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CALCULATED ACID–BASE BALANCE FOR H_2O_2 OXIDATION OF CARBONATE-POOR PYRITIC MINE-ROCK

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Abstract

An assessment of the net acid–base account following H_2O_2 oxidation of mine rock was established by chemical calculations based on the molar quantity of neutralizing cations (Na, K, Mg, Ca) and acid-generating S released during the Net Acid Generation (NAG) test. These neutralizing cations are derived from both silicates and carbonates; in carbonate-poor samples ($ANC_{carb} < 5$ kg H_2SO_4/t), however, the acid-neutralization capacity of silicate may be more important in neutralizing acidity than carbonate ANC. Testing is not recommended for samples that have significant concentrations of non-acid-forming S, non-neutralizing cations or non-acid-forming sulfide minerals, such as galena.

Keywords: acid rock-drainage, acid-neutralization capacity, net acid generation (NAG) test, H_2O_2, acid mine-drainage, pyrite oxidation, acid–base accounting.

SOMMAIRE

Un bilan global entre acidité et basicité de roches exploitées dans les mines suite à leur oxydation par traitement au H_2O_2 a été établi par calculs fondés sur la quantité molaire des cations neutralisateurs (Na, K, Mg, Ca) et de S apte à générer l'acidité en utilisant le test NAG (génération globale d'acidité). Ces cations neutralisateurs seraient dérivés à la fois de silicates et de carbonates; dans les échantillons à faible teneur en carbonate ($ANC_{carb} < 5$ kg H_2SO_4/t), il est clair que la capacité des silicates à neutraliser l'acide pourrait être plus importante que celle des carbonates. Un tel test n'est pas recommandé pour les échantillons qui possèdent une proportion importante de soufre non apte à former un acide, de cations non aptes à neutraliser, ou de minéraux sulfurés non aptes à générer de l'acidité, par exemple la galène.

(Traduit par la Rédaction)

Mots-clés: drainage minier acide, capacité à neutraliser l'acide, test NAG, évaluation de la génération d'acide, H_2O_2, oxydation de la pyrite, bilan acide–base.

INTRODUCTION

A comprehensive set of tools for predicting the geochemical characteristics of discrete samples of rock and their potential acid-forming (PAF) or non-acid-forming (NAF) behavior is available (*e.g.*, Sobek *et al*. 1978, Morin & Hutt 2001, Smart *et al*. 2002). A common predictive test in cases of acid rock-drainage (ARD) used to characterize samples as to their overall acid-production capacity is the net acid-generation (NAG) test (Miller *et al*. 1997, Smart *et al*. 2002). This test employs H_2O_2 to oxidize sulfide minerals such as pyrite, thereby generating acid, which then reacts with neutralising minerals to produce a final NAG pH that reflects the net acid-generation capacity of the sample. Back-titration of the NAG liquor to pH 7.0 provides an assessment of the NAG value (expressed in kg H_2SO_4/t). Net acid-generation in conjunction with the net acid-production potential (NAPP) can be used to further refine the classification of a sample in regard to its acid-generation potential (*e.g.*, Smart *et al*. 2002).

In this paper, we investigate the acid-neutralization reactions occurring in the NAG tests (and sequential NAG test) using calculations based on neutralizing ions (Na, K, Mg, and Ca) released to solution during the test. This is the first time that silicate acid-neutralization

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capacity (SiANC) has been addressed by these methods in the NAG test. A similar process has been described previously for carbonate dissolution in the ANC test (Weber *et al.* 2004a, 2005), and its dissolution in the NAG test (Stewart *et al.* 2003a). In combination with acid-generating reactions (determined from S release), it is possible to obtain an acid–base account for the NAG test, which provides an explanation of the final pH values in the NAG test.

BACKGROUND INFORMATION

The NAG test and variations thereof (*e.g.*, Miller *et al.* 1997, Smart *et al.* 2002) evaluate the net acid-generation potential of a sample without specific separate estimation of the maximum potential acidity (MPA) or acid-neutralization capacity (ANC) (Miller *et al.* 1997), and is based on earlier similar procedures (*e.g.*, Sobek *et al.* 1978, Finkelman & Giffin 1986, O'Shay *et al.* 1990). Acid generated during the test by sulfide oxidation reacts with carbonate and silicate minerals present in the sample and may result in their dissolution. Rapid decrease in pH during the NAG test indicates the presence of reactive sulfide minerals or acidic sulfate salts (Weber *et al.* 2004b), whereas a high final NAG pH (above 4.5) indicates the presence of carbonates and silicates with acid-neutralizing capacities in excess of acid produced.

Oxidation reactions in the NAG test can generate false readings of pyrite-induced acidity in organic-matter-rich samples (*e.g.*, coal measures) owing to the formation of organic acids under H_2O_2 oxidizing conditions, leading to overestimation of the net acid-generation capacity (derived from sulfide oxidation) of the sample during back-titration (O'Shay *et al.* 1990, Stewart *et al.* 2003a, Ahern *et al.* 2004). In samples with significant carbonaceous organic matter, these authors showed that a better indication of the acid generation is to determine the acidity in the NAG test due to pyrite, monitored by S release (Stewart *et al.* 2003a, Ahern *et al.* 2004). They reported that the total S in the NAG digestion liquor may be representative of the pyrite oxidized, and that this can be used to determine the pyrite-induced acidity generated in the NAG test (*e.g.*, $\text{Acidity}_{\text{NAG}}$; Equation 1). To determine the net acid-generation capacity of a sample requires consideration of neutralizing reactions as well as acid-generating reactions in the test. Stewart *et al.* (2003a) suggested that the neutralization of acidity occurring in the NAG test can be determined by Mg and Ca concentrations measured in the NAG solution as an indication of carbonate dissolution (*e.g.*, $\text{ANC}_{\text{NAG(Mg+Ca)}}$; Equation 2). However, in contrast to Stewart *et al.* (2003a), we suggest that Equation 2 also includes neutralization derived from Mg- and Ca-bearing silicate minerals. These two equations can be used to determine the calculated NAG value (CNV) expressed in kg H_2SO_4/t (Equation 3).

