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#### Review

# Preoperational assessment of solute release from waste rock at proposed mining operations



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#### ABSTRACT

Environmental assessments are conducted prior to mineral development at proposed mining operations. Among the objectives of these assessments is prediction of solute release from mine wastes projected to be generated by the proposed mining and associated operations. This paper provides guidance to those engaged in these assessments and, in more detail, provides insights on solid-phase characterization and application of kinetic test results for predicting solute release from waste rock. The logic guiding the process is consistent with general model construction practices and recent publications. Baseline conditions at the proposed site are determined and a detailed operational plan is developed and imposed upon the site. Block modeling of the mine geology is conducted to identify the mineral assemblages present, their masses and compositional variations. This information is used to select samples, representative of waste rock to be generated, that will be analyzed and tested to describe characteristics influencing waste rock drainage quality. The characterization results are used to select samples for laboratory dissolution testing (kinetic tests). These tests provide empirical data on dissolution of the various mineral assemblages present as waste rock. The data generated are used, in conjunction with environmental conditions, the proposed method of mine waste storage, and scientific and technical principles, to estimate solute release rates for the operational scale waste rock.

Common concerns regarding waste rock are generation of acidic drainage and release of heavy metals and sulfate. Key solid phases in the assessments are those that dissolve to release acid and sulfate (iron sulfides, soluble iron sulfates, hydrated iron-sulfate minerals, minerals of the alunite-jarosite group), those that dissolve to neutralize acid (calcium and magnesium carbonates, silicate minerals), and those that release trace metals (trace metal sulfides, hydrated trace metal-sulfate minerals). Conventional mineralogic, petrographic, and geochemical analyses generally can be used to determine the quantities of these minerals present and to describe characteristics that influence their dissolution. A key solid-phase characteristic is the mineral surface area exposed for reaction, which is influenced by mode of occurrence (included, interstitial, liberated) and the extent of mineral surface coating. Short-term dissolution tests can estimate the extent of hydrated sulfate minerals present. Longer term dissolution tests are necessary to describe the dependence of drainage pH and solute release rates on solid-phase variation. The extensive data compiled from baseline pre-development definition, the operational plan, solid-phase characterization, and dissolution testing are ultimately synthesized by means of a modeling exercise requiring considerable technical and scientific expertise. The predicted rates (model outputs) are expressed as probability distributions to allow assessment of risk. This exercise must be technically defensible and transparent so that regulators can confidently assess the results and evaluate the operational plan proposed. Technical and non-technical challenges involved in implementing such programs are identified to benefit management planning for both industry and government.

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#### Contents

1.	Introd	luction	107
	1.1.	Overview	107
	1.2.	Background	107

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	1.3.	Approach	108
	1.4.	Previous work	108
2.	Purpo	ose and objectives	109
3.	Baseli	ine water sampling	109
4.	Opera	ational plan.	110
5.	Mine	waste dissolution	111
	5.1.	Acid production	
	5.2.	Acid neutralization	112
	5.3.	Trace metal release	
	5.4.	Secondary reactions	113
	5.5.	Mine waste dissolution summary	
6.	Mine	waste characterization: solid-phase indicators of solute release.	
	6.1.	Introduction.	
	6.2.	Sample selection	
	6.3.	Conventional geochemical analyses.	
		6.3.1. Chemical composition	
		6.3.2. Mineral content and composition	
		6.3.3. Mineral surface area exposure and reactivity	
	6.4.	Mine waste specific characterization techniques	
		6.4.1. Static tests.	115
		6.4.2. Short-term leach tests	115
7.	Mine	waste dissolution testing: kinetic tests.	
	7.1.	ASTM D5744 humidity cell test	
		7.1.1. Background	
		7.1.2. Test method	115
		7.1.3. Determination of reactivity and solute release rates	116
	7.2.	Field tests.	
8.	Mode	ling.	118
	8.1.	Baseline conditions	118
	8.2.	Operational plan	119
	8.3.	Conceptual model	119
	8.4.	Quantitative description of conceptual model.	119
	8.5.	Output release rates	
	8.6.	Modeling guidance	
	8.7.	Modeling solute release rates for waste rock based on humidity cell data	120
	8.8.	Concentration limits	120
9.	Concl	usions.	
	9.1.	Technical challenges	121
	9.2.	Nontechnical challenges	121
	9.3.	Research needs	121
	Ackno	owledgements	121
	Refere	ences	122

# 1. Introduction

# 1.1. Overview

Environmental assessments are conducted prior to development of new mines to identify, quantify, and manage potential water quality impacts (and to address other objectives). The associated financial liability is then estimated and integrated into economic feasibility analyses for the proposed operations. This process has been developed in response to previous impacts of mining operations on water resources and the associated substantial financial liability. Whereas environmental assessments may also be conducted at abandoned mine sites and at different stages of mine development, this paper addresses new mines. More specifically it focuses on quantifying solute release from waste rock at such operations. It does not consider transport of the solutes from the operation or assessment of the associated environmental risk (e.g. Smith, 2007). Background is presented to provide context for the more focused discussion and describe some of the challenges of the larger process of environmental assessment. This context is intended to provide insight on the magnitude and complexity of environmental assessment of mining operations to those practicing in this field, mine management, government agencies charged with economic development, politicians, and

members of the public with economic, environmental, or other interests in proposed mining.

# 1.2. Background

Historically, mine drainage has created substantial water-quality problems. Williamson et al. (2006) cited an estimated remediation cost of \$71 billion for abandoned mine sites in the United States, much of which would be directed toward treating acidic drainage. Maest et al. (2005) identified a remediation cost on the order of \$20 billion for mine sites on the National Priorities List in the United States. Williamson et al. (2006) further cited a Canadian acid- rock drainage liability of two to five billion dollars, and an annual cost of \$60 million per year to manage potentially acid-producing wastes in Australia.

Environmental assessments are of interest to mining companies, governmental regulatory agencies, and the public. The potential liabilities are integral to the economics of resource development and must, therefore, be accounted for in the mining company's economic assessment. Governmental agencies share concerns regarding the environmental risks that accompany development and the associated financial liabilities. Reflecting these concerns, the National Research Council (NRC, 1999) recommended that financial assurance be required for reclaiming

environmental disturbances on United States' federal lands resulting from "all mining activities beyond those classified as casual use". The National Environmental Policy Act (NEPA) provided the environmental impact statement (EIS) to inform federal land managers' permitting decisions. The EIS process includes determining the scope of issues and identification of alternatives for evaluation, and ultimately "determines the content of the plan of operations and mitigation requirements" (NRC, 1999). The operational plan is fundamental to assessing potential environmental impacts and the associated financial assurance. The United States Government Accountability Office (GAO) subsequently issued critiques with recommendations to improve management of financial assurance by the United State Bureau of Land Management (USBLM; GAO, 2005, 2008, 2011) and United States Environmental Protection Agency (USEPA; GAO, 2006).

Thus, from a regulatory viewpoint the intent of environmental assessment is to avoid environmental impacts and assign to the mining company the financial responsibility for operation and closure that is compliant with regulations. Virtually all long-term water quality impacts associated with mining operations are the result of dissolution of mine wastes such as waste rock, mine walls, mill tailings, and processing wastes. A key factor in this dissolution is the oxidation of sulfide minerals that have been excavated and exposed to atmospheric oxygen and water. The combination of sulfide minerals, oxygen and water leads to the release of acid, metals, and sulfate. Mine wastes, including waste rock, tailings, metallurgical wastes, and the mine itself (e.g. mine walls, residual rock) vary substantially in their composition, including sulfide mineral content. Thus, these wastes vary in their potential for impacting water resources. Whereas some mine waste can create substantial water-quality problems, others may be comparatively benign. For example, the Berkeley pit lake pH is less than three with concentrations of some heavy metals in the hundreds of milligrams per liter (Gammons and Duaime, 2006), while several abandoned iron mine pits in Minnesota serve as municipal drinking water supplies (Walsh, 2014).

Geoenvironmental modeling allows correlation of mineral deposit types and features of the deposit types with their influence on water quality, both before and after mineral development (Plumlee and Nash, 1995). These "big picture" models are helpful in identifying, based on the mineral deposit type to be mined, water-quality constituents of concern for a proposed development and a broad description of expected water quality (Seal and Hammarstrom, 2003). However, the level of detail provided by geoenvironmental modeling is not adequate for environmental review, nor is it a replacement for site-specific data. Whereas there are similarities among mines, there are typically aspects that make each mining operation unique. Distinctive features include geology, mining method, associated processing facilities, climate, topography, hydrology, and mine waste management techniques, and each of these features can influence water quality. Thus, environmental assessment of mining and the associated processing operations cannot generally be patterned after a large population of similar situations, as may be the case for municipal waste water treatment or plating operations, for example.

# 1.3. Approach

Because each mining operation is unique, it is generally necessary to conduct a modeling exercise to project potential water quality impacts from proposed operations. Briefly summarizing this modeling, monitoring can be conducted to establish baseline conditions, and a provisional operational plan can be developed to describe the change to be imposed on these conditions. Waste rock to be generated will be described in this plan and the reactions by which solutes are released from the rock can be identified.

Waste rock characteristics influencing these reactions can be assessed and dissolution tests can be conducted to determine the relationship between waste rock composition and solute release. This information can then be extrapolated based on site-specific conditions and technical considerations to model solute release from proposed waste rock storage facilities.

#### 1.4. Previous work

The mine site modeling approach presented is not a new strategy. It is generally consistent with earlier work in Minnesota (Minnesota Environmental Quality Board, 1979) and more recent detailed developments of that approach and its components are presented in Price (2009), Environment Canada (2009), Maest et al. (2005), International Network for Acid Prevention (INAP, 2010), and Morin and Hutt (2014).

Price (2009) presented information and insight on mine waste drainage quality prediction that reflects more than a decade of guidance development. The objective of the manual is "...to be a toolbox of procedures and factors to consider in program planning, sampling, test work design and data interpretation." The guidance presented was intended to be sufficient to allow drainage quality predictions adequate to inform design and implementation of mitigation measures that "prevent significant environmental impacts". He identified and described the multidisciplinary "methods, properties, and processes" that contribute to the complexity of drainage quality prediction. Among the aspects of prediction emphasized are the needs for site-specific prediction program design, the need for adequate resources and expertise for this design, its implementation, and interpretation, and the continuation of the prediction process throughout the mine-life cycle.

