A Comparison of Kinetic NAG tests with Static and Humidity Cell Tests for the Prediction of ARD

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Abstract

This study compares data from kinetic NAG tests with data from static tests, and humidity cell tests on five different rock samples. The paper presents pH data over time in both types of kinetic tests and seeks to determine what useful information is discernable from such data. Total amounts of metals leached by the different methods are also compared. For the materials used in this study the following findings were made: NAG tests confirm the ARD categorisation conferred by standard ABA procedures, the lag-time until temperature excursion does not correlate with the time to pH< 4 in humidity cells, that running NAG tests for longer than is typical may reveal the presence of aluminosilcate NP, that NAG tests lead to the release of more dissolved constituents than up to 80 weeks of humidity cell testing, and that the 'kinetic' data from the NAG tests did not reveal any useful information that the final NAGpH would not have revealed.

Key words: Kinetic NAG, ARD, Humidity Cells, Prediction

Introduction

Of the many static test methods available for prediction of the acid generating capacity and general ARD behaviour of rocks, the Net Acid Generation (NAG) test has perhaps received the least attention in terms of research. The typical NAG procedure is based upon peroxide tests developed by numerous authors e.g. Sobek et al (1978) and Finkelman & Giffin (1986). The test involves subjecting a pulverised rock sample (<70 µm) to 15% hydrogen peroxide (H_2O_2) in a ratio of 1:100 (solids: liquid). The sample is allowed to react with the peroxide overnight, the sample is then boiled for about 2 hours, cooled and the final pH (NAGpH) is measured. The sample is then titrated to pH 4.5 and pH 7 and the volume of NaOH required recorded. The peroxide oxidises the sulfide moiety, the acidity generated reacts with readily available neutralising potential (NP) within the sample. According to the standard interpretation of these data, a final NAGpH < 4.5 indicates the sample has the potential to generate net acidity, NAGpH> 4.5 indicates zero capacity to generate net acidity. The amount of titrant required to neutralise the NAG solution can also be used to set site specific criteria for samples deemed to have a low- or high-capacity to generate acid.

The Kinetic NAG (KNAG) test is identical to the standard NAG test but pH, temperature and occasionally conductivity are measured continuously during the reaction. According to Miller et al (1997) the kinetics of the NAG test can provide an indication of lag times and oxidation rates in a similar way to leach columns. These authors go on to tentatively suggest a direct relationship (based on 33 samples) between the time for a pH unit decrease in a kinetic NAG test and the time to pH 4 in a leaching column. The relationship derived for these characteristics was: Time to leaching column acidity = 2.4 x NAG (minutes) [EQ 1]. The present study has examined five samples on which static and humidity cell (HC) data were available. Kinetic NAG tests were carried out on these materials and the results examined and compared with humidity cell and static data in order to investigate what happens during a kinetic NAG test and how the data can be used for ARD prediction.

Materials and Methods

Rock samples from three different mine sites were collected and characterised. The results of the static tests and rock type are shown in Table 1. The KNAG procedure was based on the standard NAG test but was scaled up to allow sufficient volume for continual sampling. 25 g of crushed (<70 µm) rock material was added to 2.5 L of 15% H_2O_2 (apart from Sample 2 where 2.5 g was used because of the high sulfide content). The contents of the flask was stirred using magnetic stirrers and the pH, temperature and conductivity were continuously monitored. Samples were taken during and at the end of the experiment for acidity titrations and metals analysis by ICP-OES. SO_4 releases were estimated by charge balance on the metals analyses. There was one major difference to the normal NAG protocol in that the boiling step was omitted. Humidity cell data were collected using standard humidity cell operating procedures as per Price (1997).

