Dissection of the NAG pH Test: Tracking Efficacy Through Examining
Reaction Products

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Abstract

In this study we sought to better understand the mechanics of the NAG pH test and determine the influence each variable has in controlling the resulting NAG pH, a value which is commonly used by the mining industry for waste classification. Three bulk samples (20 kg) representative of waste types A (alkaline), B (weakly-NAF) and D (PAF) were obtained from the Savage River mine, Tasmania. Variables tested included initial reaction time, heating temperature, heating length, post reaction cooling time and hydrogen peroxide (H_2O_2) strength (n=126). Our observations showed that for this suite, a multi-addition NAG pH test facilitated efficient sulphide oxidation for low sulphide-sulphur samples (i.e., < 0.3 wt. %) with an initial reaction time of at least 480 minutes given per 15% H_2O_2 addition, heating to 80 to 90 °C for 2.5 hours, and then cooling of the reaction solution overnight with the NAG pH reading taken the following morning. This study demonstrated that using the recommended standard conditions given in Smart et al. (2002) is not appropriate for general use. Rather a suite of representative waste samples should initially be selected and the optimal conditions to facilitate sulphide oxidation determined on a site-per-site basis.

Keywords: Static testing| Waste classification| Prediction | NAG testing

Introduction

Improving waste classification predictions is an ongoing area of research (e.g., Chopard et al., 2017; Dold, 2017) but despite several researchers suggesting that such classifications should be based on mineralogical data, the industry remains reliant on static geochemical data. Therefore, it is imperative to ensure that classifications made using these data are as robust a possible. One such screening tool is the net acid generation (NAG) pH test. Whilst it is typically screened against net acid producing potential (NAPP) values (Smart et al., 2002) it is now being increasingly used against other values including total-sulphur, paste pH, and acid rock drainage index (ARDI) values as a lower cost means of allowing waste classification (Weber et al., 2006; Parbhakar-Fox et al., 2011). Given the growing importance placed on this test, its reproducibility is critical, however, in confi-

dential inter-laboratory comparisons, values measured for duplicate samples across three laboratories were vastly different resulting in conflicting waste classifications. This is likely a manifestation of procedural interpretation errors of the most widely cited NAG procedure given in the AMIRA P387A Handbook (Smart et al., 2002). For example, the test is stated as suitable for samples containing <1.5% S and with low concentrations of Cu, but for samples undergoing geoenvironmental characterisation, these values may yet be unknown. Further, the procedure states that after the reaction, the beaker should be placed on a hot plate and gently heated until effervescence stops (i.e., minimum of 2 hours), but no clear recommendation of which temperature to heat to is given. Finally, on completion, the sample is to cool to room temperature with no exact length of time given as to when to take the final NAG pH measurement. Obser-

vations of procedural errors have been noted most recently by Charles et al. (2015) who stated that for carbonate-bearing samples, the pre-boil time length is critical in controlling the final pH. However, discrepancies could arise for samples with differing mineralogy (i.e., silicate or sulphide rich) with the controlling variables on these NAG results yet to be documented. Whilst dissecting the NAG test may help develop improved laboratory protocols, the industry remains plagued by one fundamental error, there is an absence of a (global) standard to use during NAG pH testing. Whilst several exist for acid base accounting tests (e.g., KZK-1, NBM-1; Canmet) commercial laboratories rarely report on the use of a similar standard for NAG pH testing, thus, how can confidence be given in resulting values if QA/QC measures cannot be demonstrated for a given analytical suite? This paper presents a snapshot of the overall study which aimed to demonstrate the importance of using site-specific NAG pH protocols with an example from the Savage River mine, Tasmania, Australia given.

Methods

Three bulk samples representative of wastes types A (alkaline), B (weakly non-acid forming; NAF) and D (potentially acid forming; PAF) were obtained from the Savage River mine, Western Tasmania. The samples were dried and prepared to <75 μm, split into four portions (1 to 4) using a riffle splitter with two parts selected (blindly) for use. The in-use portions were placed in zip-lock plastic bags and stored in a cool and dry place to limit opportunities for oxidation between experiments. The workflow adopted during

this investigation is shown in Figure 1 with all analyses performed at the University of Tasmania. X-ray diffractometry (XRD) measurements were performed using a Bruker D2 Phaser (Co-X-ray source) with data processed using Topas V4 software. A Hitachi SU-70 field emission scanning electron microscope (FE-SEM) was used to examine the reaction feed and products, with samples mounted on double-sided carbon tape placed on a 10 mm metal stub and carbon coated prior to analysis. All other analytical procedures are as given in Parbhakar-Fox et al. (2011).

