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Comparison of Actual and Calculated Lag Times in Humidity Cell Tests

Kelly Sexsmith[1], Dylan MacGregor[1] and Andrew Barnes[2]
1. *SRK Consulting, Canada*
2. *SRK Consulting, United Kingdom*

ABSTRACT

It is common practice to run humidity cell tests on potentially acid generating rock or tailings samples to determine the amount of time it will take for acidic conditions to develop—often called "lag time". Defining lag time is important for understanding when management plans need to be in place for preventing or mitigating acid rock drainage. The lag time is a function of the amount of neutralization potential (NP) present in the rocks and rate of sulphide oxidation and therefore NP depletion. Although direct observations of lag times are possible, it is relatively rare for acidic conditions to develop over the course of a laboratory test. Therefore, lag times are more often calculated.

This paper explores the relationships between actual measured lag times versus calculated lag times for two groups of samples: 1) where acidic conditions developed following a distinct lag time, and 2) where acidic conditions should have developed, but did not develop despite an extended period of testing. The results show that actual lag times tend to be shorter than calculated lag times, demonstrating the importance of using conservative assumptions in the calculations of lag time as well as running some tests for an extended period of time to obtain site specific information on lag times. In addition the paper reiterates the importance of quantifying available NP rather than simply adopting measured NP results available from commonly measured NP procedures.

Keywords: Lag Time, Humidity Cell Test, Prediction, Management

INTRODUCTION

Generation of acid rock drainage (ARD) is a time dependent process in which oxidation of sulphide minerals results in the release of sulphate and acidity. Weathering of silicate minerals and/or dissolution of carbonate minerals may produce sufficient alkalinity to buffer the pH. In addition, reactions between sulphide oxidation products and carbonate and/or silicate minerals may further buffer the pH. In potentially acid generating mine wastes, the relative rates of acid production and acid consumption will determine: 1) whether acidic conditions will develop rapidly – due to insufficient rates of neutralization; or 2) whether there will be a delay in the onset of acidic conditions - due to a finite or limited amount of neutralization potential (NP). Along with rates of acid production, the amount and the availability of the NP will determine how long buffering reactions will persist.

Where present, the delay in the onset of acidic conditions is typically referred to as the “lag time”. Lag times are important for understanding when management plans need to be in place to prevent or mitigate the effects of ARD. For example, where lag times are sufficient to ensure neutral pH conditions can be maintained for a period of time, it may be possible to backfill, place covers, or freeze the material to prevent ARD from developing. Similarly, it may be possible to delay the construction of a treatment plant, and thereby defer some of the start-up costs for period of time.

The lag time is a function of the amount and availability of NP present in the rocks and rate of sulphide oxidation and therefore NP depletion occurring as these rocks are exposed to air and water. Although direct observations of lag times are possible, it is relatively rare for acidic conditions to develop over the course of a laboratory test – even in samples that are potentially acid generating. More often, acidic conditions develop very early in the lab test due to insufficient rates of neutralization, or they don’t develop at all due to slow rates of NP depletion. Therefore, lag times are more often calculated using data from humidity cell tests. Although the calculations are based on reasonably straightforward inputs, they are subject to a number of uncertainties, including the accuracy of measuring the NP and the rates of sulphide oxidation and NP release, the availability and reactivity of the NP, and other factors such as deposition of secondary minerals on mineral surfaces which may reduce the availability of the NP or result in reduced reaction rates. Estimates of lag times are also typically adjusted to reflect field conditions such as differences in temperature which can reduce reaction rates and further delay the onset of acidic conditions.

To better understand the magnitude of uncertainty in estimating lag times in the laboratory setting, we compiled data from a number of long term humidity cell tests and explored the relationship between actual versus calculated lag times in two groups of samples: 1) where acidic conditions developed following a distinct lag time, and 2) where calculations indicated that acidic conditions should have developed, but didn’t develop despite an extended period of testing.

