

## Predominant chemical kinetics in laboratory prediction of ARD

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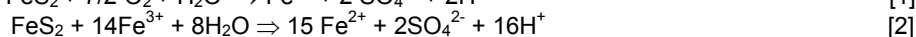
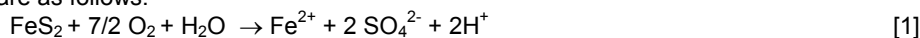
**Keywords:** Prediction, humidity cells, microbial oxidation.

### ABSTRACT

Laboratory-based leaching tests are used to predict the potential of mine wastes to generate acid rock drainage (ARD). This paper presents data on the influence of experimental procedure on generation of ARD in the laboratory. The leaching cells and operational procedures used were based on the design and operation of 'humidity cells', commonly used throughout the mining industry to define the characteristic leaching behaviour of mine wastes. The results of speciation modelling (using PHREEQC) of the generated leachates reveal that iron (III) is the dominant cation in solution during periods of maximum leaching. Data are presented that indicate that the characteristic leaching behaviour of the mine waste is ultimately controlled by the various geochemical sinks and sources of ferric iron within the leaching system. In particular, the data emphasises the critical importance of microbial oxidation of iron (II). The implications of these findings are that the leaching rates observed in the laboratory are a result of microbial dynamics occurring within the artificial laboratory environment, whether or not these rates are applicable to material leaching in real mine environments is an important question that has been raised by this research.

### INTRODUCTION

The oxidation of sulphides (predominantly pyrite) exposed as a result of mining activities can lead to acidic metal rich leachates, variously termed acid mine drainage (AMD) or acid rock drainage (ARD). Sulphide oxidation is a natural consequence of the erosion and weathering of sulphide-bearing rocks, however its impacts are more obvious in and around mine sites where sulphide-rich material has been exposed by mining operations. This greatly increases the available surface area for sulphide oxidation. If sulphide oxidation rates are significant, acidification of the mine water occurs and the subsequent mobilisation of metals can lead to significant impacts in the receiving environment. On exposure to the oxidising conditions pyrite can oxidise. The reactions with oxygen and iron (III) are as follows:



### General approach to prediction of ARD

The general process of prediction involves two steps (e.g. Policy for metal leaching and acid rock drainage at mine sites in British Columbia, 1998 and Price, 1997), these are to firstly identify and describe geological materials and secondly, to predict the ARD potential of the geological materials (e.g. waste rock, tailings), in order to identify "problematic" waste so that contingency / appropriate mitigation plans can be put into place.

The most widely used tests to quantify ARD potential are 'static' tests and 'kinetic' tests. Acid Base Accounting (ABA) is by far the method of choice for evaluating the ARD potential of a test sample (Kwong, 2000). ABA is often used as a screening process to categorise materials into 'potentially acid-generating' and 'uncertain groups'. For the uncertain group, kinetic test-work (especially 'humidity-cells') is used to define acid generation characteristics. Kinetic tests are essentially dissolution 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 (Morin and Hutt, 1998). The ultimate goal is to use static and kinetic tests in conjunction with others to assist in developing strategies for the environmentally sound management of mine wastes (Morin & Hutt, 1998).

### Interpretation of humidity cell results

Much of the available literature on humidity cell test-work 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 D5744-96 D5744-96 (1996), Lapakko (2003). ASTM D5744-96 D5744-96 (1996) explicitly refers to an observed rate of weathering of at least one order of magnitude in humidity cells over field rates. This is at odds with the view of Price (1997) and Morin and Hutt (1997) who state that humidity cells do not accelerate the weathering of a sample, rather that humidity cells measure the rate of weathering of the 'primary' minerals (original minerals) such as pyrite in the samples (Morin and Hutt, 1997). They purport that release rates from humidity cells are higher (appear accelerated) than field release rates because humidity cell releases reflect the dissolution rate of primary minerals alone whilst releases from mine site components reflect chemical loadings resulting from primary mineral dissolution but altered by precipitation of secondary minerals within the mine site component, the cause of this being the much lower liquid to solids ratio in mine site components as compared to humidity cells.

In practice humidity cell release rates (only weight corrected) have been directly applied to the field by inexperienced practitioners. Given the complexity and degree of heterogeneity in mine waste piles in terms of hydrology, oxygen fluxes, temperature (e.g. Lefebvre et al 2001) and microbiology (e.g. Edwards et al, 1999;

Edwards et al, 2001) it should be clear that humidity cell's represent (in the majority of cases) a different leaching environment than that in the field and so direct scaling-up of results in this fashion will give erroneous results.

