A Review of Scale Factors for Estimating Waste Rock Weathering from Laboratory Tests

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ABSTRACT

Authorization to start or expand most hardrock mines now requires the proponents to estimate *a priori* the environmental impacts they may have on surface and groundwater water quality. These estimates are often based on the intrinsic environmental characteristics of mine waste measured in laboratory-scale tests, including total concentrations of major minerals and regulated metals, soluble metals liberated by aqueous leach tests, and rates of sulfide-mineral oxidation and solute release under standard weathering conditions. Waste-rock leach rates under full-scale weathering are then estimated by "scaling" from these laboratory rates to field conditions. This paper reviews laboratory- and field-scale studies of sulfidic waste rock weathering, then provides updated estimates of scale factors based on moisture content, fragment size, temperature, contact (i.e., the fraction of rock actually flushed by unsaturated flow), and oxygen concentration. The results provide a basis for making screening level estimates of mine-water impacts at proposed mines. Further, the ranges in scale factors provide a basis for conducting probabilistic estimates impacts. Ultimately, the goal is to improve mine permitting by identifying the ranges for these critical scale factors that will bracket reliably estimates of pollutant release from full-scale mine waste facilities.

Key Words: Acid rock drainage, scale factor, prediction, waste rock, uncertainty, permitting

Introduction

Authorization to start or expand most hardrock mines now requires the proponents to estimate *a priori* the environmental impacts they may have on surface and groundwater water quality. These water-quality forecasts are required initially to comply with disclosure requirements (such as the U.S. National Environmental Policy Act), and are soon thereafter required to support the permits designed to prevent water pollution (such as issued under the U.S. Clean Water Act). Further, environmental effects relate directly to project financing, which considers cost estimates for mitigation required to comply with water quality permits. At the pre-mining stage, water quality predictions must rely on models using the intrinsic environmental characteristics of mined materials, primarily sulfide mineral concentrations, net acid generating potential, laboratory-scale rates of sulfide mineral oxidation and metal dissolution, and major mineral content in excavated rock. All of these parameters are readily available from tests on materials recovered during exploration. Estimates of full-scale behaviour of mine waste then follow from the geostatistical interpolation of these intrinsic environmental characteristics, providing estimates for (and uncertainty in) the environmental characteristics of rock across the entire deposit. The environmental character of tailings follows a parallel tract, with metallurgical tests on ore producing representative material for environmental testing. These environmental characteristics, when coupled with the mine plans and site-specific climate conditions, provide the basis for predicting water quality impacts using environmental models.

Yet despite active research and the improving understanding of mine waste management, great challenges remain in making these initial water-quality predictions in a manner that is efficient, reliable, and

defensible. A significant problem has been a systematic model underestimate of actual water quality effects reported in audits. A comparison of predicted versus actual water quality at 25 large US mines found that at eight of the nine mines that actually developed acid drainage, modelers had predicted "low acid drainage potential initially or had no information on acid drainage potential" (Kuipers *et al*. 2006). Past errors understandably raise concern among stakeholders near proposed mines. Related to this is the tendency for scientists to overestimate prediction accuracy, in large part by assigning zero uncertainty to all parameters omitted from their model (Morgan and Henrion 1990). To this is added the natural tendency toward increasing complexity—new phenomena are easily added to environmental assessments and tend to remain in future analyses. The result can be longer and more expensive permitting phases for mines as stakeholders request more reliable predictions.

Defensibility in mine permitting increasingly means incorporating prediction uncertainty with impact disclosure. While predictions have essentially no value without some estimate of uncertainty, the increased complexity of probabilistic simulations can reduce transparency and reliability. Analog studies help by improving clarity, providing a basis for calibrating models and illustrating ranges of solute loads to receiving waters at similar waste-rock facilities. But analogs are a trade off, losing detail in site-specific characteristics in exchange for very accurate descriptions of impacts under full-scale conditions. And predictions based on analog sites may well increase uncertainty relative to a computational model of a proposed mine-waste facility. But this too is a trade off, exchanging larger uncertainty in predictions for simplicity and, ideally, acceptance among stakeholders.

This paper provides an updated review of published studies linking the environmental behavior of mine waste under field conditions to the intrinsic characteristics of the rock. The framework for this review is the widely applied concept of using scale factors to extrapolate from laboratory conditions to field scale behavior in waste rock. In this framework, solute releases from laboratory tests are "scaled up" to field conditions by correcting for the effects known to significantly affect oxidation and pollution migration in sulfide mine waste. Specific scale effects considered here are moisture content, fragment size, temperature, contact (i.e., the fraction of rock actually flushed by unsaturated flow), oxygen concentration, and chemical attenuation. These findings, when considered in light of site-specific intrinsic rock characteristics such as sulfide sulfur concentrations, fraction of neutralizing rock, and climate, provide a basis for making screening level estimates of mine-water impacts at proposed mines.

