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Nonferrous Metal Mining

Waste Characterization and Drainage Mitigation with Alkaline Solids

Research Summary

Minnesota Department of Natural Resources Division of Minerals

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SUMMARY

Minnesota has potential for development of nonferrous mining, particularly in the Duluth Complex and the greenstone belts of the state. Prior to development of a nonferrous mine, the composition of potential mining wastes must be determined and the quality of the drainage from the wastes must be predicted. Numerous studies have been conducted on these subjects and related topics by the Reclamation Section within the Division of Minerals of the Minnesota Department of Natural Resources (MN DNR). This report summarizes studies conducted on mine waste characterization, drainage quality prediction, and the use of alkaline solids for mine drainage mitigation. Additional detail on the studies, most of which are yet in progress, is available in the references cited.

A process for the characterization of mine wastes prior to mine development was developed. The objective of this process is to identify potential adverse impacts of mine waste drainage on natural resources. With this information the design and costs of mitigation of these potential impacts can be accounted for prior to mineral resource development.

Field studies on the dissolution of Duluth Complex rock have been conducted since the mid-1970's at the Dunka Mine and test piles at the MN DNR Babbitt Research Site. Laboratory studies have been conducted on Duluth Complex rock, titanium tailings generated from Duluth Complex rock, and gold tailings from mines in greenstone belts outside of Minnesota. A study evaluating tests for predicting mine waste drainage quality was also conducted.

The use of alkaline solids to mitigate mine waste drainage problems has been examined. Laboratory experiments were conducted to examine the mitigative potential mixing of alkaline solids with acid-producing mine waste. Laboratory and field tests were conducted to determine the effectiveness of limestone beds for treating mine waste drainage.

INTRODUCTION: MINING IN MINNESOTA

Minnesota has an extensive mining industry and potential for mineral expansion and diversification. Iron mining began in Minnesota over a century ago and led to the taconite mining industry which, in 1988, produced 42.5 million long tons of iron ore valued at 1.3 billion dollars (U. S. Bureau of Mines, 1988). Nonferrous mining development shows promise for the future. The state is presently the subject of extensive metallic mineral exploration, with 101 leases covering almost 40,753 acres of state land.

Considerable mineral potential for base and precious metals is associated with Minnesota's Precambrian rocks, specifically its greenstones, metasedimentary formations and the Duluth Complex (figure 1). The greenstone and metasedimentary formations, or greenstone belts, of Minnesota extend north into Canada, where they have yielded substantial mineral production. These formations are potential hosts for gold, zinc-copper massive sulfides with various by-products, and magmatic sulfide deposits containing copper, nickel and platinum group elements. Recent exploration of greenstone belt metasedimentary formations has focused on gold, base metals, and silver-cobalt-copper deposits. The Duluth Complex contains an estimated copper-nickel resource of 4.4 billion tons (Minnesota Environmental Quality Board, 1979), as well as significant titanium resources. Drill core analyses have also revealed the presence of chromium, vanadium, cobalt, and platinum group elements.

If mineral development occurs, tailings and waste rock, as well as the mine itself will be wastes which remain after the operation is abandoned. Some mining wastes are relatively stable chemically and, therefore, are environmentally innocuous with respect to release of acid and trace metals. On the other end of the spectrum are wastes at mine sites classified by the U. S. Environmental Protection Agency as Superfund Sites. Some of these sites were abandoned in the 1800's and have generated problematic drainage for roughly a century.

Since mine waste drainage quality is variable, the degree of mitigation required for wastes is variable. In order to design and optimize mitigation methods, the quality of drainage from potential mine waste must be predicted prior to mineral resource development. The optimal method of predicting the quality of drainage from a mine waste is to study drainage from mining wastes of similar composition in the environment over an extended time period. Due to the absence of mining wastes of appropriate composition, as well as time and economic constraints, such an approach is often infeasible prior to mine development. Consequently, it is necessary to predict mine waste drainage quality based on the composition of the mine waste and laboratory dissolution tests. Presently, there are no simple tests which can predict the quality of drainage from all mine wastes. Consequently, expertise is required in design and interpretation of mine waste drainage quality predictive tests.

Mine waste drainage quality, as well as techniques of impact mitigation, have been studied in Minnesota since the mid 1970's. The studies were initiated in 1976 under the auspices of the Regional Copper-Nickel Study and, in 1978, were continued by the Minnesota Department of Natural Resources, Division of Minerals (MN DNR). This report summarizes research conducted by the MN DNR on:

- mine waste characterization,
- drainage quality prediction for Duluth Complex mining wastes,
- drainage quality predictive testing on non-ferrous mining wastes from greenstone belts,
- evaluation of predictive tests, and
- mitigation of mine waste drainage using alkaline solids.

