

# Evaluating Circum-neutral Mine Drainage: Case Studies of Advanced Testing Methods Generating Representative Empirical Data

Steven Pearce<sup>1</sup>, Andrew Barnes<sup>2</sup>, Seth Mueller<sup>3</sup>, Diana Brookshaw<sup>1</sup>

<sup>1</sup>*Mine Environment Management, 3 Vale Street, Denbigh LL16 3AD, Wales, [spearce@memconsultants.co.uk](mailto:spearce@memconsultants.co.uk)*

<sup>2</sup>*Geochemic Ltd, 3 Coghill Research Laboratories, Lower Race, Pontypool, PN4 5UH, Wales, [abarnes@geochemic.co.uk](mailto:abarnes@geochemic.co.uk)*

<sup>3</sup>*Boliden Mineral AB, Boliden, Sweden, [seth.mueller@boliden.com](mailto:seth.mueller@boliden.com)*

## Abstract

Standard acid mine drainage (AMD) characterisation testing methods focus on acidity and can underestimate risks posed by circum-neutral mine drainage. For circum-neutral sites, amended testing methods are required to provide representative empirical data. Case studies of where such amended testing methods have been used to refine assessments of discharge quality from circum-neutral drainage sites are discussed.

**Keywords:** Modified Columns, Circum-neutral Drainage, Modified NAG Test

## Introduction

The geochemical testing of mine waste materials aims to characterise their properties to allow prediction of their behaviour longer term under a range of conditions, such as when subjected to different oxygen levels or leached due to rainfall. Since the mine wastes from many sites generate acidity upon oxidation, and the mobility of most metals is enhanced in acidic solutes (e.g. Krol *et al.* 2020), the standardised testing methods are centred around determining the relative acidity of the drainage (for example acid-base accounting (ABA) testing, including net acid generation (NAG) tests and acid-neutralisation capacity (ANC) tests).

Typically, acidity causes mineral dissolution, releasing the components of those minerals, and desorption of metals due to competition with H<sup>+</sup> ions. Both of these processes, therefore, can contribute to increase in metal loading of the solute with decreasing pH.

However, many metals released through sulfide oxidation, such as cobalt and nickel, are mobile in circum-neutral pH environment, with order of magnitude difference in solute concentrations occurring over the pH range of 6-8. In environments where sufficient buffering is present to buffer the generated acidity, correct estimation of pore water pH,

and changes in metal behaviour at relatively small changes in pH are critical for rock drainage metal leaching assessments.

The behaviour of waste rock materials is characterised through a combination of static and kinetic tests. Static tests reflect 'snapshots' of the behaviour under specific conditions, for example pH-dependent leach test, or under full oxidation, with the net acid generation (NAG) tests. Kinetic tests track the evolution of the solute in response to flushing. In both cases selecting the correct conditions is key to achieving representative results. Standard kinetic tests such as humidity cells, for example, have very high flushing rates, and as such are not likely to capture the slow drain-down processes occurring at low liquid-to-solid (L:S) ratios in waste rock dumps or tailings storage facilities. Using the outputs of such standard kinetic tests to assess drainage risk from circum-neutral sites can result in underestimation of flush-out times for residual sulfate loads from processing, inaccurate simulation of pore water pH conditions and overestimation of metal release rates.

To improve prediction of water quality from circum-neutral sites, a suite of novel or adapted testing methods is needed to target the contaminant release mechanisms that dominate in those conditions such as mineral

dissolution/precipitation reactions and sorption processes. The research discussed here describes a set of tests which have been used to generate robust empirical data as part of metalliferous drainage assessment at active mine sites in Scandinavia (nickel mine in Finland, and a copper mine in Sweden). Materials analysed included samples of partially weathered waste rock material collected from waste rock storage facilities (as part of a sonic drilling program of work), in general material <22mm in size were analysed and for leach testing material <2.36mm was analysed.

