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Nonferrous Metal Mining

Impact, Mitigation, and Prediction Research

Minnesota Department of Natural Resources Division of Minerals

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NONFERROUS METAL MINING Impact, Mitigation, and Prediction Research

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SUMMARY

Since 1976 the Reclamation Section within the Minerals Division of the Minnesota Department of Natural Resources (MDNR) has been investigating potential impacts of nonferrous metal mining and techniques for their mitigation. Laboratory experiments, field test plots, and full scale operational field studies have been funded by the mining industry, the State of Minnesota, the Iron Range Resources and Rehabilitation Board, the United States Bureau of Mines, and the United States Environmental Protection Agency. The following topics have been addressed:

- 1. Quantification of the drainage quality, quantity and attendant chemical mass release from mine waste disposal facilities;
- 2. Description of the dissolution of sulfide-bearing mining wastes and the subsequent aqueous solute transport;
- 3. Assessment of low-cost, low-maintenance systems for mitigating impacts of mine drainage; and
- 4. Prediction of the quality of drainage from mining wastes generated by future operations.

These topics were examined as parts of several different projects, the first of which was the Regional Copper-Nickel Study. This study was initiated in 1976 with the intent of determining the potential impacts of proposed mining of copper and nickel in northeastern Minnesota. Some of the projects initiated by the Regional Copper-Nickel Study were adopted by the MDNR when the Regional Study concluded. These projects were conducted at several different sites.

At the Dunka Mine Site, chemical release from sulfide bearing waste rock has been quantified and the subsequent transport described. Mitigation techniques examined in conjunction with this operation include stockpile capping, wetland treatment, addition of alkaline solids to acidic mine waste drainage, and the use of various alkaline solids for neutralizing mine waste drainage. Chemical release from Duluth Complex rock was further examined at the AMAX test stockpiles, as was the effect of stockpile revegetation on chemical release. Treatment of drainage from these piles using various neutralizing agents has been examined, as has the use of several low cost solids. Finally, laboratory experiments were conducted to simulate mine waste dissolution in the field. These experiments were compared to results observed at the AMAX test site. An approach was also developed to incorporate such experiments into a program for mine waste regulation.

Technical expertise developed through these studies is presently being integrated into Minnesota's nonferrous metallic mineral mineland reclamation rules. The rules will base reclamation requirements for a given mining waste on its potential for adversely impacting other natural resources. Information from the studies will assist in assessing potential impacts and identifying viable mitigation options. The individual studies are summarized in the following pages.

MINING in MINNESOTA

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Minnesota has an extensive mining industry and vast 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 615 leases covering almost 238,000 acres of state land.

Minnesota's greatest mineral potential is associated with its Precambrian rocks, specifically its greenstones, metasedimentary formations and the Duluth Complex (figure 1). The greenstone formations of Minnesota extend north into Canada, where they have yielded substantial mineral production. They 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 metasedimentary formations associated with the greenstone 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, as well as significant titanium resources. Drill core has also revealed the presence of chromium, vanadium, cobalt, and platinum group elements.

In order to optimize mitigation design for a given mine waste it is necessary to assess the potential environmental impacts of the waste. The impact of mine waste drainage is a function of the drainage quality, drainage quantity, and extent of deleterious chemical transport. At present, there are no time-tested methods of quantifying these factors prior to operation. Likewise, there are no proven cost effective technologies for the acceptable long-term mitigation of potential impacts.

The optimal method of quantifying the factors controlling impact is to study drainage from actual mining wastes in the environment over an extended time period. Due to time and economic constraints, such an approach is often infeasible prior to mine development. However, these factors, as well as techniques of impact mitgation, have been studied since the mid 1970's. The studies were intitated in 1976 under the auspices of the Regional Copper-Nickel Study and, in 1978, were adopted by the Minnesota Department of Natural Resources. **Research includes:**

- Impacts and mitigation at the Dunka Site;
- Leaching and revegetation studies of AMAX test piles;
- Laboratory and field experiments on passive treatment of stockpile drainage with low-cost solids; and
- Laboratory experiments on the preoperational prediction of mine water quality.