The results of the studies, many of which are yet in progress, are summarized following a brief discussion of mine waste dissolution chemistry. The information generated in these studies will aid in the prediction and mitigation of acid and trace metal release from mine wastes generated by future operations.



Figure 1. Selected bedrock formations of northern Minnesota (adapted from G. B. Morey et al., 1982).

MINE WASTE DISSOLUTION CHEMISTRY

When metal sulfide minerals are exposed to the oxidizing conditions present in waste rock stockpiles, mine walls, and tailings basins, sulfide is oxidized and the associated metals (Fe, Cu, Ni, Co, Zn) are released (Nelson, 1978; Garrels and Christ, 1965; Sato, 1960a, 1960b). Acid is produced as a result of the oxidation of iron sulfide minerals present in mine waste, as indicated by reaction 1 (Nelson, 1978) and reaction 2 (Stumm and Morgan, 1981). Two moles of acid are produced for each mole of sulfur oxidized.

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

$$FeS_2(s) + (5/2)H_2O + (15/4)O_2(g) = FeOOH(s) + 4H^+(aq) + 2SO_4^{-2}(aq)$$
 [2]

The rate of oxidation is proportional to the available sulfide surface area (Nelson, 1978; Sato and Mooney, 1960; Sato, 1960a, 1960b), and dissolved oxygen concentration (Nelson, 1978; Dobrokhotov and Maiorova, 1962; McKay and Halpern, 1958), with only a slight dependence on pH (Nelson, 1978; Majima and Peters, 1966).

Dissolution of sulfate minerals such as melanterite and jarosite will also produce acid (reactions 3 and 4, respectively). As was the case for the sulfide minerals, the dissolution

$$FeSO_4 \cdot 7H_2O(s) + (1/4)O_2(g) = FeOOH(s) + SO_4^{2-}(aq) + 2H^{+}(aq) + (11/2)H_2O$$
[3]

$$KFe_3(SO_4)_2(OH)_6(s) = K^+(aq) + 3FeOOH(s) + 2SO_4^{2-}(aq) + 3H^+(aq)$$
 [4]

of melanterite yields two moles of acid per mole of sulfate dissolved. In contrast, the dissolution of jarosite yields 1.5 moles of acid per mole of sulfate dissolved. The dissolution of sulfate minerals such as anhydrite (reaction 5) or barite ($BaSO_4$) will not produce acid.

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

The most effective minerals for consuming (neutralizing, buffering) acid are calcium carbonate and magnesium carbonate (reactions 6-9). Reactions 6 and 8 are dominant above approximately pH 6.3, while reactions 7 and 9 are dominant below this pH. Other minerals,

$$CaCO_{3}(s) + H^{+}(aq) = HCO_{3}(aq) + Ca^{2+}(aq)$$
 [6]

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq)$$
 [7]

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

$$MgCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Mg^{2+}(aq)$$
 [9]

such as anorthite and forsterite, can also consume acid but their dissolution rate (and associated rate of acid consumption) is typically slow in the neutral pH range (reactions 10, Holdren and Berner, 1979; 11, Hem, 1970). These minerals dissolve more rapidly as pH decreases and, therefore provide more buffering under acidic conditions.

$$CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O = Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s)$$
 [10]

$$Mg_{2}SiO_{4}(s) + 4H^{+}(aq) = 2Mg^{2+}(aq) + H_{4}SiO_{4}(aq)$$
[11]

Iron carbonates will provide no net consumption of acid. The initial dissolution of one mole of iron carbonate will consume one or two moles of acid (reactions 12, 13). However, under environmental conditions the one mole of ferrous iron released will oxidize to ferric iron (reaction 14) which will precipitate as ferric oxyhydroxide (reactions 15). The oxidation of ferrous iron is slower than the subsequent ferric oxyhydroxide precipitation, and is reported to be second-order with respect to OH^{-} concentration (Sung and Morgan, 1980, Eary and Schramke, 1990). The oxidation and precipitation reaction will yield two moles of acid (reaction 16). Thus, iron carbonate will not contribute to acid consumption.

$$FeCO_3(s) + H^+(aq) = HCO_3(aq) + Fe^{2+}(aq)$$
 [12]

$$FeCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Fe^{2+}(aq)$$
 [13]

$$Fe^{2+}(aq) + (1/4)O_2(g) + H^+(aq) = Fe^{3+}(aq) + (1/2)H_2O$$
 [14]

$$Fe^{3+}(aq) + 2H_2O = FeOOH(s) + 3H^+(aq)$$
 [15]

$$Fe^{2+}(aq) + (1/4)O_2(g) + (3/2)H_2O = FeOOH(s) + 2H^+(aq)$$
 [16]

The oxidation of trace metal sulfide minerals releases trace metals and sulfate but does not necessarily contribute acid (reaction 17).