Environment Canada (2009) produced an Environmental Code of Practice for Metal Mines, the objective of which is to "identify and promote recommended best practices" with the intent of improving the environmental compatibility of mining facilities. This publication provides a valuable complement to the prediction manual of Price (2009), the pair of documents reflect the extensive work of the Mine Environment Neutral Drainage (MEND) program in Canada in advancing the environmentally sound management of mine wastes. The document identified environmental concerns related to mining and provides an extensive list of environmental management tools and practices to manage these concerns throughout the mine life cycle (exploration and feasibility, planning and construction, operation, closure).

Maest et al. (2005) evaluated methods and models used to predict water quality at hardrock mine sites based on four phases of mining identified by the Society of Mining, Metallurgy, and Exploration (SME, 1992): exploration (prospecting, rigorous surficial inspection, subsurface sampling), development, active mining and reclamation, closure, and post-closure. With these phases Maest et al. (2005) associated characterization activities that were grouped into classes of geology and geophysics, static tests, whole rock chemistry, mineralogy and petrography, short-term leach tests, laboratory kinetic tests, and field tests. Individual methods within each of these classes were identified along with their advantages and limitations. General concerns regarding characterization were use of representative samples, avoiding use of composite samples, continuity of characterization throughout the mine-life cycle, and scaling laboratory data to field conditions. Modeling for risk assessment is also addressed and includes development of a "site-wide conceptual model". Geochemical and hydrological models that can be applied to the conceptual model are identified and categorized based on their objective and minesite components to which they can be applied.

The Global Acid Rock Drainage Guide (GARD Guide) was produced by the International Network for Acid Prevention (INAP,

2010), an international organization of mining companies, as a "state-of-practice summary" of techniques and technology for managing problems resulting from sulfide mineral oxidation. It is a technical document aimed at an audience with background similar to that of scientists or engineers, including chemistry and engineering fundamentals. It builds on the approach used by Maest et al. (2005) and predictive information presented by Price (2009), expressing characterization objectives and activities as a function of mining phase. It is generally more expansive than Maest et al. (2005), providing greater detail on topics such as observational information to be gathered by geologists during exploration phase and mineralogical and petrographic methods. The detail includes helpful illustrations in its discussion of conceptual site models and other beneficial photos and figures. Topics beyond characterization, prediction, and mine waste management are also addressed, including corporate, regulatory and community contexts of these activities.

Further insight on drainage quality prediction can be gained from Morin and Hutt (2014) who provided commentaries regarding mine waste drainage quality prediction on their website (www.mdag.com). In addition to books and other publications, the site includes a series of case studies and essays to provide insight into mine waste drainage issues. Information presented reflects a very large collection of empirical data from both predictive testing and field studies.

There are also two publications of note that provide a broader perspective on environmental aspects associated with mining. The Mining, Minerals and Sustainable Development Project (MMSD, 2002) and Miranda et al. (2005) provided a broad holistic description of mining and acknowledged the role of environmentally sound mine waste management. MMSD (2002) examined social and technical issues ranging from large-volume wastes to human rights. Chapter 10 provides a general description of mine waste management issues. Additional detail is provided in Appendix A: Large volume waste working paper. Miranda et al. (2005) also focused on socially responsible mining and provide sections with broad overviews on critical mine waste issues, considering general issues such as safety and long-term maintenance costs.

# 2. Purpose and objectives

As indicated above, environmental assessment of each mine presents unique, complex, technical problems. This assessment seeks to quantify potential impacts from an operation that does not yet exist. Mine wastes of concern are unique to each site, as are the preexisting site conditions. Furthermore site specific geographic, hydrologic, and climatic conditions will influence solute release from mine wastes and mine waste management options. As such, it is necessary to develop a model that can be used to predict future interaction of the proposed mine with the environment.

The objective of this paper is to present a modeling approach for projecting solute release from waste rock at a proposed mining operation. In a basic sense, this modeling requires development of an operational plan and imposition of this plan onto the premining (baseline) conditions at the proposed mine site. Based on this synthesis specific operational facets will likely require more detailed description, and testing will be conducted on materials representative of mine waste from the operation to assess their potential for dissolution. This information and empirical data from external sources is then analyzed using scientific and technical principles to project solute release rates from various sources within the operation.

The presentation adopts a geochemical, as opposed to hydrological, perspective on the projected quantification of solute release from waste rock and has several specific objectives. First,

it will relate recent insights on baseline water monitoring. Second, it will describe the role of the operational plan in informing the quantification of solute release from waste rock. This includes the importance of the block model for quantifying the mass and composition of mine wastes to be generated and the description of proposed disposal facilities. Third, it will identify the minerals responsible for release of solutes commonly of concern with respect to mine waste drainage, dissolution reactions leading to solute release, and waste rock characteristics influencing these reactions. Fourth, it will identify methods of determining the waste rock characteristics affecting solute release using both conventional geochemical techniques and tests specific to mine wastes. Fifth, dissolution testing (kinetic tests) to describe solute release will be discussed, including recent revisions to the ASTM D5744 humiditycell test and examples of data generated by the test and their interpretation. Sixth, and finally, it will describe how modeling is used to extrapolate results of the characterization process to estimate solute release from waste rock in the field.

Relative to the publications discussed in the previous section, the focus is limited to projecting solute release from waste rock at proposed facilities and this process is addressed in a sequential stepwise approach. Supporting information and examples are provided from recent literature, including revisions to the ASTM 5744 humidity cell method. Applications of data generated by these tests to the modeling process are presented, as are recent recommendations for environmental regulation. Technical and non-technical considerations regarding the modeling process are provided to inform management-level decisions.

This paper intends to assist those involved in preparing and reviewing environmental assessments and permitting proposed hard-rock mining operations by providing guidance to avoid errors and inefficiencies that can easily occur in these processes. Although it is written from a governmental background, the presentation will also introduce these topics to representatives of industry, nongovernmental organizations, and interested members of the general public. Whereas there is considerable technical depth to many of the topics presented, the paper attempts to provide a general perspective on the subject matter. It is not intended to be an in-depth, comprehensive compilation, but rather a helpful and compact guide to assist those responsible for the stated assessments.

# 3. Baseline water sampling

Baseline water data for a proposed mine site can serve several environmental objectives. The phrase "water data" is used rather than "water quality data" in recognition that flow can have a strong influence on water quality and is essential to the ultimate projection of the impacts of proposed mining. To meet these objectives the sampling program design must be carefully considered with respect to factors including the location of sampling sites, sampling methods, parameters determined, sampling frequency, period of record, and variables affecting water quality aspects determined. Key to the present discussion, the data provide a foundation upon which mining conditions can be superimposed to project water resource conditions in the future. This projection is then the basis for assessing potential environmental impacts. These data also provide a basis for comparison with data collected during and after mine development, and thus can be used to help implement regulations and assess compliance. Finally, the data can be used as input for geochemical and toxicological modeling.

Smith (2011) analyzed and summarized literature addressing the variability of water quality, particularly metal concentrations, and factors affecting this variability. Temporal variation can occur both on a daily scale and a seasonal scale. The former variation can be substantial, resulting from episodic precipitation events and geochemical reactions (e.g. sorption) affected by daily changes in temperature and pH. Seasonal variations were more strongly influenced by snow melt and atmospheric precipitation trends. Spatial variation of aqueous metal concentration was reported to be affected by metal sources within the watershed (existing mine wastes, naturally occurring mineralized materials) and interactions of surface water and groundwater. A sound understanding of flow dynamics was also emphasized due to the influence of hydrologic conditions on water quality.

Technically sound methods of sampling and analysis, as well as documentation of procedures, are also essential for generating reliable data (Smith et al., 2014). The methods used and parameters targeted must comply with current regulations. Furthermore, in addition to the mine site model under discussion, the data quantity and quality must address the requirements of geochemical and toxicological modeling under consideration. Smith (2011) described some of the needs for this more complex modeling and provides numerous specific suggestions for a water-quality sampling plan.

Levitan et al. (2014) provided an example of establishing geochemical baseline conditions for surface water and sediments. They selected sampling sites with consideration of geological variability and sample timing to reflect hydrological and climatic variations. They also provided statistical methods for data analysis. A second example of of baseline assessment that applied relevant technical principles is provided by Maest et al. (2004).

# 4. Operational plan

The term "operational plan" is used to represent not only the mine itself but also associated developments such as processing facilities and mine waste storage facilities. A reasonably detailed operational plan is necessary for modeling associated with solute release from waste rock, as well as addressing other concerns (e.g. air emissions, hydrologic concerns, water balances, etc.). This plan will generally describe the proposed mining operations for a specified period (for example 20 years or life of mine, whichever is shorter) and the mine closure plan. The operational plan will likely evolve in an iterative process based on both operational resource recovery and environmental considerations. As the diligence and detail of the operational plan increase, so does the expedience of the subsequent modeling.

It is likely that operational plan deficiencies will be identified in the course of this modeling and other aspects of mine and processing evaluation. Included will be errors related to operational misconceptions, geotechnical errors, and environmental deficiencies. However, as the rigor of the plan increases, the severity of modeling deviations from the likely reality decreases and, consequently, less numerous the modeling iterations. Consequently, the time required for iteratively revising operational plans and modeling will be reduced. In contrast, ill-conceived operational plans incorporating numerous and larger flaws will require more extensive plan revisions and modeling iteration, which translate into more lost time. Careful consideration should be given to the time and effort expended on developing an operational plan that includes diligent consideration of environmentally sound mine-waste management. Time spent up front in developing a sound plan is likely to result in substantial savings over the longer term.

The operational plan contains information that conventionally has been included to define strategies for economic mineral recovery and processing. This includes a description of the ore body, mine design (including waste rock and possibly overlying unconsolidated sediments), approaches for ore blasting and excavation, and possibly ore milling, mineral processing, and metallurgical operations. The operational plan can be considered in two closely related categories: resource recovery and environmental. This distinction is artificial because both aspects must be considered in the economic evaluation of a project and are, furthermore,

interdependent. That is, changes in resource recovery aspects require changes in mine waste management and vice versa.

Resource recovery aspects of the plan are those which have conventionally been undertaken as necessary to the economic extraction and beneficiation of mineral commodities. These aspects begin with a mine development plan predicated on the ore body, which is generally described using a block model based on drill core data and an understanding of the associated geology. The block model allows determination of the composition, variability, and extent of the ore body.

From the block model a schedule for rock movement is developed. This includes the quantity and composition of ore, lean ore, and waste rock, as well as the timing of their excavation and subsequent handling. Depending on the operation, an operational plan may also include facilities for concentrating ore (e.g. flotation) and metallurgical processing (e.g. hydrometallurgy). For the mine, concentrator, and metallurgical plant specific waste streams must also be considered. Potential sources associated with the mine itself include the mine walls and floor and remnant broken rock. Immediate products from the mine also represent potential sources and these include unconsolidated sediment (overburden), waste rock, subeconomic ore, and during storage, the ore itself. Tailings from a concentrator and residues from metallurgical processing represent additional potential sources of solute release.