Results and Discussion

The bulk mineralogy of all tested parent samples (n=6) is dominated by magnesiohornblende, chlorite, quartz and albite. D-Type is the most pyrite bearing (6.6-7.7 wt. %) with 5.1-5.7 wt. % calcite + dolomite, B-Type contains moderate pyrite (0.9-1.3 wt. %) and 2.8-3 wt. % dolomite+ trace calcite, and A-Type contains the least pyrite (< 0.5 wt. %) with 5 to 5.5 wt. % calcite + dolomite. D-Type is potentially acid forming (PAF), A-Type is non-acid forming (NAF; likely an effective neutraliser), whilst B-Type fall proximal to the ANC/PAF cut-off when simple mineralogical classifications are performed (Parbhakar-Fox et al. 2011). Trace elements measured in the parent samples include Cu (65 to 443 ppm), As (11 to 29 ppm), Ni (44 to 217 ppm) and Zn (174 to 305 ppm) with the highest quantities reported for D-Type. Total sulphur values confirm mineralogical observations that D-type is the most acid forming (range: 5.94 to 6.55 %) with a predicted MPA of 182 to 200 kg H_2SO_4/t. B -Type had a calculated MPA range of 11 to 35 kg H_2SO_4/t and for A-Type
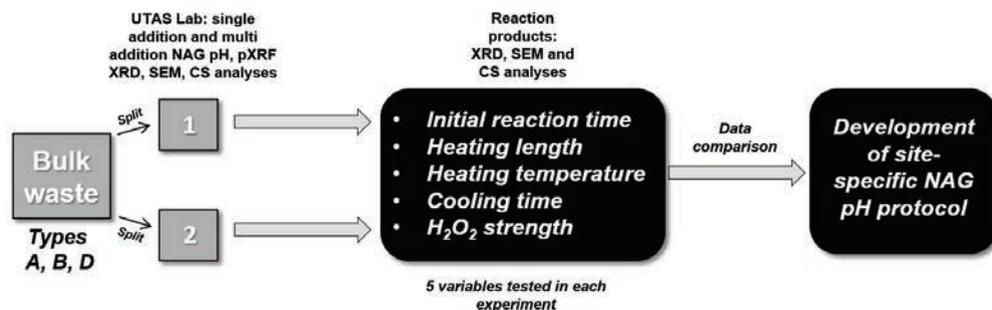

Figure 1. Experimental program followed in this study.

it was < 10.5 kg H_2SO_4/t. In these experiments, a baseline by which to bench mark results against was required, so multi-addition NAG values (performed at 15 % H_2O_2) were used (A-Type: pH 9.12 and 9.28; B-Type: pH 9.13 and 9.21; D-Type: pH 8.06 and 8.09). This test was used in preference over sequential NAG to mimic what a commercial laboratory might do when considering logistical constraints (i.e., fixed time length per experiment known reagent consumption quantity). The results for each tested variable are summarised in the next sections *NB. The reader is encouraged to download the associated presentation to view the supporting figures.*

Initial reaction time

The procedure recommends that the initial reaction evolves until 'boiling' or effervescence ceases, and may recommend a sample to be left overnight. In this study, six experiments were performed (10, 30, 60, 120, 240 and 480 minutes). A-Type is carbonate bearing (5 to 5.5 wt. %) which typically requires a long initial reaction time. Our observations showed that after 10 minutes, only mild effervescence was seen along the liquid meniscus (NAG pH: 8.49-9.42) and after 120 minutes, this had become more apparent (NAG pH: 9-9.8). Samples were allowed to continue to react until 480 minutes with effervescence only gradually decreasing (NAG pH 8.98). The 240 minute samples both best approximated the multi-addition baseline values (A-Type: pH 9.12 and 9.28), with the 480 minute experiment the only to drop below. The relative proportion of dolomite decreased with increasing time length, conversely calcite appeared to relatively increase, with discernable change observed for pyrite (though it was present in trace quantities hard to resolve by XRD). B-Type material was more reactive than A-Type with all experiments immediately showing a higher degree of effervescence with larger bubbles forming. This likely corresponds to its higher pyrite content with a contribution too from the reactive carbonates (up to 3 wt. %). Considering this, terminating the experiment at 10 minutes certainly did not allow for total reaction (pH: 9.41-9.85), indeed, the effervescence only appeared to significantly reduce again after 480 minutes, as seen for both splits (NAG pH: 8.53-8.6). Pyrite content decreased

