

OBSERVED PREFERENTIAL DEPLETION OF NEUTRALIZATION POTENTIAL OVER SULFIDE MINERALS IN KINETIC TESTS: SITE-SPECIFIC CRITERIA FOR SAFE NP/AP RATIOS¹

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Abstract: As the number of completed kinetic tests grows, an international database is forming on rates of acid generation, acid neutralization, and metal leaching. As the results become available and are compiled, valuable lessons are learned on the prediction of acidic drainage and on the variability of reaction rates caused by site-specific factors.

One of the more important lessons from the kinetic-test database pertains to acid-base accounting (ABA). A great deal of effort is expended on the development of universal ABA criteria to predict if a sample may eventually become net acidic. Based on the amount of carbonate or feldspar minerals (Neutralization Potential or NP) and sulfide minerals (Acid Potential or AP), the criteria are usually expressed as some form of Net Neutralization Potential (=NP-AP) or NP/AP ratio. Widely reported criteria for NP/AP state that a value above 2.5 to 3.0 can be considered non-net-acid-generating through time, but there is still some argument on the appropriate values. The Canadian database shows that one site required NP/AP > 4.0 for the prediction of consistently neutral pH after 40 weeks of testing.

This paper presents some of the information in the Canadian database. In particular, the rates of NP and AP depletion are presented for several kinetic tests, showing that the amount of NP often has to exceed AP by a factor of 1.3 to 4.0 for the predicted maintenance of near-neutral pH into the distant future. This is in partial agreement with theoretical relationships that show the factor should often be between 1.0 and 2.0 for carbonate-based neutralization. In effect, the kinetic database shows that attempts to identify universal ABA criteria can be either too cautious or faulty for a particular minesite. Instead, appropriate ABA criteria should be determined on a site-specific basis, reflecting reaction rates of the acid-generating and acid-neutralizing minerals at the particular site.

Additional Keywords: acidic drainage, geochemical predictions, kinetic tests, acid-base accounting

Background and Objectives

From a geochemical perspective, acidic drainage can be viewed as the result of competition between acid-generating and acid-neutralizing minerals, with the dominant mineral(s) regulating the chemistry of water passing over the material. A problem arises from the recognition that the dominant mineral at one point in time may not be the dominant one at a later time. These issues can be summarized in the pointed question: Will the sample generate net acidity *at any point* in time? The answer to this question carries major implications for mine planning, operation, closure, and bonding.

A person unfamiliar with acid-drainage prediction, but aware of acid-drainage impacts, would likely be surprised to discover that current techniques do not typically yield predictions with which mining companies and regulatory agencies are comfortable. This is understandable in light of past technical failures in prediction and

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control and because of the philosophical issues surrounding human limitations. Focusing on technical matters, past failures in prediction can be traced to two basic problems: insufficient data and incorrect interpretation.

Insufficient data is not an acceptable excuse for erroneous predictions, as additional effort would eliminate the problem. Incorrect interpretation of the data, on the other hand, is more complicated and, for this paper, we are concerned with general misinterpretation rather than individual weakness. Furthermore, we limit our discussion here to the common predictive tools for acidic drainage often labelled "static" and "kinetic" tests. Other highly specialized, research-level tools are available, but they are not as widely used and accepted as the aforementioned tests.

Predictions of acid drainage are commonly based on suites of static and kinetic tests. Static tests typically comprise bulk analyses of minerals, metals, and nonmetals that characterize a sample at one point in time. Such tests include the popular acid-base accounting (ABA), for which there are several variations (e.g., Coastech Research 1989). By their nature, static tests cannot reliably yield long-term trends in chemistry.

Kinetic tests consist of repetitive cycles of leaching and monitoring either under laboratory conditions or in the field. The trends through time in aqueous concentrations issuing from the tests yield long-term production rates of metals, nonmetals, and titration-based parameters such as acidity, which static tests cannot provide. However, kinetic tests alone often do not indicate how long the long-term production rates can be maintained, unless the tests are run for years or decades. More often, static tests on the sample provide the total mass and balances of acid-generating and acid-neutralizing minerals that are being consumed in the kinetic test. Consequently, static and kinetic tests form a codependent suite of predictive testwork, and each test must be conducted for proper interpretation of all tests. This opposes earlier views that kinetic tests were only "confirmatory" in nature and were only necessary if static tests suggested a potential problem (e.g., B.C. AMD Task Force et al. 1989).

