Humidity cell tests for the prediction of acid rock drainage

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Abstract

This paper presents a study of various geochemical humidity-style weathering tests that were carried out on waste mine rock from Avoca, County Wicklow, Ireland. The aim of this paper is to present data that demonstrate some of the geochemical controls on weathering rates together with release rates from laboratory testwork. These data are used to determine the applicability of various interpretations of humidity cell data for prediction of acid rock drainage. Furthermore, within this context the paper offers opinion on common questions related to the use of such tests: should humidity cells be aerated? How long should the test be run for? Is pre-treatment of the samples required? Is inoculation of the samples with iron and sulfur oxidising microbes required? And should these tests really be considered to be accelerated weathering tests?

1. Introduction

This paper concerns the use of humidity cell and similar leaching tests for the prediction of acid rock drainage (ARD). ARD (also known as acid mine drainage, AMD) is contaminated effluent resulting from the oxidation of iron-sulfide minerals when exposed to oxygen and water due to mining and other earth works. If the rate of acid generation due to sulfide oxidation is in excess of acid consumption by neutralising minerals then low pH mine water results. In addition to the acidity produced, the consequent solubilisation and mobilisation of metals at low pH can lead to severe impact to the receiving environment. ARD from mining operations is one of the most problematic environmental issues facing the mining and minerals industry. Once ARD begins, the process is extremely difficult to halt and long-term treatment of mine waters is often required to protect the environment. By predicting mine-waste drainage quality prior to the inception of mining, plans for mineral-resource development and mine-waste management can be made that minimize adverse environmental impacts throughout the lifetime of the working mine, and after mine closure. The task of prediction is often hindered by the complex rock types encountered and the proliferation of proposed test techniques to predict whether or not a specific rock type will produce acid. Nevertheless, a number of test techniques are commonly used to aid in the prediction of ARD. Humidity cell test work involves periodic leaching of a rock sample (typically 1 kg) over time; the generated leachates are analysed, typically for pH and dissolved constituents (Lapakko and White, 2000; White and Lapakko, 2000). The data generated from these tests are used in the prediction of ARD. The objective of this paper is to present data from a study of humidity cell and humidity cell-style tests, and using these data to examine controls on weathering rates and release rates and the consequent applicability of various common methods of data interpretation. In addition, opinions are advanced on some common and often debated questions together with recommendations for the use of humidity cell tests and the data that they generate.

The general process of prediction involves two steps: (1) identify and describe geological materials and (2) predict their ARD potential (Price, 1997). The most widely used tests to quantify ARD potential are ‘static’ tests and ‘kinetic’ tests. The ultimate goal is to use static and kinetic tests in conjunction with other relevant data to assist in developing strategies for the environmentally sound management of mine wastes (Lapakko, 2003). Kinetic tests are weathering tests conducted to aid prediction of drainage quality from mine wastes. The most common kinetic tests are laboratory-based columns, humidity cells and field-based test pads (Price, 1997; Lawrence, 1990; Lapakko and White, 2000).

According to Price (1997), kinetic tests can provide prediction information including: (1) the relative rates of acid generation and neutralisation (important in determining if a sample will “go acid”), (2) the time to ARD onset and (3) drainage chemistry and the resulting downstream loading for each of the probable geochemical conditions. This paper concentrates on ‘humidity cell’ tests. Humidity cells are widely used to estimate the rates of weathering in order to predict the rates of acid generation and neutralization potential (NP) depletion, and the lag time to ARD generation (Prostad et al., 2002; Miller et al., 1997; Price, 1997; Bowell et al., 2000; EGi, 2002). However, the limitations of these tests with regard to the validity of interpretations and extrapolation of data has not been widely discussed in the literature.

1.1. Factors influencing the reactivity of mine waste in the field and the laboratory

Ultimately the purpose of all mine drainage prediction is to predict whether the receiving environment (e.g., groundwater, surface water) will suffer any deleterious impacts from mine wastes (e.g.,Fig. 1a (3)). To predict the environmental impact at the receptor it is necessary to understand the source of the contamination (e.g.,the pile of mine waste in Fig. 1a) and the mechanisms that transport the contaminants from the source to the receiving environment (Fig. 1a (2)). Unfortunately, from the perspective of prediction of ARD, both the dissolution of contaminants from mine wastes and their transport are complex processes involving coupled physical, chemical and...
biological phenomena (Bowell et al., 1999a; Bowell, 2002; Lefebvre et al., 2001; Nordstrom and Alpers, 1999). Further complication arises because comparisons between mineral weathering rates determined in the laboratory and field commonly reveal large discrepancies, with order(s)-of-magnitude lower rates commonly observed in the field (Malmstrom et al., 2000) although there are also cases where mineral weathering rates in the field are higher than those recorded under laboratory conditions.

