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A Case Study of Important Aluminosilicate Neutralization

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Abstract

At a molybdenum-related site with more than 2 km of underground workings and 60,000 tonnes of waste rock, acid-base accounts say the drainage waters should be acidic. However, several decades of monitoring showed no ARD. We looked more closely at aqueous neutralization and solid-phase Neutralization Potential (NP), particularly the aluminosilicate-based (“silicate”) NP, based on:

- (1) the mathematical conversion of silicate minerals to NP,
- (2) the dissolution-precipitation of minerals to explain the observed water chemistry at the portal and in humidity cells and to estimate silicate neutralization, and
- (3) the dissolution (neutralization) rates of silicate minerals based on specified pH values.

Mathematical Conversion of Silicate Minerals to Neutralization Potentials

Silicate NP values were calculated from bulk solid-phase levels of aluminosilicate minerals in the five humidity-cell samples. All except the already acidic metasedimentary Cell 1 sample would be net acid neutralizing, as long as a substantial portion of this calculated silicate NP successfully neutralized pH to above 6. However, this was not true for the Cell 2, because it became acidic relatively quickly. Thus, most of its silicate NP derived from biotite, magnetite, and epidote could not fully neutralize above pH 6. The remaining three cell samples were either acidic or trending towards acidic pH after Week 130. They also contained minor carbonate, and derived most of their silicate NPs from plagioclase. Their mineralogy-based Sulphide Net Potential Ratios indicated they will not become acidic, if much of their silicate NP could neutralize fully.

Dissolution-Precipitation of Minerals to Estimate Silicate Neutralization

The U.S. Geological Survey SpreadBal-2002 software estimated the amounts of silicate minerals dissolving and precipitating to explain water chemistries seen at the on-site portal and in recent weeks of the five laboratory humidity cells. Epidote, plagioclase, calcite, and biotite were often calculated as major dissolving components to create the observed water chemistries, with substantial precipitation of quartz, ferric oxides, and aluminum oxides also needed to explain the

observed chemistries. Subsequent mathematical conversions showed that silicate neutralization played a major role in the partial (below pH 6) to full (above pH 6) neutralization in the near-neutral humidity cells. This work also showed that calcite was not needed to explain the water chemistry, with atmospheric CO₂ potentially supplying the carbon for alkalinity. However, slightly better agreement was obtained when calcite was included. This indicated calcite could be a secondary mineral accumulating in the samples, rather than a primary mineral solely accounting for neutralization.

Neutralization Rates of Silicate Minerals at Specified pH Levels

Literature-derived, pH-dependent rates of neutralization by various aluminosilicate minerals used the bulk effluent near-neutral pH from humidity cells to provide a calculated sum, or total, rate of neutralization. During extended near-neutral periods in three cells, the calculated neutralization rates were similar to, or substantially less than, the measured neutralization rates. The substantially larger measured rates apparently reflect (1) the additional contribution of calcite and/or (2) the possibility of micro-scale acidic conditions (pH < 6) around the aluminosilicate mineral grains that would cause them to react faster than calculated. However, such a small-scale pH cannot be estimated from available information.

1. Introduction

Although uncommon, standard interpretations of acid-base accounting (ABA) can predict widespread ARD for some minesites when none has been observed for decades (Morin et al., 2001; Eary and Williamson, 2006). This contradiction has particularly been noted at some molybdenum-related sites.

The contradiction can be traced to two factors associated with the surrounding rock, which is usually similar to granodiorite in these cases. First, sulphide minerals at some minesites react relatively slowly, producing acidity at a low rate. Second, slow-neutralizing aluminosilicate minerals, which are not detected in the hours-long Neutralization Potential (NP) test, can successfully neutralize the low acidity rate.

