

Tyrone Operations P.O. Box 571 Tyrone, NM 88065

March 31, 2025

#### Via Electronic & Mail

Mr. Brad Reid New Mexico Environment Department Groundwater Quality Bureau Mining Environmental Compliance Section P.O. Box 5469 Santa Fe, NM 87502

#### Via Electronic

Mr. Clint Chisler Energy, Minerals & Natural Resources Dept Mining and Minerals Division Mining Act Reclamation Program 1220 South St. Francis Drive Santa Fe, NM 87505

Dear Messrs. Reid and Chisler:

#### Re: Discharge Permit 396 (DP-396) and Permit No. GR010RE Updated Emma Material Characterization and Handling Plan Resubmittal and Response to Additional Information

In a letter dated November 8, 2024, the New Mexico Environment Department (NMED) and Mining and Minerals Division (MMD) requested Freeport-McMoRan Tyrone Inc. (Tyrone) resubmit the *Updated Emma Material Characterization and Handling Plan* and provide additional information to address joint agency comments. This submission serves as Tyrone's response to the joint agency comment letter. It begins with background information on the project's history, permitting status, and the work completed to date in support of the Emma Expansion project, followed by direct responses to each comment in the joint agency letter.

On October 22, 2021, Tyrone submitted an application to the New Mexico Environment Department (NMED) to renew and modify DP-396 to support the Emma Expansion project, a critical mining initiative for the Tyrone Mine. The project includes a 200-acre pit south of the existing Tyrone mine, two non-discharging waste rock stockpiles, and new haul roads for transporting leach ore and acid-generating waste to existing stockpiles at the Tyrone Mine.

The application includes a state-of-the-art, highly conservative Material Handling Plan (Emma MHP), developed in consultation with Life Cycle Geo (LCG), a firm specializing in geology, geochemistry, and data science. The Emma MHP outlines conservative material segregation practices for the construction of the two non-discharging stockpiles, incorporating total sulfur analysis and confirmatory acid-base accounting testing to ensure that the stockpile will not discharge contaminants in excess of water quality standards. This plan was supported by extensive preliminary geochemical evaluation, including a static and kinetic testing program developed in consultation with LCG and NMED in December 2020, and the subsequent submission of a September 13, 2021 report titled "Geochemical Characterization of Emma Waste Rock Materials" to support the renewal and modification of DP-396 for the Emma Expansion project.

On February 7, 2022, NMED deemed Tyrone's October 22, 2021 application administratively complete, as of November 5, 2021. However, on May 9, 2022, NMED found the application technically deficient and requested additional information. This initiated a lengthy process of additional information requests, ultimately delaying the Emma Expansion project and adversely impacting Tyrone's business objectives. To date, Tyrone has yet to receive a permit with conditions that are protective of the environment and reasonably developed to support mining of the Emma project while ensuring compliance with the Supplemental Permitting Requirements for Copper Mine Facilities (20.6.7 NMAC).

Tyrone acknowledges in December 2023 Tyrone requested a delay in permit issuance, in part to avoid unreasonable permit conditions, such as a requirement that no potentially acid-generating (PAG) materials be present in the Emma non-discharging waste stockpiles with no explanation given by NMED for ignoring the proposed Emma MHP

While modern material characterization and handling practices, like those proposed for the Emma Expansion project, are industry-standard, robust and environmentally sound, it is impractical to insist that no PAG materials be present as some minor amount of dilution is common for all waste piles in the mining industry. Through proper geochemical characterization and materials segregation and handling, the Emma waste stockpiles can be constructed as non-discharging units, even with incidental quantities of PAG materials, as demonstrated by the extensive discharge modeling work conducted by LCG and presented to NMED.

Tyrone also notes that multiple meetings were held with NMED, Tyrone, and Tyrone's consultants to address agency concerns about the proposed material handling processes. During these meetings, the agency asked numerous questions and requested additional information related to geochemical characterization work that was completed and submitted approximately four years prior, in 2021. Tyrone contends that the level of scrutiny given to the Emma MHP and the repeated requests for additional information are excessive, far beyond industry norms and inconsistent with past NMED practice. Additionally, Tyrone notes that during most of the communications with NMED, the agency requested more information rather than providing specific guidance on what was needed to issue a permit and the regulatory basis for such requirements. Repeated requests for additional information delay permitting processes, increase costs to the permittee (labor, consultant expenses, etc.), and negatively impact mine plans, significantly affecting the company's ability to operate efficiently and profitably.

Tyrone asserts that, with the submission of this response and a finalized Emma MHP, NMED and MMD should be able to issue permits for the Emma Expansion project that ensure regulatory compliance, environmental protection, and support ongoing mining operations aligned with Tyrone's business needs. The U.S. copper supply is projected to fall short of meeting the growing demand driven by clean energy initiatives, which, according to S&P Global, is expected to double by 2035 due to increased use in electric vehicles, renewable energy systems, and grid expansion. Therefore, prompt issuance of permits with reasonable conditions while protecting the environment is critical, not only for Tyrone but also for advancing clean energy. Tyrone is open to meeting in person in Santa Fe with NMED and MMD to ensure clarity, address any remaining concerns, and prevent further information requests and permitting delays.

Comments and additional information requests outlined in NMED and MMD's November 8, 2024 letter are summarized in italics below, followed by Tyrone's responses:

#### Comment 1:

Section 3.1. Proposed Segregation Threshold. In addition to employing total sulfur and Acid Base Accounting (ABA) material characterization analyses, please describe any other methods or material characterization and handling strategies planned to avoid and to minimize significant inclusion of PAG materials such as samples S-2.5-1, S-2.5-3, and S-5-1 described in the Geochemical Characterization report. Describe other aspects planned to safeguard or monitor the proposed Waste Rock Stockpiles (WRPs) such as ore control processes including continuous geologic mapping; blasthole logging, spacing, and sampling; interval testing; waste flagging and routing; and use of a GPS targeting system (if applicable).

Section 5 of *Updated Material Characterization and Handling Plan* discusses the Waste Rock Management plan for the Emma Expansion of the Tyrone mine. Subsection 5.1 discusses Tyrone's plan to continuously update their geologic model with total sulfur data as part of the operational blasthole analysis program. Because the blastholes are designed to represent each block of the geologic model, this will enable timely visualization of the updated distribution of total sulfur within the Emma pit. Additionally, by implementing the proposed total sulfur cut-off of 0.2 wt.%, Tyrone can plan in advance which of their mine blocks are PAG and NPAG and route them accordingly as the mine plan is updated, ensuring material is sent to its proper destination rock storage facility. Finally, this detailed mine plan and routing/dispatching information is loaded electronically onto unit GPS guidance systems or surveyed and marked manually in the shovel pit. It is also sent to the Tyrone Dispatch system which monitors and assigns trucks to dump at the specified dump locations.

Furthermore, Subsection 5.2 of the Updated Material Characterization and Handling Plan describes the adaptive monitoring and confirmatory strategy Tyrone plans to employ at each of the non-discharging facilities. Tyrone will randomly collect a blasthole sample for every 150,000 tons of waste rock material deposited at one of the two facilities. Samples will be sent to a commercial laboratory for ABA testing which includes measurement of sample acid generation potential (AGP) and acid neutralization potential (ANP). Blasthole data will be recorded for the random samples routed to NPAG waste stockpiles, so that ABA samples can be readily cross-correlated with the blast assay total sulfur database that Tyrone builds for this project. Results of random ABA testing and corresponding sulfur testing will be submitted to NMED on a semi-annual basis along with other reports required by DP-396. The ABA results will be identified according to the blasthole where the sample was collected. Maps of the Emma Pit will be included with ABA results to show where the blasthole was located within the pit.

Although very minor dilution can be expected within each of the waste piles and is considered normal for an operating mine site, the conservative case of the discharge demonstration (Section 4) was designed to address this very topic. The conservative case assumes that some material with total sulfur up to 1.2 wt.% may be placed in one of the non-discharging facilities. Each of the three samples mentioned in the question have total sulfur of 1.2 wt.% or below, and the discharge demonstration concludes that there would still not be any exceedance of surface or groundwater quality standards.

#### Comment 2:

Please specify the typical laboratory detection limits, laboratory turnaround times, and the laboratory or laboratories proposed for total sulfur and ABA analyses.

The detection limit and turn-around time for total sulfur is stated in the material handling plan on page 18 and corresponds to the same assay turn-around for copper assays. This turn-around time is only for FMI's lab in Safford, AZ. Confirmatory ABA samples will be obtained from a commercial lab and the turn-around times range from 2 to 4 weeks typically. The reporting limits at commercial labs are typically 0.01 weight percent (wt.%) for total sulfur and 0.3 tons of CaCO<sub>3</sub> equivalents per kilotons of rock (tCaCO<sub>3</sub>/kt) for Sobek (or Modified Sobek) acid neutralization potential (ANP).

#### Comment 3:

Section 4.0. Discharge Demonstration (with respect to lab testing and predictive mass-balance modeling).

- a. Figure 4 provides time-series predictions (mass-balance modeling) of sulfate concentration for both an assumed Base Case and a Conservative Case for the proposed 6HW and EMW conditionally exempt/Non-Acid Generating (NAG) WRPs.
  - *i. Please confirm that the following "input" data was employed in modeling and make any clarifications or edits as needed:* 
    - 1. Humidity cell testing results (HCT).
    - 2. Construction plan for the WRPs based on the expected progression of materials during mining. Describe deviations or simplifications.
    - 3. Construction plan: Regarding modeling of the conservative case, please describe the assumptions regarding inclusion of modest quantities of a higher weight percent (wt%) PAG material. Describe the assumed modeled quantities if relevant as a percentage of each lift of a pile and frequency of addition employed over model runs; describe any basis to support that the modeled inclusions are conservative. Describe merits of selection of the total sulfur wt% value for this assumed conservative material as based upon either of the PAG materials previously tested via HCT that demonstrated acid-generation; compare merits of modeling either 0.7 or 1.2 wt% total sulfur or the average of the two.
    - 4. Meteoric precipitation and any other meteoric site data (i.e., monthly rain/snow, pan evaporation).
    - 5. First Flush data
    - 6. Please describe if any other material characterization data such as results from the meteoric water mobility testing or XRD analysis was incorporated into the modeling.
  - ii. For the 6HW WRP, Figure 4 shows predicted results that start at Month #12 (and end at Month #36) while it shows results for EMW running from Month #Zero to Month #48. Table 5 seems to be the opposite showing that construction of the 6HW would take approximately five years and start before the construction of the EMW which is shown to be built over only approximately three years. It seems that the designations of 6HW and EMW have been mixed up either in Figure 4 or Table 5. Please review and correct as applicable.
  - *iii.* Please provide example calculations to exemplify how model inputs are employed to estimate some sulfate result(s) graphed in Figure 4. Include the following calculations and discussion topics:

- 1. "Mass release rates" are described on page 26 of the Geochemical Characterization. Please include at least one example sulfate calculation for a material type. Also include release rate answers for all types.
- 2. Description of methods to scale results from the HCT tests to conditions modeled in the proposed WRPs (e.g., meteoric precipitation, preferential flow, effective material size, contact time).
- 3. A table of input values used in the model, as described in the previous question (see part "i") over the predicted model periods.
- 4. Provide example calculations to relate to at least one numerical model base case and its corresponding conservative case calculation.
- 5. As needed, for supplementing descriptions please reference:
  - a. Previous Tyrone reports such as Geochemical Characterization report's Figure 13 titled "Sulfide Surface Area versus Cumulative Released Sulfate Mass."
  - b. Peer-reviewed literature
    - i. Note: Please provide a copy of at least Lapakko and Antonson (2002) and Price (1997). Note that "Price (1997)" was referenced but not included in the bibliography of the Geochemical Characterization report.
- 6. Please describe the basis and the assumptions used for the Conservative Case.
- 7. Please describe why the modeled result values in Figure 4 generally downtrend over the modeled period.
- 8. Please describe why the Discharge Demonstration model only contemplates sulfate generation and does not evaluate other potential water contaminants listed in Section 20.6.2.3103 NMAC.

**For 3.a.i.:** HCT data was used to derive the source terms for sulfate in the model for both the base case and conservative case that was simulated. The base case used a first flush (FF) source term calculated from weeks 0-4 in the HCTs with less than 0.2 wt.% total sulfur and the long term (LT) source term was calculated from the average of the last 4 weeks of the HCTs with less than 0.2 wt. % total sulfur. The conservative case used both meteoric water mobility procedure (MWMP) and HCT results as they provided the highest values of leached sulfur to use in the models. The HCT data used included sample S-2.5-1 which has total sulfur of 1.2 wt.%.

**For 3.a.i.2**: Yes. LCG used the Emma mine plan construction sequencing for the simulated buildout of both EMW and 6HW facilities that was provided by Tyrone. No simplifications or deviations were made. This is included in the *Updated Material Characterization and Handling Plan* as shown in Table 5.

**For 3.a.i.3**: The conservative case model was built the exact same way as the base case model. The model was simple assuming a homogenous distribution of material properties. Higher total sulfur weight percent material was included by assigning a new source term derived from the higher total sulfur weight percent material (i.e., FF was 11.5 mg SO<sub>4</sub>/kg-rock and LT was 7.4 mg SO<sub>4</sub>/kg-rock) to all of the rock in the stockpiles.

The modeled quantities of waste rock deposition were based on year as opposed to lifts and evenly distributed over monthly timesteps for modeling. Each facility was assumed to contain 10 million tons (Mt) at the end of mine life and the amount of waste rock deposited each year was based on the planned percent complete contained within Table 5 of the *Updated Material Characterization and Handling Plan*. Each year of material deposition was split into 12 equal time steps assuming each month adds the same amount of waste rock needed to achieve the planned tonnage for the year.

The conservative case model is considered conservative because it uses source terms, assigned to the entire facility, that have leaching rates for sulfate that are approximately 3x and 11x higher than the base case, for FF and LT rates, respectively. The conservative model also uses the leach test data of material with total sulfur content greater than 1 wt.%, which is 5x higher than the proposed upper sulfur threshold for segregation.

The merits of this selection are that it is the highest total sulfur material that LCG and Tyrone has data for that is relevant to the Tyrone mine. Because of this, these modeled values are considered conservative.

**For 3.a.i.4**: The meteoric data used was from the Tyrone mine general office weather station. The period of record used was from January 1, 2016 to December 31, 2020. The monthly mean precipitation was used for the infiltration values.

**For 3.a.i.5**: Yes. The model used FF data as described in the previous answers. FF was estimated from the first five weeks of the HCT testing program for samples that had total sulfur content less than 0.2 wt.% for the base case and used the MWMP data for the conservative case.

**For 3.a.i.6**: Other characterization data were used. MWMP test results were used to parameterize the FF rate in the conservative case model.

For 3.a.ii: The error is in Table 5. The 6HW and EMW headers are corrected (switched) in the final version of the *Updated Material Characterization and Handling Plan* that accompanies these responses.

**For 3.a.iii.1:** An example calculation is given for week 3 for HCT sample L-2.5-1, using Equation 1 from the *Updated Material Characterization and Handling Report*. The actual values used in the source term was based on the geometric mean of the values calculated with Equation 1 for every HCT sample.

$$[SO_4; mg/kg] = \frac{[concentration of SO_4; mg/L] \times [volume of leachate; L]}{[sample mass; kg]}$$
(1)

$$[2.37; mg/kg] = \frac{[2.7; mg/L] \times [0.877; L]}{[1; kg]}$$
(1)

**For 3a.iii.2**: The full description of how LCG scaled the HCT results to the modeled concentrations in Figure 4 is contained within Equations 1 through 3.

For 3.a.iii.3: A table of input values used in the model is provided in the Tables below. The four values in Table 1 were calculated using Equations 1 and 2 from the *Updated Material Characterization and Handling Report*. The value of  $F_{Flow}$  was variable and dependent on the climate data.

| Source Term      | Base Case | Conservative Case |
|------------------|-----------|-------------------|
| First Flush (FF) | 3.81      | 11.50             |
| Long-Term (LT)   | 0.65      | 7.36              |

| Scaling Factors                        | Value  |
|--|--|
| Surface Area (F <sub>SA</sub> )        | 0.2  |
| Preferential Flow (F <sub>Flow</sub> ) | Values for $F_{Flow}$ were scaled to the monthly value of $F_{Flow}$ . |

**For 3.a.iii.4**: An example calculation for the first model month of the Base Case and Conservative Case for the 6HW stockpile is presented below as Equation 3. Equation 1 and 2 are in the *Updated Material Characterization and Handling Report*. Equation 3 takes the FF and LT sulfate release rates calculated from Equation 1 and 2 as inputs and calculates a simulated sulfate concentration emanating from the 6HW stockpile.

There is no LT mass in the first model month, which is why that input is 0 in the example calculations. The value of 94 and 284 match the predicted sulfate concentration for the first month for the 6HW stockpile.

$$\left[SO_4; \frac{mg}{L}\right] = \frac{\left[F_{SA}; -\right] \times \left[F_{Flow}; -\right] \times \left(\left(\left[SO_{4_{FF}}; \frac{mg}{kg}\right] \times \left[Mass_{FF}; kg\right]\right) + \left(\left[SO_{4_{LT}}; \frac{mg}{kg}\right] \times \left[Mass_{LT}; kg\right]\right)\right)}{\left[Infiltration; L\right]}$$
(3)

Base Case:

$$[94; mg/L] = \frac{[0.2; -] \times [0.104; -] \times \left( ([3.81; mg/kg] \times [571,990,378; kg]) + ([0.65; mg/kg] \times [0; kg]) \right)}{[482,344; L]}$$
(3)

**Conservative Case:** 

$$[284; mg/L] = \frac{[0.2; -] \times [0.104; -] \times \left( ([11.50; mg/kg] \times [571,990,378; kg]) + ([7.36; mg/kg] \times [0; kg]) \right)}{[482,344; L]} (3)$$

Where:

 $F_{SA}$  = surface area scaling factor, unitless [-]  $F_{Flow}$  = variable preferential flow scaling factor, unitless [-]  $SO_{4FF}$  = First flush sulfate concentration from Eq. 1 and 2; mg/kg  $Mass_{FF}$  = mass of material in stockpile for FF leaching; kg  $SO_{4LT}$  = Long term sulfate concentration from Eq. 1 and 2; mg/kg  $Mass_{LT}$  = mass of material in stockpile for LT leaching; kg Infiltration = volume of rain flushing through the stockpile; L

For 3.a.iii.5: Copies of the requested reports are provided in Appendix 2.

**For 3.a.iii.6**: The basis for the conservative case was to model the highest expected sulfate concentrations based on the available, relevant laboratory data, and known construction information for the stockpiles. The assumptions for the behavior of these materials were the same as that of the Base Case with the exception of assuming a higher release rate of sulfate. The following test results were used simulating the conservative case sulfate release rates:

- First-flush (FF) release rates were modeled using the MWMP data because it had higher concentrations that the HCT results.
- Long-term (LT) release rates were modeled using the average of the last four cycles of the HCT data as that is assumed to mimic the long-term release rate potential of the material.

For 3.a.iii.7: The modeled sulfate results decrease over time because of the increase in precipitation volume over time resulting from the increase in surface area of the non-discharging facility as it is constructed. As can be seen in Equation 3, the mass of sulfate is divided by the volume of infiltrating water. Although both the mass of waste rock and volume of infiltrating water increase with time as the facility expands, the increase in surface area contributing to the precipitation acts to dilute the increasing mass.

For 3.a.iii.8: The mass-balance discharge demonstration model only simulates sulfate as that is the only constituent of notable concentration that is consistently released from waste materials in leach tests, and the only constituent expected in measurable quantities from a waste stockpile with NPAG material. Sulfate may also be released from dissolution of non-sulfide minerals such as gypsum or other secondary sulfosalt minerals and therefore represents a conservative estimate of material sulfide oxidation.

#### Comment 4:

Section 4.0. Confirm that the proposed use of total sulfur analyses is intended to augment the more traditional process of employing fewer static ABA samples. Confirm that Tyrone anticipates that the many proposed additional total sulfur analyses in this case are anticipated to enhance material characterization through significantly increasing the frequency of sampling materials. In addition to 80-90 ABA samples, NMED understands that approximately 5,000 total sulfur waste rock samples will be analyzed if 10 million US tons of NPAG waste rock (and a smaller quantity of PAG) are generated from mining the Emma Pit. Please confirm that using total sulfur analyses will also enable real-time analysis that will better correspond with actual operational WRP handling.

Yes, the proposed use of total sulfur analyses is intended to augment the traditional process of employing fewer static ABA samples. Each blasthole assay will be submitted for total sulfur analysis and the results of which will be added to the Tyrone mine plan where the distribution of sulfur will be updated for proper waste rock routing. Additionally, Tyrone plans to submit one random sample for static ABA analyses per 150,000 tons of waste rock placed in the non-discharging facilities. The total number of total sulfur assays will be based on the mine plan and the number of blastholes Tyrone uses to define the copper grade within the pit.

Because total sulfur will be measured at each blasthole and Freeport-McMoRan's internal lab has approximately 48-hour turn around, the mine plan estimates of PAG and NPAG volumes within the pit can be updated in near real-time with the update of their copper grade to achieve near real time updates for accurate mine planning.

#### Comment 5:

As discussed in meetings, a data gap was recognized from the current material characterization study. To date, no samples have been found that contain total sulfur in the range of 0.0575 wt. % to 0.248 wt. %. Therefore, a correlation between total sulfur and NPR or NAG pH has not yet been confirmed. NMED requests that Tyrone discuss this data gap and propose how this data gap can be addressed through additional characterization work in the next revision to the Updated Material Characterization and Handling Plan. NMED asks that Tyrone prioritize performing NPR and NAG pH analyses of any future samples identified to be in this total sulfur range.

Figure 3 from the *Updated Material Characterization and Handling Plan* presents the relationship between NPR, NAG pH, and total sulfur. As presented, a strong relationship between the three variables that trends from low NAG pH/low NPR/high Sulfur in the bottom left to high NAG pH/high NPR/low sulfur in the top right is seen based on the greater than 40 samples available for the expansion related material. The higher sulfur sample you mention, with a value of 0.25 wt. %, is both above the 0.2 wt. % sulfur cutoff and categorized as NPAG based on the NAG pH values. Because of this, the 0.2 wt. % cut-off is considered conservative and defensible.

#### Comment 6:

Appendix 1. Sampling Methods and Testing. Sampling frequency should be increased to match the same sampling frequency (one sample for every 150,000 tons of waste rock) as proposed in Section 5.2 of the Updated Material Characterization and Handling Plan, at a minimum.

Appendix 1 has been modified to include approximately 30 samples for each of the waste rock stockpiles which is equivalent to the sampling frequency of one sample for every 150,000 tons of waste rock.

#### Comment 7:

Appendix 1. Sampling Methods and Testing. Tyrone should consider collecting bulk samples for each lift of the stockpiles to capture sample variability across the pile by depth.

Appendix 1 indicates samples will be distributed horizontally and vertically (i.e., by lift) as the stockpile is constructed to get good representation. Samples need to be collected from a specific location (rather than bulked from several locations) to obtain estimates of rock volume.

#### Comment 8:

Appendix 1. Soil suitability testing parameters and methods for Emma EMW and 6HW stockpile samples. Recommend adding base saturation to the list of parameters to test.

Tyrone does not believe base saturation is necessary to determine the suitability of Emma overburden materials. Problems associated with low base saturation are found in agricultural soils

in humid regions where base cations are leached, increasing soil acidity over time and thus requiring periodic lime application to maintain crop productivity. Such a situation is not anticipated for the reclamation of the Emma overburden materials. Furthermore, base saturation is not identified as a necessary soil parameter in MMD's 2022 Guidance for Soil and Cover Material Handling and Suitability for Part 5 Existing Mines

Should you have questions or comments regarding this request and comment letter, please contact Sherry Burt-Kested at (575) 912-5927.

Sincerely,

Sherry BurtKested

Sherry Burt-Kested Environmental Manager New Mexico Operations

SBK:ao Enclosures 20250331-100 Appendix 1: Updated Emma Material Characterization and Handling Plan

# MATERIAL CHARACTERIZATION AND HANDLING PLAN FOR TWO NON-DISCHARGING FACILITIES:

EMMA PROJECT

#### Submitted to:



Freeport-McMoRan Tyrone, Inc. Highway 90 South Tyrone, New Mexico 88065



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December 2023



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# **1.0 INTRODUCTION**

## **1.1 PLAN OVERVIEW**

At the request of Freeport-McMoRan Tyrone, Inc. (Tyrone), Life Cycle Geo, LLC (LCG) has prepared this Material Characterization and Handling Plan (Plan) to support the permitting and operation of two nondischarging stockpiles at the proposed Emma expansion of the Tyrone Mine (Emma), in Grant County, New Mexico. The proposed Emma Pit will be part of the larger Tyrone Mine Operations (Tyrone Mine) and is located approximately 12 miles southwest of Silver City, NM and one mile south of Tyrone Mine.

Construction of the new non-discharging stockpiles will require a Material Characterization Plan, a discharge demonstration, and a Material Handling Plan (as per guidelines provided by Copper Mine Rule, Title 20, Chapter 6, part 7 of New Mexico Administrative Code). The two proposed non-discharging stockpiles are 6HW Waste stockpile, which will be constructed north of the Emma Pit and EMW Waste stockpile, which will be constructed north of the Emma Pit and EMW Waste stockpile, which will be constructed north of the Emma Pit and EMW Waste stockpile, which will be constructed north of the Emma Pit (See Figure 1). A technical memo titled "Emma Material Handling Plan: Soil Suitability Testing for Stockpiled NPAG Reclamation Cover Materials" by WSP is attached as Appendix A.

The report is organized as follows:

- Section 2 provides an overview of the acid rock drainage potential of materials at Emma based on the results of the geochemical characterization conducted on Emma materials (LCG 2021a,b)
- Section 3 provides the material handling plan for managing waste rock at Emma
- Section 4 provides the results of the discharge demonstration for the EMW Waste stockpile and 6HW Waste stockpile
- Section 5 provides a plan for waste rock monitoring and reporting

### **1.2 PLAN PURPOSE**

The purpose of this Plan is to facilitate permitting of the non-discharging 6HW Waste stockpile and EMW Waste stockpile. This plan includes information about the expected long-term environmental behavior of stockpile materials (summarized from LCG 2021a), a discharge demonstration for the two stockpiles, and a material handling plan.





Figure 1: Locations of 6HW Waste stockpile, EMW Waste stockpile, and Emma Pit

# 2.0 EMMA ACID ROCK DRAINAGE POTENTIAL 2.1 GEOLOGY

The geology of the Tyrone deposit, which includes Emma, has been described in other recent characterization and permitting reports for the Little Rock Mine, which has similar geology to Emma (SARB Consulting, Inc. [SARB] 1995, 1996; Golder Associates, Inc. [Golder] 2016) and is repeated here in brief to provide geologic context to the lithologic units excavated from Emma. There are three dominant lithologies within the projected Emma ultimate pit: 1) Precambrian granite, 2) tertiary monzonite (Tyrone stock) and 3) various dikes/sills/minor intrusives (e.g., aplite, diabase, granodiorite and hornfels). Tertiary



mineralization occurs primarily within the stock and host Precambrian granite. The proportion of the various Emma waste material lithologies destined for the non-discharging stockpiles is expected to be approximately 65% Precambrian granite, 20% tertiary monzonite porphyry, and 15% other relatively minor lithologies including aplite, hornfels, and diabase dikes.

Minerals that are typically indicative of long-term waste material environmental behavior include various sulfide and carbonate minerals as these are the primary contributors to the acid-generating potential (AGP) and acid-neutralizing potential (ANP), respectively, of waste material. Primary (hypogene) mineralization at Emma resulted in emplacement of pyrite, chalcopyrite, and to a lesser degree, bornite. Calcite occurs principally in the host rock but was also introduced as post-supergene alteration.

### 2.1 CHARACTERIZATION PROGRAM

LCG conducted a program to establish the long-term environmental behavior of future Emma waste materials. The program was initially proposed to New Mexico Environment Department (NMED) by Tyrone in 2020 (LCG 2020). The Phase 1 and 2 static testing portions of the program have been completed (LCG 2023). The Phase 3 kinetic testing (humidity cell testing [HCT]) program was proposed to NMED in 2021 (LCG 2021a) and is now also complete (LCG 2023). Results from this characterization program inform the conclusions about long-term waste material environmental behavior and discharge behavior that is summarized within this Material Characterization and Handling Plan for the two non-discharging stockpiles.

More specifically, the characterization program involved selection of 40 samples to establish the long-term environmental behavior of Emma waste rock (LCG 2020). The samples were selected to be representative of the predicted distribution of lithology and alteration/oxidation, as well as the spatial extent of the projected Emma Pit. Table 1 summarizes this distribution in terms of projected waste proportions for the 6HW Waste stockpile and EMW Waste stockpile.

| Lithology                   | Proportion of Waste | Samples | Proportion of Total Samples |
|-----------------------------|---------------------|---------|-----------------------------|
| Aplite                      | 6.0%                | 8       | 20%                         |
| Diabase                     | 2.5%                | -       | -                           |
| Fault Breccia               | 1.1%                | -       | -                           |
| Granodiorite                | 1.3%                | 1       | 2.5%                        |
| Hornfels                    | 4.3%                | -       | -                           |
| Precambrian granite         | 64.0%               | 27      | 67.5%                       |
| Tertiary monzonite porphyry | 20.7%               | 4       | 10%                         |
| Total                       | 100%                | 40      | 100%                        |

#### Table 1: Sample Selection Summary



### 2.2 SUMMARY OF ARD AND METALS LEACHING POTENTIAL

This section provides a high-level summary of the acid rock drainage (ARD) and metals leaching potential of Emma Mine waste rock, summarized from LCG (2023). The Emma characterization program results indicate that a significant majority of Emma waste rock has very low sulfur content (often near or below detect). Figure 2 shows the AGP and ANP values for the 40 samples by lithology.



Figure 2: AGP vs. ANP (based on Modified Sobek test) for Emma waste rock samples

The figure illustrates that most AGP values are close to zero, a function of very low material sulfur content. Eight samples (20%) have AGP values above  $5 \text{ TCaCO}_3/kT$  while the rest are close to zero.

Table 2 summarizes internationally accepted metrics for screening-level ARD classification using the neutralization potential ratio (i.e., ANP/AGP; NPR), net neutralization potential (i.e., ANP - AGP; NNP), and net acid generation (NAG) pH (Mine Environment Neutral Drainage Program [MEND] 2009, International Network for Acid Prevention [INAP] 2009, AMIRA 2002). These classifications are applied in Tables 3 and 4 for the 40 samples according to NPR and NAG pH, respectively, and classify the samples as either potentially acid generating (PAG), not potential acid generating (NPAG), or uncertain.

#### Table 2: ARD potential thresholds using NNP, NPR, and NAG pH criteria

| ARD Potential   | NNP<br>(tCaCO <sub>3</sub> /kt)  | NPR                                   | NAG pH |
|-----------------|--|---------------------------------------|--------|
| Likely (PAG)    | <-20   | <1                                    | <4.5   |
| Uncertain       | -20 <nnp<20< td=""><td>1<npr<2*< td=""><td>-</td></npr<2*<></td></nnp<20<> | 1 <npr<2*< td=""><td>-</td></npr<2*<> | -      |
| Unlikely (NPAG) | >20  | >2*                                   | >4.5   |

Note: A more conservative NPR of 3 has also historically been used (INAP 2009)

#### Table 3: Screening-level ARD potential classification for 40 Emma waste rock samples

| Lithology                   | n  | PAG<br>(NPR < 1) | Uncertain<br>(1 < NPR < 2) | NPAG<br>(NPR > 2) |
|-----------------------------|----|------------------|----------------------------|-------------------|
| Aplite                      | 8  | 2                | 0                          | 6                 |
| Granodiorite                | 1  | 0                | 0                          | 1                 |
| Precambrian granite         | 27 | 7                | 3                          | 17                |
| Tertiary monzonite porphyry | 4  | 0                | 1                          | 3                 |

#### Table 4: NAG pH classification for 40 Emma waste rock samples

| Lithology                   | n  | PAG<br>(NAG pH < 4.5) | NPAG<br>(NAG pH > 4.5) |
|-----------------------------|----|-----------------------|------------------------|
| Aplite                      | 8  | 1                     | 7                      |
| Granodiorite                | 1  | 0                     | 1                      |
| Precambrian granite         | 27 | 6                     | 21                     |
| Tertiary monzonite porphyry | 4  | 0                     | 4                      |



Both the NAG pH and NPR classifications reflect the AGP<sup>1</sup> data displayed in Figure 2 in that 9 (22.5%) of the 40 samples are classified as PAG; these are generally the samples with AGP values of at least 5 TCaCO<sub>3</sub>/kT (i.e., the samples that do not have sulfur concentrations near the lower detection limit) or in some cases, samples with low total sulfur, but without detectable concentrations of ANP. The consistency between the NAG and NPR classifications is helpful in developing a threshold for segregation of PAG and NPAG waste rock to ensure that only NPAG waste rock ends up on the non-discharging stockpiles. Both the NAG and NPR classifications, when compared to Figure 3, suggest that acid-generating potential is almost entirely a function of sulfur content. As such, simple sulfur concentrations could be used conservatively to segregate PAG from NPAG materials. The proposed segregation threshold (LCG 2023) is discussed in greater detail in the Waste Rock Placement (Section 3.0).

The metals leaching potential of the Emma waste rock materials also appears to be very low based on short-term and long-term leachate testing conducted to date. As indicated by results of the humidity cell testing (LCG 2023), metals release is only expected to be significant if acidic conditions are generated- this includes high sulfate and chalcophile metals.

The results of the leachate testing program were used to parameterize the discharge demonstration for the two stockpiles, which will receive NPAG materials and as such, neither stockpile will become acid generating provided the material handling plan described in Section 3 is followed. Accordingly, this discharge demonstration does not include HCT results associated with PAG materials.

# **3.0 WASTE ROCK PLACEMENT**

## 3.1 PROPOSED SEGREGATION THRESHOLD

Based on results of the characterization program, a total sulfur threshold of 0.2 weight percent (wt. %) has been proposed (LCG 2023) to segregate PAG from NPAG waste. The total sulfur threshold of 0.2 wt. % is an effective means of separating PAG from NPAG materials based on the results of the geochemical characterization program and produces similar classifications as both NPR and NAG pH. The relationship between the three metrics is illustrated in Figure 3. The primary differences in classification between using a total sulfur threshold of 0.2 wt. % vs. using a NAG pH or NPR threshold are as follows:

- Two samples have NPR values greater than 1 (classify as NPAG) but have total sulfur values > 0.2 wt. % (classify as PAG).
  - Both samples have higher ANP than AGP (*these samples plot above the NAG pH* = 4.5 line and are colored green in Figure 3) and are unlikely to become acid-generating.
  - Using the total sulfur threshold, these samples will be conservatively segregated as PAG.

<sup>&</sup>lt;sup>1</sup> AGP was calculated from total sulfur (i.e., AGP = total sulfur x 31.25)





Figure 3: NPR versus NAG pH colored by total sulfur. Black circles are non-detect values.



- One sample has NPR value less than 1 (classify as PAG) but total sulfur concentration < 0.2 wt. % (classify as NPAG).
  - This sample has very low total sulfur content (< 0.2 wt. %) but has even lower corresponding ANP (the sample plots above the NAG pH = 4.5 line and to the left of the NPR = 1 line in Figure 1).
  - LCG (2023) indicated that it is highly unlikely for waste materials with **sulfide** sulfur content < 0.2 wt. % to ever become acid-generating.

LCG (2023) points out that the total sulfur threshold of 0.2 wt. % is not only an accurate predictor of NPAG and PAG material types, but it is also conservative because:

- It does not account for material ANP
- Not all total sulfur is present as sulfide sulfur (i.e., it is not all oxidizable pyrite)
- It results in a higher proportion of samples classified as PAG than NPR or NAG pH
- Studies indicate that below a threshold of 0.2 wt. %, irrespective of neutralization potential, materials are highly unlikely to become acid-generating

Details regarding material segregation, handling and compliance are discussed in the Waste Rock Management section (5.0).

# 4.0 DISCHARGE DEMONSTRATION

## 4.1 OBJECTIVE

The purpose of the discharge demonstration is to establish whether seepage or runoff from the nondischarging NPAG 6HW Waste stockpile or NPAG EMW Waste stockpile could cause an exceedance of NMAC 20.6.2.3103 surface water or groundwater quality standards.

## 4.2 MODEL DETAILS AND STRUCTURE

Consistent with discharge demonstrations developed for other facilities at Tyrone mine (e.g., Golder 2016; LCG 2021b), LCG developed a mass balance model to assess discharge quality from the planned nondischarging, NPAG 6HW Waste stockpile and NPAG EMW Waste stockpile to groundwater. The mass balance model focused on sulfate concentrations as that is the only constituent of notable concentration that is consistently released from waste materials in leach tests, and the only constituent expected in measurable quantities from a waste stockpile with no PAG material. Sulfate may also be released from dissolution of non-sulfide minerals such as gypsum or other secondary sulfosalt minerals and therefore represents a conservative estimate of material sulfide oxidation (Golder 2016; LCG 2021b). Once released, sulfate is generally unlikely to attenuate (unless it is present in very high concentrations, along with calcium, and precipitates as gypsum).

The following data sources were used in the mass balance model:

• Historic climate data collected from the Tyrone mine general office weather station



- Expected lithologic proportions in the stockpiles
- Stockpile construction schedules
- Waste rock acid-base accounting (ABA) and metals leaching test data

The following assumptions were made in the mass balance model development:

- All water entering the stockpile comes from meteoric precipitation.
- All dissolved sulfate in the predicted discharge is released from waste rock during contact with inflowing precipitation (i.e., the inflowing water contains no sulfate) and the mass of sulfate released from waste rock is controlled by a mass release rate as calculated from HCT results (LCG 2020; LCG 2023).
- The waste rock mass was based on the expected NPAG waste tonnage going to each stockpile which is estimated to be ~10 MT for each stockpile. This mass is a conservative over-estimate of tonnage actually expected for the stockpile.
- The lithologic composition of each stockpile is assumed to be equivalent and composed of NPAG material. However, to accommodate a certain proportion of segregation inefficiency, a small proportion of higher sulfur material was modeled as a conservative scenario.
- The lithologic composition of the stockpiles is assumed to be equal to the lithologic proportions presented in Table 1.

The sulfate mass release rates used in the model were calculated in a two-step process: 1) Converting the laboratory leachate sulfate concentration to a laboratory leachate sulfate mass released per unit mass of material in the laboratory tests (equation 1), and 2) Calculating a representative sulfate mass release rate for a stockpile by taking the geometric mean of the sulfate mass release rates (i.e. equation 1) of each sample for a lithology and multiplying it by the fractional proportion of that lithology in the stockpile by using Microsoft® Excel's SUMPRODUCT function (equation 2).

$$[SO_4; mg/kg] = \frac{[concentration of SO_4; mg/L] \times [volume of leachate; L]}{[sample mass; kg]}$$
(1)

$$\left[SO_{4_{stockpile}}; mg/kg\right] = \sum_{i} \left( [lithologic proportion; \%]_{i} \times [SO_{4}; mg/kg]_{i} \right)$$
(2)

Where i in equation 2 represents each lithology in the stockpile.

Two mass release rates are used in the model, first flush (FF) and long-term (LT). The FF release rate represents freshly placed rock which has a higher propensity for rapid sulfate release from weathered material surfaces as opposed to older rock, from which readily available surface oxidation products have already been rinsed. The LT release rate reflects seepage inside the stockpile, for rock that has already been flushed, representing longer-term water-rock interaction. Both release rates were derived from HCT results (LCG 2023) and the expected lithologic distribution of waste in the stockpiles (see Table 1). Leachate mass release data was not available for all lithologies so the lithologic proportions were normalized to those lithologies for which leachate testing data was available (i.e., aplite, Precambrian granite, granodiorite, and Tertiary monzonite porphyry).

Two scenarios of sulfate release were evaluated with the model, a Base Case and a Conservative Case. The Base Case represents the expected chemistry from the waste rock assuming all material deposited has



sulfur content less than 0.2 wt. % and is classified as NPAG, while the Conservative Case represents expected sulfate concentrations assuming some material with elevated sulfur (up to 1 wt. %) is mixed in with the low-sulfur material deposited in the waste dumps.

The FF and LT sulfate release rates were assigned as follows:

- 1. Base Case: The FF rate was assumed to be equal to the average sulfate mass released from the first five cycles of the HCT tests for samples with total sulfur less than 0.2 wt. % and the LT rate was set to equal the average sulfate mass released from the last five cycles of the HCT tests.
- 2. Conservative Case: The FF and LT release rates for the Conservative Case were calculated the same way as for the Base Case except that all HCT samples with total sulfur less than 1 wt. % were used to include sulfate release data from some elevated sulfur samples.

Water infiltrating the stockpiles is not expected to contact 100% of waste rock surfaces. In practice, water infiltrating waste rock is likely to follow preferential flow paths (El Boushi 1975). Additionally, mass release will be affected by the waste rock particle size distribution (Morin 2013) which varies from lab to field. Generally, laboratory tests are conducted on materials with a finer overall particle size distribution to accelerate weathering/oxidation and mass release. To account for these concepts, two scaling factors (one for material surface area and one for preferential flow) were used to adjust laboratory-derived mass release and material surface saturation levels to the field-scale (Kempton 2012). The preferential flow scaling factor was varied according to the proportion of inflowing water, with a value of 0.05 for low water months and 0.2 for high water months (Morin 2013).

For the purposes of the discharge modeling, stockpile construction is scheduled to begin in fourth quarter of 2022, Mine Year 2, and proceed into Mine Year 5, 2026. For modeling, an equal amount of increased tonnage was assigned to each month. Table 5 outlines the estimated percent of waste rock completion of each stockpile though the 5-year mine life. The tonnage and surface areas were distributed through the model duration based on these percentages. The actual tonnage placed in the two stockpiles are likely to be lower than estimates in this plan; the tonnages in this plan are overestimated to be conservative. Both stockpiles are expected to be 54 acres. The mass-balance model was built to reflect this construction schedule and final stockpile geometry by using monthly timesteps based on mass released during each month of construction. Average monthly precipitation data collected from 1990 to 2021 was used to estimate the monthly inflow at each time step. The mass-balance model was run for four years (48 months) and three years (36 months) for the EMW Waste stockpile and 6HW Waste stockpile, respectively. The FF mass-release rate was applied to new stockpile material for three months, after which the LT mass-release rate was applied (Golder 2016; LCG 2021b).



| Model Year | EMW Waste   | 6HW Waste   |
|------------|-------------|-------------|
| 1          | 0%          | 0%          |
| 2          | 11%         | 0%          |
| 3          | 50%         | 76%         |
| 4          | <b>98</b> % | <b>99</b> % |
| 5          | 100%        | 100%        |

#### Table 5: Stockpile Construction Schedule

### **4.3 MODEL RESULTS**

Figure 4 presents the predicted monthly sulfate concentrations over time from the mass balance model for both stockpiles. Different predicted sulfate concentrations for each stockpile over time reflect their different footprint areas and construction schedules. The mass-balance model applies an equal mass of waste rock over each unit of area in the stockpile, as such different surface areas will result in releasing different concentrations of sulfate per unit area. During the modeled period, predicted sulfate concentrations range from 13 to 356 mg/L and 13 to 364 mg/L, for the 6HW Waste stockpile and EMW Waste stockpile, respectively, inclusive of both the base and conservative scenarios. Sulfate trends are driven by precipitation volumes, which are the sole source of infiltration through the stockpiles during construction. As such, sulfate concentrations vary seasonally and exhibit an inverse correlation to recharge. More sulfate is expected to accumulate and be picked up by a relatively lower volume of precipitation during the drier months, with maximum sulfate concentrations occurring in the driest months, which are April and May. This reflects flushing of sulfate from stockpile material surfaces and dissolution into a smaller volume of water. Figure 4 indicates that predicted maximum sulfate concentrations are below the NMED regulatory standard groundwater quality value for sulfate of 600 mg/L<sup>2</sup>.

<sup>&</sup>lt;sup>2</sup> NMAC 20.6.2.3103 (B) domestic water supply maximum allowable concentration





\*NMAC 20.6.2.3103 (B) domestic water supply maximum allowable concentration

Figure 4: Mass-Balance Model Predicted Sulfate Concentrations for 6HW Waste stockpile and EMW Waste stockpile

# **5.0 WASTE ROCK MANAGEMENT**

Current estimates indicate that up to 10 million tons of NPAG rock could be deposited to the two Emma non-discharging stockpiles, although the actual tonnage is likely to be lower. The proposed sulfur threshold will effectively minimize placement of waste (PAG) material on the two non-discharging stockpiles. PAG waste will be routed to existing stockpiles at Tyrone that are currently permitted to receive PAG materials. Furthermore, a small proportion of NPAG waste rock (less than half a percent of the total waste rock tonnage) will be routed to the Emma Pit to achieve the closure/closeout plan objectives and for pit water management. This material will be identified using the same proposed sulfur threshold.

The following paragraphs describe how waste rock materials are segregated, routed, tracked and monitored.

## **5.1 WASTE ROCK SEGREGATION AND HANDLING**

In order to segregate NPAG from PAG waste, Tyrone will measure the total sulfur concentration of production blastholes as part of its operational blast assay program. This data will be used to update PAG and NPAG volume estimates in real-time for accurate mine planning, and to guide Tyrone Operations staff in routing ore and waste to the correct destination.



A summary of the waste segregation workflow is as follows:

- The geologic model is used in the design of pit benches for the mine plan
- The mine plan is used to design specific blast patterns with drill patterns that are laid out in the field
- After drilling is complete, blasthole cuttings are sampled (one composite sample from each production blasthole- the average blasthole is 10 5/8" in diameter and 53-55 ft. depth)
- Random samples of blastholes for ABA confirmation are also taken at this time, and as described in Section 5.2 below.
- Each sample typically represents one mine block (with an approximate size of 25ft by 25ft by 50ft). A mineable shape typically consists of six mine blocks and represents the minimum volume that can be segregated.
- The samples are sent to the Company assay lab in Safford, Arizona. Assay results are typically returned within 48 hours.
- Assay tests include total sulfur measurement by LECO Induction Furnace (with 0.001 wt. % detection limit)
- Assay results are used to update the geologic model
- The average sulfur concentration in a mineable shape (usually based on six data points) must be below the 0.2 wt. % total sulfur threshold for the shape to be designated as NPAG. If the average is above the threshold, the shape is designated as PAG.
- Tyrone ore control uses the updated model to design the final detailed mine plan for each bench, including the routing of ore to leach stockpiles and the routing of waste-to-waste stockpiles.
- This detailed final mine plan and routing/dispatching information is loaded electronically onto loading unit GPS guidance systems or surveyed and marked manually in the shovel pit. It is also sent to the Tyrone Dispatch system which monitors and assigns trucks to dump at the specified dump locations.

Although very minor dilution can be expected within each of the waste piles and is considered normal for an operating mine site, the blast assay-based segregation program is considered robust, state-of-the-art and conservative for the following reasons:

- Blasthole assay sulfur is measured at the same frequency and resolution used by Tyrone for identifying and segregating its copper ore.
- Material neutralization potential is not accounted for hence the ARD potential of waste materials is overestimated. The threshold is conservative for other reasons summarized in Section 3.1.

Tyrone has high confidence that the proposed segregation threshold and segregation and handling procedure is effective and represents the highest industry standard. The process is also adaptive and verifiable.



### **5.2 MONITORING AND CONFIRMATION**

Tyrone recommends that periodic waste rock sampling be conducted to provide ongoing assurance that the proposed total sulfur threshold is correctly segregating NPAG from PAG rock. Tyrone initially proposes to collect one random blasthole sample for every 150,000 tons of waste rock material. Tyrone may propose a reduction in sampling frequency, for NMED approval, based ongoing evaluation of the monitoring program. Samples will be sent to a commercial laboratory for ABA testing which includes measurement of sample AGP and ANP. Blasthole data will be recorded for the random samples routed to NPAG waste stockpiles, so that ABA samples can be readily cross-correlated with the blast assay total sulfur database summarized in the previous section.

Results of random ABA testing and corresponding sulfur testing will be submitted to NMED on a semi-annual basis along with other reports required by DP-396. The ABA results will be identified according to the blasthole where the sample was collected. Maps of the Emma Pit will be included with ABA results to show where the blasthole was located within the pit.

## 6.0 SUMMARY

The purpose of this material handling and characterization plan is to identify robust material handling practices that are protective of the environment and to demonstrate that NPAG-classified waste rock placed in the EMW Waste stockpile and 6HW Waste stockpile will not generate discharge in exceedance of NMED water quality standards. The plan also provides the procedure for compiling soil suitability data and water-holding capacity data for NPAG waste rock that may be utilized as part of the cover system at closure. Based on the results of the geochemical characterization program (LCG 2021a, 2021b, 2023) and the discharge demonstration (this study), The two proposed stockpiles will not produce drainage in exceedance of NMED water quality standards provided the material handling plan (Section 5) is followed.



# **CLOSURE**

This material handling and characterization report was prepared by Morgan Warren and Dr. Tom Meuzelaar for Tyrone. Please do not hesitate to contact the undersigned with any questions or comments.

Tom peuzelas

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# APPENDICES



### **TECHNICAL MEMORANDUM**

**DATE** March 27, 2025

Project No. GL21476949

- TO Raechel Roberts FMI Tyrone Operations
- **CC** Todd Stein (WSP), Tom Shelley (FMI), Tom Meuzelaar (Life Cycle Geo)
- FROM Doug Romig, CPSS

EMAIL doug.romig@wsp.com

# EMMA MATERIAL HANDLING PLAN: SOIL SUITABILITY TESTING FOR STOCKPILED NPAG RECLAMATION COVER MATERIALS

#### **Objectives**

- Characterize and document segregated NPAG overburden that is stockpiled per the Emma Material Handling Plan for eventual use as a reclamation cover material.
- Track the suitability of NPAG overburden from Emma placed in the EMW and 6HW stockpiles.
- The following is proposed in addition to the ABA confirmation sampling that will be done on blast hole cuttings prior to placement of waste.