The idea that kinetic tests are only needed if static tests like ABA suggest a problem assumes that static tests can accurately "suggest a problem". The literature abounds with efforts to improve, refine, and properly interpret ABA results (e.g., Coastech Research 1989; Morin 1990; Lapakko and Lawrence 1993). In particular, the focus of many papers has been the proper criteria for identifying acid-drainage potential through the Acid Potential (AP or similar parameter) and Neutralization Potential (NP or similar parameter). The net potential for acid drainage is often expressed through subtraction (Net Neutralization Potential = NP - AP) or through division (NP/AP). Various criteria that have appeared include: (1) any sample with an NNP value less than -20 ppt CaCO₃ will be net acid generating at some point in time, (2) any sample with NP/AP less than 1.0 will be net acid generating, and (3) any sample with NP/AP greater than 1.0 and less than 2.5 is "uncertain" in its potential and requires further (kinetic) testwork. We find these criteria particularly interesting because our unpublished work has provided samples with negative values of NNP that are not expected to generate net acidity at any time, as well as samples with NP/AP > 4.0 that are expected to generate net acidity within several years.

The worldwide search for universal ABA criteria is useful, but an "uncertain" range seems to develop from any large compilation of ABA data. This actually means that "uncertain" samples at some mines will produce acidic drainage, whereas similarly classified samples at other mines will not. Careful examination of the preceding sentence reveals that the sample's potential is not "uncertain" at all; it is simply site-dependent. In other words, each site has its own ABA criteria for estimating acid-drainage potential, and it is only the search for universal criteria that creates the uncertain status.

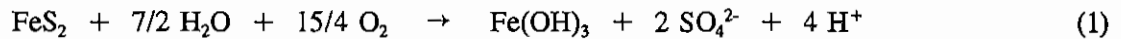
The first objective of this paper is to show how kinetic tests empirically provide the critical or "safe" NP/AP ratio above which there is no predicted potential for acidic drainage at any point in time. This is obtained by comparing the consumption rate of NP to the oxidation of sulfide. For example, if NP is consumed 2.3 times faster than sulfide oxidizes, then samples with reactive, available NP and AP at ratios above 2.3 would be predicted not to generate acidic drainage at any time. The second objective of this paper is to provide examples of "safe" NP/AP ratios at particular minesites that lie within the "uncertain" range in any universal ABA criteria. We conclude with

the recommendation that static and kinetic tests should always be conducted as one suite so that the results of all testwork can be interpreted more accurately .

Theory

Since the focus of this paper is on the relative reaction rates of acid-generating and acid-neutralizing minerals, the relevant theory addresses the geochemical reactions of the minerals and the manner in which one mineral can affect another. In this paper, the acid-generating minerals are limited to pyrite (FeS_2), and the acid-neutralizing minerals are limited to calcite (CaCO_3) and a suite of feldspar minerals. The conclusions reached for these minerals may not necessarily apply to other minerals and the appropriate reactions for other minerals should be checked independently. Furthermore, site-specific environmental conditions can sometimes invalidate the following conclusions as illustrated below.

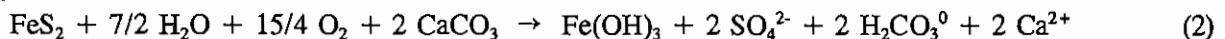
The "standard" reaction for pyrite oxidation is:



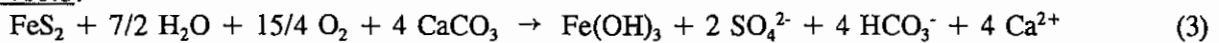
Equation 1 assumes much about mineralogy, reaction pathways, and local environmental conditions. These assumptions include: (1) all sulfur occurs in the solid phase only as S_2^{2-} , (2) S_2^{2-} oxidizes completely to sulfate, (3) pyrite is the only oxidizing sulfide mineral, (4) molecular oxygen and water are the only oxidants, (5) all iron oxidizes to the ferric (Fe^{3+}) state, and (6) all iron precipitates as $\text{Fe}(\text{OH})_3$. Obviously, these assumptions on mineralogy, reaction pathways, and environmental conditions are not always met, and thus alternative equations would apply (Morin 1990; Morin 1993). For simplicity, this paper assumes equation 1 is applicable to a site.