The "scale factor" model for estimating solute release from waste rock

The use of analog waste rock facilities to estimate environmental impacts at proposed mines is predicated on a common conceptual model for how sulfide-bearing mine waste degrades water quality. Chemically, the aeration of the excavated rock introduces oxygen that oxidizes sulfide minerals, producing directly sulfate, and dissolving metals that were bound in sulfide minerals (e.g., iron, copper, nickel, arsenic, etc.) in approximate proportion to sulfate. Pore gas in the rock is generally oxygenated as atmospheric oxygen moves through the rock, often by advection or convection in conductive coarse areas, and by diffusion into less permeable zones; but pore-gas oxygen concentrations can be depleted where oxidation is fast and transport is slow, and oxidation rates are reduced proportionally. Energy released by oxidation will heat the rock, further increasing chemical oxidation rates. Reaction rates are generally proportional to the surface area of sulfide minerals, and oxygen diffusion into fragments or through rinds of wreathing products can limit the oxygen flux to sulfide; thus the rate of oxidation decreases with increasing fragment size. The pore water chemistry generally varies with pH: in pH-neutral zones, produced acid has been neutralized by carbonate or silicate minerals, and metal concentrations are limited by precipitation of secondary minerals and adsorption; in acidic zones, chemical oxidation is much faster and pore-water metal concentrations may be limited only by oxidation rate. Some meteoric water will percolate into the waste rock, but the unsaturated flow passes preferentially, through finer fragments in dryer climates and coarser fragments in wetter climates, so acid and metals in finer materials are preferentially rinsed and produce the seepage to surface or groundwater.

The scaling factor concept described herein follows generally the concept described by Malmstrom *et al*. (2000), which assumed that these basic controls on mine waste reaction — fragment size, temperature, water flow, and oxygen concentration — could be "scaled-up" from laboratory tests to estimate solute release from full scale waste facilities. Key laboratory static analyses are sulfide sulphur (acid-generating potential), carbonate carbon (acid neutralizing potential), and acid and metals dissolved by oxidation (typically measured by hydrogen peroxide digestion). Humidity cells then indicate rates of oxidation and solute release under oxygenated moist conditions at 20 °C, ideally measuring rates in material spanning a wide range in sulfide mineral concentration and pH. Geostatistical models of deposits can then extend these environmental parameters so that each block of waste rock has an estimate for intrinsic solute release rates.

For a single parcel of waste rock under field conditions, the pollutant release rate, R_{Field}, follows from the lab rate, R_{lab}, and "Scale Factors":

$$R_{Field} = R_{Lab} * SF_{moist} * SF_{size} * SF_{contact} * SF_{temp} * SF_{O2} \qquad \text{Equation 1}$$

Where the lab-to-field Scale Factors are:
SF_{moist}: the reduction in oxidation that can arise when moisture becomes too low to support chemical oxidation,
SF_{size}: The reduction in field oxidation due to larger fragment sizes,
$SF_{contact}$: The reduction in solute leaching from fragments too coarse to be flushed by pore water,
SF_{temp}: the change (increase of decrease) in oxidation rate caused by field temperatures higher or lower than lab tests,
SF_{O2}: The reduction in field oxidation rate caused by reduced O2 concentration in pore gas,
These factors are presented in this paper as fractions for field conditions relative to laboratory conditions. The effect of chemical attenuation of pollutant due to pore-water composition is often studied in field applications, but is discussed here only conceptually.

Broad application of the scale-factor approach warrants some caution. First, water quality estimates using a facility-wide scale-factor approach provide only facility-wide average behavior. Waste rock effluent water quality varies temporally and spatially. A study at the Mine Doyon (Quebec, Canada; ~7% pyrite by mass [Lefebvre *et al*. 2001]) "revealed strong temporal (dry period vs. recharge period), and spatial (slope vs. central region of pile) variability in the formation of acid mine drainage" (Sracek *et al*. 2004). Second, some scale factors are not entirely independent, so combining scale factors can double count some effects. In particular, coarse rock in end-dumped slopes will carrying minimal unsaturated flow in all but the wettest climates (Newman *et a*l., 1997), and solute loads in Equation 1 should not also be reduced further by slow oxidation in the large fragments that have already been eliminated based on conductivity.