#### Sampling Methods and Testing

- Collect approximately 30 samples from each of the NPAG overburden stockpiles (EMW and 6HW) for soil suitability testing during the construction of the stockpiles. This is essentially equivalent to a sampling frequency of one sample for every 150,000 tons of waste rock.
- Soil suitability tests will be collected at the stockpile dump sites to obtain representative samples of the material as placed.
- Based on the construction schedule for the EMW and 6HW stockpiles, we anticipate the majority of sampling would be conducted in Years 2 and 3 of the mining at Emma.
- Distribute samples horizontally and vertically (i.e., by lift) as the stockpile is constructed to get a good representation and capture variability in material properties.
- Collect samples from the upper surface of the stockpile lifts from backhoe excavated test pits.
- Visually estimate volumetric rock content and verified by field sieving of <3-inch material on a #10 sieve and adjusted to account for oversized rock (>3-inch).
- The sieved fine-earth faction (1-gallon) will be sent to the laboratory for analytical testing (see table below).
- During the sampling program, collect a minimum of 10 samples for soil-hydraulic characterization to determine compliance with available water holding capacity requirements under the Copper Rule.

#### <u>Reporting</u>

- Compile and summarize all laboratory data and electronic lab reports and maintain a summary spreadsheet.
- Prepare a short technical memorandum for bi-annual reports to agencies that summarizes the soil suitability data, transmits laboratory reports, and provides a sample location map.

#### Soil Suitability Testing Parameters and Methods for Emma EMW and 6HW Stockpile Samples

| Analysis/Parameter   | Source-Method              |
|--|----------------------------|
| Saturated Paste pH   | SLS 1954, Method 2 and 21a |
| Electrical Conductivity, saturated paste                       | SLS 1954, Method 3a and 4b |
| Saturation Percentage  | SLS 1954, Method 27a       |
| Particle Size Analysis   | ASA 1982, Method 15-5      |
| Organic Matter (Carbon)  | ASA 1982, Method 29-3.5.2  |
| N as Nitrate   | ASA 1982, Method 33-8.1    |
| Phosphorous (Olsen)  | ASA 1982, Method 24-5.4    |
| Potassium  | ASA 1982, Method 13-3.5    |
| Cation Exchange Capacity                                       | SLS 1954, Method 19        |
| AB-DTPA extraction   | ASA 1982, Method 3-5.2     |
| Extractable Metals<br>(As, Cd, Cu, Fe, Pb, Mn, Mo, Ni, and Zn) | EPA Method 6010/6020       |

https://wsponlinenam.sharepoint.com/sites/us-albuquerquemineenvir/client freeport/tyrone/emma mhp/gl21476949\_emma mhp-soil suit testing r1 tm\_032725.docx

Appendix 2: Peer Reviewed Literature
## Preprint 02-073

## DRAINAGE PH, ACID PRODUCTION, AND ACID NEUTRALIZATION FOR ARCHEAN GREENSTONE ROCK

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## ABSTRACT

Fourteen samples of pyrite-bearing Archean greenstone rock (d < 6.35 mm, 0.04%  $\leq$  S<sub>t</sub>  $\leq$  1.22%) were characterized (particle size, chemistry, mineralogy) and subjected to laboratory dissolution testing. The only sulfide and carbonate minerals identified were pyrite and siderite, respectively. Quartz, chlorite and sericite typically comprised 90 to 98 percent of the mineral content. For the first 60 weeks, seven samples with sulfur contents less than or equal to 0.16% produced drainage pH values exceeding 6.0. Over this period, six of the seven samples with sulfur contents greater than or equal to 0.20% produced drainage pH below 6.0, with minimum values ranging from 3.2 to 4.7. The seventh sample (0.72% S) had a siderite content of 18%. Small amounts of magnesium and, to a lesser degree, calcium carbonates present in the siderite apparently dissolved to neutralize acid and maintain drainage pH above 6.0. Sulfate release rates generally increased as sulfur content increased, and the rates of pyrite oxidation estimated for individual samples were roughly half to five times that reported in the literature for the abiotic oxidation of pyrite by oxygen. Observed neutralization potentials ranged from 0.2 to 2.0 g CaCO<sub>3</sub>/g rock.

#### INTRODUCTION

Greenstone belts are hosts to numerous gold and base metal deposits. There is presently no mineral development in the Archean greenstone belts of northern Minnesota. There are, however, a number of gold and base metal mines north and northeast of Minnesota in Ontario, and these mines are located in greenstone belts which extend into Minnesota. The Minnesota Department of Natural Resources (MN DNR) is charged with both encouraging mineral resource development and protecting other natural resources, including water quality. If mineral development occurs in Minnesota's greenstone belts, characterization of mine wastes will be necessary to determine the quality of drainage which would be generated. Mine wastes that generate drainage that will not adversely impact the quality of receiving waters would require little or no mitigation, and could possibly be put to beneficial use. In contrast, mine wastes generating drainage that could severely impact receiving waters would require diligent management.

To gain insight into the drainage quality from Archean greenstones, rock samples were collected during excavation of a cavern, unrelated to mining, in the greenstone formation near Soudan, MN. The samples were characterized and subjected to laboratory dissolution testing to determine the relationship between the sulfur content of Archean greenstone rock and drainage pH. The data from this study will be added to that being gathered on other rock types in a cooperative project with the US Bureau of Land Management Utah State Office. Ultimately such information, along with information on trace metal release, will be used to help determine the extent of mitigation required for operational mine wastes.

## **Generation of Acidic Drainage**

Generation of acidic drainage is the major water quality concern regarding mine waste drainage quality, although release of metals in neutral drainage can also adversely impact water quality. Acid is released as a result of the oxidation of iron sulfide minerals, such as pyrite (equation 1), which are common to both hydrothermal quartz carbonate gold deposits and base metal deposits in greenstones.

 $FeS_{2}(s) + (15/4) O_{2}(aq) + (5/2) H_{2}O = FeOOH(s) + 2SO_{4}^{2}(aq) + 4H^{+}(aq)$  [1]

Williamson and Rimstidt (1994) used literature data to derive a rate law for the abiotic rate of pyrite oxidation by oxygen at  $25^{\circ}$ C, defined by the equation

 $dFeS_{2}/dt = 10^{-8.19 \, (\pm 0.10)} \, m_{DO}^{0.5 \, (\pm 0.04)} m_{H_{4}}^{(-0.11 \pm 0.01)}$  [2]

where the rate of pyrite destruction is expressed in mol m<sup>-2</sup> s<sup>-1</sup> and m<sub>b0</sub> and m<sub>H</sub> are the respective molalities of dissolved oxygen and hydrogen ion in units of mol kg<sup>-1</sup>. Ranges of m<sub>b0</sub> and pH for which the expression is applicable are approximately 10<sup>-5.5</sup> to 10<sup>-1.5</sup> and 2 to 10, respectively. At pH 3 and pH 7, this yields respective rates of 2.2 x 10<sup>-10</sup> and 6.2 x 10<sup>-10</sup> mol m<sup>-2</sup> s<sup>-1</sup> for oxygen saturation at 25°C .

Some or all of the acid generated as a result of iron sulfide oxidation may be neutralized by dissolution of other minerals present in a mine waste. Calcite is the most reactive carbonate, with a reported dissolution rate of approximately 2.4 x 10<sup>-3</sup> mol m<sup>-2</sup> s<sup>-1</sup> at pH 6 ( $p_{co2}$  = 0.1 atm, 25°C; Busenberg and Plummer 1986). Relative to calcite dissolution at pH 6, siderite dissolution under anoxic conditions is about three orders of magnitude slower (Greenberg and Tomson 1992) and chlorite dissolution is roughly 10 orders of magnitude slower (May et al. 1995; Sverdrup 1990; Malmström et al. 1996). The chlorite dissolution rate is roughly four orders of magnitude lower than that for pyrite oxidation at pH 6.0 (derived from Williamson and Rimstidt 1994). Thus, for a rock containing only chlorite and pyrite, chlorite dissolution could neutralize acid and maintain pH 6.0 only if pyrite content were less than about 0.3 weight percent (considering differences in mineral density and surface roughness factors).

#### OBJECTIVES

This publication reports on the solid-phase characterization of 14 Archean greenstone samples and the first 60 weeks of laboratory dissolution testing. The objectives of this report are to 1) provisionally classify solids based on their composition and their associated potential to produce acidic drainage, 2) compare observed rates of pyrite oxidation to those reported in the literature, and 3) quantify observed neutralization potentials. The classification must be viewed as provisional because laboratory testing of other low-carbonate mine wastes indicates that drainage pH decreases with time (Lapakko and Antonson 1994). This temporal variation, as well as the potential for trace metal release to neutral drainage and rates of silicate mineral dissolution, will be addressed as the project progresses. The information generated will ultimately be used to assist in mine waste management decisions for Archean greenstone waste rock.

### METHODS

## **Materials**

As part of a project unrelated to mining, the University of Minnesota Department of Physics constructed a cavern at a depth of 730 m in a greenstone formation near Soudan, MN (www.hep.umn.edu/minos). Fourteen samples used in the present study were collected from a 5-cm drill hole bored prior to excavation along the anticipated length of the cavern and were selected to provide a range of sulfur contents. Samples were stage crushed to minus 0.64-cm to limit generation of fines.

#### **Experimental**

The experimental apparatus is described by Lapakko and White (2000). A total of 18 cells were used for the fourteen samples, four of which were run in duplicate. Prior to sample addition, the cells were washed with 10% HNO<sub>3</sub>, then rinsed three times with distilled water. Each cell and the contained 1000 g dry solids was weighed, and the solids were then rinsed daily with 500 mL of deionized water for three days (week 0) to remove oxidation products which accumulated prior to the beginning of the experiment. The outlet port was capped and 500 mL of deionized water all cells were filled, the outlets were uncapped and the cells drained. Subsequently the cells were rinsed weekly in a similar manner, with the exception that a single 500-mL volume of deionized water was slowly dripped into the cell from a separatory funnel.

Between rinses the cells were stored in a room in which temperature and humidity were controlled. Over the 60-week period of record, temperature and relative humidity were measured three to four times per week, with a total of 203 readings. Temperature ranged from  $21.1^{\circ}$ C to  $27.8^{\circ}$ C and averaged 24.6°C, with a standard deviation of  $1.2^{\circ}$ C. Relative humidity ranged from 50% to 65% and averaged 59.2%, with a standard deviation of 2.4%.

#### Analyses

Particle size distribution was determined using method ASTM E-276-93 (ASTM 2000) by Lerch Brothers Inc. (Hibbing, MN). The rock samples, as well as their size fractions, were analyzed for sulfur, sulfate (sulfide was determined by difference), and evolved carbon dioxide by ACTLABS in Tucson, AZ using ASTM E-1915-97 (ASTM 2000). A 10 percent hydrochloric acid solution was used to solubilize the carbonate minerals, and the carbonate present was guantified as the difference between total carbon in the initial sample and that in the residue. The remaining solid-phase constituents of the bulk samples were determined by ACTLABS in Ancaster, ON. Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E-886-94 (ASTM 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash ENVIRO II ICP. Concentrations of Ag, Cd, Cu, Ni, Pb, Zn, and Bi were determined using a total digestion method modified from Crock et al. (1983), with analysis by ICP-AES. Other trace elements were determined using instrumental neutron activation analysis (Hoffman 1992). Mineral content was determined using sample chemistry, optical microscopy, and previous x-ray diffraction data on drill core samples. Sulfide mineral liberation was determined using optical microscopy (Louis Mattson, Mineralogical Consulting Service, Pengilly, MN).

Water samples were analyzed for specific conductance, pH, alkalinity, and acidity at the MN DNR laboratory in Hibbing, MN. Specific conductance was determined using a Myron L conductivity meter. An Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH determinations. Alkalinity (for pH  $\geq$  6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (American Public Health Association et al. 1992). Other drainage analyses were conducted at the MN Department of Agriculture. Aqueous concentrations of Ca and Mg were determined with a Varian 400 SPECTRAA. Sulfate concentrations were determined using a Lachat QuickChem 8000 or, for [SO<sub>4</sub>] <5 mg/L, a Dionex ion chromatograph.

## **Calculation of Release Rates**

Concentrations of sulfate, calcium and magnesium (as well as pH, alkalinity/acidity, specific conductance) were plotted as a function of time. Visual inspection of these graphs indicated that concentrations for weeks 20 to 60 were less variable than those in the initial 20 weeks. Solute mass release was calculated as the product of the observed concentration and the volume of drainage. Rates of solute release were calculated for weeks 20 through 60 by averaging the weekly rates determined.

## RESULTS

## Solid-phase Analyses

The 14 greenstone samples were analyzed for particle size distribution, chemistry and mineralogy. Solids were crushed to finer than 6.4 cm. Approximately 45 to 55 percent of the particles were finer than 2 mm, 17 to 22 percent finer than 0.42 mm, and 6 to 9 percent finer than 0.15 mm.

Total sulfur contents ranged from 0.04 to 1.22 percent, with virtually all sulfur present as sulfide. The sulfate content, expressed as sulfur, did not exceed 0.033 percent and exceeded 0.016 percent in only one sample. Evolved carbon dioxide contents exceeded the detection limit of 0.05 percent in only the 0.50%-S and 0.72%-S samples (1.76 and 6.85 percent CO<sub>2</sub>, respectively). The major whole rock chemical components were SiO<sub>2</sub> (49.4-84.8%), Al<sub>2</sub>O<sub>3</sub> (7.4-21.2%), FeO (3.5-14.8%), and MgO (1.1-6.4%). Contents of CaO (0.03-0.68), K<sub>2</sub>O (0.55-4.48%), and Na<sub>2</sub>O (0.07-0.97%) were low. Quartz (24-77%), chlorite (10-55%), and sericite (5-42%) contributed 90 to 98 weight percent of the mineral content in 13 of the 14 samples. The exception was the 0.72%-S sample, in which the contribution of these three minerals was 77 percent and siderite content was 17.9 percent.

Pyrite was the only sulfide mineral reported, occurring in quantities of 0.1 to 2.2 percent. Pyrite grains ranged from coarse (600  $\mu$ m) to very fine (<10  $\mu$ m) grains intergrown with host rock minerals. The degree of pyrite liberation in the individual samples ranged from 9 to 20 percent, with most liberation occurring in the -300  $\mu$ m or -200  $\mu$ m fractions (Mattson 2000). Melanterite was the only sulfate mineral detected, with contents not exceeding 0.3 percent.

Siderite was the only carbonate mineral reported and exceeded 0.1 weight percent in only the 0.50%-S and 0.72%-S samples (1.76 and 6.85 percent CO,, respectively), for which respective contents of 4.6 and 17.9 weight percent were reported. The composition of the siderite used, considering the high manganese content inferred by the chemical/mineralogical balance, was 53.8% FeO, 4.0% MnO, 2.1% MgO and 2.1% CaO. (Subsequent consideration suggests that the calcium content used may be somewhat high. Additional analysis are being conducted to determine the siderite composition.) The neutralization potentials (g  $CaCO_3$  eq (kg rock)<sup>-1</sup>) present as calcium and magnesium carbonate were calculated as 0.95 x %CO<sub>2</sub> and 1.32 x %CO<sub>2</sub>, respectively. This calculation yielded NP[(Ca/Mg)CO<sub>3</sub>] values of 4.0 and 15.5 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>, respectively, for the two samples. The siderite was well liberated in both high carbonate samples.

## Drainage Quality and Mass Release

As has been reported for laboratory dissolution of other lowcarbonate rocks (Lapakko and Antonson 1994), drainage pH generally decreased as dissolution time and sulfur content increased (Figures 1, 2). Samples in the present experiment were provisionally classified based on the minimum pH values

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observed. Since drainage pH may continue to decrease, these classifications may change as the experiment progresses.

Group 1 samples were those for which drainage pH values exceeded 6.0, a common drainage quality standard in the United States, throughout the period of record. Based on the drainage pH alone, disposal of waste rock in this class would require no rigorous reclamation. This group consisted of seven samples with sulfur contents of 0.04% to 0.16% and a sample containing 0.72% sulfur. For the first seven samples, drainage pH declined over the first 20 to 32 weeks of the experiment then plateaued. Sulfate concentrations generally decreased over the first 10 weeks then plateaued. For the 0.72% S sample, which contained 17.9% siderite, drainage pH decreased over the first 10 weeks, plateaued until week 20, then increased. The temporal trend for sulfate concentrations was similar to that for the aforementioned samples.

The extent of dissolution of these samples was fairly low. Sulfur depletion from the eight samples ranged from 2.5 to 3.8 percent. For seven of the samples, the total acid potential release based on total sulfate release ( $\Delta AP(SO_4)$ ), ranged from 0.04 to 0.13 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>, and the neutralization potential release based on calcium and magnesium release ( $\Delta NP(Ca, Mg)$ ) ranged from 0.07 to 0.1 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>. The 0.72% S sample released more AP and NP than the other samples in this group, with respective values of 0.7 and 0.8 g CaCO, eq (kg rock) The calcium and magnesium carbonates present in the siderite were the likely sources of much of the NP in this sample. The sulfur content implies an AP of 22.5 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>, which exceeds the NP implied by the calcium and magnesium carbonate content present in the siderite (15.5 g CaCO, eq (kg rock)<sup>-1</sup>). Thus the available NP[(Ca/Mg)CO<sub>3</sub>] may be depleted prior to the available pyrite, with a consequent possibility of drainage acidification.



Figure 1. Drainage pH generally decreased with increasing sulfur content and time. Sulfate concentrations generally increased with sulfur content and were fairly constant between 20 and 60, the period over which rates were determined.



Figure 2. pH of drainage from rocks with S  $\leq$  0.16% exceeded 6.0, and rocks with S  $\geq$  0.20% typically produced drainage pH below this value. The visually determined best fit curve ignores the 0.72% S sample.

Group 2 samples were those for which minimum drainage pH values in the range of 4.02 to 4.35 were observed. Moderate reclamation measures would be required to elevate drainage pH values in this range to meet a standard of 6.0. This group consisted of four samples with sulfur contents ranging from 0.20 to 0.50. The pH of drainage from these samples exceeded 6.0 for 3 to 17 weeks. For the three lower sulfur samples drainage pH generally decreased throughout the period of record, and sulfate concentrations declined for the first four to six weeks then slowly increased (Figure 1). Drainage pH from the0.50% S sample decreased through about week 15 then slowly increased, and sulfate concentrations generally declined over the course of the experiment.

The extent of dissolution of these samples was greater than that for the Group 1 samples. Sulfur depletion ranged from about 5 to 7 percent of that initially present. For the period during which drainage pH exceeded 6.0, the  $\Delta AP(SO_a)$  ranged from 0.08 to 0.12 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup> and the  $\Delta NP(Ca+Mg)$  from 0.05 to 0.08 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>. The sulfate releases observed over periods of 3 to 17 weeks (while drainage pH exceeded 6.0), are similar to those observed for the Group 1 samples over their 60-week period of record. However, the  $\Delta NP(Ca+Mg)$  during this period were less than those observed for the Group 1 samples

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over the 60-week period of record. This may reflect more effective acid neutralization at the slower sulfide oxidation levels of Group 1 samples.

Group 3 samples were those for which minimum drainage pH values of 3.1 and 3.5 were observed. Of the samples tested, waste rock producing drainage pH in this range would require the most rigorous control measures in order to meet water quality standards. This group consisted of two samples with sulfur contents of 0.59 and 1.22 percent. Drainage pH values exceeded 6.0 for no more than two weeks, declined for 24 to 40 weeks, and then plateaued. Sulfate concentrations from the 0.59% S sample increased rapidly from week 14 to 24 then plateaued, while those from the 1.22% S sample increased steadily from week 8 to week 60.



Figure 3. The rate of sulfate release (mol SO<sub>4</sub> (g rock)<sup>-1</sup> s<sup>-1</sup>) during weeks 20 - 60 generally increased as sulfur content increased and pH decreased. Solid symbols represent rates for weeks 20 - 40, and empty symbols represent weeks 40 -60. Circles represent rates with a median pH of 6.3 - 7.5, whereas triangles represent rates with a median pH of 3.5 -5.2. Square symbols represent rates for which the median pH was 3.3, This point was not included in the regression analysis.

## **Rates of Sulfate Release**

Rates of sulfate release increased with sulfur content and linear regression was conducted on data from 13 of the 14 samples (Figure 3). Data for the 0.59% S sample was omitted from the regression. Sulfate release from this sample was more than three times that anticipated based on the relationship between sulfate release rate and sulfur content for the other samples. The pH of drainage from this sample typically ranged from 3.3 to 3.5 between weeks 20 and 60. Oxidation by ferric iron, possibly mediated by bacteria, may have accelerated the oxidation of pyrite in this sample.

The sulfate release rates, normalized for sulfur content, for Group 2 samples were slightly higher than those for the Group 1 samples (Figure 3). The median pH values during the period over which sulfate release rates were calculated ranged from 4.35 to 5.04 as opposed to a range of 6.38 to 7.26 for the Group 1 Oxidation by ferric iron, perhaps mediated by samples. neutrophilic bacteria, may have contributed to the elevated sulfate release rates for the Group 2 samples.

#### **Rate of Pyrite Oxidation**

The sulfate release rates and an estimated liberated pyrite surface area were used to determine a normalized oxidation rate for the pyrite in the samples. It was assumed that 1) all sulfate release was due to oxidation of pyrite (the only sulfide mineral reported present), 2) all sulfate released by pyrite oxidation was transported with the drainage, and 3) only the liberated pyrite oxidized (i.e. oxidation of interstitial or included pyrite was very slow).

The liberated pyrite surface area of a sample was determined by summing the liberated pyrite surface area in each particle size fraction, which was calculated as:

#### $A_{vv,i} = (\% S/100)[(55.85 + 64.12)/64.12] x$ [6/(p d<sub>ave.i</sub>)]ML(SR)/100, where [3]

- A<sub>py, i</sub> %S<sub>i</sub> = pyrite area in particle size fraction i,  $m^2$ ,
- = sulfur content of particle size fraction i, percent,
- = pyrite density =  $5.02 \times 10^6$  g m<sup>-3</sup>. ρ
- d<sub>ave.</sub> = arithmetic mean diameter of particle size fraction i.
- M, = mass of rock in particle size fraction i,
- = percent liberation in particle size fraction i, and SR = surface roughness factor for pyrite estimated as 2.6. using the value reported for guartz (Parks 1990) since pyrite surfaces were reported to be smooth.

Half the rate of sulfate release (oxidation of one mole of pyrite yields two moles sulfate) observed for weeks 20 to 60 was regressed against the liberated pyrite surface area. Excluding data for samples for which pH values were below 4.0, this regression yielded a pyrite oxidation rate of  $1.6 \times 10^{-9}$  mol m<sup>-2</sup> s<sup>-1</sup> (r<sup>2</sup> = 0.93, n = 12). This is 2.7 times the 5.9 x  $10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> value predicted for the abiotic oxidation of pyrite by oxygen at pH 6.8 (Williamson and Rimstidt 1994), the median pH value for the twelve rates used.

Calculated pyrite oxidation rates for individual samples from week 20 to 60 were also compared with abiotic rates predicted by Williamson and Rimstidt (1994). The latter values were calculated using the median pH between weeks 20 and 60. For the eight samples with median pH values above 6.0, the ratio of observed to predicted rates ranged from 0.5 to 0.9. For the four samples with median pH values between 4.35 and 5.04, this ratio ranged from 1.4 to 2.1. For the two samples with median pH values of roughly 3.3 and 3.65, the respective ratios were 2.7 and Thus the ratio of observed to predicted rates of pyrite 5.2. oxidation increased as pH decreased. This suggests that pyrite oxidation by ferric iron, perhaps mediated by bacteria, became more influential as pH decreased. It is also possible that pyrite grain size in the -200 fraction decreased as sulfur content increased, yielding a larger pyrite surface area as sulfur content increased which would enhance sulfate release.

## Acid Neutralization

The observed acid neutralization potential of the samples ranged from 0.03 to 0.12 g CaCO<sub>3</sub> eq (kg rock)<sup>-1</sup>. These values are based on the release of AP observed from Group 2 and Group 3 samples (samples that ultimately produced drainage pH < 6.0) while drainage pH exceeded 6.0 (Table 1). The observed values reflect a very low capacity for acid neutralization, which is consistent with the paucity of carbonate minerals present. It should be noted that while drainage pH exceeded 6.0, the AP release exceeded the NP release indicated by calcium and magnesium. This suggests that dissolution of minerals containing potassium and sodium also neutralized acid initially to maintain pH above 6.0. Acid neutralization by silicate mineral dissolution was limited, as indicated by drainage pH values or 3.2 to 4.7 despite combined chlorite and sericite contents of 15 to 46 percent. That is, acid production by relatively small amounts of pyrite exceeded acid neutralization by the relatively large amounts of silicate minerals.

Seven of the eight Group 1 samples released 0.03 to 0.09 g CaCO<sub>3</sub> eq (kg rock)<sup>1</sup> AP. Acid neutralization was due to reaction with trace amounts of calcium or magnesium carbonates or with silicate minerals. The former possibility cannot be excluded since calcium and magnesium release has not yet exceeded the calcium/magnesium carbonate content possible based on the detection limit for solid-phase CO<sub>2</sub> (Table 1). That is, dissolution

of calcium and magnesium carbonates present at undetectable levels could be neutralizing acid. If these carbonates are solely responsible for acid neutralization, drainages may acidify as the carbonates become unavailable or depleted. More insight on this will be gained as the experiment progresses

| %S                                       | AP  | NP                          | $pH_{min}$ | Weeks Solute Release |          |        |        |          |
|--|-----|-----------------------------|------------|----------------------|----------|--------|--------|----------|
|  |     | [(Ca +Mg)CO <sub>3</sub> ]' |            | pH > 6               | pH       | > 6    | We     | eks 0-40 |
|  |     |                             |            |                      | AP       | Ca+Mg  | AP     | Ca+Mg    |
|  |     |                             |            | Group 1: p           | oH > 6.0 |        |        |          |
| 0.04                                     | 1.2 | <0.11                       | 6.94       | 60                   | 0.0367   | 0.0914 | 0.0367 | 0.0914   |
| 0.05a                                    | 1.6 | <0.11                       | 6.84       | 60                   | 0.0586   | 0.0799 | 0.0586 | 0.0799   |
| 0.05b                                    | 1.6 | <0.11                       | 6.86       | 60                   | 0.0387   | 0.0727 | 0.0387 | 0.0727   |
| 0.10(1)                                  | 3.1 | <0.11                       | 6.55       | 60                   | 0.0911   | 0.128  | 0.0911 | 0.128    |
| 0.10(2)                                  | 3.1 | <0.11                       | 6.49       | 60                   | 0.0966   | 0.132  | 0.0966 | 0.132    |
| 0.12                                     | 3.7 | <0.11                       | 6.49       | 60                   | 0.109    | 0.112  | 0.109  | 0.112    |
| 0.16a                                    | 5.0 | <0.11                       | 6.55       | 60                   | 0.134    | 0.145  | 0.134  | 0.145    |
| 0.16b(1)                                 | 5.0 | <0.11                       | 6.23       | 60                   | 0.125    | 0.0955 | 0.125  | 0.0955   |
| 0.16b(2)                                 | 5.0 | <0.11                       | 6.27       | 60                   | 0.128    | 0.0958 | 0.128  | 0.0958   |
| 0.72                                     | 22  | 15.5                        | 6.19       | 60                   | 0.747    | 0.784  | 0.747  | 0.784    |
| Group 2: 4.02 • pH <sub>min</sub> • 4.35 |     |                             |            |                      |          |        |        |          |
| 0.20                                     | 6.2 | 0.11                        | 4.15       | 17                   | 0.0952   | 0.0745 | 0.345  | 0.198    |
| 0.26                                     | 8.1 | <0.11                       | 4.06       | 16                   | 0.117    | 0.0688 | 0.487  | 0.327    |
| 0.39                                     | 12  | <0.11                       | 4.02       | 11                   | 0.120    | 0.0828 | 0.610  | 0.373    |
| 0.50                                     | 16  | 4.0                         | 4.35       | 3                    | 0.0822   | 0.0471 | 1.167  | 0.627    |
| Group 3: 3.1 • pH <sub>min</sub> •3.5    |     |                             |            |                      |          |        |        |          |
| 0.59(1)                                  | 18  | <0.11                       | 3.11       | 0                    | 0.0278   | 0.0078 | 1.927  | 0.490    |
| 0.59(2)                                  | 18  | <0.11                       | 3.08       | 0                    | 0.0304   | 0.0099 | 1.997  | 0.498    |
| 1.22(1)                                  | 38  | <0.11                       | 3.46       | 1                    | 0.0446   | 0.0309 | 1.405  | 0.539    |
| 1.22(2)                                  | 38  | <0.11                       | 3.39       | 2                    | 0.0777   | 0.0579 | 1.521  | 0.587    |

| Table 1. Drainage pH and AP and NP release for weeks 0 to 60. A | AP. NP. and Ca+M                        | a expressed as ( | a CaCO, ea/ka rock. |
|---|---|------------------|---------------------|
|   | ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,, |                  |                     |

<sup>1</sup> NP present as calcium and magnesium carbonate = 2.27 x %CO<sub>2</sub>. Assumes all CO<sub>2</sub> present as siderite, with magnesium and calcium contents indicated by the mineralogical analyses.

It is also possible that the rate of acid generation by these solids is so low (Figure 3) that the slow dissolution of silicate minerals is adequate to neutralize the acid produced. Group 1 solids with low carbonate contents were able to neutralize acid produced by inferred pyrite oxidation rates (based on sulfate release rates) less than 1.7 x 10<sup>-14</sup> mol FeS<sub>2</sub> (g rock)<sup>-1</sup> s<sup>-1</sup>. The silicate mineral content of these solids is considerably higher than the pyrite content. Consequently, if the acid is being neutralized by silicate mineral dissolution, the drainage from these samples will remain neutral as long as rates of pyrite oxidation do not increase and rates of silicate mineral dissolution do not decrease.

The 0.72% S Group 1 sample, in which calcium and magnesium carbonates were present in siderite, exhibited anomalous behavior. The AP release from this sample was comparable to that of Group 2 samples, nonetheless its drainage pH remained above 6.0. This was most likely due largely to the dissolution of the calcium and magnesium carbonate components present in the siderite, which was reported to be relatively fine grained.

Calcium and magnesium carbonates were also present in the 0.50% S Group 2 sample, yet this sample produced drainage pH below 6.0 after three weeks of dissolution (Table 1). The siderite in this sample was fairly coarse, which may have limited the dissolution rate. Furthermore, the rate of sulfate release, and implied acid production, from this sample was faster than that from the previously mentioned sample (Figure 3, Table 1).

## CONCLUSIONS

Fourteen samples of pyrite-bearing Archean greenstone rock were characterized and subjected to laboratory dissolution testing for 60 weeks. Rocks with sulfur contents less than or equal to 0.16% produced drainage pH values exceeding 6.0, and rocks with sulfur contents greater than or equal to 0.20% typically produced drainage pH below 6.0. The rates of pyrite oxidation estimated for individual samples were roughly half to five times that reported in the literature for the abiotic oxidation of pyrite by oxygen. Observed neutralization potentials ranged from 0.2 to 2.0 g CaCO<sub>3</sub>/g rock.

This systematic approach for determining drainage quality from a given waste rock lithology as a function of compositional variations within the lithology and quantifying observed neutralization potentials provides information for the environmentally sound management of waste rock. Relating empirical data to established rates of mineral dissolution provides a scientific basis for data interpretation and facilitates extrapolation of laboratory results to operational applications. In the longer term, systematically generating empirical data on dissolution of mine waste lithologies, relating these data to scientific fundamentals, and compiling this information will build a stronger foundation for future mine waste management decisions.

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## DRAFT

# Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia

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Location: 3973 Alfred Avenue

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Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage - DRAFT #1

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The Mine Reclamation Section (MRS) of the British Columbia Ministry of Employment and Investment have produced this manual with the objective of improving the practice of metal leaching and ARD prediction, enabling the Ministry's goal of supporting the productive use of the province's mineral resources where it occurs in a manner that protects land and watercourses. More effective prediction should result in quicker mine reviews, less conservative depositional criteria, greater public trust and consequently a more profitable mining industry.

The MRS's goal in prediction is informed material excavation and deposition, with the necessary level of understanding provided by comprehensive monitoring and testwork. Assistance is provided in this document in the form of a tool box of procedures for laboratory analysis and data interpretation, and a proposed framework for testing. While the final decision about which tests and analysis are required to build the necessary level of understanding should be based on the specific site conditions, there are some generic tests that are almost always needed to provide the required information.

One can never completely remove the uncertainty surrounding metal leaching and ARD. The objective in drainage prediction is to reduce the uncertainty to a level at which the liability can be identified and the appropriate monitoring, mitigation and contingency plans can be selected.

Detailed methodologies are provided for analyses that may not be standard laboratory procedures. Detailed explanations or descriptions are provided where additions or modifications are suggested to standard laboratory analyses, tests or terminology, and for controversial items that are presently the subject of debate. In some cases, such as NP (neutralization potential), there is no one clearly best method. There are a number of procedures, all with strengths and weaknesses. The recommended method has some clear advantages. However its disadvantages are also noted. In other cases, such as the prediction for mine walls, there is presently only one field measurement procedure, which despite its flaws can provide valuable information about the metal leaching from that source.

The length and level of detail in this document reflects the complexity of this topic. No apology-is made for this. It reflects the level of knowledge required of researchers and of those carrying out prediction work for major mines. A table of contents is provided to assist those who are only interested in a portion of prediction.

Much is still to be discovered about minesite weathering, and future improvements in the materials and methods are expected from the world-wide research and detailed minesite monitoring. Consequently this is by nature a working document. Additions and revisions will be made to reflect changes in technology and the experiences of practitioners.

The Manual attempts to provide clear, comprehensive guidance without limiting the options and approaches. Critical guidance is provided as to the methods, the manner in which they are used and reported, their limitations and how the tests may be used to address overall project prediction needs. Hopefully the document will be a useful reference tool.

Readers should not conclude that the authors are of the opinion that there is only one right way of doing things, and all other approaches are wrong. The authors are however of the opinion that:

- users of the Manual should consider the specific site conditions and materials when deciding which and how rules and procedures should apply,
- the prediction questions should be clearly understood prior to sample selection and analysis,
- the selected materials and methods should be defensible,
- the terminology must be clear and
- predictions should be informed by comprehensive measurement, thorough data interpretation and all available knowledge about the site and metal leaching/ARD.

Lastly and perhaps most importantly, this document was produced to allow the public and industry to see how prediction testwork and individual projects are reviewed by the MRS. It is a lot of work to write it all down, and perhaps that is why MRS's efforts in this regard are somewhat unique. However it is part of the MRS's policy to be transparent with regards to the rationale for its decision making. It is hoped that this open approach will help prevent the repetition of past mistakes and that the subsequent review of this working document will provide a clearer understanding of where improvements are required.

## ACKNOWLEDEMENTS

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## **1. INTRODUCTION**

## 1.1 Rationale and Objective

Mining is an industrial activity that exposes, comminutes and redistributes bedrock and overburden. The exposure of bedrock to oxygen and water can cause significant changes in mineral stability. Physical changes to the landscape, and the movement and alteration of materials will alter the hydrological conditions. The combined effects of mineral instability and changes in drainage will result in the weathering processes and leaching that can dramatically change site drainage chemistry. The primary concerns addressed in this document are acidic rock drainage (ARD) and metal leaching, both of which can have a major environmental impact.

In British Columbia, 37 existing mine sites either had or have a potential for significant metal leaching and acid rock drainage (ARD). Metal leaching is also a concern at a large proportion of new projects, with fourteen advanced exploration projects rated as potentially ARD generating (PAG). Consequently acid rock drainage (ARD) is the major environmental concern for the B.C. mining industry. Due to the inherent uncertainty and past mistakes in prediction, metal leaching is one of the most contentious, complicated and costly issues faced by the mining industry.

The British Columbia Ministry of Employment and Investment's (BC MEI) legal requirement to prevent ARD problems is contained in the B.C. Mines Act: Health, Safety and Reclamation Code, which states:.

"All potential acid generating material shall be placed in a manner which minimizes the production and release of acid mine drainage to a level that assures protection of environmental quality (Section 10.6.16)."

In practice this requirement is extended to all aspects of metal leaching, and all British Columbia mines with a potential to generate significant metal leaching must develop acceptable plans for prediction and if necessary mitigation. The overall goals in prediction planning are to prevent significant off-site impacts, to minimize onsite impacts and to identify the risks and possible consequences of the mine plan for land and watercourses. To achieve this goal requires an understanding of the metal leaching potential of all the materials that will be affected or disturbed by mining. Because weathering conditions and the consequent drainage chemistry may change over time, a prediction of future performance is required.

Proposed mines must predict future water chemistry to identify the magnitude of potential risks and to determine what mitigation is necessary to protect the surrounding environment. Operating mines need monitoring and on-site testwork to verify laboratory predictions with field data, to determine the performance of mitigation works, to determine if additional

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## Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage - DRAFT #1

measures are needed to protect, maintain, or restore the local environment, and to allow timely implementation of cost-effective mine-closure strategies. Closed mines must continue prediction/monitoring to inform site management, to increase understanding of materials or mitigation strategies whose performance is still uncertain and to verify that the implemented closure strategies has resulted in the predicted long-term environmental protection and reclamation success.

From previous project review, regulation and research, the Mine Reclamation Section (MRS) of BC MEI has developed a set of guidelines that guide its assessment of projects with issues involving ARD and other metal leaching concerns. To advise regulators, mining companies and the public, and to improve existing practices, MRS publishes and periodically updates them. As a result of the frequent errors in prediction laboratory analysis and data interpretation and the many requests for advice, this year MRS has also produced this "Manual of Guidelines and Recommended Methods for the Prediction of Metal Leaching and ARD".

This manual was developed in conjunction with the MRSs' General Metal Leaching and ARD Guidelines and in recognition of both the importance of drainage-chemistry predictions and the frequent errors and omissions by proponents when they do the work. Prediction to enable prevention is critical because once ARD starts, it may persist for hundreds of years. Past errors coupled with the severe consequences when things go wrong have resulted in conservative depositional criteria, a lack of public confidence and overly long regulatory reviews. To counteract this, the MRS promotes a philosophy of informed decision making, recommending thorough, ongoing material characterization and weathering studies, and monitoring of the resulting minesite drainage.

The guidelines outline the common questions and discuss the materials and methods appropriate to each phase of a prediction project. The proper program planning, testwork and the interpretation of the resulting data requires the following:

- a) A basic understanding of mining, geology, weathering and environmental chemistry.
- b) Selection of test materials and methods.
- c) Interpretation of the test results.
- d) An understanding of the limitations and potential flaws in test procedures.
- e) Adequate sample characterization, particularly with regards to mineralogical data.
- f) Consistency in test procedures if one is comparing results and learning from previous experiences at similar sites.

This manual attempts to address the items listed above for the information and procedures to be used when carrying prediction work. This includes generic questions, policies, screening criteria and recommended procedures for laboratory analysis and for interpretation of the resulting data. The guidelines are intended to assist regulators, mining companies and the public, to improve the standard of work, to reduce the uncertainty and make the resulting product more accurate, to avoid unnecessary work and to permit constructive criticism of the

MRS practices.

Adherence to the recommended methods in this manual should lead to faster regulatory reviews, more dependable prediction and less onerous waste-handling strategies. Nevertheless, there is clear recognition that much still remains lots to be learnt and new research developments will undoubtedly require changes and refinements. Site-specific factors may sometimes justify a deviation from the recommendations in this manual. Such deviations should be discussed with regulatory agencies early in the predictive studies to maintain timely reviews and to ensure that the necessary information is collected.

The suggested procedures presented here were derived from experience gained in British Columbia and some items may not apply to other biogeoclimatic conditions. Users of the guidelines both in this province and in other jurisdictions must consider the specific site conditions and materials when deciding which and how rules and procedures apply.

Comments and suggestions on the guidelines and any related issue should be directed to the authors at the following address:

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## 1.2 Summary

The suggested procedures are divided by topic into several chapters. Each of these chapters is summarized below and the overall approach to prediction is illustrated in Figure 1-1. The suggestions are consistent with the general principles of the main Metal Leaching/Acid Rock Drainage Guidelines (Price and Errington, 1997), which provide general, overall guidance on this complex topic.

- Chapter 2 introduces the general questions associated with the prediction of ARD and metal leaching, and the generic techniques used to answer the questions.
- Chapter 3 provides some general background information and theory on weathering and drainage chemistry, information needed in the selection of procedures and for the proper interpretation of test results.

Chapter 4 outlines the geologic information required to initially identify the rock and waste units that will form distinct portions of the mine components described in Chapter 5.

- Chapter 5 explains the information needs for each mine component, such as physical and geochemical inventories and the manner in which water and solids (Chapter 4) are exchanged among them and the surrounding environment.
- Chapter 6 provides recommendations on the number, size, description and handling of samples for each rock, waste unit and mine component discussed in Chapters 4 and 5.
- Chapter 7 lists the rationale and recommended procedure for each of the static tests recommended for drainage-chemistry predictions, conducted on samples collected under Chapter 6.
- Chapter 8 provides recommendations on the proper presentation and interpretation of the results from the static tests outlined in Chapter 7.
- Chapter 9 lists the rationale and recommended procedure for each type of kinetic test recommended for drainage-chemistry predictions. Kinetic tests are conducted on samples collected under, the precepts outlined in Chapter 5 and selected for further testing based on results discussed in Chapter 8.
- Chapter 10 provides recommendations on the proper presentation and interpretation of the results of the kinetic tests outlined in Chapter 9.
- Chapter 11 describes some basic geochemical models that can be used to interpret the results of static and kinetic tests (Chapters 8 and 10) and to predict of drainage chemistry.
- Chapter 12 provides examples of how to predict the drainage chemistry for each mine component (Chapter 5), based on the results of static and kinetic testwork (Chapters 8 and 10), the geochemical modeling (Chapter 11) of the selected samples (Chapter 6) and expected degree of aeration or submergence.

Chapter 13 contains a list of references used in the development of this manual.

Chapter 14 contains a glossary for some terminology used in this manual.

## Recommended Flowchart the Prediction of Minesite-Drainage Chemistry in British Columbia

Review and understand the general questions (Chapter 2) and the general background information (Chapter 3) before proceeding.

Identify rock and waste units exposed or disturbed by mining, milling, concentrating and construction (Chapter 4).

Determine the form and extent of each rock and waste unit that will occur in each mine component, such as tailings and waste-rock dumps, and describe how water will move through and over the components (Chapter 5).

Collect samples of rock and waste units that are representative of the units and the mine components they form, following recommendations on sample numbers, size, mass, description and handling (Chapter 6).

Conduct (Chapter 7) and interpret (Chapter 8) static tests to determine the composition of samples selected in Chapter 6.

Conduct (Chapter 9) and interpret (Chapters 10 and 11) kinetic tests based on static-test results (Chapter 8) for selected samples (Chapter 6).

Predict drainage chemistry through time for each mine component (Chapter 12), based on adjustments to static-test and kinetic-test results (Chapters 8, 10 and 11) for the expected flow, contributing mass and degree of aeration or submergence.

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Carry out after each phase:

- Revise classification of rock and waste units
- Tentatively create management units and determine their monitoring, mitigation and materials handling requirements, and the resulting exposure conditions

Figure 1-1. Overall Recommended Approach to Drainage-Chemistry Predictions in British Columbia

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## 1.3 General Principles

To operate a mine in an informed, environmentally responsible manner, a proponent must predict the metal leaching potential of all the materials excavated, exposed or otherwise disturbed. Prediction information will be required to determine the potential environmental impact and the (if-necessary) extraction, waste handling and mitigation conditions required to prevent unacceptable impacts.

The overall goal is to prevent metal leaching and ARD through prediction and design, avoiding long-term mitigation and risk wherever possible.

The mitigation requirements will be determined according to the available information, with precautionary conditions based on conservative assumptions established in the absence of refuting data. The use of onerous conservative depositional criteria is not a valid excuse for uninformed materials handling. Better prediction work will be required where conservative prevention strategies may sterilize ore and/or create additional risk.

Conservative screening criteria based on worst-case assumptions are used to prevent uninformed material use. Screening criteria should be used to determine whether additional testwork is required. The final criteria used for waste handling and remediation decisions should be based on site-specific test results.

The required materials and methods will vary according to the questions being asked and the phase of the operation.

Because there will always be a degree of uncertainty regarding material composition and the potential for metal leaching and ARD, post-extraction QA/QC, drainage collection and ongoing monitoring and test work will usually be required. Sampling and analysis are required both to predict and verify the composition of all excavated and exposed material. Ongoing testwork and monitoring are required to check the rate and form of weathering and the resulting drainage chemistry, and to refine predictions.

To avoid testwork for its own sake, to identify the critical management/mitigation questions and to ensure that the resources are used efficiently, each phase in the testwork selection and data evaluation should be done with an eye towards possible waste handling and mitigation strategies. A preliminary evaluation of different mitigation strategies will be critical in identifying significant information gaps and in developing a work plan that is compatible with the entire project.

ARD and metal leaching prediction studies tend to be jargon-filled, highly technical and detailed affairs carried out by specialized consultants. Despite the prohibitive level of technical detail, it is critical that the mine operator stay intimately involved and informed, and be the primary contact for communication between regulators and their consultants.

The persons responsible for metal leaching and ARD data, interpretation and conclusions must be clearly identified at the front of reports submitted to the MRS.

Due to the significant time required to do the predictive work, the cost, and the site-specific needs of each mining project, a proponent is advised to carefully review its prediction plans prior to their implementation.

The onset of metal leaching is controlled by geochemical thresholds which may take many years to reach. Consequently, the absence of acidic conditions, both on the mine site and in testwork, does not in itself prove that there will not be future metal leaching or ARD.

These guidelines are an attempt to provide clear, comprehensive guidance, while not limiting the options and approaches. Users must consider the specific site conditions and materials when deciding which and how rules and procedures apply. While modifications or additional requirements for individual mines may result from their site specific conditions, there is some generic information which almost all mines require. It is for this reason that the following guidelines are provided and methods are recommended.

Through research, the MRS will continue to assist the development of improved metal leaching/acid rock drainage technology and will revise the guidelines to reflect changes in technology.

Most methods provided here have been used at mines in British Columbia for many years, and are accepted by regulatory agencies in the province. All methods have strengths and weaknesses, and both are noted.

## 1.4 Overall Approach

To determine the metal leaching potential and environmental protection requirements for each waste material or exposure type, it will be necessary to:

- 1. Identify all the different areas and geological materials potentially affected by the mine and determine the manner in which they will disturbed. For each impacted geological material and area, the proponent should provide a description of the general geological parameters and a map showing its size, shape and location.
- Predict the metal leaching/ARD potential of each different geological material in the form(s) (for example, waste rock, tailings and mine walls) and environmental condition(s) in which it is or will be exposed (for example, deposited aerially or underwater). This is the main phase of a prediction program and includes the static and kinetic testing.

## Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage - DRAFT #1

3. Create management units and determine their requirements for monitoring, mitigation, and materials handling based on the site conditions, the metal leaching potential and the environmental protection needs. Management units should consist of waste type/exposure type/geological material combinations that will perform alike, and that can and should be handled together.

While Step 2 includes the static and kinetic testwork which comprises much of any prediction program, proponents are cautioned not ignore Steps 1 and 3, which provide terms of reference and the means for properly interpreting the testwork results. Step 3 should include consideration of cost and risk reducing avoidance or mitigation measures which would preclude a need for detailed prediction.

The questions to be answered and the procedures used in prediction will depend on the biogeoclimatic conditions, the status of the operation, the waste and exposure types, the post-excavation environment and the availability of test materials such as drill core. To carry out the prediction work in a cost effective manner, a proponent should focus on the questions critical to their particular waste handling and remediation options. For example, if there are no dissolution concerns, the critical ARD prediction question for flooded tailings will be the effectiveness and long term maintenance of the oxygen barrier rather than the composition of the waste.

## 1.4.1 Phased Approach

The large number of factors to consider (geological, mining, environmental, and ARDspecific information requirements) and the long duration of some of the testwork can make prediction an onerous undertaking, both in the time and the resources necessary for data collection, and the expertise necessary for its interpretation. Commonly the most efficient and effective way to characterize geological units, create management units, and determine disposal needs will be an iterative process of testwork, analysis and review, similar to that used to determine other geological characteristics such as ore reserves. An iterative or phased approach should help ensure that the proponent:

- Detects all potentially problematic materials.
- Avoids unnecessary work on materials for which there is no concern.
- Makes informed decisions regarding the materials and methods for more costly, time consuming test procedures, such as kinetic tests, with cheaper, more easily collected Acid Base Accounting (ABA) and elemental data.
- Implements timely refinements in response to unforeseen conditions.

Each phase in the prediction program should be informed by the preceding work. Based on the results of the first round of sampling and analysis, it may be necessary to further subdivide some of the original geological classification units, to refine the prediction questions and to modify the test procedures. Conversely, it may be possible to reduce the

number of management units by compiling geological materials whose differences are not significant with regards to mitigation and waste handling.

## 1.4.2 Avoiding Errors

At every iterative stage, the proponent must determine the applicability of the testwork, samples, and analysis to the questions being asked. Metal leaching tests, which are often misused or misinterpreted, provide very specific information. Common errors include testing unrepresentative samples, incomplete analysis of the test materials and erroneous assumptions pertaining to the parameters measured by the test. All test assumptions, rules, and analyses, including those provided here, should be verified for their applicability to the specific project, site conditions and prediction questions.

The screening criteria, outlined later in this manual, should be used to avoid unnecessary work and to focus the effort on the materials of greatest concern or uncertainty. The screening criteria, which are based on a few simple tests, are not intended to serve as final prediction criteria.

Owing to the significant analytical costs, the potential for delays, the site-specific requirements and the uncertainty regarding proper test protocols, the proponent should carefully review each phase of the prediction program with the responsible regulatory agencies prior to its implementation and as testwork progresses.

## 1.4.3 Mixed Wastes

Assessments of the potential for metal leaching and acid rock drainage are typically done in two steps:

- 1. Assessment of potential for individual samples; and
- 2. Assessment of potential for mixed wastes.

A description of the information requirements for mixed PAG and non-PAG are provided in the Section on Blending to Create a Benign Composite in the Mitigation Portion of the General Metal Leaching and ARD Guidelines.