This is (to some extent) recognised by Price (1997) and Morin & Hutt (1997) and is the same reasons why they state that humidity cell rate release rates simply give the rate of primary mineral reaction rate, they go further to suggest that once (arbitrarily defined) steady-state release rates has been established they can be used for predictions of drainage chemistry and depletion times for various acid-generating, acid-neutralizing, alkaline generating and metal-leaching minerals. According to Price (1997), kinetic test-work procedures can provide prediction information including; the relative rates of acid generation and neutralisation, important in determining if a sample will "go acid"; the time to ARD onset; drainage chemistry and the resulting downstream loading for each of the probable geochemical conditions. The veracity of these claims is discussed later in this paper, the underlying assumption of these claims is that the steady-state rate of primary mineral dissolution measured in humidity cells in the laboratory is the same as the rate of primary mineral dissolution in the field; this is a particular point which this paper seeks to address.

## METHODS

Metalliferous mine waste 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 sulphide type. Ore mineralisation is dominated by pyrite (16.7%) in association with smaller quantities (< 1%) chalcopyrite, sphalerite, galena, and arsenopyrite (Platt, 1977; Howell et al, 1999; Sapsford, 2003). The sulphides are hosted by a gangue of quartz and chlorite; there is negligible carbonate neutralisation potential.

All materials were dried at 40°C for 2 days and then crushed to < 10 mm. The leaching cells used and procedures followed were based upon the ASTM D5744-96 (1996) and Price (1997), which in themselves are modifications of a basic procedure developed by Sobek et al (1978) and others.

Two different shape leaching cells were used (details are given in Table 2) 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. Distilled water was used to flush (once weekly) the interstitial water content of the cells; the water was allowed to contact the sample for approximately 2hrs before draining into a collection flask (as per Price 1997).

**Table 2 Details of cell construction and operating procedures**

Cell name	Cell dimensions (mm)		Approx. bed height	Aerated or non-aerated	Number of weekly leaches
	Height	I.D			
<b>A1</b>	200	94	100	<i>Aerated</i>	47
<b>A2</b>	200	94	100	<i>Aerated</i>	47
<b>B1</b>	150	144	50	<i>Aerated</i>	47
<b>B2</b>	150	144	50	<i>Aerated</i>	47
<b>N1</b>	200	94	100	<i>Non-aerated</i>	47
<b>N2</b>	200	94	100	<i>Non-aerated</i>	73
<b>N3</b>	200	94	100	<i>Non-aerated</i>	73
<b>N4</b>	200	94	100	<i>Non-aerated</i>	73

For the initial leach, all cells were flushed with 750 ml of distilled water; on subsequent weeks a leach of 500 ml was employed. Four of the leaching cells were aerated for 6 days / week (see Table 1). The aeration cycle included 3 days of dry air, followed by 3 days of humid air. The air (supplied at approximately 1 L/min/cell) was introduced to the cell from a compressed air line via a plastic manifold attached to the bottom of the (aerated) cells.

## RESULTS AND DISCUSSION

Figures 1-4 show the concentration of sulphate and iron in cell the cell leachates for the aerated cells. Typical results show the cells were leaching significant amount of iron and sulphate and that releases from the cells show a 'hump-shaped' trend over the duration of the experiment. PHREEQC was used to speciate the dissolved load and calculate saturation indices. The speciation of dissolved iron (the dominant cation in solution) was important. Speciation calculations revealed that there was a significant amount of Fe(III) in the leachate solutions, all measured pH values were between 2.03 and 3.71.

Literature values for the rate of oxidation of pyrite by Fe<sup>3+</sup> at pH~ 2 are 1 to 2 x 10<sup>-8</sup> mol m<sup>-2</sup>s<sup>-1</sup> (McKibben and Barnes, 1986; Rimstidt et al, 1994) an order of magnitude faster than by oxygen: 0.3 to 3 x 10<sup>-9</sup> mol m<sup>-2</sup>s<sup>-1</sup> (McKibben and Barnes, 1986; Olson, 1991). Pyrite will be oxidised by iron (III) at low pH whilst there is a constant source of Fe(III) in solution. Figures 1-4 show that times of maximum sulphate and iron concentrations coincide with times when Fe(III) dominates the speciation of dissolved iron.

