



CASE STUDIES TO DEMONSTRATE THE IMPORTANCE OF LIQUID TO SOLID RATIOS FOR GEOCHEMICAL TESTING METHOD SELECTION AND WATER QUALITY PREDICTION

J. Dent^A, S. Pearce^A, D. Brookshaw^A, R. Savage^A, A. Barnes^B, S. Mueller^C and H. Kaasalainen^D

^AMine Environment Management, Denbigh, UK; jdent@memconsultants.co.uk;
spearce@memconsultants.co.uk; dbrookshaw@memconsultants.co.uk;
rsavage@memconsultants.co.uk

^BGeochemic Ltd, Pontypool, UK; abarnes@geochemic.co.uk

^CBoliden, Vasterbotten, Sweden; seth.mueller@boliden.com

^DSweco AB, Lulea, Sweden; hanna.kaasalainen@sweco.se

ABSTRACT

A range of well-developed standardised geochemical static and kinetic leach tests described by industry-standard protocols, guidance and laboratory method statements are currently widely used to determine AMD risk.

Industry-standard leach tests use variable liquid to solid (L:S) ratio, including 2:1 for a paste pH test, 20:1 for SPLPs or TCLPs, to greater than 10:1 for HCTs run over a period of greater than 6 months. In contrast, field conditions for a typical WRSF may have a L:S ratio as low as 0.01-0.001:1. It is a common situation for laboratory conditions not to be representative of field conditions with respect to L:S ratio. Corrections or “scaling factors” used for geochemical modelling are assumed to correct for the more dilute conditions used in the laboratory tests, but direct empirical evidence for this assumption is lacking.

Case study data is presented for major mine sites in Sweden, Finland and Nigeria which demonstrates direct empirical data to evaluate the importance of L:S ratios for geochemical prediction. Methods used include upflow leach testing, customised column testing, equilibrium testing and field IBC tests, alongside industry-standard methods, to demonstrate how the choice of method and ultimately the L:S ratio impacts on the results and outcome.

Case study empirical data show that higher L:S ratios tests can result in porewater chemistry with higher overall metal loads or relative concentrations due to underestimated pH following dilution of pore water alkalinity or metals to below detection limits, or from suppression of sorption processes. Lower L:S tests or field data can more accurately simulate solubility constrained circum-neutral porewater conditions where mixed secondary calcium and magnesium sulfate minerals exist.

Results of the study demonstrate that the L:S ratio, and thus method selection, is a critical factor for accurate simulation of pore water geochemistry and water quality prediction from WRSFs and will have wide ranging applicability for mine waste geochemical assessment.

Keywords: L:S ratio, pore water prediction, solubility, scaling, waste rock dump



1.0 INTRODUCTION

The prediction of water quality drainage from mine waste is typically based on industry-standard testwork which uses established methods to allow comparison between tests. These methods often define the mass of waste rock to be evaluated as well as the volume (or equivalent mass) of water to be used to leach the rock.

The liquid to solid (L:S) ratio is a simple assessment of the water mass used within a laboratory test or percolating through a waste rock storage facility (WRSF) compared with the mass of waste in the test or waste pile. The L:S ratio found in the field will depend on the hydrological conditions of the site including those dictated by a closure cover system, but could be as low as 0.001:1 (assuming a 30 m high WRSF has 400 mm of net percolation per annum) (Pearce et al. 2015). Also, residence times within a WRSF vary greatly due to both percolation and particle size. In comparison, standard laboratory tests can range from 2:1 for a paste pH test to greater than 10:1 for humidity cell tests (HCTs) run over a period of greater than 6 months. Over a one year period a HCT has a L:S ratio of approximately 27. Overall, this paper focuses mainly on dynamic tests such as column tests.

