

# PROTOCOLS AFFECTING THE REACTIVITY OF MINE WASTE DURING LABORATORY-BASED KINETIC TESTS<sup>1</sup>

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**Abstract.** This paper presents data from a number of humidity cell style weathering tests for the evaluation of ARD behaviour. These tests indicate that the results of such test work can be influenced by particle size, mineralogy, as well as the effects of aeration versus non-aeration; of sample mass; of flushing frequency; solution-mineral interaction in the cell and the duration of the testwork. The work undertaken to date indicates that many of the concerns and idiosyncratic details insisted in many protocols do not appear to have a significant impact on leaching rates. Far more important appears to be sulfide and secondary mineralogy; grain size and length of exposure to aeration.

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## **Introduction**

Acid Rock Drainage (ARD) is water that is contaminated as a result of water leaching products of sulfide mineral oxidation (principally pyrite) exposed to air and water. ARD emanating from base-metal, precious-metal and coal mining operations is one of the most problematic environmental issues facing the mining and mineral industries. Once ARD begins, the process is difficult or financially expensive to limit and long-term treatment of mine waters is often required to prevent deleterious impacts on receiving environments. By predicting mine-waste drainage quality prior to the inception of mining, plans for mineral-resource development and mine-waste management can be made to minimize adverse environmental impacts throughout the lifetime of the mine, and after mine closure (Bowell et al., 1999). The task of prediction is often hindered by the complex rock types encountered and the lack of simple, inexpensive 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 prediction including 'kinetic' (or 'dynamic') tests.

Kinetic tests are essentially time-dependant 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; Morin and Hutt, 1998). The ultimate goal is to use static and kinetic tests in conjunction with chemical and mineralogical data to assist in developing strategies for the environmentally sound management of mine wastes.

This paper highlights some of the important findings from a number of different kinetic test studies of different materials conducted over a ten year period by the ARD Research Group in the School of Engineering at Cardiff University. It should be noted that this paper does not go on to make definite predictions about the behaviour of the same materials in the field because the leaching behaviour of a rock sample within a laboratory leaching test can be very different from its leaching behaviour in a field setting where a wide range of different physical, chemical and biological conditions may prevail (see Lebreve, 2001). This paper primarily addresses the behaviour of mining wastes under different experimental conditions in the laboratory and the potential for laboratory artefacts to influence results of such testwork.

## **Methods**

Background information and characterisation data for the materials used in the weathering dissolution tests are detailed in Table 1. Although no ABA data are available for these rocks, it is clear from the mineralogy and the chemical analyses that these rocks would be classed as 'strongly acid generating' (perhaps with the exception of the porphyry-Cu ore). Various different weathering cells were used during the course of the experiments; the details of these cells are given in Table 2.

The kinetic testwork apparatus and procedures employed were based upon the similar 'humidity cell' protocols given in ASTM D5744-96 (1996), Lawrence (1990), Morin & Hutt (1997), Price (1997), which in themselves are modifications of a basic procedure adapted and developed by Sobek et al (1978) from work done in the 1960's.

The crushed material (typically 100% passing 5 mm) was blended and riffle split to ensure homogenous split was used in each cell. Great care was taken in preparing representative splits

of the VMS material in particular, as a large number of these cells were run in parallel. Approximately 200 kg of VMS material was collected and dried at 40°C for 2 days and then passed through two jaw crushers, larger boulders were manually crushed with a sledge hammer before jaw crushing. The material was then passed through a gyratory crusher, achieving a grain size of approximately 100% passing 5 mm. The VMS material was homogenised by repeatedly passing and recombining all the material through a large spinning cone riffle. Once homogenised the sample was riffled through the same cone riffle to obtain a sample of approximately 50 kg. This sub-sample was transferred to a smaller spinning riffle, which further subdivided the sample into twenty sub-samples (approx. 2.5 kg). These were then passed through a box riffle to obtain 2 samples, one of which was bagged and labelled ‘Pre-test’ and stored (for later use in characterisation studies) in a freezer at –18°C. The other sample was taken for use in the leaching experiments, before loading into the cell these samples were riffled down to approximately 1 kg. Pre-test samples (from 1 kg splits) and post-test wet sieve analysis showed no significant differences in particle size distribution between samples (See Table 1 and Sapsford, 2003).

The different materials used in the studies presented were loaded into cells of varying construction (see Table 2) and for the aerated cells, subject to a weekly aeration cycle: 3 days of dry air, 3 days of humidified air (air supplied at 1-10 litres/min (ASTM, 1996)) and flushed on the final (7<sup>th</sup>) day of the cycle. Non-aerated cells were simply left to stand in between cycle flushes. Distilled water was used to flush the cell contents at the end of a cycle. A liquid to solid ratio of 1:2 was used to flush the cells. Since most cells contained 1 kg of waste rock, leaches were typically 500 ml. An exception to this was the initial leach was in some cases 750 ml was used (e.g. following the protocol of Morin & Hutt, 1997).

The nomenclature used in this paper to refer to different materials and procedures used is summarised in Fig. 1. Further, detailed information on the methods selected and characterization of the test material is given in Sapsford (2003).

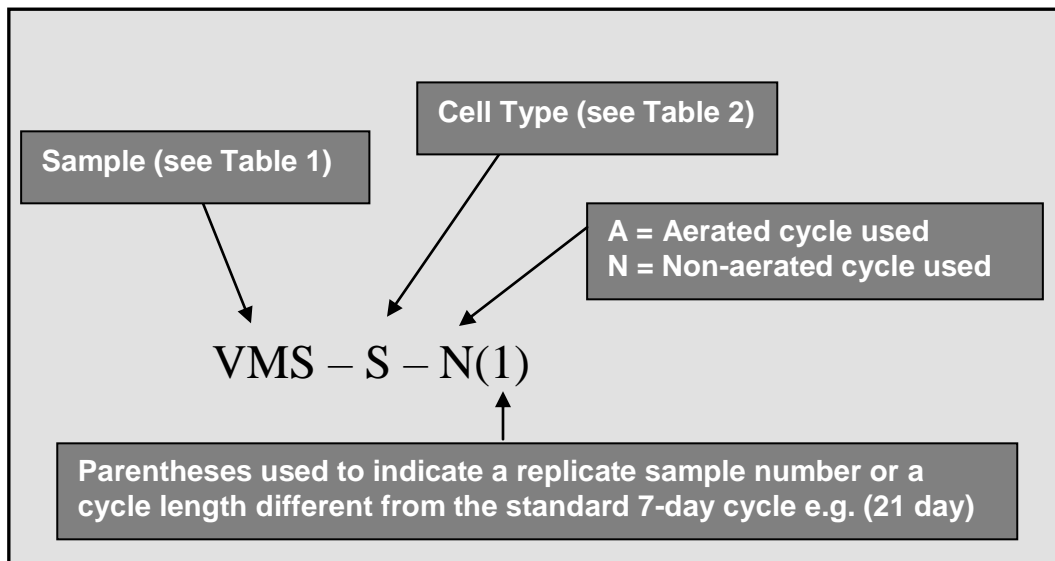


Figure 1. Explanation and example of nomenclature used in this paper for referring to materials and methods used.

Table 1 Background information and characterisation data for the materials used in the kinetic tests

Sample	Deposit Type	Location	Major Mineralogy	Chemical Analyses (Whole rock)		Particle Size Information	Notes
				S	Fe		
VMS	<i>Volcanogenic Massive Sulfide</i>	Ireland	Pyrite (16.7%), chalcopyrite, sphalerite, galena, quartz chlorite	11.6%	9.7%	< 5 mm d <sub>50</sub> ~ 1.6 mm	Abundance of fines, with 15% passing 100µm
VMS 2	<i>Volcanogenic Massive Sulfide</i>	Ireland	Pyrite (16.7%), chalcopyrite, sphalerite, galena, quartz chlorite	11.7%	9.3%	-8 mm, + 5.6 mm	Coarser fraction (sieved)
IBN	<i>Volcanogenic Massive Sulfide</i>	Iberian Pyrite Belt	Massive pyrite with chalcopyrite, bornite, sphalerite, galena, chalcocite tennantite, quartz, calcite	43%	42%	< 5 mm	Only a small amount of fine material (< 100 µm) present
IBN 2	<i>Volcanogenic Massive Sulfide</i>	Iberian Pyrite Belt	Massive pyrite with chalcopyrite, bornite, sphalerite, galena, chalcocite tennantite, quartz, calcite	48%	48%	< 5 mm	Only a small amount of fine material (< 100 µm) present
IBN 3	<i>Volcanogenic Massive Sulfide</i>	Iberian Pyrite Belt	Massive pyrite with chalcopyrite, bornite, sphalerite, galena, chalcocite tennantite, quartz, calcite	48%	48%	< 150 µm	IBN 2 milled to tailings size
IBN 4	<i>Volcanogenic Massive Sulfide</i>	Iberian Pyrite Belt	Massive pyrite with chalcopyrite, bornite, sphalerite, galena, chalcocite tennantite, quartz, calcite	30%	32%	< 5 mm	Only a small amount of fine (< 100 µm) material present
IBN 5	<i>Volcanogenic Massive Sulfide</i>	Iberian Pyrite Belt	Semi-massive pyrite in kaolinite, quartz and illite matrix	24%	23%	< 5 mm	Only a small amount of fine (< 100 µm) material present
AP	<i>Porphyry-Cu</i>	Andes	Pyrite, chalcopyrite, molybdenite, bornite, chalcocite, quartz, feldspar, biotite, fluorite, kaolinite	< 1%	6%	< 5 mm	
C	<i>Coal associated sulfide seam</i>	South Wales	Pyrite, Kaolinite	28.4%	30%	< 5 mm	Pyrite occurring free as 1 – 4 mm chunks

**Table 2** Cell construction and specifications

Cell Type	Coding	Diameter (mm)	Height (mm)	Sample Mass (kg)	Bed Height* (mm)	Construction material
Standard	S	94	200	1	100	Clear Perspex™
Broad	B	144	150	1	50	Clear Perspex™
Large	L	395	600	46	250	Grey Plastic

\*Bed Height; approximate height of sample within cell

### **Results and Discussion**

The following sections present data from numerous leaching tests. It is important to note that a number of the graphs combine data points and lines without data points. This is solely to enhance the clarity of the presented data on charts which contain multiple data sets; there is no implied interpolation of any kind. The results and discussion are split into six sections which cover important factors in kinetic testwork.