Most humidity cell tests are designed to reveal something about the source of contamination, although specific interpretations differ. Full chemical digests will reveal whether contaminants are present and their concentration, whereas humidity cells are weathering experiments designed to reveal some information about the acid producing potential of a sample, the rate of weathering of minerals within the sample and concomitant contaminant release rates.

1.2. Weathering rates and release rates

‘Weathering rate’ and ‘release rate’ are two often poorly defined terms that are commonly used interchangeably in the literature describing humidity cell data and other kinetic test data. For the purposes of this paper and as a recommendation for future work these terms are ascribed more exact meanings to aid in dispelling confusion in the literature surrounding humidity cells and other leaching tests.

**Weathering rate** – The rate (mass per unit time) at which a primary mineral is transformed into a secondary product (soluble species or insoluble mineral, congruently or incongruently). Many of the reactions of importance are dissolution reactions and therefore depend on the amount of mineral surface area contacting solution. In geochemical studies kinetic data is often normalised to mass per unit time per unit area. However, as it is difficult to accurately measure the reactive surface area of minerals within a mine waste sample, other ways of expressing the rates of weathering are commonly employed that relate the rate to unit sample mass rather than surface area. Typically it is the sulfide (often pyrite) oxidation rate that is the critical weathering rate of importance in mine waste studies.

**Release rate** – The mass efflux (per unit mass of bulk rock) of an element or species away from a unit mass of rock, per unit time. For example, protocols for humidity cells tests often specify that cell contents are flushed weekly, in this case the release rate units are mg/kg/week. Where all of the reaction products are flushed from the interstitial water, then the release rate is the same as the weathering rate (under the conditions of the test) expressed in unit of mass per unit bulk mass per unit time, e.g., mg/kg/week.

In the case of sulfide oxidation, if all the reaction products are flushed from the humidity cell interstices in the weekly rinse then the sulfate release rate (mg/kg/week) is also the same as the sulfate production rate within the cell, which is stoichiometrically proportional to the rate of sulfide oxidation (assuming no other sources of soluble sulfate).

This can also then be expressed in units of mass of sulfide reacted per unit bulk mass per unit time, usually mg/kg/week. However, when not all reaction products are flushed from a system, e.g., due to secondary mineral precipitation or incomplete leaching, then the release rate becomes different from the weathering rate and the actual weathering rate will be underestimated. Conversely, if attempting to quantify the weathering rate of primary minerals in the sample, the later dissolution of any secondary minerals present containing the component of interest will mean that the release rate will define a weathering rate that is an over-estimate of the true rate. The difference between weathering and release rates so defined is clear in application when considering actual mine waste dumps where sulfide minerals will continue to weather (as long as oxidising conditions persist) despite the residual amounts of some weathering products not being removed from the site of reaction.

The same distinction between weathering rates and actual releases in the field is also made by Price (1997). In this reference however, the term ‘release rate’ from humidity cells to describe the weathering rate of pyrite and other primary minerals within the cell. As discussed this is perfectly applicable if there are no secondary minerals present in precursor material or precipitated during testwork (which the protocols of these authors stress should be avoided) or dissolution within the humidity cell. For the purposes of this paper the authors adhere to the two separate definitions given above for weathering rates and release rates to attempt to add clarity. Some cases of the observed scale-dependence of weathering rates may in fact be due to the erroneous use of on-site effluent concentrations (reflective of release rates moderated by secondary mineral precipitation) for the calculation of weathering rates.

1.3. Comparing weathering rates and release rates in the field and laboratory

Humidity cell and similar leaching tests are often run to determine the chemical behaviour of various mine wastes, specifically to determine weathering rates and/or release rates depending on specific interpretations that exist. Fig. 1a and b frame the important question to be answered, that is whether any given 1 kg of material in the field (Fig. 1a) and 1 kg rock in a humidity cell in the laboratory (Fig. 1b) weather and release contaminants at the same rate. Does the release rate data generated by humidity cell tests (Fig. 1b) give us information about the same release rates and/or weathering rates of an identical 1 kg of material in the field (Fig. 1a). This paper presents a study of various humidity-style weathering tests that were carried out on waste mine rock. The aim of the paper is to present data that demonstrates some of the geochemical controls on weathering rates and release rates.

This informs a discussion on the applicability of various interpretations of humidity cell data. Considering the enormous liability both financial and environmental of ARD, the authors feel that an in depth discussion into ARD prediction (in this case leaching tests) is both timely and important.
2. Materials and methods

Metalliferous mine waste used in the study was collected from the Avoca mine site, county Wicklow, Ireland. This site is a former Cu–Pb–Zn mine. The Avoca ore deposit is of the volcanogenic massive sulfide type. The mineralisation is hosted by Ordovician volcanic rock. Ore mineralisation is dominated by pyrite in association with chalcopyrite, bornite, chalcocite, covellite, sphalerite, galena, arsenopyrite, pyrrhotite, Ag-, Bi-, Sb-sulfosalts and tetrahedrite (Platt, 1977; Bowell et al., 1999a,b). Approximately 200 kg of metalliferous mine waste (typically 10–20 kg blocks) was collected from the mine site. The material was dried at 40 °C for 2 days and then passed through two jaw crushers and a gyratory crusher, achieving a grain size of approximately 100% passing 5 mm (d50 ~ 1.6 mm). The crushed material was homogenised by repeatedly passing all the material through a large spinning cone riffler. Once homogenised the sample of approximately 200 kg was riffled down into 1 kg samples for leaching tests and sample characterization.