## Methods

### *Amended NAG test*

To understand the interplay between oxidation, sorption and metal release, and provide additional data in the circum-neutral to slightly-acidic pH range, conditional NAG test leaching was performed with AMIRA P387A-Appendix D as a guideline, with modifications applied to the described method. The amount of solid and 15% H<sub>2</sub>O<sub>2</sub> reagent were doubled relative to the standard method, to provide sufficient sample while maintaining the liquid to solid ratio (L:S ratio). After H<sub>2</sub>O<sub>2</sub> addition, the test was run for 24 h and monitored. No boiling step was performed, since this was demonstrated to report unrepresentative pH and leachate quality (see Barnes *et al.* 2021) because of the material type (ultramafic mineralogy with carbonates). The NAG pH, EC and temperature were measured and 50 mL aliquot collected, filtered through 0.45 µm polyethersulfone (PES) filter into bottles and preserved with 0.57 mL 40% nitric acid for analysis by ICP. The pH of the NAG liquor solution was then adjusted via titration and samples were taken for analysis at various pH steps including pH 5, 6, 7, 7.5 and 8.

### *Amended pH dependent leach test and sorption-desorption assessment*

The effect of pH on the release of metals and sulfur/sulfate from the partially weathered samples was tested through a series of pH controlled or amended tests. A set of samples of <2.36mm material were equilibrated with deionised water through bubbling with

nitrogen during overhead stirring, and in the absence of CO<sub>2</sub>. If the starting ‘rest’ pH after this equilibration was below 8, this was corrected by addition of 100 µL aliquots of 1 M KOH until the rest pH was above 8. The sample solutions were then sparged with CO<sub>2</sub> to achieve precise amendment of the pH to pH 8, 7.5, 7 and 6. Allowing equilibration at each step for 30 minutes before recovering liquid sample aliquot for analysis. This method of controlling pH allows better control to ensure the correct pH is achieved at each step. It also decreases the effect of addition of competing cations to amend pH, which may compound sorption processes.

### *Mixed leach test*

A mixed leach test was designed to better understand the role of the solids (i.e. presence of fine grained mineral particles) in controlling solution chemistry. Initially two DI leaches were performed on <2.36 mm size fraction of higher risk and lower risk waste samples, both at 2:1 L:S ratio, performed for 24 h while mixing by end-over-end tumbling. After the mixing period, equal amounts of each leachate were recovered and filtered with 0.45 µm PES filter, and mixed by end-over-end tumbling for 24 h. An aliquot of the higher risk waste leachate was used as a leachant for a leach test on a new <2.36mm size fraction sample of the lower risk waste sample in a 2:1 L:S ratio. The leachate and waste rock were contacted for 24 h and mixed by end-over-end tumbling.

### *Amended leach columns testing*

The mineral precipitation/dissolution dynamics and their effect on drainage evolution over time were investigated using kinetic columns. The standard method defined in EN 14405:2017 explores solution chemistry at liquid:solid ratios of 0.25 to 10.

Customised column tests were prepared, with bespoke amendments to the standard method to capture specific aspects to provide representative results in a practical timescale (Table 1). Liquid samples were recovered from the seepage from each column and analysed for a suite of physical and chemical parameters including pH, sulfur and metals of interest.

Table 1 Comparisons of amended vs standard upflow column test method.

Test	Flow rate mL/h	Cumulative L:S ratio in first six steps	Temp °C	Atmosphere
Standard upflow test	10	0.25, 0.5, 1, 2, 4, 8 24 hours to L:S ratio of 0.5	25	N <sub>2</sub>
Small column (start)	0.95	0.25, 0.38, 0.51, 0.65, 0.8, 0.9 14 days to L:S ratio of 0.5	8	Air
Small column (long term)	0.22	0.25, 0.38, 0.51, 0.65, 0.8, 0.9 14 days to L:S ratio of 0.5	8	Air
Large column (start)	0.95	0.25, 0.27, 0.29, 0.31, 0.34, 0.36 98 days to L:S ratio of 0.5	8	Air
Large column (long term)	0.22	0.25, 0.27, 0.29, 0.31, 0.34, 0.36 98 days to L:S ratio of 0.5	8	Air

**Results**

*Metal release rates*

The standardised NAG testing reported generally NAG pH values above 8 for the nickel mine waste samples (and up to pH 10), with a cluster of results at pH<4, and limited results in the range 8-4. The standardised testing results indicated that at this site NAG pH tests produced results that are spuriously high and are not likely representative of field pore water conditions. This has been confirmed by other studies (Barnes *et al* 2021). The leachate results are considered as a ratio of metal to sulfate concentration to focus on the release mechanisms without bias due to elemental composition of the samples. Based on the leachate quality from this testing, an exponential Ni/S relationship to pH is estimated (Figure 1).