Where calcite is present and reactive, the overall oxidation-neutralization reaction depends on pH (Ferguson and Morin 1991). Two simplified neutralization reactions with calcite, assuming no calcium and sulfate are lost to secondary mineral precipitation, are:

for $\text{pH} < 6.3$:



for $6.3 < \text{pH} < 10.3$:

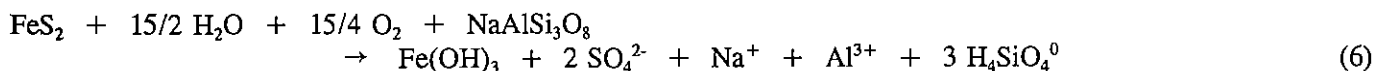
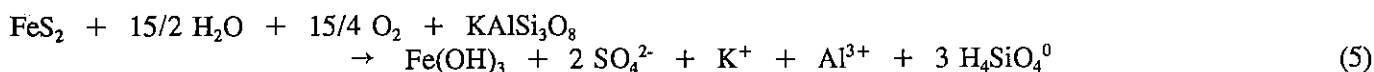
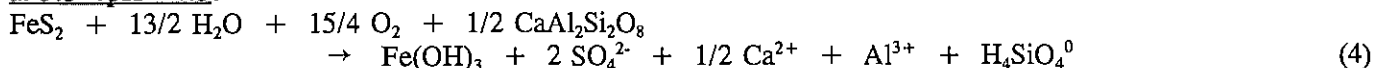


Equations 2 and 3 show that twice as much calcite is needed to neutralize the pyrite-derived acidity to neutral levels than to slightly acidic levels. Additionally, the resulting aqueous ratio of calcium to sulfate is 1:1 at acidic levels and 2:1 at neutral levels. Again, equations 2 and 3 are simplifications of mineral-water reactions; potentially important factors such as aqueous complexation and chemical activity are ignored and other complications are discussed below.

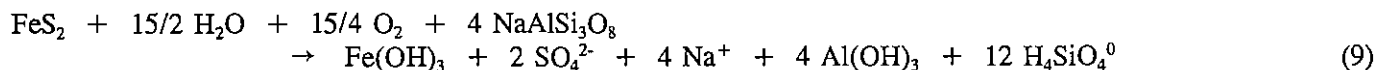
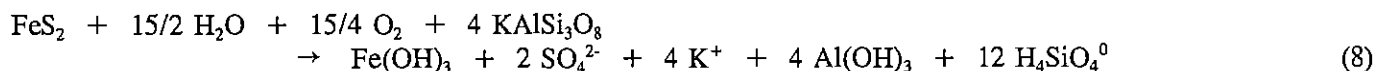
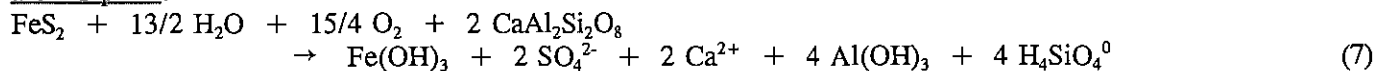
If carbonate is absent or non-reactive, slower-reacting feldspar and accompanying mafic minerals can provide some neutralization of acidity (Lapakko 1988; Lapakko and Antonson 1993; Moss and Edmunds 1992). However, the stoichiometry of these neutralization reactions can be complex and site-specific (Melchoir and Bassett 1990; Stumm 1990) and the understanding of the mineral-dissolution mechanisms is evolving quickly (Schott 1990). In general, the rates and nature of feldspar neutralization are dependent on several factors (Sverdrup and Warfvinge 1993) and complete neutralization may only be possible where mineral-surface areas are high, feldspar minerals comprise a significant percentage of the overall mineralogy, and the rate of acid generation is relatively low. Such a case is discussed below as Mine "E". In many cases, though, only partial neutralization can be expected from feldspar and accompanying mafic minerals.