For one site with more than 2 km of underground workings and approximately 60,000 t of waste rock (not included in Morin et al., 2001), we look more closely here at three aspects of that rock's capacity to neutralize acidity:

- 1) The amount of NP represented by the bulk amounts of aluminosilicate minerals initially in the rock, which cannot be detected in the standard, short, hours-long acid bath (see Section 2). In this study, this is called "silicate NP", and will provide another estimate of NP for this site.
- 2) The amounts of aluminosilicate minerals and carbonate minerals that must dissolve or precipitate to explain the water chemistry from the humidity cells and from the underground drainage (Section 3).
- 3) The kinetic rates at which the aluminosilicate minerals reportedly dissolve and neutralize aqueous acidity and pH (Section 4), labelled "rate of silicate neutralization" in this study.

Ideally, the silicate information should come from site-specific testwork. For this site, the testwork included expanded acid-base accounts, total-element contents, mineralogy including the types and amounts of silicate minerals, and long-term kinetic tests for bulk reaction rates including small-scale laboratory tests and large-scale monitoring of the existing minesite components.

2. Calculation of Silicate, Slow-Reacting, and Effective Neutralization Potential

As one type of acid-base accounting (ABA), a small amount of pulverized sample is placed in an acid bath and heated until the reaction (visible bubbling, usually created by fast-reacting carbonate minerals) ceases. A subsequent titration with hydroxide then shows how much of the original acid had been neutralized by minerals in the sample. This is known as bulk or "Sobek" Neutralization Potential (NP; Sobek et al., 1978). It can also be considered fast-reacting "short-term NP", often representing calcium-magnesium-bearing carbonate minerals.

It is important to note that fast-reacting carbonate minerals can still be found in rock types like granodiorite, despite the abundance of aluminosilicate minerals. White et al. (2005) frequently

identified calcite in granitoid rocks around the world, at levels of 0.028 to 18.8 kg/tonne, with a mean of 2.52 kg/t. Jambor et al. (2006) also detected carbonate minerals in rocks ranging from granitic to ultramafic. This may reflect the sequestration of carbon dioxide by silicate minerals, and may explain why smaller-scale tests become acidic while larger-scale tests do not.

Bulk NP often represents the actual amount of neutralization to a pH greater than 6.0, which is important for in situ control of ARD. However, theoretical cases (Eary and Williamson, 2006) and actual cases (Morin et al., 2001) show measured short-term NP can substantially underestimate total neutralizing capacity (called “Effective NP” here to distinguish it from measured NP). This is due to the presence of aluminosilicate minerals that can neutralize water to pH above 6.0 under certain conditions.

Morin and Hutt (1997 and 2001) provided the following equation for Effective NP:
Effective NP = measured (short-term, Sobek) NP + Slow-Reacting NP (SRNP) - Unavailable NP

This equation recognized that additional NP (SRNP) is not detected by the NP procedure, and that some measured NP (UNP) is “unavailable” for neutralization. SRNP in rock is the focus of this case study, with SRNP assumed to be the same as silicate NP. UNP, often around 5-15 kg/t, has been discussed elsewhere (Morin and Hutt, 1997, 2001, 2008a, and 2008b).

Because the additional silicate NP (SRNP) provided by aluminosilicate minerals cannot be detected using standard ABA procedures, the NP represented by these minerals can be calculated. This is not a simple task, because several assumptions must be made about the minerals and about the water into which they are dissolving (Morin and Hutt, 2006). Nevertheless, a general estimate of silicate NP and SRNP can be obtained by setting the final neutralized pH to near-neutral values (around 7-8) so that, simplistically, all iron precipitates as $\text{Fe}(\text{OH})_3$, all aluminum precipitates as $\text{Al}(\text{OH})_3$, and all silicon forms aqueous H_4SiO_4^0 .