Kinetic tests are often used to predict field scale water quality using a weathering or release rate based on the leachate produced from laboratory kinetic tests. The weathering (or oxidation rate) of the waste rock may not be simply linked to the solute release rate in laboratory scale leachate. If following weathering or oxidation of a mineral a secondary mineral precipitates or there is incomplete dissolution of the oxidation products the residual products and precipitates will build up within the waste mass since they are not removed from the system (Sapsford et al. 2009). This is more likely to occur within a WRSF at field scale (MEND, 2009) but may be less likely to occur within some laboratory leaching tests such as HCTs (Parbhakar-Fox and Lottermoser, 2015). Equally, a laboratory test may provide insufficient residence time for alkalinity equilibration or sorption reactions and thus the results of the test may suggest acidic conditions would develop or release of sorption sensitive elements occurs. The residence time of porewater within a test is often directly influenced by the L:S ratio, as higher L:S ratios require higher flushing rates and thus lower residence times. Equilibration of chemical reactions is not instantaneous, particularly the precipitation of oversaturated minerals. This in turn effects the ability for sorption to occur, as less mineral surface has formed and is available for sorption reactions. The L:S ratio is a key consideration when interpreting laboratory results and the potential inaccuracy between laboratory results and field scale prediction (MEND, 2009).

This paper provides case study examples where different L:S ratios lead to varying controls and effects on leachate chemistry and thus the importance for scaling to field scale water quality prediction.

2.0 EFFECTS OF LIQUID TO SOLID RATIOS

2.1 Solubility Constraints

Solubility-constrained conditions likely dominate in mine waste pore water where the sulfide oxidation rate generates a higher sulfate mass load than can be dissolved in pore water flux



(i.e., rate infiltrating into the mine waste). Sulfate precipitation will occur if these supersaturated solutions are created which depends on nature of the lowest-solubility mineral that is stable. Typically, this is gypsum in pore water impacted by the presence of sulfate and Ca^{2+} cations released from carbonate dissolution (related to buffering reactions). Figure 1 illustrates the theoretical maximum sulfate concentration formed from sulfides in mine waste under different oxygen ingress rates (as $\text{O}_2 \text{ g m}^{-2} \text{ year}^{-1}$) and net percolation (NP) rates. An oxygen ingress rate of more than $1,000 \text{ g m}^{-2}$ is typical of uncovered mine waste and less than $1,000 \text{ g m}^{-2}$ for a covered and compacted mine waste. If equilibrium and saturation limits are ignored this would equate to porewater sulfate concentrations. The theoretical example mine waste used to calculate the potential maximum sulfate porewater concentrations has an initial sulfide content sufficient to exhaust oxygen ingress rates shown under all conditions in pH conditions over pH 4 and where calcium is present in excess, thus gypsum precipitation is possible. In the field any sulfate in solution over the gypsum saturation limit (approximately $2,500 \text{ mg L}^{-1} \text{ SO}_4$) will result in formation of secondary sulfate minerals as excess sulfate is not able to dissolve in the volume of water available. Thus, the sulfate concentrations in seepage produced from the waste would be capped at approximately $2,500 \text{ mg L}^{-1} \text{ SO}_4$ and so wherever the theoretical sulfate porewater concentration is greater than the gypsum saturation limit then precipitation of excess sulfate occurs as gypsum. These conditions can prevail over extended periods of time (decades typically) due to continued oxidation of fresh sulfide minerals and once this source declines, the dissolution of secondary sulfate minerals begins. It is also worth noting that the precipitation of gypsum builds up secondary minerals in the waste and therefore limits the mass transport from the waste rock.

The typical net percolation rate within a narrow (100 mm diameter) HCT using a 1 litre weekly flushing event will equate to around 6,624 mm annually which is illustrated in Figure 1. A HCT of this method assuming 1 kg waste sample has an annual L:S ratio of approximately 52. The HCT is designed to continually release all oxidation products, as the volume of leachate within a flush is greater than the sulfate mass released by oxidation. HCT tests are generally designed to provide a release rate rather than an oxidation rate (Sapsford et al. 2009) and are not an accurate predictor of theoretical maximum pore water sulfate concentrations, thus leading to the build-up of longer-term oxidation products within the HCT.

