

# ADVANCES IN ACID ROCK DRAINAGE (ARD) CHARACTERISATION OF MINE WASTES<sup>1</sup>

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**Abstract.** Research was carried out to improve acid rock drainage (ARD) prediction methodologies, focussing on resolving uncertainties in acid base accounting (ABA) methods. Advancements, their application, and interpretation are reported. Consideration of both net acid production potential (NAPP) and net acid generation (NAG) test results provide a more reliable routine screening technique than either test alone, increasing confidence in acid potential classification and identifying apparent conflicts requiring further investigation. Techniques such as sequential NAG, modified organic carbon NAG, modified ANC methods to account for siderite and acid buffering characteristic curve (ABCC) testing can be used to help resolve these conflicts in a relatively short time frame. Samples with abundant siderite require complex modified ANC methods, involving excess addition of H<sub>2</sub>O<sub>2</sub> to ensure all dissolved ferrous ion is oxidised before completion of the back titration step. It is demonstrated that at siderite abundances of less than 15 wt %, standard ANC methods are sufficient, improving the efficiency of ANC assessment by reducing the number of modified ANC tests required.

Comparison of ABCC profiles with the developed set of standard carbonate curves provides an indication of the relative reactivity of the ANC measured in waste rock samples, something not evident in ANC test results alone. A relationship was established between kinetic NAG and leach column test results, which provides an indication of lag times without the need to carry out leach columns on all samples. This has the great advantage of allowing kinetic prediction on a broad sample set in a short time frame. The test refinements and developments described in this paper improve the reliability of ARD prediction from short duration tests, provide information on relative reactivity of acid forming and neutralising phases, and improve predictions of acid forming potential.

**Additional Key Words:** NAG, ANC, NP, NAPP, NNP, ABA, ABCC, kinetic NAG, siderite, leach column

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## Introduction

This paper describes advances made in improving acid rock drainage (ARD) prediction methodologies to help resolve uncertainties in acid base accounting (ABA) approaches. The paper focuses on application of these improved techniques, using case study sample to illustrate where appropriate.

ABA methods are widely used for classifying samples according to their acid forming potential. ABA involves the subtraction of an acid neutralising capacity from a maximum potential acidity of a sample. Results are expressed as a net acid producing or acid consuming capacity per mass unit of rock. In Australia the ABA test is reported as a Net Acid Producing Potential (NAPP) value in units of kg H<sub>2</sub>SO<sub>4</sub>/t. The NAPP is calculated as follows (Miller and Jeffery, 1995):

$$\text{NAPP} = \text{MPA} - \text{ANC} \quad (1)$$

where: *MPA is Maximum Potential Acidity = % S × 30.6*

*ANC is Acid Neutralising Capacity*

In North America, ABA results equivalent to NAPP are normally expressed as a net neutralisation potential (NNP) in units of kg CaCO<sub>3</sub>/t, but the components in the calculation are the same, with the MPA normally expressed as AP (acid potential, although AP is often based on sulfide-S content) and ANC expressed as NP (neutralising potential). When ABA methods are used in isolation for ARD classification, they are subject to a number of limitations, including:

- The MPA may overestimate the acid generation potential due to the presence of non acid forming S-bearing phases such as gypsum, epsomite, barite, galena, sphalerite, etc. (The use of sulfide-S content to determine AP eliminates some of these interferences.);
- The ANC is affected by Fe carbonates such as siderite, and its presence may result in over estimation of the effective acid neutralising mineral content in a sample;
- The ANC test provides no indication of the relative reactivity of the acid neutralising component of a sample, nor whether it may be available at the same rate of acid generation; and
- The NAPP value provides no measure of lag times before acid production.

The objectives of the research were to address the limitations described above with modified test methodologies, and improve the reliability of ARD prediction from short-term tests. This paper provides an overview of the following specific advancements and how they are applied and interpreted:

- use of the single addition and sequential net acid generation (NAG) tests in combination with solution analysis to identify and resolve uncertainties in ABA predictions;
- use of a modified H<sub>2</sub>O<sub>2</sub> ANC test to overcome siderite effects and triggers for when to apply it;
- use of the acid buffering characteristic curve (ABCC) test to predict the reactivity of the ANC measured; and

- use of kinetic NAG tests to predict leach column lag times.

### **Methodology**

Details of standard ARD methods, which include single addition NAG, sequential NAG, standard ANC, kinetic NAG and leach column tests, are available in Ian Wark Research Institute & Environmental Geochemistry International (2002). Brief descriptions of these standard methods together with new modifications are provided in this section.

#### **NAG Test Methods**

The single addition NAG test involves a single addition of 250 ml of 15% H<sub>2</sub>O<sub>2</sub> to a 2.5 g of pulverised (less than 75 µm) sample. The sample is allowed to react overnight. The entire sample is heated until gently bubbling for approximately 1-2 h to remove excess H<sub>2</sub>O<sub>2</sub> and encourage release of inherent neutralising capacity. Once the sample has cooled to room temperature, the pH and titrated acidity to pH 4.5 and 7.0 (in kg H<sub>2</sub>SO<sub>4</sub>/t of sample) of the solution are measured. A NAGpH less than 4.5 indicates the sample is acid producing. A temperature rise is commonly observed in NAG testing of sulfidic samples as a result of catalytic decomposition of peroxide by metal ions released during sulfide oxidation. Complete decomposition of the peroxide may occur before all the reactive sulphides have oxidised. Thus the single addition NAG test may not account for the total acid potential of a given sample.

Sequential NAG test is used to overcome peroxide decomposition effects through successive additions of peroxide to the same sample. Results provide a better estimate of total acid generating capacity. This test involves the sequential reaction of a sample with 15% H<sub>2</sub>O<sub>2</sub> and is essentially a series of single addition NAG tests (250 ml of 15% H<sub>2</sub>O<sub>2</sub> solution) on the one sample. At the end of each NAG test stage, the sample is filtered and the NAGpH and titrated NAG acidity of the solution are measured. The NAG test is then repeated on the solid residue. The cycle is normally repeated until the NAG pH is ≥ 4.5. All of the individual NAG acidities are then summed to give a total sequential NAG acidity in kg H<sub>2</sub>SO<sub>4</sub>/t. Solution assays of sequential NAG solutions were carried out by filtering solutions from each stage, topping up the filtered solutions to the original 250ml with deionised water to account loss by evaporation, and analysis of solutions for S by ICP-OES.

The kinetic NAG test is a single addition NAG test in which the pH and temperature are monitored during the NAG reaction (Miller et al., 1997). Profiles of pH and temperature provide an indication of the reaction kinetics of sulfide oxidation and acid generation during the NAG test.

#### **ANC Test Methods**

The standard ANC test is based on that developed by Sobek et al. (1978), and involves digestion of 2g of pulverised sample in HCl at selected concentrations and volumes depending on the amount of reactive carbonate expected in the sample. The amount of reactive carbonate in a sample is estimated before testing based on a fizz rating, in which one or two drops of 8% HCl is added to the sample and the scale of the “fizzing” (effervescence) reaction is given a “fizz rating”. Different concentrations and volumes of acid are used in the ANC digestion according to the fizz rating. The fizz rating can be somewhat subjective, and a more objective check is carried out by measuring the ANC solution pH after digestion is complete, which should be between pH 0.8 and 1.5. ANC digest solutions outside of this range require repeating or

adjustment of acid volume. The digestion involves heating the combined solid and HCl solution at 80-90°C for 1-2 hours or until the reaction is complete (no further evolution of gas bubbles).

After digestion the solution is back titrated to pH 5, two drops of H<sub>2</sub>O<sub>2</sub> are added to promote oxidation of dissolved Fe<sup>+2</sup> and precipitation of Fe(OH)<sub>3</sub>, and the titration continued to pH 7 to determine the amount of HCl consumed. The HCl consumed is converted to units of kg H<sub>2</sub>SO<sub>4</sub>/t.