Table 1 *Static Test Data for Materials Used*

Sample #	1	2	3	4	5
Deposit Type	Porphyry	Porphyry	Porphyry	Porphyry	Porphyry
Rock Type	Meta Arkose	Massive Sulfide	Breccia	Contact Breccia	Granite
Tot S %	0.06	13.14	3.54	2.41	0.04
Sulfide S %	0.04	12.00	2.50	2.41	0.03
Contact pH[1]	7.25	3.41	7.18	7.03	8.82
AP[2]	1.16	375	78.13	75.24	0.94
Carb-NP[2]	3.08	9.13	0.90	0	8.19
NPR[3]	2.66	0.02	0.01	0	7.66
NNP	1.92	-366	-77.23	-75.24	7.12
NAGpH	-	-	3.49	2.81	-
ARD Potential[4]	Low	Likely	Likely	Likely	None

[1] Water contact test either paste pH or similar

[2] Units of tonnes of $CaCO_3$ equivalent per 1000 t of rock

[3] NPR based on Carb-NP

[4] Based on ABA Screening Criteria from Price (1997)

Results and Discussion

Samples 1 and 5

The NPR for these samples (Table 1) suggests low/no likelihood for ARD, in fact Price (1997) suggest that samples with a sulfide content of <0.3% and a water contact pH > 5.5 have no potential to produce ARD. The KNAG (Fig 1(a)) reveals a final pH > 4.5 for Sample 1, indicating the rock is non-acid forming (NAF), this is in agreement with 80 weeks of humidity cell (HC) testing (Fig 1(b)). For Sample 5 the final KNAGpH < 4.5 suggesting ARD potential, however the boiling step was omitted and this may have raised the pH above 4.5. Fig 1(c) shows that the temperature remained close to ambient throughout both the tests.

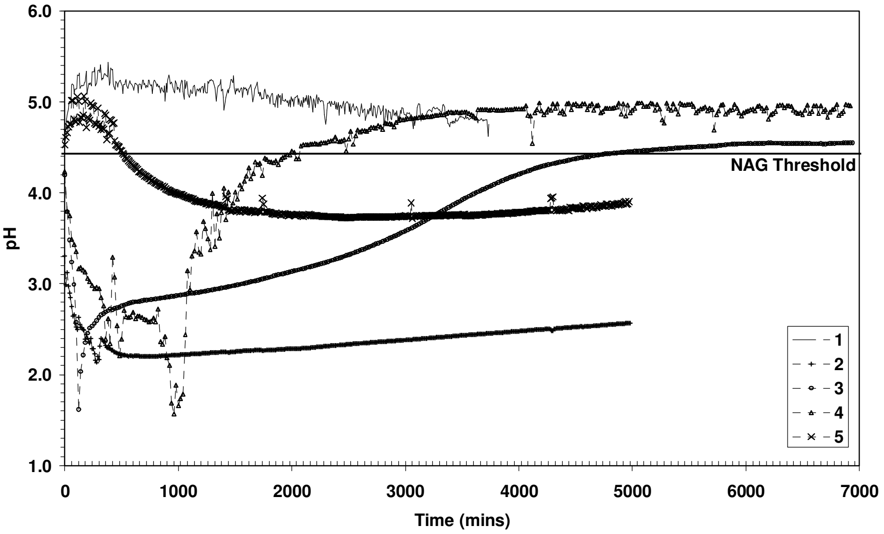
Sample 2

The final NAGpH of < 4.5 (Fig 1 (a)) confirms the acid potential of this sample and agrees with the NPR and NNP. The KNAG pH was < 4 from the start of the test, this concurs with the contact pH data (Table 1) and the 72 weeks of HC data (Fig 1 (b)). Over the course of the test the pH recovery was minimal suggesting that the NP of the sample was consumed and/or very slow reacting. Fig 1(b) reveals that Sample 2 displayed a considerable 'temperature excursion' reaching temperature of 86°C after about 5 hours. Clearly the relationship in EQ 1 does not hold for this sample as it was acidic from the start in the humidity cell. Table 2 indicates that the NAG test is more aggressive than HC (apart from Zn) and leached considerably more than HC in 72 weeks of oxidation, especially for Ca and Ni. Calculations suggest that only 50% of the sulfide S was oxidised – this is probably related to the early decomposition of the peroxide as indicated by the temperature excursion (Fig 1(c)).