Detailed mineralogy of rock in this study is available from five samples tested in humidity cells (Table 1, and Figures 1 to 3) and from hundreds of related historical thin sections. The five humidity-cell samples contained mixtures of minerals that can partially or fully neutralize acidity. These included:

- carbonates mostly as calcite (calcium carbonate) detected at levels below 1% in the three cell samples that were near neutral for an extended period of testing (Cells 3, 4, and 5),
- plagioclase containing more sodium than calcium in the granodiorite,
- potassium feldspar (K-feldspar),
- muscovite (mostly in metasedimentary Cell 1 and lesser amounts in the granodiorite) and biotite (mostly in the volcanics), which in their ideal forms release potassium,
- biotite (mostly in the volcanics) and chlorite and clinocllore (both at low levels in four cell samples), which in their ideal form release magnesium, and
- clinozoisite and epidote (seen visually in both volcanics cell samples and one granodiorite cell sample), which in their ideal forms release calcium.

Table 1. Summary of mineralogy for the five humidity-cell samples

Sample	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5	
<u>Rock Unit</u>	<u>Metasedimentary</u>		<u>Volcanics (High NP)</u>		<u>Volcanics (Low NP)</u>		<u>Granodiorite (High NP)</u>		<u>Granodiorite (Low NP)</u>	
Analytical Method ¹	P	X	P	X	P	X	P	X	P	X
Quartz	50	37.8	25	24.3	35	37.6	45	49.3	40	40.8
Illite-sericite	40									
Muscovite-sericite		42.6					3	2.8	2	
K-feldspar	trace	1.3	5	4.6	40	13.6	40	8.4	40	18.4
Plagioclase		11.1		38.0		41.8	2	34.4	3	36.3
Biotite	trace-1%		35	15.3	10	3.5	trace-1%		3	1.3
Clinozoisite-epidote			10		1				2	
Magnetite			10	7.2	2	0.8	trace		1	0.4
Pyrite			3	2.1	2	0.6	1	0.7	trace-1%	0.3
Pyrrhotite	4	2.1	1	2.3	trace-1%	1.0	1	1.3	trace	
Chalcopyrite			2	0.2	trace	0.1	trace		trace	
Molybdenite					trace-1%	0.1	trace-1%	<0.1	trace	0.1
Powellite								0.2		
Carbonate					trace-1%		2		2	
Calcite								0.9		0.7
Siderite?				0.4						

Sample	Cell 1		Cell 2		Cell 3		Cell 4		Cell 5	
<u>Rock Unit</u>	<u>Metasedimentary</u>		<u>Volcanics (High NP)</u>		<u>Volcanics (Low NP)</u>		<u>Granodiorite (High NP)</u>		<u>Granodiorite (Low NP)</u>	
Fe-oxides							trace			
Rutile	3		4		1		trace		1	
Actinolite			2	5.5						
Clinocllore		3.1				1.0		2.0		1.7
Chlorite			1		1		trace-1%		2	
Andalusite		2.1								
Gypsum?	1									
Covellite			trace							
Clay	trace-1%									
Bornite?			trace		trace					

¹ Analytical methods: P = petrographics (visual) results in volume-%; X = Rietveld x-ray powder diffraction in wt-%.

Based on more than three years of humidity-cell testing (Figures 1 to 3), aqueous calcium concentrations dominated over those of magnesium, sodium, and potassium in most humidity cells, and in drainage from the full-scale underground portal. The major exception was acidic Cell 2, with elevated potassium. Thus, calcite, plagioclase, and clinozoisite-epidote appear to be the most important minerals. However, ion exchange and secondary-mineral precipitation (like smectites) can remove potassium, sodium, and/or magnesium from solution and thus mask their contributions to neutralization.

