (1989) were consistent with this value. Day (1989) suggested that a Net NP value of +10 kg CaCO₃/t be used as the threshold for acid production, while Morin (1989) observed values of -15, +10, and +20 kg CaCO₃/t for a modified procedure on various sets of samples. Ferguson (1989) indicated that it was difficult to determine the acid generating character of samples with Net NP values in the range of -20 to +20 kg CaCO₃/t.

Drafts of California regulations proposed a NP:APP ratio of three as the acid production threshold value for the initial mine waste screen (Krull, 1988). Although this value appears to be conservative, no published reference for its establishment was found. In particular, the ratio provides a more conservative threshold value if the APP is high. For example, using a threshold Net NP value of 5 kg CaCO₃/t seems relatively safe if the APP is 1 kg CaCO₃/t (i.e., APP = 1, NP = 6 kg CaCO₃/t). However, if the APP is 150 kg CaCO₃/t, the 5 kg CaCO₃/t difference between APP and NP may provide a less comfortable safety factor. An interesting feature of this approach is observed when sulfur content reaches eight percent, at which point the carbonate content necessary to meet the 3:1 criterion occupies the remaining 92 percent of the solid. Thus, all solids exceeding eight percent sulfur would be classified as acid producers in the initial mine waste screen.

A potential shortcoming of the Sobek et al. (1978) technique is the possible overestimation of the NP due to three factors. First, the strong acid used in this method may dissolve minerals which would not consume acid under the conditions typical of the environmental dissolution (Lutwick, 1986). Furthermore, the strength of acid addition is based on the qualitative interpretation of the "fizz" test. Adding an excessive amount of acid based on this qualitative interpretation would further compound this problem. A second potential problem with techniques using boiling HCl digestion is that iron and manganese carbonates (e.g., siderite, rhodochrosite), which provide no net neutralization, may contribute to the measured neutralization potential. Consequently, these techniques may overestimate the neutralization provided by wastes containing significant amounts of these carbonates. Thirdly, the neutralization potential determined by this method may also be overestimated due to contributions from metal hydroxides which precipitate during the titration with sodium hydroxide (Ferguson and Erickson, 1988).

The Modified Acid Base Account bases the APP on the sulfide sulfur content and uses a 24-hour ambient temperature digestion to determine the neutralization potential (Coastech, 1989). The pH is checked at least once after six hours of reaction, and for the test to be valid, a pH in the range of 1.5 to 2.0 must be attained. The solution is then titrated to pH 8.3 to determine the amount of acid consumed by the sample.

To address the problem of adding excessive or inadequate amounts of acid, Lawrence (1989) has measured the pH following the addition of acid to the sample. If the pH is not in the range of 1.5 to 2.0, the acid addition is modified. An excessively low pH may indicate depletion of the carbonate minerals and subsequent attack of the host rock. Consequently, minerals which buffer less effectively may contribute to the measured neutralization potential. A high pH indicates incomplete digestion of carbonate minerals and, consequently, an underestimate of neutralization potential.

Conducting the acid digestion at a low temperature, as opposed to boiling, may reduce potential contributions to the measured NP from iron carbonate minerals. Coastech (1989) examined a 24-hour digestion at room temperature. Data presented by Frisbee and Hossner (1989) suggest that decreased dissolution of iron carbonates would be expected at the lower temperature. If so, this digestion may more accurately determine neutralization potential for samples containing siderite (FeCO₃) and possibly rhodochrosite (MnCO₃). However, the presence of these minerals was not reported in the samples tested by Coastech (1989), and the NP determined by this technique was generally higher than that by the standard technique.

To gain insight into the components which provide buffering, Lawrence (1989) constructed titration curves describing the neutralization of the acid digestate. The pH 7.0 endpoint for the NaOH titration has also been reported as unstable, and an endpoint of pH 8.3 has been proposed (Coastech, 1989).

The Alkaline Production Potential: Sulfur Ratio Test was developed by Caruccio et al. (1981) to evaluate the potential of coal mine wastes to produce acid. It is similar to the ABA procedure in that it uses total sulfur content to reflect the potential for a sample to produce acid. The ability of a sample to consume acid is referred to as the Alkaline Production Potential (APP). This value is quantified by adding 20 mL of 0.1N HCl to 500 mg of minus 23 micron sample. After two hours at room temperature the mixture of acid and solids is titrated to pH 5.0. The acid consumption is compared to values of know calcium carbonate standards.

4.3. Kinetic Tests

The rates of acid production and consumption can be addressed in kinetic tests, which are typically more expensive and time consuming than static tests. In these tests mine waste samples are allowed to oxidize under prescribed conditions. The resultant drainage quality is then assumed to represent that which would be generated by the actual mine waste under field conditions. Detection of acid generation after an initial lag period requires an extended period of experimentation (Hedin and Erickson, 1988; Miller and Murray, 1988). Erroneous conclusions could be drawn based strictly on the drainage quality observed during the tests. Neutral drainage could be observed over the relatively short duration of the test but, over a longer period in the field, the neutralization potential could be depleted with resultant drainage acidification. Thus, the rates of acid production and consumption can be determined from kinetic tests, but it may be time consuming to experimentally determine if the acid neutralizing capacity will be depleted before the acid producing capacity.

5. **METHODS**

5.1. Sample Collection

Tailings and feed samples were received from eight North American gold mines. Samples of magnetic and table tailings generated in pilot plant testing of a North American titanium ore bulk sample were also collected.

5.2. Solids Analysis

The samples were analyzed for particle size distribution in the Hibbing DNR office and by Hanna Research. Samples were analyzed by Bondar Clegg for parameters of regulatory interest, major solid phase components, and a set of miscellaneous parameters included in the ICP analytical package. The analyses were conducted on a solution generated by digestion of the solids in a heated 3:1 mixture of hydrochloric and nitric acid. Most metals were analyzed directly by ICP, with the following exceptions. Thallium was extracted with MIBK and analyzed by graphite furnace. Gold was analyzed using fire assay extraction with analysis by gravimetric finish and/or atomic absorption. Mercury was analyzed by graphite furnace atomic absorption. Silica was analyzed by peroxide fusion with gravimetric finish.