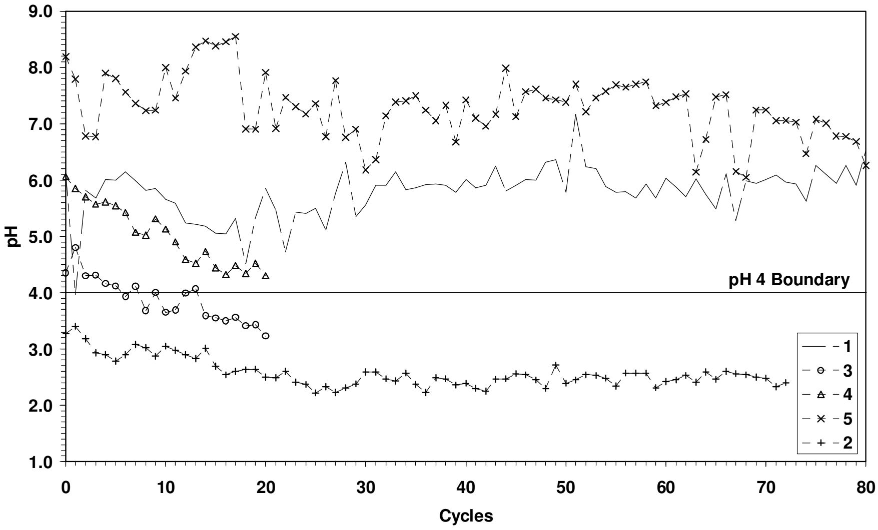
Sample 3

Static testwork confirms that this sample has a high ARD potential, the standard final NAGpH was 3.49 (Table 1). Interestingly, in the KNAG after a 100hrs the pH had recovered to >pH 4.5 (see Fig 1(a)) suggesting the presence of slow reacting NP that was not detected in the standard NAG or by using Carb-NP. A Sobek-NP test may have indicated this NP, although it was not detected after the boiling step of the standard NAG which may be analogous to Sobek-NP. The HC data for Sample 3 (Fig 1(b)) over 20 weeks of available data shows a rapidly declining pH. EQ 1 would suggest a lag time in the columns of 120 weeks, however it ca be seen that the lag time before pH < 4 was 6 weeks. Experimental data suggests that only ~15% of the available sulfide S was oxidised –

Figure 1 *(a) Kinetic NAG pH profiles (b) Humidity Cell pH profiles (c) Kinetic NAG temperature profiles*



(a)



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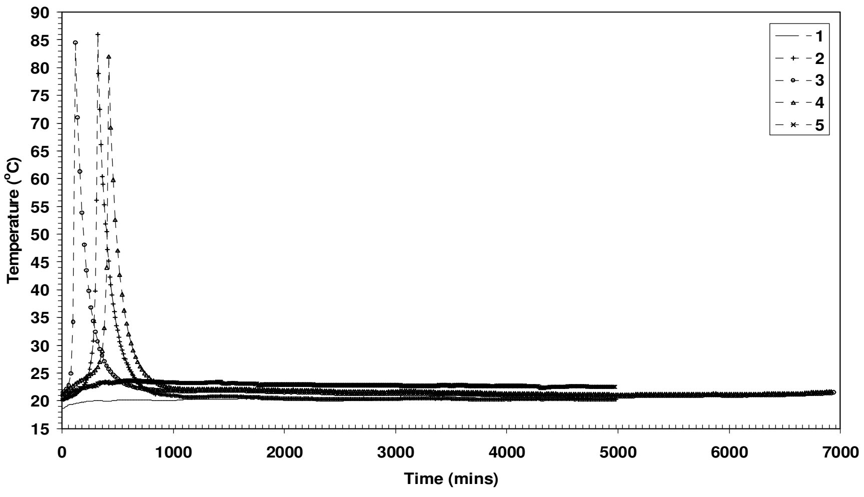

(c)

