SUBAQUEOUS DISPOSAL OF MINE WASTE: LABORATORY INVESTIGATION[1]

Kim A. Lapakko[2]

Abstract: Laboratory experiments were conducted for 120 weeks to examine the effect of three different subaqueous disposal techniques on the oxidation of sulfide minerals present in Virginia Formation hornfels rock containing about 14 wt % pyrrhotite ($Fe_{0.9}S$). The subaqueous techniques were unmodified subaqueous disposal, subaqueous disposal with alkaline addition, and pretreatment (rinsing and neutralization) of rock prior to subaqueous disposal and subsequent alkaline addition. The pH of drainage from the two controls, representing on-land disposal, ranged from 3.7 to 4.2 during the initial 100 weeks, then decreased rapidly to 3.2 at 120 weeks. During the first 100 weeks the sulfate release rates averaged roughly 2.0×10^{-12} mol per gram rock per second; concurrent with the pH decrease, rates for controls increased to 5.6×10^{-12} and 13×10^{-12} mol per gram rock per second. For unmodified subaqueous disposal, pH declined steadily from 4.5 initially to 3.5 after 120 weeks. The pyrrhotite oxidation rates for the three subaqueous disposal techniques were 1.5×10^{-12}, 1.7×10^{-12}, and 2.2×10^{-12} mol per gram rock per second, respectively. With the exception of some initial rapid sulfate release from rock that was not pretreated, these rates were relatively constant over the course of the experiment. The rates observed in the laboratory were used, in conjunction with existing knowledge on oxygen transport, to determine rates of acid production for subaqueous disposal of similar mine waste in an open pit.

Additional key words: acid mine drainage, pyrrhotite, oxidation, rates, kinetics

Introduction

Subaqueous disposal has been gaining favor as a preferred option for mine waste disposal. This trend is the result of documentation of cases in which the oxidation of the sulfide minerals present in tailings has been retarded as a result of their disposal in lakes (Rescan Environmental Services Ltd 1989, Pedersen et al. 1990, Pedersen et al. 1991, Robertson 1991) and in mines (Rescan Environmental Services Ltd 1989). Ritcey (1991) cautioned that subaqueous disposal of partly oxidized waste, such as this waste rock, would result in release to the water of acidic reaction products that had accumulated on the mine waste surface. Disposal of partly oxidized waste in pits in British Columbia (Equity Silver Ltd. 1988) and the Yukon (Morin 1993b) resulted in acidification of the mine pit water. In another case, waste rock that produced acidic drainage while stored on land was relocated, along with a limestone amendment, into an open pit in 1988. The pit was subsequently flooded, and Veillette and Desrochers (1991) reported that the results through 1990 were favorable.

Although the rate of oxidation may be inhibited, sulfide minerals can oxidize in a subaqueous environment (City Resources Limited and Norecol Environmental Consultants Ltd. 1988, Moses and Herman 1991, Yanful and Payant 1992). The rates of oxidation and the resultant water quality are dependent upon site-specific conditions (Morin 1993a). Empirical determination of sulfide mineral oxidation rates for specific mine wastes in the laboratory, in conjunction with the existing knowledge on the diffusion of oxygen in water, allows calculation of site specific oxidation rates and the resultant water quality. Morin (1993a) used this approach to calculate rates of pyrite oxidation, and the attendant acid production, under various subaqueous disposal conditions.

In the present study the subaqueous oxidation of pyrrhotite ($Fe_{0.8-1}S$) present in mineralized Virginia Formation hornfels is examined. The complete oxidation of $Fe_{0.9}S$ is expressed as follows:

https://doi.org/10.21000/JASMR94010270

$$10Fe_{0.9}S + (87/4) O_2 + (47/2) H_2O = 9 Fe(OH)_3 + 10 SO_4^{2-} + 20 H^+ \tag{1}$$

The water quality associated with this oxidation and the rates of oxidation under laboratory conditions are compared for on-land (subaerial) disposal and three variations of subaqueous disposal. The rates determined in conjunction with existing knowledge of oxygen transport are used to extrapolate the laboratory data to in-pit disposal in the field.

Objectives

The objectives of this experiment were to describe the oxidation of sulfide minerals present in mineralized Virginia Formation rock under the following conditions:

1. In a subaerial (on-land disposal) environment in which the mine waste is subjected to wet-dry cycling,
2. In a submerged environment,
3. In a submerged environment with regular alkaline addition, and
4. In a submerged environment with regular alkaline addition, after removal of trace metal and acid reaction products from the hornfels surface.