To overcome the potential effects of siderite on ANC tests, a modified H<sub>2</sub>O<sub>2</sub> ANC method was carried out using the same digest procedure as the standard ANC, but different procedures for the back titration. This method is a variation on those described by Skousen et al. (1997), involving incremental additions of 30% H<sub>2</sub>O<sub>2</sub> and NaOH after addition of a single 5ml aliquot of H<sub>2</sub>O<sub>2</sub>, as follows:

- a) Filter digestion solution before back titration.
- b) Titrate (auto titration acceptable) the ANC digestion solution with NaOH to pH 5 with constant mixing.
- c) Add 5ml of 30% H<sub>2</sub>O<sub>2</sub> and let sit for 1 hour.
- d) Manually back-titrate with NaOH (using burette) to pH 7.0 over 1-2 hours or until stable (no pH change to two decimal places in 10 minutes).
- e) Let solution sit overnight.
- f) Check pH and adjust with further manual back titration to pH 7.0 if required.
- g) Add 8 drops of H<sub>2</sub>O<sub>2</sub>, leave for 15 minutes.
- h) Check pH and adjust with further manual back titration to pH 7.0 if required.
- i) Repeat steps g and h until solution pH is stable at pH 7.0.
- j) Repeat steps e to i once more.
- k) Sum the total volume of NaOH used to calculate the final ANC.

*Note: filtering of the ANC digestion solution before back titration is essential for the modified H<sub>2</sub>O<sub>2</sub> ANC method, since the amount of H<sub>2</sub>O<sub>2</sub> used in the test could cause oxidation of pyrite in the solid residue, releasing acid and causing underestimation of the ANC.*

#### ABCC Test Method

The ABCC test was developed by Miller and Jeffery (1995) and involves slow titration of a sample with acid while continuously monitoring pH. ABCC results provide an indication of what portion of the ANC measured in a sample is readily available for acid neutralisation.

The refinements of the test involved the optimisation of test configurations for ranges of ANC values, and generation of a set of standard carbonate curves for each ANC range. The volume and concentration of HCl at each addition is varied according to set ANC ranges, but the time between additions (approximately 15 minutes) is kept constant. High HCl volumes and concentrations are used for high ANC samples and low HCl volumes and concentrations are used for low ANC samples. Table 1 shows the optimal test configuration for a given ANC value.

Table 1. Optimal sample sizes, HCl concentrations, HCl increment volumes and target pH values for ABCC testing of various ANC ranges.

ANC Range (kg H <sub>2</sub> SO <sub>4</sub> /t)	Sample Weight (g)	HCL Increments (ml)	HCl Concentration (M)	pH End Point	Carbonate Standard Set To Use For Comparison
700-1000	1g	0.5	0.5	2.5	Sample Set 1 ANC ≈ 500
300-700	2g	0.5	0.5	2.5	Sample Set 1 ANC ≈ 500
150-300	2g	0.2	0.5	2.5	Sample Set 2 ANC ≈ 200
75-150	2g	0.4	0.1	2.5	Sample Set 3 ANC ≈ 100
35-75	2g	0.3	0.1	2.5	Sample Set 4 ANC ≈ 50
17-35	2g	0.2	0.1	2.7	Sample Set 5 ANC ≈ 25
<17	2g	0.1	0.1	2.8	Sample Set 6 ANC ≈ 13

The refined ABCC procedure is carried out as follows:

- Slowly titrate appropriate weight of sample in a conical flask, using optimal HCl concentrations and increment volumes according to the ANC range.
- Plot cumulative kg H<sub>2</sub>SO<sub>4</sub>/t added (x-axis) against pH measured (y-axis) to obtain the buffering curve.
- Rescale appropriate carbonate standard curves to match the total ANC of the sample and plot on same graph for comparison.

#### Leach Column Method

Leach column test procedures involve application of wet and dry cycles to a crushed sample (generally 2-3kg) under atmospheric oxidation conditions. Water is added once per week at rates of 100ml/kg in the first three weeks, and 400ml/kg in the fourth week to flush the oxidation products into a collection vessel. Heat lamps are used to dry the sample between water additions to promote oxidation throughout the sample.

Column leachates are tested for a variety of parameters, including leachate volume, pH, EC, acidity/alkalinity and multi-elements.

### Results

#### Use of the NAG Test in ARD Assessment

The NAG test is a static ARD prediction tool usually used in conjunction with other static methods, such as the NAPP determination, to give an indication of acid forming potential. It

involves the addition of H<sub>2</sub>O<sub>2</sub> to a prepared sample of mine rock or process residue to oxidise reactive sulfide minerals, followed by measurement of the pH of the reaction solution and titration of any net acidity produced.

Single Addition NAG Testing and Comparison with NAPP. The single addition NAG test can be used to critically assess the validity of NAPP predictions and vice versa, highlighting conflicts and potential issues with ANC and MPA estimates requiring further investigation. Using NAG tests in conjunction with ABA methods to classify samples results in better definition of acid forming potential and reduces the risks of misclassifying non acid forming (NAF) materials as potentially acid forming (PAF) (Type 1 error) and PAF material as NAF (Type 2 error). Miller et al. (1997) presented a scheme whereby the NAPP result is plotted against the pH of the NAG (NAGpH) solution to classify samples.

Table 2 shows ABA (NAPP) and NAG results for a case study set that will be used to illustrate the way NAG test results can be used to assess ABA results. Figure 1 is an ARD classification plot for these samples, showing the NAPP value on the x-axis and the NAGpH on the y-axis. Potentially acid forming (PAF), non acid forming (NAF) and uncertain (UC) classification domains are indicated. A sample is classified PAF when it has a positive NAPP and NAGpH < 4.5, and NAF when it has a negative NAPP and NAGpH ≥ 4.5. Samples are classified uncertain when there is an apparent conflict between the NAPP and NAG results, i.e. when the NAPP is positive and NAGpH ≥ 4.5, or when the NAPP is negative and NAGpH < 4.5.

Table 2. ABA (NAPP) and NAG test results for a case study sample set.

Sample No	Material Type	Total S	MPA	ANC	NAPP	NAGpH	NAG <sub>(pH4.5)</sub>	NAG <sub>(pH7.0)</sub>	ARD Classification
		%	kg H <sub>2</sub> SO <sub>4</sub> /t		kg H <sub>2</sub> SO <sub>4</sub> /t				
1	Carbonaceous Mudstone	0.05	2	14	-12	6.9	0	1	NAF
2	Hydrothermal Breccia	4.30	132	182	-50	3.2	4	14	UC
3	Carbonaceous Siltstone	0.12	4	10	-6	2.7	32	56	UC
4	Basaltic Volcanics	0.42	13	113	-100	8.9	0	0	NAF
5	Monzodiorite	0.79	24	11	13	4.0	1	4	PAF
6	Tailings	1.97	60	106	-46	8.8	0	0	NAF
7	Carbonaceous Mudstone	2.02	62	10	52	2.5	29	35	PAF
8	Basalt	1.53	47	1	46	7.9	0	0	UC
9	Basalt	3.28	100	2	98	6.2	0	6	UC
10	Black Shale	4.93	151	3	147	2.2	50	57	PAF
11	Silty Mudstone	0.78	24	16	8	4.9	0	4	UC
12	Mudstone	1.60	49	11	38	2.7	9	15	PAF
<b>Calculations</b>		<b>Classification</b>							
MPA = 30.6 x %S		PAF = NAPP > 0 and NAGpH < 4.4							
NAPP = MPA - ANC		NAF = NAPP ≤ 0 and NAGpH ≥ 4.4							
		UC = (NAPP ≤ 0 and NAGpH < 4.5) <b>or</b> (NAPP > 0 and NAGpH ≥ 4.5)							

Samples that plot in the upper left hand NAF domain and lower right hand PAF domain of Fig. 1 have consistent NAPP and NAG classifications. These samples can be classified as NAF and PAF with a greater degree of confidence than if the ABA test was used alone. However, the samples that plot in the uncertain domain have conflicting NAPP and NAG results, and the reasons for this illustrate why reliance on only ABA methods to predict acid potential can lead to misclassifications.

