Reflooded Mine Source Term Technical Memoranda for the Proposed Crandon Mine, Forest County, Wisconsin

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James M. Robertson, Director and State Geologist

State of Wisconsin

CORRESPONDENCE/MEMORANDUM

DATE: January 31, 2004

TO: Crandon Project Files

FROM: Chris Carlson – WA/3

SUBJECT: Crandon Project Reflooded Mine Source Term Report

Attached are three memos that were originally intended to be merged to form the Department's "Reflooded Mine Source Term Report for the Proposed Crandon Mine," which was to be a support document for the project's Environmental Impact Statement. Since Nicolet Minerals Company withdrew their permit applications for the proposed mine in late October 2003, these memos represent the state of the review and analysis of the reflooded mine source term at that time. Efforts were made to document the already completed work, but no efforts were made by the source term review team to evaluate the individual work products, merge them together into a final source term document, or to expose the effort to wider internal or external review. Therefore, the memos must stand on their own, as is, and be considered together as a status report on the Department's reflooded mine source term review at the time of permit application withdrawal. Any readers should consider them to be draft in nature, and not to represent the final perspective of individual members of the source term review team, the source term review team as a whole, or of the Department. Any users of the content of the memos do so at their own risk.

LIST of REFLOODED MINE SOURCE TERM TECHNICAL MEMORANDA

I Oxygen Fluxes in Stope Access Cross-Cuts After Bulkhead Installation – Civil Engineering Consultants
II Summary Evaluation of Laboratory Waste Characterization for the Proposed Crandon Mine Reflooded Mine Source Term – Kim Lapakko
III Source Term Calculations for the Reflooded Mine, Proposed Crandon Project – Sala Groundwater and Wisconsin DNR

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MEMORANDUM

To: Christopher Carlson, PhD, WDNR

From: Craig H. Benson, PhD, PE

Date: November 23, 2003

Re: Oxygen Fluxes in Stope Access Cross-Cuts After Bulkhead Installation

Enclosed is the material I drafted for the report on the reflooded mine source term. A copy of this document was sent to Kim Lapakko in June 2003.

OXYGEN TRANSPORT TO BACKFILLED STOPES

Paste backfill will be exposed to oxygen at the top surface of the stopes or cut-and-fill lifts, and through the cross-cuts. A schematic showing each of these areas of oxygen contact is shown in Fig. 1. Oxygen transport to each of the contact areas was evaluated independently.

STEFFEN, ROBERTSON, AND KIRSTEN (SRK) ANALYSIS

Cross-Cuts

A schematic of a cross-cut is shown in Fig. 2. The cross-cut is blocked by a bulkhead and the space between the bulkhead and backfill is assumed to be completely filled with waste rock. Oxygen traveling to the stope first passes across the bulkhead, then passes through the rock backfill, and finally penetrates the backfilled stope. Steffen, Robertson, and Kirsten (SRK) assumed that the transport through the cross-cut could be bounded by two different scenarios, referred to as BEJ and UB (see Appendix A of Addendum No. 1 to the *Mine Permit Application, Reflooded Mine Management Plan*, Foth and Van Dyke 2000).

In the BEJ analysis, the oxygen flux is assumed to be controlled by the rate at which oxygen diffuses into the backfill. The bulkhead is assumed to readily transmit oxygen, rendering pore gas in the waste rock at atmospheric conditions (8.9 moles/m^3). The UB scenario assumes that oxygen transport is limited by the rate at which oxygen can diffuse through the waste rock. The oxygen concentration at the interior face of the bulkhead is assumed to be atmospheric. To maximize the oxygen flux, the oxygen concentration was assumed to be zero at the interface between the waste rock and backfill. Advection and consumption of oxygen in the waste rock were ignored in the UB and BEJ cases.

SRK assumed that the oxygen flux in the BEJ case could be described by the average rate of oxygen consumption obtained from the humidity cell tests (0.50 mol O_2/m^2-yr) (Appendix A, page A-21, Foth and Van Dyke 2000). For the UB case, SRK computed the flux using the steady-state form of Fick's First Law. The effective diffusion coefficient in the waste rock was assumed to be 6x10^{-6} m^2/s based on data reported in Ritchie (1994). The oxygen flux for the UB case was determined to be 139 mol O_2/m^2-yr (Appendix A, page A-21, Foth and Van Dyke 2000).

Surfaces of Stopes and Cut-and-Fill Lifts

Oxygen transport into the surfaces of the stopes and cut-and-fill lifts occurs while the surfaces are exposed during mining (i.e., while mining directly above the upper surface of a stope or a backfilled layer). This scenario is similar to the BEJ case assumed for transport in the cross-cuts, which assumes that diffusion into the backfill controls the oxygen flux. SRK indicates that the humidity cell tests are representative of this scenario, but did not report an oxygen flux. However, based on the previous analysis used for the cross-cuts, the oxygen flux can be assumed to be 0.50 mol O_2/m^2-yr.

No analysis was conducted for the case where the access to the cut-and-fill lifts is isolated by a bulkhead. However, this analysis is similar to that assumed for the cross-cuts. Accordingly, the BEJ and UB fluxes reported by SRK for the cross-cut analysis (0.50 and 139 mol O_2/m^2-yr) apply to the surfaces as well. As noted in the previous section, both of these fluxes ignore advection and oxygen consumption in the waste rock.

ADDITIONAL ANALYSIS

Additional analyses were conducted to evaluate the importance of advection and oxygen consumption in the waste rock. Van Genuchten's (1981) solution to the advection-diffusion-reaction equation (ADRE) with zero order consumption was used for the analysis (Appendix C of van Genuchten 1981). Using this solution to analyze transport in the access cross cut implies that transport occurs under isothermal conditions and pressure differentials are small.

Van Genuchten's solution assumes that the gas traveling from the main cross cut to the stope has an initial concentration C_i and travels at a pore velocity v, the source concentration (at the interior face of the bulkhead) is constant and equals C_o, and the porous medium (waste rock) has a diffusion coefficient D and zero-order consumption rate γ. Retardation due to sorption is included in the solution, but was ignored in this analysis (the retardation factor R was set to 1).

For this analysis, C_i and C_o were both assumed to equal the atmospheric concentration of oxygen (8.9 moles/m^3), D and v were defined using typical values, and γ was set using the consumption rates reported by Lapakko (2003). A summary of the computations used to define the consumption rate is in Benson (2003).

Two cases were considered: Case L and Case U. Case L used lower bound values for the diffusion coefficient, pore air velocity, and consumption rate. Case U used upper bound values for the diffusion coefficient, pore air velocity, and consumption rate. A summary of the input parameters is in Table 1. Results of the simulations are shown in Fig. 3. In both cases, oxygen transport is dominated by oxygen consumption in the waste rock. Within two days, oxygen concentrations in the waste rock reach zero for Case L and within one day for Case U. Also, in both cases the concentration across the waste rock is negligible. These results indicate that the rate of oxygen transport is controlled by the rate at which oxygen can be delivered to the waste rock, i.e., the flux across the bulkhead. Diffusion thorough the waste rock and diffusion into the stope backfill are negligible.

An additional analysis was conducted to estimate the flux across the bulkhead. Steady-state oxygen transport across the bulkhead due to advective and diffusive transport was assumed. The input parameters that were used for this steady-state analysis are summarized in Table 2, and the computations are summarized in Benson (2003). The diffusion coefficient was based on data reported by Elberling (1996) for cemented porous media, assuming that the timber bulkhead would be coated with shotcrete. This steady-state analysis indicates that the flux across the bulkhead ranges between 3.47 and 34.7 mol $0_2/m^2$-yr. These fluxes fall within the range of fluxes predicted by SRK. That is, even though the analyses conducted by SRK do not simulate the key mechanisms driving oxygen transport, the fluxes reported by SRK are reasonable.

REFERENCES

Benson, C. (2003), Oxygen Flux in Stope Access Cross-Cuts After Bulkhead Installation, Memorandum to Christopher Carlson of Wisconsin Dept. of Natural Resources, April 13, 2003.

Elberling, B. (1996), Gas Phase Diffusion Coefficients in Cemented Porous Media, J. Hydrology, 93-108.

Foth and Van Dyke (2000), *Mine Permit Application, Reflooded Mine Management Plan* , Crandon Project, Crandon, Wisconsin, prepared for Nicolet Minerals by Foth and Van Dyke, Green Bay, WI.

Ritchie, A. (1994), Sulfide Oxygen Mechanism-Controls and Rates of Oxygen Transport, in *The Environmental Chemistry of Sulfide Mine Wastes*, D. Blowes and J. Jambor, eds, CANMET.

Lapakko, K. (2003), Oxygen Consumption Rates for Waste Rock and Pyritic Paste Backfill, personal communication.

van Genuchten, M. (1981), Analytical Solutions for Chemical Transport with Simultaneous Adsorption, Zero-Order Production, and First Order Decay, *J. of Hydrology*, 49, 213-233.

Table 1. Summary of Input Parameters for Cases L and U.

Parameter	Case L	Case U
Initial Gas Concentration in Pore Space, C_i (mol/m^3)	8.9	8.9
Source Gas Concentration, C_o (mol/m^3)	8.9	8.9
Retardation Factor, R	1	1
Gas Velocity, v (m/yr)	0.365	3.65
Gas Diffusion Coefficent, D (m^2/yr)	31.6	316
Consumption Rate, γ (mol/m^3-yr)	-1890	-8750

Table 2. Transport Parameters Used for Computing Flux Across Bulkhead.

Parameter	Case L	Case U
Source Gas Concentration, C_o (mol/m^3)	8.9	8.9
Gas Flow Rate, q (m/yr)	0.365	3.65
Gas Diffusion Coefficent, D (m^2/yr)	0.0073	0.073
Bulkhead Thickness (m)	0.3	0.3

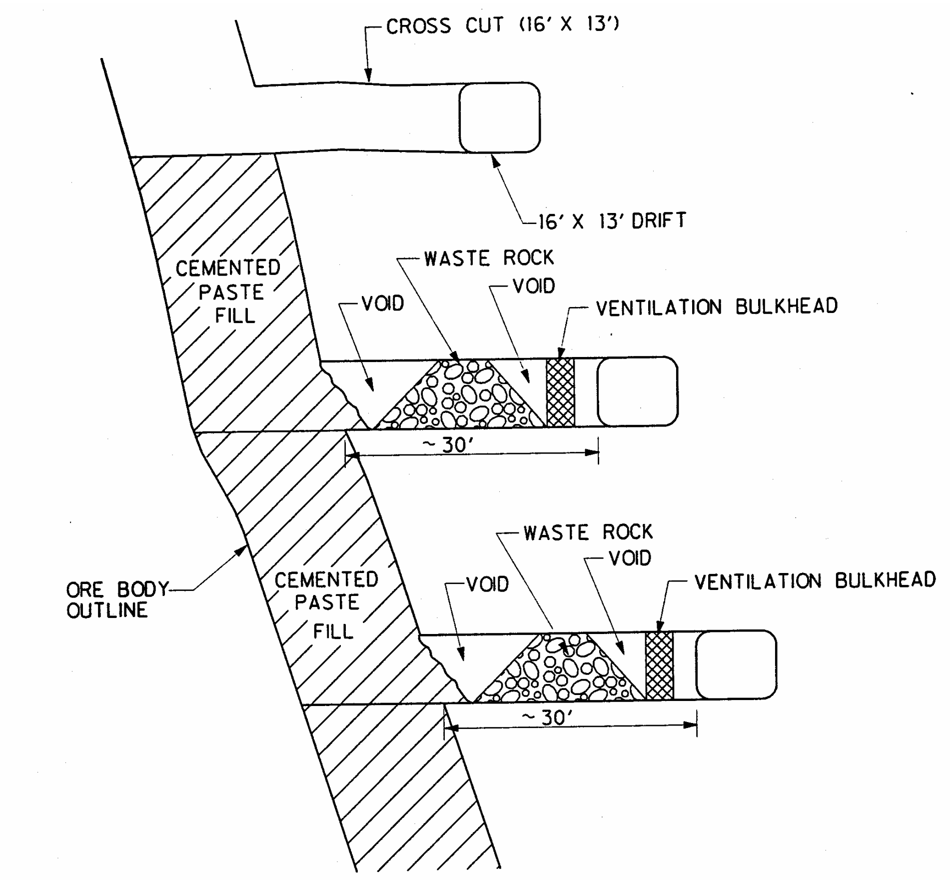
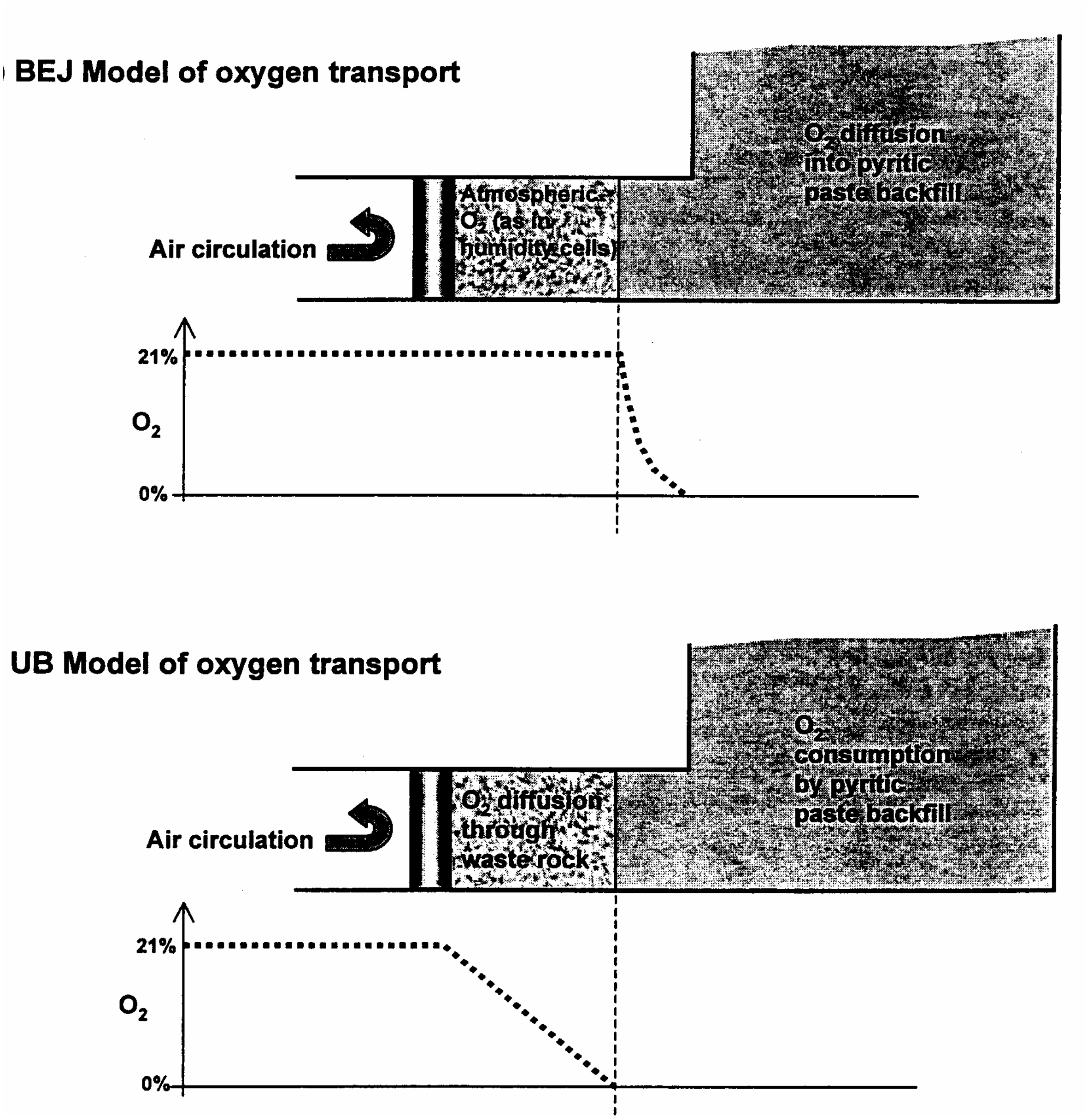


Fig. 1. Schematic of backfilled stope access cross cut (from Foth and Van Dyke 2000).


