Predicting Water Quality at Hardrock Mines

Methods and Models, Uncertainties, and State-of-the-Art

Buka Environmental

Kuipers & Associates

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Front cover: Left – Partially filled open pit at the Equity Silver Mine (silver) in British Columbia, Canada. Center – Open pit at the Bingham Canyon Mine (copper) in Utah USA. Right – Two-year kinetic tests at the Montana Tunnels Mine (gold, silver, lead, zinc) in Montana USA. Back cover: Construction of the heap leach pad at the Marigold Mine (gold) in Nevada USA. All Photos by Ann Maest.

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FOREWORD

The prediction of water quality at mine sites, the focus of this report, is a challenging topic because of its technical complication and inherent uncertainties. The quantity and characteristics of mine wastes are among the most important determinants of water quality at a mine site. Mine wastes or mined materials include the extraction area (open pit or underground mine), waste rock, unprocessed lean ore, heap or dump leach piles, tailings, and metallurgical processing wastes, although all of these wastes may not be present at a specific operation. The quantity of material generated can be very large, with mine waste areas covering hundreds of acres and amassing to tens or hundreds of million tons. The quality of mine waste drainage can be environmentally innocuous, circumneutral to basic with elevated concentrations of metals and oxyanions, or highly acidic with very high heavy metal concentrations. In addition to the potentially large physical size of mine waste disposal facilities, these materials remain on the ground long after mining and processing operations cease and can generate problematic drainage for centuries. Thus, in the absence of remediation, mine wastes are potentially sources of contaminants that may be transported from the mine site and adversely impact environmental or human receptors for many years.

Mine waste characterization techniques, in conjunction with geochemical and physical modeling and relevant existing data, have been applied to predict the quality of drainage that will be generated by mine wastes over time. These predictions are intended to contribute substantially to the fundamental information required to design and cost remediation that will allow compliance with water quality standards in a technically and economically efficient manner. Designing remediation measures in advance of mining allows their costs to be factored into the economics of mineral resource recovery, and for environmental mine waste management measures to be integrated effectively into the mine plan. Whereas this concept is fairly simple, the prediction of mine waste drainage quality over time can be a difficult proposition.

Factors that complicate drainage quality prediction range in scale from small to large. First, on a small scale, drainage quality is influenced by the dissolution of minerals present in the mine wastes, as well as secondary reactions among solutes, gas phases, and solid surfaces. The mineral surface areas available for reaction can be difficult to quantify, and the rates of reaction in a complex system are not well known. Second, on the large scale, geology, climate, methods of mining and mineral processing, and mine waste management approaches vary among and within operations. Variability of these large-scale factors means that characterization problems and results can be unique to an operation or operational component, and this limits the degree to which information from one site can be applied to another. Third, extrapolation from laboratory to operational scale must address complicating factors such as differences in particle size, environmental conditions, water and gas transport, and how these variables affect drainage quality over periods of decades or centuries. There is virtually no available information describing the effect of variables such as these on well characterized operational mine wastes over extended periods of time. The lack of this field information introduces uncertainty into predictions, and this uncertainty must be accounted for. Finally, characterization results and subsequent modeling must lead to environmental mine waste management programs that are practical and verifiable in the field. Given the large masses of material often moved in mining operations, this consideration is far from trivial.

Despite these difficulties, geochemical characterization techniques can provide predictive information on mine waste drainage quality that is beneficial to the environmentally sound management of mine wastes. Given the complexity of long-term predictions and the associated uncertainty, mine waste characterization should be viewed in the context of a program, integrating results from a variety of characterization techniques over time, rather than a single test or a one-time series of tests. This program begins with testing in the exploration phase and extends through closure and post-closure in the form of monitoring. Technical expertise from those experienced in the field will most likely be required to develop and apply a well-designed waste characterization program.

This report identifies various techniques for the geochemical characterization of mine wastes, including conventional geochemical and mineralogical analyses, static tests, short-term dissolution tests, and

kinetic tests. For each technique, the report addresses advantages and limitations and sources of uncertainty, and makes concise recommendations for improvements. Sources of uncertainty in characterization and modeling identified in this report can be used to evaluate mine characterization and management plans. The characterization flow chart presented in the report provides a strategy that can be used at a wide variety of mine sites and recognizes that the specific characterization techniques can vary among these sites. Collection of an adequate suite of samples for testing is also discussed, and is a cornerstone for a reliable characterization program.

The application of characterization techniques during various phases of mineral resource development (exploration, development, active mining, and reclamation, closure, and post-closure) is discussed in this report. A modeling approach including development of a conceptual model, input data collection (including characterization results), model selection, sensitivity analysis, and evaluation of results is presented. The information presented in this report addresses many of the challenges associated with predicting water quality at mine sites noted above and will be useful to regulators, mine operators, and the public who are involved in mine waste characterization and modeling projects.

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August 2005

AUTHORS

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REVIEWERS

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LIST OF ACROYNMS

1D, 2D, 3D	1, 2, 3 dimensional
µg/L	microgram/liter
µm	micrometers
AAS	atomic absorption spectrometer
ABA	acid base accounting
ACMER	Australian Center for Minerals Extension and Research
ADTI	Acid Drainage Technology Initiative
AG	acid generating
AGP	acid generation potential
AMD	acid mine drainage
AP	acid production potential
ARD	acid rock drainage
AVIRIS	Airborne Visual and Infra-Red Imaging Spectrometer
BCRC	British Columbia Research Confirmation test
BCRI	British Columbia Research Initial test
BC SWEP	British Columbia special waste extraction procedure and modification
^{o}C	degrees Celsius
cm	centimeter
DI	deionized water
EP Toxicity	extraction procedure toxicity test
eq/t	equivalents of calcium carbonate per ton
gm	gram
HCT	humidity cell test
hr	hour
ICMM	International Council on Mining and Metals
ICP-MS	Inductively-coupled plasma – mass spectrometer
IGWMC	International Groundwater Modeling Center
INAP	International Network for Acid Prevention
K_d	distribution coefficient
kg	kilogram
L	liter
m	meter
M	molar
MEP	multiple extraction procedure
MEND	Mine Environmental Neutral Drainage
min	minute
mL	milliliter
mm	millimeter
MWMP	meteoric water mobility procedure
N	normal
NAA	neutron activation analysis
NAG	net acid generating test
NCV	net carbonate value test
NEPA	National Environmental Policy Act
NP	neutralization potential
NPL	National Priorities List
NRC	National Research Council
OD	outside diameter
P	pressure
PVC	polyvinyl chloride
QA/QC	quality assurance/quality control

RCRA	Resource Conservation and Recovery Act
SC	specific conductance
SEM/EDS	scanning electron microscopy/energy dispersive system
SME	Society of Mining, Metallurgy, and Exploration
SPLP	synthetic precipitation leaching procedure
T	temperature
TCLP	toxicity characteristic leaching procedure
TIC	total inorganic carbon
UNEP	United Nations Environmental Programme
USACOE	United States Army Corps of Engineers
USDA	United States Department of Agriculture
US EPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	volatile organic compound
WET	California waste extraction test
WWG	World Wide Acid Rock Drainage Guide
XRD	X-ray diffraction
XRF	X-ray fluorescence

OVERVIEW

In order to determine if a given hardrock mine project will be protective of water resources during and after mining, regulators at state and federal agencies review Environmental Impact Statements or other types of environmental assessment documents submitted by mine proponents. In these assessments, the potential of the mined materials to generate acid and contaminants and to affect water resources is evaluated using a number of laboratory and field techniques and a variety of predictive modeling approaches. The regulator's job is to evaluate, sometimes with incomplete information, whether the tests and modeling that were conducted were appropriate for the site-specific conditions at the mine and whether the predictions and the mining approach are reliable enough to guarantee that future environmental liability is adequately addressed.

According to the U.S. EPA's Abandoned Mine Land Team, the cost of remediating mine sites on the National Priorities List (NPL) in the United States is on the order of $20 billion. Recent increases in the prices of precious and base metals on the world market have triggered an increase in the number of new mines being proposed in the United States and around the world. In the United States alone there are on the order of 170 large hardrock mines – in nearly all regions of the country – that are in various stages of being proposed, in permitting, in construction, operating, or recently closed and require oversight and ongoing evaluations by state and federal agencies. In order to reduce liability costs associated with hardrock mining, improvements must be made in mine evaluations before mining begins and also throughout the life of the mine. This report lays out a framework for evaluating the methods and models used to predict water quality at hardrock mine sites and makes recommendations for their improvement. It is intended to be used by regulators, the interested public, and mine operators and managers.

The companion study to this report, *Comparison of Predicted and Actual Water Quality at Hardrock Mines: The reliability of predictions in Environmental Impact Statements* (Kuipers et al., 2005), reviews predictions made in Environmental Impacts Statement for large hardrock mines in the United States – predictions based in part on characterization and modeling approaches – and evaluates their reliability using operational water quality data. Findings from that study highlight the importance of obtaining characterization data through all stages of mining and using this information in forecasts of mine site water quality.

Although predictive modeling is by its nature uncertain, it is valuable for helping to describe and understand the physical, chemical, and biological changes that can occur to natural systems from mining activity. Much of the uncertainty related to predicting water quality at mine sites derives from inadequate or inaccurate conceptual models, hydrologic and geochemical characterization data, and input data to hydrogeochemical models.

The creation of a site conceptual model is an important first step in predicting water quality at mine sites. In order to create a useful conceptual model, baseline hydrogeologic and geochemical data from the proposed mine must be collected and interpreted. The pathways through which contaminants can travel from mine sources to receptors should be identified and characterized, and the effects of any proposed mitigation measures on contaminant transport should be estimated. Conceptual models are not unique and can change over time as mining progresses. Therefore, it is necessary to revisit conceptual models and modify mining plans and predictive models based on new site-specific information.

One of the biggest challenges in predicting water quality is estimating the long-term geochemical behavior of mined materials. Unlike other industrial facilities, contaminant discharges from mine sites can take years, decades, or longer to develop and are subject to climatic and seasonal variability in concentrations and flow. Laboratory and field geochemical testing and careful measurements of hydrologic and meteorologic conditions at the site over time are needed for improved water-quality predictions. Mineralogic characterization is an underutilized tool in the prediction of the geochemical behavior of mined materials. Static tests and short-term leach tests are not designed to simulate long-term behavior of mined materials. Properly conducted static tests can instead provide estimates of the total amount of acid-generating and -neutralizing material present, and short-term leach tests can be used to simulate the short-term interaction of water with weathered, mined materials. Results from static tests can be useful as an

initial screening method to determine which materials should be examined further for acid-generation potential but should not be used to predict the long-term ability of mined materials to generate acid. Similarly, results from short-term leach tests may be useful for estimating leachate concentrations in, for example, waste rock runoff after a storm event but should not be used to predict concentrations of leachate in seeps whose waters derive from slower pathways within the pile. Kinetic tests are designed to estimate longer-term geochemical behavior of mined materials. However, there are a number of issues, mostly related to particle size and length of the tests that can cause kinetic tests to be poor predictors of long-term water quality. These issues require that kinetic testing start as early as possible in the development of a proposed mine, and that the results be reported in terms of available surface area of minerals that control acid generation, acid neutralization, and contaminant leaching. Involvement of a person with in-depth understanding and experience in mine waste characterization approaches and interpretation will help prevent misinterpretation of characterization test results and result in a well-designed and applied waste characterization program.

At mine sites, much of the modeling performed is "forward" modeling, or modeling of conditions that do not yet exist. In the case of pit lakes, steady-state water quality and quantity conditions may not exist for hundreds of years, yet predictions about the quality of pit water are often requested for regulatory purposes. The difficulty in checking modeling results against actual water quality results in large uncertainties in the accuracy of predictive water quality modeling. Most of the other uncertainties in predictive modeling at mine sites relate to values used as inputs to the models rather than to the validity of the model itself. The model or models chosen to predict water quality should be representative of the site (as reflected in the site conceptual model) and be applied at a level of complexity that is appropriate for the available data and the regulatory decisions that must be made. In many cases, available data may limit the model application, and it may be more appropriate to develop a less-complex, screening-level model when data are not available to support a more complex model. For mines that are already developed, field sampling will provide the best measure of water quality. Site-specific values used as inputs to models must be as accurate of the range of conditions at a mine site as possible and should consider seasonal and other types of temporal variability.

The inherent uncertainty in model predictions is rarely stated or recognized. Methods used to evaluate or account for model uncertainty include Monte Carlo analysis, other stochastic methods, and evaluating a range of model input values to develop a range of outcomes (e.g., a range of water quality in a given receptor). These methods account for the fact that, rather than being well described by a single value as required in the model, parameters are better described with a probability distribution. However, uncertainty evaluation of parameter input will not address inaccuracies in conceptual models. Presenting potential contaminant concentrations at receptors as ranges rather than absolute values will better reflect the uncertainty inherent in predictive modeling.

Hydrologic and geochemical codes still solve the same basic equations and reactions that were identified 80 or more years ago. Some of the most notable improvements in both hydrologic and geochemical codes are the operating systems and the graphic interfaces, which allow more user-friendly operation of the codes and better visual output of the modeling results. Individual codes have slight advantages and disadvantages, depending on the application, but the experience of the modeler, the choice of input parameters and data, and the interpretation of the modeling output are more important than the choice of the code itself. The ability of today's codes and advanced computers to predict an outcome far exceeds the ability of hydrogeologists and geochemists to represent the physical and chemical properties of the site. The degree of confidence in the models is severely limited in part because the models are so complex that they cannot be easily reviewed by regulatory staff and the public. Water quality predictions should always be re-evaluated over time at mines sites and compared to site-specific water quality information as it becomes available. The efficacy of the mitigation measures should also be tested using predictive models and later confirmed with active monitoring. For this analysis, possible ranges in effectiveness of the mitigation measures (e.g., ranges in permeability values of liners) should be used in predictive models.

Predictive modeling of water quality at mine sites is an evolving science with inherent uncertainties. However, using the approaches described in this report, predictive water quality modeling and site characterization information can be reliably used to design protective mitigation measures and to estimate the costs of future remediation of hardrock mine sites.

1.0 INTRODUCTION

The art of predicting future water quality at hardrock mine sites has been practiced for at least the past 30 years. As part of the National Environmental Policy Act (NEPA), mines and other industrial facilities in the United States on federal land are required to estimate impacts to the environment, including direct impacts to water quality and indirect impacts that are later in time but still reasonably foreseeable (Kempton and Atkins, 2000; Bolen, 2002). Facilities on private land in the United States are often subject to State processes that may or may not require prediction of potential impacts to water resources. Other countries have followed a similar approach, largely based on the Environmental Impact Statement or Assessment of NEPA. A wide array of approaches has been used to predict water quality that could result from construction, proposed expansion, or other action at an industrial facility.

In this study, we review the methods and models used to predict water quality at hardrock mine sites, with an emphasis on the state of the art and on advantages and limitations of these techniques. Because water quantity and quality are interrelated, methods and models used to predict water quantity will also be discussed, but the emphasis will be on how these methods relate to water quality. This study brings together technical information on water-quality predictions at mine sites in a single report, and attempts to present a straight forward approach to using and evaluating the results of the methods and models used to predict water quality at mine sites. Approaches developed primarily in the United States, Canada, and Australia and applied in these countries and in other parts of the world, especially in the last 10 years, are discussed, and the format of the study is geared toward use by regulators of hardrock mines. The approach and results of this study could also be used by environmental managers at mine sites and community groups, and allows for the creation of a checklist for prediction methodology used at mine sites. Recommendations are made for improvements in water quality prediction methods and models.

2.0 THE NATURE OF PREDICTIONS

Although future predictions are often part of the business of science, most notably in the fields of meteorology and more recently climate change, scientists are generally uncomfortable with forward (future) predictions (Sarewitz, 1996). Forward predictions cannot be checked for accuracy until the future comes to pass. In the mining industry, the most common example of forward modeling is the prediction of pit lake water quality over time. Predictions of pit lake water quality and water-quality predictions in general have been acknowledged as having large uncertainties (Kempton, 2002), yet results from these predictions often form the basis of permit granting to the mining industry.

The principal use of modeling, according to Oreskes et al. (1994), should be to understand discrepancies between observed data and simulated results, test hypotheses, conduct sensitivity analyses, and explore "what-if" scenarios. If detailed site-specific information is available, an adequate conceptual model of the mine site, for example, can be developed to simulate current conditions or conditions in the recent past. If this is successful, an increased level of confidence can be placed in the use of this model to assess future site conditions (Mayer et al., 2003). However, because natural systems are never closed systems, because inputs to hydrologic and geochemical models are incompletely or only approximately known, and because of scaling problems in natural systems, models used to simulate natural processes cannot be verified (Oreskes et al., 1994).

The length of time over which a mine site will deviate from baseline or pre-mining conditions can be on the order of centuries to tens of thousands of years, as a result of potential delays in the generation or appearance of acid drainage (e.g., Morin et al., 1995; Kempton and Atkins, 2000*)* and the long "half-life" of releases from mining wastes. Therefore, the "future" at hardrock mine sites approximates the period of interest for nuclear waste disposal rather than that for more conventional industrial facilities. In addition, changes in the mine plan after permitting can add uncertainty to the predictions made early in the mining process. Inherent uncertainties, lag times, and the duration of contamination have led some practitioners of modeling at mine sites to emphasize ranges rather than precise values for water-quality predictions. At least three Environmental Impact Statements for mines in Nevada (Battle Mountain Phoenix Project, 2001; Round Mountain, 1996; Twin Creeks, 1996) contain general statements about uncertainty, such as, "…there is considerable uncertainty associated with long-term predictions of potential impacts to groundwater quality from infiltration through waste rock...for these reasons, predictions should be viewed as indicators of long-term trends rather than absolute values." While these statements are certainly true, modeling and predictions do have value as management tools and for helping to understand the biological and physicochemical systems at mine sites (Oreskes, 2000). In addition, water-quality predictions are used to make decisions about mitigation approaches at a mine site, and realistic predictions will ensure that the appropriate type of mitigation is chosen.

An optimistic approach to modeling would consider that our understanding of hydrochemical systems and the problem of relating models at different scales (from the atomic to the watershed level) will continue to advance by implementation of field and laboratory experiments that carefully extract one variable at a time to isolate and compare with the coupled numerical models available today, and by conducting post-audits of predictions. The level of complexity chosen for the model must reflect the scale at which the problem is addressed (White and Brantley, 1995), the availability of information, and the level of detail and accuracy/precision that is required (Banwart et al., 2002). In general, for problems of larger scale (e.g., predicting groundwater flow under a 20-km^2 area at a mine site) and with less available information, a less complex the model should be employed.

3.0 PREVIOUS AND ONGOING INVESTIGATIONS

A number of other studies have reviewed and evaluated methods and models used to predict water quality at hardrock mine sites, and a number of studies are currently under way to review prediction methodologies. For example, INAP (International Network for Acid Prevention) and ADTI (Acid Drainage Technology Initiative) an industry-based organization consortium is in the process of developing a World Wide ARD Guide (WWG) that will capture and summarize the best science and a risk-based approach to acid-drainage management. The first scoping meeting for the WWG was held in December, 2004.

ICMM (International Council on Mining and Metals), in partnership with the UK's Department for International Development, the United Nations Conference on Trade and Development, and the United Nations Environment Programme (UNEP), launched an online library of good practice in mining and metals (www.goodpractice-mining.org) in August 2004. The library contains references for guidelines, standards, case studies, legislations, and other related areas.

Other major players in prediction of water quality at hardrock mine sites are MEND (Mine Environmental Neutral Drainage), a program funded by Canadian federal and provincial governments and the mining industry that ended in 1997; InfoMine/EnviroMine, sponsored by Robertson GeoConsultants, Inc. of Canada, with a website (http://technology.infomine.com /enviromine/) devoted to the identification and dissemination of mining environmental technology; ACMER (Australian Centre for Minerals Extension and Research), an industry initiative to address environmental issues relevant to the minerals industry with a focus on sustainable development; the British Columbia Ministry of Employment and Investment, Energy and Minerals Division (BC Ministry) in Canada; the U.S. Environmental Protection Agency; the Minnesota Division of Natural Resources; and the U.S. Geological Survey.

Although the laboratory and field tests and hydrogeochemical models used for prediction are continually undergoing modifications, the basic characterization and modeling approaches remain relatively unchanged over the past 20 years. As reviewed in later sections of this study, the effectiveness of these methods and models has been questioned by a number of workers, and the advantages and disadvantages of using these approaches have also been discussed at length. Among the previous studies of methods and models used to predict water quality at mine sites, MEND and Infomine have conducted the most thorough reviews, and the BC Ministry, the U.S. Environmental Protection Agency, and the Ian Wark Institute in Australia have also conducted reviews. White, Lapakko and Cox (1999) wrote a thorough review of geochemical characterization methods and the issues affecting their validity.

Acid drainage is considered to be one of the most important and long-lasting environmental concerns at hardrock and coal mines. However, the emphasis on acid drainage prediction has eclipsed concern over neutral and basic mine drainage, which can nonetheless contain elevated and potentially injurious concentrations of metals, metalloids, anions, and other contaminants (Scharer et al., 2000a). For example, elements that form oxyanions in natural waters, such as arsenic, antimony, and vanadium, often have elevated concentrations at higher pH values such as those typical of cyanide heap leach facilities (Miller et al., 1999). Heap leach pads and tailings impoundments are examples of mined materials that may produce neutral or basic drainage with potentially elevated concentrations of contaminants.

This study synthesizes existing reviews and other relevant information in one document that can serve as a stand-alone review and provide a gateway to both broader and more in-depth information on the subject of water-quality predictions in hardrock mining. Methods and models used to predict acid drainage are addressed, but the study takes a more general and simplified approach that allows for the evaluation of any type of contaminant release from mined materials. This study also emphasizes the advantages and limitations of the characterization methods and models used to predict water quality at mine sites, rather than providing an exhaustive review of these techniques themselves. However, an extensive bibliography is provided for readers who would like more detailed information on the specifics of characterization methods and models.

4.0 STUDY APPROACH

The study approach included reviewing available literature on methods and models used to predict water quality at hard rock mine sites; developing a "toolbox" approach for discussing and evaluating these methods and models; and using information from the literature review and toolboxes to evaluate uncertainties associated with methods and models used to predict water quality at hardrock mine sites.

4.1 Bibliography

A review of the available literature was conducted as a first step in the study. Much of the information available on water-quality predictions at hardrock mine sites is contained in the "gray" literature, that is, in conference proceedings, agency handbooks or manuals, and short course summaries rather than more extensively peer-reviewed papers in journals and books. Bibliographic database searches were conducted using GeoRef, AltaVista, WorldCat, IMMAGE, Proceedings First, Google, Biosis, and Yahoo using the following keywords: prediction, characterization, acid mine/rock drainage, modeling, geochemistry, alkaline drainage, alkaline mine drainage, pit lake, pit lakes model, pit lakes modeling, pit lake water quality, and pit lake characterization. Personal files of the authors and other associates were also searched for documents relating to water quality prediction at hardrock mine sites. The documents were reviewed and categorized according to the characterization method or model that they discuss. An Excel file containing the references and information about their content is available electronically at www.kuipersassoc.com as part of this study.

4.2 Toolbox Approach

The current study uses a "toolbox" approach for reviewing and evaluating methods and models used to predict water quality at mine sites. A similar approach was taken by Plumlee and Logsdon (1999) in the much broader context of methods for conducting "environmentally-friendly" mineral development. Two toolboxes cover the gamut of methods and models of interest for this study: geochemical characterization and modeling. The geochemical characterization toolbox contains field and laboratory methods and tests used to evaluate or predict water quality. The geochemical characterization methods rely heavily on methods used for geologic and mineralogical characterization of rocks and sediments and geochemical characterization of weathering and dissolution of geologic materials. The results from the geochemical characterization methods are in some cases used in models and in other cases are used on their own to evaluate the potential of mined materials to release contaminants. The modeling toolbox contains separate hydrologic and geochemical models as well as mass balance or fate and transport models that combine hydrologic and geochemical information and models. Information from the literature was used to identify advantages and limitations of the characterization methods and models in the toolboxes, and to discuss sources of uncertainty and recommendations for improvements for both the characterization methods and the hydrogeologic models used to predict water quality at hardrock mine sites.

5.0 MINE SITE CONCEPTUALIZATION

Creation of a conceptual model is a necessary first step in the process of successfully predicting water quality at a mine site (Mayer et al., 2002, p. 290). Errors in modeling and especially in long-term predictions often derive from errors in conceptualization (Bredehoeft, 2005). A conceptual model is a qualitative description of the hydrology and chemistry of the site and their effects on mined and natural materials. It includes baseline conditions, sources (mining-related and natural), pathways, biological and physicochemical processes, mitigation measures, and receptors. Information about sources and mitigation measures will generally come from the mine plan. A generalized mine site that illustrates the elements of a conceptual model is depicted in Figure 1.

Baseline conditions at a mine site may include existing contamination from historic or pre-existing mining or other human activities, as well as natural mineralization and naturally elevated concentrations of constituents in water, soil, rocks, and plants. Baseline conditions also include examining the effects of seasonal and temporal variability and storm events on pre-project water quality and quantity.

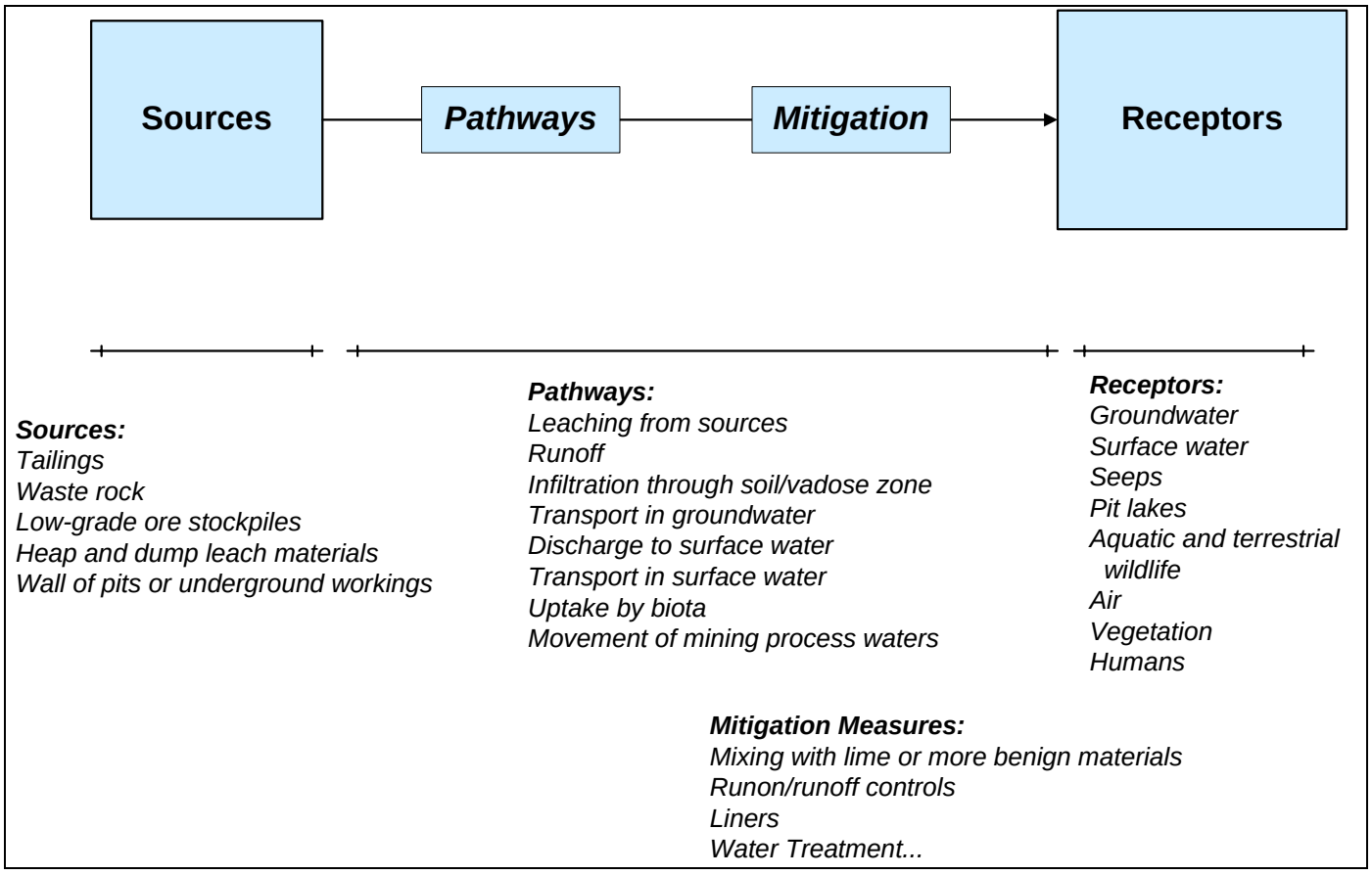

Figure 1. Generalized conceptual model of sources, pathways, mitigations, and receptors at a mine site.