### **Sources and sinks of dissolved ferric iron in the leaching system**

The chemistries of the weekly leachates are the product of reactions taking place within the interstitial water (within the cells) during the intervening time between flushes. The leachate chemistry is in effect, a 'snap-shot' of the chemistry of the interstitial water at that time, because each leach event flushes out a large proportion of the interstitial water and the dissolved components it contains. The apparent (calculated by PHREEQC) ratio of

Fe(III)/Fe(II) in the cell's interstitial waters reflects the relative rates of Fe(III) production and consumption as compared to the relative rates of Fe(II) production and consumption.

There are a number of possible sources and sinks for Fe(III) in the reacting interstitial water. Fe(III) is consumed by sulphide oxidation by equation [2]. Fe(III) can also be removed (consumed) from solution by precipitation of Fe(III)-bearing minerals, e.g. ferrihydrite precipitation [3]. Sources of Fe(III) are dissolution of Fe(III)-bearing minerals, e.g. ferrihydrite dissolution, reverse of [3],

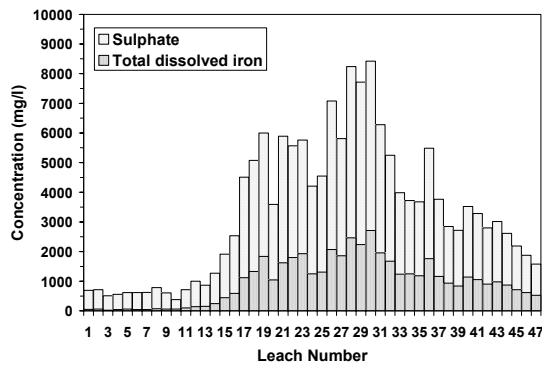


and regeneration of Fe(III) by the oxidation of Fe(II),

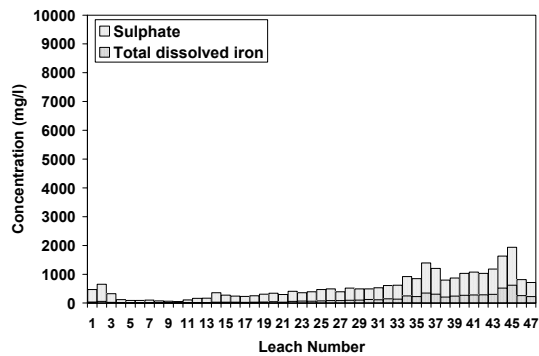


**Ferrous-oxidising microbial activity**

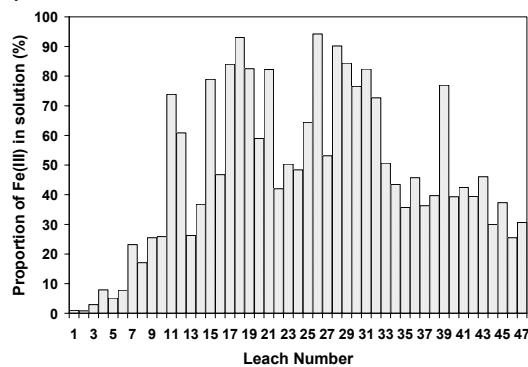
As can be seen by Figures 1-4 for much of the time the greater proportion of dissolved iron existed as Fe(III). Therefore, in the reacting interstitial water the rate of Fe(III) production > the rate of Fe(III) consumption. Because Fe(III)-bearing solid dissolution was not a significant source of Fe(III) in these experiments (Sapsford, 2003), oxidation of Fe(II) must account for the presence of Fe(III). Abiotic ferrous oxidation rates at pH < 4 are extremely slow - of the order of years (Singer and Stumm 1968, 1970). It is well established that ferrous-oxidising microbes have been reported to increase the oxidation rate under acidic conditions by a factor of up to 10<sup>6</sup> (Singer and Stumm, 1970), changing t<sub>1/2</sub> for equation [4] from years to minutes. Sulphide minerals were oxidising within the cells and consuming Fe(III) by equation [2], this strongly implies the presence of a Fe(II)-oxidising microbial population within the cells, as this is the only way in which the rate of Fe(III) production could have exceeded the consumption rate, leaving the observed excess of Fe(III) in solution.