$$\text{Acidity}_{\text{NAG}} = [\text{S} \times 2] \times 49/\text{wt} \quad (\text{in kg } H_2SO_4/\text{t}) \qquad (1)$$

$$\text{ANC}_{\text{NAG(Mg+Ca)}} = [(\text{Mg} + \text{Ca}) \times 2] \times 49/\text{wt} \quad (\text{in kg } H_2SO_4/\text{t}) \qquad (2)$$

$$\text{CNV} = \text{Acidity}_{\text{NAG}} - \text{ANC}_{\text{NAG(Mg+Ca)}} \quad (\text{in kg } H_2SO_4/\text{t}) \qquad (3)$$

where S, Mg and Ca are in mg/L, wt is the sample weight in g. Conversion of S in NAG solution to equivalent H_2SO_4/t assumes that all S is derived from pyrite oxidation and 1 mole of H_2SO_4/t is generated for every mole of S in solution, and all Mg and Ca are derived from acid dissolution of carbonates and silicates. However, Na- and K-bearing silicate minerals also can neutralize acidity. This has been demonstrated in the modified Sobek ANC test (Weber *et al.* 2005), and can similarly be determined for the NAG test, *e.g.*, Equation 4.

$$\text{ANC}_{\text{NAG(Na+K)}} = [(\text{Na} + \text{K})] \times 49/\text{wt} \quad (\text{in kg } H_2SO_4/\text{t}) \qquad (4)$$

where Na and K are in mg/L, and wt is the sample weight in g. All Na and K are assumed to be from silicate neutralization. Thus this source of neutralization should be considered when assessing the net acid–base balance.

The assumption that all S released to solution during the NAG test (or in other H_2O_2 methods) is derived from pyrite dissolution and thus equates to the release of 2 H+ ions is erroneous. For instance, Jennings *et al.* (2000) showed that arsenopyrite, pyrite, marcasite, pyrrhotite, and chalcopyrite generate acidity, and (low-Fe) sphalerite, chalcocite, and galena do not. This finding is similar to that of Stewart *et al.* (2003b), who demonstrated that there are significant differences between the acid-forming potentials of different sulfide minerals in the NAG test and that, of the sulfide minerals examined, only pyrite, pyrrhotite, arsenopyrite and chalcopyrite are acid-producing, whereas sphalerite, galena, bornite, chalcocite and covellite are not. Results also showed that for samples with up to 5 wt% S (present as sulfides), a single-step NAG test is sufficient to oxidize the majority of sulfides present as pyrite, pyrrhotite, arsenopyrite, and sphalerite. However, this finding is at odds with calculations based on stoichiometry, which suggest that >5 wt% S should be oxidized. It can be determined that 15 vol.% H_2O_2 (6.35 mol/L) or 1.6 mol H_2O_2 is available in the NAG test (250 mL) to react with any pyrite present. According to Equation 5, this amount is sufficient to oxidize up to 0.21 mole of pyrite. If the 2.5 g NAG sample was entirely pyrite (0.02 mole of pyrite), then theoretically there is ample H_2O_2 is for oxidation purposes. However, owing to H_2O_2 loss associated with its catalytic decomposition, this is not the case:

$$FeS_2 + 15/2\ H_2O_2 \rightarrow Fe(OH)_3 + 2\ SO_4^{2-} + 4\ H_2O \quad (5)$$

Samples tested by the NAG test will commonly experience a temperature excursion during the test procedure, which is associated with the catalytic exothermic decomposition of the H_2O_2 (Stewart *et al.* 2003b) (*e.g.*, Fig. 1). This temperature excursion has previously been incorrectly attributed to the exothermic reactions of minerals with H_2O_2. The cessation of effervescence was taken to indicate that the reaction had run to completion (Jennings *et al.* 2000). Catalytic decomposition of the H_2O_2 is triggered by metals such as Pb, Cu, Mn, and Fe (Cotton & Wilkinson 1988) that are typically released during oxidation of sulfide minerals in the NAG test. Following decomposition of the H_2O_2, no further significant oxidation of pyrite occurs.

Since total oxidation of sulfide may not occur in samples with high sulfide-bound S (owing to decomposition of the H_2O_2), the final NAG pH may be circumneutral, if there is sufficient acid-neutralization capacity in the sample to neutralize the acid released, when in fact, the acid-production potential (*e.g.*, MPA) is far greater than the ANC. To determine the acid-production potential in such samples requires a sequential NAG test (Smart *et al.* 2002), which involves repeated additions of H_2O_2 to the sample residue (after removal of the previous NAG solution by filtering) to determine the true acid-generating potential of the sample. Some problems with this method occur if the sample has a high clay content that can clog the filter paper. In this instance, the liquor must be decanted off, which leaves a portion of solution and dissolved ions in the sample residue. Unfortunately, these ions can then be calculated as being released again from the next sequential stage.

TABLE 1. MINERALS QUANTITIES AND ACID–BASE ACCOUNTING TEST RESULTS FOR ROCK SAMPLES TESTED

Sample	PAF-H	PAF-L	C	U	T	PF
Quartz	49.3	16	9	45.1	44	19.2
Kaolinite						21.5
Illite						3.9
Smectite						3.4
Biotite				1.9		
Muscovite	31.7	11				12.7
Chlorite $(Mg,Al,Fe)_{12}(Si,Al)_8O_{20}(OH)_{16}$	2.2	0.1	1		1.6	
Orthoclase	7.6	54	36		6.8	
Albite		9	35		41	
Ca Plagioclase			6	4.1		
Pyroxene				3.8		
Olivine (Mg_2SiO_4)			3			
Calcite	0.1	0.1	0.25	0.33	0.2	
Ferroan magnesite $(Mg_{0.53}Fe_{0.44}Ca_{0.03}CO_3)$						0.04
Siderite						0.08
Pyrite (Euhedral)	9.1	3	1	5.1	2.3	1.7
Pyrite (Framboidal)						7.5
Pyrrhotite				Tr		
Chalcopyrite	0.03	0.8	0.6		0.4	
Sphalerite			Tr			
Magnetite	0.1			39.9		
Fe-Oxides (Fe_2O_3)		6	9		3.7	
Organic matter						30
LECO inorganic C	0.01	0.01	0.03	0.04	0.02	0.01
Total LECO S	4.6	1.7	0.8	2.4	1.5	4.67
ANC_{carb}	1	1	2	3	2	0.4
ANC	6.3	17.2	11	18	5.1	-36.4
ANC_{Actual}	11.1	21.3	NA	NA	5.6	7.1
MPA	141	52	24	73	46	143
NAPP	130	31	13	55	40	136

ABA data (MPA, ANC, and NAPP) in kg H_2SO_4/t; all other units in wt%; Tr: trace. NAPP uses ANC_{Actual} if available. Mineral contents have been normalized to 100% (slight increase in wt%); hence MPA does not match pyrite-bound S. NA: not analyzed.