Sulfur was analyzed by LECO induction furnace and sulfate was analyzed using a sodium carbonate leach. Carbon dioxide was analyzed using a Coolermetrics carbon dioxide analyzer.

The Bondar-Clegg chemical analyses did not account for 100% of the material present, therefore, Hanna Research reanalyzed for the major rock forming elements. There were two apparent reasons for this problem. First, Bondar-Clegg reported some parameters as simply "greater than" a given value, thus there was no accurate quantification. Secondly, the digestive technique selected for the Bondar-Clegg analyses did not dissolve the entire sample, therefore, some the major rock forming elements were not released to solution for analysis.

For analysis of Ca, Mg, Na, K, Fe, Mn, Al, and P Hanna Research used a multi-acid digestion with hydrochloric, hydrofluoric, and 50% sulfuric acids. The solid/acid mixture was baked dry and redissolved with a solution of distilled deionized water and hydrochloric acid. For analysis of Cr, Ti, and V samples were digested with a mixture of sulfuric and phosphoric acid.

Mineralogical analyses were conducted by Louis Mattson of the Hanna Research Center. X-ray diffraction (XRD) was used for mineral identification as well as determination of the approximate modal composition. This analysis was applied to the bulk sample and to a heavy mineral concentrate. The heavy mineral concentrate was analyzed to more accurately identify the sulfides and other heavy minerals present. This was necessary since the sulfide content of the tailings was fairly low.

The chemical analyses were used in conjunction with XRD data to more accurately determine the mineral composition. The formula for dolomite used by Hanna was 30% CaO, 22% MgO, and 48% carbon dioxide. The corresponding contents for ankerite were 30%, 15%, and 45%, with the remaining 10% composed of iron oxide. The values for dolomite composition are theoretical while those for ankerite are "typical" for ankerite. The extent of sulfide and carbonate mineral liberation was determined by wet screening on 100, 270, and 500 mesh sieves, and using optical microscopy to examine the fractions separated.

The Acid-Base Accounting static test was conducted using the method of Sobek et al. (1978). The sulfur content was determined by LECO furnace and multiplied by 31.25 to tield the Acid Production Potential in units of kg/metric ton rock. The "fizz" test was used to determine the acid addition required for the Neutralization Potential determination. Hydrochloric acid (about 25 percent concentration) was added to the sample and the extent of "fizzing" was observed. Based on the vigor of this reaction, the volume and concentration of hydrochloric acid (HC1) to be added to 2 grams of minus-60 mesh mine waste was determined (no fizz: 20 mL 0.1N HCl; slight fizz: 40 mL 0.1N HCl, moderate fizz; 40 mL 0.5N HCl; strong fizz: 80 mL 0.5N HCl). The mixture of acid and mine waste was then boiled until the reaction ceased, as indicated by the termination of the production of bubbles. The volume was increased to 125 mL and the mixture was boiled for one minute then cooled. The solution was then titrated to pH 7.0 with sodium hydroxide (NaOH) to determine the amount of acid consumed by reaction with the rock.

For the Modified Acid Base Account the APP was based on the sulfide sulfur content (Coastech, 1989). As with the ABA procedure, the "fizz" test was used to determine the acid addition. The mixture of acid and the 2.00 g, minus 60 mesh sample was digested for 24 hours at room temperature on a shaker table (25 to 30° C). The pH was checked at least once after six hours of reaction, and for the test to be valid, a pH in the range of 1.5 to 2.0 was required. The solution was then titrated to pH 8.3 to determine the amount of acid consumed by the sample.

For the Alkaline Production Potential: Sulfur Ratio Test, total sulfur content was used to determine the potential for a sample to produce acid. The capacity to consume acid was quantified by adding 20 mL of 0.1N HCl to 500 mg of minus 23 micron sample. After two hours at room temperature the mixture of acid and solids was titrated to pH 5.0.

5.3. Dissolution Experiment Procedure

Several techniques have been used in laboratory leaching of mining wastes (Caruccio, 1986; Ferguson and Mehling, 1986). The method used was based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water (Gottschalk and Buehler, 1912; Caruccio et al., 1980; Lawrence et al., 1989). Samples (75 g) of tailings were placed into the upper segment, or reactor, of a two-stage filter unit (figure 1). To each reactor, 200 mL of distilled deionized water was added and allowed to drain through the tailing sample overnight. This rinsing was repeated weekly for 52 weeks. Between rinses the solids were retained in the reactors and stored in a box to undergo further oxidation. All samples were run in duplicate.

A cover was placed about 3 cm above the upper edge of the box to allow drying of the solids and prohibit the input of airborne debris. A thermostatically controlled heating pad was placed beneath the box to maintain a constant temperature. The box was stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. Temperature and relative humidity in the box were monitored four to five times per week.

5.4. Water Quality Analysis

The rinse water, or drainage, was analyzed for pH directly in the lower stage of the reactor. Samples were then filtered and analyzed on site for alkalinity, acidity, and specific conductance. Samples were also collected for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.1 mL Instra-Analyzed nitric acid (Baker) per 50 mL sample. An Orion SA 72 pH meter, with a Ross combination pH electrode (8165), was used for pH analysis and a Myron L conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al., 1975). The barium sulfate turbidimetric technique was used for sulfate analysis (APHA et al., 1975). Metals were analyzed by Bondar-Clegg using either ICP or a Perkin Elmer 603 atomic absorption spectrophotometer.

6. **RESULTS AND DISCUSSION**

6.1. Solid Phase Analysis

6.1.1. Particle Size

The ten gold mine tailings, samples T1-T10, were quite fine. The -500 fractions of these samples comprised from 26% to 91% of the total samples mass, and from 47% to 97% of the samples were finer than 270 mesh (table 1). Samples T5 and T6 were the coarsest, while sample T7 was the finest. In contrast, titanium tailing samples T11 and T12 contained only 0.75% and 16.08%, respectively, in the -500 mesh fraction.

6.1.2. Chemistry

As presented in earlier discussion, sulfur content is an indicator of the potential presence of iron sulfide minerals and/or jarosite. In turn, dissolution of these minerals will lead to acid production. The total sulfur contents of the samples ranged from less than 0.02% to 7.63% (table 2). With the exception of samples T2, T9, and T10, the sulfate concentrations in the tailings were less than 0.2%, and typically less than 0.1%. Subtraction of the sulfate-sulfur from the total sulfur values yields sulfide-sulfur values in the range of less than 0.01% to 7.3%.