BEJ Model of oxygen transport

UB Model of oxygen transport

Fig. 2. Oxygen transport mechanisms assumed by SRK (from Foth and Van Dyke 2000).

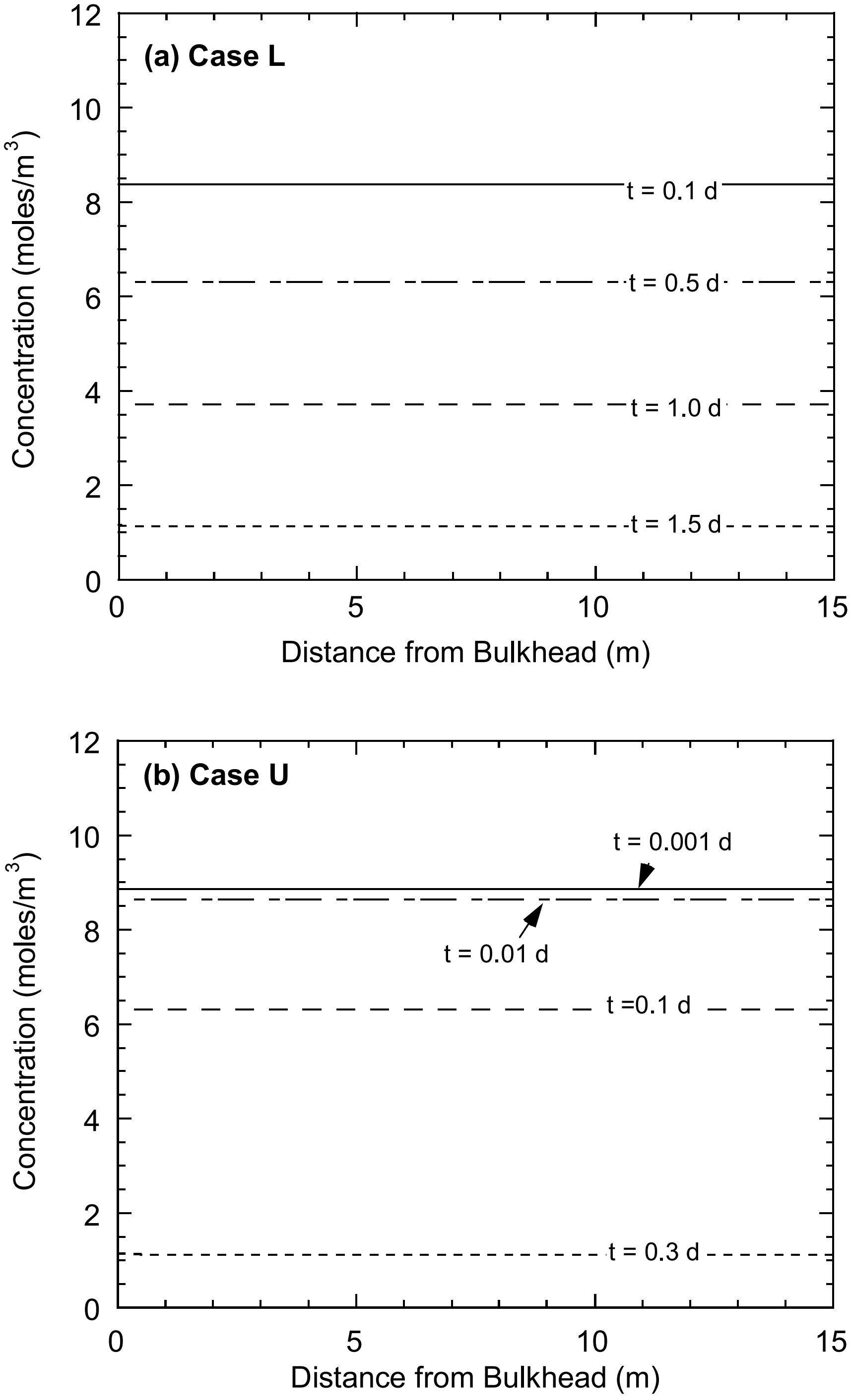


Fig. 3. Oxygen concentrations in the stope access cross cut assuming advective-diffusive transport with zero order consumption in the waste rock: (a) Case L and (b) Case U.

Summary Evaluation of Laboratory Waste Characterization for the Proposed Crandon Mine Reflooded Mine Source Term

Final Draft Memorandum

31 December 2003
Kim Lapakko

1. Introduction

Water quality in the reflooded mine will be influenced by the pyritic paste backfill, waste rock, mine walls, and the crown pillar. NMC characterized and conducted laboratory dissolution tests on samples selected to represent the various components. Geochemical and physical (gas transport, hydrology) modeling were used to extrapolate laboratory data to estimate the solute release under field conditions. The objective of this presentation is to summarize the characterization and laboratory testing conducted and its applicability for estimating solute release in the field.

The pyritic paste backfill and the pyritic tailings that constitute the majority of the paste were subjected to characterization and laboratory dissolution testing. Similarly, composite samples of waste rock were characterized and subjected to laboratory dissolution tests. This waste rock characterization and testing is described in the section of the TMA and Reclamation Pond Source Term Report entitled TMA Laboratory Waste Characterization. No tests were conducted specifically on mine wall or crown pillar materials. The aforementioned waste rock testing was used for projecting the dissolution behavior of mine walls. This information, in conjunction with data from ore dissolution tests, was used to estimate dissolution behavior of the crown pillar.

Solute release in the field is largely a function of the materials that are present and the reaction conditions to which they are exposed. Determining, prior to mine development, the extent and character of these materials, the conditions to which they are exposed, the reactions that occur, and the rates of those reactions is not a trivial process. Furthermore, there is a dearth of empirical information on solute release from underground mine workings, much less the solute release under conditions specific to the proposed site. Consequently, there is considerable uncertainty involved in extrapolating solid-phase characterization and laboratory dissolution test data to field conditions for the long term over which mine waste dissolution will occur.

There are several general steps that can be taken to reduce the uncertainty of solute-release predictions. First, steps can be taken to ensure that samples selected for characterization and laboratory dissolution testing are representative of those that will be present in the field. This may involve examination of a compositional range of materials to simulate the compositional variability of materials in the field. Second, samples subjected to dissolution testing must be thoroughly characterized with respect to particle size distribution, chemistry, mineralogy, and petrology. Third, dissolution tests must be carefully designed to ensure accurate collection of all data needed for estimations. Fourth, the data collected must be extrapolated diligently. Available empirical data and scientific principles, including those of geochemistry, gas transport, and hydrology, must be rigorously applied. Furthermore, a range of hypotheses must be considered to account for potential variations in solid-phase compositions and reaction conditions in the field.

2. Tests for Pyritic Paste Backfill Solute Release Calculations

2.1. Materials

Tests on pyrite concentrate and pyritic paste backfill were used to calculate solute release from the pyritic paste backfill. Bulk zinc tailings were generated in metallurgical testing on a master zinc ore composite created from drill core samples (Foth & Van Dyke 1999/2000, Environmental Impact Report (EIR) Appendix 4.2-15, p. 4.2-15-10). Pyritic paste backfill was prepared from a mixture of two pyrite concentrates generated from flotation of bulk zinc tailings with five percent cement and water (Foth & Van Dyke 1999/2000, EIR Appendix 4.2-15, p. 4.2-15-11 to 4.2-15-12). The paste was placed into a mold to form cubes with an edge length of approximately 1 cm and cured for 28 days before being subjected to humidity cell testing. Two batches of pyritic paste backfill cubes, designated NMC-1 and NMC-2, were prepared.

2.2. Solid-Phase Analyses

2.2.1. Introduction

This section discusses particle size distribution analyses, bulk chemical analyses, acid base accounting, mineralogical analyses, and leach extraction tests conducted on the pyrite concentrate and pyritic paste backfill. Solid-phase characterizations of the pyrite concentrate and pyritic paste back fill are presented in Appendix 4.2-15 of Foth & Van Dyke (1999/2000). Further details on the chemical analyses, acid base accounting, mineralogic analyses, and leach extractions are presented in Appendix 4.2-15 Attachments C, B, A, and F, respectively. Refined chemical analysis of the carbonate minerals present in the pyrite concentrate is presented in Appendix 4.2-16a of Foth & Van Dyke (1999/2000).

Process and pore water analyses were also conducted on the pyrite concentrate (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment D) and multiple step batch tests were conducted on both the pyrite concentrate and the pyritic paste backfill (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment G). These results were not used in the estimation of solute release from the reflooded mine and are not assessed in this report. The available neutralization potential determined from multiple step batch testing of the pyritic paste backfill is compared with the available neutralization potential observed in humidity cell tests in Appendix 1 of this report.

2.2.2. Pyrite Concentrate

2.2.2.1. Particle Size Distribution

No data on the particle size distribution of the pyrite concentrate were found.

2.2.2.2. Bulk Chemical Analyses

Solid-phase chemical analyses were conducted by Lakefield Research Limited in Lakefield, Ontario, Canada. The laboratory is "certified by the Standards Council of Canada, the Canadian Association of Environmental Analytical Laboratories, and has been accredited at the ISO/IEC Guide 25 level for various inorganic and organic parameters" (Black 2000). The methods are presented in the EIR (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-13, Table 2.3), with details provided in Black (2000).

Abbreviated chemical analyses (duplicated) for the pyrite concentrate are summarized in Table 3.18 and detailed results are presented in Table C-1 of Attachment C (Foth & Van Dyke 1999/2000. EIR, Appendix 4.2-15, p. 4.2-15-41 and 4.2-15-173, respectively). The duplicate results for are in good agreement, within seven percent of the mean value with the exception of strontium (15 percent). Both the total sulfur and sulfide content were reported as 43.25 percent, indicating no sulfate was present (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment C, Table C-1, p. 4.2-15-173). The average carbonate, calcium and magnesium contents were reported as 0.95%, 2900 and 5400 mg/kg, respectively. Trace metal contents near or exceeding 1000 mg/kg (0.1%) were copper (995 mg/kg), arsenic (3600 mg/kg), lead (4200 mg/kg), and zinc (12,100 mg/kg).

Although methods for ferric iron are provided in Table 2.3, no results are provided. Results are provided for silicon in Table 3.18 and C-1, but the method for obtaining these results is not identified in Table 2.3. Sulfur values are higher than the 40 percent total sulfur and sulfide averages reported for acid base accounting in Table 3.16 (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-40). It is curious that on both replicates, total sulfur was equal to sulfide content.

2.2.2.3. Acid Base Accounting (ABA)

The duplicated ABA results for the pyrite concentrate indicate an average AP(S_T) of 1250 kg $CaCO_3$ eq/tonne, based on an average total sulfur content of 40% (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.16, p. 4.2-15-40). The sulfide content reported for the ABA analyses was also 40%, indicating the absence of solid-phase sulfate. The total sulfur and sulfide contents were slightly lower than associated values reported for the chemical analysis (43.25%; see previous paragraph).

The neutralization potential (NP) values reported were calculated both by assuming 100% of the carbonate was associated with calcium and magnesium and using the modified Sobek (?) method, although a citation for this method was not found. It should be noted that the text in section 3.2.2 and Table 3.16 (Foth & Van Dyke 1999/2000, Appendix 4.2-15) indicates the NP was determined by the Sobek method, while section 2.3.2 and Attachment B indicate the method used was the modified Sobek (?) method (Table B-1, p. 4.2-15-169). Chapman (2002a) indicated the word “modified” was omitted from tables “due to formatting and space limitations”, however the text in section 3.2.2 also refers to “Sobek neutralization potential”. Due to this inconsistency, and the fact that no reference is cited for the modified Sobek method, the method will be referred to in this report as modified Sobek (?). The modified Sobek (?) method yielded an average value of 16.15 kg $CaCO_3$ eq/tonne.

The average value based on the carbonate content of 0.95% was 15.85 kg $CaCO_3$ eq/tonne (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.16, p. 4.2-15-40).

2.2.2.4. Mineralogical Analyses

Optical microscopy indicated that sulfide minerals, largely pyrite (86%), comprised over 93 weight percent of the pyrite concentrate, with quartz contributing another 5.4 weight percent (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.13, p. 4.2-15-37). Major pyrite and minor quartz were also reported present by the x-ray diffraction (XRD) analysis, as was minor chlorite (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.14, p. 4.2-15-38). XRD did not detect carbonates or jarosite, although it was noted that XRD "detection limits for carbonate minerals are typically in the range of 1 to 3%" (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-38).

Electron microprobe analysis indicated the carbonate minerals consisted of ferroan dolomite 43.3 atomic percent), magnesian siderite (23.3 atomic percent) and siderite (33.3 atomic percent). The analysis further indicate that 43% of the carbonate was associated with calcium and magnesium (Tables 1, 2, Foth & Van Dyke 1999/2000, Appendix 4.2-16a, p. 4.2-16a-6).

2.2.2.5. Leach Extraction Testing

Three different leach extractions were performed on the pyrite concentrate (and pyritic paste backfill), and the methods are described in Foth & Van Dyke 1999/2000 (EIR Appendix 4.2-15, p. 4.2-15-15 to 4.2-15-16). The objective of these extractions is to determine the composition of iron oxyhydroxides. This allows quantification of the extent of components released due to mineral dissolution and subsequently sequestered by iron oxyhydroxides. The dithionate extraction (Fuller et al., 1996) is intended to leach weakly crystalline iron oxyhydroxides using a moderate reductant at pH 8.5. The hydrochloric acid is intended to leach weakly crystalline iron oxyhydroxides and siderite at pH 3.5 to 4.0. The hydroxylamine hydrochloride extraction (Ribet et al., 1995) is conducted with a strong reductant at pH 4.3 for 24 hours at 90 degrees Centigrade. It is designed to leach high levels of crystalline ferric hydroxides and trace metal sulfides containing ferric iron.

Leach extraction testing of the pyrite concentrate indicated that with the exception of selenium, release was greatest using the hydroxylamine hydrochloride leach (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.21, p. 4.2-15-44). Consistent with the large release, mineralogic examination of the residue from this extraction indicated it induced moderate changes in pyrite and major changes in the iron oxyhydroxides, carbonates, and chlorite (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment A, p. 4.2-15-62). The dithionate leach released the greatest amount of selenium, and the second largest amounts of arsenic, antimony, chromium, copper and iron (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.21, p. 4.2-15-44). Mineralogical examination of the leach extraction residues indicated that the dithionate extraction also induced moderate changes in pyrite but little change in iron oxyhydroxides, carbonates, and chlorite. The hydrochloric acid extraction induced only minor changes in pyrite but major changes in the iron oxyhdroxides, carbonates and chlorite. These results will be used for comparison with leached solids from the humidity cell testing.

2.2.3. Pyritic Paste Backfill

2.2.3.1. Particle Size Distribution

The paste was placed into a mold to form cubes with an edge length of approximately 1 cm.

2.2.3.2. Bulk Chemical Analyses

Abbreviated bulk chemical results (duplicated) for the pyritic paste backfill are summarized and compared to those for the pyrite concentrate and cement in Table 3.19, and detailed results are presented in Table C-1 of Attachment C (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-42 and 4.2-15-174, respectively).

The duplicate results are in good agreement, within five percent of the mean value with the exception of mercury (6.7 percent) and boron (9.8 percent). The total sulfur and sulfide contents were reported as 39.9 and 38.5 percent, respectively. Only one sulfate analysis was reported, with a value of three percent, somewhat less than the 4.2 percent value calculated from the difference of total sulfur and sulfide contents. Trace metal contents near or exceeding 1000 mg/kg (0.1%) were copper (1000 mg/kg), arsenic (2500 mg/kg), lead (3750 mg/kg), and zinc (10,900 mg/kg). It was noted that although the cement addition to the pyrite concentrate generally produced lower trace concentrations in the pyritic paste backfill (relative to the pyrite concentrate), "concentrations of antimony, chromium, cobalt, copper and nickel in the pyritic paste backfill were higher than in the pyrite concentrate." It was concluded that "variability in the samples or in the analyses (analytical error) could account for some of these differences" (Foth and Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-42).

The chemistry of the cement presented indicated that calcium (54.9%), iron (1.4%), magnesium (1.2%), and sulfur (1.2%) were the only components present at concentrations greater than one percent. Concentrations of calcium, magnesium, sodium, barium, nickel, and strontium reported for the cement exceeded those for the pyrite concentrate.