Sample 8, 9 and 11 plot in the upper right hand uncertain domain, having positive NAPP values but NAGpH values greater than 4.5. Samples 8 and 9 have high total S contents of 1.5-3.3%S (Table 2) and low ANC (<3 kg H<sub>2</sub>SO<sub>4</sub>/t), and the resulting high positive NAPP values indicate a high acid forming potential. However, the NAG test results indicate the sample is non acid producing. Closer examination of samples 8 and 9 showed that these samples were highly weathered, and the majority of S was likely present as gypsum, the presence of which was visually confirmed by site geologists.

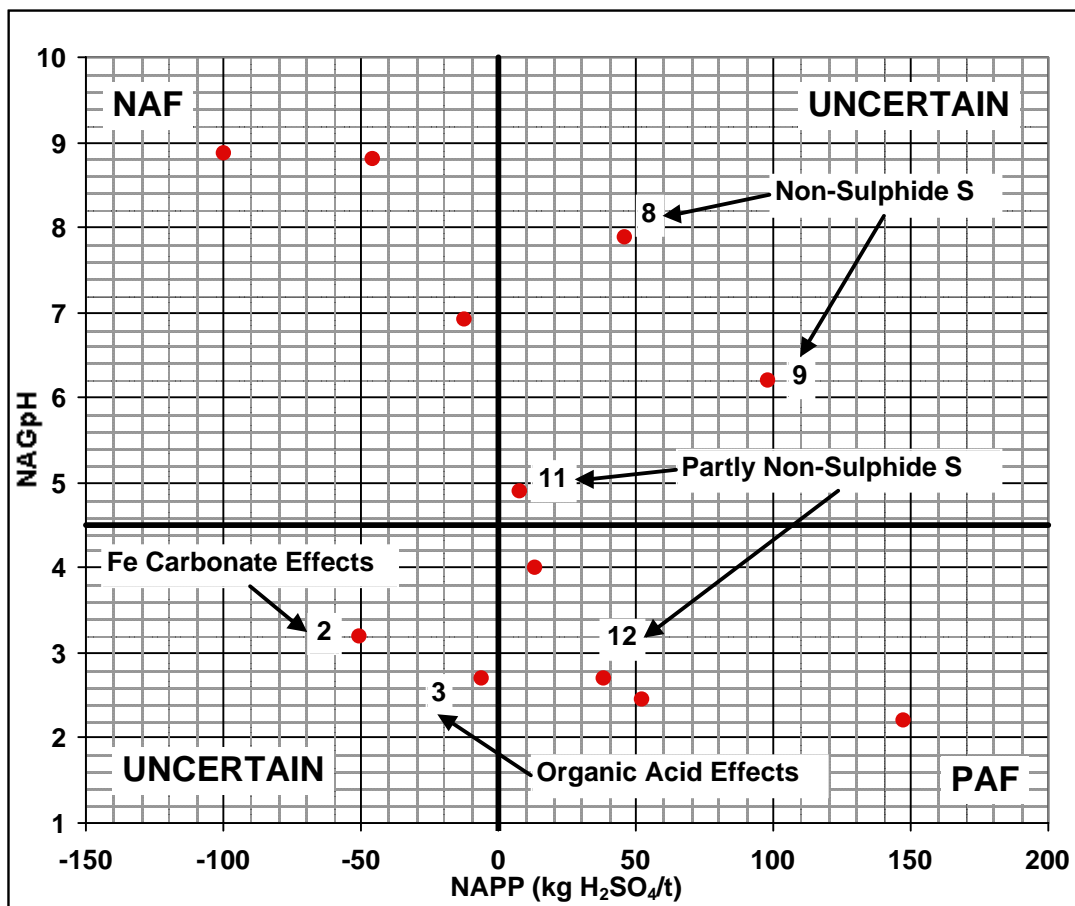


Figure 1. ARD classification plot for a case study sample set.

Although sample 11 was unweathered, it had a relatively low NAPP value of 8 kg H<sub>2</sub>SO<sub>4</sub>/t, and sequential NAG testing was required to resolve the apparent conflict between NAG and NAPP values (see next sub-section).

Sample 2 plots in the lower left hand uncertain domain, having a negative NAPP value but a NAGpH value less than 4.5. This sample has a high total S of 4.3%S and high ANC (182 kg

H<sub>2</sub>SO<sub>4</sub>/t), and the resulting negative NAPP value indicates the sample would be non acid forming. However, the NAG test results indicate the sample is acid producing, with a NAGpH value of less than 4.5. In this case the ANC measured was affected by iron carbonates, and not all of the measured ANC was effective. Reliance on the NAPP value alone would have misclassified the sample as NAF. Use of modified ANC methods and ABCC testing to measure the effectiveness of total ANC values and help resolve these types of NAG-NAPP conflicts is discussed in sections to follow.

Sample 3 also plots in the lower left hand uncertain domain, but in this case the sample is carbonaceous and has very low S, and the low NAGpH value measured is due to organic acid effects. In this case the standard NAG test does not produce a reliable result and the NAPP value is a better indication of acid forming potential. However, the effects of organic matter can be overcome with a modified organic carbon NAG test as described by Stewart et al. (2003b). These effects are only a significant issue in carbonaceous (>5% organic C) samples with low S (<0.7%), and there are a number of triggers and checks described in Stewart et al. (2003b) that can be used to determine when organic acid effects on the NAG test are likely from a sample, and when modified organic carbon NAG test methods are required.

The case study sample results demonstrate the effectiveness of the NAG test in highlighting potential issues in ABA results. Identifying conflicts between the NAG and NAPP results helps identify when further investigation is warranted. Techniques such as sequential NAG, modified organic carbon NAG, modified ANC methods to account for siderite and ABCC testing can be used to help resolve these conflicts in a relatively short time frame.

Sequential NAG Testing to Help Resolve Uncertainty in Sample Classification. Sequential NAG testing is used to provide a total acid producing potential for samples in which oxidation of sulphide S is incomplete (typically when pyritic S is greater than 0.7 to 1%S). Sequential NAG testing normally involves titration of the liquor from each NAG stage to produce a total acid potential from a sample, which is directly comparable to a positive NAPP result. However, analysis of the NAG solution for key elements can also be carried out, which greatly improves the interpretation of acid potential in a sample. This is illustrated by application of sequential NAG testing with S solution assay to case study samples 11 and 12.

Sequential NAG testing to four stages (each stage is equivalent to a single addition NAG test) was carried out on sample 11 with S assay of NAG solutions to track the release of S into solution relative to the total S measured in the sample. Results are presented in Table 3, which shows that all S in the solid was accounted for in the sequential NAG solution, but that none of the NAG solutions produced a pH less than 4.5. The results confirm that despite having a positive NAPP value, sample 11 is unlikely to be acid producing, consistent with the single addition NAG result. The results show that the fraction of the total S present in non acid generating forms (most likely as primary sulphate salts) is sufficient to make the sample non acid producing overall. This was later confirmed with column leach testing.

Sample 12 plots in the PAF domain, and sequential NAG testing was carried out with S assay of NAG solutions to provide a better measure of the total acid potential and track the release of S into solution relative to the total S measured in the sample. Results are presented in Table 4, which show a total sequential NAG acid potential of 10 kg H<sub>2</sub>SO<sub>4</sub>/t, considerably less than the NAPP potential of 38 kg H<sub>2</sub>SO<sub>4</sub>/t. Sulfur assay confirmed that all S in the solid was accounted for in NAG solution, and the missing acidity is therefore either due to non acid forming S forms,



or the presence of neutralising species not measured by the ANC test. In this case electron microprobe analysis confirmed the presence of Mg-S species (Weber et al., 2004), and the discrepancy between the sequential NAG and NAPP results could be attributed to the presence of non acid forming sulphate salts in the sample.

Table 3: Sulphur in solution by sequential NAG stage for sample 11.