This scale-factor approach was demonstrated clearly in a study of the Aitik mine site in northern Sweden, where small-scale (0.15 kg), short-term (20 week or longer), kinetic tests at room temperature were scaled to larger columns (1.82×10^3 kg, aerated and with constant water flow, and operated for 85 weeks at temperature of 4 to 10 °C) and full-scale field piles (9.5×10^{10} kg), where effluent load was determined from water recovered from drainage ditches with temperatures ranging from 1 to 4°C (Malmstrom *et al*. 2000). The study indicated that "the scale dependence is to a large degree predictable by quantification of the effects of a few critical and readily available, bulk-averaged, physicochemical characteristics."

A second study compared oxidation rates in large-scale kinetic tests (20- to 30-tonne piles of run-of-mine rock) against laboratory-scale kinetic tests in a temperate climate, where temperature scaling was less important (Bennett *et al*. 2000). The study found good comparison between laboratory kinetic tests and field scale piles in terms of sulfate production rate per kg of rock (ranging from 1×10^{-9} to 1×10^{10}

kg(O_2)/kg(rock)/s). This consistency in field-to-lab comparisons led the authors to conclude "oxidation rates measured in the laboratory can be confidently applied to full-size dumps if the materials tested in the laboratory represented the composition of the dump" (Bennett *et al*. 2000)

These lab-to-field comparison studies provide a rough estimate of prediction accuracy and the magnitude of the various scale factors. At the Aitik Mine full-scale tests, the factors producing the greatest effect on lab-to-field scaling, from largest to smallest, were temperature, particle size, specific mineral concentration, and surface area of minerals (Malmstrom *et al*. 2000). For pyrite oxidation, the total estimated lab-to-field scale reduction factor for solute release was approximately 50, and the discrepancy between predicted and observed field-scale results was approximately 20%. The scale effects were similar for trace metals based on copper release from chalcopyrite reaction rates; the lab-to-field scaling factor was approximately 50, but the discrepancy between observed and predicted field-scale results was much larger, at 500 to 1,000 % (i.e., factor of 5 to 10 error), apparently due to complex metal attenuation processes. In the present literature review, these scale factors are extended to include the effects of low moisture and pore-gas oxygen.

Parameter Ranges for Water Quality Modeling at Hard Rock Mining

Presented here is a discussion of each scale factor. The discussion starts with an explanation of how and why the effect alters reaction rates or transport under field conditions, followed by ranges for the scale factor based on parameters collected from published studies.

Moisture content effect on oxidation rate

Measurements of mine waste under field conditions indicate that moisture is unlikely to appreciably limit oxidation in waste rock or pit wall rock in any but the most extreme arid climates. Hollings *et al*. (2001) found that oxidation rates decreased when gravimetric moisture increased above ~10%, apparently because water reduced oxygen transport. Pyrite oxidation in waste rock does in fact slow dramatically at low moisture. A study focused on drier conditions found oxidation rates steady at gravimetric moisture between 10% and 2%, but then decreasing by ~85% at 1% moisture (Kempton *et al*. 1997). Moisture profiles through waste rock in Arizona, US, where potential evaporation [~180 cm/yr] was ~8 times greater than precipitation [23 cm/yr], indicated that moisture in the pile at hydraulic equilibrium waste was ~ 4% to 6%, which is not low enough to inhibit oxidation, and that surface drying from uncovered waste rock extended only to ~1 m (Swanson *et al*. 2000). Approximately 30% of the rock below 1-m depth had gravimetric moisture below 2%. However, this drier rock was still reactive, with ~1% moisture. Unless a closure cover effectively restricts infiltration, the waste rock should eventually wet up to the ~4 to 6% gravimetric moisture, which is high enough that sulfide mineral oxidation will not be restricted by low moisture. In general, low moisture will, therefore, not restrict oxidation in waste rock. This finding extends to pit walls, where reactive fracture zones (1 to 15 m thick) are usually far thicker than the zone affected by seasonal drying (Kempton and Atkins 2009). The SF_{moist} should thus be 1 unless site conditions demonstrate that *in situ* waste rock will be dryer than ~2% gravimetric moisture.

