

Justification For Modification Of The NAG Test Method To Suit Varied Mining Waste Geochemical Characteristics On A Site-Specific Basis

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Abstract

The Net Acid Generation (NAG) test is generally carried out using a consistent method, irrespective of the site or the geochemical properties of material being tested. There are significant risks posed by utilising standard methods to assess processes which are inherently site specific like AMD. This can lead to misleading interpretations of results which is particularly true where the NAG liquor is being used to give an indication of elemental mobility during sulfide oxidative weathering. Examples include an average 3 pH unit increase between pre and post boiling, and greater than 60% reduction in nickel release to the NAG liquor.

Keywords: Net Acid Generation (NAG) Test, Hydrogen Peroxide Leach, Acid Mine Drainage

Introduction

Net acid generation (NAG) testing has been widely used by mine waste geochemists globally to aid in prediction of acid rock drainage and metals leaching (ARDML) since the mid 1990's. The test method allows the rapid determination of the acid generation potential through the use of hydrogen peroxide (H₂O₂) to rapidly oxidise sulfide minerals and release associated acidity. The oxidation process occurs in the same manner as would occur with oxygen as the primary oxidising agent albeit much more rapidly. The generated acidity in turn reacts with any rapidly available neutralising potential (carbonates and some silicates) allowing the determination of Net acidity through back titration. In combination with Acid Base Accounting (ABA) methods and other ARDML prediction techniques, the test can be a very effective tool to aid mine waste characterisation.

The concept, and ultimately the NAG method used today has been developed by a number of pioneer researchers over the past

40 years. These include; Sobek *et al* (1978), Finkelman & Giffin (1986), O'Shay *et al* (1990) and Miller *et al* (1997). The work culminated in the currently accepted 'quasi' standard as published by Smart *et al* (2002) in the AMIRA ARD test handbook.

The leachate generated during NAG testing can be analysed to give an indication of the potential mobility of contaminants from a waste material during weathering. Several authors have also suggested the use of NAG test leachate data as an aid to prediction of mine water discharge chemistry (Miller *et al*, 1997; Stewart *et al*, 2006; Sapsford *et al*, 2010; Barnes *et al* 2015). However, a number of recent studies have observed that the standard NAG testing methodology can greatly under or over predict the leachate pH (see Stewart *et al*, 2006; Charles *et al* 2015; Karlsson *et al* 2018) influencing the concentrations of dissolved trace elements (noting that the solubility of many key metal species is highly pH dependant).

Karlsson *et al* (2018) undertook NAG testing on waste rock from a number of

Scandinavian mine sites and compared the results to actual site seepage data. The study found that the standard NAG testing method often over predicted pH from circum-neutral deposits (i.e. was overly optimistic) and under predicted pH from mine wastes which themselves were generating acidic seepage. Previous work by Charles *et al* (2015) following similar observations of high pH values (in excess of pH 10) from post boiling stage NAG test data (i.e. NAG pH) showed that the high pH conditions were potentially attributed to CO₂ disequilibria following degassing of the sample during the 2 hour boiling step.

The generation of elevated pH may not be a concern when the tests are solely used to give an indication of potential acid forming and non-acid forming behaviour. However, the large deviation in pH from that which would be expected in the field can result in very large error when using NAG leachate data to assess mobility risk of key toxic metal or metalloid species. This is due in part to the sensitivity of the mobility of these species to pH.

This paper presents the justification for modification of the NAG test on a site-by-site basis as demonstrated through particular experience at the Kevitsa mine site in northern Finland.

Kevitsa Case Study

Kevitsa ore deposit is a Ni-Cu-PGE mineralisation hosted in a mafic / ultra-mafic cumulate. The waste rock from the deposit comprises largely of amphibole ‘tremolite’ ≈30%, and diopside ‘augite’ ≈35%. With minor amounts of Mg olivine ‘forsterite’ ≈5%, orthopyroxene ‘enstatite’ ≈7.5% with relatively low concentrations of serpentine. Carbonates are present as calcite and dolomite, but concentrations are generally less than 1% (total inorganic carbon content = 0.8% equivalent as calcite). Sulfide minerals are present in the waste typically at concentrations less than 1% mainly as pyrrhotite, chalcopyrite and pentlandite. Nickel is recognised as a key element potentially mobilised under circum neutral conditions as a result of sulfide oxidation.

Due to the presence of calcite and dolomite, and generally low sulfide content, the majority of the waste rock at Kevitsa is Non-Acid Forming (NAF) having and excess of acid neutralising capacity to acid generating capacity.