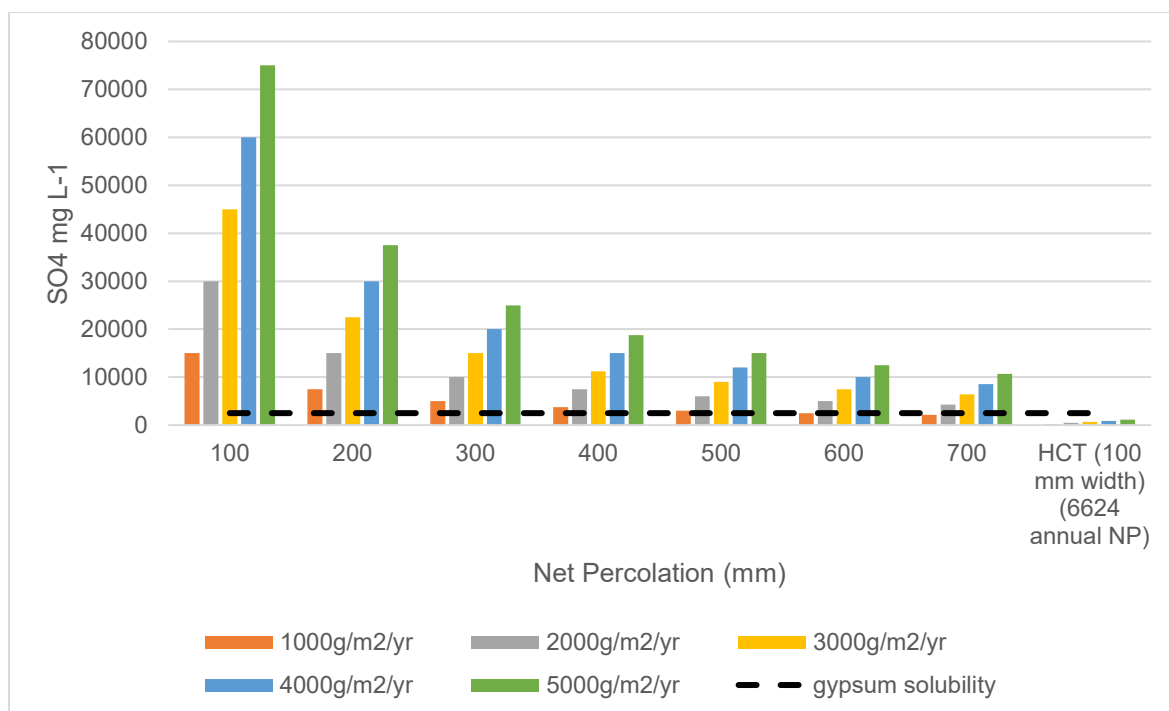


Fig. 27. Maximum porewater sulfate concentrations in relation to gypsum solubility generated from mine waste with sulfide content sufficient to exhaust all oxygen ingress rates (as O_2 g m^{-2} year $^{-1}$) shown. Net percolation rates typical of those experienced by mine waste facilities, including an example of the equivalent net percolation rate (6624 mm) in a narrow 100 mm diameter HCT