Since roughly 1990, the attention directed toward environmentally sound management of mine wastes has increased markedly. This aspect of planning focuses on the mine wastes to be generated and their environmentally sound management. Domestic wastes (refuse, sanitary wastes) and operational wastes (e.g. oil and grease, chemicals) must also be considered but are not within the scope of the present paper. The quantity of these materials and their compositional variation must be determined.

The extent and composition of mine walls and waste rock can be estimated based on drill core data and the mine design. Drill core data and geostatistical "kriging" techniques to interpolate those data are commonly used to develop a block model for a mineral resource that is used to describe the extent and grade of the deposit for economic evaluation. As the amount of information increases the confidence in the deposit evaluation increases. The increasing confidence is reflected in the terminology identifying the resource as "inferred", "indicated", and ultimately "measured" (presented in order of increasing confidence). Because of the importance of such information to investors, the Toronto Stock Exchange requires the evaluation conform to National Instrument 43-101 (NI 43-101) in order for properties to be listed on the exchange. This conformance includes independent third party review of the economic evaluation. This evaluation is complex and must consider criteria such as the continuity of mineralization, geology, and grade of the resources when evaluating the physical proximity of drill core and the internal agreement of the data. Consequently, the reviewer must be well-versed in economic geology and geostatistical evaluation of drill core data. NI 43-101 requires that the review be conducted by a "qualified person" and provides the attributes of such a person.

A similar review for estimation of waste rock quantity and composition would be required to vet the accuracy of block models for waste rock zones and constituents of concern. Because block models focus on describing an ore body, their application to waste rock might be less accurate. For example, drilling for resource definition might be less dense in areas identified as containing inadequate quantities of targeted economic commodities. Similarly, analyses of core samples from areas of waste rock might be less detailed or might not target constituents of potential environmental interest. Thus, in order to rigorously define the extent and composition of rock units contributing to waste rock, a block model reviewed by an independent third party is required. Drilling program design

should consider the importance of waste rock characterization in order to enhance the integrity of block modeling in areas of waste rock. This importance of such rigor is a function of the potential for problematic drainage from the waste rock. For example, if the mass of waste rock to be generated is negligible, accurate determination of its mass and composition might be moot.

The mineral assemblages present, their mass, and their composition will serve as an initial guide for mine waste management plans and a basis for further solid-phase characterization of waste rock. The term "mineral assemblage" is used to represent rock that has a given degree of compositional uniformity (mineral content, mineral chemistry, petrography) and, therefore, a degree of uniformity in dissolution behavior. It is used to account for mineralogic and petrographic variability within rock units. In particular, in some geological situations rock units might be altered by heat, pressure, or reactive fluids, and it might be necessary to subdivide the unit into alteration packages to represent different mineral assemblages. The essential point is to identify units with a degree of compositional uniformity to serve as a basis for drainage quality predictions and potential mine waste management assessment.

A reliable block model can be used to document and help describe the mineral assemblages present, the mass of each mineral assemblage, and the range of chemical composition of each assemblage. In particular, the masses will allow an initial assessment of relative potential for solute release. The compositional ranges will allow determination of "representativeness" in samples selected for testing. Thus, mass and representativeness, in conjunction with the proposed mine waste management plan, are necessary inputs to planning an effective and efficient characterization program.

Beyond the focus on waste rock, the following three paragraphs provide a brief commentary on characterization of the mine walls (and the associated broken rock) and tailings. The block model can be used to estimate the composition of mine walls by imposing the model onto the proposed mine design. For waste rock, the rock units present are identified and their masses determined. Then block model data can be applied to describe the compositional variation and masses within compositional categories for each rock unit. This information is fundamental to the description of the waste rock source term. The operational plan that the block model informs will also include the schedule of waste rock excavation. This schedule must also be considered in the ultimate mine waste management plan.

The mass of tailings anticipated is based on the production rates provided in the mine model. Analysis of pilot plant materials will provide compositional information. Such processing tests should provide a variety of compositions based on runs under different conditions (e.g. chemical addition, processing rate, ore feed composition). Testing might also generate coarse and fine fractions of tailings, both of which should be targeted for characterization and dissolution testing to evaluate the tailings source term.

Processing tests should be conducted with an awareness of environment information that might benefit environmental review. This would include not only solid-phase characterization but also water quality in the processing circuit. It should be noted that the degree to which pilot plant results simulate operational conditions is dependent on the scaling required. Pilot plants are likely to provide a better simulation than bench scale tests, and large scale pilot plant tests are likely to better simulate operational conditions than small scale tests (Bacon, 2008). Similar characterization and testing of metallurgical wastes would also be required.

# 5. Mine waste dissolution

Much of this paper focuses on waste rock dissolution and solidphase characteristics that influence dissolution. The following presents some key mine-waste dissolution reactions, those resulting in acid production, acid neutralization, and release of trace metals. The discussion identifies a few of the minerals of interest and characteristics of those minerals that are pertinent to drainage quality prediction and, therefore, environmental assessments. A brief summary of reactions subsequent to dissolution is also presented. Much of the information has been extracted from Lapakko (2002), and it is included and expanded on here for the convenience of the reader and because of its immediate relevance to the present report. More detailed discussion on a wider range of aqueous geochemistry fundamentals and geochemistry of acid mine drainage is presented by Nordstrom (1999), Nordstrom and Alpers (1999), Smith (1999) and Smith and Huyck (1999).

#### 5.1. Acid production

There are three general types of acid releases from mine wastes: iron sulfide oxidation, dissolution of soluble iron sulfate minerals, and the dissolution of less soluble sulfate minerals of the alunite/jarosite series. The oxidation of iron sulfide minerals such as pyrite (FeS<sub>2</sub>) and pyrrhotite (Fe1<sub>-x</sub>S, 0.7 < x < 1.0) is responsible for the majority of acid production by mine wastes. Eqs. (1) and (2) represent pyrite and pyrrhotite oxidation by oxygen (after Stumm and Morgan, 1981; Nelson, 1978). In addition to acid (H<sup>+</sup>), sulfate is also released to solution. It should be noted that dissolution of sulfate minerals such as anhydrite (CaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) also releases sulfate, but there is no attendant acid release with this dissolution.

$$FeS_2(s) + (15/4)O_2(aq) + (7/2)H_2O$$

$$= Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 4H^+(aq)$$
(1)

$$Fe_{1-x}S(s) + [(9-3x)/4]O_2(aq) + [(5-3x)/2]H_2O$$

$$= (1-x)Fe(OH)_3(s) + SO_4^{2-}(aq) + 2H^+(aq)$$
(2)

The rate of iron sulfide oxidation and attendant acid production is dependent on solid-phase compositional variables, drainage pH, microbial activity, and climate as well as the availability of oxygen and water. Oxidation rates vary among sulfide minerals, and it is often reported that reactivity decreases in the order marcasite > pyrrhotite > pyrite (e.g. Kwong and Ferguson, 1990; Nordstrom and Alpers, 1999). However, different reactivity rankings have been reported by other authors and may be a function of reaction conditions, trace element concentrations of the minerals, and crystal-morphology characteristics, among other factors (Jambor, 1994; Plumlee, 1999). Of particular importance to the ensuing discussion is the importance of exposed mineral surface area. In particular, for a given sulfide mineral the oxidation rate per unit mass increases with the available mineral surface area.

The abiotic rate of pyrite oxidation by oxygen decreases slightly as pH decreases, but the overall abiotic rate (oxygen and ferric iron) increases as pH decreases into a range where ferric iron becomes the dominant oxidant (Williamson and Rimstidt, 1994). Nordstrom (1982) reported that as "pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent". As pH further decreases, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm, 1970), which is the only significant oxidizing agent in this pH range (Nordstrom, 1982; Singer and Stumm, 1970; Kleinmann et al., 1981). Laboratory tests inferred that the oxidation rate of pyrrhotite present in Duluth Complex rock in the pH range of 3.5-4.1 was roughly six to seven times that in the range of 5.3-6.1, and the higher rate was attributed to bacterially mediated oxidation (Lapakko and Antonson, 1994). Olson (1991) reported the biotic rate of pyrite oxidation in the approximate pH range of 1.5–2.0 in the laboratory was roughly 34 times the abiotic rate. Data presented by Nordstrom and Alpers (1999) suggest that the bacterially mediated rate of pyrite oxidation by ferric iron is roughly two to three orders of magnitude faster than the abiotic oxidation by oxygen at pH 2. It should be noted that the discussion above is largely based on oxidation of pyrite occurring in a water saturated condition. In mine waste facilities such as waste rock piles, this oxidation can also occur as a vapor phase reaction (Jerz and Rimstidt, 2004).

The reaction of iron sulfides produces acidic, iron- and sulfaterich waters which can (1) react with sulfide minerals and accelerate their oxidation, (2) evaporate partially or totally to precipitate hydrated iron-sulfates and other minerals, and/or (3) contact host rock minerals, which react to neutralize some or all of the acid. Acidic flow that is not neutralized within the mine waste will exit as acid rock drainage (ARD).