METHODOLOGY

SRK has compiled an inventory of results from over 229 humidity cell tests representing 33 sites internationally. Of these, 42 tests from 15 of these sites were identified as possible candidates for this study either because acidic conditions developed after distinct lag time to onset of acidic conditions, or acidic conditions had not developed, but the predicted lag times were reasonably close to or less than the test duration, indicating that acidic conditions could have developed. Key static and kinetic test results for each of these samples were compiled, and the calculations of NP depletion were checked to ensure that consistent calculation methods were applied. On further review, 12 of the non-acidic tests were eliminated because the calculated lag times exceeded the test duration (i.e. there was no reason to expect that acidic conditions should have developed). The final dataset was comprised of 30 tests from 14 sites, with test durations ranging from 80 to 520 weeks. Thirteen of these tests are still operating.

Due to the large number of programs and the time frame over which these tests were completed – dating back almost 20 years, there were some minor variations in the static and kinetic testing methods. Most of the ABA tests included analysis of total inorganic carbon (TIC), and either Modified Sobek NP (MEND 1991), Sobek NP (Sobek et al., 1978), or with the European Standard EN15875 (CEN, 2011) procedure which itself is based on the Modified Sobek NP procedure. All of the humidity cell tests were completed using either flood or trickle leach variations of the MEND or ASTM method for humidity cell tests (ASTM 2001, MEND 1991). Lastly, the mineralogy was characterized using petrographic analysis and/or Reitveld XRD for most of the samples.

The actual lag time was defined as the point in time where the pH dropped below a value of pH 5, as shown in Figure 1. This pH was selected to ensure that acidic conditions were due to sulphide oxidation, rather than equilibrium with atmospheric carbon dioxide.

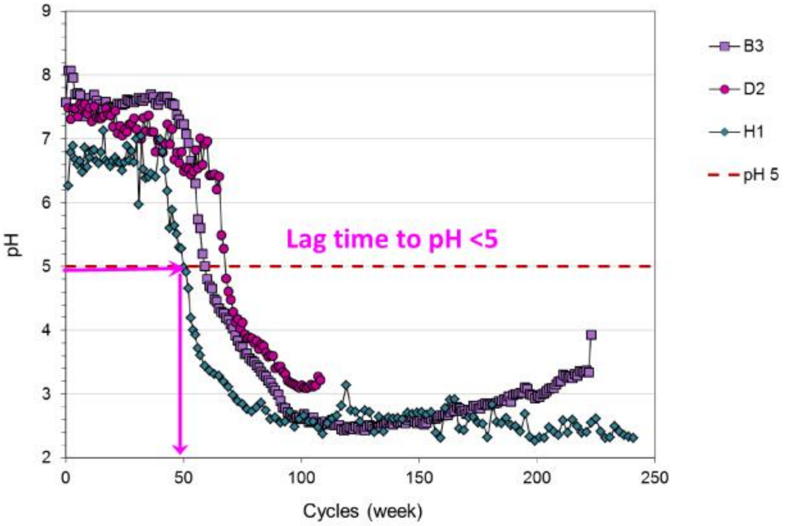


Figure 1 Definition of "actual lag times" used in this study

Calculated lag times were determined using the following two methods:

$$Time\ to\ NP\ depletion\ = \frac{NP^*}{(Ca+Mg)\ release\ rate} \qquad \text{(equation 1)}$$

or,

$$Time\ to\ NP\ depletion\ = \frac{NP^*}{SO_4\ release\ rate} \qquad \text{(equation 2)}$$

Where: NP* is the available NP in units of kg $CaCO_3$ eq/t (described below)

(Ca+Mg) and SO_4 release rates are the steady state non-acidic release rate from the humidity cell test in units of kg $CaCO_3$ eq/t/year.

For most of the samples examined in this study, these two calculation methods gave similar depletion times because the molar ratios of SO4/(Ca+Mg) in the humidity cell leachate were close to unity.