The final objective was to extrapolate laboratory results to conditions of in-pit disposal in the field.

The wet-dry cycling environment represents disposal of the hornfels on land, with alternate periods of oxidation and flushing of oxidation products. The second condition represents the disposal of partly oxidized rock in an underwater environment, with no subseqent mitigation. The third condition includes addition of alkalinity after the disposal described by condition 2. The fourth condition includes "pretreatment" of the hornfels by removing the metals and acid on the rock surface. The rock is then handled as described in condition 3. This pretreatment was investigated as a means of removing acid and trace metals from partly oxidized wastes prior to subaqueous disposal.

Methods

Materials

The rock used in the experiment was mineralized Virginia Formation hornfels (VFH) which was collected, crushed, and wet-sieved in March 1989. The plus 270-minus 100-mesh fraction ($0.053 <$ particle diameter $\leq$ 0.149 mm) was retained for experimental use and stored in plastic bags until the inception of this experiment in September 1990. Sulfur contents, as determined by LECO furnace, of the two samples used in the study were 5.13% and 5.96%, respectively. Acid digestion (U. S. Bureau of Mines 1980) and digestate analysis by atomic absorption spectrophotometry (Perkin Elmer 603) indicated that over 97% of the sulfur was associated with iron (table 1). X-ray diffraction and electron microscopy (SEM/EDS) of a heavy mineral concentrate indicated the

Table 1. Sulfur, trace metal, and pyrrhotite content of mineralized Virginia Formation hornfels samples. (All values in wt %.)

Sample	S	Cu	Ni	Co	Zn	Pyrrhotite
A[1]	5.13	0.11	0.052	0.011	0.083	12.8
B[2]	5.96	[3].14	[3].068	[3].012	[3].084	14.9

[1] Used for on-land, unmodified subaqueous, and subaqueous with alkaline addition simulation.

[2] Used for pretreated subaqueous with alkaline addition.

[3] Average of analyses of duplicate samples.

presence of both hexagonal ($Fe_{0.9}S$) and monoclinic ($Fe_{0.875}S$). The pyrrhotite content of the samples was calculated based on the chemical analyes and the hexagonal pyrrhotite formula. Transmitted light microscopy of a similar

mineralized VFH sample (Graber 1990) indicated the rock contained 32% quartz, 32% opaques (sulfides, oxides, and graphite), and 19% of a clay mineral, probably kaolinite. Feldspar and chlorite each contributed 5%, and phlogopite and muscovite each contributed 4%.

Dissolution Procedures

To simulate on-land disposal, duplicate 75-g samples were placed onto a perforated plastic plate (covered by a glass fiber filter) in the upper segment, or reactor, of a two-stage filter unit (fig. 1). Prior to the inception of the experiment, the reactor was placed onto the lower segment (receiving flask) of the unit, upon which was placed a 0.45-μm filter. Samples were then rinsed with three distilled water volumes of 200 mL, to remove products that accumulated from oxidation during sample storage. To each reactor, 200 mL of distilled water was added and allowed to stand for 5 min; it was then drawn by vacuum through the mine waste sample and 0.45-μm filter into the receiving flask. This rinsing was repeated weekly for 120 weeks.

Between rinses the solids were retained in the reactors to oxidize further and stored in individual compartments of a wooden housing. A thermostatically controlled heating pad was placed beneath the housing to control temperature. The reactors were stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. Temperature and relative humidity were monitored two to three times a week. The average weekly temperature ranged from 21.7° to 28.6° C, with an average of 25.8° C and a standard deviation of 1.1° C (n=118). The relative humidity ranged from 38% to 67%, with an average of 53.6%, and a standard deviation of 5.6%.