The most common sources of contamination at hardrock mine sites are tailings, waste rock, low-grade ore stockpiles, heap leach piles, dump leach piles, and the walls of open pits and underground workings. A number of these sources are depicted in Figure 2. These sources can leach constituents found in them before they are mined, such as metals and sulfate, and can also leach constituents added by the mining process, such as cyanide in precious metals operations, flotation reagents in tailings, and nitrate from blasting. The mine plan should be used to identify the nature, location, and extent of contamination sources at the mine. Natural sources of metals and other mine-related constituents may also exist and should be identified. In addition to acid-generation potential, sources should be examined for the potential to leach metals and any other constituents of concern identified in the source materials. The location and size/volume of the sources need to be estimated for the conceptual model, and much of this information will be available in the mine plan.

Pathways are physical or biological conduits through which or by which constituents released from mining-related sources can move. Typical pathways at mine sites include transport through air, leaching, infiltration through the soil/vadose zone, movement through alluvial aquifers and fractures in bedrock, transport in groundwater, discharge to surface water, transport in surface water and sediment, and uptake and transfer via biological pathways.

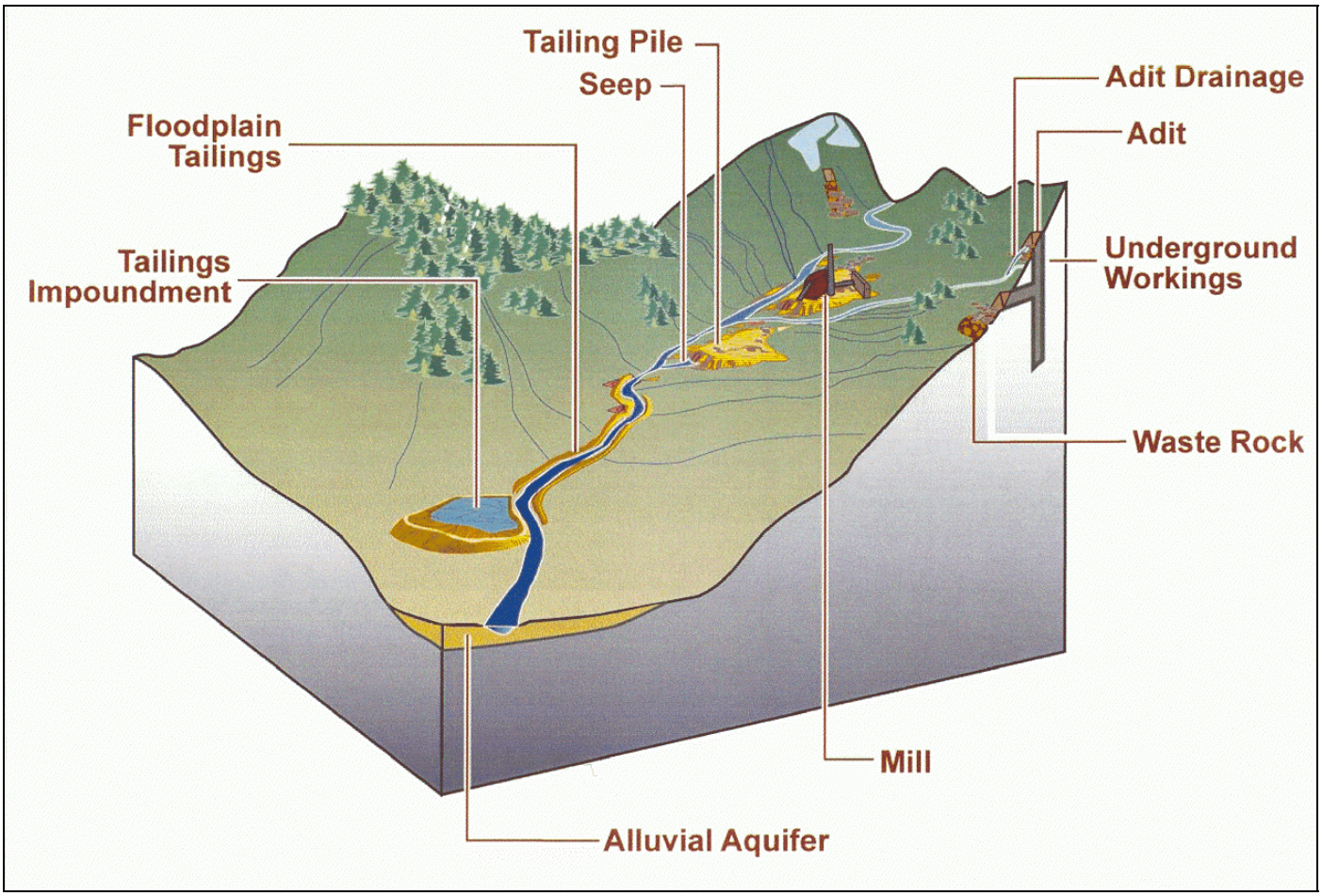

Figure 2. Some typical sources of contamination at hardrock mine sites.

For example, Figure 3 depicts the movement of contaminants from tailings along pathways to a stream. The same pathways would apply to movement of contaminants from a waste rock dump or a heap or dump leach facility. Contaminants from the tailings pile are leached by precipitation, transported along the surface of the tailings pile and the ground in runoff, and transported through the pile and the vadose zone as infiltration to groundwater. Contaminants can also adsorb to material in the vadose zone. Once in groundwater, contaminants can adsorb to aquifer materials and move through groundwater to surface water. Once in surface water, the contaminant can be adsorbed onto stream sediment, dissolved in the water column, resuspended during storms and high-water events, and/or consumed by macroinvertebrates, and then eaten by fish. Another way that constituents can move at mine sites is through the transfer of waters around the site as part of the mining process. For example, groundwater can be pumped to prevent groundwater inflow and allow mining of an open pit, and the water can be used in the mill, discharged to surface water, returned to groundwater via infiltration basins or reinjection wells, or sent to a treatment facility – depending on its quality and the needs of the mining operation. All potential natural pathways and transfer of waters during mining must be known to construct a suitable conceptual model.

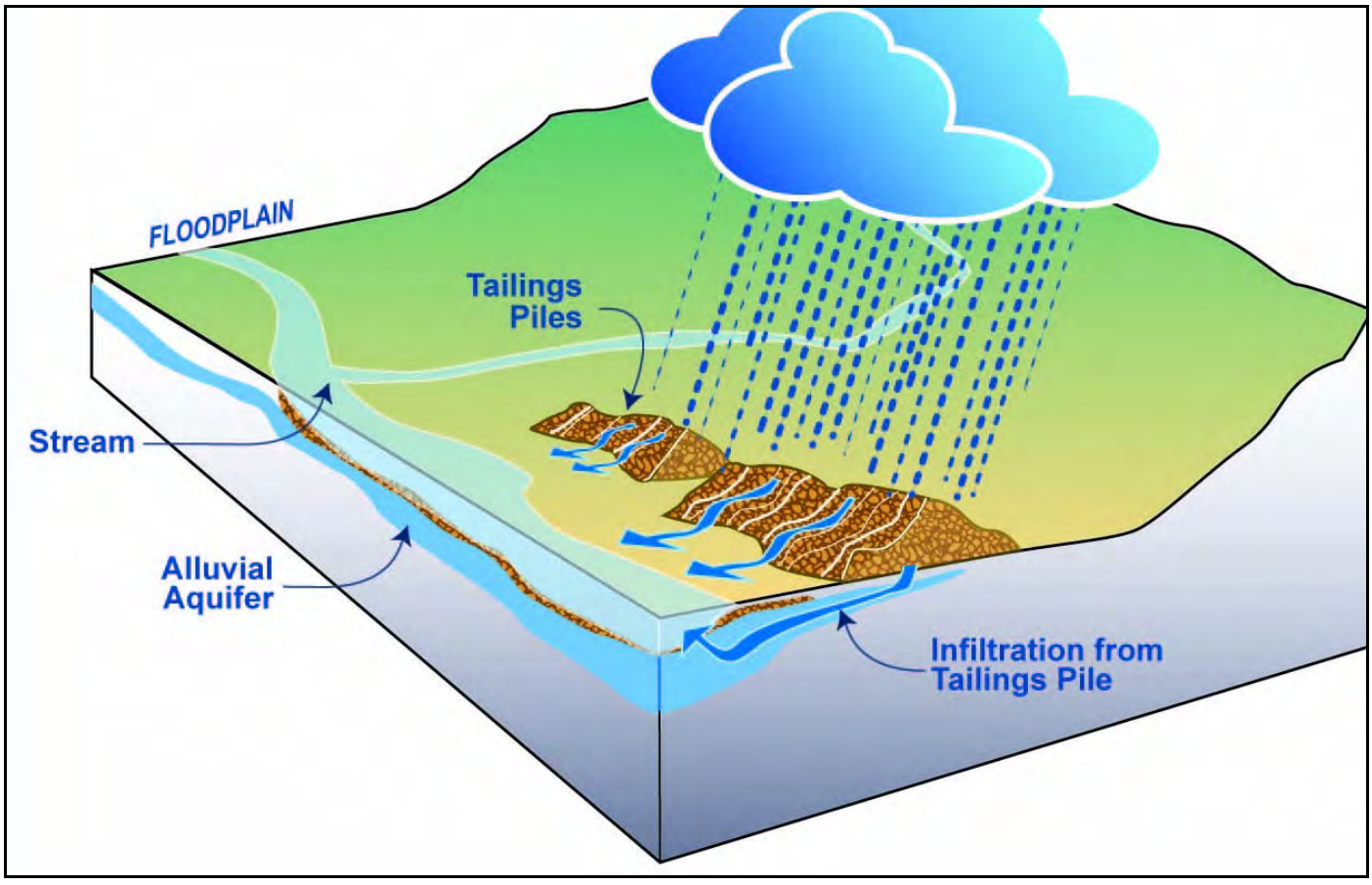

Figure 3. Transport pathways for contaminants in a hypothetical tailings pile.

In the pathways, biological and physicochemical processes control the movement and composition of constituents released from mining sources. Biological and physicochemical processes include: precipitation, evaporation, runoff, infiltration, gas advection (e.g., flow of air into a waste rock pile), erosion, advection/dispersion in groundwater and surface water, geochemical reactions (e.g., dissolution, precipitation, redox reactions, adsorption, acid/base reactions), and reactions involving biota (e.g., uptake of metals and redox transformations). It is these processes that are often the subject of hydrogeochemical modeling predictions at mine sites.

Mitigation measures are used to reduce the likelihood that contaminants will adversely affect receptors. Mitigation and remediation measures can be similar, but mitigation generally refers to up-front measures employed from the start of mining of the site or a unit, while remediation generally refers to measures used after mining of the site or a mining unit occurs. The mine plan should be used to identify the types of mitigations that will be used and which mine units (or mine facilities, such as waste rock dumps, tailings disposal facilities, heap leach facilities) and waters will be affected by the mitigations. Mitigation measures can include: mixing of mined materials with lime or more benign soils/rocks to decrease the acid generation and metal leaching potential, runon/runoff controls, installation of liners, treatment of contaminated waters, and backfilling pits to prevent formation of lakes with poor water quality. Although mitigation measures are not often considered explicitly in prediction models, they can have a profound effect on the concentrations that actually reach receptors. In addition, natural mitigating effects can improve water quality at receptors. Such effects include natural attenuation in soils, the vadose zone, and aquifers; dilution in groundwater and surface water; and biological transformation of substances to more benign forms. Natural processes can also diminish water quality from mine-related discharges at receptors. For example, evaporation can concentrate metals and other ions, and biological transformations can create more toxic species.

Potential receptors include groundwater, surface water (springs, lakes, streams, marine waters), vegetation, air, aquatic biota (e.g., macroinvertebrates, fish), terrestrial wildlife (e.g., birds, mammals), and humans. The location and degree of sensitivity to mine releases must be known for each receptor for development of the conceptual model.

A mine is an ever-evolving entity, and the conceptualization of the mine site must, of necessity, change as the mine evolves. Changes in the mine plan can appreciably affect uncertainty about future water quality, and NEPA, for example, requires that if there is a significant change in the mine plan or operations, a supplemental EIS must be performed. Short of a significant change, however, the accumulation of many small changes in the mine plan can make it difficult to accurately predict water quality. Therefore, predictions themselves must be continually updated as new environmental information from the mine site becomes available.

6.0 GEOCHEMICAL CHARACTERIZATION TOOLBOX

For the purposes of this study, which focuses on prediction of water quality at hardrock mine sites, characterization is defined as field and/or laboratory tests or measurements that help define the biological and physicochemical environment that will be or has been mined and the potential for water quality impacts. A characterization program includes scientific and engineering studies that describe the physical, chemical, and biological characteristics of the site, its rocks and minerals, and its fluids. The program will allow one to describe (a) the nature and extent of potential physical and chemical impacts to ground and surface water, and (b) the engineering or institutional steps to control the potential water-quality impacts. The program put forward to achieve these objectives is called "characterization." The opportunities for characterization (geochemical and hydrogeologic) during different phases of mining are discussed.

A characterization toolbox was assembled that contains methods and approaches used by mine operators currently or in the past. The characterization toolbox mainly focuses on geochemical characterization. The types of hydrogeologic information used as inputs to models are covered under section 6.1 and in the modeling toolbox section (sections 7.1.1, 7.1.2, 7.3, 7.4.2, Table 3, and Table 5). Each geochemical characterization method is briefly described, its advantages and disadvantages are discussed, and the uses of the test for water quality prediction are presented. The major sources of uncertainty associated with the use of geochemical characterization tools and recommendations for improvement are also discussed. Finally, a state-of-the-art approach to geochemical characterization of mined materials is presented.

6.1 Characterization during Different Phases of Mining

The amount of information available and therefore the ability to successfully characterize a mine site in terms of its potential to degrade water resources is directly related to the phase of mine development. During the earliest exploration stages, relatively little site-specific information is available. In contrast, during the post-closure phase potential water quality impacts are better known and the mine site can be characterized with a higher degree of certainty. Characterization cuts across all facilities/sources, pathways, and receptors, but different methods are needed to characterize each.

The extent of a geochemical characterization program should be dictated by site conditions and the nature of the deposit, with complex geology and mineralogy requiring a greater sampling and characterization effort. For example, a complex mixed oxide/sulfide ore body might require a highly rigorous program, while a deposit with distinct oxide/sulfide zoning might require a less rigorous program. Important features of an effective program include adequate sampling to ensure representation of the source materials, sampling of distinct geology or mineralogy types when they are encountered, and a level of environmental characterization that is commensurate with the level of ore characterization. In general, the amount and type of data should also be commensurate with the phase of development, with more detailed evaluations taking place with more advanced phases of the regulatory and economic decision-making processes. The characterization program should be both reactive and proactive so that results are received and evaluated in a timely fashion and the mine plan can change in response to any unexpected findings.

This section describes the site conditions and types of geochemical and hydrogeologic characterization that can occur during different phases of mining, including the exploration, development, active mining, closure/reclamation, and post-closure.

6.1.1 Exploration

The prospecting and exploration stages of mining involve long periods of investment with a high risk of failure (SME, 1992). The primary objective of exploration is to find an economic mineral deposit (NRC, 1999). There are three generally recognized stages of exploration: (1) prospecting, which involves the search for directly observable natural features associated with ore mineralization, or geologic and literature research in geologically favorable areas; (2) detailed surface reconnaissance, which includes geologic mapping, geochemical and/or geophysical coverage and use of other special techniques; and (3) surface drilling and/or underground exploration via adits or shafts (SME, 1992). The exploration phase can last for a few years to more than 10 years.

Geologic and mineralogic information collected from drilling or underground exploration programs is combined with information from geological mapping, and geophysical, stratigraphic, and other studies to delineate the geologic and mineralogic nature of the ore deposit. Borehole data will typically include depth to water, which can be the first step toward a preliminary understanding of the mine-site hydrologic characteristics. As shown in Figure 4, the ore reserve and the location and amounts of associated waste and low-grade ore can be estimated, often by using a geologic model.

The recommended characterization methods to be employed during the exploration phase are:

- Whole rock analysis
- Mineralogy
- Drill core descriptions (petrology and mineralogy)
- Block model or similar model (a computerized estimate of the quantity and characteristics of ore and waste)
- Available literature on the ore deposit
- Mineral occurrences (e.g., on fracture surfaces, in groundmass, using hand specimens and thin section) with an emphasis on sulfides and carbonates
- Acid-base accounting
- Startup of long-term kinetic testing; possible startup of test pads if sufficient material and access to site are available
- Baseline surface and ground water quality and flows (including springs)
- Potentiometric surface for groundwater
- Hydraulic properties (e.g., hydraulic conductivity, porosity, permeability) of soil, vadose zone, and groundwater aquifers, especially under proposed locations of mine facilities
- Examination of characteristics of similar mines in region/area
- Hydrogeochemical models for prediction of water quality.

This information can allow for a gross characterization of potential environmental conditions, including the extent of oxide, mixed oxide/sulfide, and sulfide ore; net acid generation potential (net AGP); and contaminants of concern. However, because long-term characterization has not been conducted, estimates of water quality impact potential made during this stage should be viewed as preliminary and highly uncertain.

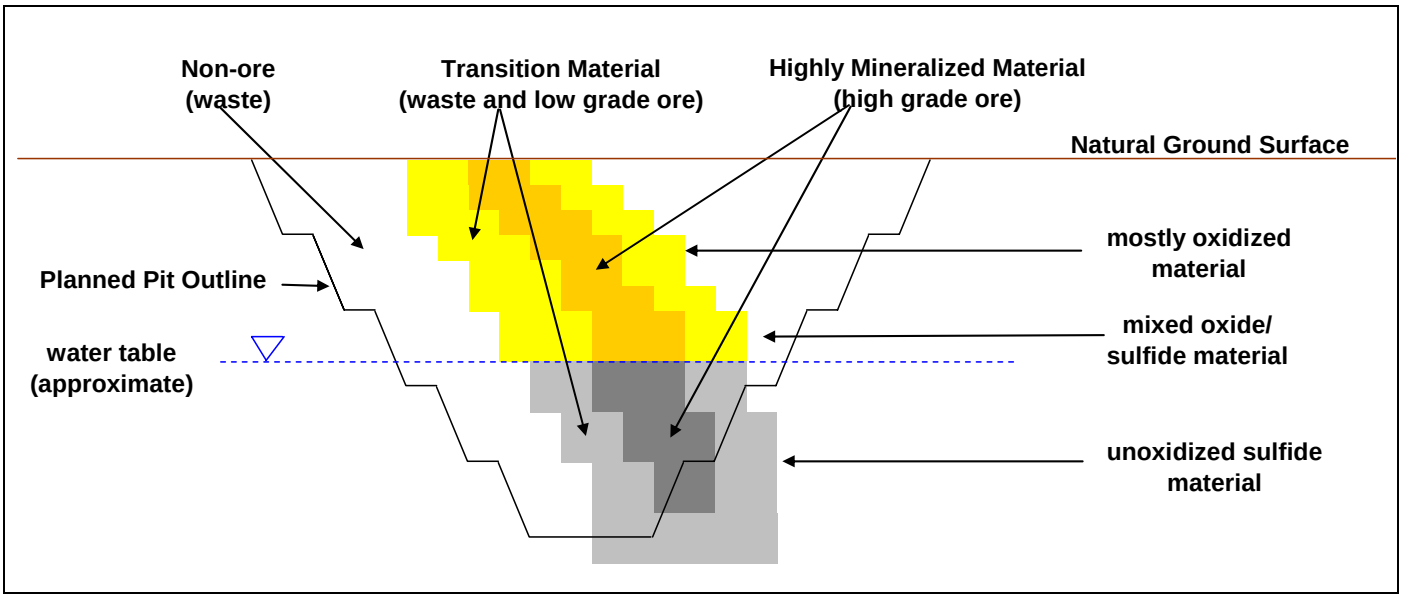

Figure 4. Site conditions and characterization opportunities during the exploration phase of mining.

6.1.2 Development

The development stage of mining projects is intended to take the resource identified by exploration efforts and to determine by what means (e.g., open pit versus underground mining) and at what revenue stream (return on investment) the ore deposit might actually be mined and processed. Before development proceeds, the deposit must be judged to be economic, and the required permits must be obtained. During mine development, infrastructure (power, roads, water, etc.) is put in place, and physical facilities are built, including the mineral processing facility. During the development phase, overburden and waste in open-pit mines are removed and placed in surface waste dumps. For underground mines, the deposits are developed by gaining access to the mineralization through shafts or adits (NRC, 1999).

During the development phase, the following types of characterization should be conducted:

- Continued sampling of geology and mineralogy of ore and waste
- Continued acid-base accounting and kinetic testing of mined materials; startup of field test plots, if waste will be stored at surface. (Note: the design of the test plots must correspond to the conceptual model for how the waste would ultimately be stored.)
- Continued testing of hydraulic properties of soils, vadose zone, and aquifers
- Tailings bench scale testing
- Creation of a mine waste management plan
- Study of changes in groundwater potentiometric surface from dewatering or other mining-related stresses
- More detailed hydrogeochemical models for prediction of water quality.

Figure 5 depicts the site conditions during development and active mining of the deposit. As depicted, due to dilution and inexact characterization methods, some mineralized ore typically reports with the waste material, and some sulfide ore can report to processes typically intended for oxide ores. These errors, which typically originate during the development phase, can result in water quality impacts during later phases of mining.

6.1.3 Active Mining

The active mining phase includes extraction of the in-place mineralized material and associated waste rock by drilling, blasting, mucking (loading), and transporting (hauling). During the active mining phase, the ore is processed, typically by crushing and grinding of the ore and subjecting the ore to various physical or chemical processes to separate and concentrate the valuable minerals from the waste in the ore. Wastes include waste rock, spent leach pad material from heap leach and dump operations (at gold and low-grade base metal mines), and tailings from flotation and vat leach operations (at certain gold and higher grade base metal operations). Heap leach and dump operations also involve the creation of barren and pregnant (containing the valuable metal) solution ponds or conveyances. The potential impacts resulting from release or discharge of tailings, leached rock, or pregnant leach solutions can be substantial (NRC, 1999).

As the mine matures, the amount and degree of useful characterization information increases substantially, allowing for either confidence in the original source characterizations and water-quality predictions, or the realization that errors in previous characterization and prediction work may require changes in the site conceptual model and potentially the mine plan itself. It is almost always more efficient and less expensive to adapt to changes in characterization information by modifying the project than to ignore the information received during the operations phase of mining. The segregation of ore and waste depicted in Figure 5 is realized during the mining operations stage.

During the active mining phase, the following types of characterization are recommended:

- Continued geochemical characterization of mined materials (field test plots and laboratory tests)
- Continued predictive and laboratory verification of the mine waste management plan (e.g., validity of using <0.2% sulfur as cutoff for non acid-generating wastes)
- Collection and sampling of leachate from waste rock, tailings, and other facilities
- Sampling of water quality in streams and groundwater upstream/gradient and downstream/gradient of mine facilities

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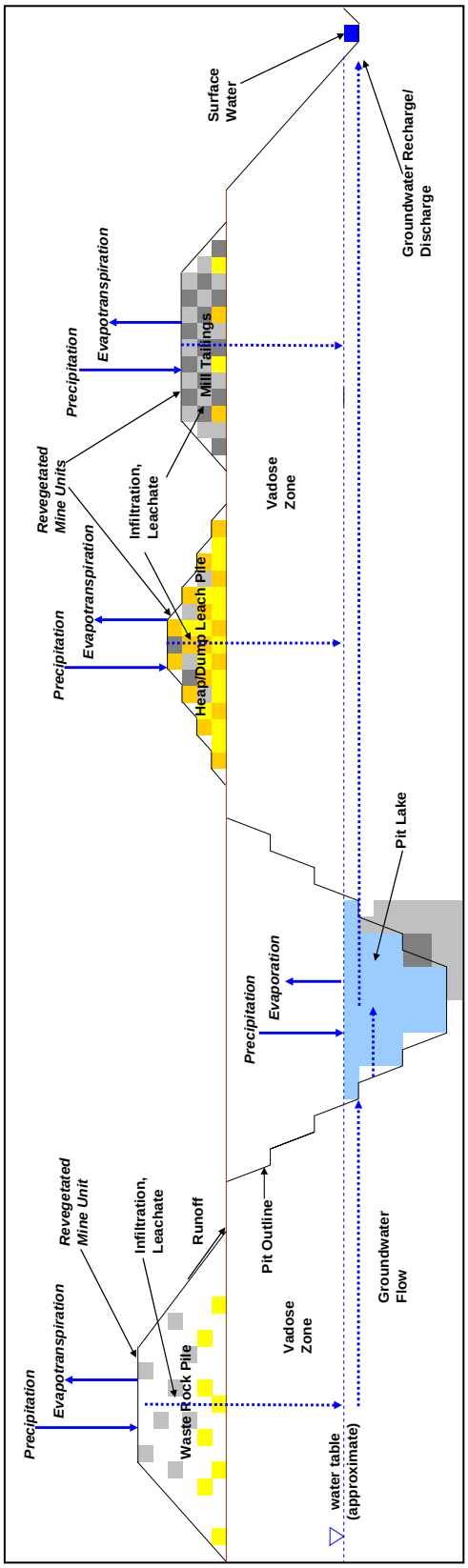

Figure 5. Site conditions and characterization opportunities during development and extraction phases of mining.