This thorough homogenisation and subsampling was done to ensure that the samples in each cell were practically identical. The Avoca material was characterised, the sulfur chemistry was found to be dominated by pyrite (16.7%) in association with smaller quantities of chalcopryite (0.4%), sphalerite (0.4%), galena (0.2%), and arsenopyrite (0.2%). Of the 11.6% total S in the samples, 2.4% of the S was present as sulfates (Sapsford, 2003). The sulfides are hosted by a gangue of quartz and chlorite. Although no neutralisation potential tests were performed on the rock the mineralogy outlined above in combination with the more detailed mineralogical studies of Bowell et al. (1999a,b) clearly demonstrate the high potential for acid generation from these wastes.

The kinetic test apparatus and procedures employed were based upon the similar ‘humidity cell’ protocols given in ASTM D5744-96 (1996), Lawrence (1990), Price (1997), White and Lapakko (2000), which in themselves are modifications of a basic procedure adapted and developed by Sobek et al. (1978) from earlier work carried out in various institutes in the 1960’s. Two different shape leaching cells were used (details are given in Table 1) in the experiment. All cells were loaded with approximately 1 kg (accurately known) of crushed Avoca waste rock, the sample sat on a 22 µm polypropylene mesh on a perforated base plate. 500 ml of distilled water was used to flush (once weekly) the interstitial water content of the cells. An exception to this was the initial leach where 750 ml was used, following the protocol of Morin and Hutt (1997) and Price (1997). The water was allowed to contact the sample for approximately 2 h before draining into a collection flask (as per Price, 1997). ‘Aerated’ cells were subjected to a weekly aeration cycle: 3 days of dry air, 3 days of humidified air (air supplied at 1–10 l/min (ASTM, 1996)) and flushed on the final (7th) day of the cycle.

Non-aerated cells were simply left to stand in between cycle flushes. After the cells finished draining (typically 1 h or less) the volume of leachate collected was recorded. Leachate pH was measured with a Russel K-series pH electrode in conjunction with a Corning 240 pH meter, which was calibrated against commercial buffer solutions (pH 4 and pH 7) before each batch of measurements. Leachate redox potential was measured using a BDH Gelplas combination redox probe (Ag/AgCl) in conjunction with a Corning 240 m. Conductivity (specific conductance) of the samples was measured using a Hanna H1932000 Conductivity meter.
Cell leachates were filtered through a 0.45 µm Cellulose Nitrate filter paper. Samples were taken and acidified with 10% HNO₃.

Table 1. Details of cell construction and operating procedures

<table>
<thead>
<tr>
<th>Cell name</th>
<th>Cell dimensions (mm)</th>
<th>Approx. bed height (mm)</th>
<th>Aerated or non-aerated</th>
<th>Number of weekly leaches</th>
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<td>200</td>
<td>94</td>
<td>Aerated</td>
<td>47</td>
</tr>
<tr>
<td>A2</td>
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<td>47</td>
</tr>
<tr>
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<td>94</td>
<td>Non-aerated</td>
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</tr>
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</tr>
<tr>
<td>N6</td>
<td>200</td>
<td>94</td>
<td>Non-aerated</td>
<td>73</td>
</tr>
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</table>

Figure 2 Calculated Sulphate Release Rates from leaching cells
4. Discussion

4.1. Controls on the rate of sulfide mineral weathering

Humidity cells are often run in an attempt to define a sulfide weathering (or oxidation) rate for a given waste material. It is useful to know how fast acid-producing reactions such as pyrite oxidation are occurring in the samples, and a sulfide oxidation rate determined from a humidity cell may be used as input into geochemical prediction models such as in the assessment of pit water–Wallrock interactions (Bowell and Parshley, 2005) or in the assessment of waste rock pile weathering (Ritchie, 1994). It is possible to measure the sulfide oxidation rate of material in humidity cells; this is usually done by measuring the sulfate concentrations in the weekly flush although has occasionally been done by measuring oxygen consumption rates (Hollongs et al., 2001). The former approach is (as discussed in section 1.2) only valid if the release rates have not been modified by dissolution or precipitation of secondary minerals salts.