## 2. GENERIC PREDICTION QUESTIONS AND TEST PROCEDURES

## 2.1 Questions

Prediction is one word which covers a wide range of procedures and objectives. Consequently, before proceeding with the sampling, analysis and other testwork that form the bulk of any prediction program for ARD or metal leaching, a practitioner or a researcher should consider what questions need to be answered by their "prediction". Of course, the kinds of questions will depend on the mine, whether it is closed, operating or proposed, whether ARD is present, probable or uncertain, the types of wastes and depositional environments, and the present knowledge. For example, an active-ARD producer where much of the rock is potentially acid generating (PAG), like Equity Silver, may be primarily concerned with predicting the amount and source of future loadings, to reduce them, and to determine the size of the financial security. A proposed mine like Huckleberry may be looking to distinguish PAG from non-PAG rock in order to prevent ARD and to reduce the costs of disposing of the non-PAG rock.

As the degree of knowledge increases regarding the geological materials, the mine components, their performance and mitigation constraints, the questions will become more refined. To maximize the effectiveness of the prediction work, a proponent should consider all relevant questions as soon as possible. In some cases it may become apparent that avoidance or mitigation are more effective uses of resources than refined prediction.

Generic prediction procedures and questions faced by mining operations are as follows.

# Step 1: Determination of the spatial and geological variability of the excavated, exposed, or otherwise disturbed materials.

Identify all the different areas and geological materials potentially affected by the mine and determine the manner in which they will disturbed. For each impacted geological material and area provide a description of the general geological parameters and a map showing its size, shape and location.

• What is the range in geological variability laterally and vertically?

## Step 2. Predict the Extent of Metal Leaching and Potential for ARD Potential

Determine the metal leaching/ARD potential for each different geological material, in the forms (for example, waste rock, tailings and mine walls) and conditions (for example, deposited aerially or underwater) in which they are or will be exposed.

Ouestions to be addressed at this stage include:

## Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage - DRAFT #1

- Which trace elements occur in abnormally high concentrations and what is the potential for significant release under the different possible geochemical conditions?
- In what minerals do the metals, trace elements, acidity and neutralization potential (NP) occur? The mineral source, along with the magnitude and the geochemical conditions, will determine the rate of release.
- What are the critical weathering reactions? For example, is dissolution a concern? Will primary metal release occur almost entirely from sulphide oxidation?
- Under what physical and geochemical conditions does present, and will future, weathering occur? Some parameters, such as redox, will be largely determined by the depositional environment and mitigation procedures. Other parameters will be controlled by concurrent weathering reactions. One of the most important determinants of the rate of metal leaching is whether there will be ARD.
- What is the expected present and future metal loadings from each mine component/geologic unit?
- What criteria should be used to identify and separate problematic materials? A most important issue is what criteria should be used to distinguish materials capable of producing acidic drainage.

## Step 3. Determine the Mitigation and Materials Handling Requirements

Based on the site, the metal leaching potential and the environmental protection requirements, determine the mitigation and materials handling requirements for waste type/exposure type/geological unit combinations that will perform alike, and that can be handled together. Mitigation and materials handling prediction questions include:

- What disposal/remediation methods are needed? This will depend on the prediction answers to questions regarding the critical weathering reactions and the potential drainage quality and quantity (see Step 2).
- What are the volume and area requirements for waste disposal? This requires a determination of the mass or volume of material with the critical composition. For lime treatment, this will require an evaluation of total acidity and metal loadings, and the sludge disposal requirements.
- What QA/QC procedures will be required for the extraction, waste handling and disposal operations? The sampling requirements and the laboratory and data analysis procedures will be determined from the results of previous testwork and from the operational and environmental requirements.

• How long will it take for significant metal leaching/acid drainage to develop in materials for which there will be a delay prior to the application of remedial measures? This question, pertinent to most prevention measures, is particularly important for the PAG mine walls or for PAG wastes back-filled into active or slowly filling pits or underground workings. For mine wastes, the kinetic testwork required to answer this question should include humidity cells. Wall washing stations are presently the recommended kinetic procedure for mine walls.

The questions listed above pertain both to proposed and existing mines. An additional question for existing mines with ARD is:

• What portion and mass of the component in question is generating ARD?

While Step 3 is the last stage in prediction, proponents should start considering the materials handling and deposition conditions, constraints and questions as soon as possible after the initial static test information has been collected from each of the impacted areas and geological units (Step 2), and before proceeding with more detailed testwork. There is something of a chicken and egg relationship between Steps 2 and 3, as all stages of research and planning should include a consideration of cost effectiveness, and of the limitations, needs and opportunities provided by management and mitigation. The final assessment of mitigation requirements will be based on the metal leaching potential and the environmental protection requirements determined in Step 2. However the probable mitigation requirements (Step 3), along with the geological variability (Step 1), must also be considered in the design of the testing program. Considered hypothetically at first, the mitigation requirements will be come more refined as testing proceeds.

## 2.2 Procedures

To predict the metal leaching/ARD potential and to address the prediction questions listed previously, the proponent is advised to carry out a program of testwork and analysis. Although there are generic procedures that will be common to all programs, each mine must consider the effects of its unique site and geological conditions. Prediction criteria should be based on site-specific factors such as the mine plan, weathering environment, the composition of exposed surfaces and the rates of critical reactions.

Prediction data may be obtained from a great variety of materials and methods, including detailed mineralogical characterization, comparisons with other sites, drainage monitoring, static laboratory tests, kinetic laboratory tests and on-site field trials. Usually, there is no one piece of evidence or conclusive test, and the proponent must combine information from a variety of sources. For example, the drainage chemistry from historic sites might be presented with detailed ABA and geological data showing that the rock types and exposure conditions are very similar to the site in question.

While a degree of site-specific interpretation is always necessary, generic prediction methods will almost always be required. These procedures provide a complementary mix of geological and kinetic information which can be used to answer the major prediction questions listed above. At a minimum, the following generic procedures are recommended:

## Static Testing

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- a) Trace Element Content
  - Total Concentration
  - Soluble Concentration
- b) Acid Base Accounting
  - Total-Sulphur, Sulphate-Sulphur and Sulphide-Sulphur
  - Bulk Neutralization Potential
  - Carbonate Neutralization Potential
  - pH
- c) Mineralogy and Other Geological Properties
  - Mineralogical Examination
- d) Particle Size Separation and Determination (for unconsolidated and crushed materials)

## Kinetic Testing

- a) Reaction Rates and Drainage Chemistry
  - Pre-Test and Post-Test Characterization
  - Humidity Cell
  - On-Site Test Pads
  - Minewall Stations (for existing rock exposures)
  - Site Drainage Monitoring

More detailed descriptions of these procedures, their use, the methods of data analysis and interpretation, and other recommended methods are provided in subsequent chapters. Clearly there are situations where site-specific factors may justify deviation from the standard procedures. To ensure their acceptability, such deviations should be discussed with the regulatory agencies prior to use.

## 3. BACKGROUND KNOWLEDGE

Metal leaching and ARD result from the combined effects of mineral weathering, drainage geochemistry and site hydrology. Persons or groups of persons carrying out major prediction studies need to have an understanding of mineral weathering processes, such as dissolution, oxidation/reduction and of the possible effects of important geochemical parameters like pH (Section 7.8).

The major factors contributing to ARD or metal leaching which are commonly measured in a prediction program can be divided into five categories:

- 1. The potential acidity, alkalinity and metals in physically exposed, rapidly weathering minerals. This is measured using static test procedures.
- 2. The amount of drainage. This can be estimated from site hydrology and climate data.
- 3. The reactivity of the acid producing and neutralizing minerals.
- 4. The geochemical conditions under which weathering will occur. Particularly whether the material will generate net acidity, which can be predicted from the rates of acid generation and neutralization under non-acidic conditions (#3), and the amount of acidity and alkalinity (#1).
- 5. The rates of metal leaching and loadings for the probable geochemical condition(s). This can be predicted from the rates of primary-mineral metal release and degree of secondary mineral precipitation or dissolution.

A proponent should have an understanding of the inter-relationship between these factors before they start excavating material.

Drainage chemistry is primarily determined by secondary mineral solubility. Even under acidic conditions, much of the released primary reactants may precipitate as secondary minerals. It is the dissolution of the primary reactants and precipitation of the secondary precipitants that determine drainage chemistry.

The main factors influencing the rate at which aerobic weathering products are created and the magnitude of secondary mineral precipitation/dissolution are the original metal concentration, the minerals forms, and the environmental conditions, particularly pH. Other factors sometimes affecting the concentrations of trace elements are concentrations of other elements, drainage quantity, temperature and oxygenation.

Primary minerals often react under kinetic conditions and thus generate aqueous concentrations (mg/L) that depend on the amounts and ratio of water and minerals. On the other hand, secondary minerals often react under equilibrium conditions and thus generate concentrations (mg/L) that are not affected by the amounts and ratio of water and minerals. Morin and Hutt (1997) used these general features to divide the evolution of drainage chemistry into three stages (Figure 3-1), although complexities such as the flow of water can

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affect interpretations (Table 3-1).



Figure 3-1 Three Stages in Minesite Drainage Chemistry (from Morin and Hutt, 1997).

The First Stage begins when sulphide and metal-bearing primary minerals are first exposed to air and precipitation. Because primary minerals are often far from equilibrium, their kinetic dissolution rates are relatively high (Rate1, First Stage, Figure 3-1). Over this period, the primary rates typically exceed the solubility of various secondary minerals like sulphates, carbonates, and hydroxides, causing them to precipitate within or below the mine component. The precipitation of secondary minerals is purposely avoided in kinetic tests like humidity cells in order to obtain primary rates (Rate1). However, it is the metals and acidity remaining in the drainage after secondary-mineral precipitation that create the measurable drainage chemistry flowing from each minesite component (Rate2, Figure 3-1). This first stage can reportedly last for years to millennia.

After most of the reactive primary minerals have been dissolved, the accumulated secondary minerals begin dissolving (Figure 3-1). Because the precipitation and dissolution of many secondary minerals is an equilibrium process, Rate2 (Figure 3-1) is expected to remain

relatively constant and predictable for specific geochemical conditions. The First and Second Stages of drainage chemistry can apparently last for decades to millennia.

| TABLE 3-1       Kinetic vs. Equilibrium Mineral Reactions   |   |  |  |  |
|---|---|--|--|--|
| Kinetic   | Equilibrium   |  |  |  |
| aqueous concentrations (mg/L) change with time  | aqueous concentrations (mg/L) do not change with time   |  |  |  |
| aqueous concentrations (mg/L) can be<br>dependent on the ratio of water to mineral                                      | aqueous concentrations (mg/L) are<br>independent of the amount of mineral and<br>water  |  |  |  |
| if water remains in contact with minerals<br>long enough (stagnant drainage), equilibrium<br>will eventually be reached | if drainage moves into contact with other<br>minerals, equilibrium will change, resulting<br>in either new equilibrium or kinetic<br>conditions |  |  |  |

The Third Stage of drainage chemistry involves the dissolution of only low-reactivity primary and secondary minerals like quartz. As a result, drainage concentrations fall to relatively low levels and there is no acidic drainage.

Predictive modeling of elemental concentrations in drainage during the first two stages must therefore focus on Rate2, whereas predictive modeling of duration of drainage chemistry up to Stage 3 must focus on the cumulative difference between Rate1 and Rate2 during the First Stage (Chapters 9 and 10).

Because of the large ranges in contaminant concentrations found in drainage chemistry, the prediction of minesite drainage is difficult and must include significant uncertainty. The objective in drainage prediction is to reduce the uncertainty to a level at which the liability can be identified, and the appropriate monitoring, mitigation and contingency plans can be selected.

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## 4. GENERAL GEOLOGICAL INFORMATION

## 4.1 Introduction

This chapter focuses on the critical first task in any prediction program; that is, the identification, general description, and mapping of all the bedrock and overburden that will be (for new mine proposals) or have (for existing or historical mines) been affected by mining (Step 1 in Chapter 2). Since most of the variability in metal leaching and ARD results from, or is associated with, differences in the spatial distribution and properties of geological materials, this information is required to ensure that all the possible sources of metal leaching are evaluated. The form and hydrology of mine components composed of these units will be discussed in Chapter 5.

The information required in this initial reconnaissance of the rock and overburden types can generally be derived from existing terrain mapping, drill logs, exploration reports, metallurgical testwork and other relevant geological studies. While often overlooked in the rush to do more problem-specific testing, this reconnaissance is necessary to ensure that the entire range of spatial and geological variability is addressed, and that the subsequent testwork is representative and comprehensive. Usually one or more of the properties used to separate different geological units directly affect or are correlated with the occurrence of weathering processes like ARD.

The following subsections provide more detailed explanations of the minimum description expected for various geologic materials.

## 4.2 Genesis of the Ore, the Surrounding Waste Rock, and the Overburden

A detailed description of the paleoenvironment and the geologic processes that formed the ore, the surrounding rock, and any overlying unconsolidated overburden is usually required. This information may suggest both micro and/or macro depositional patterns which could be expected in acid-generating and acid-neutralizing minerals. The macro depositional patterns of minerals, such as calcite and pyrite, could affect the distribution of potentially acid generating (PAG) bedrock. The micro spatial distribution of minerals in relation to each other and to fractures could affect their relative exposure and subsequent reactivity. This information should be used when designing a sampling plan (Chapter 6).

## 4.3 Identification and Classification of Geological Units

For the purposes of this manual, the most useful delineation of geologic units would be according to their effect on drainage chemistry. For example, Unit 1 may be capable of generating acidic drainage, whereas Unit 2 would consistently yield pH-neutral drainage.

However, mining companies usually delineate rock units on the basis of other factors, such as mineralogy, physical appearance, origin, or whether the rock is ore or waste. As a result, metal leaching-specific information is initially not available.

The basic separation or differentiation of units at an early stage will be into categories such as sedimentary, igneous, or metamorphic rock and basal till. Within each of these categories there will be subcategories, such as intrusive, extrusive, and pyroclastic for igneous rocks, and the various forms of alteration that can transform part of one rock unit into another distinct type. The delineation of units is not a simple matter and should be carried out with the assistance of a Professional Geoscientist registered with the British Columbia Association of Professional Engineers and Geoscientists.

Ideally the geological materials can be separated into discrete, homogeneous materials or "geological units". However, it is recognized that both bedrock and overburden can be highly variable, with changes occurring over small distances. Several mining projects and mines in British Columbia have found that some portion of each unit is capable of acidic drainage and another portion maintains pH-neutral conditions. This variation within rock units greatly complicates the prediction of future drainage chemistry.

Where changes occur irregularly, along continuums or so often that it is impossible to separate the overburden or rock mass into discrete homogeneous units, the proponent should divide the rock mass into "manageable" units, based in part on size and location. For example, bench or adit heights may be used to divide separately manageable units of waste rock.

## 4.4 Spatial Distribution

In some cases, spatial distribution is a critical parameter and the recognition of spatial differences can significantly increase predictive accuracy and greatly reduce the amount of PAG waste. For example, the sulphide content in till overlying mineralized bedrock is often only significant in the 1 or 2 m above the bedrock contact.

The possibility of spatial differences should always be considered when extrapolating sample results from available near-surface areas to unsampled, deeper occurrences of the same lithology. Spatial effects on the metal leaching potential may depend on the proximity to the source of ore mineralization. In other cases the primary control is some other distal source of alteration. Spatial differences may only be significant in one or two adjacent waste lithologies. An example of where location may be significant are porphyry systems where discrete pyrite alteration halos occur outside the zone of economic mineralization. This may be an important consideration if, as is sometimes the case during mine development, drill core is not available beyond the ore perimeter.

## 4.5 Mapping

Geologic cross-sections and plan maps should be presented to show the location and distribution of all significant geologic units. The mapping should show the proposed openpit excavation, other mine features, the shape and location of all impacted bedrock and overburden, and the proximity to sources of mineralization, alteration, weathering, or leaching.

## 4.6 Description of Each Unit

Written descriptions should be provided for each unit, including the physical appearance, and the general mineralogy and elemental composition. This information usually available from the exploration program, is critical in designing an appropriate sampling plan (Chapter 6).

To the degree possible, the description should focus on the central tendency and variability in properties of importance to metal leaching. Ideally the parameters reported should include the mass, dimensions, mode of genesis, lithology, bulk and vein mineralogy, sulphide mineralization, hydrothermal and supergene alteration features, degree of oxidation, colour, results of the hydrochloric acid fizz test, grain size, texture, structure, fracturing, strength, competency and spatial distribution of the above. Properties such as colour, grain size and texture will be used in field identification. Mineralogical information should include descriptions of the primary, secondary and alteration minerals for each significant geologic unit.

If possible, the description should include the eventual or existing forms of exposure (for example, pit wall, tailings, ore or waste rock - see Chapter 5).

## 4.7 Existing Mines

For existing operations and where new mining projects will affect or be affected by historical mining, geologic descriptions should include the characterization and mapping of existing mine wastes and excavations. In addition to the properties listed previously, the information reported for existing mine wastes and naturally unconsolidated materials, like glacial till, should include the particle size distribution, the mode of deposition and/or exposure, and the quantity (weight, volume and/or aerial extent). Existing mining-related disturbance should be mapped in sufficient detail to show the topography of both the mined areas and the surrounding terrain, the underlying strata and the location of any permanent or intermittent water courses. The mapping should also indicate if any other mining has or is occurring in the same immediate watershed.

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# 5. DESCRIPTION OF THE MINE AND MINE COMPONENTS

## 5.1 Introduction

Various geologic units (Chapter 4) are disturbed, exposed, excavated, reworked and deposited, and become various mine components (Table 5-1). In addition to this exchange of solids, water may also be passed among components until finally discharged to the local environment. A detailed, but not exhaustive, example of solid and water distribution is shown in Figure 5-1.

The eventual form and depositional conditions for each waste type/ exposure type/ geological unit combination, the waste volumes or surface area and the rates of these exchanges, as well as the overall physical and geochemical inventories of the components, are important in the prediction of future drainage chemistry. Considerations for each component and the recommended information for prediction are discussed in the following subsections.

| TABLE 5-1     Common Mine Components at Minesites in British Columbia |   |  |  |  |
|---|---|--|--|--|
| Open Pits   | Underground Workings                                      |  |  |  |
| Waste-Rock Dumps  | Low-Grade Ore Stockpiles                                  |  |  |  |
| Ore Stockpiles  | Tailings Impoundments                                     |  |  |  |
| Roads   | Disturbed-Rock Foundations for Buildings                  |  |  |  |
| Dams surrounding another component if built of different material     | Ditches surrounding or extending between other components |  |  |  |

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Figure 5-1. Schematic Diagram of a Mining Operation (from Morin and Hutt, 1997). Interactions among components are indicated by arrows (solid = liquid exchange, dashed = solids exchange).

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#### 5.2 Waste Rock

The following factors should be considered when predicting the future drainage chemistry from a waste rock dump.

- The coarseness of some waste rock will allow unrestricted air movement. In the absence of some form of oxygen barrier or sink, aerobic conditions may be expected to persist throughout a waste rock dump.
- Typically in B.C. more than 75% of the mass occurs as coarse particles in which the mineralogy is almost entirely occluded from oxygen and water, and thus relatively inert. Drainage chemistry will be controlled by the relatively small portion of the mass which occurs as fine-sized particles. The more cohesive the rock, the smaller the proportion of fines.
- The proportional composition of the fine-sized particles may deviate from that of the whole, with less drainage input expected from more cohesive, stronger grains and a greater contribution expected from grains along plains of weakness.
- While much remains to be understood about waste dump hydrology, evidence to date indicates that drainage occurs along preferred pathways. Significant volumes of the dump appear to be hydraulically isolated and thus to varying degrees do not contribute their weathering products to the effluent drainage.
- In typical dump construction, each truck load is dropped or pushed over the advancing terrace face, where to varying degrees it spreads from crest to toe. As a result, a portion of each truckload used to construct a single lift will remain at or near the surface.

Specific prediction needs for waste rock are as follows:

- Regular operational sampling and analysis of the fine fraction<sup>\*</sup> is usually necessary to verify pre-mining material characterization, and to determine the relationship between the composition of the fine fraction and whole rock analysis. Predictions based on drill core should be modified according to observed differences.
- For proposed operations which do not yet have wastes to analyze, petrographic methods can be used to estimate the relative contribution of critical minerals to the fine-sized fraction and to the surfaces of coarse particles. Comminution effects may also be

<sup>\*</sup> Based on MEI research, the <2mm fraction is suggested as typically being representative of the fine particle size and as for sand-sized grains is the particle size in which typically most of the mineral grains will be exposed. The diameter of the size fraction in which all the grains are exposed and which dominates sample reactivity is a material specific characteristic, requiring material specific considerations.

predicted using weathering simulation methods, such as slaking or coarse crushing.

• Sampling requirements will depend on the questions being addressed. However, a generic recommendation for drainage-chemistry prediction for a single lift of a waste rock dump is to sample the fines exposed in shallow surface trenches.

## 5.3 Tailings

The following factors should be considered when predicting the future drainage chemistry of tailings.

- Pre-mining predictions based on ore should consider the changes in composition that will result from milling. For example, the milling procedures used by metal mines remove some sulphides and can add alkalinity, both of which reduce the potential for metal leaching or ARD. Other milling practices can increase the potential through the addition of metal-bearing reagents, like copper sulphate. The precise effect on the metal leaching potential will depend on the milling process, the pertinent mineralogy and particle size/grain size relationships.
- Tailings are often fine textured with most, if not all, of the mineralogy exposed and able to contribute to weathering processes.
- The fine texture of tailings creates, relative to waste rock, a reduced pore size and a lower permeability for both air and water. This may result in a raised water table and/or restricted drainage loss into surrounding, more porous strata. Restricted air movement may limit the rate of oxygen replenishment, reducing acid generation and metal leaching and perhaps changing the balance between acid generation and neutralization.
- Significant mineralogical and particle-size segregation may occur when the tailings are deposited. The selective deposition of heavy minerals and the creation of raised sandy beaches may create zones of higher metal leaching potential close to the deposition point. The potential separation of sulphides and carbonates on tailing beaches may result in localized ARD.

Specific prediction needs for tailings are as follows:

- Regular operational tailings sampling and analysis, necessary to verify pre-mining material characterization, should include monitoring to determine whether mineralogical and particle size segregation create zones of higher metal leaching potential close to the deposition point. Predictions should be modified according to observed differences.
- Hydrological or gaseous limitations should be investigated whenever prediction tests

suggest a metal leaching potential.

• Pre-mining prediction should include a milling/metallurgical study to determine the removal of sulphides, additions of alkalinity and additions or removal of metals for the range in ore composition, and a determination their effect on the metal leaching/ARD potential. The study should identify the milling process, the pertinent mineralogy and particle size/grain size relationships.

## 5.4 Open Pits and Underground Workings

The chemistry of drainage from open pits and underground workings will be determined by the quality and quantity of waste rock, talus, mine walls and fractures, and the frequency with which they are drained. In some cases, only a small portion of the mass will be exposed to weathering processes, so the resulting drainage chemistry will be generated from a very small portion of the whole.

Significant amounts of waste materials (waste rock or tailings) or talus from wall collapse may be present in open pits and underground mines. Often, these materials contribute more reactive surface area than the mine walls and fractures.

## 5.5 Stockpiles of Ore and Low Grade Ore

Ore is often stockpiled for relatively short periods of time, but can release drainage with unacceptable chemistry if highly reactive. The composition and fate of low grade ore stockpiled at a minesite is determined by transitory economic factors and is therefore somewhat uncertain. Consequently predictive testwork is required to determine the composition of any stockpiled materials. If there is a potential for ARD or significant metal leaching, thorough kinetic testing supported by detailed on-site monitoring will be required to determine the time to initial onset of unacceptable drainage chemistry. In essence this work should follow the procedure for waste rock (Section 5.2).

# 5.6 Physical Inventory of Mine Components and Exchange of Solids and Water

The following data must be collected in order to inventory the mine components and the exchange of solids and water.

- Climatic data, including temperature and precipitation, and the surface and ground water flows in the area.
- For each proposed or existing mine component (Table 5-1), the volume/tonnage and

lateral area at various times in the minesite's history.

• The amount of each geologic unit (Chapter 4) reporting to, or exposed in, each component.

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The information should be summarized in tabular format. Based on the climatic and waterflow data, the flows of water into and from each component through time should be calculated on a monthly or more frequent basis.

The times at which each unit was/will be exposed and expanded should be tabulated based on the mine plan and schedule.

#### 5.7 Geochemical Inventory of Mine Components

Based on the physical distribution of geologic units within each mine component (Chapter 5) and each unit's overall geological and mineralogical composition (Chapter 4), rough estimates of each component's composition can be made. Of primary importance is the inventory through time of all acid-generating and acid-neutralizing minerals as well as minerals that can leach metals of environmental concern. The level of detail for each component will depend primarily on its depositional environment and on its potential for unacceptable drainage chemistry.

#### 6. SAMPLING REQUIREMENTS

#### 6.1 Introduction

One of the most important parts of any prediction program is the sample selection and preparation prior to analysis. The objective in sample selection is to choose samples representative of all the different types of materials that will be excavated or exposed. Without the selection of representative samples, all subsequent analyses and interpretations may be invalid. This chapter will focus primarily on the purpose and rationale of proper sample collection, rather than the collection techniques. Appropriate techniques for extracting rock and tailings have been discussed in various reports for the British Columbia Acid Mine Drainage Task Force and the federal Mine Environment Neutral Drainage (MEND) Program.

Every program will be faced with questions regarding the location, number, size and type of samples to collect. The answer to each of these questions will depend on the prediction questions, on the particular site, on the mine plan and on what test material is available. Different materials provide different information. For example, geochemical testwork on both comparable old and new drill core may provide pre-mining information on mineral reactivity at the site; testwork on both old and newly exposed tailings may reveal changing geochemical conditions, how quickly different minerals react and the fate of released metals.

Owing to the significant cost involved, the importance, the complexity and the specific requirements of each mining project, a proponent is advised to discuss the sampling program with regulatory agencies prior to its implementation.

#### 6.2 Number of Samples

Every sampling program faces the question of how many samples should be analyzed. The simple answer is that sufficient samples should be collected and analyzed to determine the statistical distributions (e.g., Table 8-1) of relevant geochemical parameters.

As significant variability can result from differences in mineralization, alteration and lithology, sufficient samples should be taken to accurately characterize the variability and central tendency over the entire area of disturbance and for each significant geological unit. The actual number of samples required for a particular area or material will depend on the variability of critical parameters, the questions being asked, and the degree of accuracy required. Obviously, the answer to the question of how many samples to collect will be different for each geologic unit and mine component.

A proponent should be guided by all available site specific information and use statistical guidelines for selecting the appropriate number of samples. Ideally sampling will be an

iterative task involving several phases of sampling and analysis, with each phase informed by the results from the previous campaigns.

The following arbitrary recommended minimum number of samples from each rock unit or a mine component based on tonnage of disturbed rock is provided for use in the first phase of testing, in the rare case where no other guidance is available for initial sampling (Table 6-1).

| TABLE 6-1   Minimum Number of Samples for Preliminary Static Testing   (from Price and Errington, 1997) |                           |  |  |
|---|---------------------------|--|--|
| Tonnage of Unit (metric tonnes)   | Minimum Number of Samples |  |  |
| < 10,000  | 3                         |  |  |
| < 100,000   | 8                         |  |  |
| < 1,000,000   | 26                        |  |  |
| <10,000,000   | 80                        |  |  |

A relatively new technique of ABA interpretation, block modeling, provides a statistical basis for determining how many samples to collect and generally would require significantly more samples than indicated in Table 6-1. Block modeling involves the conceptual discretization of a proposed pit or underground working into blocks, often several metres in each dimension. Geostatistical techniques like Kriging are then used with analytical data from core to designate each block as either ore or waste. Similarly, each block can be designated net acid generating or net-acid neutralizing based on ABA data. For this to be statistically significant, ABA core samples must be collected no further apart than 50 m laterally and vertically (Morin and Hutt, 1997). For larger pits, this may lead to more than 1000 ABA samples.

#### 6.3 Source of Material to Sample

The second major issue in sample selection is the type of material to sample. Where a mine component exists, the actual in-situ material should be collected. However, this is not always possible. For example, a proposed mining project cannot collect samples of non-existent waste rock. As a result, crushed drill core may have to substitute for blasted waste rock.

One advantage in using drill core is that it is available for all the areas of disturbance. Another advantage is that the location, grade, and visually detectable geological conditions have usually been recorded, allowing a preliminary separation into "operational" geological units (rock types) and management units.

Prior to mining, the choice of test materials for predictive work is often restricted to drill

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core. Notable exceptions are the tailings created in the pilot scale testing of the mill circuit, and waste rock and large bulk samples extracted from exploration adits. Exploration waste rock may provide valuable information on the composition of the fine size fractions and relative mineral exposure. The analyses of tailings from mill testwork may indicate proportional sulphide removal and the effect of milling on the ABA characteristics of ore. In both cases, caution is required in extrapolating the results from a limited sample population to the entire range of site conditions.

For existing waste dumps or rock walls, the spatial distribution of composited subsamples should cover a geochemically functional area or mass. This could be the depth of mixing that occurs in waste handling, the minimum area that could be handled if separate mitigation were required (e.g., a pit bench or adit rock face, or one lift of a dump or a muck pile), or the depth of a significant iron-stained layer.

For most purposes, waste rock dump sampling can be restricted to the fine-grained portion of the dump, typically the terraced dump bench. Non-destructive/comminuting sampling techniques will be required for waste rock or overburden where particle size differences are important or for weathering studies where surface measurements are required. This generally precludes drilling and may pose an insurmountable problem if the material of interest is buried.

Sampling requirements will depend on the questions being addressed. However, a generic recommendation for drainage-chemistry prediction for a single lift of a waste rock dump is to sample the fines exposed in shallow trenches which presumably will be representative of the type of fines found throughout the dump. The rationale for this is that, in typical dump construction, each truck load is dropped or pushed over the advancing terrace face, where to varying degrees it spreads from crest to toe. As a result, a portion of each truckload used to construct a single lift will remain at the surface.

When sampling tailings, a critical factor to consider is the effect of alluvial deposition on particle size and mineral segregation, and its consequent effects on metal leaching. In a typical impoundment, discrete samples should be collected from the slimes in the center and the sands on the periphery.

Where the objective is to characterize the range, rate and form of weathering at the site, discrete-geochemical zones are often identified by colour, primarily the red or yellow discolouration indicating iron release and consequent precipitation. When using colour as an indicator of weathering, a proponent should be aware that while the association between iron release and the degree of weathering generally holds true, this rule is not universally applicable. Leached iron may precipitate in unweathered materials or be completely removed if the pH is very low.

There are two examples in British Columbia (Cinola and Kitsault) where waste rock would, based on its grey, unoxidized colour, be visually classified as unweathered, when in fact the

opposite is true. In both cases the site has high precipitation, and the materials in question are hydrothermally altered, with a moderate pyrite content (1 to 3% sulphide-S) and little or no NP. Upon weathering the leachate pH dropped below 3, so ferric iron remained soluble. As a result, all the iron released by oxidation has been removed by leaching.

#### 6.4 Sample Size

The issue of sample size involves two separate questions: the area or volume over which a sample is collected (this section) and the actual mass collected (Section 6.5).

The area, volume or length over which a sample is collected (or subsamples are composited) should be based on:

- the proposed modes of extraction, exposure and deposition;
- the geochemically functional area;
- the material variability; and
- the prediction questions.

Composting of widely spaced samples is not acceptable. For drill core, the sampled length (and thus weight) of core for each individual sample should be the proposed bench heights for open pits or the proposed adit heights for underground workings. Ideally all the core or a split can be used. Where no continual sample over the desired length is available, discrete-interval subsamples should be combined to create a representative sample (for example, compositing three to five subsamples collected at regular intervals over a bench or adit height).

In general, stratified random subsampling can be used to create a representative sample for a "mining" functional area or length (e.g., dump height or bench height). The exception to this is where a sampling unit, such as a bench height, is split to avoid compositing lithologically or otherwise very different materials, whose performance may be very different and which occur in volumes large enough to handle separately. Where possible, compositing should be designed to allow the discrete subsamples to be analyzed separately, if this is required to determine small-scale variability. For example, a program of testing drill core samples, prepared by compositing over a length equivalent to the bench height, could include the occasional analysis of discrete subsamples separated to permit the measurement of lithological variability.

### 6.5 Sample Mass

The minimum sample mass or volume is controlled in part by the laboratory's requirements for testing. Additional material beyond the minimum should be collected in case there are additional analysis or QA/QC requirements (e.g., replicate testing). There is a minimum

weight of 2 kg needed to conduct all static tests in Chapter 7, with a 4 kg sample preferred. To conduct the laboratory kinetic tests of Chapter 9, a minimum of 2 kg is also required, with 4 kg preferred, in addition to the minimum of 2 kg for pre-kinetic static tests. The field kinetic tests of Chapter 9 typically require several kg to many tonnes depending on the design of the test.

#### 6.6 Sample Description

It is very important that a geological description be provided with each sample. This information can be used for field identification and will show where the sample fits within the group it represents. Geological information, which for proposed mines can usually be derived from drill logs, will also be used to reassign samples if the geological units are reclassified, and can be used to explain anomalous ARD test results.



Figure 6-1. Example of Required Geologic Cross-sections for Core Samples

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In all cases, every sample should be accompanied by a unique sample name, sampling date, and descriptions of sampling location, sample size, and visual characteristics like Munsell colour, visible mineralogy and apparent grain size. The Munsell colour chart provides a standard procedure for reporting the colours of weathered materials. All this information can be critical in the correct interpretation of analytical results.

Samples sites should be plotted and shown on plan and cross-section maps. Where drill core is used, the locations of the samples should be plotted on geologic cross-sections (e.g., Figure 6-1). The sections should include a depiction of sample intervals along drill holes and rock units.

### 6.7 Particle Size and Exposed Surface Effects

Two factors that should be kept in mind during sample selection, in sample preparation prior to analysis and in the interpretation of analysis results are that:

- significant mineral reactivity requires exposure to oxygen and/or water, and
- most laboratory analyses do not distinguish the exposed, potentially reactive portion of a sample from the portion that is physically occluded and at least for now, largely unreactive.

The requirement for surface exposure is one of the reasons why ore is crushed prior to milling. Crushing can make physically unreactive grains reactive. It has a similar effect when the whole sample, stones and all, is crushed prior to bulk assays. Before crushing a sample, one should consider the effect on the resulting analysis results and whether some other analysis would create more accurate information. Considerations include:

- The reactive (exposed) portion may have a significantly different composition from that of the whole.
- The proportional magnitude of the reactive fraction should be considered when extrapolating laboratory results to the field.
- The possibility that a lack of physical exposure prevents chemical reactivity should be considered when studying mineral weatherability in excavated materials and exposed surfaces.

There are two features to consider 1) whether or not mineral grains are exposed, and 2) that the rate of mineral reactivity is determined in part by the area of surface exposure.

One of the main parameters controlling surface area and mineral exposure is particle size (Section 7.9). Surface area increases exponentially as particle size decreases (Brady, 1990). Consequently most of the surface area and mineral exposure in a stoney unconsolidated material will occur in the fine particles. In contrast to the sand, silt and clay, relatively few mineral grains in coarse fragments occur on exposed surfaces. Because most of the mass is

physically occluded from oxygen and water, competent coarse fragments and mine walls typically can contribute relatively little to drainage chemistry.

For materials like tailings, consisting entirely of finely crushed particles in which almost all the mineralogy is exposed, the "whole" sample should also be analyzed.

For stony materials like waste rock or till, where only a small proportion of the whole is physically available to react, greater prediction accuracy will be achieved by selectively analyzing the "reactive" size fraction. This is particularly important for a waste rock in which most of the mass occurs in coarse particles. At the Whistle project in Ontario (K. De Vos, personnel communication) and from the Kitsault mine (McLaren, 1986) less than 3% of the mass was estimated to occur in the < 2 mm particle size fraction. These two sites are likely typical of the competent, indurate rock types found at most precious and base metal mines.

When sampling an existing waste rock, a representative sample of the fines containing material should be collected (i.e., stones and all). Because of the difficulty in sampling boulders, there is generally a particle size cut off around 12 cm. A recommended initial particle size separation for waste rock samples is by dry sieving to separate the >12 mm (stones), 2-12 mm (gravel) and <2 mm fractions.

Depending on the prediction objective, subsequent testing can be carried out on the particle size(s) that illustrate the effects of weathering or whose weathering will determine drainage chemistry. Ideally the decision regarding the upper particle size cut-off for the "reactive" fraction should be a site specific evaluation that considers a number of features including the grain size of reactive minerals, the extent of previous weathering and the competency and porosity of the coarse fragments. Based on observations of mineral reactivity made on waste rock with a wide range of grain size (Price and Kwong, 1997), if there is no site specific information, a general rule of thumb used by MRS is to recommend that the < 2 mm fraction be considered the reactive fraction, and that this size fraction be separately analyzed whenever appropriate in static and kinetic test work. The validity of this generalization should be assessed for each site and material.

Ideally analysis should be done on stony media and should be done on size fractions representative of both the reactive fines (e.g. < 2 mm) and the coarse fragments (e.g. > 12 mm). -

Some of the possible drawbacks associated with using the < 2 mm fraction to represent the reactive fraction are that:

- sieving is required, and additional handling could alter the quality of the sample;
- a large enough subsample of the < 2 mm fraction may be unavailable, and too small a sample size may not yield representative data;
- the analysis will not measure the contribution from the coarse fragments, which may be

significant if coarse fragments are incompetent or porous, or the < 2 mm fraction is unreactive;

• the analysis assumes that most contaminant release comes from this size fraction. This assumption may not be correct for historic mine wastes and for naturally weathered materials in which weathering has progressively removed reactive minerals from the finer particles;

Other advantages with separately analyzing the < 2 mm size fraction are:

- it requires a small mass to provide a representative sample;
- discrepancies in the coarse fragment content won't significantly effect precision;
- the smaller sample size requires smaller containers and apparatus;
- provided the particle size distribution is known, the results can be applied for a material which has a widely ranging stone content.

Where pre-mining waste rock characterization was based on some form of total sample analysis (i.e., drill core or drill chips), QA/QC analysis of the resulting post extraction "reactive" size fraction is required to verify the predicted composition. Predictions should be modified according to observed differences.

Historical waste rock and overburden can also contain non-reactive coarse fragments, but with the extra feature that previous weathering may have removed reactive minerals from the finest size fraction. An example of this was seen in talus samples at the Red Mountain site near Stewart, where the finest fraction (< 230 mesh) often had the lowest sulphide content. Consequently, most of the reactive capability in well weathered samples may be in intermediate particle sizes (e.g., 2 to 12 mm). Depending on the degree of previous weathering, "reactive fraction" analysis should be carried out on a larger particle size distribution for already strongly weathered materials (e.g., < 12 mm versus < 2 mm).

When only a portion of the whole material is collected or analyzed, the proportional amount should be determined. For rock walls, this may require a visual assessment in the field. For a waste dump, the proportion of the fines-containing material (versus fines-free stones and boulders) should be estimated in the field. Laboratory sieve analysis of the "total" samples taken from the fines-containing material should be used to quantify the proportional contribution of the analyzed size fraction (Section 12.2).

Distinguishing the composition of the reactive size fraction or surfaces may not be possible in the pre-excavation prediction of consolidated material like bedrock. For cohesive samples like drill core, it is usually only possible to analyze the total sample. Where drill core is used to predict the composition of waste rock, petrographic methods can be used to estimate the relative contribution of critical minerals to the fine-sized fraction and to the surfaces of coarse particles. Comminution effects may also be predicted using weathering simulation methods, such as slaking or coarse crushing.

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When attempting to identify the reactive fraction in a particular waste rock, overburden or on a rock wall, one should consider the composition, porosity, friability, previous exposure and hydrology. Even for cohesive strata like drill core or rock walls, it might be possible to selectivity sample and analyze the composition of friable, potentially incompetent or water bearing veins and fractures, if the goal is to make a more refined prediction of the reactivity.

## 6.8 Sample Preparation

After being collected a sample should be air dried or oven dried at a low temperature. Oven drying at temperatures no higher than 40 °C will ensure most minerals are not altered. Prior to drying, the sample should be kept cool. However, drying will cause additional secondary minerals to precipitate during evaporation of the porewater, which could complicate testwork and predictions.

If the sample contains stones, it should be separated by dry sieving into the >12 mm (stones), 2-12 mm (gravel), and <2 mm size fractions. The weight of each fraction should be measured and recorded. Where particles are cemented together, they may be separated through some form of mechanical vibration or chemical pretreatment.

Depending on the test requirements, a subsample should be split-off for crushing. Crushing is required for consolidated, surface-less bedrock samples and for bulk, whole, or total sample assays. Depending on the laboratory, crushing is usually to < 74  $\mu$ m (200 mesh) or 120  $\mu$ m (120 mesh). Typically crushing occurs to an unspecified degree on an unspecified particle size distribution. This is no longer acceptable practice.

Crushing the entire sample is said to provide a representative subsample. Since crushing also creates new surfaces, exposing minerals otherwise occluded from weathering processes, it should not be done on the test material intended for surface measurements of pH or soluble metals.

In sample preparation and subsampling prior to analysis, care should also be taken to collect samples which are large enough to limit "nugget effects" due to the non-uniform distribution of minerals in clusters. For example, if pyrite occurs as large porphyroblasts, the sample volume should be large enough to limit sub-sampling errors due to the random variation of the number of porphyroblasts in the sample.

#### 7. STATIC TESTS

#### 7.1 Introduction

Static test is a term used in ARD and metal-leaching studies to describe analyses that measure the quality and quantity of different constituents in a sample at one point in time, for example, the total and soluble concentration of a particular metal. There is an almost unlimited variety of static test analyses. The tests described below, which measure parameters specific to metal leaching, should be considered for inclusion in any metal leaching/ARD prediction program.

The information derived from the recommended static tests, in conjunction with previous experience, can form the basis for preliminary estimates of metal leaching or ARD. For example, by comparison with other samples, whose performance is known, static test results may suggest how a sample has been altered in the past, or may weather in the future. Static test screening criteria can be very useful for identifying materials with no ARD potential or elements of little concern. However, the reader is cautioned that given the present ignorance regarding rock and mineral reactivity, and the lack of detailed historic site characterization and monitoring, static test criteria are generally coarse and conservative.

A static test result may suggest, but it cannot on its own show temporal performance. Kinetic tests (experimental designs that simulate or allow the measurement of weathering - Chapter 9), are required to assess or predict reaction rates and geochemical evolution (Chapters 8, 10, 11 and 12). Kinetic testing in combination with static tests, is required to develop more refined and precise, site-specific estimates.

This chapter describes recommended analysis procedures for the following important static test parameters. These tests include:

a) Elemental Analysis

- Whole-rock major element analyses by XRF;
- Multi-element trace analysis by ICP after strong acid digestion (major, minor and trace constituents);
- Soluble constituents;
- Other selective-dissolution analyses including delineation of accumulated reaction products;
- b) Sulphur species, including sulphide, leachable sulphate and total sulphur;
- c) Neutralization potential;
  - Sobek neutralization potential;
  - Carbonate-based neutralization potential, including detection of iron and manganese carbonates;
- d) pH

- Surface rinse pH;
- Crushed sample pH (crushed pH);
- e) Particle-size analyses; and
- f) Mineralogical determinations/examinations;

The recommended procedures for whole-rock major element analyses (Section 7.2), multielement analyses (Section 7.3), solubility and other selective extraction tests (Section 7.4), particle-size analyses (Section 7.9) and mineralogical examinations (Section 7.10) follow generally available procedures commonly used in geology and soil science.

The combined measurements of sulphur species (Section 7.6), neutralization potentials (Section 7.7), and paste (crushed) pH (Sections 7.8), accompanied by the calculation of net neutralization potentials (Section 8.1.1) and net potential ratios (Section 8.1.2), are typically known as acid-base accounting (ABA). There are several variations of ABA. However, the basic procedure by Sobek et al. (1978), also known as the EPA-600 method, has been the procedure most commonly used in British Columbia and around the world. Because of its extensive use, the Sobek procedure permits validation against field observations collected over the past approximately 20 years.

Many of the static tests discussed in this chapter provide complementary, somewhat redundant information. These seeming redundancies provide critical cross-checks on predictive information, with discrepancies pointing to unusual conditions warranting further examination and clarification.

The procedures provided in this manual refer to the required particle size by diameter in mm or  $\mu m$ . A conversion table of diameter to U.S. Standard Mesh Sizes can be found in Appendix 1.

In order that static test results are properly applied and interpreted for the specific project and natural site conditions, the results should be evaluated by personnel knowledge of both with ARD/metal leaching technology and weathering/drainage chemistry-study requirements. Informed, site-specific decision making requires comprehensive testing and is only possible if the necessary information is obtained and correctly interpreted.

### 7.2 Whole-Rock Major Element Analyses

The objective of whole-rock major element analyses is to measure the total amounts of common mineral-forming cations. This relatively cheap analysis can be used to:

Measure the concentration of Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Si, Ti (all to 0.01%), Ba (to 5 ppm), Nb, Rb, Sr, Y (all to 2 ppm) and Zr (to 3 ppm), all reported as oxide equivalents. In samples with a low sulphur content, sulphur can be measured down to 0.01%.

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- Identify materials with very low levels of matrix alkalinity (little Ca or Mg), a situation where anomalously low sulphide contents may result in ARD or where ARD onset may be instantaneous.
- Measure the Ba concentration. Assuming that all the Ba occurs in this form, the XRF-Ba content can be used to estimate the barite content, providing a possible correction to the sulphide determination (Section 7.6). Ba should only be assumed to be barite if the geology supports it. Ba may also occur in feldspars to quite high levels.
- Provide a general measure of chemistry which can be compared to crustal and/or rock type averages (Appendix 2). This data may be used to check the lithological classification.
- Assist in the determination of all or part of the bulk mineralogy. This ranges from the "relatively" simple use of elemental data to predict the concentrations of individual minerals, the only ones in which they occur, to normative computer programs that attempt to predict the entire mineral suite. Both assessments require additional mineralogical information showing which minerals are present and the cation ratios in solid solution minerals. To determine the mineral forms in which various metals occur requires a mineralogical examination (Section 7.10). While it holds great hope for the future, normative computer programs are presently unable to account for the heterogeneous mix of hydrated, alteration minerals common in mined rock.

Due to cost and ability to provide the necessary level of accuracy, XRF is the recommended procedure for whole-rock analysis. Other low cost options such as wet chemical digestion procedures, may result in incomplete sample dissolution with a resulting biasing of the results. Another common non-dissolution method, neutron activation NAA - gamma spectroscopy analysis, is an appropriate exploration tool as it provides gold concentrations in addition to related gold trace elements. The disadvantage of NAA is the possibility of matrix interference caused by mineralized samples.

Limitations on the use of XRF are that:

- Sulphides may prevent a clean disk from being produced, causing signal interference in the analysis which will not allow for the optimum detection limits to be achieved. XRF is therefore not recommended for high sulphide samples (usually ≥5% sulphides).
- Samples with high amounts of Fe can also cause signal interference, and high levels of metals such as Cu and Zn can cause serious damage to the crucibles used during the analysis.
- XRF is not suitable for the detection of elements which occur at low levels in a sample. Detection of trace (<100 ppm) elements can be done more reliably using other techniques such as ICP (Section 7.3).

If samples are known to have elevated sulphide and/or metal contents, the proponent should discuss the nature of the samples with laboratory personnel, and together decide if XRF analysis is possible. The recommended option for high sulphide samples is to use a lithium

metaborate fusion and digestion technique with an inductively-coupled plasma or inductively-coupled plasma atomic emission spectroscopy (ICP or ICP-AES) analysis.

Whole-rock results are usually reported as oxide equivalents: "Al<sub>2</sub>O<sub>3</sub>", "MgO", etc. which show the cation levels balanced with oxygen. This is the traditional way of reporting the data and does not mean that the cations in the sample necessarily occur in these oxide forms. Elemental concentrations can be derived from the atomic-weight ratios shown in Table 6-1. The sum of a whole rock analysis, including loss on ignition (LOI), will typically approximate 100%. A significant deviation from 100% can indicate an analytical error, or the presence of large amounts of sulphides, carbonates, phyllosilicates and/or hydrated minerals.

| Table 7-1<br>Atomic Weight Conversions of<br>Oxide Mineral Concentrations to Equivalent Elemental Concentrations |               |             |  |  |  |
|--|---------------|-------------|--|--|--|
| To convert from  | To equivalent | Multiply By |  |  |  |
| Al <sub>2</sub> O <sub>3</sub>   | Al            | 0.5292271   |  |  |  |
| CaO  | Ca            | 0.7146933   |  |  |  |
| Cr <sub>2</sub> O <sub>3</sub>   | Cr            | 0.3421052   |  |  |  |
| Fe <sub>2</sub> O <sub>3</sub>   | Fe            | 0.3497182   |  |  |  |
| MgO  | Mg            | 0.6030761   |  |  |  |
| MnO  | Mn            | 0.7744572   |  |  |  |
| P <sub>2</sub> O <sub>5</sub>  | Р             | 0.2181907   |  |  |  |
| K <sub>2</sub> O   | K             | 0.4150562   |  |  |  |
| SiO <sub>2</sub>   | Si            | 0.4674654   |  |  |  |
| Na <sub>2</sub> O  | Na            | 0.3709261   |  |  |  |
| TiO <sub>2</sub>   | Ti            | 0.5994993   |  |  |  |

The method(s) used for XRF whole rock analysis may vary slightly between laboratories. This variation in technique may be due to differences in the instruments. For example, one manufacturer may suggest operational methods and sample preparation techniques which are different from another instrument manufacturer. Also, a certified laboratory will have established sample preparation, analysis and QA/QC procedures which have been developed over years of performing the analyses and these procedures may vary slightly from other laboratories. Despite the slight variations, each laboratory should use similar method(s) for whole-rock major element analyses.

For whole-rock XRF and ICP methods, as with all multi-element analyses, accuracy requires careful calibration with a range of appropriate standards. Likewise, analytical precision requires that the techniques used are consistent between samples and between laboratory personnel.

### General Procedure - XRF Technique

- 1. A finely ground sample is mixed with lithium metaborate flux and fused in a furnace at approximately 1000°C.
- 2. From the resulting melt a thin glass disk is prepared and analyzed by XRF.
- 3. To analyze for Ba, Nb, Rb, Sr, Y and Zr about 2 g of sample is combined with a liquid binder, compressed on a boric acid backing in an aluminum mold, dried and analyzed by XRF spectrometry.
- 4. To determine loss on ignition (LOI), approximately 1 g of sample is placed in a dry porcelain crucible, weighted, and ashed at 1000°C for about 1 hour. The sample and crucible are then cooled in a desiccator, re-weighed and the LOI calculated.