with increased reaction time, with <0.3 wt. % difference measured for dolomite, with a net decrease over time only observed for B-Type sample 3. D-Type material was the most exothermic and reactive of all waste types with vigorous effervescence and very large bubbles frequently produced after H_2O_2 addition and a constant 'scum' forming on the surface. This reaction appeared to abate after 240 minutes; but no discoloration of the solution occurred (i.e., changing from black to orange/brick red, which can occur for high-sulphide bearing samples). NAG pH values measured after 480 minutes (pH 8.53-8.6) were closest to the multi-addition baseline data. Pyrite decreased in D-Type sample 2 from 6.6 to 5 wt. % however it did not significantly vary for D-Type sample 1 (except at 240 minutes where it dropped to 1.8 wt. %). When evaluating the rate of pyrite dissolution, these results suggest that extending the reaction time beyond 480 minutes will still not oxidise even 50% of the pyrite contained in this waste material.

Heating length

This part of the procedure is designed to i) break down residual H_2O_2 in the sample and ii) encourage carbonate dissolution allowing for an assessment of neutralising potential. In the previous experiment, lower pH values were measured prior to heating, confirming that alkalinity is realised on heating. The heating length times used in these experiments were 30, 60, 90, 120 and 150 minutes. The initial reaction time used in this experiment was 480 minutes (as informed by the previous experiment) with a heating temperature of 80 to 90 °C with NAG pH readings taken after 1-hour cooling time. For A-Type sample 2, the NAG pH slightly dropped with increased heating length (pH 11.8 to 11.3) with similar values measured for A-Type sample 3. However, NAG pH values for both samples were higher than their respective baseline values by at least 2 pH units. These highly basic values support observations given in Charles et al. (2015) and suggest that the maximum length of time allowed may still be too short, with bulk-mineralogical analysis on post-reaction residues from the 150 minutes samples still reporting calcite (3- 3.4 wt. %) but only trace dolomite (< 0.4 wt. %). For Type-B, basic NAG pH values were again

measured in each experiment ranging from pH 10.1 to 11 for Type-B sample 1, and pH 10.6 to 11.3 for Type-B sample 3. In general, results were lower after 150 minutes than 10 minutes with classifications remaining NAF but were still approximately 1 unit above the multi-addition baseline value. Whilst pyrite decreased over time, dolomite content varied by only 0.2 wt. %. The NAG pH values for D-Type samples were notably lower than those measured for A- and B-Type (D-Type sample 1: pH 8.1- 8.61, baseline pH: 8.06; D-Type sample 2: pH 8.17 to 8.41; baseline pH 8.09), with a much smaller range recorded due to the increased pyrite oxidising (as confirmed by bulk mineralogical measurements on the reacted residues) and overshadowing the alkalinity generated by carbonate dissolution. At the end of the reaction, between 5-6 wt. % pyrite remained, indicating that up to 12% only had reacted. Similarly only 30% of carbonates had reacted after 150 minutes. These results suggest that for these samples, a minimum heating length of 150 minutes should be used.

Heating temperature

The original procedure states that after the reaction, the beaker should be placed on a hot plate and gently heated, however the temperature at which this 'gentle' heating is performed at is not clearly stated. Weber et al. (2005) stated their heating as 80-90 °C therefore this was the temperature used in the previous two experiments, but, this is considerably higher than a gentle heating. Experiments were conducted at room temperature (≈25°C), 60, 80 and 90 °C. Two pH measurements were made, soon after cooling (i.e., 1 hour) and after overnight cooling (approximately 10 hours) with an initial reaction time of 480 minutes used, and heating length of 120 minutes (NB. These experiments were performed in parallel to the previous, thus the recommended minimum of 150 minutes was not used). For both A-Type samples, the NAG pH values increased considerably with heating temperature, with the lowest values measured at 25°C (pH 7.2), both of which were lower than the benchmark values (pH 9.12 and 9.28), suggesting these are too acidic. The on-cooling NAG pH values for 60 to 90 °C showed remarkable consistency with increased temperature, with a slight overall increase in NAG pH noted for A-Type sample 2 (pH 11.2 to 11.3) and pH 11.3 consistently measured for A-Type sample 3. These values are two units about the baseline value, suggesting they are too basic. However, the overnight cooling values better show the effect of heating temperature, with a net-decrease in pH clearly noted for A-Type sample 2 (pH 10.2 to 8.8), but for A-Type sample 3 this peaked at 80 °C (pH 10.4) and decreased at 90 °C, with a value approximating the baseline achieved (i.e., pH 9.1). This suggests, if a higher temperature is used, then the NAG pH should be taken after leaving the sample overnight, otherwise a temperature of 40-45 °C is optimal. Bulk contents of pyrite and dolomite measured in post reaction residues confirmed it to decrease with temperature. Results from B-Type are similar, with carbonates measured in post reaction residues showing a general decrease for calcite (less so for dolomite) though pyrite showed no linear trends with a range of 0.4 wt. %. However, for D-Type, it appeared that heating temperature had little effect on the final NAG pH when measured after overnight cooling with a range of 7.8 to 8.2 for D-Type sample 1 (baseline: pH 8) and pH 7.9 to 8.1 for D-Type sample 2 (baseline: pH 8.1). If measured after 1 hour of cooling, an increase in pH was noted as temperature increased (7.5 to 9.3: Type D sample 1; 7.56 to 9.1: Type D sample 2), thus, an optimal reaction temperature of 55 °C identified. Despite this recommendation, pyrite remained between 4 to 5 wt. % in all D-Type samples.