For the five humidity-cell samples (Table 1), petrographic-based values were considered more representative for most minerals, and any minerals at levels considered “trace” were ignored (Table 1). Also,

- all illite, sericite, and muscovite were combined as muscovite;
- gypsum, actinolite, and rutile were ignored as sources of neutralization;
- all sulphides were combined as pyrite although they might not all be acid generating;
- due to the significant discrepancies between petrographics and XRD for K-feldspar and plagioclase, the XRD proportions of K-feldspar and plagioclase that appear more reasonable for a granodiorite were applied to the petrographics values (e.g., for Cell 2, its petrographics-based 5% K-feldspar was adjusted to 0.5% K-feldspar and 4.5% plagioclase);
- plagioclase was assigned an Anorthite ratio of An20 (20% calcium and 80% sodium), which has slightly less neutralizing capacity than the rough average of An30 reported in the historical thin sections for this site, and
- weight-percent was assumed equal to volume-percent, which may underestimate sulphide levels but is offset by assuming all sulphides were acid-generating pyrite.

This resulted in mineralogy-based NP values of 54 to 230 kg CaCO₃ equivalent/tonne based on mineralogy (Table 2), compared to measured Sobek NP values of 5-15 kg/t. Silicate NP, rather than carbonate NP, represented most to all of the summed mineralogy-based NP values. The two cell samples with the highest and lowest NPs were acidic in early weeks, so their mineralogy-based NPs derived mostly from muscovite and biotite were not applicable. The remaining three cells, becoming acidic much later, drew most of their mineralogy-based NP from plagioclase.

For the Cell 1 metasedimentary sample, its 40% illite-sericite (considered as muscovite) provided most of the silicate NP of 54 kg/t, with biotite supplying the remainder. This failed to raise its SNPR values above 1.0 and thus it was still considered net acid generating. More important, it became acidic quickly (Figure 1), so the silicate minerals provided virtually no NP to maintain near-neutral conditions.

For the high-NP volcanics sample (Cell 2), roughly half its silicate NP of 230 kg/t was derived from biotite, with most of the remainder from epidote and magnetite. This raised its mineralogy-based SNPR above 2.0. Thus, it would be net acid neutralizing using standard SNPR criteria, but it became acidic relatively quickly during testing (Figure 1), so its actual effective NP was very low. Nevertheless, unlike the other cells, weekly effluents show that potassium has been dominant (Figure 3), with calcium not far less on a mg/L basis. The elevated potassium would be consistent with dissolution of biotite and K-feldspar, but much lower magnesium would rule out biotite as the primary source of potassium. This is discussed further in Section 3 of this case study.

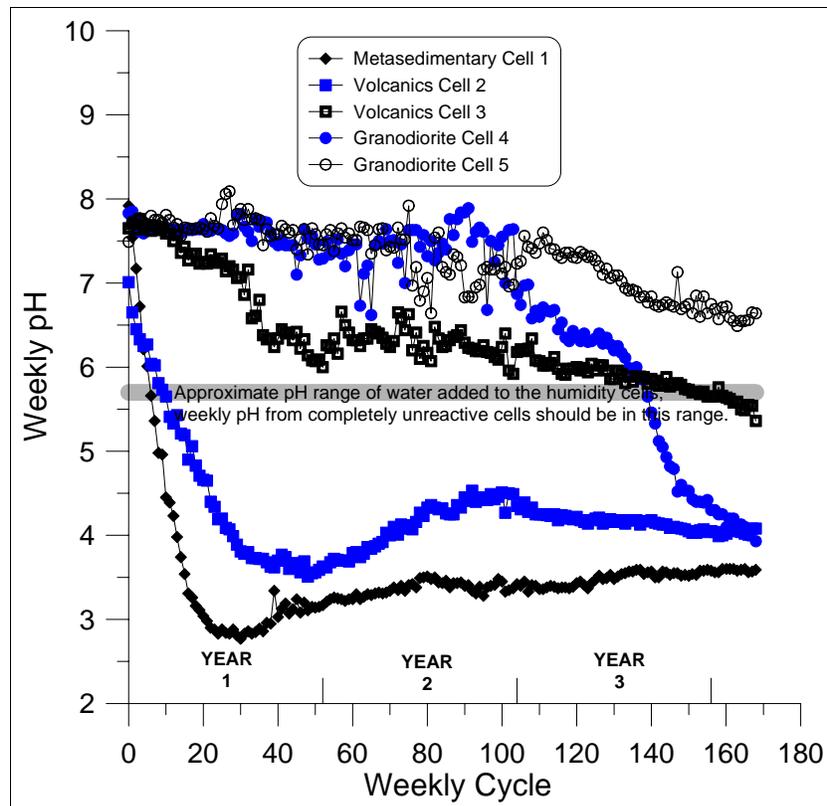


Figure 1. Weekly effluent pH from the five humidity cells.