LECO determinations of inorganic C are a common and useful way to determine the carbonate content, and hence, the calculated ANC derived from carbonates (ANC_{carb}), provided Fe carbonate is not an issue (*e.g.*, Paktunc 1999, White *et al.* 1999, Weber *et al.* 2004a). The difference between the ANC_{carb} and the $ANC_{NAG(Mg+Ca)}$ is therefore due to silicate ANC. The difference between $Acidity_{NAG}$ and the ANC_{NAG} should provide an overall indication of the net acid–base account of the NAG test (ABA_{NAG}). In this paper, we investigate these acid–base balances.

METHODS AND MATERIALS

Rock samples

Eight samples of rock were characterized as part of the Australian Minerals Industry Research Association (AMIRA) P387A project, which involved X-ray diffraction (XRD), X-ray fluorescence (XRF), LECO total S, LECO organic and inorganic C, optical mineralogy and scanning electron microscopy (SEM). Mineral assemblages were determined by XRD–XRF mineralogical reconciliation (similar characterization was reported previously by Weber *et al.* (2004b). Two samples were deemed unsuitable for ABA_{NAG} calculations because of significant non-acid-forming sulfides or non-acid-forming sulfate salts. Thus six of the original eight samples were assessed. Mineralogical data for

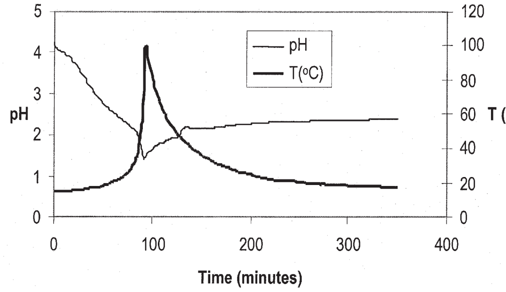

FIG. 1. Kinetic NAG test pH and temperature profiles for sample PAF–H. The rapid decrease in pH from 90 to 120 minutes is due to the inability of the pH-measuring system to compensate for the sudden increase in temperature.

these rock samples are presented in Table 1. Maximum potential acidity (MPA) is based on total wt% S, as determined by LECO total S analysis, multiplied by the stoichiometric factor 30.6 to determine the MPA in kg H_2SO_4/t; the ANC is determined by the Modified Sobek ANC test, although the ANC_{Actual} (Weber *et al.* 2004b) was determined on samples that were affected by acid generation during storage and the testing process itself (derived from acidic sulfate salts and reactive sulfides). The NAPP is based on the difference between MPA and ANC (using ANC_{Actual} where available; *e.g.*, see Weber *et al.* 2005).

The Modified Sobek ANC test

The Modified Sobek ANC test is based on the methodology of Sobek *et al.* (1978) as adapted by Environmental Geochemistry international (Smart *et al.* 2002). The test involves adding the prescribed quantity and molarity of acid to 2 g dry pulverized sample (<75 μm) in a 250 mL flask. Twenty mL of deionized water is used to flush any sample adhering to the flask walls and the bottom. The flask covered by a watch-glass is heated to 80–90°C on a hot plate for 2 h and then cooled at room temperature for 1 h. A back-titration using the prescribed quantity and molarity of NaOH (see Smart *et al.* 2002, Weber *et al.* 2004a) is then made. This is stopped at pH 4.5 to add 2 drops of 30% H_2O_2 to oxidize the remaining Fe^{2+} in solution. The titration is continued to pH 7.0, and the volume of NaOH recorded. The pH of the solution was measured with a Meterlab PHM201 pH – T meter calibrated with standard buffers at pH 4.0 and 7.0. Blanks were also run to quality-check results and to improve the ANC calculation process (Weber *et al.* 2005).

Previously, it has been shown that reactive sulfides and acidic sulfate salts can generate acidity in the ANC test (Weber *et al.* 2004b), which needs to be addressed to determine the actual ANC (ANC_{Actual}) that is not biased by acid formation masking ANC. This sulfide and sulfate acidity (SA_{max}) was determined by assessing the Modified Sobek ANC digestion liquor for dissolved S, which can be used to determine the ANC_{Actual} of the sample. Further details of this method are provided elsewhere (Weber *et al.* 2004b, 2005).

Net Acid-Generation (NAG) test

The NAG test involves the addition of 250 mL 15 vol.% (unstabilized) H_2O_2 to 2.5 g of pulverized sample (<75 μm), to encourage the rapid oxidation of reactive sulfides. Unstabilized H_2O_2 with a pH of 4.5 is used rather than stabilized H_2O_2 with a pH of 3.5 to prevent the sample being classified as acid-generating, when it may simply be a function of the pH 3.5 stabilized H_2O_2. After digestion, the final pH is recorded (NAG pH), and the sample is back-titrated with either 0.1 M or 0.5 M NaOH first to pH 4.5 and then to pH 7.0, and the net acid-generation (NAG) capacity is calculated. The sample is back-titrated initially to pH 4.5, as this is the starting pH of the solution. Titration to pH 7.0 accounts for acidity derived from metals such as Cu and Zn (Smart *et al.* 2002). To obtain information on the acid-generation kinetics of a sample, the pH and temperature of the NAG liquor are monitored during the single-addition NAG test to produce a pH–temperature profile for the duration of the test. This is known as the kinetic NAG test (Fig. 1).

To determine the acid-production potential in samples that experience H_2O_2 decomposition prior to total oxidation of sulfide minerals requires a sequential NAG test, which involves repeated additions of H_2O_2 to the sample residue (after removal of the previous NAG solution by filtration) to determine the true acid-generating potential of the sample. The NAG liquor is back-titrated to determine the net generation of acid for that stage. The test is usually repeated until there is no further reaction, and the pH remains above 4.5. Further details of the NAG test and sequential NAG tests are provided in the ARD Test Handbook (Smart *et al.* 2002).