Due to the complexity of feldspar dissolution, only simplified examples will be discussed here. For these examples, (1) all sulfur in pyrite oxidizes fully to sulfate, (2) iron from pyrite oxidizes and precipitates as Fe(OH)₃, (3) the silicon from the feldspar forms aqueous H₄SiO₄⁰ or solid-phase SiO₂, (4) aluminum does not hydrolyze between pH 3.5 and 4.5, but hydrolyzes and precipitates as Al(OH)₃ around pH 7, and (5) the alkali metals do not hydrolyze and do not precipitate between pH 3.5 and 7.0. Consequently, the neutralization reactions for the three most common end-member feldspar minerals are:

at 3.5 < pH < 4.5:



around pH 7:



Based on equations 2 through 9, the ratios of the cation from the neutralizing mineral (calcium, potassium, or sodium) to sulfate range from 1:1 to 2:1 around neutral pH and from 1:1 to 4:1 at acidic pH (table 1). These ratios represent the depletion rate of neutralizing minerals relative to that of the sulfide mineral, which in turn reveals the relative amount of reactive NP to AP needed to ensure the maintenance of pH-neutral conditions into the future.

Table 1. Ratio of cation (Ca, K, Na) to sulfate during selected neutralization reactions¹.

Mineral	~ pH 4	~ pH 7
CALCITE	1.00	2.00
ANORTHITE (Ca feldspar)	0.25	1.00
ALBITE (Na feldspar) . . .	0.50	2.00
K FELDSPARS (various) .	0.50	2.00

¹ See equations 1 through 9

At this point, two complications should be considered. First, if feldspar minerals provide significant neutralization in a sample, their contents should be converted into CaCO₃ equivalent for comparison to ABA values. One mole of calcium feldspar (anorthite) around neutral pH neutralizes two moles of acidity (equation 7) and thus this mineral can be twice as effective per mole as calcite at neutral pH (equation 3). Consequently, NP_{feldspar as CaCO₃} = 2 x Ca-feldspar content on a molar basis, or NP_{feldspar as CaCO₃} = 5.56 x Ca-feldspar content on a weight basis such as tonnes/1000 tonnes (not the same as visual and volume percent). Other conversion factors apply depending on

the mineralogy and environmental conditions (e.g., table 2). Second, there is no reason that the ratios of cation to SO_4 should match exactly those of table 1. For the mineralogy and environmental conditions involved in equations 1 through 9, the actual value of the ratio can lie anywhere within a factor of two for calcite (1.0 to 2.0) and a factor of four (0.25 to 1.00, or 0.50 to 2.00) for the feldspar minerals. Also, additional reactions such as the exsolution of CO_2 gas from the water upon neutralization by calcite can prevent the ratio from reaching 2.0 at $\text{pH} > 6.3$ (Ferguson and Morin 1991), and minerals other than those examined here can produce other ratios. Furthermore, carbonate and feldspar minerals can be dissolved and leached even in the absence of sulfide oxidation by dilute water. The point being brought forward here is that there are definable ratios based on simplified theory, but the actual ratios of cation to SO_4 could be higher or lower than expected. Therefore, it is more appropriate and more reliable to now examine actual ratios obtained from kinetic testwork for some Canadian mines.

Table 2. Conversion of parts-per-thousand weight measurements of a neutralizing mineral to $\text{NP}_{\text{mineral}}$ as CaCO_3 equivalent as tonnes $\text{CaCO}_3/1000$ tonnes of sample¹.