Cooling length

The cooling length time can considerably impact the final NAG pH reading as indicated in the previous section. The original procedure stipulates that the sample should be allowed to cool to room temperature. However, the amount of time this may take is not quoted and therefore could be as quick as 30 minutes (or less if a cold water bath is used) or could be left overnight to react (particularly if experiments were performed over several working hours in a commercial laboratory). In this experiment, NAG pH measurements were taken after 10, 30, 60, 120, 240 and 720 minutes cooling, with these samples also left overnight and additional pH reading tak-

en. For both A-Type samples, the NAG pH maxima were measured after 240 minutes (pH 11.2 and 11.7) and minima at 60 minutes (pH 9 to 9.3). This trend was mimicked again after overnight cooling for all samples, however the pH values had all uniformly dropped with several values (10, 30 minutes and overnight) similar to the benchmark values for both splits (i.e., pH 9.28 and 9.12). For B-Type, the NAG pH values ranged from pH 10.6 (10 minutes) to 8.4 (240 minutes). The lowest values were measured after cooling overnight, with a small range measured (0.3 to 0.6 pH units) and readings very close to the benchmark values for B-Type sample1 (pH 9.13). However, when measured again after being left overnight, all readings were near-identical to the benchmark pH. For B-Type sample 3 it was also very close, with the 10 and 240 min samples the closest to the baseline (pH 9.21). For D-Type samples, NAG pH values on cooling were reasonably similar to the benchmark values ranging from pH 7.8 to 8.7. The maximum value for D-Type sample 1 was measured at the start with a mild progressive decline observed over time. In contrast, values appeared to increase with cooling time length for D-Type sample 2. The overnight pH for both samples were closest to the mNAG benchmark values. These observations show that measuring the pH of the NAG solution after an overnight rest period is most likely to yield a more accurate pH measurement.

Hydrogen peroxide strength
All experiments up to this point focused on changing variables in the experimental procedure. It is evident from B-Type and D-Type materials that changing or fine-tuning these variables does not results in total pyrite oxidation, or indeed, full consumption of effective carbonate neutralisers. Considering this, our final experiment focussed on changing the strength of the H2O2, with 7.5 %, 15% and 30 % tested following a single-addition methodology (480 minutes initial reaction time, 120 minutes on hot plate at 80-90 ˚C, with the final pH taken after overnight cooling). Lower pH readings were consistently measured for all samples when using 7.5 % strength relative to 15% H_2O_2, with values for all waste types around pH 8. It is likely that carbonates

are mildly reacting with only very minor pyrite oxidation (if at all) allowed as the H2O2 strength is simply too weak. At 15% H2O2, the highest results were measured for A-Type and B-Type samples suggesting, that sufficient oxidative capacity is present to attack pyrite generating acidity causing carbonate dissolution and elucidating alkalinity. Bulk mineralogical measurements provided no evidence of intermediate reaction products (i.e., calcium or magnesium hydroxides) influencing the final pH. At 30 %, lower pH values are reported for all samples showing pyrite oxidation is now the dominant reaction with mineralogical classifications approximated, particularly for D-Type, with both samples classified as PAF (pH 2.16 and 2.75). These data show that this is the most important factor controlling NAG pH values. These results show that the standard single NAG pH test is not appropriate for samples containing > 0.3 % sulphide-sulphur, which is much less than that stated by Smart et al. (2002) and yet, it is widely performed. As a final piece of supporting evidence, SEM investigations on NAG residues showed that even at 30% strength, unreacted sulphides remained in a single addition test. Therefore, adopting a multi-addition approach should be mandatory and supersede the single-addition test entirely. Whilst it will add time (and costs) to the overall experimental run, it will improve NAG testing accuracy.