The information gathered in these studies will aid in the impact assessment and mitigation of mine waste drainage from future operations. The results of the studies to date are summarized following a brief discussion of mine waste dissolution chemistry and previous mitigation research. Due to the complexity of these topics, and the relatively short time over which they have been studied, additional examination will be required.



Figure 1. Selected Precambrian rock formations of Minnesota.

MINE WASTE DISSOLUTION and MITIGATION

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):

$$MeS(s) + 2O_2 = Me^{2+}(aq) + SO_4^{2-}(aq)$$
(1)

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, 1977).

Reactions subsequent to the sulfide dissolution affect the net chemical 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 release of iron from sulfide minerals leads to the formation of iron oxyhydroxide minerals (Sung and Morgan, 1980; Nelson, 1978) and the generation of acid:

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

The acid that is generated can be consumed by the dissolution of the silicate minerals (Holdren and Berner, 1979) present in the rock:

$$CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O = Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s)$$
 (3)

The balance between the rates of acid generation and acid consumption determines the drainage pH. An excess of acid generation also elevates trace metal release, since trace metal concentrations increase as pH decreases. Other aspects of solution composition also affect trace metal transport, as well as the chemistry of the released component, and the chemical character and surface area of solid surfaces present.

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 ever present 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).

Mitigation attempts at other operations in the United States have focused on reducing contaminant release from the stockpile and removing contaminants from the drainage. Physical barriers, the most common of which is a vegetated soil layer, have been used to reduce the input of water and oxygen to mining wastes (Doyle, 1976; Grim and Hill, 1974). Addition of alkalinity (Ladwig et al., 1985) and bactericides (Erickson et al., 1985) to mine waste stockpiles, as well as drainage treatment by alkaline beds and/or wetlands (Kleinmann, 1985), have also been employed to reduce acid release from coal mining waste.

REGIONAL COPPER - NICKEL STUDY

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). Development of these deposits would require extensive open pit mining which, based on conceptual mining models, could produce an estimated 4 to 10 square km of waste rock stockpiles, depending on the stripping ratio and stockpile height (Veith, 1978; Sturgess, 1981).

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 (figure 2), monitoring of a bulk sample site, and laboratory experiments.



Figure 2. Locations of Dunka Mine and AMAX exploration site.

The earliest reports focused on the impact of potential copper-nickel operation on water resources (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 reports concluded that development of this resource could produce a number of environmental impacts, some of which could be due to leachate generation (Johnson and Lieberman, 1979). One of the principal sources of leachate could be lean ore and waste rock stockpiles (Thingvold et al., 1979). These stockpiles would generate an estimated 1.5 to 3.8 million cubic meters of drainage in a year of average precipitation (Hewett, 1980). Copper and nickel concentrations as high as 1.7 and 40 mg/L, respectively, have been observed in leachate generated by Duluth Complex waste rock stockpiles at the Dunka Mine, near Babbitt, Minnesota (Eger et al., 1981a). Both copper and nickel background concentrations in undisturbed streams of the area are approximately 0.001 mg/L (Thingvold et al., 1979). These trace metals have been shown to cause adverse biological impacts at aqueous concentrations less than 0.010 mg/L (Lind et al., 1978).

IMPACTS and MITIGATION at the DUNKA SITE

Impacts

The quantity and quality of waste rock and lean ore stockpile drainage were 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 trace metal content (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.

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 a mass load of over one ton of nickel into Bob Bay on Birch Lake. The majority of the flow passes through Unnamed Creek (figure 3). The most recent and comprehensive report (Eger et al., 1981b) presented the results of monitoring from 1976 to



Figure 3. Dunka Mine site.

1980, and earlier reports are available (Eger and Lapakko, 1980a; Eger et al., 1977). After 1980 the monitoring was conducted by Erie.