The results presented in Table C-1 indicate the presence of sulfate, whereas analysis of pyrite concentrate indicated no sulfate was present (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment C, p. 4.2-15-174 to 4.2-15-174). Although methods for carbonate and ferric iron are provided in Table 2.3, no results are provided. Results are provided for silicon in Tables 3.19 and C-1, but the method for obtaining these results is not identified in Table 2.3.

2.2.3.3. Acid Base Accounting

No AP or sulfur values are presented for the pyritic paste backfill in section 3.2.2 of Appendix 4.2-15 (Foth and Van Dyke 1999/2000). The modified Sobek (?) (see section 2.2.2.3) neutralization potential (NP) and the neutralization potential present as carbonate (NP-CO_3) were determined. The carbonate content, used to determine the NP-CO_3, was determined using LECO furnace.

NP was determined in duplicate on eight samples with curing times of 7 days (1 sample), 28 days (6 samples), and 90 days (1 sample), using the modified Sobek (?) method and carbonate content (Foth and Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-40, Table 3.17). The modified Sobek (?) values ranged from 26 to 57 kg $CaCO_3$ eq/tonne, and values determined based on carbonate content ranged from 19.2 to 27.5 Neither of the measurements showed a clear dependence on curing time.

The pyritic paste humidity cells used paste from batches NMC-1 and NMC-2. NP was determined on duplicate samples of NMC-1, cured for 7 days, and NMC-2, cured for 28 days. The average NP for the duplicate samples of NMC-1 was 55.95 kg $CaCO_3$ eq/t (57.3 and 54.6 kg $CaCO_3$ eq/t) and the corresponding value for NMC-2 was 25.8 kg $CaCO_3$ eq/t (25.5 and 26.1 kg $CaCO_3$ eq/t) (Foth & Van Dyke 2000, Appendix 4.2-15, p. 4.2-15-40, Table 3.17; Steffen Robertson and Kirsten 2000, Table 2.3).

The short-term cells contained pyritic paste from both NMC-1 and NMC-2. The average NP of these batches, 40.9 kg $CaCO_3$ eq/t, was used for these cells (Foth & Van Dyke 2000, Appendix 4.2-16, Attachment A, Tables A-9.1 and A10.1). The intermediate term cell contained pyritic paste from batch NMC-2, and the 25.8 kg $CaCO_3$ eq/t determined for this batch was used for this cell (Foth & Van Dyke 2001, Appendix C, Table C1).

The neutralization potential present as carbonate (CO_3-NP) was also determined on duplicate samples. The average of duplicates of NMC-1 was 20.85 kg $CaCO_3$ eq/t (19.2 and 22.5 kg $CaCO_3$ eq/t) and the corresponding value for NMC-2 was 21.25 kg $CaCO_3$ eq/t (21.7 and 20.8 kg $CaCO_3$ eq/t) (Foth & Van Dyke 2000, Appendix 4.2-15, p. 4.2-15, Table 3.17). The value used for the short term cells was 21.0 kg $CaCO_3$ eq/t (Foth & Van Dyke 2000, Appendix 4.2-16, Attachment A, Tables A-9.1 and A10.1). The CO_3-NP reported for the intermediate cell was 21.25 (Foth & Van Dyke 2001, Appendix C, Table C1).

Determining the NP and NP-CO_3 for the short term cells as an average of those for the two batches suggests an equal mass from each batch was used in both of the short term cells. This is not stated in the methods. It should be further noted that whereas NP values were determined for both the short term and long term cells, only one analysis was presented for sample bulk chemistry and leach extraction testing (Foth & Van Dyke 2000, Appendix 4.2-15, Tables 3.19 and 3.22, respectively). It is unclear how a single sample was selected to represent both the mixture of two pyritic paste batches used in the short term cells and the single batch used in the intermediate term cell.

2.2.3.4. Leach Extraction Testing

With the exception of selenium, release was greatest using the hydroxylamine hydrochloride leach (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.21, p. 4.2-15-44). Mineralogical examination of the residue from this extraction indicated it induced minor changes in pyrite and major changes in iron oxyhydroxides, carbonates, and chlorite (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Attachment A, p. 4.2-15-62). The dithionate leach released the greatest amount of selenium, and the second largest amounts of arsenic, antimony, chromium, copper and iron (Foth & Van Dyke 1999/2000, Appendix 4.2-15, Table 3.21, p. 4.2-15-44). This extraction induced only minor changes in pyrite and virtually no changes in iron oxyhydroxides, carbonates, or chlorite. The hydrochloric acid extraction also induced only minor changes in pyrite as well as iron oxyhydroxides, moderate changes in carbonates and major changes in chlorite. These results are used for comparison with leached solids from the humidity cell testing.

2.3. Laboratory Dissolution Tests

Saturated column tests were conducted on 3.2 kg of pyritic paste backfill that had been cured for 28 days and crushed prior to column testing. These tests are described in EIR Appendix 4.2-15 (Foth & Van Dyke 1999/2000). A closed system was used to recycle water through the pyritic paste backfill at a rate of approximately three pore volumes per day for 28 days (EIR Appendix 4.2-15, Foth & Van Dyke 1999/2000, p. 4.2-15-58, Figure 3.2). Solution pH, Eh, and conductivity were determined on weekdays until values stabilized . A variety of solutes were determined at the end of the test (Attachment I, EIR Appendix 4.2-15, Foth & Van Dyke 1999/2000).

Humidity cell tests were conducted on both the pyrite concentrate and the pyritic paste (Foth & Van Dyke 1999/2000, EIR Appendix 4.2-16; SRK 2001). Duplicate samples of pyrite concentrate were conducted for 58 weeks. Two 20-week and one 107-week humidity cell tests were conducted on the pyritic paste. Cubes from both pyritic paste backfill batches were used in each of the short term humidity cell tests, and cubes from batch NMC-2 were used for the intermediate term tests (Chapman 2002b). The leached samples were subjected to bulk chemical and ABA analyses (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Attachment A, Tables A7.1, A8.1 [pyrite concentrate]; Tables A9.1, A10.1 and Attachment B, Appendix 5 [pyritic paste backfill short term cells]; SRK 2001, Appendix C, Table C1 [pyritic paste backfill intermediate term cell]) and mineralogical analyses (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Attachment B [pyritic paste backfill short term cells]; SRK 2001, Appendix B [pyritic paste backfill intermediate term cells]).

Leach extraction tests were conducted on leached cubes removed from the cells after tests were completed. The leached cubes were removed systematically with the objective of obtaining representative samples (e.g., SRK 2001, p. 3). These tests were used in conjunction with analyses of humidity cell drainages to determine the magnitudes and rates of reaction and solute release. The leach extraction residues were subjected to bulk chemical and acid base accounting analyses (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Attachment C [pyrite concentrate, pyritic paste backfill short term cells]; SRK 2001, Attachment C [pyrite paste backfill intermediate term cells]), and mineralogical analyses (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Attachment B [pyritic paste back fill short term cells]; SRK 2001, Appendix B [pyritic paste backfill intermediate cells]).

2.4. Calculations

Laboratory dissolution tests were used to estimate solute release for unoxidized pyritic paste backfill, oxidized pH-neutral pyritic paste backfill, and oxidized acidic paste backfill. With the exception of chloride, solute release from the unoxidized pyritic paste backfill was estimated based on concentrations observed in the saturated column test and subsequent geochemical equilibrium modeling on these values (SRK 2000, p. A-29). The chloride concentration used was based on the amount of chloride present in the pyritic paste tested rather than that reported for the column test leachate. The “Best Engineering Judgement” (BEJ) case used concentrations observed in the saturated column test for all solutes except barium, calcium, iron, lead, and nickel. These concentrations were reduced based on geochemical modeling (SRK 2000, p. A-32, Table 2.13). Other than the calculated chloride concentration, the “Upper Bound” (UB) case used observed concentrations for all solutes.

Solute release from the oxidized neutral pyritic paste backfill was estimated based on results from short-term (20 weeks) humidity cells HC-CPT-ST1 and HC-CPT-ST2 (SRK 2000, p. A-26). Solute release to humidity cell drainages during the first five weeks was used for the BEJ case, and results for aluminum, barium, calcium, fluoride, silver, and sulfate were adjusted based on geochemical equilibrium modeling (SRK 2000, p. A-28, Table 2.11). Release through week 20 was used for the UB case, and concentrations of calcium and sulfate were adjusted based on geochemical equilibrium modeling. All calculations considered only release observed in humidity cell drainages (Foth & Van Dyke 1999/200, Appendix 4.2-16, p. 4.2-16-228 to 4.2-16-230, Table A9.3 and p.4.2-16-242 to 4.2-16-244). Leach extraction tests conducted on the residues (Foth & Van Dyke 1999/200, Appendix 4.2-16, p. 4.2-16-379 to 4.2-16-380, Table C3-4) were not included in these calculations.

Solute release from the oxidized acidic pyritic paste backfill was based on drainage quality from the pyrite concentrate (58 weeks), leach extraction tests, and equilibrium modeling of these results (SRK 2000, p. A-23). Pyrite concentrate results were used rather than those from the short-term pyritic paste humidity cells because 1) drainage from the pyrite concentrate was acidic throughout most of the test, while that from the short-term pyritic paste cells remained neutral, and 2) rates of metal release (relative to sulfate release) for the short-term pyritic paste cells was more prone to error due to the low sulfate release rates (SRK 2000, p. 18-19).

If leach extractions indicated net solute removal from the solid phase, this value was subtracted from the observed release in dissolution testing. Thus, it was possible to have rates lower than those observed based on release of solutes during humidity cell testing. For the short term cells this approach did not greatly affect release rates from the short-term pyritic paste backfill cells. The calculated rates for silver from CPT-ST-1 and calcium from CPT-ST-2 were reduced by less than 10 percent relative to the rates observed in the humidity cell drainages (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Tables 3.19, C3-4). Rates calculated (considering leach extraction results) for the pyrite concentrate were generally lower than those observed in the humidity cell drainages (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Table C2-4). For example, the calculated nickel release was 40 percent of that observed in the humidity cell drainages. Rates for other solutes were reduced to a lesser degree. The BEJ case adjusted concentrations of barium, calcium, lead, silver, and sulfate using geochemical equilibrium modeling. The UB case assumed no solubility controls.

2.5. Assessment

The pyrite concentrate and pyritic paste backfill were created reasonably by using the available materials. Were additional materials available, a variety of concentrates and paste backfill mixtures would have been beneficial to assess the effects of variability in composition on dissolution behavior and solute release. With regard to this concern, it should be noted that the compositions of the pyrite concentrate and paste backfill under operational conditions will likely vary from those tested. The solid-phase characterization was generally thorough, although it omitted determination of the particle size distribution of the pyrite concentrate. Dissolution tests were designed fairly reasonably. One unfortunate aspect was the lack of adequate pyritic paste backfill cells to continue some additional tests for a longer duration.

Solute release from the unoxidized pyritic paste backfill was estimated based on concentrations observed in the the saturated column test and subsequent geochemical equilibrium modeling on these values (SRK 2000, p. A-29). Chemical analyses of the saturated column leachate indicated a charge imbalance, with anions roughly 1.5 (using sulfate analyses) to 2.8 (calculating sulfate concentration from total sulfur) times cations (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-251, Table I-1). SRK (2000) accounted for this imbalance by adjusting the chloride concentration, however, errors in other analyses may have contributed to the imbalance. Unfortunately, there was no duplicate analysis or a duplicate test to address this possibility. The lack of such replication introduces uncertainty to the calculations presented for the unoxidized pyritic paste backfill.

Solute release from the oxidized neutral pyritic paste backfill was estimated based on results from short-term (20 weeks) humidity cells HC-CPT-ST1 and HC-CPT-ST2 (SRK 2000, p. A-26). Subsequent to the issuance of SRK (2000) the intermediate humidity cell test on pyritic paste backfill was terminated after 107 weeks of operation. The pH of drainage remained above 6.0 for the first 60 cycles of the test. These results should be considered in prediction of solute release from the oxidized neutral pyritic paste backfill.

Solute release from the oxidized acidic pyritic paste backfill was based on drainage quality from the pyrite concentrate (58 weeks), leach extraction tests, and equilibrium modeling of these results (SRK 2000, p. A-23). Rates calculated considering leach extraction results for the pyrite concentrate were generally lower than those observed in the humidity cell drainages (Foth & Van Dyke 1999/2000, Appendix 4.2-16, Table C2-4). No solubility controls were used for the UB case.

To reduce uncertainty in prediction, additional results should be examined, and twelve cases are proposed to be considered for the solute release from the acidic pyritic paste backfill. The first six additional cases consider only solute release in humidity cell drainage, ignoring leach extraction test results. This will eliminate use of release rates that are lower than those observed in the humidity cell test. Two additional cases can be based on pyrite concentrate humidity cell test results. First, release during weeks 0-10 will provide a relatively high rate of release. Second, drainage quality results for the entire period of record can be used (as opposed to rates adjusted for leach extraction used by SRK (2000)). Use of averaged results from the two short-term tests on pyritic paste humidity cells, ignored in SRK (2000), can be considered as a third case. Additional cases four through six can be based on intermediate pyritic paste backfill (CPT IT-1) using data from cycles 0-107 (entire period of record), cycles 60-107 (period during which pH was below 6.0), and cycles 101-107 (during which drainage was most acidic).

Four additional cases can be created using release rates adjusted based on leach extraction results. Leach extraction data should be applied in a manner that does not reduce rates below those observed in humidity cell tests. The averaged results from the two short-term tests on pyritic paste humidity cells provide one case. Leach extraction results can also be used to adjust observed solute release from the intermediate-term pyritic paste backfill test using data from cycles 0-107, 60-107, and 101-107.

Two additional cases can be developed from the intermediate-term pyritic paste backfill test using data from cycles 101-107, both with and without adjustment using leach extraction results. These results should be multiplied by five to account for the facts that 1) drainage pH was decreasing at this time and rates were correspondingly increasing, and 2) only two samples were analyzed for metals during this period.

The median and maximum values for each parameter from this set of twelve relative release rates are recommended for use as the range of reasonable potential release rates (Table 1).

The following comments are directed specifically toward calculations of sulfide mineral oxidation rates. These calculations did not adequately consider certain aspects of the data. SRK (2000) used sulfate release rates in humidity cell drainage as one estimate of sulfide mineral oxidation rates, and did not consider total sulfur release in humidity cell tests. Furthermore they ignored the more rapid sulfate release to solution during cycles 102-107, when the lowest drainage pH values of the test were observed, and the variation of measurements of sulfate accumulation in the solid phase. For cycles 0-107, total sulfur release yielded oxidation rates that were 30 percent higher than those calculated using sulfate release. This was due to elevated total sulfur concentrations during the first 30 cycles of the experiment. For cycles 102-107 the rates determined using total sulfur release were in good agreement with those determined using sulfate release.

Solid phase sulfate accumulation based on bulk chemical analyses yielded oxidation rates roughly 3.3 times those based on leach extraction testing. Oxidation rates determined for cycles 102-107 were roughly 2.2 times those determined for cycles 0-107. This indicates that oxidation rates will increase if the pH of the pyritic paste backfill decreases, and this is consistent with the scientific knowledge of sulfide mineral oxidation. Based on these results, an oxidation rate of 1.05E-7 mole O_2 kg^{-1} s^{-1} (4.01E-7 mole O_2 m^{-2} s^{-1}) should be considered in addition to values reported in SRK (2000).

3. Tests for Wall Rock and Stope Plug Solute Release Calculations

3.1. Materials

Large-scale humidity cell tests were conducted on waste rock master composites and high sulfur composites from each of the Skunk Lake, Rice Lake, Upper Mole Lake, and Lower Mole Lake formations. These composites were formed from samples of drill core from the individual formations.

3.2. Solid-Phase Analyses

The samples were characterized with respect to particle size distribution, bulk chemistry, and acid-base accounting. No mineralogical analyses were reported, and no leach extraction tests were conducted on these materials.