An upflow test can be used to consider porewater more effectively, where L:S ratio conditions between 0.1 – 1 can be simulated. This provides a more realistic assessment of field conditions where L:S ratios are less than 1. The sulfate concentrations produced from an upflow column on mine waste from a copper mine in the Nordic region show (Figure 2) that initially the sulfate flushed from the system at low L:S ratios (<0.2) is much higher in concentrations (>4000 mg L $^{-1}$) likely equating to melanterite dissolution (melanterite is an Fe-sulfate mineral). The solubility constant of melanterite is higher than that of gypsum, resulting in this melanterite being dissolved before gypsum and therefore controlling initial seepage quality (Appelo and Postma, 2005). At L:S ratios greater than 0.2 the sulfate concentration declines to approximately 2000 mg L $^{-1}$, which is indicative of gypsum at equilibrium within the system. This shift in mineral dissolution occurs also in pH circum-neutral mine waste seepage (Figure 3). The concentrations of Mg, Ca and SO $_4$ released in an upflow test of circum-neutral mine waste show that at low L:S ratio high Mg and SO $_4$ and low Ca concentrations prevail, suggesting an epsomite-equilibrium controlled system initially (epsomite is a Mg-sulfate mineral and is more soluble than gypsum so dissolves first). As the L:S ratio increases with reaction progress, the epsomite is dissolved and at L:S ratios between 0.7 to 2.1 the system transitions from epsomite dissolution to gypsum equilibrium (~ 2000 mg L $^{-1}$ SO $_4$).

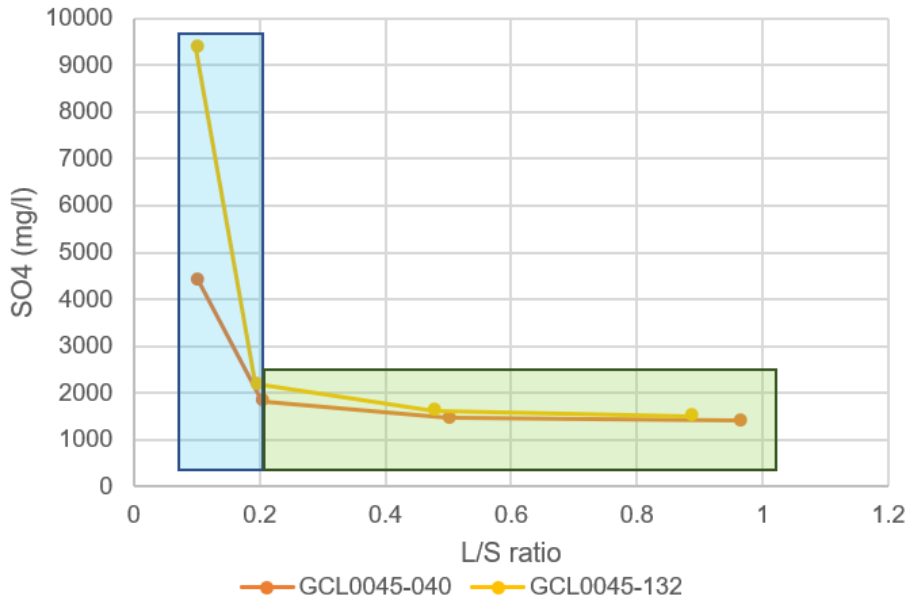


Fig. 28. Upflow sulfate results at evolving L:S ratio. The blue box is where L:S < 0.2 and melanterite dissolution results in high sulfate concentrations. The green is where L:S > 0.2 and gypsum equilibrium occurs