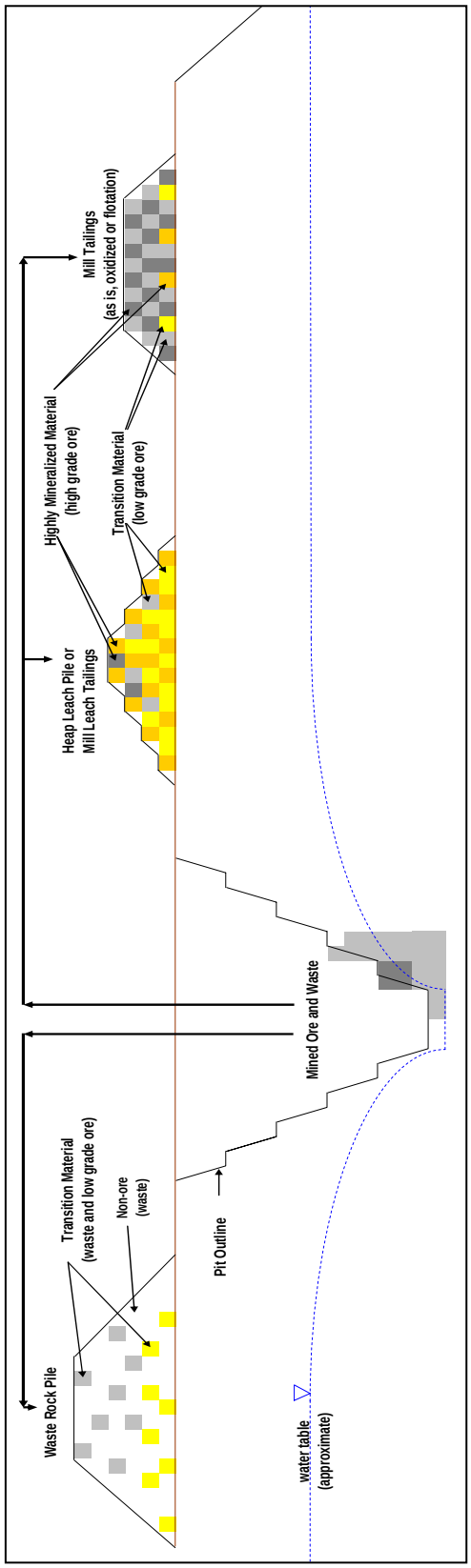

Figure 6. Site conditions and pathways for potential contaminant transport during the closure/post-closure phases of mining. Refer to Figure 5 for definition of shaded areas in waste units and pit areas.

- Testing of hydraulic properties of mined materials (e.g., waste rock, heap leach material, tailings)
- Continued observation of changes in groundwater potentiometric surface resulting from mining-related stresses
- Comparison of predicted (from characterization and modeling efforts) and actual water quality
- Routine evaluation of the results of ongoing characterization for significance to monitoring programs, operational controls, mine planning, and closure planning.

6.1.4 Reclamation, Closure, and Post-Closure

Additional maturation of water quality emanating from the various sources is likely to occur during the closure and post-closure periods. These changes may take place over a period of as little as two years to as many as thousands of years, depending on the nature of the wastes (especially rates of weathering of acid-producing and neutralizing components in mined materials) and the proximity to water resources. At mines in Nevada, for example, that have deep unsaturated zones and great depths to groundwater, acid and sulfate from oxidizing sulfides in waste rock dumps can take tens of thousands of years to reach groundwater resources (Kempton and Atkins, 2000), and pit lakes can take 100 to 300 years to reach hydraulic steady state for large open-pit mines (Bolen, 2002). Figure 6 depicts the site conditions, including potential pathways for transport of contaminants from sources to water resources, during the closure/post-closure period.

Where reactions are occurring and water quality has already been impacted during or shortly after mining, empirical evidence may serve as a good predictor of future water quality. However, in cases where maturation has not occurred, or similarly where leachate has not yet reached water resources, existing data may not adequately predict future impacts even though mine operations may have ceased. In these cases, forward models using existing water quality and mineralogic information can be used to predict potential future water quality years after mining has ceased. Reclamation and closure planning must take into account both existing and future conditions in order to be effective at restoring post-mining utility to the land and at protecting future water quality.

During the closure, reclamation, and post-closure phases of mining, the following characterization methods should be employed:

- Comparison of predicted and actual water quality
- Continued sampling of quality and quantity of water resources, including springs, leachate, surface water, and groundwater at points of compliance and other locations
- Measurement of rate of change in groundwater levels over time after groundwater pumping has ceased
- Monitoring of effectiveness of mitigation measures and comparison to predicted performance.

6.2 Geochemical Characterization Methods Used in Water-Quality Predictions

Table 1 presents a description of geochemical characterization methods used in the prediction of water quality at hardrock mine sites. Included in the table are method descriptions, method references, how the characterization tool is used in water-quality predictions, and the advantages and limitations of the method. The geochemical characterization tools described include geology, whole rock analysis, paste pH, mineralogy, sulfur analysis, static testing (Sobek and modified Sobek methods, and other modifications of neutralizing potential methods, net acid generating test (NAG), and net carbonate value test (NCV)), total inorganic carbon, short-term leach tests, sequential extraction, and modified shake extraction), kinetic tests (humidity cell and column), and field testing of mined materials. A description of the sources of uncertainty associated with their use and recommendations for improvement are contained in the following sections.

A brief overview of each general type of characterization tool is contained in this section, and details are provided in Table 1. Geologic methods are used to identify rock type, mineral occurrences, and alteration types of samples and include geologic mapping, sample logging, petrographic and mineralogic analysis, ore assay, creating a three-

Table 1. Description of Geochemical Characterization Methods used to Estimate Water Quality at Hardrock Mine Sites.

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Geology and geophysics	Geologic mapping, sample logging, petrographic and mineralogic analysis; ore assay; 3D block model of ore body and wastes; structural, fracture density and orientation, and rock competency information; geomorphology; geophysics	See mineralogy; AVIRIS; various.	Downing and Giroux, 2004; SME, 1992; Plumlee, 1999; Lapakko, 2002; Diehl et al., 2004.	Information on rock type, mineralogy, and alteration type used to evaluate acid generation and neutralization capacity of site. Information on structure and fractures used to estimate porosity in competent bedrock. Geomorphology used for effects of landforms on hydrology and geochemistry. AVIRIS used for remote spectral imaging of minerals.	Provides information on ore reserves and potential pathways for transport of contaminants in subsurface.	Representativeness of samples; difficulty in defining structural and fracture information.
Whole rock analysis	Whole rock analysis	Grind sample to ~200 mesh (~50 µm) or finer and digest with aqua regia, HNO_3/perchloric/HF (or make $LiBO_2$ (lithium metaborate) bead by mixing sample with $LiBO_2$ in Pt crucible, heat to 1000°C, dissolve in HNO_3/HF); analyze by ICP-AES, ICP-MS (for trace metals), AAS, neutron activation analysis (NAA), or XRF (for semi-quantitative analysis) for elements of interest.	Johnson and Maxwell, 1981 (as cited in Tremblay and Hogan, 2000); APHA/AWWA/WEF, 1998; Lapakko, 2002.	Determines total potential load of constituents to environment.	Can identify rock types with higher total levels of contaminants; can be used with CIPW normative calculations (e.g., Lawrence and Sheske, 1997) to determine likely mineralogy of sample.	Volatile elements such as As, Sb, Hg may be lost in HNO_3/perchloric/HF acid digestion (use HCl/K chlorate instead); high S^- may precipitate insoluble sulfates and underestimate concentrations of Be, Pb, etc. (Tremblay and Hogan, 2000).
Paste pH	Paste pH	Mix 20 g air-dried test material with 20 mL DI (for 1:1 ratio methods) for 5 sec, let stand 10 min, measure pH.	Sobek et al., 1978; Lapakko, 2002.	Determines potential effect of acid-forming salts in mine waste over short term.	Quick, inexpensive, easy to perform.	Provides no indication of long-term acidity/neutralizing potential of soils/rocks.

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Mineralogy/microscopy/microprobe/petrology	Optical microscopy; XRD; petrographic analysis (reflected and transmitted light); SEM/EDS; electron microprobe; Sulfide Alteration Index; Rietveld analysis	Optical: hand lens, binocular microscope; XRD: grind to powder, place in X-ray goniometer; Petrography: slice solid rock sample into thin section (30-µm thick), polish, examine with reflection/ transmission petrographic microscope; SEM/EDS: use polished section or filter with suspended material from water sample, coat with carbon or gold, expose to electron beam scan, examine composition using back-scattered electrons (if EDS available). Electron Microprobe: like SEM but optimized for chemical analysis; Sulfide Alteration Index: petrographic analysis of alteration of sulfide grains.	Jambor and Blowes, 1994; Blowes and Jambor, 1990 (Sulfide Alteration Index); Raudsepp and Pani, 2003 (Rietveld analysis).	IDs primary/secondary minerals alternation that could affect neutralization potential (NP) and acid generation potential (AGP); degree of alteration of minerals (e.g., Sulfide Alteration Index); type of sulfide minerals and crystal forms (e.g., framboidal) to help evaluate reactivity of minerals; availability of minerals for weathering reactions (liberation) that can affect AGP and contaminant leaching potential.	Provides information about AGP, NP, and availability of minerals for weathering; corroborates rock type information.	Not easy to understand results if not trained in geology; semi-quantitative at best; small sample size/representative-ness; no database for comparison of results; XRD: no information on grain size or condition, not good for identification of secondary minerals (Tremblay and Hogan, 2000, Shaw and Mills, 2004).
Sulfur analysis (different forms of sulfur)	Total S, pyritic S, sulfide S, organic S, sulfate S	Oxidation of ground sample with acid and measurement of S by spectrophotometer (LECO); removal of non-sulfide minerals to determine sulfide S.	ASTM Method 1915-97 (2000, for total sulfur); ASTM method E-1915-99 (2000, for sulfide S).	Potential of samples to generate acid; used in combination with ABA tests.	Distinguishes between forms of S with more (pyritic S, sulfide S) and less (organic S, sulfate S) acid generation potential.	Does not confirm identity of minerals that contain the sulfur; can overestimate (for jarosite, iron sulfates) or underestimate (for chalcopyrite, galena) sulfide content (Lapakko, 2002).

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Static testing	Acid-base accounting (ABA) methods: Sobek Method	Dry pulverized (-60 mesh) samples at ≤ 60°C): AP: total S (by combustion to SO_2 and measurement by infrared detection); subtract sulfate S (by dissolution in HCl) to obtain AP. NP: add 1:3 HCl (pH endpoint usually between 0.8 and 2.5),rate fizz of sample, heat to near boiling, add water and boil, back-titrate to pH 7.0 with 0.1N NaOH.	Sobek et al., 1978.	To evaluate overall amounts of acid-generating and acid-neutralizing materials in a sample; to identify samples that need kinetic testing.	General for Static testing: Gives operationally defined estimate of total neutralizing and acid generating content of samples; well-established technique; relatively fast and inexpensive technique; less labor-intensive than identifying complete mineralogy.	General for Static testing: Provides no information on relative rates, availability, texture, or identity of AG and NP minerals; assumes NP and AG minerals are completely available for weathering; can over- or under-estimate AGP and overestimate NP (see below); testing can be time-consuming. For Sobek Method: Can overestimate AGP (use of Total S); can overestimate NP (boiling, pH endpoint) (Price, 1997; White et al., 1999; Li, 2000; Scharer at al., 2000b).
Static testing	Other ABA and Neutraliza-tion Potential Procedures	Lapakko: 1.0N H_2SO_4 to pH 6.0, AP = total S, 4-120 hrs; BC Research Inc. Initial (BCRI): 0.1N H_2SO_4 to pH 3.5, AP = total S, 4+ hrs; BC Research Confirmation (BCRC): 6 or 12N H_2SO_4 to pH 2.5 - 2.8, inoculate with active *T. ferrooxidans* culture, monitor pH (decrease indicates biochemical oxidation of sulfides); Modified Sobek: -200 mesh, uses sulfide rather than total S, 24-hr ambient-T digestion using 0.1-0.5N HCl, with pH 1.5-2.0, for NP, with titration to pH 8.3 rather than 7.0; Sobek - siderite correction: as Sobek, but with H_2O_2.	Mills, 2004b; White et al., 1999.	As above .	Prevents overestimation of NP and AP that can occur using Sobek et al., 1978; confirms presence/absence of bacteria (BCRC).	BC Research Test requires more equipment and takes longer to run than ABA; Variable estimates of NP: NP-Sobek>NP-Modified Sobek>NP-BCRI Initial>NP-Lapakko (Tremblay and Hogan, 2000; Mills, 2004a; White et al., 1999; Plumlee, 1999).

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Static testing	NAG (Net acid-generating)	Add 15% H_2O_2, react until effervescing stops, boil for at least 2 hr (do not let sample dry out), add DI, titrate to pH 4.5 with .1 or .5N NaOH.	Miller et al., 1997.	As above. Widely used in SE Asia and Australia for management and screening tool.	Evaluates net acid-base balance; arrives quickly at estimated net value for AGP; uses simple laboratory equipment and reagents.	Does not distinguish between AP and NP; screening method only; use with caution in carbonaceous rocks (can produce acid in error) or in high-sulfide rocks (elevated temperatures can drop pH) (Tremblay and Hogen, 2000; Stewart et al., 2003b).
Static testing	NCV (Net carbonate value)	Uses combustion-infrared detection for carbon and sulfide analysis. NCV=NP+AGP, where NP=(Total C) - (C after HCl digestion) (=TIC), AGP=(Total S) - (residual S after pyrolysis at 550^o C for 1 hr). XRD, XRF used to confirm NCV results.	Bucknam, 1997. http://www.bucknam.com/ncv.html	As above. Used principally by Newmont.	Procedure can be conducted quickly; includes only carbonate minerals in NP if pyrolysis working as expected; good for screening-level and operational testing tool.	Does not confirm presence of minerals that generate or consume acid; requires sophisticated instrumentation; can overestimate NP when siderite is main carbonate mineral.
Total Inorganic Carbon	TIC	Measure total C by infrared analysis using pulverized sample. Treat split w/ HCl to remove inorganic C and subtract from total for TIC.	Hillebrand et al., 1953.	Measures NP associated with carbonates.	Avoids inclusion of non-carbonate minerals in NP; less expensive than NP.	Only provides carbonate fraction of NP; can overestimate NP when siderite is main carbonate; can only complement total NP results.
Short-term leach tests	SPLP (Synthetic Precipitation Leaching Procedure, Method 1312) and modification by USGS	#1 reagent water to pH 4.2 with 60/40 HNO_3/H_2SO_4; #2 reagent water to pH 5.0 with 60/40 HNO_3/H_2SO_4; 20:1 liquid:solid ratio; 18±2 hours. USGS modification: composite sample of <2-mm fraction; leach 50g in 1L of distilled water, shake for 5 min; settle for 10 min; measure pH and SC; preserve samples for chemical analysis.	US EPA, 1996; http://www.epa.gov/epaoswer/non-hw/industd/guide.htm (for all leach tests); Diehl et al., 2004; Smith et al., 2000.	Measures readily soluble components of mine wastes (all leach tests). SPLP: developed to evaluate metal mobility in an engineered landfill subjected to acid rain. USGS modification used to measure fraction that controls rapid leaching.	Provides indication of extent of leaching of salts and readily dissolvable constituents from dried mine materials (for all short-term leach tests).	Provides no information on long-term leach rates; only simulates short-term interaction with rain/snowmelt; high liquid:solid ratio may underestimate leachability.

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Short-term leach tests	TCLP (Toxicity Char-acteristic Leaching Procedure, Method 1311)	0.1N acetic acid, pH 2.9, for alkaline wastes; 0.1N sodium acetate buffer solution, pH 5.0 for non-alkaline wastes; 20:1 liquid:solid ratio, 18±2 hours.	US EPA, 1996.	Use to determine if waste is hazardous under RCRA; to evaluate metal mobility in a sanitary landfill.	Applicable standards available.	Use of acetic acid not appropriate for mining applications; only simulates the release of contaminants to groundwater.
Short-term leach tests	MEP (Multiple Extraction Procedure, Method 1320)	Same as EP Toxicity test (see below), but with synthetic acid rain (60/40% H_2SO_4/HNO_3); 20:1 liquid:solid ratio; 9 or more extractions, 24 hr/extraction.	http://www.epa.gov/epaoswer/non-hw/industd/guide.htm	Same as TCLP and SPLP.	Longer procedure than TCLP and SPLP.	Provides no information on long-term leach rates; only simulates short-term interaction with rain/snowmelt; high liquid:solid ratio may underestimate leachability.
Short-term leach tests	MWMP (Meteoric Water Mobility Procedure)	Place 5 kg of <2-in mine rock (crush material >2 in and combine with fraction < 2 in) in 15-cm OD PVC column, apply a volume of reagent-grade water equal to mass of dry solids in column (assume 1 mL/g) to top of column over <48 hr, collect effluent and measure pH, elements of interest (filtered).	Nevada Mining Association, 1996.	Same as for SPLP.	Commonly used in Nevada; uses larger sample size than SPLP and solution more similar to rainwater in western US; higher solid:liquid ratio than SPLP.	Similar to SPLP but weaker (less aggressive) than SPLP (uses only water).
Short-term leach tests	California WET (waste extraction test)	0.2 M sodium citrate (pH 5.0), 10:1 liquid:solid ratio, 2mm maximum particle size, 48 hrs.	http://www.epa.gov/epaoswer/non-hw/industd/guide.htm (for all leach tests).	Same as for TCLP.	Commonly used in California; lower liquid:solid ratio and longer tests time than SPLP and TCLP.	Similar to EP Toxicity test, but sodium citrate makes test more aggressive; sodium citrate not appropriate for mining applications.
Short-term leach tests	EP Toxicity (Extraction Procedure, Method 1310)	0.5N acetic acid, pH 5.0, 16:1 liquid:solid ratio during extraction, 20:1 final dilution, 24 hrs.	US EPA, 1996.	Similar to TCLP.	Applicable standards.	Replaced by TCLP.

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Short-term leach tests	BC SWEP (British Columbia Special Waste Extraction Procedure) and Modification	Mix 50 g crushed/ground (<9.5mm) sample and reagent water, measure pH, if >5.2, lower to 5.2 with 0.5N acetic acid, if <5, make no adjustments. Cap bottle and place in tumbling apparatus, check pH after 1, 3, 6, 22 hr; if >5.2, lower to 5.2 with acetic acid. Record amount acid added and final pH. Separate liquid and solid phases, filter, analyze for metals, etc. Modification: use reagent water instead of acetic acid; Cap bottle and agitate in rotary extractor for 1 hr total. (in BC, DI or 0.1N HCl is used as extractant at a 3:1 liquid:solid ratio for 24 hr).	Province of British Columbia, 1992.	Similar to TCLP for normal procedure; similar to SPLP/MWMP for modification.	Similar to TCLP for normal procedure; similar to SPLP/MWMP for modification. Lower liquid:solid ratio than other short-term leach tests.	Similar to TCLP for normal procedure; similar to SPLP/MWMP for modification.
Short-term leach tests	Sequential Extraction	To 1 gm dry sample add $MgCl_2$, shake for 1 hr (salts); to residue add Na-acetate, shake 5 hr (adsorbed); to residue add hydroxylamine HCl in 96^{o}C waterbath for 6 hr (amorphous Fe oxyhydroxides); to residue add ammonium acetate solution in 85^{o}C waterbath for 5 hr (Mn oxides); to residue add HF extract, digest. Analyze extracts from different extractions for constituents of interest.	Tessier et al., 1979; Ribet et al., 1995.	To evaluate associations of constituents of interest, especially metals, with different solid phases (e.g., salts, loosely-bound/adsorbed, iron and manganese oxides/hydroxides, inside mineral lattice); to determine how easily metals can be released to the environment	Understanding associations of metals with different phases of the solid will assist in understanding geochemical conditions under which they may be released to environment	Long procedure, many reagents, mostly research application, no applicable standards/criteria.
Short-term leach tests	Modification of Shake Extraction of Solid Waste with Water	Dilution water is ASTM D1987 water adjusted to pH 5.5 by carbonic acid, use a 4:1 liquid:solid ratio, agitate for 18 hr, decant surface water and analyze for pH, metals, etc.	ASTM, 1992; Mills, 2004d: Metal leaching test procedures.	For extraction of tailings solids.	Can simulate conditions where the solid waste is the dominant factor in determining the pH of the extract; lower liquid:solid ratio than some other leach tests.	Test only approved for certain inorganic constituents, and is not applicable to organic substances and volatile organic compounds (VOCs).

Character-ization Tool	Test Names	Method Description	Method Reference	Use in Water-Quality Predictions	Advantages	Limitations
Laboratory kinetic testing	Humidity cell tests (HCT)	Before test analyze sample for ABA, TIC, metal concentrations, size fractions, mineralogy, petrology. For material 100% passing 6.3mm (waste rock), use 10.2 cm ID x 20.3 cm h column, for material passing 150 µm (fine tailings), use 10.2-cm high x 20.3-cm diameter, expose material to 3-day alternating wet (humid air) and dry cycles, then pour water over sample every week and measure pH, SO_4, alkalinity, metals, etc. in leachate. HCT can run for 20 weeks to years. Modification: ASTM, 2003.	Sobek et al., 1978; ASTM, 2003; Mills, 2004c; Lapakko, 2003a.	To estimate longer-term potential of fully oxygenated mined materials to generate/consume acid and produce contaminated leachate; to estimate rates of sulfide oxidation and neutralizing mineral dissolution; to evaluate acid generation lag time; to determine relative reactivities of rocks of a given mineral assemblage as a function of solid-phase compositional variation; to provide rates for modeling.	Standardized test; provides kinetic and steady-state leaching information and information on weathering rates of primary minerals (e.g., sulfides).	Additional size reduction, if used, causes discrepancies between laboratory results and field conditions; not appropriate for saturated mined materials (e.g., submerged tailings); if NP>AP, AG lag time for metal/acid production may be longer than test (Benzaazoua et al., 2001; Mills, 2004e; Nicholson and Rinker, 2000; Lapakko, 2003a and b).
Laboratory kinetic testing	Column tests	Analyze sample before test, as for HCT's set-up options available, including maintaining water over sample, alternating flooding and draining, and recirculating leachate to top of column. Sub-aerial columns = "trickle leaching." Column typically 76-, 152-mm diameter x 1- to 3-m high; generally DI water used as leachate; commonly run on material <~25 mm; test length variable.	Tremblay and Hogan, 2000; Lawrence and Day, 1997.	As above, but can simulate leaching conditions in variably saturated or oxygen-deprived conditions; to simulate effects of mixing mined material with lime/alkaline additions.	Closer to field conditions than HCT; can simulate different weathering/ saturation conditions and mitigations; simulates combined weathering of primary and secondary phases.	Channeling of leachate along preferential flow paths or sides of column; must examine mineralogy before and after tests for estimation of weathering rates of primary minerals (Tremblay and Hogan, 2000).
Field testing of mined materials	Multiple; waste rock or tailings test piles; wall washing; Minewall Approach	Application of characterization methods to existing tailings, waste rock, (also oxidation depth, depth to water table, pore gases and fluxes); creation of waste rock/tailings test piles for new material; wall washing: isolate section of pit wall or underground working, spray water on wall, collect and analyze resulting leachate.	Tremblay and Hogan, 2000; for estimation of field oxidation rates: Blowes and Jambor 1990 (as cited in Shaw and Mills, 2004); Nicholson et al. 1995; Morin and Hutt, 1997, 2004.	To estimate long-term potential of mined materials to generate acid and contaminated leachate.	Tests are conducted under actual field conditions; can collect samples after transient events, such as thunderstorms and snowmelt.	For field test piles: requires consideration of sampling and sample handling for proper scaling to full-scale system (e.g., for particle distribution, chemical composition, water movement, rate of weathering, effect of climate, gas transport, etc.).

dimensional block model of the ore body and wastes, and structural and rock competency information.

Whole rock analysis determines the total concentrations of constituents in a rock sample, which can assist in identifying constituents of concern. Paste pH is used to evaluate the effect of soluble salts on the short-term pH of mined materials. Mineralogic examinations identify minerals that can affect acid generation and neutralization potential and include optical microscopy, X-ray diffraction (XRD), reflected and transmitted light petrographic analysis, scanning electron microscopy/energy dispersive system (SEM/EDS), electron microprobe, sulfide alteration index, and refinement of the XRD information using the Rietveld technique.

Sulfur analysis is used to help determine the potential of samples to generate acid and is used in static testing methods. Static testing determines the total amount of acid-generating (using sulfur analysis and titrations) and acid-neutralizing (using various tests) material in a mine sample and includes the acid-base accounting methods and modifications, net acid-generating test, and net carbonate value test. Neutralization potential procedures, which are part of acid-base accounting, include the Lapakko pH_6 method and the BC Research Initial and confirmation tests. Total inorganic carbon determinations are used to measure the total amount of carbon for estimations of the carbonate content in a sample (also used in acid-base accounting).

Short-term leach tests measure the readily soluble components of mine wastes and include the synthetic precipitation leaching procedure (SPLP), the multiple extraction procedure (MEP), the toxicity characteristic leaching procedure (TCLP), the Nevada meteoric water mobility procedure (MWMP), the California waste extraction test (WET), the extraction procedure toxicity test (EP Toxicity), the British Columbia special waste extraction procedure and modification (BC SWEP), various sequential extraction techniques, and the shake extraction test.

Kinetic testing is used to estimate the longer-term potential of mined materials to generate and consume acid and produce contaminated leachate and to estimate rates of oxidation and dissolution of materials. Kinetic tests include the humidity cell test and column tests. Finally there are a number of field tests for mined materials that are also used to estimate the long-term potential of mined materials to generate contaminants under direct field conditions. Field tests include waste rock or tailings test piles, wall washing, and the Minewall approach (Morin and Hutt, 2004).

Additional and general references used to create the table, especially the advantages and limitation of geochemical characterization methods, include Tremblay and Hogan (2000), Price (1997), Blowes and Jambor (1990, as cited in Shaw and Mills, 2004), Downing and Mills (2004), Jambor (1994), White et al. (1999), Mills (2004a-d), Lawrence and Wang (1997), Logsdon (2002), Kwong (2000), Lawrence and Day (1997), EPA (1994 and 1978), Smart et al. (2000), Zhu and Anderson (2002), White et al. (1999), Smith (1997), and Lapakko (2003a and b). Lapakko (2003a) provides a review of the history of humidity cell testing methods. Lapakko (2002) also contains an overview of geochemical characterization methods, including non-invasive techniques such as AVIRIS (Airborne Visual and Infra-Red Imaging Spectrometer). MEND has a produced a list of information requirements that can serve as a starting point for assessment of metal leaching and acid drainage (Price, 2005).