The carbon dioxide concentrations in the samples ranged from 0.16% to 21.85%. These values indicate the presence of variable amounts of carbonate minerals. Samples T11 and T12 were distinct from the remaining samples in that they were very low in both sulfur and carbon dioxide content. These two samples were titanium tailings while the remaining samples were from gold mining operations.

Trace metal analyses indicate elevated concentrations of arsenic in samples T7, T8, and T9. Sample T9 had slightly lower arsenic levels and the highest concentrations of mercury, molybdenum, and antimony. Sample T11 had the highest chromium and copper concentrations.

6.1.3. Mineralogy

The key parameters with respect to acid generation are the iron sulfide minerals. The iron sulfide content of the samples ranged from near zero for samples T11 and T12 to 13.6 percent for sample T7 (table 3). Calcium carbonate and magnesium carbonate are the dominant minerals for acid neutralization. The major forms of these two minerals are calcite and dolomite, respectively, although both compounds are also present in ankerite. The typical calcite content of the samples ranged from 0.2 to 1.5 percent, with two samples beyond this range. The frequency distribution with respect to dolomite content was bimodal. Six of the samples contained virtually no dolomite while the remaining six contained 10 to 21 percent (table 3).

The release of trace metals from mine waste samples is largely a function of the trace metal content, the mineral form in which the metal is present, the chemistry of the individual metal, and the pH of the drainage. With the exception of samples T11 and T12, the trace elements of regulatory concern are present as sulfides (table 3). With samples T11 and T12, olivine and serpentine contained most of the nickel. Arsenopyrite, galena, and sphalerite, as well as their oxidation products, were most likely the respective sources of arsenic, lead, and zinc in these two samples.

As indicated in table 1, most of the samples were very fine, typically 50 to nearly 100 percent in the minus 270 mesh fraction. With the exception of samples T11 and T12, the pyrite, pyrrhotite, and carbonate minerals were all well liberated (table 4). These two samples were coarser than the others and contained only trace amounts of sulfides and carbonates. The sulfides observed in these samples were partially oxidized and generally poorly liberated.

6.2. Static Tests

The determination of Acid Production Potential (APP) for the ABA and APP:S methods is based on the total sulfur content, while that for the Modified ABA technique is based on the sulfide-sulfur content. Since there was little difference between the total sulfur content and the sulfide-sulfur content of the samples (i.e., the samples contained little sulfate), the APP values did not vary greatly among the three techniques. The Neutralization Potential (NP) values were variable. With the exception of sample T11, the NP determined by the ABA method exceeded that determined by the Modified ABA method. In eight of the 12 samples, the NP determined by the APP:S method was the lowest.

The ABA technique identified samples T9 and T2 as acid producers, based on Net NP values of -151 and -26 kg $CaCO_3/t$, respectively. Sample T6 yielded a Net NP of 1 kg $CaCO_3/t$, in the range of -20 to +20 kg $CaCO_3/t$. Ferguson (1989) indicated it was difficult to determine the acid generating character of samples in this range. The Net NP of the remaining samples, using the ABA method, ranged from 65 to 260 kg $CaCO_3/t$ (table 5).

The Modified ABA Test requires that a pH in the range of 1.5 to 2.0 following the acid addition for determination of Neutralization Potential. Of the 12 tailings samples subjected to the test, only one of the samples met this requirement initially. The remaining samples were tested again using an increased or decreased acid addition. Although the target pH zone was attained in only one additional case, the pH values observed were adequate for reasonable extrapolation of the NP value for the target zone. More detailed data on the ABA and Modified ABA tests are presented in appendix 3.

The Modified ABA technique also identified sample T9 and T2 as acid producers, based on respective Net NP values of -141 and -66 kg $CaCO_3/t$. Samples T6 and T10 were in the marginal range of -20 to +20 kg $CaCO_3/t$. The Net NP of the remaining samples ranged from 30 to 211 kg $CaCO_3/t$ (table 5).

The APP:S technique was consistent with the previous two techniques in identifying sample T9 as having the strongest potential to produce acid (Net NP = $-150 \text{ kg CaCO}_3/t$). Samples T2 and T10 were also identified as acid producers, with Net NP values of -81 and $-32 \text{ kg CaCO}_3/t$. Samples T6 and T11 were in the marginal range, although it seems most unlikely sample T11 would produce acid due to the very low sulfur content (table 5). The Net NP of the remaining samples ranged from 34 to 179 kg CaCO₃/t.

The NP/APP ratio is generally a more conservative quantifier for potential acid producers. The NP and APP from the Modified ABA technique were used to calculate this ratio. As with the previous classifications, this approach identified sample T9 as having the greatest potential to produce acid. This is indicated by the lowest NP:APP ratio of 0.10. In accord with the previous classifications, samples T2 and T6, respectively, exhibited the next highest potential for acid production. In addition, samples T8 and T10 also had NP/APP ratios less than three (table 5).

Thus, there was general, but not precise, agreement among the various methods of identifying acid producing samples. The various Neutralization Potential analyses generally

estimated the buffering mineral content fairly well (tables 5, 9). All methods identified samples T9 and T2 as acid producers. Assuming all of the Neutralization Potential in sample T2 were available to neutralize the acid produced by oxidation of the iron sulfides, a long time would be required before this sample produced acid drainage. In contrast, sample T9 has one-tenth the NP and would acidify much sooner. With the exception of the ABA technique, samples T6 and T10 were identified as having some potential for acid production, while the potential for acid production by sample T8 was slight. The remaining seven samples (T1, T3, T4, T5, T7, T11, T12) exhibited very little potential for acid production.

The NP determined by the ABA method was highly reproducible and tended to increase as the acid addition increased. Four of the samples were subjected to this test in duplicate. The difference from the mean for these pairs ranged from 0.65% to 7.6%, with an average value of 3.8% (table 6). Samples T8 and T11 were each subjected to two different acid additions. At the higher acid addition the NP values exceeded those at the lower acid addition by factors of 2.2 and 1.7, respectively (table 7). The amount of acid added in this test is determined by a subjective evaluation of the "fizz test" (see Section 4.2). The results presented in table 7 indicate that the NP value could readily vary by a factor of two, depending upon the laboratory technician's interpretation of the "fizz test".