Over the period from 1976 to 1980, 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 (Eger et al., 1981b). Concentrations of trace metals (Cu, Ni, Co, Zn) exceeded ambient levels by 10 to 10,000 times. Copper and nickel concentrations exceeded the 48 hr LC50 for *Daphnia pulicaria*, while nickel concentrations also exceeded the 96 hr LC50 for the fathead minnow. (The LC50 is the concentration which is lethal to 50 percent of the test organisms, for the designated time interval.) Nickel contributed more than 90 percent of the trace metal load, and its removal by natural processes was less than 40 percent. Consequently, in the absence of mitigative measures, nickel concentrations will be elevated downstream from gabbro stockpiles. Concentrations of calcium, magnesium, and sulfate in the stockpile drainage were also elevated, but these parameters are of lesser environmental impact than the trace metals. Indeed, these parameters can reduce the toxic effects of trace metals.

Individual 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, 1988a; 1988b), Unnamed Creek (Eger and Lapakko, 1980b; Strudell, 1986), and Bob Bay (Lapakko and Eger, 1981b; Strudell et al., 1984). The Seep 3 stockpile drainage flows through a white cedar swamp prior to entering Unnamed Creek. From July 1976 through August 1977, average nickel and copper concentrations were 17.9 and 0.62 mg/L, respectively. The runoff moved across the surface and through the upper 30 cm of the peat. Travel times through the swamp were estimated to be about 50 days for flow across the surface and 250 days for flow through the upper 30 cm of peat. Analysis of water quality and peat samples indicated that at least 30 percent of the nickel and essentially 100 percent of the copper was being removed from the drainage by peat sequestration. Maximum trace metal concentrations in the peat, as determined by acid digestion, were 0.64 percent nickel and 0.36 percent copper. Information on the kinetics, mechanisms, and capacities of metal sequestration by peat has also been collected and is presented in the form of literature reviews (Lapakko et al., 1986b; Otterson, 1978).

The field study on trace metal transport through Unnamed Creek was augmented by chemical equilibrium computer modeling (Eger and Lapakko, 1980b). The studies indicated that nickel transport was greater

than that of copper in both the wetland (10-70 percent vs. 1-14 percent) and the creek (60-100 percent vs 26-51 percent). Aqueous and solid phase analyses indicated that metal removal resulted from adsorption onto peat, organic stream sediments, and mineral sediments. Results of chemical equilibrium computer modelling were consistent with field results and further suggested that zinc would behave similar to nickel, and cobalt similar to copper.

The transport of trace metals through Bob Bay was investigated in 1976-1977 and again in 1983. Additional studies will be conducted in the summer of 1990. The initial study (Lapakko and Eger, 1981b) indicated that concentrations of SO4, Ni, Ca, Mg, Cl, Cu, and alkalinity in the bay were higher than the regional average concentrations and decreased with distance from the point of input. Elevated metal concentrations were also observed in the sediments, as well as in plant and clam tissue. Nickel removal, based on sediment composition and sedimentation rate, ranged from 3 to 34 ug/cm²-yr. Nickel removal rates based on water quality data were 2 to 8 times as high.

The elevated concentrations were restricted to a high density flow along the bottom of the bay (Strudell et al., 1984). This flow occupied less than five percent of the bay volume during the 1983 study. The metal concentrations in the high density flow were higher than those observed in the previous study, due largely to higher input concentrations from the mining watershed. In this study, no nickel removal from the density flow was observed during the one to three days required for flow to pass through Bob Bay. The nickel concentrations did decrease but, based on concentrations of conservative parameters such as sulfate and calcium, this decrease was due to dilution.

Mitigation

The Minerals Division is presently involved in developing and implementing a program to mitigate release of trace metals and acid at the Dunka site. Monitoring to describe the trace metal sources within the Unnamed Creek watershed will continue. 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. These data will be used to design measures to reduce the release of trace metals and acid to the environment.