The volume of rinse water, or drainage, was determined by weighing the receiving flask. pH was analyzed directly in the lower stage of the reactor, and aliquots were withdrawn for on-site determinations of specific conductance, acidity, and alkalinity Samples were also taken for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

The three underwater disposal conditions were all examined in duplicate. In each case 200 g hornfels and 1.8 L of distilled water were added to a 2-L Erlenmeyer flask. Glass wool was placed in the mouth of the flask to retard evaporation while allowing oxygen transport into the flask. The flasks were stored in the same controlled temperature and humidity room as the wet-dry cycle reactors. The pH of the solution was measured directly by inserting the electrode into the flask. Samples were withdrawn from a depth of about 8.3 cm in the flasks, which had an average water depth of 13 cm, for determination of specific conductance and alkalinity or acidity. The remaining sample was filtered (0.45 μm) for subsequent determination of sulfate, calcium, and magnesium. Samples taken for metal analyses were
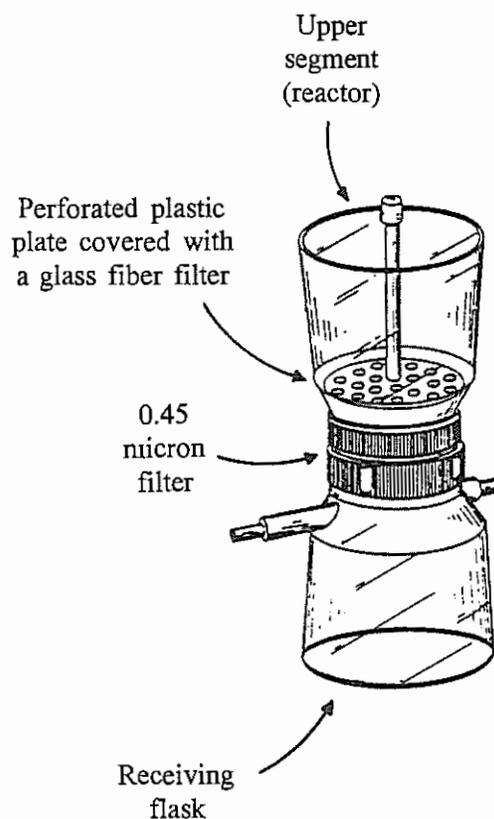

Figure 1. Reactor design.

272

acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample. Distilled water was added to maintain a constant volume within the flasks.

For the first subaqueous disposal condition, untreated rock was placed into the flasks with no further modification. For the second disposal condition, untreated rock was placed into the flasks, and an alkaline solution (hydrated lime dissolved in distilled water) was added when the pH in the flask dropped below 7.25. The alkalinity of this solution typically ranged from 1,400 to 2,000 mg/L as $CaCO_3$.

For the third subaqueous disposal condition, the 200-g rock samples were first rinsed with approximately 5.7 L of distilled water to remove acid and other products generated by weathering. The samples were next rinsed with 4.1 L of a solution of hydrated lime and distilled water (average alkalinity 1,030 mg/L as $CaCO_3$). A subsequent rinsing with 6.4 L of a solution of sulfuric acid and distilled water (average acidity 310 mg/L as $CaCO_3$) because the alkaline solution rinses produced a pH in excess of 11 on the rock sample surface. In total, each sample was subjected to 151 rinses of 100 to 120 mL. For the final rinse, 100 mL of distilled water was passed through the solids bed, and the pH of the effluent was between 7.6 and 7.8.

Analysis

An Orion SA 720 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. 1992). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Calcium and magnesium were analyzed at the MN DNR Minerals Office in Hibbing using a Perkin Elmer 603 atomic absorption spectrophotometer in the flame mode.