 $CuS(s) + 2O_2(g) = Cu^{2+}(aq) + SO_4^{2-}(aq)$ [17]

Reactions subsequent to the sulfide dissolution affect the net trace metal release to the environment. The transport of a given component in the environment is the net result of release to solution by dissolution and removal from solution by precipitation, coprecipitation, exchange reactions, and adsorption. The degree of trace metal transport is dependent upon drainage composition (in particular pH), the chemistry of the released component, and the chemical character and surface area of solid surfaces present. Concentrations of trace metals tend to increase exponentially as solution 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.

Chemical release is also affected by the amount of water percolating through the stockpile, which is dependent on the input volume and subsequent flow routing. Precipitation is an everpresent input, but surface water and groundwater can also contribute under certain conditions. The water input will be incorporated as storage or discharged as evapotranspiration, surface runoff, subsurface flow (or interflow) and baseflow (Hewett, 1980).

MINE WASTE CHARACTERIZATION

The quality of mine waste drainage is variable, largely due to the variability in mine waste composition. The preoperational characterization of mining wastes allows siting, construction and reclamation of waste disposal facilities in a manner that will reduce contaminant release and the associated drainage treatment cost. A mine waste characterization process has been designed for application on a site specific basis (Lapakko, 1990c; 1988b).

The approach and analytical techniques used for mine waste characterization are similar to those employed for evaluation of potential for resource recovery. The extent of rock units potentially contributing to mine waste is delineated and pertinent compositional aspects of these units are quantified. The quality of drainage from the potential wastes is then projected. Existing data on a mine waste of similar composition, generated by similar mining methods, and exposed to similar environmental conditions for an extended time provide the best indicator of drainage quality. A directory of contacts has been compiled to facilitate information collection on mine waste composition and drainage quality across the United States (Wessels et al., 1991).

Since data on the drainage quality from a mine waste of specific composition are often not available, it may be necessary to conduct laboratory dissolution tests for drainage quality projection. These tests could be conducted on a variety of representative samples from individual rock units to determine the relationship between mine waste composition and drainage quality. Additional sampling, analysis, and dissolution testing may be required based on the information compiled. The relationship between solid composition and chemical behavior is then extrapolated to the waste as a whole. A mine waste management program would be designed based on the projected drainage quality and quantity.

The mine waste composition and predicted drainage quality would be subject to verification during operation if mine development proceeded. Small scale field tests on well characterized waste, representative of operational scale waste, allow more accurate extrapolation to operational scale, estimation of drainage volume, and assessment of mitigation design. Initiating such tests as soon as resource development begins, maximizes the benefit of these tests for drainage quality prediction and mine waste management.

By characterizing mine wastes and predicting mine waste drainage quality prior to mineral resource development, waste disposal facilities can be sited, constructed and reclaimed in a manner that will more effectively reduce contaminant release and the associated drainage treatment cost. Mitigation can be tailored to the predicted drainage quality and directed toward meeting water quality objectives. Wastes with mitigative capacity (e.g., limestone) can be identified during the characterization process. Finally, the cost of reclamation can be considered along with other mining costs in the assessment of resource development economics. Mine development can then progress with consideration of both metal recovery and the environmentally sound management of mine wastes.

DRAINAGE QUALITY FROM POTENTIAL MINNESOTA MINE WASTES

Potential for base and precious metal development is associated with the Duluth Complex and the greenstone belts (greenstones and metasedimentary formations) of Minnesota (figure 1). Drainage quality data have been collected from Duluth Complex wastes generated from operational stockpiles as well as small scale test piles. Predictive tests have been conducted to determine the drainage quality from Duluth Complex mining wastes and nonferrous mining wastes from greenstone belts.

Duluth Complex Mine Waste Drainage

The Duluth Complex is a massive gabbroic intrusion in northeastern Minnesota containing low grade copper and nickel sulfides. These deposits represent one of the largest known copper and nickel resources in the U. S. (Kingston et al., 1970; Minnesota Environmental Quality Board, 1979). In 1976, the Regional Copper-Nickel Study was formed in response to public concerns for the environmental impact of copper-nickel mining. The final summary report was completed in 1979 (Minnesota Environmental Quality Board, 1979). The investigations conducted included operational scale field studies at the Dunka Mine (an active iron ore operation), pilot scale field studies at the AMAX exploration site, monitoring of a bulk sample site, as well as laboratory experiments.