#### **Influence of Particle Size**

The influence of particle size in kinetic tests is two-fold. Firstly, particle size distribution will determine the available surface area for kinetically-controlled reactions; there is a dramatic increase in surface area with decreasing particle size, the fine material in a leaching test will contribute proportionally more to mass transfer from the solid to dissolved phase. The surface area of particular minerals will be controlled by its mode of occurrence.

Another possibly important consideration (which may be particularly important for non-aerated procedures) is the amount of water retention within the leaching cells. Finer particles will tend to retain more of the water that is applied each week to flush reaction products out. This could potentially impact the reactivity of pyrite rich samples. In water-saturated portions of cell material sulfide oxidation can occur but may be limited by the rate of supply of oxygen by diffusion through pockets of interstitial water to the sulfide surfaces, which is several orders of magnitude slower than through air (this familiar ‘diffusive barrier’ concept is behind the application of water covers to reactive mine wastes). As a result sulfide oxidation within weathering cells containing a large proportion of fine material may be suppressed compared to well-drained coarser materials whose entire contents are open to air. Even though most protocols include aeration for tailings samples (Price, 1997; ASTM 1996; Morin & Hutt, 1997), these protocols simply state that air should be directed over the surface of the sample, meaning sulfide oxidation may be limited in the same fashion. The proposed influence of particle size on pyrite oxidation rate is qualitatively summarised in the cartoon illustration in Fig. 2.

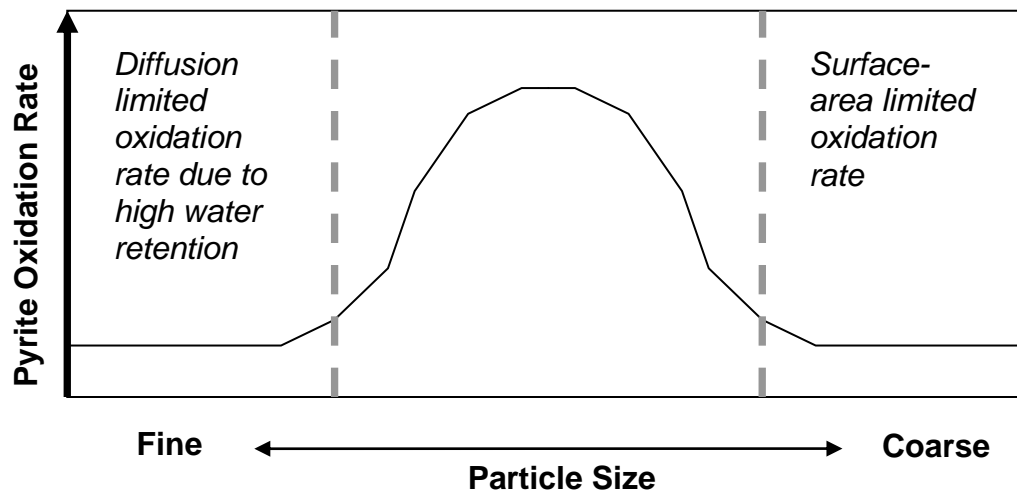


Figure 2 Schematic showing possible influence of particle size on pyrite oxidation rate in laboratory weathering cells, especially relevant to non-aerated procedures.

Sample C-S-A was a crushed coal sample with 1-4mm free pyrite grains dispersed throughout it. Fig. 3(a) shows that the C-S-A cell pH recovered from initial low pH (probably due to the dissolution of effervescent sulfate salts on the surfaces of the pyrite or deprotonation of oxide mineral surfaces) and was circumneutral thereafter. C-S-A cell sulfate releases shown in Fig. 3(b) were correspondingly high in initial leaches but dropped off to consistently low values thereafter. Only 10 data points are shown as sulfate monitoring was subsequently discontinued, conductivity was monitored for the remaining 32 weeks and indicated that the concentration of total dissolved load was consistently low (< 1000 mg/l). Analyses (not shown) showed that Fe concentrations were consistently lower than 5 mg/l after the first 5 cycles. This sample would have been classed as strongly acid generating on account of the high sulfide-sulfur content (28%) and lack of neutralising potential (NP) as indicated by no fizz on application of weak HCl. However, leachates generated by this material remained circumneutral. This is likely due to the large grains of pyrite with limited surface area available for reaction. In addition it is possible that the crystallized nature of the pyrite in this sample increases stability of the  $\text{FeS}_2$  compound compared to less crystalline materials, as demonstrated in studies summarized by Thornber (1992; 1993).

IBN-S-N was a massive pyrite with 43 wt. % S and 42 wt. % Fe. Figure 3(a) shows that this sample did consistently produce low pH leachates (~ pH 3), but surprisingly seemed relatively unreactive in terms of pyrite oxidation, sulfate releases were consistently < 100 mg/kg/cycle after the first 4 cycles (see Fig. 3(b)). Fe releases were consistently < 25 mg/kg/cycle after the first 4 cycles, and often below 10 mg/kg/cycle. Again this is a sample with no NP and large amounts of pyrite yet the sulfide oxidation rates are relatively low. The lack of fine material in this cell and the resultant paucity of available surface area for reaction is probably the main reason for the low oxidation rates observed.

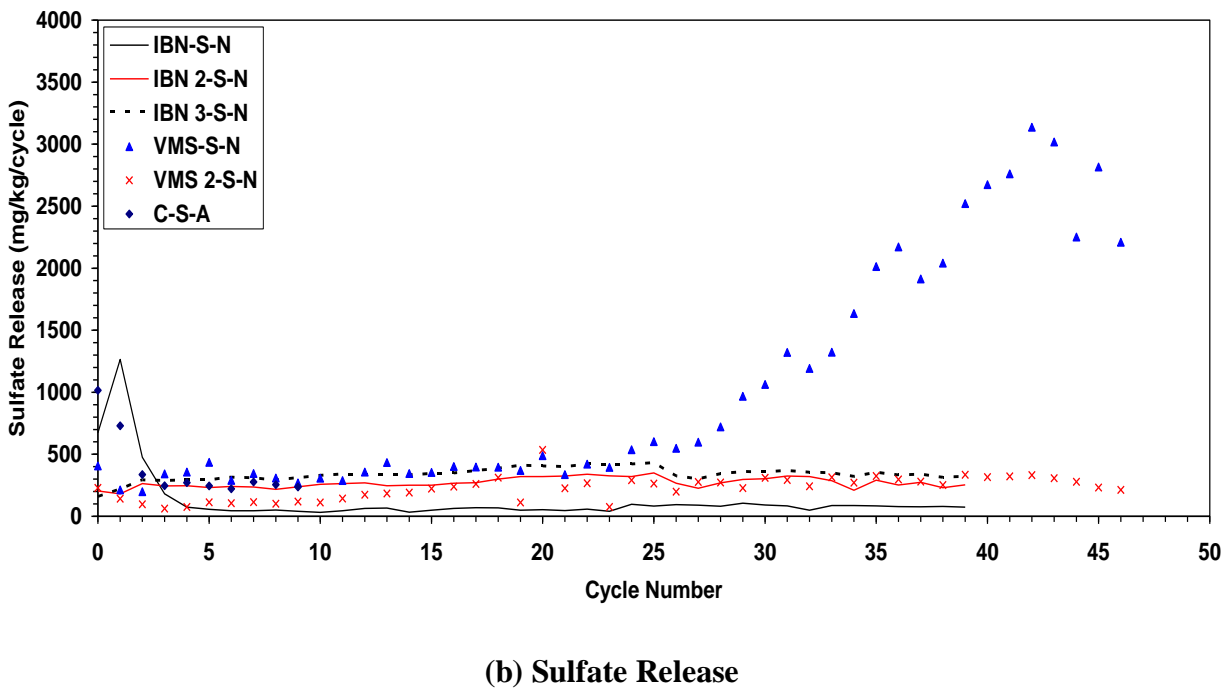
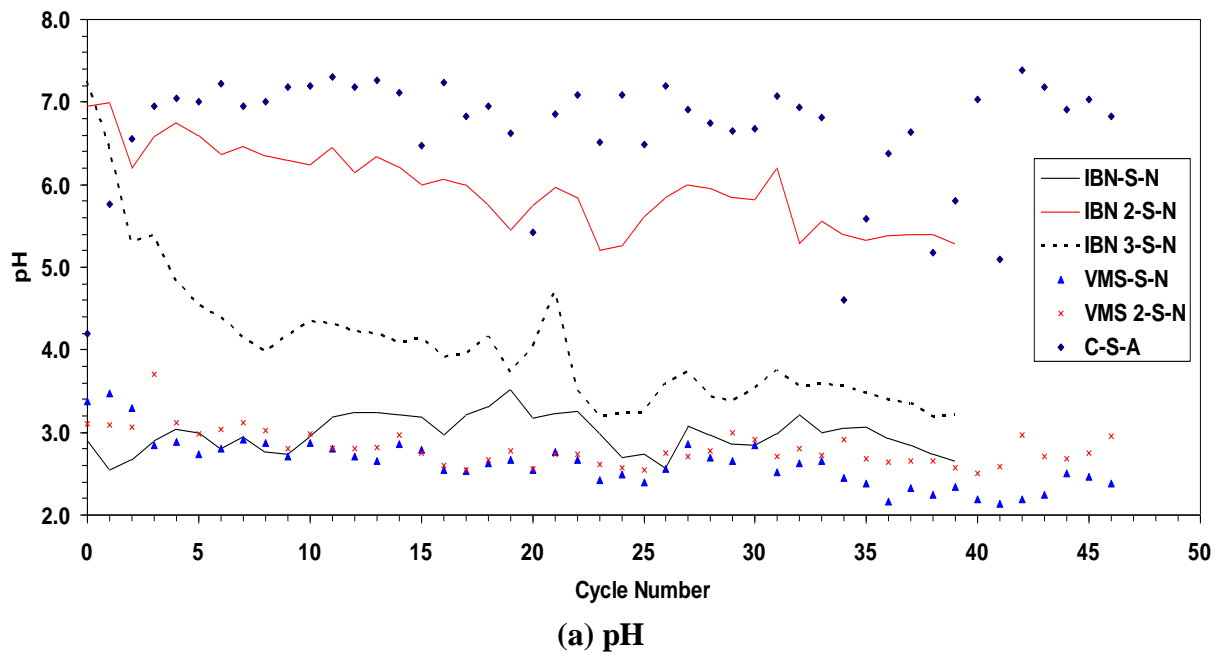