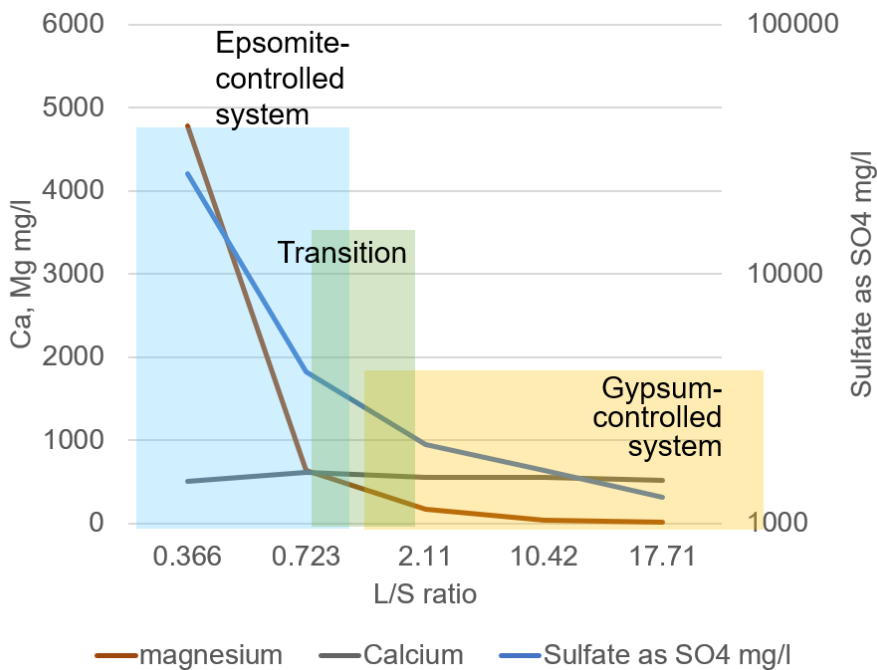


Fig. 29. Mg, Ca, and Sulfate concentrations released in circum-neutral mine waste in an upflow test



The evolution of mine waste drainage will often require evaluating mine waste at varying L:S ratios to enable the effect of evolution of mineral solubility controls to be accurately assessed.

2.2 Detection Limits

Kinetic tests at higher flushing rates, such as HCTs, may mean that pore water pH and EC is affected by dilute conditions in the test (L:S ratio >27) leading to the pore water ionic strength being unrealistically weak. Dilute leachate means that metals may be reported at limit of detection (LOD) in the HCT leachates but in the field may be significantly higher. If this is not taken into account during field scaling key contaminants of concern maybe missed. If these high L:S ratios (>27) are scaled to lower L:S ratio field conditions then the mass load from these elements could be much greater. Table 1 shows the potential range of scaling of different species using simple dilution from high L:S ratios to lower L:S ratios, being more realistic of field conditions.

Table 15. Potential field concentrations if HCT leachates are at detection limits

Elements	HCT leachate (L:S >27)	Potential field concentration ($\mu\text{g L}^{-1}$)		
	LOD ($\mu\text{g L}^{-1}$)	L:S 1	L:S 0.1	L:S 0.01
As, Co, U	0.5	13.5	135	1,350
Cr, Mn, Se	1	27	270	2,700
Al	10	270	2,700	27,000

An example of scaling using site data is the comparison of HCTs and large column tests on mineralogically similar circum-neutral mine waste from a Finnish Ni/Cu mine (Table 2). Both test scales have variability relating to grain size and availability of oxygen as well as the difference between sample mass and flushing rate (i.e., L:S ratios). As such, not all parameters measured in the leachate maybe directly comparable. However, the example of lithium is used here as the release of lithium from mine waste is likely to be less directly controlled by sulfide minerals and sulfide oxidation. In the HCTs lithium is measured below the detection limit of $1 \mu\text{g L}^{-1}$ and the L:S ratio ranges from around one at the start of the test to 31 after 60 weekly cycles. In the large column tests, where the L:S ratio ranges between 0.01 – 0.41 between the starting flush and the final flush (over ~30 weeks), the lithium concentration is much higher ranging between $1.2 - 39.1 \mu\text{g L}^{-1}$.