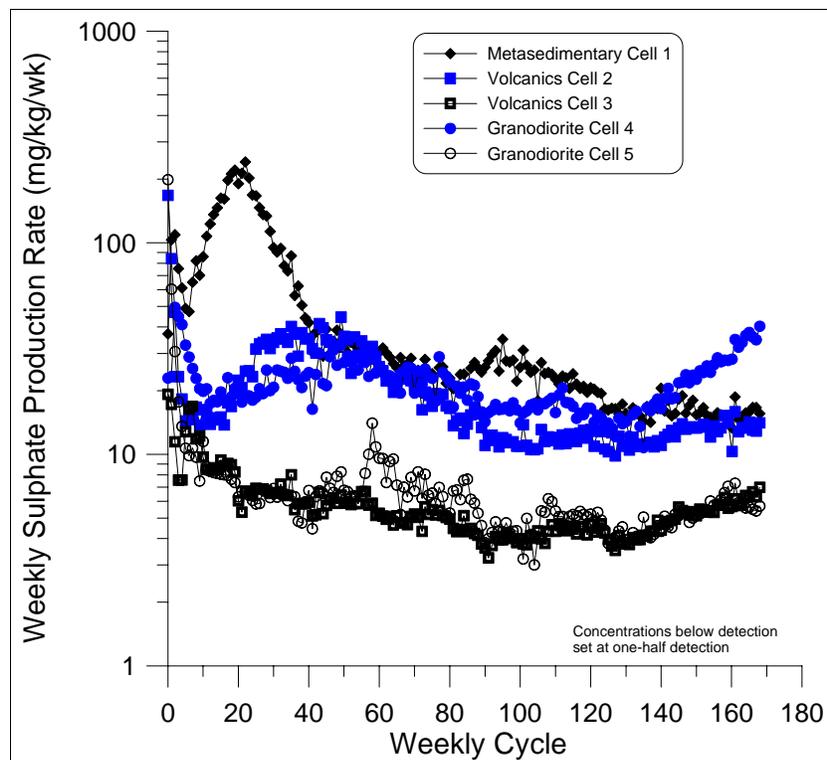


Figure 2. Weekly sulphate-production rate from the five humidity cells.