## General Procedure - ICP-AES Procedure

- 1. A finely ground sample is mixed with lithium metaborate flux and fused in a furnace at approximately 1000°C.
- 2. The resulting melt is allowed to cool and is then dissolved in a known volume of  $\sim$ 5% nitric acid.
- 3. The resulting solution is analyzed by ICP or ICP-AES techniques with all inter-element interference (both major and trace elements) being corrected.
- 4. To determine loss on ignition (LOI) approximately 1 g of sample is placed in a dry porcelain crucible, weighted, and ashed at 1000°C for about 1 hour. The sample and crucible are then cooled in a desiccator, re-weighed and the LOI calculated.

## 7.3 Strong Acid Digestion Multi-Element Trace Analysis by ICP

The objective of multi-element trace analysis is to provide a measure of the solid-phase levels of various metals that maybe of environmental concern. Combined with metal-leaching rates (Chapter 9) these levels allow the calculation of metal depletion times and can be used as a screening tool to detect constituents which occur in anomalously high concentrations and may, under unfavourable geochemical conditions, be a drainage-chemistry concern. It should be noted that if ARD occurs even elements occurring in "normal" concentrations may become a concern. Determination of which elements occur in high concentrations can be made by comparing the results with the normal range of concentrations found in rock and soil. A list of normal trace element concentrations is provided in Appendix 3. In weathered samples, metals below the normal range may indicate previous rapid metal leaching and depletion. These results should be used to focus future work on the materials and elements requiring further investigation.

Where one mineral is the only source for a particular element, trace element concentrations may be used to estimate this mineral's concentration. For example, the Pb concentration may be used to estimate the amount of galena. This procedure should be used with caution as many trace elements occur as a trace constituents in other more common minerals, like pyrite. Submicroscopic techniques should be used to check the assumption that there is a sole mineral source.

All geologic materials impacted by the mine should be screened using the multi-element analytical techniques.

Obviously total concentrations provide no information about the form in which the elements exist and therefore are not to be taken as a direct measure of their threat to the environment. In many cases the mineral source may be inert or only sparingly soluble. Where elements are present in high concentrations, further testing and analysis should be done to determine the mineral source(s) (Section 7.10), the potential rates of release (Chapters 9 to 11) and the environmental significance (Chapter 12).

#### Strong Acid Digestion Multi-Element Analyses by ICP

As the recommended XRF procedure for whole-rock major cation analysis (Section 7.2) cannot detect the required lower concentrations of many trace metals, a strong acid dissolution using aqua regia, or some other similar concentrated acid combination combined with low detection ICP analysis is the recommended multi-element trace analysis procedure. Advantages of the aqua regia method include the cost, its ubiquitous use and the ability to detect a large number of elements. Triple-acid or four-acid digestion methods are typically more expensive but provide a more complete digestion.

For a standard 32 element aqua-regia digestion and low level ICP analysis, the optimum minimum detection limit varies between elements. Examples of minimum detection limits that can be expected include Ag to 0.2 ppm; Be and Cd both to 0.5 ppm; Cr, Co, Cu, Hg, Mo, Ni, Sc, Sr and V all to 1 ppm; Sb, As, Bi, Pb and Zn all to 2 ppm; Mn to 5 ppm; Ba, Ga, La, P, Th, W and U all to 10 ppm; Al, Ca, Fe, Mg, Na and Ti all to 0.01%; K to 0.1%. It should be noted that detection limits and the elements reported may vary slightly between laboratories due to differences the standards and in the techniques used to calibrate individual instruments.

It should also be noted that aqua regia does not dissolve the whole sample, and therefore it may underestimate the concentration of some elements that dissolve slower or form more inert minerals. Elements whose concentration may be underestimated include Al, Ba, Be, Ca, Cr, Ga, La, Mg, Sc, Na, Sr, Th, Ti and W. In many cases, incomplete dissolution during trace element measurements may not be much of a concern, as most of the mineral sources are soluble, and those minerals that remain inert in the test procedure are expected to be similarly unreactive in the field. However, this is clearly not a total assay and whenever the resulting concentrations are reported, they should be prefaced by the analytical procedure. If aqua regia is used, the results should be referred to as the aqua regia metal concentrations, and any unusual problems with incomplete sample dissolution should be reported. A more complete digestion will occur with the more expensive concentrated triple-acid digestion

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method (perchloric, nitric, and hydrofluoric acids).

The main drawback with the standard 32 element aqua-regia digestion and low level ICP analysis done at some laboratories is that some of the potentially important trace elements are not assayed (Se) or the detection limits may be too high (As, Hg and Sb). Selenium can only be reliably determined using alternate digestion/extraction techniques and other non-ICP (i.e. atomic absorption) detection methods, by analyzing the original sample solution separately and by using background correction. Detection limits lower than those available with the standard aqua-regia ICP analysis may also be achieved with alternate digestion techniques and/or quantitative non-ICP methods. Until it is determined that As, Hg, Sb and Se are not a concern, modification or additional analyses will be required.

As with the XRF whole rock major element analyses (Section 7.2), specific aqua regia - ICP multi-element analysis methods may vary slightly between laboratories. Again the reason for this variation in technique may be due to differences in the instruments used and the certified laboratory's established sample preparation, analysis and QA/QC procedures. Despite the slight variations, each laboratory should use similar method(s).

### General Procedure

- 1. A finely ground sample is placed into a numbered test tube. Every tenth sample should be a duplicate sample or an internal known reference standard.
- 2. Add a small known volume of aqua regia solution (concentrated HCl:HNO<sub>3</sub> 3:1).
- 3. Place test tubes in racks in a hot water bath making sure that the water level in the pan is above the level of the sample solution. Digest at approximately 95°C for 2 hours.
- 4. Cool the sample and bring up to a known volume in a volumetric flask with *demineralized/deionized* water. Cap, shake and centrifuge the samples.
- 5. Using a macro pipettor take an exact aliquot of the sample solution and transfer it to a clean autosampler tube, adding additional *demineralized/deionized* water, if necessary, and shake to mix sample.
- 6. Analyze sample on an Inductively Coupled Plasma (ICP) instrument using matrix matched calibration standards. The ICP instrument should be calibrated according to internal laboratory QA/QC procedures and the instrument Operator's Manual supplied by the manufacturer. The analytical results should also be corrected for spectral interelement interference.

## 7.4 Analysis for Soluble Constituents

In addition to primary-mineral weathering effects, such as sulphide oxidation, significant contaminant release may also occur from the dissolution of surface coatings or soluble minerals, such as carbonates and salts (Chapter 3). Solubility is generally only a concern where materials are already oxidized as a result of historic supergene processes, previous mining or a delay in the use of prevention measures. Metal release through dissolution tends

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to occur as a result of changes in the leaching rate or through the removal of solubility constraints. These latter processes can result from submergence, exposure to precipitation or movement of material into a drainage path.

The presently recommended solubility testing procedure is a modification of the shake flask, leachate extraction procedure outlined in the Special Waste Regulation of the British Columbia *Waste Management Act*. The sample should be shaken for 24-hours, using distilled water, at a 3:1 water to solid ratio by weight. The use of a 3:1 solution (excess water or weak acid) is to ensure all soluble products can dissolve without solubility limitations. The gentle agitation for 24 hours is to ensure continuous exposure of all surfaces and mixing of the rinse solution.

To determine the presently leachable components, the recommended procedure is a distilled water leach. The distilled water can be replaced with a weak acid solution to determine solubility under the low pH conditions that would result from ARD.

For unconsolidated materials, the test material should be an "as is" (uncrushed) subsample. For consolidated materials like drill core, crushing is required and it is therefore only possible to measure the "crushed" soluble constituents. For fine textured materials (e.g., tailings) or pulverized bedrock, the analysis should be done on a subsample of the total sample. For materials containing coarse fragments (e.g., till and waste rock), the analysis should be done on a subsample of the whole sample or if there are logistical problems on a subsample of a size fraction that is representative of the reactive material. The drawbacks associated with using the < 2 mm fraction to represent the reactive fraction are noted in Section 6.7. The advantages to the use of the < 2 mm size fraction, in addition to those noted in Section 6.7, are that a smaller (50 to 100 g) sample is required and therefore smaller containers and "shaking" apparatus.

Because solubility is only a concern in a limited number of situations, soluble-constituent testing should be used selectively. The potential for metal solubility, and consequent need for testing, should be determined from the initial characterization of geological materials (Chapter 4), the sulphate content (Section 7.6) and the results of petrographic examinations (Section 7.10).

### 7.4.1 Distilled Water Extraction

#### Chemicals

1. Deionized or distilled water  $(H_2O)$ .

### Materials

1. 400 mL polyethylene or glass container.

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2. Rotary extractor or shake flask extractor.

#### <u>Method</u>

- 1. Weigh a representative 250 g subsample and place into a cleaned 1000 mL container. Add 750 mL of distilled or deionized water of known chemical composition, as defined through chemical analysis, to the container.
- 2. Gently agitate the samples on a rotary extractor for 24 hours. On completion of the 24-hour agitation, let the samples stand for a minimum of three hours allowing suspended materials to settle.
- 3. Collect the supernatants, recording their volume. Measure pH of the subsample and then immediately process the water (filter, preserve, etc.) and submit for chemical analysis (multi-element analysis, etc.). Dissolved parameters are important to determine readily soluble components. Total parameters would reflect release of retained products during handling and physical abrasion of rock or tailings.
- 4. Transfer the wet solids from the containers to pre-weighed drying trays, ensuring all the sample has been removed.
- 5. Air dry the wet samples for 24 hours, or dry in an oven on low heat (<40°C) if necessary. If the samples were dried in an oven, cool in a desiccator prior to weighing. Record the final weights of the dry samples.
- 6. Take a representative split from the samples. Submit the splits for desired static tests such as whole-rock (Section 7.2), total-metal (Section 7.3), sulphur species (Section 7.6) and NP analyses (Sections 7.7).

#### Interpretation of the Results

In the absence of site-specific objectives, the elements of potential concern can be selected by comparing the shake flask results with the discharge objectives, such as those reported in Table V of the provincial Pollution Control Objectives for the Mining, Smelting and Related Industries (Appendix 4). This comparison is only a screening approach for use prior to the development of site-specific objectives. Values above or below the Pollution Control Objectives have no legal meaning. The determination of potential impact and a need for mitigation will depend on the site-specific conditions.

Obviously the test results are determined by conditions such as the solid-to-water ratio which may be very different from the actual site conditions.

#### 7.4.2 Weak Acid Extraction

The procedure for the weak acid extraction is identical to that for the distilled water extraction, except that water is replaced by dilute 0.1 N HCl (pH between 1 and 2). If significant NP (Section 7.7) is present, additional acid may be required to maintain an acidic pH.

#### 7.5 Acid-Base Accounting

The combined measurements of sulphur species, neutralization potential (NP) and pH, accompanied by the calculation of acid potential (AP), net neutralization potential (NNP) and neutralization potential ratio (NPR), are known as acid-base accounting (ABA). ABA provides a useful rough guide as to whether a sample is potentially ARD generating (PAG), an assessment that can be refined and calibrated with more detailed mineralogical characterization, site specific observation and kinetic testing. Although universal ABA rules do not exist, ABA characteristics, particularly the NPR, are often used for operationally identifying and separating potentially ARD generating (PAG) materials, or as screening criteria in the early phases of the prediction program.

There are several versions of ABA. The simplest procedure would be to use sulphide-S to calculate AP and only one procedure to determine NP. The analysis suite recommended is an expanded version of the Sobek or EPA-600 method (Sobek et al., 1978), which includes a determination of all sulphur species. Modifications include the additional measurement of carbonate-carbon, a revision in the procedure for measuring pH and possible corrections for barite, iron and manganese carbonates, based on refined mineralogical characterization.

The resulting list of recommended ABA analyses are:

- Total-Sulphur, Acid Leachable Sulphate-Sulphur, Acid Insoluble Sulphate-Sulphur and Sulphide-Sulphur
- Bulk Neutralization Potential
- Carbonate-Carbon (Carb-NP)
- pH

### 7.6 Sulphur Species

Sulphur minerals are the primary sources of acidity and contaminant trace metals in mined materials, and their measurement is a critical requirement in minesite drainage chemistry prediction. The main variables for sulphur species are the various oxidation states and the bonding with different cations. The chemical behaviour of sulphur depends to a large degree on its oxidation state. The most oxidized state commonly found in nature is sulphate-S  $(SO_4^{-2})$ . The most common sulphate minerals are the Ca sulphates, gypsum and anhydrite. Under acid pH conditions, sulphate may occur in Al and Fe minerals. Most sulphate minerals are soluble and acid leachable. However, one of the most problematic sulphate minerals from an analytical point of view is barite, which is insoluble and not removed in an acid leach.

The primary reduced sulphur species, sulphide  $(S^2)$  and disulphide  $(S_2^2)$ , primarily occur combined with Fe in minerals such as pyrrhotite and pyrite, whose oxidation generates acidity. Notably, pyrite and pyrrhotite may contain other metals as trace constituents or as

foreign inclusions. Other common sulphide minerals include chalcopyrite (Cu, Fe) and other Cu species, arsenopyrite (As, Fe), sphalerite (Zn, Fe), and galena (Pb). Intermediate sulphur species such as elemental sulphur and thiosulphate are reportedly capable of generating some acidity upon oxidation, however, they are not common and there are no well documented examples where they have had a significant effect.

The third common category of sulphur species are organic forms which may be common in coal or in unconsolidated materials that have supported plant growth.

Under acid conditions significant potential acidity may reside in acid sulphate minerals and in certain forms of iron and aluminium. However, ABA is generally carried out to determine the likelihood of ARD from neutral pH samples. Under these conditions, the maximum potential for future mineral acid generation is calculated from the sulphide-S content. Ideally the sulphide-S content will be determined using the recommended expanded sulphur analyses. Short-cuts are possible if there is no organic-S or sulphate-S. However, these assumptions must always be checked. The initial ARD predictions at Huckleberry Mine were based on the assumption that all total-S and sulphide-S were synonymous. This assessment was based on the assumption that all the sulphur occurred as pyrite (FeS<sub>2</sub>). In fact a large proportion (up to 3% S) occurred in the non-acid generating forms of gypsum and anhydrite (calcium sulphates). As a result, the mine greatly exaggerated the acid generation potential (AP), erroneously predicting that all the Main Zone waste rock and all the tailings would be potentially acid generating (PAG).

The recommended procedures for determining sulphur species follow the basic procedures of Sobek et al. (1978), also known as EPA-600 acid-base accounting (ABA). Recommended expansion and modifications of the EPA-600 method are provided in *italics*.

Different species of sulphur are isolated using the various leaching procedures prescribed below. The sulphur concentration in each subsample is measured with a Leco sulphur analyzer, with the results used to determine or calculate:

- total-S,
- sulphide-S,
- acid-leachable Sulphate-S,
- acid-insoluble Sulphate-S and
- organic-S.

The detailed procedures for the preparation and analysis of sulphur with Leco equipment can be found in the equipment manuals.

For organic-free samples, the sulphide-S content may be calculated from the difference between acid-leachable sulphate and total-S, with a possible correction for barite. Obviously this short cut should be avoided for coal samples or samples including roots, woody debris, leaves, etc. Direct determination of sulphide provides a QA/QC assessment when compared

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to the calculated sulphide.

Chemicals (from Sobek et al., 1978)

- 1. Hydrochloric acid (HC1), 2 parts acid to 3 parts water: mix 400 mL of concentrated HCl with 600 mL of distilled water.
- 2. Nitric acid (HNO<sub>3</sub>), 1 part acid to 7 parts water: Mix 125 mL of concentrated HNO<sub>3</sub> with 875 mL of distilled water.
- 3. Silver nitrate (AgNO<sub>3</sub>), 10%: Dissolve 10.0 g of AgNO<sub>3</sub> in 90 mL of distilled water. Store in amber bottle away from light.
- 4. Nessler's Solution (Fisher Scientific Co. No. So-N-24 or equivalent).

## Materials (from Sobek et al., 1978)

- 1. Leco Induction Furnace and Automatic Sulphur Titrator, prepared and operated according to the Operator's Manual and internal laboratory QA/QC and operating procedures.
- 2. Funnels, 28" I.D. polyethylene.
- 3. Filter paper, 5.5" glass fibre.
- 4. Flasks, Erlenmeyer, 250 mL.
- 5. Beakers, 100 mL.
- 6. Syringe.
- 7. Baiance, can be read to 0.001 g.

## Procedure (from Sobek et al., 1978)

1. Take three 0.500 g subsamples of less than 60 mesh material.

## Total-S (from Sobek et al., 1978)

2. Take one subsample and analyze for total sulphur.

# Acid-Leachable Sulphate-S (from Sobek et al., 1978)

- 3. Taking care not to sharply crease the glass fibres, fold filter paper to fit a polyethylene funnel.
- 4. Place second subsample in filter. NOTE: Make sure all material is placed in the filter.
- 5. Place subsample and filter onto funnel holder in sink or other suitable pan which can receive outflow from funnel.
- 6. Using a syringe, pipette, or other graduated dispenser, add 2:3 HCl to almost the top of the filter paper. Caution: During this step and all other leaching steps, be careful not to lose any sample by runover, splashing, or breaking through the filter paper.

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- 7. Repeat step 6 until a total of 50 mL of acid has been added.
- 8. Place funnel holder, containing funnel and subsample, over a 100 mL beaker.
- 9. Leach subsample with 50 mL of distilled and deionized water. Discard leachate. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Samples must be kept moist.

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- 10. Leach subsample with another 50 mL of distilled and deionized water.
- 11. Test leachate for chlorides by adding 3 drops of 10% AgNO<sub>3</sub> with a dropper. NOTE: The presence of chlorides will be detected by a white precipitate.
- 12. Discard leachate and repeat steps 10 and 11 until no precipitate forms.
- 13. Discard leachate.
- 14. Air dry subsample and filter overnight.
- 15. Carefully fold glass fibre filter around the sample and transfer to ceramic crucible for [residual] total sulphur analysis.

#### Sulphide-S (from Sobek et al., 1978)

- 16. Place third subsample in a 250 mL Erlenmeyer flask. NOTE: Make sure all of the subsample is placed in the flask.
- 17. Add 50 mL of HNO<sub>3</sub> (1:7).
- 18. Let stand overnight at room temperature.
- 19. Taking care not to sharply crease the glass fibres, fold a filter to fit a polyethylene funnel.
- 20. Place a funnel holder over a sink or other suitable pan which can receive outflow from funnel.
- 21. Carefully pour subsample and acid from the Erlenmeyer flask into the funnel. NOTE: Do not get material above top of filter paper.
- 22. Repeat step 21 using distilled and deionized water to wash all materials remaining in the Erlenmeyer flask into the funnel.
- 23. Place funnel holder containing funnel and subsample over a 100 mL beaker. NOTE: Stop here if procedure cannot be completed in one day. CAUTION: Sample must be kept moist.
- 24. Leach subsample with 50 mL of distilled and deionized water. Discard leachate.
- 25. Leach subsample with another 50 mL of distilled and deionized water.
- 26. Test leachate for presence of nitrates by adding 3 drops of Nessler's Solution with a dropper. NOTE: If nitrates are present, the leachate will turn yellow within 30 seconds as seen against a white background.
- 27. Discard leachate and repeat steps 25 and 26 until no nitrates are detected.
- 28. Discard leachate.
- 29. Air dry subsample and filter overnight.
- 30. Carefully fold glass fibre filter around the sample and transfer to a ceramic crucible for [residual] total sulphur analysis.

Comment: It is necessary to remove chlorides and nitrates by water leachings after the hydrochloric and nitric acid (respectively) extractions before running total sulphur.

Calculations (adapted from Sobek et al., 1978; expansions and modifications in *italics*)

- 1. Total-S (%) = total sulphur of untreated sample.
- 2. Acid-leachable sulphate-S (%) = Total-S (%) minus Total-S after HCl treatment (%).
- 3. Sulphide-S (%) = Total-S after HCl treatment (%) minus Total sulphur after HNO<sub>3</sub> treatment (%).
- 4. Insoluble sulphate-S (%) = Barium as %Ba from total-metal analyses \* (32.06/137.34) assumes all insoluble sulphate-S occurs as barite and all barium occurs as barite; this should be confirmed through mineralogical examinations (Section 7.10).
- 5. Organic-S (%) = Total-S after HNO<sub>3</sub> treatment minus Insoluble Sulphate-S (%).
- 6. Sulphur discrepancy or del-S (%) = Total-S (%) minus (acid-leachable sulphate-S (%) + insoluble sulphate-S (%) + sulphide-S (%) + organic-S (%)); if positive in value, assumed to be acid-generating sulphide unless demonstrated otherwise.

## 7.7 Laboratory Bulk Neutralization Potentials

## 7.7.1 Introduction

The drainage pH of weathering rock is primarily determined by the balance between acid and alkalinity generating reactions. All materials containing acid generating minerals like pyrite are acid producing, but ARD will only result if there is insufficient production of neutralizing alkalinity. Neutralization ability is therefore a primary determinant of drainage chemistry and the static test measure of neutralization potential (NP) is a major part of acid base accounting (Section 8).

It is important to realize the limitations inherent in any "static laboratory measurement". This is especially true for Lab-NP, which is a completely different parameter, and should be clearly distinguished, from the actual production/manifestation of NP in the field (Field-NP). However much of what is said below equally pertains to other static tests like AP. The static test neutralization potential procedure is a measurement of the capacity of a crushed sample to neutralize strong acidity. Obviously static laboratory NP procedures will never be able to match all the nuances in contributing mineralogy, the limitations on physical exposure/availability and the geochemical determinants of reactivity under the site and mine component specific environmental conditions.

Laboratory neutralizing potential is not intended to be an accurate measurement of the

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effective "field" neutralization capacity. Rather the goal is to provide a preliminary guide as to the available NP, a value that, in conjunction with a measure of the maximum available acidity, can be used to make crude conservative predictions, and that can be refined and calibrated with more detailed mineralogical characterization, site specific observation and kinetic test work.

Part of the difficulty in measuring NP compared to AP, for which there is a clearly defined contributing mineralogy (sulphides) and usually one or two dominant minerals (pyrite or pyrrhotite), is that most common rock forming minerals are capable of producing some alkalinity, but in widely varying reactions and rates. Even if the sample remains the same, alkalinity production can be altered by the measurement procedure, the weathering (or simulated-weathering) conditions, physical properties, the rate of acid generation and over time. The amount of variation resulting from changes in the above is strongly affected by the potentially NP contributing minerals.

One of the most important concepts to be understood in NP work is the distinction between effective field NP and other forms of alkalinity generation (e.g., Morin and Hutt, 1994; Morin and Hutt, 1997). Effective NP is defined as the ability of a potential NP source to maintain a neutral drainage chemistry. Obviously the ability of a potential NP source to maintain a neutral drainage chemistry depends in part on a the rate of acid generation (Chapters 6 and 8). To be effective NP, alkalinity must be available to neutralize that acidity. Alkalinity generated after the onset of ARD is a totally different phenomena. The distinction of effective NP and the determination of whether or not a mine component will produce ARD depends to a large degree on the relative kinetic rates, a factor not measured in a static NP analysis.

The concern regarding a possible discrepancy in relative acid generation and neutralization rates is generally not significant when the NP comes from carbonate minerals whose solubility will be stimulated by a pH decrease. However, it is very important if the NP comes from slowly dissolving aluminosilicate minerals which will only contribute significant, effective Field-NP, if the in-field rate of acid generation is also slow. If the in-field rate is relatively fast, the aluminosilicate minerals containing lots of alkalinity may not react fast enough to neutralize much acidity, and thus these minerals would not represent significant effective Field-NP. As field performance can depend in large part on the reaction-rates, the evaluation of Lab-NP results should include an assessment of NP mineral reaction rates. If non-carbonate minerals are an important potential NP source the prediction of the effective Field-NP requires kinetic test information.

The term NP is presently used to refer to a wide range of phenomena. The examples provided above illustrate the importance of defining the form of NP and the type(s) of measurements. It is especially important to state whether it is the field or the laboratory property that is being referred to. One of the objectives of this manual is to encourage practitioners to be more precise in their NP terminology.

While there can be various Lab-NP and Field NP predictions, depending on the test procedures, a sample in a specific depositional environment has only one Field-NP, an "effective NP", that represents its actual neutralization capacity relative to its rate and total capacity for acid generation (Chapter 6). Significant improvements in the measurement of Lab-NP can really only be achieved if there is an understanding of what mineralogy's NP is being measured and of each mineralogy's field performance under different site specific conditions.

The present best practice for Field-NP prediction is to interpret the Lab-NP measurements in combination with whatever knowledge exists regarding the:

- resulting manifestation of Field-NP,
- the potentially contributing mineralogy and how its quantities vary on exposed surfaces and
- rates of acid and alkalinity generation under the site specific environmental conditions for the general sample and for specific minerals.

Although the bulk mineralogy remains constant, the effective Field-NP will change with changes to the quantity and quality of exposed surface, and the weathering conditions. Changes may result from:

- the effect of extraction and comminution on surface area and exposure,
- the effect of deposition and previous weathering on the reaction environment and
- changes in environmental inputs.

For example, a material may have different "effective Field-NP values" as a result of differences in the rate of acid generation caused by restrictions in the oxygen supply.

The laboratory static test procedures available for measuring NP can be split into two categories: 1) the traditional procedure of determining bulk neutralization which measures the samples ability to neutralize an excess of strong acid; and 2) a test, or group of tests, aimed at measuring the carbonate neutralization potential.

## 7.7.2 Bulk Neutralization Potential

The critical objective in any bulk laboratory NP measurement is to provide data that can contribute to and be used in conjunction with the available weathering and mineralogical data. A standard procedure is necessary so that the test results can be repeated. A standard procedure also allows a comparison to be made with the results at other sites. To facilitate calibration, the static NP procedure should measure the possible sources of

alkalinity. Weathering and mineralogical measurements can then be used to determine the size, reactivity and significance of the different sources.

The procedure recommended here, the Sobek et al. (1978) procedure, also known as the EPA-600 method, involves soaking a sample in excess acid, heating the mixture to ensure good dissolution, and then determining the remaining, un-neutralized acidity. The NP is then reported in any of three equal units: tonnes (t) of CaCO<sub>3</sub> equivalent/1000 t of sample, or kg of CaCO<sub>3</sub> equivalent/t of sample, or parts per thousand (ppt) CaCO<sub>3</sub> equivalent. The Sobek procedure includes an initial determination of the rate of NP dissolution ("fizz rating" of carbonate dissolution) to ensure sufficient acid is added to dissolve all readily reactive NP.

Possible discrepancies between the Sobek Lab-NP and the Field-NP, that should be considered in the interpretation of test data, may result from the fact that the Sobek Lab-NP:

- 1. Is done on a crushed sample, removing surface area and mineral exposure constraints on reactivity.
- 2. Is only carried out for a limited duration, and thus if the field rate of acid generation is slow, it may underestimate the NP content of slowly dissolving aluminosilicate minerals.
- 3. Involves both a very strong acid and heating, neither of which occur in neutral pH weathering, and which may overestimate the contribution of some minerals, like clays, to provide significant effective Field-NP.

While the Sobek method is the standard procedure, there are a number of alternate methods for measuring laboratory NP, many of which are promoted as being more accurate because they reduce the lab./field discrepancy in one or more of the above. Recently there has been support for the use of a modified Sobek Lab-NP test procedures that replaces heating with a longer acid digestion. Judgment of whether this or other static laboratory methods make the resulting field-NP assessments easier or more accurate awaits the provision of evidence that they more accurately predict field experience or are more easily calibrated with mineralogical information and with reaction rates recorded in field and laboratory kinetic tests.

To date, most ARD research in British Columbia and in the eastern USA have used or have been calibrated with the Sobek et al. (1978) NP procedure. The knowledge gained about the relationship between this form of Lab-NP and the resulting Field-NP more than compensates for any predicted, but as yet unverified, gains in Lab-NP "accuracy". Since there is no body of field evidence with which to interpret other Lab-NP procedures, the Sobek method remains the recommended procedure. Practitioners wishing to use other procedures should have a good kinetic/mineralogical basis for interpretation and are recommended to also carry out the Sobek method on a subset of samples.

## Method (from Sobek et al., 1978; expansions and modifications in *italics*)

During digestion, do not boil samples. If boiling occurs, discard sample and rerun. Before titrating with acid, fill buret with acid and drain completely. Before titrating with base, fill buret with base and drain completely to assure that free titrant is being added to the sample.

## Chemicals (from Sobek et al., 1978)

- 1. Carbon dioxide-free water: Heat distilled water just to boiling in the beaker. Allow to cool slightly and pour into a container equipped with ascarite tube. Cool to room temperature before using.
- 2. Hydrochloric acid (HCl) solution, 0.1 N, certified grade.
- 3. Sodium hydroxide (NaOH), approximately 0.5 N: Dissolve 20.0 g of NaOH pellets in carbon dioxide-free water and dilute to 1 liter. Protect from CO<sub>2</sub> in the air with ascarite tube. Standardize solution by placing 50 mL of certified 0.1 N HCl in a beaker and titrating with the prepared 0.5 N NaOH until a pH of 7.00 is obtained. Calculate the normality of the NaOH using the following equation:

Note: Other methods of standardizing prepared NaOH solutions, such as the use of triplicate accurately weighed samples of potassium acid phthalate, can be employed and should be consistent with a laboratory's QA/QC procedures.

4. Sodium hydroxide (NaOH) approximately 0.1 N: Dilute 200 mL of 0.5 N NaOH with carbon dioxide-free water to a volume of 1 liter. Protect from CO2 in air with ascarite tube. Standardize solution by placing 20 mL of certified 0.1 N HCl in a beaker and titrating with the prepared 0.1 N NaOH until a pH of 7.00 is obtained. Calculate the normality of the NaOH using the equation in No. 3 above.

Note: Other methods of standardizing prepared NaOH solutions, such as the use of triplicate accurately weighed samples of potassium acid phthalate, can be employed and should be consistent with a laboratories QA/QC procedures.

5. Hydrochloric acid (HCl), approximately 0.5 N: Dilute 42 mL of concentrated HCl to a volume of 1 liter with distilled water. Standardize solution by placing 20 mL of the known normality NaOH prepared in No. 3 above in a beaker and titrating with the prepared HCl until a pH of 7.00 is obtained. Calculate the normality of the HCl using the following equation:

Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage - DRAFT #1

- N1 = (N2V2)/V1, where:
  - V2 = Volume of NaOH used.
  - N2 = Normality of NaOH used.
  - V1 = Volume of HCl used.
  - N1 = Calculated Normality of HC1.
- 6. Hydrochloric acid (HC1), approximately 0.1 N: Dilute 200 mL of 0.5 N HCl to a volume of 1 liter with distilled water. Standardize solution as in step 5 above, but use 20 mL of the known normality NaOH prepared in No. 4 above.
- 7. Hydrochloric acid (HC1), 1 part acid to 3 parts water: Dilute 250 mL of concentrated HCl with 750 mL of distilled water.

#### Materials (from Sobek et al., 1978)

- 1. Flasks, Erlenmeyer, 250 mL.
- 2. Buret, 100 mL (one required for each acid and one for each base).
- 3. Hot plate, steam bath can be substituted.
- 4. pH meter equipped with combination electrode.
- 5. Balance, can be read to 0.01 g.

#### Procedure (from Sobek et al., 1978)

- 1. Place approximately 0.5 g of sample (less than 60 mesh) on a piece of aluminum foil.
- 2. Add one or two drops of 1:3 HCl to the sample. The presence of CaCO3 is indicated by a bubbling or audible "fizz."
- 3. Rate the bubbling or "fizz" in step 2 as indicated in Table 7-2.

| TABLE 7-2   Volumes and Normalities of Acid Addition for NP Determination Based on Fizz Rating (from Sobek et al., 1978) |               |                        |  |  |
|--|---------------|------------------------|--|--|
| Fizz Rating  | Add mL of HCL | Normality of Added HCl |  |  |
| None   | 20            | 0.1                    |  |  |
| Slight   | 40            | 0.1                    |  |  |
| Moderate   | 40            | 0.5                    |  |  |
| Strong -   | 80            | 0.5                    |  |  |

- 4. Weigh 2.00 g of sample (less than 60 mesh) into a 250 mL Erlenmeyer flask.
- 5. Carefully add HCl indicated by Table 7-2 into the flask containing sample.
- 6. Heat nearly to boiling, swirling flask every 5 minutes, until reaction is complete. NOTE: Reaction is complete when no gas evolution is visible and particles settle evenly over the bottom of the flask.

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- 7. Add distilled water to make a total volume of 125 mL.
- 8. Boil contents of flask for one minute and cool to slightly above room temperature. Cover tightly and cool to room temperature. CAUTION: Do not place rubber stopper in hot flask as it may implode upon cooling.
- 9. Titrate using 0.1 N NaOH or 0.5 N NaOH (concentration exactly known) to pH 7.0 using a pH meter and buret. The concentration of NaOH used in the titration should correspond to the concentration of the HCl used in No. 5 above. NOTE: Titrate with NaOH until a constant reading of pH 7.0 remains for at least 30 seconds.
- 10. If less than 3 mL of the NaOH is required to obtain a pH of 7.0, it is likely that the HCl added was not sufficient to neutralize all of the base present in the 2.00 g sample. A duplicate sample should be run using the next higher volume or concentration of acid as indicated in Table 7-1.
- 11. Run a blank for each volume or normality of acid using steps 5, 7, 8, and 9 above.

## Calculations (from Sobek et al., 1978)

- 1. Constant (C) = (mL acid in blank) / (mL base in blank).
- 2. mL acid consumed = (mL acid added) (mL base added multiplied by C).
- 3. Neutralization Potential (as t CaCO3 equivalent/1000 t material) = (mL of acid consumed) \* (25.0) \* (N of acid).

#### Interpretation of Results

Effective Field-NP is a site-specific value, estimated through static and kinetic tests as explained above and in Chapters 8 and 10. Nevertheless, some general interpretation guidelines are available.

- 1. All Lab-NP procedures underestimate Field-NP where aluminosilicate minerals are sufficiently reactive and alone provide effective neutralization (Morin and Hutt, 1994 and 1997). In these cases, NP should be calculated from whole-rock (Section 7.2), multi-element (Section 7.3) and mineralogical (Section 7.10) data.
- 2. For carbonate systems, studies in British Columbia have shown that the NP method of Sobek et al. (1978) may slightly overestimate Field-NP (e.g. Minesite Drainage Assessment Group, 1996).

## 7.7.3 Carbonate Neutralization Potential

The second recommended Lab-NP determination is based on a measurement of inorganic carbon. The resulting calculation of Carbonate Neutralization Potential (Carb-NP) is a measure of the maximum theoretical neutralization capacity if all the carbonates reacted like calcite. This a useful measure, in part because carbonate minerals are a rapidly

available NP source, capable of matching the fastest rates of acid generation. However this generalization is only true of calcium and magnesium carbonates (Table 7-3).

When Fe and Mn carbonates weather, hydrolysis of the Fe and Mn creates acidity, so there is no net alkalinity generation. Also kinetic dissolution rates can be slow. The possible contribution of non-neutralizing Fe and Mn carbonate minerals, including commonly occurring minerals such as siderite and ankerite, must always be checked when Carb-NP is used. It should also be noted that Fe and Mn carbonate minerals can distort Sobek NP measurements (Lapakko, 1994).

| Table 7-3   Theoretical Compositions of Some Relevant Carbonate Minerals (taken from Jambor and Blowes, 1994) |                                     |                 |       |       |       |       |  |
|---|-------------------------------------|-----------------|-------|-------|-------|-------|--|
| Mineral   | Formula                             | CO <sub>2</sub> | CaO   | MgO   | FeO   | MnO   |  |
| Calcite   | CaCO <sub>3</sub>                   | 43.97           | 56.03 |       |       |       |  |
| Magnesite   | MgCO <sub>3</sub>                   | 52.19           |       | 47.81 |       |       |  |
| Siderite  | FeCO <sub>3</sub>                   | 37.99           |       |       | 62.01 |       |  |
| Rhodochrosite   | MnCO <sub>3</sub>                   | 38.29           |       |       |       | 61.71 |  |
| Dolomite  | $CaMg(CO_3)_2$                      | 47.73           | 30.41 | 21.86 |       |       |  |
| Ankerite  | CaFe(CO <sub>3</sub> ) <sub>2</sub> | 40.76           | 25.97 |       | 33.27 |       |  |
| 1:1   | $Ca(Mg,Fe)(CO_3)_2$                 | 43.97           | 28.01 | 10.07 | 17.95 |       |  |
| Kutnohornite  | $CaMn(CO_3)_2$                      | 40.93           | 26.08 |       |       | 32.99 |  |

Various procedures are available to measure inorganic carbon (inorganic-C). In organicfree samples, where all the carbon is inorganic, a total-C measure can be used to calculate the Carb-NP. This is the case for most bedrock and subsurface waste samples. However, organic-C is likely to occur in coal and other organic containing sedimentary rocks or as a result of plant and microflora growth. One of the easiest total-C procedures uses the same Leco equipment used for the analysis of sulphur (Section 7.6). If organic-C is present, either carbonate-C must be measured directly or organic-C must be determined separately as explained below and subtracted from the Leco total-C value.

#### Method

1. Obtain total carbon value from Leco equipment.

2a). If Leco total carbon is reported as %C:

Carb-NP (as t CaCO3 equivalent/1000 t sample) = (Leco %C) \* (100.09/12.01) \* (10). 2b).If Leco total carbon is reported as %CO2:

Carb-NP (as t CaCO3 equivalent/1000 t sample) = (Leco %C) \* (100.09/44.01) \* (10).

3. If there are other significant sources of non-carbonate carbon, an independent
determination of inorganic carbonate is required. This determination can be made in one of several ways:

- a) measurement of Leco total carbon before and after the bulk NP analysis (Section 7.7.2); the subtraction of the two values provides the amount of carbon dissolved by acid and assumed to be inorganic carbonate (should be confirmed by mineralogical examinations Section 7.10);
- b) dissolution of carbonate in acid within a sealed chamber, followed by analysis of the evolved gas by Gas Chromatography to determine the original, solid-phase carbonate content; or
- c) dissolution of carbonate in acid within a sealed chamber; the measurement of gaspressure increase will indicate the carbonate content after calibration of the chamber with known carbonate standards.

#### Interpretation of Results

A comparison of Carb-NP and bulk Sobek NP values can provide useful information about potential NP sources and the NP capacity of the carbonate minerals (Chapter 8). For example if Carb-NP is greater than the Sobek-NP, a measurable portion of the inorganic carbon is not generating alkalinity or is unreactive. This suggests either the presence of iron- or manganese-rich carbonates or, if a total carbon assay was used, the presence of organic matter. These possibilities should be evaluated before Carb-NP is used as a measure of the rapidly available neutralization capacity.

More Sobek-NP than Carb-NP in a sample indicates that there may be significant neutralization from non-carbonate minerals. Because of the potentially slow reaction rate and possibly multiple sources of aluminosilicate alkalinity, further work is required to determine the sources and their reactivity relative to the rate of acid generation, before it can be concluded that laboratory measured, non-carbonate NP will provide effective Field-NP.

One clue as to the alkalinity source may be the base cation released in humidity cell testing (Chapters 9 and 10).

Great care is required when working with rocks containing low AP and NP levels because minor variations can significantly alter the interpretation.

It bears repeating that effective Field-NP, like the field manifestation of many other static test measures, depends on mineral abundance and reaction rates and therefore the Field-NP prediction must include consideration of the mineralogy and the results of field and laboratory kinetic tests.

#### 7.8 pH

#### 7.8.1 Introduction

In addition to sulphur species (Section 7.6) and neutralization potential (Section 7.7), the measurement of sample pH has traditionally been a fundamental part of acid-base accounting (ABA). pH is a principal determinant of both primary mineral reaction rates and secondary mineral solubility, and therefore can have a large effect on drainage chemistry. For example, increases in the concentration of potentially biologic limiting trace metals such as Cu and Mo are often linked to pH changes, with Cu solubility increasing and Mo solubility decreasing as the pH decreases.

pH is a measure of the hydrogen ion activity of a solution, made with a combination pH electrode inserted in a test solution. Despite its simplicity and importance, the wrong test procedure is often used, the results are often misinterpreted and the descriptive terminology is imprecise or misleading.

The first considerations in pH analyses are the measurement objective and type. The objective in most waste characterization programs is to determine the resulting pH of the corresponding pore water. Measurements can be made:

- a) directly on the actual pore water,
- b) indirectly on down gradient seepage water, or
- c) on simulated pore water solutions artificially created by adding a solvent to a subsample of the material under investigation.

Both a) and b) are made in the field and are radically different parameters from c) which is generally a laboratory measurement.

Of the different procedures a) is the preferred option. However, in many cases direct pore water pH measurement is not logistically possible. For example in a waste rock dump, with hard coarse particles, there is usually no free water to sample and it is practically impossible to remove water under tension. Usually the only way to collect the actual pore water is with a lysimeter, an expensive, time consuming, disruptive procedure, which is usually not available.

The best available procedure for determining the approximate pore water pH is commonly a measurement made on a simulated pore water solution. In the simulation there are two major considerations:

- the quality and quantity of the solvent, and
- the origin and any pre-treatment of the sample.

Much of the current confusion and errors in the interpretation of laboratory pH data result

from the inaccurate descriptive terminology and from a failure to recognize that variations in pre-treatment and in the solvent can markedly change the parameter being measured.

pH values reported in ABA testwork are usually recorded as "paste pH" measurements. According to Sobek et al. (1978) and other standard texts (Page et al., 1982b), a paste pH measurement is made by inserting a combination electrode into a paste created from material that has a  $< 250 \mu m$  particle size. The solid:solution weight ratio is recommended to be 2:1. Alternatively, water may be added to bring the paste to "near saturation conditions" where water should not pond on the surface nor should dry material appear (Sobek et al., 1978).

Disadvantages with the Sobek paste pH procedure include:

- In some cases, solvent quantities may vary from the recommended 2:1 solid:solution ratio.
- If the paste is not thoroughly mixed, the procedure of inserting a combination pH electrode into the paste may put the electrode in contact with a limited number of particles. Depending on the heterogeneity and chemistry of the particles, the resulting pH measurement may not be reproducible and may not reflect the pH of the entire sample.
- If crushing the sample is not appropriate it may be difficult to find material which is  $< 250 \mu m$ . For example, the fine particles in waste rock are usually predominantly sand-sized and thus not conducive to paste formation.
- Rough and angular particles may scratch the electrode.

Although the ABA pH values reported by most laboratories are reported as paste pH, the procedure used usually contains two significant modifications:

- The analysis is carried out on a crushed sample, which is a necessity when the analysis is carried out on drill core, large rock fragments or if the sample does not naturally contain enough material with a particle size of  $< 250 \ \mu m$  (-60 mesh). Some laboratories may crush samples to as fine as  $< 100 \ \mu m$  (-100 mesh);
- The solid:solution ratio is increased to 1:1, allowing the electrode to measure the pH of the overlying supernatant. The increased solid:solution ratio allows the electrode to be immersed without contacting the charged solid particles.

With regards to estimating pore water pH, the main problem with the so-called paste pH is that crushing creates new surfaces, exposing minerals occluded from weathering processes, which can potentially alter the resulting measurement. While the creation of new surfaces is irrelevant for bulk ABA assays, it may have a large effect on a measurement like pH.

The pH of rock and overburden crushed underwater is called the abrasion pH: underwater crushing is used to dissipate any heat that may be produced. The results have been used as an indicator of mineralogy and previous weathering (Clarke, 1900; Stevens and Carron, 1948; Grant, 1969; Ferrari and Magaldi, 1983). The effect of crushing intensity on the quantity of

ions released and the resulting pH is also documented in the literature (Grant, 1969). Data from a number of British Columbia mine sites shows that the pH values of crushed > 19 mm waste rock material may be three to four units higher than that measured for an uncrushed, < 2 mm surface rinse pH measurement (Price and Kwong, 1997).

Preliminary conclusions that can be drawn from the above and from Price and Kwong (1997) include:

- As the term pH can refer to such drastically different parameters, any reporting of test results should specify laboratory test procedures, including any pre-test sample preparation or solvent additions.
- Crushed pH values (Section 7.8.2) vary according to the degree of weathering, particle size, the effects of mineral abrasion and the residual alkalinity.
- A < 2 mm size fraction, uncrushed, surface rinse pH (Section 7.8.3) is a recommended measurement for weathering studies and drainage chemistry predictions done on unconsolidated wastes.
- The laboratory pH measurement of a solid material like waste rock is in fact a measurement of the "associated" solution, and is strongly affected by the quantity and quality of the solvent, and by any pretreatment that affects surface quantity and quality. A field pH measurement of pore water or surface drainage is a radically different parameter from the laboratory measurement, and therefore not directly comparable.

In this manual, we are only going to concern ourselves with pH measurements made on air dried solid samples tested in the laboratory. As described previously there are several considerations and interferences which may affect the final pH measurement:

- whether or not to crush the sample;
- the effect prior wetting and drying has on the sample;
- particle size considerations for unconsolidated samples;
- the solvent;
- the ratio of solid-to-solvent;
- amount of sample handling and preparation; and
- the geochemical effects of particle surfaces and aqueous diffusion rates on the combination pH electrode.

Due to various limitations, pH values cannot be detected to more significant figures than 0.2 to 0.5 pH units.

Two pH measurements are recommended for the laboratory pH procedures: first, a crushed pH used\_primarily for bedrock, drill core, minewalls, or other consolidated materials, and second, a surface rinse pH for waste rock, tailings, overburden, or other unconsolidated materials. In both cases, the recommended test procedure is to use distilled water as the solvent and a 1:1 weight ratio of solid to solvent weights.

The recommended procedure is to measure pH with a glass electrode and meter. The basic procedure for both crushed pH (Section 7.8.2) and surface rinse pH (Section 7.8.3) have been modified from Sobek et al. (1978), also known as the EPA-600 paste pH (below). Recommended modifications to the original procedure are in italics. Adaptations have also been taken from Page et al. (1982b).

# Measurement Methods (adapted from Sobek et al., 1978; recommended expansions and modifications in italics)

Care must be taken to insure electrode life and accurate pH measurements:

- 1. Electrode should not remain in the sample longer than necessary for a reading, especially if more alkaline than pH 9.0 or more acidic than pH 2.0.
- 2. Electrode should be washed with a jet of distilled water from a wash bottle after every measurement (sample or buffer solution).
- 3. Electrode should be dipped in dilute (0.1 N) hydrochloric acid for a few seconds and washed with distilled water to remove any calcium carbonate film which may form, especially from alkaline samples.
- 4. Drying out of the electrode should be avoided.
- 5. Electrode is cleaned and suspended in distilled water (which is protected from evaporation) for storage.
- 6. Place pH meter in standby position when electrode is not in a solution.

The pH meter and electrode should be standardized with buffers differing by 3 or 4 pH units, such as 7.0 and 4.0, before beginning a series of measurements. After every tenth measurement, recheck the standardization with both buffers. Care should be taken not to contaminate one buffer with the other buffer or with the test solution. Never return used standard buffers to their stock bottles.

#### Chemicals (from Sobek et al., 1978)

- 1. Standard buffer solutions, pH 4.00 and pH 7.00.
- 2. Distilled water (H2O).

#### Materials (from Sobek et al., 1978)

- 1. pH meter equipped with combination electrode.
- 2. Paper cups, 30 mL capacity.
- 3. Plastic cups.
- 4. Stirring rod.
- 5. Wash bottle containing distilled water.
- 6. Balance, can be read to 0.1 g.

# Procedure (1:1 Solid:Solution Ratio)

- 1. Turn on pH meter, adjust temperature setting and "zero" pH meter per instruction manual.
- 2. Place pH 4.0 and pH 7.0 standard buffers in two plastic cups (one buffer in each cup). NOTE: NEVER return used buffers to stock bottles.
- 3. Place electrode in the pH 7.0 buffer.
- 4. Adjust pH meter to read 7.0.
- 5. Remove electrode from buffer solution and wash with a jet of distilled water from a wash bottle.
- 6. Place electrode in the pH 4.0 buffer and check the pH reading. NOTE: If pH meter varies more than ±0.1 pH units from 4.0, something is wrong with the pH meter, electrode or buffers.

# Note: the following adapted from Page et al. (1982b).

- 7. Weight or measure 20g of air-dry test material and 20 mL of distilled water.
- 8. Mix thoroughly for 5 sec, preferably with a portable mechanical stirrer.
- 9. Let stand for 10 min.
- 10. Insert electrode(s) into the container, and stir the supernatant by swirling the electrodes slightly. Protect the electrodes taking care not to contact settled particles, moving the electrode carefully about to insure removal of water film around the electrode. Electrodes are easily scratched.
- 11. When reading remains constant, record pH and remove electrode from the supernatant. Carefully wash electrode with distilled water. If all pH measurements are completed, the electrode should be stored in a beaker of distilled water. NOTE: After every 10 samples, check meter calibration with standard buffers.

# 7.8.2 Crushed pH (Crushed Sample pH)

For crushed pH, the preceding procedure has an augmented sample preparation: pulverization of the whole sample to a < 100  $\mu$ m size or smaller. The method can be used on a wide range of materials (including waste rock and overburden). It is the only possible approach for bedrock, drill core or other consolidated sample materials. The prescribed sample comminution exposes and abrades previously occluded materials, creating fresh new surfaces that were not previously in contact with drainage. Differences in crushed sample pH can result from differences in:

- mineral alkalinity;
- base leaching and other weathering processes; and
- the size and quality of pre-pulverization surface area.