The earliest reports on the Duluth Complex focused on the impact of potential copper-nickel operation (Thingvold et al., 1979), and addressed the hydrology (Hewett, 1980) and chemistry of stockpiles. The early laboratory studies (Lapakko, 1980; Eisenreich et al., 1977a, 1977b) investigated the kinetics and mechanisms of gabbro dissolution as well as trace metal equilibria. The findings of the early field monitoring, the laboratory experiments, and chemical equilibrium computer models were compiled in a comprehensive report (Eger and Lapakko, 1980c), and summarized in shorter papers presenting the chemical mechanisms of leaching (Lapakko and Eger, 1980a, 1980b).

The Dunka Mine

The quantity and quality of Duluth Complex waste rock and lean ore stockpile drainage have been investigated at the LTV Steel Mining Company Dunka Site (previously Erie Mining Company), a full scale open pit taconite operation near Babbitt, Minnesota. Typical Minnesota iron mining wastes have low sulfur and trace metal contents (Lapakko and Wagner, 1989). However, this open pit intersects the geological contact between the Duluth Complex and the iron formation, and removal of gabbro from the Duluth Complex was required to mine the underlying taconite. The gabbro, which contains metal sulfide minerals, has been stockpiled on the site. Since 1976, data have been collected on the drainage quality, annual quantity, mass release and maximum flow rates associated with stockpile drainages at the site. The stockpiles containing gabbro exceed 50 million tons in mass and cover an area of 320 acres. Total flow from the watershed is about 500 million gallons per year, with the majority of the flow passing through Unnamed Creek (figure 2). The most recent and comprehensive report (Eger et al., 1981b) presented the results of monitoring from 1976 to 1980, and earlier reports are available (Eger and Lapakko, 1980a; Eger et al., 1977). After 1980 the monitoring was conducted by Erie Mining Company and LTV Steel Mining Company.

During the period from 1976 to 1980 (Eger et al., 1981a), greater than 95% of all leachate samples had pH values between 6.0 and 8.5, but values as low as 4.5 were reported. Concentrations of trace metals (Cu, Ni, Co, Zn) exceeded ambient levels by 10 to 10,000 times. Nickel contributed more than 90 percent of the trace metal load from the stockpiles, and its subsequent removal by natural processes in the Unnamed Creek system was less than 40 percent. Consequently, in the absence of mitigative measures, nickel concentrations will be elevated downstream from Duluth Complex stockpiles. Concentrations of calcium, magnesium, and sulfate in the stockpile drainage were also elevated, but these three parameters are of lesser environmental impact than the trace metals. Indeed, elevated concentrations of calcium and magnesium can reduce the toxic effects of trace metals.

Other studies at the Dunka site have focused on the transport of trace metals leached from the stockpiles through a white cedar swamp (Eger et al., 1980; Eger and Lapakko, 1988; 1989), Unnamed Creek (Eger and Lapakko, 1980b; Strudell, 1986), and Bob Bay (Lapakko and Eger, 1981b; Strudell et al., 1984). Information on the kinetics, mechanisms, and capacities of metal sequestration by peat has been compiled in the form of literature reviews (Lapakko et al., 1986b; Otterson, 1978) and laboratory experiments on metal removal by peat have been conducted (Lapakko et al., 1986a).





AMAX Test Piles

Six test piles containing 820 to 1300 metric tons of low grade copper-nickel Duluth Complex rock were constructed in 1977. For runoff collection, each pile is underlain by an impervious Hypalon liner which is sloped toward a 15.2 cm perforated plastic pipe. The runoff collected flows to a common sump and is subsequently pumped to settling basins. In 1982 approximately 40 percent of test pile FL4 was removed for use in another study of stockpile reclamation techniques. The most recent and comprehensive report on the leaching and revegetation studies (Eger and Lapakko, 1985) was published in 1985, although additional progress reports (Eger et al., 1981a, 1980a, 1979) and symposium publications (Eger and Lapakko, 1981; Eger et al., 1980b) are available.

The following conclusions on Duluth Complex rock drainage quality were drawn based on this small scale field monitoring program.