3.3. Laboratory Dissolution Tests

Large scale humidity cell tests were conducted on master composites and high sulfur composites of Skunk Lake, Rice Lake, Upper Mole Lake, and Lower Mole Lake formations, with one cell being run for each of the eight samples. The physical dimensions and test conditions are described in Table 1a of EIR Appendix 3.5-33 (Foth & Van Dyke 1997). In summary, the large scale humidity cells were constructed from polyethylene containers (30 gallons) with a conical base. A spigot was installed at the lowest part of the base. The cell diameter was 45.7 cm, yielding a cross sectional area of 0.164 m^2. (This is erroneously reported as 1.64 in Table 3.5-22 in Foth & Van Dyke [1998].) From 73.64 to 133.18 kg of rock was placed into the master composite cells, yielding depths of 30.5 to 50.8 cm (EIR Appendix 3.5-33, Table 1a).

The experimental procedure is summarized in Foth & Van Dyke (1998, p. 3.5-159). For two periods a day (0400-0800, 1600-2000) saturated air was introduced to each cell from two ports on opposite sides of the cell, slightly above the base. Deionized water was added to each cell twice a day (at 1200 and 2400) for six days of each one-week cycle. The total amount of water introduced weekly by these additions was equal to the average weekly precipitation in the Crandon area (4.8 L, Foth & Van Dyke 1998, Table 3.5-22 and Foth & Van Dyke 1999/2000, Appendix 3.5-34, Table 1). A volume equal to the average weekly precipitation in the Crandon area was also added on the seventh day, simulating a storm event.

Drainage from the cells was collected weekly, prior to the simulated storm event. The leachate volume, pH, conductivity, and temperature were measured weekly at Foth & Van Dyke. Samples were also collected and submitted to an analytical laboratory for determination of alkalinity, acidity, aluminum, antimony, arsenic, barium, beryllium, bismuth, cadmium, calcium, chromium, cobalt, copper, gallium, germanium, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, silver, sodium, sulfate, tellurium, thallium, tin, titanium, uranium and zinc.

The test duration for master composites of the Skunk Lake and Rice Lake formations was 106 weeks, while that for the Upper and Lower Mole Lake formations was 70 weeks (Foth & Van Dyke 1999/2000, Appendix 3.5-34, Table 1). During this time10 to 18 pore volumes of drainage were collected from the cells (Foth & Van Dyke, 1998, Table 3.5-22). The test duration for high sulfur composite of the Skunk Lake formation was 106 weeks, while that for the Rice Lake, Upper and Lower Mole Lake formations was 65 weeks. During this time 17 to 32 pore volumes of drainage were collected from the cells (Foth & Van Dyke, 1998, Table 3.5-22).

3.4. Calculations

Solute release rates were calculated based on the volume and chemistry of the drainages. No leach extraction tests were conducted on the solids to account for products of mineral dissolution that were retained in the leached solids during the test.

Solute release rates from the hanging wall rock were calculated based on rates of release from humidity cell tests on waste rock composites from the Lower Mole Lake, Upper Mole Lake, Rice Lake, and Skunk Lake formations for 54 weeks. From cycle 10 to cycle 54, trace metals were analyzed only on cycles 17, 33, and 54. For samples that were not analyzed, concentrations were estimated by linear interpolation (SRK 2000, Attachment F). Release rates were normalized based on an estimated surface area present in each humidity cell (SRK 2000, Attachment G). The results from the various formations were scaled to the amount of rock surface from each formation estimated to be present (SRK 2000, p. A-36).

No rates were calculated for broken waste rock left in the mine as stope plugs.

3.5. Assessment

3.5.1. Materials

The master and high-sulfur composites were reasonably assembled.

3.5.2. Solid-Phase Analyses

Although the samples were characterized with respect to particle size distribution, bulk chemistry, and acid-base accounting (Foth & Van Dyke 1995), no mineralogical analyses or leach extraction tests were conducted. The problems associated with the lack of these data are discussed below.

3.5.3. Laboratory Test Methods

Particle size distribution analyses, chemical analyses, and acid-base accounting were conducted by accepted methods. No mineralogical analyses or leach extraction tests were conducted. The lack of mineralogical characterization limited the understanding of reactions occurring during testing, particularly the extent of calcium and magnesium carbonate minerals available to neutralize acid. The lack of leach extraction tests, before and after testing, prohibited calculation of the amount of reaction products that accumulated in the solid phase during testing.

The kinetic tests were developed "to determine the ability of the material to produce acidic drainage and specifically to determine oxidation rates, neutralization rates, metal leaching rates, and water quality as a function of time" (Foth & Van Dyke 1995). These tests are not well suited to achieve these objectives.

There are several problems associated with using the humidity cells for determination of rates. First, the cells are much larger than cells commonly used for waste rock testing. The cells contained roughly 74 to 133 kg as compared to 1 kg in more commonly used cells (e.g. White and Lapakko 2000). The flow path through the larger cells is long relative to that of the smaller cells used more commonly. As mentioned previously, the rock depths in the large cells ranged from 27 to 51 cm as compared to approximately 7.5 cm in the smaller cells. The longer flow path increases the probability of the development of preferential flow paths. This reduces the efficiency of reaction product transport.

Second, the amount of water added relative to the amount of rock is relatively small. The water addition to the waste rock humidity cells was not designed to remove all reaction products but rather, "deionized water was added to each column to simulate precipitative inputs in two different ways" (Foth & Van Dyke 1998, p. 3.5-159). As mentioned previously, the water added to the cells was 4.8 liters per week, and this represents 0.16 to 0.36 pore volumes per cycle. More commonly used protocols apply 500 mL of water to a 1 kg sample (White and Lapakko 2000), representing approximately 1.5 to 3 pore volumes per cycle. Despite the higher water application to the smaller cell, removal of reaction products is less than 100 percent. The lower rinse water application rate in the larger provides less efficient transport of reaction products from the cell. Both the longer flow path and the lower rinse water addition contribute to underestimation of chemical reaction rates based on drainage quality.

Third, there were no analyses conducted on the leached solids to determine the extent of reaction products that were not transported from the waste rock cells. Consequently it was not possible to quantify the rinsing efficiency. Such analyses were conducted on leached solids from tests on depyritized tailings, pyritic paste backfill, and pyrite concentrate.

The two short term humidity cell tests designated HC-DPT-ST1 and HC-DPT-ST2, were conducted on depyritized tailings. The pore volume reported for cell HC-DPT-ST2 was 33.5 cm^3 (EIR Appendix 4.2-16, p. 4.2-16-69, Table A-2.1). Although no pore volume was reported for cell HC-DPT-ST1 (EIR Appendix 4.2-16, p. 4.2-16-55, Table A-1.1), it is assumed it was similar. These cells yielded approximately 600 mL of drainage per cycle (EIR Appendix 4.2-16, p. 4.2-16-56, Table A1.2 and p. 4.2-16-70, Table A2.2), representing an approximate average drainage of 18 pore volumes per cycle. Leached products from the short term humidity cell tests on depyritized tailings were examined. Rates considering the accumulation of sulfate in the solids were roughly 2.5 times steady state rates based on drainage quality alone (EIR Appendix 4.2-16, p.4.2-16-49, Table 4.1).

The average pore volumes drained per cycle for the short term depyritized tailings cells was 50 to 120 times that in the waste rock tests. Consequently, less efficient removal of reaction products would be expected for the waste rock tests. However, it is difficult to quantify the degree to which reaction products accumulated in the waste rock tests.

Fourth, determination of sulfate concentrations in the laboratory were subject to error (Moe 1997). This problem was identified after the waste rock humidity cells were terminated; therefore, there are no data available to assess the potential degree of this error. Examination of data from the depyritized tailings humidity cells indicates that some reported values were half those expected based on a charge balance.

Fifth, the frequency of trace element analysis was very low. From cycle 10 to cycle 54, trace metals were analyzed only on cycles 17, 33, and 54. This represents only three samples over a period of 45 weeks. No samples were analyzed for trace metals from cycle 55 to the end of the tests. Sixth, cells were not replicated and, consequently, the variability in drainage quality for a given solid-phase composition cannot be determined.

Seventh, due to the small number of samples tested, there are no empirical data describing the variation of drainage quality with solid-phase composition. This applies to the rate of sulfide oxidation and the rate of acid neutralization, as well as the resultant drainage pH. These relationships can not be quantified nor can, more generally, the type of functional relationships between the solid-phase and chemical behavior be empirically determined. The type of testing required to determine these relationships for individual lithologies has been described in the literature (Lapakko and Antonson 1994, 2002). Eighth, the lack of mineralogical characterization of the solids further complicates the interpretation of the drainage quality data.

3.5.4. Extrapolation of Laboratory Results to the Field

There are several uncertainties involved in extrapolating laboratory rates to field conditions in the stope plugs and the walls of the mine workings. These include the problems with the laboratory tests mentioned above. Additional problems include differences in specific surface area between the laboratory samples and waste rock in the field (i.e. as stope plugs) and differences in the degree of spatial concentration of high sulfur rock between the laboratory samples and waste rock in the field.

First, the specific surface area of waste rock in the humidity cells may be lower than that for broken rock in the field (i.e. as stope plugs). For example, the -200 fractions in the laboratory tests were 1.9 and 1.5 percent for the Skunk Lake and Lower Mole Lake composites, respectively (EIR Appendix

3.5-31 p. 3.5-31-20 and 3.5-31-23). In contrast, the -200 fraction of rock from an underground exploration shaft in the Duluth Complex is reported as 3.1 percent (Lapakko 1993). Since most of the surface area, as well as much of the liberated sulfides, may be associated with this fraction, release from the humidity cell tests may underestimate release in the field.

Second, the rock in the laboratory cells was relatively well mixed. As a result, high sulfur rock in the master composites was in close proximity with the more abundant low sulfur rock. Consequently, acid generated by high sulfur rock would be more readily neutralized by the surrounding low sulfur (non-acid producing) rock. In both waste rock piles and in the underground mine, high sulfur rock will tend to be concentrated. Consequently, there will be greater potential for development of acidic zones associated with high sulfur rock in the field. Due to the low pH in these zones, the rate of sulfide mineral oxidation will accelerate and trace metals will reach higher concentrations.

Markart (2003) estimated that at least 6 percent and as much as 20 percent or more of the Lower Mole Lake Composite could be categorized as acid producing. This rock could create acid producing zones that would yield higher release of some trace elements. For example, rates of copper and zinc release from the Lower Mole Lake High Sulfur Composite were roughly 100 and 900 times, respectively, those from the Lower Mole Lake Master Composite. In a waste rock pile it is conceivable that the acid could migrate and create acidic conditions in surrounding rock also.

It is difficult to quantify the fraction of acidic rock, with attendant elevated metals release. As a result several fractions of acidic rock can be considered. NMC calculated releases without using data from the Lower Mole Lake High Sulfur Composite. As a lower bound for acidic zones it can be assumed that six percent of the Lower Mole Lake rock is represented by the high sulfur composite. Additional cases to consider would be 20 and 40 percent. The last value assumes acid from the Lower Mole Lake high sulfur rock has migrated and affected rock that would otherwise be neutral. The use of 100 percent high sulfur composite would clearly represent an upper bound.

To account for the aforementioned uncertainties in applying laboratory rates to the field, the following is proposed. For extrapolation of laboratory rates to broken rock, respective factors of 20 and 10 may be used for rates of sulfate and metal release. If rock with high sulfur content is present, rates from the high sulfur composites should be used. Furthermore, the possibility of drainage from high sulfur rock creating acidic environments in surrounding rock must be considered. For application of laboratory rates to mine walls, respective factors of 5 and 10 may be used for sulfate and metals. If rock with high sulfur content is present, rates from the high sulfur composites should be used. The waste rock rates reported in the TMA/RP review document (Benson and Carlson 2003) should be used for all waste-rock-based calculations.

4. Ore Dissolution Tests used for Crown Pillar Solute Release Calculations

4.1. Materials

A dissolution test was conducted on an unweathered zinc ore composite and is described by Thresher (2000). The objective of the test was to generate acidic water with elevated concentrations of solutes to be used for testing waste water treatment methods. The dissolution test was conducted on a 174.6-kg composite comprised of drill core samples, the diameter of which was reduced by hand to less than two inches.

4.2. Solid-Phase Analyses

Thresher (2000) reported the mean diameter of the sample as "about 1-1½ inches. The particle size distribution of the sample was determined and, based on visual examination of the particle size distribution graph presented by Chapman (2003), the median diameter appeared to be approximately 0.4 inches. Based on this distribution, Chapman (2003) reported a specific surface area of 13.9 ft^2/kg for the sample. The chemistry of the sample is presented in Table 2 of Appendix 3.5-32 (Foth & Van Dyke 1999/2000). The sulfur content of the sample is reported as 29.1 percent, and concentrations of zinc, lead, copper, arsenic, and cadmium are reported as 9.66, 1.12, 0.33 and 0.025 percent, respectively. Thresher (2000) indicated the sample mineralogy was not representative of the Crandon ore, and was dominated by pyrite with lesser sphalerite. It also contained more galena and arsenopyrite than the Crandon ore.

4.3. Laboratory Dissolution Test

The laboratory dissolution test was conducted using the same apparatus described for waste rock dissolution tests (section 3.5.3 above) using methods described by Thresher (2000). The test was conducted from 12 August to 19 December 1993, a period of 122 days, during which the sample was rinsed 21 times at varying intervals. During the first nine rinse cycles the sample was saturated with approximately 50 liters of deionized water for 24 hours, then drained into a collection vessel for four days. Water additions during cycles 10 though 19 were similar, but samples were allowed to drain for seven days. After cycle 19 approximately 1.4 L/day of deionized water was pumped onto the sample and drainage samples were collected every seven days.

All drainage samples were analyzed for temperature, pH, and specific electrical conductivity. More detailed chemical analyses were conducted after cycles 1, 2, 4, 8, 16, 19, and 21. The drainage volumes were determined only after cycles 20 and 21. All other drainage volumes were estimated as 50 L (Thresher 2000).

Drainage pH in this test was initially 4.1, increased to 6.3 at cycle 4, typically remained above 6.0 through cycle 19, then decreased to 5.3 at the end of the test (cycle 21). Concentrations of several solutes in the initial sample were elevated, for example zinc, copper, aluminum, and cadmium concentrations were 970, 120, 17, and 5.3 mg L^{-1}. As pH increased and stabilized, these concentrations decreased and stabilized at approximate concentrations of 13, 0.25, 0.03, and 0.06 mg L^{-1}. When pH decreased at the end of the test, concentrations of zinc, copper, and cadmium increased to 53, 1.8, and 0.19 mg L^{-1}. The observed inverse relationship of metal concentrations with drainage pH suggests that metal concentrations were controlled by their solubility with respect to oxide, hydroxide, and carbonate phases as opposed to their solid-phase availability.

4.4. Data Analysis

Solute release rates for the BEJ case were calculated based on the solute release observed during cycles 3 to 21 (SRK 2000, p. A-49). The UB case release rates were calculated using solute release over all 21 cycles. Rates were expressed per unit surface area based on the estimated surface area of the unweathered ore composite. These rates were extrapolated to the field based on the estimated surface area of the crown pillar.

4.5. Assessment

4.5.1. Materials

The dissolution test was conducted on an unweathered ore composite. This was deemed the best surrogate for the crown pillar. However, the degree to which this simulated the material in the crown pillar is unknown. One particular concern is the presence of a small amount of neutralization potential that maintained drainage pH above six for most of the test. As discussed in section 4.3, the elevated pH maintained trace metal concentrations at a fairly low level. In the absence of this neutralization potential, drainage pH could easily have been much lower and, consequently, trace metal concentrations could have been considerably higher. As is clear from data presented in section 4.3, drainage pH values in the realm of 3 to 4 could have resulted in trace metal concentrations that were orders of magnitude higher than those observed in the test. For example, trace metal concentrations at pH 3.3 would be expected to be more than three orders of magnitude higher than those at pH 6.3 if they were constrained only by the solubility of trace metal hydroxides.

A second concern is that the sample used was an unweathered ore composite. The crown pillar has undergone significant weathering over time. Consequently, it is likely that there are soluble acid and trace metal salts present. This would result in a large initial flush of soluble oxidation products when water contacted the rock. A similar, but less substantial, flush of soluble oxidation products was observed at the beginning of the test on the unweathered ore composite. It should be noted that the extent of soluble oxidation products on the unweathered ore composite was far less than that which would be expected on the rock in the crown pillar.