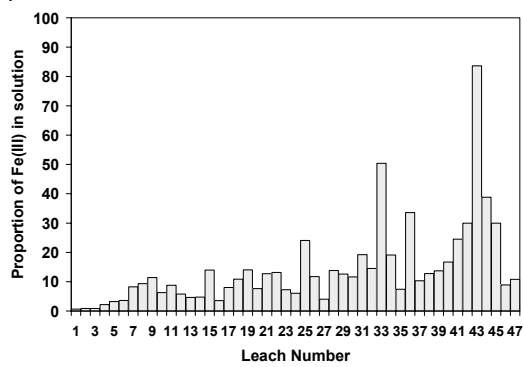
(a) Cell A1



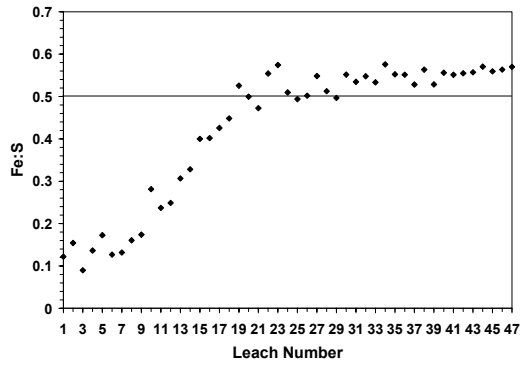
(d) Cell A2



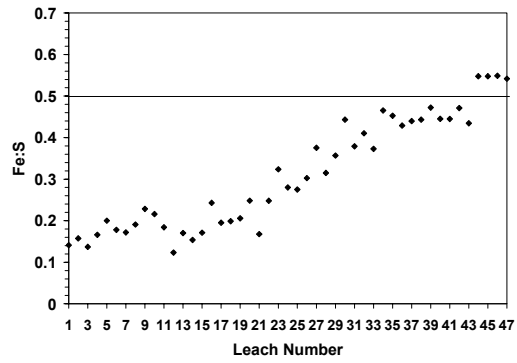
(b) Cell A1



(e) Cell A2



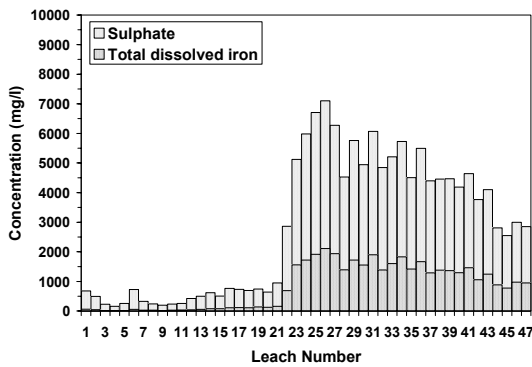
(c) Cell A1



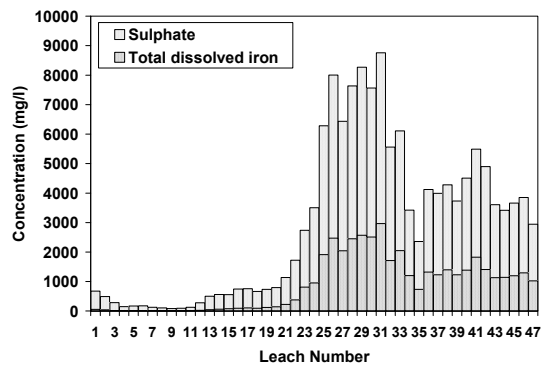
(f) Cell A2

Figure 1 Results of leaching tests

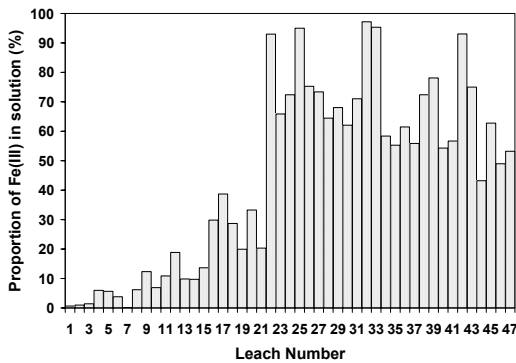
- (a) Cell A1 concentrations of dissolved sulphate and iron in leachates
- (b) Cell A1 Proportion of Fe in solution as Fe(III)
- (c) Cell A1 Molar ratio of Fe to S over duration of the test
- (d) Cell A2 concentrations of dissolved sulphate and iron in leachates
- (e) Cell A2 Proportion of Fe in solution as Fe(III)
- (f) Cell A2 Molar ratio of Fe to S over duration of the test