Table 16. Comparison of HCT and column leachates on circum-neutral mine waste

Parameter	HCT cell 1	HCT cell 2	HCT cell 3	Large column 1	Large column 2	Large column 3	Large column 4
L:S ratio range		1 - 31		0.084 - 0.41	0.085 - 0.38	0.079 - 1.33	0.01 - 0.33
Li concentration range ($\mu\text{g L}^{-1}$)	<1	<1	<1	12.5 - 29.4	18.2 - 39.1	7.96 - 13.5	1.22 - 10

2.3 pH Sensitivity

The pH of leachate produced from waste rock can be sensitive to the L:S ratio. Waste rock samples from a gold mine in Nigeria classified as either MPAF (moderate potentially acid forming) or PNAF (probable not acid forming) were leached using two different kinetic test methods: standard HCTs using 1 kg samples and approximately 0.5 litre weekly deionised water irrigation; and a downflow percolation column test (DPT) where a much larger sample (~4 kg) is flushed using a relatively small volume of deionised water (~0.4 litres every four weeks). These larger DPT columns are designed to simulate more realistic field conditions. The HCT generates a lower pH in both the PNAF (by around 0.5 pH units) and the MPAF (by around four pH units), where as drainage from the DPT columns maintains a pH of approximately 8 on both waste classifications (Figure 4). The pH is sensitive to the flushing rate of the columns: in the higher flushing rate of the HCTs pore water alkalinity is potentially more dilute and due to the quicker flushing time (and potentially shorter reaction time), less able to buffer the acidity produced in the porewater. Alternatively, the dissolution rate of the carbonates may be too low relative to the flushing rate, preventing buffering occurring. Metal solubility and mobility is often strongly pH dependent; therefore pH sensitivity can have major implication on the test results and subsequent interpretation.

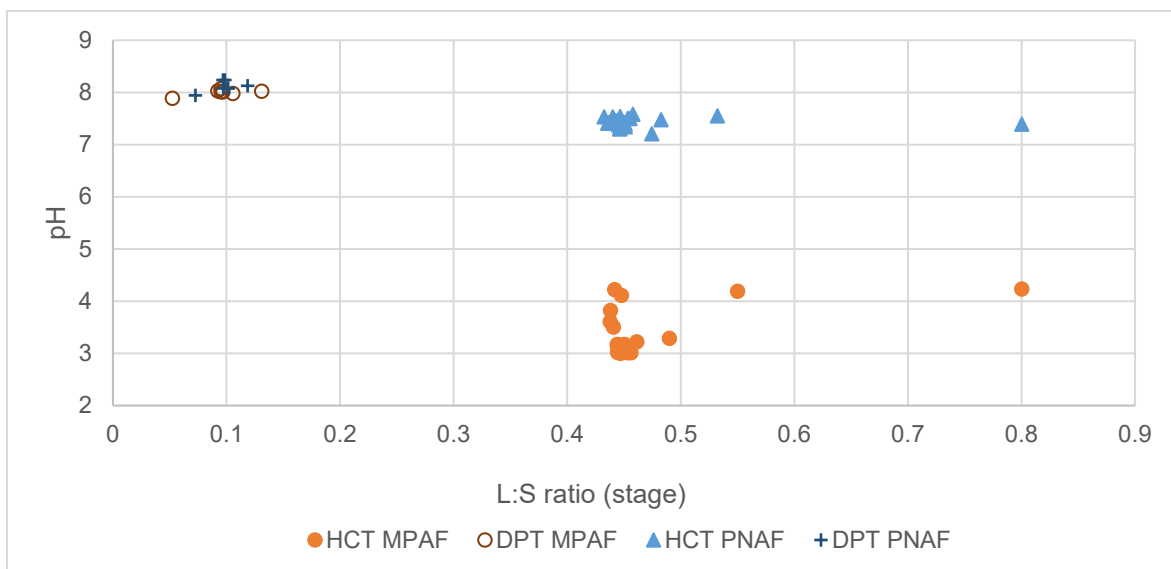


Fig. 30. pH measured in HCT and DPT MPAF and PNAF waste rock leachates by stage L:S ratio