4.5.2. Solid-Phase Analyses

The particle size distribution and chemistry of the unweathered ore composite were determined. However, no mineralogical analyses for the sample were provided. Furthermore, no leach extractions were conducted to determine the amount of reaction products retained in the cell during the test.

4.5.3. Laboratory Dissolution Test

The objective of the test was to generate acidic water with elevated concentrations of solutes to be used for testing waste water treatment methods. It was poorly designed to determine solute release from the crown pillar. First, it is not known how closely the rock used approximated the composition of the crown pillar, and this is a critical concern. The unweathered ore contained a small amount of neutralization potential, and this maintained drainage pH above 6.0 for most of the test. Since much of the crown pillar has oxidized to some degree, it is likely that calcium and magnesium carbonate minerals have been dissolved and no neutralization potential remains. If this were the case, drainage would likely readily acidify and trace metal concentrations would be quite high. Furthermore, rock in the crown pillar is likely to contain a much higher content of soluble acid and trace metal salts. This would result in a rapid release of acid and trace metals from the crown pillar rock.

Second, rinse intervals and volumes were not held constant throughout the test, and rinse volumes were not accurately determined for each cycle. During the first nine cycles the sample was rinsed every four days with approximately 50 liters of deionized water. During cycles 10 through 19 the rinse volume was the same but the addition occurred every seven days. After cycle 19 the water addition decreased to 1.4 liters per day. Although the effect of these variations is unknown, the approach cannot be viewed as systematic. It is likely that reaction product transport was reduced after cycle 19 because the water addition was decreased by about 80 percent.

Third, the schedule for chemical analyses was erratic. Analytical intervals varied from four days (cycles 1 to 2) to 46 days (cycles 8 to 16). A more diligent design would provide a more systematic approach to sample collection and analysis.

Fourth, no leach extractions were conducted and, consequently it is not possible to determine the extent of reaction products that were retained in the solids bed.

4.5.4. Data Analysis

Solute release rates for the BEJ and UB cases were calculated based on the solute release observed during cycles 3 to 21 and 1 to 21, respectively (SRK 2000, p. A-49). As discussed above, critical concerns are the lack of consideration for acidic conditions and release of soluble trace metal salts. Both of these possibilities would result in increased trace metal release.

To account for accelerated trace metal release two additional cases can be considered. First, data from the first eight cycles of the ore composite sample test can be considered (Table 2). This places more weight on the initial samples for which pH was relatively low and metal concentrations were relatively high. This also places more weight on the release of soluble trace metal sulfates present on the solids.

Second, data from the Lower Mole Lake High Sulfur Composite (LMLHSC) humidity cell can be considered. This cell produced acidic drainage throughout the test and the long-term mass release rates can be used. These rates were determined as average release rates for cycles 17, 33 and 54; 5, 9 and 54 (Cd, Cr, Co, Pb, Ni, Ag); or 5 and 9 (Sb, Be, Mo, Hg). Due to the paucity of data, and consequent potential for error, multiplying these values by a safety factor of five should be considered. Trace metal concentrations in the LMLHSC rock were lower than those in the ore composite. To account for this discrepancy, the release rate for a specific component from the LMLHSC should be multiplied by the ratio of component concentration in the ore composite to that in the LMLHSC (Table 3).

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Table 1.

Potential Alternative Relative Release Rates from Pyritic Paste

	MAX IMUM VALUE	MEDIAN VALUE
SO4 (mol/mol SO4)	1.00E+00	1.00E+00
S (T) (mol/mol SO4)	2.52E+00	1.03E+00
Cl (mol/mol SO4)	1.38E+00	4.86E-03
Al (mol/mol SO4)	4.12E-01	3.14E-02
Sb (mol/mol SO4)	4.09E-04	1.01E-05
As (mol/mol SO4)	1.22E-01	4.91E-03
Ba (mol/mol SO4)	7.73E-05	4.19E-06
Be (mol/mol SO4)	3.34E-04	2.25E-05
B (mol/mol SO4)	1.50E-06	
Cd (mol/mol SO4)	4.37E-03	3.32E-04
Ca (mol/mol SO4)	1.31E+00	2.60E-01
Cr (mol/mol SO4)	2.32E-04	1.89E-05
Co (mol/mol SO4)	3.61E-03	3.74E-04
Cu (mol/mol SO4)	1.24E-01	7.92E-03
F (mol/mol SO4)	5.60E-03	1.61E-03
Fe (T) (mol/mol SO4)	4.70E+00	2.55E-01
Pb (mol/mol SO4)	6.17E-03	3.45E-04
Mg (mol/mol SO4)	1.86E-01	9.88E-02
Mn (mol/mol SO4)	4.23E-02	6.70E-03
Hg, Low Level (mol/mol SO4)	1.99E-07	9.50E-09
Ni (mol/mol SO4)	4.28E-03	2.47E-04
K (mol/mol SO4)	1.11E-01	4.13E-04
Se (mol/mol SO4)	2.98E-04	6.91E-05
Ag (mol/mol SO4)	2.73E-05	1.96E-06
Na (mol/mol SO4)	7.91E-02	5.12E-02
Sr (mol/mol SO4)		
Zn (mol/mol SO4)	2.55E+00	2.28E-01

Table 2.

Crandon Ore Composite Leaching Data - Estimating Constituent Release from the Crown Pillar

Sample Size = 174.6 kg

			Cycle Number								Cum. Release (mg/kg)	Crown Pillar Low RangeEstimate Weekly Flux Rate (mg/kg/wk)
		GW	1	2	3	4	5	6	7	8		
Date collected			19-Aug-94	24-Aug-94	29-Aug-94	03-Sep-94	08-Sep-94	13-Sep-94	18-Sep-94	23-Sep-94	Cycle 1 - 8	Cycle 1 - 8
Volume	(L)		50	50	50	50	50	50	50	50		
pH			4.14	4.84	5.7	6.27	6.43	6.64	6.66	6.6		
EC			2560	730	483	425	341	313	331	305		
Al	(mg/l)		17	1.6	0.831	0.061	0.053	0.046	0.038	0.030	5.63	0.99
Sb	(mg/l)		0.040	0.040	0.040	0.040	0.043	0.045	0.048	0.050	0.10	0.02
As	(mg/l)	<.005	0.03	0.013	0.009	0.005	0.005	0.005	0.005	0.005	0.02	0.0039
Ba	(mg/l)		0.016	0.017	0.013	0.009	0.008	0.008	0.007	0.006	0.02	0.0042
Be	(mg/l)	<.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.01	0.0020
B	(mg/l)											
Cd	(mg/l)	<.005	5.3	0.7	0.45	0.2	0.166	0.131	0.097	0.062	2.03	0.36
Ca	(mg/l)	25	55	33	30.5	28	27.500	27.000	26.500	26	72.59	13
Cl	(mg/l)											
Cr	(mg/l)	<.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.01	0.0020
Co	(mg/l)		1.7	0.61	0.41	0.21	0.170	0.131	0.091	0.051	0.97	0.17
Cu	(mg/l)	0.027	120	16	8.8	1.6	1.270	0.940	0.610	0.28	42.81	7.5
CN	(mg/l)											
F*	(mg/l)											
Fe	(mg/l)	0.03	70	6	3.21	0.42	0.370	0.320	0.270	0.22	23.14	4.0
Pb	(mg/l)	<.04	0.77	0.28	0.16	0.04	0.040	0.040	0.040	0.04	0.40	0.07
Mg	(mg/l)		50	27	22.5	18	16.750	15.500	14.250	13	50.69	8.9
Mn	(mg/l)	0.011	2	1	0.785	0.57	0.488	0.405	0.323	0.24	1.66	0.29
Hg	(mg/l)	<.0002	0.0004	0.0002	0.0002	0.0002	0.000	0.000	0.000	0.0002	0.00	0.00009
Ni	(mg/l)	<.015	0.31	0.081	0.054	0.027	0.025	0.024	0.022	0.02	0.16	0.028
K	(mg/l)		0.97	0.50	0.50	0.50	1.575	2.650	3.725	4.8	4.36	0.76
Se	(mg/l)	<.005	0.097	0.063	0.051	0.039	0.034	0.029	0.023	0.018	0.10	0.018
Ag	(mg/l)		0.005	0.005	0.005	0.005	0.013	0.021	0.028	0.036	0.034	0.0059
Na	(mg/l)		5.0	3.0	2.7	2.4	2.300	2.200	2.100	2.0	6	1.1
SO4	(mg/l)	9.9	2040	435	309	183	161	139	116	94.2	996	174
Zn	(mg/l)	0.44	970	100	68.5	37	31.25	25.50	19.75	14	363	63

* fluoride data not available. Data from HC-UPT-IT1 (uncemented pyritic tailings) was used.

Measured at less than detection limit. The detection limit value is used in these calculations

Interpolated value.

Nb: beginning at cycle 20, sample was leached twice a day at a rate of ~1.4 L/day. After 7 days, the collected leachate was submitted for analysis.

Table 3.

Crandon Ore Composite Leaching Data - Estimating Constituent Release from the Crown Pillar

		Lower Mole Lake High Sulfur Composite (mg/kg/wk)	Ore Composite Bulk Chemistry mg/kg	Ore Composite Bulk Chemistry mg/kg	Ore Composite Bulk Chemistry mg/kg	Lower Mole Lake High Sulfur Composite Bulk Chemistry mg/kg	Bulk Chemistry Ratio	High RangeEstimate Crown Pillar Release Rate (mg/kg/wk)
Date collected			**Sample 1**	**Sample 2**	**average**			
Volume	(L)							
pH								
EC								
Al	(mg/l)	0.28	12000	12700	12350	63500	0.19	0.27
Sb	(mg/l)	0.00314	60	60	60	60	1.00	0.016
As	(mg/l)	0.000945	2300	2600	2450	190	12.89	0.061
Ba	(mg/l)	0.000542	31	20	25.5	260	0.10	0.00027
Be	(mg/l)	0.000283						
B	(mg/l)							
Cd	(mg/l)	0.00825	240	240	240	16	15.00	0.62
Ca	(mg/l)	20	5100	3800	4450	6600	0.67	67.4
Cl	(mg/l)							
Cr	(mg/l)	0.000298	27		27	9	3.00	0.0045
Co	(mg/l)	0.0432	77	66	71.5	25	2.86	0.62
Cu	(mg/l)	1.06	3100	3400	3250	490	6.63	35.2
CN	(mg/l)							
F*	(mg/l)							
Fe	(mg/l)	0.38	250000	263000	256500	78300	3.28	6.2
Pb	(mg/l)	0.00248	8400	9300	8850	480	18.44	0.23
Mg	(mg/l)	8.75	7800	8100	7950	19800	0.40	17.6
Mn	(mg/l)	1.06	450	560	505	640	0.79	4.18
Hg	(mg/l)	0.0000177	8.9	6.1	7.5	2.3	3.26	0.00029
Ni	(mg/l)	0.00609	6.5	5	5.75	8	0.72	0.022
K	(mg/l)	0.302	3300	4300	3800	21200	0.18	0.27
Se	(mg/l)	0.0129	72	123	97.5	3	32.50	2.10
Ag	(mg/l)	0.000298	44.4	37.2	40.8	0.28	145.71	0.22
Na	(mg/l)	0.101	360	350	355	3500	0.10	0.051
SO4	(mg/l)	94.8	946640	964614	955627	133013.9	7.18	3405
Zn	(mg/l)	4.08	93000	93100	93050	4200	22.15	452
		S(total)	31.6	32.2	31.9	average	13.19	

Appendix A.
Multiple Step Batch Test Results and Assessment of Available Neutralization Potential of Pyritic Paste Backfill

A1. Introduction

Multiple batch tests were used to assess the available neutralization potential of the pyritic paste backfill. The following presentation describes multiple batch tests on the pyrite concentrate and the pyritic paste backfill. Results from the pyritic paste backfill were used to calculate its available neutralization potential. These calculations are compared to the available neutralization potential observed in humidity cell tests on the pyritic paste backfill.

A2. Multiple Batch Tests

A2.1. Methods

The Multiple Step Batch Test were conducted on the pyrite concentrate and pyritic paste backfill, and the methods are described in section 2.3.7 of Foth & Van Dyke (1999/2000) (Foth & Van Dyke 19999/2000, Appendix 4.2-15, p. 4.2-15-18). A single 40-g sample of pyrite concentrate was subjected to six 0.99-L volumes of leachate at pH 4 and 50 mgL^{-1} ferrous iron. A 50-g sample of pyritic paste backfill were subjected to six 1.00-L volumes of leachate at pH 4.0 and 300 mgL-1 ferrous iron (Foth & Van Dyke 1999/2000, Appendix 4.2-15-19, Table 2.7).

The procedure was described as follows (Foth & Van Dyke 1999/2000, Appendix 4.2-15, section 2.3.7).

> The exact amount of solids was weighed out and placed in a 2-L narrow mouth vessel. Two holes were augured through the stopper through which glass tubes were inserted. The first was short and only passed through the stopper so that the end within the vessel was not in contact with the solution and was used to control the atmosphere inside the vessel with argon. The second tube was longer and extended to the bottom of the vessel and was used to extract samples, or replace solution as required.
>
> Once the sample was placed in the vessel and the atmosphere had been displaced with argon gas, the de-aerated leachant was introduced into the vessel. The vessel was then sealed and placed on a shaking table to agitate the slurry.
>
> Every second day, the vessel was removed from the shaker, and the solids were allowed to settle for a period of 4 - 6 hours. A small aliquot of sample was then extracted from the vessel while maintaining anoxic conditions. The sample pH, Eh, temperature, alkalinity/acidity and conductivity were obtained, and a total iron analysis was completed. Each stage of the tests was continued for a minimum period of 10 days. At the end of each stage, taking care not to extract solids, the leachate was extracted by vacuum. The extracted

leachate was sampled and preserved as required for analysis. The leachate was replaced with fresh leachant by pumping the fresh leachant back into the system. This process was repeated until all six stages of the tests had been completed.

The addition of acidity was calculated to be adequate to dissolve all available neutralization potential during the six stages. The NP (modified Sobek (?)) and CO_3 NP of the residues were determined and the residues were subjected to analysis by optical microscopy and SEM-EDS. There is ambiguity regarding the method that was used to determine Sobek NP as described in Section 2.2.2.3 of the main body of this document.

The extent of neutralizing minerals reacted, or available neutralization potential, during the six leaching stages was calculated by 1) comparison of the unleached samples and the leached residues using both modified Sobek (?) NP and CO_3-NP measurements and 2) based on neutralization of solution acidity during all six leaching stages for the pyrite concentrate and during the first three stages for the pyritic paste backfill, and 3) based on the release of calcium and magnesium during all six leaching stages for the pyrite concentrate and during the first three stages for the pyritic paste backfill.

A2.2. Results

A2.2.1. Pyrite Concentrate

It is reported that anoxic conditions were not maintained in the test, and acid neutralization and iron removal was essentially limited to the first three cycles (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-46). It is further suggested that "the results may be used as a provisional estimate of NP availability for the pyrite concentrate under oxidizing conditions" (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-46).

The leachate pH were for the six stages were 4.9, 5.5, 4.9, 4.9, 4.7, and 4.1, respectively (Table 3.23, p. 4.2-15-48, Foth & Van Dyke 1999/2000, Appendix 4.2-15). Total iron concentrations in the leachate increased from 0.62 mg/L in the first stage to 39 mg/L in the sixth stage. Leachate acidities in the final two stages were higher than those present in the leachate, indicating a net release of acidity. The fraction of modified Sobek (?) NP and CO_3-NP availability were calculated by 1) analysis of initial solids and post-test residue, 2) calculation of acidity consumed during the test (accounting for change in acidity, release of alkalinity, and dissolution of manganese carbonate), 3) calculation of the total calcium and magnesium release during all six stages. The respective availabilities of modified Sobek (?) NP for the three calculations were 0, 34, and 64 percent. The associated values for CO_3-NP availability were 0, 35 and 65, percent (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-49, Tables 3.24, 3.25). The values based on residue analyses were "considered to be erroneous and were disregarded" (p. 4.2-15-47, Foth & Van Dyke 1999/2000, Appendix 4.2-15).