Although the data results from a slightly different procedure (underwater crushing), the abrasion pH data provided by Stevens and Carron (1948) indicates the pH of various crushed

#### minerals (Table 7-4).

| Table 7-4                              |  |                   |             |        |       |      |   |   |         |   |   |        |    |    |
|--|--|-------------------|-------------|--------|-------|------|---|---|---------|---|---|--------|----|----|
| Field Test for Minerals by Abrasion pH |  |                   |             |        |       |      |   |   |         |   |   |        |    |    |
|  | (Taken from Stevens and Carron, 1948)                                    |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Composition                            |  |                   | Abrasion pH |        |       |      |   |   |         |   |   |        |    |    |
| Mineral                                | Formula  | Type <sup>1</sup> |             |        | Ac    | idic |   |   | Neutral |   |   | lkalin | 1e |    |
|  |  |                   | 1           | 2      | 3     | 4    | 5 | 6 | 7       | 8 | 9 | 10     | 11 | 12 |
| Coquimbite                             | Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>1</sub> .9H <sub>2</sub> O       | b A               |             |        |       |      |   |   |         |   |   |        |    |    |
| Alunogen                               | Al <sub>2</sub> (SO <sub>4</sub> ) <sub>1</sub> ·16H <sub>2</sub> O      | b A               |             |        |       |      |   |   |         |   |   |        |    |    |
| Pickeringite                           | MgAl2(SO2)4-22H2O  | BbA               |             |        |       |      |   |   |         |   |   |        |    |    |
| Potash Alum                            | KAI(SO4)2-12H2O  | BbA               |             |        |       |      |   |   |         |   |   |        |    |    |
| Aluminite                              | Al,SO, 9H,O  | b A               |             |        |       |      |   | T |         |   |   |        |    |    |
| Scorodite                              | rodite FeAsO, 2H,O b A   |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Sessolite                              | solite H <sub>3</sub> BO <sub>3</sub> a                                  |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Jarosite                               | Disite $K_2Fe_4(OH)_{12}(SO_4)_4$ b a                                    |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Siderite                               | FeCO <sub>1</sub>  | ba                |             |        |       |      |   |   |         |   |   |        |    |    |
| Gypsum                                 | CaSO, 2H <sub>2</sub> O  | Ba                |             |        |       |      | T |   |         |   | 1 |        |    |    |
| Pyrophyillite                          | Al <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub>        | ba                |             |        |       |      |   |   |         |   |   |        |    |    |
| Quartz                                 | SiO,   | a                 |             |        |       |      |   |   |         |   |   |        |    |    |
| Gibbsite                               | Al(OH),  | b                 |             |        |       |      |   |   |         |   | I |        |    |    |
| Andalusite                             | Al <sub>2</sub> SiO <sub>5</sub>   | ba                |             |        |       |      |   | Ι |         |   |   |        |    |    |
| Muscovite                              | KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>       | Bba               |             |        |       |      | ŀ |   |         |   |   |        |    |    |
| Calcite                                | CaCO,  | Ba                |             |        |       |      |   | Ι |         |   |   |        |    |    |
| Anorthite                              | CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>                         | Bba               |             |        |       |      |   |   |         |   |   |        |    |    |
| Microcline                             | KAlSi <sub>1</sub> O <sub>2</sub>  | Bba               |             |        |       |      |   |   |         |   |   |        |    |    |
| Taic                                   | lc Mg <sub>1</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>2</sub> B a |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Albite                                 | ite NaAlSi,O <sub>a</sub> Bba  |                   |             |        |       |      |   |   |         |   |   |        |    |    |
| Dolomite                               | CaMg(CO <sub>3</sub> ) <sub>2</sub>                                      | BBa               |             |        |       |      |   |   |         |   |   |        |    |    |
| Borax                                  | Na, B, O, 10H, O   | Ba                |             |        |       | · ·  |   |   |         |   |   |        |    |    |
| Phlogopite                             | KMg,AlSi,O <sub>10</sub> (OH),   | BBba              |             |        |       |      |   | Ι | Ι       |   |   |        |    |    |
| Magnesite                              | MgCO <sub>1</sub>  | Ba                |             |        |       | Ι    | Γ | Γ | Ι       |   | T |        |    |    |
| Brucite                                | Mg(OH) <sub>2</sub>  | В                 |             |        |       |      |   |   |         |   | Ι |        |    |    |
| Merwinite                              | Ca <sub>3</sub> Mg(SiO <sub>4</sub> ) <sub>2</sub>                       | BBa               |             |        |       |      |   |   |         |   |   |        |    |    |
| Shertite                               | $Na_2Ca_2(CO_1)$   | BBa               |             |        |       |      |   |   |         |   |   | Τ      |    |    |
| <sup>1</sup> A = strong ad             | id B = strong base   | a = weak a        | id I        | b = we | ak ba | se   | • |   |         |   |   |        |    |    |

#### 7.8.3 < 2 mm Surface Rinse pH (1:1 Rinse pH)

For this pH method, the procedure at the end of Section 7.8.1 is carried out on a dry sieve sorted < 2 mm particle size fraction (no particle comminution). The < 2 mm particle size fraction is considered to be representative of the fine particles, which due to their disproportionately greater surface area will determine the pore water chemistry. This type of pH measurement should be used for all unconsolidated materials. Crushed pH determinations (Section 7.8.2) should also be carried out on unconsolidated materials, such as waste rock, if additional information is required on the residual alkalinity within the particles.

#### 7.9 Particle-Size Analyses

#### 7.9.1 Introduction

Particle size distribution can play an important role in drainage chemistry prediction because of its effect on:

- mineral reactivity; and
- water and gas movement (Chapter 12).

The effect of particle size on mineral reactivity results from the relationship between particle size and grain exposure and exposed surface area. For example, in large particles (coarse fragments) most of the mineral grains are physically occluded and denied access to oxygen and water, and are thus unable to react. For many chemical processes, the larger the surface area the higher the reaction rates, and there is typically an exponential increase in mineral exposure (surface area) with a decrease in particle size. The particle size distribution may be especially critical if the relative proportions of critical minerals varies from the fine to the coarse sized particles.

Factors that will determine the particle size distribution and the proportion of fines in a waste rock dump include:

- features of the blast;
- methods of materials handling including deposition;
- the strength and competency of the rock; and
- weathering.

Compositional differences between particle-size fractions will result from:

- skewed or selective release of different primary minerals, as a result of their strength, cohesion and distribution in the original rock, during initial mining and from later weathering of coarser particles.
- weathering effects causing the preferential removal of primary minerals and the accumulation of secondary minerals and surface coatings in fine particle size fractions.
- grain size may provide a lower limit on the possible particle size in which a mineral may exist.

For example, a waste-rock boulder may contain a much higher concentration of hard minerals like quartz and K-feldspar, while softer minerals like calcite, gypsum and phyllosilicates are concentrated in the fine size fractions. In some cases it is the lack of the cohesiveness between grains that causes their preferential occurrence in the finer particle size fractions. Phenocrysts like quartz and K-feldspar will be largely absent from the < 50  $\mu$ m size fraction,

which will largely consist of softer, silt-size minerals like the phyllosilicates. The effect of softness, grain size and spatial distribution in the original rock may play a significant role in the eventual location and consequent differential reactivity of different sulphide minerals.

Particularly at metal mines, much of the waste rock remains isolated in competent, coarse fragments. Samples taken from existing waste dumps, should be sieved to permit separate analysis of the fine fraction (Section 6.7).

A more refined particle size separation can be used to calculate "geometric" surface areas for the entire sample based on the assumption that the surface area of each particle is proportional to the cube of its diameter/width (Sections 7.9.3 and 8.1.4). Surface-areadependent reaction rates for kinetic tests (Chapter 10) can then be calculated and scaled to fit other particle sizes.

It should be noted that the use of geometric surface areas for calculation of surface-area rates is prone to significant errors. Since mineral grains are rarely cubes and do not necessarily have smooth surfaces and regular shapes, the calculated geometric area may be anomalously low. Other, more direct methods like nitrogen-adsorption BET (which have their own problems) have shown that surface areas can be 100-1000 times higher than the geometric value. On the other hand, studies in British Columbia, particularly for Cinola Stage II studies, have shown that normalization of rates to geometric surface area lessens the discrepancies among samples.

Particle size separation can be divided into three procedures:

- dry sieving which can separate > 100 μm particle size fractions, and can therefore be used to separate stones (> 12 mm), gravel (2 12 mm), soil (< 2 mm) and sand (> 2 mm 50 μm) sized particles (Page et al., 1982a);
- wet sieving which is required to separate the silt and clay (< 50  $\mu$ m) sized particles from larger > 50  $\mu$ m particles; and
- differential liquid settling procedures to separate different < 50  $\mu$ m particle sizes, such as silt (2 50  $\mu$ m) and clay (< 2  $\mu$ m) -sized.

The procedure should be chosen according to the proposed use of the data. Methodology is provided here for the separation of:

- soil, gravel and stones; and
- sand from silt and clay.

In both procedures the particles are separated using a nest of sieves. The duration of sieving will depend, to a degree, on the sample size and the sensitivity of the particles to abrasion. Reducing the sample size is a preferred option to prolonged sieving. For similar weights, more time may be required for smaller particles because of the progressive reduction in the percentage of open area as the aperture size decreases. According to Allen (1981), for

routine control purposes the cut-off for machine sieving is recommended to be 20 minutes or a 1% per minute rate fall. Standardization of the procedure is crucial if one is to get reproducible results.

# 7.9.2 Separation of Soil, Gravel, and Small and Large Stone Size Fractions

# Materials

- 1. At least 500 g of air dried sample.
- 2. <sup>1</sup>/<sub>2</sub>", 11 mm and 2 mm diameter sieves; all screens should be stainless steel as brass sieves can cause trace element contamination.

# Method

- 1. Ensure that all screens to be used for samples that will be chemically analyzed are clean and made of stainless steel.
- 2. Prior to starting separation, record total weight of the sample and each of the screens.
- 3. Dry sieve for 5 to 20 minutes. Greater time periods may cause significant particle comminution and abrasion.
- 4. Record the resulting weights of each screen. Calculate the weights for each of the following size fractions:
  - $> \frac{1}{2}$ " large stones
  - <sup>1</sup>/<sub>2</sub>" 11 mm small stones
  - 2 11 mm gravel
  - < 2 mm soil

#### Additional Notes:

In strongly oxidized, calcareous or samples with a high organic content, smaller particles may be cemented or aggregated together. In these cases, a pretreatment will be required prior to sieving, at least for the soil and gravel fractions to remove the cement. However, it should be noted that chemical and/or physical pretreatment may alter the original sample by dissolution or destruction of some minerals (Page et al., 1982a).

Additional sieves may be added to avoid having excess material on the finer screens.

# 7.9.3 A More Refined Particle Size Separation for Surface Area Determinations

- 1. Ensure that all screens to be used for the testwork are clean and made of stainless steel.
- 2. Prior to starting separation, record total weight of the sample and each of the screens.
- 3. Wet screen the sample on a 400 mesh screen. If the sample is coarse, pass through a larger size screen(s) first and report its' screen diameter or mesh size. Retain the grains

passing through this fine screen for possible later sizing using an alternative method for fine silts and clays.

- 4. Filter and dry the two screen fractions. Flocculating the -400 mesh fraction will enhance the filtering.
- 5. Weigh and record the dry weight of the sands and finer material.
- 6. Weigh and record the weight of each screen then assemble the nest of screens required for the test. The mesh size and number of screens will be dependent upon the weight and coarseness of the sample. For example, a screen nest may start with the largest screen being 6 mesh or 8 mesh and the smallest screen being 200 to 400 mesh with up to 10 or 12 screens between. In addition to the sample size, weight and coarseness the number of screens used will be determine by the type of shaking apparatus available (i.e., how large a screen nest will fit on the shaking table).
- 7. Pour the sample onto the top screen and secure the lid. Sample size will be determined by the size of the sieve apparatus and the amount of the available sample/subsample.
- 8. Place the nest of screens onto the shaker and secure them to the machine. If grains agglomerate (clump), add water periodically or continuously.
- 9. Set timer to 20 minutes duration and turn on the machine.
- 10. At the end of the 20 minutes remove the screens. Weigh each of the screens and record the weights. If the contents are moist, dry and weigh. NOTE: drying, especially above 40°C, can change mineralogy.
- 11. Subtract the weight of each screen plus sample fraction (dry) from the original weight of that screen. Record each fraction weight on the screen analysis report.
- 12. Where assays or other analyses are required each fraction should be prepared as required. If no assays or analyses are required the fractions can be recombined and stored as one sample, or stored separately.

# 7.10 Mineralogical Examinations

#### 7.10.1 Introduction

Previously described static tests measuring parameters such as trace multi-elements (Section 7.3) and Carb-NP (Section 7.7) provide a measure of the concentrations of various elements in a sample or specific size fraction of the sample. They do not however identify the contributing minerals. This maybe a significant limitation for prediction because the mineralogical form(s) in which the elements occur in large part determine their contribution to drainage chemistry. For example, total iron identified by whole-rock analysis (Section 7.2) may occur in acid-generating pyrite, acid-neutralizing calcium-iron carbonate, and/or some form of iron oxide. Identification of the participating mineralogy is therefore necessary for interpreting kinetic test results and most other aspects involved in predicting drainage chemistry.

Minerals are frequently invoked as critical parameters controlling the type and rate of metal leaching. Yet despite an almost universal agreement about the importance of mineralogy

(e.g., Kwong, 1996; Kwong and Ferguson, 1997), it is property that is generally measured poorly, if at all, and almost never accurately quantified. This results in an often rudimentary assessment of the roles played by various minerals during chemical weathering.

Omissions in mineralogical measurement are due to a number of factors.

- a) While mineralogy is a single, simple word, it actually includes a wide range of factors and properties beyond the already very difficult task of assigning a mineral name; critical parameters include grain size, elemental composition and elemental distribution.
- b) Mineralogy terminology is often too imprecise for the purpose of metal leaching prediction. For example, the term "plagioclase" covers a range of minerals which differ greatly in their weathering capability and consequent effective Field-NP. Minerals can be very difficult to precisely identify.
- c) The available mineralogical procedures all have major flaws or limitations.
- d) More accurate and comprehensive methods are prohibitively expensive.
- e) Mineralogy is recognized as an independent field of science.

Although it is rarely investigated in any detail, mineralogy plays a large role in determining the rates of metal release, acid generation and neutralization, and is therefore required information for site-specific predictions of drainage chemistry.

#### 7.10.2 Visual Rock Description

The first comprehensive mineralogical information is usually obtained from drill logs (Chapter 4). This information is usually determined with the naked eye, and implicitly expressed in a rock name. While a rock name infers some mineralogical composition as well as textural information, the accompanying notes, should be consulted for a detailed description of the individual minerals within the specimen.

Geological descriptions based solely on visual examination of hand-specimens are often comprehensive. However, the procedure is subjective and the accuracy of identification depends largely on the practitioners' experience and familiarity with the local geology of the area hosting the specimen. If highly altered specimens are involved, correct rock identification is made even more difficult.

#### 7.10.3 Detailed Information Requirements

While it can provide a good start, the terminology and information resulting from a visual assessment is usually too vague and of uncertain accuracy for the prediction of drainage chemistry. Once the static testing starts, a more detailed and accurate enumeration of the component minerals is required to add important weathering information and to fill in any gaps in the initial characterization of geological materials (Chapter 4).

Suggested information requirements include:

- Identify the potential acidity and metal sources, with particular emphasis on sulphide minerals;
- Determine the potential contribution of barite to the sulphide-S measurement;
- Identify the potential neutralization sources, with particular emphasize on carbonate minerals, but also including any potentially significant slow alkalinity release aluminosilicate sources;
- Identify clay or carbonate (e.g., siderite and ankerite) minerals which contribute to the laboratory NP, but may not provide similar contributions in the field;
- Evaluate the potential for the most reactive acid generation and neutralization sources (carbonates and sulphides) to preferentially occur in the finer particle size fraction, where they can contribute to geochemical reactions, as opposed to large blocks, where they would be encapsulated and inert. This will involve consideration of the relative exposure of sulphides and carbonates along fracture planes;
- Identify any readily soluble constituents; and,
- Identify any mineralogical and rock fabric characteristics that will influence weathering.

The properties of interest will depend in part on the questions raised by other testwork and the specific conditions of each site, material and disposal option.

Some information will be available in existing drill logs, exploration reports, metallurgical testwork and academic geological publications, which should be analyzed prior to static testing. In most cases, it will be necessary to augment this information with prediction-specific detailed microscopic (petrographic, Section 7.10.4), submicroscopic (for example, SEM and XRD, Sections 7.10.5 and 7.10.6) and/or geochemical (including both major and trace elements, Sections 7.2, 7.3, and 7.10.7) analyses. Generally speaking, the more lines of evidence-available for consideration, the more accurate is the resultant mineral identification.

Inasmuch as the mineral constituents of a geologic sample ultimately determine its overall acid generation/neutralization potential (Kwong, 1993), an accurate measure of mineral abundance is essential in predicting the metal leaching potential of the sample or interpreting its ABA\_characteristics. The most common techniques to acquire mineral abundance data are petrographic analysis, XRD analysis and SEM.

#### 7.10.4 Petrographic Examination

A petrographic examination, traditionally the first method used for determining the mineralogical composition, is a microscopic examination of thin sections, thinly shaved, translucent slices of rock mounted on glass slides. Petrographic data can come from either a visual scan or a more tedious point-counting procedure. A visual scan can be relatively quick (30 minutes) and will provide information on the major and minor mineral phases, their shapes, grain size, spatial relationships and an estimate of their relative proportions.

Disadvantages of petrographic analysis are that:

- Subsampling errors may be large for sections made on coarse fragments and drill core.
- A thin section is very small and may not be representative.
- Minerals at levels less than roughly 0.5% will not normally be detected.
- Petrographic techniques cannot be used to detect features smaller than approximately 100 µm.
- Quantitative analysis is labour-intensive and the results are somewhat subjective.
- Incipient alteration of primary minerals may not be readily detected, leading to possible erroneous predictions with regard to the quantity of, and the minerals accountable for, the acid neutralization capacity in a test sample.
- Petrographic methods are limited in their ability to determine the precise elemental composition of minerals, which occur as solid solutions and whose composition can vary significantly from minesite to minesite. For example, petrographic methods cannot always distinguish different carbonate minerals.

Despite the disadvantages, petrographic examinations provide useful general information and it is generally recommended for a subset of representative samples, preferably those samples for which ABA and elemental data already exist.

Point counting can be used to make a more accurate estimate of mineral percentages. Given that this procedure is very time consuming and with the limitations listed above, point counting is better carried out using submicroscopic procedures like SEM and microprobe analysis.

#### 7.10.5 X-Ray Defraction

X-ray defraction (XRD) can be used for a general mineralogical assessment or to identify specific phyllosilicate minerals. Semi-quantitative mineralogical data can be derived through a direct of comparison of reflection peak sizes. More quantitative information is provided if the peaks heights are compared to internal/external standards or reduced according to the corresponding mineral's absorption characteristics. Unlike petrographic techniques, XRD detection is not limited to grains larger than 100  $\mu$ m.

Disadvantages with XRD are that it has a poor precision, it is unable to detect minor mineral constituents (those occurring in < 5 wt%), some minerals cannot be distinguished and mineral identification is often operator-dependent. For example, biotite may not be readily recognized in the XRD analyses mainly because of overlapping reflection peaks with those of illite/muscovite. Quantitative XRD analysis incorporating corrections for mineral absorption effects can be quite accurate but remains unable to detect minor mineral constituents. For ARD assessment purposes, semi-quantitative XRD analysis ranking minerals as major, minor or trace components does not lead to a more quantitative predictions.

XRD is not recommended for general mineral identification because of the problems with cost effective accuracy and precision.

# 7.10.6 Other Submicroscopic Procedures

More sophisticated investigative procedures can be used to identify fine-grained minerals, to describe small, potentially important, mineral alteration features and to identify the elemental composition of specific minerals. The general availability of SEM instrumentation makes point-counting using a SEM-EDX setup an increasingly attractive option, especially if it can be run automatically.

In addition to mineral identity and abundance, mineral grain size and composition are important factors that affect the reactivity of a mineral, and hence the subsequent acid generating and metal leaching rates. For example, some researchers have found that fine grained pyrite weathers twice as fast as coarse granular pyrite; Kwong (1993 and 1996) and Kwong and Lawrence (1994) have provided evidence that Co substituting for Fe in pyrite may retard the weathering rate of the acid-generating sulfide. Mineral grain size, morphology, and textural relationship with other co-existing minerals are usually assessed by petrographic analysis or scanning electron microscopy. Image analysis is becoming a popular way to render the same information (e.g. Kwong and Lawrence, 1994; Mountjoy, 1997). Detailed mineral composition data is most readily determined by electron-probe microanalysis (EPMA).

Due to the expense, submicroscopic analysis should be carried out on a small, carefully chosen, subset of samples.

# 7.10.7 Mineralogy Calculated From the Whole Rock Geochemical Data

The use of geochemical data can range from the "relatively" simple use of elemental data to predict the appropriate concentrations of individual minerals to a prediction of the theoretical mineral assemblage calculated using normative computer programs and all the element concentration data (Sections 7.2 and 7.3). Using optimization techniques and taking the

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observed mineral assemblages into consideration, recent research has improved the accuracy of the theoretical calculation of normative minerals based on whole rock geochemical data (e.g., de Caritat et al., 1994; Cheng and Sinclair, 1995). However, the computer codes produced thus far apply only to limited scenarios, typically in sulfide-deficient systems. Until more work is done on sulfide-rich systems, accurate prediction of mineralogy based on geochemical analyses for ARD assessments remains a novel idea with great potential for practical application.

While it does not yet support quantitative assessment, qualitative differences in critical major and minor minerals can often be detected in the geochemical data. The ideal situation is where there is only one source for a particular element. For example, the Pb concentration can usually be used to estimate the amount of galena. This procedure should be used with caution as many trace elements occur as a trace constituents in common minerals like pyrite. Submicroscopic techniques should be used to check assumptions regarding the composition of solid solution minerals or the mineral hosts for a particular element.

#### 7.10.8 Conclusion

Depending on the questions and the level of sophistication sought, different forms of mineralogical data may serve the purpose of an investigation. In the early stage of an exploration program, implicit mineralogical data based on rock classification may give a general idea of the overall susceptibility of the country rocks to acid generation or their capability to neutralize acid. Implicit mineralogical data in the form of a rock name may also be useful in selecting samples for more detailed analysis (Chapter 6).

More detailed mineralogical information derived from petrographic and submicroscopic analyses should be used to interpret ABA, elemental concentration and kinetic data. To accurately predict the weathering behaviour of a mineral, detailed EPMA data may be required. Until sulphide-rich systems are addressed, however, recasting of mineralogy from whole rock analyses remains a promising but unreliable tool.

Given the importance of mineralogical information in ARD assessment and the difficulty in acquiring accurate quantitative mineralogical data, careful planning is required to obtain useful information at a reasonable cost. As briefly mentioned above, the level of sophistication of the data required depends on the purpose of the investigation. Whereas there are currently no firm guidelines specifically requiring the acquisition of mineralogical data for ARD assessment, a better understanding of the acid generation/neutralization and metal leaching processes through the application of such data will facilitate devising more cost-effective preventive and/or mitigation measures for ARD problems.

Taking the above into consideration, a suggested cost-effective strategy for acquiring the necessary mineralogical data to support predictive testwork is as follows:

- 1. Comprehensive coverage can be provided by geochemical analysis, informed by a subset of petrographic and/or SEM analysis. If supported by mineralogical data, geochemical assays should permit the detection of pronounced mineralogical differences.
- 2. Conduct additional SEM-EDX analyses to fill in petrographic blind-spots and as a confirmation test for assumptions of geochemical composition.
- 3. Perform quantitative measurement of solid solution and trace contaminant mineral composition by EPMA only if more accurate mineral weathering rates constitute an essential component of the proposed ARD prevention/mitigation scheme.
- 4. Mineralogical and geochemical data are invariably collected during various stages of mineral exploration and in the metallurgical testwork; as it becomes available this information should be incorporated into the metal leaching prediction.

#### 8. PRESENTATION AND INTERPRETATION OF STATIC TEST DATA

#### 8.1 Calculated Parameters

The first phase in the interpretation of static test data is the calculation of a number of derived parameters:

- neutralization potential ratios;
- proportion of retained reaction products;
- surface area.

The default parameter used to calculate the AP (acid potential) of a sample is sulphide-S. AP is then used to calculate other ABA parameters. If sulphide-S is not available and total-S is used to calculate it, the acid potential of the sample it is known as TAP.

#### 8.1.1 Net Neutralization Potentials

Net Neutralization Potential (NNP) is a traditional part of acid-base accounting, like sulphur species (Section 7.6), neutralization potential (Section 7.7), and crushed/surface rinse pH (Sections 7.8). NNP is a calculated parameter and does not require any unique additional chemical analysis.

- 1. Obtain sulphide-S (%), and del-S (%) from Section 7.6.
- 2. Calculate:

Acid Potential (AP, as t  $CaCO_3/1000 t$ ) = (sulphide-S (%) + del-S (%))\* 31.25

- 3. Obtain Sobek NP and Carb-NP from Section 7.7.
- Calculate: NNP (NNP as t CaCO<sub>3</sub>/1000 t) = NP - AP Carbonate NNP (CNNP, as t CaCO<sub>3</sub>/1000 t) = Carb-NP - AP

The analysis for each of the different sulphur species is done on a separate sub-sample (Section 7.6). Different extraction methods are used on some of the sub-samples to differentiate between the sulphur species. After the tests have been completed, sometimes when sulphide-S, sulphate-S and organic-S are subtracted from total-S some of the sulphur is unaccounted for. In this case a del-S is reported, and in the calculation of AP is assumed to be sulphide-S.

If there is no sulphide-S, sulphate-S and organic-S data available, or no sulphate-S and organic-S in the sample, total-S may be used in place of sulphide-S. If total-S is used the calculations will be:

1. Obtain total-S (%) from Section 7.6.

- 2. Calculate: Total Acid Potential (TAP, as t CaCO<sub>3</sub>/1000 t) = total-S (%) \* 31.25
- 3. Obtain Sobek NP and Carb-NP from Section 7.7.
- Calculate: Total NNP (TNNP, as t CaCO<sub>3</sub>/1000 t) = NP - TAP Carbonate TNNP (CTNNP, as t CaCO<sub>3</sub>/1000 t) = Carb-NP - TAP

# 8.1.2 Net Potential Ratios

Net Potential Ratio (NPR) is a part of acid-base accounting that is calculated and does not require any unique chemical analysis. Because it provides a measure of the proportions of NP and AP, the NPR criteria can be used over the wide range of AP values. Consequently the NPR rather than the NNP is to be used for operationally identifying and separating potentially acid generating (PAG) materials, and as screening criteria in the early phases of the prediction program (see Section 8.3.4).

- 1. Obtain sulphide-S (%) and del-S (%) from Section 7.6.
- Calculate: Acid Potential (AP, as t CaCO<sub>3</sub>/1000 t) = (sulphide-S (%) + del-S (%))\* 31.25
- 3. Obtain Sobek NP and Carb-NP from Section 7.7.
- Calculate: NPR (NPR, dimensionless) = Sobek NP / AP Carbonate NPR (CNPR, dimensionless) = Carb-NP / AP

If there is no sulphide-S, sulphate-S and organic-S data available, or no sulphate-S and organic-S in the sample, total-S may be used in place of sulphide-S. If total-S is used the calculations will be:

- 1. Obtain total-S (%) from Section 7.6.
- 2. Calculate: Total Acid Potential (TAP, as t CaCO<sub>3</sub>/1000 t) = total-S (%) \* 31.25
- 3. Obtain Sobek NP and Carb-NP from Section 7.7.
- Calculate: Total NPR (TNPR, dimensionless) = Sobek NP / TAP Carbonate TNPR (CTNPR, dimensionless) = Carb-NP / TAP

# 8.1.3 Proportion of Soluble Constituents

The interpretation of soluble-constituent static tests (Section 7.4) involves the calculation of the weight of a soluble-constituent in the sample and its comparison to the total amount (Sections 7.2 and 7.3) in the sample.

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Soluble-Constituent Amount (e.g., mg Cu/kg) = Concentration (e.g., mg Cu/L) \* Water Volume (L) / Weight of Sample (kg)

Percentage of Total Amount of Soluble-Constituent = (Surface-Retained Amount / Total Amount) \* 100%

The percentage of soluble-constituents can be used to estimate metal loadings and the drainage chemistry resulting from thorough rinsing by precipitation or after submergence. The information is also useful for interpreting the early weeks of humidity cell tests during which most of the soluble components should be removed.

#### 8.1.4 Particle Surface Area

Particle-size analyses (Section 7.9) are reported in tabular form or graphically. For estimating surface area, the average weight, volume, and number of particles retained on each sieve is calculated. The average surface area for each particle is then estimated and summed. This provides the geometric surface area for the sample and on a per-kg basis. Equations for calculating geometric surface area are found in the textbooks addressing particle-size area, or free software like Grain 2.0 provides automatic calculations upon entry of sieve data.

#### 8.2 Data Presentation for Interpretation

The second step in the evaluation of static test data is the presentation of the information in a form that allows for proper interpretation. In most cases this requires data tabulation, calculation of descriptive statistics and plotting critical parameters. The calculated parameters should include means and various percentiles (Table 8-1). Tabulation and derivation of descriptive statistics should be done for each potentially unique geological unit and waste or exposure type (Table 8-2).

| Required Statistical                              | TABLE 8-1         Parameters for Static Tests (Sections 7.2 to 7.9) |
|---|---|
| Percentiles                                       | 10%, 50% (median), 90%  |
| Central Tendency - moments                        | arithmetic mean, arithmetic standard deviation <sup>1</sup>         |
| <sup>1</sup> if the distribution is not normal of | or log normal, other statistics should be used                      |

Arithmetic means and standard deviations are based on the assumption that data are distributed normally. This is not always the case. Therefore, the distribution of important static-test results should be displayed graphically. Based on the observed distribution, appropriate statistical summaries can be created and, if desired, percentages of statistical

populations within specified categories (e.g., NPR <1) can be estimated.

In addition to tabulation and the calculation of descriptive statistics, preliminary data evaluation requires the production of scatterplots which graphically illustrate the relationship between key parameters. Scatterplots of one parameter against another from whole-rock, multi-element, and acid-base accounting (ABA) analyses can reveal correlations, relationships and population differences not apparent in the statistical data. For example, a scatterplot of surface rinse pH vs. NP may reveal the amount of unreactive NP in weathered samples after the sample "goes acid", and a plot of iron vs. sulphide will show any additional amount of iron not accounted for by iron-sulphide minerals. Mineralogical examinations (Section 7.10) will also assist in these interpretations.

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Table 8-2 Bislictical Presentation of ABA Date

| Project:<br>Classic<br>Data:<br>Rock Type:<br>Comments: | Red Mou<br>Royal Oai<br>ABA Data<br>Marc Zon<br>Data taka<br>The cartific |       |          | P-91 LAC Minarab Manazan<br>a ABA analysis was 19-Hor-<br>on 20-Ost-90 by Dive Kann | dum from Dave Kann<br>90. cartificata number<br>eay, ho Bond Gold C | ndy lo Ge<br>Nadis - A | orga Hope.<br>PAI to Or<br>talyak was | -1046 PAL |                        |  |                    | Couver, B          | ų                    |              |     |  |  |                           |   |              |    |   |
|---|---|-------|----------|---|---|------------------------|---------------------------------------|-----------|------------------------|--|--------------------|--------------------|----------------------|--------------|-----|--|--|---------------------------|---|--------------|----|---|
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| 27806   | MC80-66   | Ξ     | 112.5    | Zana Mu   |   | 4.42                   |                                       |           | 0.00                   |  |                    | 8                  | 87                   |              | 2   | 1  |  |                           | ſ | 1            |    |   |
| 27606   | MC80-65   | 112.5 | T.       | Zone Mu   |   | 6.14                   |                                       | 2         | 0.000                  |  |                    | 101                | : 3                  |              | ; 3 | ģ  | . 10                                   |                           | a | Į            |    |   |
| 27622   | MC80-56   | 134.5 | ž        | Zane the  |   | 3.62                   |                                       | -         | 0.000                  |  |                    | 110                | Š                    |              | ğ   | ÷ ÷  |  |                           | 9 | 8            |    |   |
| 27623   | MC80-55   | ž     | 130.5    | Zone for  |   | 35                     |                                       | -         | 0000                   |  |                    | 123                | 2                    |              | 2   | 5  | _                                      |                           | 0 | 3            |    |   |
| 27629   | MC80-66   | 147   | 140.5    | Zuna Ma   |   | 1.06                   |                                       | -         | 0.000                  |  |                    | 8                  | 8                    |              | 8   | •  |  |                           | - | 3            |    |   |
| 27630   | MC80-55   | Ţ     | ğ        | Zone Mu   |   | 0.0                    |                                       | -         | 0.000                  |  |                    | 8                  | <b>8</b> 2           |              | 8   | 0  |  |                           | • | 2110         |    |   |
| 27637   | MC80-56   | ğ     | 100.5    | Zone Pe   |   | 0.19                   |                                       | -         | 0.000                  |  |                    | •                  | 1                    |              | 1   | 8  | _                                      |                           | ~ | 4816         |    |   |
| 27636   | MC80-55   | 160.5 | ä        | Zone the  |   | 0.36                   |                                       | -         | 0.000                  |  |                    | Ξ                  | ₿                    |              | Š   | 8  | -                                      |                           |   |              |    |   |
| 11106   | MC80-31   | 151.7 | ž        | Zone Nv   |   | 24                     |                                       | -         | 0.000                  |  |                    | 128                | 8                    |              | 8   | ?  |  |                           | 0 | 101          |    |   |
| 11106   | MC80-31   | Ş     | 154.5    | Zone Mu   |   | 24                     |                                       | ,         | 0.000                  |  |                    | 2                  | 8                    |              | 2   | ē  | •                                      |                           | 0 | 2047         |    |   |
| 11113   | MC80-31   | 6.6M  | ž        | Zame Nw   |   | 5.14                   |                                       | -         | 0.000                  |  |                    | 101                | ส                    |              | 2   | -12  | -                                      |                           | 0 | 2075         |    |   |
| 11114   | NC80-31   | ä     | 10.0     | Zone Pe   |   | 3.62                   |                                       | -         | 0.000                  |  |                    | 130                | 8                    |              | 8   | ŕ  | _                                      |                           | o | 2536         |    |   |
| 11267   | MC 80-32  | 101   | Ş        | Zone Ne   |   | 5.30                   |                                       | -         | 0.000                  |  |                    | ž                  | ñ                    |              | ñ   | Ę.   | 5                                      |                           | 0 | Ĩ            |    |   |
| 11250   | MC 80-32  | 2     | ļ        | Zone Mer  |   | 341                    |                                       | -         | 0000                   |  |                    | 107                | 2                    |              | 8   | 5 <u>7</u> -   |  |                           | G | 2808         |    |   |
| 11206   | MC 80-32  | R.    | 171      | Zana Mu   |   | 2.22                   |                                       | -         | 0.000                  |  |                    | 2                  | 8                    |              | 3   | Ę  | _                                      |                           | 0 | 3            |    |   |
| 11206   | MC 80-32  | 170.5 | 2        | Zione Pru   |   | 3.16                   |                                       | -         | 0.000                  |  |                    | 8                  | 2                    |              | 3   | Ť  |  |                           | 0 | 2005         |    |   |
| 200178  | MC 00-26  | 17    | 172.6    | Zone Me   |   | 6.11                   |                                       | -         | 0000                   |  |                    | ē                  | 2                    |              | 2   | 121-   |  |                           | 0 | 2087         |    |   |
| 200106  | MC 80-28  | 121   | ž        | Zena Ma   |   | 5.40                   |                                       | -         | 0000                   |  |                    | 171                | 4                    |              | 11  | 15   | •                                      |                           | 0 | C100         |    |   |
| 2002  |   |       | R        |   |   | 2                      |                                       | -         | 0000                   |  |                    | 3                  | 5                    |              | 5   | •  |  |                           | - | 1612         |    |   |
|   |   | R     | R        | ALL DATE  |   | Ŗ                      |                                       | -         | 0000                   |  |                    | ŧ                  | 72                   |              | 2   | 8  |  |                           | - | 200          |    |   |
|   |   |       | ₽į       | Zane hiv  |   | 2                      |                                       | -         | 0.000                  |  |                    | 5                  | 8                    |              | 8   | -12  | _                                      |                           | 0 | 7833         |    |   |
|   | MC 80-30  | 5     | 11.6     | Zane Mu   |   | 3                      |                                       | 2         | 000                    |  |                    | ą                  | 8                    |              | 8   | Ļ  | •                                      |                           | 0 | 1000<br>1000 |    |   |
| 31021   | MC 80-36  | 211.5 | 2        |   |   | 7.16                   |                                       |           | 0.000                  |  |                    | ន                  | =                    |              | Ξ   | 21   | ~                                      |                           | 0 | 7040         |    |   |
| 31022   | MC 90-36  | 22    | 214.5    |   |   | 9.3                    |                                       |           | 0.000                  |  |                    | ã                  | 11                   |              | 11  | , and a second s | -                                      |                           | 0 |              |    |   |
| 13077   | MC 80-43  | ŝ     |          | Zana Inv  |   | 8                      |                                       |           | 0.000                  |  |                    | ž                  | 114                  |              | 11  | Ŗ  |  |                           | 0 | 012          |    |   |
| 13078   | NC 81-43  | E.    | <u> </u> | Zana Mu   |   | 89                     |                                       | -         | 0000                   |  |                    | ŝ                  | 78                   |              | 2   | 0  |  |                           | o | 8            |    |   |
|   | 2100 CM   |       |          | Zana (w   |   | 12.63                  |                                       |           | 000.0                  |  |                    | ą                  | 8                    |              | ង   | 5  |  |                           | Ó | 1990         |    |   |

1100 0 0.0410 0.007 0.0047 0.0470 0.0440 0.1080 0.1080 0.1080 0.2510 0.1122 İ 0 05314 8 8942 0 4605 0 00171 - 00689 0 0098 0 0 1518 0 7728 0 1128 0 0 13428 1 7728 0 1283 0 0 0000 0 0 1728 0 00148 0 0 0000 0 0 1157 0 0 00148 0 1 157 8 0 2481 0 1 157 9 11 0.0734 0.0304 0.0308 0.0419 0.0569 0.0569 0.0419 0.0569 0.0548 0.0419 0.0561 0.0553 0.0149 0.2564 0.2564 0.1119 0.116 0.5227 0.4665 0.5110 0.5229 0.4665 0 1302 0.1206 0.1120 0.0171 0.0170 0.0173 And the detection 29 <u>29 25 29 29 29</u> 919 191 ŧ **888**55585 Ĭ ÷ \*\* . . 拦걸걸쳤음ㅎㅎㅎㅎ -141 -174 8 등 두 별 않 은 ~ 8 ŝ 9 F -----~ = = = 3 2 • : アッセン • ⊼= 400000 . 0 0 4 0 1 - 0 0 0 - - - -2 • ¥ & = # 8 # 5 NPR = Sobel AP / AP TNPR = Sobel AP / TAP CNPR = CarbAP / AP CTNPR = CarbAP / AP 2822886528 ğ ~ <u>5</u> 8 8 <u>5</u> 2 8 38 3 82826283 Ş ğ ē 800 0.798 0.246 0.112 0.112 0.112 0.112 0.124 0.124 0.124 0.124 0.124 0.058 0.110 0.00 0.005 0.005 0.005 11 8.8 8.0 44585854 44585854 5 5 5.16 NNP = Sobei: NP - AP TNNP = Sobei: NP - TAP CNNP = Carb-NP - AP CTNNP = Carb-NP - TAP 8 5 8 5 5.10 -----5 3 8 19 7 8 8 T 53= Indergraund mine wat but sample, With ore zone in creasout is hanging at contact. Light grey with indexind Å 8 855 AP = %S (Sumde + dei) \* 31 25 TAP = %S (Totei) \* 31 25 Carb-NP = (% CO2 / 44 01) \* 100 09 \* 10 288885 1388 MC 80-43 A8A-010 MC 80-43 A8A-017 MC 96-08 A8A-021 MC 96-55 A8A-020 MC 90-55 A8A-030 MC 90-55 MC 90-23 166-172 MC 90-23 MC 90-23 166-172 MC 90-23 MC 90-23 166-172 MC 90-23 Crystal Tuff On AL PAR Mudmun Mutum Mutum 10 Percento 00 Percento Court

The required plots will depend on the site and the prediction questions. However, there are some ABA scatterplots that are almost always required and usually should be reported (Table 8-3), while others can be helpful to interpretations and should be checked.

| Ge                                 | nerically Required  | TABLE 8-3<br>Scatterplots for Acid-Base Accounting   |
|------------------------------------|---------------------|--|
| Parameter #1                       | vs. Parameter #2    | Potential Purpose  |
| < 2 mm Surface<br>Rinse pH         | Crushed pH          | comparison of pH methods   |
| Total Sulphur                      | Sulphide            | portion of total sulphur comprised of sulphide;<br>implications of substituting total sulphur for sulphide |
|                                    | Sulphate (optional) | portion of total sulphur comprised of sulphate;<br>relationship of sulphate to total sulphur               |
| Sulphide                           | Sulphate            | oxidative relationship of sulphide to sulphate   |
| •                                  | pH'                 | correlation showing any control by sulphide (for weathered materials only)                                 |
| Sobek NP<br>(Carb-NP) <sup>2</sup> | Carb-NP             | portion of NP comprised of carbonate minerals;<br>general reactivity of carbonate minerals                 |
|                                    | pH1                 | correlation showing any control by NP; estimation of<br>unavailable NP (for weathered materials only)      |
|                                    | NPR                 | available NP in samples with high PAG  |
|                                    | Sulphide            | balance between AP and NP  |
|                                    | Particle Size       | for weathered samples shows the contribution of various particle sizes and possible occlusion              |
| NPR                                | NNP                 | relationship of two bulk-balance parameters;<br>substitution of one parameter for another                  |
|                                    | pH <sup>1</sup>     | preliminary adherence to critical NPR values based<br>on pH (for weathered materials only)                 |
| <sup>1</sup> The use of both       | < 2 mm surface rins | se pH and crushed pH should be reviewed.   |
| <sup>2</sup> The use of both       | Sobek-NP or Carb-   | NP should be reviewed.   |

The tabulated raw data scatterplots and descriptive statistics should be examined to:

- determine which if any trace elements occur in anomalous amounts;
- evaluate the ABA data to determine which measurements most effectively describe the AP and NP;
- compare descriptive statistics with ABA screening criteria to provide an initial assessment of the ARD potential for 10%, median, and 90% of the samples in each category.
- identify any anomalous sample or sub group of samples whose performance may

significantly differ from or alter that of the group, and determine whether these materials can be "treated" separately.

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It should be noted that pertinent geological location and sample type information is required to carry out the latter. Where possible the data for sample groups whose spatial occurrence, ore grade, and static test parameters suggest they can treated alike should be combined. Examples of scatterplots and the resulting data interpretation for mines and mining projects in British Columbia are shown in Figure 8-1 through 8-10.







Figure 8-2 Scatterplots of Total Sulphur vs. Sulphate Sulphur from B.C. Mines



Figure 8-3 Scatterplots of Total/Sulphide Sulphur vs. Crushed pH from B.C. Mines



Figure 8-4 Scatterplots of Sobek-NP vs. Crushed pH from B.C. Mines



Figure 8-5 Scatterplots of Sobek-NP vs. Carb-NP from B.C. Mines



Figure 8-6 Scatterplots of xNNP vs. Crushed pH from B.C. Mines



Figure 8-7 Scatterplots of xNPR vs. Crushed pH from B.C. Mines







Figure 8-9 Scatterplots of xNPR vs. Total Sulphur and Sobek-NP from B.C. Mines



Figure 8-10 Scatterplots of xNPR vs. xNNP from B.C. Mines

#### 8.3 Static Test Screening Criteria

#### 8.3.1 Introduction

The information derived from recommended static tests, in conjunction with previous experience, can form the basis for preliminary estimates of metal leaching or the ARD potential. Static test screening criteria can be very useful for identifying materials with no ARD potential or elements of little concern. However, the reader is cautioned that given the present ignorance regarding rock and mineral reactivity, and the lack of detailed historic site characterization and monitoring, static test criteria are coarse and conservative.

#### 8.3.2 Total Concentration of Trace Elements

All materials impacted by the mine should be screened using the multi-element analytical techniques (Sections 7.2 and 7.3).

Determination of which trace elements occur in high concentrations can be made by comparing the results with the normal range of concentrations found in rock and soil (Appendix 3).

Obviously total concentrations provide no information about the form in which the elements exist and therefore are not to be taken as a measure of their threat to the environment. In some cases the mineral source will be inert or only sparingly soluble. Where elements are present in high concentrations, further testing and analysis should be done to determine the mineral source(s), the potential rates of release and the environmental significance.

## 8.3.3 Concentration of Soluble Constituents

In the absence of site specific objectives, elements of greatest concern can be identified by comparing the shake flask results with the discharge objectives reported in Table V of the provincial Pollution Control Objectives for the Mining, Smelting and Related Industries: Ministry of Environment, 1979 (Appendix 4). The determination of potential impact and a need for mitigation will depend on the site-specific conditions.

Because solubility is only a concern in a limited number of situations and due to the inherent high cost of testwork, solubility testing should be used selectively. The dissolution potential, and the consequent need for testing, should be determined from the initial characterization of geological materials, the sulphate content (ABA) and the results of petrographic examinations.

#### 8.3.4 Acid/Base Accounting (ABA) ARD Screening Criteria

- 1. No testing is required on unconsolidated materials such as glaciofluvial and fluvial deposits, derived from wide areas, and having little opportunity for either sulphide or trace element concentration or deposition.
- 2. Materials with a sulphide-S content less than 0.3 % and a subsoil pH greater than 5.5, require no further ARD testing and, if there is no other metal leaching concern, will be considered safe to excavate. A cutoff of 0.3% sulphide-S is appropriate for most geological conditions. The exceptions are where the rock matrix consists entirely of base poor minerals (for example, quartz and sericite, in pervasive phyllic alteration) or where the sulphide minerals contain heavy metals, such as As and Zn, which are soluble in weakly acidic leachate.

If the sulphide content is 0.3% or more, an ABA assessment is required. Due to the greater solubility of metals at low pH, if the pH is less than 5.5, a 24 hour shake flask extraction is required to determine the soluble metal content (see Analysis of Soluble Constituents, Section 7.4).

This abbreviated ABA screening criteria is intended for situations, like road construction in non-mineralized terrain, where there is no reason to expect a low NP or significant trace element release. Where materials are likely to be mineralized or hydrothermally

altered, a proponent is advised to carry out the full ABA/metal leaching analysis, and to use the NPR screening criteria listed in #3.

3. Where materials are mineralized, the full suite of ABA testing should be carried out. ARD Screening criteria based on the results of standard ABA test results are as follows:

|                      | Acid-Base Acc                 | Table 8-4<br>ounting (ABA) Screening Criteria   |
|----------------------|-------------------------------|---|
| Potential<br>for ARD | Initial Screening<br>Criteria | Comments  |
| Likely               | NPR < 1                       | likely ARD generating unless sulphide minerals are non-reactive   |
| Possibly             | 1 < NPR < 2                   | possibly ARD generating if NP is insufficiently reactive or is depleted at a faster rate than sulphides   |
| Low                  | NPR 2-4                       | not potentially ARD generating unless significant<br>preferential exposure of sulphides along fracture<br>planes, or extremely reactive sulphides in<br>combination with insufficiently reactive NP |
| None                 | NPR > 4                       |   |

The main conclusion to be drawn from the above is that samples with an NPR greater than 4 are judged to be of no ARD concern and no further ARD testwork is required, unless the materials are to be used as a source of alkalinity.

The ratio of 4:1 is a conservative screening criteria selected to ensure the detection of all sites where there is an unfavorable balance between acid generation and neutralization reactions or where the composition of the reactive fraction (for example, a waste rock's fine-sized fraction) varies significantly from the analysis of the entire sample. It is recognized that a 4:1 ratio is conservative and will be higher than the maximum NPR of acid drainage generating materials.

Without additional information, samples with an NPR less than 4 will be considered to have an uncertain ARD potential. Where the acid rock drainage potential of a waste material or geological unit is uncertain, it will be considered acid drainage generating until the prediction can be refined through further testing. The type and amount of additional testwork required for material will, to some degree, depend on the ARD potential. For example, the designation of low ARD potential NPR 2 to 4 will be changed from low to non-ARD

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generating when it is shown that either the sulphides will not be preferentially exposed or the NP is sufficiently reactive.

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It is cautioned that acid-base accounting on its own provides only a rough assessment of the potential for acid drainage. More accurate site and material-specific interpretation or testing should be used to develop less conservative, more refined materials handling criteria. Typically, the more refined NPR distinction between potentially and non-ARD generating materials is between 1 and 2. With very slowly reacting sulphides and significant slow release alkalinity, ARD may not occur in materials with an NPR less than one.

To date the only materials with an NPR greater than 2 reported to have produced ARD or NP/AP depletion rates that would result in ARD are field test pads (Ziemkiewicz and Meek, 1994) and other forms of testing (Morin and Hutt, 1993b). In other cases where ARD was initially ascribed to an NPR > 2 mine component, it was later discovered that the source was incorrectly characterized or it was a discrete portion that was NPR < 2 (for example, low grade ore in a generally benign waste rock dump), and the problem rests with characterization and material handling.

The present lack of documentation of NPR 2 - 4 materials producing ARD, is qualified by the understanding that there is a general lack of well characterized minesites in the range of NPR 1 to 4. The shortage of evidence and the hypothetical possibilities of chemically unreactive NP and of selective NP occlusion in coarse fragments detract from a blanket statement that ARD is impossible above an NPR of 2 or 3. The MRS therefore requires additional evidence to justify the use of less conservative NPR numbers.

The ABA screening criteria listed above apply to individual samples. The development of criteria for rock dumps containing a mix of potentially acid generating (PAG) and non-PAG waste is more difficult. Data for predicting acid drainage for mixed waste rock dumps are limited, especially for hard rock mines.

#### 9. KINETIC TESTS FOR AERIALLY EXPOSED MATERIALS

Kinetic information is a critical part of drainage chemistry prediction and kinetic testing is usually required for any project resulting in significant new exposure of potentially metal leaching rock. This chapter describes the recommended technique for laboratory and fieldbased kinetic tests. The recommended laboratory test for aerially exposed materials is a humidity cell. The recommended field-based procedures are on-site test pads, wall washing stations, and the monitoring of the actual dumps, pits, impoundments or underground workings.

## 9.1 Objectives and General Form

Kinetic tests provide a measure of the dynamic performance or "reactivity" of excavated and exposed materials. The previously described static tests (Chapters 7 and 8) such as acid-base accounting (ABA) provide data on the composition of the sample. Site specific kinetic information is required to show how that composition will perform.