Sequential NAG Stage	S in Solution by Stage (mg/l)	Portion of Total S Released	NAGpH	NAG to pH 4.5 (kg H <sub>2</sub> SO <sub>4</sub> /t)
Stage 1	60.7	78%	5.2	0
Stage 2	12.0	15%	4.7	0
Stage 3	5.3	7%	5.1	0
Stage 4	3.3	4%	5.3	0
Total		104%		0

Table 4: Sulfur in solution by sequential NAG stage for sample 12.

Sequential NAG Stage	Sulfur in Solution by Stage (mg/l)	Portion of Total S Released	NAGpH	NAG to pH 4.5 (kg H <sub>2</sub> SO <sub>4</sub> /t)
Stage 1	135	84%	3.0	6
Stage 2	64	40%	2.9	4
Stage 3	11	7%	4.1	0.1
Stage 4	4	3%	7.3	0
Stage 5	1.4	1%	7.2	0
Total		135%		10

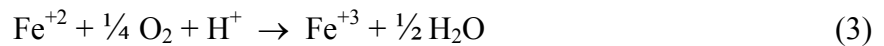
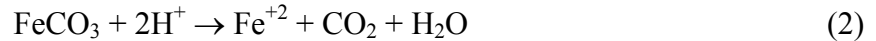
These examples confirm the reliability of NAG testing in detecting the presence of non acid forming S forms. The simple addition of S assays of the NAG solutions greatly improved confidence in the NAG test results, and thus resulted in a more reliable prediction of acid potential. More complex NAG solution assay can be used in specific circumstances to improve interpretation of NAG results and understanding of sample geochemistry, for example:

- Analysis of NAG solutions for S, Ca, Mg, Na and K can be used to track the balance of acid generating and neutralising reactions, which may include partial dissolution of reactive silicates at low pH (e.g. Jambor et al., 2000).
- The addition of anions such as Cl<sup>-</sup> may be included where Cl<sup>-</sup> (e.g. KCl and NaCl) or other soluble salts may be present in a sample to help partition cations and anions according to mineral phases present in the sample.

- Analysis of metals such as Cu and Zn in mixed sulphide samples can assist in assessing the contribution to the acidity measured by the NAG titration to specific sulphide phases.

#### Siderite Effects on the ANC Test

Siderite provides no acid neutralising benefit (Paktunc, 1999), because the acid consumed during dissolution is re-released upon oxidation of  $\text{Fe}^{+2}$  iron to  $\text{Fe}^{+3}$  iron and subsequent precipitation to  $\text{Fe}^{+3}$  oxyhydroxides under normal field conditions as follows:



In standard acid neutralising capacity (ANC) tests (equivalent to North American neutralisation potential or NP tests) based on Sobek et al. (1978) methods, a sample is digested in acid according to its fizz rating, and the digest solution is back titrated with NaOH to determine the amount of acid consumed. Commonly, two drops of 30%  $\text{H}_2\text{O}_2$  are added to the solution during back titration once the pH reaches around pH 5 to promote oxidation of  $\text{Fe}^{+2}$  iron in solution (Ian Wark Research Institute & Environmental Geochemistry International, 2002). However, in these standard ANC tests the oxidation of  $\text{Fe}^{+2}$  iron and subsequent precipitation to  $\text{Fe}^{+3}$  oxyhydroxides may not be complete in the time frame of the test. The acid consumed by the siderite in equation 2 contributes to the ANC value determined during back titration, and thus the resulting ANC values may overestimate the actual ANC.

Figure 2 compares standard ANC values for a siderite mineral sample (which includes a portion of Ca and Mg carbonate) with that calculated based on contained Mg and Ca carbonate in the sample, showing a very large discrepancy. It is apparent that in this case the two drops of 30%  $\text{H}_2\text{O}_2$  added to the solution was not sufficient to account for all of the ferrous ions released to solution.

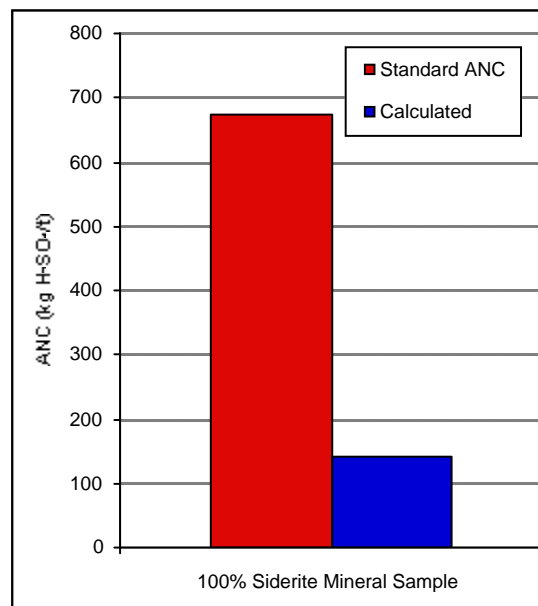


Figure 2. Standard ANC compared to that calculated from Mg and Ca carbonate content for a siderite mineral sample.

The potential effects of siderite on the ANC test have been well documented previously in Day, Hope and Kuit (1997), Meek (1981), Skousen et al. (1997), and Jambor et al. (2000). The purpose of the modified H<sub>2</sub>O<sub>2</sub> ANC method is to add an excess of oxidant (H<sub>2</sub>O<sub>2</sub>) to the ANC digestion solution, so that all Fe<sup>+2</sup> iron has oxidised and hydrolysed, and any acid consumed on dissolution of siderite is re-released before completion of the back titration. A significant drawback of the modified H<sub>2</sub>O<sub>2</sub> ANC test and predecessors such as Skousen et al. (1997) is they are more time consuming than standard methods, and thus more costly for routine analysis. It is important, therefore, to know when modified tests are required and when standard ANC tests are sufficient.

It is apparent that the effects of siderite on the ANC test will be controlled by its abundance in the sample. At low siderite concentrations the two drops of H<sub>2</sub>O<sub>2</sub> added during the back titration in a standard ANC test will be sufficient to oxidise the Fe<sup>+2</sup> to Fe<sup>+3</sup>, and longer more complex test methodologies will be unnecessary. Higher siderite concentrations lead to greater requirement for oxidant (i.e. H<sub>2</sub>O<sub>2</sub>) and a longer time for complete oxidation of Fe<sup>+2</sup> to Fe<sup>+3</sup>.

A set of siderite standards were prepared to determine the siderite abundance at which modified H<sub>2</sub>O<sub>2</sub> ANC methods are required. The standards covered a range of equivalent siderite abundances from 5 wt % to 100 wt %. The standard ANC method (including the addition of two drops of H<sub>2</sub>O<sub>2</sub>) and a modified H<sub>2</sub>O<sub>2</sub> ANC method were carried out on the standard samples, and compared to the calculated ANC based on Ca and Mg carbonate in the samples. Results are shown in Fig. 3. The trends of the standard ANC (red line) and modified H<sub>2</sub>O<sub>2</sub> ANC (blue line) converge with decreasing siderite abundance, and it is apparent that samples with less than 15 wt % siderite, a high siderite content, do not require more complex modified ANC test methodologies. Note also that the modified H<sub>2</sub>O<sub>2</sub> ANC and the calculated ANC correspond closely, supporting the effectiveness of the modified H<sub>2</sub>O<sub>2</sub> ANC method used in accounting for siderite.