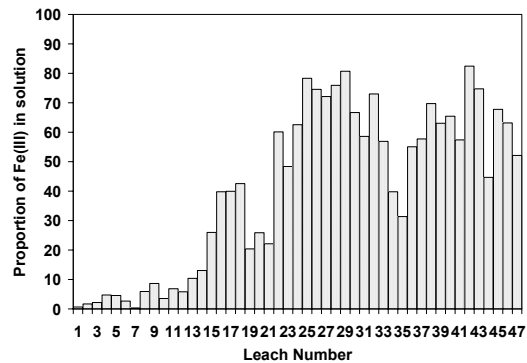
(a) Cell B1



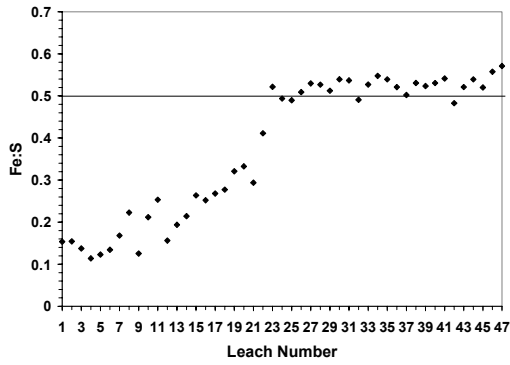
(d) Cell B2



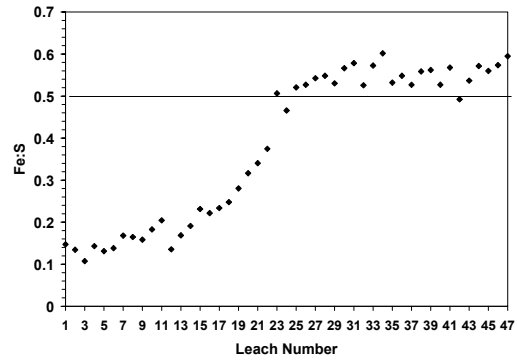
(b) Cell B1



(e) Cell B2



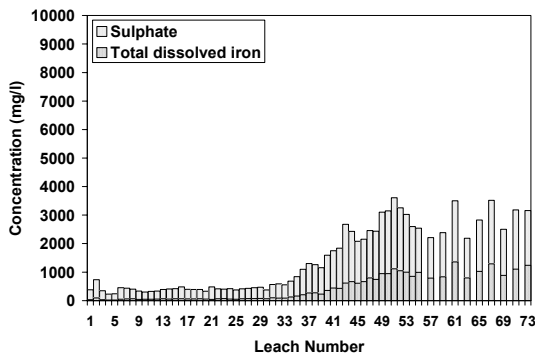
(c) Cell B1



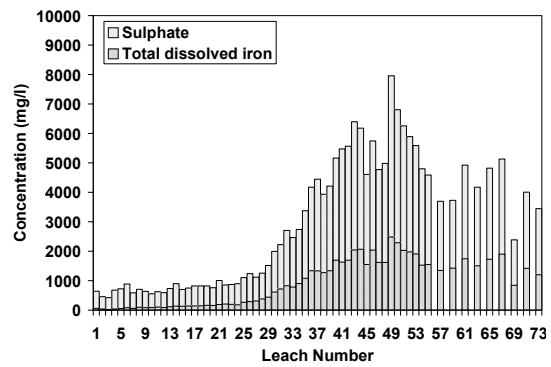
(f) Cell B2

Figure 2 Results of leaching test

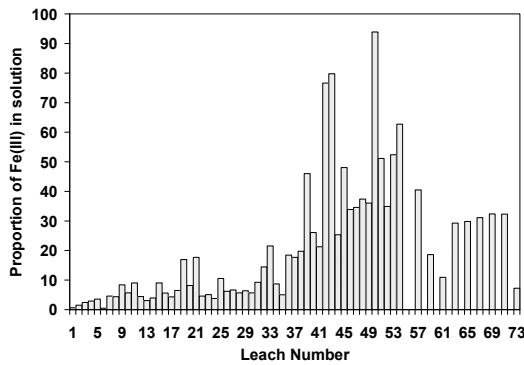
- (a) Cell B1 concentrations of dissolved sulphate and iron in leachates
- (b) Cell B1 Proportion of Fe in solution as Fe(III)
- (c) Cell B1 Molar ratio of Fe to S over duration of the test
- (d) Cell B2 concentrations of dissolved sulphate and iron in leachates
- (e) Cell B2 Proportion of Fe in solution as Fe(III)
- (f) Cell B2 Molar ratio of Fe to S over duration of the test