***Table 2** Total Leached Metals and Sulfate from Kinetic NAG tests (KN) and Humidity Cells (HC).*

	Sample 1			Sample 2			Sample 3			Sample 4			Sample 5		
	KN	HC[1]	RATIO	KN	HC[2]	RATIO	KN	HC[3]	RATIO	KN	HC[3]	RATIO	KN	HC[1]	RATIO
	mg/g	mg/g		mg/g	mg/g		mg/g	mg/g		mg/g	mg/g		mg/g	mg/g	
Na	1.23	0.04	28.7	12.2	0.78	15.5	1.63	0.42	3.87	1.41	0.38	3.72	1.23	0.03	46.6
Mg	0.29	0.10	2.8	1.29	0.90	1.4	0.86	0.66	1.29	0.37	0.46	0.80	0.069	0.01	6.0
K	0.41	0.04	11.4	3.80	-	-	0.72	0.10	7.29	0.84	0.12	7.20	0.54	0.02	30.0
Ca	0.88	0.18	4.9	3.80	0.02	192.5	1.01	0.74	1.35	16.8	6.01	2.79	0.73	0.17	4.4
Ti	0.001	0	-	0.007	0	-	0	0	-	0	0.01	-	0.003	0	-
Cr	0.004	0	-	0.020	0	-	0.02	0.002	11.3	0.007	0.001	12.4	0.004	0	-
Mn	0.010	0.003	3.5	0.18	0.06	2.9	0.10	0.06	1.55	0.01	0.01	1.47	0.075	0.002	41.2
Fe	0.16	0.003	864	70.4	29.3	2.4	5.64	0.003	1790	3.72	0.002	2393	0.31	-	4600
Co	0.002	0	-	16.8	0	-	0.27	0.003	197	1.36	0.001	1840	0.08	0	-
Ni	0.006	0.001	23.2	6.55	0.06	118	0.11	0.001	57.3	0.53	0.001	587	0.04	0	1670
Cu	0	0	-	0.43	0.43	1.0	0.74	2.02	0.36	3.64	0.03	131	0.04	0	282
Zn	0.004	0.001	7.02	0.80	3.89	0.2	0.23	0.13	1.75	0.024	0.002	11.8	0.03	0	147
Al	0.17	0.01	24.9	7.66	1.76	4.4	0.82	0	-	0.25	0.001	368	0.25	0.001	185
Cd	0	0	-	0	0.01	-	0.028	0.02	1.15	0.005	0	151	0.002	0	-
SO_4	2.36	0.60	4.0	168	93.2	1.8	10.6	7.09	1.49	26.1	7.09	3.69	2.56	0.14	18.8

[1] Samples subject to 80 weeks humidity cell testing [2] Sample subject to 72 weeks humidity cell testing [3] Samples subject to 20 weeks humidity cell testing

again probably due to the decomposition of the oxidant peroxide at an early stage of the test which is indicated by the temperature excursion to 85°C after only 120 minutes of the test. Apart from Cu Table 2 shows that the KNAG test is more aggressive leach than 20 weeks of humidity cell testing.

Sample 4

Again, static testwork confirms that this sample has a high ARD potential, the standard final NAGpH was 2.41 (Table 1). After a 100hrs the KNAG pH had recovered to circa pH 5 (see Fig 1(a)) once again suggesting the presence of slow reacting NP that was not detected in the standard NAG or by the Carb-NP. Aluminosilicate buffering is once again the likely explanation for the behaviour of this sample. The trend of the HC data in Fig 1(b) indicates that the HC will become acidic (<pH 4) but future data will be scrutinised to see if the slow reacting NP indicated in the KNAG affects the HC pH. Fig 1 (c) indicates the sample underwent a temperature excursion to 70°C after 440 minutes. If the trend of pH in the HC continues a pH of < 4 would be expected in 23 weeks, not the 440 x 2.4 = 1056 weeks before pH < 4 if EQ 1 held true. S data indicates that only 36% of the available sulfide S was oxidised – again probably related to the oxidant decomposing during the test.

Conclusions

Over the typical 20 hrs of a standard NAG test, the NAG criteria generally confirmed the predictions of the standard Carb-based ABA. Over longer periods pH in some samples recovered, indicating slower reacting NP. The data in this paper suggest no correlation between the time for unit drop in pH in the KNAG test and the time to pH<4 in humidity cells, although this does not rule out site specific relationships. For higher sulfide contents the decomposition of the peroxide leads to less of the available sulfide reacting. The data in this paper shows that the NAG and KNAG tests are generally an aggressive leach for metals and sulphate and despite a few exceptions leads to greater releases than substantial periods of humidity cell testing. This paper demonstrated that for the samples tested there is no clear advantage in carrying out intensive pH and temperature monitoring during NAG style tests.

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