Fragment size effect on oxidation rate

Published studies report that sulfide mineral oxidation rates in mine waste decrease dramatically with increasing fragment size, consistent with the proportionality between surface area and heterogeneous reaction rates. Models based on diffusion-limited oxidation into shrinking-core spheres demonstrate fragments greater than 200 mm contribute very little to total waste-pile oxidation, even after hundreds of years (Davis and Ritchie 1987). More recently, studies have found that only waste-rock fragments less than ~ 20 to 30 mm are flushed by percolating water, reducing the oxidation focus to this small size. In rock from the Cluff Lake Mine, Canada, oxidation rates (based on O_2 consumption) vs. diameter in uniformly sized waste-rock at 20 °C indicated that the 13 mm fraction was only ~ 30% as reactive as the 1 mm fraction, and the 25 mm fraction only ~20% as reactive as the 1 mm fraction (Hollings *et al*. 2001). A second study, which measured oxidation rate (based on sulfate release) vs. fragment size in mine waste

rock, found that the cumulative <25 mm fraction released 80% of the total sulfate compared to larger material of 25 to 76 mm diameters (Stockwell *et al*. 2003).

Surface area measurements (based on geometry in fragments >6.3 mm and BET nitrogen adsorption in less than 6.3 mm) for five field-scale barrel tests (275 to 325 kg in each, 100 mm maximum diameter fragments) at the Antamina Mine, Peru, indicated that 65% of the surface area was in material < 6 mm (35% gravimetric fraction), and 88% of the surface area in material < 20 mm (55% gravimetric fraction Aranda *et al*. 2009).

Scaling to correct for fragment size in waste thus has two components:

- Scaling the oxidation rates in the fraction flushed by water (<20 mm diameter [Neuner *et al*. 2009]) to the entire pile; and
- Scaling the oxidation rate measured in humidity cell tests (<6.4 mm diameter) to estimate the slower reaction rates in the entire fraction flushed by water (<20 mm diameter).

This first component follows directly from fragment size distributions in waste rock (Figure 1), but the second component (i.e. scaling for reactivity) can be achieved using small fragments in laboratory-scale measurements.

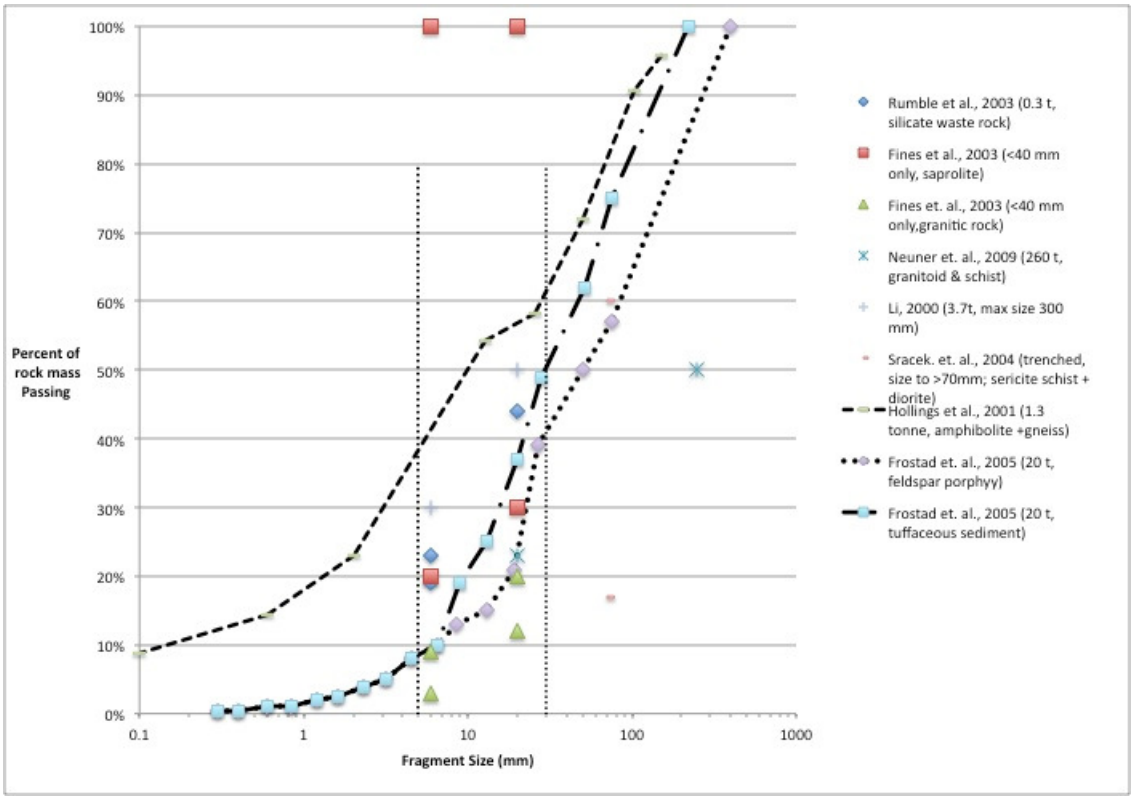

Figure 1. Fragment size distributions reported for large samples of waste rock. The most representative run-of-mine samples shown with connected lines.