Mineral	~ pH 4	~ pH 7
CALCITE	1.00	0.50
ANORTHITE (Ca feldspar)	11.12	5.56
ALBITE (Na feldspar) . . .	5.56	2.78
K FELDSPARS (various) .	5.24	2.62

¹ See equations 1 through 9.

Examples of Geochemical Ratios of Neutralization

The first example is drawn from the extensive testwork of the Cinola Gold Project in British Columbia (City Resources/Norecol 1988). This testwork included over 200 acid-base accounts, 44 humidity cells, 13 laboratory-scale leach columns, and 4 on-site 30-mt leach pads. Although the mine application is no longer pursued, the British Columbia AMD Task Force and the Canadian MEND Program continued some tests for a total period of 5 years, and a draft report has recently been submitted (Norecol, Dames, and Moore 1993). Geochemical molar ratios were calculated for initial humidity cells that were pH-neutral and had analyses for one or more of calcium, magnesium, manganese, strontium, and barium (fig. 1). These cations are taken as indicators for dissolution of all potential

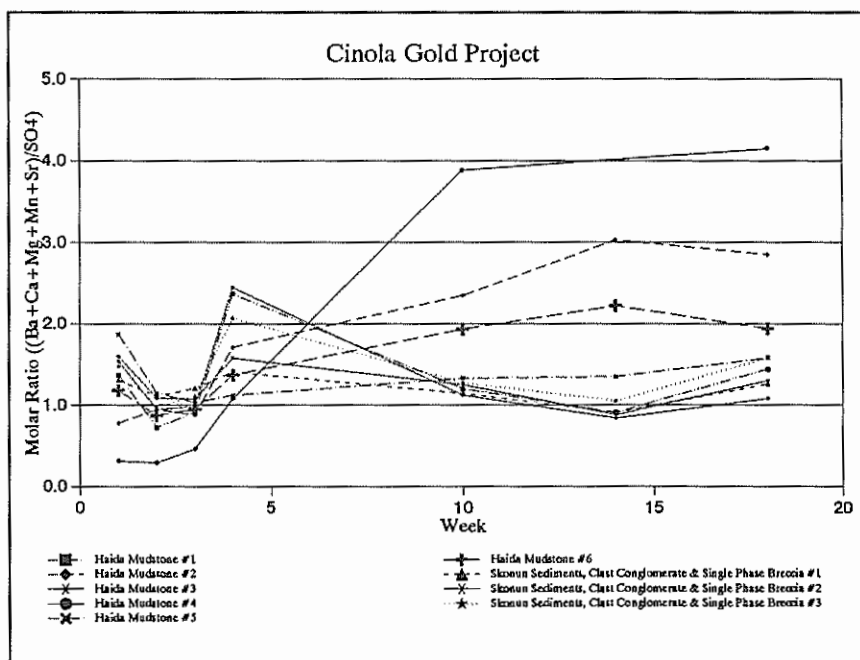


Figure 1. Geochemical ratios versus week for Cinola kinetic tests.

carbonate minerals, although calcium dominated the sum. Pyrite was the dominant sulfide mineral.

After the Cinola humidity cells began stabilizing by Week 5, the geochemical ratios usually exceeded 1.0 for most of the Skonun rock type and 2.0 for three samples of Haida mudstone (fig. 1). The ratios above 1.0 for $\text{Ca}:\text{SO}_4$ suggested neutralization was derived from calcite (table 1), which was consistent with other information that indicated calcium-dominated carbonate minerals were present and available in the rock. Furthermore, in agreement with figure 1, later studies of limestone addition to Skonun sediments showed that NP/AP values close to 1 were not sufficient to maintain pH-neutral conditions over decades, but that a ratio of 2.0 should indefinitely maintain neutral conditions (Norecol, Dames, and Moore 1993). The higher ratios for some Haida mudstone over the Skonun show that the carbonate minerals can be more quickly leached relative to sulfide in this rock type. As a result, a "safe" NP/AP ratio from ABA would be a maximum of 4.2 based on figure 1.