The available NP (NP*) was estimated based the TIC or NP titration method (Sobek, Modified Sobek or EN15875) that was considered to be most appropriate for the sample or project site, and further adjustments to account for limitations on the availability and/or reactivity of the NP. The following types of adjustments were made to account for these limitations:

- Site specific "unavailable" NP was estimated based on the TIC or NP found in samples with acidic paste pH values, and was subtracted from the TIC or NP.
- TIC was multiplied by a factor that represented the Ca+Mg content of the carbonates (Day 2009).
- TIC or NP was divided by a factor representing the relative availability of NP/AP (NP/AP_{crit}) established through kinetic testing. (NP/AP_{crit}) is typically a value between 1 and 1.5.
- For sites where there was no specific information as to whether TIC or NP was more appropriate for a site, or where site specific correction factors could not be established, the lesser of the TIC or NP value was selected and this was divided by an NP/AP_{crit} factor of 1.5.

For one site (Site N), NP was measured using both the normal EN15875 method in finely pulverized material, and an alternative method on samples with a particle size distribution equivalent to that used in the humidity cell test – without size reduction, making it possible to determine the amount of NP that was physically available in the humidity cell test. The results ranged from 0.34 to 0.66 (average of 0.53), indicating that roughly half of the NP was physically available. However, for consistency with the other data sets which did not have this type of data, these results were not explicitly considered in determining of NP* for these tests.

The (Ca+Mg) and SO_4 release rates were based on the steady state release rates established for the period of the test prior to the onset of acidic conditions. This is an important point because these rates often increase in response to decreasing pH conditions, and since the point of the calculation is to determine the time to onset, rates must reflect the period prior to onset of acidic conditions. Additionally, it was important to establish that these rates were not governed by dissolution of primary gypsum or anhydrite in the samples or by gypsum precipitation – which can occur in samples with very high oxidation rates and large amounts of calcite.

The comparisons of actual and calculated lag times inherently consider the combined effects of the variables that are included in these calculations – notably NP* and the (Ca+Mg) or SO_4 release rates. To explore secondary relationships, regression analysis was used to establish the relationship between actual and calculated values, and the residuals were plotted against other variables, including the rate of acidification (i.e. pH unit/week), the difference between NP* and TIC, (Ca+Mg)/SO4 release rates, sulphur content and sulphate production rates. A more qualitative approach was used to assess potential influences of mineralogy on the results.

RESULTS AND DISCUSSION

Sample Characteristics

Table 1 presents key results from the static and kinetic tests, and the actual and calculated lag times for each of the samples.

The ABA results (Table 1 and Figure 2) indicate that the majority of these samples had very low TIC and NP and high AP, with TIC/AP and NP/AP ratios consistently well below 1, indicating that they were all samples with a strong potential for ARD. As indicated previously, these samples represent a relatively small portion of the total number of samples in the kinetic test inventory, which suggests that delayed onset to acidic conditions is relatively rare and almost always occurs in material with very low NP and relatively high sulphide contents.

The pH profiles from the humidity cell tests (Figure 3) show a range of patterns. In some tests (Figure 3a), there is a distinct period when pH conditions are maintained at constant levels in the range of pH 6.5 to 8, and then a rapid drop in pH. In some (Figure 3b, 3c), there is a distinct period with constant pH, but then a more gradual drop in pH that is sometimes accompanied by large oscillations in pH over an extended period of time. In others (Figure 3d), the pH starts to drop early on in the test, but decreases very gradually, resulting in effective delays of more than 20 weeks before dropping below a pH of 5. Arguably samples from this last group does not show a distinct lag to onset of ARD, but were retained for use in the study to see if they would provide further insights in the determination of lag time.

Calculated versus Actual Lag Times

Comparisons of calculated versus actual lag times are shown in Figure 4. The results indicated that a small number of tests (5/30) had calculated lag times that were shorter than actual lag times. However, in most tests, calculated lag times were longer than actual values, and there was a reasonable relationship between these values (r = 0.62 and 0.67 for the two calculation methods respectively). A small number of tests were also treated as outliers because they had calculated lag times that were much longer than actual values. Further discussion of the outlier results is provided in the following section.