Figure 3 pH and Sulfate Releases from six cells highlighting the effects particle size on test results

IBN 2-S-N and IBN 3-S-N are the same material, the latter sample crushed to tailings size ( $< 150 \mu\text{m}$ ). The effect of increasing the available surface area for reaction can be seen in the more rapid evolution of lower pH in IBN 3-S-N and the slightly higher sulfate releases. However, the sulfate releases are not as high as was anticipated for the sulfide content in the

material with respect to previously studied sites, but it must be borne in mind that the cell was non-aerated and sulfide oxidation in portions of the cell contents may have been limited by the rate of oxygen diffusion through the sample related to the small particle size (as discussed above)

VMS-S-N (11.6 % S) contains material with a significant fines fraction (15% passing 100 $\mu$ m), VMS 2- S-N (11.7 % S) is a coarse fraction (-8 mm + 5.6 mm) of the same material separated out before crushing. Figure 3 (a) shows that although both VMS samples consistently generate low pH leachates (< 3.5), Fig. 3(b) shows that VMS-S-N goes on to be the far more reactive of any of the materials with sulfate releases reaching a peak of 3,130 mg/kg/cycle on cycle 42.

The data presented in this section clearly show that despite very high sulfide sulfur contents of up to 48%, materials tested can be relatively unreactive during kinetic tests if there is an absence of fine (< 1mm) material within the cells. However, where all the material is fine (e.g. IBN 3-S-N) then more of the leach water is retained within the cell. The rate of sulfide oxidation may be controlled by the rate of oxygen supply by diffusion (as discussed above).

An example of the effect of particle size distribution on water retention is given in Sapsford (2003). 8 x 1 kg samples of crushed VMS material with a  $d_{50} \sim 1.6$  mm, and a substantial proportion of fine material (approximately 15 % passing 100  $\mu$ m) were loaded into weathering cells, these cell retained on average 19 % (max 25 %, min 11 %) of the initial 750 ml water leach. A cell containing 1 kg of a fine grained fraction of the VMS material (- 500 + 250  $\mu$ m) retained 55 % of the initial 750 ml leach. One kg of a coarser fraction of the VMS material (- 8 + 5.6 mm) loaded into a cell retained only 3 % of the initial 750 ml leach.

Problems may also arise when particle size reduction is performed (particle size reduction is suggested in some cases by ASTM, 1996 and Price, 1997). This can result in the preferential exposure of different minerals. If greater amounts of neutralising minerals are exposed then humidity cell drainage may suggest that there is enough NP to prevent ARD from occurring even though in the field this NP is occluded within the interior of grains and so is not available (e.g. Lapakko et al, 1998). The same can in some cases be true for sulfide minerals, resulting in them concentrating in the fines after crushing (e.g. Wise, 1997), in these cases sulfide oxidation rates may be accelerated within kinetic test cells.

Although not considered here it should also be noted that the crystallinity of the sulfides will influence behaviour in kinetic testing. Essentially the more crystalline the sulfide, the greater the energy required to exceed the enthalpy of reaction and thus de-stabilize the crystal structure allowing oxidation reactions to occur (Thornber, 1983; 1992, 1993). In addition the trace element chemistry will influence the conductive nature of some sulfides, such as pyrite.

#### Effects of Aeration versus Non-aeration

The incorporation of forced aeration into kinetic testwork cells has been common since the widespread adoption of the methodology of Sobek et al (1978). Humidity cells have (as indicated by their name) included periods of introduction of dry and humid air. The original intent of forced aeration was to ensure that the oxygen-consuming sulfide oxidation reactions were not limited by the rate of oxygen supply by diffusion. Numerous authors have recently evaluated the effects of aeration versus non-aeration (e.g. Frostad et al, 2002; Lapakko and White, 2000). These studies suggest that actively aerating a cell has no appreciable effect on weathering rates; this is demonstrated with sulfide contents of up to ~ 7% (Lapakko and White, 2000). The implication is that oxidation rates are unaffected, suggesting that the reactions were



not limited by the change of oxygen supply into the cell. This is reasonable given the cells are run under aerobic conditions.

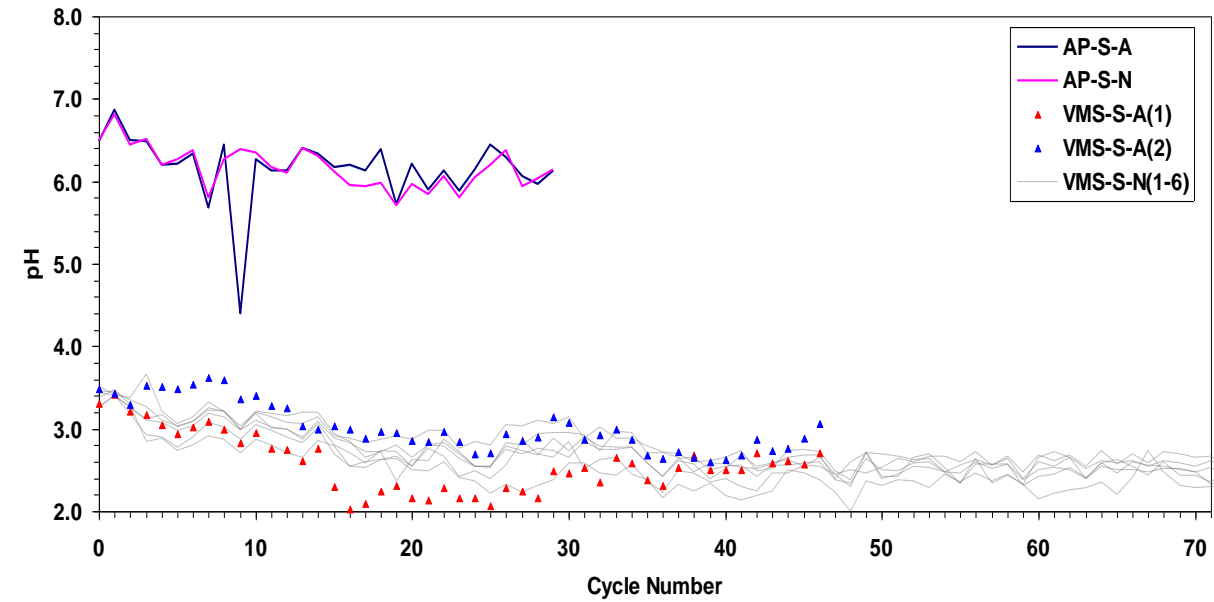
Figure 4 shows leaching results from a typical low sulfide (<1 wt% sulfide-S) Andean style porphyry Cu-Mo deposit Fig. 4(a) shows that the pH of the leachates produced from aerated (AP-S-A) and non-aerated (AP-S-N) cells were very similar (~ pH 6) for the duration of the experiment (apart from an aberration for AP-S-A, cycle 9). The sulfate release rates (Fig. 4(b)) from these cells were also similar and the cumulative sulfate leached over the 20 cycles was 7,983 mg/kg for AP-S-A and 7,717 mg/kg for cell AP-S-N (within 5 % of each other). The results are in agreement with the findings of Frostad et al (2002) and Lapakko and White (2000). These results are not unexpected where low (bulk) oxidation rates are a consequence of low sulfide content, the rate of supply of oxygen by diffusion to sulfide surfaces is fast enough to ensure that the oxygen supply is not limiting. However, such studies should be treated with caution where aqueous releases are dominated by sulfate salt dissolution. Because such processes are independent of oxygen availability, little difference will be observed in sulfate releases rates.