The prediction information which kinetic testing is used to provide include:

- 1. The relative rates of acid generation and neutralization, which play a major role in determining the geochemical conditions, including whether the sample will go "acid".
- 2. The time to ARD onset, which determines how long a delay is permissible before prevention measures are required.
- 3. Drainage chemistry and the resulting downstream loadings for each of the probable geochemical conditions.

The items listed above can be estimated from measurements of the:

- Reactivity of acidity and metal sources, with particular emphasize on sulphide minerals.
- Reactivity of neutralizing minerals, particularly if non-carbonate minerals contribute critical NP.
- Probable geochemical conditions.
- Solubility of the released metals.

Unlike the relatively simple, single-analysis static tests, kinetic tests are complex procedures typically requiring:

- a) A field situation (weathering) and/or laboratory test procedures (simulated weathering) that illustrate or simulate one or more facets of the weathering of the test materials.
- b) Detailed pre-weathering characterization of the test material. This requires thorough static testing and is needed to determine:
- If the test sample is the appropriate test material;
- Possible mineral sources for critical components identified in the drainage. This information is required in part to ensure that the desired parameters are measured and to identify situations where a pretreatment may be required. Pretreatment may be required when one component or reaction may mask one of the critical features being measured, for example where gypsum or some other sulphate source masks sulphate release by sulphide oxidation;
- Differences between the test material and the actual mine component under investigation.
- c) A temporal monitoring regime showing the changes in composition as a result of weathering. Because test material sampling can be destructive to the test, monitoring usually consists of regular geochemical analysis of the drainage. Destructive sampling is usually not a concern in the monitoring of mine components.
- d) Post-weathering characterization of the test material, again requiring thorough static testing. A comparison with the results of the pre-test results can be used as a check on the results of (c). Testing should also be used to identify any (secondary) weathering products and to separate them from the unreacted initial or primary mineral content

Kinetic testing includes a variety of procedures, measuring quite distinct parameters. The tests are not interchangeable and one should be aware of the differences when selecting a test and interpreting the results. Test selection should be based on the information requirements, the site, the exposure environment and the specific materials being tested. One of the most critical aspects, and a common source of error when it is not recognized, is the distinction between tests designed to measure the primary weathering reactions and those designed to measure the drainage chemistry resulting from secondary mineral solubility.

#### 9.2 Possible Sources of Kinetic Information

Kinetic data may be obtained from a variety of sources including:

- Similar materials, at other similar sites, whose performance is already known.
- Talus (colluvial) soils and outcrops developed under similar climatic conditions on similar materials.
- Existing mine wastes, surfaces and seepage at the same site.
- Laboratory tests.
- Small field tests.

Often, there is no one piece of evidence or conclusive test, and the proponent must combine information from a variety of sources. For example, experience at other sites might be

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presented in combination with detailed geological data and laboratory kinetic test results that show that the rock or waste types are very similar. Usually static test data is used in conjunction with previous industry experience to make preliminary estimates of the potential for ARD and/or metal leaching. Given the present ignorance regarding the reactivity of rock, site-specific kinetic testwork are generally required to verify and refine these estimates. In all but the most exceptional circumstances, site-specific predictions require a complementary mix of static and kinetic test information.

Any kinetic test information presented for review should generally include:

- Detailed static test information showing that the test material has the same composition as the material it is purported to represent. Documentation will typically include the ABA, elemental and mineralogical data and for waste rock the properties that affect mineral exposure (e.g., composition relative to planes of weakness and occlusion in coarse fragments). This data should be used to select the test material.
- The identity of minerals contributing to the measured drainage chemistry, and evidence that the parameters measured are true indicators of the properties under investigation. In humidity cell testing, this should include data to support assumptions regarding the mineralogical origins of constituents like sulphate and base cations, the parameters which are used to estimate rates of acid generation and neutralization.
- Drainage concentration and flow data. The environmental impact of drainage chemistry will depend on downstream loadings and its effect on receiving water quality. Any drainage monitoring should therefore include a measure of the flow rate. This applies to laboratory tests as well as to field monitoring.
- Consideration of the possible differences between the test and the actual deposition, exposure and leaching conditions, including effects on mineral availability, reactivity, metal solubility and metal concentrations.

The onset of ARD is controlled by geochemical processes, such as calcite dissolution, which may take many years to complete. Consequently, both on the mine site and in testwork, the absence of acid conditions does not in itself prove that there will not be future ARD.

Laboratory kinetic tests will be empowered where it can be shown that the test results are correlated with field rates or that they simulate the actual balance of important processes, such as oxidation, dissolution and entrainment.

Depending upon the materials and site, it may be necessary to consider the effect of additions from biotic and climatic sources.

The major variables to be considered in test selection are:

- Whether the test occurs in the laboratory, at the minesite or at some other suitable field site. This is particularly critical for direct measurement of drainage chemistry and secondary mineral solubility.
- The scale of the test real or reduced. Size reduction will alter potentially influential factors such as heat conservation and drainage heterogeneity, and may preclude large particles from the test.
- Whether the test accelerates weathering processes.
- Whether the measurement objective is primary mineral weathering or secondary mineral solubility. Measurement of primary mineral weathering requires an action to remove the solubility constraints. Usually this is accomplished with aggressive leaching or flushing. Measurement of primary mineral weathering and secondary mineral solubility are mutually exclusive for obvious reasons.

Large disparities obviously exist between laboratory tests and those carried out at the minesite due to differences in sample preparation, climate conditions, sample size, limitations in scale and, in the case of waste rock, particle size. To distinguish the artificial nature of laboratory climate conditions, laboratory induced changes should be referred to as simulated weathering.

A synopsis of the test conditions for various kinetic tests is shown in Table 9-1. A comparison of the different procedures is provided in the subsequent sections.

| Table 9-1        A Synopsis of the Test Conditions for Various Kinetic Tests |   |                           |     |                                 |  |  |  |  |  |
|--|---|---------------------------|-----|---------------------------------|--|--|--|--|--|
| Test Procedure   | Test Procedure Field/Lab Scale Primary Weather Drainage Chemistry |                           |     |                                 |  |  |  |  |  |
| Humidity Cell  | Lab   | Bench, <6<br>mm particles | Yes | With MINTEQ<br>or site drainage |  |  |  |  |  |
| Column   | Lab   | Bench to<br>pilot         | No  | Yes                             |  |  |  |  |  |
| Soxhlet Extraction   | Lab   | Bench                     | Yes | No                              |  |  |  |  |  |
| Field Test Pads  | Field   | Pilot                     | No  | Yes                             |  |  |  |  |  |
| Wall Washing<br>Stations   | Field   | 1 m <sup>2</sup>          | Yes | With MINTEQ<br>or site drainage |  |  |  |  |  |
| Site Drainage  | Field   | Real                      | No  | Yes                             |  |  |  |  |  |

Three on-site procedures are recommended:

• pilot scale field test pads for waste rock and tailings;

- wall washing stations for mine walls;
- operational monitoring of the actual mine components.

The recommended procedure for measuring primary reaction rates is the humidity cell.

In an attempt to more accurately predict field weathering, some researchers have advocated using laboratory test apparatus that more closely mimic field conditions. Examples of this are the use of real precipitation rates and the use of bigger particles in column studies. Given the size and climate constraints of a laboratory, the laboratory and field conditions will always be markedly different. Clearly the best place to measure secondary mineral precipitation and dissolution is at the minesite, using the real climate and, in the case of waste rock, the real particle size distribution.

In some cases, column studies have been used to measure both the primary reaction rate and the results of secondary mineral precipitation and dissolution. One critical feature for any procedure measuring primary reaction rates is the requirement that all the reactants are in fact being measured. Without flushing out the products of weathering, it is impossible to measure the primary reaction rate. Primary reaction rates are required to predict the future balance of acid generating and neutralizing reactions, conditions which determine whether the material become acidic. With the present tools, measurements of primary reaction rates and secondary dissolution are mutually exclusive.

Trickle leach column tests have the following disadvantages:

- The primary weathering products may be retained and therefore leachate chemistry cannot be used as a measure of the relative rates of acid generation and neutralization, and of times to mineral depletion.
- They are run at the laboratory temperature often with a reduced particle size, and without seasonal variation and the extremes of both temperature and precipitation. Consequently, they provide poor analogues for heterogeneous drainage and the secondary mineral precipitation and dissolution, the controlling factors for metal leaching under all but the most acidic pH values.
- Without the entire load of primary weathering products, leachate results cannot be used either with MINTEQ to predict the extent of secondary precipitation or release, or with field data to predict metal leaching based on the predicted evolution in drainage chemistry (i.e. pH conditions).

For these reasons, laboratory columns are not recommended as a primary tool for the prediction of drainage chemistry. However, column studies may contribute useful drainage chemistry information if they simulate the critical geochemical conditions.

# 9.3 Humidity Cell Procedure

The humidity cell is the recommended kinetic test for predicting primary reaction rates under aerobic weathering conditions (Figures 9-1 and 9-2). The resulting data provides a measure of the rates of metal release, acid generation and acid neutralization under the geochemical conditions encountered in the test. Measured rates can be used to estimate the time to mineral exhaustion and the balance between the rates of acid generation and acid neutralization can be used to predict future geochemical conditions like pH, one of the critical information needs for setting site-specific waste disposal criteria (Chapters 7, 8, 10 and 11).

Although it is a secondary consideration, humidity cell results can also be used to crudely predict drainage chemistry. There are two possible approaches.

- a) When sufficient parameters are measured to permit geochemical modeling (Section 11.2) with programs such as MINTEQ, the primary humidity cell weathering data can be used to predict the resulting secondary precipitation products and their solubility. This procedure can be used prior to the availability of on-site tests and monitoring.
- b) Detailed site monitoring data showing metal concentrations for different pH conditions can be combined with geochemical conditions predicted by the humidity cell and flow rates calculated for different mine components (for example, Cu concentrations at different pH values, as discussed in Morin et al., 1995a and 1995b; Morin and Hutt, 1997) to predict loadings. This procedure for data analysis is discussed in greater detail in Section 11.1.

# Advantages of the Humidity Cell

- Well characterized test material.
- The consistent reproducible test conditions of humidity cell testing permit the comparison with results from other sites.
- Weekly flushing permits measurement of the primary reaction rates.

The statement that weekly flushing permits the measurement of primary reaction rates, which is the main reason for carrying out the procedure, should be qualified. Flushing will only remove those weathering products that are water soluble. The assumption that base cations and sulphate, which are the parameters used to determine the rates of acid generation and neutralization, are water soluble should be checked as part of the test.

# Simulated-Weathering in a Humidity Cell versus Weathering in the Field

- Logistically restricted to fine particles, typically less than 10 mm in diameter.
- Room temperature, a regular cycle of dry and humid air, and regular rinsing with distilled water.

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- No heterogeneity in leaching.
- No conservation of heat generated by oxidation.
- Minimal accumulation of soluble secondary weathering products.

Because of the differences noted above, the humidity cell procedure clearly does not simulate the precipitation and dissolution of secondary weathering products.

Laboratory conditions in tests like humidity cells may enhance or depress rates of sulphide oxidation, leaching rates and carbonate dissolution relative to field conditions. Some processes which can cause discrepancies between laboratory and field rates include:

- Differences in the accumulation of secondary minerals (e.g., Table 10-3).
- Pretreatment grinding and crushing may damage mineral grains, exposing soluble base cations and hydroxides, making the minerals more susceptible to weathering and creating additional neutralization potential compared to that operationally available. This is primarily a concern for waste rock and wall rock, where only a limited portion of the mass ends up in the fines. However, damaged, highly reactive grains normally dissolve within the first few weeks of testing. This accounts for the often observed peak concentrations in early weeks of leaching.
- For a similar mass of material, the portion able to contribute to drainage chemistry will be much larger in a crushed humidity cell sample than in the actual waste rock and pit walls. Consequently the available amount of sulphide-S and NP will be proportionally be much higher in the test sample.
- Pretreatment comminution does not discriminate between high and low strength portions of the rock. Consequently the fines in the test sample may include material that due to its physical stability would normally occur as coarse fragments or relatively unfractured mine walls, with its NP effectively inert. This may pose a prediction problem if the 'usually inert' material has a higher AP or NP content than the "real operational" fines.

#### The Procedure

The following description of the humidity cell procedure includes:

- the apparatus;
- an outline of the general procedure;
- sample preparation; and
- detailed descriptions of start-up, operating and closedown procedures.

This information follows to the original procedure of Sobek et al. (1978) with a minor modification to handle larger sample sizes.

#### Apparatus

The recommended humidity cell design is a plexiglass cylinder fitted with a base plate and equipped with a drain hole, a detachable lid and various other air and drainage ports. Approximately 2.5 cm (1 inch) from the bottom of the base plate is a removable perforated plate or screen which supports the sample. Filter materials such as polypropylene landscape fabric should be used to minimize the amount of fine particles passing through the perforated plate.

The size and shape of the humidity cell will depend on the particle size of the material being tested (e.g., waste rock versus tailings). If the sample consists of relatively porous material, predominantly sand and gravel sized particles, the humidity cell should be approximately 8 inches high and 4 inches wide (Figure 9-1). This tall slender humidity cell is typically used for waste rock samples which are crushed to approximately -6 mm (-¼ inch). If the sample consists of a material like tailings, with finer particles (approximately 150  $\mu$ m) and less permeability, a shorter, wider cell should be used to facilitate leaching and aeration (Figure 9-2).



Figure 9-1 Humidity Cell for Rock



Figure 9-2 Humidity Cell for Tailings

#### General Outline of the Procedure

One critical requirement for humidity cell testwork that is often, but should never be omitted, is the pre-test and post-test characterization of the original sample and the resulting residue. Analyses should include expanded ABA, strong acid digestion multi-element analysis by ICP, mineralogy, whole-rock major-element analysis and particle size (Chapter 7). This information is used to identify possible sources of element release and to calculate the rates and times to depletion for different minerals, elements, acidity and alkalinity sources. Posttest characterization is also required to identify any accumulated weathering products.

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Where a component of the pre-test composition will mask a significant weathering reaction, a pretreatment may be required to remove it. The most common example of this is where a sample contains a soluble sulphate mineral (e.g., gypsum) whose dissolution products cannot be distinguished from the sulphate released by sulphide oxidation and the calcium released from calcite.

After sample preparation and pre-test characterization, approximately 1 kg of the test sample (dry weight) is placed in the humidity cell and arranged so that it has a relatively flat surface. In the initial week (Week 0) the test sample is wetted and flushed/rinsed (Section 9.3.1). What follows is a repetitious, weekly cycle of dry air, humid air and flushing (Section 9.3.2). For the air treatments, air is continuously pumped into and through the cell. A dry-air manifold is required for the three-day-per-week dry-air treatment. A humidifier is required for the water-saturated air treatment.

The pattern of air flow differs between the tailings and waste-rock cells. This difference mirrors differences in field deposition and water-retention characteristics. Tailings are typically fine materials with a high moisture content and are usually placed as a slurry into an impoundment. Usually the only "fresh" air in constant contact with the tailings is that which passes over the top of the tailings mass. Subsequent air movement into the tailings is through diffusion, a slow process (Chapter 12) that limits the downward movement of oxygen. Waste rock, on the other hand, is usually coarser than tailings, and is placed in piles or dumps. The larger particle size allows for better drainage, more contact between the waste rock and air, and greater air circulation. As a result, air in a waste rock cell is introduced below the sample so that it can more freely circulate through it, while in a tailings cell air is passed over top of the sample.

One testing "cycle" takes place over seven days (Section 9.3.2). The first three days of the cycle is the "dry" portion during which filtered laboratory air is passed over a tailings sample or through a waste rock sample. The next three-day period is the "wet" portion of the testing cycle, when laboratory air is first pumped through a humidifier unit and then into a cell.

On the final day of the testing cycle, 500 mL of distilled/deionized water is added to the top of the cell and allowed to soak the sample for a specified period to dissolve the accumulated weathering products. Fine-grained samples should be gently stirred to ensure particle surfaces are rinsed. The rinse water is then drained for analysis. The purpose of the weekly rinse/flush is to wash out any weathering reaction products that have accumulated in the cell during the wet and dry segments of the cycle. The day after collecting the rinse/flush sample, another cycle is initiated with the introduction of dry air. A detailed description of the startup, operating and closedown procedures are presented below.

The weekly "leachate" or rinse water should be analysed for pH, sulphate, conductivity, acidity, alkalinity, and multi-element ICP analysis. Metal samples should be filtered to provide dissolved concentrations. From the analyses, leaching rates should be calculated, typically in units of mg of parameter/kg of sample/week (Table 10-1). Using pre-test static

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tests such as ABA and multi-element ICP analysis (Chapter 7), times to metal depletion can also be calculated.

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The duration of a humidity cell test is until the rates of sulphate generation and metal leaching have stabilized at relatively constant rates for at least five weeks. Experience in British Columbia shows that stabilization often takes 40 weeks, and can sometimes take over 60 weeks, and significant changes may take place even after several years. Therefore, the criteria on which to close down a cell depend on the site-specific objectives and the degree uncertainty in the predictions. Because of uncertainty and associated risks, some British Columbia mines have continued kinetic tests for up to five years (and some are still continuing).

# Sample Preparation

Sample preparation requirements depend on the specific material, site and depositional conditions. The main guideline is that the test material, particle size and mineral exposure should, to the extent possible, match the material that will react in the field. General recommendations for different materials are as follows:

- do not comminute existing fine-grained materials;
- for existing waste rock, use a particle size fraction representative of the "reactive material" (e.g., the < 2 mm fraction), which can be separated by sieving;
- for existing tailings use the entire sample;
- for bedrock or drill core samples of future waste rock use a total rock sample ground to 80% < 6 mm (< ¼ inch); and</li>
- for bedrock or drill core samples of future ore, use the entire rock sample ground to 80%
  < 6 mm to simulate ore stockpiles or < 150 μm to simulate tailings.</li>

# 9.3.1 Humidity Cell Startup Procedure

- 1. A minimum 2 kg of sample is required for humidity cell testing. Record sample information on a humidity cell pre-test sample information sheet (Figure 9-3).
- 2. The beginning of the humidity cell test program will be Week 0. Humidity cells are operated on a weekly cycle.
- 3. If the sample is rock, crush the sample as required above. If the sample is tailings, crushing is not required and the sample is normally tested as received.
- 4. Split out sufficient representative portions of the sample and send for all static tests discussed in Chapter 7. Record information on pre-test sample information sheet. Label these results "pre-test data".
- 5. Weigh 1000 g of sample, record the weight and carefully place in the appropriate humidity cell, either for waste rock or tailings (Figures 9-1 and 9-2). If the sample is moist, determine water content so a dry weight can be calculated. Ensure the sample has a relatively level surface in the cell.

# HUMIDITY CELL TESTING PROGRAM PRE-TEST DESCRIPTIVE SAMPLE INFORMATION SHEET

Company:

Project:

Sample Id.:

Sample Type (waste rock, tailings, etc.):

Sample Submission Date:

Submitted To:

Submitted By:

Sample Description (colour, smell, texture, size distribution, moisture content, etc.):

# Figure 9-3 Pre-Test Sample Description Form for Kinetic Samples

Procedures For Week 0

- 6. Clamp the drain hose at the bottom of the cell. Carefully add a known volume of demineralized/deionized water, approximately 750 mL, to the top of the humidity cell. Enough demineralized/deionized water should be added to the sample to thoroughly moisten the sample and allow for collection of at least 300-500 mL of leachate. Record the amount of water added on a weekly data sheet (Figure 9-4). Put a collection flask under the cell so that the hose drains into it. All of the sample must have good contact with the water, therefore gently agitate (gently stir so that all of the sample is in contact with water) fine, low permeability samples for about one minute.
- 7. Allow rock samples to soak for approximately 2 hour and tailings samples to soak for approximately 4 hours allowing dissolution reactions to occur and any suspended particles to settle. Disconnect the hose clamp and drain off the leachate into the collection flask. If the cell will not drain in a reasonable time (i.e. about an hour) check to see if the drainage hose is blocked. If the leachate still will not drain carefully decant the

leachate off the top of the sample. Record the volume of leachate collected (Figure 9-4).

| KINETIC TEST - WEEKLY DATA SHEET  |   |   |  |  |  |  |  |  |  |
|---|---|---|--|--|--|--|--|--|--|
| PROJECT: Mine A<br>CELL NO.: A-4<br>SAMPLE ID./DESCRIPTION: Sample 45964 (Dump #6 - Waste Rock) |   |   |  |  |  |  |  |  |  |
| Date  | Leachate<br>Volume<br>Added<br>(mL)   | Leachate<br>Volume<br>Recovered<br>(mL)   | рН   | Conductivity<br>(µS/cm)  | Humidifier<br>Water<br>Temp<br>(°C)  | Comments<br>/Analyst   |  |  |  |
| 12-Feb-96   | 750   | 430   | 6.68   | 425  | 30.5   | Filtered solids returned<br>to cell. Water drained<br>well. NH   |  |  |  |
| 19-F eb-96  | 500   | 427   | 6.96   | 505  | 30.5   | Filtered solids returned<br>to cell. Water drained<br>slowly. K M  |  |  |  |
| 26-F cb-96  | 500   | 471   | 7.21   | 311  | 30.5   | Filtered solids returned to cell. N H  |  |  |  |
|   | F: Mine A<br>D.: A-4<br>: ID./DESCR<br>Date<br>12-F eb-96<br>19-F eb-96<br>26-F eb-96 | F: Mine A      D: A-4      Date    Leachate      Volume      Added      (mL)      12-F eb-96    750      19-F eb-96    500      26-F eb-96    500 | KINETIC TE:      F: Mine A      D: A-4      : ID./DESCRIPTION: Sample 45964 (E      Date    Leachate      Volume    Volume      Added    Recovered      (mL)    12-F eb-96      19-F eb-96    500    427      26-F eb-96    500    471 | KINETIC TEST - WEE      F: Mine A      D: A-4      : ID./DESCRIPTION: Sample 45964 (Dump #6 -      Date    Leachate    Volume      Added    Recovered    pH      12-Feb-96    750    430    6.68      19-Feb-96    500    427    6.96      26-Feb-96    500    471    7.21 | KINETIC TEST - WEEKLY DATA SH      F: Mine A    Date    Leachate    Leachate    pH    Conductivity (μS/cm)      Date    Leachate    Volume    pH    Conductivity (μS/cm)      12-Feb-96    750    430    6.68    425      19-Feb-96    500    427    6.96    505      26-Feb-96    500    471    7.21    311 | KINETIC TEST - WEEKLY DATA SHEETI: Mine A<br>D: A-4<br>: ID./DESCRIPTION: Sample 45964 (Dump #6 - Waste Rock)DateLeachate<br>Volume<br>Added<br>(mL)pH<br>Volume<br>( $\mu$ S/cm)Conductivity<br>Water<br>Temp<br>(°C)12-Feb-967504306.6842530.519-Feb-965004276.9650530.526-Feb-965004717.2131130.5 |  |  |  |

Figure 9-4 Weekly Report Form for Humidity Cell Kinetic Testing

NOTE: if excess solids flow from the humidity cell with the leachate it may be necessary to filter the leachate, through coarse filter paper into a clean weighed filter flask. Transfer as much of the solids as possible from the collection flask to the filter apparatus by swirling before transferring. Weigh the filtrate plus the filter flask; record the weight. Record the volume of the filtrate. Keep a record of all weights and calculations.

- 8. Immediately filter the leachate through a 45 μm filter into a 500 mL polyethylene bottle ("raw") and a 100 mL polyethylene bottle acidified with HNO<sub>3</sub> to a pH < 1.5. Label the bottles with the project name, sample id., cycle number and date. Record all data for this initial rinse as Week or Cycle 0.
- 9. Place approximately 25 mL of the "raw" leachate in a 30 mL beaker and perform pH and conductivity measurements on the sample using calibrated instruments. Record all results. For all analyses keep a record of the instruments used, all QA/QC procedures, and any data resulting from calibration.
- 10. Submit the remaining "raw" leachate immediately for acidity, alkalinity and sulphate analysis. Submit the acidified sample for ICP metals. This suite of analyses is a standard request. Additional work may be required according to the sample and the type of information needed (i.e. some samples may require low level arsenic and/or mercury analyses, etc.).

11. Carefully scrape any residue in the filter apparatus back into the humidity cell. Place the filter paper on top of the humidity cell to dry ensuring it will not be disturbed. When the filter paper and residue have dried return any solids back to the humidity cell.

#### OA/OC Procedures for Week 0

- 12. Take a sample of the demineralized water used as humidity cell rinse water, and process through a blank cell. Handle and filter the sample as was done with the humidity cell leachate. Measure pH and conductivity in the sample. Label the sample "Method Blank" and submit it for analysis.
- 13. Take a sample of demineralized/deionized water used for leaching the cells (do not process in any way). Label it "Rinse Water" include the cycle/week number and date, and submit it for analysis.

# 9.3.2 Humidity Cell Weekly Operating Procedure

This procedure generally adheres to the objectives of Sobek et al. (1978), but is modified in places to allow for larger samples

- 1. For the first three days after the weekly rinse, dry air is pumped into the humidity cell. Connect the humidity cell to a dry air source, use a gentle flow rate to move the air through (waste rock) or over (tailings) the sample. If more than one humidity cell is running, splits can be taken from a main air line leading to each humidity cell. Use hose clamps to ensure that each cell receives roughly the same rate of air flow.
- 2. On the morning of the fourth day, a three day wet air cycle begins. Switch the air supply from a dry source to a humid one. Disconnect each humidity cell from the main dry air supply line. Connect each cell to a nipple on the humidifier. The humidifier should be roughly half full of water and contain an immersion heater which is set to 30 °C. The air from the main dry air supply is switched to pass through the humidifier unit. This air passes through the humidifier and exits from an aquarium-type diffuser. The air pressure is adjusted to provide an adequate air flow without causing rolling waves in the humidifier. Again, if more than one humidity cell is running, use hose clamps associated with each humidity cell to ensure that each cell receives roughly the same air flow rate.
- 3. On the seventh day, the rinsing and sampling procedures begin. Shut off the main air supply. Disconnect the air supply hose from each of the humidity cells and clamp shut.

NOTE: The waste rock cells have the air inlet at the bottom and will allow leach water to drain back into the humidifier if not clamped. Disconnect the immersion heater and record the water temperature and pH of each humidifier.

4. Ensure that the drain hose at the bottom of the cell is clamped. Place a clean 500 mL beaker under each cell with the hose draining into it. Carefully add 500 mL of demineralized/deionized water, to the top of each humidity cell. Record the amount of

water added. All of the samples must be in contact with the water, therefore gently agitate fine, low permeability samples for about one minute before and/or after the addition of water. Make note of how each cell is treated in the weekly records (Figure 9-4).

5. Allow rock samples to soak for approximately 2 hour and tailings samples to soak for approximately 4 hours to allow complete dissolution and any suspended particles to settle. Disconnect the hose clamp and drain off the leachate into the collection flask. If the cell will not drain in a reasonable time (i.e. about an hour) check to see if the drainage hose is blocked. If the leachate still will not drain carefully decant the leachate off the top of the sample. Record the volume of leachate collected.

NOTE: If excess solids flow from the humidity cell with the leachate it may be necessary to filter the leachate through coarse filter paper into a clean weighed filter flask. Transfer as much of the solids as possible from the collection flask to the filter apparatus by swirling before transferring. Weigh the filtrate plus the filter flask and record the weight. Record the volume of the filtrate. Keep a record of all weights and calculations. Return as much of the solid material as possible back into the humidity cell being careful not to cross-contaminate the material.

- 6. Immediately filter the leachate through a 45  $\mu$ m filter into two subsamples; a 500 mL polyethylene bottle ("raw") and a 100 mL polyethylene bottle acidified with HNO<sub>3</sub> to a pH < 1.5. Label the bottles with the project name, sample id., cycle number and date.
- 7. Place approximately 25 mL of the "raw" leachate in a 30 mL beaker and perform pH and conductivity measurements on the sample using calibrated instruments. Record all results. Keep a record of the instruments used, all QA/QC procedures and any data resulting from the calibration.
- 8. Submit the remaining "raw" leachate immediately for acidity, alkalinity and sulphate analysis. Send the acidified sample for ICP metals, and arsenic and mercury analysis if necessary. Laboratories will provide analysis of a standard suite of elements (usually approximately 32 elements) as a standard request and this should always be done. Additional assays may be added depending on the type of information needed (i.e., some samples may not require low level arsenic analysis, etc.).
- 9. Carefully scrape any residue in the filter apparatus back into the humidity cell taking care not to introduce contamination into the humidity cell. Place the filter paper on top of the humidity cell to dry, ensuring it will not be disturbed. When the filter paper and residue have dried, return any solids back to the humidity cell.

# OA/OC Procedures for Weekly Operation

- 10. Take a sample of the demineralized/deionized water used as humidity cell rinse water, and process through the blank cell. Handle and filter as was done with the humidity cell leachate. Measure pH and conductivity in the resulting leachate sample. Label the sample "Method Blank" and send it for analysis.
- 11. Take a sample of the demineralized water used for leaching the cells (do not process in

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any way). Label it "Rinse Water", include the cycle/week number and date, and submit it for analysis.

- 12. Humidifier maintenance: Humidifiers should be cleaned out every three months or if water appears turbid. Also replace tubing whenever necessary.
- 13. Interpretation of the results is discussed in Chapter 10.

# 9.3.3 Humidity Cell Closedown Procedure

- 1. When the cell has stabilized geochemically (Chapter 10), it can be terminated if desired. To allow a proper interpretation of the cell results, specific closedown sampling and analysis procedures must be carried out and included in data interpretation.
- 2. After the last cycle, rinse and collect leachate as per the humidity cell operational procedures (Section 9.3.2).

NOTE: The rinse from the last cycle must be submitted for the full suite of analysis.

- 3. Remove the sample from the test cell and place it into a clean 4 L polyethylene rotary jar. To ensure that the test cell has been thoroughly cleaned and all of the sample and its precipitates have been transferred to the rotary jar, use a known amount of demineralized/deionized water of known composition to wash the cell. Add enough additional demineralized/deionized water to the rotary jar so that a total of 3 L of demineralized/deionized water has been added.
- 4. Gently agitate the sample on a rotary extractor for a period of 24 hours. On completion of the 24 hour agitation, let the sample stand for a minimum of three hours allowing suspended materials to settle.
- 5. Collect the supernatant, recording its volume. Handle and prepare the sample in the same manner as was done during normal humidity cell operation. Label the sample "Final Leach" and submit it for leachate analysis.
- 6. Transfer the wet solid from the rotary jar to a pre-weighed drying tray, ensuring all the sample has been moved. Record the weight of the wet sample.
- 7. Air dry the wet sample, or dry in an oven on low heat (<40 °C) if necessary. Record the final weight of the dry sample. If sample was dried in an oven, cool in a desiccator prior to weighing.
- 8. Take a representative split from the sample and label it "Final Residue". Submit the split for all static tests defined in Chapter 7. These analyses will be known as "Post-Test Data".
- 9. Package the remaining sample, label it "Final Residue". Place it in cold storage for possible later examination.
- 10. Interpretation of the results is discussed in Chapter 10.

### 9.4 On-Site Field Tests and Monitoring

Because humidity cells are operated in a laboratory (Section 9.3), they are not subjected to annual patterns and climatic events that can occur at a minesite. On-site tests and monitoring provide for site specific verification and calibration of the generic humidity cell results, particularly with regards to the quality of drainage chemistry and the resulting metal leaching. Three procedures are recommended:

- pilot-scale kinetic test pads;
- wall washing stations; and
- monitoring of the actual mine components.

# 9.4.1 On-Site Pilot Scale Kinetic Test Pads

On-site field test pads (this section) and wall washing stations (Section 9.4.2) are a recommended field tool for keeping track of the drainage chemistry resulting from each different combination of mine waste and geological materials. Operating mines should construct on-site leach pads and wall washing stations and carry out ongoing monitoring.

Characteristics of field test pads include:

- fairly well characterized test material;
- some uncertainty regarding flow paths;
- real particle size distribution;
- natural weather conditions, air temperature, humidity, precipitation rate and quality;
- irregular, incomplete flushing, allowing accumulation of soluble secondary weathering products, permitting measurement of resulting drainage chemistry, but preventing measurement of primary reaction rates;
- irregular seepage impedes sample collection; and
- limited conservation of heat generated by oxidation.

# Field Test Pads as compared to Humidity Cells

- field-temperature and precipitation;
- natural variation and extremes in temperature and precipitation, including seasonal changes; and
- natural flushing/incomplete leaching allows accumulation of the soluble secondary weathering products stable under the given geochemical conditions; therefore permits measurement of drainage chemistry.

Field Test Pads as compared to Large Scale Dump or Impoundment

- permits drainage collection as compared to the diffuse drainage through a large waste rock dump;
- permits measurements to be made on a known composition and volume/mass of material as compared to heterogeneous waste rock dump where it is impossible to tell what portion contributes what to the eventual output;
- permits more detailed characterization; and
- may not simulate the large scale features of a large dump
  - ⇒ insulation from external temperature variations; importance on ARD weathering conditions unknown

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 $\Rightarrow$  particle size, mineralogy and drainage heterogeneity.

Experience in British Columbia with field test pads has shown that they can behave more or less like humidity cells (Section 9.3) or full-scale mine components (Section 9.4.4), depending on the volume of rock and the amount of precipitation (Norecol, Dames and Moore, 1994; Redfern Resources Ltd., 1997). Higher volumes of rock or proportionally less precipitation lead to significant geochemical retention typical of full-scale behaviour. Lower volume pads or proportionally more precipitation provide more complete rinsing of reaction products typical of humidity cells.

#### Method

- 1. Obtain or build a large container, open on top and with a basal drain hole. Some designs that have been used in British Columbia are:
  - a) portable drilling mud tanks that hold about 2 t;
  - b) V-shaped trenches lined with geotextile holding 20 t; and
  - c) above-ground wooden cribs holding over 100 t.

The important criteria are:

- a) the volume of rock is known;
- b) this volume is isolated from runoff and only exposed to precipitation; and
- c) all water passing through the rock is collected at one point.
- 2. Daily measurements of temperature ranges and precipitation are required from a nearby location.
- 3. Whenever a significant rainfall event occurs, a clean bucket should be placed at the discharge point to collect all water. After flow from the container ceases, retrieve the bucket, determine water volume and process the water for chemical analysis (filter, preserve, etc.).
- 4. Interpretation of the results is discussed in Chapter 10.

#### 9.4.2 Wall Washing Stations

This Minewall Procedure for using wall washing stations was developed in British Columbia for the B.C. AMD Task Force and the Canadian MEND Program. It has been used in British Columbia at Bell Mine, Island Copper Mine, Equity Silver Mine, Mt. Washington, the Tulsequah Chief Project, as well as at other sites in Mexico, the USA and Indonesia. Limitations of the procedure include the difficulties of setting up wall washing stations on fractured rock and in estimating the source area contribution of unseen fractures.

Small fractures may be sealed to prevent water loss, but to a large degree the requirement for water retention restricts testing to cohesive walls. Practitioners must therefore determine whether the sampling sites are representative of the weathering conditions in locations which cannot be tested. One possible means for collecting information from highly fractured zones is with complementary humidity cell testing of rock chips. Alternatively, a surface area correction may be applied to regular humidity cell test results.

Further information on the wall washing stations and the procedure for data analysis and interpretation may be obtained from the Minewall documentation (MEND, 1995). While still in its infancy, this procedure provides information that may not be obtained from other kinetic tests. As with any procedure its strength and weaknesses will become clearer as it is used at additional sites. Presently the test permits a very useful order of magnitude calculation of the contributions from possible contaminant sources.

#### Equipment (for each station)

- 1. 3 m of 90E-bent, flexible plastic bathtub edging
- 2. 2 tubes of pure silicon bathroom sealant (must be pure silicon)
- 3. 1 sheet of clear plastic 1 m by 1 m
- 4. 8 black metal clasps often used for holding unbound reports
- 5. 1 L of distilled water in a squeeze bottle which allows the direction and pressure of water to be controlled

Installation Procedure (see Figure 9-5)

- 1. Select a relatively flat surface of rock, preferably with no surface fractures, measuring no more than 1 m by 1 m.
- 2. Mark the intended perimeter of the station on the surface with a pencil, with three, four, or five limbs.
- 3. The lowest, or bottom, limb must slope downwards from horizontal so that all water caught on it will drain in one direction for collection and later analysis.
- 4. Cut the plastic edging to the length required for each limb.
- 5. Install each limb by using pure silicon sealant as glue.

- 6. Ensure silicon sealant fills all open spaces between the edging and the rock surface so that no water can pass through.
- 7. Ensure each limb overlaps so that no gaps exist at any junction.
- 8. Ensure the upper limb(s) will divert water around the sides of the station so that the water will not flow over the isolated area.
- 9. With 1 L of distilled water, wash the entire isolated surface within the edging, rinsing out any loose rock/dust and ensuring all water is caught by the edging and directed to the bottom limb where the water can then be caught in a bottle.
- 10. Cut the clear plastic sheet to extend 2 cm over each limb, then loosely attach the plastic sheet with the metal clasps, ensuring the plastic sheet does not touch the rock surface but prevents all precipitation or runoff from reaching the isolated rock surface.



Figure 9-5 Diagram of Minewall Station Assembly

#### Regular Sampling

1. Carefully remove the plastic sheet and place it somewhere clean and dry.

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- 2. Inspect the station for loose edging and broken seals against the rock; repair any problems AFTER sampling (below), but avoid losing rinse water through any broken seals.
- 3. Record a note if there is any condensation and if any water may have condensed and trickled out of the station between sampling events.
- 4. Place a calibrated collection bottle at the downstream (outflow) end of the lower limb (trough) to catch all subsequent rinse water.
- 5. With a calibrated squeeze bottle, spray at least 200 mL onto the isolated rock surface to rinse the entire area thoroughly; use as little water as possible; it is important to catch all rinse water in the collection bottle; record the volume of water sprayed on the rock.
- 6. Record the amount of water recovered in the collection bottle.
- 7. Analyze the water in the collection bottle like any other water sample. Measurement should include pH, acidity, alkalinity, sulfate, dissolved metals and total metals as desired.
- 8. As a quality-assurance procedure, for one round of sampling also filter a similar volume of the distilled water through a 0.45  $\mu$ m filter, then analyze like all other water samples.

Interpretations of Minewall Stations parallel those of humidity cells (Section 9.3), but rates are reported as mg/m<sup>2</sup>/wk, rather than mg/kg/wk as used in Table 10-1.

# 9.4.3 On-site Monitoring of Mine Components and the Resulting Drainage

Although it is usually not intended as such and is not commonly recognized as a kinetic test, on-site monitoring can provide very useful information about;

- the range of weathering,
- drainage chemistry under different geochemical conditions,
- trends in metal leaching over time,
- solubility constraints,
- fine particle replenishment, and
- the correlation of contaminants with diagnostic drainage parameters.

The accumulated operational drainage monitoring data collected over the life of a mine is often one of the main sources of prediction data consulted in the review of closure plans. Intermittent analysis of the solid phase of tailings and waste rock is required to verify premining predictions of the form and rate of weathering.

The main advantage in field monitoring is that the measurements are of the "real" weathering and drainage. Pilot scale and smaller testing precludes potentially significant factors such as the conservation of heat generated by oxidation in acidic dumps.

The primary disadvantages in field monitoring are that:

• The diagnostic ability is usually limited to the existing geochemical conditions.

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- It is often difficult to determine what portion of the whole has contributed to or is represented by the results.
- It is sometimes impossible to separate additional uncontrolled factors, such as the contribution of off-site groundwater discharge, which can distort the results.
- Natural conditions such as the wide particle size distribution of waste rock and the irregularity of natural weather conditions, air temperature, humidity, precipitation rate and quality will introduce variability that may be very costly to remove or impossible to account for.

Important features to consider in analysis of field monitoring results are that:

- There may be more than one source of drainage resulting in variable waste flushing and irregular dilution. All drainage sources should be identified prior to analysis. However some uncertainty may remain.
- One of the most difficult tasks in waste analysis is estimating what portion of the whole a particular sample or analysis result represents. Given the complexity, the contributing (test) materials are never going to be completely characterized.
- The flow path through mine wastes are uncertain and there is therefore some uncertainty regarding which portion of whole contribute to the drainage chemistry.
- Irregular, incomplete flushing, will result in the accumulation of soluble secondary weathering products.
- Irregular leaching may impede drainage collection.

Both the drainage and the solid phase should be monitored. Drainage monitoring is facilitated by the drainage collection required whenever there is a potential for significant metal leaching from a particular mine component. Several valuable observations on the range in contaminant concentration, the regularity of annual chemical cycles, and the application of humidity cells for predictions have been gained from the drainage monitoring at Bell and Island Copper Mines with up to 25 years of drainage monitoring results (Morin et. al. 1995a, 1995b, 1994, 1993). Any and all water-chemistry data should be regularly compiled into spreadsheets and regularly examined for trends and revisions of predictions. The procedure for data interpretation is discussed further in Chapter 11.

In addition to drainage monitoring, intermittent sampling and analysis is required to characterize the form and rate of weathering in the solid phase of tailings, waste rock and mine walls. When the composition is similar to that of wastes from new mines, field evidence from historic mine sites may provide a very good prognostic tool for new mining developments.

Due to complexities and confounding features such as geochemical retention, various drainage sources and material heterogeneity (Chapters 7 and 8), site monitoring results must be interpreted with caution and with the assistance of data from smaller scale tests on more completely characterized materials (Sections 9.3, 9.4.1, and 9.4.2). Field monitoring and humidity cell results have been shown to be similar at several sites once weathering product retention is taken into account (Morin and Hutt, 1997).

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# 10. PRESENTATION AND INTERPRETATION OF TEST DATA FROM THE RECOMMENDED KINETIC TESTS

Guidance is given here on the presentation and interpretation of data from the recommended kinetic tests (Chapter 9). For example, the various equations for calculating neutralization depletion in a humidity cell, based on pre-test static tests and weekly rinse analyses, are listed and explained. This interpretation, in combination with general modeling (Chapter 11), leads to detailed predictions of drainage chemistry through time for each component (Chapter 12).

#### 10.1 Initial Comments

Kinetic tests (Chapter 9) with supporting static tests (Chapters 7 and 8) can contribute valuable information to the prediction of drainage chemistry at a minesite. However, without proper interpretation the data can be misleading. Proper interpretation of the test results is just as important as conducting the tests and using the proper laboratory procedures.

Kinetic tests provide a measure of the reaction rates and a generalized indication of the potential mineral leaching from the sample. Proper interpretation of this data requires consideration of the sample type, its physical properties, the depositional environment and the contributing elements and minerals. As a result, the general guidelines for interpretation provided here may be adjusted if required by unique site-specific conditions or where refinements are suggested by previous site experience.

# 10.2 Interpretation of Humidity Cell Tests

The primary objectives of humidity cell tests are to (a) measure stable reaction rates under specific geochemical conditions and (b) to calculate depletion times for acid-generating, acid-neutralizing, and metal-leaching minerals. The first step in the interpretation of kinetic test results is the calculation of these values.

One of the major problems with humidity cell work in the past was the short duration of the tests. Kinetic tests should be operated (Chapter 9) until weekly rates become relatively stable. For humidity cells this can require at least 40 weeks of testing, and may require more than a year. In order to remove the effect of natural weekly variations, stable rates are arbitrarily defined as the average of the last five weeks of testing. Stable rates should be compiled into a table for ease of prediction (Chapter 11) and for reporting.

One of the major weaknesses in the present interpretation of humidity cell results is the lack of long-term rate data. Calculations of the time to NP depletion and ARD onset include the inherent assumption that the measured "stable rates" will persist. This allows the results to be extrapolated into future. Unfortunately, there is very little long-term data to check this

# assumption.

Studies in British Columbia have indicated that stable rates from humidity cells can persist within a factor of two for at least five years. Other studies at B.C. mines have shown that stable rates from fresh rock are similar to five-year old rates (Norecol, Dames and Moore, 1994). Obviously rates will not remain the same forever. However, if the mineralogical data shows the contributing minerals will not be exhausted, it can be assumed that the calculated rates, which will be used for predictions of drainage chemistry (Chapter 11), will persist for decades. Hopefully the accuracy of this assumption will be addressed by future research.

The calculation of stable rates and depletion times are best accomplished by entering all weekly data into spreadsheets that will allow data manipulation. Recommended equations for calculating derived parameters are listed in Table 10-1. The Acid Generation section includes calculations for the rates of total and measurable (remnant) acid generation by weight and surface area, and the remaining amounts of acid-generating sulphur. The Molar Ratio section lists two of many possible ratios of NP:AP consumption, based on the mineralogy of the NP minerals (Section 7.10). The rates for Acid Neutralization and NP Consumption vary according to the (1) mineralogy of NP minerals and (2) environmental conditions, particularly whether the system is opened or closed to  $CO_2$ . Depletion equations for NP under various conditions are included. The final section of the table on Metal Leaching provides the basic equations for rate and depletion, which should be applied to all metals. Where metal concentrations in mg/L are below detection, one-half the of the limit can be used for rate calculations.

# **TABLE 10-1**

# Recommended Equations for Interpreting Laboratory Kinetic Tests

Acid Generation

<u>Acidity Production Rate</u> (mg CaCO<sub>3</sub>/kg/wk) = Acidity (mg CaCO<sub>3</sub>/L) \* Volume Leachate Collected (L) / Sample Weight (kg)

<u>Sulphate Production Rate</u> (mg/kg/wk) = Sulphate (mg/L) \* Volume Leachate Collected (L) / Sample Weight (kg)

<u>Remaining total-S</u> (% of original) = {[Initial total-S (%) - ((Cumulative Sulphate Production Rate (mg/kg) \* 32.06 / 96.06) / 10000))] / Initial total-S (%)} \* 100%

<u>Remaining sulphide-S</u> (% of original) = {[Initial sulphide-S (%) - ((Cumulative Sulphate Production Rate (mg/kg) \* 32.06 / 96.06) / 10000))] / Initial sulphide-S (%)} \* 100%

<u>Sulphate Production Rate By Surface Area</u>  $(mg/m^2/wk) =$  Sulphate Production Rate (mg/kg/wk) / Surface Area  $(m^2/kg)$ 

# NP Molar Ratios

<u>Carbonate Molar Ratio</u> = [(Ca (mg/L)/40.08) + (Mg (mg/L)/24.31)] / (SO<sub>4</sub> (mg/L)/96.06)

Other ratios may be used depending on the source of alkalinity, for example:

Anorthoclase Molar Ratio = (Ca (mg/L)/40.08) / (SO<sub>4</sub> (mg/L)/96.06)

Acid Neutralization and NP Consumption

<u>Carbonate Ratio NP Consumption</u> (mg CaCO<sub>y</sub>/kg/wk) = Carbonate Molar Ratio \* Theoretical NP Consumption (mg/kg/wk);

based on:

 $2H^{+} + SO_{4}^{2} + (Ca_{x}Mg_{1-x})CO_{3(s)} = xCa^{2+} + (1-x)Mg^{2+} + SO_{4}^{2-} + H_{2}CO_{3}^{0}$  or  $2H^{+} + SO_{4}^{2-} + 2(Ca_{x}Mg_{1-x})CO_{3(s)} = 2xCa^{2+} + (2-2x)Mg^{2+} + SO_{4}^{2-} + 2HCO_{3}^{-}$ 

<u>Theoretical NP Consumption at pH 6</u> (mg CaCO<sub>3</sub>/kg/wk) = Sulphate Production Rate (mg SO<sub>4</sub>/kg/wk) \* 100.09 / 96.06;

based on:

 $2H^{+} + SO_{4}^{2} + CaCO_{3(s)} \approx Ca^{2+} + SO_{4}^{2-} + H2CO_{3}^{0}$ 

<u>Empirical Open-System NP Consumption around neutral pH</u> (mg CaCO<sub>y</sub>/kg/wk) = Theoretical NP Consumption (mg/kg/wk) + Alkalinity Production Rate (mg/kg/wk) - Acidity Production Rate (mg/kg/wk);

based on:

 $2H^{+} + SO_4^{2} + CaCO_{3(s)} = Ca^{2+} + SO_4^{2-} + H_2CO_3^{0}$ plus  $H_2CO_3^{0} + CaCO_{3(s)} = Ca^{2+} + 2HCO_3^{-}$ minus un-neutralized acidity

<u>Theoretical Closed-System NP Consumption above pH 6.5</u> (mg CaCO<sub>3</sub>/kg/wk) = [Theoretical NP Consumption (mg/kg/wk) \* 2] - Acidity Production Rate (mg/kg/wk); based on:

 $2H^{+} + 2CaCO_{3(s)} = 2Ca^{2+} + 2HCO_{3}^{-}$ minus un-neutralized acidity

<u>Remaining NP</u> (% of original) = {[Initial NP (t CaCO<sub>3</sub>/1000 t) - (Cumulative NP Depletion Rate (mg/kg) / 1000)] / Initial NP (tonnes CaCO<sub>3</sub>/1000 tonnes)} \* 100%

#### Metal Leaching

<u>Metal Leach Rates</u> (mg/kg/wk) = Metal Concentration (mg/L) \* Volume of Leachate Collected (L) / Sample Weight (kg)

<u>Remaining Metal</u> (%of original) = {[Initial Metal Content (mg/kg) - Cumulative Metal Leach Rate (mg/kg)] / Initial Metal Content (mg/kg)} \* 100%

NOTES: At later stages of some humidity cell testing programs, analyses for sulphate, alkalinity and metals are not necessarily done on a weekly basis but may be decreased to monthly. In this circumstance, weekly values for rates can be calculated through interpolation of the preceding and subsequent measured values.

All the humidity cell data must be submitted in a tabular form both on paper and on a computer disc. The best way to show trends or the association between different parameters is to plot the results. Examples of plots of the humidity-cell results for pH, rates of sulphate production (sulphide oxidation), NP consumption rates and metal-leaching rates for British Columbia mine rock are shown in Figure 10-1 to 10-4. Discussions accompanying these figures illustrate the interpretations of humidity-cell results.



# Figure 10-1 B.C. Humidity Cells that Remained Acidic or Near Neutral, Showing Leachate pH and Rates of Sulphate Production (Sulphide Oxidation) and NP Consumption.