Although we expected to find a number of tests where the acidic conditions should have developed but didn’t develop over the course of the test, only one test met this criterion (plotted on Figure 4 using test duration in lieu of actual lag time). This also supports the conclusion that acidic conditions tend to develop more rapidly than expected based on standard calculation methods used to assess lag times.

Linear regressions on these relationships indicate that, on average, predictions of lag time would be improved if the calculated lag times are multiplied by a factor of 0.73 (based on the calculation shown in equation 2). In other words, predicted lag times should be calculated as follows:

$$predicted\ lag\ time\ = 0.74 \times \frac{NP*}{SO_4\ release\ rate} \qquad \text{(equation 3)}$$

Interestingly, this factor is reasonably close to the “physical availability” that was measured in samples from Site N, suggesting that more rapid onset of acidic conditions could be, in part, a function of reduced NP availability in coarser particles in these samples.

Table 1 Sample Characteristics, Actual and Calculated Lag times

Test	Duration	S(T)	S(SO4)	AP	TIC	NP	NP*	NP*/AP	Release rates		Calculated Lag		Actual Lag time		Rate of	Mineralogy
									Ca+Mg	SO4	eqn 1	eqn 2	to pH<6	to pH<5	pH change	
	weeks	%	%	kg CaCO3/t					kg CaCO3 eq/yr		years		years		su/wk	
A1	295	0.71	0.01	22	0.83	10	0.83	0.04	0.38	0.33	2.2	2.5	3.3	4.5	0.01	no carbonate, Ca+Mg silicates
A2	295	1.86	0.01	58	1.7	9.2	1.7	0.03	0.67	0.61	2.5	2.7	1.4	2.1	0.04	calcite > analytical TIC, Ca+Mg silicate
A3	266	2.21	0.02	68	12	18	12	0.17	1.3	1.4	(8.7)	(8.3)	1.1	1.3	0.09	calcite, Ca+Mg silicates
B1	442	0.73	0.01	23	7.5	7.0	5.4	0.24	0.8	0.31	6.4	(17.4)	4.1	4.7	0.02	Ankerite/ankerite dolomite
B2	223	0.93	0.02	29	4.2	4.0	3.1	0.11	1.4	1.4	2.1	2.2	1.0	1.1	0.25	Ankerite/ankerite dolomite
B3	223	0.98	0.02	31	5.0	3.0	2.3	0.08	1.7	1.6	1.4	1.4	1.1	1.2	0.25	Ankerite/ankerite dolomite
B4	223	1.1	0.02	34.4	52	5	3.8	0.11	2.3	1.3	1.7	3.0	>4.3	>4.3	na	
C1	154	3.27	0.06	100	5.8	10	4.9	0.05	1.7	2.2	2.8	2.2	1.2	1.7	0.04	tr calcite, 40% quartz, 40% illite.
D1	98	0.57	0.01	18	0.80	3	0.53	0.03	0.43	0.52	1.2	1.0	0.7	0.8	0.14	no carbonate
D2	108	0.27	0.02	6	1.7	3.5	1.1	0.19	0.42	0.33	2.7	3.4	1.3	1.3	0.18	tr carbonate
D3	81	0.38	0.01	11	0.80	1.2	0.53	0.05	0.18	0.28	3.0	1.9	0.5	0.7	0.10	no carbonate
D4	104	0.59	0.01	16	0.83	8.5	0.56	0.03	0.27	0.37	2.1	1.5	0.6	1.0	0.06	tr carbonate
E1	313	36	0.72	1087	72	62	41	0.04	32	32	1.3	1.3	1.4	1.8	0.06	calcite
F1	173	2.91	0.34	80.3	20	11	7.1	0.09	2.0	2.0	3.5	3.4	2.3	2.8	0.05	no data
F2	118	1.15	0.11	35.9	39	19	6.2	0.17	1.8	1.8	3.5	3.5	1.9	2.3	0.05	no data
G1	296	9.1	0.04	283	11	15	7.6	0.03	0.36	0.44	(21.0)	(17.2)	1.2	1.5	0.05	no carbonate by XRD
G2	296	6.7	0.1	198	6.8	6.5	4.3	0.02	2.4	2.8	1.8	1.6	0.0	0.9	0.03	calcite
G3	296	6.4	0.1	189	6.8	6.2	4.1	0.02	4.3	4.8	1.0	0.9	0.0	0.3	0.11	no carbonate
H1	241	6.04	0.1	186	8.0	1.0	4.7	0.03	4.3	4.3	1.1	1.1	0.8	1.0	0.20	calcite and dolomite, but low mod NP
H2	369	2.48	0.05	76	58	5.2	3.1	0.04	1.2	1.3	2.6	2.4	2.1	3.0	0.02	high siderite
I1	96	1.6	0.01	50	4.1	6.8	2.8	0.05	2.0	2.2	1.4	1.3	0.5	0.6	0.15	no data
J1	520	4.4	0.01	136	11	6.0	7.3	0.05	1.7	1.8	4.2	4.1	2.7	4.0	0.02	pale brown carbonate (poss ankerite)
J2	520	2.4	0.01	73	48	57	32	0.43	3.8	4.4	8.3	7.2	3.4	5.2	0.01	calcite vienlets
K1	201	13.2		243.5	na	7.3	4.9	0.02	na	0.96	na	5.1	1.4	2.1	0.01	no carbonate
L1	113	1.16	0.01	36	2.0	6.4	1.4	0.04	1.0	0.90	1.4	1.5	1.1	1.7	0.04	calcite with minor ankerite and
M1	79	1.06	0.04	30	25	23	20	0.65	5.2	7.0	3.8	2.8	0.6	0.7	0.25	no data
N1	169	3.25	0.27	93	8.3	11	5.6	0.06	2.0	1.8	2.7	3.0	1.9	2.9	0.03	calcite
N2	169	2.92	0.11	88	57	36	24	0.27	1.5	1.5	(16.3)	(15.9)	1.9	2.5	0.02	-
N3	169	0.76	0.05	22	3.3	4.8	2.2	0.10	0.5	0.4	4.8	5.5	1.9	2.8	0.03	-
N4	169	3.07	0.29	87	3.3	3.8	2.2	0.03	0.9	1.0	2.5	2.2	1.5	2.1	0.03	-