Hydrated iron-sulfate and trace-metal sulfate minerals precipitate during the evaporation of acidic, metal- and sulfate-rich water within mine-waste materials and store acid and metals released by sulfide mineral oxidation. The stored acid and metals can be subsequently released by additional flow through the mine waste (e.g. rain events, snow melt). The more common hydrated iron-sulfate minerals that occur as efflorescent salts on the surfaces of weathering pyrite include melanterite (FeSO<sub>4</sub>·7H<sub>2</sub>O), rozenite (FeSO<sub>4</sub>·4H<sub>2</sub>O), szomolnokite (FeSO<sub>4</sub>·H<sub>2</sub>O), römerite (Fe<sup>2+</sup>(Fe<sup>3+</sup>)<sub>2</sub>  $(SO_4)_4 \cdot 14H_2O)$  and copiapite  $(Fe^{2+}(Fe^{3+})_4(SO_4)_6(OH)_2 \cdot 2OH_2O)$ (Alpers et al., 1994). These efflorescent salts are highly soluble and provide an instantaneous source of acidic water upon dissolution and hydrolysis (Nordstrom, 1982; Cravotta, 1994; Chou et al., 2013). They are partially responsible for increased acidity and metals loadings in the receiving environment during rain events, and these increased loadings can result in fish kills (Jambor et al., 2000). Their cumulative storage and incremental release may help explain the lag from mine-waste placement to AMD-formation, particularly in arid climates. As an example, Eq. (3) represents the dissolution of melanterite, indicating production of two moles of acid for each mole of melanterite dissolved. Cravotta (1994) showed that a similar aqueous dissolution of römerite produced six moles of acid for each mole of römerite dissolved.

$$\begin{aligned} \text{FeSO}_4 \cdot 7 \text{H}_2 \text{O} \left( s \right) + (1/4) \text{O}_2 \left( g \right) &= \text{Fe}(\text{OH})_3 \left( s \right) + \text{SO}_4^{2-} \left( \text{aq} \right) \\ &+ (9/2) \text{H}_2 \text{O} + 2 \text{H}^+ \left( \text{aq} \right) \end{aligned} \tag{3} \end{aligned}$$

The alunite–jarosite mineral group consists of sulfate minerals that are less soluble than the efflorescent sulfate salts. Bigham and Nordstrom (2000) reported on the biogeochemistry of these poorly crystalline hydroxysulfates of iron (e.g. jarosite ([K, H<sub>3</sub>O, Na]Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, schwertmannite (Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub>·nH<sub>2</sub>O)) and aluminum (e.g. alunite (KAl<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>, basaluminite (Al<sub>4</sub>(SO<sub>4</sub>) (OH)<sub>10</sub>·4H<sub>2</sub>O) commonly associated with acidic sulfate waters draining from mine sites. They discussed formation and decomposition of these "less soluble" sulfate–bearing minerals as well as their sorption of and coprecipitation with cations and oxyanions that occur in mine–site drainages. Additional technical information on alunite–jarosite, including thermodynamic data, are also available (Stoffregen et al., 2000).

According to Nordstrom (1982), the evaporative concentration of efflorescent iron sulfates leads to the precipitation of the more common iron minerals such as goethite (FeOOH) and jarosite. Similar reaction of efflorescent aluminum sulfates will produce alunite. Alpers et al. (1994) reported that jarosite is slightly soluble and can generate acid as indicated by potassium jarosite dissolution presented in Eq. (4). It should be noted, however, that jarosite composition is variable, and the associated reactivity is also variable (e.g. Lapakko and Berndt, 2003).

$$\label{eq:KFe3} \text{KFe}_3 \; (\text{SO}_4)_2 (\text{OH})_6 \; (s) = \text{K}^+ + 3 \text{FeOOH} \; (s) + 2 \text{SO}_4^{2-} \; (\text{aq}) + 3 \text{H}^+ \; (\text{aq})$$

#### 5.2. Acid neutralization

The balance between the rates of acid production by iron-sulfide mineral oxidation and host-rock mineral neutralization will determine the acidity of mine-waste drainage. The most effective minerals for neutralizing acid are those containing calcium carbonate and magnesium carbonate, including calcite (CaCO<sub>3</sub>), magnesite (MgCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), and ankerite (CaFe(CO<sub>3</sub>)<sub>2</sub>). Eq. (5) represents the dominant acid-neutralizing reaction of calcite (CaCO<sub>3</sub>) above pH 6.4, whereas Eq. (6) is the dominant reaction below pH 6.4 (Drever, 1988):

$$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq)$$
 (5)

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3^-(aq) + Ca^{2+}(aq)$$
 (6)

Of the carbonate minerals, calcite (CaCO<sub>3</sub>) dissolves most rapidly with a reported rate of  $2.7 \times 10^{-6}$  mol m<sup>-2</sup> s<sup>-1</sup> (pH 6,  $p_{\text{CO}_2} = 0.0000$  atm, 25 °C; Busenberg and Plummer, 1986). Relative to calcite, the rate of dolomite [(Ca,Mg)CO<sub>3</sub>] dissolution is about an order of magnitude slower (Busenberg and Plummer, 1982) and the rate of magnesite (MgCO<sub>3</sub>) dissolution is about four orders of magnitude slower (Chou et al., 1989). The rate of siderite dissolution under anoxic conditions is reported to be three orders of magnitude slower than that of calcite at pH 6 (Greenberg and Tomson, 1992), although under more acidic conditions this difference appears to decrease (Golubev et al., 2009). However, iron and manganese carbonates do not provide net acid neutralization under oxidizing conditions, due to oxidation of the released iron or manganese, the subsequent hydrolysis and precipitation of these metals, and the consequent acid production.

Dissolution of silicates such as plagioclase-feldspars (e.g. anorthite in Eq. (7), Busenberg and Clemency, 1976) and olivine (e.g. forsterite in Eq. (8), Hem, 1970) can also neutralize acid. However, their rates of dissolution and consequent acid neutralization are slow relative to the carbonate minerals (Nesbitt and Jambor, 1998). For example, White et al. (1999a) noted that "at near neutral pH, the dissolution rate of calcite is approximately seven orders of magnitude faster than the dissolution of plagioclase feldspar". Nonetheless, silicate mineral dissolution can maintain neutral conditions if the rate of acid production is quite slow (Lapakko and Antonson, 1994, 2002; Lapakko et al., 1997). The effectiveness of silicate minerals in neutralizing acid increases with increasing mineral surface area, which in turn, increases with increasing mineral content and decreasing grain size.

$$\begin{split} &\text{CaAl}_2 \text{Si}_2 \text{O}_8 \; (s) + 2 \text{H}^+ \; (a \text{q}) + \text{H}_2 \text{O} \; (a \text{q}) \\ &= \text{Ca}^{2+} \; (a \text{q}) + \text{Al}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4 \; (s) \end{split} \tag{7}$$

$$Mg_{2}SiO_{4}\left( s\right) +4H^{+}\left( aq\right) =2Mg^{2+}\left( aq\right) +H_{4}SiO_{4}\left( aq\right) \tag{8}$$

#### 5.3. Trace metal release

Trace metals are metals that occur at low average concentrations in the earth's crust but can be present at elevated levels in mineralized areas. Trace metals commonly occur as sulfide minerals, the oxidation of which releases the trace metal from the highly insoluble sulfide phase (e.g. Eq. (9)). They can also occur as hydrated metal-sulfates and be released to solution upon dissolution of these phases (Jambor et al., 2000).

$$ZnS\left( s\right) +2O_{2}\left( aq\right) =Zn^{2+}\left( aq\right) +SO_{4}^{2-}\left( aq\right) \tag{9}$$

#### 5.4. Secondary reactions

Once released to solution, there are several types of reactions that can influence the migration and fate of these solutes. Smith and Huyck (1999) presented a series of diagrams for the generalized relative mobility of elements under different environmental conditions, for use as an initial estimate of metal behavior in surficial environments. At a regional scale, generalizations frequently can be used to estimate broad trends in metal mobility. However, as the scale becomes increasingly finer, estimating metal behavior generally becomes increasingly difficult (Smith and Huyck, 1999).

In general, components released from mineral phases may remain in solution or be removed in secondary phases, perhaps after oxidation (e.g. iron hydroxide precipitation after oxidation of iron in Eq. (1)). For removal from solution, trace metals may precipitate as oxides, hydroxides, or carbonates, be adsorbed onto surfaces of minerals such as iron oxyhydroxides (Smith, 1999), or coprecipitate with other solid phases. In acidic solutions trace metal removal is limited, and elevated trace metal concentrations are often associated with these solutions. However, circumneutral drainages can also contain elevated concentrations of trace elements such as nickel, copper, cobalt (Lapakko, 1993), zinc, manganese (Smith and Huyck, 1999), molybdenum (Brown, 1989), arsenic, and antimony. Concentrations of molybdenum, arsenic, and antimony in particular can be elevated even as pH increases above 7.

Oxidation of arsenic and antimony sulfides can produce acid, as can oxidation of the iron sulfide fraction of mixed sulfide minerals such as chalcopyrite (Plumlee, 1999). Other trace metal sulfide oxidation will produce acid if and only if the metal released hydrolyzes (Eq. (10)) or precipitates as a hydroxide, oxide, or carbonate (e.g. Eq. (11)). For most trace metals this will occur only at pH levels above 6, and as pH decreases below this level the secondary phases will dissolve. Consequently, they do not generally contribute to acid production observed at lower pH levels.

$$Zn^{2+}(aq) + H_2O(aq) = Zn(OH)^+(aq) + H^+(aq)$$
 (10)

$$Zn^{2+}(aq) + 2H_2O(aq) = Zn(OH)_2(s) + 2H^+(aq)$$
 (11)

# 5.5. Mine waste dissolution summary

There are three general groups of minerals, the dissolution of which is a major influence on mine waste drainage quality. Acid producing minerals include iron sulfides that react with oxygen (or ferric iron) over an extended period of time; soluble iron sulfate minerals that dissolve rapidly, and less soluble sulfate minerals that dissolve slowly. Minerals that neutralize acid include fast-reacting calcium and magnesium carbonates and comparatively slow-reacting silicate minerals. Trace metal sulfides are the major source of trace metal release from waste rock. Critical to the dissolution of all these minerals is the surface area exposed for reaction. The minerals present and their extent of exposure are prominent targets of mine waste characterization. Once released from the original mineral phase, solutes may remain in solution or be removed in secondary phases.

# 6. Mine waste characterization: solid-phase indicators of solute release

# 6.1. Introduction

Information regarding mine waste characteristics is fundamental to projection of their geochemical behavior. Consequently a program to characterize relevant solid-phase aspects of the mine

wastes is required. This program includes conventional geochemical analyses to determine the chemistry, mineralogy, and petrography of the mine wastes and tests designed specifically for describing characteristics that affect mine waste dissolution. Some of this characterization occurs as a natural by-product of conventional mine development planning such as drill core logging and more detailed analysis of drill core and pilot plant materials. However, more focused analyses and testing are likely necessary to aid in predicting drainage quality from the various mine wastes. Ultimately laboratory dissolution tests will be required to assess the pH of drainage and solute release rates from individual mine wastes. This information will then be used as inputs for modeling to extrapolate the characterization data and dissolution test results to field conditions. The extrapolation is likely to involve application of technical and scientific principles in order to forecast over the large change in scale and reaction conditions that spans the gap between laboratory testing and the operational setting.