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Figure 10-2 B.C. Humidity Cells that Remained Acidic or Near Neutral, Showing Leachate pH and Rates of Copper and Zinc Leaching.



a) waste rock; sulphate rate exceeded NP rate from start; acidic conditions after Week 15; sulphate rate accelerated below pH 4; relatively constant NP rate of ~ 30 mg/kg/wk independent of pH; accidental addition of strong acid to cell at Week 34; unavailable NP ~ 8 t/1000 t



b) tailings, pH initially acidic, then near neutral, then acidic around Week 135; sulphate and NP rates erratic but within defineable ranges; sulphate rate accelerated below pH 5; lateNP rate steady despite onset of acidification; unavailable NP uncertain due to discrepancy between calculated remaining and post-test value, possibly attributable to erroneous pre-test analysis or neutralization by non-carbonate minerals

Figure 10-3 B.C. Humidity Cells that Became Acidic, Showing Leachate pH and Rates of Sulphate Production (Sulphide Oxidation) and NP Consumption.



Figure 10-4 B.C. Humidity Cells that Became Acidic, Showing Leachate pH and Rates of Copper and Zinc Leaching.

After a kinetic test is terminated, the closedown procedure (Section 9.3.3) should include a final rinse to determine the amount of accumulated reaction products. Detectable retained weathering products can be redistributed evenly over all weeks of the test. This arbitrary practice is based on the assumption that the weekly amount of retained product was constant. As a result, all calculated weekly rates may increase somewhat after the termination of the test. If the weekly increase is significant, the sample was not properly prepared or was inadequately rinsed during the test (Section 9.3.2).

Humidity cell estimates of the relative rates of acidity production and NP consumption should be used to improve the crude, preliminary estimates of the likelihood of ARD provided in the ABA screening criteria (Section 8.3.4). For example, if kinetic tests produce a stable molar ratio of 1.75 NP:AP consumption at non-acidic pH, then all samples with NPR values less that 1.75 should be considered net acid generating (Table 10-2). This assumption should of course include the qualifier "if the presently available NP persists". This assumption should always be checked. For both preliminary and final interpretations, the percentage of rock units or mine components falling into each category should be reported, based on the statistical values (Table 8-1).

| TABLE 10-2        Final Criteria for Interpreting Crushed/Rinse pH and xNPR   |  |  |  |  |  |  |
|---|--|--|--|--|--|--|
| Criteria Prediction/Current Condition   |  |  |  |  |  |  |
|   | Crushed/Rinse pH   |  |  |  |  |  |
| crushed/rinse pH < 5.0  | currently acidic; future unknown   |  |  |  |  |  |
| crushed/rinse pH 5.0 currently near-neutral; future unknown   |  |  |  |  |  |  |
|   | xNPR   |  |  |  |  |  |
| xNPR < safe value <sup>1</sup>  | eventually acidic  |  |  |  |  |  |
| xNPR safe value <sup>1</sup>  | indefinitely near-neutral or alkaline  |  |  |  |  |  |
| <sup>1</sup> "safe value" is the molar ratio of the<br>or component obtained from labor<br>xNPR value needed to maintain no<br>to modification of xNPR values | e rates of acid generation and acid neutralization for a unit<br>atory and field kinetic tests, which defines the minimum<br>on-acidic conditions; any NP which is unavailable will lead |  |  |  |  |  |

# 10.3 Interpretation of the Drainage Monitoring Results from On-Site Kinetic Tests

As explained in Chapter 9, excavated mine wastes, exposed walls and field test pads are intermittently and incompletely leached, resulting in at least some retention of the products of primary mineral weathering. As a result, equilibrium solubility processes and reactionproduct retention (e.g., Table 10-3) will play a significant role in determining the chemistry of site drainage and the drainage from on-site field test pads.

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| Table 10-3        A Comparison Between Humidity Cell and Field Test Pad Results Indicates the |   |                         |                        |                        |                         |            |  |  |
|---|---|-------------------------|------------------------|------------------------|-------------------------|------------|--|--|
| Proportional Retention of Weathering Products   |   |                         |                        |                        |                         |            |  |  |
| Parameter   |   | Acidic Condition        | \$                     | pH                     | Neutral Condition       | 20C        |  |  |
|   | Cell Rate   | Field Rate <sup>2</sup> | Retention <sup>3</sup> | Cell Rate <sup>1</sup> | Field Rate <sup>2</sup> | Retention' |  |  |
| pH <sup>4</sup>   | 2.90  | 2.6-4.5                 |                        | 7.08                   | 6.3-7.5                 |            |  |  |
| Acidity   | 231   | 0.318                   | 99.86                  | 0.92                   | 0.00811                 | 99.12      |  |  |
| SO.   | 575   | 1.74                    | 99.70                  | 12.2                   | 0.188                   | 98.46      |  |  |
| Ca  | 8.81  | 0.144                   | 98.37                  | 5.0                    | 0.0919                  | 98.16      |  |  |
| Cđ  | 0.00134   | 0.000169                | 94.62                  | 9.60e-05               | 7.65e-07                | 99.20      |  |  |
| Cu  | 0.0793  | 0.00894                 | 88.73                  | 1.90e-03               | 1.31e-05                | 99.31      |  |  |
| Ni  | 0.0161  | 0.000300                | 98.14                  | 7.20c-04               | 8.23e-07                | 99.89      |  |  |
| Pb  | 0.0127  | 0.000143                | 98.87                  | 8.70e-04               | 5.14e-07                | 99.94      |  |  |
| Zn  | 0.214   | 0.0351                  | 83.60                  | 4.50c-03               | 4.33e-05                | 99.04      |  |  |
| <sup>1</sup> From humid   | ity cells (mg/kg  | /wk)                    |                        |                        |                         |            |  |  |
| <sup>2</sup> Average rate   | <sup>2</sup> Average rates calculated from field-test concentrations, water recovered, and weight |                         |                        |                        |                         |            |  |  |
| (mg/kg/wk)  |   |                         |                        |                        |                         |            |  |  |
| <sup>3</sup> Retention Fa   | actor = {[Cell R  | ate - Field Rate]/      | Cell Rate}*100         | *                      |                         |            |  |  |
| <sup>4</sup> pH is presen   | ted in pH units   | and not as a rate       |                        |                        |                         |            |  |  |

Scatterplots showing changes in the data over time and geochemical speciation models such as MINTEQ (Chapter 11) can be used to identify trends and to assist in identifying equilibrium conditions (e.g., Table 10-4). While it is often a powerful tool, speciation modeling will not always be capable of explaining the observed mine site geochemistry. Studies at mines in British Columbia have shown evidence of equilibrium processes which operated for decades, while modeling of the data failed to identify the mineral causing equilibrium (Morin and Hutt, 1997). Modeling predictions regarding equilibrium solubility conditions should be interpreted with caution and wherever possible the conclusions should be supported by long-term monitoring of water chemistry.

Two of the best examples of drainage monitoring are the many years of water chemistry monitoring at the Island Copper Mine and Bell Mine. Compilations of the data from both sites have shown that year after year the elemental concentrations vary within definable ranges, for a particular range of pH (Table 11-1). The consistent behaviour is consistent with equilibrium conditions. MINTEQ identified possible mineral equilibrium for cadmium and copper, but not for zinc despite its equilibrium-like behaviour. The lack of an identified mineral for zinc probably reflects weaknesses in MINTEQ and other related programs. These issues are examined further in Chapter 11.

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| Table 10-4                  |                                     |                             |   |                                       |                             |   |  |
|-----------------------------|-------------------------------------|-----------------------------|---|---------------------------------------|-----------------------------|---|--|
| A Com                       | Limitation Pr                       | n Drainag<br>edicted w      | e Chemistry Me<br>tith an Empirica  | easured for a Fie<br>d Model at the T | ld Test Pa<br>ulsequah (    | d and the Equilibrium<br>Chief Project  |  |
| Parameter                   |                                     | cidic Ran                   | ge  |                                       | pH-Neut                     | ral Range   |  |
|                             | Field-kinetic<br>range <sup>1</sup> | Model<br>value <sup>2</sup> | Control <sup>3</sup>  | Field-kinetic range <sup>1</sup>      | Model<br>value <sup>2</sup> | Control'  |  |
| pH                          | 2.6-4.5                             | 2.7                         |   | 6.2-7.5                               | 7.0                         |   |  |
| Acidity                     | 420-965                             | 1175                        |   | 7-11                                  | 17                          |   |  |
| SO₄                         | 1120-8800                           | 2000                        | CaSO <sub>4</sub> ·2H <sub>2</sub> O;<br>AlOHSO <sub>4</sub><br>(+0.5);<br>jarosites? | 130-250                               | 225                         | KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub> (+0.4)             |  |
| Ca                          | 131-286                             | 255                         | CaSO4.2H2O  | 62-114                                | 0.36                        |   |  |
| Cd                          | 0.11-0.80                           | 0.58                        | mineral<br>unidentified   | 0.0005-0.0011                         | <0.000<br>1                 | CdCO <sub>3</sub> (-1.3)  |  |
| Cu                          | 4.0-5.2                             | 27                          | mineral<br>unidentified   | 0.0083-0.016                          | <0.000<br>1                 |   |  |
| Ni                          | 0.069-0.74                          | 1.58                        | mineral<br>unidentified   | 0.00025-<br>0.0018                    | <0.000<br>01                |   |  |
| РЪ                          | 0.07-0.41                           | 0.4                         | PbSO4 (-1.5)  | <0.0001-<br>0.0016                    | 0.004                       | PbAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> 6H <sub>2</sub> O |  |
| Zn                          | 23-162                              | 78                          | mineral<br>unidentified   | 0.008-0.050                           | <0.000<br>1                 |   |  |
| <sup>1</sup> From hum       | idity cells (mg/k                   | g/wk)                       |   |                                       | ·                           |   |  |
| <sup>2</sup> Average ra     | ites calculated fr                  | om field-t                  | est concentration   | s. water recovered                    | 1 and weigh                 | tht (malea /ade)  |  |
| ' From MIN                  | TEQ results; val                    | lues in par                 | entheses reflect  | diustments to gen                     | eral solubi                 | lity values in MINTEO   |  |
| personal provides in MINIEO |                                     |                             |   |                                       |                             |   |  |

#### **11. GEOCHEMICAL MODELS**

Geochemical models can assist with the interpretation of testwork results (Chapters 8 and 10) and may improve the prediction of drainage chemistry (Chapter 12). However, models can not substitute for good site specific measurement and understanding. They are tools to assist, but not direct, the work. Only techniques and programs that are widely used and tested should be employed. Custom or in-house models that are unpublished or are not widely released will be regarded with suspicion, and will require a great deal of justification and explanation before acceptance.

#### 11.1 Empirical Modeling

There are two basic requirements for the prediction of acidic drainage and metal leaching.

- 1. The rates and abundance of primary mineral dissolution from static and kinetic tests (Chapters 7 and 9).
- 2. The formation and dissolution of secondary minerals (Chapter 3).

| Table 11-1      Annual Statistics for Drainage Chemistry at a Monitoring Station      at Island Copper Mine      (adapted data from Morin et al., 1994, and 1995a) |       |                   |       |       |       |                     |        |       |  |
|--|-------|-------------------|-------|-------|-------|---------------------|--------|-------|--|
|  |       | LOG <sub>10</sub> | MEAN  |       |       | LOG <sub>10</sub> S | TD DEV |       |  |
| Year   | 90-91 | 91-92             | 92-93 | 93-94 | 90-91 | 91-92               | 92-93  | 93-94 |  |
| pH (arithmetic)  | 6.27  | 6.93              | 7.08  | 6.86  | 0.71  | 0.85                | 0.67   | 0.69  |  |
| Conductivity   | 3.06  | 3.09              | 3.10  | 3.16  | 0.12  | 0.09                | 0.11   | 0.06  |  |
| Alkalinity (mg/L)  | 1.74  | 1.71              | 1.70  | 1.62  | 0.07  | 0.45                | 0.36   | 0.35  |  |
| Acidity (mg/L)   | 1.32  | 1.33              | 1.51  | 1.60  | 0.00  | 0.33                | 0.24   | 0.05  |  |
| Cu (mg/L)  | -0.94 | -1.23             | -1.49 | -1.43 | 0.41  | 0.46                | 0.42   | 0.46  |  |
| Zn (mg/L)  | 0.41  | 0.22              | 0.25  | 0.41  | 0.38  | 0.44                | 0.40   | 0.34  |  |
| Cd (mg/L)  | -1.74 | -1.82             | -1.79 | -1.72 | 0.17  | 0.22                | 0.23   | 0.21  |  |
| Sulfate (mg/L)   | 2.89  | 2.90              | 2.91  | 2.93  | 0.06  | 0.09                | 0.08   | 0.08  |  |
| Ca(mg/L)   | 2.37  | 2.39              | 2.43  | 2.44  | 0.04  | 0.09                | 0.06   | 0.07  |  |
| Mg (mg/L)  | 1.46  | 1.51              | 1.59  | 1.60  | 0.04  | 0.16                | 0.07   | 0.07  |  |
| Al(mg/L)   | -0.78 | -0.71             | -0.56 | -0.57 | 0.68  | 0.33                | 0.35   | 0.37  |  |

Morin and Hutt, 1993a; Morin et al. (1993, 1994, 1995a, 1995b) found that annual means and standard deviations of drainage chemistry at Island Copper and Bell mines were relatively constant as long as pH remained relatively steady (e.g., Table 11-1 and Figure 11-1). Because the precipitation and dissolution of many secondary minerals are often equilibrium controlled, a narrow range of concentrations at a particular pH can be observed annually over

years of monitoring and are thus predictable. The prediction of this range, or Rate2 (as labeled in Figure 3-1), does not require the identification of the secondary minerals, although identification may be possible.

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A compilation of best-fit lines relating pH or another parameter to aqueous concentrations, and the corresponding standard deviations, is known as an "empirical drainage-chemistry model" (e.g., Table 11-2). It is important to note that Table 11-2 shows that some parameters do not correlate well with pH, and instead are relatively constant across the observed range of pH or correlate better with another parameter like sulfate. Under the assumption that past processes that created the correlation in various pH ranges will continue, the empirical drainage-chemistry model becomes a predictive tool. However, such an empirical model may not be possible for minesites with less than a few hundred data points (Norecol, Dames and Moore, 1996). More detailed instructions and discussions of empirical drainagechemistry models can be found in Morin and Hutt (1993a and 1993b) and Morin et al. (1995a and b).

| Example<br>Waste | e of an Empirical l<br>-Rock Dumps, and  | Table 11-2<br>Drainage-Chemistry Model Including an Ope<br>i a Tailings Impoundment at a Mine in Britis | en Pit, Several<br>h Columbia |
|------------------|--|---|-------------------------------|
|                  |  | (adapted from Morin et al., 1995b)  |                               |
| Parameter        | pH Range   | Best-Fit Equation   | Log(Std. Dev.)                |
| Acidity          | pH < 3.5   | $\log(Acid) = -0.932pH + 5.864$   | 0.345                         |
|                  | pH > 3.5   | log(Acid) = -0.360pH + 3.862  |                               |
| Alkalinity       | pH > 4.5   | log(Alk) = +0.698pH - 3.141   | 0.654                         |
| Diss Aluminum    | pH < 6.0   | $\log(AI) = -0.925 pH + 4.851$  | 0.429                         |
|                  | pH > 6.0   | A1 = 0.2 mg/L   |                               |
| Diss Arsenic     |  | < 0.2 mg/L  | 0                             |
| Diss Cadmium     | pH < 3.0   | Cd = 0.07 mg/L  | 0                             |
|                  | pH > 3.0   | Cd = 0.015 mg/L   | -1                            |
| Diss Calcium     |  | log(Ca) = +0.619log(SO4) + 0.524  | 0.375                         |
| Diss Copper      | pH < 3.4   | $\log(Cu) = -1.485pH + 6.605$   | 0.692                         |
|                  | 3.4 <ph<5.4< td=""><td><math>\log(Cu) = -0.327 pH + 2.666</math></td><td></td></ph<5.4<> | $\log(Cu) = -0.327 pH + 2.666$  |                               |
|                  | pH > 5.4   | $\log(Cu) = -1.001 \text{pH} + 6.307$   |                               |
| Total Copper     |  | log(Cu-T) = +0.962log(Cu-D) + 0.180   | 0.230                         |
| Diss Iron        | pH < 4.4   | $\log(Fe) = -1.429 pH + 6.286$  | 0.807                         |
|                  | pH>4.4   | $\log(Fe) = -0.455pH + 2.000$   |                               |
| Total Iron       |  | If diss Fe>1.0, total Fe-diss Fe  | 0                             |
| Diss Lead        |  | Pb = 0.05  mg/L   | 0                             |
| Diss Nickel      |  | $\log(Ni) = -0.317 pH + 0.853$  | 0.607                         |
| Diss Selenium    |  | Se = 0.2 mg/L   |                               |
| Diss Silver      |  | Ag = 0.015 mg/L   |                               |
| Diss Zinc        |  | $\log(Zn) = -0.441 pH + 1.838$  | 0.667                         |
| Total Zinc       |  | total Zn = diss Zn  | 0.144                         |



Figure 11-1 Empirical Drainage-Chemistry Correlations with pH (adapted from Morin et al., 1995a).

There are two important issues that should be clarified about the statistical values in the models (Table 11-2): their physical implications and the frequency of monitoring needed to obtain them reliably. The physical implications are derived from the use of probability tables for predicting maximum or minimum concentrations over a duration of time like one day or one week. The physical implications also include the probability that a particular concentration will be encountered through a year. Standard probability tables applied to one year (Table 11-3) indicate that the maximum concentration of one-month duration will be 1.73 log standard deviations above the best-fit line. With dissolved zinc at pH 4.0 in Table 11-3 as an example, the average annual concentration is:

| log(average annual zinc, | mg/L) = -0.441pH + 1.838 | (11-1) |
|--------------------------|--------------------------|--------|
|                          | = -0.441 * 4.0 + 1.838   | ()     |
|                          | = +0.074                 |        |
| Average annual zinc      | = 1.19  mg/L             |        |

The corresponding maximum one-month-duration concentration of dissolved zinc at pH 4.0 is:

| log(maximum one-month-duration zin | c) = -0.441 pH + 1.838 + (1.73*0.667)   | (11-2) |
|------------------------------------|---|--------|
|                                    | = -0.441 * 4.0 + 1.838 + (1.73 * 0.667) | ()     |
|                                    | = +1.23                                 |        |
| Maximum one-month-duration zinc    | = 17.0  mg/L                            |        |

This approach was validated at one site using high-frequency analyses, collected every four hours at several stations over three years. Although normal and lognormal distributions theoretically continue to positive and negative infinity, distributions of aqueous concentrations cannot. At lower values, the distribution is truncated by analytical detection limits. At higher values, the distribution is truncated by the maximum solubility of secondary minerals, and thus the actual concentrations for one second, one minute, and one hour durations may be the same despite the differing statistical predictions.

| Table 11-3        Probability Levels and Corresponding Time Intervals over One Year |                    |                  |             |       |        |  |  |
|---|--------------------|------------------|-------------|-------|--------|--|--|
| Time interval   | 1 Year             | 1 Month          | 1 Week      | 1 Day | 1 Hour |  |  |
| Probability   | 100%               | 8.3%             | 1.9%        | 0.27% | 0.011% |  |  |
| No. of std deviations above mean'   | +0.00              | +1.73            | +2.34       | +3.00 | +3.85  |  |  |
| <sup>1</sup> obtained from normal-distribution table                                | es (e.g., Pollard, | , 1977) after di | viding by 2 |       |        |  |  |

The second issue on the annual standard deviation is the frequency of sampling required to obtain the value. Although two samples a year are adequate for calculating statistical values of means and standard deviations, these values may be found inaccurate if more frequent

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sampling were conducted. Therefore, high-frequency sampling and analysis are required. Such studies in British Columbia have shown that, with an acceptable level of error reflecting analytical error, weekly to monthly analyses would be sufficient to obtain reasonably accurate statistical values (Morin et al., 1993 and 1994). No special timing of the sampling was needed.

#### 11.2 Mineral-Equilibrium Modeling

An important model in the prediction of drainage chemistry involves equilibrium speciation and calculation of mineral saturation indices. There are many programs in wide distribution that can perform the calculations, such as MINTEQ (U.S. EPA) and PHREEQE (U.S. Geological Survey). MINTEQ (Allison et al., 1990) is recommended for drainage predictions in British Columbia because (1) it is available free of charge, (2) it is not copyrighted and thus the program and its input/output can be freely distributed and discussed, (3) it is maintained and occasionally expanded by the U.S. EPA, and (4) training courses in its use are relatively common and regular.

MINTEQ requires as input water-chemistry analyses of all significant cations, anions and pH, similar to those measured in kinetic tests (Chapters 8 and 9). The output requires some knowledge of aqueous complexation and mineral precipitation-dissolution. The output shows which minerals may be forming or dissolving to account for observed water chemistry (Table 10-4). The implicit assumption is that minerals will be at chemical equilibrium if present, which is not correct for kinetically controlled systems (Chapter 3). Therefore, equilibrium modeling should be used with caution.

Other, more complex models are available to assist in predictions. A notable example is WATAIL, a physical-chemical program developed for the Canadian MEND Program. This program simulates some aspects of acid generation and neutralization in tailings, as well as physical movement of groundwater through a tailings area. WATAIL and related models have recently been described and reviewed in detail by Perkins et al. (1995). Further discussion of the application of empirical modeling (Section 11.1) and equilibrium modeling (this section) to specific mine components is discussed in Chapter 12.

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# 12. PREDICTION OF DRAINAGE CHEMISTRY WHERE THE OXIDATION RATE IS LIMITED

## **12.1 Initial Comments**

A common basic ingredient required for sulphide oxidation and acid generation is the presence of oxygen, whether as a gas or in dissolved aqueous form. If the supply rate of oxygen to a mine component exceeds the rate of oxygen consumption, then the rate proceeds unhindered. This is the situation in a humidity cell. However, if the consumption rate exceeds the supply rate, then the rate of oxidation is reduced and kinetic rates based on humidity cell testing must be adjusted. The adjustments available for limitations in gaseous oxygen are discussed first (Section 12.2), followed by adjustments for subaqueous disposal (Section 12.3).

Published literature is contradictory on whether ferric iron can also oxidize sulphide minerals in the absence of oxygen (e.g., Morin, 1993). The effect of ferric iron is not included in the following approaches, but should be added if site-specific information indicates that it contributes to oxidation.

# 12.2 Components Exposed to Air and Water

The supply rate of air with gaseous oxygen can be controlled by air transport or convection, or by slow diffusion in the absence of convection. No matter which process controls oxygen movement, there are two basic outcomes. In the first, the supply rate of oxygen exceeds the consumption rate, and measurable gaseous oxygen exists near the minerals. Alternatively, the consumption rate exceeds the supply rate, and gaseous oxygen is depleted. For portions of mine components that meet, or are predicted to meet, the first outcome, no adjustments of reaction rates from humidity cells are necessary. For the second outcome, humidity cell reaction rates can be set to zero. As explained in Section 12.1, there is some debate on the extent that other oxidants, like ferric iron, can oxidize minerals in the absence of oxygen. Due to this uncertainty, the second outcome of zero rates may have to be modified on a sitespecific basis if other oxidants are present in significant quantities.

For detailed predictions of Rate1 (Figure 3-1), the total weight of portions of a component that will have measurable gaseous oxygen nearby is multiplied by rates from humidity cells:

$$Rate1 = WT * HCR$$
(12-1)

where Rate1 = total reaction rate of a mine component in units of mg/wk (see Figure 3-1) WT = total weight of oxidizing material in the component in units of kg HCR = humidity-cell rate for acidic or near-neutral conditions in units of mg/kg/wk

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For example, if cells give a near-neutral rate of 15 mg Cu/kg/wk and 10,000,000 t of a 30,000,000 t waste-rock dump is expected to be oxygenated and 10% of that physically exposed (proportion of fines), then Rate1 of copper for the dump will be:

Rate1 = 1,000,000 kg \* (15 mg Cu/kg/wk)  
= 15 t Cu /wk or 
$$1.5 \times 10^{10}$$
 mg Cu/wk (12-2a)

Of course, a different rate would develop if the dump became acidic. Rate1 can be converted to a hypothetical concentration by division with the expected flow rates through the reactive portions, e.g.:

Concentration based on Rate1 =  $1.5 \times 10^{10}$  mg Cu/wk / (10,000,000 L/wk) = 1,500 mg/L (12-2b)

Obviously such a concentration is prohibited by secondary-mineral solubility. This indicates a great deal of the copper released from primary minerals in this dump would precipitate as secondary minerals. If the on-site solubilities are known (Section 11.1) or are predicted from MINTEQ (Section 11.2), Rate2 (Figure 3-1) and the degree of retention can be calculated:

$$Rate2 = EC * Flow$$
(12-3)

where Rate2 = total release of a component through drainage in units of mg/wk (see Figure 3-1) EC = equilibrium concentration in mg/L (from methods in Chapter 11)

Flow = total flow through reactive portions of the component in units of L/wk

In the preceding example, if equilibrium copper is 100 mg/L, then Rate2 will be  $1.0x10^9$  mg Cu/wk (100 mg/L \* 10,000,000 L/wk) as a loading. As a result, the amount retained in the component will be 99.3%.

As another example, an HCR rate of 2 mg Cu/kg/wk is predicted for a relatively small wasterock dump with 100,000 t of rock with 10% physically exposed, for a total weekly production rate of 200,000,000 mg Cu/wk. This dump is located in a wet climate, so it receives 2,100,000 L/wk of infiltration. The predicted Ratel is:

Rate1 = 
$$20,000,000 \text{ mg Cu/wk} + 2,100,000 \text{ L/wk} = 9.5 \text{ mg/L}$$
 (12-4)

Unlike the preceding example (Equation 12-2), this predicted concentration is likely to be soluble at acidic pH. Therefore, no precipitation of secondary copper and no retention (0%) may occur in this situation. Again, this should be confirmed by checking on-site solubilities (Section 11.1) or through MINTEQ modeling (Section 11.2).

These two examples highlight the importance of not only geochemical rates and physical exposure, but of flow rates when calculating concentrations from kinetic rates.

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Consequently, the climate, hydrology, and hydrogeology in and around a minesite are critical in predicting kinetic-based concentrations and determining if any metals will be retained. On the other hand, concentrations controlled by equilibrium reactions are relatively insensitive to flow rates.

The remaining issue in the prediction of air-exposed sections of mine components is the portion of a component that will be in contact with oxygen. Air exposure varies with the component and its physical and chemical composition. Nevertheless, there are a few general expectations (Table 12-1). For example, in coarse-grained waste rock without seals and in open-pit walls, a reasonable assumption is 100% exposure to air. For underground workings, oxygen availability depends on air circulation and layout of the workings. Oxygen availability may be uncertain in inactive workings. Active workings will normally have full oxygen levels for the health of miners.

| Anticipated Extent of Air E<br>in B      | Table 12-1<br>Exposure for Typical Mine Components<br>ritish Columbia |
|--|---|
| Component                                | Typical Air Exposure  |
| Open Pits                                | fully oxygenated  |
| Underground Workings                     | fully oxygenated unless sealed or inactive                            |
| Waste-Rock Dumps                         | fully oxygenated if coarse; limited oxygen if fine grained            |
| Ore and Low-Grade Ore Stockpiles         | fully oxygenated if coarse; limited oxygen if fine grained            |
| Tailings Impoundments                    | limited oxygen  |
| Roads                                    | fully oxygenated  |
| Dams                                     | fully oxygenated unless fine grained                                  |
| Disturbed-Rock Foundations for Buildings | fully oxygenated  |

If there is some oxygen consumption in fine-grained waste rock and tailings, oxygen may be depleted at some depth below the surface. This situation is illustrated in field studies where oxygen levels decrease with increasing depth. An oxygen gradient with depth is often provided as evidence for diffusion, although slow convection is an equally plausible explanation. For either case, depths of oxygen diffusion and the thickness of material in contact with sufficient oxygen for reaction can be estimated with relatively simple equations. More complex models and equations are available, but the required assumptions, boundary conditions, the need for rarely measured input data and the omission of important processes like barometric pumping reduce their accuracy.

One difficulty with predicting oxygen diffusion is that there is no agreement in published literature on whether the rate of pyrite oxidation (1) is independent of oxygen level until a certain minimum (often reported around  $1\% O_2$ ) is attained, (2) decreases linearly with oxygen level, or (3) depends on some exponential factor of oxygen level.

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In most cases, of oxygen independence above 1% O<sub>2</sub> is acceptable for approximate predictions, even when there is some linear dependence. The following simplified method assumes this to be the case.

This simple predictive method for the initial depth of oxidation (dZ1) in a vertical column of  $1 \text{ m}^2$  lateral area (Figure 12-1) begins with an assessment of the effective diffusion coefficient for oxygen within the mine component. Some literature values and equations are provided in Table 12-2. These values by definition must range between the diffusion coefficient of oxygen in air ( $1.78 \times 10^{-5} \text{ m}^2/\text{s}$ ) and the diffusion coefficient of oxygen in water ( $2.1 \times 10^{-9} \text{ m}^2/\text{s}$ ) with some modification for pore space tortuosity and other factors. Since it is assured that there is some exposure to air, higher values of the coefficient around  $10^{-7}$  to  $10^{-5} \text{ m}^2/\text{s}$  should be expected in most situations.





Figure 12-1 Conceptual Column for Calculating Oxygen Diffusion and Depth of Oxidation.

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| Examples of Values a                           | Table 12-2           and Equations for Effective Diffusion Coefficients for G           Drygen Within Mine-Component Materials   | ascous                           |
|--|--|----------------------------------|
| Material                                       | Value (m <sup>3</sup> /s) or Equation  | Reference                        |
| Waste-rock column, Woodlawn<br>Mine, Australia | 7.86x10 <sup>-1</sup>  | Jeffery et al.<br>(1988)         |
| Waste-rock dump, Woodlawn,<br>Australia        | 3.49-5.07x10 <sup>-4</sup>   | Ritchie (1994)                   |
| Waste-rock dump, Aitik Mine,<br>Sweden         | 2.25-6.85x10 <sup>4</sup>  | Ritchie (1994)                   |
| Waste-rock dump, Heath Steele,<br>Canada       | 2.65-3.35x10 <sup>-4</sup>   | Ritchie (1994)                   |
| Tailings                                       | $D_{eff} = \tau D_{s}^{\circ} (1-S)^{\circ} + \tau D_{w}^{\circ} / H$ where:<br>$D_{eff} = \text{effective diffusion coefficient (m2/s)}$ $\tau$ and $\alpha$ = fitting parameters from laboratory<br>column data of tailings from an Ontario<br>mine ( $\tau = 0.27$ and $\alpha = 3.27$ )<br>$D_{s}^{\circ} = \text{coefficient for free diffusion of oxygen in air}$ (1.78x10 <sup>-5</sup> m2/s)<br>$D_{w}^{\circ} = \text{coefficient for diffusion of oxygen in water}$ (2.1x10 <sup>-5</sup> m2/s)<br>S = dimensionless degree of water saturation<br>(dry = 0.0 to saturated = 1.0)<br>H = modified dimensionless Henry's constant<br>(26.32 at 10 °C) | David and<br>Nicholson<br>(1995) |
| Tailing <b>s</b>                               | D <sub>eff</sub> = 3.98x10 <sup>-7</sup> [(G-0.05)/0.95] <sup>1.7</sup> T <sup>1.5</sup><br>where:<br>Deff = effective diffusion coefficient (m <sup>2</sup> /s)<br>G = gas-filled pore space<br>T = temperature (K)   | Stuparyk et al.<br>(1995)        |

In an adaptation of Fick's First Law of Diffusion (e.g., Freeze and Cherry, 1979):

$$F = D^{*aC}/_{aZ1} * TC$$
 (12-5)

where F = flux of oxygen in units of mol  $O_2/m^2/wk$ 

- D = effective diffusion coefficient of gaseous oxygen within a mine component in units of m<sup>2</sup>/s (see Table 12-2)
- dC = change in concentration of O<sub>2</sub> from atmospheric to zero in units of mol O<sub>2</sub>/m<sup>3</sup> (approximately 8 mol O<sub>2</sub>/m<sup>3</sup>)
- dZ1 = initial depth from the open atmosphere to no oxygen in m (to be calculated)

TC = conversion factor of seconds in one week (604,800 s/wk)

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Based on the vertical column of material (Figure 12-1), the initial total volume of material in this column that would oxidize according to Equation 12-5 is dZ1 m<sup>3</sup>.

Based on humidity-cell rates (Rate1, Figure 3-1), the consumption of oxygen by a certain weight of material is:

$$CO = HCR * Weight * Conv * Ratio$$
(12-6)

where: CO = consumption rate of oxygen in units of mol O<sub>2</sub>/wk/column; the column has a lateral area of 1 m<sup>2</sup>
HCR = humidity-cell rate (in units of mg SO<sub>4</sub>/kg/wk) for near-neutral pH if effective NP still present or for acidic pH if effective NP exhausted
Weight = weight of material oxidizing at HCR to consume all oxygen in the column in units of kg (to be calculated)
Conv = conversion factor for mg SO<sub>4</sub> to moles S (1/96000)
Ratio = ratio of sulphur in moles to oxygen in moles according to the standard pyrite equation (15/8)

When the constants are inserted into Equation 12-6, the result is:

$$CO = 1.95 \times 10^{-5} + HCR + Weight$$
 (12-7)

To estimate the depth of oxidation when an entire column contains sulphide minerals, that is, before there is any significant depletion or coating of shallow sulphides, Weight in Equation 12-7 is related to dZ1 in Equation 12-5 through bulk density:

Weight = BD 
$$*$$
 dZ1 (12-8)

where: Weight = weight of oxidizing material in kg oxidizing in a column of 1 m<sup>2</sup> lateral area (to be calculated, see Equation 12-7)

BD = bulk density of material in units of  $kg/m^3$ 

dZ1 = depth from the open atmosphere to no oxygen in m (to be calculated, see Equation 12-5)

Substituting Equation 12-8 into 12-7 and equating F (Equation 12-5) with CO (Equation 12-7) yields:

$$dZ1 = 4.98 \times 10^{5*} [D/(BD^*HCR)]^{0.5}$$
(12-9)

Equation 12-9 provides a rough estimate of the initial thickness of oxidizing material. When multiplied by total lateral area of reactive portions, the total oxidizing volume and weight within a component can be determined. Rate1 and Rate2 can then be determined from total weight using Equations 12-1 and 12-4.

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(1 A A)

After the uppermost zone (dZ1) is fully oxidized, a deeper interval (dZ2) begins oxidizing (Figure 12-1). At this point, Equation 12-5 must be adjusted to:

$$F = D^{**C}/_{(dZ_1+dZ_2)} TC$$
(12-10)

Equation 12-8 must be adjusted to:

$$Weight = BD * dZ2$$
(12-11)

When the adjusted equations are combined, Equation 12-9 becomes a more complex, quadratic equation:

$$(dZ2)^{2} + dZ1dZ2 - 2.48x10^{11} + D/(BD^{+}HCR) = 0$$
(12-12)

in which only dZ2 is unknown. This equation and those for deeper intervals (dZ3, dZ4, etc.) can be solved as quadratic equations. The time to depletion of sulphide minerals for each interval can also be calculated based on the initial sulphide content and reaction rates (HCR). The calculated the thickness of progressively deeper dZ intervals and their time of activity, shows that the migration of the oxidation front into the mine component slows with time and eventually becomes negligible.

The thickness of the resulting active dZ interval multiplied by lateral area will provide an estimate of Rate1 (Figure 12-1) at a particular time. If Rate1, when divided by flow through the zone, has a concentration less than secondary-mineral solubility, then Rate2 will equal Rate1 and no secondary minerals will form. If Rate1 exceeds Rate2, secondary-mineral retention will occur, similar to that illustrated in the first example, Equations 12-1 to 12-4.

## 12.3 Components Exposed to Water Only

The calculation of oxidation rates in the submerged portions of mine components is both easier and more difficult than exposed portions. In any case, humidity-cell results will often be of little value in subaqueous scenarios.

When a mine component is first submerged, rapid dissolution of soluble minerals will occur (Section-7.4), causing short-term peaks in concentrations in surface and ground waters. If the component has been exposed to air for some time, the level of retained secondary minerals could be high and the high concentrations could persist for weeks to years. After the initial dissolution peak concentrations have subside, much slower metal-release rates will likely occur.

Laboratory and field studies of tailings and waste rock have shown that metals can migrate upwards into an overlying water column or downwards into the component depending on the relative concentrations of pore waters and surface water, and the direction of groundwater flow. The chemistry and residence times of surface waters prior to its entry into a component is relatively easy to estimate. Greater effort must be spent estimating pore water concentrations and flows.

Morin (1993) pointed out that unless the grain size of a component is less than most tailings, around 10-100  $\mu$ m, dissolved oxygen is supplied primarily by advection of water through, rather than by diffusion into, the component. Consequently for most mine wastes, physical factors like hydraulic conductivity and hydraulic gradients will determine the extent of long-term oxidation and metal release into a litre of pore water, rather than the diffusion coefficient of oxygen in water (2.1x10<sup>-9</sup> m<sup>2</sup>/s).

At saturation dissolved oxygen can exist in water, at levels of approximately 8 to 10 mg/L. The standard equation for pyrite oxidation by oxygen shows that the maximum amount of sulphate and acidity that would be created by 10 mg/L dissolved oxygen is 51 mg SO<sub>4</sub>/L and 33 mg CaCO<sub>3</sub>/L. If there is no other oxygen supply to a litre of water and no entrained air bubbles, then acidic conditions cannot develop if alkalinity exceeds the generated acidity of 33 mg CaCO<sub>3</sub>/L. If ferric iron also contributes to sulphide oxidation, then its effect will have to be included. However, at near-neutral pH levels, the aqueous concentrations of ferric iron are often low and thus minor in importance relative to dissolved oxygen.

For submerged materials with a low hydraulic conductivity, residence times of porewaters will be relatively high and thus equilibrium chemistry may be attained. The resulting concentrations can be predicted based on approaches discussed in Chapter 11. If residence times are low due to high hydraulic conductivities or gradients, then kinetic conditions may apply (Chapter 3). Kinetic rates from submerged samples and groundwater flow rates will be required to predict pore water chemistry. Based on this, the interaction of pore water with surface waters and overall predictions of surface- and ground-water chemistries can be made.

# 13. THE MRS METAL LEACHING AND ARD DATABASES

### 13.1 The MRS Kinetic Database

Humidity cells have been used in prediction testwork for at least three decades and some of the test results have been compiled in an international database, providing and opportunity for comparison with mines with similar geology and/or whose drainage chemistry is known. To further empower the collective knowledge of metal leaching and ARD in British Columbia, and our ability for prediction, proponents are encouraged to submit new results for inclusion in the MRS Kinetic Database. Regular updates of the database will be available to mines contributing their data to it.

Data for inclusion in the British Columbia Kinetic Database should include the following fields of information:

- 1. <u>General Information</u> mine name, location, sample id., type of test (humidity cell, column, on-site leach pad, etc.), type of sample (waste rock, tailings, ore, etc.), number of weeks test run, sample weight, surface area (m<sup>2</sup>/kg);
- <u>Pre-Test Data</u> total-S (%), sulphide-S (%), S (%) used for NPR, log<sup>10</sup> S (%), NP (tonnes CaCO<sub>3</sub> / 1000 tonnes), Carb-NP (tonnes CaCO<sub>3</sub> / 1000 tonnes), crushed/paste pH, NNP, NPR, initial metal concentrations (mg/kg) (e.g., Cu and Zn);
- Data for the Entire Length of the Test lowest pH, highest pH, average sulphate production rate (mg/kg/wk), average acidity production rate (mg CaCO<sub>3</sub>/kg/wk), average alkalinity production rate (mg CaCO<sub>3</sub>/kg/wk), average carbonate NP consumption rate (mg CaCO<sub>3</sub>/kg/wk), average carbonate ratio ((Ca + Mg)/SO<sub>4</sub>), feldspar molar ratio ((Ca + (Na/2) + (K/2))/SO<sub>4</sub>), metal leach rates (mg/kg/wk);
- 4. Data for the Late-Stage of the Test After Data Has Stabilized number of weeks used in late-stage averages, average pH, average sulphate production rate (mg/kg/wk), average acidity production rate (mg CaCO<sub>3</sub>/kg/wk), average alkalinity production rate (mg CaCO<sub>3</sub>/kg/wk), average carbonate NP consumption rate (mg CaCO<sub>3</sub>/kg/wk), average carbonate ratio ((Ca + Mg)/SO<sub>4</sub>), feldspar molar ratio ((Ca + (Na/2) + (K/2))/SO<sub>4</sub>), metal leach rates (mg/kg/wk);
- <u>Post-Test Data</u> total-S (%), sulphide-S (%), S (%) used for NPR, log<sup>10</sup> S (%), NP (tonnes CaCO<sub>3</sub> / 1000 tonnes), Carb-NP (tonnes CaCO<sub>3</sub> / 1000 tonnes), crushed/paste pH, NNP, NPR, metal concentrations (mg/kg) (e.g., Cu and Zn).

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#### 15. GLOSSARY

Grain: Separate crystals in multi-grain consolidated matrix.

- Ore: Rock that contains sufficient amounts of the economically valuable elements to warrant its extraction.
- Overburden: At metal mines, the term overburden usually only refers to naturally unconsolidated surficial materials. At coal mines, overburden includes both bedrock and naturally unconsolidated surficial materials on top of the coal seams. In this manual the metal mining definition will be used.
- Particle: Defined as separate fragments in unconsolidated matrix.
- Soil: The rooting medium, present or potential. Man-made media on the surface containing soil-sized particles and which can support plant growth are often called proto-soils. In this manual the term soil was used for both natural and man-made rooting media.
- Soil-sized: Particles < 2 mm in diameter.
- Tailings:Material remaining after the economically valuable elements are removed<br/>from the ore. To remove the valuable elements, the blasted rock goes through<br/>several steps of crushing and extraction. The resulting residue or tailings<br/>usually consists of a slurry of sand and/or silt-sized particles in water.
- Waste rock: Rock that does not contain sufficient amounts of the economically valuable elements to warrant its extraction, but which has to be removed to allow access to the ore. The waste rock is blasted into smaller particles to allow its removal by truck and shovel.

Appendix 1 Conversion Table for Standard Mesh Sizes

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| Sieve De | signation              | Nominal Sieve          | Nominal Wire |
|----------|------------------------|------------------------|--------------|
| Standard | Alternative            | Opening                | Diameter     |
| (mm)     | (inches)               | (inches <sup>•</sup> ) | (mm*)        |
| 125      | 5                      | 5                      | 8            |
| 106      | 4.24                   | 4.24                   | 6.4          |
| 100      | 44                     | 4                      | 6.3          |
| 90       | 3.5                    | 3.5                    | 6.08         |
| 75       | 3                      | 3                      | 5.8          |
| 63       | 2.5                    | 2.5                    | 5.5          |
| 53       | 2.12                   | 2.12                   | 5.15         |
| 50       | 24                     | 2                      | 5.05         |
| 45       | 1.75                   | 1.75                   | 4.85         |
| 37.5     | 1.5                    | 1.5                    | 4.59         |
| 31.5     | 1.25                   | 1.25                   | 4.23         |
| 26.5     | 1.06                   | 1.06                   | 3.9          |
| 25       | 14                     | 1                      | 3.8          |
| 22.4     | 0.875                  | 0.875                  | 3.5          |
| 19       | 0.75                   | 0.75                   | 3.3          |
| 16       | 0.625                  | 0.625                  | 3            |
| 13.2     | 0.53                   | 0.53                   | 2.75         |
| 12.5     | 0.504                  | 0.5                    | 2.67         |
| 11.2     | 0.438                  | 0.438                  | 2.45         |
| 9.5      | 0.375                  | 0.375                  | 2.27         |
| 8        | 0.312                  | 0.312                  | 2.07         |
| 6.7      | 0.265                  | 0.265                  | 1.87         |
| 6.3      | 0.250 <sup>d</sup>     | 0.25                   | 1.82         |
| 56       | No. 3 1/2 <sup>e</sup> | 0.223                  | 1.68         |
| 4.75     | No. 4                  | 0.187                  | 1.54         |
| 4        | No. 5                  | 0.157                  | 1.37         |
| 3.35     | No. 6                  | 0.132                  | 1.23         |
| 2.8      | No. 7                  | 0.111                  | 1.1          |
| 2.36     | No. 8                  | 0.0937                 | 1            |
| 2        | No, 10                 | 0.0787                 | 0.9          |
| 1.7      | No. 12                 | 0.0661                 | 0.81         |
| 1.4      | No. 14                 | 0.0555                 | 0.725        |
| 1.18     | No. 16                 | 0.0469                 | 0.65         |
| 1        | No. 18                 | 0.0394                 | 0.58         |
| 0.85     | No. 20                 | 0.0331                 | 0.51         |
| 0.71     | No. 25                 | 0.0278                 | 0.45         |
| 0.0      | NO. 5U                 | 0.0107                 | 0.39         |
| 0.3      | NO. 33                 | 0.0197                 | 0.34         |
| 0.425    | No. 40                 | 0.0105                 | 0.29         |
| 0.333    | No 50                  | 0.0137                 | 0.247        |
| 0.25     | No 60                  | 0.0098                 | 0.215        |
| 0.212    | No. 70                 | 0.0083                 | 0.152        |
| 0.18     | No. 80                 | 0.007                  | 0.131        |
| 0.15     | No. 100                | 0.0059                 | 0.11         |
| 0.125    | No. 120                | 0.0049                 | 0.091        |
|          |                        |                        |              |

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| U.S. Stan | dard Sieve Series (AS' | TM Designation E11") | - Continued    |
|-----------|------------------------|----------------------|----------------|
| Sieve D   | signation              | Nominal Sieve        | Nominal Wire   |
| Standard  | Alternative            | Opening              | Diameter       |
| (mm)      | (inches)               | (inches)             | (m <b>m*</b> ) |
| 0.106     | No. 140                | 0.0041               | 0.076          |
| 0.09      | No. 170                | 0.0035               | 0.064          |
| 0.075     | No. 200                | 0.0029               | 0.053          |
| 0.063     | No. 230                | 0.0025               | 0.044          |
| 0.053     | No. 270                | 0.0021               | 0.037          |
| 0.045     | No. 270                | 0.0017               | 0.03           |
| 0.038     | No. 270                | 0.0015               | 0.025          |

For complete specifications including permissible variations from nominal apertures and wire diameters and method of checking and calibrating, see the most recent ASTM Designation E11, issued by American Society for Testingand Materials, 1916 Race St., Philadelphia, PA 19103.

These standard designations correspond to the values for test sieve apertures recommended by the International Standards Organization, Geneva, Switzerland.

Only approximate equivalent to the metric values in column 1.

<sup>4</sup> These sieves are not in the standard series but they have been included because they are in common usage.

<sup>\*</sup> These numbers (3.5 to 400) are the approximate number of openings per linear inch but it is preferred that the sieve be identified by the standard designation in millimeters or µm.