Fig. 3 shows the molar ratio of Fe to S in the cell leachates generated in this study. At early periods of the leaching the Fe:S ratio is less than 0.5. This is attributable to Fe-mineral precipitation, nonferrous sulfide dissolution or sulfate mineral dissolution. For a brief period the ratio reaches 0.5 the stoichiometric ratio of Fe:S in pyrite, suggesting pyrite oxidation is the dominant reaction contributing dissolved Fe and S to the pore water. Thereafter the ratio climbs to _0.6, this can be interpreted as either a consequence of dissolution of Fe-bearing phases, and/or sulfate precipitation within the cells, the earlier explanation is favoured because the material contained only a small amount (1.8%) of non-sulfur-bearing Fe phases and jarosite minerals were consistently shown (by PHREEQC modelling) to be over-saturated with respect to cell leachates (Sapsford, 2003). As implied by Fig. 3, secondary mineral dissolution and precipitation can at various times lead to under and over-estimates of the pyrite oxidation rate. It is interesting to note that secondary mineral precipitation occurred despite the 2:1 solid:liquid flushing applied weekly.

Other studies have indicated the precipitation of jarosite–alunite within humidity cells (Bowell et al., 1999a,b; White and Lapakko, 2000). Morin and Hutt (1998) have shown that gypsum precipitation within humidity cells is probably responsible for erroneous interpretations of weathering rates in a small number of humidity cell studies. In all of these situations precipitation of sulfate precludes the use of the sulfate release rate as a means of quantifying the sulfide weathering rate. Where the occurrence and effects of secondary mineral precipitates in a humidity cell is of concern, appropriate termination analyses should be performed. A suggested protocol is as follows: On decommissioning the cell, the sample should be homogenized and split into sub-samples. These sub-samples can be submitted for diagnostic testing including Mineralogy (SEM, XRD and optical microscopy), sulfur and carbon speciation, and total element content following acid digestion. In addition selective extractions should be used as a diagnostic leach to determine “reactive element load” still available in the sample. Many schemes exist for these and the exact steps utilized will be dependent on the precursor mineralogy of the material being tested (Tessier et al., 1979; Hall, 1999). The “reactive element load” can then be factored into the release rate calculation using a kappa value method.

4.2. Microbial contributions

It has long been recognised that certain microbes have the ability to catalyse the oxidation of metal sulfides. A number of bacteria and archaea can catalyse the oxidation of sulfides. Many cell protocols include instructions for inoculation of humidity cells with sulfide oxidising microbes, especially Acidithiobacillus ferroxidans (e.g., ASTM, 1996; Sobek et al., 1978). Sulfide oxidising microbes will grow if the necessary environmental conditions are provided, as they are in a humidity cell, without the necessity of them being artificially introduced as they are ubiquitous in the environment. Morin and Hutt (1997) report that inoculation either makes no difference to sulfate release rates from humidity cells, or that a temporary increase in rates occurs, followed by a return to the rates observed in cells which have not been inoculated. According to Morin and Hutt (1997) microbiological contributions to pyrite oxidation can usually be regarded as a constant and therefore ignored. Consistent application of bioleach liquor to humidity cells has been shown to increase pyrite oxidation rates (Paredes, 1995).

Fig. 3 shows plots of the iron and calculated sulfate release rates from the Avoca material compared to the percent proportion of dissolved Fe present as aqueous Fe(III). These are derived data calculated using PHREEQC version 2 (Parkhurst and Appelo, 1999) to speciate the cell leachates based on the analyses of dissolved solids and measured redox potentials (corrected wrt SHE). Fig. 4a shows results from aerated broad cell A2 and Fig. 4b shows results from cell B1. Fig. 4 show that times of maximum sulfate and iron releases coincide with times when Fe(III) species dominate the dissolved iron pool. This is not surprising considering that Fe(III) is such an effective pyrite oxidant. However, the maintenance of significant concentrations of Fe(III) in the presence of reactive sulfides (reducing agents in this context) at the low pH of the generated leachates (typically pH <2.5, data not shown) requires continual replenishment of the aqueous Fe(II) pool. With the absence of significant quantities of dissolving Fe(II)-bearing phases, and considering the extremely slow rate of abiotic Fe(II) oxidation at low pH, this is strong circumstantial evidence for the presence of an Fe(II)-oxidising microbial population within the humidity cells.

By regenerating the Fe(III) oxidant, the microbes through their activity appear to indirectly control the rate of pyrite oxidation within the cells. These data are consistently reproduced in all of the leaching tests conducted using this waste material (Sapsford, 2003).