6.3 Sources of Uncertainty in Geochemical Characterization and Recommendations for Improvement

The validity of geochemical characterization data is linked to a number of issues, including those related to sample representativeness, methods used to extrapolate characterization results to field conditions, and the use of and interpretation of mineralogic information and test conditions. Some of the more important issues related to uncertainty in geochemical characterization are discussed below, and recommendations for improvements are provided. General issues discussed include: extent of environmental sampling (representativeness of field conditions); compositing of samples, changes in geochemical characterization as the mine evolves; and field/laboratory discrepancies. The issues related to static testing include: the effect of particle size; the effect of temperature, pH, and test duration on neutralization potential estimates; the effect of mineralogy and organic matter on neutralization and acid generation potential; estimating neutralization potential (NP) and acid production potential (AP) in low-S, low NP wastes; and interpretation of static testing results using NP/AP ratios**.** Issues related to short-term leach testing include: the water:rock ratio; the use of unweathered materials; and the interpretation and use of test results. The issues related

to kinetic testing include: the effect of particle size and mineral availability; the length of kinetic tests; the effect of column size and shape; the effect of temperature; and the applicability of standard kinetic testing for materials under low-oxygen or reducing conditions.

The geochemical characterization issues are discussed in terms of problems statements, background information, and recommendations to address the stated problem.

6.3.1 General Issues

Extent of environmental sampling (representativeness of field conditions).

Problem Statement: The extent of sampling of mined materials is often inadequate for representing the range of potential environmental impacts at a mine site, especially for mines with variable geology and mineralogy.

Background: The purpose of environmental sampling is to have the information necessary to tailor waste management strategies to the potential for adverse impacts to the environment. Environmental sampling of mined materials can be done as a parallel to economic resource evaluation in terms of both method and timing. Bennett et al. (1997), for example, discuss the application of geological block models to environmental management. Both environmental and economic evaluations delineate, based on representative samples, the extent of rock units of interest/concern and quantify pertinent aspects of their composition (Lapakko, 1990). In practice, the number of representative samples for resource evaluation is almost always substantially larger than that for environmental evaluation. According to Robertson and Ferguson (1995), “Placer (Dome) has adopted the principle that the economic significance of acid drainage liability is as important to a project as the ore reserve inventory.” To put this principle into practice, the number of samples for environmental impact prediction (e.g., acid generation potential) should be more commensurate with the number of assays for ore reserve, although in practice, economics dictate that fewer environmental samples will be analyzed because of the greater number of parameters that must be examined to predict future water quality. The analytes determined for resource evaluation, however, can be extensive, especially for platinum group metals, for example. Analyses for resource evaluation are similar to whole rock analysis and can provide direction for future environmental sampling.

According to Farmer (1992), “The principal reason that current methods rarely, if ever, provide a reliable result is the failure to test a representative number of samples in each geologic rock unit in the proposed mine.” Price and Errington (1994) recognized that the most important phase of the prediction program is sampling and that a sufficient number of samples should be analyzed to accurately characterize the potential for environmental impact. They suggest the guidelines contained in Table 2 as the minimum number of samples that should be collected for each rock type during initial sampling. Samples must be representative of all geologic, lithologic, and alteration types and of the relative amounts and particle size of each type of material; the compositional range within mineral assemblages or rock types must be known (Downing, 2004).

Table 2. Example of Recommended Minimum Number of Samples of Each Rock Type for Geochemical Characterization of Mined Materials for Potential Environmental Impact.
(adapted from Price and Errington, 1994)

Mass of Each Separate Rock Type (tonnes)	Minimum Number of Samples
<10,000	3
<100,000	8
<1,000,000	26
10,000,000	80

Runnells et al. (1997), however, argue against this approach and emphasize the importance of site-specific variability in dictating the number of samples collected and analyzed. Using this approach, more homogeneous materials such as tailings would require fewer samples than the more heterogeneous waste rock at any given site. This approach reflects the fact that fundamental error, which results from the compositional heterogeneity of particles, is often the main source of sampling error (Pitard, 1993). Important factors in the fundamental error include heterogeneity, particle size, and sample mass. If the population is very heterogeneous or the particle size is large, more sample mass is required to minimize the fundamental error associated with sampling. Smith et al. (2000) provide a discussion of sampling errors.

Given that a 200-ft deep drill hole can be used to project ore resources 100 ft away from the hole in all directions, a core from such a drill hole would

represent approximately 200,000 tonnes of material. According to the recommendations of Price and Errington (1994), at a minimum, between eight and 26 samples would be required to adequately characterize the rock type represented in this particular drill hole. If the drill hole were split and sampled on 10-ft intervals, 20 samples would be taken, approximately meeting the recommendations. This amount of sampling is consistent with industry practice for ore resource estimates; however, this extent of sampling is rarely performed for environmental characterization.

An alternative approach to characterizing existing waste-rock dumps was suggested by Wickham et al. (2001) using a model to integrate lithology and mineralogy from the exploration core-hole database with information on pit development, ore handling (to separate out rock sent to processing facilities and waste rock), and dispatch records. The approach is less costly than extensive sampling of the waste rock piles and relies on existing mine information. It also was found to provide an accurate accounting of total tonnage and lithologic characterization in the waste rock dumps, distinguishing between total sulfur, sulfide-sulfur, and pyrite-sulfur materials for each dump. A geochemical sampling program for acid potential was based on the model, and the classification scheme accurately classified waste rock exhibiting similar geochemical behavior, as determined by static and kinetic testing. The approach allowed a proportional sampling according to total tonnage for each compositional type (using cores and test pits in each dump), and the results were used to estimate net acid potential for each dump. The approach is not applicable to a prospective mine, but aspects of the method, particularly the essential Bayesian approach, could be adapted for new mines, with some customizing.

In addition to an adequate level of sampling, every study of acid generation potential or other type of environmental characterization at mine sites should include a sampling and analysis plan with data quality objectives and a quality assurance/quality control (QA/QC) plan. The QA/QC plan should include using standard reference samples (e.g., Canadian Reference Material for Standard Acid Base Accounting) and chain-of-custody forms to help increase the confidence in the results of the environmental analyses (Downing and Mills, 2004). The best QA/QC programs are multi-level and involve both the corporate culture and every level of operations. QA/QC reports should be available and provided with every analysis. The basic elements of any QA/QC program should include the following: laboratory accreditation; proficiency testing; documentation; assessment procedures, sample preparation; quality control; and confidentiality of data and data security.

Recommendation: The variability in the potential to impact the environment should be examined initially by extensive geologic and mineralogic analysis of all mined materials and wastes. The extent of geologic and mineralogic sampling should be commensurate with the extent of sampling for ore characterization. The observed degree of geologic and mineralogic variability should then dictate the extent of sampling for environmental characterization. Fewer samples should be required for tailings than for waste rock, wall rock, and other types of heterogeneous material. The minimum number of samples suggested in Table 2 should be applied to each different type of mineralogy (for example, addressing the range of hydrothermal and supergene alteration for each lithology), rather than to each rock type. The mine proponent must be responsible for showing that the data provided are sufficient for environmentally protective decision making.

Compositing of samples.

Problem Statement: Compositing of samples for environmental characterization leads to a lack of knowledge about where potential environmental problems can develop on the mine site.

Background: Compositing rock samples across rock types leads to the masking of potential acid drainage and other potential environmental problems due to the mixing of different rock types in the composites that may not be representative of the actual placement of the rock types in the mining process (Farmer, 1992). For example, compositing has the effect of assuming a perfect mixture of rock types will occur, whereas in the real world the different rock types might be mined from different places and at different times and might be placed in separate repositories or processed during different periods. Price and Errington (1994) recommend that compositing be avoided in the absence of highly certain information indicating it is advisable (e.g., compositing could be advisable for a highly homogenous deposit). Compositing also obfuscates information on the source of any potential environmental problem related to the mined materials because there are too many variables.

Depending on the objectives of the sampling, compositing of mine waste samples can be appropriate, especially if the "average" properties of a deposit are of interest. Smith et al. (2000) uses a statistically based compositing approach to sample waste rock dumps at abandoned mines. Their target population for sampling was the upper 15 cm of a mine waste dump, because this surficial material is most likely to impact runoff from snowmelt and rain storms (although the approach could be modified to apply to drilling or subsurface trench sampling). They collected the <2mm size fraction of the material, assuming that smaller size fractions are generally the most reactive and would control leaching behavior over the short term. This hypothesis was tested and confirmed by performing the synthetic precipitation leaching procedure (SPLP, EPA Method 1312) on various size fractions. To minimize grouping and segregation errors (another type of error associated with sampling), they collected at least 30 sub-samples for each composite sample. The results showed that the <2-mm size fraction provided a worse-case scenario for short-term leaching of acidity and zinc.

Recommendation: Compositing of samples is only recommended for mined material that is consistent in size and composition, for example, existing tailings material that is known to be from a consistent ore type and a single process. For example, autoclaved and non-autoclaved tailing should not be composited, and complex ore bodies, such as those including skarn adjacent to intrusive rocks in a porphyry copper, should be evaluated carefully in terms of understanding the compositional range of tailing. Compositing should not be used for any other types of mined materials or for water-quality samples. Compositing can be appropriate if the average properties of mined materials are of interest. Guidelines recommended above should be used to determine the extent of sampling of mined materials for environmental characterization.

Changes in geochemical characterization as mine evolves.

Problem Statement: Geochemical characterization conducted before mining begins may not accurately reflect conditions after mining has progressed.

Background: As mining progresses, there is an opportunity to test assumptions upon which mined-material characterization and water-quality predictions are based. Changes in geology, such as a change in rock type or in the mineralogy (sulfide versus oxide minerals, for example), as the mine expands or develops, can impact all aspects of mining from development to waste disposal (SME, 1992). Changes in geology can result in significant changes in the results of materials characterization and water-quality predictions and in environmental impacts.

Recommendation: Geochemical characterization should be conducted throughout the active life of the mine and used to continually evaluate potential environmental impacts.

Field/lab discrepancies.

Problem Statement: Laboratory geochemical characterization tests are generally not representative of field conditions. Results from laboratory tests will generally overestimate field weathering rates and underestimate the length of contaminant generation from mined materials.

Background: For most mine waste, laboratory oxidation and weathering rates are generally two to three orders of magnitude higher than field rates (Ritchie, 1994; Banwart et al., 2002; Schnoor, 1990; Sverdrup and Warfvinge, 1995; Drever and Clow, 1995). This discrepancy can be explained by considering a relatively small number of bulk physical and chemical properties of mine rock at field sites: temperature, particle size, spatial variability of sulfide-bearing rock at the site, hydrological factors such as preferential flow, and the availability of oxygen (Banwart et al., 2002; Banwart et al., 2004). Malmstrom et al. (2000) was able to obtain reasonable agreement between field and laboratory weathering rates when these factors were taken into account numerically (Banwart et al., 2002, Banwart et al., 2004). Bennett et al. (2000) found that in the shorter term, oxidation rates should be similar under laboratory and field conditions, although this would apply only to materials with similar mineralogy and leaching behavior. However, extrapolation of decreases in humidity cell oxidation rates over time may underestimate longer term field rates because larger-sized particles will still be oxidizing under field but not under humidity cell test (HCT) conditions, due to the small particle size (max size = 2 mm) used in the test. This issue can be avoided by using larger-scale cells (or columns), rather than HCT's, for waste rock. These results also imply that the size distribution and available surface areas for sulfide and neutralizing minerals in a waste pile must be known to accurately

predict long-term oxidation rates of sulfides under field conditions. Sverdrup and Warfvinge (1995) were able to completely resolve discrepancies between laboratory and field (watershed scale) weathering rates for individual minerals by taking into account partial wetting of field minerals, temperature differences between the laboratory and the field, and the effect of product inhibition (of aluminum and base cations) in the field. Laboratory conditions such as the effect of buffers, using freshly ground minerals in laboratory experiments, and CO_2 overpressure in experiments contributed in a minor way to laboratory-field discrepancies. Generally, if weathering rates are expressed on a per available surface area basis, rather than on a unit time or unit mass basis, the agreement between field and laboratory rates is improved. The bulk of the surface area occurs in the fine fraction, which should not be ignored in laboratory testing.

The accumulation of solutes that are not flushed from the system is an important factor in accounting for the apparently slower weathering rates under field conditions. Banwart et al. (2004) were able to successfully model field solute concentrations when water and solutes held in stagnant zones in a waste pile were included in the model. Smith and Beckie (2003) also found that incomplete knowledge about hydrologic processes controlling unsaturated flow in waste rock made modeling of drainage water quality difficult. In addition to controlling the chemical reactivity in mine waste deposits, grain-size variability can lead to structural heterogeneities that affect fluid flow in the piles, including preferential flow. Mineralogy (including secondary phases), porewater chemistry, sequential and other extractions for different size fractions, and measuring the grain-size distribution were considered important characterization approaches for predicting the geochemical and hydrologic behavior of solutes in waste piles (Smith and Beckie, 2003).

Recommendation: Site-specific measurements of temperature, particle-size distributions, available sulfide and neutralization mineral surface areas, spatial variability of sulfide-bearing rock, hydrological factors such as preferential flow, and the availability of oxygen should be determined for all waste units, especially waste rock and leach dumps. Mineralogic analysis, including mineral availability, should be completed before laboratory testing begins. To the extent possible, field-scale testing or laboratory columns, with minimal changes in grain size distribution compared to the actual mined material, should be conducted as supplements to or replacements for laboratory characterization testing, especially for waste rock. Site-specific estimates of scaling factors between laboratory and field conditions should be determined and used in predictive modeling studies.

6.3.2 Issues Related to Static Testing

Effect of particle size.

Problem Statement: Static ABA tests use crushed rock, which will overestimate the association of acid-producing and acid-neutralizing minerals under field conditions and overestimate the neutralizing, and possibly the acid-generation, potential of the samples.

Background: When a sample is crushed or ground, it makes grains more reactive. Producing a fine-grained, homogenous assemblage changes the spatial relationship between the acid-generating and acid-neutralizing minerals. If the newly-exposed surfaces have a significantly different composition from those available to weathering under field conditions, the laboratory test will not effectively simulate reality (Price, 1997). If sulfide mineralization, for example, occurs in veins or along fractures, crushing the rock will tend to underestimate AGP and overestimate NP. Static testing does not consider the association of the sulfide in the rock under field conditions (e.g., disseminated, inclusions, fully liberated along fractures); rocks with the same pyrite content would show the same AP, regardless of their availability to weathering because of sample crushing. White et al. (1999) noted that the reduction of particle size leads to overestimation of the NP. The largest size fraction examined in their experiments (- ¼ inch) approximates the particle size commonly used in HCT's. The overestimation of NP was attributed to increased dissolution of acid-neutralizing minerals that were not available for weathering under field conditions. Stromberg and Banwart (1999) found that particles <0.25 mm contributed ~80% of the sulfide and silicate dissolution, and calcite particles larger than 5 to 10 mm react too slowly (due to intra-particle diffusion) to neutralize acid produced from sulfides. Scharer et al. (2000b) also found that the availability of neutralization potential (NP) from limestone was mass-transfer limited when particles were >6.4 mm. Under mass-transfer limitations, the rate of pyrite oxidation may exceed the rate of neutralization by buffering minerals. Therefore, under field conditions where limestone or other neutralizing minerals are larger grained, crushing will overestimate the

contribution of that mineral to neutralization potential. The same conditions may apply to the crushing of larger sulfide grains and the overestimation of acid generation potential.

Recommendation: Static ABA tests cannot be used to quantify acid generation and neutralization under field conditions and should only be used as an initial screening technique to estimate the total amount of acid-generating and acid-neutralizing material present in rock that is representative of the samples collected. Evaluation of mineralogy, including available weathering surface area for sulfides and carbonates, may be a more accurate approach than ABA testing for estimating the acid generation potential of mined materials.

Effect of temperature, pH, and test duration on neutralization potential estimates.

Problem Statement: Neutralization potential tests that are conducted at elevated temperatures or that use pH endpoints of <6.0 will overestimate the amount of neutralization potential available under field conditions. For samples with low carbonate content, neutralization potential tests conducted for short time frames may underestimate the neutralization potential.

Background: The U.S. Bureau of Mines examined the NP of five samples using the NP(pH6) test (Lapakko modification) at 4, 24, and 120 hrs (White et al., 1999). NP increased consistently with time, with 120-hr tests typically having 1.1 to 2.3 times higher NP values than the 4-hr tests. The calcite-containing samples produced NP relatively quickly (≤ 4 hr), while samples with magnesium carbonate dissolved more slowly (4 to 120 hr). The Lapakko modification NP procedure has the longest test duration (up to 1 week), while the original Sobek procedure has the shortest (3 hr); the BCRI Initial test lasts for 16-24 hr, and the modified Sobek has a 24-hr duration (Mills, 2004a). Downing and Madeisky (1997, as cited in Mills, 2004a) used the BCRI Initial Method to evaluate changes in NP over time (up to 40 to ~92 hours) for four low-carbonate samples and the Canadian Reference Material for Standard Acid Base Accounting (NBM-1), and found that NP did not change substantially over time for samples dominated by carbonate (NBM-1), while samples with low carbonate content had increasing NP values over time and the NP was contributed by mica, chlorite, pyroxene and amphibole. The conclusion reached by Mills (2004a) was that the Lapakko modification and TIC methods will give the lowest NP values (only carbonates are credited), Sobek will give the maximum NP values (lowest test pH and elevated temperature), and BCRI Initial and Modified Sobek will give intermediate results (carbonates and only most reactive silicates credited).

Neutralization potential is defined operationally as the buffering of a sample by minerals at a pH of at least 6.0 (White et al., 1999). Buffering at lower pH values will not be adequate to keep site waters in compliance with regulatory standards. Conducting the neutralizing potential test at pH values <6 will overestimate field neutralization potential because under field conditions, calcite may produce bicarbonate ion rather than CO_2 gas (for tests that use fizz method (Sobek and NAG tests) and all NP tests with endpoint pH values <6). Conducting NP tests at elevated temperature values or low pH values (<6) will also overestimate NP because minerals that do not contribute to neutralization potential at pH values >5 (silicates such as kaolinite, montmorillonite, albite) will be included in NP at these elevated temperatures and low pH values (for original Sobek method, NAG test, BC Research tests) (Tremblay and Hogan, 2000).

Recommendation: Evaluation of mineralogy is a necessary step for determining the neutralization potential of mined materials. If using ABA testing, some general guidelines include: for most mineralogies, the original Sobek method will overestimate neutralization potential; use NAG testing only as a screening method for estimating neutralization potential; assuming siderite is not a dominant carbonate mineral, Lapakko and modified Sobek methods are the most reliable and reasonably conservative tests for estimating NP.

Effect of mineralogy and organic matter on neutralization and acid generation potential.

Problem Statement: Mineralogy is the most important control on acid-generation and neutralization potential, yet until the last few years, mineralogy has rarely been confirmed as part of static or kinetic testing procedures. Lack of knowledge about the mineralogy of mined material can cause either overestimation or underestimation of net acid-generation potential.

Background: ***Effect on NP***. As an example of the importance of mineralogy, the presence of siderite, a reduced-iron carbonate, can cause an overestimation of

NP, depending on the pH of the static test method back titration. If siderite dissolves at low pH values, it can contribute to alkalinity; if it dissolves at pH values above about 3.5 under oxidizing conditions, ferric hydroxide will precipitate and add acidity (Balestrieri et al., 1999; Plumlee, 1999; Nordstrom, 2000). The higher pH of the NP(pH6) resulted in good agreement between test results and known neutralization potential (NP) values for a pure siderite sample, while the Sobek and modified Sobek methods, which use a lower titration pH, caused an overestimation of NP (White et al., 1999). White et al. (1999) also discuss "mineralogic NP," which is an estimate of NP from the amount of calcium and magnesium carbonate minerals present. Values for NP derived from ABA testing can be compared to mineralogic NP values as a check on the validity or calibration of the ABA results. If NP values from ABA testing are higher than the mineralogic NP, minerals with less effective buffering capabilities (e.g., silicates) are being counted as contributing to the neutralization potential.

The extent to which minerals other than calcium and magnesium carbonates contribute to the ability to neutralize acid at reasonable rates is debatable and dependent on the pH at which the material weathers in the field over time. Certain silicates can contribute neutralizing potential to mine wastes over the long term or if the wastes are in a low-pH environment (Nicholson, 2003; Bliss et al., 1997). In static tests conducted on three pure feldspars (oligoclase – the sodic plagioclase, bytownite, and microcline – the potassic K-feldspar), bytownite, the calcic-endmember plagioclase feldspar, was the only feldspar that produced measurable NP in static tests (White et al., 1999). Kwong and Ferguson (1997), using XRD and NP tests, determined that biotite, chlorite, and amphibole contributed to NP, while quartz, muscovite, plagioclase, and K-feldspar did not. After reviewing the contribution of many silicates to the results of static tests, Jambor (2000) recommends that the most realistic measure to use for predicting whether rocks will be acid producing is the carbonate content. In ultramafic rocks, olivine and its deuteric alteration products such as lizardite can provide efficient neutralization (Jambor, 2000 and 2003). If ferrous iron is present in silicate minerals and it dissolves and subsequently oxidizes to ferric iron/iron oxyhydroxide, the buffering capability of the silicate will be reduced (Nicholson, 2003). Generally, feldspars will only be effective neutralizing agents if they are largely calcic and if the sulfur content is relatively low. Morin and Hutt (1994) found that feldspar (50% calcium) effectively neutralized acid produced by the oxidation of 1.9% pyrite in tailings. However, the subaqueous conditions may have limited the rate of pyrite oxidation in the tailings.

Aluminosilicates weather (releasing base cations such as calcium that can neutralize acidity) at slower rates than carbonates (Lawrence and Wang, 1997; Sverdrup and Warfvinge, 1995; Brantley and Chen, 1995). This discrepancy in weathering rates has led some researchers to propose a short-term index based on carbonate content and a long-term index based on Ca+K content (Downing and Madeisky, 1997, as cited in Mills, 2004a) and relative reactivity rates, based on the minerals present (Mills, 2004a and Plumlee, 1999, pg. 74). However, as noted above, White et al. (1999) observed that potassium feldspars were not effective neutralizing agents.

Effect on AGP. If sulfates and organic S are present (only expected in certain sediment-hosted sulfide deposits, or if secondary sulfates have formed), using total S may overestimate AGP. However, some soluble sulfates can store and produce acid when solubilized, especially certain iron sulfates (Nordstrom and Alpers, 1999; Mills, 2004a). Depending on the type of sulfide present (and the pH and oxidant present in the natural setting), using sulfide S for acid potential (AP) tests may also overestimate AGP. For example, when oxygen (rather than ferric iron) is the oxidant, Plumlee (1999) states that sphalerite, galena, and chalcopyrite will not generate acid. On the other hand, he notes that chalcopyrite and other sulfide minerals that do not contain iron will produce acid when oxidized by ferric iron (which could be present at low pH values). Although balanced equations can be written for these reactions, there does not appear to be empirical evidence for the results, and more experiments need to be conducted to conclusively evaluate oxidation of sulfides by oxygen and ferric iron.

By closely examining mineralogy in humidity-cell experiment samples, Newbrough and Gammons (2002) found that pyrite in samples with higher leachate pH values was coated with chalcocite, which can consume protons. Stewart et al. (2003a) has shown that there are significant differences among the acid-generation potentials of sulfide minerals, using the net acid generation (NAG) test. According to their results, only pyrite, pyrrhotite, arsenopyrite, and chalcopyrite are able to produce leachate with a pH <4.5. The presence of carbonaceous matter can produce organic acids during the peroxide oxidation step in the NAG test and lead to overestimation of acid generation potential by this method (Stewart et al., 2003b). The

effects were most pronounced in samples with sulfur content <0.5% and total organic carbon contents >7%, which would be rare in most hardrock mines. The precipitation of gypsum (mostly in kinetic tests) can underestimate the AGP because there will be lower concentrations of sulfate in the effluent after gypsum precipitates. However, Morin and Hutt (1998) found this was rare in kinetic results from the International Kinetic Database (IKD, version 98.3, MDAG Publishing, 1998).

Recommendation: Mineralogy should be thoroughly examined as part of the environmental characterization process, with special attention paid to identifying the types of metal sulfides, silicates, and carbonates in mined materials and the surface area of these minerals available for reaction. In many cases, this will involve mineralogical examination that is more detailed and sophisticated than simple bulk powder X-ray diffraction. If siderite is a dominant carbonate, the NP tests should be modified to ensure that siderite is not included in NP. As a check on NP, use mineralogic NP (based on the amount of calcium and magnesium carbonates present) for samples of lithologies of interest. Use of total sulfur for AGP may result in slight overestimations of AGP, but using total S would result in more protective and supportable management decisions. However, if there is a substantial amount of non-acid producing sulfates or organic sulfur, they should be subtracted from the total sulfur value.

Estimating NP and AP in low-S, low NP wastes.

Problem Statement: Rocks with low sulfur content can produce acid, and rocks with low NP can buffer acid, yet standard ABA tests may not predict these results.

Background: Rocks with low sulfur content can produce acid, and rocks with low neutralization potential can produce neutralizing ability. For example, Lapakko and Antonson (1994) observed that samples from the Duluth Complex in northeastern Minnesota (a large copper/nickel resource with elevated levels of platinum group metals) with %S values from 0.41 to 0.71% produced pH values from 4.8 to 5.3, and samples with %S values from 1.12 to 1.64% produced pH values of 4.3 to 4.9 after 150 weeks. Also, as noted above, a number of researchers have found that certain feldspars can effectively neutralize acid at low %S values.

Li (2000) presents a method for predicting the acid drainage potential for wastes in this category. He defines low-sulfide, low-neutralization potential waste as those with sulfur contents <1% and neutralizing potential <20 kg $CaCO_3$ equivalents per ton (eq/t). Li notes that there are many documented cases of acid generation by mine waste with a sulfide-sulfur content of 0.1 to 1.0% S. At these low S contents, the addition of neutralizing potential by silicates becomes more important, and the procedure includes using mineralogic and kinetic information to evaluate the importance of silicate buffering. If the silicate dissolution rate is greater than the sulfate production rate, the material may be buffered initially but eventually form acid, although the common silicates do not yield alkalinity at appreciable rates until the pH falls to <3 (Stumm, 1997). In this case, the relative availability of acid-producing and -neutralizing material is evaluated to determine whether or not the waste is expected to generate acid. Scharer et al. (2000a) note that wastes with neutral drainage (such as some in the low-S, low-NP category) will have slower sulfide oxidation rates (because sulfides oxidize more slowly at neutral pH values) but can produce elevated concentrations of sulfate, base cations, and metals.

Recommendation: For rocks with low S content and/or low NP, standard ABA testing must be supplemented early in the mining process with additional information on mineralogy, availability of acid-producing and neutralizing material, and kinetic tests to determine the relative weathering rates of sulfides and neutralizing minerals.

Interpretation of static testing results using NP/AP ratios.

Problem Statement: NP/AP ratios are routinely used to predict the likelihood of acid generation at a mine site. Depending on the amount and availability of neutralizing material, material with even “safe” ratios (e.g., >3:1) may produce acid in the longer-term.