Between 2013 and 2017 in the region of 400 NAG tests were undertaken on samples of waste rock and tailings from the Kevitsa deposit using the Smart *et al* (2002) method. Associated NAG liquor analysis was undertaken on a small sub-set of 17 of these samples. As is conventional the NAG liquor was collected following the boiling step and prior to the NAG back titration. The NAG pH and electrical conductivity (EC) was also measured following the boiling step. The results of the standard NAG testing showed nickel release less than 1 mg/kg for the waste rock samples with an average pH of 8.85.

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On review of the data with respect to observations made by Charles *et al* (2015), it was thought likely that the high NAG pH and low Ni mobility may be attributed to the boiling step used in the standard NAG method. This can have the effect of increasing the leachate pH due to degassing of dissolved CO₂ in the sample and forming a CO₂ disequilibrium between the solution and the atmosphere.

Based on the above, during the most recent waste characterisation study undertaken on the Kevitsa waste rock during 2017 / 2018, it was decided to utilise a modified NAG method. This method included a pre-boil NAG pH and EC measurement together with pre-boil sample of NAG liquor.

Results of revised testing

To understand the effect of the boiling step on leachate quality, NAG testing with pre-boil and post-boil pH measurements were undertaken on six samples (See Figure 2). All samples showed a post-boil pH increase ranging from 0.79 pH units (GCL0046-058) and up to 2.7 pH units (GCL0046-052) with an average increase of 1.47 pH units. To determine the impact of pH on the leach samples, the concentration of dissolved constituents sampled prior to boiling were

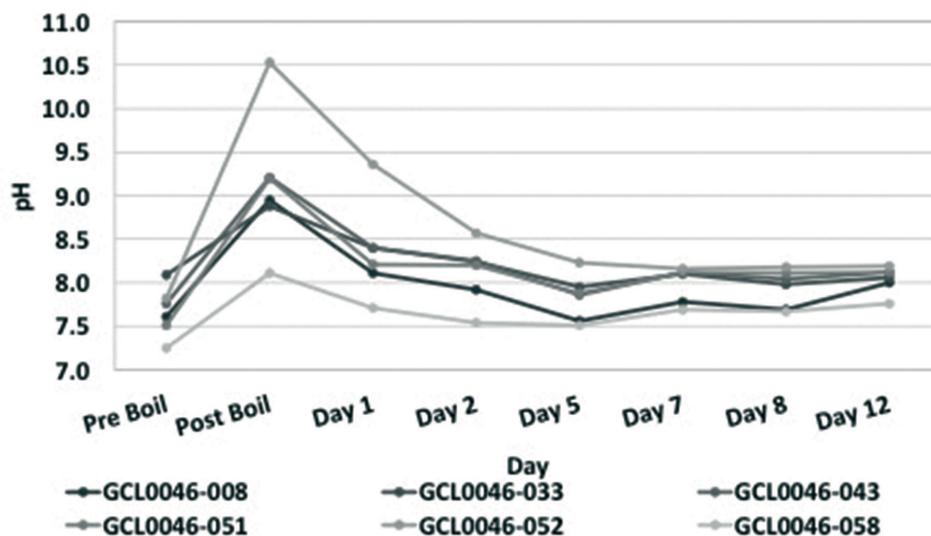


Figure 1 Evolution of pH following boiling of NAG solution.

compared to those sampled at the end of the 12 day equilibration period. The results of boiling support the findings of Charles *et al* (2015) showing that the initial post boil pH increase recovers to near the pre-boiling pH given roughly 5 days which is attributed to equilibrium with atmospheric CO₂ as indicated in Charles *et al* (2015). It is clear however, that if NAG liquor samples are taken for analysis immediately following the post boiling stage, that the leachate pH will be out of equilibrium which is likely to affect the solubility of many elements that are of interest in a geochemical characterisation study.

In the above analysis, and also in all NAG tests undertaken for the current stage of work in the project, leachates were routinely sub-sampled for elemental analysis prior to the heating stage. In the case of the NAG pH equilibrium tests shown above, samples were also taken after the 12-day equilibration period for GCL0046-058 and 052. The results of nickel release for the pre-boil and post 12-day re-equilibration period analysis are shown in Figure 3. The graph demonstrates that the nickel release in the NAG leachates post-boil equilibration are roughly 60% lower than the pre-boil concentrations despite the solution pH largely recovering to pre boil levels.

The lower concentrations of metals in the NAG liquor following boiling can be attributed

to reduced mobility of nickel at elevated pH through such processes as precipitation of hydroxides and adsorption on to mineral surfaces however, the failure of concentrations to recover to pre-boil levels indicates that the processes that are responsible for reducing the mobility are not completely reversible.