The surface area study of waste rock at the Antamina Mine by Aranda *et al*. (2009) illustrates a method for scaling from the <6.4 mm fraction to the <20 mm fraction. This study reported that:

- 65% of surface area is in material < 6 mm (35% gravimetric fraction),
- 88% of surface area is in material < 20 mm (55% gravimetric fraction).

The ratio of *surface area : mass* in the <6 mm fraction is 1.9 (i.e., 65% of area / 35% of mass), which is ~1.2 times greater than the ratio of *surface area : mass* for the <20 mm fraction (i.e., 88% of area / 55% of

mass = 1.6). Thus the scale factor for converting reaction rate in humidity cells (<6 mm diameter) to reaction rate in the rock that will be flushed by water (<20 mm size fraction) is ~1/1.2, or ~0.83.

Estimates of fragment-size distributions in waste rock vary widely primarily due to the small number of sieve analyses on large run-of-mine rock samples, and the variable effect of blast methods and rock strength. However, a review of published studies of fragment size distribution in large-scale (e.g., tens to hundreds of kg run-of-mine rock) identified the following relevant results (Figure 1):

- Modeling study of full-scale waste-rock facilities (Davis and Ritchie 1987)
    - 90% of the material less than 200 mm
- Large-scale column tests (1.2 m diameter, 2 m height, mass = 1.2 to 3.7 tonne; Li 2000)
    - 50% of rock less than 20 mm
    - 30% of rock less than 6 mm
- Large-scale waste rock sieve analysis, low-strength friable schist waste-rock at Mine Doyon, Canada (Sracek *et al*. 2004)
    - Between 17% and 60% of the rock fragments greater than 70 mm
- Large-scale sieve test (1,300 kg sample) from waste rock at the Cluff Lake Mine, Canada (Hollings *et al*. 2001)
    - 58% of rock less than 20 mm
    - 23% to 40% of the rock less than 6 mm
- Sieve of 0.5 m cubic excavation from waste-rock at Ok Tedi Mine, New Guinea (Rumble *et al*. 2003)
    - 45% less than 20 mm diameter
    - 23% less than 6 mm diameter
- Large-scale sieve analysis of very weathered (saprolite) bulk waste-rock sample, South Carolina, US; (Fines *et al*. 2003)
    - 30% to 100% of rock less than 20 mm diameter
    - 20% to 100% of rock less than 6 mm diameter
- Large-scale sieve analysis of granitic bulk waste rock sample, Sudbury, Canada; (Fines *et al*. 2003)
    - 12% (granitic rock) to 20% (volcanic rock) less than 20 cm
    - 3% (granitic rock) to 9% (volcanic rock) less than 6 mm
- Large-scale (20 tonne) sieve analysis of rock subjected to field kinetic tests (Frostad *et al*. 2005):
    - 20% to 35% of waste rock is less than 20 mm diameter
    - 10% of waste rock less than 6 mm diameter
- Large-scale (two test pads, 15 m high and 60 m x 50 m) field experiment at the Diavik Diamond Mine, Northern Canada (Neuner *et al*. 2009):
    - 23% of the rock less than 20 mm

Temperature effect on oxidation rate

The effect of temperature on oxidation rate is described by the Arrhenius equation:

$$k = Ae^{[-Ea/RT]} \qquad \text{Equation 2}$$

Where:

k = reaction rate [1/s, or same units as used for A]
A = empirical constant, determined at given temperature [1/s]
Ea = activation energy of the reaction [kJ/mole]
R = Universal gas constant [0.008314 kJ/mole/K]
T = temperature [Kelvin]

The factor to correct reaction rate measured under laboratory conditions to field temperature is derived by dividing the Arrhenius equation under field temperature by the equation at laboratory temperature

(Malmstrom *et al*. 2000):

$$k_{field}/k_{lab} = e^{[-Ea/R[(1/Tlab - (1/Tfield)]} \quad \text{Equation 3}$$

The activation energy of pyrite oxidation varies from 50 to 88 kJ/mole for a variety of experimental conditions [Nicholson *et al*. 1988], and the value between 20-40 °C was measured to be 56.9 ± 7.5 kJ/mole (McKibben and Barnes 1986). The reported activation energy for the oxidation of pyrrhotite is between 47 and 63 kJ/mole (Nicholson and Sharer 1998).