The pH-dependent leach testing provided more detailed results between pH 8 and 4, predicting an exponential relationship between Ni/S ratio and pH. The pH-dependent leach results predicted higher Ni concentrations relative to sulfur for the same pH compared to the standardised NAG leach test. This difference arises because of test conditions and solubility constraints with mineral dissolution at circum neutral pH where gypsum is likely the main sulfate mineral precipitated, but at lower pH conditions sulfates such as jarosite may form. When pH is varied in a sample that has been subject to sulfide oxidation at circum neutral pH the concentration of nickel changes but the concentration of sulfate does not as gypsum is not sensitive to pH but nickel is. In

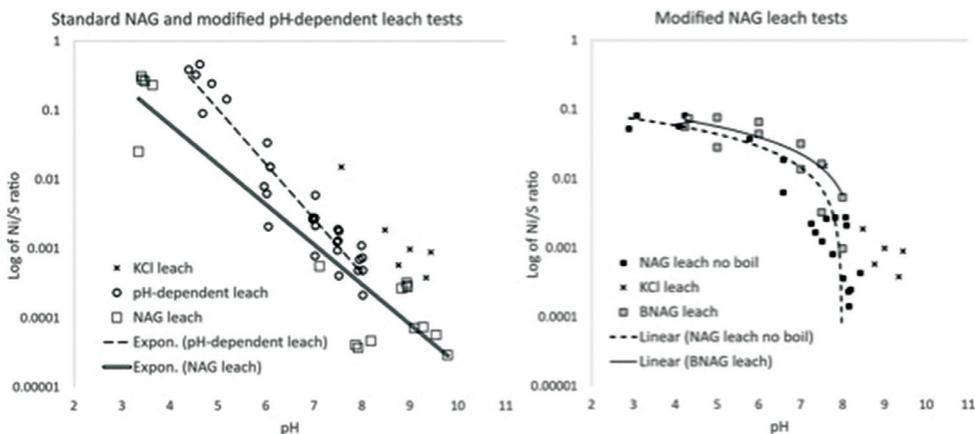


Figure 1 Scatter plots of the nickel to sulfur ratio in leachates of different pH values generated by the tested analytical method. Left: standard NAG leach tests and modified pH-dependent leach test. Right: Modified NAG tests. Potassium chloride (KCl) leach test results are included in both graphs for comparison.

the NAG test high dilution rates of  $\approx 50$ -100:1 liquid to solid mean that sulfate is not likely limited by solubility constraints, however in test with lower liquid solid ratios sulfate may be solubility constrained. Further where a sample has been subject to sulfide oxidation at lower pH values ( $< \text{pH } 4.5$ ) other sulfate minerals such as jarosite may form which in turn effects the release of nickel. As such the ratios of nickel to sulfate in the NAG test are not likely to accurately represent field conditions when dealing with circum neutral sites, and in particular where they are subject to pH changes over time. This observation is important when considering field conditions where liquid solid ratios in pore water are significantly lower (generally  $< 0.5$ ) and where pore water pH may change over time (for example a decrease over time from  $\approx 8$  to  $\approx 5$ ).

When NAG testing was carried out without the boiling step, NAG pH values were typically between 6.5 and 8.5. The available data shows a relationship with pH interpreted as linear (seen curved on a log y axis scale, Figure 1). This was also the case for results where the NAG solution was back-titrated to specific pH steps, with a hysteresis relative to the NAG leach (no boil) results. For both of these tests the Ni/S ratio was higher than the pH-dependent leach, reflecting the effect of oxidative Ni release on the leachate quality (Table 2). The difference in the Ni/S ratio between the results of the no-boil NAG leach test and the BNAG test suggests that less sorption is available in this test (e.g. due to loss of sorption sites relative to material exposed to solute of the same pH where the pH did not decrease further).

The results suggest that the method of assessment to estimate metal/sulfate release and relative solute concentrations has a significant effect on results and as such assumptions that may be used for modelling.

For circumneutral sites very careful method design and selection is required. Reliance on standard test methods therefore carries a high degree of risk.

### Sorption

Leach test results from low-risk and high-risk solids (standard 2:1 L:S ratio DI method) had similar pH (6.21 and 6.18 respectively), but had very different concentrations of cobalt, nickel and manganese, reflecting the source metal abundance-associated circum-neutral metal leaching potential of the waste rock materials at this site. Copper mobility is highly pH sensitive, reflected in the very similar copper concentrations reported in the 2:1 L:S ratio leachate.