Several different mitigative measures are being studied:

- stockpile capping,
- wetland treatment,
- addition of alkaline materials to mine wastes that have potential to generate acid,
- addition of alkaline solids to acidic mine waste drainage, and
- the use of various alkaline solids for neutralizing mine waste drainage in an active treatment program.

Results of these studies will be incorporated as appropriate into LTV's mitigation program at the Dunka site.

The stockpile capping study plots were constructed in 1988 and data collection began in 1989. Four types of infiltration barriers were examined:

- 12 inches of compacted minus 2.5-inch glacial till,
- 12 inches of compacted minus 0.5-inch glacial till,
- two 6-inch lifts of compacted minus 2.5-inch glacial till, which was mixed with five percent bentonite, and a
- 20 mil PVC membrane, with six inches of pit run sand above and below the liner.

The plots were constructed as four lysimeter collection systems on a single rock stockpile. At the bottom of each plot was a liner for drainage collection. A six-inch layer of sand was placed on each liner and overlain by four feet of mine run waste rock. One foot of compacted sand was placed between the rock and the overlaying barrier. The barrier was

covered with one foot of unscreened glacial till upon which sod was placed, to simulate a well-established vegetative cover (figure 4).

The results generated from July 1 to November 21 were assumed to be reliable and were used for the initial comparison among the plots. The plot with the minus 0.5-inch till was not constructed properly and extensive repairs were required. The accuracy of the data from this plot was questionable and could not be used to measure the performance of the barrier. Additional tests conducted in 1990 indicated some problems with Plots 3 and 4 and with some of the instrumentation. These problems are being corrected. The plot with the PVC membrane produced the least bottom flow, while the minus 2.5-inch compacted glacial till produced the largest amount of bottom flow.



Figure 4. Capping test plot construction.

	Yield, inches of water				
	Input ^a ,	Surface	Barrier	Bottom	
Field Plot	inches	Runoff	Flow	Flow	
-2.5 inch till	19.2	0	0.37	6.6	
-0.5 inch till	19.2	0	0.04	3.7	
20 mil PVC	17.9	0	2.2	2.2	
5% Bentonite	18.3	0.13	1.9	2.3	
a					

Table 1. Stockpile capping field results July 1 - Nov. 30, 1989 (accuracy of flow measurement instrumentation is being checked).

^aInput includes water added through sprinklers plus natural precipitation.

The EPA HELP model was applied to the measured flows to estimate hydraulic conductivities for the barriers, the cover layer, and the drainage layer above the PVC liner. In general, the 20 mil PVC and the five percent bentonite mixture had hydraulic conductivities less than 10^{-6} cm/sec, while the minus 2.5-inch compacted till exceeded this value. The hydraulic conductivity of the cover material was on the order of 10^{-3} cm/sec, while that for the drainage layer above the PVC liner was on the order of 10^{-2} cm/sec. The evaporative depth on the plots was four to six inches and the maximum leaf area index was 1 to 1.5. More detail on the study is presented in a DNR report and symposium paper (Eger et al. 1990a, 1990b). This study will continue in order to more accurately assess the effectiveness of the four infiltration barriers.

The wetland treatment study objectives are to: 1) optimize treatment efficiency with different flow distribution methods and vegetation types; 2) measure system life; and 3) develop data for application to full scale treatment systems.

In 1988 four treatment cells were designed and constructed. Each cell is 6m x 30.5m and is surrounded by compacted peat berms (figure 5). Stockpile drainage is collected by a small dam near the toe of the stockpile, piped to the plots, and distributed to each cell through a series of valves and pipes.

Four treatments were selected, two low water plots (Cells 1 and 2, 5cm depth) with natural vegetation and two high water plots (15cm depth) with cattails (Typha). Cell 1 is a control cell containing native vegetation, sedges (*Carex sp.*) and grasses (*Calamograstis sp.*). In Cell 2 the peat was trenched perpendicular to the flow path to increase peat-drainage con-



Figure 5. Wetland treatment cell design.

tact. After trenching, sedges and grasses from the surrounding area were transplanted into this cell.