If the evolution of concentration of Fe(III) in solution is, as surmised, due to Fe(II) oxidation microbial activity, it is interesting to note the similarity to classical microbial growth/activity kinetics in batch systems. Fig. 4b show that release rates tended to decrease and stabilise during the latter stages of these experiments. It is possible that this decrease could be due to the establishment of a mature biofilm or nutrient depletion (due to the continual flushing with distilled water).
It is also suggested that the lag-time (20 weeks) until rapid pyrite oxidation occurs could be a result of the time that it takes to establish sessile microbial populations on pyrite surfaces. The successful attachment of microbes to pyrite surfaces can be mediated by Fe(III) concentrations. Bioleaching experiments by Sand et al. (2001) demonstrated that 200 mg/l of Fe(III) was required in solution before bioleaching started, if enough Fe(III) was initially in solution, then leaching started without the commonly seen lag phase. This may have possible implications for attempts to inoculate systems with microbes, if the microbes contained within the inoculum are unable to adhere to the pyrite surfaces then they will be washed out of the cell during the weekly flushes.

In addition, Sapsford (2003) and Sapsford et al. (2004, 2005) postulated that secondary mineral precipitates may directly control the rate of sulfide oxidation under acidic conditions. The Eh (w.r.t SHE) of the non-aerated cell leachates stabilised around a consistent value of around 660 mV (data not shown) after around 50 weeks. This coincided with stable and similar sulfate release rates (see Fig. 3c). It is proposed that a steady-state Fe(III) concentration was achieved in the interstitial water of the reacting material. This Fe(III) concentration reflected the combined buffering effects of contributions of microbial Fe(II) oxidation and aqueous Fe(III) consumption by pyrite oxidation and Fe(III) mineral precipitation. The Eh buffering effect of these mechanisms operating together could serve to stabilise aqueous Fe(III) concentrations and explain the concomitant observation of stabilised rates of pyrite oxidation and sulfate release. A similar mechanism is proposed by Ganor et al. (2005) for the kinetic dissolution of plagioclase, where precipitation of a secondary phase (nontransite) explained the observed stabilisation of the dissolution rate.

4.3. Predictions of sulfide oxidation rate in the field

If the modification of the effluent sulfate concentrations by precipitation and dissolution reactions is neglected and it is assumed that the cell release rates quantify the sulfide oxidation rate, then the data gives a number of measurements of sulfide oxidation rate (amount of sulfide reacted per week) for the material in the laboratory. Much of the literature on humidity cell data interpretation contains a fundamental and explicit assumption that the material in the laboratory and the material in the field will both ultimately display the same zero-order reaction rate (e.g., Lawrence et al., 1989; Lapakko and White, 2000). Laboratory studies in the literature are unanimous in that sulfide minerals undergo complex kinetically controlled dissolution. The abiotic rate of pyrite oxidation has been studied extensively (e.g., Lowson, 1982; Wiersma and Rimstidt, 1984; McKibben and Barnes, 1986; Luther, 1987; Moses et al., 1987; Williamson and Rimstidt, 1994). Due to the complexity of the reaction chemistry, no consensus on rate laws has been reached. Based on statistical analysis of published FeS2 oxidation rates and their own work Williamson and Rimstidt (1994) produced the following rate law for the oxidation of pyrite by ferric iron in the presence of dissolved oxygen (DO):

\[
r = 10^{6.07} \left[ \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right]^{0.93} / \left[ \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \right]^{0.40}
\]

where \( r \) = pyrite destruction rate (mol m\(^{-2}\) s\(^{-1}\)) and \( \log (\text{Fe}^{3+}/\text{Fe}^{2+}) \) for their experiments was 0.5–1.5 with \( [\text{Fe}^{2+}]_0 \times 10^{-3} \) M. Other studies of pyrite oxidation have reported different rate laws, e.g., McKibben and Barnes (1986), Lowson (1982) and Nicholson et al. (1990). The complex oxidative dissolution kinetics of pyrite (and other sulfides) suggests that for the rates of oxidation to be same in the laboratory and the field then the material necessarily must have experienced identical evolution in chemical, microbiological and physical environment.
Figure 4 Sulfate, iron releases and the proportion of total iron present as ferric iron with leaching cycle number for non-aerated and aerated cells
Given the differences in flushing rates, flushing frequencies, lixiviant type, temperature, rate of oxygen supply, rate of accumulation of secondary-mineral precipitates (that can passivate sulfide surfaces), particle size distribution and degree of liberation (if for example the laboratory sample has undergone further crushing) it very unlikely that this evolution is the same. It is possible that sulfide oxidation in real environments tends to zero-order kinetics and that sulfide oxidation is not sensitive to changes in the local physico-chemical environment. However, the differences in reactivity displayed in the laboratory are not trivial for different intersitial water chemistries. This is clear from the order of magnitude difference in sulfate release rates for the Avoca material shown over time in the leaching tests conducted (see Fig. 4).

Some of the controls on overall reaction rates warrant further discussion. Passivation of sulfide minerals can occur because accumulations of secondary minerals are much more likely in the field where flushing rates are lower. In many leaching cell protocols accumulation of secondary minerals is expressly undesirable and minimised by use of large leach volumes and sample stirring during leaching, yet many literature references suggest that diffusion of reactant through secondary mineral coatings becomes the rate limiting step during sulfide oxidation (e.g., Cruz et al., 2001; Cabral and Ignatiadis, 2001; Nicholson et al. (1990) and necessarily should be take into account when simulating field oxidation rates.