Background: The results of static ABA tests are usually presented as either NNP (NP – AP) or NP/AP. Use of the NP/AP ratio is preferred because it allows comparison of acid generation and neutralization potentials over a wide range of results (Tremblay and Hogan, 2000). Practitioners of ABA methods have used various NP/AP ratios to define acid-generating, uncertain, and non-acid-generating screening criteria for mined materials, with suggested non-acid-generating ratios ranging from 1:1 to 4:1 (White et al.,

1999). The use of ratios assumes that measured NP and AP values are representative of field conditions, and this premise has been questioned by many practitioners, as discussed above. Ferguson and Morin (1991, as cited in US EPA, 1994) discussed the validity of extrapolating a sample's ability to generate acid into short (< 1 year), medium (a few years), and long-term (many years) time frames, with ABA tests being appropriate only for short-term projections. Robertson and Ferguson (1995) used a non-acid-generating NP/AP ratio of 2:1; Price (1997) and Mills (2004a) recommended a conservative screening criterion of 4:1; and Morin and Hutt (1994) used a range of >1.3 to 4.0. Scharer at al. (2000b) concluded that for heterogeneous waste rock piles, the NP/AP ratio is a reliable indicator only for short-term predictions, and that kinetic data on depletion rates of neutralizing minerals suggest that NP/AP ratios as high as 5.0 may become acidic in the long term. Mined materials with NP/AP values below the selected screening criterion and above a ratio of 1:1 are considered to have an uncertain ability to form acid and would fall into a "gray zone" that would require longer term kinetic testing. Skousen et al. (2002) found that NNP and NP/MPA (MPA = maximum potential acidity using total S, ~NP/AP) ratio were best at predicting actual drainage pH from surface coal mines, and that 96% (50/54 mines, excluding 4 anomalous sites) of the mines had good agreement between NNP or NP/AP ratios and drainage pH. They used NP/AP ratio ranges of <1 (acid drainage), 1-2 (acid or alkaline drainage), and >2 (alkaline drainage) for predicting post-mining drainage quality. Although the predictability is quite high for these mines, all are coal mines. Hardrock mines have more complicated mineralogy and likely more variability in the predictability of drainage water quality. Lapakko (2003a) states that there is no agreement on a "safe" value for NP/AP ratios, and that determining sample-specific mineralogy is a better approach for predicting drainage quality.

Recommendation: Static ABA tests and NP/AP ratios should only be used as initial screening tools for samples to be used for kinetic testing and as estimates of the total amount of acid-generating and neutralizing material present. Knowledge of mineralogy is essential in interpreting ABA results. To estimate medium- and longer-term acid-generation and metal-leaching potential, static test results must be supplemented with mineralogic, mineral availability, and kinetic testing data.

6.3.3 Issues Related to Short-Term Leach Testing

Water:Rock Ratio, Use of Unweathered Materials, and Interpretation and Use of Short-Term Leach Testing Results.

Problem Statement: Short-term leach tests are used routinely to determine the identity and concentrations of constituents of concern leaching from mined materials. Although the intent of the tests is to simulate short-term leaching conditions, the results of the tests are often misapplied to longer-term leaching. Two other issues that confound the interpretation and of the tests is the water:rock ratio and the use of unweathered mined materials.

Background: The purpose of short-term leach tests, as the name implies, is to simulate the leaching of constituents of concern over short time frames by meteoric water. The majority of the constituents (hydrated metal sulfate salts) that are rapidly released from mined materials are on the weathered surfaces of the fine fraction (< 2 mm) of the sample (Smith et al., 2000; Hageman and Briggs, 2000). Therefore, without a weathered surface, short-term leach tests are meaningless, and only the longer-term weathering behavior can be studied. Fresh drill core generally will not have a weathered surface, and short-term leach tests should not be conducted on this material until a weathered surface develops.

The water:rock ratio is never known definitively, but the 20:1 ratio used in many of the US EPA leach test methods is too dilute. The higher ratio used may ensure the complete solubility of all products (Hageman and Briggs, 2000), but the dilution may cause leached concentrations to be below detection limits, especially if lower detection limits (e.g., for metals) cannot be achieved in the laboratory performing leachate analysis. On the other hand, a low water:rock ratio (e.g., MWMP test) may underestimate the amount of poorly soluble constituents such as arsenic that may be released.

Recommendations: The use of unweathered materials in leach tests should be avoided. Short-term leach tests may have limited use as a scoping tool if weathered rock is used, but the results should only be applied to short-term leaching of mined materials after they have been weathered in the field. Involving an experienced geochemist in testing design and analysis will minimize misinterpretation of test results. Taking short-term leach test results from long-term kinetic

tests (e.g., "first flush" results from humidity cell or column tests) would eliminate the need for separate short-term leach tests and would better link short-term and long-term predictions for leaching of contaminants. In addition, releases can then be quantified on a per unit mass basis if short-term leach results are taken from kinetic testing.

6.3.4 Issues Related to Kinetic Testing

There are two distinct purposes for conducting kinetic tests: to predict the onset of acid drainage, especially in samples with equivocal results for static testing; and to generate data that can be used to model or predict water chemistry. For kinetic testing conducted before the early- to mid-1990's, the main purpose was to predict the onset of acid drainage. Today, most projects would require the development of a technical basis for estimating future water quality, and the prediction of the onset of acid drainage would come as a byproduct of that analysis. The purpose of conducting kinetic testing must be understood by all parties, and then the details of how to conduct the test can be worked out for decision-making purposes.

Effect of particle size and mineral availability.

Problem Statement: With the exception of tailings, crushing is required for humidity cell tests, yet, especially for heterogeneous and larger grained material, such as waste rock, humidity cell test results will not accurately represent field conditions.

Background: The effect of particle size on static testing results and field/laboratory discrepancies has been discussed above, and these same issues apply to kinetic testing. In particular, the availability of acid-generating and neutralizing minerals to weathering will be overestimated if the sample is crushed (Lapakko, 2003a). This is especially true for minerals in the rock groundmass or those coated in less reactive minerals or precipitates. Benzaazoua et al. (2001) showed that both HCT's and column leach tests had similar results for sulfidic mine tailings; however, for more heterogeneous and larger grained material, such as waste rock, the crushing required for HCT's will make results deviate more from actual field conditions. In a column test with minimal grinding, only acid-generating and neutralizing material that is "liberated" (available to weathering, for example, along fractures or on surface of rocks) will be counted as contributing to acid-generation and metal leaching potential (Mills, 2004e). The availability of minerals, especially sulfides and carbonates, is one of the most important factors controlling the rate of acid development and contaminant leaching at mine sites. Lapakko and Antonson (2002) show the importance of determining the sulfur content as a function of particle size and liberation (available surface area) when determining sulfide dissolution rates (also see Lapakko, 2003b). Lapakko (2003a) shows that kinetic test results at 30 weeks (pH values) were dependent on both lithology and particle size. The drainage pH for the mudstone samples decreased as particle size increased, with a large drop in pH for sizes above 2.0 mm. Drainage pH increased with increasing particle size for the latite and gabbro samples, but the drainage pH of the latite sample dropped for sizes above 2.0 mm.

Recommendation: Humidity cell testing should not be used to predict weathering rates for waste rock or wall rock or other types of heterogeneous, large-grain size material unless the results are expressed in terms of available mineral surface area. This requires that the surface area of specific minerals in the kinetic-test samples be known and – to permit scaling up to field conditions – that the surface area of minerals in the actual waste be known or well estimated. Column testing with no or minimal reduction of particle size or field techniques, such as mine wall washing, will provide results that will be more representative of field conditions. Samples must be well characterized in terms of mineralogy and mineral availability before and after tests are conducted.

Length of kinetic tests.

Problem Statement: The minimum recommended length of time for kinetic testing is 20 weeks, but a number of practitioners of kinetic testing have shown that this time frame is inadequate for accurate prediction of the onset of acid drainage and/or metal leaching, especially in samples with higher neutralization potential.

Background: Many different lengths of time are recommended for kinetic testing, but none are shorter than 20 weeks. As noted in Section 6.3.2, silicates weather more slowly than carbonates, and carbonates weather more slowly than sulfides. The relative weathering rates of carbonates, sulfides, and silicates can produce drainage with changing quality over time. Depending on mineralogy and availability of minerals for reaction, a 20-week kinetic test may not capture all the potential changes in drainage quality over time, in particular the production of acid. Price (1997)

recommends that HCT's should last until weekly rates become relatively stable (then use the average of the last five weeks); this could require substantially more than 20 weeks and possibly more than a year. Robertson and Ferguson (1995) state that kinetic tests should be at least 20 weeks in duration, but suggest that this is inadequate unless samples are extremely high in sulfur content, low in buffering capacity and/or potentially highly reactive, and recommend that typical lengths should be two to three years. ASTM (2003) requires a minimum of 20 weeks duration for HCT's. Lapakko (2003a) states that the 20-week duration recommended by ASTM is too short to allow for potential acidification from mine-waste samples in general, and recommends substantially longer periods if the objective is to see if the rock will acidify over the long term. Morin and Hutt (1997) recommend 60 to 120 weeks or longer.

Lapakko notes that a tailings sample with 1.3 wt% calcite and 6.6 wt% pyrite generated circumneutral drainage for 112 weeks before generating acidic drainage, and that a mixture of rotary kiln fines and rock with 2.1 wt% sulfur from the Duluth complex had a lag time of 581 weeks before it started producing acid (Lapakko, 2003a). Samples with higher NP or NP/AP>1 can have large lag times before generating acid, and Tremblay and Hogan (2000) recommend that the length of the HCT should depend on sample composition, but be at least 20 weeks long and typically last at least one year. Nicholson and Rinker (2000) show that sulfate and nickel concentrations in leachate from both humidity cell and column leach tests did not start to increase until after 20 weeks, and that peak concentrations of nickel in humidity cell tests were not reached until over 60 weeks had passed (Figure 7 a and b). The results further showed that a substantial amount of nickel was leached from the wastes under neutral pH conditions.

The length of kinetic tests also depends on the objectives of the test. For example, if the objective is to examine relative weathering rates, tests may be longer or shorter than if the objective is to determine if the sample will ever produce acid.

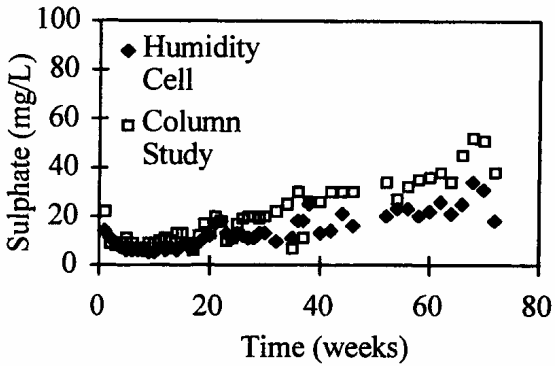

Figure 7a. Sulfate vs. time for humidity cell and column tests. (Source: Nicholson and Rinker, 2000.)

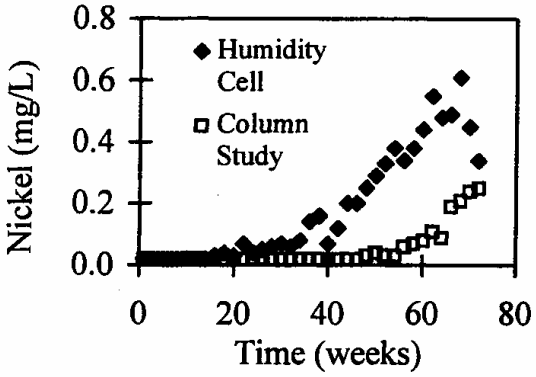

Figure 7b. Nickel vs. time for humidity cell and column tests. (Source: Nicholson and Rinker, 2000.)

Recommendation: The objectives of kinetic testing should be clearly stated. If the objective is to determine if the sample will produce acid, kinetic tests should be conducted for longer than 20 weeks, unless earlier results indicate that acid will be produced. The length of the test should depend on the sample composition. Mineralogy (including available surface areas) should be examined initially and after the test and used to help determine if the sample could eventually produce significant amounts of acid or contaminants. For kinetic test samples with static test NP:AP>1 that have not produced acid within one year, test lengths should be longer than one year.

Effect of column size and shape.

Problem Statement: Column testing of larger grain size material may result in incomplete contact of leachate with the sample material and inaccurate prediction of water quality unless the experiment is carefully designed and implemented.

Background: Leachate may be channeled down the sides of a column if the ratio of the column diameter to the size of the largest particles is low; a ratio of ≥6 is recommended (Tremblay and Hogan, 2000). Ratios of 10 and as high as 40 have been discussed as well. Channeling is more likely to occur in column rather than humidity cell tests (HCT's). The larger the column, and the more representative the size distribution is of that of the actual mine unit, the less scaling is required to approximate full-scale field conditions.

Recommendation: For larger grain size material, such as waste rock, larger columns should be used for kinetic testing, using a ratio of column diameter to largest particle size of six or greater. To reduce grain size somewhat, the material can be broken by hand, for example, using a hammer, if necessary, so that the breakage would occur along faces that would naturally be exposed to weathering.

Effect of temperature and weather conditions.

Problem Statement: Laboratory temperatures and conditions deviate from field conditions, and these deviations may result in under- or overestimation of metal leaching and acid production rates and concentrations.

Background: The temperature of kinetic tests conducted in the laboratory generally will be different and more consistent than actual field conditions. Kinetic tests conducted in the laboratory will not simulate weather conditions in the field, such as precipitation, snowmelt, and the variability in ambient temperatures, nor or they designed to. Cooler temperatures can slow the rate of mineral dissolution, including sulfide oxidation, and warmer temperatures will increase weathering rates. For small molecules, reaction rates double for every 10^{o}C increase in temperature (Pauling, 1970).

Recommendation: To the extent possible, field kinetic tests should be conducted as a supplement to laboratory kinetic testing. Mine proponents and regulators should acknowledge that the results of kinetic testing, unless the tests are conducted in the field, will not represent dynamic hydrologic and weathering conditions such as snowmelt and precipitation. Results from kinetic tests conducted under oxygenated conditions can be used to model the effect of different temperatures on sulfate production using experimental data on the effect of temperature on activation energies for the reactions (e.g., Ritchie, 2003).

Applicability of standard kinetic testing for materials under low-oxygen or reducing conditions.

Problem Statement: Humidity cell tests have been used, among other things, to estimate leaching characteristics of tailings material, some of which may be fully saturated under field conditions. Humidity cell tests are not designed to represent low-oxygen or reducing conditions.

Background: Humidity cell tests are conducted under partially saturated and high oxygen-content conditions and are not intended to simulate acid production and consumption or contaminant generation under fully saturated and anoxic conditions (Tremblay and Hogan, 2000; Price, 1997), such as would exist in portions of tailings impoundments. Column tests more closely simulate the leaching processes operating in mine waste deposits and can be adapted to conditions other than complete oxygen saturation (Mills, 2004c) using experimental data on the relationship of reaction rates to the fugacity of oxygen.

Recommendation: Humidity cell tests should not be used to represent leaching characteristics of materials under low-oxygen or reducing conditions. Continuous-flow column tests or batch tests can be used to estimate the behavior of mined materials under low-oxygen conditions.

6.4 State-of-the-Art Methodology for Geochemical Characterization of Mined Materials

The steps for state-of-the-art geochemical characterization of mined materials are described below and shown schematically in Figure 8. The rationale for the selection of these approaches is contained in the preceding sections. The full list of steps is most appropriate for proposed or expanding

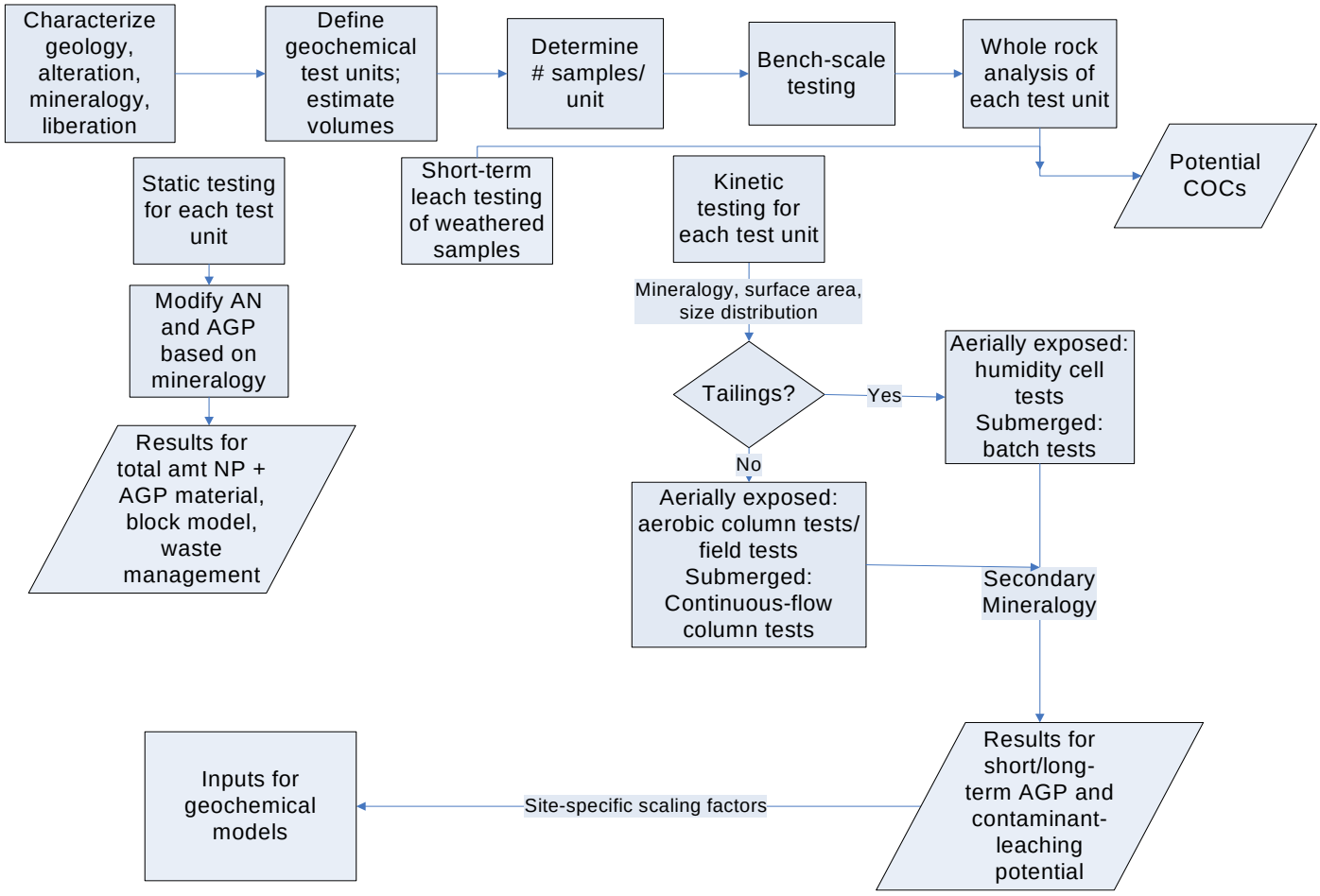

Figure 8. Steps for state-of-the-art geochemical characterization of mined materials.

operations. Characterization of mined materials at inactive or abandoned mines sites would instead rely more on existing site- or unit-specific water chemistry (e.g., seep, pore water, pit water, surface water, or groundwater quality) or a smaller list of approaches.

The first step in characterizing mined materials is to determine the geology and mineralogy of the rocks at the mine site. Such analyses include the determination of rock type, alteration, primary and secondary mineralogy, the availability of acid-producing and -neutralizing and metal-leaching minerals (liberation, e.g., veins, disseminated, encapsulated, etc.), and the locations and dimensions of oxidized and unoxidized zones for all waste types, pit walls, and underground workings. The geologic and mineralogic analysis also includes defining all geologic units that will become waste, pit or underground workings walls (and areas behind the walls), and stockpiles, and defining the ore types by delineating ore grades.

The next step in the geochemical characterization of mined materials is defining the geochemical test units. Geochemical test units are rock types of distinctive lithology, mineralogy, and/or alteration. The units should be as homogeneous as possible, based on information on lithology, mineralogy, alteration, and the availability of minerals to weathering. Geochemical test units should be maintained throughout the life of the mine, although new test units may be defined based on future exploration. Examples of geochemical test units are peridotites, feldspathic peridotites, pyroxenites, gabbros, and olivine gabbros (possibly for ultramafic deposits), an oxidized marble skarn, or propylitically-altered rhyolite. Extensive geochemical characterization should be performed on each of the identified test units. Depending on the results of the characterization, some of the test units may be grouped together in the mine waste management plan. Alternatively, if an initial unit designation provides a wide range of test outcomes, it may be necessary to subdivide the unit for waste management purposes. For example, if the initial designation included sulfur concentrations < 0.2 wt %, but the characterization data showed widely varying results for acid generation potential, the samples would be reclassified and a more prudent sulfur limit would be determined. Within a given lithology and mineralogy, the sulfide content can often be the controlling factor in determining the ability of a test unit to produce acid and leach contaminants.

The third step in characterizing mined materials is to estimate the volumes of each type of material to be generated and the distribution of types of material in waste, pit, and underground workings. The number of samples for geochemical testing of each unit should be based on the volume of material in each unit. The information on geochemical test units should be coordinated with the mine waste management plan.

The fourth step in characterization is conducting bench-scale testing of the ore, which involves creating tailings and/or heap leach materials in a laboratory. In addition to any metallurgical testing, the tailings or heap leach material can be subjected to geochemical and hydraulic testing. The general categories of geochemical testing that will be performed on the geochemical test units are whole rock analysis, static testing, short-term leach testing, and kinetic testing.

Whole rock analysis includes analyzing the samples for potential contaminants of concern and major element chemistry in each test unit. Results from whole rock analysis can be used to define constituents of concern. Whole rock analysis should be performed on the identified geochemical test units, including the ore, tailings, and leached heap materials.

Static testing is then performed on potential sources of acid drainage, including waste rock, pit wall rock, underground working wall rock, tailings, ore, leached heap materials, and stockpile materials. The number of samples for each unit will be defined by the volume of material to be generated. For acid-generation potential (AGP), the modified Sobek method using total sulfur is recommended. The mineralogy and composition of the sulfides should be confirmed using mineralogic analysis. For the acid-neutralizing potential (NP), the modified Sobek method, and the Lapakko modification for siderite, are recommended. Carbonate and silicate mineralogy should be confirmed using mineralogic analysis. For interpretation of static test results, mineralogy should be used to stoichiometrically modify the AGP and NP results. For example, if sulfides are present that will not generate acid, or if sulfur is present from organic or non-acid-generating sulfate salts, the AGP should be reduced accordingly. If the NP is from siderite or silicates, the NP should be reduced accordingly. At this stage of geochemical testing, no credit should be given for siderite or silicates, and the results should apply only to estimating the total potential acid generation and neutralization potentials. However, depending on the mineralogy and sulfide content, certain silicates in

ultramafic rocks – olivine and lizardite – can neutralize low percentages of sulfide and could be given credit, if kinetic test work shows that these silicates can neutralize acidity at reasonable rates. Thus, at the static-testing stage, an "effective" NP should be assigned to olivine and lizardite on a contingent basis that requires confirmation through kinetic testing.

Another possible characterization test is short-term leach testing if it has been performed on materials that have had an opportunity to weather before the test is conducted. Short-term leach tests on fresh core, for example, have no significant relevance to field conditions for managed mine wastes. Results from short-term leach tests can be used to estimate the concentrations of constituents of concern after a short event (e.g., a storm event) but are not appropriate to use for estimation of long-term leaching. Standard short-term leach tests with a lower liquid:solid ratio (e.g., MWMP or BC SWEP modification – see Table 1) can be conducted on samples from each geochemical test unit. However, using first flush results from longer-term kinetic testing will help coordinate the short-term and longer-term weathering results and will allow the determination of weathering on a per mass basis. The leachate samples should be analyzed for constituents of concern (based on whole rock analysis and known contaminants of concern) using detection limits that are at least ten times lower than relevant water quality standards (e.g., for arsenic, which has a drinking water standard of 10 µg/L, the detection limit should be 1 µg/L or lower). Major cations and anions should also be determined on the leachate samples, and the cation/anion balance should be checked for each sample.

The last step in geochemical characterization is kinetic testing. The objectives of kinetic testing should be clearly defined. Kinetic testing should be conducted on a representative number of samples from each geochemical test unit. Special emphasis should be placed on kinetic testing of samples that have an uncertain ability to generate acid. Column tests are recommended over humidity cell tests for all aerially-exposed mined materials, including natural on-site construction materials, with the exception of tailings. However, either type of kinetic test can be useful depending on the objectives of the testing and if the available surface areas for reaction are determined in advance of the testing. Grinding of samples should be minimized to avoid exposure of acid-producing or acid-neutralizing minerals that would not be exposed under field conditions. If necessary, samples could be broken by hand or using another method so that the breaks occur, as much as possible, along preferential structures such as fractures. This is especially important if mineralogic analysis shows that the acid-generating and -neutralizing minerals are largely present in veins or as coatings along fracture surfaces. The dimensions of the column should be appropriate for the size of material in the sample.

Surface area, particle size distribution, and volume of the material in the column should be measured before the test begins. If not available already, the mineralogy and whole rock chemistry of each kinetic test sample should be defined. The particle size distribution for the kinetic samples can be performed using sieves. The overall available surface area for sulfides, carbonates, and silicates (and also within a given size fraction, if possible) should be determined on a small subset of samples. It is often the small size fractions (<~2mm) that will control weathering behavior on a short-term basis, and the larger size fractions that will control weathering/leaching on a longer-term basis (Diehl et al., 2004; Smith et al., 2000; see Table 1). Particle size distribution is needed not only for the test samples, but also for field-scale wastes. A field-scale particle size distribution can be estimated by direct measurement (sieving) or calculated from the blasting plan. During the column test, pH, specific conductance, effluent volumes and flow rates, and all constituents of concern (as defined by whole rock analysis and leach testing) should be determined for each sample of column effluent. Detection limits should be at least ten times lower than relevant standards, and major cations and anions should also be determined in order to check for cation/anion balance. Secondary minerals should be identified in column material at the beginning and at the end of the column test. The tests should be conducted for one to two years, or until effluent pH values drop below 4.5 or contaminant concentrations are greater than ten times relevant standards.

For the interpretation of column tests, the tests should be continued until effluent parameter values are relatively constant with time. The amount of sulfide and carbonate (or neutralizing silicates, if relevant) depleted over the course of the test should be noted to ensure that sulfide grains have been sufficiently weathered. Initial concentrations and pH values should also be noted, as these "first flush" concentrations and values are relevant for behavior in storm events. The effect of secondary mineralogy on oxidation and dissolution rates for minerals of interest should be evaluated for use as inputs to geochemical or mass balance models. Weathering rates from kinetic tests

should be applied to field-scale materials and on a surface-area basis.

Humidity-cell tests can be used for aerially-exposed tailings, without grinding the samples. Tests should be conducted on well characterized samples, and the objectives of the test should be defined. The same measurements of surface area and volume, mineralogy and whole rock chemistry, and effluent parameters, volumes, and flow rates, and length of testing are relevant for both column tests and humidity cell tests. For waste rock and heap or dump leach materials, field-scale kinetic tests (e.g., on pads) are recommended rather than humidity-cell tests. Minewall washing can be used to evaluate leaching from the walls of open pits. Loads, weathering rates, and concentrations in leachate from the field-scale test should be measured over time and related to site climate/meteorology. For example, leachate should be collected during or immediately after a storm event. The surface area of material in the field test should also be measured before the test begins. For subaqueously deposited non-tailings materials (e.g., waste rock), continuous flow-through tests can be conducted (see, e.g., Newbrough and Gammons, 2002). Batch tests can be used for subaqueously-deposited tailings.