For all metals, mixing the supernatants at 1:1 ratio, resulted in leachate quality approximately equal to the average of the concentrations of the metals in the constituent leachates (Table 2), which given the pH was similar this results is not surprising. When however the same experiment is carried out but in the presence of the low risk solid, the concentrations of all metals except Cu decreased by an order of magnitude, indicating that the presence of solids has a material effect on solute concentration. The results confirm that at circum-neutral pH, sorption processes are a very significant control metal mobility, and that testing method can significantly effect solute concentrations and implied metal mobility. The results are particularly relevant when leaching test results of different materials are assessed in combination (for example taking averages of leach test results for example).

### Kinetic solute evolution

Results of the upflow test (Figure 2) show that flushing of the soluble salts occurred within the first 24 hours (or when 1:1 L:S ratio was

**Table 2** Leachate quality in mixed leachate tests.

Metal/Sample	Co mg/kg	Cu mg/kg	Mn mg/kg	Ni mg/kg
Low-risk solids leach	0.00224	0.00842	0.033	0.0612
High-risk solids leach	1.24	0.01968	21.4	14.84
Composite supernatant mix	0.626	0.01084	10.68	7.56
Low-risk solids leach with high-risk sample leachate	0.01492	0.01542	1.052	0.496

reached). Typically, most parameters had relatively constant concentrations at L:S ratios of over 1, indicating that the majority of soluble salts had been flushed out.

The pH remained above 7.5 in all tests, indicating circum-neutral conditions (Figure 2) however pH was lower in the upflow tests indicating that the faster flushing rate in this test materially influenced pore water pH conditions. The pH results in the small and large column mirrored one another in time, although this was reflective of a different L:S ratio. The results therefore indicate that pH may be controlled by residence time, and therefore related to the kinetics of dissolution of mineral phases rather than the amount of percolation.

In the amended columns, sulfur concentrations had lower initial concentrations and decreased at a slower rate when compared to the upflow test relative to L:S ratio. The greater contact time within these columns was a likely significant

influence on sulfate mineral dissolution kinetics and also potentially indicative of greater dissolution of less labile sulfur-containing minerals. These effects likely contributed to a longer time frame to flush out sulfate minerals in the amended relative to the upflow test and are critical to consider when scaling results to field interpretations of timeframes for removal of sulfate minerals from mine waste facilities.

The concentrations of nickel and manganese had a different pattern to sulfate, correlating to time since start of the experiment to a greater extent than L:S ratio, and are significantly lower in the upflow test. These results suggest that nickel and manganese solute concentrations are controlled by pore water residence time to a great extent. Over the initial period of the test to L:S ratio of  $\approx 0.5$  sulfate concentrations were higher in the large column for example but nickel concentrations were lower.