In practice, a simpler estimate of the change in oxidation rate with temperature is often described as the "Q10", which is the change in oxidation rate with a change in temperature of 10 °C. The Q10 for pyrite oxidation has been reported to be between 2 and 3 at temperatures between 3 and 25 C (Nicholson *et al*. 1988). Ideal temperatures for iron-oxidizing bacteria are between 25 and 45°C, though some thermophilic bacteria thrive between 60 and 80 °C (Hiskey and Schlitt 1981)

Elevated temperatures in waste rock are observed in a wide range of climates. In semi-arid climates (e.g., Nevada, US), studies of field-scale waste rock piles include one report with steady temperatures of ~20-40 °C through the year (~10-30 °C above ambient air), indicating active oxidation across the entire depth (up to 39 m deep; Milczarek *et al*. 2009). Another study in older sulfide bearing waste rock at the Robinson District found rock temperature ~6 °C above ambient and ~50% reduction in oxygen; temperatures 10 – 20 °C above ambient conditions were observed in oxygenated facility edges (Helgen *et al*. 2000). Unfortunately, neither of these studies report sulfide sulfur content in the rock. In wetter climates, the Mine Doyon waste-rock facility (Quebec, Canada; ~7% pyrite by mass, ambient air temperature ~5 °C) has zones with advective oxygen flow that maintain rapid oxidation and internal temperatures of 45 to 70 °C over the 6 to 30 m depth interval (Sracek *et al*. 2004). However, in zones where oxidation is diffusion-limited and thus slower, overall average temperatures vary less and are closer to ambient air temperature. The Nordhalde waste rock (Germany; ~3 % pyrite by mass) has internal temperatures of 15 – 20 °C (6 to 11 °C above ambient air temperature (Levebvre *et al*. 2001). In arctic conditions, the well-studied Aitik Mine waste rock in Sweden (average air temperature ~0 °C, average gravimetric pyrite content ~1 % [range 0 – 5%]; Bennett *et al*. 1994) is well oxygenated throughout the dump (Malmstrom *et al*. 2000), but has internal temperatures of only 1 – 4 °C. Finally, in very wet climates, a study of waste rock at the Mt. Lyle Mine (Tasmania, average air temperature ~11 C, average gravimetric sulfide S ~5%, rock age ~40 years at time of study) found temperatures of 10 to almost 30 °C above ambient through the rock (monitored from surface down to 30 to 40 m; Garvie *et al*. 1997). Calculations based on thermal and oxygen profiles indicated that reactive pods that comprised ~15% of the rock accounted for ~70% of the total oxidation. Scale factors for temperature can thus range from ~0.3 or lower in artic conditions (e.g., 0^{o}C or colder) up to ~6 (i.e., corresponding to ~40^{o}C) in well oxygenated sulfidic waste rock.

Water contact: fraction of waste flushed by unsaturated flow

The internal structure observed in waste rock facilities produces enormous zonal variability in unsaturated hydraulic conductivity. Careful excavation and study of mine waste finds compacted horizontal layers develop by heavy equipment, and the structure created by end-dumping, including a basal layer of coarse boulders and lenses on angle-of-repose slopes (~40 degrees) that are 10 – 20 cm thick with extreme variability between adjacent layers (Herasymiuk 1996, Newman *et al*. 1997). Studies using unsaturated-flow models and column studies of waste rock structures demonstrate that unsaturated flow is conveyed preferentially through fine materials at low water flux typical of capped waste rock facilities (Newman *et al*. 1997; Fala *et al*. 2003). A similar study of waste-rock hydrology concludes that "transient water flow in mine waste-rock reflects the summation of water flow and transport in multiple pathways of varying properties . . . that range in scale from macro-sized variations in properties to differences in properties at the pore scale" (Marcoline *et al*. 2003). Ideally, preferential flow layers can be designed to isolate

reactive waste (Fala *et a*l. 2003); but at pre-feasibility planning stage, a simple range for contact factors may be adequate.