The NP values determined by the Modified ABA digestion technique also tended to increase as the acid addition increased (table 8). Since this technique also requires a pH in the range of 1.5 to 2.0 after the acid addition, more consistent readings would be expected. That is, the acid addition would be determined by the objective criterion of the target pH range rather than the subjective interpretation of the "fizz test."

6.3. Dissolution Experiments

Due to an equipment problem at the analytical laboratory (Bondar-Clegg), the final set of metal analyses have not been completed. When their ICP is repaired, the samples will be analyzed. The data generated and the attendant data analysis and discussion will be incorporated into a revision of this report.

The weekly rinse volume and a total of 44 water quality parameters were analyzed at varying frequencies throughout the 52 week experiment. Over the course of the 52 week experiment the temperature ranged from 18.9° C to 30.6° C, with a mean of 26.9° C and a standard deviation of 1.6° C. The relative humidity ranged from 35% to 80%, with a mean of 54.9% and a standard deviation of 8.8% (figure 2). The complete set of water quality data for the weekly rinses is presented in Appendix 4. A summary tabulation of the number of analyses, minimum, mean and maximum values, standard deviation, and range is presented in appendix 5.

The primary concern regarding the impact of mine waste on water quality is mine waste drainage pH. The oxidation of iron sulfide minerals leads to acid production, while dissolution of calcium carbonate and/or magnesium carbonate minerals will neutralize acid present in the drainage. If the rate of acid production exceeds the rate of acid consumption, the drainage will become acidic. As drainage pH decreases below 6 the drainage toxicity

increases. Trace metal concentrations also tend to increase with decreasing pH, and these metals tend to be toxic to aquatic organisms at low concentrations.

The pH of drainage from all reactors was in the neutral to basic range. For samples T1 to T10, median pH values (weeks 7-52) were in the approximate range of 7.9 to 8.2. The median pH of drainage from samples T11 and T12 was lower, with values of 7.1 and 7.4, respectively (figure 3). The median drainage pH values approximate those observed during a period of relatively stable pH, which followed a trend of increasing pH over the first 10 weeks of the experiment (figure 4). Figures 5 through 16 present the drainage pH values recorded from week 7 through week 52. This period was chosen to permit more refined presentation of water quality variation over the long term, rather than obscure these variations by scaling graphs to accomodate elevated concentrations observed during the initial rinsing phase, particularly sulfate.

For weeks 7 through 52, the median drainage alkalinities for samples T1 through T10, the gold mine tailings, were typically the range of 35 to 55 mg/L. The median drainage alkalinity for T9 was slightly below this range, while values for T2 and T10 were above it (figure 3). As was the case for drainage pH, median drainage alkalinities for samples T11 and T12 were lower, in the neighborhood of 6 and 15 mg/L, respectively (figure 3). Alkalinity values became fairly stable after increasing during the first 10 weeks of the experiment, a similar temporal variation to that observed for pH (figures 4-16).

The typically elevated alkalinities are consistent with the dissolution of calcium carbonate or magnesium carbonate in the solid phase (reactions 8-11). This presence was suggested by the chemical analysis for carbon dioxide, and generally verified by x-ray diffraction analysis of the solids. The elevated buffering capacity was also reflected in the Neutralization Potentials determined.

As was the case with pH and alkalinity, sulfate concentrations also became fairly stable over time (figures 5-16). The sulfate concentrations were generally highest for the initial rinse, then decreased to a relatively constant range (figure 4). The elevated initial concentrations were the result of two occurrences. First, sulfate was produced by sulfide mineral oxidation which occurred between the time of sample collection and the beginning of the experiment. This period ranged from weeks to months. This contention is supported by the increase in the initial rinse sulfate concentration with sulfur content of the tailings (figure 17).

The dissolution of sulfate minerals, such as gypsum and anhydrite, present in the tailings may also have contributed to the initial elevated sulfate concentrations. The sulfate concentrations subsequently decreased, as the products of this long-term oxidation and sulfate mineral dissolution were rinsed from the solids. The concentrations observed after this initial rinsing period were the result of sulfide mineral oxidation which occurred in the standard experimental oxidation period of one week. During this period some sulfate would also be contributed by dissolution of sulfate minerals present. This contribution would most likely be from calcium sulfate minerals. Barite was also detected in some samples, but barium sulfate is fairly insoluble, therefore, its contribution of sulfate would be expected to be small. It is assumed that the dissolution of sulfate minerals after the initial reaction phase was a relatively small contributor to the observed aqueous sulfate concentrations. For weeks 7 through 52, the median sulfate concentrations in drainage from the various samples ranged from less than 1 mg/L to almost 90 mg/L (figure 18). Much of the observed variation apparently resulted from variation in the total sulfur content of the solid phase (figure 19). The median sulfate concentrations for samples T8 (1.73% S) and T9 (5.58% S) were lower than would be expected based on the other samples. Much of the sulfur in sample T9 is present as sulfate in barite (BaSO₄), which is fairly insoluble. This may also contribute to the lower sulfate release per unit mass sulfur in the solid phase. (Note: The sulfate concentration in the static test analysis did not agree with the initial sulfate analysis of sample T9. The barite content based on the initial sulfate analysis is also in question.)

Despite the elevated barite content of sample T9, both T8 and T9 contain significant amounts of pyrite (table 3), but it is apparently oxidizing at a slower rate than the pyrite present in other samples. It is possible that the pyrite in samples T8 and T9 has a lower reactivity than that present in the other samples. Such variation in reactivity among different types of pyrite has previously been reported by Lai et al. (1989), Hammack et al. (1988), and Hammack (1985). Means of readily identifying these less reactive forms of pyrite would be important in accurately predicting mine waste drainage quality.

The total sulfur contents of samples T1 to T10 used in the dissolution experiment ranged from 0.1% to 7.6%. (Note: The sulfur contents of the samples used in the dissolution tests were different than those of samples used for static tests.) The mineralogical analyses indicated that iron sulfide minerals contributed the majority of this sulfur. The sulfate release from the tailings to the various drainages (figures 5-16), and the dependence of this release on sulfur content (figure 19) indicate that the iron sulfides were oxidizing and, therefore, that acid was being produced.