Notes: Blue text indicates less than detection limits. Red text indicates outliers.

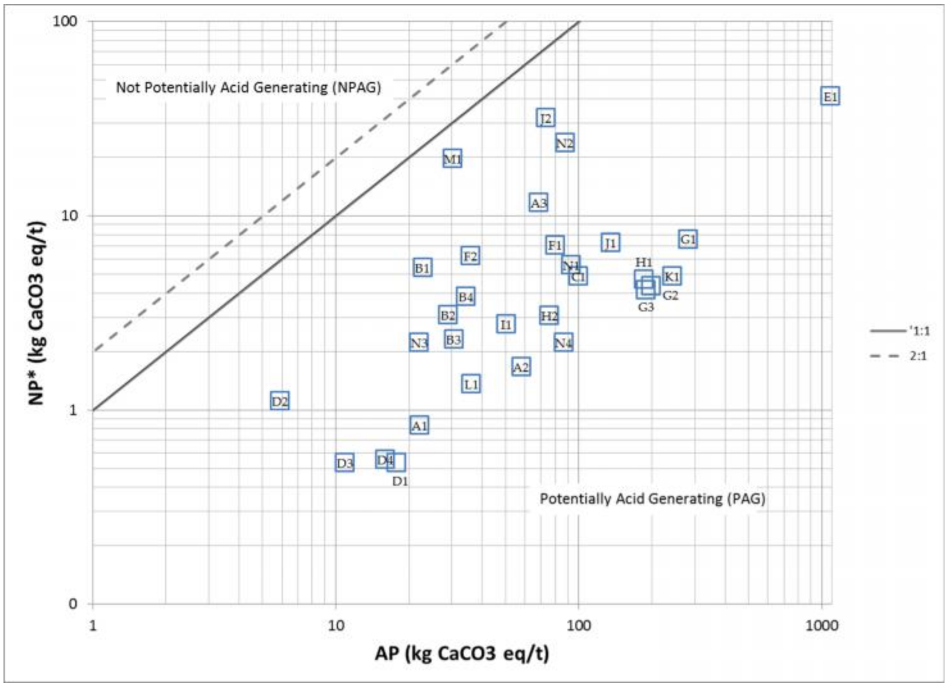


Figure 2 NP versus AP results for this dataset. Labels indicate the site and test number