Passivation can apply to both acid producing components like pyrite but also equally may decrease the reactivity of NP minerals (Scharer et al., 2000; Al et al., 2000) such as calcite and contaminant releasing components e.g. galena. Probably the most common example of this is the passivation of calcite by gypsum precipitation in response to sulfuric acid consumption. Oxygen supply is a critical parameter because although it may be possible to measure a relatively fast pyrite oxidation rate in the laboratory the actual nodal pyrite oxidation rate may be limited and slowed considerably by the rate of oxygen transfer to it, which is controlled by various macro-scale phenomena (Ritchie, 1994). Particle size reduction is often carried out on rock samples to be submitted for leaching tests, the consequent change in the liberation of minerals contained within the test material can vastly alter the behaviour of a material (e.g., Lapalcko et al., 1998; Bowell et al., 2006).

The authors note that there is a surprising lack of studies that compare rates of sulfide oxidation in the laboratory and at full field scale – perhaps a reflection of the difficulty in defining the latter. Bennett et al. (2000) set out to answer whether the rate of sulfide weathering is comparable in the field and the laboratory. They concluded that the sulfide oxidation rate measured in a well designed kinetic cell (e.g., humidity cell) provide a reasonable measure of the oxidation in the field. However, this statement must be taken in the context of their study that also concludes that this ‘similarity’ is similarity in the range of orders-of-magnitude. These authors point out that modelling studies (e.g., Ritchie, 1994) often indicate that the global (rock pile) oxidation rate is relatively insensitive to the exact value of the intrinsic oxidation rate (IOR), and therefore the IOR only needs to be known to the nearest order of magnitude. It is that apparent that the question of whether humidity cell and other leaching tests can be used to simulate the sulfide oxidation rate of material in the field is currently unresolved. The data presented in this paper and the literature indicates that sulfide oxidation rates are sensitive (to differing degrees) to the exact nature of the weathering environment. As shown in Figs. 4 and 5 sulfate release rates can vary by an order-of-magnitude during a humidity cell test and between tests for the same material, in some cases the sulfide oxidation rate can be altered by an order-of-magnitude by differences in protocol. In addition to the measurement of sulfide oxidation rates, there is the question of how to apply this data to obtain useful prediction information. Although beyond the scope of this paper it should be noted that there are no universally accepted techniques or models for converting laboratory measured sulfide oxidation rates into predictions of the overall rate of oxidation within waste rock materials and how these can be related to the rate of contaminant release. Fig. 5 displays the frequency of occurrence of sulfate release rates from this study (grouped by hundred of mg/kg/cycle). Which sulfate release rate of all of the rates measured for the Avoca material would be appropriate to model sulfide oxidation in the field? The approach of many protocols is to take the ‘steady-state’ rate at the end of the test (Price, 1997). When judged by frequency of occurrence (Fig. 5) the 100–400 mg/kg/cycle, and 1200–1300 mg/kg/cycle would seem to be likely candidates. Ending humidity cell testing when ‘stable rates’ are obtained (as per Price, 1997) may be a useful criteria if it is intended to use such modal sulfate releases for modelling because if the duration of the tests was extended and a ‘steady-state’ rate persisted, the modal value in Fig. 5 would gradually skew towards this ‘steady-state’ value.

As described above there is currently no data available that would indicate that this ‘steady-state’ is nothing other than the ‘steady-state’ for the particular conditions within the humidity cell apparatus. It should be emphasised that the information provided by such tests still contribute greatly to the improvement of a prediction model, but clearly there is scope to include not only the modal rate (or steady-state rate), but also the mean, minimum and maximum observed rates. It is also noteworthy that in all of these tests maximum sulfate release rates were observed after week 20 and so would have been missed by a shorter duration test.

From a conservative modelling perspective, the maximum observed rate is useful (e.g., 4101–4200 mg/kg/cycle bracket for Avoca material, Fig. 5). The results outlined above and literature suggest that the maximum observed rates (<80 mg/kg/cycle) are achieved under the high redox potentials developed by microbial oxidation of aqueous Fe(II). This raises an intriguing question of whether a lengthy humidity style test is necessary to define sulfide oxidation rates when possibly a much shorter microbial leach test would suffice to provide the maximum likely rate for a conservative prediction model.