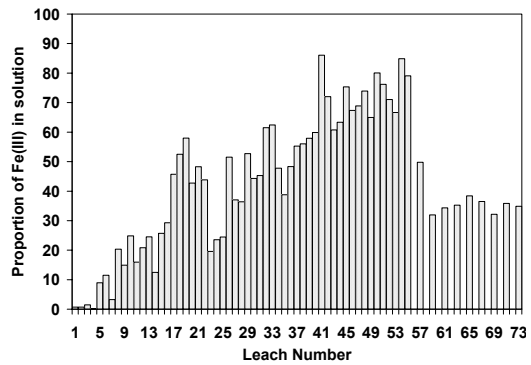
(a) Cell N1



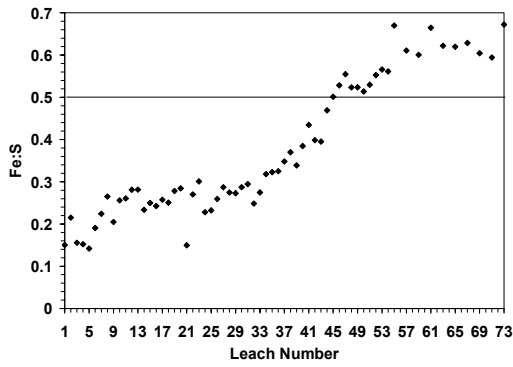
(d) Cell N2



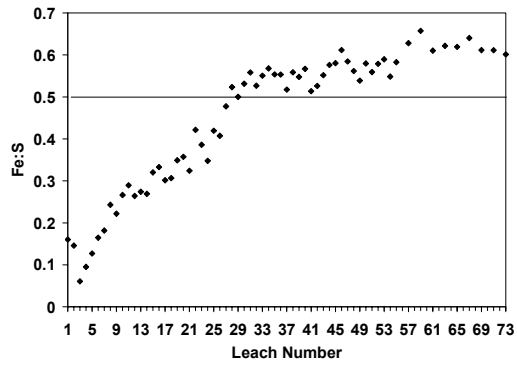
(b) Cell N1



(e) Cell N2



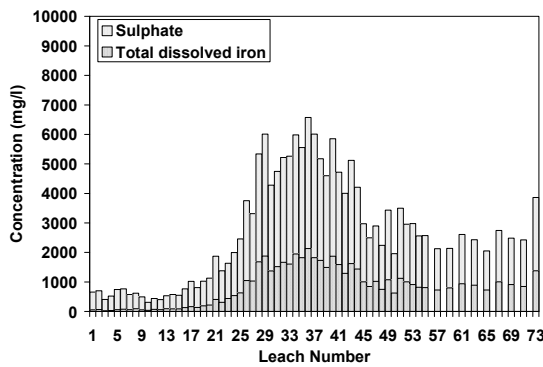
(c) Cell N1



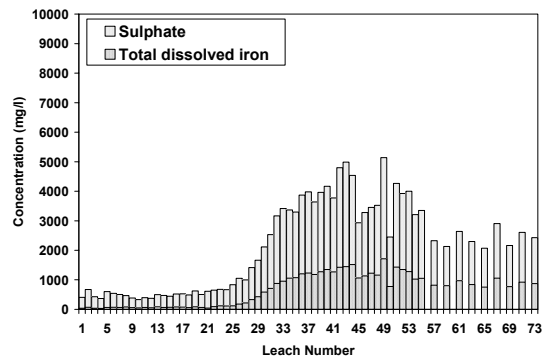
(f) Cell N2

Figure 3 Results of leaching test

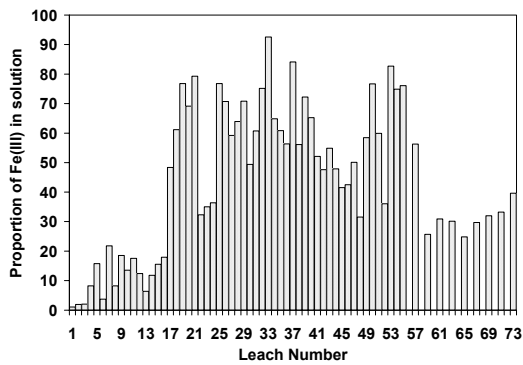
- (a) Cell B1 concentrations of dissolved sulphate and iron in leachates
- (b) Cell B1 Proportion of Fe in solution as Fe(III)
- (c) Cell B1 Molar ratio of Fe to S over duration of the test
- (d) Cell B2 concentrations of dissolved sulphate and iron in leachates
- (e) Cell B2 Proportion of Fe in solution as Fe(III)
- (f) Cell B2 Molar ratio of Fe to S over duration of the test