The results of the characterization tests should be applied to the block model of the deposit or to a watershed model of the mine to predict the ability of the wastes or mined materials to generate acid and contaminants across the entire mine site and to affect specific drainages or groundwater. Any new materials encountered in mining will require full characterization, as described above.

7.0 MODELING TOOLBOX

A scientific model is a testable idea, hypothesis, theory, or combination of theories that provide new insight or a new interpretation of an existing problem (Nordstrom, 2004). Therefore, a model is not necessarily limited to mathematical formulations or always performed on a computer. In addition, models should be able to explain a large number of observations while maintaining simplicity (Occam's razor), and are always a simplification of reality (Nordstrom, 2004).

As discussed in Section 2.0, predictions of the future using forward, or scenario, (non-scientific) modeling cannot be checked until the future comes to pass. However, regulatory agencies can directly or indirectly require the use of forward modeling at some level as part of ensuring that mining operations will not contaminate groundwater and surface water resources. Predicting the effect of mine facilities and operations on future water quality often involves the use of multiple models to simulate the important processes occurring at the mine site. In many cases, the output from one model may be used as input for another model, or the models may be used iteratively to develop a prediction. In this document, a distinction is made between a code and a model. A code is a computer program, or set of commands, that is used to solve the governing equations that describe biological and physicochemical processes. A code is generic in the sense that it can be applied to many different sites, using different input parameters and conditions. A model is a simplified representation of the site-specific conditions at a particular site, and may be a conceptual model or one created using a computer code. For example, MODFLOW is a computer code that can be used to create a model of groundwater flow at a particular mine site.

Because codes are continually being revised, and new codes may be developed to replace older ones, this section is not intended to provide a complete review of all available codes, or to be an endorsement of any particular code. The codes listed in this section are examples of commonly applied codes that can be used to simulate specific processes at mine sites. This section describes the preparatory steps for predictive modeling (Section 7.1), available codes for predicting water quantity and quality (Section 7.2), modeling water quality from specific mine units (Section 7.3), and sources of uncertainty in modeling and recommendation for improvement (Section 7.4).

7.1 Preparatory Steps for Predictive Modeling of Water Quality at Hardrock Mine Sites

The stages in developing a predictive hydrogeochemical model of water quality for a mine site include developing a conceptual model and selecting an appropriate computational code; gathering site-specific geologic, geochemical, and hydrologic data and fundamental (e.g., thermodynamic) information as inputs for the model; verification and calibration of the model (for hydrologic models); and analysis of uncertainty.

7.1.1 Development of a Conceptual Model and Selection of Appropriate Predictive Codes

The conceptual model is the foundation and starting point of the creation of a model. As discussed in section 5, a conceptual model is a qualitative description of the hydrology and chemistry of the site and their effects on mined and natural materials. Models are always simplifications of reality, and a conceptual model may not be unique. The completeness of a conceptual model is limited and affected by numerous factors that must be considered and identified. The site conceptual model must be representative of the most important processes and reactions that will occur over time on the mine site, and it can change with time at the mine site and as more information is collected (Bredehoeft, 2005). The type of general information needed for such a model is depicted schematically in Figure 9.

The baseline conditions are those that exist before a project commences; in a number of cases, baseline conditions also include pre-existing mining sources. The modeler must determine the potential receptors and possible pathways through which contaminants travel from sources to receptors. The modeler must also identify the hydrologic and geochemical processes that operate on the sources, along the pathways, and in the receptors. The conceptual model also includes mine-project activities such as mitigation

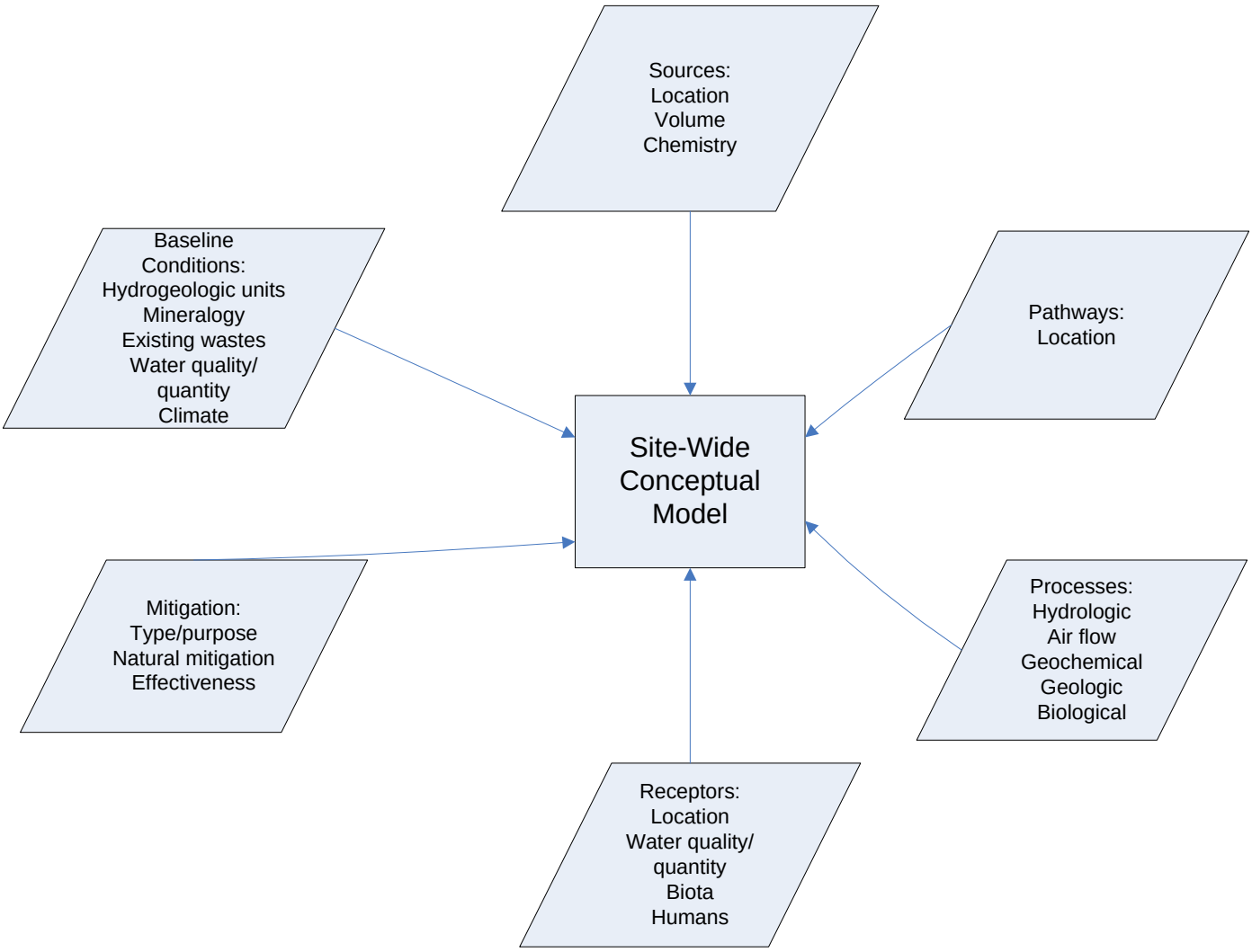

Figure 9. General information needed for development of a site-wide conceptual model.

measures and movement of process and mine-related waters at the site. The type of information needed for a site-wide conceptual model includes:

- Baseline conditions
  - Description of all geologic units (lithology/mineralogy)
  - Spatial characteristics of geologic units (e.g., depth, thickness, locations)
  - Physical, hydraulic, and geochemical characterization of any existing wastes or contaminant sources (including mineralogy, volumes, locations, physical characteristics, acid-drainage potential, contaminant-leaching potential)
  - Location and quality of springs and seeps, including seasonal/temporal variability in water quality
  - Existing groundwater and surface-water quality, including seasonal/temporal variability in water quality
  - Hydrology and hydrogeology, including depth to groundwater, composition and location of unsaturated zone and aquifers/aquitards; spring and stream flow rates, recharge/ infiltration rates, groundwater flow directions and fluxes, gaining/losing reaches of stream, hydrologic parameters (hydraulic conductivity, porosity, permeability, etc.), seasonal/temporal variability of all hydrologic components, and the effect of man-made structures (e.g., dams, wells, intake structures) on water flows and levels
  - Climatic conditions (precipitation, evaporation, climate type, seasonal/long-term climatic variability, dominant wind directions,

typical storm events, temperature) for locations at or close to mine
- Sources
  - Location, volume, mass, chemistry of proposed mining-related sources
  - Nature and extent of natural background sources
- Pathways
  - Possible travel paths from movement of contaminants from sources to receptors (e.g., air, infiltration, runoff, vadose zone, groundwater, transport in streams, transfer among solid and aqueous phases in groundwater and surface water)
- Processes
  - Hydrologic (e.g., advection/diffusion, dispersion, mixing, convection)
  - Geochemical (e.g., sorption, precipitation, dissolution, redox)
  - Air flow (e.g., movement of air into mined material/waste units)
  - Biological (e.g., uptake of contaminants by wildlife, aquatic biota; oxidation/reduction of contaminants by bacteria)
- Receptors
  - Streams, springs, lakes, groundwater, wildlife, aquatic biota, human, etc.
  - Location
  - Quality and quantity (covered under baseline conditions)
  - Interconnectedness of receptors
- Mitigation
  - Proposed mitigations for mine units
  - Natural mitigation (e.g., dilution in surface water/groundwater, adsorption onto alluvial material)
  - Effectiveness of mitigation measures

Predictive water-quality models are nearly entirely dependent on the conceptual model on which they are based and on the parameterization of the different geochemical or hydrogeologic units (e.g., alteration zones superimposed on lithologies) in the model (in other words, how the characteristics of aquifers or other geologic units are represented in the model, including thickness, hydraulic properties, ability to sorb contaminants, etc.). In many cases, there may be more than one conceptual model that could fit the data at the site, and it is important that these different conceptual models be tested (Neuman and Wierenga, 2003). The modeler should consider whether more than one conceptual model could be described and if collection of additional information would better constrain the conceptual model. If the conceptual model is flawed, the model will be flawed, and its predictive capability will be questionable. New information can make an existing conceptual model invalid and lead to major uncertainties in terms of long-term predictions (Bredehoeft, 2005).

Selection and use of the most complex hydrogeochemical code to predict water quality at a mine site does not necessarily provide realistic predictions. As noted by Nordstrom (2004), the sophistication of software has outdistanced our capacity to evaluate, constrain, and test the software. Selection of a computer code to develop a prediction of water quality should be based on factors such as: 1) modeling objectives; 2) capability of the code to simulate important processes affecting water quality at the mine site, as described by the site conceptual model(s); 3) ability of the code to simulate spatial and temporal distribution of key input parameters and boundary conditions; 4) availability of the code and its documentation to the public; and 5) ease of use of the code, including availability of pre- or post-processors and graphical interfaces.

Prior to initiating a modeling project to predict water quality at mining sites, currently available codes should be reviewed, and a code should be selected that simulates the processes identified in the conceptual model that are relevant to the specific mine site. The overall objectives of the modeling project and the availability of supporting data should be considered in selecting a code. The code or codes chosen to predict water quality should be representative of the site (as reflected in the site conceptual model) and be applied at a level of complexity that is appropriate for the available data and the regulatory decisions that must be made. In many cases, available data may limit the code application, and it may be more appropriate to develop a less-complex, screening-level model when data are not available to support a more complex model. Some of the issues to consider when selecting a code include:

- What are the objectives and endpoints of the modeling
- What specific processes at the mine site will influence water quality, and what codes are capable of simulating these processes
- Whether reactions are better represented by equilibrium or kinetic codes (or both)
- Whether to use coupled or separate water quantity and quality codes

- The type and quality of environmental data available (or that could be collected) versus the type of data needed for the code
- Importance of colloids, microbiology, and transport by bacteria to resulting water quality
- Presence of graphical interfaces in codes and ease of use
- Availability of the code to others.

These issues are discussed in more detail in Sections 7.1.2 and 7.4.

7.1.2 Collection of Data for Modeling Inputs

Site-specific inputs to computer codes are needed to make a model that will have relevance to a given mine site. The quality and representativeness of input data will affect the results of the models. Site-specific inputs to hydrogeochemical codes used to predict water quality are similar to certain information needed for conceptual models and can include:

- Spatial characteristics of geologic or geochemical units (e.g., depth, thickness)
- Hydraulic characteristics (e.g., hydraulic conductivity, porosity, storage characteristics) of mined materials, aquifers, and vadose zone)
- Water (leachate) quality and quantity of contaminant sources
- Rate of leaching of contaminants from mined materials
- Rate of pyrite oxidation
- Mineralogy of mined materials
- Reactive surface area of wastes
- Presence and type of bacteria
- Oxygen diffusion rates
- Partitioning of contaminants between soil/rock/waste/sediment and water
- Groundwater and surface water quality and temporal variability in quality
- Groundwater and surface water flow and temporal variability in flow
- Depth to groundwater and distance to surface water
- If a pit lake will form, pit lake bathymetry and dimensions
- Climate data (precipitation, temperature, wind speed, solar radiation, etc.)
- Information on mitigations.

Issues related to site-specific inputs that may affect the accuracy of models are discussed in the Modeling Issues section (Section 7.4). The inputs required for specific codes or types of codes are included in Tables 3, 4, and 5.

Site-specific values used as inputs to codes must be as representative of the range of conditions at a mine site as possible. Modelers need to request and use input data that are appropriate for their conceptual model and provide a rationale for why the values used are appropriate for site-specific conditions. Modelers also need to explain how inadequacies in the characterization and input data used lead to uncertainties in predictions. Sensitivity and uncertainty analysis is discussed in Section 7.1.4.

In addition to site-specific data used as inputs to a code, data usually included in a code (e.g., thermodynamic data) should also be reviewed to ensure that the data are adequate for the intended purpose of the model and the site-specific conditions. Examples of data or parameters that can be included in hydrogeochemical codes include:

- Thermodynamic data, including thermodynamic data for secondary minerals (Perkins et al., 1995, p. 54), solid solutions, and aqueous species (e.g., iron, arsenic, selenium)
- Activity coefficient corrections capable of handling high-ionic strength solutions (e.g., Pitzer formulations) (Perkins et al., 1995; Alpers and Nordstrom, 1999)
- Reaction rate/kinetics data (Perkins et al., 1995; Zhu and Anderson, 2002) if non-equilibrium reactions are expected to be important
- Microbiological data (Nordstrom, 2000). The rate of production of acid, sulfate, and metals is dependent on the presence of microbes such as *T. ferrooxidans*. Information on rates with and without microbes can be used in certain codes.
- Geochemical reactions (e.g., sorption).

Hydrologic and geochemical data or parameters used in codes should be representative of site conditions and include parameters and reactions that are relevant for a given site. In most cases, a range of values (e.g., sensitivity analysis) will be needed to characterize the site, and an explicit evaluation of uncertainties in the

data and model structure should be conducted (Section 7.1.4).

7.1.3 Code Verification and Model Calibration

A water-quality model is a simplified representation of the complex hydrologic and geochemical conditions at a mining site. The success of the model predictions will depend on how well the model represents the actual conditions and processes that influence water quality at the site. Verification of the modeling software and calibration of the selected model should be performed as part of hydrologic modeling; geochemical codes are neither verified nor calibrated, although test cases can be used to determine that the code is operating properly. "Verification" of the modeling software means that the code that is selected for the predictive modeling accurately solves the mathematical equations that describe the processes that the code simulates for conditions similar to those at the site in question. For hydrologic codes, the software is verified by comparison to analytical solutions for simple simulations, and this provides some assurance that the basic programming in the code is accurate. Modeling software may also contain "bugs" that will be identified and corrected as a code is used and applied by more users in more situations; therefore, more widely-used and available codes are generally more reliable in predicting water quality at mine sites.

Model calibration is the process of comparing site-specific observations (e.g., stream flows, groundwater elevations, or pit lake concentrations) with model simulations. Calibration includes adjusting model parameters (e.g., hydraulic conductivity or porosity) so that the output from the model reproduces observed field conditions (see, e.g., Hill, 1998). Several authors have suggested that environmental models can be calibrated but never validated. Oreskes and Belitz 2001) state that even the term validation is unfortunate, because "valid" implies a legitimacy that may not be justified.

At mine sites, much of the modeling performed is "forward" modeling, or modeling of conditions that do not yet exist. In the case of pit lakes, steady-state water quality and quantity conditions may not exist for hundreds of years, yet predictions about the quality of pit water are often required for regulatory purposes. Even though "final" water quality in pit lakes and other receptors may not develop for decades to centuries, water quality at other similar mines can be used to estimate the degree of uncertainty in the prediction. For example, limnologic and water quality conditions at existing pit lakes can be used to understand possible conditions at other mines where pit lakes do not yet exist. Wetting front migration and water in existing waste rock dumps can be used to understand possible conditions in future dumps. Inconsistencies with observed conditions are cause for concern. For example, if a model indicates that no seepage will be observed from a waste rock dump for hundreds of years, and toe seepage has been observed from existing waste rock dumps in the field, the model's predictive capability and degree of uncertainty should be questioned. After several years of site-specific data have been collected at the mine site, the model can be calibrated to a longer data record that will incorporate more temporal variability, and confidence in the model predictions can increase.

7.1.4 Estimation of Uncertainty

The inherent uncertainty in model predictions is rarely stated or recognized. Substantial uncertainty is inherent in determining many of the parameters that are required for modeling water-quality evolution at mining sites, especially hydrologic parameters such as hydraulic conductivity and recharge. Uncertainties in hydrologic modeling may be very large as a result of the inherent range in hydraulic conductivity and other hydrologic parameters, and the effects of these uncertainties on net water-quality predictions (via mass flux) need to be addressed in the uncertainty evaluation. The uncertainty may derive from incomplete characterization or incomplete knowledge of the geochemical and hydrogeologic conditions at the site. Many authors have written about the necessity of quantifying uncertainty in model predictions (Beven, 1993 and 2000; Draper, 1995; Kundzewicz, 1995; Meyer and Gee, 1999; Neuman and Weirenga, 2003). Methods used to evaluate or account for model uncertainty include Monte Carlo analysis, stochastic methods, and evaluating a range of model parameters to develop a range of deterministic outcomes (e.g., a range of water quality in a given receptor). These methods account for the fact that, rather than being well described by a single value as required in the model, parameters are better described with a probability distribution (i.e., a mean, variance, skewness, etc.).

Another aspect of uncertainty relates to estimating the efficiency of mitigation or remediation measures, which often cannot be completely quantified. The predicted water quality from a facility will in part determine what kind of mitigation measures will be taken. If the predictions aren't realistic, it is much harder to "retrofit" mine design than to make it right or prevent pollution in the first place. Adaptive management in the absence of predictions can be useful only if mitigations can be designed and implemented at a later date and be effective. Regulators will still need to rely on predictions for the initial design of the mine waste unit.

Model uncertainty should be acknowledged in predicting water quality at mining sites, and some methodology (conducting sensitivity analyses using a range of values as input parameters, Monte Carlo approaches) should be employed to evaluate the effect of uncertainty on model output. For example, a desired confidence level could be determined (e.g., 95%), and this confidence level on environmental data could be used throughout the model. The computer program Excel has add-ins that can be used to incorporate parameter distributions into a model for the evaluation of uncertainty. The add-ins include @Risk (available from www.palisade.com), and Crystal Ball (available from www.decisioneering.com). These approaches will be useful only if the uncertainty derives from site variability in parameters but will not address uncertainties in the conceptual model. Uncertainties in the conceptual model can be addressed by collecting as much site-specific hydrogeochemical data as possible and keeping an open mind to rethinking the original conceptual model (Bredehoeft, 2005).

7.2 Hydrogeochemical Models Used to Predict Water Quality at Hardrock Mine Sites

Many of the hydrogeologic and geochemical codes available for use in predicting water quality at hardrock mine sites are listed in tables 3 and 4, respectively. Table 3 lists the category and subcategory of hydrogeologic code (near-surface process, vadose zone, groundwater, limnologic, stream/river codes, sediment generation, and integrated hydrologic/watershed codes), commonly used codes, the inputs required, and the processes that are modeled/outputs. Table 4 lists the category of geochemical code (speciation and reaction path, pyrite oxidation, and coupled reaction path/flow codes), available codes, special characteristics of the codes, inputs required, and the type of simulation that the code performs. Figure 10 depicts a mine site, pathways, and receptors and shows where hydrologic and geochemical models are used at mine sites.

Table 3. Description of Selected Hydrogeologic Codes Used for Predicting Water Quality at Hardrock Mine Sites.

Category of Code	Subcategory	Available Codes	Inputs Required	Modeled Processes/Output
Near Surface Process Hydrologic Codes	Water balance (infiltration, runoff, evapotranspiration)	HELP (Schroeder et al., 1994a, b); SOILCOVER (MEND 1994) CASC2D; CUHP; CUHP/SWMM; DR3M; HEC-HMS (US ACOE 2000); PRMS; PSRM; SWMM; TR20	Precipitation, temperature, wind speed, incident solar radiation, vegetative cover (for evapotranspiration) (climate data can be estimated using CLIGEN or WGEN; USDA ARS); hydraulic conductivity/permeability of soil/geologic material; soil moisture storage and transmission requirements.	Partitioning of precipitation into runoff, evapotranspiration, infiltration; estimation of runoff, infiltration, evaporation rates through/from mine facilities and covers; estimation of amount of precipitation entering pit lake.
	Water balance (infiltration, runoff, evapotranspiration) + contaminant transport	SESOIL (Bonazountas and Wagner, 1981, 1984); PRZM 3 (Version 3, Carsel et al., 1984; US EPA, 2003a); HSPF (Bicknell et al., 1997); LEACHM (Wagenet and Hudson, 1987)	Same as above plus source concentrations/loads, initial soil concentrations, contaminant fate/transport parameters (e.g., adsorption, precipitation).	Quantity and quality of infiltration and runoff from/to mine facilities.
Vadose Zone Codes	Vadose zone percolation	1D codes: SESOIL; HELP; CHEMFLO-2000 (US EPA, 2003b); Hydrus-1D (U.S. Salinity Lab; Simonek et al., 1998); SWACROP (IGWMC); SWIM HEAPCOV (Sulphide Solutions); Unsat-1 (IGWMC); Unsat-H (Pacific Northwest Laboratory); 2D codes: Hydrus-2D (U.S. Salinity Lab); FEFLOW (Waterloo Hydrogeologic); SEEP/W (Geo-slope Intl., 1994); SUTRA (USGS); VS2D (Lappala et al. 1987; Healy, 1990; USGS)	Infiltration rates; any layering or heterogeneity in geologic materials; hydraulic properties of soils/geologic units such as moisture retention properties (measured or modeled).	Seepage through unsaturated portions of mine facilities (e.g., waste dumps) and underlying vadose zone .
	Vadose zone percolation and contaminant transport	SUTRA (USGS); VS2D/T (USGS, Lappala et al., 1987; Healy, 1990); FEFLOW (Waterloo Hydrogeologic)	Same as above plus quality of water entering the vadose zone and initial concentrations of constituents in vadose zone; parameters describing partitioning between soil/rock and water.	As above, but with contaminant transport.

Category of Code	Subcategory	Available Codes	Inputs Required	Modeled Processes/Output
Groundwater Codes	Groundwater flow	MODFLOW (McDonald and Harbaugh, 1988; Harbaugh and McDonald, 1996; MODFLOW 2000); FEFLOW (Waterloo Hydrogeologic)	Hydraulic conductivity, porosity, storage characteristics, thickness of geologic units, areal recharge, surface water recharge, pumping or re-injection of water from wells, discharge to surface water; model boundaries (streams, flow barriers, etc.). For fracture flow/transport: also need fracture spacing, orientation, aperture.	Simulate mine dewatering and reflooding; flow and transport in saturated tailings.
	Groundwater flow + contaminant transport	MODFLOW with MT3D; MODFLOW-SURFACT; SUTRA (USGS); FEFLOW (Waterloo Hydrogeologic); FEMWATER (US EPA). Groundwater flow and solute transport in fractured rock: FRAC3DVS and FRACTRAN (Waterloo Hydrogeologic); TRAFRAP-WT (IGWMC)	Same as above plus contaminant input concentrations; dispersion properties of aquifer, retardation characteristics of contaminant. For fracture flow/transport: also need fracture spacing, orientation, aperture.	Contaminant transport and loading from a mine facility to groundwater or surface water.
Limnologic Codes	2D, finite difference hydrodynamic and water quality model.	CE-QUAL-W2 (Cole and Wells, 2001)	Detailed bathymetry, flow rates, climate data, nutrient concentrations of inflows.	Can be applied to rivers, lakes, reservoirs, and estuaries to simulate nutrient/primary productivity of lakes and mixing characteristics (e.g., turnover), sediment, eutrophication kinetics.
	1D (DYRESM) or 3D (ELCOM) hydrodynamic and aquatic ecological (CAEDYM) models	DYRESM/ELCOM-CAEDYM (University of Western Australia, 2005)	Nutrient and suspended sediment concentrations; Fe, Mn, Al concentrations; dissolved oxygen; biota (e.g., zooplankton, fish, macroinvertebrates, algae).	Primary/secondary production, nutrient and metal cycling (Fe, Mn, Al only), oxygen dynamics, sediment movement, changes in biomass.

Category of Code	Subcategory	Available Codes	Inputs Required	Modeled Processes/Output
Stream/River Codes	Streamflow/ quantity	Single-event rainfall-runoff codes: HEC HMS (US ACOE, 2000); TR-20, TR-55 (USNRCS). Continuous streamflow simulations: SWRRB (USDA); PRMS (USGS); SHE (European Hydrologic System code). Flood hydraulics codes: HEC-2 (US ACOE); FLDWAV (US Nat. Weather Service).	Channel geometry, flow data, tributary flow data.	Flood hydrograph simulation from a specific hydrologic event. Simulate continuous streamflow, effect of transient runoff events on streamflow, evapotranspiration changes in soil moisture, base-flow recharge. Flood hydraulics: predict surface flow in rivers and engineered channels.
	Stream water quality and quantity	WASP4 (US EPA); OTIS-OTEC (USGS); SWMM (US EPA); Mike-11 (Danish Hydraulic Institute)	Point and non-point contaminant source data; concentrations in stream and tributary inputs, temporal streamflow data; channel geometry; sediment/water contaminant partitioning.	Fate and transport of constituents in surface water.
Sediment-Generation Codes	Soil erosion from rainfall and overland flow	Revised Universal Soil Loss Equation-RUSLE (USDA ARS National Sedimentation Laboratory)	Soil characteristics, slope, rainfall/runoff relationship.	Sediment production rates.
Integrated Hydrologic/ Watershed Codes		MIKE SHE (British Institute of Hydrology, Danish Hydraulic Institute); PRMS/MMS (Leavesley et al., 1981; 1983; USGS); HSPF (Bicknell et al., 1997; US EPA)	Same as near-surface process and groundwater codes.	Simulate all components of hydrologic flow regime (snowmelt, overland, channelized, unsaturated/saturated zone flow) and interaction between components.