A2.2.2. Pyritic Paste Backfill

The pyritic paste backfill test CPT-1 was reported to be anoxic for three cycles and CPT-2 for five cycles. Leachate pH decreased from about 11 to 9 in the first three stages, and values of 6.1 and 5.8 were reported for the fourth stage (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-48, Table 3.23). The respective availabilities of Sobek (?) NP based on change in solid-phase composition, acidity consumption (stages 1-3), and calcium and magnesium release (stages 1-3) averaged 93%, 93.5%, and 83.5%. The corresponding availabilities for CO_3-NP were 86%, 182%, and 162.5% ((Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-49, Tables 3.24, 3.25).

The residue from the CPT-1 test was subjected to mineralogical analysis, and the following paragraphs are excerpted from the results (Foth & Van Dyke 1999/2000, Appendix 4.2-15, p. 4.2-15-95 with summary on p. 4.2-15-62).

> "Carbonate minerals (0.5 wt%) were present as both 1) extensively iron oxyhydroxide-stained liberated grains up to 25μm and as 2) liberated iron oxyhydroxide-staining along fractures and rims up to 75μm. SEM-EDS analysis identified carbonate compositions rich in Fe, with minor Mg and Mn. Minor amounts primary Ca(Fe,Mg)Mn carbonate were also identified."
>
> "Iron sulphates / iron oxyhydroxides consisted of minor orange-brown cementing of sulphide grains and staining on fine-grained phyllosilicates (muscovite). SEM-EDS analysis identified compositions of iron and sulphur, with minor silica for these minute grains. SEM-EDS analysis of pseudomorphed carbonate grains identified compositions of Fe, with minor S and lesser Zn. These compositions are indicative of an intergrowth of iron oxyhydroxides and iron sulphate."

The summary of mineralogical analyses indicates a carbonate content of <0.2%, traces of fine (<5μm) disseminated iron sulphate occurring in minor amounts as replacement of carbonates and extensive staining of muscovite.

A3. Available Neutralization Potential Observed in Humidity Cell Tests

An upper bound for NP release was determined based on the total calcium and magnesium release during the first 60 cycles of the intermediate term humidity cell test. In this test drainage pH equaled or exceeded pH 6.0 for the first 60 cycles (Foth & Van Dyke 2001, Appendix C, Table C2). Cumulative mass releases of calcium and magnesium at cycle 60 were 5700 and 610 mg/kg, respectively (Foth & Van Dyke 2001, Appendix C, Table C3). This implies an NP depletion of 16.7 kg $CaCO_3$ eq/t ($5.7 \times 100/40.1 + 0.61 \times 100/24.3 = 16.7$). This represents available modified Sobek (?) NP and CO_3-NP values of 65 and 79 percent, respectively (Table 1). This is an upper bound for NP release (available NP) because some of the calcium release was probably due to gypsum dissolution rather than calcium carbonate dissolution. This calculation could not be made with the short term tests because the pH of their drainage remained above 6.0 throughout the 20 cycle duration of the tests.

A lower bound was determined by assuming 1) all acid neutralization that occurred was the result of carbonate mineral dissolution, 2) the only carbonate minerals present were those in the pyrite concentrate, and 3) the dissolution of carbonate minerals present in the pyrite concentration was stoichiometric. The neutralization potential present as carbonate (CO_3 NP) is reported as 15.85 kg $CaCO_3$ eq/ton (Foth & Van Dyke 2000, Appendix 4.2-15, p. 4.2-15-40, Table 3.16). The fractions of carbonate with associated with calcium and magnesium are 23.6 and 22.2 percent, respectively (Foth & Van Dyke 2000, Appendix 4.2-16a, p. 4.2-16a-6, Table 2).

The magnesium release during the first 60 cycles of the intermediate term humidity cell test was 610 mg/kg, and this represents an NP release of 2.5 kg $CaCO_3$ eq/t. Assuming the stoichiometric dissolution of carbonate minerals implies calcium carbonate dissolution would release 2.7 kg $CaCO_3$ eq/t of NP. This yields a total NP release of 5.2 kg $CaCO_3$ eq/t. This indicates availabilities of modified Sobek (?) and CO_3-NP of 20 and 24 percent, respectively (Table A1.1).

The NP availabilities determined from humidity cell results were considerably lower than those estimated based on the multiple step batch tests (Table A1.2).

A1.4. References

Foth & Van Dyke. 2000. Crandon Project Tailings Management Area Groundwater Quality Performance Evaluation (Depyritized Tailings). Included as Appendix 4.2-12 of the Environmental Impact Report.

Foth & Van Dyke. 2001. Corroborative Testing Program, Final Results from the Intermediate Term Humidity Cell Test on Pyritic Paste Backfill (CPT-IT1). Report prepared by Steffen Robertson and Kirsten (Canada) Inc. for Foth & Van Dyke, June 2001. 26 p. plus appendices.

Steffen Robertson and Kirsten. 2000. Reflooded Mine Source Concentration - Crandon Project, WI. 90 p. plus appendices. Included as Appendix A in Foth & Van Dyke. 2000b. Addendum No. 1 to the Mine Permit Application, Reflooded Mine Management Plan, Crandon Project, Crandon, Wisconsin, December 2000. 75 p. plus figures and appendices.

Table A1.1. Pyritic paste backfill NP availability observed in the intermediate term humidity cell test.

NP depletion method	NP depletion, kg $CaCO_3$ eq/t	Initial, NP kg $CaCO_3$ eq/t		Percent NP Available	
		Modified Sobek	CO_3-NP	Modified Sobek	CO_3-NP
Ca+Mg release through cycle 60	16.7	25.8	21.25	65	79
Carbonate dissolution based on Mg release through cycle 60	5.2	25.8	21.25	20	24

Table A1.2. Comparison of pyritic paste backfill estimated available NP with NP availability observed in the intermediate term humidity cell test.

	Modified Sobek NP	CO_3-NP
Initial NP[1], kg $CaCO_3$ eq/ton	25.8	21.25
Availability[2], percent		
Multi Step Batch Test[3]		
Residue analysis	93	86
Leachate acidity consumption	93.5	182
Leachate Ca + Mg release above pH 6.0	83.5	162.5
Intermediate Term Humidity Cell		
Maximum[4]	65	79
Minimum[5]	20	24

[1] Foth & Van Dyke 1999/2000, Appendix 4.2-15, page 4.2-15-40, Table 3.17.

[2] Calculated using average NP or NP(CO_3).

[3] Foth & Van Dyke 1999/2000, Appendix 4.2-15, page 4.2-15-49, Tables 3.24, 3.25.

[4] Based on cumulative Ca + Mg release at pH $\geq$ 6.0 (60 cycles)

[5] Using Mg release at pH $\geq$ 6.0 (60 cycles) and assuming 1) all neutralization due to dissolution of carbonate minerals, 2) dissolution of carbonate minerals was stoichiometric.

Technical Memorandum

Date: December 31, 2003

To: Wisconsin DNR Crandon Project Files

From: David Blowes, PhD – Sala Groundwater, Inc., Waterloo, Ontario
Christopher Carlson, PhD – Wisconsin DNR

Subject: Source Term Calculations for the Reflooded Mine, Proposed Crandon Project

This document reports on the status of the review of the reflooded mine source term calculations submitted by Nicolet Minerals Company at the time the permit applications were withdrawn at the end of October 2003. Though revised calculations of the estimated source term were largely completed by the WDNR review team at that time, those calculations had not been documented or reviewed in detail by the project team. This document describes the procedures used to develop source term estimates for the reflooded mine. The source term estimates developed at the time the mine permit application was withdrawn were based on parameter estimates (e.g., solute release rates, gas transport rates, sulfide oxidation rates) derived from other portions of the review, conducted largely by other members of the review team. There has been no opportunity for those individuals to review how these values were used in the source term estimates or to confirm that these values were used in a manner that is consistent with their development. Furthermore, some of the components of the review completed by the other members of the DNR review team had not been documented at the time the mine permit application was withdrawn, making it impossible to be certain that the values used in this work were correct. As a consequence some aspects of the reflooded mine source term calculations may not be supported by other associated review documents.

A. EXPECTED REACTIONS OF IMPORTANCE IN THE REFLOODED MINE

1. Sulfide Oxidation

A principal cause of environmental concern associated with the reflooded mine is the oxidation of sulfide minerals contained within the paste tailings and waste rock components of the backfill material, the mine workings wall rock and the crown pillar, and the subsequent transport and release of these oxidation products to water flowing through the underground workings. The principal sulfide mineral in the backfill materials and the wall rock is pyrite. The oxidation of pyrite can be described through the equation:

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2\,SO_4^{2-} + 2\,H^+ \qquad [1]$$

This reaction consumes pyrite, oxygen and water, generates low pH conditions and releases Fe(II) and SO_4 to the water flowing through the mine waste. The Fe(II) released by sulfide oxidation may be oxidized to Fe(III) through the reaction:

$$Fe^{2+} + \frac{1}{2}O_2 + H^+ \Leftrightarrow Fe^{3+} + \frac{1}{2}H_2O \qquad [2]$$

The resulting Fe(III) may precipitate as a ferric oxyhydroxide phase, through a reaction of the form:

$$Fe^{3+} + 3\,H_2O \Leftrightarrow Fe(OH)_3 + 3\,H^+ \qquad [3]$$

Alternatively, Fe(III) may oxidize additional pyrite or other sulfide minerals through reactions of the form:

$$FeS_2 + 14\,Fe^{3+} + 8\,H_2O \rightarrow 15\,Fe^{2+} + 2\,SO_4^{2-} + 16\,H^+ \qquad [4]$$

Within mine wastes, sulfide oxidation proceeds rapidly, and is catalyzed by chemolithotrophic bacteria of the *Acidithiobacillus* group (Boorman and Watson, 1976; Southam and Nordstrom, 1997; Gould and Kapoor, 2003). Within the paste materials the pore water is initially anticipated to be basic, ranging between pH 9 and pH 11. Under these conditions the activity of *Acidithiobacillus ferrooxidans*, and related species is expected to be limited. This limitation may not be sufficient to prevent sulfide mineral oxidation for several reasons. The rate of abiotic oxidation of pyrite increases as the pH increases (Williamson and Rimstidt, 1994). Neutrophillic bacterial species are active under neutral pH conditions (Gould and Kapoor, 2003); these bacteria may catalyze steps in the overall oxidation process. Furthermore, there is potential for development of acidic microenvironments within the more basic tailings mass (*e.g.*, Southam et al., 2003).

In addition to the iron-sulfide minerals, other metal-sulfide minerals are susceptible to oxidation, releasing elements such as As, Cd, Co, Cu, Ni, Pb, Zn to the water flowing through or adjacent to the tailings-paste mass, wall rock and crown pillar.

The fine grain size and the cementation of the paste material are anticipated to lead to low gas permeabilities within the bulk of the backfill. The permeability of tailings materials is typically too low to permit significant advective transport, or convective transport, of gas-phase oxygen. In the paste material, the transport of oxygen is expected to be dominated by gaseous diffusion. The rate of oxygen gas diffusion is dependent on the concentration gradient and the diffusion coefficient of the paste material. The diffusion coefficient of tailings is dependent on the air-filled porosity of the tailings, with the diffusion coefficient increasing as the air-filled porosity increases, and decreasing as the moisture content increases. A steady supply of oxygen to the surface of the paste backfill is required to support rapid oxidation of sulfide minerals. As the sulfide minerals near the surface of the cemented tailings backfill are depleted, the rate of sulfide oxidation is expected to decrease due to the longer diffusion distance through the paste tailings.

2. Carbonate and Hydroxide Mineral Dissolution and Acid Neutralization

The oxidation of sulfide minerals in the wall rock, the crown pillar, and the tailings and waste rock components of the backfill will release H^+ to the pore water. This H^+ will react with the portland cement included in the paste and the non-sulfide gangue minerals within the mine wastes, wall rock, and crown pillar. Acid-neutralization reactions consume H^+, resulting in a progressive increase in the pH along the groundwater flow path. The most significant pH-buffering reactions expected in the paste backfill are the dissolution of the portland cement components, dissolution of carbonate minerals, aluminum hydroxide and ferric oxyhydroxide minerals, and aluminosilicate minerals. Similar reactions, including portland cement dissolution from grout, are expected to be significant in the wall rock and crown pillar.

The most abundant carbonate minerals in the Crandon tailings are dolomite ($CaMg(CO_3)_2$), ankerite ($CaFe(CO_3)_2$), siderite ($FeCO_3$) and calcite ($CaCO_3$). These are also anticipated to be the most abundant carbonates in the wall rock and crown pillar. The dissolution of dolomite can be described as:

$$CaMg(CO_3)_2 + 2H^+ \Leftrightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \qquad [7]$$

Dissolution of the portland cement and the dissolution of these carbonate minerals has the potential to raise the pH of the pore water to near neutral. Carbonate mineral dissolution releases Ca, Mg, and cations such as Mn that are included as impurities, and increases the alkalinity of the water. Initially the masses of portland cement and carbonate minerals present may be sufficient to neutralize the H^+ released by sulfide oxidation. After prolonged oxidation, however, some portions of the oxidized backfill material, the wall rock, and the crown pillar are expected to become acidic because the acid generating sulfide contents of the backfill material and portions of the wall rock and crown pillar exceed the mass and availability of the acid-neutralizing carbonate minerals. As the carbonate content of the paste backfill is depleted a sharp decline in pH is expected, the decline in pH is likely to be accompanied by an increase in the concentrations of dissolved metals.

3. Secondary Mineral Formation

Sulfide oxidation and acid neutralization reactions occurring in the backfill, wall rock, and crown pillar will release high concentrations of dissolved constituents. The concentrations of these dissolved constituents may exceed the solubilities of secondary minerals, which would accumulate in the backfill, on the surfaces of the mine workings, or within the crown pillar. The precipitation of secondary minerals limits the concentrations of dissolved major ions and dissolved metals in the waste-derived waters (Alpers et al., 1994; Jambor et al., 2003). The most abundant dissolved constituents derived from sulfide oxidation and acid neutralization reactions are SO_4, Fe(II), Fe(III), and the major cations Ca, Mg, K, Na, and HCO_3^-. These dissolved constituents react in the effluent waters, resulting in the precipitation of a number of secondary minerals including gypsum ($CaSO_4 \cdot 2H_2O$), jarosite ($KFe_3(SO_4)_2(OH)_6$), goethite ($\alpha FeOOH$), ferrihydrite ($Fe_8(OH)_9$), siderite ($FeCO_3$), and rarely, melanterite ($FeSO_4 \cdot 7H_2O$). The precipitation and dissolution of these phases limits the dissolved concentrations of the major ions in the pore water and provides substrate for the attenuation of dissolved metals. In the underground workings and the crown pillar, accumulations of secondary minerals may provide reservoirs of dissolved constituents that may be released as geochemical conditions change after the workings are allowed to flood (for example, soluble minerals such as gypsum may dissolve).

4. Adsorption and Ion Exchange

The precipitation of secondary minerals may limit the maximum concentrations of many dissolved elements within the backfill, the wall rock, and the crown pillar. At concentrations that do not attain saturation with respect to secondary minerals, dissolved metal concentrations may also be limited by adsorption on the surfaces of primary minerals or to the surfaces of secondary iron and aluminum hydroxide minerals. Although adsorption during groundwater transport may provide an important sink for dissolved metals within the backfill or the underlying aquifers, these mechanisms were not considered by

NMC in the evaluation of the potential concentrations of dissolved elements and will not be addressed in detail here.

5. Fuel combustion

During mining, combustion of fuels underground will release emission products. The three principal sources of these combustion products were identified by SRK (2000) as:

- Natural gas used for mine air heating and
- Fuel oil used for mobile equipment.

Gaseous emissions from these sources include sulfur dioxide, volatile organic compounds, carbon monoxide. In addition, polycyclic aromatic hydrocarbons (PAH's) derived from the incomplete combustion of fuel oils and trace metals, originally present in the fuel oil will be released. Much of the combustion by products will be removed from the mine workings by the mine ventilation system and the mine-water collection and pumping system.

6. Blasting Residues

The explosive to be used in the mining operation is ANFO, a mixture of ammonium nitrate and fuel oil. SRK (2000) indicates that during mining, the majority of the nitrogen compounds derived from the combustion of the explosives will be in the gaseous form and will be removed from the mine workings by the ventilation system. Much of the remainder is expected to be removed by the mine-water collection and pumping system. Dissolution of any remaining unexploded ANFO will release ammonium, nitrate and nitrite, as well as fuel oil components to the reflooded mine.