Figure 4 also shows data from material from a VMS deposit (S = 11.6 %, with 16.7% pyrite). Figure 4 (a) shows that these cells all produced leachates of < pH 4. There are differences, both between two replicate aerated cells VMS-S-A(1) and VMS-S-A(2) and the six non-aerated replicate cells VMS-S-N(1) – VMS-S-N(6) but pH for all the cell leachates stabilise at similar values of around 2.5 in latter stages of the experiments.

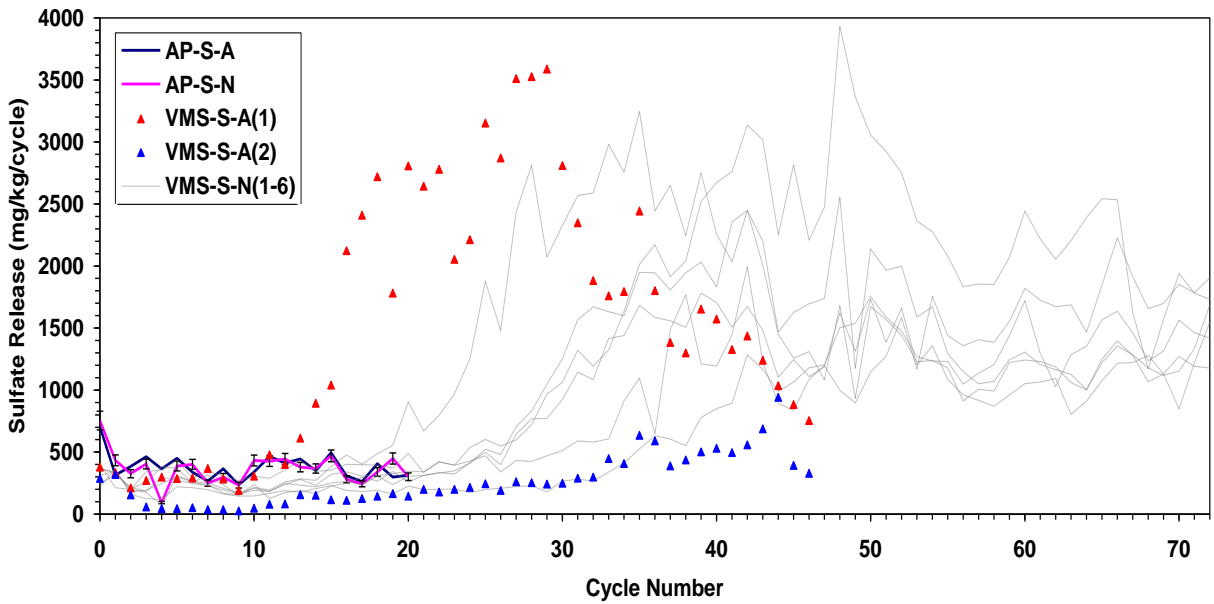
Figure 4(b) shows the sulfate releases for these cells. The difference in sulfate release rates between cell VMS-S-A(1) and VMS-S-A(2) can be attributed to a malfunctioning air-flow into cell VMS-S-A(2). The cell contents were drier than other cells, this was apparent from visual observations, the drier material being noticeably lighter grey than the dark grey moist material. The excessive drying in this cell is thought to be due to an increase in air-flow through it. Splits of a single airline were used to supply these cells, a total of 8 cells were supplied with air from splits from this line. The air flow through the single line was monitored with a rotatameter and was 8 L/min, the intention being to supply each of the 8 cells with ~1 L/min. The air flow through cell VMS-S-A(2) that resulted from the malfunction is unknown but obviously could not have exceeded 8 L/min. In contrast the contents of the other three humidity cells (run in parallel), including cell VMS-S-A(1) never completely dried despite the 3 day dry air cycle. It should also be noted that these other two humidity cells displayed almost identical leaching behaviour to cell VMS-S-A(1) (data in Sapsford, 2003) so that the differences in reactivity of VMS-S-A(1) and VMS-S-A(2) are unlikely to be attributable to sample variability.

After 46 cycles the sulfate release rates from VMS-S-A(1) and VMS-S-A(2) are comparable, but between the times there is a very big difference in reactivity. It is proposed that the reduced moisture content suppressed sulfide oxidation. In the case of cell VMS-S-A(1), the large sulfate releases are attributed to rapid pyrite oxidation rates. The pyrite oxidation rate in this case is thought to have been high due to the maintenance of a high Fe(III)/Fe(II) ratio in solution by the action of Fe(II)-oxidising microbes (see later section on microbiology). Since maintenance of Fe(III) as the oxidant clearly requires the presence of an aqueous solution, then it is clear why complete drying of the interstitial water could be prohibitive for sustaining high pyrite oxidation rates. This may also be a relevant mechanism (in addition to the lack of surface area) affecting the reactivity of samples where all the material is coarse and there is a lack of fine material e.g. cell IBN-S-N. For example, for a coarse fraction of the VMS material (-8 + 5.6 mm) only 23 ml

of the 750 ml of rinse water applied was retained in the cell after the initial rinse. In such cases, the water is retained as a thin film around the particles; these particles may be more prone to drying completely (than cells with finer material which retain more water).



(a) pH



(b) Sulfate Release

Figure 4 pH and sulfate release from 10 cells highlighting the effect of aeration versus non-aeration.

Note: The grey dotted lines are results from six replicate cells (1-6).

It is proposed that due to the suppression of pyrite oxidation in cell VMS-S-A(2), the pH of the cell leachates was slightly higher than for VMS-S-A(1) (see Fig. 4(a) and the sulfate release is much lower.

VMS-S-A(1) did produce very similar sulfate releases to two other aerated cells (data not shown). However, it is clear from the comparison of the pH and sulfate release rates from the six replicate cells VMS-S-N(1) – VMS-S-N(6) that the non-aerated cells produce variable releases, and the majority of the peak releases are less than the peak releases for the aerated cells. Although variability in releases could be due to sample heterogeneity, every effort was made to reduce heterogeneity in splits by careful handling procedures (see Methods section).

The variability is thought to be caused by the inconsistent water retention characteristics of these cells caused by the fines within these cells. Accumulations of fine material have been observed occurring on the upper surface of a cell, settling out after suspension by a flood leach. Accumulations of fines have also been observed to occur in the bottom and middle of leaching cells (Sapsford, 2003). Bradham and Caruccio (1990) also highlighted problems with fine materials within kinetic tests. In addition to the occurrence of accumulations of fine material, the VMS material also displayed ‘water sensitivity’.

Water sensitivity occurs where the presence of clay minerals (even a small amount) can control the permeability and water retention characteristics of porous media. If the leaching cell contains clay mineral particles in a flocculated state then the permeability is not adversely affected, if however the clay minerals are in a peptised state then the permeability can be adversely affected. The reason for this is that when clay minerals are in a flocculated state, the clay is fixed as a loosely built voluminous frame work (‘house-of-cards’ structure) between larger mineral grains, water flow is consequently not greatly impeded. Where the clays are in a peptised state, the electrostatic repulsion between particles causes them to slide and roll past each other without agglomerating. The peptised clay particles become entrained in the water as it flows through the rock material, this results in the clogging of narrow pores with microscopic ‘filter cakes’, which consequently results in lower permeability and higher water retention (Van Olphen, 1977). Whether or not the clay minerals are in a peptised state is reflective of, and very sensitive to the pore-water chemistry. The water retention characteristics of a leaching cell can therefore change dramatically from cycle to cycle; this in turn can dramatically affect the sulfate release rates. Data on water retention and releases which provide evidence for this mechanism and reveal its dramatic effect on sulphide oxidation in a fine grained sample (-500  $\mu\text{m}$  + 250  $\mu\text{m}$ ) is presented in detail in Sapsford (2003).

### Sample Mass

Various different sample masses have been used in weathering cells, for example Sobek et al (1978) suggest the use of 200 g of sample, the protocols of Price, (1997); Morin and Hutt (1997) and ASTM (1996) use 1 kg samples. Frostad et al (2002) compared the use of an aerated cell containing 50 kg of rock to the standard humidity cell sample size of 1 kg. Average sulfate production rates were 58 and 19 mg/kg/week respectively. These results suggest that sulfate release rates are reduced for larger scale samples. However the rinse volume to solid ratio was smaller for the larger sample, which may have caused a decrease in sulfate release due to incomplete flushing of the cell contents and secondary mineral precipitation. Soregaroli and Lawrence (1998) similarly reported a decreased metal release rates in a humidity cell containing 3 kg of rock as opposed to standard 1 kg run under the same conditions. Again the relative ratio of leach volume to solids was smaller for the larger cell, which may explain the results.

Figure 5(a) and (b) show data for the of large sample mass cells, VMS-L-N(1) and VMS-L-N(2) that contained 41 and 46 kg respectively, the samples were flushed with 20.5 L and 23 L of distilled water respectively each week. The results can be compared to the data shown for the six replicate VMS-S-N cells that contained 1 kg (grey dotted lines on Fig. 5). All cells were non-aerated. Figure 5 (a) show that the pH of the cell effluents is indistinguishable from those from the smaller cells. Figure 5 (b) shows that the sulfate release rates are comparable to some of the lower sulfate releases recorded for the 1 kg samples.