NAG acid-base account (ABA) calculation

The acid-neutralization capacity of a sample subjected to the NAG test (ANC_{NAG}) can be determined by calculation (Equation 6) and includes ions derived from both carbonates and silicates:

$$ANC_{NAG} = [(Na + K) + (Mg + Ca) \times 2] \times 49/wt \text{ (in kg } H_2SO_4/t) \quad (6)$$

where Na, K, Mg, and Ca are the mmoles of each cation released in the test, 49 is the conversion factor to convert to kg H_2SO_4/t, and wt is the weight of sample used in the test (2.5 g). The NAG acid–base account (ABA_{NAG}) can therefore be determined by:

$$ABA_{NAG} = ([(S \times 2)] - [(Na + K) + (Mg + Ca) \times 2]) \times 49/wt \text{ (in kg } H_2SO_4/t) \quad (7)$$

and should be comparable to the NAG value determined by back-titration to pH 4.5, the starting pH of the initial NAG solution. This calculation assumes that there are no significant sulfide minerals other than pyrite, that no undetermined non-acid-forming sulfate salts or non-acid-neutralizing cations are present, and that there is no significant precipitation of secondary minerals (excluding Fe and Al) during the test. Where the ANC_{NAG} is greater than $Acidity_{NAG}$, negative ABA_{NAG} results may occur. This typically occurs where the final NAG pH is greater than, or close to, the starting pH of the H_2O_2 solution (pH 4.5), and indicates that neutralizing reactions have dominated over acid-generating reactions in the NAG test. In this instance, the neutralization capacity in the NAG test can be determined by titration with HCl down to pH 4.5 to determine a negative NAG value that matches the ABA_{NAG} value. Further details and examples are provided by Weber (2003).

Results

Sample PAF–H

Sample PAF–H is derived from the PT Freeport Grasberg mine, Papua Province, Indonesia. It is described as a potentially acid-forming sample with a high capacity to generate ARD and low acid-neutralization capacity. A classification system for this site has been previously described (Neale *et al*. 2003). For sample PAF–H, the ABA_{NAG} calculation provided a good indication of the NAG value determined by titration (Table 2). $Acidity_{NAG}$ is invariably greater than the NAG value, which is expected if neutralization reactions are occurring. In this instance, the neutralization is essentially derived from silicate minerals, as only 1 kg H_2SO_4/t ANC is due to carbonates (*e.g*., ANC_{carb}; Table 1). The majority of this neutralization is derived from Na- and K-bearing silicates (*e.g*., $ANC_{NAG(Na+K)}$). After an initial surge in neutralization during Stage 1, which is predominantly derived from Na and K minerals, the ANC_{NAG} remains stable at an average of 8.4 kg H_2SO_4/t for stages 2–4. In Figure 2A, we summarize the individual $Acidity_{NAG}$ and ANC_{NAG} released during the PAF–H sequential NAG test as compared to final NAG pH. Acid-generating reactions dominated over acid-neutralization reactions during the first three stages, as indicated by the low pH and the $Acidity_{NAG}$ being greater than ANC_{NAG} (Fig. 2A). Most acidity is released during the first two stages. By Stage 4, neutralization reactions (ANC_{NAG}) dominated over acid generation, as shown, and the pH remains at 4.5. Results indicate that neutralization (ANC_{NAG}) derived over four sequential NAG stages was 36.7 kg H_2SO_4/t, which is significantly greater than the ANC_{Actual} of 11.1 kg H_2SO_4/t.

Sample PAF–L

Sample PAF–L is also derived from the PT Freeport Grasberg mine, Papua Province, Indonesia. It is described as a potentially acid-forming sample with a low capacity to generate ARD and low acid-neutralization capacity (Neale *et al*. 2003). ABA_{NAG} provided a good indication of the NAG value determined for sample PAF–L (Table 3). Again, $Acidity_{NAG}$ is greater than the NAG value, indicating significant silicate-induced neutralization reactions are occurring during the test, as only 1 kg H_2SO_4/t ANC is derived from carbonates (Table 1). Figure 2B summarizes the individual $Acidity_{NAG}$ and ANC_{NAG} released during the sequential NAG test as compared to final NAG pH. Acid-generation reactions dominated over acid-neutralization reactions during the first two stages, although ANC_{NAG} is also significant in proportion to the total acid load. For Stage 4, the final NAG pH was 7.4 (Table 3), which indicates that neutralization reactions dominate; no analysis of the solution was undertaken for this stage. During Stage 3, ANC_{NAG} is greater than $Acidity_{NAG}$, which indicates that although acidity has been generated (as evident by the pH drop from 4.5 to 3.2), the ABA_{NAG} calculation does not indicate that acid-generating reactions are dominating over acid-neutralization reactions. This could either be related to precipitation of sulfate compounds such as jarosite, or non-neutralizing cations that have been released from soluble salts such as gypsum. This will affect the chemical calculation process by either overestimating the acid-generation or the acid-neutralization reactions. During Stage 2, the difference between $Acidity_{NAG}$ and ANC_{NAG} is greatest, and this is reflected by the lowest pH recorded. Results indicate that the ANC_{NAG} derived over three stages is 28.9 kg H_2SO_4/t, which is greater than the ANC_{Actual} of 21.3 kg H_2SO_4/t.

Sample C

Sample C is derived from the Newcrest Mining's Cadia mine in Australia. It is a rock-chip sample derived from blast hole drilling and is classified as potentially acid-forming, with a low capacity to generate acid and with a moderate ANC. Sequential NAG testing indicated that strongly acid conditions developed during stages 2 and 3 (Table 4) after exhaustion of the readily available ANC. This was determined to be 11 kg H_2SO_4/t, as measured in the Modified Sobek ANC test. Analysis of the solution data shows that the initial ANC surge in the sequential NAG test is derived from approximately equal proportions of $ANC_{NAG(Mg+Ca)}$ and $ANC_{NAG(Na+K)}$. By Stage 2, the $ANC_{NAG(Mg+Ca)}$ is only 30% of the initial value, and $ANC_{NAG(Na+K)}$ is only 10%. Although the $ANC_{NAG(Na+K)}$ is low, its contribution to ANC_{NAG} is significant. Figure 2C shows that $Acidity_{NAG}$ dominates over acid-neutralization reactions during the first four NAG stages, which is reflected in final NAG pH values being less than 4.5. The lowest values of pH occur at

TABLE 2. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE PAF–H

	Stage 1	Stage 2	Stage 3	Stage 4	Total
NAG (titration)	37	43	16	0	96
Final NAG pH	2.4	2.2	3.2	4.5	
wt%S removed	34.1	32.0	14.1	3.0	83.2
$Acidity_{NAG}$	48.0	44.9	19.9	4.3	117.1
$ANC_{NAG(Mg+Ca)}$	2.7	3.1	2.8	2.6	11.2
$ANC_{NAG(Na+K)}$	9.0	5.6	5.4	5.5	25.5
ANC_{NAG}	11.7	8.7	8.2	8.1	36.7
ABA_{NAG}	36.3	36.2	11.7	-3.8	84.2 (80.4)

wt% S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g*., where $ANC_{NAG} > Acidity_{NAG}$).