- 1. Trace metal concentrations in leachate from test piles containing low grade sulfide mineralization exceeded concentrations in undisturbed streams of the area by as much as five orders of magnitude.
- 2. Drainage pH decreased while trace metal concentrations and mass release rates increased with time and the iron sulfide content of the stockpile (figure 3).
- 3. A critical iron sulfide content appears to occur at approximately 1.1 weight pct FeS (0.6 pct total sulfur) in the bulk rock. Rock of similar mineralogy and particle size distribution which contains more than this critical amount would generate acidic leachate.
- 4. Only through long term studies can the influence of time and environmental processes be adequately measured. Predictions based on data from the first years of this study would have underestimated trace metal release rates by as much as two orders of magnitude.

The second phase of an experimental program funded by the U.S. Bureau of Mines was also conducted at the AMAX/Kennecott site. This two phase program examined the feasibility of removing trace metals (Cu, Ni, Co, Zn) from stockpile drainage using readily available materials in low-cost, low maintenance systems. The results of the entire program are presented in a final report (Lapakko et al., 1986a), and synopses of various research segments are presented in several symposium proceedings (Eger et al., 1984; Lapakko and Eger, 1988, 1983, 1981a; Lapakko et al., 1983).



Figure 3. Annual median pH of test pile drainage from 1978-1991.

Laboratory Predictive Tests

The variation of laboratory drainage quality with Duluth Complex rock composition was initially examined in batch reactor and column tests (Lapakko, 1980). Subsequently, an experimental method based on the principle that sulfide minerals oxidize in the presence of atmospheric oxygen and water was used (Gottschalk and Buehler, 1912; Caruccio et al., 1980). The experiments were conducted in units designed to permit the rinsing of solids and filtration of the rinse solution in one step (U.S. Patent No. 4,783,318). The mixtures were placed onto a 1.6 micron Whatman GF/A glass fiber filter (5.5 cm diameter) which covered a plastic plate in the upper section of a two-stage filter unit or reactor.

The reactors and solids were stored in a box to dry and oxidize. A thermostatically controlled heating pad was placed beneath the box to maintain a constant temperature. Water containers were placed in the box, and a humidifier and dehumidifier were placed in the room, to maintain a fairly constant humidity. The solids were rinsed weekly with 200-mL volumes of distilled deionized water.

This technique was used to investigate the effect of solid phase sulfur content on the **quality** of drainage from AMAX drill core samples of Duluth Complex rock over periods of 30 to 49 weeks (Lapakko, 1988a). These samples contained from 0.47 to 2.57 percent sulfur, with typical copper and nickel ranges of 0.13 to 0.23 percent and 0.05 to 0.09 percent, respectively. Samples containing 0.9 percent sulfur produced drainage pH as low as 4.25, while samples of lower sulfur content produced drainage in the neutral range (figure 4). The pH data observed in the laboratory were found to correlate reasonably well with data from the test piles discussed previously. Additional samples are being examined to verify the initial results and to examine other variables of solid composition.







The composition of the Duluth Complex rock examined in the aforementioned experiment was subsequently characterized using more sophisticated methods (Pignolet-Brandom and Lapakko, 1990). The QEM*SEM automated scanning electron microscope image analysis system was used to quantify the volumetric abundances of iron sulfides, copper-iron sulfides, nickel-iron sulfides, calcite, as well as the general categories of silicate, oxide, and phosphate minerals. The sulfur, nickel, and copper contents based on these volumetric abundances were typically within 20 percent of the values determined by standard chemical analyses, indicating that the QEM*SEM analyses were quite accurate.

The pH and sulfate concentrations of the rinse water from the laboratory experiment described above correlated well with the mineralogical data. In addition to accurate mineralogical abundance data, QEM*SEM can also determine mineral and particle size, particle surface mineralogy, extent of sulfide liberation, surface area per unit volume, sulfide surface area per unit volume, and free sulfide surface area per unit volume. These parameters affect the dissolution of mine waste and, therefore, the quality of drainage generated by the waste.

The same dissolution procedure was used to examine the drainage quality from sixteen Duluth Complex samples collected from blast holes at the Dunka site (Lapakko and Antonson, 1992). The sulfur contents ranged from 0.18 to 3.12 percent, and the test duration ranged from 69 to 150 weeks at the time of the aforementioned publication. Testing of most of these samples is yet in progress to examine long-term dissolution behavior of the rock.