The sulfate release is an indicator of acid production by most of the tailings. The fact that the drainage from the tailings is typically neutral to basic indicates that the acid produced is being neutralized. This reflects the ability of the tailings to neutralize the acid produced to date. The ability to neutralize the acid produced is roughly indicated by ABA Neutralization Potential values ranging from 18 to 373 kg $CaCO_3/t$ (table 5). These values indicate that one metric ton of tailings is capable of neutralizing 18 to 373 kg acid (as $CaCO_3$). Mineralogical analyses, in conjunction with chemical analyses of carbon dioxide, indicate the presence of calcium carbonate and/or magnesium carbonate in the samples most likely is providing the majority of the buffering (table 9).

When calcium carbonate and magnesium carbonate minerals are present, drainage pH in the neighborhood of 8, such as those observed, would be expected. As iron sulfide minerals oxidize, sulfate is released and acid is ultimately produced. The acid produced is neutralized by dissolution of calcium carbonate and magnesium carbonate, which releases calcium or magnesium, respectively. This phenomenon is qualitatively demonstrated by the positive correlation of calcium and magnesium concentrations with sulfate concentration (figure 20).

Since the drainages are presently basic, the acid produced by iron sulfide oxidation has been neutralized. This indicates that the buffering minerals originally present in the tailings have not been depleted. As acid production continues, due to continued iron sulfide oxidation,

the Neutralization Potential of the tailings may be depleted. Factors which contribute to this condition include depletion of the buffering minerals and coating the surface of buffering minerals. The latter leads to a decrease in the rate of buffering mineral dissolution. If the Neutralization Potential is depleted while a significant amount of reactive iron sulfide minerals remain, the drainage will become acidic.

The static test results indicate that samples T9 and T2 are the most likely to generate acidic drainage, as indicated by their low Net Neutralization Potentials (table 5). Based on the static test data, the T9 tailings would be the first to generate acid since the NP is only 18 kg CaCO₃/t. This indicates that once acid generation exceeds 18 kg CaCO₃/t, the drainage will become acidic. The acid generation has apparently not yet reached this value.

The trace metals of most interest for water quality regulation are antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, silver, thallium, and zinc. Regulatory water quality standards for some of these metals are presented in appendix 6. The trace metal concentrations were typically highest in the initial rinse values. Concentrations then typically decreased to asymptotically approach a constant level, as was the case with sulfate. This similarity is not unexpected, since most of the trace metals are commonly associated with sulfide minerals. The trace metals are discussed based on the frequency with which they were detected in the rinse samples. The concentrations are typically fairly low, reflecting the elevated pH of the drainages. If pH decreases, an increase in trace metal concentrations would be expected.

The most frequently detected parameters were barium, zinc, and mercury. Barium concentrations in drainage from samples T1-T10 were, more often than not, above the detection limit. The median barium concentrations for T1, T2, T6, and T9 ranged from 55 to 110 ug/L (figure 21). Barium concentrations were also elevated during the initial rinses of other tailings, but decreased to below detection limits over time. In operational scale mine waste drainage, which typically contains elevated sulfate concentrations, barium concentrations were initially at detectable levels for all samples except for T3 (figure 22). Median zinc concentrations ranged from 0 to 18 micrograms per liter. After week 13 virtually all zinc concentrations were reported as below the 10 microgram per liter detection limit.

Mercury was also detected regularly in the drainage samples, although typically at levels less than 1 microgram per liter (figure 23). These analyses are presently in question since elevated mercury concentrations were also reported for distilled water blanks submitted for analysis. The elevated release of mercury is particularly curious given the low mercury levels in the solids phase (table 2). The accuracy of the mercury concentrations reported for the drainages is clearly in question. More refined analytical techniques are required to more accurately assess the mercury release from the tailings.

A few notable exceptions to the aforementioned trend were:

- 1) the elevated concentrations of arsenic from samples T7,T8, and T9;
- 2) elevated concentrations of antimony from samples T7, T8, and T9; and
- 3) elevated concentrations of molybdenum from sample T9.

All of these elements are more soluble than most trace metals in the neutral pH range common to the drainage from the tailings.

Detectable concentrations of arsenic and antimony were commonly observed in drainage from samples T7, T8, and T9 (figures 24, 25). The median arsenic concentration in drainage from T7 was about 1200 micrograms per liter, although it appears concentrations may stabilize at 200 to 300 micrograms per liter (figure 26). Elevated arsenic concentrations in the drainage from these tailings in the field was also reported. The arsenic is elevated in the solid phase content of the tailings samples T7 and T8 (table 2). However, the arsenic content of sample T6 was also of similar magnitude without elevated arsenic release, and the arsenic content of sample T9 was moderate. The antimony release was highest from sample T9, followed by T8 and T7. This is the same order as the presence of stibnite (Sb₂S₃) in the tailings themselves (table 3).

The elevation of both arsenic and antimony from these samples suggests the possible presence of minerals of the tetrahedrite series, which has end members of $Cu_{12}Sb_4S_{13}$ (tetrahedrite) and $(Cu, Fe)_{12}As_4S_{13}$ (tennantite). This is further suggested by elevated copper concentrations in the drainage from samples T7 and T8 (figure 27). The mineralogical analyses, however, reported the arsenic and antimony to be present in arsenopyrite and stibnite, respectively (table 3). It is possible that minerals of the tetrahedrite series, as well as pyrargyrite (Ag₃SbS₃), proustite (Ag₃AsS₃), realgar (AsS), and orpiment (As₂S₃), are present in the samples but were not detected in the initial analysis (Mattson, 1991). A more detailed study would be required to examine this possibility (Mattson, 1991).

In addition to samples T7 and T8, copper release was also slightly elevated from samples T1 and T12 (figure 27). The median copper concentrations in drainage from these four samples ranged from 0 to 17 micrograms per liter. Concentrations of copper were initially elevated in drainage from most of the tailings samples, but typically decreased below the detection limit over time (figure 28). Nickel concentrations were also elevated in the initial drainage from most of the tailings but, as was typically the case with copper, decreased below the detection limit over time (figure 29).