The second example in this paper is taken from a copper mine in Canada in which five humidity cells contained pH-neutral samples of waste rock and tailings with known calcium-based carbonate minerals and pyrite. The geochemical ratios from these cells (fig. 2) showed that there was often an accelerated depletion of neutralizing minerals relative to sulfide oxidation beyond that attributable to sulfide oxidation alone (table 1). Interpretation of results by Week 40 suggested a safe NP/AP ratio for this site was approximately 4.0, and continuation of two cells beyond Week 40 continued to support this value as a maximum. Although the samples were pH-neutral and were expected to remain so for years, their ABA ratios were less than 4.0. Consequently, eventual net acid generation was predicted for them.

The third example is a coal-tailings area with no known occurrences of acidic drainage in the tailings area, but acidic seepage was common in nearby waste piles due to oxidation of pyrite. The geochemical ratios from the one pH-neutral cell remained relatively consistent during the 40-week period, around values of 1.0 to 1.5 (fig. 3). The safe NP/AP ratio for this sample in the long term is 1.4. This relatively

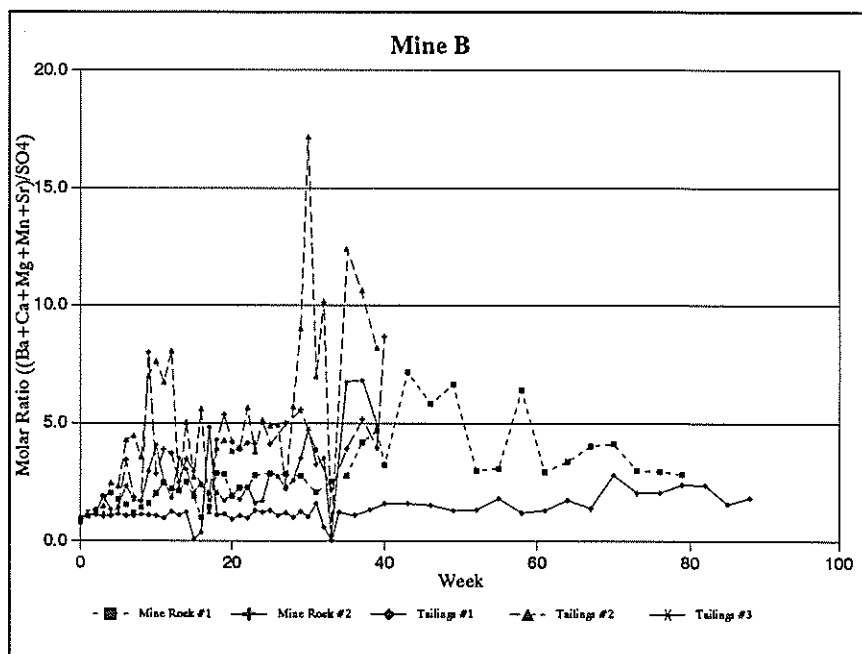


Figure 2. Geochemical ratios versus Week for kinetic tests at Mine B.