Comparison of Historic NAG Data

In order to test the theory, modified NAG tests were undertaken on 64 of the samples from the 2013 to 2017 sampling which had previously been run with the Smart *et al* (2002) method. This allowed the pre-boil NAG pH from the NAG re-runs to be compared to the post-boil NAG pH values from the historic testing (see Figure 4). There is a clear difference in the overall NAG pH distribution, with no samples having a pre-boil NAG pH exceeding pH 8, while three quarters of the post-boil NAG pH for the same samples exceeding pH 8.5. The maximum post boil pH values were pH 11.5 with the average pH increase between pre and post boil NAG pH of 3 pH units.

Historical NAG liquor data was also compared to new data obtained at the pre-boiling stage of the standard NAG test (expressed as a ratio of nickel release relative to sulfur on a logarithmic scale, as above). The resultant graph resembles a pH

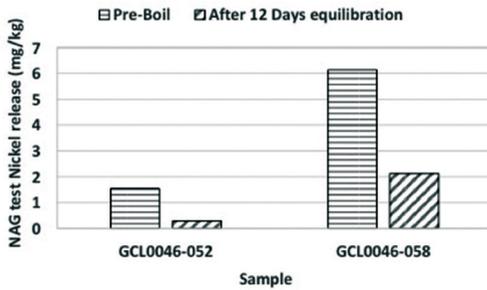


Figure 2 Difference in nickel release Pre-boil and post equilibration for sample GCL0046-052 and GCL0046-058.

dependant leach curve which demonstrates the importance of pH to nickel mobility (Figure 5). It is clear that the historical NAG data plots in the pH range >8.5 and relative nickel:sulfur ratios are significantly lower. Because the relative change in nickel mobility was found to be in the orders of magnitude between the pH range of 7-9. It is clear that estimation of nickel mobility using the NAG test is very sensitive to testing method, and that by using liquor data from the standard method to make initial assessment of nickel mobility will result in a large underestimation of nickel concentrations.

Key Observations

NAG liquor / hydrogen peroxide leach analysis is an important tool for initial assessment of metal mobility from mining waste. This is especially true on un-weathered sulfidic

material such as drill core where water leaching tests would yield little usable information.

Observations made in the current study broadly agree with the findings of Charles *et al* (2015) and Karlsson *et al* (2018). The current study shows that even following an extended re-equilibration period, the metals concentrations and in some cases the pH does not fully recover to their pre-boil levels. The current study is limited as the elemental analysis was only undertaken at the end of the equilibration period. It would aid the study to understand the behaviour of dissolved metals over the full equilibration period including the period immediately following boiling.

The results of this study and the work of previous authors clearly demonstrate that NAG liquor data obtained from the standard NAG test, should be used with caution and that the standard NAG method, although reliable as an indicator of ARD properties (i.e. NAF or PAF), especially when used in conjunction with acid base accounting and mineralogical assessment, may be misleading when used to assess potential leachate pH and elemental mobility. This is especially true when assessing circum neutral and alkaline drainage situations, and when dealing with NAF samples, as the standard method can lead to a large over-estimation in pH. This in turn can lead to significant decrease in metals concentrations in the leachate, and therefore an under-estimation of concentrations if then inferred to the deposit.

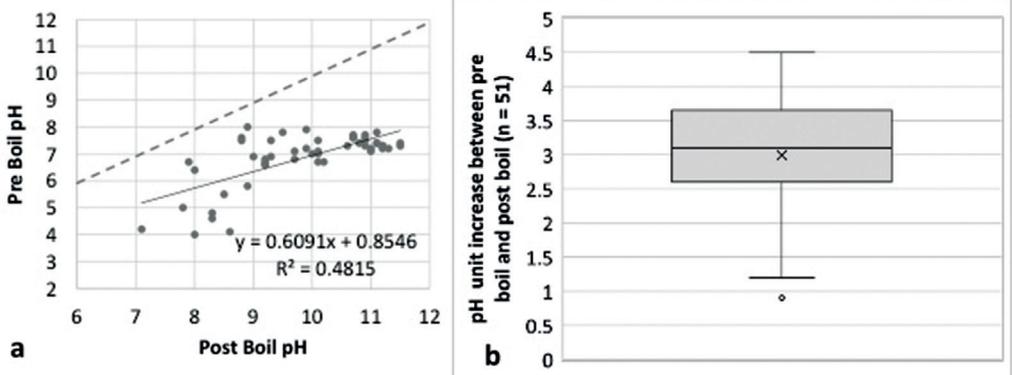


Figure 3 Comparison of the distribution of pH values obtained for the same 51 samples at a post-boil stage and pre-boil stage (a) and box and whisker plot showing the pH unit difference between pre and post boil NAG pH values for the same samples (b).