Appreciable molybdenum release was observed only from sample T9, which had a median molybdenum concentration of about 50 micrograms per liter in its drainage (figure 30). The molybdenum concentration in tailings sample T9 was 1130 ppm, while the corresponding concentration in the remaining samples did not exceed 2 ppm. The variation of the molybdenum concentration over time in the T9 drainage is presented in figure 31. Although elevated concentrations were observed in the T10 drainage, these all occurred during the initial three weeks of reaction.

Concentrations of beryllium, silver, lead, and cadmium were occasionally detected in the initial rinse of the tailings and subsequently decreased below the detection limit (figures 32-35). Chromium was below the detection limit in all drainage samples.

Selenium and thallium were analyzed only in the initial rinse. Selenium was not detected in any of the samples. Thallium was detected seven times at 1 microgram per liter and once at 2 micrograms per liter. Detectable thallium concentrations were not observed for any pair of duplicate reactors. The solid phase concentrations of selenium were usually less than three ppm and did not exceed seven ppm in any of the tailings samples. Although the thallium concentration in sample T9 was 33 ppm, the corresponding value for the remaining samples did not exceed four parts per million (appendix 1). Due to the low aqueous concentrations observed for the initial rinse, the low solid phase concentrations, and the additional analytical cost, analysis of these parameters was discontinued.

7. **NEED FOR ADDITIONAL STUDY**

Following the completion of this project several needs are clear. These needs have been identified based on existing data and will not be met within the scope of the present project.

1. This project is predicated on the assumption that the tailings collected and examined are similar to those which might be generated by future Minnesota mining operations. Although this assumption appears to basically sound, it should be evaluated by comparing the geology of the mines from which the tailings were collected with that of precious metal exploration areas in Minnesota. The mineralogical analyses of the tailings samples can further aid this comparison.

2. Additional dissolution testing will be required to determine if some of the samples will produce acid drainage. Mineralogical analyses and static test data suggest that samples T2 and T9 are likely to produce acid, and that T6 and T10 have a moderate potential to produce acid. Two types of laboratory tests can be conducted to verify these predictions based on solid phase analyses.

First, the reactor tests presently being conducted can be continued on selected samples until either acidic drainage is produced or the amount of iron sulfide remaining in the tailings is no longer a threat to produce acid. In concert with this continuation, the drainage quality data will be analyzed to determine the rates of acid production and consumption. The continued data collection will be used to determine changes in these rates over time. If these rates remain fairly constant the ultimate acid character of the drainage can be projected using the method proposed by Lapakko (1990).

The second laboratory test which can be conducted is a high temperature oxidation test. The rate of sulfide oxidation in this test is quite high and, therefore, the time required for reaction is reduced. Such tests will be evaluated in an upcoming project, and may be highly beneficial in reducing the time required for predictive testing. However, at present the drainage generated in these accelerated tests must be compared to drainage generated under less severe conditions to determine if the relative rates of acid production and consumption are altered.

3. Chemical and mineralogical analyses should be conducted on the leached solids and compared to analyses of the unleached solids. This will provide insight into the relative dissolution rates of the minerals present and ultimate solid phase reaction products.

4. The specific surface area of the solids should be analyzed to better assess the effects of surface area on the observed water quality. This would be particularly beneficial in more accurately assessing the effects of sulfur content on sulfate release.

5. Additional data analysis should be conducted to determine the rates of mineral dissolution and examine variables which may influence these rates.

6. Dissolution tests should be conducted on selected samples using a longer oxidation period. This will allow investigation of the effect of longer term dry cycle oxidation on drainage quality. Sulfide oxidation will continue during such dry cycles but may not be accompanied by attendant neutralization reactions.

7. Firms which submitted samples for testing should be contacted in order to compare the water quality generated in laboratory tests to that generated in the field. This comparison will aid in future extrapolation of laboratory results to field conditions.

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Sample	+100M	+270M	+500 M	-500M
T1	0.58	16.63	18.16	64.63
T2	13.72	27.77	15.87	42.64
Т3	7.99	24.49	17.19	50.33
Т4	1.42	28.90	28.05	41.63
T5.	12.88	40.32	20.54	26.26
Т6	14.37	35.01	16.66	33.96
Т7	0.27	2.48	6.24	91.01
Т8	4.04	22.77	19.06	54.13
Т9	1.83	18.25	18.60	61.32
T10	· 8.97	26.82	19.45	44.76
T11	83.75	14.28	1.22	0.75
T12	56.04	15.04	12.84	16.08

Particle Size Distribution, Weight Percent

	Concentrations in PCT					<u> </u>					Conc	entratio	ns in PPI	1					
	s _{TOT}	50 ₄	s ²⁻	со ₂	Ag	As	Ba	Be	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	τι	Zn
								_									_		
τ1	.51	.06	.49	9.86	<.5	38	67	<.5	1	146	26	.23	<1	32	15	<5	<1	<1	339
T2	7.63	1.00	7.3	8.91	<.5	429	36	<.5	3	165	155	1.80	<1	125	122	<5	2	<1	931
T 3	1.03	.05	1.01	7.50	<.5	151	22	<.5	<1	209	117	.05	<1	118	22	<5	7	3	114
т4	1.15	. 14	1.10	6.84	<.5	115	25	<.5	<1	212	149	.03	<1	110	19	<5	<1	1	110
T5	.67	.04	.66	2.94	<.5	47	38	<.5	1	64	39	.02	2	27	55	<5	1	2	84
T6	2.12	.16	2.07	7.54	<.5	1240	42	<.5	<1	104	67	.03	<1	18	21	<5	3	4	66
17	.10	.05	0.08	10.23	<.5	1346	53	<.5	<1	281	33	.05	<1	126	14	18	2	1	60
т8	1.73	.07	1.70	4.88	<.5	>2000	102	<.5	<1	213	124	1.38	<1	140	106	41	1	<1	85
T9	5.58	5.83	3.64	.61	1.0	234	402	<.5	1	78	32	21.6	1130	19	26	288	<1	33	152
T10	4.08	.57	3.89	21.85	<.5	281	90	<.5	2	52	23	.06	<1	26	28	<5	2	4	61
T11	<.02	.02	<.01	.17	<.5	72	72	<.5	5	2368	1098	.04	<1	463	40	<5	<1	<1	97
T12	<.02	.03	<.01	.16	<.5	17	42	<.5	<1	156	1615	.03	<1	620	19	<5	<1	1	103

Table 2. Sulfur, carbonate, and trace metal content of tailings.