Results

The drainages from the duplicate reactors simulating on-land disposal exhibited similar temporal variations in quality over the 120-week period of record. The drainage quality clearly indicated that the rock was a fairly strong acid producer. During the initial 90 to 105 weeks the drainage composition was fairly stable, with pH ranging from 3.6 to 4.0 and sulfate concentrations typically between 40 to 65 mg/L (fig. 2). It should be noted that sulfate concentrations were highest in the initial rinse and decreased until
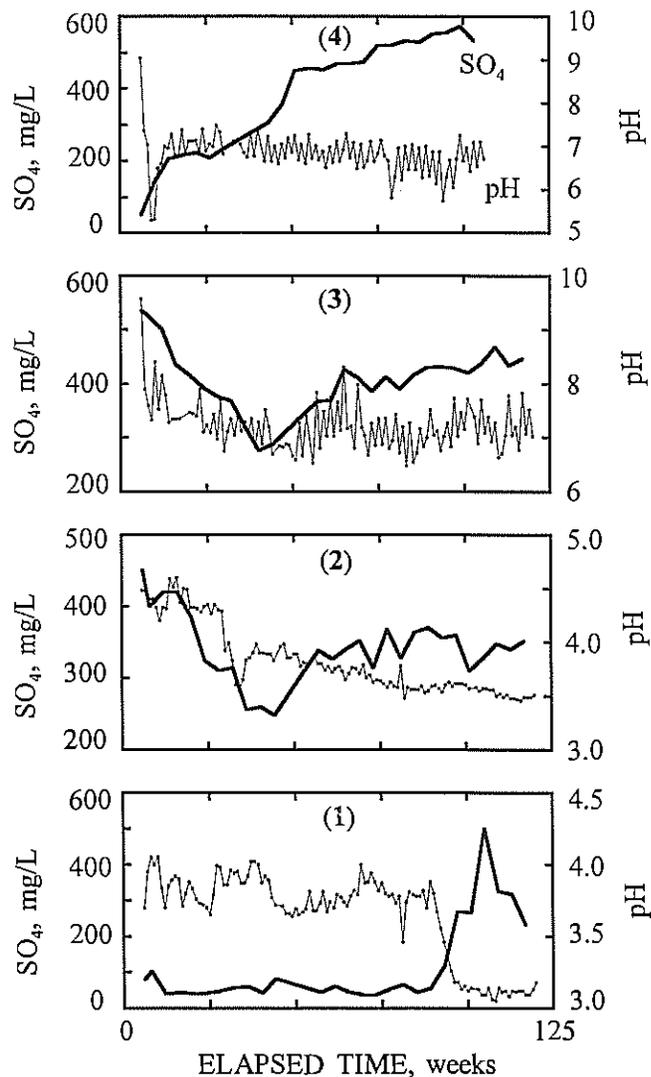

Figure 2.   Solution pH and sulfate concentrations for (1) on-land disposal, (2) unmodified subaqueous disposal, (3) subaqueous with alkaline addition, (4) pretreated rock, subaqueous disposal with alkaline addition. Acidic solutions were produced by (1) and (2).

273

week 10, reflecting the release of oxidation products which accumulated between sample crushing and the inception of the experiment. For all four experimental conditions the amount of sulfate on the rock surfaces ranged from 5 to 8 mg per gram rock. Subsequently, the aqueous sulfate observed was the product of sulfide mineral oxidation, since no sulfate minerals were present in the rock. Between weeks 90 and 100 drainage pH decreased to 3.1 while sulfate concentrations increased to the neighborhood of 300 mg/L. This transitional phase was followed by a period of fairly stable drainage quality during which drainage pH was lower and sulfate concentrations were greater than the corresponding values in the initial phase.

The rates of sulfate release in the final phase were three and six times higher than those in the initial phase for the two on-land reactors (table 2). This accelerated release was probably due to increased biologically mediated ferric iron oxidation of the sulfide minerals in the lower pH range. The rate of chemical oxidation also may have increased, but this increase would be slight relative to the increase in the rate of biological oxidation (Nordstrom 1982).

For the unmodified subaqueous disposal, pH declined steadily from 4.5 initially to a value of 3.5 after 120 weeks. The initial sulfate concentrations were about 450 mg/L. These elevated concentrations and the initial low pH reflected the release of acidic reaction products that had accumulated on the rock owing to oxidation prior to the experiment. During the initial 40 weeks sulfate concentrations decreased from roughly 450 to 250 mg/L; they \subsequently increased and stablized in the approximate range of 350 to 400 mg/L (fig. 2). The initial decrease in sulfate concentrations was due to dilution by the distilled water added to replace the sample volume withdrawn. During the first 40 weeks this volume averaged 75 mL/week. Subsequently the sample volume was reduced to about 44 mL/week.

The sulfate release for the unmodified subaqueous disposal was relatively rapid during the initial 10 weeks, owing to release of oxidation products accumulated on the solids prior to the experiment. Subsequent sulfate release was fairly linear and was the result of oxidation of pyrrhotite present in the rock. The rate of this oxidation was about 75% of that during the initial phase for the on-land disposal environment (table 2).