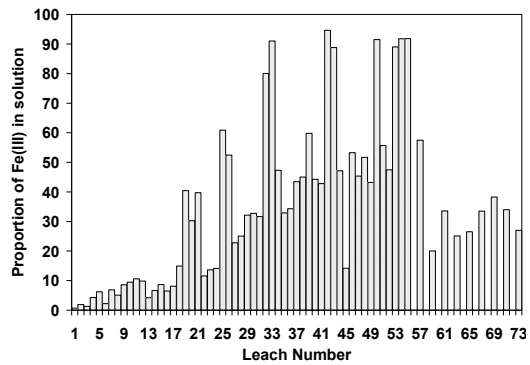
(a) Cell N3



(d) Cell N4



(b) Cell N3



(e) Cell N4

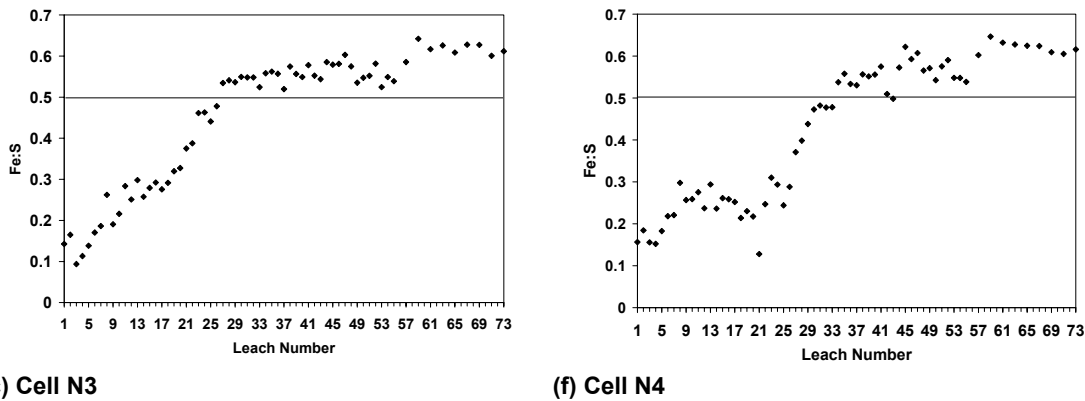


Figure 4 Results of leaching test

- (a) Cell N3 concentrations of dissolved sulphate and iron in leachates
- (b) Cell N3 Proportion of Fe in solution as Fe(III)
- (c) Cell N3 Molar ratio of Fe to S over duration of the test
- (d) Cell N4 concentrations of dissolved sulphate and iron in leachates
- (e) Cell N4 Proportion of Fe in solution as Fe(III)
- (f) Cell N4 Molar ratio of Fe to S over duration of the test

Maximum concentrations of iron and sulphate coincide with periods where Fe(III) dominates the leachate chemistry. Concentrations drop off subsequently and the proportion of Fe(III) in solution is seen to decrease concurrently.

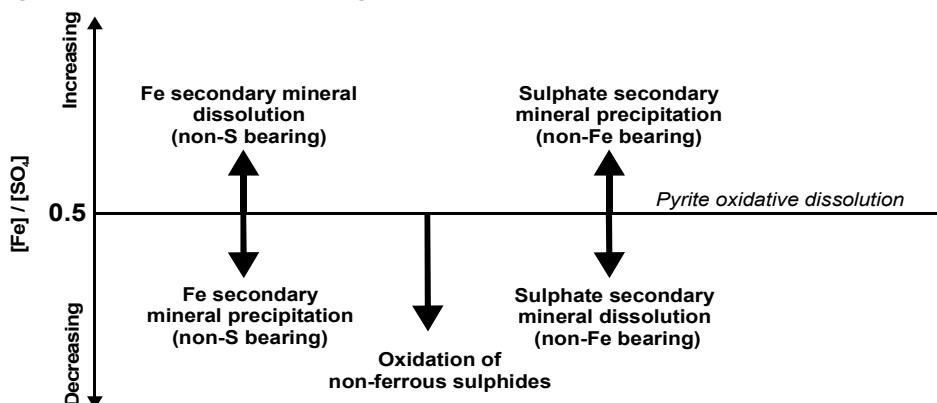
It is interesting to note that the shape of the graphs of proportion of iron (III) in solution (and therefore iron (II) oxidation microbial activity in the leaching experiments) resemble the classical graphs of microbial population (and therefore activity) dynamics in batch reactors (e.g. Shleigal, 1986). There is an initial lag-phase where microbes become acclimatised to their surroundings, followed by an exponential growth phase, then a steady-state period followed by a death phase where microbe numbers (and therefore activity) decrease in response to nutrient depletion. Because iron (II) oxidation only yields a small amount of energy ( $\Delta G$  per mole oxidised), microbes have to process a lot of iron (II) to get the energy to grow. Consequently, only a small population of microbes can be responsible for a lot of the iron (II) oxidation. Although only a small population is required in the leaching cells, the cell contents are leached with distilled water. It is suggested this repeated flushing may have depleted any nutrients (e.g. phosphate / nitrates) present and that this could explain the rapid decline in the Fe(III)/Fe(II) ratio, and the consequent decrease in pyrite oxidation rates.