Stage 2, when the difference between $\text{Acidity}_{\text{NAG}}$ and ANC_{NAG} is the greatest for any stage. For the final three stages, ANC_{NAG} dominates over $\text{Acidity}_{\text{NAG}}$, which is reflected in gradually increasing values of pH. By Stage 7, ANC_{NAG} dominates over $\text{Acidity}_{\text{NAG}}$, and the final NAG pH remains at 4.5. In this instance, the total ANC_{NAG} (13.0 kg H_2SO_4/t) is similar to the ANC determined by the modified Sobek ANC test, 11 kg H_2SO_4/t.

Sample U

Sample U is from the Placer Pacific Osbourne mine. It is a composite tailings sample characterized as potentially acid-forming, with a moderate ANC and a lag period prior to acid rock-drainage. Acid generation dominates over acid-neutralization reactions during the first two stages of the sequential NAG test, as evidenced by the low pH. However, by Stage 3, neutralization reactions dominated over acid-generating reactions, and the pH is greater than the starting pH, 4.5 (Table 5).

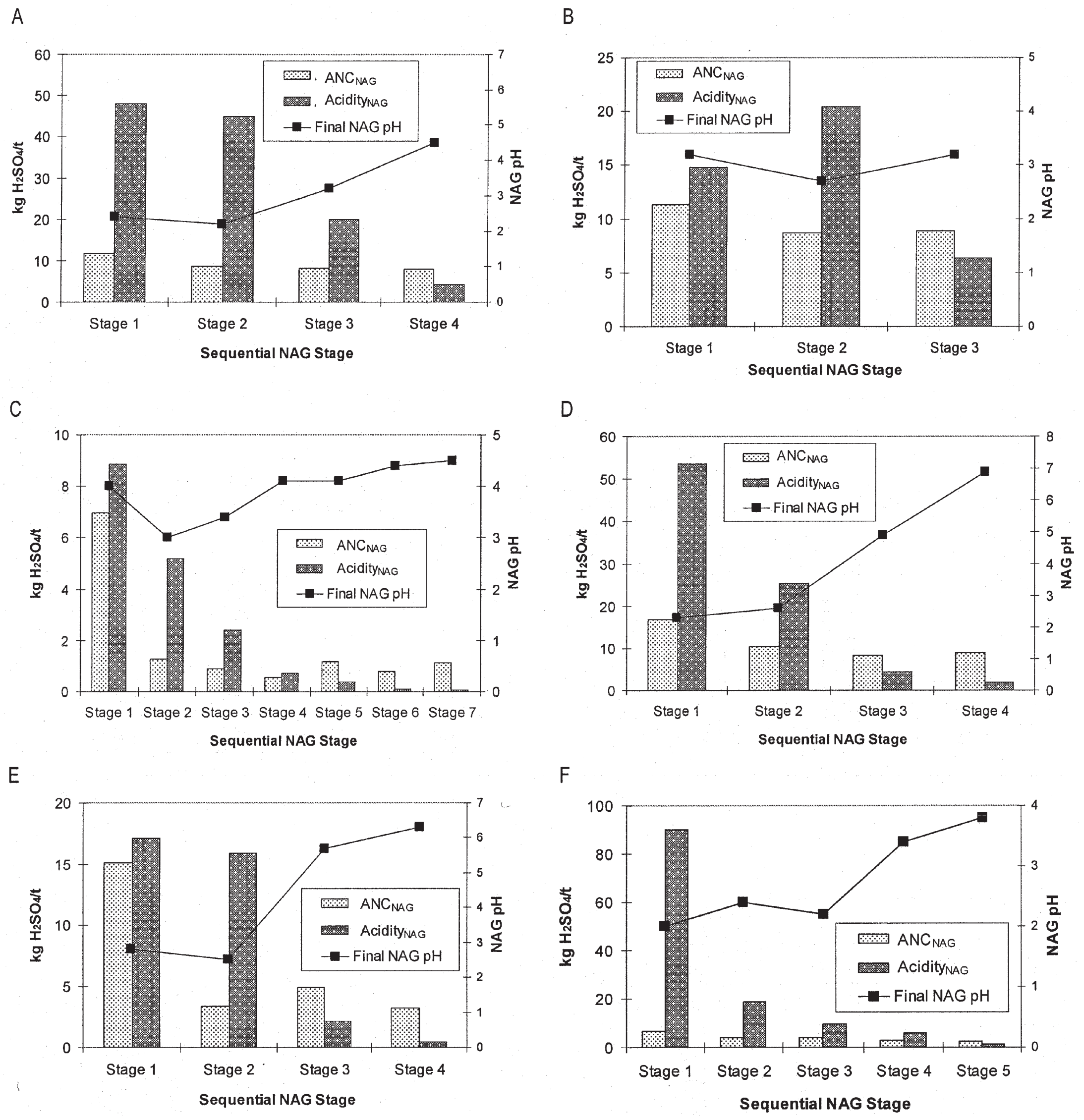

FIG. 2. Comparison of ANC_{NAG}, $\text{Acidity}_{\text{NAG}}$ and final NAG pH for six waste-rock samples. A. Sample PAF–H. B. Sample PAF–L. C. Sample C. D. Sample U. E. Sample T. F. Sample PF.

This trend continues in Stage 4, with an even higher final NAG pH value and a greater disparity between Acidity_{NAG} and ANC_{NAG}. On average, the ANC_{NAG} is 9.2 kg H_2SO_4/t after Stage 1, The total ANC_{NAG} over four sequential NAG stages for this sample is 44.4 kg H_2SO_4/t, which is half of the total Acidity_{NAG} (Table 5). At all stages, the AcidityNAG was greater than the NAG value, suggesting significant silicate-induced neutralization of acid as the carbonate ANC (ANC_{carb}) was only 3 kg H_2SO_4/t. Acidity_{NAG} and ANC_{NAG} released during the sequential NAG test as compared to final NAG pH are shown in Figure 2D. The trend of increasing final NAG pH subsequent to sulfide exhaustion in stages 2–3 is clearly visible.