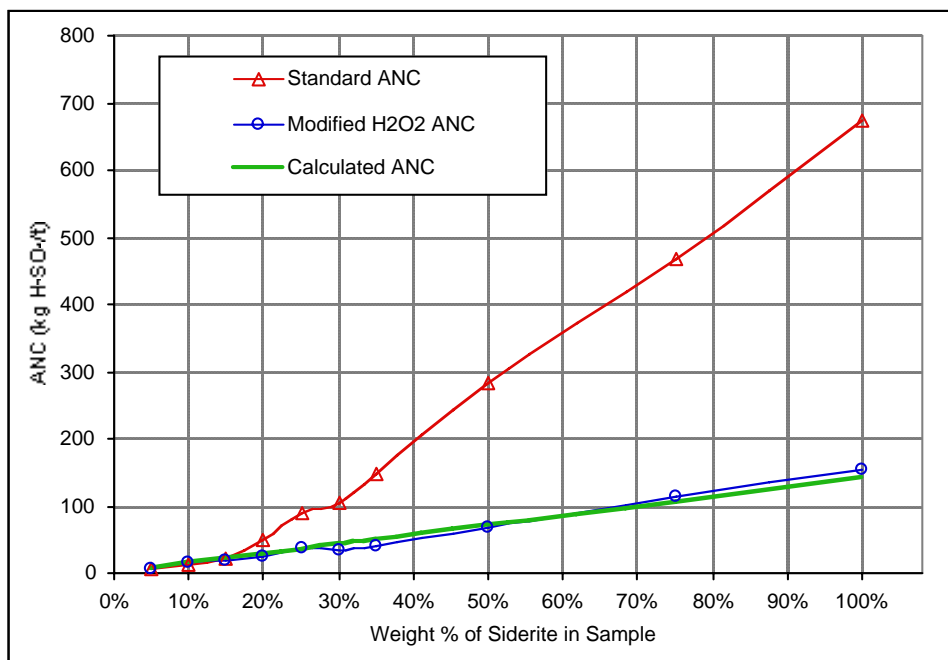


Figure 3. Standard ANC and modified H<sub>2</sub>O<sub>2</sub> ANC results by wt % siderite abundance. Calculated ANC from Ca and Mg carbonate is provided for comparison.

Thus the modified H<sub>2</sub>O<sub>2</sub> ANC method should be used in cases where the siderite abundance is expected to be high or measured as high (approximately > 15 wt %). Mineralogical information from drill logs and quantitative/semi-quantitative mineralogical investigations will provide an indication of the siderite abundance. Where mineralogy is not known, there are several other triggers for application of the modified H<sub>2</sub>O<sub>2</sub> ANC test, including:

**Conflicting NAG and NAPP Results:** Samples that have a negative net acid producing potential (NAPP) value but a low net acid generation (NAG) solution pH may indicate that the ANC has been overestimated and that high siderite abundances in the sample are a possibility (see previous NAG section).

**Sharp Drop in ABCC pH Profiles:** The shape of the acid buffering characteristic curve (ABCC) profile (see section below) provides an indication on the availability of the ANC measured. The ABCC profile for samples with ANC values affected by siderite will show very sharp drops with acid additions.

**Green/Black Colouration of Titrated ANC Solution:** Green or black colouration in the ANC solution after back titration is an indication of the presence of un-oxidised ferrous iron, and therefore further H<sub>2</sub>O<sub>2</sub> oxidation may be needed before determining the ANC value to avoid overestimation. The left plate (I) of Figure 4 shows an example of the distinctive green/black colouration typical of ferrous (i.e. Fe<sup>+2</sup>) hydroxides. The orange/red colouration on the right plate of Figure 4 is due to oxidation of ferrous ions and precipitation of Fe(OH)<sub>3</sub>. The reliability of the color trigger will depend on the type of sample tested. Many samples will contain materials that will mask these colors, and the apparent absence or presence of a green/black coloration may be misleading.

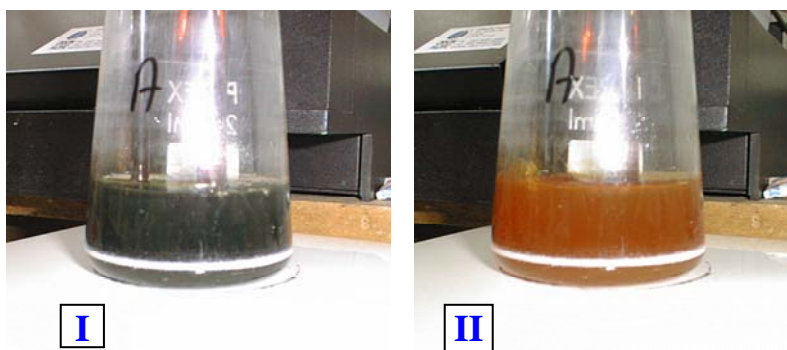


Figure 4. Left plate (I) shows green/black coloration of ANC solution after standard ANC titration to pH 7 indicating the presence of Fe(OH)<sub>2</sub>. Right plate (II) shows characteristic orange/red Fe(OH)<sub>3</sub> precipitates after oxidation of Fe<sup>+2</sup> ions.

#### Use of Standard Carbonate Curves to Interpret ABCC Test Results

The refined ABCC procedure involves generation of an ABCC profile for the test sample and comparison of this with standard carbonate curves to interpret the ANC reactivity. The method is valid for ANC values as low as approximately 10 H<sub>2</sub>SO<sub>4</sub>/t. Figure 5 shows a typical example of the ABCC carbonate standard profiles generated for one of the ANC standard sets (Set 1 with ANC values of 400 kg H<sub>2</sub>SO<sub>4</sub>/t, see Table 1). Note that although all carbonate standard samples

had similar standard ANC values of around 400 kg H<sub>2</sub>SO<sub>4</sub>/t, the buffering curves vary. The plot demonstrates that the ABCC test is effective in discriminating between carbonates of different reactivity, with limestone and calcite effectively neutralising acid, and siderite and magnesite neutralising little acid. The curves for other sample sets show similar relative carbonate buffering characteristics, although the exact shapes of the curves vary somewhat due to differences in acid concentration and volumes.

Table 5 shows four examples that will be used to demonstrate the application of the refined ABCC test. The case study set comprises a tailings sample, and three waste rock samples with varying ANC.

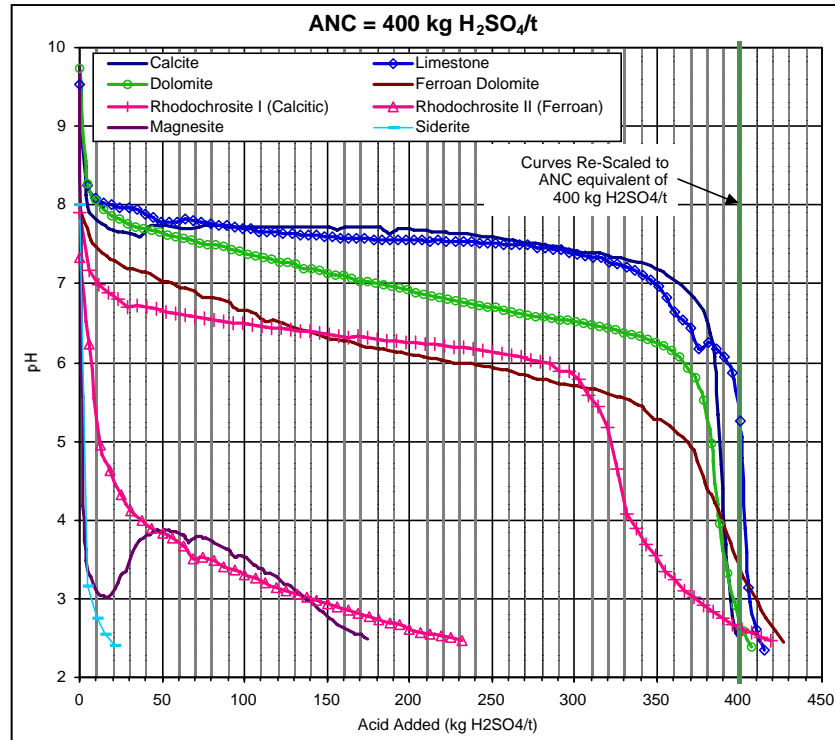


Figure 5. Example ABCC curves for carbonate standard set 1 rescaled to a total ANC equivalent of 400 kg H<sub>2</sub>SO<sub>4</sub>/t.

Table 5: Case study sample set to demonstrate the application of the ABCC test.