# 6.2. Sample selection

A variety of very useful analytical techniques are available to provide information on the solid-phase variables that influence solute release from mine wastes. It is, however, of utmost importance that analyses be conducted on samples that are representative of the mine wastes of concern. Thus the number of samples analyzed must be adequate to describe the variability of the mine wastes of concern (after Hoal et al., 2013). The collection and testing of samples must be based on clearly defined objectives, and these objectives must consider the baseline conditions, the operational plan (including the mass and compositional variation of the mine waste), rock characteristics that control mineral dissolution, and the ultimate conditions under which the mine wastes will be stored. Similar to strategies for economic recovery, mine waste characterization plans begin with the block model. Focusing specifically on waste rock, the block model should identify the rock units present, their masses, and compositional ranges. This information in conjunction with the mine waste management plan will inform selection of samples for characterization.

Solute release prediction requires an understanding of the reactions that produce acid, neutralize acid, and release trace metals and the solid-phase variables that affect these reactions. Solid-phase analyses can describe these variables and provide qualitative assessments regarding potential solute release. Numerous analytical techniques were identified and their applications described by Lapakko (2002). The techniques included conventional methods of geochemical, mineralogic, and petrographic analysis and tests commonly applied or specifically developed to characterize mine wastes. The following paragraphs provide a brief summary of that information and include pertinent updates.

# 6.3. Conventional geochemical analyses

# 6.3.1. Chemical composition

Conventional chemical analyses quantify the elements present in geological materials and this information indicates what constituents may be of environmental concern. Common approaches for these analyses are X-ray fluorescence and sample digestion with subsequent analysis of the digestate (Lapakko, 2002). Chemical analysis can also provide initial assessments of potential acid production (based on sulfur, sulfide, and sulfate determinations) and potential acid neutralization present as carbonate minerals (based on inorganic carbon determinations). Chemical analysis can reasonably quantify sulfur present as sulfide in most samples and therefore provide a good indication of sulfide mineral content. This determination will not describe the distribution of sulfide if multiple sulfide minerals are present. Likewise, the presence of

sulfate minerals such as jarosite, alunite, anhydrite (CaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), and barite (BaSO<sub>4</sub>) can confound discrimination of sulfide and sulfate during chemical analysis. (Note that dissolution of anhydrite, gypsum, and barite does not produce acid.) Consequently, more sophisticated strategies including mineralogical analyses may be required to develop effective chemical analytical approaches (Lapakko, 2002).

#### 6.3.2. Mineral content and composition

Mineralogical and petrographic analyses are required to determine the minerals in which elements are present, the crystal form of minerals, the mineral grain size, and extent of mineral exposure for reaction (liberation). Conventional techniques applied for such analyses include optical microscopy, X-ray diffraction (XRD), XRD with Rietveld refinement (Raudsepp and Pani, 2003), scanning electron microscope (SEM), and electron-probe microanalysis (EPMA). These techniques can be applied to determine whether the sulfur-bearing phases are acid producing (as opposed to, for example, anhydrite, gypsum or barite) and, if so, if they are iron sulfides, efflorescent salts, or less soluble sulfate minerals. This discrimination is relevant because of the difference in the acid production behavior of the different minerals. The efflorescent salts provide a rapid release that is not sustained.

Relative to the efflorescent salts, sulfide and less soluble sulfate mineral dissolution can provide a sustained release of acid, sulfate, and any trace metals associated with these phases. In general, the iron sulfide minerals provide a more rapid release of acid and sulfate (Lapakko and Berndt, 2003; Linklater et al., 2012). More specifically Lapakko and Berndt (2003) reported that drainage pH values from two pyritic samples were one to two units lower and acidities were ten to 70 times higher than associated values from two potassium jarosite samples of similar sulfur content. The acid release from alunite and jarosite was limited by their relatively low solubility. It should be noted that the authors did attribute rapid initial release of acid and sulfate to dissolution of hydronium jarosite, demonstrating that jarosite minerals have variable reactivity. The presence of this phase was inferred based on EPMA and other solid-phase analyses (Desborough et al., 2010).

Similarly, the presence of inorganic carbon alone is not adequate to assess the extent of acid neutralizing carbonate minerals present. In particular, carbonate quantified by chemical analysis could be associated with neutralizing phases (i.e. carbonate associated with calcium or magnesium) or phases that do not contribute net neutralization in oxidizing environments (e.g. carbonate associated with iron or manganese). Mineralogical analyses are necessary to determine if the minerals will neutralize acid. Furthermore, carbonate mineral identification, in conjunction with existing information on rates of dissolution, will provide a qualitative to semi-quantitative assessment on the relative reactivity of the phases present.

#### 6.3.3. Mineral surface area exposure and reactivity

Whereas the acid-producing (e.g. iron sulfide) and acid-neutralizing (e.g. calcium and magnesium carbonate minerals) mineral contents, and the balance of these contents, influence mine waste drainage quality, there are several subtle mineralogical and petrographic factors which are also influential. Oxidation of sulfide minerals and dissolution of carbonate and silicate minerals are surface reactions and, therefore, their rates are dependent on the surface area available for reaction. Mineral surface area is dependent on mineral grain size, the "roughness" of the mineral surface, and the extent to which the mineral is liberated from the rock matrix. For a given mass of a mineral, the surface area increases as mineral grain size decreases. For example, breaking a grain in half will expose new surfaces although the mineral mass does not change. The surface area per unit mass is referred to a specific surface area.

Specific surface area also increases as the roughness of the mineral surface increases. As a common example for acid production, framboidal pyrite has a very irregular surface and, therefore, a high surface area per unit mass relative to euhedral pyrite. Consequently, the oxidation rate per unit mass of framboidal pyrite is reported to be much more rapid than that of euhedral pyrite (Pugh et al., 1984; White and Jeffers, 1994).

The fraction of mineral surface area exposed and available for reaction is affected by the mode in which the mineral occurs. Iron sulfide and other minerals may be entirely liberated from the rock matrix, occur interstitial to other minerals and be partially liberated or surrounded by host rock minerals, or occur as inclusions within other minerals. The extent of liberation, or mineral surface exposure, affects availability for reaction. For example, acid-producing or acid-neutralizing minerals liberated from the rock matrix will have their entire surface area available for reaction. Minerals occurring in veins and along bedding planes will also be highly exposed if rocks break along these features. In contrast, iron sulfide and calcium and magnesium carbonate minerals surrounded by relatively stable host rock minerals, such as quartz, will be essentially unavailable for reaction. Examples of the influence of modes of occurrence and particle size on mineral dissolution rates and drainage quality are presented by Lapakko et al. (2006, 2012) and Lapakko and Antonson (2006).

Because mineral surface area exposed (liberated) is a critical variable in mineral dissolution, quantifying the extent of exposure provides valuable information regarding potential rates of solute release. Solid-phase variables of concern are similar to those relevant to mineral processing, and similar analytical techniques can be applied for their assessment (Hoal et al., 2013). QEMSCAN® (Quantitative Evaluation of Minerals by Scanning Electron Microscopy) and mineral liberation analysis (MLA) use software to interpret data collected with a scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDS). Smith et al. (2013) identified numerous characterization capabilities of these techniques that are relevant to mine waste dissolution; they also provided an example of application of the techniques to characterize fluvial materials. Other researchers have applied these automated techniques to assess both mineral content and important petrographic aspects such as mineral liberation (exposed mineral surface) (Barazzuol et al., 2012; Smith et al., 2012; Buckwalter-Davis et al., 2012). These techniques are more refined than automated techniques demonstrated previously for mine waste characterization (Pignolet-Brandom and Lapakko, 1990).

Reactivity decreases as mineral surfaces are covered with coatings, such as iron oxyhydroxides. Such coatings commonly develop on sulfide mineral surfaces as oxidation progresses and inhibit the rate of reaction. Similar coatings can form on carbonate minerals to limit their effectiveness in neutralizing acid. Such coatings can be identified, measured for thickness, and analyzed using SEM and EPMA.

# 6.4. Mine waste specific characterization techniques

Static tests, short-term dissolution tests, and kinetic tests have been developed to assess the potential for acid generation and solute release from mine wastes. Static tests and kinetic tests were originally developed for application to coal mining and data back to at least 1978 (Sobek et al., 1978). The term static test has historically been used to identify designed to determine the balance of acid-producing and acid-neutralizing potentials of mine wastes by fairly quick and inexpensive methods (e.g. Ferguson and Erickson, 1987; USEPA, 1994; Adam et al., 1997; White et al., 1999b; Lapakko, 2002; Jambor et al., 2003; Chotpantarat, 2011). Development of short-term leach tests is more recent. The

following test classifications are based on test objectives, although methods within the test classes have broad similarities as well.

#### 6.4.1. Static tests

Static tests were developed to provide a rapid estimation of whether or not a mine waste would produce acid and are commonly applied as a first-cut screening strategy. Most of these tests determine the potentials of a sample to produce and neutralize acid. Whether or not acidic drainage will be generated is predicted based on the balance of acid production and acid neutralization potentials of mine waste (e.g. balance of Eqs. (2) and (4)). These tests have also been referred to as acid-base accounting tests, or ABA. These tests were reviewed in detail by White et al. (1999b). There are also methods of estimating potential for acid production that use hydrogen peroxide to oxidize sulfide minerals present and allow the acid produced to react with neutralizing mineral present (net acid generation or NAG test). The resultant solution provides a measure of the balance of these reactions. As a recent addition to these tests, sulfur and inorganic carbon techniques have been incorporated into an ASTM method (ASTM E1915-13) for estimating acid-generating and acid-neutralizing potential (Bucknam et al., 2009). A method for determining neutralization potential by titration has also been incorporated into the method.

#### 6.4.2. Short-term leach tests

Short-term leach tests were developed to assess the presence of readily soluble components available for immediate release from mine or process wastes. This release includes that from the dissolution of presence of soluble sulfate minerals such as the hydrated trace-metal sulfates discussed earlier. This dissolution is also manifested by elevated sulfate (and possibly acid and trace metal) release in the initial rinse from humidity cell tests. Short-term leach tests include the Meteoric Water Mobility Procedure (MWMP, ASTM E2242) and Synthetic Precipitation Leach Procedure (SPLP, ASTM D6234).

# 7. Mine waste dissolution testing: kinetic tests

Solid-phase characterization provides a sound qualitative to semi-quantitative description of the potential reactivity of mine wastes. Dissolution tests, commonly referred to as kinetic tests, are required for more quantitative information on drainage quality and rates of solute release. Although kinetic tests can be conducted either in the laboratory or field, testing for purposes of environmental review of proposed mines may be limited to laboratory tests because of limited sample availability. They can be designed to address several objectives and are generally conducted under oxidizing conditions for relatively long periods, on the order of months to years.