The pH of water in the two flasks simulating subaqueous disposal with subsequent alkaline addition was maintained in the typical range of 6.7 to 7.5. Sulfate concentrations followed the same trend observed for the unmodified subaqueous disposal. Concentrations decreased from about 520 to 300 mg/L during the first 40 weeks and subsequently increased to around 450 mg/L (fig. 2). As was the case for the unmodified subaqueous disposal, the initial elevated sulfate concentrations were the result of release of reaction products that had accumulated on the rock surface. Similarly, the subsequent decrease in concentrations was due to dilution by the distilled water used to replace the sample volume withdrawn.

The linear rate of release, representing the oxidation of pyrrhotite, was slightly faster than that observed for the unmodified reactors, and was about 88% of the initial rate for the on-land disposal simulation (table 2). The rates of alkalinity addition and the sum of calcium and magnesium release were in good agreement with the sulfate release rates.

For the rock that was treated prior to subaqueous disposal, the initial pH values were elevated due to some residual alkalinity on the solids. The solution pH declined steadily, decreasing below 6.0 at week 9. Alkalinity was added subsequently at regular intervals to maintain neutral pH. Sulfate concentrations were near 20 mg/L at the beginning of the experiment, indicating, as did the elevated initial pH, that the pretreatment was effective in removing reaction products from the rock surfaces. Subsequently, sulfate concentrations increased steadily over the course of the experiment (fig. 2).

Sulfate release for the pretreated subaqueous disposal was linear throughout the period of record (fig. 3). The rate of sulfate release per gram rock was higher than that observed for the other subaqueous disposal reactors, and was slightly higher than that during the initial phase of the on-land disposal simulation (table 2). When

normalized for the difference in pyrrhotite content (table 1), the rate of oxidation per unit area pyrrhotite approximated that observed for the on-land disposal simulation (table 3). The sum of the calcium and magnesium release rates was within 6% of the sulfate release rate (table 2). However, the rate of alkalinity addition was about 20% less than the sulfate release rate. Some of the acid generated as a result of iron sulfide oxidation was apparently neutralized by dissolution of host rock components and/or by the release of alkalinity accumulated on the solids during their pretreatment.

The data indicate that pyrrhotite can oxidize in a subaqueous environment with a consequent generation of acid and provide rates for that oxidation. The oxidation rates expressed as a function of the mathematically derived pyrrhotite surface area (table 3) also allow extrapolation of the data to particles larger than those used in the present study. For the sample masses used in this experiment, the rate of oxidation in the subaqueous setting was approximately equal to that observed in the intial phase for the wet-dry cycling environment. This indicates that, under the experimental conditions, oxygen transport was not the rate-limiting step for sulfide mineral oxidation. However, as the depth of pyrrhotite-bearing rock increases, oxygen transport would become limiting.
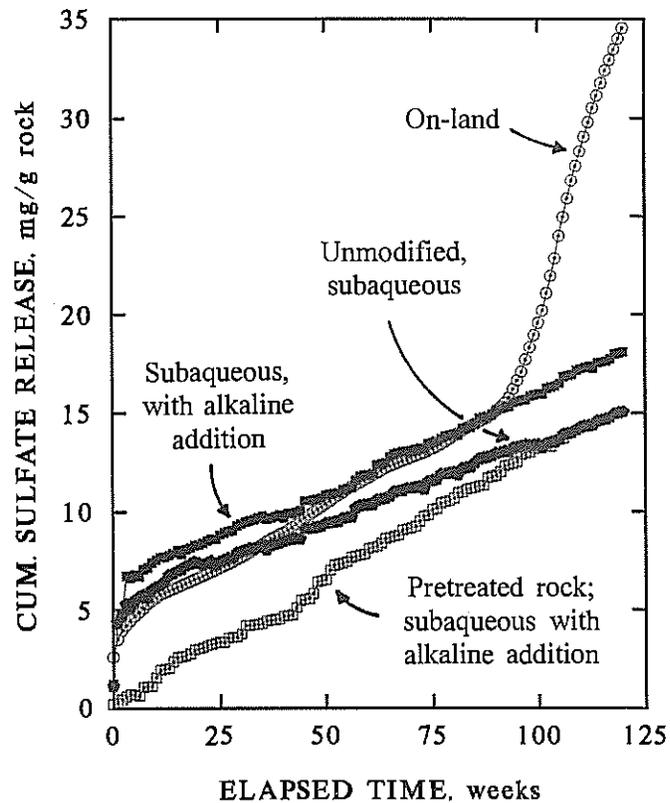

Figure 3. Cumulative sulfate release for on-land and subaqueous disposal. The rates of sulfate release and attendant acid production for the disposal options did not differ greatly. Data presented are from the second replicates.