Sample ID	Commodity	Sample Type	ANC kg H <sub>2</sub> SO <sub>4</sub> /t
A	Au	Tailings	50
B	Cu	Waste Rock	50
C	Coal	Waste Rock	15
D	Coal	Waste Rock	25

Figure 6 is a plot of the ABCC curve for sample A, together with standard curves as reference. Sample A shows effective acid neutralisation, producing a gradual decrease in pH

with acid added and pH dropping rapidly below pH 4 once the equivalent total measured ANC capacity is consumed. The curve closely corresponds to that of the dolomite standard, indicating that the carbonate in the sample is dolomitic, and readily available. In this case the ANC value is predicted to be a reliable estimate of the available acid buffering in the sample.

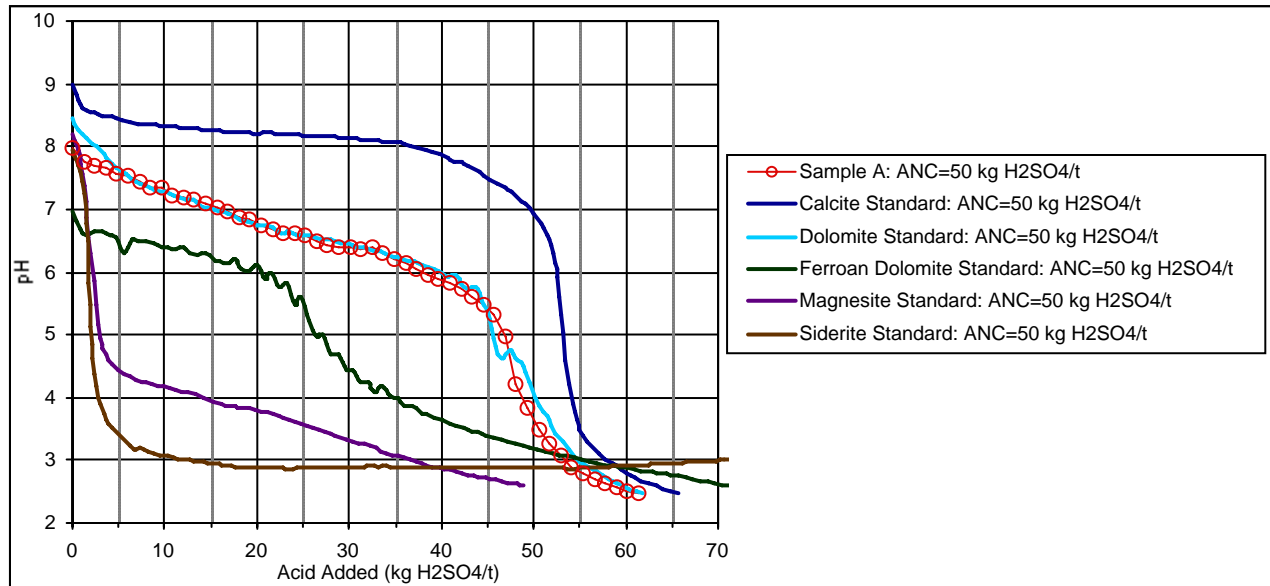


Figure 6. ABCC profile for sample A (Au Tailings) with a standard ANC value of 50 kg H<sub>2</sub>SO<sub>4</sub>/t. Carbonate standard curves are included for reference.

Sample B has the same ANC as sample A, but the ABCC curve is different. Figure 7 is an ABCC plot of sample B, which shows that in this case the curve drops sharply after the equivalent of 20 kg H<sub>2</sub>SO<sub>4</sub> of ANC is consumed, and drops below pH 4 after approximately 30 kg H<sub>2</sub>SO<sub>4</sub> of ANC is consumed. The curve shows a steady drop thereafter with acid added. Some portion of the ANC appears to be of calcitic origin, resulting in the strong buffering in the early part of the test. The rest of the carbonate appears to be more typical of ankerite or ferroan dolomite. Results indicate that the ANC value should be treated with caution, with a portion of the ANC likely to have a slow rate of buffering. Slow flushing rates and long residence time in the waste material would be required for the entire ANC to be effective.

Figure 8 is a plot of the ABCC curve for sample C, which drops relatively quickly and is very similar to the ferroan dolomite profile, indicating slow reactivity. The ABCC profile for sample D shown in Figure 9 trends between ferroan dolomite and siderite/magnesite, indicating poor ANC reactivity. The ABCC curves for C and D indicate that the ANC measured may be ineffective. Column testing would be required to determine the availability of the total ANC measured for acid buffering.

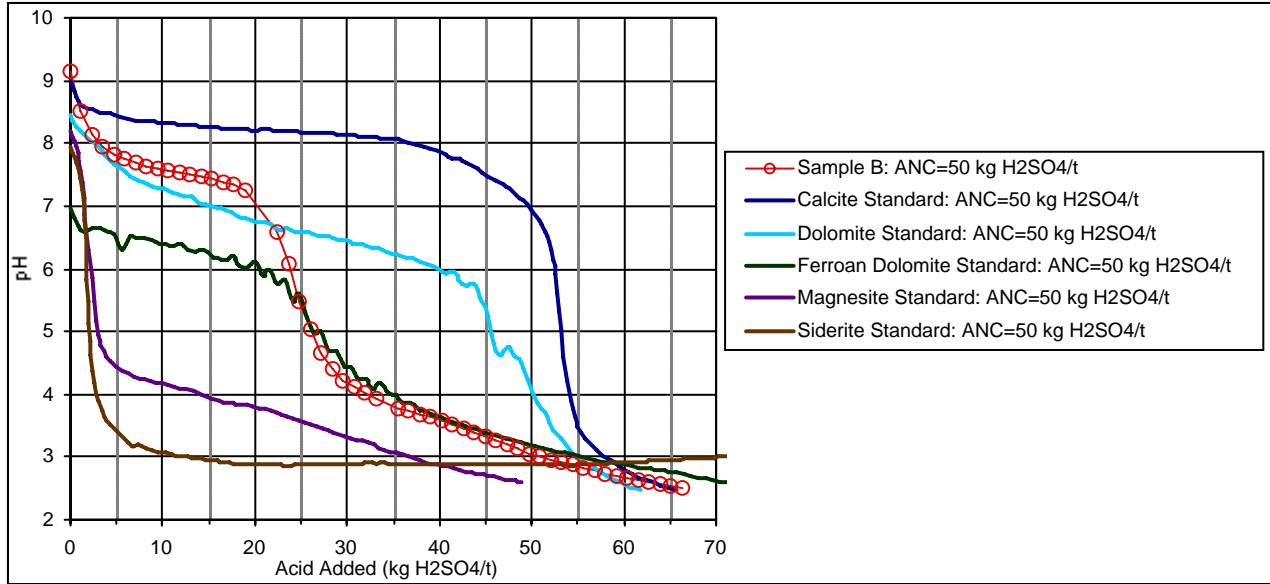


Figure 7: ABCC profile for sample B (Cu Waste Rock) with a standard ANC of 50 kg H<sub>2</sub>SO<sub>4</sub>/t. Carbonate standard curves are included for reference.