From a practical perspective, if the aim of humidity cell test work is to measure sulfide oxidation rate then the following has to be born in mind: (1) That a representative sample should be used that does not incorporate artificial particle sizes. (2) That there are no significant sources (other than sulfide oxidation) or sinks of sulfate in the humidity cell if using sulfate releases to define the sulfide oxidation rate. And (3) That significant drying of acidic samples during the dry air cycle can lead to lower sulfide oxidation rates being measured for acidic samples (see Fig. 2a).
4.4. Predictions of release rates of metals in the field

The majority of the waste rock in the field is likely to be in the base flow domain where continual slow movement of water means that the flushing rate will be orders-of-magnitude smaller than in humidity cells. In these circumstances dissolution products are likely to accumulate in solution because they are not being transported (flushed) away. This typically results in secondary mineral precipitation and is therefore no surprise to find that secondary minerals often control aqueous loadings at mine sites (e.g., Alpers et al., 1994; Bowell and Parshley, 2005). In general, the lower the flushing rate, the more secondary mineral accumulation is expected to decrease the mobility of reaction products. Anecdotal evidence suggests that around 80% of mine waste piles display equilibrium controlled releases, i.e., concentrations independent of flow controlled by dissolution/precipitation of secondary minerals (Morin and Hutt, 1998). Comparisons of release rate data between humidity cells and field test pads from an anonymous material in Price (1997) show that under both acidic and neutral conditions sulfate releases from the field test pads were 0.3% and 1.5% of releases measured from humidity cells for the material in question. Similar reductions in release rates of Ca, Cd, Cu, Ni, and Pb were also reported. Fig. 6 shows the total amount of copper leached from the cells containing the Avoca material after 46 weeks of testing and ranges from 143 mg/kg for cell A1 to 499 mg/kg for cell N2. These figures are the sums of the Cu release rates from the cells. Such release rates do not often relate to the expected release rates (see Section 1.2) in the field. Exceptions will exist where weathering rates are extremely low, or where mine wastes are very well flushed by high annual rainfalls or where major (water) flow paths of low residence time dominate the overall hydrology of the waste dump.

In this regard then humidity cells may provide a crude estimate of releases from the field. Generally, the release rates from the humidity cell do not reflect release rates in the field but may be used to estimate the weathering rates of the different minerals such as Cu from chalcopyrite, Zn for sphalerite. The actual release rate in the field will be determined by flushing rates and immobilisation due to secondary mineral precipitation. In addition, peak releases of metals such as Cu from waste dumps and mines may not be related to any of the processes that are simulated in humidity cell tests. Efflorescent salt deposits may become (considering their high solubility) a significant sink of acidity and metals and conversely be an important source of contaminants upon high flow (e.g. storm) events in the field.

4.5. Do humidity cells accelerate weathering?

Much of the available literature on humidity cell tests and its application is contradictory. For example, the majority of authors in the literature refer to humidity cell tests as ‘accelerating’ the rate of weathering of a sample e.g., ASTM (1996), Lapakko (2003). ASTM (1996) explicitly refers to an observed rate of weathering of at least one order of magnitude in humidity cells over field rates, no data are presented to qualify this assertion.
This is contrary to Price (1997) and Morin and Hutt (1997) who claim that humidity cells do not accelerate the weathering of a sample, rather that humidity cells provide information on the ‘primary’ rate of weathering.

Whether humidity cells represent accelerated weathering depends on the definition of ‘weathering’ used. If weathering is taken to mean the rate of weathering as defined by the authors above (the same as the Morin & Hutt and Price, 1997 ‘release rate’ from primary minerals) then weathering is not necessarily accelerated in the laboratory compared to the field and the only available data (Bennett et al., 2000) indicates that there is an order-of-magnitude similarity between these rates. Large differences in temperature between the laboratory and field could mean that the rate of weathering is actually considerably faster in the field. Alternatively, oxygen transport limitation on the macro-scale or microscale (e.g. passivation of mineral surfaces by secondary precipitates) can mean that weathering rates measured in the laboratory are considerably faster than those in the field.

Rates of release (removal of alteration products) will typically be accelerated in the laboratory relative to field conditions where secondary mineral precipitation reduces release rates. If therefore, weathering is defined in a looser sense as removal of mass, then ‘weathering’ in this sense in the laboratory should be considered to be accelerated. The difference can be perhaps made clear by the use of the geological terminology weathering (implying alteration) and erosion (implying efflux of weathering products). In this context research has shown that the rates of sulfide weathering can be similar in the laboratory humidity cell and field (e.g. Bennett et al., 2000); however the rates of (chemical) erosion in the laboratory are likely to be accelerated relative to the field.

4.6. Is inoculation necessary?

Generally inoculation is unnecessary, as microbes will naturally flourish due to their ubiquitous nature. However, there may be circumstances where an indication of microbial assisted sulfide oxidation rates is required but there is not enough time to allow them to develop naturally in the humidity cell. In such cases, inoculation may be justified. If the addition of a microbial culture is required by protocol then it is recommended that in future the inoculating solution contain Fe(III) sulfate, where Fe(III) > 200 mg/l. This may assist in the attachment of the added microbes to mineral surfaces and prevent them being flushed from the humidity cell during subsequent sample flushes. It might be possible to measure the maximum microbial sulfide oxidation rates in a humidity cell (or equivalent kinetic test) without having to wait for them to establish significant numbers naturally. Further research into developing a standardized approach to inoculation of kinetic tests for this purpose may be fruitful wherever sulfide oxidation rates are required for modelling purposes.