For larger sample masses, the effects of water saturation in portions of the cell may become more pronounced (in line with previous explanations), this is simply a reflection of the depth of material in the cells, and the longer distances through which oxygen has to diffuse to supply inner regions of the cell. These are the likely explanations for the lower sulfate releases from the large cells.

### Effects of Flushing Frequency and Secondary Mineral Interactions

Flushing Frequency. If interpreting humidity cell data in the same way as Price (1997) and Morin & Hutt (1997), the flushing (or leach) frequency of the humidity cells has to have been high enough to ensure the removal of dissolution products without letting them accumulate within the interstitial water to an extent where they become saturated and secondary minerals precipitate. This is of particular importance for sulfate because it is used as a tracer (assumed to be conservative) to track for pyrite oxidation rates. The choice of a 7-day cycle has arbitrarily been set in most protocols, probably due to the convenience rather than any specific scientific criteria. The duration of time between leaches (controlled by the leach frequency) dictates the duration that the interstitial water has to react with the solid phase. Reaction rates are controlled by the concentration of dissolved species, so it is possible that the leach frequency affects dissolution rates by allowing reactants to build up in solution e.g.  $H^+_{(aq)}$  and sulfate.

Figure 6 (a) shows that the longer 21 day cycle of cell IBN 2-S-N (21 day) makes little difference to the pH of cell effluent compared to the 7-day cycle of IBN 2-S-N. Figure 6 (b) shows that there is only a marginal effect on sulfate release rates between IBN 2-S-N (21 day) and the 7-day cycle of IBN 2-S-N. In the first 6 cycles sulfate release are actually less than for the 7-day cycle. This suggests that pyrite oxidation is not the dominant mechanism producing dissolved sulfate. Similar to comparisons made in the effect of aeration versus non-aeration, caution is required where readily-soluble secondary mineral dissolution reactions contribute significantly to dissolved constituent release. This is because readily-soluble secondary mineral dissolution may occur predominantly during the flushing events and therefore the time between leaches will be largely irrelevant, whereas the rate of pyrite dissolution may be sensitive to the chemistry of the interstitial water which changes over time as reaction products accumulate within it.

Where pyrite oxidation is a large contributor to sulfate release rates differences are observed. Samples VMS-S-N (14 day) and VMS-S-N (28 day) in Fig. 6 (a) generally produced lower pH leachates than for the six VMS-S-N replicates (grey dotted lines). VMS-S-N (14 day) and VMS-S-N (28 day) produced significantly more sulfate per cycle. For example VMS-S-N (28 day) and VMS-S-N (14 day) produced peak releases of 9361 mg/kg (cycle 21) and 3778 mg/kg (cycle 26) respectively. Cell VMS-S-N (28 day) releasing more sulfate per cycle than VMS-S-N (14 day).

However, these are per cycle releases and when the data is normalised to time in weeks (see Fig. 6(c)) the sulfate release rates (or accumulation rate in VMS-S-N (14 day) and VMS-S-N (28

day)) from all of the non-aerated VMS cells are comparable, although sulfate releases are toward the lower end of the sulfate releases from the cells flushed weekly, VMS-S-N(1-6).

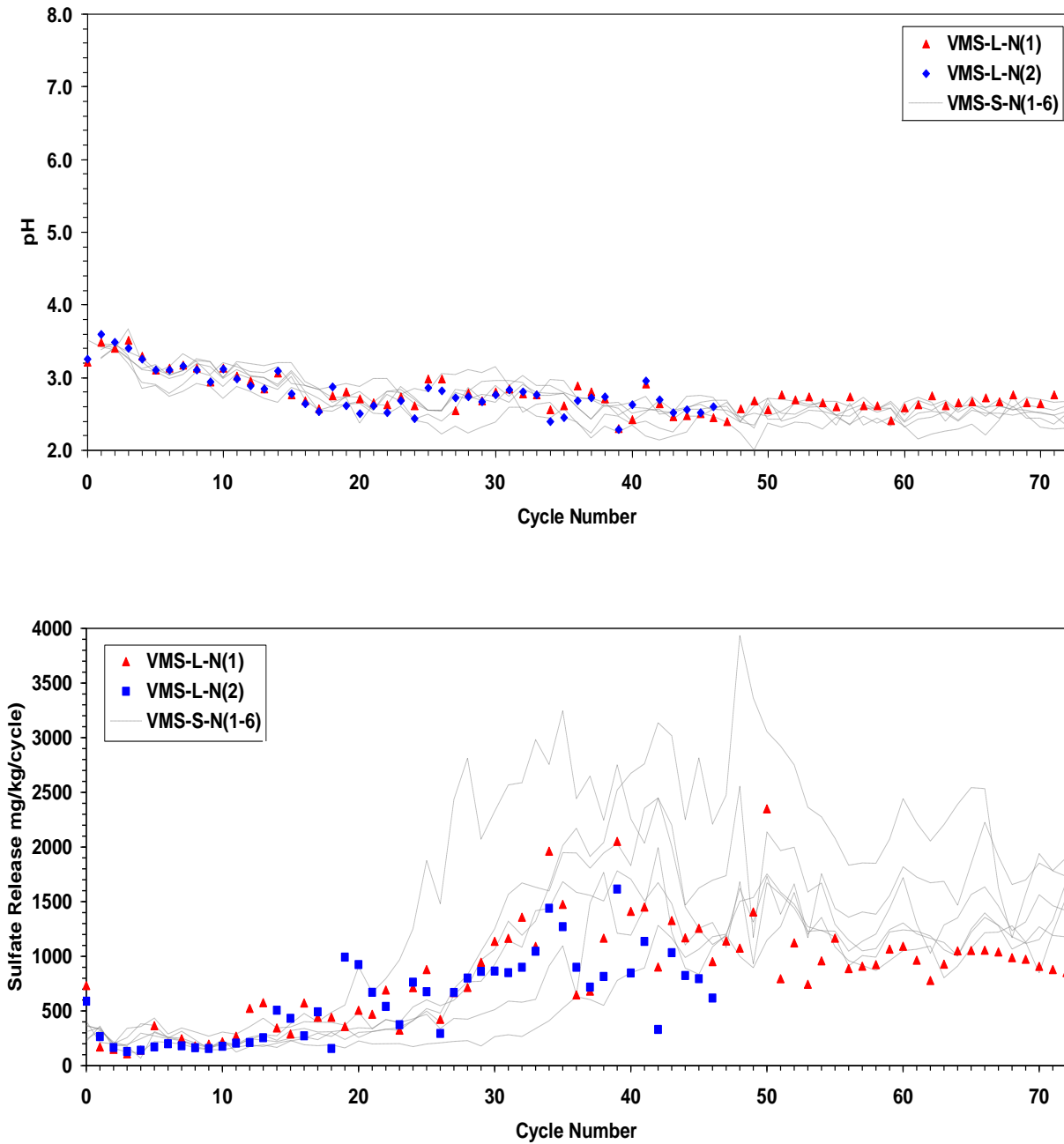
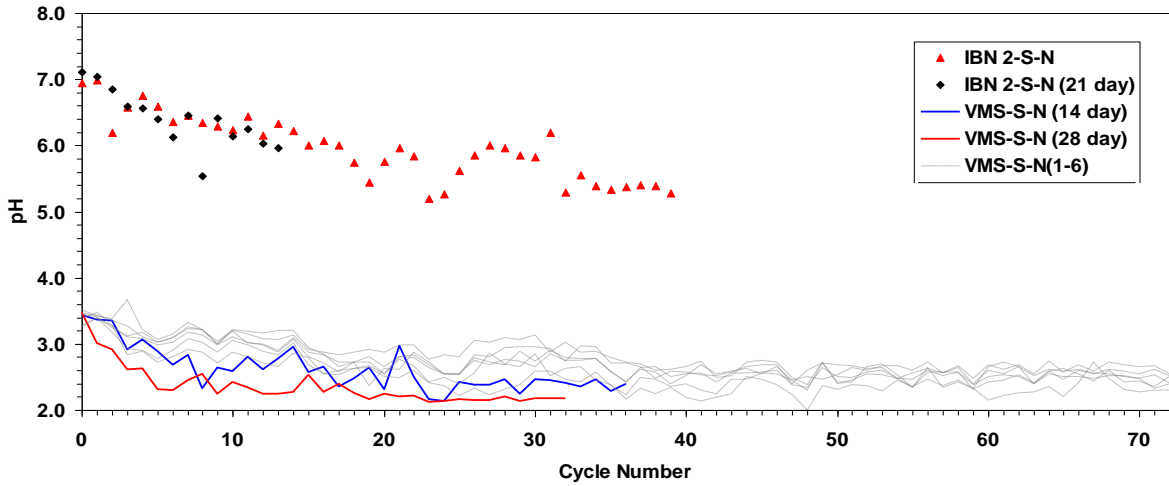
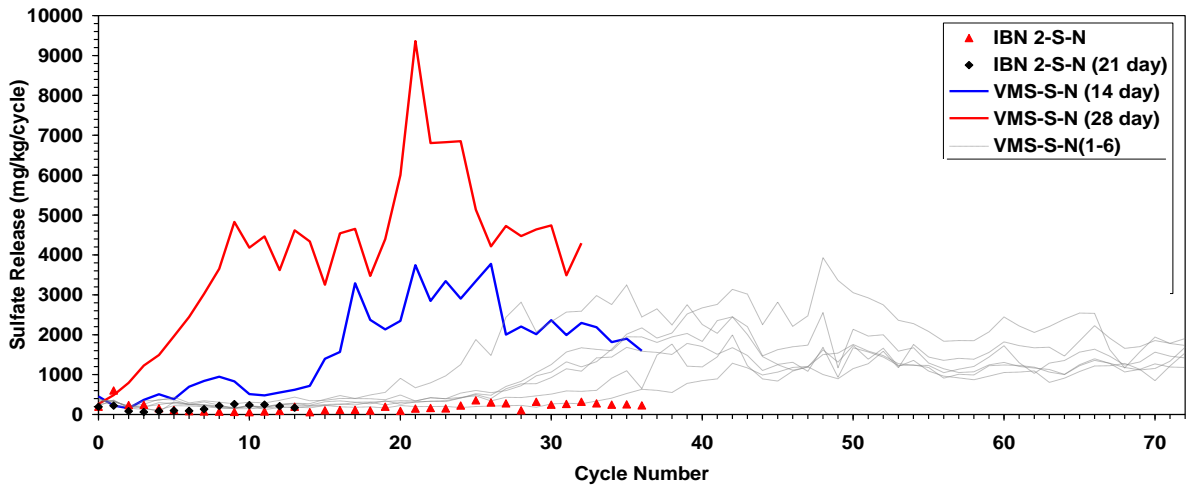