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							Weight	Percent Mine	rals				
		T1	T2	т3	T4	T5	Т6	17	т8	T9	T10	T11	T12
<u>Carbonates</u>													
Calcite Dolomite Ankerite Siderite		0.2 18.9 - 1.9	1.5 16.1 - 1.3	0.5 14.5 - 0.9	0.6 13.0 - 1.1	6.0 0.5 0.2	1.3 3.6 14.0	0.2 20.9 0.2	10.1 0.1	1.4 - -	2.1 19.7 31.4	0.4 - -	0.4
Regulatory E	lement-Be	aring Mine	rals										
Pyrite Pyrrhotite Barite Arsenopyrite Chalcopyrite Molybdenite Galena Stibnite Sphalerite	S S Ba,SO ₄ As Cu Mo Pb Sb Zn	0.86 0.04 - 0.01 0.01 - <0.01 - 0.05	13.58 0.02 - 0.09 0.04 - 0.01 - 0.14	1.82 0.10 - 0.03 0.03 - <0.01 - 0.02	1.99 0.05 	1.09 0.22 0.01 0.01 <0.01	1.29 3.50 0.27 0.02 <0.01	0.04 0.54 - - - <0.01 <0.01 <0.01 0.01	2.43 1.04 - 0.04 0.04 - 0.01 0.01 0.01	6.57 0.13 14.22 0.05 0.01 0.19 <0.01 0.04 0.02	7.32 0.06 0.01 <0.01 0.01	See Text See Text See Text See Text See Text	See Text See Text See Text See Text

Table 3. Sulfide and carbonate mineralogy of tailings (analysis by Hanna Research Center).

Notes:

1) Barite was the only sulfate mineral detected. Sulfate in other samples is probably due to pyrite and/or pyrrhotite oxidation which often forms melanterite, FeSO4'7H20.

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Percent Liberation (Weight Percent)

Sample	Pyrite	Pyrrhotite	Calcite	Dolomite	Ankerite	Siderite
T1	94	-	97	-	95	93
T2	87	86	93	89	-	-
тз	91	89	-	91	+	ł
Т4	92	92	95	-	-	-
Т5	85	84	92	-	87	86
Т6	86	86	-	88	-	86
Т7	97	97	99	98	-	97
Т8	93	90	96	92	· -	93
Т9	94	94	96	93	-	93
T10	89	87	93	-	92	
T11	-	-	40	-	-	-
T12	-	-	63		-	-

			ABA			мо	DIFIED	ABA				
SAMPLE	s _T 1	s²	APP ³	NP	NET NP ⁴	APP ⁵	NP	NET NP ⁵	APP ⁶	NP ⁷	NET NP ⁴	NP/APP ¹⁰
T1	0.55	0.50	17	230 ⁸	213	16	200	184	17	162	145	12
T2	8.19	7.87	256	230	* -26	246	180	* -66	256	175 ⁸	* -81	* 0.73
ТЗ	1.12	1.08	35	195 ⁸	160	34	130	96	35	150 ⁸	115	3.8
T4	1.23	1.18	38	184 ⁸	146	37	130	93	38	150	112	3.5
T5	0.63	0.59	20	98 ⁸	78	18	92	74	20	83 ⁸	63	5.1
T6	2.18	2.10	68	69	M 1	66	64	M -2	68	58	* -10	* 0.97
T7	0.31	0.30	9.7	270	260	9.3	220	211	9.7	189 ⁹	179	24
T8	1.86	1.79	58	174	116	56	120	64	58	134	76	* 2.1
Т9	5.40	5.03	169	18	*-151	157	16	*-141	169	19	* -150	* 0.10
T10	6.51	6.30	203	373	170	197	200	М 3	203	171	* -32	* 1.0
T11	0.04	0.01	1.2	66	65	0.31	30	30	1.2	19	M 18	97
T12	0.04	0	1.2	139	138	0	150	150	1.2	35	34	large

Table 5. Static test results.

1 Total sulfur, percent. Analyzed by Lerch Brothers, Inc.

2 Sulfide sulfur calculated as the difference between total sulfur and sulfate sulfur, percent.

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5

Acid Production Potential in kg $CaCO_3$ /metric ton = 31.25 x total sulfur Net Neutralization Potential in kg $CaCO_3$ /metric ton = NP-APP Acid Production Potential in kg $CaCO_3$ /metric ton = 31.25 x sulfide sulfur Acid Production Potential in kg $CaCO_3$ /metric ton = 31.25 x total sulfur. Calculated for comparison with other methods. 6

7 Net Neutralization Potential refers to the Alkaline Production Potential defined by Caruccio et al. (1981)

8 Average of duplicate values.

9 For pH 5.05 endpoint

10 Neutralization Potential to Acid Production Potential Ratio for Modified ABA Method

* Indicates samples identified by the test as a potential acid producer.

Indicates moderate potential for acid production, with Net NP in the range of -20 to +20 kg CaCO3/metric ton. М
Table 6. Duplication of neutralization potentials (NP, kg $CaCO_3/t$) determined by method of Sobek, et al. (1978).

Tailing	mL HCl	N HCl	Equiv. H ⁺	рН _о	NP (pH 7)
Tl	40	0.500	0.020	1.14	228
	40	0.500	0.020	1.18	231
Т3	40	0.500	0.020	1.21	188
	40	0.500	0.020	1.17	202
T4	40	0.500	0.020	1.15	190
	40	0.500	0.020	1.17	178
Т5	40	0.500	0.020	0.98	106
	40	0.500	0.020	1.05	91

Table 7.Effect of initial acid addition on NP determined by method of Sobek, et al.
(1978).