The rate of sulfate release was approximately first order with respect to the solid phase sulfur content. Drainage pH decreased with increased solid phase sulfur content and time of reaction. Based on drainage pH and sulfate release rates, the solids were divided into four groups of variable sulfur content. For a 150-week period of record the pH of drainage from the first group (0.18-0.40% S) was continuously above pH 6.0, while the minimum drainage pH for samples from the second group (0.41-0.71% S) ranged from 4.82 to 5.30. The samples from the third group (1.12-1.64% S) generated minimum pH values of 4.32 to 4.92 over a period of 69 weeks, while the two samples in the fourth group (2.06 and 3.12% S) generated minimum drainage pH values of 3.5 to 4.3 over a period of 78 weeks (Lapakko and Antonson, 1992).

Two tailings samples generated from bench scale tests on titanium ore from the Duluth Complex were also subjected to solid phase characterization and dissolution testing described above (Lapakko, 1991a). These tailings were relatively coarse 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. These tailings generated drainage of neutral pH during the 52-week dissolution test, and present virtually no potential for acid production since the sulfide content of both samples was reported as less than 0.01 percent. Copper, nickel, and zinc concentrations (to a lesser extent) 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 (Lapakko, 1991a).

Drainage Quality from Greenstone Belt Gold Mine Tailings

No gold mines have been developed in greenstone belts in Minnesota. To investigate the quality of drainage from such wastes, samples were collected from other mines in greenstone belts. Ten tailings samples from operating North American gold mines were compositionally characterized (particle size, chemistry, mineralogy) and subjected to dissolution testing to examine the relationship between the solid phase characteristics and drainage quality (Lapakko, 1991a). The tailings were quite fine, with roughly 50 to 100% in the minus 270 mesh size fraction. They 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 degree of liberation of the sulfide and carbonate minerals typically exceeded 90 percent. The neutralization potential (NP) determined by the method of Sobek et al. (1978) typically exceeded the total calcium carbonate and magnesium carbonate and magnesium carbonate and magnesium carbonate determined by the method of Lawrence (1990) more closely approximated this value (Lapakko, 1992c).

None of the samples produced acidic drainage during the 52-week dissolution experiment, despite oxidation of iron sulfide minerals present in the tailings (Lapakko, 1990a). Drainage quality data, in conjunction with mineralogic data, indicated that the acid produced by iron sulfide oxidation was neutralized by the dissolution of the calcium carbonate and magnesium carbonate minerals in the tailings. However, these data suggested that the additional dissolution of some samples may deplete their neutralization potential and ultimately produce acidic drainage. Dissolution testing of these samples was continued in a subsequent project (Lapakko, 1992d). The pH of drainage from one of the samples (T9) decreased below pH 6.0 after 122 weeks and below pH 5.0 after 126 weeks (MN DNR Babbitt Research Laboratory, 1992, unpublished data). The comparison of oxidation rates with solid phase sulfur contents indicated that the pyrite present in some samples was oxidizing more slowly than that present in others (Lapakko, 1992c).

Barium, zinc, arsenic, antimony, and molybdenum were the most commonly release trace metals. Barium concentrations in mine waste drainage in the field, where sulfate concentrations are typically high, would probably be controlled by the limited solubility of barium sulfate. Arsenic, antimony, and molybdenum, when occurring in elevated concentrations as sulfide minerals, may produce elevated concentrations even if drainage is neutral.

EVALUATION OF PREDICTIVE TESTS

Several static and kinetic tests have been developed for predicting mine waste drainage quality. Static tests base predictions on solid phase analyses, while kinetic tests base predictions using dissolution tests on mine waste samples. To evaluate these various tests the U. S. Environmental Protection Agency provided funding to the MN DNR for a project which was administered by the Western Governor's Association. A literature review was produced as a foundation for the laboratory studies conducted (Lapakko, 1991b; 1992a).

In the laboratory studies, ten mine waste samples were subjected to four static tests and six kinetic tests to evaluate the ability of the tests to predict mine waste drainage pH (Lapakko, 1992b). The particle size distribution, chemistry, and mineralogy of the samples were analyzed to improve data interpretation. Static tests base drainage quality prediction on measurements of the maximum capacity of a mine waste to produce acid (Acid Production Potential or APP) and neutralize acid (Neutralization Potential or NP). The study addressed the accuracy of Acid Base Accounting, Modified Acid Base Accounting, and the B. C. Research Initial Tests for quantifying APP and NP. It concluded that the APP could be accurately quantified, and that the tests tended to overestimate the ability of mine wastes to neutralize acid while maintaining a neutral pH. Mineralogic factors contributing to this overestimation were enumerated. A modification of the Net Acid Production Test compared favorably with the Net NP (NP - APP) values of the aforementioned static tests.