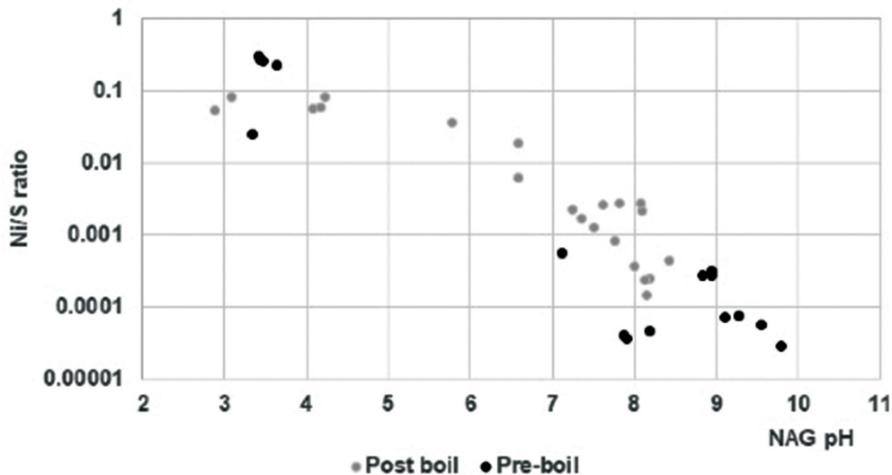


Figure 4 Comparison between Ni/S ratio determined in pre-boil and post-boil NAG leachates.

We would recommend that pre and post boil NAG pH is determined for all NAG testing as a matter of routine. The authors believe that this can give important information on the materials behaviour. In addition, if leachate samples are to be collected, the authors recommend that, when NAF material is being tested, that this is done prior to the boiling step to avoid limitations in element mobility due to the pH increase that can occur during the boiling step.

References

- Barnes, A., Sapsford, D.J., Bowell, R.J., Dey, B.M. (2013). An assessment of Rapid-Turnaround Tests for ARD Prediction. Presentation given at the 23rd World Mining Congress. August 11th to 15th 2013, Montreal, Canada.
- Charles, J.C., Barnes, A., Declerq, J., Warrender, R., Brough, C., Bowell, R.J. (2015). Difficulties of interpretation of NAG test results on net neutralizing mine wastes: initial observations of elevated pH conditions and theory of CO₂ disequilibrium. In: Proceedings of the 10th International Conference on Acid Rock Drainage and IMWA Annual Conference. April 21 – 24, 2015. Santiago, Chile. ppTBC
- Finkelman, R.B. and Giffin, D.E. (1986). Hydrogen Peroxide Oxidation: An Improved Method for Rapidly Assessing Acid-Generating Potential of Sediments and Sedimentary Rocks.
- Karlsson, T., Räisänen, M. L., Lehtonen, M., Alakangas, L. (2018). Comparison of static and mineralogical ARD prediction methods in the Nordic environment. *Environmental Monitoring and Assessment* 190. 719
- Miller, S., Robertson, A., & Donahue, T. (1997). Advances in acid drainage prediction using the net acid generating (NAG) test. In Proceedings fourth international conference on acid rock drainage, (pp. 533–547). Vancouver, B. C. Canada May 31 – June 6, 1997, volume II.
- O'Shay, T.A., Hossner, L.R., Dixon, J.B. (1990) A modified hydrogen peroxide oxidation method for determination of potential acidity in pyritic overburden. *Journal of Environmental Quality* 19. 778-782.
- Sapsford, D. Bowell, R., Dey, M., Williams, C. and Williams, K. 2010. A Comparison of Kinetic NAG tests with Static and Humidity Cell Tests for the Prediction of ARD
- Smart, R., Skinner, W. M., Levay, G., Gerson, A. R., Thomas, J. E., Sobieraj, H., Schumann, R., Weisener, C. G., Weber, P. A., Miller, S. D., & Stewart, W. A. (2002). ARD test handbook: Project P387A, A Prediction and Kinetic Control of Acid Mine Drainage. Melbourne: AMIRA international Ltd 42 p.
- Sobek, A.A., Schuller, W.A, Freeman, J.R. and Smith R.M. (1978). Field and Laboratory Methods Applicable to Overburdens and Mine soils. Report EPA-600/2-78-054, US National Technical information Report. PB-280495.
- Stewart, W.A., Miller, S.D., Smart, R. (2006). Advances in Acid Rock Drainage (ARD) Characterisation of Mine Wastes. Paper Presented at the 7th International Conference on Acid Rock Drainage (ICARD), March 26-30, 2006, St Louis MO. R.I. Barnhisel (ed.) Published by the American Society of Mining and Reclamation (ASMR), 3134 Montavesta Road, Lexington, KY 40502. Pp 2098 - 2119