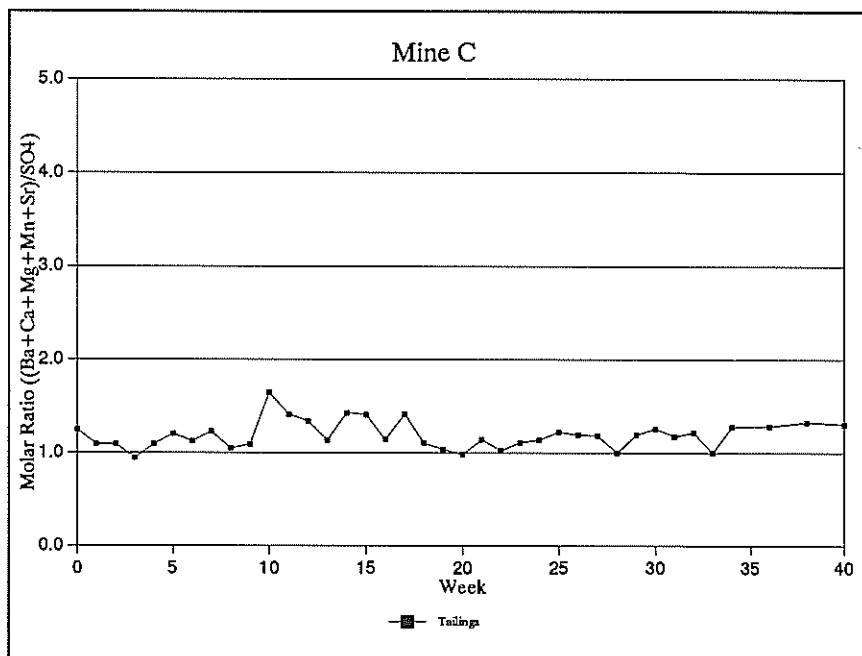


Figure 3. Geochemical ratio versus Week for the kinetic test from Mine C.

low value is attributed to the loss of CO₂ gas during neutralization within the cell (Ferguson and Morin 1991), but the safe value may have to be raised to 2.0 or more if CO₂ is not similarly lost under field conditions.

The fourth example in this paper is drawn from a Canadian copper mine with no known occurrences of acidic drainage, although elevated sulfate values in mine drainage point to active oxidation of the pyrite. Geochemical ratios from the four pH-neutral rock types placed in humidity cells were less than 3.0 after the cells began stabilizing by Week 10 (fig. 4). After 40 weeks, the ratios indicated each rock type could be assigned its own safe value, but the overall value for the minesite could be set at 2.3 at Week 40.

The fifth and last example is taken from a Canadian mine with little to no carbonate minerals in the rock and tailings. This mine has been closed for over a decade and no acidic drainage has appeared despite the general lack of carbonate minerals since closure. There is one dominant rock type and this rock and its tailings contain 50% feldspar, 1%S as pyrite, and most of the remainder is quartz with minor magnetite and hornblende. Two geochemical ratios were calculated from the humidity-cell results: a carbonate ratio including calcium and magnesium and a feldspar ratio including calcium, potassium, and sodium (fig. 5). Because calcium was the dominant cation, both ratios are similar. Although there were apparently some occasional errors in analyses of the cations and/or anions, the ratios often centered around 1.0, which is the theoretical value for dissolution of calcium feldspar under pH-neutral conditions (table 1). However, due to erratic values towards the end of the testwork, a conservative safe NP/AP ratio would be 1.5. This, however, is not an important issue since the conversion of the 50% feldspar to an NP value (table 2) far exceeds the potential acidity from 1%S sulfide.

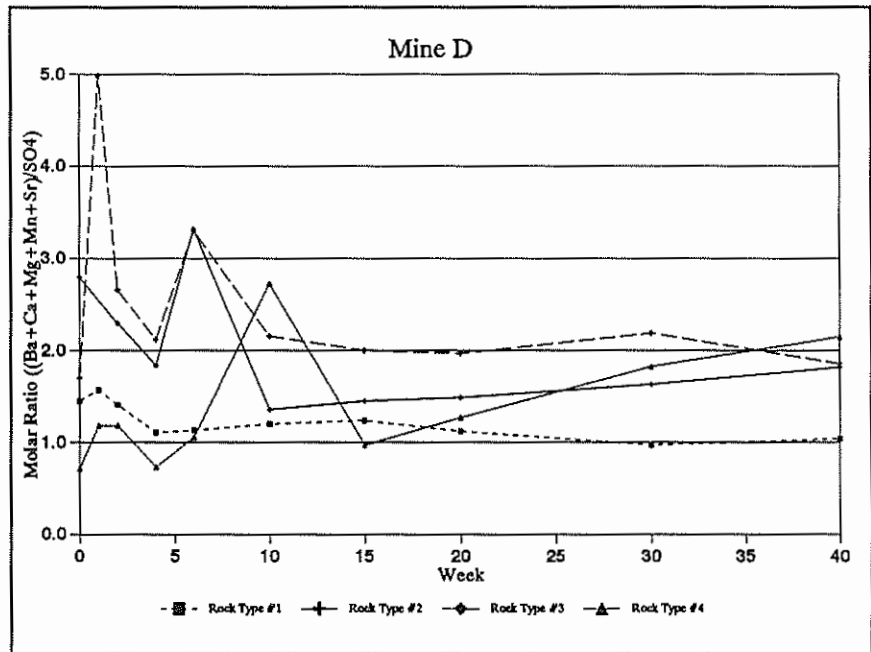


Figure 4. Geochemical ratios versus Week for kinetic tests at Mine D.