Appendix 2 Average Oxide-Equivalent Concentrations in Selected Rock Types

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| -                  |          | Averag    | e Amount | s of Chemi | cal Element   | ts in Grani | te Rocks ( | <b>?</b>           |          |                   |
|--------------------|----------|-----------|----------|------------|---------------|-------------|------------|--------------------|----------|-------------------|
|                    | -        | ,         |          | (taken fr  | om Mielke, 15 | (22)        |            |                    |          |                   |
|                    | Alkali   | Alkali    |          | Dhundian   | Quartz        | Quartz      | Grano-     | <b>Phyndacites</b> | Quartz   | Decine            |
| Element            | Granites | Rhyolites | Same 5   | Kuyoutes   | Monzonites    | Laites      | diorites   |                    | Diorites |                   |
| No. of Analyses)   | (48)     | (21)      | (2)      | (22)       | (121)         | (58)        | (137)      | (115)              | (58)     | ( <del>S</del> 0) |
| SiO,               | 73.86    | 74.57     | 72.08    | 73.66      | 69.15         | 70.15       | 66.88      | 66.27              | 66.15    | 63.58             |
| ,<br>Oj            | 0.2      | 0.17      | 0.37     | 0.22       | 0.56          | 0.42        | 0.57       | 0.66               | 0.62     | 0.64              |
| Al-O-              | 13.75    | 12.58     | 13.86    | 13.45      | 14.63         | 14.41       | 15.66      | 15.39              | 15.56    | 16.67             |
| Fe,O,              | 0.78     | 1.3       | 0.86     | 1.25       | 1.22          | 1.68        | 1.33       | 2.14               | 1.36     | 2.24              |
| FeO.               | 1.13     | 1.02      | 1.67     | 0.75       | 2.27          | 1.55        | 2.59       | 2.23               | 3.42     | 3                 |
| MaO                | 0.05     | 0.05      | 0.06     | 0.03       | 0.06          | 0.06        | 0.07       | 0.07               | 0.08     | 0.11              |
| MeO                | 0.26     | 0.11      | 0.52     | 0.32       | 0.99          | 0.63        | 1.57       | 1.57               | 1.94     | 2.12              |
| 0                  | 0.72     | 0.61      | 1.33     | 1.13       | 2.45          | 2.15        | 3.56       | 3.68               | 4.65     | 5.53              |
| Na.O               | 3.51     | 4.13      | 3.08     | 2.99       | 3.35          | 3.65        | 3.84       | 4.13               | 3.9      | 3.98              |
| K,0                | 5.13     | 4.73      | 5.46     | 5.35       | 4.58          | 4.5         | 3.07       | . 3.01             | 1.42     | 1.4               |
| H,O <sup>•</sup>   | 0.47     | 0.66      | 0.53     | 0.78       | 0.54          | 0.68        | 0.65       | 0.68               | 0.69     | 0.56              |
| P20,               | 0.14     | 0.07      | 0.18     | 0.07       | 0.2           | 0.12        | 0.21       | 0.17               | 0.21     | 0.17              |
| ouartz             | 32.2     | 31.1      | 29.2     | 33.2       | 24.8          | 26.1        | 21.9       | 20.8               | 24.1     | 19.6              |
| K-feldspar         | 30       | 27.8      | 32.2     | 31.7       | 27.2          | 26.7        | 18.3       | 17.8               | 8.3      | 8.3               |
| albite             | 29.3     | 35.1      | 26.2     | 25.1       | 28.3          | 30.9        | 32.5       | 35.1               | 33       | 34.1              |
| anorthite          | 2.8      | 2         | 5.6      | 5          | 11.1          | 9.5         | 16.4       | 14.5               | 20.8     | 23.3              |
| corridum           | 1.4      | •         | 0.8      | 0.9        |               | •           |            | •                  | •        | •                 |
| CaSiO <sub>3</sub> | •        | 0.1       | ł        | •          |               | 0.2         | 1          | 1.3                | 0.3      | 1.3               |
| MgSiO,             | 0.6      | 0.3       | 1.3      | 0.8        | 2.5           | 1.6         | 3.9        | 3.9                | 4.9      | 5.3               |
| FeSiO <sub>3</sub> | 1.1      | 0.6       | 1.7      | •          | 2.2           | 0.8         | 2.9        | 1.3                | 4.1      | 2.8               |
| acmite             | •        | •         | •        | •          | •             | 1           | •          | •                  | •        | •                 |
| magnetite          | 1.2      | 1.9       | 1.4      | 1.9        | 1.9           | 2.5         | 1.9        | 3                  | 2.1      | 3.3               |
| ilmenite           | 0.5      | 0.3       | 0.8      | 0.5        | 1.1           | 0.8         | 1.1        | 1.4                | 1.2      | 1.2               |
| apatite            | 0.3      | 0.2       | 0.4      | 0.2        | 0.5           | 0.3         | 0.5        | 0.3                | 0.5      | 0.3               |

|                                  |                 | Average /      | Amounts o | f Chemical | Elements     | in Interme | diate Rock | s (%)             |          |           |
|----------------------------------|-----------------|----------------|-----------|------------|--------------|------------|------------|-------------------|----------|-----------|
| •                                | -               |                |           | (taken fr  | om Mielke, 1 | 977)       |            |                   |          |           |
| Element                          | Alkali          | Alkali         | Syenites  | Trachytes  | Monzonites   | Laites     | Monzo-     | Latite            | Diorites | Andonines |
| No. of Analyses)                 | Syeutes<br>(25) | Tracbytes (15) | (18)      | (77)       | (46)         | (42)       | (56)       | Abucalica<br>(38) | (20)     | (49)      |
| SiQ                              | 61.86           | 61.95          | 59.41     | 58.31      | 55.36        | 54.02      | 54.66      | 56                | 51.86    | 54.2      |
| Tio,                             | 0.58            | 0.73           | 0.83      | 0.66       | 1.12         | 1.18       | 1.09       | 1.29              | 1.5      | 1.31      |
| N.O.                             | 16.91           | 18.03          | 17.12     | 18.05      | 16.58        | 17.22      | 16.98      | 16.81             | 16.4     | 17.17     |
| Fe,O,                            | 2.32            | 2.33           | 2.19      | 2.54       | 2.57         | 3.83       | 3.26       | 3.74              | 2.73     | 3.48      |
| FeO                              | 2.63            | 1.51           | 2.83      | 2.02       | 4.58         | 3.98       | 5.38       | 4.36              | 6.97     | 5.49      |
| OnM                              | 0.11            | 0.13           | 0.08      | 0.14       | 0.13         | 0.12       | 0.14       | 0.13              | 0.18     | 0.15      |
| MeO                              | 0.96            | 0.63           | 2.02      | 2.07       | 3.67         | 3.87       | 3.95       | 3.39              | 6.12     | 4.36      |
| 0.0                              | 2.54            | 1.89           | 4.06      | 4.25       | 6.76         | 6.76       | 6.99       | • 6.87            | 8.4      | 7.92      |
| Na <sub>2</sub> O                | 5.46            | 6.55           | 3.92      | 3.85       | 3.51         | 3.32       | 3.76       | 3.56              | 3.36     | 3.67      |
| K,0                              | 5.91            | 5.53           | 6.53      | 7.38       | 4.68         | 4.43       | 2.76       | 2.6               | 1.33     | 1.11      |
| Н,О*                             | 0.53            | 0.54           | 0.63      | 0.53       | 0.6          | 0.78       | 0.6        | 0.92              | 0.8      | 0.86      |
| P2O5                             | 0.19            | 0.18           | 0.38      | 0.2        | 0.44         | 0.49       | 0.43       | 0.33              | 0.35     | 0.28      |
| ouartz                           | 1.7             |                | 2         | ũ          | •            | 0.5        | 2          | 7.2               | 0.3      | 5.7       |
| K-feldepar                       | 35              | 32.8           | 38.4      | 43.9       | 27.8         | 26.1       | 16.7       | 15.6              | 7.8      | 6.7       |
| albite                           | 46.1            | 5              | 33        | 28.8       | 29.3         | 27.8       | 31.9       | 29.9              | 28.3     | 30.9      |
| anorthite                        | 4.2             | 3.3            | 10        | 9.7        | 15.8         | 19.2       | 21.1       | 22.2              | 25.8     | 27.2      |
| cormdum                          | •               | 0.6            | ł         | 2          | £            | 8          | •          | •                 | ŧ        | •         |
| CasiO <sub>3</sub>               | 3               | 2.1            | 3         | 4.2        | 6.3          | 4.5        | 4.5        | 4.1               | 5.6      | 4.2       |
| MgSiO,                           | 2.4             | 1.6            | S         | 3.2        | 8            | 9.7        | 9.9        | 8.5               | 15.3     | 10.9      |
| FeSiO,                           | 2.1             | •              | 2.1       | 0.5        | 4.1          | 2.4        | 5.4        | З                 | 8.5      | 5.3       |
| Mg <sub>2</sub> SiO <sub>4</sub> | •               | •              |           | 1.4        | 0.8          |            | I          | 4                 | •        | •         |
| Fe <sub>2</sub> SiO <sub>4</sub> | •               | •              | 1         | 0.2        | 0.4          | 1          | •          | •                 | 1        | 1         |
| magnetite                        | 3.3             | 3.3            | 3.3       | 3.7        | 3.7          | 5.6        | 4.9        | 5.3               | 3.9      | 5.1       |
| ilmenite                         | 1.2             | 1.4            | 1.5       | 1.2        | 2.1          | 2.3        | 2.1        | 2.4               | 2.9      | 2.4       |
| apatite                          | 0.5             | 0.4            |           | 0.5        | 1            | 1.2        | 1          | 0.8               | 0.8      | 0.7       |

| Periodia  | oounts of Chemi<br>& Anorthositic | cal Elements<br>Rocks (%) |
|-----------|-----------------------------------|---------------------------|
| Ð         | ken from Mielke, I                | 623)                      |
|           | Periodite                         | Anorthoeite               |
| Analyses) | (23)                              | (6)                       |
|           | 43.54                             | 54.54                     |
|           | 0.81                              | 0.52                      |
|           | 3.99                              | 25.72                     |
|           | 2.51                              | 0.83                      |
|           | 9.84                              | 1.46                      |
|           | 0.21                              | 0.02                      |
|           | 34.02                             | 0.83                      |
|           | 3.46                              | 9.62                      |
|           | 0.56                              | 4.66                      |
|           | 0.25                              | 1.06                      |
|           | 0.76                              | 0.63                      |
|           | 0.05                              | 0.11                      |
|           | •                                 | 1.4                       |
| sper      | 1.7                               | 6.7                       |
|           | 4.7                               | 39.3                      |
| te        | 7.5                               | 45.9                      |
| inc       | •                                 | •                         |
|           | 3.9                               | 0.3                       |
| 5         | 14.8                              | 2.1                       |
|           | 2.6                               | 1.2                       |
| ð         | 49.1                              | •                         |
|           | 9.6                               | •                         |
| tite      | 3.7                               | 1.2                       |
| 2         | 1.5                               | 0.9                       |
|           | 0.1                               | 0.3                       |

| Ave              | race Amounts o | Chemical Elen                     | hents                     |
|------------------|----------------|-----------------------------------|---------------------------|
| -                | in Gabbroic-Ba | saltic Rocks (%)<br>Mielke, 1977) |                           |
| Slement          | Gabbros        | Tholeiitic Basalts                | Alkali Olivine<br>Basalts |
| No. of Analvace) | (160)          | (137)                             | (%)                       |
| Ċ                | 48.36          | 50.83                             | 45.78                     |
|                  | 13.2           | 2.03                              | 2.63                      |
| 10               | 16.81          | 14.07                             | 14.64                     |
| e.0.             | 2.55           | 2.88                              | 3.16                      |
| 60<br>60         | 7.92           | .6                                | 8.73                      |
| Ouv              | 0.18           | 0.18                              | 0.2                       |
| U <sub>o</sub> N | 8.06           | 6.34                              | 9.39                      |
| 000              | 11.07          | 10.42                             | 10.74                     |
| Na.O             | 2.26           | 2.23                              | 2.63                      |
| 4,0<br>X,0       | 0.56           | 0.82                              | 0.95                      |
| -0-H             | 0.64           | 16.0                              | 0.76                      |
| P,O,             | 0.24           | 0.23                              | 0.39                      |
| owartz           |                | 3.5                               | ٩                         |
| K-feldspar       | 3.3            | 5                                 | 6.1                       |
| albite           | 18.9           | 18.9                              | 18.3                      |
| anorthite        | 34.2           | 25.9                              | 24.7                      |
| nepheline        | •              | #                                 | 2.3                       |
| CaSiO,           | ∞              | 10.3                              | 10.8                      |
| MrSiO,           | 14             | 15.8                              | 7.1                       |
| FeSiO            | 7.4            | 11.2                              | 2.9                       |
| Mg,SiO,          | 4.3            | •                                 | 11.5                      |
| Fe,SiO,          | 2.5            | •                                 | 5                         |
| magnetite        | 3.7            | 4.2                               | 4.6                       |
| ilmenite         | 2.4            | 3.8                               | ٢                         |
| apatite          | 0.6            | 0.5                               |                           |

|                                  |           | Average /         | Amounts of | Chemical E   | lements in . | Alkalic Roc      | ka (%)  |         |         |
|----------------------------------|-----------|-------------------|------------|--------------|--------------|------------------|---------|---------|---------|
|                                  |           |                   |            | AKED ITOM MI | elke, 1977)  |                  |         |         |         |
| Element                          | Nepheline | <b>Phonolites</b> | Essexites  | Nepheline    | Leucite      | Ijolit <b>es</b> | Olivine | Olivine | Olivine |
| (No. of Analyses)                | 5)(80)    | (47)              | (15)       | (8)          | (31)         | (11)             | (21)    | (11)    | (10)    |
| SiO <sub>2</sub>                 | 55.38     | 56.9              | 46.88      | 44.82        | 47.05        | 42.58            | 40.29   | 43.64   | 37.08   |
| TiO1                             | 0.66      | 0.59              | 2.81       | 2.65         | 1.54         | 1.41             | 2.9     | 2.54    | 3.31    |
| Al <sub>2</sub> O,               | 21.3      | 20.17             | 17.07      | 15.42        | 16.05        | 18.46            | 11.32   | 10.82   | 8.08    |
| Fe <sub>2</sub> O <sub>3</sub>   | 2.42      | 2.26              | 3.62       | 4.28         | 3.49         | 4.01             | 4.87    | 5.11    | 5.12    |
| FeO                              | 2         | 1.85              | 5.94       | 6.61         | 5.78         | 4.19             | 7.69    | 5.89    | 7.23    |
| MnO                              | 0.19      | 0.19              | 0.16       | 0.16         | 0.17         | 0.2              | 0.22    | 0.15    | 0.18    |
| MgO                              | 0.57      | 0.58              | 4.85       | 7.27         | 6.2          | 3.22             | 13.28   | 13.86   | 16.19   |
| CaO                              | 1.98      | 1.88              | 9.49       | 10.32        | 10.8         | 11.38            | 12.99   | 10.66   | 16.3    |
| Na <sub>2</sub> O                | 8.84      | 8.72              | 5.09       | 5.3          | 2.35         | 9.55             | 3.14    | 2.16    | 2.3     |
| K,O                              | 5.34      | 5.42              | 2.64       | 1.26         | 5.38         | 2.55             | 1.44    | 4.09    | 1.36    |
| H,O⁺                             | 0.96      | 0.96              | 0.97       | 1.56         | 9.0          | 0.55             | 1.08    | 0.72    | 1.89    |
| P <sub>2</sub> O <sub>5</sub>    | 0.19      | 0.17              | 0.48       | 0.35         | 0.59         | 1.52             | 0.78    | 0.63    | 0.96    |
| Ś                                | 0.17      | •                 | •          | •            | -            | 0.38             | •       | •       | •       |
| U                                | •         | 0.23              | •          | •            | •            | 1                | ٩       | •       | •       |
| so,                              | •         | 0.13              | ۱          | •            | 1            | ٩                | 1       | •       | •       |
| ztrenp                           | 31.1      | 31.7              | 15.6       | 7.8          | 22.2         | 10               | -       | 6.9     | •       |
| albite                           | 32        | 36.2              | 14.7       | 12.6         | •            | -                | -       | -       | •       |
| anorthite                        | 2.8       | 1.7               | 16.1       | 14.5         | 17.5         | -                | 12.8    | 6.1     | 7.5     |
| leucite                          | 1         | •                 | •          | •            | 7.4          | 3.9              | 6.5     | 13.8    | 6.5     |
| ncpheline                        | 23.3      | 18.7              | 15.3       | 17.3         | 10.8         | 43.7             | 14.2    | 9.9     | 10.5    |
| Ca <sub>2</sub> SiO <sub>4</sub> | ŧ         | 1                 | •          | •            | •            | •                | 1.6     | 1       | 12.8    |
| Casio,                           | 2.1       | 2.9               | 11.6       | 14.3         | 13.6         | 18.5             | 17.2    | 17.8    | 10.6    |
| MgSiO,                           | 1.2       | 1.4               | 8.2        | 10.4         | 9.3          | 8                | 13.1    | 14.5    | 8.6     |
| FeSiO <sub>3</sub>               | 0.8       | 0.9               | 2.4        | 2.5          | 3.2          | 2.4              | 2.2     | 1.1     | 0.8     |
| Mg <sub>2</sub> SiO <sub>4</sub> | 0.1       |                   | 2.8        | 5.5          | 4.3          | •                | 14.1    | 14.1    | 22.3    |
| Fe <sub>2</sub> SiO <sub>4</sub> | 0.1       | ł                 | 0.8        | 1.5          | 1.7          | -                | 2.7     | 1.2     | 2.5     |
| magnetite                        | 3.5       | 3.3               | 5.3        | 6.3          | 5.1          | 5.8              | 7.2     | 7.4     | 7.4     |
| ilmenite                         | 1.4       | 1.2               | 5.3        | ۶            | 2.9          | 2.7              | 5.5     | 4.9     | 6.2     |
| apatite                          | 0.4       | 0.3               | 1.2        | 0.8          | 1.3          | 3.6              | 1.8     | 1.5     | 2.3     |
| calcite                          | 0.4       | •                 | '          | ·            |              | 0.9              | •       | •       |         |

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Appendix 3 Normal Trace Element Concentrations in Selected Rock Types

British Columbia Ministry of Employment and Investment, Energy and Minerals Division

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| Atomic Element         Symbol         Igneous Rocts         Schimentary           No.         i         i         Iultrabasic         Basaltic         Granitic Rocts         Shales         Standston           89         Attinium         Ac         E                           | Sedimentary Rocks Deer<br>Sandstones Carbonates Carb |                |
|---|--|----------------|
| Atomic         Element         Symbol         Bataltic         Granitic Rocka         Shales         Standson           No.         i         I         Ultrabasic         Rocka         High         Low         Syenites         Shales         Standson           89         Actinium         Al         2000         72000         8800         80000         25000           13         Aluminum         Al         2001         0.2         0.2         0.2         0.2         0.2         0.0         2500           31         Aluminum         Ar         B                 | Sandstones Carbonates Carb                           | -sea Sodiments |
|   | L Sandstones Carbonates Carbo                        |                |
| 89         Actinium         Ac         E <th< th=""><th></th><th>Date Clay</th></th<>           |  | Date Clay      |
|   | н<br>Н<br>Н<br>Н                                     | E              |
| 51         Antimony         5b         0.1         0.2         0.2         0.2         0.2         0.2         1.5         1.5         0.0X           18         Argon         Ar         B   | 0 25000 4200 200                                     | 0 84000        |
|   | 0.0X 0.2 0.1   | 5 1            |
| 33         Argenic         Aa         1         2         19         1.5         1.4         13         1           85         Asteine         Ai         E <td>B B E</td> <td>A</td>                         | B B E  | A              |
| 85         Attaine         At         E <the< th=""><td></td><td>13</td></the<>                 |  | 13             |
| 56         Barium         Ba         0.4         330         420         840         1600         580         X0           4         Beryllium         Be         0.X         1         2         3         1         3         0.X           8         Beryllium         Be         0.X         1         2         3         1         3         0.X           8         Bismuth         Bis         D         0.007         D         0.01         D         D         D         D         D           3         Bornine         Br         1         3.6         4.5         1.3         2.7         4         1           35         Bornine         Br         1         3.6         4.5         1.3         2.7         4         1           48         Cathon         Ca $\Delta$ $\Lambda$ <td>E</td> <td>Ξ</td>  | E  | Ξ              |
| 4         Beryllium         Be $0.X$ 1         2         3         1         3         0.X           83         Bismuth         Bi         D         0.007         D         0.01         D         D         D         D         D         D         D         3 $3$ 5         9         10         D  | X0 10 15   | 2300           |
| 83         Bismuth         Bi         D $0.007$ D $0.01$ D          | 0.X 0.X 0.   | r 2.6          |
| 5         Boron         B         3         5         9         10         9         100         35           35         Bromine         Br         1         3.6         4.5         1.3         2.7         4         1           48         Cadmium         Cd         0.X         0.22         0.13         0.13         0.3         0.03           6         Carbon         C         A         B  | DDD  | ۵              |
| 35         Bromine         Br         1         3.6         4.5         1.3         2.7         4         1           48         Cadmium         Cd         0.X         0.22         0.13         0.13         0.13         0.3         0.03           20         Calcium         Ca         0.X         0.22         0.13         0.13         0.3         0.0X           50         Calcium         Ca         25000         76000         25300         5100         18000         22100         39100           58         Carbon         C         A         B         B         B                                       | 35 20 5  | 230            |
| 48         Cadmium         Cd $0.X$ $0.22$ $0.13$ $0.13$ $0.03$ 58         Cenum         Ce $0.X$ $48$ $81$ $92$ $161$ $59$ $0.7$ $4$ 55         Cesium         Ce $0.X$ $1.1$ $2$ $4$ $0.6$ $5$ $0.X$ 17         Chlorine         C1 $83$ $60$ $170$ $22$ $4.1$ $2$ $90$ $35$ 27         Cobalt         Co $170$ $22$ $4.1$ $2$ $90$ $35$ 29         Cobalt<   | 1 6.2 7  | 70             |
| 20         Calcium         Ca $25000$ $76000$ $25300$ $5100$ $18000$ $22100$ $39100$ 58         Carbon         C         A  | 0.0X 0.035 0.(                                       | X 0.42         |
| 6         Carbon         C         A </th <td>39100 302300 312</td> <td>00 29000</td> | 39100 302300 312                                     | 00 29000       |
| 58         Cerium         Ce         0.X         48         81         92         161         59         92           55         Cesium         Ca         0.X         1.1         2         4         0.6         5         0.X           17         Chlorine         C1         85         60         130         200         520         180         10           24         Chromium         Cr         1600         170         22         4.1         2         90         35           27         Cobalt         Co         150         48         7         1         1         19         0.3           27         Cobalt         Co         150         87         30         10         5         45         X           29         Copper         Cu         10         87         30         10         5         45         7           66         Dysprosium         Dy         0.X         2.1         3.5         4         7         13         4.6         7.2           68         Erbium         Eu         0.X         2.1         3.5         4         7         2.5         4  | `<br>~<br>~  | <              |
| 55       Cesium       Ca       0.X       1.1       2       4       0.6       5       0.X         17       Chlorine       C1       85       60       130       200       520       180       10         24       Chronium       Cr       1600       170       22       4.1       2       90       35         27       Cobalt       Co       130       200       52.0       180       10         29       Copper       Cu       10       87       30       10       5       45       X         29       Copper       Cu       10       87       30       10       5       45       X         29       Copper       Cu       10       87       30       10       5       45       X         66       Dysprosium       Dy       0.X       3.8       6.3       7.2       13       4.6       7.2         68       Erbium       Er       0.X       3.8       6.3       1.4       1.6       2.55       4         63       Europium       Er       0.0       50.0       850       1200       740       2.70         9  | 92 11.5 3  | 345            |
| 17       Chlorine       C1       85       60       130       200       520       180       10         24       Chromium       Cr       1600       170       22       4.1       2       90       35         27       Cobalt       Co       150       48       7       1       1       19       0.3         29       Copper       Cu       10       87       30       10       5       45       7.2         66       Dysprosium       Dy       0.X       3.8       6.3       7.2       13       4.6       7.2         68       Erbium       Er       0.X       2.1       3.5       4       7       2.5       4         63       Europium       Eu       0.X       0.8       1.4       1.6       2.5       4         63       Europium       Fu       0.0       870       166       2.8       1       1.6         7       Fue       F       100       400       520       850       1200       740       270         64       Fue       E       E       E       E       E       E       E       E       E <t< th=""><td>0.X 0.X 0.</td><td>0</td></t<>   | 0.X 0.X 0.   | 0              |
| 24       Chromium       Cr       1600       170       22       4.1       2       90       35         27       Cobalt       Co       150       48       7       1       1       19       0.3         29       Copper       Cu       10       87       30       10       5       45       X         66       Dysprosium       Dy       0.X       3.8       6.3       7.2       13       4.6       7.2         68       Erbium       Er       0.X       2.1       3.5       4       7       2.5       4         63       Europium       Eu       0.X       0.8       1.4       1.6       2.5       4         63       Europium       Eu       0.X       0.8       1.4       1.6       2.5       4         63       Europium       F       100       400       520       850       1200       740       270         77       F       E  | 10 150 21(   | 21000          |
| 27       Cobalt       Co       150       48       7       1       1       19       0.3         29       Copper       Cu       10       87       30       10       5       45       X         66       Dysprosium       Dy       0.X       3.8       6.3       7.2       13       4.6       7.2         68       Erbium       Er       0.X       2.1       3.5       4       7       2.5       4         63       Europium       Eu       0.X       0.8       1.4       1.6       2.5       4         63       Europium       Eu       0.X       0.8       1.4       1.6       2.5       4         7       Function       Function       Function       Function       70       70       70  | 35 11 1  | 8              |
| 29     Copper     Cu     10     87     30     10     5     45     X       66     Dysprosium     Dy     0.X     3.8     6.3     7.2     13     4.6     7.2       68     Erbium     Er     0.X     2.1     3.5     4     7     2.5     4       63     Europium     Eu     0.X     0.8     1.4     1.6     2.8     1     1.6       9     Fluorine     F     100     400     520     850     1200     740     270       87     Fancium     Fr     E     E     E     E     E     E     E   | 0.3 0.1 7  | 74             |
| 66         Dysprosium         Dy         0.X         3.8         6.3         7.2         13         4.6         7.2           68         Erbium         Er         0.X         2.1         3.5         4         7         2.5         4           63         Europium         Eu         0.X         0.8         1.4         1.6         2.8         1         1.6           9         Fluorine         F         100         400         520         850         1200         740         270           87         Fancium         Fr         E   | X 4 3  | 250            |
| 68         Erbium         Er         0.X         2.1         3.5         4         7         2.5         4           63         Europium         Eu         0.X         0.8         1.4         1.6         2.8         1         1.6           9         Fluorine         F         100         400         520         850         1200         740         270           87         Francium         Fr         E <th< th=""><td>7.2 0.9 2.</td><td>27</td></th<>    | 7.2 0.9 2.   | 27             |
| 63         Europium         Eu         0.X         0.8         1.4         1.6         2.8         1         1.6         1.5         1         1.6         1         1.6         1         1         1.6         1         1         1.6         1         1         1         1         1         1         1         0         1         0         1         0         1         0         1         <                                  | 4 0.5 1.   |                |
| 9         Fluorine         F         100         400         520         850         1200         740         270           87         Francium         Fr         E         <  | 1.6 0.2 0.   | ø              |
| 87 Francium   Fr   E   E   E   E   E   E   E   E  | 270 330 54   | 1300           |
|   | ш  | ω              |
| 64 Gadolinium Gd 0.X 5.3 8.8 10 18 6.4 10   | 10 1.3 3.  | 38             |
| 31 Gallium Ga 1.5 17 17 17 30 19 12   | 12 4 1.  | 20             |
| 32 Germanium Ge 1.5 1.3 1.3 1.3 1.3 1.6 8   | 8 0.2 0.   | 2              |
| 79 Gold Au 0.006 0.004 0.004 0.004 0.007 0.00X 0.00X 0.00X  | 0.00X 0.00X 0.00                                     | X 0.00X        |
| 72 Hafhium Hf 0.6 2 2.3 3.9 11 2.8 3.9  | 3.9 0.3 0.4  | 4.1            |
| 2 Helium He B B B B B B B B B B   | BBBB   | B              |

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|        |              | Dist   | rribution o | f the elen | nents in th     | ne Earth's     | : crust (in | parts per m | uillion) <sup>1</sup> - Con | tinued     |           |           |
|--------|--------------|--------|-------------|------------|-----------------|----------------|-------------|-------------|-----------------------------|------------|-----------|-----------|
|        |              |        |             | I          | preous Rock     | 5              |             | Se          | dimentary Ro                | cks        | Deep-sea  | Sediments |
| Atomic | Blement      | Symbol |             | Basaltic   | Ū               | ranitic Rock   | 8           |             |                             |            |           |           |
| No.    |              |        | Ultrabasic  | Rocks      | High<br>Calcium | Low<br>Calcium | Sycnites    | Shales      | Sandstones                  | Carbonates | Carbonate | Clay      |
| 16     | Protactinium | P      | ш           | E          | щ               | ய              | Э           | B           | E                           | B          | ш         | a         |
| 88     | Radium       | R      | Э           | Е          | Э               | Э              | Э           | щ           | Э                           | B          | Э         | Э         |
| 88     | Radon        | 8      | ш           | ш          | Э               | ല              | E           | E           | E                           | E          | E         | E         |
| 75     | Rhenium      | Re     | Q           | ۵          | ۵               | ٩              | D           | ٥           | D                           | D          | ۵         | ۵         |
| 45     | Rhodium      | କ୍ଷ    | D           | ۵          | D               | ٥              | D           | D           | ۵                           | D          | D         | D         |
| 37     | Rubidium     | Rb     | 0.2         | 30         | 110             | 170            | 110         | 140         | 60                          | 3          | 10        | 110       |
| 4      | Ruthenium    | Ru     | D           | ۵          | D               | ۵              | D           | D           | D                           | ۵          | ۵         | D         |
| 62     | Samarium     | Sm     | 0.X         | 5.3        | 8.8             | 10             | 18          | 6.4         | 10                          | 1.3        | 3.8       | 38        |
| 21     | Scandium     | ß      | 15          | 30         | 14              | 7              | 3           | 13          | 1                           | 1          | 2         | 19        |
| 8      | Selenium     | ઝ      | 0.05        | 0.05       | 0.05            | 0.05           | 0.05        | 0.6         | 0.05                        | 0.08       | 0-17      | 0.17      |
| 14     | Silicon      | Si     | 205000      | 230000     | 314000          | 347000         | 291000      | 73000       | 368000                      | 24000      | 32000     | 250000    |
| 47     | Silver       | Ag     | 0.06        | 0.11       | 0.051           | 0.037          | 0.0X        | 0.07        | 0.0X                        | 0.0X       | 0.0X      | 0.11      |
| 11     | Sodium       | °Z     | 4200        | 18000      | 28400           | 25800          | 40400       | 9600        | 3300                        | 400        | 20000     | 40000     |
| 38     | Strontium    | Sr     | 1           | 465        | 440             | 100            | 200         | 300         | 20                          | 610        | 2000      | 180       |
| 16     | Sulphur      | S      | 300         | 300        | 300             | 300            | 300         | 2400        | 240                         | 1200       | 1300      | 1300      |
| 73     | Tantalum     | Ta     | 1           | 1.1        | 3.6             | 4.2            | 2.1         | 0.8         | 0.0X                        | 0.0X       | 0.0X      | 0.X       |
| 43     | Technetium   | Tc     | ပ           | ပ          | ပ               | C              | ပ           | ບ           | с<br>С                      | v          | ပ         | ပ         |
| 52     | Tellurium    | Te     | D           | D          | Q               | ۵              | D           | D           | D                           | D          | D         | ۵         |
| 65     | Terbium      | £      | 0.X         | 0.8        | 1.4             | 1.6            | 2.8         | 1           | 1.6                         | 0.2        | 0.6       | 9         |
| 81     | Thallium     | F      | 0.06        | 0.21       | 0.72            | 2.3            | 1.4         | 1.4         | 0.82                        | 0.0X       | 0.16      | 0.8       |
| 8      | Thorium      | Ę      | 0.004       | 4          | 8.5             | 17             | 13          | 12          | 1.7                         | 1.7        | x         | 7         |
| 69     | Thulium      | Tm     | 0.X         | 0.2        | 0.3             | 0.3            | 0.6         | 0.2         | 0.3                         | 0.04       | 0.1       | 1.2       |
| 50     | Tin          | Sn     | 0.5         | 1.5        | 1.5             | 3              | ×           | ه           | 0.X                         | 0.X        | 0.X       | 1.5       |
| 22     | Titanium     | Ϊ      | 300         | 13800      | 3400            | 1200           | 3500        | 4600        | 1500                        | 400        | 770       | 4600      |
| 74     | Tungsten     | M      | 0.77        | 0.7        | 1.3             | 2.2            | 1.3         | 1.8         | 1.6                         | 0.6        | 0.X       | X         |
| 92     | Uranium      | Ŋ      | 0.001       | 1          | 3               | 3              | 3           | 3.7         | 0.45                        | 2.2        | 0.X       | 1.3       |
| 23     | Vanadium     | >      | 40          | 250        | 88              | 4              | 30          | 130         | 20                          | 20         | 20        | 120       |
| 54     | Xenon        | Xe     | В           | B          | B               | B              | B           | B           | B                           | B          | B         | æ         |
| 2      | Ytterbium    | ድ      | 0.X         | 2.1        | 3.5             | 4              | 7           | 2.6         | 4                           | 0.5        | 1.5       | 15        |
| 39     | Yttrium      | ۲      | 0.X         | 21         | 35              | 4              | 20          | 26          | 40                          | 30         | 42        | 8         |
| 8      | Zinc         | Zn     | 50          | 105        | 60              | 39             | 130         | 95          | 16                          | 20         | 35        | 165       |

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|             |              | Dist     | ribution o | f the elen | nents in t      | he Earth'      | s crust (in | parts per n | nillion) <sup>1</sup> - Coi | ntinued    |           |           |
|-------------|--------------|----------|------------|------------|-----------------|----------------|-------------|-------------|-----------------------------|------------|-----------|-----------|
|             |              |          |            | ľ          | gneous Roci     | cs             |             | Х           | edimentary Ro               | xcks       | Deep-sea  | Sediments |
| Atomic      | Element      | Symbol   |            | Basaltic   | 5               | iranitic Rocl  | S           |             |                             |            |           |           |
| No.         | -            | -        | Ultrabasic | Rocks      | High<br>Calcium | Low<br>Calcium | Syenites    | Shales      | Sandstones                  | Carbonates | Carbonate | Clay      |
| 67          | Holmium      | Ho       | 0.X        | 1.1        | 1.8             | 2              | 3.5         | 1.2         | 2                           | 0.3        | 0.8       | 7.5       |
| -           | Hydrogen     | Н        | ×          | ۷          | ۷               | V              | V           | ۲           | <                           | V          | <         | <         |
| 53          | lodine       |          | 0.5        | 0.5        | 0.5             | 0.5            | 0.5         | 2.2         | 1.7                         | 1.2        | 0.05      | 0.05      |
| ٢           | Iridium      | Ч        | ۵          | D          | D               | D              | D           | D           | D                           | D          | D         | ٩         |
| 26          | Iron         | Ъс       | 94300      | 86500      | 29600           | 14200          | 36700       | 47200       | 9800                        | 3800       | 9006      | 65000     |
| 36          | Krypton      | ۲r       | B          | B          | B               | 8              | B           | B           | В                           | B          | B         | B         |
| 57          | Lanthanum    | L        | 0.X        | 15         | 45              | 55             | 70          | 92          | 30                          | X          | 10        | 115       |
| 82          | Lead         | å        | -          | 6          | 15              | 19             | 12          | 20          | 7                           | 6          | 6         | 80        |
| m           | Lithium      | Li       | 0.X        | 17         | 24              | 40             | 28          | 66          | 15                          | 5          | S         | 57        |
| 6           | Indium       | Ъ        | 0.01       | 0.22       | 0.0X            | 0.26           | 0.0X        | 0.1         | X00                         | 0.0X       | 0.0X      | 0.08      |
| 71          | Lutetium     | Ľ        | 0.X        | 0.6        | 1.1             | 1.2            | 2.1         | 0.7         | 1.2                         | 0.2        | 0.5       | 4.5       |
| 12          | Magnesium    | Mg       | 204000     | 46000      | 9400            | 1600           | 5800        | 15000       | 7000                        | 47000      | 4000      | 21000     |
| 25          | Manganese    | Å        | 1620       | 1500       | 540             | 390            | 850         | 850         | 0X                          | 1100       | 1000      | 6700      |
| 8           | Mercury      | Hg       | 0.0X       | 0.0        | 0.08            | 0.08           | 0.0X        | 0.4         | 0.03                        | 0.04       | 0.0X      | 0.X       |
| 42          | Molybdenum   | °W       | 0.3        | 1.5        | 1               | 1.3            | 0.6         | 2.6         | 0.2                         | 0.4        | 3         | 27        |
| 8           | Neodymium    | PZ       | 0.X        | 20         | 33              | 37             | 65          | 24          | 37                          | 4.7        | 14        | 140       |
| 2           | Neon         | ž        | B          | m          | B               | B              | B           | B           | B                           | B          | B         | B         |
| 93          | Neptunium    | ź        | ц          | щ          | íL,             | ц              | Ξ.          | í.          | F                           | ц          | Ľ         | Ľ         |
| 28          | Nickel       | ź        | 2000       | 130        | 15              | 4.5            | 4           | 68          | 2                           | 20         | 30        | 225       |
| 4           | Niobium      | £        | 16         | 6          | 20              | 21             | 35          | 11          | 0.0X                        | 0.3        | 4.6       | 14        |
| -[;         | Nitrogen     | z        | 0          | 2          | 20              | 20             | 30          | <           | <b>v</b>                    | V          | ۷         | <b>v</b>  |
| <b>و</b>  • | Comun        | 5        | a) ·       | аļ,        |                 | ٩              | ٥           | ۵           | ٩                           | ۵          | D         | D         |
| ×           | Uxygen       |          |            | <          | <               | <              | <           | <           | <                           | V          | V         | <         |
| <b>\$</b>   | Palladium    | Pa       | 0.12       | 0.02       | 0.00X           | 0.00X          | D           | D           | D                           | D          | D         | ٩         |
| 2           | Phosphorus   | <u>م</u> | 220        | 8          | 920             | 800            | 800         | 700         | 170                         | 400        | 350       | 1500      |
| 8           | Platinum     | æ        | ٩          |            | ۵               | ۵              | D           | ۵           | D                           | D          | ٥         | ۵         |
| <b>z</b>    | Plutonium    | æ        | ц.         | ſL.        | ц               | <u>ند</u>      | Я           | ٤.          | F                           | Ľ.         | <u></u>   | 11        |
| 2           | Polonium     | Po       | ш          | ш          | Ē               | ш              | Э           | Е           | Е                           | Э          | ш         | ш         |
| 2           | Potassium    | ×        | 40         | 8300       | 25000           | 42000          | 48000       | 26600       | 10700                       | 2700       | 2900      | 25000     |
| 5           | Praseodymium | <u>ح</u> | 0.X        | 4.6        | 11              | 8.8            | 15          | 5.6         | 8.8                         | 1.1        | 3.3       | 33        |
| 5           | Promethium   | M        | -<br>      | 0          | ပ<br>ပ          | с<br>V         | с<br>V      | с<br>U      | ပ                           | ပ<br>ပ     | c         | c         |

|         |                        |                        | (in parts) | per millio   | n)                   |                     | 1003       |
|---------|------------------------|------------------------|------------|--------------|----------------------|---------------------|------------|
| Element | Continental<br>Crust   | Crust as a<br>Whole    | Chondrites | Element      | Continental<br>Crust | Crust as a<br>Whole | Chondrites |
| н       | $(1,530)^{1}$          | 1,520                  | -          | Rh           | -                    | -                   |            |
| Li      | 20                     | 18                     | 3          | Pd           | 0.015                | 0.01                | 1          |
| Be      | 3                      | 2                      | 3.6        | Ag           | 0.075                | 0.08                | 0.1        |
| B       | 10                     | 9                      | 2          | Cd           | 0.15                 | 0.16                | 0.1        |
| C       | 200                    | 180                    | 400        | In           | 0.25                 | 0.24                | 0.01       |
|         | (5,070)'               | (5,220)'               |            |              |                      |                     |            |
| N       | 19                     | 19                     | 1          | Sn           | 2.3                  | 2.1                 | 1          |
| 0       | 461,000                | 456,000                | 350,000    | Sd           | 0.2                  | 0.2                 | 0.1        |
|         | (472,650)'             | (468,780) <sup>1</sup> |            |              |                      |                     |            |
| F       | 585                    | 544                    | 28         | Te           | -                    | -                   | 0.5        |
| Na      | 23,550                 | 22,700                 | 7,000      | F I          | 0.45                 | 0.46                | 0.04       |
|         | (22,060) <sup>1</sup>  | (21,370)               |            |              |                      |                     |            |
| Mg      | 23,300                 | 27,640                 | 140,000    | Cd           | 3                    | 2.6                 | 0.1        |
|         | (18,500) <sup>1</sup>  | (23,400) <sup>1</sup>  |            |              |                      |                     |            |
| Al      | 82,300                 | 83,600                 | 13,000     | Ba           | 425                  | 390                 | 6          |
|         | $(80,210)^1$           | (80,950) <sup>1</sup>  |            |              |                      |                     |            |
| Si      | 281,500                | 273,000                | 180,000    | La           | 39                   | 34.6                | 0.3        |
|         | (279,380) <sup>1</sup> | (277,970) <sup>1</sup> |            |              |                      |                     | _          |
| P       | 1,050                  | 1,120                  | 500        | Ce           | 66.5                 | 66.4                | 0.5        |
|         | (1,040) <sup>1</sup>   | (960) <sup>1</sup>     |            |              |                      |                     |            |
| s       | 350                    | 340                    | 20,000     | Pr           | 9.2                  |                     | 0.1        |
|         | (530) <sup>1</sup>     | (400) <sup>1</sup>     |            |              |                      |                     |            |
| CI      | 145                    | 126                    | 70         | Nd           | 41.5                 | 39.6                | 0.8        |
|         | (620) <sup>ı</sup>     | (500) <sup>1</sup>     |            |              |                      |                     |            |
| K       | 20,850                 | 18,400                 | 850        | Sm           | 7.05                 | 7.02                | 0.2        |
|         | (23,620) <sup>1</sup>  | (19,420) <sup>1</sup>  |            |              |                      |                     |            |
| Ca      | 41500                  | 46,600                 | 14,000     | Eu           | 2                    | 2.14                | 0.08       |
|         | (40,000) <sup>1</sup>  | (49,960) <sup>1</sup>  |            |              |                      |                     |            |
| Sc      | 22                     | 25                     | 6          | Gd           | 6.2                  | 6.14                | 0.4        |
| Ti      | 5650                   | 6,320                  | 500        | $\mathbf{n}$ | 1.2                  | 1.18                | 0.05       |
|         | (4,380) <sup>1</sup>   | (5,040) <sup>1</sup>   |            |              |                      |                     |            |
| v       | 120                    | 136                    | 70         | Dy           | -                    | •                   | 0.35       |
| Cr      | 102                    | 122                    | 2,500      | Но           | 1.3                  | 1.26                | 0.07       |
| Mn      | _950                   | 1,060                  | 2,000      | Er           | 3.5                  | 3.46                | 0.2        |
|         | (1,110) <sup>1</sup>   | (1,240) <sup>1</sup>   |            |              |                      |                     |            |
| Fe      | 56,300                 | 62,200                 | 250,000    | Tu           | 0.52                 | 0.5                 | 0.04       |
|         | (46,810) <sup>1</sup>  | (50,880) <sup>1</sup>  |            |              |                      |                     |            |
| Co      | 25                     | 29                     | 800        | УЪ           | 3.2                  | 3.1                 | 0.2        |
| Ni      | - 84                   | 99                     | 13,500     | Lu           | •                    | •                   | 0.03       |
| Cu      | 60                     | 68                     | 100        | HI           | 3                    | 2.8                 | 0.5        |
| Zn      | 70                     | 76                     | 50         | Ta           | 2                    | 1.7                 | 0.02       |
| Ga      | 19                     | 19                     | 3          | W            | 1.25                 | 1.2                 | 0.15       |
| Ge      | 1.5                    | 1.5                    | 10         | Re           | 0.0007               | 0.0007              | 0.0008     |
| AS      | 1.8                    | 1.8                    | 0.3        | US           | -                    | •                   | 0.5        |

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|                     |  | Dist                    | ribution o                     | f the elen                 | nents in th         | ie Earth's   | s crust (in   | parts per n  | illion) <sup>1</sup> - Coi | tinued                    |            |           |
|---------------------|--|-------------------------|--------------------------------|----------------------------|---------------------|--------------|---------------|--------------|----------------------------|---------------------------|------------|-----------|
|                     |  |                         |                                | Ig                         | gneous Rock         | 8            |               | Š            | dimentary Ro               | cks                       | Deep-sea ? | sediments |
| Atomic              | Element                                    | Symbol                  |                                | Basaltic                   | ତ                   | ranitic Rock | 5             |              |                            |                           |            |           |
| °.<br>Ž             | -  | -                       | Ultrabasic                     | Rocks                      | High                | Low          |               | Shales       | Sandstones                 | Carbonates                | Carbonate  | Clay      |
|                     |  | •                       |                                |                            | Calcium             | Calcium      | oyenues       |              |                            |                           |            |           |
| 40                  | Zirconium                                  | 21                      | 45                             | 140                        | 140                 | 175          | 500           | 160          | 220                        | 19                        | 20         | 150       |
| <sup>1</sup> In som | e cases only orde                          | r of magn               | itude estima                   | tes could be               | made. The           | se are indic | ated by the s | ymbol X.     |                            |                           |            |           |
| A : The<br>lithosph | te elements are th<br>ere, whereas carb    | e basic cc<br>on is imp | matituents of<br>ortant in sed | the biosphi<br>imentary ro | ere, hydrosp<br>ck. | here and atr | nosphere. C   | xygen is al: | the most in                | iportant elem             | ent of the |           |
| B: The r            | are gases occur in                         | the atmo                | sphere in th                   | e following                | amounts (vo         | olume per co | ent: He, 0.00 | 052; Ne, 0.  | 0018; A. 0.93              | : Kr. 0.0001:             | Xe.        |           |
| 0.00000             | 8. He is produced                          | by radio                | active decay                   | of U and T                 | h but is also       | lost to oute | r space. A4(  | ) is produce | d by the radio             | active potass             | ium 40 and |           |
| is the m            | ajor isotope of ar                         | çon in the              | atmosphere                     | The argon                  | and helium          | contents of  | rocks will v  | ary with the | ir age owing               | to the effect o           | of         |           |
| radioact            | ive decay. The en                          | stimated r              | are-gas conte                  | ents of igne               | ous rocks an        | e (in cc per | gm of rock):  | He, 6 * 10   | <sup>5</sup> ; Ne, 7.7 * 1 | 0 <sup>+</sup> ; A, 2.2 + | 10°5: Kr,  |           |
| 4.2 + 10            | <sup>•</sup> ; Xe. 3.4 • 10 <sup>-10</sup> |                         |                                |                            |                     |              |               |              |                            |                           |            |           |
| C: These            | clements do not                            | occur nat               | urally in the                  | Earth's crue               | st.                 |              |               |              |                            |                           |            |           |
| D: The c            | lata for these clen                        | nents are               | missing or w                   | nreliable.                 |                     |              |               |              |                            |                           |            |           |
| E: All d            | cse elements are                           | present as              | : radioactive                  | nuclides in                | the decay so        | hemes of U   | and Th.       |              |                            |                           |            |           |
| F: These            | elements occur I                           | aturally (              | only as a con                  | sequence of                | f neutron cal       | sture by una | nium.         |              |                            |                           |            |           |
| Source:             | <b>Turckian and We</b>                     | depohl, 1               | 961                            |                            |                     | -            |               |              |                            |                           |            |           |

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# Abundances of Chemical Elements in the Earth's Crust and Chondrites Continued (in parts per million)

| Element   | Continental<br>Crust | Crust as a<br>Whole | Chondrites       | Element       | Continental<br>Crust | Crust as a<br>Whole | Chondrites |
|-----------|----------------------|---------------------|------------------|---------------|----------------------|---------------------|------------|
| Se        | 0.05                 | 0.05                | 10               | Г             | •                    | -                   | 0.5        |
| Br        | 2.4                  | 2.5                 | 0.5              | Pt            | •                    | •                   | 2          |
| Rb        | 90                   | 78                  | 5                | Au            | 0.004                | 0.004               | 0.17       |
| Sr        | 370                  | 384                 | 10               | Hg            | 0.085                | 0.086               | 3          |
| Y         | 33                   | 31                  | 1                | π             | 0.85                 | 0.72                | 0.001      |
| Zr        | 165                  | 162                 | 30               | Pb            | 14                   | 13                  | 0.2        |
| Nb        | 20                   | 20                  | 0.3              | Bi            | 0.0085               | 0.0082              | 0.003      |
| Mo        | 1.2                  | 1.2                 | 0.6              | Th.           | 9.6                  | 8.1                 | 0.04       |
| Ru        | •                    | •                   | •                | U             | 2.7                  | 2.3                 | 0.015      |
| . The abu | indance of the n     | nain elements of    | btained by a qui | intitiative r | nethod based or      | the volume          |            |

measurements are shown in parentheses; Source: Ronov and Yaroshevsky, 1972.

| Crustal Abundance of Minerals |                   |                     |                   |  |  |  |
|-------------------------------|-------------------|---------------------|-------------------|--|--|--|
| Mineral                       | Volume percentage | Mineral             | Volume percentage |  |  |  |
| Plagiociase                   | 42                | Biotite             | 4                 |  |  |  |
| Potash feldspar               | 22                | Magnetite, ilmenite | 2                 |  |  |  |
| Quartz                        | 18                | Olivine             | 1.5               |  |  |  |
| Amphibole                     | 5                 | Apatite             | 0.5               |  |  |  |

Appendix 4 Pollution Control Objectives for British Columbia

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British Columbia Ministry of Employment and Investment, Energy and Minerals Division

| (Province of British Colum)   | bia. Ministry of Environment                                       | 1979)                                  |  |  |  |
|---|--|--|--|--|--|
|   | Ran  | ne                                     |  |  |  |
| Parameter   | (mg/L dissolved in effluent unless otherwise stated <sup>5</sup> ) |  |  |  |  |
| Total suspended solids <sup>1,2</sup>   | 25   | 75                                     |  |  |  |
| Total dissolved solids  | 2500   | 5000                                   |  |  |  |
| Toxicity (96-hour LC50 static bioassay <sup>3</sup> )                             | 100%   | 80%                                    |  |  |  |
| pH (pH units)   | 6.5-8.5  | 6.5-10                                 |  |  |  |
| Radioactivity: Gross Alpha pCi/L  | 10   | 100                                    |  |  |  |
| Radium <sup>226</sup> pCi/L (dissolved in effluent passing through a 3 µm filter) | less than 10   |  |  |  |  |
| Specific elements and compounds:  | I  |  |  |  |  |
| Aluminum (Al)   | 0.5  | 1                                      |  |  |  |
| Ammonia (as N)  | 1  | 10                                     |  |  |  |
| Antimony (Sb)   | 0.25   | 1                                      |  |  |  |
| Arsenic (as trivalent As)   | 0.05   | 0.25                                   |  |  |  |
| Arsenic (total dissolved)   | 0.1  | 1                                      |  |  |  |
| Cadmium (Cd)  | 0.01   | 0.1                                    |  |  |  |
| Chromium (Cr)   | 0.05   | 0.3                                    |  |  |  |
| Cobalt (Co)   | 0.5  | 1                                      |  |  |  |
| Copper (Cu)   | 0.05   | 0.3                                    |  |  |  |
| Cyanide (as CN)   | 0.1  | 0.5                                    |  |  |  |
| Fluoride (F)  | 2.5  | 10                                     |  |  |  |
| Iron (Fe)   | 0.3  | 1                                      |  |  |  |
| Lead (Pb)   | 0.05   | 0.2                                    |  |  |  |
| Manganese (Mn)  | 0.1  | 1                                      |  |  |  |
| Mercury (total) (Hg) <sup>4</sup>   | nil  | 0.005                                  |  |  |  |
| Molybdenum (Mo)   | 0.5  | 5                                      |  |  |  |
| Nickel (Ni)   | 0.2  | 1                                      |  |  |  |
| Nitrite/Nitrate (as N)  | 10   | 25                                     |  |  |  |
| Phosphate (Total P biologically available in e                                    | 2  | 10                                     |  |  |  |
| Selenium (se)   | 0.05   | 0.5                                    |  |  |  |
| Silver (Ag)   | 0.05   | 0.5                                    |  |  |  |
| Uranyl (UO <sub>2</sub> )   | 2  | 5                                      |  |  |  |
| Zinc (Zn)   | 0.2  | 1                                      |  |  |  |
| Oil and Grease (Total)  | 10   | 15                                     |  |  |  |
| Not applicable to approved direct discharge of                                    | tailings solids.   |  |  |  |  |
| <sup>2</sup> Variances may be allowed during periods of ex                        | ccess runoff.  |  |  |  |  |
| Bioassay on salmonid species.   |  | ······································ |  |  |  |
| Natural background concentration will be asse                                     | ssed.  |  |  |  |  |
| Analysis for Total Elements in tailings may be                                    | required prior to and during                                       | operations and                         |  |  |  |

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