B. EXPECTED SOURCES OF SOLUTES

1. Introduction

There are several sources of solutes in the reflooded mine. These sources include the pyrite concentrate that will be contained in the cemented paste backfill to be placed into the mined-out stopes; the waste-rock plugs used to retain the paste backfill; the wall rock of the mined out access workings and mined out stopes which are not backfilled; unmined ore, including the crown pillar; and blasting residues and combustion byproducts. SRK (2000) provided estimates of the concentrations of solutes that are expected from each of these sources, both an expected case “Best Engineering Judgment” and a reasonable worst case “Upper Bound”. These solute concentrations were integrated with the solute transport modeling results to estimate the potential for release of dissolved constituents from the reflooded mine to result in excedances of groundwater quality standards.

2. Stopes – Paste Backfill & Waste Rock Plugs

2.1 Stope Development and Backfilling

The development and operation of the Crandon mine will involve excavation of underground workings to gain access to the ore body and the removal of portions of the orebody. NMC proposes to use cemented pyritic tailings with waste rock plugs to backfill the mined out stopes. The use of backfill would enhance mine stability and maximize ore recovery. The use of the pyritic tailings for backfill would return the sulfide minerals underground, where they would be submerged following mine reflooding. Pyritic paste backfill is to be placed in both types of stopes proposed for the mine, blasthole open stopes and cut and fill stopes.

2.1.1 Blasthole Stopes

The configuration of the blasthole stopes is described in the Reflooded Mine Management Plan (Foth and Van Dyke, 2000). The blasthole stopes are proposed to be 75 feet long (along the strike of the ore body), 200 feet high, and 100 feet in orebody width. Typical blasthole stopes would contain 170,000 tons of ore. About 12 stopes are expected to be operated in any year, resulting in an annual production of 2,000,000 tons of ore. Access to the blasthole stopes would be via 13 foot by 16 foot cross-cuts from the development workings into the ore body. The blasthole stopes would be filled by placing a waste rock plug in the cross-cut at the base of the stope. Pyritic paste backfill would be pumped into the stope from the top. The cross-cut would be sealed with a ventilation bulkhead for safety and to limit air flow to the backfill.

2.1.2 Cut and Fill Stopes

The configuration of the cut and fill stopes is described in the Reflooded Mine Management Plan (RMMP; Foth and Van Dyke, 2000). The cut and fill stopes are proposed to be 120 feet along the strike of the ore body and 100 feet wide. The cut and fill stopes would be mined in four lifts. Each lift is expected to be 11 to 13 feet high, for a total height of 45 feet. A typical cut and fill stope would contain 60,000 tons of ore. Pyritic paste backfill would be pumped into the stope to backfill the stope and provide a working surface as each lift is removed. A tight fill procedure is proposed to be used for the final lifts to minimize the residual void space left between the top of the backfill and the crown pillar.

2.1.3 Pyritic Paste Backfill

NMC proposes to backfill the blasthole stopes and the cut and fill stopes will be backfilled with pyritic paste. The stopes would be filled with the backfill material shortly after excavation of the stope is complete. The outer surfaces of the pyritic paste backfill present in the mine-out stopes would be exposed during mining and would remain exposed during the period of time required for the mine to flood. During this period of exposure, there is potential for the sulfide minerals contained in the pyritic paste backfill to oxidize, releasing solutes that may be stored in the backfill or in secondary oxidation products. After the mine is allowed to flood, the solutes released from the pyritic paste backfill could be released to the water flowing through the mine workings. The bulk of the pyrtic paste backfill, contained in the central portions of the stopes, will be isolated from oxygen by the surrounding backfill material. SRK has labelled this portion of the backfill the *Unoxidized Backfill*. The backfill present at the stope margins may be exposed to oxygen during mining and reflooding. Where exposure to oxygen is limited the acid-neutralizing capacity of the pyritic paste backfill will be sufficient to consume the H^+ generated by oxidation of the sulfide component of the backfill. SRK has labelled this portion of the backfill as *Oxidized Neutral Backfill*. Where exposure of the backfill is extensive, the H^+ released by sulfide oxidation is expected to exceed the neutralization capacity of the pyritic paste backfill. In this case the pore water of the backfill will become acidic, and the concentrations of dissolved metals will increase. SRK has labelled this portion of the backfill as the *Oxidized-Acidic Backfill*. Data derived from the laboratory testing program was used to estimate the solute concentrations associated with each of these backfill types.

3. Wall Rock

3.1 Introduction

During mining, NMC proposes to excavate underground workings, including shafts, ramps, development workings, drifts, cross-cuts and ventilation raises into the country rock surrounding the ore body. The Crandon mine workings development would occur for the two portions of the orebody to be mined, the Massive Zinc Ore and the Copper Stringer Ore. Some of this exposed rock will contain sulfide minerals, which will oxidize when exposed to atmospheric oxygen by mining activities.

3.2 Hanging Wall

Mine workings and access drifts for the Massive Zinc Ore would occur in the hanging wall host rock, the Skunk Lake, Rice Lake, Upper Mole Lake and Lower Mole Lake Formations. All orebody access would be in the Lower Mole Lake Formation and the Crandon Formation (the massive sulfide deposit). NMC has conducted a waste characterization program to evaluate the potential for release of dissolved constituents from the hanging wall formations. NMC provided an estimate of the exposed surface area and acid-base accounting results from each of the formations that would be encountered during the mining of the Massive Zinc Ore (Foth and Van Dyke, 2000). This summary is reproduced in Table 1.

Table 1. NMC estimates of development wall rock exposure surface area and waste rock acid base accounting (from Addendum No. 1 to the Mine Permit Application, Reflooded Mine Management Plan, Foth and Van Dyke, 2000).

Formation	Exposed Wall Rock	Composite	ABA			
			Sulfide (%)	AP	NP	NNP
Lower Mole Lake	2,617,000 ft^2	Master	0.27	8.4	46	38
Upper Mole Lake	566,000 ft^2	Master	0.1	3.1	48	45
Rice Lake	1,610,000 ft^2	Master	0.05	1.6	1.6	0.0
Skunk Lake	201,000 ft^2	Master	0.14	4.4	1	-3.4

3.3 Foot Wall

The Copper Stringer Ore is situated in the foot wall, primarily the Sand Lake Formation. NMC has not undertaken detailed waste characterization studies on the Sand Lake Formation (foot wall) rock.

3.4 Crown Pillar

As proposed, the crown pillar would vary in thickness from 100 feet to 300 feet, and includes portions of the saprolite, the underlying orebody, hanging wall rocks, and foot wall rocks. The saprolite includes the gossan zone and a limited zone of supergene enrichment. These units are underlain by the unaltered massive sulfide zone. The gossan is the weathered zone of the orebody, which is typically less than 100 ft thick, but may locally be less or much more extensive. The supergene zone is characterized by copper enrichment, as indicated by the occurrence of the secondary sulfide minerals including chalcocite, covellite and bornite (Foth and Van Dyke, 2000).

Waste characterization studies have been conducted on the massive sulfide ore materials and on the hanging wall rock. No waste characterization studies were conducted on the gossan materials, the supergene enrichment zone, or on the foot wall rocks.

C. PREDICTION OF WATER CHEMISTRY OF SOURCES

1. Solutes Derived from the Stopes

The backfill present in the stopes is anticipated to be a major source of dissolved constitutes available for release to the groundwater system. The segregation of the backfill follows the classification system that was developed by SRK (2000; see section 2.1.3), the unoxidized backfill, the oxidized neutral backfill and the acidic backfill. Solute concentrations or solute loads associated with each of these components were developed and reviewed. A summary of the differences between the approach and assumptions used in the estimates made for this assessment and those made for NMC by SRK (2000) and presented in the RMMP (Foth and Van Dyke, 2000) is presented in Attachment 1.

1.1 Acidic Backfill and Waste Rock Plugs

1.1.1 Oxidized Acidic Backfill

The approach used to calculate the volume of acidic paste backfill was similar to that used by SRK in the RMMP (2000). These calculations were modified in the following manner:

- The oxidation rates were set considering the review of the laboratory test results (Lapakko, 2003). The Lower Range case was limited by the laboratory paste tailings sulfide oxidation rate. The Upper Range case was based on the rate of diffusion of oxygen through the cross-cut bulkhead adjacent to the backfill. This rate is limited by the rate of diffusion through the waste rock plug behind the bulkhead.
- The Neutralization Potential (NP) values were set to values recommended from the DNR review of the laboratory testing program results (Lapakko, 2003).
- The mass release ratios (masses of metals released per mass of sulfate released) were set to values recommended by the review of the laboratory testing program (Lapakko, 2003). Two values for these ratios were selected for each element, a median case and a maximum case. The median case was used for the Lower Range estimates and the maximum case was used for the Upper Range estimates.
- The MINTEQA2 equilibration step was not conducted since only a bulk mass for each constituent of oxidation product was developed. The bulk mass approach was used due to the way these values were integrated with the solute transport modeling results.

These values were then used to estimate the masses of constituents released per stope, and summed to estimate the masses released throughout the mine workings. Eight estimates were developed based on the combination of oxidation rates and mass release ratios derived from the DNR review of the laboratory experimental data. These estimates were selected to provide a range of the potential solute masses that will be released from the acidic paste backfill. The Lower Range estimates combined the median sulfate release rate estimate derived from the experimental data with the lower estimates of the metal release ratios. The Upper Range estimate combines the maximum release rate estimate with the upper estimates for the metal release ratio. These masses are listed in Tables 2 and 3 for the Lower Range and Upper Range estimates, respectively.

1.1.2 Oxidation of the Waste Rock Plugs in the Blast Hole Stopes

During mining, the ore would be drawn from the base of the blasthole stopes at drawpoints connected to the main mine drifts by cross-cuts. After mining is complete in a stope, the cross-cut would be filled with a waste rock plug and the stope would be backfilled with pyritic paste. A sealed bulkhead would be installed between the waste-rock plug and the external mine workings to limit the transport of oxygen from the mine workings into the cross-cut. Although the bulkheads would be sealed, it is anticipated that oxygen gas would pass through the bulkhead. SRK assumed, therefore, that the rate of oxidation of the paste backfill behind the bulkhead would be limited by diffusion through the waste rock plug or by the rate of sulfide oxidation at the backfill surface. The DNR review of the SRK estimates of the diffusion of oxygen through the waste rock plug, indicates that these estimates are reasonable (Benson, 2003).

SRK did not consider the release of solutes due to oxidation of the waste rock between the bulkhead and the surface of the paste backfill. As an alternative to SRK's assumption of the oxygen being consumed by the paste backfill, Benson (2003) estimated the rate of oxygen consumption by the waste rock within these cross cuts. This analysis included a Lower Range estimate and an Upper Range estimate. These estimates were combined with the metal release rates for the waste rock (Lapakko, 2003) to estimate the masses of metals released by oxidation of the waste rock plugs. These masses were summed over all the blasthole stopes and added to the masses derived from the acidic paste backfill in the cut and fill stopes to develop alternative Lower and Upper Range estimates of release from the cross-cuts. These values are also included in Tables 2 and 3.

1.2 Oxidized Neutral and Unoxidized Paste Backfill

1.2.1 Oxidized Neutral Paste Backfill

A portion of the acidity released by sulfide oxidation would be neutralized by the NP of the paste backfill material. The high pH associated with this water would result in the precipitation of secondary minerals within the paste backfill, decreasing the concentrations of some dissolved constituents. To estimate the concentrations of dissolved metals in the Oxidized Neutral portion of the paste backfill an approach similar to that used by SRK (2000) was used. Differences between the approach used by SRK, and the approach used here are:

- To estimate short-term conditions, solute release rates from Cycle 20 of the Short Term Cemented Backfill tests (CPT-ST 1/2) were combined.
- To estimate longer term conditions, solute release rates from Cycle 62 of the more prolonged leaching of the Intermediate Term Cemented Backfill tests (CPT-IT1) were used in the analysis. The Intermediate Test results were not available at the time the SRK estimates were developed.
- The selection of secondary phases allowed to precipitate in the MINTEQA2 simulations for the Lower Range calculations included barite, gypsum, anglesite, calcite, ferrihydrite, gibbsite, $Ni(OH)_2$, cerargyrite, fluorite, $Zn(OH)_2$, and brochantite.
- In the Upper Range case, only gypsum was allowed to precipitate in the MINTEQA2 simulations.
- A calculation was added to account for the formation of a narrow zone of oxidized neutral paste backfill which may develop at the interface of the paste backfill and the stope walls due to anisotropies that are anticipated to develop in the paste backfill prior to the mine reflooding (Mine Systems Design, 2003)

The thickness of the oxidized neutral zone in the backfill exposed in the stope tops was estimated to be 0.05 m by SRK (2000). This estimate was used in current the calculations. To account for oxidation along the discontinuities along stope margins (Mine Systems Design, 2003), a 0.005 m thick layer of oxidized neutral paste backfill was assumed to surround the backfill in each stope. To estimate the solute concentrations in the oxidized neutral zone of the cemented paste backfill, solute release rates were determined from the cemented paste backfill tests (CPT-ST 1/2 - Cycle 20, and CPT-IT1 - Cycle 62) were used. These leach rates are expressed in mg kg^{-1}. To convert these rates to release rates expressed in mg L^{-1}, calculations were conducted incorporating the bulk density (2332 kg m^{-3}) and the expected porosity (0.4 m^3 m_T^{-3}). The estimated concentrations of some solutes exceed the solubility limits of secondary minerals commonly observed in mines and mine wastes. Due to the longer duration of the CPT-IT1 test, the results from that test were selected to be used to develop the Lower and Upper Range estimates. To account for these solubility limitations, simulations were conducted using MINTEQA2. For the Lower Range case, concentrations estimated using the solute release rates were equilibrated with respect to barite, gypsum, anglesite, calcite, ferrihydrite, gibbsite, $Ni(OH)_2$, cerargyrite, fluorite and $Zn(OH)_2$. To provide estimates of the Upper Range case the estimated concentrations were equilibrated only with gypsum.

1.2.2 Unoxidized Paste Backfill

The contribution from the unoxidized paste backfill was estimated using the approach described by SRK (2000). The concentrations of Ca, Cl and S_2O_3 were modified to remove a negative value for the concentration S_2O_3 (not physically possible) and to maintain charge balance in the water chemistry (based on the fundamental condition of electroneutrality). The resulting water was equilibrated using MINTEQA2, the solid phases included in the simulations were barite, calcite, ferrihydrite, gibbsite, gypsum, rhodochrosite, $Ni(OH)_2$, and $Pb(OH)_2$. The pH of the water was assumed to be pH 11 SU and the Eh was assumed to be -170 mV. These Eh and pH conditions are the same as was used by SRK (2000).

Two cases were developed, a Lower Range case and an Upper Range case. The Lower Range case was based on the saturated column test results, with the MINTEQA2 results included when they resulted in lower concentrations. The Upper Range case was based on the saturated column tests only.

1.2.3 Unacidic Paste Backfill

The results from the oxidized neutral and unoxidized paste backfill estimates were averaged by volume to produce bulk Lower and Upper Range estimates for the unacidic paste backfill. The final estimates are presented in Tables 2 and 3.

2. Solutes Derived from the Workings Wall Rock

2.1 Solutes Derived from the Wall Rock

The masses of solutes released by oxidation of the wall rock were estimated using the same approach as used by SRK (2000). The masses were calculated using the formula:

Constituent Release (mg) = specific release rate (mg ft^2 yr^{-1}*) x exposed surface area (*ft^2*) x time (yr)*

Differences in the approach used were:

- The solute release rates were based on the waste rock release rates presented in Benson and others (2003).
- The Lower Range estimate of the solute release was based on the Lower Range estimate of the proportion of high sulfur rock present in the mine workings (represented by 80% Master-Composite equivalent and 20% High Sulfur equivalent; K. Lapakko, pers. comm.).
- The Upper Range estimate was based on the Upper Range estimate of the proportion of high sulfur rock present in the mine workings (represented by 60% Master-Composite equivalent and 40% High Sulfur equivalent; K. Lapakko, pers. comm.).

The exposed wall rock surface area and the exposure times used in these calculations were the same as used by SRK (2000). The solute contributions calculated based on these assumptions for the Lower and Upper Range cases are presented in Tables 2 and 3. An additional sensitivity analysis, evaluating the potential effect of an increase in the reactive surface area of the mine workings, was planned prior to the withdrawal of the Mine Permit Application. This sensitivity analysis was not completed.