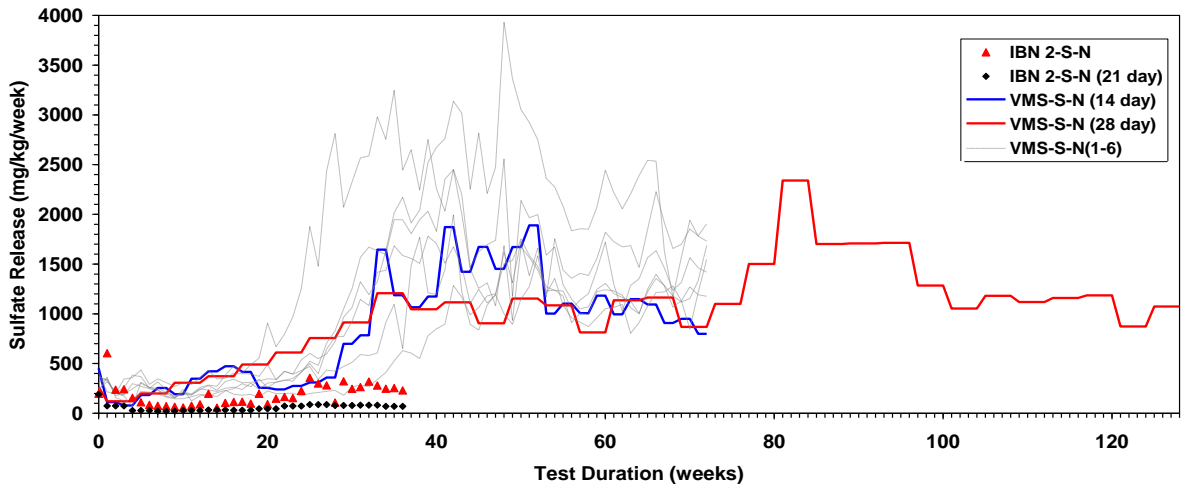
Figure 5 pH and sulfate release from 8 cells contrasting the effect of sample mass. Note: The grey dotted lines are results from six replicate cells (1-6).



(a) pH



(b) Sulfate Release (on a per cycle basis)



(c) Sulfate Release (on a weekly basis)

Figure 6 pH and Sulfate releases from 10 cells of differing cycle length. Note: The grey dashed lines for 6 replicate VMS-S-N samples of standard 7-day cycle are included for comparison.

Secondary mineral interactions. If reaction rates are fast then dissolved constituents in the interstitial water may precipitate secondary minerals. Different authors have different views on the way in which humidity cells should be run and the data interpreted. According to the common humidity cell protocols of Price (1997) and Morin and Hutt (1997), the precipitation of secondary minerals is unwanted. Precipitation may remove a constituent of interest from solution. For example for these authors interpretation of humidity cell data, if sulfate concentrations are being used to calculate the rates of sulfide oxidation then sulfate mineral precipitation (e.g. as gypsum or jarosite) will remove sulfate from solution and give the impression that sulfide oxidation rates are slower. Morin and Hutt (1998) demonstrate how gypsum precipitation has led to erroneous interpretations of weathering rates in a number of humidity cell studies.

When examining the data shown in Fig. 6(b), it is interesting to note that after large differences in sulfate leaching rates in the middle period of leaching the VMS cells all appear to have stabilising sulfate release rates of between 1000 and 2000 mg/kg/cycle, this is also the case for the time normalised data for cells VMS-S-N (14 day) and VMS-S-N (28 day) in Fig. 6(c). The Eh (versus SHE) of the VMS cell leachates also stabilised around a remarkably consistent value of around 660 mV at these times (data in Sapsford, 2003). This suggests that secondary mineral precipitation may be exerting a control on the concentrations of the dominant redox pair in these solutions i.e.  $Fe^{3+}/Fe^{2+}$ , which would also have the concomitant effect of stabilising the pyrite oxidation rate and therefore sulfate releases.

The contribution of precipitation and secondary-mineral dissolution reactions could not have been observed directly. However, by plotting the ratio of total iron concentration [Fe], against total sulfate concentration [SO<sub>4</sub>] over the duration of the experiments, certain conclusions can be

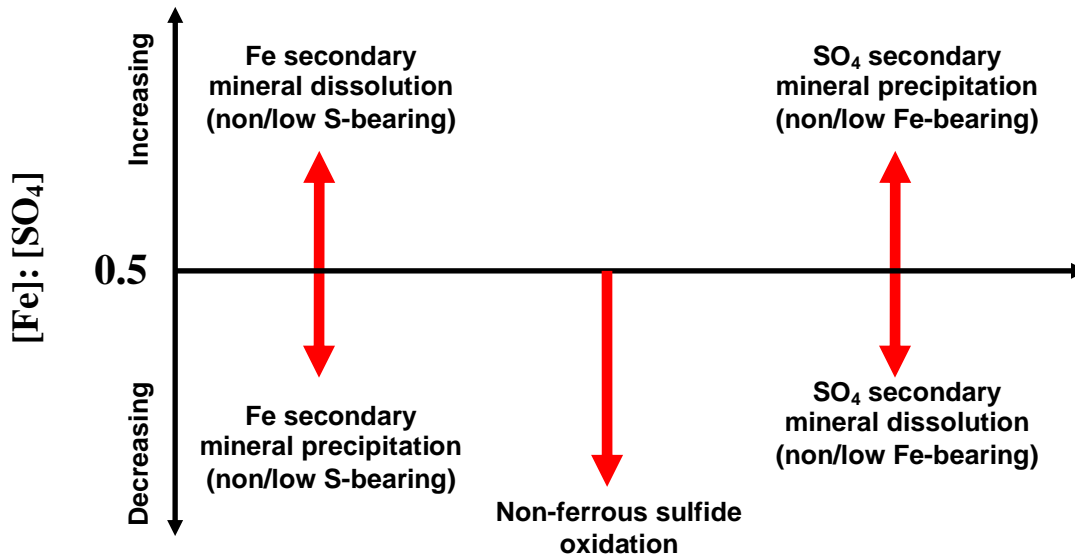


Figure 7 Conceptual explanations for the variation in iron:sulfate ratio in kinetic cell leachates.

drawn. If pyrite dissolution is the dominant reaction contributing to the measured dissolved solids in the interstitial water, then the molar ratio of Fe:S (note: Molar S = molar  $\text{SO}_4^{2-}$ ) should be 0.5, since the stoichiometric formula of pyrite is  $\text{FeS}_2$ . Figure 7 shows how deviations from this value can be interpreted accordingly. An increase in the ratio can be interpreted as either due to dissolution of non-sulfide Fe-bearing phases, and/or sulfate precipitation. A decrease in this ratio can be attributed to Fe-mineral precipitation and/or sulfate mineral dissolution. The dissolution of other sulfides aside from pyrite (e.g. sphalerite) can also decrease this ratio.

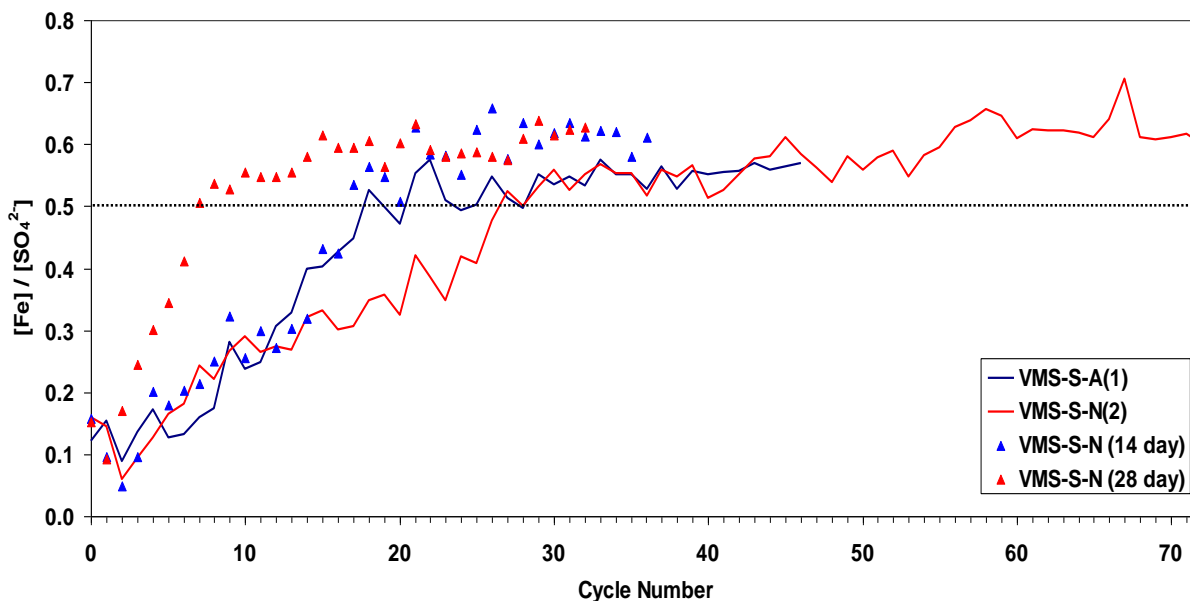


Figure 8 Total iron to sulfate ratio in VMS leachates.