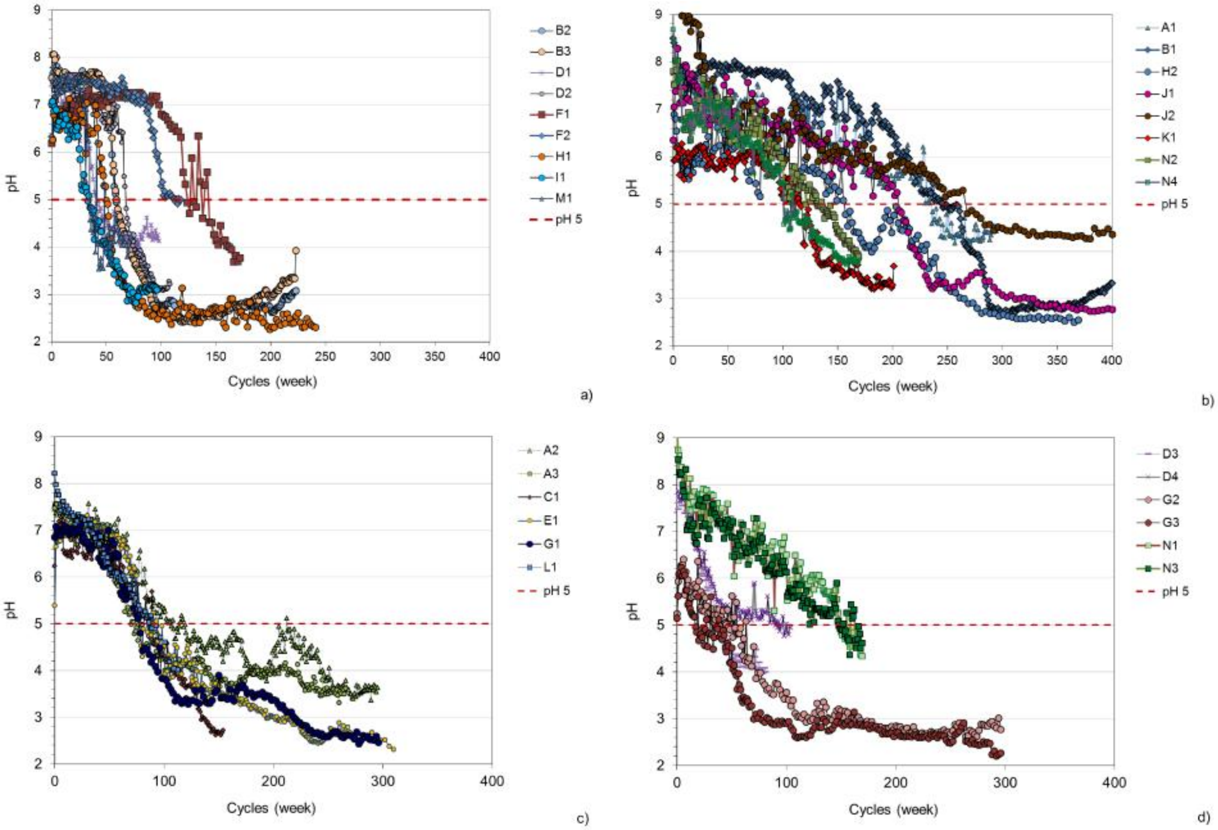
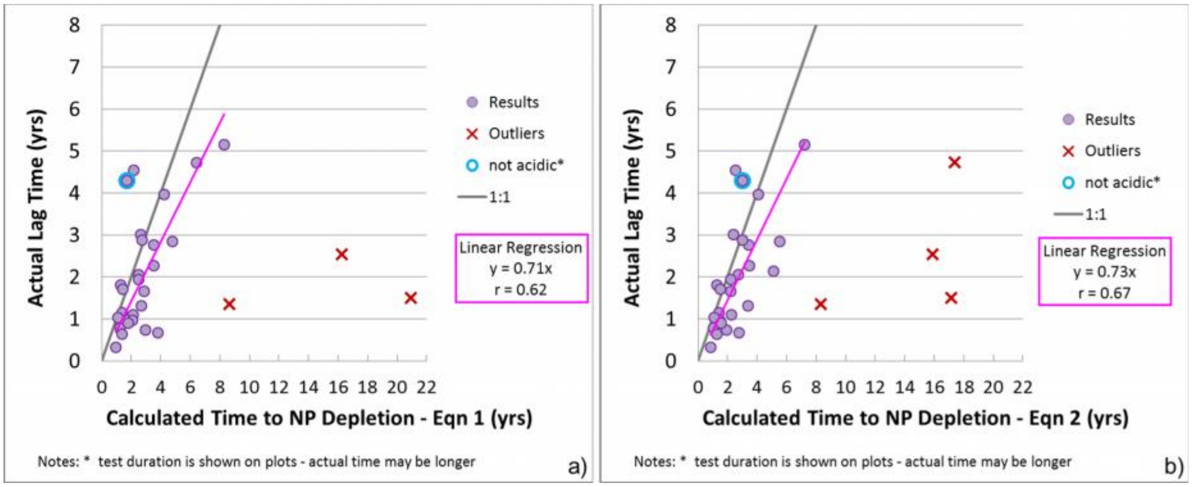