Table 4. Description of Selected Geochemical Codes Used for Predicting Water Quality at Hardrock Mine Sites.

Category of Code	Available Codes	Special Characteristics	Inputs Required	Modeled Processes/ Outputs
Geochemical Speciation and Reaction Path Codes	WATEQ4F v.2 (Ball and Nordstrom, 1991 and database updates)	Most complete mineral database for acid drainage, redox species; database updates for uranium, chromium, and arsenic redox species.	Variable, can include: concentrations in inflows and other waters of interest (filtered), pH, temperature, redox species concentrations and/or Eh, mass and surface area, identity of minerals, infiltration rates/volume, reactive surface area; bacteria, rate constants.	Estimate concentrations of species in solution, amount of minerals precipitating from solution/dissolving from rock, pH, Eh, amount adsorbed to/desorbed from solids.
	MINEQL (Schecher and McAvoy, 1991); MINEQL+ v. 4.5 (Environmental Research Software, 2005)	Basis for MINTEQ (along with WATEQ); v. 4.5 is windows MINTEQA2 with a user interface for relational databases; temp = 0-50^{o}C, ionic strength <0.5M.		
	MINTEQ (Allison et al., 1991)	Most complete ion exchange and sorption, supported/approved by EPA, with PHREEQE, most often applied to acid drainage problems.		
	HYDRAQL (Papelis et al., 1988)	Speciation, adsorption, organic ligands.		
	Geochemist's Workbench (Bethke, 1994; 1996 - REACT is mass transfer module)	Can include bacteria, Pitzer formulation, evaporation, mass transfer, isotopic calculations, temperature dependence for 0-300^{o}C, sorption, complex kinetics and decoupled redox reactions.		
	PHREEQE/PHRQPITZ (Parkhurst, 1995; Plummer and Parkhurst, 1990); PHREEQC v. 2 (Parkhurst and Appelo, 1999)	With MINTEQ, most often applied to acid drainage problems, includes Pitzer formulation, can define kinetic reactions, mass transfer, reaction path, ion exchange fluid mixing, sorption, solid-solution equilibria, 1D transport, inverse modeling (NETPATH; Plummer et al., 1991; Parkhurst, 1997), carbon isotope compositions.		
	SOLMINEQ.88 (Kharaka et al., 1988); SOLMINEQ.GW (explained in Hitchon et al., 1996)	Most user-friendly, Pitzer, organic ligands, covers temperature range from 0-350^{o}C and 1-1,000 bar pressure, mass transfer options (fluid mixing, mineral precipitation/dissolution, ion exchange, sorption).		
	GEOCHEM (Parker et al., 1995)	Speciation and mass transfer, adsorption, soil-water interactions.		

Category of Code	Available Codes	Special Characteristics	Inputs Required	Modeled Processes/ Outputs
	EQ3/6 (Wolery and Daveler, 1992)	Path-finding, Pitzer, evaporation, solid solution, best documented mass transfer program, kinetics, organic species.		
	SOLVEQ-CHILLER (Spycher and Reed, 1990a and b)	Reaction of fluids with solid phases, mixing of fluids, gases, evaporation, boiling, requires user to define rates and step size for reactant addition.		
	PATHARC (Alberta Research Council; Bill Gunter and Ernie Perkins)	Most user-friendly reaction path program, dissolution/ precipitation kinetics and equilibrium reactions, gases, evaporation; isothermal, does not include solid solution.		
Pyrite Oxidation Codes	PYROX implementation of the Davis/Ritchie shrinking core model (Wunderly et al., 1995)	Simulates diffusion-limited pyrite oxidation only.	Geometry/structure of waste rock dump, pyrite content, particle size distribution, water content of rock matrix, estimates of diffusion rates of oxygen in bulk and rock matrix.	Simulate generation of acid and sulfate from oxidation of sulfides in mine units; results used with kinetic test results to estimate release of metals from oxidation; effects of barometric pumping not incorporated into the models.
	Davis/Ritchie approach (Davis and Ritchie, 1986; Davis et al., 1986; Davis and Ritchie, 1987; Ritchie, 2003)	Simulates oxygen diffusion as only mechanism for pyrite oxidation using analytical solutions.		
	FIDHELM (Kuo and Ritchie, 1999; Pantelis, 1993; Pantelis and Ritchie, 1991)	Simulates oxygen diffusion and convection as mechanisms of pyrite oxidation; output also tracks temperature.		
	TOUGH AMD (Lefebvre et al., 2002; Lefebvre and Gelinas, 1995)	Simulates unsaturated water flow, oxygen diffusion and convection, heat generation and transfer, and solute transport.		
Coupled Reaction Path/Flow Codes	PHREEQM (Appelo and Postma, 1993)	1D, uses PHREEQE, no kinetics, mixing cell, simple.	Variable, can include: infiltration rates, concentrations in inflows (e.g. kinetic test results and background groundwater), moisture contents, reactive surface area, porosity, hydraulic conductivity, soil hydraulic function parameters, diffusion coefficients, dispersivities, bacteria (if used in model),	Fate and transport of constituents in and downgradient of mine waste units, mineralogy, porosity, fluid composition.
	REACTRAN (Ortoleva et al., 1987)	1D, user-defined reaction rates, temperature gradients.		
	MPATH (Lichtner, 1985)	1D, concentration varies only with distance along flow path.		
	MINTRAN (Walter et al., 1994)	2D, uses MINTEQA2 but more rigorous calculation of flow/transport than PHREEQM, for transport in groundwater, assumes total equilibrium between fluid and rock, like PHREEQM, includes shrinking core model and 1D gas oxygen diffusion, kinetics.		

Category of Code	Available Codes	Special Characteristics	Inputs Required	Modeled Processes/ Outputs
	CIRF.A (Potdevin et al., 1992; University of Illinois)	2D, T and P corrections for thermodynamic properties, multiple rate laws; output = mineralogy, porosity, fluid composition, etc.	equilibrium constants, mineralogy of downgradient aquifer and mine unit, secondary mineral-phase formation (from reaction of mine seepage with aquifer minerals), rate constants, sorption/cation-exchange capacity.	
	1DREACT (Steefel, 1993)	1D, finite difference, steady-state and transient, uses rate laws.		
	FMT (Novak, 1993 and 1994)	2D, finite difference, can simulate flow through fractures, Pitzer and Extended Debye-Huckel activity coefficient corrections.		
	TOUGHREACT and TOUGH2-CHEM (Xu et al., 2001)	Can simulate acid generation and buffer reactions in unsaturated media, kinetics.		
	TOUGH-AMD (Lefebvre et al., 2001)	Designed specifically for waste rock and heap leach systems, includes heat generation by acid production and oxygen convection, no attenuation mechanisms.		
	KGEOFLOW (Sevougian et al., 1992)	1D, similar to 1DReact, uses simple kinetic equations, uses EQ3/6.		
	RETRASO (Saaltink et al., 2002)	Kinetics, sulfide mineral oxidation, transient flow, secondary mineral precipitation.		
Coupled Reaction Path/Flow Codes (cont.)	OTIS-OTEC (Runkel et al, 1996, 1999)	1D in-stream solute transport and stream-bank storage combined with MINTEQA2, can simulate redox chemistry and sorption.		
	RT3D (Clement, 1997)	3D, multi-species, reactive transport in groundwater.		
	SULFIDOX (based on Ritchie, 1994; see Appendix 1)	Release and attenuation of acid drainage in waste rock and heap leach pads.		
	MINTOX (Gerke et al., 1998)	Tailings, 2D, sulfide oxidation and transport, diffusive gas transport.		
	MIN3P (Mayer et al., 2002)	Update of MINTOX; Finite element, steady-state and transient, variably saturated, user-set rate laws, diffusive gas transport in unsaturated zone, kinetics, sulfur redox, pH buffering, can define rate expressions.		
	MULTIFLO (Lichtner, 1996)	Comprehensive general-purpose code of reactive transport, kinetic dissolution of aluminosilicate minerals.		

Category of Code	Available Codes	Special Characteristics	Inputs Required	Modeled Processes/ Outputs
	PHAST (USGS)	3D transport; combines solute-transport code HST3D (Kipp, 1998) and iterates at every time step with PHREEQC.		
	CRUNCH (Steefel, 2000; see Appendix 1)	Unsaturated-zone processes, can simulate release and attenuation of acid drainage.		
Biogeochemical and Reactive Transport Codes	BIOKEMOD (Salvage and Yeh, 1998) coupled to HYDROGEOCHEM (Yeh and Tripathi, 1989)	Simulation of reactive transport modeling with biogeochemical transformation of pollutants in groundwaters.		Complexation, adsorption, ion-exchange, precipitation/ dissolution, biomass growth, degradation of chemicals by metabolism of substrates, metabolism of nutrients, and redox, biogeochemical transformations in groundwater.

Alpers and Nordstrom (1999) provide a review of the history of geochemical codes used to simulate water-rock interactions in mining environments. Nordstrom (2004) provides a good summary of geochemical modeling approaches and available codes, some of which are summarized in Table 4. Some of the codes listed are no longer in use and have been superseded by newer versions or by codes that use different approaches. Mayer et al. (2003) provide a history and recent summary of reactive transport modeling. Web resources for obtaining selected environmental codes are presented in Appendix 1.

A general type of modeling that can incorporate hydrologic, geochemical, economic, and other types of codes and models is dynamic modeling. Dynamic modeling can be used to see how systems change over time and can be useful when evaluating oscillating systems and systems with feedback loops. An example of a feedback loop would be the oxidation of pyrite to form ferric iron, which in turn would oxidize pyrite. The filling of an open pit with water after mining can be simulated using dynamic modeling. A dynamic model can be set up so that discharge of pit water to groundwater would occur at a certain pit water elevation or volume, and this in turn would change groundwater chemistry. Dynamic modeling codes vary in cost and complexity, ranging from Vensim to STELLA (probably the most widely used in the mining industry) to GoldSim, which is the most expensive and the most comprehensive of the currently available dynamic models (see Appendix 1). One potential drawback of dynamic modeling is that because there is no standard way to assemble a dynamic model and because they can become so complex (because of pulling in many types of information), they can become difficult to evaluate or replicate. However, for understanding systems with temporal and other types of changes, they are a valuable addition to the modeling toolbox.

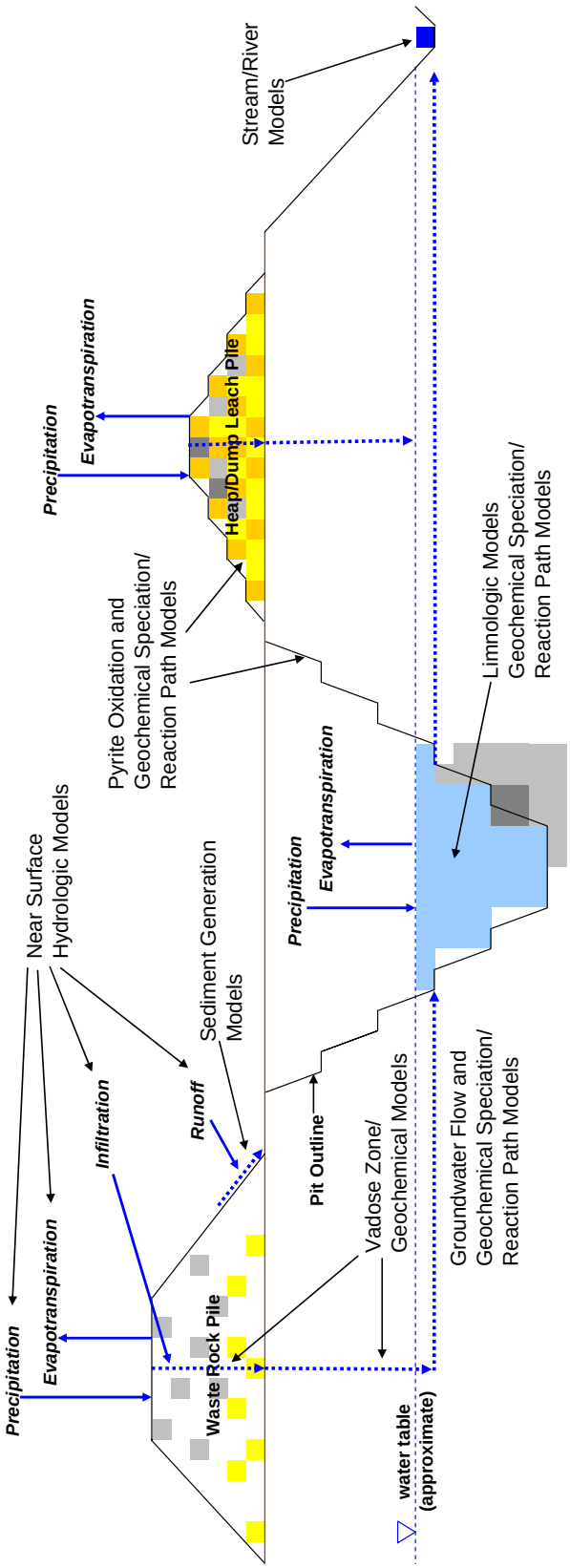

Figure 10. A mine site, pathways, and opportunities for hydrologic and geochemical modeling, using codes in Tables 3 and 4.

7.3 Modeling Water Quality at Specific Mine Sites

The geochemical characterization and modeling tools discussed in Sections 6 and 7 can be used to predict water quality in and from specific mine units or facilities at hardrock mine sites, such as waste rock piles, pits, heap leach pads, and tailings impoundments. The modeling of water quality in or emanating from mine units requires the use of a combination of hydrogeologic and geochemical modeling approaches and inputs from site characterization studies. In some cases, codes have been created to predict water quality from specific mine units. Such codes couple and combine the basic codes shown in Tables 3 and 4 (coupled hydrologic and geochemical codes are also listed in Table 4). As discussed in the following section, there are issues with coupling hydrologic and geochemical processes, as is generally done in facility-specific codes. Modeling of waste rock piles is especially challenging because of physical and chemical heterogeneities and the fact that local equilibrium is not universally applicable (Perkins et al., 1995). Table 5 lists, by mine facility, the types of water-quality predictions that are typically performed using models; the characterization and modeling inputs required for these predictions; the potentially applicable hydrogeochemical codes; and any facility-specific codes that are available.

After the development of a conceptual model and the gathering and checking of model input data, the use of a hydrogeochemical code to predict water quality requires entering site-specific characterization data into a computer code. General step-by-step procedures for predicting water quality related to pit lakes, dry pits, underground workings, waste rock dumps, tailings impoundments, and heap leach facilities are included in this section. Refer to Table 5 for facility-specific inputs to codes (geochemical and hydrologic characterization), potentially applicable hydrogeochemical codes, and available facility-specific codes.

The prediction of water-quality in a mine facility and in downgradient groundwater and surface water involves the following general steps. Depending on the modeling objectives, not all steps may be required:

1. **Develop site-specific conceptual model:** Develop a conceptual model for prediction of water quality from the mine unit of interest (see Section 7.1). Identify all significant processes and pathways that could influence water quality. Also determine the end point of modeling (e.g., composition of pore fluid in tailings impoundment vs. concentrations of constituents at a receptor). The modeling end point will determine which of the following steps need to be implemented.

2. **Characterize hydrogeologic and chemical conditions:**

   - Estimate the length of time that mined materials will be exposed to the atmosphere, based on the mine plan
   - Determine the geochemical test units
   - Characterize the geology, geochemistry, and hydrology of the facility and the site using the relevant tests and procedures described in Table 1, Section 6.4, and Section 7.1.
   - Determine the number and type of hydrogeologic units
   - Estimate sulfide mineral oxidation rates during exposure (ideally using laboratory-measured rates on site-specific materials (e.g., from long-term kinetic testing) or field-scale measurements
   - Evaluate contaminant releases (constituents, rates, and chemical mass load) from mined material using results from kinetic tests and/or water quality samples
   - Assess chemical loads and volume of water from any other water sources entering the facility, if relevant (e.g., tailings pond seepage, process water, stormwater runoff collected from mine area or waste rock, water pumped into the pit to enhance/accelerate pit infilling).

Table 5. Application of Characterization and Modeling Toolboxes to Modeling of Water Quality at Mine Units.

Mine Unit	Water Quality Prediction	Characterization/Modeling Inputs	Potentially Applicable Codes	Available Facility-Specific/Reactive Transport Codes
Pit Lakes and Backfilled Pits (at least partially below the water table)	• Pit water quality over time • Downgradient water quality (if pit lake discharges to groundwater) • Surface water quality (if pit lake discharges to springs, streams, lakes)	• Pit wall mineralogy, specifically sulfide content • Inflowing groundwater quality and quantity; exiting groundwater flow rate • Rate of rise of water in pit • Release rates from wall rock • Release rates from backfill, if relevant • Oxidation rate of sulfides in wall rock • Quantity and quality of water entering pit due to runoff from pit high walls • Precipitation rate • Evaporation rate • Pit dimensions • Pit lake limnology/ hydrodynamics • Mitigation (e.g., enhanced filling, partial backfill) • Groundwater transport characteristics, if pit lake discharges to groundwater • Surface water characteristics, if pit lake discharges to surface water	1,2,3,4,5,7,8,9, 10	• Proprietary codes typically developed by consultants to the mining industry. • There is no publicly available, commonly used model for simulating pit lake water quality, with the exception of MINEWALL (MEND, 1995), but it does not calculate chemical speciation and geochemical reactions in the pit water, nor does CAEDYM (University of Western Australia, 2005).
Underground Workings/Dry Pits	• Water quality in underground workings, if flooded • Runoff/infiltration from dry pits • Downgradient water quality (if underground working/dry pit infiltration impacts groundwater) • Surface water quality (if underground working/dry pit infiltration impacts springs, streams, lakes)	• Wall rock mineralogy, specifically sulfide content • Release rates from wall rock Oxidation rate of sulfides in wall rock • Inflowing groundwater quality and quantity • Rate of flooding of mine workings • Groundwater elevation/depth over time • Groundwater transport characteristics, if UW/dry pit infiltration impacts groundwater • Surface water characteristics, if underground working/dry pit infiltration discharges to surface water • Releases/effects of plugging/backfilling, if relevant	2,3,4,6,7,10	• MINEWALL (MEND, 1995)

Mine Unit	Water Quality Prediction	Characterization/Modeling Inputs	Potentially Applicable Codes	Available Facility-Specific/Reactive Transport Codes
Waste Rock Dumps	• Potential for and quality of seepage from waste rock dumps • Downgradient groundwater quality • Surface water quality (if waste rock seepage impacts seeps, springs, streams, lakes)	• Waste rock mineralogy (sulfide content) • Oxidation rate of sulfides in waste rock • Chemical release rates from waste rock • Quantity and quality of waste rock seepage • Infiltration rates through unsaturated zone • Runoff (amount and chemistry) • Dump dimensions • Physical composition of waste rock dump • Mitigations (cover, liners, etc.) • Upgradient groundwater quality • Distance to water table over time • Distance to surface water • Characteristics of vadose zone and aquifer that affect hydraulics and transport • Groundwater transport characteristics, if waste rock seepage impacts groundwater • Surface water characteristics, if waste rock seepage discharges to surface water	1,2,3,4,5,6, 7,10	• ACIDROCK (Scharer, et al., 1994) • FIDHELM (Pantelis, 1993) • TOUGHAMD (Lefebvre, 2001) • SEEP/W and SOILCOVER (quantity only) • SULFIDOX (See Appendix 1)
Tailings Impoundments	• Tailings pore water quality • Potential for and quality of seepage from impoundments • Downgradient groundwater quality • Surface water quality (if tailings seepage impacts seeps, springs, streams, lakes)	• Tailings mineralogy (sulfide content) • Contaminant release rates from tailings • Dimensions of tailings impoundment • Tailings impoundment water management during mining and post-closure (presence of pool, degree of saturation) • Sulfide mineral oxidation rates • Liner specifications (release/zero discharge) • Surface water proximity • Distance to water table over time • Infiltration rate through unsaturated zone • Characteristics of vadose zone and aquifer that affect hydraulics and transport • Groundwater transport characteristics, if tailings seepage impacts groundwater • Surface water characteristics, if tailings seepage discharges to surface water	1,2,3,4,5,6, 7,10	• WATAIL (Scharer et al., 1993) • RATAP (Scharer et al., 1994) • MINTRAN (Walter et al., 1994) • MIN3P (Mayer et al., 2002)

Mine Unit	Water Quality Prediction	Characterization/Modeling Inputs	Potentially Applicable Codes	Available Facility-Specific/Reactive Transport Codes
Heap Leach Facilities	• Potential for release from heap leach facility (often designed to be zero-discharge) • Quality of runoff/seepage water • Downgradient groundwater quality • Surface water quality (if heap leach pad seepage impacts seeps, springs, streams, lakes)	• Concentrations of constituents in process solutions • Contaminant release rates (from kinetic tests) • Liner specifications (permeability/hydraulic conductivity) • Upgradient groundwater quality and quantity • Dimensions of heap • Distance to groundwater over time, and surface water • Heap leach pad water management during mining and post-closure (presence of pool, degree of saturation) • Infiltration rates through heap after closure • Characteristics of vadose zone and aquifer that affect hydraulics and transport • Groundwater transport characteristics, if heap leach seepage impacts groundwater • Surface water characteristics, if heap leach seepage discharges to surface water	(1,2,3,4,5,6, 7,10)	• FIDHELM (Pantelis, 1993) • TOUGHAMD (Lefebvre, 2001) • SULFIDOX (See Appendix 1)

Refer to Tables 3 and 4 for specific codes.

1 Equilibrium thermodynamic geochemical codes
2 Mass transfer codes
3 Coupled mass transfer/flow codes
4 Pyrite oxidation codes
5 Near surface process hydrologic codes
6 Vadose zone codes
7 Groundwater codes
8 Watershed codes
9 Limnologic codes
10 Stream/river codes

3. **Determine mass fluxes into the facility:**

   - Determine *water balance* for the facility using basic meteorological data and numerical or analytical models. For pit lakes, estimate precipitation and evaporation from lake surface, runoff from pit high walls, groundwater flow rate into and out of the pit (if relevant), discharge rate of any surface water entering or leaving the pit. The water balance can be used to predict rate of inundation of pit walls with groundwater. For underground mines, estimate the rate of flooding of the mine workings. For tailings and waste rock, estimate the infiltration of meteoric water into the facilities.

   - Determine *chemical releases* to the unit from mined material outside of the facility, using short-term and/or long-term leaching data (depending on objectives) or water quality samples. For pits, these releases may be derived from oxidized wall rock, runoff from pit high walls, and possibly waste rock backfill. Oxidation of sulfide minerals in the walls of underground workings and dry pits may also release metals and acid to the environment. Run-on water entering tailings and waste rock facilities may be affected by leaching of upgradient mined or unmined materials.

   - Determine *mass flux rates into facility*. For pits or underground workings, determine the amounts of contaminants entering the facility from surrounding groundwater and run-on by combining fluid flow rates and representative water-chemistry values for each flow component. This provides both a water and chemical mass flux input to the facility.

4. **Determine water quality in the facility:** If water quality samples are available, and the modeling endpoint is downgradient of the facility, modeling of water quality in the facility may not be required. If water quality in the facility is a modeling endpoint (e.g., pore water quality for waste rock, tailings, leach dumps; pit or mine water quality for pit lakes and underground workings), use inflowing water chemistry (if relevant), releases from mined material, and water balance information. A mass-balance geochemical code (e.g., PHREEQE) can be used to mix waters and calculate concentrations of constituents, taking precipitation and adsorption into account. Include an uncertainty analysis in the prediction of water quality. Consider physical, chemical, and biological processes that can change the water quality within the facility. For example, in pit lakes, limnologic conditions in the lake may influence water quality. If relevant, limnologic conditions in the lake can be predicted over time using empirical observations on analogue lakes in the area, or using a numerical or analytical lake model.

5. **Evaluate mass fluxes out of the facility:** Evaluate migration of contaminants from the mine unit. For waste rock, tailings, or dry pits, this could require estimating water and chemical mass fluxes discharging from the bottom or toes of the dump or tailings impoundment, or infiltrating through the floor of the dry pit. For a pit lake or flooded underground workings, the chemical mass flux out of the facility would be the amount of water and quantity of constituents released to groundwater or the vadose zone.

6. **Evaluate migration to environmental receptors:** Environmental receptors include groundwater and surface water resources where water will be used by humans or wildlife, or where water quality standards are relevant (e.g., points of compliance). In some cases, a receptor can be pit water (discussed in 4 above). If considering vadose zone transport to groundwater (mass flux from facility initially enters vadose zone rather than groundwater), use an unsaturated zone flow and transport analytical or numerical code (see vadose zone percolation and contaminant transport codes in Table 3). Downgradient transport of constituents in groundwater can be evaluated using a groundwater flow and solute transport code, or a reaction path code (see groundwater flow + contaminant transport codes in Table 3). For evaluating potential surface water quality impacts, transport and mixing processes can be evaluated using a surface-water-quality code (see stream water quality and quantity codes in Table 3). In some cases, it may be necessary or desirable to link models that simulate water quality in different environmental media (e.g., groundwater and surface water), or to use an integrated hydrologic/watershed model. An uncertainty analysis should be included for the prediction of

water quality and quantity in the unsaturated zone, groundwater, or surface water.

7. **Evaluate effects of mitigation:** Assessing the effects of mitigations on the predicted water quality at downgradient locations may require creating a conceptual model for mitigations. Based on the conceptual model, values for releases of water and constituents from or to the facility can be modified. For example, if a cover will be added to a tailings impoundment at Year 10, the infiltration rates to the impoundment would need to be decreased after Year 10 in the model. Decreasing infiltration rates will affect the flux of constituents leaving the facility and migrating to receptors.

7.4 Sources of Uncertainty in Hydrogeologic and Geochemical Modeling and Recommendations for improvement

The computational capabilities of today's codes and advanced computers far exceeds the ability of hydrogeologists and geochemists to represent the physical and chemical properties of the site or to test the outcome of the model (Nordstrom, 2004; Oreskes, 2000). The degree of confidence in the models is severely limited in part because the models are so complex that they cannot be easily reviewed by regulatory staff and the public. Considering the difficulty in representing physical and chemical properties of mined materials, the meaning of "accuracy" in water-quality modeling must be reconsidered in the regulatory process. Many of the issues in modeling relate to the conceptual model of the mine site and the data used as inputs to the code, which have been discussed in Section 7.1. And, as discussed in the previous section, the uncertainties inherent in predictions should be evaluated as part of the modeling process. Predictions for conditions outside of the calibration data, such as those that occur in transient hydrologic systems (e.g., stream flows), are especially suspect. Regulatory decisions using models should recognize these limitations and be based on a conservative approach that takes into account the likelihood and consequences of all reasonably foreseeable outcomes.

Some of the major issues that affect uncertainty in modeling are discussed in the following section and address: general issues, including coupling of models, timeframe for predictions, and use of proprietary codes; issues related to modeling inputs, including hydrogeologic and geochemical inputs; and issues related to modeling limitations or lack of information.

7.4.1 General Issues

Coupling of models.