Since cattails have been used extensively in constructed wetlands, and quickly produce a dense stand and large biomass, they were planted in the two high water cells. Cell 3 has a serpentine flow path and contains a 5 cm layer of straw, which was added to stimulate sulfate reduction by consuming oxygen during its decomposition. Cell 4 uses peat berms perpendicular to the flow to distribute flow and increase the peat-stockpile drainage contact.

Data collection began in August of 1989. The nickel input concentration to the cells varied from a minimum value of 0.11 mg/L in early August and generally increased throughout the fall to a maximum of 1.82 mg/L in November. Preliminary results indicated that the average nickel removal ranged from a maximum of 78 percent in Cell 1 to 26 percent in Cell 4. Additional data will be collected and a final report will be prepared in February 1991.

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). Concentra-





tions 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).

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 experi-



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

ment 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).

A field scale limestone treatment bed (1.4 cubic meter 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 7.1 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 at Seep 1 was recommended (Lapakko, 1990a). Although this bed was not constructed, treatment with larger limestone particles was examined briefly in the summer of 1990.

The use of various alkaline materials for active treatment of mine waste drainage is described in the section on the AMAX test stockpiles.

LEACHING, REVEGETATION, and ACTIVE DRAINAGE TREATMENT STUDIES on AMAX TEST STOCKPILES

Six test stockpiles containing 820 to 1300 metric tons of low grade copper-nickel material 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 collected runoff 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 have been 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 9).



Figure 9. Annual median pH of test pile drainage from 1978 to 1989 (modified from Eger and Lapakko, 1985).

- 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.
- 5. Covering piles with topsoil (18 cm) or a combination of sandy till (30 cm) over coarse sand (28 cm), and establishing vegetation on these piles reduced drainage volume, and therefore mass release, by 30 to 50 pct.
- 6. Reclamation treatments were effective in reducing the drainage volume and mass release, but did not improve leachate quality. Concentrations of trace metals in the leachate are at least one to three orders of magnitude greater than proposed EPA effluent guidelines for mining discharge.

Additional small scale tests have been proposed to evaluate the effectiveness of lime stabilization, bactericide application, and low permeability soil covers on further reducing trace metal mass release from stockpiled material.

Neutralization Studies

Laboratory neutralization tests were conducted on drainage from AMAX test piles FL5 and FL6 to determine dosage rates, contact times, and the amount of metal removal. Drainage representing both the typical pH and metal concentrations, and the worst case conditions, were tested with three neutralizing agents: lime, sodium hydroxide and magnesium hydroxide.

Dosage rates generally varied from 1 gram of neutralizing agent per liter of solution to 10 grams per liter, and contact times varied from 1 to 120 hours. The pH increased and metal concentrations decreased as both time and dosage rate increased. All the materials were successful in raising pH and removing over 99% of the copper, cobalt, nickel and zinc from the solution. Due to the limited solubility of magnesium hydroxide, the maximum pH was maintained around 9.5 while in some experiments the pH exceeded 12 with both lime and sodium hydroxide.

A magnesium hydroxide slurry was chosen as the neutralizing agent for the test pile drainage. Although more costly than lime or sodium hydroxide, the slurry does not require continuous agitation, is easy to dispense, maintains pH at or below 9.5 (table 2), and produces a nonhazardous sludge which settles quickly. The treatment system was installed during the spring of 1990.

Table 2.	Effects of	treating	FL6	leachate	with	various	$Mg(OH)_2$	
loadings.								

Mg(OH) ₂ Loading (g/L)	pH	Cu (mg/L)	Ni (mg/L)	Co (mg/L)	Zn (mg/L)
Control	4.0	70	78	4.62	4.17
1	8.6	0.03	0.16	0.05	0.02
2	9.2	0.02	0.07	0.06	0.02
5	9.4	0.01	0.04	0.04	0.02
10	9.5	0.02	0.05	0.02	0.02

Note: All values correspond to a contact time of 96 hours.