Figure 8 shows that for cell VMS-S-N(2) the initial  $[\text{Fe}] / [\text{SO}_4]$  ratio was below 0.5 suggesting that dissolution of a sulfate salt and non-ferrous sulfide oxidation were dominant controls on leachate chemistry. The period where pyrite oxidation dominated leachate chemistry was between cycle 25 – 40, thereafter the ratio climbs to  $\sim 0.6$  indicating the precipitation of a sulfate salt (with little or no iron content). An amorphous member of the alunite-jarosite mineral group being likely (PHREEQC modelling suggesting jarosites were oversaturated). The data for the other VMS cells in Fig. 8 show the same trend in ratios of  $[\text{Fe}] / [\text{SO}_4]$ . The  $[\text{Fe}] / [\text{SO}_4]$  ratio of 0.6 is reached in fewer cycles by cells VMS-S-N (14 day) and VMS-S-N (28 day), which suggests that an increase in the time between flushing encourages secondary mineral precipitation.

### Microbiological Considerations

Many cell protocols include instructions for inoculation of humidity cells with sulfide oxidising microbes, especially *Thiobacillus ferrooxidans* (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. It has been shown that inoculation either makes no difference to sulfate release rates, or that a temporary increase in rates occurs, followed by a return to the rates observed in cells which have not been inoculated (Morin and Hutt, 1997). However, consistent application of bioleach liquor



to humidity cells has been shown to increase pyrite oxidation rates (Paredes, 1995). The choice of the specific addition of *T.ferrooxidans* in these protocols is questionable, as it has been shown that a consortium of microbes is present in sulfide oxidising environments (e.g. Edwards et al, 2000). According to Morin & Hutt (1997) microbiological contributions to pyrite oxidation can usually be regarded as a constant and therefore ignored.

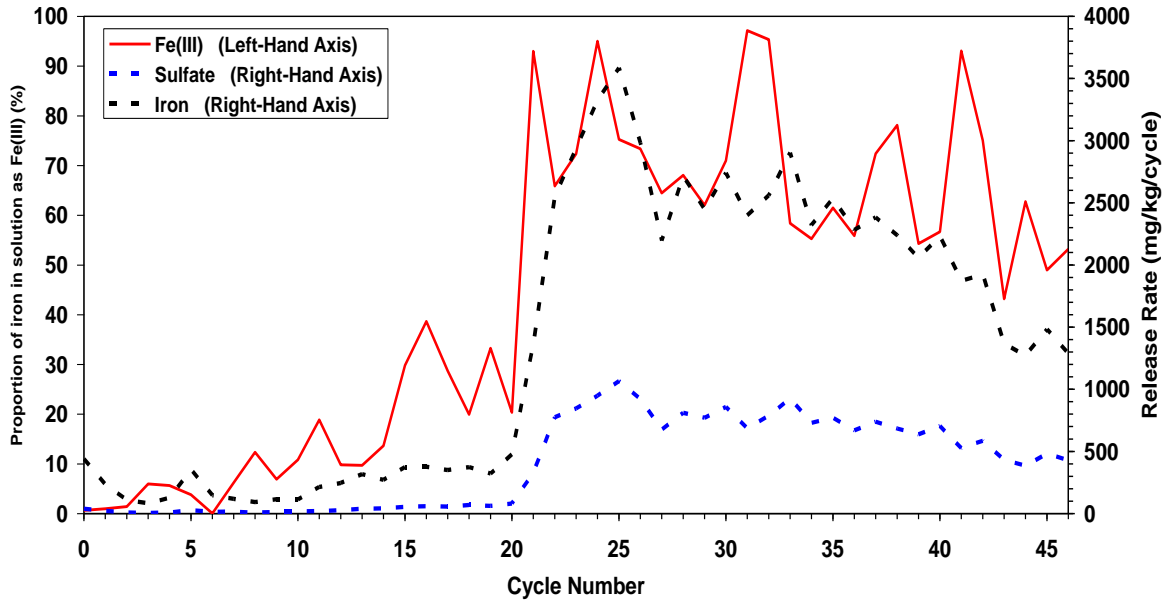
Figure 9 shows plots of the iron and sulfate release rates from VMS material compared to the proportion of iron present as Fe(III). These are derived data calculated using PHREEQCI version 2 (Parkhurst and Appelo, 1999) to speciate the cell leachates based on the analyses of dissolved loads and measured redox potentials. Figure 9(a) shows results from aerated broad cell VMS-B-A(1) and Fig. 9 (b) shows results from a non-aerated standard cell, VMS-S-N(3).

Literature values for the rate of oxidation of pyrite by Fe(III) at pH~ 2 are 1 to  $2 \times 10^{-8}$  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  $3 \times 10^{-9}$  mol m<sup>-2</sup>s<sup>-1</sup> (McKibben and Barnes, 1986; Olson, 1991). Three m<sup>2</sup> of pyrite per litre of solution will reduce 50% of the initial Fe(III) concentration in approximately 50 mins at pH 1. Pyrite will be oxidised by Fe(III) at low pH whilst there is a constant source of Fe(III) in solution.

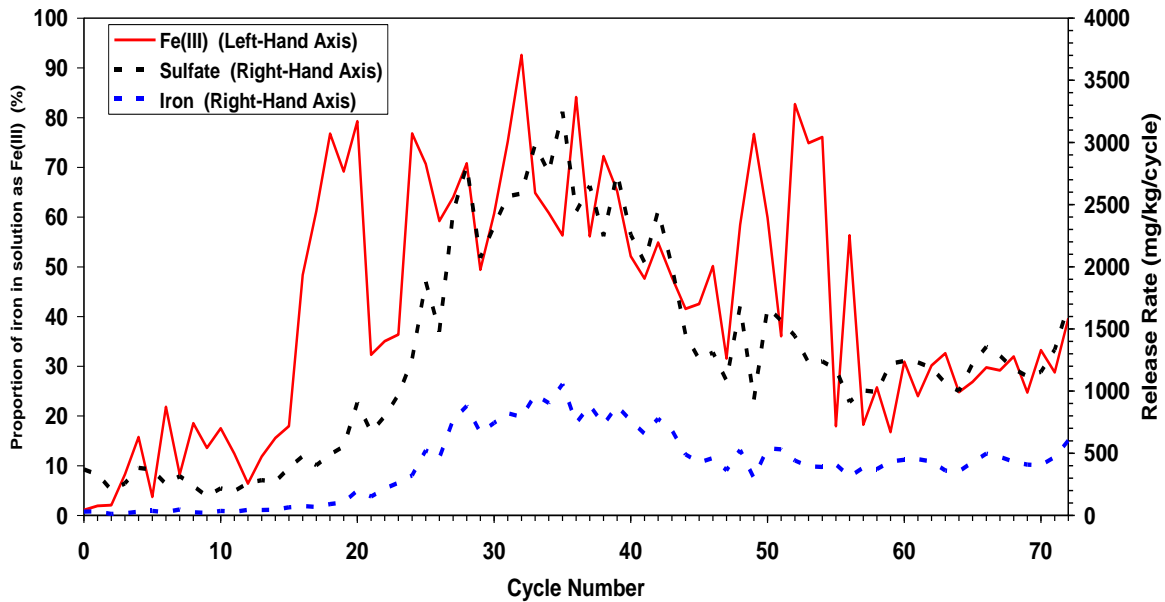
Figures 9(a) and 9(b) show that times of maximum sulfate and iron releases coincide with times when Fe(III) dominates the speciation of dissolved iron, this is not surprising considering that Fe(III) is such an effective pyrite oxidant. However, the prevalence of Fe(III) in the leachates indicates that there must be a continuous regeneration of Fe(III) to account for its continual rapid reduction by pyrite. The only possible way to sustain such high levels of Fe(III) in the presence of pyrite at the low pH of the leachate water (typically pH < 2.5, see Fig. 6(a)) is to have an Fe(II)-oxidising microbial population within the cells, which 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 cells with using the VMS material. It is also suggested that the lag-time until rapid pyrite oxidation occurs is reflective of the time that it takes to establish sessile microbial populations on pyrite surfaces.

It is interesting to note that the shape of the graphs of proportion of Fe(III) in solution (and therefore Fe(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). An initial lag-phase is followed by an exponential growth phase, and then a steady-state period is followed by a death phase where microbe numbers (and therefore activity) decrease typically in response to nutrient depletion. The interpretation of Fig. 9(a) and (b) is that release rates tend to decrease and stabilise during the latter stages of these experiments. Whether this is due to the establishment of a mature biofilm or nutrient depletion (due to the continual flushing with distilled water) is unknown.