Standard development
These investigations have highlighted the difficulty in performing consistent analyses when undertaking the NAG pH test and clearly show that the first step to overcoming this is to develop a specific NAG pH standard which can be analysed as part of a sample suite when sent to a laboratory for analysis. Thus, the final part of this study sought to initiate the develop of such standards using TASBAS and TASDOL which are routinely used in whole rock geochemical analyses performed in Tasmanian laboratories (and present in abundant quantities). TASDOL contains more sulphur but less carbon than TASBAS with both contain less than 0.1 and 0.05% respectively suggesting an absence/trace presence of sulphide and carbonate phases (thus negligible variability is likely

during NAG pH testing). TASBAS is dominated by augite, forsterite, analcime and sanadine, whilst TASDOL is anorthite, augite, quartz and sanadine dominated. For both, Si, Al, Fe, Mg, Ca and Sr (higher in TASBAS) are measured in both with F also measured in TASDOL. Trace elements include Zr, Ba, Cr, V, Ni and Zn. Ten split samples of these materials were individually prepared and tested using a standard single addition NAG test (2 hours reaction time, 2 hours heating at 80-90 ˚C with the final NAG pH measured after 2 hours cooling time). For the TASBAS, NAG pH values ranged from pH 6.7 to 6.8 (standard deviation: 0.03). For TASDOL, NAG pH values were consistently lower ranging from pH 5.9 to 6.4 with an average of pH 6.19, and a higher standard deviation (0.17). The post reaction residues of four of these samples were analysed by XRD to help indicate which silicates may have reacted (i.e., imparting a mild neutralising potential), as relative to the standard pH of both H_2O_2 and H_2O (pH 5- 5.5), these values are slightly alkaline. TASBAS values show that after NAG testing, phillipsite ($3Al_6Si_{10}O_{32}\cdot 12H_2O$) appears to have reacted with a minor net proportion decrease, along with laumontite ($Ca(AlSi_2O_6)_2\cdot 4H_2O$) both of which belong in the zeolite group. Similar net-changes were not observed in the TASDOL NAG residues suggesting this is a more inert. Further standard development using these materials is ongoing with additional test work focussing on testing a larger number of samples and exploring how the NAG pH values change with different parameters (as performed in this study).

Conclusions

The single-addition net acid generation (NAG) test is used to forecast the acid generating properties of mine wastes with results used to assist in mine waste management. In recent times, the industry-trend has been to only perform the test is to the stage whereby pH measurements are made and a waste classification assigned (i.e., no back-titration to quantify maximum potential acidity). However, discrepancies between laboratory results have been reported when testing splits of the same samples resulting in vastly different, and occasionally, erroneous waste classifications. In this study, the influence of several

experimental variables on the final NAG pH value was explored using three waste types obtained from the Savage River mine, Tasmania. For these materials a multi-addition NAG should be used for low sulphide-sulphur (i.e., < 0.3 wt. %), carbonate-bearing samples with an initial reaction time of at 480 minutes given per 15% H_2O_2 addition, heating to 80 to 90 °C for 2.5 hours and then cooling of the reaction solution overnight with the NAG pH reading taken the following morning. For high sulphide-sulphur materials (i.e., > 0.3 wt.%) 30% H_2O_2 should be used instead, as XRD and SEM studies performed on powder residues revealed that 15% H_2O_2 does not cause substantial sulphide oxidation (even when experimental variables are changed), thus the final waste classification may be incorrect (i.e., underestimating acid forming potential). Where commercial laboratory discrepancies are reported, it may be due to poor preparation of 15% H_2O_2 and erroneously high values are most likely due to reading pH when sample has not reacted for long enough during the heating step and the reading is taken too quickly after cooling (confirming observations given in Charles et al. 2015). This study highlights i) the importance of understanding a sample's mineralogy prior to commencing static testing; ii) the necessity for developing a site-specific NAG testing protocol prior to starting work on a new waste classification project to optimise experimental efficiency; and iii) the importance of developing and using a standard reference material during NAG testing to ensure waste classifications are based on robust values.

Acknowledgements

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