PASSIVE TREATMENT with LOW-COST SOLIDS

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), but synopses of various research segments are presented in several symposium proceedings cited in the following paragraphs.

Before experiments were initiated a literature review was conducted on the trace metal removal abilities of several solids (Lapakko et al., 1986b). The first experimental phase was a laboratory screening program using: 1) batch experiments to screen wood chips, peat, till, tailings, zeolite, lime and sponge iron for treatment efficiency; and 2) column experiments to select the most promising materials for field trials. Based on the laboratory results (Lapakko and Eger, 1988, 1983, 1981a), low sulfide tailings were chosen for the phase two field testing.

The field tests utilized both treatment beds and joint disposal bins. In the saturated and unsaturated flow tailings treatment beds, the mass metal removal decreased in the order Ni, Cu, Zn, and Co; the removal efficiency (percent removal), however, decreased in the order Cu, Zn, Co, with percent nickel removal being the least (Lapakko et al., 1983). A model was developed to describe the output flow at a given distance as a function of the input flow.

In the joint disposal study, tailings containing 0.38 percent sulfur were incorporated with waste rock during the construction of the plots. Initially, mixing the tailings with the waste rock reduced metal concentrations by 88%, reduced flow by 38% and prevented acid drainage (Eger et al., 1984). Recently, the treatment effect has diminished as the pH has decreased and metal concentrations increased. The overall mass release from the treated plots is still less than 50% of that from the untreated plots. These tests are continuing.

PREOPERATIONAL PREDICTION OF DRAINAGE QUALITY

The preoperational prediction of the quality of drainage from 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. Projection of drainage quality requires mass quantification and characterization of mining wastes from the proposed mining site. 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. Since these data are rarely available, it is necessary to conduct predictive tests on characterized samples representative of the compositional range of the mine wastes.

The variation of drainage quality with solid phase 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, 1919; 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, in an attempt 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 generated by leaching of Duluth Complex solids (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 10). Additional samples must be examined to verify the initial results and to examine other variables of solid composition.

The solids examined in the aforementioned experiment were 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, and 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.



Figure 10. Drainage pH vs sulfur content of the solid phase. Horizontal lines represent 25, 50, and 75 percentiles, as well as the minimum and maximum values during the entire experiment.

Kinetic tests such as this one permit identification of some acid-producing solids based on the laboratory drainage pH. However, 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). An experiment was designed to examine the feasibility of such an approach.

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 11).

Predictive tests such as these (several other predictive test methods exist) are an important part of a mine waste evaluation program. Such a program has been designed for application on a site specific basis (Lapakko, 1990c; 1988b). The approach is similar to that applied for evaluation of potential for resource recovery. The extent of rock units of concern is delineated, and pertinent aspects of their composition are quantified. Tests are conducted on a variety of representative samples to determine their chemical behavior under prescribed conditions. The relationship between solid composition and chemical behavior is then extrapolated to the waste as a whole.



Figure 11. Predicted depletion of neutralization potential and observed pH vs time.

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. Such programs must begin as soon as resource development appears viable, so that closure and post-closure waste management plans can be developed and approved with minimum disruption of resource development. The ultimate verification of waste composition and particle size can occur only during operation.

With this information, 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. Wastes with mitigative capacity (e.g. limestone) can be identified, and reclamation design can be tailored to the potential for drainages adversely impacting other natural resources. Secondly, design can be directed toward meeting regulatory water quality standards. Thirdly, 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 ultimate reclamation of mine wastes. To further address these goals, two additional projects have been initiated. The Minerals Coordinating Committee has supplied funding to evaluate the environmental leaching behavior of several non-ferrous tailings samples. The particle size, chemistry, and mineralogy of the samples will be determined, and the samples will be subjected to the leaching procedure described previously (Lapakko, 1988a). The laboratory drainage quality will then be correlated with the solid phase characteristics. Secondly, funding has been obtained from the US EPA through the Western Governors' Association to compare and contrast various predictive techniques presently in use.

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