There are possible implications for pyrite oxidation rates in the field where nutrient limitation is not likely, also where mine sites are adjacent to agricultural land, an abundance of NPK fertilizer in the local groundwater may also sustain higher microbiological Fe-oxidation rates and therefore potentially sustain higher pyrite oxidation rates. This work is discussed in more detail in Sapsford, 2003; Sapsford et al, 2004; Sapsford et al, 2005.



(a) VMS - B - A



(b) VMS - S - N

Figure 9 Sulfate and iron releases (mg/kg/cycle) (right-hand axis) vary with the calculated (see text) proportion of iron in solution as Fe(III).

### Testwork Duration

The recommended number of cycles (usually weeks) to run humidity cell tests varies in the literature. Up until the 1990's tests were usually run for 10 – 15 weeks (Morin and Hutt, 1999). ASTM (1996) gives a minimum test period of 20 weeks, although acknowledging that it may be advisable to run for longer. This duration has increased in the more recent protocols as it has been recognised that leachate concentrations from humidity cells tend to take time (commonly more than 40 weeks) to geochemically 'stabilise' (the definition of stabilise here is weekly release varying less than a factor of 2 from the previous 5 week average release). This is also the criterion recommended by Price (1997) and Lapakko (2003). It is clear that the choice of when to terminate the cell is relatively arbitrary, but still this seems a more sensible approach than terminating the cells after a fixed length of time as earlier protocols suggested. A study by Morin and Hutt (2000) analysed data from a database of humidity cell tests. Their results suggested that there was a 50% chance that cells would stabilise within a year, the other 50% fluctuating significantly through the test period. Often the number of cycles that a leaching cell is exposed to is limited to about a year, due to the practicalities in time involved in mining permit applications.

Figure 10 show data from two 40 cycle tests, both materials show increasing sulfate release and decreasing pH over time, especially IBN 4-S-N which is showing a sharp increase in sulfate release rates just at the time of test cessation.

It is clear from the data in Fig. 10, but also Fig. 3 and Fig. 4 that very different rates of sulfate release would be measured depending upon when the experiments were terminated. For example, sample VMS-S-N(2) in the first 20 cycles of the test displayed a mean sulfate release rate of 348 mg/kg/cycle, for the next 20 cycles of the test the mean sulfate release rate was 2673 mg/kg/cycle, almost eight times higher. The higher rates are attributed to the increased activity of Fe(II)-oxidising microbes, this discrepancy also reiterates the impact that microbiology can have on pyrite oxidation rates in dynamic leaching tests.

### Conclusions

This paper provides evidence suggesting that demonstrates that the results of kinetic testwork can be influenced by internal factors (particle size, mineralogy, solution-mineral interaction in the cell induced by biotic and abiotic interactions) in the sample being tested and by external factors of the conditions under which testing takes place such as variation versus non-aeration; of sample mass; of flushing frequency; and the duration of the testwork.

The work undertaken to date indicates that many of the concerns and idiosyncratic details insisted in many protocols do not appear to have a significant impact on leaching rates. Far more important appears to be the internal processes and extent of aeration.

Data presented suggests that in some cases (low pH) the complete drying of cell contents during weekly cycles can suppress pyrite oxidation rates by removing interstitial water which consequently prevents the accumulation of aqueous Fe(III) which is a can oxidise pyrite at a faster rate than O<sub>2</sub> under acidic conditions.

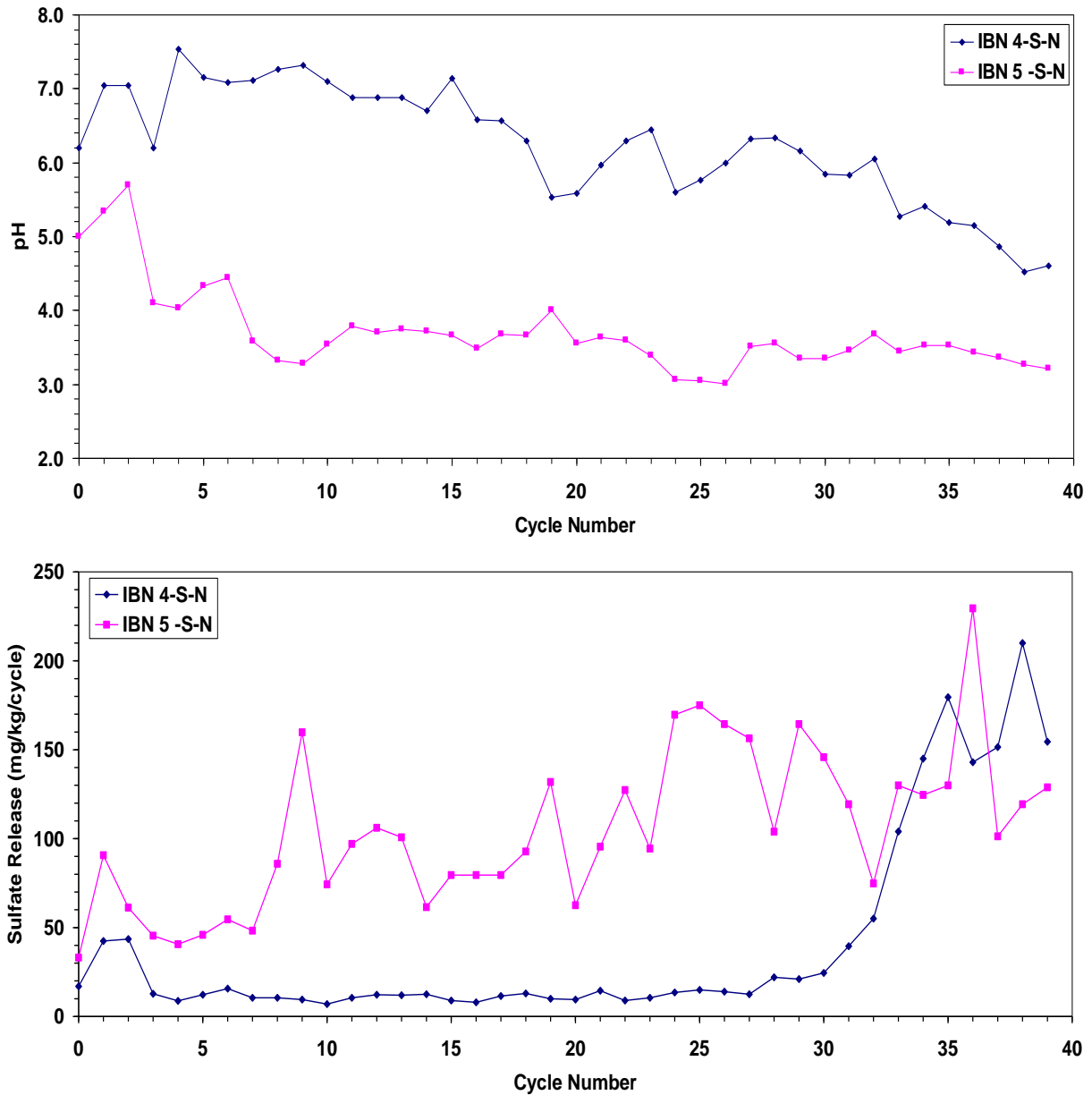


Figure 10 pH and Sulfate releases from two cells emphasising duration

Particle size distribution will influence the available surface area for kinetically-controlled reactions, with an increase in surface area occurring with decreasing particle size, which in turn can influence reactivity (depending on the specific mineral's mode of occurrence). In addition particle size will also influence the amount of water retention within the leaching cells. This may decrease or increase the reactivity of the sample. Finer particles can retain more of the water that is applied each week to flush reaction products out; this may lead to sulfide oxidation rates (especially in non-aerated protocols) being limited by rates of oxygen diffusion through pockets of interstitial water. Conversely, if the samples have limited fines content then they will retain very little water and be more prone to complete desiccation. In these cases fast sulfide

oxidation rates under acidic conditions may be curtailed by the removal of the fast reacting aqueous oxidant Fe(III).

If operating and interpreting humidity cells in the same ways as Morin & Hutt (1997) and Price (1997), the leach frequency in kinetic testing needs to be sufficient to ensure the removal of dissolution products without letting them accumulate within the interstitial water to an extent where they become saturated and secondary minerals precipitate. This is of particular importance for sulfate because it is often used as the tracer (assumed to be conservative) to track for sulfide oxidation rates.

The contribution of precipitation and secondary-mineral dissolution reactions could not have been observed directly. However, based on the indirect evidence utilizing the ratio of iron to sulfate in solution, dissolution and precipitation of sulfate salts were dominant controls on leachate chemistry. Longer periods of aeration (i.e. increased time between flushing episodes) appears to promote formation of secondary minerals and influence effluent chemistry, thus duration of exposure to air and principally to oxygen diffusion in air appears to exert a major role on effluent chemistry.

Although not measured directly in this study on the basis of other studies and indirect observations it is considered very likely that Fe(II)-oxidising microbes are present in the weathering cells and at times significantly increase the rate of sulfide oxidation (indirectly) by regeneration of Fe(III). This emphasises the impact that microbiology can have on pyrite oxidation rates in dynamic leaching tests (Sapsford et al., 2004).

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