Humidity cells are the laboratory tests most commonly conducted for environmental review. Objectives of particular importance to mine waste management are (1) assessment of relative potentials of mine wastes to produce acidic drainage under controlled conditions and (2) determination of rates of solute release. These tests are designed to assess mineral dissolution reactions and are not generally effective for evaluating the secondary reactions discussed in the section on mine waste dissolution. The amount of water added to remove reaction products in humidity cell tests is large relative to the amount of rock tested and the rinse interval is fairly frequent. This enhances removal of products of mineral dissolution, thus allowing calculation of reaction rates. These conditions generally preclude elevation of solute concentrations to levels at which they are limited by secondary reactions such as chemical precipitation, coprecipitation, or adsorption. The secondary reactions can be more appropriately addressed using laboratory column tests or field tests in which rinse water to rock ratios are lower and contact times between water and rock are longer. As with any test, the design of column and field tests must carefully consider and clearly articulate the experimental objectives. In particular, if the objective is to evaluate reactions controlling maximum concentrations of solutes, the test must be designed carefully to attain this objective.

For a laboratory testing, the following section focuses on the ASTM D5744 humidity cell method, revisions to the original method (ASTM D5744-96) that were approved in 2007 to yield ASTM D5744-07, and more recent revisions incorporated into ASTM D5744-13e1 (ASTM International, 2013). Column testing is also a viable laboratory method of kinetic testing but has been employed far less frequently than humidity cell tests. Price (2009) provides a brief discussion on these tests. Some recent applications of field tests are summarized below.

# 7.1. ASTM D5744 humidity cell test

# 7.1.1. Background

Humidity cell tests are one source of information to help guide environmentally sound mine waste management decisions. As opposed to solid-phase analyses, humidity cell tests provide an empirically determined relationship between solid-phase composition and drainage quality under controlled laboratory conditions. Because drainage quality is a function of the solid-phase composition, humidity cell testing is typically conducted on specific mineral assemblages (or rock types) that will be among the mine wastes generated. By testing individual mineral assemblages, many of the mineralogical and petrographic variables are normalized (e.g. mineral content, mineral chemistry, grain size, etc.) and testing can focus on the effects of solid-phase variables such as sulfur content. Thus diligent testing of a relatively small number of well-characterized samples representative of the compositional range of a mineral assemblage can describe the weathering behavior of a large mass of waste rock from that mineral assemblage. The resultant data then can be used, for example, to determine critical sulfur cutoffs for acidic drainage production and as a basis for modeling solute release rates from mine waste facilities. These results can be used to inform mine waste management decisions.

The extent of published data describing the relationship between well-characterized samples from individual rock types and their drainage quality in humidity cell tests is limited. Even more limited are examples of long-term field drainage quality associated with mine wastes of well-known composition. Consequently developing waste characterization programs in general, and more specifically humidity cell testing programs, is a unique exercise for each operation and possibly for mine waste disposal facilities within each operation. Details of the characterization program design are dependent on variables that are specific to individual mine settings, both physical and political. Therefore, it is not possible to pull a testing program "off the shelf." Design of a test program is best addressed on a site-specific basis, where appropriate consideration can be given to the multitude of technical and nontechnical factors that are unique to the locale and affect these decisions. Design of site specific testing programs and interpreting their output must be handled by personnel adept in the scientific and technical aspects of environmentally sound mine waste management. This includes geochemical expertise, experience with dissolution testing, and an understanding of mining/environment modeling to which the results will be applied.

# 7.1.2. Test method

ASTM D5744 is a kinetic test method originally designed to assess the relative potentials of mine-waste samples to produce acidic drainage under closely controlled laboratory conditions,

rather than to simulate field drainage quality (White and Jeffers, 1994; White and Sorini, 1996). The motivation for developing the protocol was to provide in one readily accessible document a more detailed description of the modified humidity cell protocol than was previously available in the literature. The intention was to promote method consistency and provide a helpful guide to new users of the modified humidity-cell protocol. A rigorous consensus review process was required before the protocol was established as and ASTM standard (White and Lapakko, 2000).

The method was revised and published in 2007 as D 5744-07, and details of the revision are described in Bucknam et al. (2009). The revision was informed by data from and interlaboratory study (ILS), the ASTM International peer review, solicited input, and comments presented by Lapakko (2003). The ILS was substantial. Twenty-five well-characterized samples (particle size distribution, chemistry, mineral content) from six lithologies were subjected to dissolution testing for periods of 20–265 weeks. Drainage pH and rates of sulfate, calcium, and magnesium release were used to assess the intralaboratory repeatability and interlaboratory reproducibility of D 5744-96 and compare the method with an alternative protocol referred to as the MN DNR (Minnesota Department of Natural Resources) method. The ILS data were reported by Lapakko and White (2013) and included in the precision and bias statement of the present version of the method (ASTM 5744-13e1, ASTM International, 2013).

Briefly, the method provides guidance on rock sample preparation, analysis (particle size distribution, chemistry, mineralogy, petrography) of the sample to be tested, detailed methods of humidity cell testing, and post-test solids analysis. At the core of the method is a laboratory weathering test in which a 1-kg sample of rock (diameter less than 6.35 mm) is rinsed weekly with 500 or 1000 mL of deionized water and the resultant leachate is weighed and analyzed to quantify the extent of reaction during the week. Two options for the reaction conditions during the weekly cycle are presented. Option A requires introduction of dry air for three days followed by introduction of humidified air for three days, with rinsing occurring on the seventh day of the weekly cycle. Option B does not prescribe introduction of air (Fig. 1).

The characterization of rock tested prior to testing is consistent with that described in the characterization discussion above. That is, analyses are conducted to determine elemental composition, mineral content and composition, and to assess the mineral surface



**Fig. 1.** Weekly rinsing of solutes from a suite of Duluth Complex rock samples tested using ASTM 5744-13e Option B at the Minnesota Department of Natural Resources Hibbing laboratory. 500 mL of deionized water is dripped from the separatory funnels onto the 1-kg rock samples and leachate is collected in the bottles below the humidity cells for subsequent analysis.

area available for reaction. The latter analyses include particle size distribution, chemical analysis of size fractions and petrographic analyses. These analyses are intended to inform description of the relationship between rock composition and the water quality resulting from rock weathering. Post-test analyses of the rock are intended to provide further insight on the weathering reactions. These analyses include sequential extractions that can be used to determine the partitioning of trace metals among various phases (e.g. Piatak et al., 2007). Such analyses lend insight on the accumulation of trace metals, initially released from sulfide minerals, in labile phases from which they are subject to subsequent release upon minor changes in pH. To guide those unfamiliar with weathering tests, the method provides extensive commentary describing the rationale for various aspects of the protocol.

Contrary to a fairly popular misconception, the method does not prescribe a test duration. Specifically, the method dictates (1) test duration is to be "...determined by the user's objectives of the test..." (paragraph 1.3); (2) "...Criteria for ending the testing will depend on the objective of the test, which may be site specific..." (paragraph 11.4.1); and (3) if the objective is to determine the relative reactivity as a function of compositional variations within individual mine-rock lithologies for the purpose of segregating mine wastes, "...then a specific test duration is not prescribed ..." (paragraph 11.4.2). To apply this guidance test objectives must be clearly defined prior to testing. Checkpoints can then be established at specified time intervals, for example annually, to examine data and determine if objectives have been met (ASTM International, 2013).

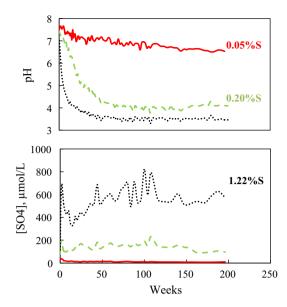
# 7.1.3. Determination of reactivity and solute release rates

Lapakko (2003) used data from humidity cell testing of greenstone rock to provide an example of evaluating the reactivity of a waste rock lithology, and the following discussion expands on that example. Testing was conducted on 14 greenstone samples with sulfur contents ranging from 0.04 to 1.22 wt% using ASTM D5744-07 Option B (Lapakko and Antonson, 2006; Lapakko et al., 2012). The samples were characterized with respect to particle size distribution, chemistry, mineral content, and mineral chemistry. Individual size fractions were analyzed for sulfur content and sulfide mineral liberation. The samples were subjected to dissolution testing for periods of 154–204 weeks.

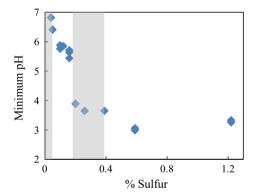
Pyrite was the only sulfide mineral present in the samples and carbonate minerals were essentially absent in all but two samples, which contained siderite. A small fraction of the carbonate in the siderite was associated with magnesium. This fraction of the siderite was capable of providing relatively rapid acid neutralization. For the remaining samples, the silicate minerals sericite (muscovite) and chlorite were the major acid-neutralizing minerals. Thus, for 12 of the 14 samples, acid-neutralizing was limited to that provided by the relatively slow dissolving silicate minerals.

Over the course of the experiment, the weekly drainage samples were analyzed for pH, sulfate, and other solutes. Fig. 2 presents the temporal variation of pH and sulfate for three of the samples. It indicates drainage pH decreased and sulfate release increased with increasing sulfur content. These trends were generally consistent throughout the sample set, as indicated by the variation of minimum drainage pH with sulfur content (Fig. 3).

It should be noted that drainage pH values from the samples containing siderite were higher than expected for samples of their sulfur content and these values were omitted from the graph. For reference, samples with sulfur contents of 0.5 and 0.72 wt% produced respective minimum pH values of 4.35 and 6.40. These relatively elevated pH values were due to the relatively rapid dissolution of the magnesium carbonate phases in these samples and the associated acid neutralization. Acid neutralization in the



**Fig. 2.** Drainage pH and sulfate concentration vs time for three of the greenstone rock samples. The lowest sulfur sample (0.05 wt%S, solid red line) yielded the lowest sulfate concentrations and highest pH. The highest sulfur sample (1.22 wt%S, dotted black line) yielded the highest sulfate concentrations and lowest pH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

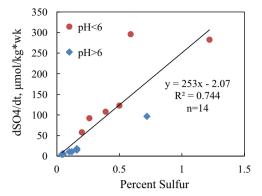


**Fig. 3.** Minimum drainage pH tended to decrease as sulfur content of the rock increased. Differences in shading delineate sample categories based on sulfur content and minimum pH.

remaining samples was provided by the slower dissolution of sericite and chlorite.