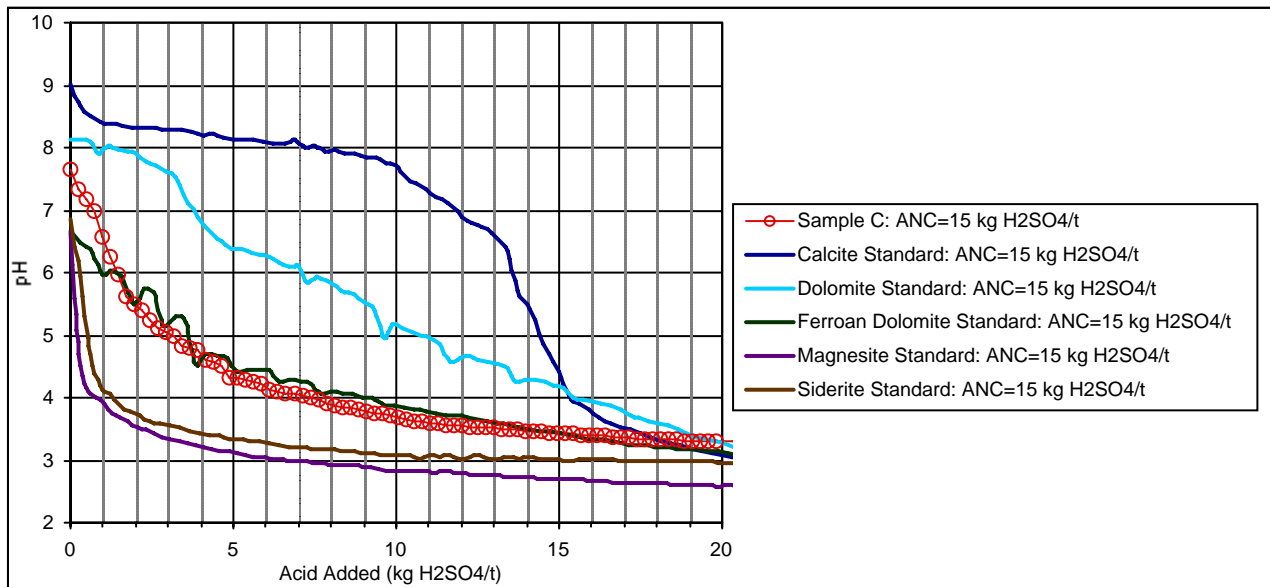


Figure 8: ABCC profile for sample C (Coal Waste Rock) with an EGi standard ANC of 15 kg H<sub>2</sub>SO<sub>4</sub>/t. Carbonate standard curves are included for reference.

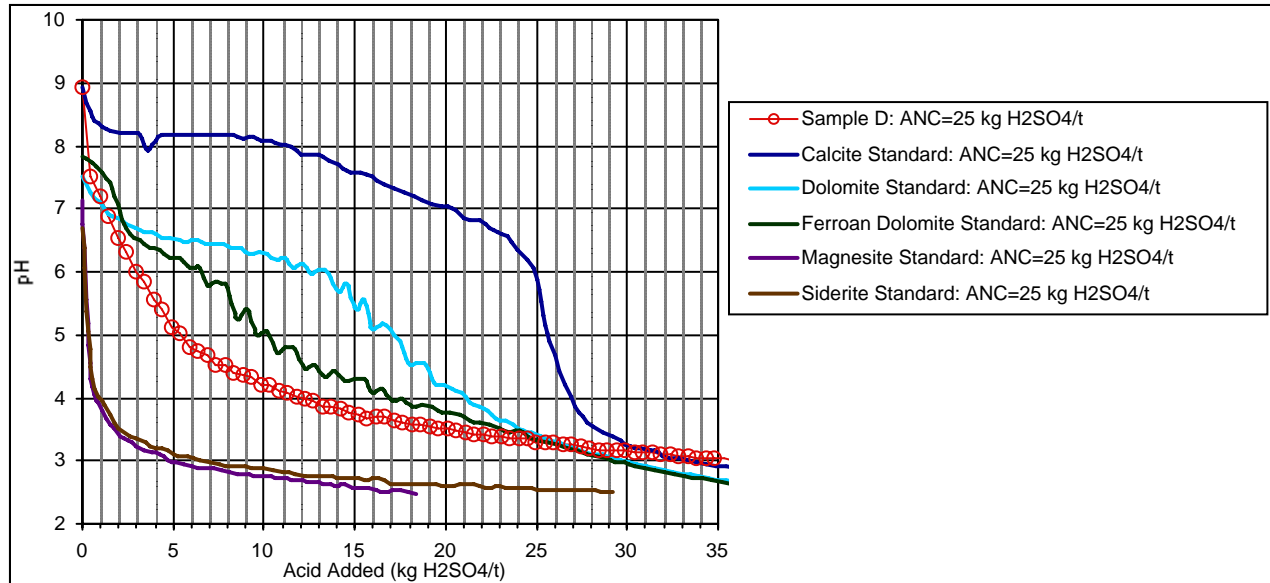


Figure 9: ABCC profile for sample D (Coal Waste Rock) with an EGi standard ANC of 25 kg H<sub>2</sub>SO<sub>4</sub>/t. Carbonate standard curves are included for reference.

#### Using Kinetic NAG Tests to Predict Column Lag Times

Sulfidic samples commonly result in heat generation during the NAG test due to the decomposition of the peroxide solution, catalysed by metal ions released during sulphide oxidation (Stewart et al., 2003a). The high temperature can destroy the peroxide and halt further oxidation of the sample. The pH trend before the temperature excursion gives an estimate of the relative reactivity, which may be related to prediction of lag times and oxidation rates similar to those measured in leach columns. An indicative relationship between kinetic NAG test results and column lag times for pyritic samples has been established based on research work using a geochemical data set provided by EGi. The basis of this relationship and how to apply it are described in this section.

Figure 10 shows the reaction time to reach pH 4 in the kinetic NAG test in minutes compared to the time to attain pH 4 in leach columns of the same samples for the EGi data set, comprised of 37 samples with pyrite the dominant sulfide. The plot shows a broad trend for NAG reaction time greater than 10 minutes when plotted on a log scale, demonstrating that the relationship is sufficient to distinguish between column lag times of days, weeks, months and years.

Figure 11 shows the time to pH 4 in the kinetic NAG test according to broad groupings based on the lag to pH 4 in column leachates. The plot shows a distinct increase in kinetic NAG time with column lag time for the column lag groupings used.



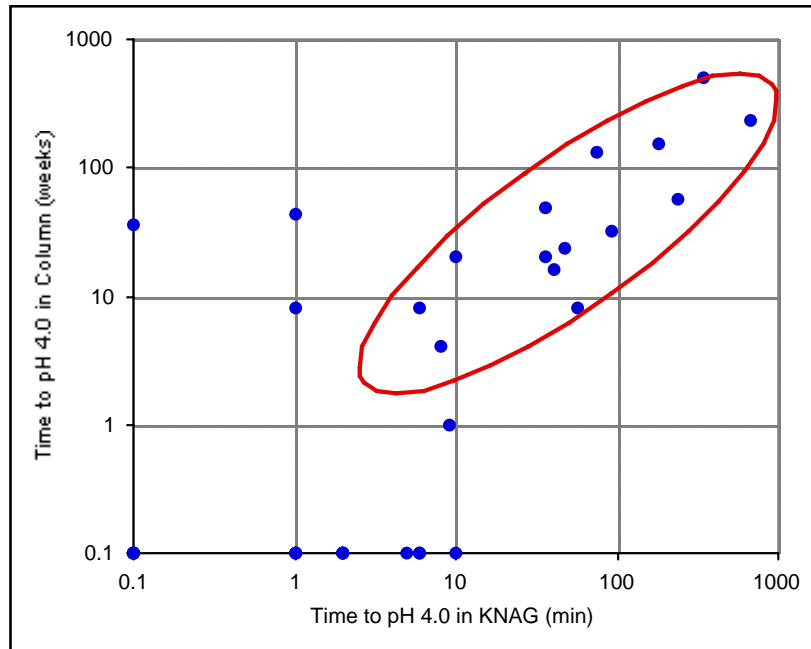


Figure 10: Time to pH 4 in kinetic NAG tests verses time to pH 4 in column leach tests.

Figure 12 is a plot of the median lag to pH 4 in the kinetic NAG test values against the median column lag times to pH 4 according to the column lag groupings in Fig. 11. The plot shows that when grouped according to broad column lag ranges, the median values of the time to pH 4 in the kinetic NAG test shows a linear correlation with median time to pH 4 in columns.

The correlation in Fig. 12 can be expressed as follows:

$$\text{Weeks to pH 4 in column} = 0.54 \times [\text{minutes to pH 4 in kinetic NAG}] \quad (5)$$

However, in practice the column lag times calculated from the kinetic NAG profiles should be reported in broad terms to reflect the indicative nature of the relationship, as shown in Table 6.