Sample T

Sample T is from the Newcrest Telfer mine in Western Australia. It is a rock-chip sample considered potentially acid-forming, with a short lag prior to acid rock-drainage. Sequential NAG geochemical data for this sample are shown in Table 6. Most ANC is derived from Stage 1 of the sequential NAG test (15 kg H_2SO_4/t), and this is predominantly derived from $\text{ANC}_{NAG(Na+K)}$, which indicates acid neutralization by Na- and K-bearing silicate minerals. Acidity_{NAG} is greater than the final NAG value, suggesting that significant neutralization by silicate occurred in Stage 1 as the carbonate ANC (ANC_{carb}) is only 2 kg H_2SO_4/t (Table 1). Predominantly, this acid-neutralization capacity of silicates is related to potassium release at Stage 1. Figure 2E summarizes the Acidity_{NAG} and ANC_{NAG} results as compared to final NAG pH values. ANC_{NAG} results indicate that there is significant neutralization occurring during Stage 1, and this is almost equal to the acidity generated in that stage. However, following its exhaustion, the ANC_{NAG} in subsequent sequential NAG steps is much lower. With the removal of this inherent ANC and continued formation of acid, Stage 2 generates the lowest pH values recorded during the sequential NAG test, which agrees with the greatest disparity between Acidity_{NAG} and ANC_{NAG}. In subsequent stages, ANC_{NAG} reactions dominated over Acidity_{NAG}, which is reflected in the final NAG pH being greater than pH 4.5.

Sample PF

Sample PF is from the Rio Tinto Kaltim Prima coal mine, Kalimantan, Indonesia. It is a potentially

TABLE 3. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE PAF–L

	Stage 1	Stage 2	Stage 3	Stage 4	Total
NAG (titration)	2.4	10.0	2.4	0.0	14.8
Final NAG pH	3.2	2.7	3.2	7.4	
wt%S removed	28.5	39.3	12.2	N.A.	80.0
Acidity_{NAG}	14.8	20.4	6.3	N.A.	41.5
$\text{ANC}_{NAG(Mg+Ca)}$	2.4	3.1	3.1	N.A.	8.6
$\text{ANC}_{NAG(Na+K)}$	8.9	5.6	5.8	N.A.	20.3
ANC_{NAG}	11.3	8.7	8.9	N.A.	28.9
ABA_{NAG}	3.5	11.7	-2.6	N.A.	15.2 (12.6)

wt% S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g.*, where $\text{ANC}_{NAG} > \text{Acidity}_{NAG}$).
N.A.: not analyzed.

TABLE 4. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE C

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Total
NAG (titration)	0.4	3.0	1.0	0.2	0.0	0.1	0.0	4.7
Final NAG pH	4.0	3.0	3.4	4.1	4.1	4.4	4.5	
wt%S removed	36.7	21.5	10.0	3.0	1.5	0.4	0.3	73.4
Acidity_{NAG}	8.9	5.2	2.4	0.7	0.4	0.1	0.1	17.8
$\text{ANC}_{NAG(Mg+Ca)}$	3.4	1.0	0.6	0.4	0.7	0.4	0.7	7.2
$\text{ANC}_{NAG(Na+K)}$	3.6	0.3	0.3	0.2	0.5	0.4	0.5	5.8
ANC_{NAG}	7.0	1.3	0.9	0.6	1.2	0.8	1.2	13.0
ABA_{NAG}	1.9	3.9	1.5	0.1	-0.8	-0.7	-1.1	7.4 (4.8)

wt% S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g.*, where $\text{ANC}_{NAG} > \text{Acidity}_{NAG}$).

TABLE 5. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE U

	Stage 1	Stage 2	Stage 3	Stage 4	Total
NAG (titration)	28.0	11.0	0.0	0.0	39.0
Final NAG pH	2.3	2.6	4.9	6.9	
wt%S removed	72.9	34.6	5.8	2.6	115.9
Acidity_{NAG}	53.5	25.4	4.3	1.9	85.1
$\text{ANC}_{NAG(Mg+Ca)}$	11.2	6.0	4.5	3.2	24.9
$\text{ANC}_{NAG(Na+K)}$	5.7	4.3	3.8	5.7	19.5
ANC_{NAG}	16.9	10.3	8.3	8.9	44.4
ABA_{NAG}	36.6	15.1	-4.0	-7.0	51.7 (40.7)

wt% S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g.*, where $\text{ANC}_{NAG} > \text{Acidity}_{NAG}$).

TABLE 6. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE T

	Stage 1	Stage 2	Stage 3	Stage 4	Total
NAG (titration)	8.0	14	0	0	22
Final NAG pH	2.8	2.5	5.7	6.3	
wt% S removed	37.1	34.4	4.6	0.9	77.0
Acidity_{NAG}	17.1	15.9	2.1	0.4	35.5
$\text{ANC}_{NAG(Mg+Ca)}$	3.2	1.5	2.0	1.2	7.9
$\text{ANC}_{NAG(Na+K)}$	11.9	1.8	2.9	2.0	18.6
ANC_{NAG}	15.2	3.3	4.9	3.2	26.6
ABA_{NAG}	1.9	12.6	-2.8	-2.8	14.6 (8.9)

wt%S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g.*, where $\text{ANC}_{NAG} > \text{Acidity}_{NAG}$).

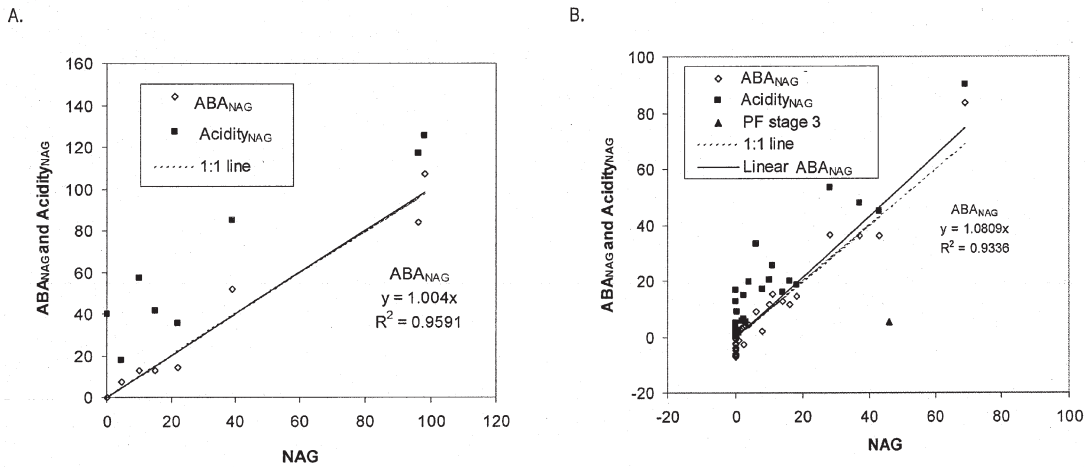

FIG. 3. ABA_{NAG} and $Acidity_{NAG}$ *versus* NAG (titration) in kg H_2SO_4/t. A. Total ABA_{NAG} and $Acidity_{NAG}$ *versus* total NAG for six samples. Total NAG for sample PF corrected to 97 kg H_2SO_4/t. B. ABA_{NAG} and $Acidity_{NAG}$ *versus* NAG for individual sequential NAG stages for six samples. NAG for sample PF (Stage 3) is not included in the correlation, but is shown to indicate significant variance due to organic acids.