Kinetic tests involve dissolution of mine waste samples and analysis of the resultant water quality. All kinetic tests simulated the field drainage pH from a sample with a reasonably high sulfur content and an NP near zero. In general, the sulfide oxidation and attendant acid production during most tests was not adequate to overcome the buffering available in samples with a moderate amount of NP. Indeed, less than ten percent of the sulfide present in the samples was oxidized over the course of the tests. This underlines the importance of considering the solid phase characteristics, particularly the NP, of samples when designing kinetic tests and interpreting their results (Lapakko, 1992b).

Kinetic tests such as these permit identification of some acid-producing solids based on the laboratory drainage pH. However, results from Lapakko (1992b) suggest it is possible that solids which generated alkaline drainage during the kinetic test time frame would have generated acid drainage had the experiments been continued. This possible error in classification was addressed by determining the time required to deplete the available acid producing potential (APP) and the acid neutralization potential (NP) using laboratory experimental data. A mixture of an alkaline solid and sulfide-bearing rock was subjected to wet-dry cycle dissolution (Lapakko, 1990b). The APP of the mixture was determined based on sulfur content, while the NP was determined by standard methods and corrected for background. The background contribution was quantified as the NP of samples of similar mineralogy after they had been allowed to oxidize to the point of generating acid. Since the samples had generated acid the remnant NP was used as the "background" contribution. This background was an artifact of the analytical technique rather than the

actual capacity for effectively neutralizing the acid produced by oxidation of iron sulfides present in the rock.

A 20-week period was selected as the experimental duration of a predictive test, and the drainage pH was alkaline over this period. The rate of neutralization by carbonate mineral dissolution was determined based on the appearance of calcium and magnesium in solution over this period. The time of neutralization potential depletion was calculated based on the initial neutralization potential of the mixture, adjusted for background contributions, and the observed neutralization rate. The calculated value was in good agreement with the drainage quality observed subsequent to week 20 (figure 5).

Subsequent data support the contention that results from short-term tests may not be accurate reflections of long-term drainage quality (Lapakko and Antonson, 1991; MN DNR Babbitt Research Laboratory, 1992). Furthermore, results from Lapakko and Antonson (1991) indicate that not all of the NP present in a mine waste will react to neutralize acid generated by the oxidation of the iron sulfide minerals present. In this study only about 80 percent of the calcium carbonate present reacted at the time drainage pH decreased below pH 6.0. It was hypothesized that the larger particles may have been less effective in neutralizing the acid produced.



Figure 5.

5. Predicted depletion of neutralization potential and observed pH vs. time.

MITIGATION USING ALKALINE SOLIDS

Blending Alkaline Solids with Mine Waste

The mitigative potential of adding alkaline solids to potentially acid generating mine waste was examined in a laboratory experiment. The experiment began in May 1988 to determine the effectiveness of mixing rotary kiln fines (a waste generated during the conversion of limestone to lime), minus 10 mesh limestone, and minus 0.25-inch/+10 mesh limestone with Duluth Complex rock containing 2.1 percent sulfur (minus 100/+270 mesh). Loadings of 1.05 to 10.5 g/100 rock were used for each alkaline solid, along with two control reactors containing only the Duluth Complex rock. The following three paragraphs summarize results for the first 80 weeks of the experiment.

The drainage pH from the control reactors was below 6 after 8 weeks and reached pH 3.7 after 70 weeks. With the exception of the lowest loading of RK fines, all of the RK fines and -10 mesh limestone produced drainage with a pH above 7. The drainage from the lowest RK fines loading remained below 6.0 after week 75, indicating that the neutralization potential of the RK fines had been depleted (figure 6). Concentrations of nickel, cobalt, and zinc from this mixture reached maximums after the pH dropped below 7.0, and copper concentrations increased steadily as pH decreased.

All other loadings of the RK fines and all loadings of the -10 mesh limestone neutralized the acid produced as a result of oxidation of iron sulfides present in the rock. Typical drainage pH values ranged from 8.0 to 9.2, with net alkalinities of 10 to 30 mg/L (net alkalinity = alkalinity - acidity). In addition to acid neutralization, sulfate concentrations indicated that these treatments reduced the rate of sulfide oxidation by approximately 70 to 85 percent. Trace metal concentrations from these treatments were 80 to 99 percent lower than those from the controls, and the reduction in iron concentration typically exceeded 99 percent.

The minus 0.25-inch/+10 mesh limestone treatment was discontinued after 40 weeks, having produced drainage similar to that of the controls. The experiment will continue to examine the duration of effective treatment by the RK fines and the minus 10 mesh limestone. These solids show potential for reducing release of acid and trace metals when mixed with potentially acid producing mine wastes. Additional detail on this study is available in two annual status reports (Lapakko and Antonson, 1989a; 1990a) and the most recent data analysis was presented in the Proceedings of the Second International Conference on the Abatement of Acidic Drainage (Lapakko and Antonson, 1991).