Table 6: Indicative column lags to pH 4 based on kinetic NAG results

Range of Time to pH 4.0 in KNAG (min)	Indicated Column Lag to pH 4
<5	<1 Month
5 to 15	1-2 Months
15 to 30	2-4 Months
30 to 50	4-6 Months
50 to 100	6-12 Months
100 to 200	1-2 Years
>200	>2 Years

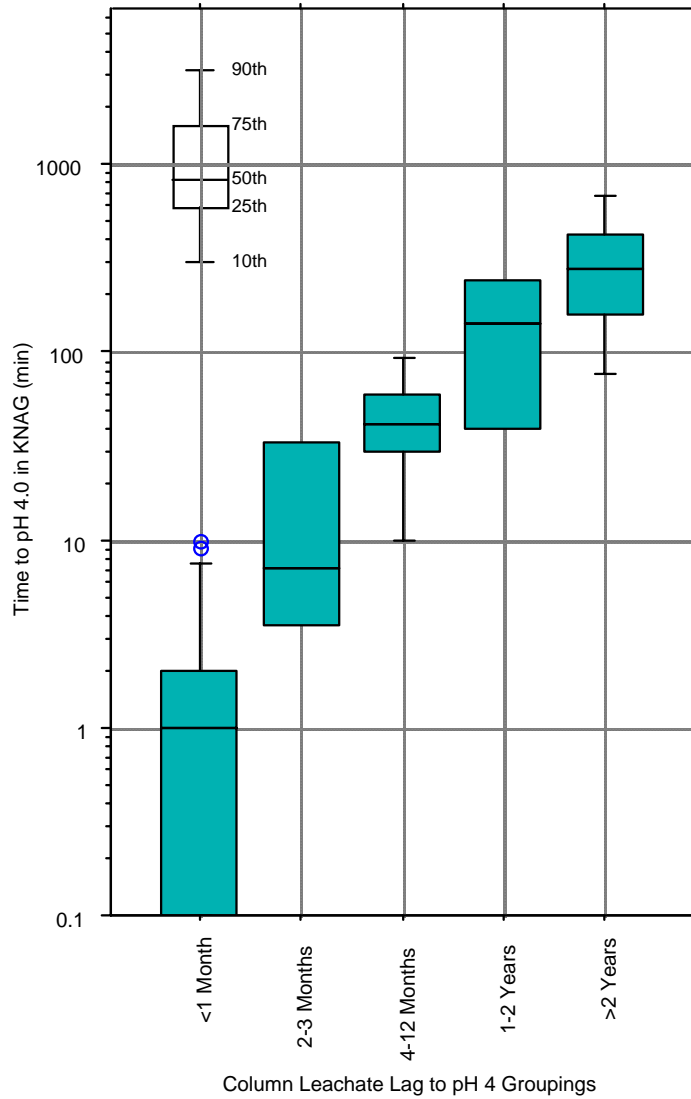


Figure 11: Box plot showing distribution of time (min) to pH 4 in the kinetic NAG for each of the column lag time groups. Box plots have 10th, 25th, 50th (median), 75th and 90th percentiles marked.

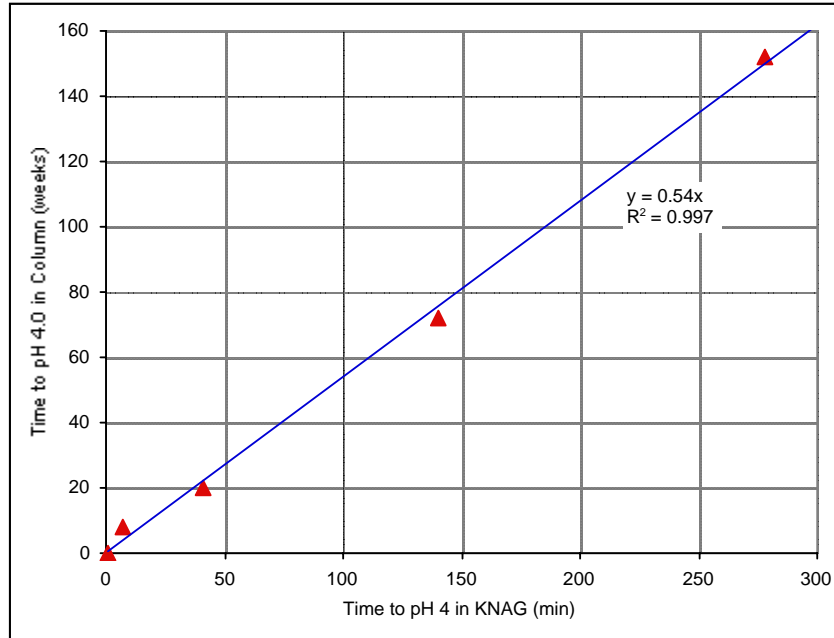


Figure 12: Plot of median time to pH 4 in the kinetic NAG versus median time to pH 4 in column leachates according to column leachate lag time groupings.

When interpreting kinetic NAG profiles, a number of limitations must be taken into account. Significant deviations from the relationship given in Table 6 may occur in the following cases:

- Samples with significant chalcopyrite and other sulphide species in addition to pyrite, since different sulphides in different combinations react at different rates in the kinetic NAG test (Stewart 2003a);
- Samples in which pyrite armoring inhibits oxidation under leach column conditions, resulting in longer column lags than those predicted by kinetic NAG tests;
- Samples with neutralising phases of low reactivity that are not readily available for acid buffering in the short duration of NAG tests but are available in the longer contact time offered by column tests, resulting in longer column lags than those predicted by kinetic NAG tests;
- Samples in which a high proportion of pyrite is encapsulated at the particle size used in the leach column test, but which is partly or fully liberated when pulverised, resulting in longer column lags than those predicted by kinetic NAG tests; and
- Samples in which a high proportion of the acid neutralising minerals are encapsulated at the particle size used in the leach column test, but which are partly or fully liberated when pulverised, resulting in shorter column lags than those predicted by kinetic NAG tests.

## **Conclusions**

The test refinements and developments described in this paper improve the reliability of ARD prediction from short duration tests. These improvements help bridge the gap between short term tests and longer term kinetic methods such as column leach and humidity cell tests, providing information on relative reactivity of acid forming and neutralising phases, and improving predictions of acid forming potential.

Comparison of NAG and NAPP results demonstrated the effectiveness of the NAG test in highlighting potential issues in ABA predictions. Used together, NAPP and NAG results provide a more reliable routine screening technique than either test alone, increasing confidence in acid potential classification and identifying apparent conflicts requiring further investigation. Techniques such as sequential NAG, modified organic carbon NAG, modified ANC methods to account for siderite and ABCC testing can be used to help resolve these conflicts in a relatively short time frame.

The sequential NAG test was shown to be useful in detecting the presence of non-acid forming S forms in a sample, which was enhanced significantly by the addition of NAG solution assay.

Investigations of siderite effects on the ANC test show that the standard ANC test is suitable for samples with less than 15 wt % siderite. Samples with greater than 15 wt % siderite require more complex ANC methods, involving larger additions of  $H_2O_2$  to ensure all dissolved  $Fe^{+2}$  ion is oxidised before completion of the back titration step. The establishment of this siderite abundance cut off, together with a number of other indicators of siderite effects, define a set of triggers that clearly determine when modified  $H_2O_2$  ANC methods are necessary, improving the efficiency of ANC assessment by reducing the number of complex ANC tests required.

The development of a set of standard carbonate curves and refinement of ABCC procedures has greatly improved the use and application of the test. ABCC test results provide an indication of the relative reactivity of the ANC measured in waste rock samples, something not evident in ANC test results alone. The use of standard carbonate curves in ABCC testing provides more confidence in assessment of ANC reactivity.

The kinetic NAG column relationships described in this paper between the time to pH 4 in the kinetic NAG tests and the time to pH 4 in the column test provides an indication (order of magnitude basis) of lag times without the need to carry out leach columns on all samples. This has the great advantage of allowing kinetic prediction on a broad sample set in a short time frame (approximately 24 hours), which is not possible with column tests. Note that the kinetic NAG test does not replace column leach or humidity cell tests, but is complementary to them.

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