4.7. Is sample pre-treatment necessary?

To avoid problems associated with passivated mineral surfaces and flushing of secondary minerals interfering with weathering rate measurements, some authors propose that samples should be pre-leached with solutions that remove these secondary precipitates. Dagenais and Poling (1997) used a sulfuric acid leach to remove oxidation products whilst Price and Kwong (1997) used a dithionate-citrate solution buffered with sodium bicarbonate (CBD). Whether these pre-treatments permanently alter the reactive nature of the sulfide particles is unknown. If using sulfate to quantify sulfide oxidation rates then sample pretreatment may be useful.
However in the field the accumulations of secondary minerals within the rock material may have been passivating the surfaces from oxidation – by removing them it is possible that higher sulfide weathering rates than in the field would be measured. Using oxygen consumption as means of quantifying sulfide oxidation rates instead of pre-treatment will side step this problem whilst retaining the properties of the material in the field but may be impractical to be widely utilised.

4.8. Aeration versus non-aeration

Aeration is usually provided to ensure that there is sufficient oxygen available so that reaction rates are not limited. This is important for high sulfide samples (>7%), in these cases there is a possibility that the measured sulfide oxidation rate will be lower than the maximum that could be achieved if all the cell contents were well aerated. However, this will probably be largely irrelevant because if the sulfide oxidation rate of 1 kg of material in the laboratory is limited by oxygen transport then oxygen transport is going to be limiting the oxidation rate in the field so the material in the field could never achieve higher oxidation rates anyway [unless the oxygen transfer mechanism became more efficient, i.e., convective]. The effect that air supply rate has on weathering rates remains largely unknown. It is interesting to note that many of the protocols, such as those of Morin and Hutt (1997) and Price (1997) do not give a suggested airflow, whilst the ASTM (1996) protocol recommends a wide range of airflow (-10 L/min). There is a potential that this variation in suggested flow rates may give rise to poor reproducibility in humidity cell release rates for low pH samples if no set value is adhered to as drying can cause orders of magnitude difference in sulfate releases (see for comparison cell A1 and A2 Fig. 2a). One potential advantage of aeration is (if other materials behave like the Avoca material in this study), that it appears to reduce the lag-time until peak release rates are observed (see Fig. 2).

4.9. Test duration

The length of time that humidity cells are run for has been the subject of considerable debate. There is some conflict between the need for a sensible turn-around time for tests and the requirement for longer tests that many regulatory authorities would like to dictate. It is also extremely important to define what prediction data is required from the humidity cell when considering the test duration. If the purpose of a humidity cell is to assess the rate of leaching of constituents from a mine waste under controlled conditions, the test should be executed until prolonged periods can be greatly facilitated by the simple, inexpensive, yet effective monitoring of pH and conductivity. As a general recommendation (with practicalities in mind), once constituent leaching reports the same rate of removal for more than four consecutive weeks then steady state can be assumed. Typically this has been observed to require at least 40 weeks of humidity cell testing although it must be noted that mine waste materials have to be judged on a material by material basis. Consequently determining the accession of steady state is a scientifically more appropriate criterion than an arbitrarily defined period of time.

5. Conclusions

The generation of ARD and metal leaching are very complex phenomena that cannot easily be recreated in the laboratory and as such in some cases the interpretation of the data requires extremely specialist knowledge – which currently resides at the forefront of research. Yet humidity cells were originally designed to answer a simple and pragmatic question of whether a material will generate acidic effluent. A simple ‘yes’ or ‘no’ criteria can then identify potentially problematic rock and inform rock handling procedures during the life cycle of the mine (including closure). Since the handling procedure is often independent of actual releases but dependant upon this acid ‘yes or no’ then this provides a relatively simple prediction. Therefore humidity cells and similar tests are often useful for assessment of ARD potential. For a multiplicity of reasons, caution should be exercised when using data from humidity cells for ‘higher’ level predictions, e.g., predictions of metal releases, sulfide oxidation rate and predictions that depend on these data (e.g., time until neutralising potential is depleted). For example, the data presented in this paper indicates that sulfide oxidation rates are sensitive to the exact nature of the weathering environment, can vary by an order-of-magnitude during a humidity cell test, and between tests for the same material. In some cases the sulfide oxidation rate can be altered by an order-of-magnitude by differences in protocol. It is recommended that the operation humidity cells (and similar tests) and application of the data generated should only go ahead after careful consideration of the specific data requirements of a particular project. By presenting the questions in advance that need answers or data, the predictive study can be designed to yield information in a timely and cost effective manner. This will also avoid misuse of data. In conjunction with other prediction tests, humidity cells can provide valuable information to inform waste handling plans provided the limits of their applicability have been clearly delineated.

References