Two studies measured average water contact factors in field scale waste rock. At the Aitik Mine (Sweden), hydrological tests using unreactive tracers found that approximately 65% of the water in the field-scale waste rock was mobile and 35% was immobile (Malmstrom *et al*. 2000). At the Island Copper Mine (Vancouver, BC, Canada), the effluent at the toe of the waste-rock was correlated with precipitation events, and interpretation using a kinematic wave-theory model estimated that "…approximately 42% of the total area of the pile contributes to flow through channels or macropores", with "…only a small fraction of the water lost to the porous matrix from these channels" (i.e., $SF_{contact}$ ~42%; Lopez *et al*. 1997).

Additional research has demonstrated that this preferential flow usually occurs in small fragments, a finding that yields a parallel approach for estimating the contact factor. Hydraulic tracer studies (Br^- and Cl^-) of waste rock at the Diavik diamond mine indicated that under unsaturated conditions, flow occurs primarily through material that is less than ~20 mm (Neuner *et al*. 2009). Another detailed study of two waste-rock piles (one in a wetter temperate climate, South Carolina, U.S.; the other in a seasonally frozen climate, Sudbury, Canada) found that materials between 5 mm and 30 mm were most effectively flushed, and that materials above this size showed evidence of accumulation of oxidation products (Tran *et al*. 2003). Particle size distributions in run-of-mine waste rock indicate that the 5 to 30 mm size fractions can correspond approximately to the 0.1 to 0.6 mass fraction (Figure 1). Conveniently, the upper estimates for the fragment size carrying moisture (i.e., up to 20 mm in Neuner *et al*. (2009) and up to 30 mm in Tran *et al*. (2003)) are close to the maximum size contributing appreciably to sulfide oxidation. Therefore, correcting for the reactive size fraction in waste rock can eliminate the need to correct for water contact fraction.

An important caveat in assuming that solutes released by oxidation in coarse fragments (e.g., greater than ~30 mm) are permanently immobilized is the risk that these salts could be flushed out during infrequent larger storm events that produce flow in larger pores. A review of various studies of water discharge from uncovered mine waste-rock (Stockwell *et al*. 2003) reported that "…rapid outflow within hours of infiltration through tens of metres of waste-rock has been observed at numerous field sites . . . and in large-scale experiments . . . and that chemical analyses of outflow waters indicate differences exist between slower and faster moving waters." This is consistent with observed water flow through the waste rock at the Island Copper Mine, where effluent at the toe of the waste-rock was correlated with precipitation events (Lopez *et al*. 1997). One of the few specific examples was a tracer study at the Diavik Mine, which found that 15 mm rainfall event over 1.5 hrs did not produce macropore flow, but that a 29 mm event over 3.8 hours may have produced some flow in preferential paths (Neuner *et al*. 2009). As a result, the assumption that large waste-rock fragments (e.g., >30 mm diameter) remain isolated from percolating pore water is most defensible in reclaimed waste rock where covers dampen water flux and prevent storm-induced flushing of pollutants accumulated in coarse fragments. Collectively, these field measurements suggests a wide range for $SF_{contact}$, from ~0.1 to 0.65, with even higher values possible in rock with highly variable water flux.

Oxygen concentrations in waste rock

Oxidation rates in mine waste are approximately proportional to oxygen concentrations in diffusion- and kinetic-limited mine waste (Davis *et al*. 1986; McKibben and Barnes 1986), so the fraction of macro scale zones with depleted pore-gas oxygen is a basis for scaling down oxidation rates under field conditions. Waste rock facilities are typically heterogeneous, and gas transport occurs through a complex mix of advection, diffusion, and convection (e.g., Garvie *et al*. 1997; Fala *et al*. 2003). While computational models can mimic these phenomena, their accuracy is not widely demonstrated, and at a feasibility stage, the volume fraction of oxygen-depleted waste rock may be estimated best using ranges at analog facilities.