Problem Statement: Water quantity and water quality must be jointly considered in predictions of water quality at mine sites. Often, the uncertainty and variability in water quantity and flow are not adequately considered in predictive modeling of water quality. Coupling of water quantity and quality (and different aspects of each) in a reactive-transport model has certain advantages in terms of ease of use but may result in loss of information in dealing with a complex chemical system.

Background: Some codes couple different physical and chemical processes together such as flow, transport, and chemical speciation, whereas other codes simulate a smaller number of closely related processes, sometimes in more detail. The codes that couple hydrologic and geochemical processes are listed in Table 4 under the heading "Coupled Reaction Path/Flow Codes." In addition, some of the codes listed in Table 3 couple different hydrologic processes. For example, codes such as VS2DT and HSPF can simulate near-surface hydrologic processes as well as flow and transport in the vadose zone. These codes are useful in assessing solute transport in unsaturated waste rock and tailings, but they have simplified algorithms for computing the partitioning of rainfall into runoff, evapotranspiration, and infiltration - processes that can be assessed in greater detail and with a more extensive climate record in a code such as HELP. However, HELP contains a more simplified algorithm for simulating unsaturated zone flow. In general, the more sophisticated a code becomes, the more difficult it is to test its reliability (Oreskes, 2000). Coupling hydrologic and geochemical processes in a reactive-transport code can make it more difficult to add or delete a process and to independently choose time steps for the transport and chemistry functions. In addition, changes in one portion of the model, whether geochemical or hydrologic (e.g., calibration of the hydrologic portion of the model), may result in changes in the results that could be wrongly attributed to other processes.

However, coupling of codes in a reactive-transport model will allow the simultaneous treatment of all processes in time, physical space, and chemical reaction space (Mayer et al., 2003).

Recommendations: If separate codes are to be used for different processes or spatial or temporal domains, there must be a careful evaluation of how those codes are coupled so that the output will be useable. Site-conceptual models and modeling efforts should include the effect of varying water quantity on water quality. Often, prediction should be evaluated using both coupled and discrete-process codes to help determine processes that control critical model results, such as the movement of constituents through a waste rock dump.

Timeframe for predictions.

Problem Statement: Hydrologic and geochemical conditions change over time at a mine site. The timeframe over which predictions are made can vary considerably from site to site and for different predictions at the same site. Depending on the timeframe chosen, substantially different modeling results can be obtained.

Background: In many situations, the model-predicted water quality is influenced by the time frame over which the predictions are made. Particularly in arid and semi-arid environments, the impacts of mining on downgradient water quality may be delayed. For example, in waste rock, infiltrating precipitation will result in a wetting front migrating through the dump over time. This wetting front will provide a mechanism for the migration of oxidation products (i.e., sulfate and metals) through the waste rock dump. However, it may take tens to thousands of years for metals to migrate through a waste rock pile and the unsaturated zone and affect downgradient groundwater quality in an arid environment (Kempton and Atkins, 2000; Swanson et al., 1998). Pit lakes with no outflow will evaporatively concentrate over time, with concentrations of constituents of concern steadily increasing (Shevenell, 2000), and the length of time for future forecasts is a technical and policy issue (Kempton et al., 1996). In other cases, water quality may improve over time, due to increased dilution with uncontaminated waters, or depletion of unoxidized sulfide minerals. As an example of the importance of time frame in water-quality predictions, Scharer et al. (2000b) determined, through modeling based on laboratory experiments that the availability of neutralizing potential in mined materials affected the time period for onset of acidification. Simulations with 33% calcite availability began to produce acid after 12.5 years, while piles with 67% of the calcite available started to produce acid after ~30 years. Therefore, using identical simulation methods would produce different conclusions if a short-term (e.g., 10-yr) or a long-term (e.g., 500-yr) simulation period were chosen.
Furthermore, uncertainty in the model predictions increases as the timeframe for forward predictions increases. For longer-term predictions, such factors as global climatic change may influence water quality.

The time frame over which model predictions of water quality are to be made may be determined by a regulatory statute, such as a required period of post-closure monitoring. However, this does not provide assurance that the predictions will be made sufficiently far into the future to include delayed impacts. For example, CERCLA requires an assessment period of 30 years after closure at Superfund sites, and the Nevada Department of Environmental Protection has frequently adopted this timeframe for environmental impact assessments at mine sites. However, particularly in arid and semi-arid environments, impacts may not be predicted to occur for hundreds to thousands of years after mining ceases at a site.

Recommendation: To the extent possible, while still recognizing the uncertainty, predictions must be extended to the timeframe required by the regulatory context (such as 100 or more years for financial assurance determination purposes). However, timeframes for model predictions should not end at an arbitrary cutoff point (based on regulatory guidance or precedent, for instance), but rather should be based on the physical conditions of the modeled system. For example, pit lake chemistry could be modeled until steady state water quality is reached or certain ecological thresholds are exceeded. Models should be used to predict the timing and magnitude of impact from waste rock units even if these impacts are far into the future.

Use of proprietary codes.

Problem Statement: The use of proprietary codes prevents the independent examination by other consultants, regulators, and public interests and creates uncertainty about the legitimacy of modeling results.

Background: Codes used to predict water quality at mine sites can be categorized based on their availability, ownership, and restrictions on use. Some codes were developed by public agencies, such as the USGS and US EPA, and are available, free of charge, for use. These "public domain" codes are typically supported by the government agency that developed them, although they may also be sold and supported by another entity, such as the International Groundwater Modeling Center (IGWMC) or Scientific Software. In many cases, pre- and post-processors (i.e., user interfaces) for public domain codes have been developed to assist model users with developing model input files and viewing and processing the output from the models. Although some pre- and post- processors are available free of charge, many are only available for purchase through a company or other entity. Other codes have been developed by a specific group or company and can be purchased for use from that company or another entity. The code often is sold with pre- and post-processing software, a user interface, and is maintained and supported by that entity. Proprietary codes are developed by a group or company, and are used solely by that company. In general, these codes may not have been verified and have not been widely applied by the modeling community. According to Sverdrup and Warfvinge (1995), a "good" model is one that is transparent (possible to inspect and understand the rules and principles the model is using) and able to be tested (inputs can be defined and determined and outputs can be observed). On both counts, most proprietary codes fall short.

Recommendation: Codes developed by a group or company that are not available for sale or distribution outside of that company should not be used in predicting water quality at mining sites. These codes cannot be verified or tested by those outside of the company. It is uncertain whether such codes accurately simulate the processes that are important for predicting water quality at the mine site. They may have "bugs" that have not been identified by wide code use. Furthermore, because the code itself is not available, it is not possible for a reviewer to reproduce the model simulations. In the same vein, any code that is so expensive that it is not feasible for a reviewer to purchase or lease the code should be avoided. Codes used for prediction of water quality at mining sites should be available for purchase and use by anyone. Similarly, models created using available codes but that do not provide an understandable record of all inputs and approaches should not be accepted for use by regulatory agencies.

In most cases, several widely-available, reasonably-priced codes are available to simulate the relevant processes influencing water quality at mining sites. Some may argue that a specific proprietary code is necessary to simulate a specific process, and that no other more available codes simulate this process. In this case, the importance of the simulated process to the water- quality predictions should be carefully considered prior to selecting a proprietary code.

7.4.2 Issues Related to Modeling Inputs

A number of important issues related to modeling inputs are listed below, with abbreviated problem statements, background, and recommendations.

Hydrologic and hydrogeologic inputs

- *Limited data on aquifer properties*. Predicted contaminant transport rates in the vadose zone and groundwater are highly influenced by hydrologic parameters for geologic units in the models. For example, groundwater velocity is dependent on hydraulic conductivity values assigned to the aquifer materials. Hydraulic conductivity can range over many orders of magnitude, and, therefore, corresponding estimated transport rates can vary over many orders of magnitude. Hydraulic conductivity measurements of aquifer materials are often quite limited and may not be representative of different conditions within the aquifer. Pump tests and lithologic descriptions may provide initial hydraulic and transport parameters, but these must be fine-tuned by calibration. The uncertainty in hydraulic parameters should be acknowledged, and an effort should be made to account for uncertainty in the model predictions, as described in Section 7.1.4.

- *Improper representation of hydrogeologic units*. After a modeler parameterizes the hydrogeologic units, each unit typically is treated as completely homogeneous in the model. Within a hydrogeologic unit, aquifer properties and geochemical characteristics are effectively averaged over the unit. Hydrogeologically complex areas such as those with fractures or variable mineralization may require more units than more homogeneous areas. Alternatively, a

range of aquifer properties and geochemical characteristics can be used for a single unit.

- *Simulation of recharge.* In arid environments, potential evaporation (i.e., the amount of water that could evaporate from a surface if the surface was perpetually wet) is greater than precipitation. However, this does not mean that there will be no infiltration or recharge to groundwater. Even in arid or semi-arid environments, infiltration can occur during precipitation events and be transferred to depths in waste piles beyond the evaporative zone, resulting in infiltration. The timing and nature of precipitation events are key determinants of whether water will infiltrate the surface of the facility or evaporate. The wetting front will move downward into the waste pile over time, bringing with it solutes dissolved from the waste material. The code used to simulate infiltration and percolation of meteoric water into mine facilities such as waste rock dumps must be sophisticated enough to account for infiltration resulting from individual storm events (e.g., HELP, HSPF, PRMS, MIKE-SHE).

- *Handling of preferential flow, macro-pores, and fractures in models.* Many hydrologic models assume uniform soil properties in geologic materials and are unable to simulate macro-pores, preferential flow, and fractures in the vadose or saturated zones, or in a groundwater aquifer. In many mining areas, the subsurface is composed of fractured bedrock. Although codes are available that simulate fracture flow and transport, application of such codes requires an extensive amount of data related to fracture density, aperture, and orientation that is not typically available at sites. In many cases, the fractured rock is assumed to behave as an "equivalent porous medium." This may be adequate for some sites, but could also result in inaccurate predictions of flow and contaminant migration. The inaccurate modeling of preferential flow paths and fractures could result in errors in prediction of flow and contaminant transport rates in the vadose zone or saturated zone. The prediction of flows in springs resulting from dewatering and groundwater rebound after mining are complicated by difficulties in accurately modeling flow along fractures and preferential flow paths. Even the most sophisticated code cannot accurately predict the fine detail of flow of fluids at a mine site, which may encompass thousands of hectares and billions of tons of rock, in the absence of currently-unattainable site-specific data. In many cases, preferential flow, macro-pores, and fractures control real-world flow (e.g., the location of springs), and the inability to model preferential flow represents a major shortcoming in water-quality predictions that must be acknowledged. Additional research is needed in this area if predictions are to be considered at all accurate or useful in determining potential for impacts and identifying mitigations to address such impacts.

Geochemical inputs

- *Completeness of water quality data used in modeling* (Perkins et al., 1995; Alpers and Nordstrom, 1999). Analytical data used to characterize groundwater, surface water, leachate, or porewater chemistry may not include all the important and necessary analytes. For example, if major cations and anions are not included, charge balances cannot be calculated, and a good charge balance is one indication that the laboratory analysis is adequate. A full analytical suite should be used for analysis of leachate from kinetic and short-term leach testing, and any identified constituents of concern should be included in the model. If thermodynamic data for an important constituent of concern is not present in the code, the modeler should consider modifying the database to include that constituent or selecting a code that has thermodynamic data for that/those constituents. If modeling is conducted using a limited water quality database, the user should state explicitly that the results do not adequately consider reactions involving the missing constituents.

- *Elevated detection limits*. For some minor and trace constituents, analytical detection limits can be higher than concentrations that could pose a risk to human health or the environment. For a number of mining-related metals, criteria for the protection of aquatic life can be lower than drinking water standards (e.g., copper, zinc, cadmium, lead), especially in low-hardness waters common in mountain streams. Detection limits should be substantially lower than the most protective and relevant water-quality standards.

- *Incomplete characterization of medium- and long-term environmental behavior of mined materials*. As noted in the geochemical characterization issues section, longer term leaching of metals, acid, and other constituents may not be well represented by results from acid-base accounting, short-term leach, or even kinetic tests. Extrapolation of data applicable to short-term conditions to longer-term conditions will add to uncertainty of longer-term water-quality predictions. Well designed long-term kinetic leaching tests should be conducted on representative materials that pose a potential threat to water quality, and results from these tests (including how leachate concentrations change over time) can be used as inputs to hydrogeochemical models.

- *Use of distribution coefficient (K_d) values in transport models*. Distribution coefficients, or K_d values, describe the tendency of dissolved constituents to adhere to solid surfaces (e.g., soils and aquifer materials) and are only relevant to equilibrium conditions (Stumm and Morgan, 1996), yet they have been used extensively to model fate and transport of kinetically controlled reactions in aquifers. K_d values are often taken from the literature rather than conducting site-specific experiments on adsorption/desorption reactions in alluvial and bedrock aquifers. Their improper use in hydrogeochemical models can produce errors in the prediction of contaminant transport rates in groundwater and of recovery times. Site-specific information on the transport of contaminants in aquifers and mined materials should be used as inputs to predictive models.

- *Application of characterization data as source terms to reaction path/mass balance models*. Steady-state pH values and concentrations from humidity-cell tests are often used as input data for geochemical reaction path or mass balance models. These inputs are used to predict future water quality based on laboratory or field-scale experiments. However, differences in weathering rates and reactants produced under field and laboratory conditions can cause large differences between experimental and actual conditions, especially if reactive surface areas are not included in the model. Applying an across-the-board scaling factor (e.g., 10^{-3} or 10^{-4}) to account for higher oxidation rates in laboratory tests (compared to field conditions) is not warranted without examining the longer term leaching behavior of the wastes. If appropriate long-term kinetic testing has been conducted (see Section 6.4), steady-state concentrations can be used without scaling factors, or site-specific scaling factors can be applied. A number of scaling issues are discussed in Section 6.3.1, Field and Laboratory Discrepancies.

- *Concentrations of contaminants that are affected by seasonal variability* (e.g., seepage and streams downgradient of mine facilities). The timing of precipitation events and other types of climatic processes can affect water chemistry. During dry periods, weathering products (secondary minerals) from the oxidation of sulfide minerals will accumulate in test piles, mine units, and unmined materials (Tremblay and Hogan, 2000). Early snow melt and storm precipitation following a dry period will flush these accumulated products from the piles and result in high concentrations of solutes and generally low pH values, while more continuous rain will result in a more constant volume of acid and other contaminants and lower concentrations in surface water and groundwater (Jambor et al, 2000; Maest et al., 2004). Sampling of mined materials, field-scale characterization tests, and water quality and quantity sampling must at least initially be conducted to capture the variability in seasonal and climatic conditions. A sensitivity analysis using linked end-members of the environmental data (i.e., concentrations and flows most likely to occur under, for example, high and low flow conditions) will better bracket actual field conditions than an average or median value.

8.0 THE STATE-OF-THE-ART IN PREDICTIVE MODELING

Over the last 20 years, the inner workings of hydrologic and geochemical codes have not changed substantially. Hydrologic and geochemical codes still solve the same basic equations and reactions that were identified 80 or more years ago. There have been improvements in the thermodynamic databases used in geochemical codes, in particular for clay mineral dissolution and precipitation and iron oxyhydroxide precipitation, and there have also been additions for the kinetics of dissolution using rate equations established in the laboratory. One of the most notable improvements in both hydrologic and geochemical codes are the operating systems (MS DOS vs. Windows) and the graphic interfaces, which allow more user-friendly operation of the codes and better visual output of the modeling results. In general, there has been movement toward the use of codes that will handle multiple processes simultaneously (e.g., coupled hydrogeologic and geochemical codes).

For modeling at mine sites, the most commonly used groundwater flow code is MODFLOW (MODFLOW 2000), and the most commonly used geochemical speciation and reaction path code is PHREEQE (Parkhurst, 1995; Plummer and Parkhurst, 1990; Parkhurst and Appelo, 1999). However, modelers can chose from a variety of hydrologic and geochemical codes, as shown in Tables 3 and 4, and from a number of coupled codes, as shown in Tables 4 and 5. Individual codes have slight advantages and disadvantages, depending on the application, but the experience of the modeler, the choice of input parameters and data (see Tiedeman et al., 2001 for guidance in selecting model input parameters for hydrologic modeling), and the interpretation of the modeling output are more important than the choice of the code itself.

A generalized flow chart for state-of-the-art modeling of water quality at hardrock mine sites is shown in Figure 11. Many of the steps have been discussed in more detail in Sections 6 and 7. The first step in predictive modeling is to identify the objectives of the modeling and develop a site (or unit) conceptual model (see Figure 7, Section 7.1.1). The next step is to gather geochemical, physical, and hydrogeologic input data for the geochemical test units and receptors (see Figure 7 and Section 7.1.2). An appropriate code is selected for predicting water quality from mine units and in receptors (see Tables 3-5, Section 7.1.1). Much of the input data for the model may already be available, but required inputs for the selected code(s) can help guide additional field and laboratory data collection.

Using site-specific input data, hydrogeochemical modeling is conducted to determine potential concentrations at receptors or other points of interest. A numeric uncertainty analysis should be conducted using possible ranges of input values. Presenting potential contaminant concentrations at receptors as ranges rather than absolute values will better reflect the uncertainty inherent in predictive modeling.

If the modeled ranges of potential concentrations are all below relevant water quality standards, additional mitigation measures will not be necessary (e.g., natural attenuation in aquifers or dilution may be sufficient to limit concentrations in receptors). However, when realistic modeled concentrations at receptors exceed water quality standards, mitigation measures will be necessary to ensure that concentrations of contaminants at receptors meet regulatory requirements. The efficacy of the mitigation measures should also be tested using predictive models and later confirmed with active monitoring. For this analysis, possible ranges in effectiveness of the mitigation measures (e.g., ranges in permeability values of liners) should be used in predictive models. If the mitigation measure is determined to be ineffective at limiting concentrations of contaminants at receptors, alternative mitigation measures should be chosen and tested again, using predictive modeling and active monitoring.

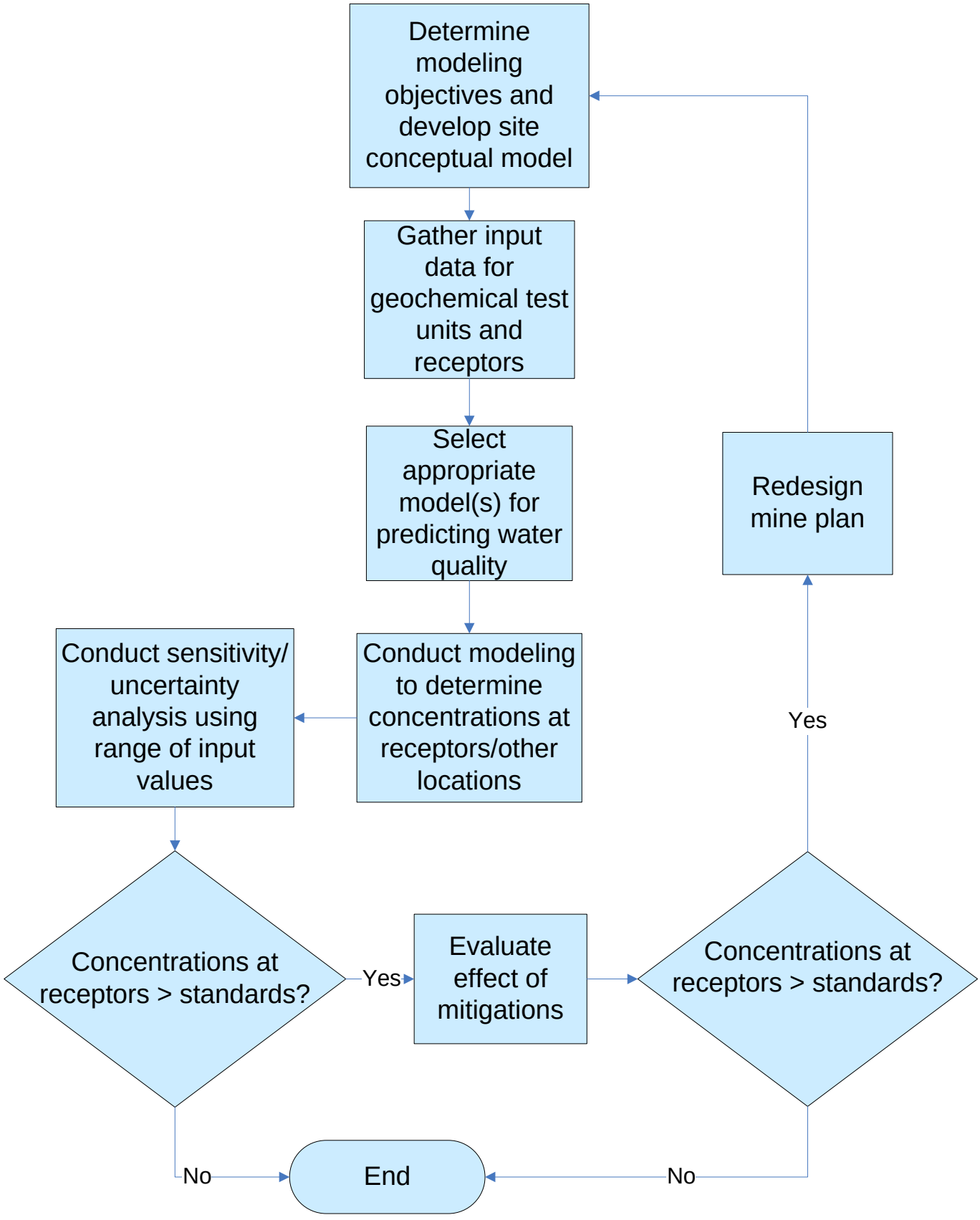

Figure 11. Steps for state-of-the-art predictive modeling at hardrock mine sites.

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Appendix 1. Web Resources for Environmental Models

Because model state-of-the-art and availability changes frequently, this appendix provides a list of web resources that offer up-to-date versions of models as well as the current availability status. This list is not meant to be comprehensive nor endorse any particular agency or vendor, but merely to provide information.

Models available from U.S. government agencies free of charge:

U.S. Geological Survey (USGS) Water Resources Applications Software (http://water.usgs.gov/software/). The software and related material (data and (or) documentation) are made available by the USGS to be used in the public interest and in the advancement of science. Models include assessment tools for groundwater (including the MODFLOW groundwater model and MT3D contaminant transport model), vadose zone flow and contaminant transport (VS2DT), continuous stream flow (HSPF and PRMS), geochemistry (PHREEQC) and water quality (OTIS). Many other models for specific applications are also available.

U.S. Environmental Protection Agency (USEPA) Center for Exposure Assessment and Modeling (CEAM) (http://www.epa.gov/ceampubl/). Models focus on groundwater (PRZM, MULTIMED) and surface water (QUAL2E, SWMM, WASP) quality and contaminant transport.

U.S. Department of Agriculture (USDA) Agricultural Research Service (ARS) (http://www.ars.usda.gov/) develops and distributes models to simulate erosion, crop production, and watershed hydrology. The Hydrology and Remote Sensing Laboratory also distributes the Snowmelt Runoff Model (SRM) that simulates the hydrograph in snowmelt dominated systems.

U.S. Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS), http://www.nrcs.usda.gov/technical/techtools/, develops and distributes the TR-20 and TR_55 single-event rainfall-runoff models.

U.S. National Weather Service (http://www.nws.noaa.gov/) develops and distributes weather forecasting tools and flood models.

Hydrological models available from agencies and other entities for purchase:

Environmental Modeling Systems, Inc. distributes models developed by the U.S. Department of Defense and Brigham Young University including GMS (Groundwater Modeling System), SMS (Surface Water Modeling System), and WMS (Watershed Modeling System) (http://www.ems-i.com/home.html).

ESRI (the developers of the ARC-View and ARC-Info GIS software) have developed GIS based environments for rainfall/runoff models such as the U.S. Army Corps of Engineers HEC models (http://www.esri.com/news/arcuser/arcuser498/hydrology.html).

The Danish Hydraulic Institute develops and distributes watershed models for planning and flood management including MIKE SHE, MIKE BASIN, MIKE FLOOD, and MIKE 11 (http://www.dhisoftware.com).

The Centre for Ecology and Hydrology, Wallingford, United Kingdom develops and distributes a wide range of models (http://www.ceh.ac.uk/).

Waterloo Hydrogeologic distributes a variety of modeling tools and modeling environments for publicly available models primarily oriented toward groundwater (http://www.waterloohydrogeologic.com/index.htm).

Entities that distribute and provide support for models developed by government agencies or companies:

The International Groundwater Modeling Center at the Colorado School of Mines, Golden, Colorado, evaluates and distributes groundwater, geochemical and contaminant transport models (http://www.mines.edu/igwmc/).

Rockware distributes earth science software with more focus on geology, geochemistry and groundwater hydrology (http://www.rockware.com/).

The Scientific Software Group distributes groundwater, surface water and water quality models (http://www.scisoftware.com/).

Boss International develops and distributes public domain models such as the U.S. Army Corps of Engineers HEC models with a custom interface, the Danish Hydraulic Institute MIKE models, and the DOD/BYU GMS, SMS, and WMS models. (http://www.bossintl.com/).

Sources that describe characteristics and identify contact information for a wide range of hydrologic models:

The USGS Surface Water and Water Quality Models Information Clearinghouse (SMIC). Allows downloads of a number of models, including: CE-QUAL, DR3M, HEC, HSPF, MIKE, MIKE SHE, OTEC, OTIS, PRMS, QUAL2E, WASP5, and others. http://smig.usgs.gov/SMIC/SMIC.html

The Hydrological Operational Multipurpose System (HOMS) of the World Meteorological Organization (WMO), Geneva, Switzerland, (http://www.wmo.ch/web/homs/).

The University of Kassel, Germany, irrigation software database (http://www.wiz.uni-kassel.de/kww/irrisoft/irrisoft_i.html).

The University of Kassel, Germany index of ecological models, which contains a detailed section on hydrologic and contaminant transport models (http://eco.wiz.uni-kassel.de/ecobas.html).

The Batelle Memorial Institute environmental software resource list (http://terrassa.pnl.gov:2080/EESC/resourcelist/hydrology/software.html).

The United Nations University surface water modeling software list (http://www.inweh.unu.edu/inweh/environmental_software/surfacewatermodelling.htm).

The InfoMine technology web site (http://technology.infomine.com/hydromine/tools/GWModeling.asp).

Information for Specific Models:

Geochemist's Workbench: www.rockware.com/catalog/pages/gwb.html.

SULFIDOX: www.ansto.gov.au./sulfide/sulfidox.html

CRUNCH: http://wwwearthsci.unibe.ch/ggww/WebCrunch/WebCrunch.htm

RT3D: http://bioprocess.pnl.gov/rt3d.htm

CAEDYM: http://www2.cwr.uwa.edu.au/~ttfadmin/cwrsoft/doc/caedym_science/index.html

MINEQL + v. 4.5: http://www.mineql.com/

Visual MINTEQ (a Windows version of MINTEQA2 v. 4.0, available at no cost from the Royal Institute of Technology, Sweden; supported by two Swedish research councils, VR and MISTRA): http://www.lwr.kth.se/English/OurSoftware/vminteq/

Vensim® PLE: www.vensim.com

STELLA: www.iseesystems.com

ModelMaker: www.modelkinetix.com

GoldSim: www.goldsim.com