2.2 Solutes Derived from the Crown Pillar

Lower Range and Upper Range estimates of the release of solutes from the crown pillar were developed using the same approach as used by SRK (2000). These estimates were modified in the following manner:

- The Lower Range Estimates were based on Cycles 1 – 8 of the Ore Composite leach test as recommended in the review of the laboratory testing program results (Lapakko, 2003).
- The Upper Range Estimates were based on the release rates from the Lower Mole Lake High Sulfur Composite test cell, as presented in Benson and others (2003) and recommended by Lapakko (2003). The leaching rates were multiplied by a factor of five to account for limitations in the High Sulfur Composite test results (Lapakko, pers. comm., 2003). The concentrations of dissolved constituents were individually adjusted for each parameter by the ratio between the average bulk chemistry of the Ore Composite samples and the bulk chemistry of the Lower Mole Lake High Sulfur Composite.
- The assumed exposure time was increased to one year.

Lower and Upper Range estimates for the crown pillar source term are presented in Tables 2 and 3, respectively. A sensitivity analysis using the water quality data from the saprolite pump test was also completed.

D. EFFECTIVENESS OF PROPOSED CLOSURE SOURCE CONTROL STRATEGIES

1. Proposed Strategies for Removal of Solutes from the Underground Mine and Expected Effectiveness

1.1 Removal of oxidized material from bulkheaded cross cuts

SRK (2000) assumed that 100% of the oxidized waste rock and paste tailings could be removed from the cross cuts following mining. The revised calculations presented herein assumed that only 80% removal would be possible. The results of these calculations are presented in Tables 2 and 3.

1.2 Washing of wall rock along access workings

SRK (2000) assumed that 100% of the oxidation products accumulated on the walls of the mine workings during mining could be removed by washing the walls prior to reflooding. The revised calculations presented herein assumed that only 50% removal would be possible. The results of these calculations are presented in Tables 2 and 3.

E. TOPICS NOT ADDRESSED IN THIS REVIEW

The Mine Permit Application was withdrawn during the course of the review of the NMC Reflooded Mine Management Plan and associated documents supporting the development of the reflooded mine source term. Topics that were intended to be included, but were not completely addressed prior to the withdrawal of the Mine Permit Application are as follows:

- Explosive residues
- Combustion by-products
- Effects of reflooding waters
    - Leakage from glacial system through/near crown pillar
    - Injected glacial aquifer water to enhance reflooding
    - Seepage from the surrounding bedrock

Table 2. Lower Range Estimates of solute release from the mine following reflooding.

Parameter	Oxidized-Acidic Cross Cuts								Unacidic Backfill	Wall Rock		Crown Pillar
	Paste Backfill Only				Waste Rock Plugs/Backfill				Paste Tailings	Weighted Average Concentration in Open Workings		Solute Concentration
	Median Available for Release to Workings No Removal (kg)	Maximum Available for Release to Workings No Removal (kg)	Median Available for Release to Workings Removal (kg)	Maximum Available for Release to Workings Removal (kg)	Median Available for Release to Workings No Removal (kg)	Maximum Available for Release to Workings No Removal (kg)	Median Available for Release to Workings Removal (kg)	Maximum Available for Release to Workings Removal (kg)	Weighted Average Solute Concentration (mg/l)	No Washing (mg/l)	Washing (mg/l)	(mg/l)
Al	67.272	8441.458	13.45	1688.29	1868.143	3843.187	373.629	768.637	0.024	22.662	11.331	1.958
Sb	0.098	37.798	0.020	7.56	99.881	108.772	19.976	21.754	0.017	0.208	0.104	0.034
As	29.262	6955.159	5.85	1391.03	71.470	1704.936	14.294	340.987	0.041	0.118	0.059	0.0077
Ba	0.046	8.056	0.009	1.61	21.450	23.339	4.290	4.668	0.006	0.047	0.023	0.0083
Be	0.016	2.284	0.0032	0.46	10.002	10.537	2.000	2.107	0.003	0.022	0.011	0.004
B	na	0.012	na	0.0025	na	na	na	na	0.005	na	na	na
Cd	2.963	372.417	0.59	74.48	14.595	101.730	2.919	20.346	0.094	0.087	0.044	0.708
Ca	829.593	39900.938	165.92	7980.19	50471.324	59686.263	10094.265	11937.253	934.385	206.317	103.158	25.248
Cl	13.688	37083.656	2.74	7416.73	3.228	8746.145	0.646	1749.229	250.989	na	na	na
Cr	0.078	9.141	0.016	1.83	11.009	13.146	2.202	2.629	0.005	0.024	0.012	0.004
Co	1.754	161.381	0.35	32.28	32.722	70.370	6.544	14.074	0.249	0.520	0.260	0.336
Cu	40.017	5958.676	8.00	1191.74	218.175	1614.085	43.635	322.817	0.012	12.467	6.233	14.890
F	2.426	80.807	0.49	16.16	0.572	19.058	0.114	3.812	0.133	na	na	na
Fe	1132.680	199243.330	226.54	39848.67	2509.738	49233.948	501.948	9846.790	0.263	17.380	8.690	8.049
Pb	5.688	969.934	1.14	193.99	56.565	283.982	11.313	56.796	0.062	0.122	0.061	0.140
Mg	190.933	3429.305	38.19	685.86	20737.599	21501.366	4147.520	4300.273	132.032	117.341	58.670	17.629
Mn	29.260	1762.775	5.85	352.56	321.034	729.881	64.207	145.976	5.314	9.045	4.523	0.579
Hg	0.0002	0.030	0.00003	0.0061	0.483	0.490	0.097	0.098	0.0030	0.0011	0.00054	0.00018
Ni	1.154	190.665	0.23	38.13	48.869	93.565	9.774	18.713	0.064	0.144	0.072	0.056
K	1.283	3288.210	0.26	657.64	10093.758	10868.977	2018.752	2173.795	177.534	20.814	10.407	1.516
Se	0.433	17.851	0.09	3.57	16.587	20.695	3.317	4.139	0.412	0.130	0.065	0.035
Ag	0.017	2.237	0.0034	0.45	9.990	10.513	1.998	2.103	0.0010	0.021	0.010	0.012
Na	93.615	1379.568	18.72	275.91	6309.903	6613.193	1261.981	1322.639	75.177	10.398	5.199	2.161
SO_4	7636.216	72907.685	1527.24	14581.54	55529.322	70923.536	11105.864	14184.707	1703.585	1078.937	539.469	346.302
Zn	1185.889	126621.870	237.18	25324.37	821.797	30405.755	164.359	6081.151	7.725	33.363	16.682	126.091

na = no information available

Table 3. Upper Range Estimates of solute release from the mine following reflooding.

Parameter	Oxidized-Acidic Cross Cuts								Unacidic Backfill	Wall Rock		Crown Pillar
	Paste Backfill Only				Waste Rock Plugs/Backfill				Paste Tailings	Weighted Average Concentration in Open Workings		Solute Concentration
	Median Available for Release to Workings No Removal (kg)	Maximum Available for Release to Workings No Removal (kg)	Median Available for Release to Workings Removal (kg)	Maximum Available for Release to Workings Removal (kg)	Median Available for Release to Workings No Removal (kg)	Maximum Available for Release to Workings No Removal (kg)	Median Available for Release to Workings Removal (kg)	Maximum Available for Release to Workings Removal (kg)	Weighted Average Solute Concentration (mg/l)	No Washing (mg/l)	Washing (mg/l)	(mg/l)
Al	7015.312	92200.678	1403.06	18440.14	17313.703	38997.823	3462.741	7799.565	0.237	42.028	21.014	0.308
Sb	10.208	412.845	2.04	82.57	755.827	853.176	151.165	170.635	0.017	0.210	0.105	0.018
As	3051.500	75966.775	610.30	15193.35	495.273	18402.359	99.055	3680.472	0.041	0.101	0.051	0.069
Ba	4.768	87.992	0.95	17.60	163.490	184.235	32.698	36.847	0.589	0.054	0.027	0.00030
Be	1.683	24.948	0.34	4.99	75.879	81.719	15.176	16.344	0.003	0.023	0.011	na
B	na	0.135	na	0.027	na	na	na	na	0.005	na	na	na
Cd	308.977	4067.677	61.80	813.54	111.993	1070.702	22.399	214.140	0.094	0.146	0.073	0.699
Ca	86512.050	435812.570	17302.41	87162.51	398121.884	500398.790	79624.377	100079.758	961.180	344.650	172.325	76.215
Cl	1427.381	405041.195	285.48	81008.24	9.496	95528.584	1.899	19105.717	636.408	na	na	na
Cr	8.166	99.844	1.63	19.97	83.485	106.996	16.697	21.399	0.005	0.025	0.013	0.0051
Co	182.879	1762.660	36.58	352.53	303.511	718.501	60.702	143.700	0.249	0.981	0.491	0.698
Cu	4173.095	65082.832	834.62	13016.57	3121.441	18455.678	624.288	3691.136	0.300	24.776	12.388	39.736
F	252.942	882.606	50.59	176.52	3.140	208.162	0.628	41.632	4.038	na	na	na
Fe	118118.825	2176208.188	23623.76	435241.64	19489.817	532247.661	3897.963	106449.532	0.291	30.578	15.289	7.036
Pb	593.162	10593.977	118.63	2118.80	419.681	2917.586	83.936	583.517	0.096	0.129	0.065	0.258
Mg	19910.947	37456.120	3982.19	7491.22	166863.138	175503.919	33372.628	35100.784	132.033	194.323	97.162	19.857
Mn	3051.349	19253.671	610.27	3850.73	3426.569	7954.427	685.314	1590.885	5.314	17.613	8.806	4.727
Hg	0.016	0.331	0.00316	0.066	3.652	3.730	0.730	0.746	0.0030	0.0011	0.00053	0.00033
Ni	120.377	2082.518	24.08	416.50	372.067	862.744	74.413	172.549	0.090	0.179	0.090	0.025
K	133.779	35915.023	26.76	7183.00	76455.202	84924.919	15291.040	16984.984	177.545	21.584	10.792	0.306
Se	45.197	194.973	9.04	38.99	135.496	181.345	27.099	36.269	0.412	0.228	0.114	2.370
Ag	1.755	24.430	0.35	4.89	75.588	81.346	15.118	16.269	0.032	0.021	0.010	0.245
Na	9762.425	15068.143	1952.48	3013.63	47467.530	50921.187	9493.506	10184.237	75.184	9.535	4.768	0.058
SO_4	796324.280	796324.280	159264.86	159264.86	539238.354	725095.601	107847.671	145019.120	1755.391	2059.48	1029.739	3849.415
Zn	123667.541	1383010.171	24733.51	276602.03	8155.842	333891.442	1631.168	66778.288	59.546	66.375	33.187	510.884

na = no information available

Attachment 1
Summary of Differences in Approach from that of Applicant in the Reflooded Mine Management Plan (FVD, 2000)

1) *Unacidic Backfilled Paste Tailings – Volume Weighted Average of Unoxidized and Oxidized-Neutral*
The volume-weighted average of the estimated contributions from the unoxidized paste backfill and the oxidized-neutral paste was determined for this portion of the source term.

a) *Unoxidized Paste Tailings*
The contribution from the unoxidized paste was estimated using the approach of SRK. However, the saturated column test results were modified for Ca, Cl, and S_2O_3 to make them more realistic, MINTEQ input was regenerated, and the simulation was rerun. Lower Range estimates were based upon the lower of the MINTEQ output or the saturated column test results, and Upper Range estimates were based upon the modified saturated column test results.

b) *Oxidized-Neutral Paste Tailings*
The contribution from the oxidized-neutral paste was estimated using the approach of SRK modified to include the use of the results from the intermediate term humidity cell at Cycle 62 and the average of the two short-term humidity cells at Cycle 20. MINTEQ simulation input was regenerated for the average short-term case (only gypsum as a controlling phase) and for three alternatives of the intermediate-term case (1. only gypsum as a controlling phase; 2. barite, gypsum, anglesite, calcite, ferrihydrite, gibbsite, $NiOH_2$, cerargyrite, and fluorite as controlling phases; and 3. barite, gypsum, anglesite, calcite, ferrihydrite, gibbsite, $NiOH_2$, cerargyrite, fluorite, $ZnOH_2$(amorph), and brokantite as controlling phases). The Lower Range estimates were based upon the intermediate-term humidity cell results and the Case 3 MINTEQ results, with the MINTEQ results used where they resulted in lowered estimates. The Upper Range estimates were based upon the intermediate-term humidity cell results and the Case 1 MINTEQ results, with the MINTEQ results used where they resulted in lowered estimates. In addition to the stope tops considered by SRK to contain oxidized-neutral tailings, stope margins were also included based upon Brackebusch (2003) discussion of anisotropies likely to be present in the backfill. An arbitrary estimate of the depth of oxidized-neutral tails on the stope margins of 0.5 cm was assumed.

2) *Oxidized-Acidic Cross Cuts*
Total mass release was estimated for the oxidized-acidic cross cuts, rather than concentration, due to the approach for utilization of the information in solute transport. The efficacy of the removal of the oxidation products from the cross cuts proposed by the applicant was revised and assumed to be 80%.

a) *Paste Tailings Only*
Median and Maximum estimates of constituent release rates relative to sulfate release for oxidized-acidic tailings were estimated in Lapakko (2003) and provided the basis for these estimates. Average exposure times for the blast-hole stopes and the cut-and-fill stopes were assumed to be the same and equal to 14 years. Estimates of constituent release were based on estimates of oxygen utilization to the paste using the approach of SRK. For the Lower Range oxygen utilization estimates (limited by oxidation rate), the Upper Range and Lower Range estimates of the paste tailings oxidation rate and available neutralization potential from Lapakko (2003) were used. For the Upper Range oxygen utilization estimates (limited by bulkheads), the Upper Range and Lower Range estimates of the available neutralization potential from Lapakko (2003) were used. Lower Upper Range estimates of total mass release were developed for both the Median and Maximum relative release rates

b) *Waste Rock – Blast-hole Stopes, Paste Tailings – Cut-and-Fill Stopes*
The same approach used for the paste tailings was used to develop the estimates of total mass release for the cut-and-fill stopes. Upper Range and Lower Range estimates of oxygen flux to the waste rock plugs behind the bulkheads of the blast-hole stopes were developed by Benson (2003) using the waste rock

oxidation rates from Lapakko presented in Benson and others (2003). Those oxygen flux estimates were combined with waste rock constituent release rates from Lapakko presented in Benson and others (2003) to develop Upper and Lower Range estimates of the total mass released from oxidation of the waste rock plugs. These were added to the release from the cut-and-fill stopes for estimates of the total mass release due to oxidation in the cross cuts.

3) Wall Rock – Weighted Average of Expected Host Rock Types

The Upper and Lower Range estimates of crown pillar release rates were developed using the approach of SRK, and the estimates of waste rock release rates cell from Lapakko presented in Benson and others (2003). The Lower Range estimate was based upon a Lower Range estimate of the distribution of high sulfur rock in the mine workings (represented by 80% master-composite equivalent and 20% high-sulfur-composite equivalent) (Lapakko, personal communication, 2003). The Upper Range estimate was based upon a Upper Range estimate of the distribution of high sulfur rock in the mine workings (represented by 60% master-composite equivalent and 40% high-sulfur-composite equivalent) (Lapakko, personal communication, 2003). The efficacy of the wall rock washing proposed by the applicant was revised and assumed to be 50%.

4) Crown Pillar

The Upper and Lower Range estimates of crown pillar release rates were developed using the approach of SRK, with the exposure time increased from 6 weeks to 1 year. The Lower Range estimate was based upon the estimated release information from Cycles 1-8 of the Ore Composite leach test as presented by Lapakko (2003). The Upper Range estimate was based upon the release rates from the Lower Mole Lake High Sulfur Composite test cell from Lapakko presented in Benson and others (2003) individually adjusted for each parameter by the ratio between the average bulk chemistry of the Ore Composite samples and the bulk chemistry of the Lower Mole Lake High Sulfur Composite, and multiplied by a factor of 5 to account for the limitations in the High Sulfur Composite test results (Lapakko, personal communication, 2003).