Table 2. Rates of sulfate, calcium, and magnesium release and alkalinity addition (moles per gram rock per second x 10^{-12}.)

Simulation	Replicate	Sulfate	Calcium	Magnesium	Alkalinity Addition[1]
On-land initial	A	1.9	0.41	0.46	0
	B	2.1	.40	.46	0
On-land final	A	5.6	.13	.86	0
	B	13	.20	2.7	0
Unmodified subaqueous	A	1.6	.20	1.1	0
	B	1.4	.18	1.0	0
Subaqueous with alkaline addition	A	1.8	[2]1.3	.40	1.7
	B	1.7	[2]1.2	.38	1.7
Pretreated subaqueous with alkaline addition	A	2.1	[2]1.9	.01	1.7
	B	2.3	[2]2.0	.01	1.7

[1] Rate of alkalinity addition as equivalent moles $CaCO_3$.
[2] Includes calcium released to solution from rock and that supplied by the addition of alkalinity.

Table 3. Pyrrhotite oxidation rates expressed as a function of mathematically derived pyrrhotite surface area. (d = 1 x 10^{-4} m, specific gravity = 4.6, specific surface area = 0.013 m^2/g.)

Simulation	Rate: nmol $Fe_{0.9}S$ per m^2 $Fe_{0.9}S$ per second		
	Replicate 1	Replicate 2	Average
On-land, initial[1]	1.1	1.2	1.2
On-land, final[2]	3.3	7.5	5.4
Unmodified subaqueous	.92	.77	.84
Subaqueous with alkaline addition	1.0	1.0	1.0
Pretreated subaqueous with alkaline addition	1.1	1.2	1.1

[1] pH 3.6 to 4.0.
[2] pH 3.1.

The rates of pyrrhotite oxidation and acid generation, when oxygen transport is limiting, can be calculated using the approach presented by Morin (1993a). This approach assumed a first-order dependence of pyrite oxidation rate on dissolved oxygen concentration, a relationship that was previously reported for the oxidation of pyrrhotite present in Duluth Complex rock (Lapakko 1980). Examination of the equations presented by Morin (1993a) and subsequent discussion with the author (Morin 1993b) led to the conclusion that the following corrections should be made in Morin (1993a). Equation 7(a) should read $J = DO(pond)(kDe)^{0.5}$; FACT1=1.00 and FACT2=1.67 for equation 1; FACT1=1.07 and FACT2=0.90 for equation 2.

The aforementioned corrections were incorporated to calculate the rates of acid production for pyrrhotite-bearing tailings and waste rock disposed under water in a mine pit. The calculation assumes the water overlying the mine waste is saturated with dissolved oxygen and the water within the mine waste pores is stagnant. Under these conditions pyrrhotite oxidation and the consequent acid production will occur only as oxygen diffuses into the mine waste. As mentioned by Morin (1993a), it is necessary to characterize the physical and chemical hydrology of the system to ensure that these assumptions are correct.

Oxygen saturation at 26° C temperature in the present study would be approximately 8 mg/L and at 5° C would be near 13 mg/L (APHA 1992). For the calculation the following values were used: dissolved oxygen = 10 mg/L; pyrrhotite oxidation rate = 1 nmol/m^2 $Fe_{0.9}S$/s; average porosity = 0.3; pyrrhotite content = 14%; tailings diameter = 0.0001 m; and waste rock diameter = 0.1 m. The calculated acid production rates for tailings and waste rock were 1 x 10^{-3} mg $CaCO_3$/m^2 horizontal cross-sectional area/s and 5 x 10^{-5} mg $CaCO_3$/m^2 horizontal cross-sectional area/s, respectively. The value for tailings is slightly less than the observed laboratory value of 2 x 10^{-3} mg $CaCO_3$ /m^2/s. Despite the approximations applied in the calculation, the similarity of values suggests that observed laboratory rate is close to being limited by oxygen transport. This seems curious since the depth of solids in the laboratory was less than 3 cm. The equations used will be examined further and additional laboratory study will be undertaken to evaluate the implication of oxygen-transport limitation in the laboratory.