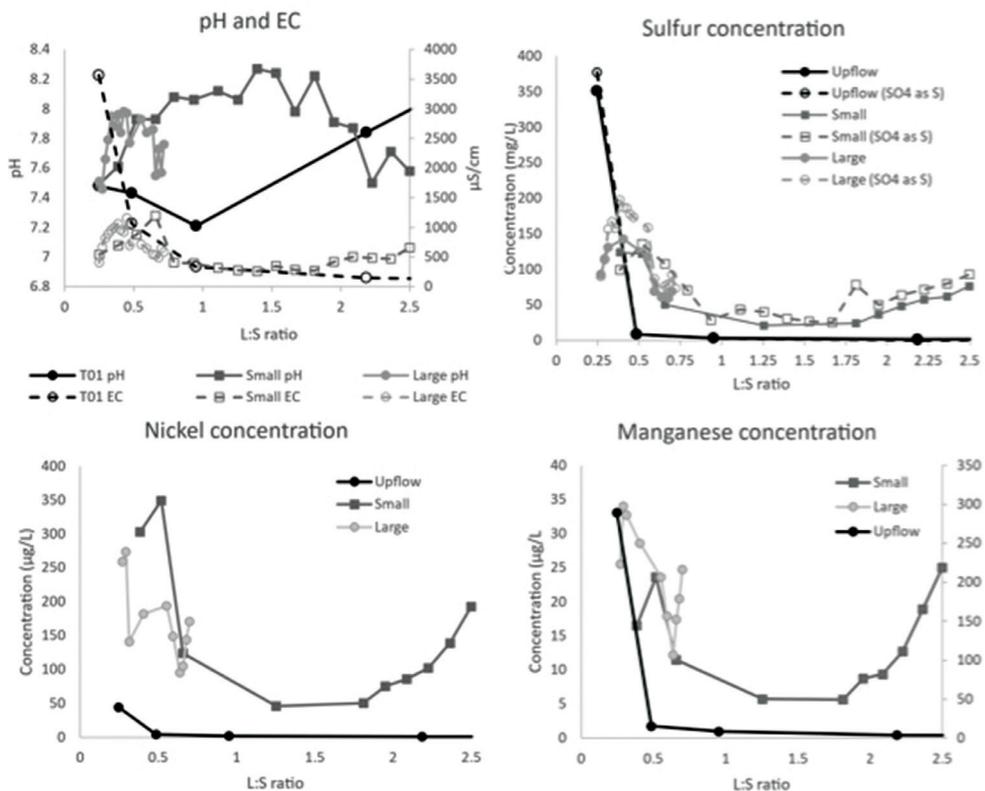


Figure 2 Scatter plots of results of amended columns of tailings relative to standard upflow test results: Top Left: the pH and EC; Top Right: sulfur and sulfate concentrations; Bottom Left: nickel concentrations; Bottom Right: Mn concentrations.

The longer-term testing shows that after approximately 150 days sulfate, nickel and manganese concentrations are increasing but this is related to the effects of sulfide oxidation presenting in the seepages and interpretation of this data is beyond the scope of this brief paper.

## Conclusions

The use of modified geochemical testing methods to better understand and predict the behaviour of waste materials under circum-neutral conditions has been evaluated.

Standard methods like the NAG test have been proven to produce spurious results when considering “real” field conditions with regards to solute pH, and as such modifications are suggested to improve the “representativeness” of this test as applied to the types of materials investigated (ultramafic carbonate containing mineralogy).

The main source of sulfate and metal release from waste materials tested was found to be the dissolution of secondary sulfate (gypsum and epsomite) mineral products that contain free base metals. NAG liquor analysis indicates that these sulfate minerals are formed as a direct result of the oxidation of iron sulfides (pyrrhotite/pyrite) and base metal sulfides (pentlandite and chalcopyrite) and subsequent dissolution/buffering with the magnesium/calcium carbonates dolomite and calcite. The mechanism of dissolution of these sulfate minerals and associated metals within pore water was interpreted from site specific and modified testing to be limited by pH mediated sorption and solubility constrains (in particular gypsum). These processes control the both the rate of dissolution and absolute pore water concentrations of sulfate and key metals such as nickel and as such understanding them is key for making accurate predictions of future water quality.

The key mechanisms for the control of solute metal concentration appears to be

related to pH dependant sorption, and the form of the dominant sulfate mineral phase (which is controlled by the pH at which sulfate mineral formation occurs). Based on assessment of testing data, a strong case can be made for adoption of site specific modified testing methods to establish likely metal mobility.

The results of the column testing show that where circum-neutral drainage condition prevail, understanding of kinetic mineral dissolution rates and metal mobility under site specific flushing rates is likely key to be able to predict likely long term pore water concentrations. The results of the testing carried out indicate the high value of empirical data to achieve a thorough understanding of these site specific factors.

In general the results indicate that while the standardised tests play a role in determining the context within which the materials should be considered, where waste materials are likely to generate circum-neutral drainage, standardised tests need to be supplemented with further analysis aimed at providing empirical data that can be used to inform predictive modelling.

## References

- Krol A, Mizerna K, Bozym M (2020) An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. *J Hazardous Materials* 348: 1-9, doi:10.1016/j.jhazmar.2019.121502
- Barnes A, Sapsford DJ, Bowell RJ, Dey M (2013) An assessment of rapid turnaround tests for ARD prediction. Presentation at 23rd World Mining Congress, August 11-15th, 2013, Montreal, Canada
- Karlsson t, Raisanen ML, Lehtonen M, Alakangas L (2018) Comparison of static and mineralogical ARD prediction methods in the Nordic Environment. *Env Mon Assess* 190(719), doi:10.1007/s10661-018-7096-2