acid-forming sample with a high capacity to generate acid rock-drainage. It has been described previously in detail (Weber *et al.* 2004b) and contains a significant amount of organic matter. In sample PF, the majority of the acid-neutralization capacity calculated from the NAG test solution data is derived from silicate minerals. Assuming that all Mg and Ca was derived from carbonates in this sample, one could incorrectly infer that 4.9 kg H_2SO_4/t of carbonate ANC was present (Stage 1). However, only 0.4 kg H_2SO_4/t carbonate ANC is available (Table 1). The Mg and Ca are most likely derived from clays, such as smectite-group minerals, present in the sample. The $Acidity_{NAG}$ calculated from solution analyses is in reasonable agreement with the NAG as determined by back-titration. This is with the exception of Stage 3, where the NAG value for Stage 3 was much higher than expected owing to the release of organic acids. Organic acids have previously been discussed by Stewart *et al.* (2003a) for similar samples. This stage was ignored to determine a correlation between ABA_{NAG} and NAG (ABA_{NAG} = 1.19 × NAG; R_2 = 0.98). The correlation between $Acidity_{NAG}$ and NAG was determined to be $Acidity_{NAG}$ = 1.3 NAG (R_2 = 0.99). The Stage-3 NAG measured by back-titration can be corrected using this correlation for NAG *versus* $Acidity_{NAG}$, which therefore indicated a NAG value of 7 kg H_2SO_4/t. Thus the total NAG value can be recalculated using a Stage-3 NAG of 7 kg H_2SO_4/t to give a total NAG of 97 kg H_2SO_4/t, which is in agreement with the ABA_{NAG} (corrected stage-3 NAG values are given in brackets in Table 7). In Figure 2F, we summarize the individual $Acidity_{NAG}$ and ANC_{NAG} released during the PF Sequential NAG test as compared to final NAG pH. Results indicate that with depletion of pyrite within the sample during the sequential NAG stages, there is a corresponding increase in final NAG pH. Although Stage 5, the final stage of the sequential testing, did not reach pH 4.5, the general trend in pH increased as acidity was exhausted (Fig. 2F).

TABLE 7. SEQUENTIAL NAG ACID–BASE ACCOUNTING DATA FOR SAMPLE PF

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Total
NAG (titration)	69	18	46 (7)	2	1	136 (97)
Final NAG pH	2	2.4	2.2	3.4	3.8	
wt% S removed	62.8	13.0	6.6	4.0	0.8	87.2
$Acidity_{NAG}$	90.2	18.6	9.5	5.8	1.2	125.3
$ANC_{NAG(Mg+Ca)}$	4.9	0.8	0.2	0.2	0.1	6.2
$ANC_{NAG(Na+K)}$	1.7	3.3	3.9	2.6	2.5	14.0
ANC_{NAG}	6.6	4.1	4.1	2.8	2.6	20.2
ABA_{NAG}	83.6	14.5	5.4	3.0	-1.4	106.6 (105.1)

wt% S removed indicates total S lost to solution (as analyzed). Numbers in brackets for Total ABA_{NAG} include negative contributions (*e.g.*, where ANC_{NAG} > $Acidity_{NAG}$). Stage-3 NAG results in brackets are corrected for organic acids as discussed. Total NAG results in brackets are based on the corrected Stage-3 acidity of (7).

DISCUSSION

Neutralization by carbonate versus silicate

Stewart *et al.* (2003a) suggested that the neutralization of acidity occurring in the NAG test can be determined by the molar concentration of Mg and Ca measured in the NAG solution (Equation 2). Furthermore, using the S release as a measure of acid generation, the calculated NAG value (Equation 3) could then be determined based on S, Mg, and Ca (Stewart *et al.* 2003). This is a suitable approach for rock samples with high carbonate content, such that this carbonate neutralization-source dominates. However, for carbonate-poor samples, such as those assessed in this work, this approach is unsuitable, as significant neutralization is derived from Na- and K-bearing silicate minerals. For samples PAF–L, C, U, and PF, a better match to the NAG associated with each sequential NAG stage occurred if Na and K ions released to solution are considered to be derived from neutralization processes. For samples PAF–H and T, the addition of these ions (Na and K) did not provide a convincing argument that they were important sources of acid neutralization.

There is no correlation between the carbonate ANC (ANC_{carb}) and $ANC_{NAG(Mg+Ca)}$ measured at Stage 1, even though final NAG pH ranged from 2.0 to 4.0, which is sufficient for rapid dissolution of carbonate. The assumption that Ca and Mg measured during the NAG test (and subsequent sequential stages) are derived entirely from carbonates is thus incorrect.

NAG acid–base accounting

In Figure 3A, we compare the total calculated ABA_{NAG} and the $Acidity_{NAG}$ to the total NAG determined by back-titration to pH 4.5 for the samples investigated (*e.g.*, the sum of all sequential stages). In the values calculated for ABA_{NAG}, we consider the negative values (as determined by ABA_{NAG} calculation) to be zero, as the NAG does not address the neutralization capacity if the final NAG pH is greater than 4.5. The trend has the following correlation: $ABA_{NAG} = 1.004 \times NAG$. For comparison, the 1:1 line is directly over the ABA_{NAG} trend line, which represents the true ABA_{NAG} : NAG ratio if for every mole of S released to solution, there are two hydrogen ions neutralized by cations such as Na, K, Ca, and Mg. Total $Acidity_{NAG}$ also is plotted to show that it is invariably greater than the NAG value, which indicates that acid neutralization is occurring during the test.

TABLE 8. NAG_{ANC} SUMMARIES

Sample	ANC_{NAG} Stage 1	ANC_{NAG} (average) Stage 2 to end	ANC_{NAG} total
PAF-H	11.7	8.4	36.7
PAF-L	11.3	8.8	28.9
C	7.0	1.0	12.8
U	16.9	9.2	44.5
T	15.2	3.8	26.6
PF	6.6	3.4	20.2

All results in kg H_2SO_4/t.