The rates of acid generation for subaqueous conditions must be considered to ensure that acid conditions would not develop in a pit upon disposal of pyrrhotite-bearing mine wastes. The potential for residual acid salts on the mine wastes prior to disposal must also be taken into account. The neutralization required for the acid inputs can then be quantified. Sources of neutralization include alkaline water inputs to the pit, dissolution of alkaline components in the pit walls, and addition of alkaline amendments. The possibility of placing an oxygen consuming material above the mine waste could also be considered as a means of slowing the acid generation. Furthermore, the release of trace metals from sulfide minerals into neutral waters must be assessed.

Acknowledgments

References

American Public Health Association (APHA), American Water Works Association, Water Environment Federation. 1992. Standard Methods for the Examination of Water and Wastewater, 18th edition. American Public Health Association, Washington, D. C.

Cathles, L. M. 1982. Acid mine drainage. Earth and Mineral Sciences 51: 37-41.

City Resources (Canada) Limited and Norecol Environmental Consultants Ltd. 1988. Cinola gold project, stage II report, v. V and v. V appendices. Submitted to British Columbia Ministry of Energy, Mines, and Petroleum Resources. (cited in Morin 1993).

Equity Silver Ltd. 1988. Decommissioning and closure report. Houston, BC.

Graber, R. 1990. Telephone conversation with Ron Graber, Pickands Mather Services, Inc., Research Center, Hibbing MN.

Lapakko, K. A. 1980. The kinetics and mechanisms of the oxidative dissolution of metal sulfide and silicate minerals present in the Duluth Gabbro. M.S. Thesis, Univ. MN, Minneapolis, MN. 199 p. plus appendices.

Morin, K. A. 1993a. Rates of sulfide oxidation in submerged environments: Implications for subaqueous disposal. p. 235-247. In Proceedings Seventeenth Annual British Columbia Mine Reclamation Symposium. (Port Hardy, BC, May 4-7, 1993).

Morin, K. A. 1993b. Telephone conversation with Kevin Morin, Morwijk Enterprises Ltd., Vancouver, BC.

Moses, C. O. and J. S. Herman. 1991. Pyrite oxidation at curcumneutral pH. Geochimica et Cosmochimica Acta 55: 471-482. http://dx.doi.org/10.1016/0016-7037(91)90005-P

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. p. 37-56. In Acid Sulfate Weathering. Soil Sci. Soc. Am. Madison, WI.

Pedersen, T. F., B. Mueller, and J.J. McNee. 1991. Diagenetic reactivity of mine tailings in mesotrophic and oligotrophic lakes in Manitoba and British Columbia. p. 199-226 In Proceedings Second International Conference on the Abatement of Acidic Drainage, v. 4. (Montreal, PQ, September 16-18, 1991).

Pedersen, T. F., B. Mueller, and C. A. Pelletier. 1990. On the reactivity of submerged mine tailings in fjords and a lake in British Columbia. p. 285-293. In Acid Mine Drainage: Designing for Closure. Proceedings GAC/MAC Joint Annual Meeting. (Vancouver, BC, May 16-18, 1990).

Rescan Environmental Services Ltd. 1989. Subaqueous disposal of reactive mine wastes: An overview. Report to British Columbia Ministry of Energy, Mines, and Petroleum Resources. Vancouver, BC.

Ritcey, G. M. 1991. Deep water disposal of pyritic tailings. p. 421-442. In Proceedings Second International Conference on the Abatement of Acidic Drainage, v. 1. (Montreal, PQ, September 16-18, 1991).

Robertson, J. D. 1991. Subaqueous disposal of reactive mine waste: An overview of the practice with case studies. p. 185-200. In Proceedings Second International Conference on the Abatement of Acidic Drainage, v. 3. (Montreal, PQ, September 16-18, 1991).

United States Bureau of Mines. 1980. A simple low-cost method for the dissolution of metal and mineral samples in plastic pressure vessels. BuMines RI 8480. 14 p.

Veillette, G. and C. J. Desrochers. 1991. Reclamation of the Solbec Mine by flooding waste rock in open pit. p. 219-238. In Proceedings Second International Conference on the Abatement of Acidic Drainage, v. 3. (Montreal, PQ, September 16-18, 1991).

Yanful, E. K. and S. C. Payant. 1992. Evaluation of techniques for preventing acidic rock drainage. First Milestone Research Report submitted to MEND.