To provide a simplistic example, the dependence of drainage pH on sulfur content could be used to provisionally categorize waste rock for management purposes based on their potential for generating acidic drainage. Samples with sulfur contents of 0.04–0.05 wt% produced drainage pH above 6.0, thus meeting the typical pH standard. Samples containing 0.10–0.16 wt%S produced values slightly lower and may require a modest degree of mitigation to meet standards. Sulfur contents of 0.20–0.40 wt% yielded values in the upper threes, and samples with 0.59 and 1.22 wt%S produced values between 3.0 and 3.5. Rock with sulfur content in these ranges would require progressively more rigorous management.

Sulfate release tended to increase as sulfur content increased, reflecting the dependence of sulfate release rate on pyrite surface area (Fig. 4). Rates for samples generating lower pH tended to be higher, likely reflecting the influence of pyrite oxidation by ferric iron and/or biological mediation of the oxidation reaction. These dependences are described in greater detail by Lapakko and



**Fig. 4.** Sulfate release tended to increase as sulfur content increased. The rates for samples generating pH below 6 tended to be higher than those for samples generating circumneutral pH. Period of record is weeks 20–204.

Antonson (2006). This analysis provides a scientific foundation for the empirical data generated, which in turn increases confidence in the understanding of the waste rock behavior. This in turn reduces uncertainty in the development of waste rock management strategies.

In addition to assessments of reactivity, humidity cell tests also provide rates of solute release. Solute release rates can be calculated for each drainage sample for which solute concentrations and drainage volume are determined. Solute release from individual samples will vary over time, and average rates are calculated over selected periods (Fig. 5). The standard deviation for a selected period can be calculated to provide a measure of variability.

# 7.2. Field tests

As mentioned above, kinetic tests can also be conducted in the field, and Price (2009) provided design considerations for such "onsite field cells". Compared to laboratory tests, field tests more readily accommodate larger size rock particles and are conducted under environmental conditions, thus accounting for factors such as variations in temperature, precipitation intensity, precipitation timing, and snow melt. Consequently these tests more closely approximate those of full-scale waste rock piles in the field. Relative to ASTM 5744-13e1 humidity cells, the field tests generally have a much lower water:rock ratio (water added relative to mass rock tested) and a much longer residence time (time water is in contact with rock). Shaw and Samuels (2012) indicated the water:rock ratio was the most influential variable with regard to differences between results from laboratory humidity cells and field barrel tests. They further concluded that their results indicated alkalinity release rates from humidity cells may not reflect field rates and that ultimate drainage pH values must be considered when estimating metal concentrations in field drainage. The low water:rock ratios and longer residence times in field tests tend to produce higher solute concentrations than humidity cell tests, but concentrations may not reach levels at which they are controlled by secondary reactions. That is, higher concentrations may be reached under operational conditions.

Field testing has been conducted at various scales, ranging from barrels (Costin et al., 2011; Shaw and Samuels, 2012; Aranda et al., 2009) to test bins (Soto et al., 2012; Salzsauler et al., 2012; Bertrand et al., 2012) to test piles of various sizes (Lapakko, 1993, 1994; Bailey et al., 2012), and full-size operational monitoring (Fig. 6). Testing of this nature has been typically conducted at operational mine sites where larger masses of material are readily available and mining personnel and equipment are available to assist in construction and monitoring. Conceptually, barrel tests

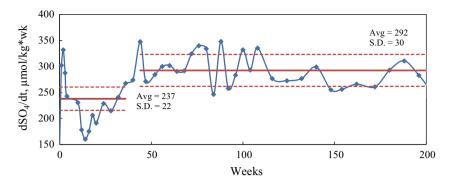


Fig. 5. Sulfate release rates ( $\mu$ mol (kg rock)<sup>-1</sup> week<sup>-1</sup>) for the 1.22%S sample were determined for different time periods. Consideration was given to capturing rates for periods during which release tended to remain within a constant range.







**Fig. 6.** The top two photos depict tank tests and test piles used for field dissolution testing of greenstone rock at the MN DNR Hibbing research site. The bottom photo depicts the weir at a site used for monitoring flow and water quality at the Dunka taconite mine in northeastern Minnesota.

are more conducive to testing prior to operation than test piles because they require less rock, potentially available from drill core or bulk samples, and have a lower construction cost.

Price (2009) cited potential compositional and flow heterogeneity, difficulty in determining mineral dissolution rates, "irregular seepage", and heat dissipation as disadvantages of field test cells. To elaborate, unknowns regarding the fraction of rock contacted and flow path complicate interpretation of data. Heterogeneity (size, chemistry, mineral content, mineral chemistry, petrography) of the larger rock sample can futher complicate this interpretation. Consequently normalizing solute release rates based on rock mass or mineral surface area is difficult, therefore interpretation and extrapolation of test data is subject to substantial uncertainty. In contrast, humidity cell rock samples (1 kg) are more homogeneous and readily characterized; the water:rock ratio is, by design, large so that reaction products are more readily transported from the cell. Thus, solute release rates can be more confidently normalized to rock mass or mineral surface area.

#### 8. Modeling

The simplified view of a mining proposal being a potential change to an existing condition provides an approach for assessing the problem. First, establish the existing conditions. Second, describe the proposed changes based on the operational plan and the additional characterization of waste rock described above. Third, project the effects of the proposed changes by conceptually imposing them onto existing conditions. Fourth, assess the results of the proposed changes. These steps comprise a modeling exercise that can be used to quantify solute release from proposed mine waste storage facilities. Beyond this quantification, and the scope of the present discussion, is assessment of risk.

# 8.1. Baseline conditions

In order to assess changes that may occur due to mining (or changes that have occurred once mining has begun) it is necessary to establish baseline conditions. This includes climate (e.g. precipitation, temperature), topography, surface-water and groundwater hydrology, surface-water and groundwater quality, bedrock properties, soil inventories, and existing features from previous mines or other industry (Maest et al., 2005; Price, 2009). Included in this assessment should be identification of the compliance points and associated water quality standards for the site. This information will specify the targets for any mitigation measures required.

The baseline conditions provide constraints for the design of the mine and associated facilities. For example, the topography will limit options based on the amount of available area that is suitable for specific purposes. Water resources on the site will affect mining considerations such as mine dewatering, availability of make-up water for processing, and environmental concerns including existing "impacts" and ultimate water quality requirements. The baseline conditions also provide a foundation onto which the operations can be imposed. This superimposition provides a basis for modeling. That is, imposing the aspects of the operational plan onto the baseline setting provides the conditions from which modeling projections will be made. Maest et al. (2005) provided additional guidance on relevant baseline information and Price (2009) delved into greater detail on this issue.

# 8.2. Operational plan

The operational plan must have adequate detail for environmental modeling. This includes mine dimensions and mine wall composition, and the mass and composition of waste rock, tailings, and processing wastes. The water balances for operational components are also necessary. Key aspects for the modeling exercise are the initial plans for mine waste management facilities. These plans are likely to evolve in an iterative process as the modeling effort progresses.

# 8.3. Conceptual model

A conceptual model is developed to describe logically the interaction of the operational plan and the environment. Given the baseline conditions and operational plan, a question at the core of the modeling is, "What affects the quantity and quality of drainage?" Addressing this question requires application of scientific and technical principles, pre-existing data, data generated during the project (including mine waste characterization and dissolution testing), and assumptions. For a specific source term such as waste rock, the model will impose the planned waste rock disposal facility onto the environmental setting. The mass, composition, and facility size, design and location will be provided by the operational plan. More detailed description of the waste rock will be provided by the characterization study.

Fig. 7 provides a schematic depicting some of the features on which a conceptual model for waste rock can be developed.

Baseline hydrologic aspects identified include groundwater elevation and flow, precipitation, and evaporation. Hydrologic aspects of the waste rock pile include input from precipitation infiltration and outputs to surface water (runoff, face and toe seepage), seepage to groundwater, and evaporation.

Fig. 7 indicates that the pile is constructed by dumping waste rock at the edge of a pile. This dumping provides a physical segregation of waste rock, with larger particles naturally falling to the base of the pile. This segregation enhances the potential for air flow up through the pile, as depicted by the colored arrows. Such flow has been observed to accelerate oxidation reactions, and the consequent release of acid and other solutes, in waste rock piles.

# 8.4. Quantitative description of conceptual model

Once a soundly conceived conceptual model is developed, a quantitative model is constructed to reflect the interactions identified. This aspect can be viewed as the computational machinery that digests inputs using sound, quantitative, technical principles to yield quantitative outputs. This machinery consists of a series of computations procedures, or algorithms. With regard to the schematic presented in Fig. 7, the quantitative model would calculate how much water would infiltrate the rock pile and how much would exit as runoff, face seepage, toe seepage, and groundwater. It would also quantify solute release from the rock based on assessment of the geochemical reaction of input water with the rock. Considerations for these calculations might be extensive, including variables such as precipitation, temperature, wind, and physical characteristics of the waste rock affecting flow through the pile.

# 8.5. Output release rates

Inputs for source term modeling are unlikely to be confidently quantified by single values. Similarly, the assumptions used in modeling are likely to be subject to uncertainty. Overall, the combination of inputs and assumptions will likely provide for a number of calculations yielding a range of output values. These outputs are perhaps best expressed as a probability distribution that describes both the range of outputs and the likelihood of their occurrence.

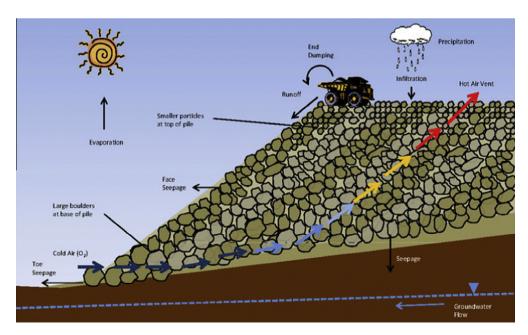


Fig. 7. Schematic of baseline conditions, construction method, and hydrologic and gas transport features of a waste rock pile (adopted with permission from The International Network for Acid Prevention (INAP), 2009. Global Acid Rock Drainage Guide (GARD Guide): http://www.gardguide.com).

#### 8.6. Modeling guidance

The National Research Council (2007) provided guidance on modeling related to environmental regulatory decisions, and their recommendations are generally consistent with guidance presented by Maest et al. (2005). Key recommendations include the following. (1) Models should be transparent. The use of proprietary models or extremely complex models makes it extremely difficult to check the structure of the model. Because a model must often deal with complicated questions, it is necessary to balance the rigor of modeling with transparency. A critical point is that regulators cannot approve results from a model they do not understand and cannot trust. (2) Conceptual models must be scientifically sound. (3) Algorithms must accurately reflect the conceptual model. (4) Inputs to the model and assumptions applied must be technically sound. (5) Computational checks must be conducted on model output. This checking might be done using simplified models, other models addressing similar problems, or by comparison with available empirical data. (6) Sensitivity analyses must be conducted to rank the relative importance of inputs and assumptions. One example of the importance of such analyses is presented by Ross and Verburg (2012), who provided five examples of how small changes in input values can have large effects on the model output. (7) Output should be presented as a probabilistic distribution rather than a single value.