2.4 Limitation of Sorption

The higher flushing rate and higher L:S ratio may also impact the sorption occurring on the surface of mine waste. The As:SO₄ ratio in HCT leachates from mine waste from a gold mine in Northern Europe is shown in Figure 5 and the monitoring results from an in waste dump



lysimeter in Figure 6. Given the humidity cells are highly flushed (i.e., contact time is lower) and it is suspected that sorption to iron oxides is a key process in limiting arsenic mobility it is possible that sorption is being suppressed in the HCT test. This is potentially due to reduced formation of iron hydroxides and thus available sorption surface from a higher flushing rate. Overall, this results in higher arsenic release rates relative to waste rock lysimeter conditions, which typically show a As:SO₄ ratio in field lysimeters of less than 1 (Figure 6) compared with the HCT As:SO₄ ratios between 1 and 300 (Figure 5). The HCTs in this example have a stage (monthly) L:S ratio of approximately two where as the field L:S ratio is expected to be around 0.1.

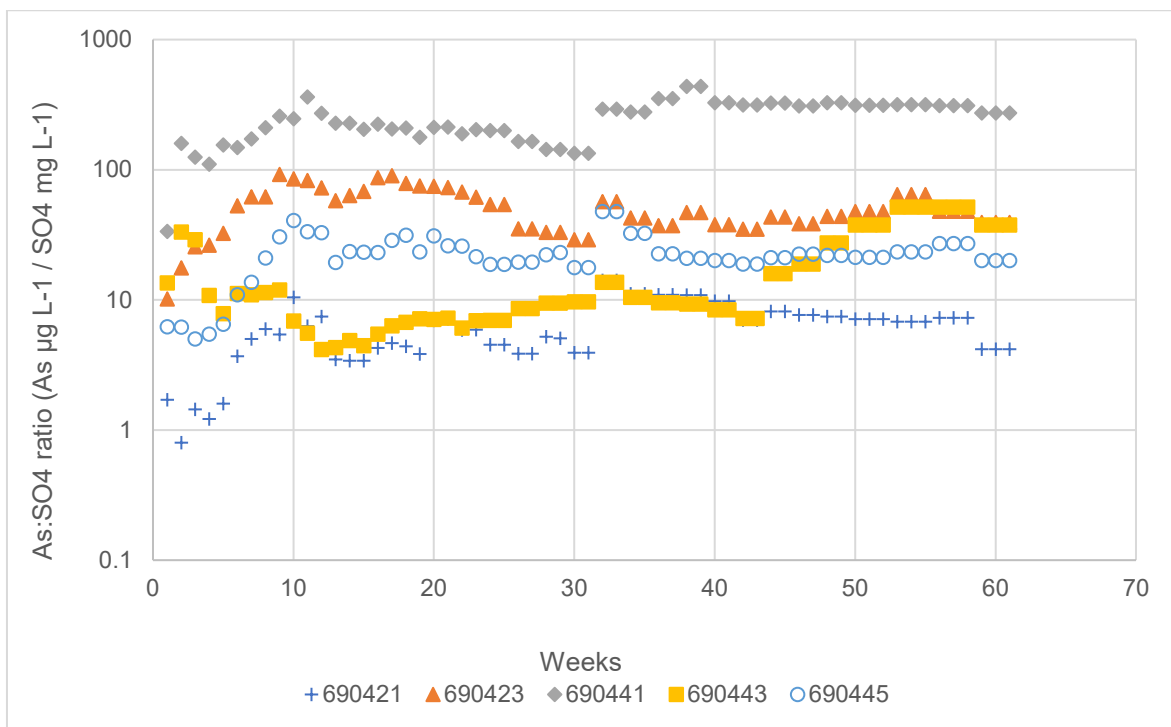


Fig. 31. As:SO₄ ratios in HCT leachates of waste rock at pH 7 – 8 (note, the numbering in the legend numbering relates to HCT sample numbers)