Figure 3 pH profiles from humidity cell tests.



Notes: * test duration is shown on plots - actual time may be longer

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Figure 4 Comparison of actual versus calculated lag times a) using NP release rates (equation 1), b) using SO4 release rates (equation 2).

To assess the potential effects of other variables, the difference between actual and predicted lag times (equation 3) was calculated, and these residuals were plotted against other variables, including the rate of acidification, the difference between NP and TIC, (Ca+Mg)/SO4 release rates, sulphur content and sulphate production rates. The results are summarized as follows:

- The rate of pH change showed the strongest secondary relationship explaining 25% of the remaining variance (r^2 = 0.25) (Figure 5a). Samples that exhibited more gradual (slow) acidification tended to show longer than expected lag times, while samples that exhibited faster acidification tended to show shorter than expected lag times. This may be explained in part by the choice of pH used to define lag time in this study. If a higher pH threshold had been selected, actual lag times would be much shorter in the samples with slow pH changes, and essentially unchanged for the samples with more rapid pH changes.
- Samples with large differences between NP and TIC also tended to show longer than expected lag times (Figure 5b). However, this is based on only two samples with large differences between NP and TIC, and may not be statistically significant. In these samples, the TIC may have been contributing some buffering capacity not accounted for by the NP titration, or the discrepancy could indicate that the NP was underestimated.
- There was essentially no relationship between the residuals and ratios of (Ca+Mg)/SO4, total sulphur content or sulphate production rates.

A more qualitative approach was used to evaluate potential relationships with mineralogy, specifically the presence of calcium magnesium carbonates, iron carbonates, and calcium magnesium silicate minerals. Samples with relatively low carbonate, but with favorable silicate minerals tended to have longer than expected lag times, and samples with iron carbonates tended to have longer than expected lag times. However there were several exceptions and no clear patterns were evident. We also note that samples with shorter than expected lag times had NP measurements that were inconsistent with mineralogy or TIC, suggesting that the differences could have been due to analytical variability. Given that this dataset tended to have such low NP, it is not surprising that variability in lab measurement could be an important factor.