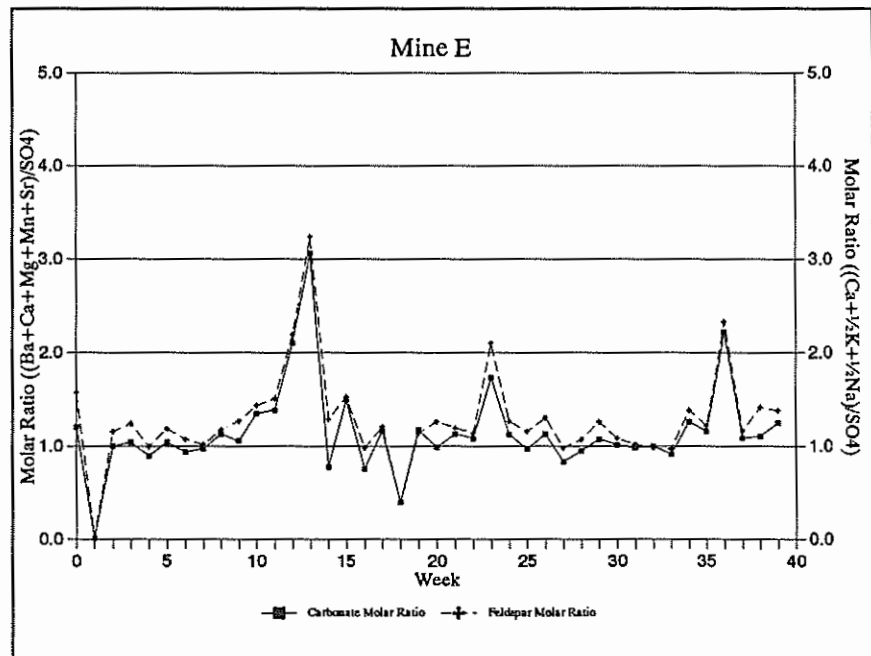


Figure 5. Geochemical ratios versus Week for the kinetic test from Mine E.

Conclusion

This paper has examined the simplified dissolution reactions of carbonate and feldspar minerals through theory and through examples from common predictive testwork known as "kinetic" tests. When the dissolution of carbonate or feldspar is driven by pyrite oxidation, the aqueous ratios of the cations to sulfate can occur within theoretically definable ranges. The occurrence of a value within or beyond a theoretical range can sometimes reveal an important aspect of the mineralogy or environmental conditions within the test chamber. When the mineralogy and environmental conditions are known, the ratio identifies the relative rate at which neutralizing minerals are consumed relative to the acid-generating minerals, which leads two important conclusions. First, in association with the results of static tests which define the total amounts of all relevant minerals, the eventual "winner" in the geochemical competition between acid-generating and acid-neutralizing minerals can be predicted, and the times to complete consumption can be calculated. Second, the long-term ratio from the testwork indicates the "safe" NP/AP ratio needed from ABA to declare a specific sample to be net acid-generating or acid-consuming indefinitely. Such an assessment should ensure that environmental conditions in the test chamber, like the exsolution of CO₂ gas, resemble those in the field.

Based on these observations, static and kinetic tests should be performed as one suite of testwork because each relies on information from the other for proper interpretation. Additionally, the search for universal criteria in this situation, where site-specific factors dominate, can lead to the delineation of an "uncertain" range that will grow as the worldwide database grows. However, the "uncertainty" is simply the result of the search for universal criteria in the first place, and gives the false impression that predictive tests for acidic drainage are not dependable or appropriate.

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'Ua mau ke ea o ka 'āina i ka aloha 'āina

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