#### **Dissolution and precipitation in the leaching system**

Figures 1-4 also show the molar ratio of Fe:S in the cell leachates. A molar Fe:S ratio of 0.5 is expected when the products of pyrite oxidation are dominant in solution (Fig 5) as this reflects the stoichiometry of Fe to S in pyrite ( $\text{FeS}_2$ ). For all cells the initial ratio of Fe:S is less than 0.5, likely to be caused by flushing of secondary sulphate salts. Later in the tests, the leachates approach a Fe:S value of 0.5 reflecting times when pyrite oxidation is the dominant reaction. The non-aerated cells (run for longer than the aerated cells - 72 weeks) display Fe:S ratios that climb to  $\sim 0.6$ , suggesting that sulphate secondary mineral precipitation occurred.

Iron and sulphate concentrations stabilise as do Fe(III) proportions (see Fig 1-4) and redox potentials (data not shown), it is suggested that an amorphous iron sulphate mineral (possibly jarosite-alunite) is precipitating in the cells and buffering the redox potential and stabilising the rate of pyrite oxidation.

Figure 5 Interpretations of changes in the molar ratio of dissolved iron to sulphate.



**Aeration versus non-aeration**

Figures 1 – 4 clearly (with the exception of Fig 1(d)) show that aeration of the cell material has an effect of reducing the time till peak concentrations are seen in the leachates. The differences can be attributed to differences in hydrology, water retention and microbial attachment phenomena (Sapsford 2003). The aerated cell A2 shows much smaller sulphate and iron concentration in solution, as well as lower proportions of Fe(III). When running the test, the contents of the cell were noticeably drier than other cells, this is attributed to malfunctioning air supply. This highlights that simple differences in methodology (in this case rate of air supply) in a standard humidity cell test can substantially alter the results obtained.

**IMPLICATIONS FOR PREDICTION OF ARD**

Humidity cells (as per the protocols of Price, 1997; Morin and Hutt, 1997; and ASTM D5744-96, 1996) protocols are designed to determine the rate of release of dissolved species from waste rock. The release rate is ascribed to the reaction of primary minerals within the sample. It is clear from the data presented that depending on the experimental procedures used and when the leaching experiment was terminated, that a wide range of reaction rates could be recorded (and in some circumstances different rates between different leaching cells operated in exactly the same fashion). The critical question is which one of these rates simulates the intrinsic reaction rates in the field?

If the humidity cell protocols of Price (1997) and Morin and Hutt (1997) were followed, the leaching cells would have been terminated where stable release rates were observed, i.e. in the latter stages of the experiment. The pyrite oxidation rate at this time was low. This is attributed to slow rates of Fe(III) generation, because at this time in the experiment, Fe(II)-oxidising microbial contributions were low (possibly due to nutrient depletion). In the field however, rapid microbial Fe(II)-oxidation rates might occur and be sustained because nutrient depletion is not as likely in the natural environment. The protocols of Price (1997) and Morin and Hutt (1997) may therefore underestimate the intrinsic pyrite oxidation rates for well flushed mine wastes. Further to this, the implications of these findings are that the leaching rates observed in the laboratory are a result of microbial dynamics occurring within the artificial laboratory environment, whether or not these rates are applicable to material leaching in real mine environments is not known.

The approach of Price (1997) and Morin and Hutt (1997) acknowledges that observed field releases will be lower than indicated by the primary weathering rate, due to the effects of secondary mineral precipitation. However, data presented suggest that in low pH environments where Fe(III) is the principal pyrite oxidant, secondary mineral precipitation may actually control the 'intrinsic' rate of sulphide oxidation by buffering Fe(III) concentrations.

Due to the ambiguity in the meaning of release rates measured in laboratory leaching tests, it is difficult (if not futile) to use the data to make meaningful predictions of actual drainage from mine waste deposits. Instead mine operators and regulatory bodies should concentrate on the development of waste management procedures based upon large numbers of more simple and inexpensive screening tools (such as 'static' tests) to establish site specific empirical relationships, which can be used more widely and cost-effectively in risk-assessments for efficient management of mine wastes.

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