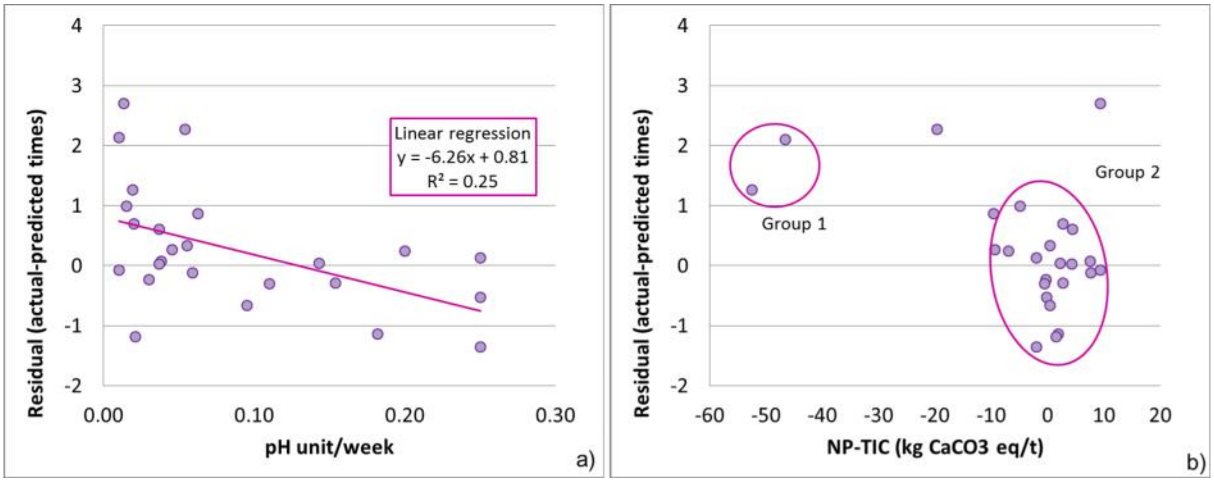

Figure 5 Relationships between residuals and a) rate of pH change and b) NP minus TIC

Outliers

Both calculation methods resulted in a small number of samples with calculated lag times that were substantially longer than the lag times actually observed in those tests. The calculated lag times based on equation 1 produced three outliers, while the calculated lag times based on equation 2 produced four outliers. The outliers were all from different sites. The outliers were closely examined to determine whether there were any unique features that could explain the large discrepancies between calculated and actual lag times, however, none were identified. Although it is believed that these differences could be due to inaccuracies in the quantification of available NP, they do suggest that calculations of lag time can lead to erroneous results. This finding emphasizes the importance of considering a range of samples in the determination of lag time, conducting quantitative mineralogy to provide independent verification of chemical determinations and having thorough QA measures in place to validate analytical results through duplicates and re-checks.

CONCLUSIONS

Data were compiled from a number of long term humidity cell tests to explore the relationship between actual versus calculated lag times. These number of tests in which lag time can be measured is rare and represents a relatively small portion of the total number of tests that were reviewed (30 out of 229 tests). The vast majority of samples that showed a distinct lag time prior to onset of acidic conditions had very low NP and relatively high sulphide concentrations. Key findings of this study are as follows:

- Calculated lag times were typically longer than actual lag times, but were significantly correlated (r = 0.67).
- Estimates of lag time can be improved by selecting the most appropriate NP (usually the lesser of TIC or NP), and by applying correction factors to account for availability/reactivity. These may be further improved by considering limitations on the physical availability.

- Tests with the longer than expected lag times showed a relatively gradual change in pH.
- The results emphasize the value of running some tests for an extended period of time either to determine actual lag times or to demonstrate that there is a prolonged period of neutral pH conditions in cases where the lag times are expected to last for an impractically long time.

It is emphasized that these conclusions may not be appropriate for samples with higher NP and/or lower sulphide content. However, there is insufficient data on lag times for those types of samples due to the long times required to measure onset of acidic conditions. Estimation of lag times in the field present further challenges and should be verified through appropriate monitoring programs.

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NOMENCLATURE

AP	acid potential
ARD	acid rock drainage
NP	neutralization potential
NP*	available neutralization potential
TIC	total inorganic carbon (a measure of carbonate content)

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