The wide variability in measured pore-gas oxygen distributions in field-scale waste rock facilities reflects the effects of intrinsic reactivity, temperature, and advective flow. At Nordhalde, Germany (~3 % pyrite by mass, ambient air temperature ~9 C), oxygen flux is diffusion limited, and O_2 is depleted within ~15 meters below the surface and near zero to the total 70 m depth (Lefebvre *et al*. 2001). Lefebvre *et al*. contrast this to the Mine Doyon, Quebec, Canada (~7% pyrite by mass, ambient air temperature ~5 °C), which is dominated by advective flow, producing average oxygen concentrations of approximately 10% through the pile (i.e., approximately 50% reduction below 21% atmospheric oxygen; Sracek *et al*. 2004). Rock in semi-arid climates exhibits similar reactivity and associated oxygen depletion. Borings near angle-of-repose slopes at one Nevada, U.S. mine found oxygen concentrations near atmospheric (21%) through the entire depth (23 to 69 m), but at 400 m back from exposed slopes, oxygen partial pressures diminished to between 0 and 10 % (Milczarek *et al*. 2009). Studies at another Nevada mine indicated oxygen concentrations of 10 -15% in most of the vertical profiles in young sulfide rock (9 m to 30 m total depth; Helgen *et al*. 2000). (Sulfide sulfur was not reported in either Nevada study). Finally, studies at the Mt. Lyle Mine, Tasmania (average sulfide S ~5%) found that advective flow maintained oxygen at atmospheric concentrations in most of the waste rock between 0 and 40 m below the surface, but that reactive zones comprising 20% to 80% of vertical profiles were completely depleted in oxygen (Garvie *et al*. 1997). For prediction purposes, assuming SF_{O2} values less than 1 are warranted primarily in rock with sulfide S concentrations of ~1% to 5% (or higher). In these conditions, SF_{O2} ranges between ~0.2 and 0.5 appear reasonable, though facility designs that inhibit convective air flow could create even lower values.

Solute attenuation effects in mine waste effluent

A computational method that reliably brackets the concentrations of major ions and trace elements in effluent from oxidizing sulfidic mine waste remains elusive. In developing an approach, there is a strong incentive to link metal release to sulphate production. Sulfide oxidation is a well-studied and measurable parameter, and many regulated metals are bound as sulfides and thus dissolve in proportion to sulphate. However, extrapolating the dissolution of each metal independently from short-term kinetic tests often produces enormous mass-balance errors and neglects entirely solution charge balance. A partial remedy is to bracket the *solute: sulphate* ratio in leachate between slight oxidation (e.g., cumulative leachate during a 20-week kinetic test) and complete oxidation (peroxide oxidation extraction), then maintain charge balance in estimates of average solute composition by bootstrapping from complete water analyses (Kempton *et al*. 2009). But this simplification does not incorporate temporal changes in water quality as oxidation proceeds.

Promising approaches used to predict trace metal concentrations in mine waste leachates include: 1) measurements of metal:sulphate dissolution ratios using stepwise partial-oxidation extractions, 2) identification of solubility caps using sequential equilibration of leachate with partially-oxidized mine waste, and 3) equilibrium geochemical models calibrated to these dissolution and attenuation tests.

Recommendations

Screening level estimates of waste-rock pollutant production based on scaling factors and analog sites will have large uncertainty. Considering only the fragment sizes identified as carrying the majority of unsaturated flow (from <5 to <30 mm) and the fragment size distributions in waste rock (Figure 1) produces an almost 8-fold range in contact factors (i.e., from 0.08 to 0.6). A large component of uncertainty is timing of pollutant discharge. The duration over which solutes will leach from waste rock is poorly constrained, but is typically estimated in decades to centuries, and two of the effects that can scale down initial reaction rates - temperature and oxygen concentration - result in extending the duration of pollutant release.

Environmental analyses should focus early on refining values for those parameters that will improve the accuracy in extrapolating laboratory tests to full-scale conditions. Determination of the waste rock water

balance and unsaturated flux supports identification of the size fraction of the conductive material that will carry most pore water under site conditions. Oxygen consumption tests can be quick and inexpensive method to measure oxidation rates in waste (Hollings *et al*. 2001); these should be conducted on samples over a wide range of fragment sizes, sulfide sulfur concentrations, pore water pH, and lithologic types.

Consider early development of a method that estimates the dissolution and attenuation of metals and anions from waste rock and tailings over the entire period that it oxidizes. This is most easily bracketed between minimal oxidation (humidity cells) and complete oxidation (peroxide oxidation), but could include interim stages of reaction. Helpful attributes of effective models include empirical tests of solute release at different stages in sulfide oxidation (maintains mass balance on pollutant sources), tracking sources as linear combinations of complete aqueous analyses (maintains charge), simulating transport and attenuation using an equilibrium chemical model with mineral phases fit to the empirical tests (maintain mass and charge balance), and estimating loads from waste as convolution sums of rock parcels that are drawn from the geologic block model (source represents the entire deposit). Ideally, any solute release model would allow propagation of parameter ranges to yield prediction uncertainty.

Finally, simple engineered designs can reduce oxidation and/or solute release. Principal among these are configurations that use preferential flow in fine fragments to divert water around reactive waste (Fala *et al*. 2003) and low-permeability layers on waste slopes to reduce advective air flow; but full-scale examples of waste constructed using these remedial designs were not identified in this review.

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