Tailing	mL HCl	N HCl	Equiv. H ⁺	рН _о	NP (pH 7)
Т8	40	0.100	0.004	4.87	80
di.	40	0.500	0.020	1.17	174
T11	40	0.500	0.020	0.95	66
	80	0.500	0.040	0.62	113

Tailing	mL HCl	N HCl	Equiv. H ⁺	рН _о	NP (pH 8.3)
	40.0	0.100	0.004	4.83	200.0
T1	40.0	0.300	0.012	1.37	186.8
	40.0	0.500	0.020	0.65	205.0
Τ2	30.0	0.300	0.009	2.09	170.2
	40.0	0.500	0.020	0.64	200.0
	40.0	0.100	0.004	4.39	78.0
ТЗ	20.0	0.527	0.010	1.20	146.5
	40.0	0.500	0.020	0.81	148.0
	40.0	0.100	0.004	4.39	76.0
Т4	20.0	0.527	0.010	1.14	144.1
	40.0	0.500	0.020	0.62	152.0
	40.0	0.100	0.004	2.14	69.0
Т5	60.0	0.105	0.006	1.65	91.6
	40.0	0.500	0.020	0.51	88.0
Т6	40.0	0.100	0.004	2.14	41.0
	60.0	0.105	0.006	1.76	62.3
Т7	30.0	0.527	0.016	1.28	218.9
	40.0	0.500	0.020	0.74	226.0
Т8	40.0	0.100	0.004	4.59	69.0
	20.0	0.527	0.010	2.18	109.3
Т9	20.0	0.105	0.002	1.85	22.4
	40.0	0.100	0.004	1.51	16.0
T10	35.0	0.527	0.018	1.22	203.7
	40.0	0.500	0.020	1.00	210.0
T11	35.0	0.105	0.004	0.53	20.3
	40.0	0.500	0.020	0.62	53.0
T12	20.0	0.527	0.010	1.37	136.9
	40.0	0.500	0.020	0.93	188.0

Table 8.Effect of acid addition on NP determined by Modified ABA method.

	T1	T2	ТЗ	T4	T5	T6	17	Т8	T9	T10	T11	T12
Calcite	0.2	1.5	0.5	0.6	6.0	1.3	0.2	0	1.4	2.1	0.4	0.4
Dolomite	18.9	16.1	14.5	13.0	0	0	20.9	10.1	0	0	0	0
CaCO ₃	10.1	8.6	7.8	7.0	0	0	11.2	5.4	0	0	0	0
MgCO3	8.7	7.4	6.7	6.0	0	0	9.7	4.7	0	0	0	0
Ankerite	0	0	0	0	0.5	3.6	0	0	0	19.7	0	0
CaCO ₃	0	0	0	0	0.27	1.9	0	0	0	10.6	0	0
MgCO3	0	0	0	0	0.16	1.1	0	0	0	6.2	0	0
FeCO3	0	0	0	0	.08	.6	0	0	0	3.3	0	0
Siderite	1.9	1.3	0.9	1.1	0.2	14.0	0.2	Q.1	0	31.4	0	0
Total												
CaCO ₃	10.3	10.1	8.3	7.6	6.3	3.2	11.4	5.4	1.4	12.7	0.4	0.4
MgCO3	8.7	7.4	6.7	6.0	.2	1.1	9.7	4.7	0	6.2	0	0
FeCO3	1.9	1.3	0.9	1.1	.3	14.6	0.2	0.1	0	34.7	0	0

Table 9.	Summary	of	carbonate	content	tailings.

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	CaO	MgO	Fe	CO2
Calcite	56	0	0	44
Dolomite	30	22	0	48
Ankerite	30	15	8	45
Siderite	0	0	48	.38

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Dolomite x 0.536 = $CaCO_3$ Dolomite x .462 = $MgCO_3$

Ankerite x
$$0.314 = MgCO_3$$

Ankerite x $0.166 = FeCO_3$

 $CaCO_3/CaO = 1.786$ MgCO_3/MgO = 2.092 FeCO_3/Fe = 2.077

Figure 1. Dissolution test reactor.











Figure 5. pH, alkalinity and sulfate concentration in drainage from T1, weeks 7-52 (0.51% total S; 0.49% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit. pH values from weeks 32-34 are questionable due to faulty electrode.



Figure 6. pH, alkalinity and sulfate concentration in drainage from T2, weeks 7-52 (7.63% total S; 7.30% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit. pH values from weeks 32-34 are questionable due to faulty electrode.



Figure 7. pH, alkalinity and sulfate concentration in drainage from T3, weeks 7-52 (1.03% total S; 1.01% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 8. pH, alkalinity and sulfate concentration in drainage from T4, weeks 7-52 (1.15% total S; 1.10% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 9. pH, alkalinity and sulfate concentration in drainage from T5, weeks 7-52 (0.67% total S; 0.66% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 10. pH, alkalinity and sulfate concentration in drainage from T6, weeks 7-52 (2.12% total S; 2.07% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 11. pH, alkalinity and sulfate concentration in drainage from T7, weeks 7-52 (0.10% total S; 0.08% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 12. pH, alkalinity and sulfate concentration in drainage from T8, weeks 7-52 (1.73% total S; 1.70% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 13. pH, alkalinity and sulfate concentration in drainage from T9, weeks 7-52 (5.58% total S; 3.64% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 14. pH, alkalinity and sulfate concentration in drainage from T10, weeks 7-52 (4.08% total S; 3.89% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 15. pH, alkalinity and sulfate concentration in drainage from T11, weeks 7-52 (0.01% total S; <0.02% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 16. pH, alkalinity and sulfate concentration in drainage from T12, weeks 7-52 (0.01% total S; <0.02% sulfide). Sulfate values listed as being less than the detection limit are represented as half of the detection limit.



Figure 17. Initial rinse sulfate concentration versus solid phase sulfur concentration.



Weeks 7 and on



Tailings Type

Figure 19. Mean sulfate concentration versus solid phase sulfur content, data from weeks 7 - 52.



52

Figure 20. Mean magnesium and mean calcium concentrations versus mean sulfate concentration (data from weeks 7 - 52).











Tailings Type



Tailings Type





Tailings Type





Tailings Type





Time (weeks)

Figure 27. Box plot for copper concentrations in drainage from tailings.







Time (weeks)









Figure 31. Molybdenum concentration versus time for T9 drainage.



Figure 32. Box plot for beryllium concentrations in drainage from tailings.






Figure 34. Box plot for lead concentrations in drainage from tailings.