Figure 6. pH and net alkalinity vs. time for 1.05 RK fines/100 g rock.

Drainage Treatment with Limestone Beds

Laboratory Tests

Column laboratory experiments to examine the ability of limestone beds to neutralize acidic stockpile drainage began in April 1988. In the laboratory experiments triplicate columns containing 780 g of minus 0.25-inch/+10 mesh high calcium limestone were used to treat each of three different drainages. Flow rates were adjusted to maintain an effluent in which the alkalinity exceeded the acidity.

As of 9 November 1989, a period of 584 days, the columns have been successful in treating all three drainages. The median influent pH and mean net alkalinity of the three drainages were Seep 1: 5.35, -18 mg/L; FL3: 4.90, -210 mg/L; and FL6: 4.15, -600 mg/L, respectively. The corresponding effluent values were Seep 1: 7.5 and 15 mg/L (figure 7); FL3: 7.9 and 37 mg/L; and FL6: 7.95 and 120 mg/L. The flow rates required to maintain an effluent alkalinity in excess of effluent acidity were 5, 0.16, and 0.55 bed volumes per day, respectively. The corresponding volumes treated were 2680, 84, and 370 bed volumes (1380, 43, and 190 L, respectively).

The results indicate that limestone beds are capable of neutralizing these stockpile drainages if adequate detention time is allowed. This experiment will continue in an attempt to quantify the capacity of the limestone to neutralize each of the three drainages. Additional detail is available in two annual status reports (Lapakko and Antonson, 1989b; 1990b) as well as a shorter technical publication in the Proceedings of the Geological Association of Canada-Mineralogical Association of Canada Annual Meeting (Lapakko and Antonson, 1990d).



Figure 7. Effluent net alkalinity and pH vs. cumulative volume: Seep 1.

Field Test

A field scale limestone treatment bed (1.4 m^3 bed volume) went on line at the Seep 1 drainage at the Dunka site on September 26, 1988. The objectives of this project were to

- 1) elevate the pH and alkalinity while reducing the acidity and trace metal concentrations in the Seep 1 drainage;
- 2) describe the variation of treatment efficiency with the volume of drainage treated; and
- 3) describe the variation of treatment efficiency as a function of detention time or, equivalently, flow rate.

The bed contained 2020 kg of high-calcium limestone (minus 1/4 inch), and was 1.3 m in diameter and 1 m deep. It received Seep 1 flow from September 26 until October 28, 1988 and from April 26 until October 31, 1989. Operation was terminated each year when freezing conditions were impending.

The total flow through the bed during the 32 day period in 1988 was 580 cubic meters or 410 bed volumes, yielding an average flow of 13 bed volumes per day. Input pH ranged from 5.2 to 5.6 as compared to an effluent range of 7.15 to 7.7. The median value for the input net alkalinity (net alkalinity = alkalinity - acidity) was -30 mg/L, indicating that acidity exceeded alkalinity by 30 mg/L. The median effluent value was +38 mg/L, indicating an increase of almost 70 mg/L (Lapakko and Antonson, 1989c).

In 1989 the bed received 6600 cubic meters (4700 bed volumes) of flow at an average rate of 0.41 L/s or about 25 bed volumes per day. The bed raised the median pH from 5.0 to 6.85 and the median net alkalinity from -51 to +24 mg/L (figure 8). Copper concentrations were reduced by almost 50%, while nickel, cobalt, and zinc concentrations were reduced by about 10%.

The rate of alkalinity release in 1989 was used to quantify treatment efficiency. This release rate varied from 4.5 to 144 mg/s, with a mean value of 32 mg/s. Multiplying this mean release rate by the 188 days of operation indicates that a limestone mass of 0.52 T was dissolved. The release rate was independent of the volume treated, indicating that the treatment capacity of the bed was not taxed. The release rate did increase with flow, indicating that for the range of flows observed, the bed raised the influent alkalinity to an apparent equilibrium value. Additional detail on this study is available in an annual progress report (Lapakko and Antonson, 1990c; 1990d). Based on the observed neutralization by both the limestone columns and the pilot scale limestone bed, construction of a larger limestone bed was designed for potential pH elevation at Seep 1 (Lapakko, 1990a).



Figure 8. pH and net alkalinity vs. time for field scale limestone bed: 1989.

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