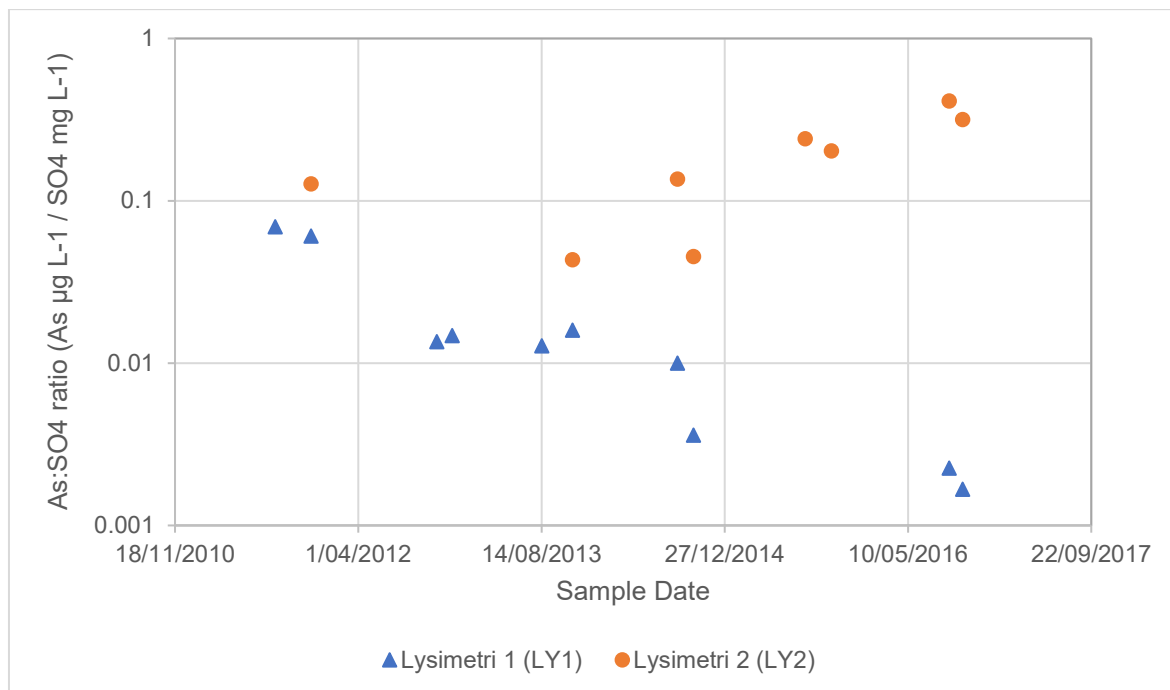


Fig. 32. As:SO₄ ratios in WRSF field lysimeters at pH 7 – 8

3.0 CONCLUSIONS

The effects of differing L:S ratios in analytical and field scale tests range from differences in the solubility constraints visible in leachates, limitations of detection limits and dilution at higher flushing rates, pH sensitivity and decreased sorption resulting in higher contaminant loads than observed in the field. These effects and the correct scaling and interpretation of analytical results is a key issue for accurate mine waste geochemical assessment and water quality prediction. In particular, under or overestimating final metal or sulfate loads could result in significant cost variations in water treatment or waste management from selection of inefficient or insufficient operational management methods and closure measures.

REFERENCES

- Appelo, C, and Postma, D (2005) *Geochemistry, Groundwater and Pollution*. 2nd Edition, Balkema, Rotterdam.
- MEND (2009) MEND Report 1.20.1: Prediction manual for drainage chemistry from sulphidic geologic material. Prepared by Bill Price, December 2009.
- Parbhakar-Fox A and Lottermoser BG (2015) A critical review of acid rock drainage prediction methods and practices. *Minerals Engineering* **82**, 107 – 124.



Pearce S, Scott P, and Weber P (2015) Waste rock dump geochemical evolution: matching lab data, models and predictions with reality. In '10th International Conference on Acid Rock Drainage and IMWA Annual Conference'.

Sapsford DJ, Bowell RJ, Dey M and Williams KP (2009) Humidity cell tests for the prediction of acid rock drainage. *Minerals Engineering* **71**, 25 – 36.