Figure 3b shows the correlation between ABA_{NAG} and NAG values (as determined by titration) for each sequential NAG stage (a total of 27 stages). Again, the results show that $Acidity_{NAG}$ generally overestimates the NAG value, and that the neutralization reactions occurring during the test need to be addressed to provide an accurate acid–base account that is comparable to the NAG value determined by back-titration. Figure 4 is a close-up of the ABA_{NAG} *versus* NAG diagram for each sequential stage (Fig. 3B) for values below 20 kg H_2SO_4/t. Of particular interest is the sudden cessation of the ABA_{NAG} : NAG trend below the NAG value 0 kg H_2SO_4/t. This occurred wherever the final NAG pH is greater than or close to pH 4.5. The calculated ANC_{NAG} thus was in excess of any acidity ($Acidity_{NAG}$) generated during the test. This could have been determined by back-titrating the NAG solution with HCl down to the starting pH of 4.5 to produce a negative ABA_{NAG} value.

To determine the suitability of the derived ABA_{NAG} value (Equation 7), which addresses the neutralization derived from Na, K, Mg, and Ca *versus* the CNV value (Equation 3), which only addresses Mg and Ca neutralization, the ABA_{NAG} and the CNV are plotted in Figure 5A (total NAG values) and Figure 5B (individual sequential NAG values). Results conclusively demonstrate that ABA_{NAG} provides a better indication of the NAG (as determined by back-titration) than the CNV (in which the neutralizing effects of Na- and K-bearing minerals are not considered) for these samples.

The ANC_{NAG} values for Stage 1 and the average ANC_{NAG} values for Stage 2 through to the final sequential NAG Stage are shown in Table 8 for all samples tested. Results conclusively demonstrate that subse-

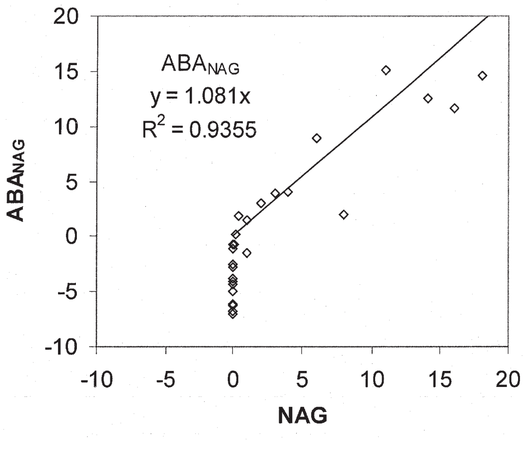

FIG. 4. Close-up of the ABA_{NAG} values shown on Figure 3B. This plot illustrates the effects of pH values that are greater than 4.5 on the ABA_{NAG} values. Results suggest that the trend line should continue into negative numbers.

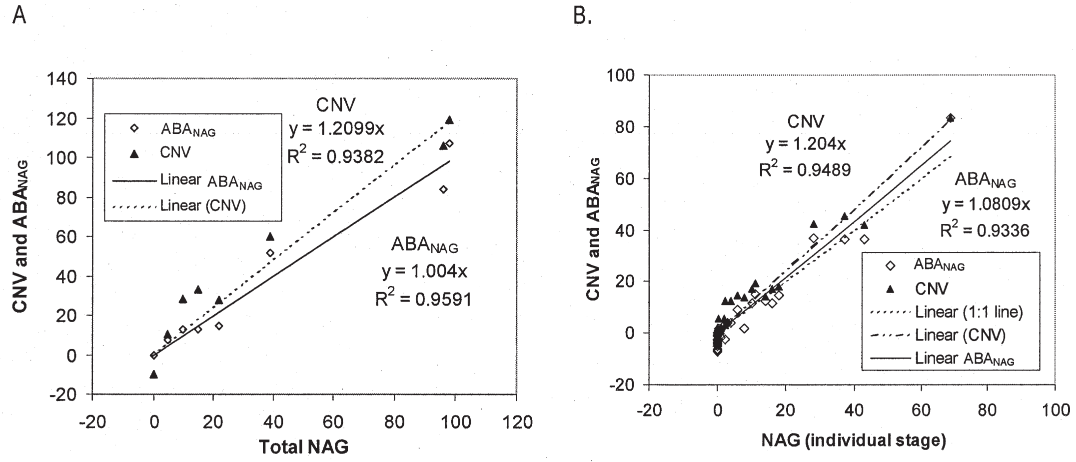

FIG. 5. ABA_{NAG} and CNV (calculated NAG value) *versus* NAG (as determined by titration). Values in kg H_2SO_4/t. A. Total NAG (Total NAG for sample PF corrected to 98 kg H_2SO_4/t). B. Individual sequential NAG stages (NAG for sample PF not included in correlation owing to the presence of organic acids). Negative ABA_{NAG} values are assumed to be zero.

quent NAG_{ANC} values are lower than the initial surge occurring in Stage 1 (carbonate dissolution and reactive surface-sites and rapid cation–proton exchange on the silicates), yet are still significant. In the case of the silicates, the initial rapid-dissolution surge and cation release, and the subsequent decrease in dissolution rates with time, which generates a parabolic dissolution-trend, have been identified by many researchers investigating the dissolution kinetics of these minerals in batch and flow-through kinetic tests (*e.g.*, Busenberg & Clemency 1976, Chou & Wollast 1984, Amrhein & Suarez 1992, Suarez & Wood 1996). Further testing is required to determine if ANC_{NAG} (Stage 1) is comparable to the ANC derived from the Modified Sobek ANC test for potentially acid-forming samples with a low content of carbonate.

CONCLUSIONS

A satisfactory method was developed to determine the net acid-generation and net acid-neutralization occurring during the H_2O_2 NAG test based on calculations using the molar quantity of neutralizing cations and acid-forming S released to solution. This provided an overall acid–base balance for the test, which provided an explanation for NAG pH trends. However, this method is unsuitable for samples that contain significant salts and significant quantities of non-acid-forming sulfide minerals.

Furthermore, results demonstrate that subsequent to H_2O_2 oxidation of sulfidic samples, the ANC derived from silicate minerals can be greater and more significant than carbonate ANC in carbonate-poor samples (*e.g.*, $ANC_{carb} < 5$ kg H_2SO_4/t). In some instances, the ANC derived from Na- and K-bearing silicate minerals is more important than neutralization derived from Mg- and Ca-bearing minerals (carbonate and silicate). We do not imply that the ANC measured by this test is applicable to kinetic tests such as the column leach test or the field situation. Another approach is still required to assess silicate ANC under those conditions.

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