# 8.7. Modeling solute release rates for waste rock based on humidity cell data

Waste rock samples subjected to dissolution in humidity cell tests are often used as a basis for projecting solute release from waste rock in the field. The solids used in the laboratory tests are intended to be representative of those in waste rock piles. In both cases the rock is subjected to cycles of oxidation and solute rinsing. Therefore an initial estimation of solute release in the field can be made using the rates observed in the laboratory that are expressed per unit mass rock (e.g. Fig. 5) and multiplied by the mass of rock in the field. However, there are substantial differences in the two situations that complicate extrapolation.

Specific differences between the laboratory and field are particle size, temperature, and water input rates. Differences in particle size are important because they influence rates of solute release, and this dependence is rock type specific (Lapakko et al., 2006). Rock particles used in humidity cell tests are finer than 6.35 mm whereas waste rock in an open pit mine can be larger than a meter in diameter. Particle size data reported for operational-scale waste rock from an open pit at the Diavik project were used to estimate that 14 wt% of the rock was finer than 6.35 mm (estimated by author using data from Smith et al., 2013). Rock taken from underground shafts and drifts tends to be smaller, with maximum sizes on the order of 0.3 m. The maximum diameter of such rock excavated from the Duluth Complex in northeastern Minnesota was in this size range. Particle size distribution determined by sieving five samples yielded (by weight) 11-22% in the -6.4 mm fraction, 5-14% in the -2.0 mm fraction and 1-3% in the -0.1 mm fraction (Lapakko et al., 2004). Additional operational particle size distribution data from several studies were summarized by Kempton (2012).

Humidity cell tests are conducted at a temperature of  $25\,^{\circ}$ C. However, in locations such as northeastern Minnesota average temperatures are in the of  $2\text{--}3\,^{\circ}$ C range. It is common to use the Arrhenius equation for scaling temperature differences in the absence of empirical data. Maest et al. (2005) recommended conducting field tests to augment data generated in the laboratory in order to better scale for temperature and other weather-related variables.

Using a similar comparison, the rinse water input in humidity cell tests is equivalent to an annual precipitation of 320 cm, and this addition is intended to remove all soluble reaction products from the cell. This input is considerably higher than, for example, the 72 cm average precipitation in northeastern Minnesota and, consequently, a lesser degree of reaction product transport would be expected in the field. In contrast, some areas in British Columbia average 650 cm of precipitation in a year. Differences such as these must be accounted for in scaling laboratory results to the field.

Malmström et al. (2000) used an approach incorporating scaling factors to account for differences between laboratory and field rates of mineral dissolution. These scaling factors represented the fraction by which laboratory rates were reduced due to specific influences on rates. For example using the rule of thumb that reaction rates double for a temperature increase of 10 °C, a temperature scaling factor of 0.5 would be used to project rates for laboratory tests conducted at 25 °C to field conditions at 15 °C. The scaling factors were intended to account for differences in preferential flow and trapped water, temperature, pH, and particle size. Malmström et al. (2000) found reasonable agreement between their modeled mineral dissolution rates and those observed in a waste rock pile.

Despite the promising results reported above, there is no general agreement on the magnitude of scaling factors. The variability of reported scaling factors is demonstrated in a literature summary by Kempton (2012) who indicated an 8-fold range in factors cited to scale water contact (and inferred solute transport) alone. Robertson et al. (2012) empirically determined field:laboratory scaling factors using data from operational scale piles (~5 million tonnes) and humidity cells. They calculated empirical sulfate release scaling factors (observed field rate/observed laboratory rate) in the range of 0.05-0.3. Hanna and Lapakko (2012) reported that sulfate release rates from Biwabik iron formation waste rock piles were roughly 1.2 times those in the initial 26 weeks of humidity cell testing of drill core (i.e. an empirical scaling factor of 1.2). However, laboratory sulfate release rates on samples of weathered rock from the field were about 10 times those from the drill core. Use of the weathered rock rates would yield a scaling factor on the order of 0.12. It is possible that the magnitude of scaling factors is a function of variables such as rock type, sulfur content, and climate. In any case it is clear that scaling is not a trivial issue. Consequently, sensitivity and uncertainty analyses must lend careful consideration to their application.

#### 8.8. Concentration limits

Scaling using the approach outlined above often yields solute concentrations in drainage that are unrealistically high. In such cases an attempt is made to establish concentration limits, often using available geochemical equilibrium models. This can be difficult for trace elements for which concentrations may be controlled by adsorption. Modeling such reactions can be a sensitive exercise due to their dependence on adsorbent surface area and solution pH. A systematic compilation of empirical data would be helpful in clearing this hurdle. Eary (1999) initiated such a compilation for pit lakes but a companion effort for waste rock has not been undertaken.

A second complexity involves solutes that may be present in laboratory drainage samples at concentrations at or below detection limits and are both highly soluble and highly toxic. Particular examples are beryllium and thallium. For such situations, laboratory concentrations may be estimated as the detection limit or perhaps half the detection limit. Extrapolating laboratory results to field conditions using scaling factors based on waste rock mass (even with consideration of factors such as temperature and solute transport efficiency) can yield predicted concentrations well above

water quality standards. The accuracy of predictions for these environmentally sensitive elements is clearly problematic. If actual concentrations, for example, are one-tenth the detection limit, use of the detection limit or half the detection limit as concentration estimates (estimation approaches presented for consideration for humidity cell tests in ASTM D5744-13) would over predict concentrations by factors of 10 and 5, respectively. On the other hand, if actual concentrations are just below the detection limit and half the detection limit is used as a concentration estimate, then predictions would under predict concentrations by a factor of 0.5. Additional research appears warranted to describe both the solid-phase occurrence of elements such as beryllium and thallium, particularly at low concentrations, and the phases controlling their transport. Research on standardizing laboratory methods for empirically determining concentrations also would be beneficial.

#### 9. Conclusions

# 9.1. Technical challenges

As indicated above, detailed empirical information correlating specific geology, mineral development methods, well-characterized mine waste components, and climate with the associated drainage quality is limited. Consequently, the process of predicting mine-waste drainage quality and the associated chemical mass release for proposed mining operations is an analytical process involving consideration of mineralogic, petrographic, geochemical, hydrological, and climatic factors that influence dissolution of the specific mine wastes at a given site. Ultimately the prediction process involves selecting samples that are representative of the waste rock to be generated and subjecting them to characterization and dissolution testing that allows results to be scientifically extrapolated to predict drainage quality from a large mass of excavated material. The fact that these predictions must address not only the period of operation but the decades and centuries after closure, further complicates an already daunting technical challenge.

The expertise required to address this challenge is both broad and deep. Industry specific expertise is required in areas such as economic geology, mining engineering, geotechnical engineering, mineral processing, and metallurgy. Additional scientific and technical expertise is required for environmental assessment and reclamation. Geology, geostatistics, mineralogy, petrography, geochemistry, hydrology, chemical engineering, and civil engineering are among the disciplines that may be required for environmental aspects of mine waste management and environmental assessments. Reclamation science and geotechnical expertise in cover applications will help inform closure design. In general, substantial expertise in these fields is required to comprehend the complex aspects of mine and processing design and the associated environmental concerns.

# 9.2. Nontechnical challenges

For regulatory agencies the challenge of environmental assessments is magnified by the size of personnel pool with adequate technical expertise. Due, in part, to the cyclic nature of mining, personnel educated to address mining related environmental issues are at a premium. The U.S. graduated 700 mining engineers in 1981 when there were 30 accredited programs, as opposed to 2010 when only 170 graduates were produced by the 13 accredited engineering programs remaining (Sevim and Honaker, 2012). This concern and was more recently echoed and elaborated on by a collection of academic and industry personnel (Mining Engineering Staff, 2014). Graduates with degrees in environmental geochemistry are also in short supply, especially considering the expertise

required for environmental review is that of a masters or doctoral level education. These shortages further increase the challenge to adequately conduct environmental assessments of mining proposals.

There is also a challenge for industry to communicate technical information to regulatory agencies. These agencies are responsible for approving plans for managing mine wastes and meeting water quality standards. In order to meet their responsibilities they must have a sound understanding of the operational plan and its environmental implications. Communicating plans, data, and associated analyses is not always done clearly among those within an operation. The difficulty of these communications, often involving a high degree of complexity, is further amplified when dealing with those not involved in the step-by-step development of the plans.

Communication is also required with other stakeholders, such as nongovernmental organizations and the general public. In a simplified sense, a mining proposal represents a potential change to existing condition and, consequently, questions regarding potential deleterious effects of this change arise. The apprehension surrounding these questions is amplified by a daunting history of the industry, the physical size of many operations, the technical complexities of mining and the associated processing and, ultimately, the magnitude and longevity of the potential impacts posed by mine waste dissolution. These concerns lead to a degree of public involvement that is beyond that for many other types of projects. Issues addressed on a local level for many types of projects might attract a national or international audience for mining operations. Consequently, the environmental review process must clearly describe the proposed operation and communicate its potential impacts and associated mitigative measures to the general public.

Thus, environmental review goes beyond the complex technical and scientific problems associated with mine development and environmental assessment. It includes the additional challenge of communicating complex information to those who might lack the breadth and depth of technical foundation necessary to readily digest the varied complexities of proposed projects, their potential impacts, and mitigative approaches. Realistic scheduling for the environmental review and permitting processes must give due consideration to these communications, including the associated educational activities inherent to this process.

# 9.3. Research needs

As indicated by the lack of agreement regarding factors to scale laboratory results to field conditions, this area merits additional research. Concentration limits that provide ceilings for rock mass extrapolations of laboratory solute concentrations to the field also merit further examination. In particular, existing and future data should be compiled to provide an empirical data base for waste rock drainage concentrations. These data should then be interpreted in terms of likely controlling solid phases (e.g. Eary, 1999). Tests should also be developed to allow assessment of concentration limits for specific operations as part of the environmental assessment process. Finally, a repository for mining related information should be developed to store and catalog information generated during environmental review, mine operation, and after closure. Critical to such an effort is the capture and analysis of data collected by regulatory agencies. Such an empirical data base will inform future mine waste solute release predictions and allow for systematic advance of environmentally sound practices of mine waste management.

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