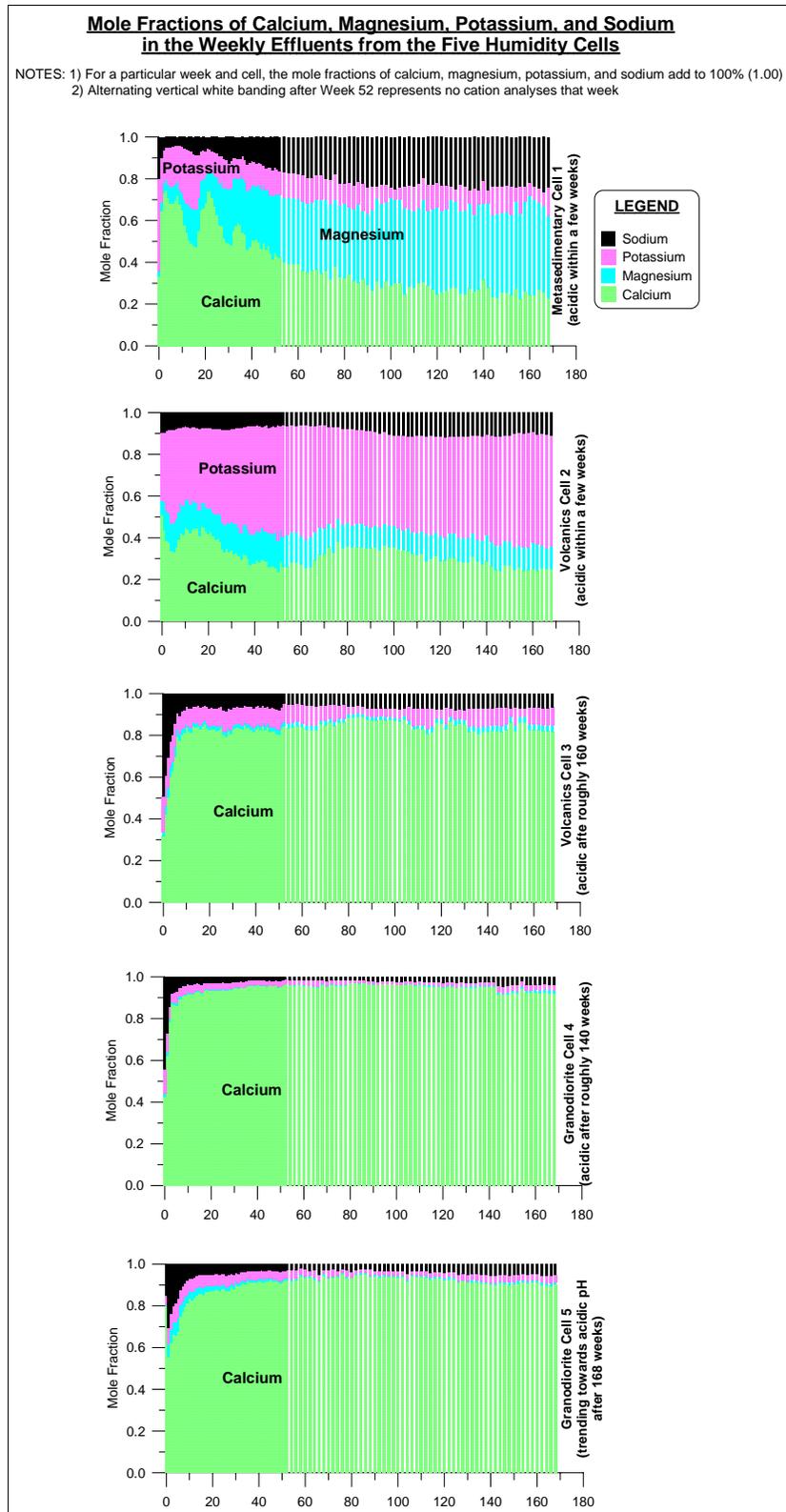


Figure 3. Temporal trends of weekly mole ratios of calcium, magnesium, sodium, and potassium from the five humidity cells.

Table 2. Calculated Neutralization Potentials and Net Potential Ratios based on acid-base accounting and mineralogy for the five humidity-cell samples					
<u>Parameter</u>	Humidity-Cell Sample:				
	Cell 1 <u>Metasedimentary</u> ²	Cell 2 <u>Volcanics</u> ²	Cell 3 <u>Volcanics</u> ³	Cell 4 <u>Grano-diorite</u>	Cell 5 <u>Grano-diorite</u>
<i>ABA-Based Sulphide-Related Parameters</i>					
Sulphide (%S)	0.75	0.63	0.44	0.86	0.23
Sulphide Acid Potential (kg CaCO ₃ equivalent/tonne)	29.2	21.9	15.1	29.5	9.2
<i>ABA-Based Neutralization Potentials (kg CaCO₃ equivalent/tonne)</i>					
Sobek NP	5	15	8	8	8
ABA-based Carbonate NP	<5	<5	<5	9	5
<i>Calculated Mineralogy-Based Neutralization Potentials (kg CaCO₃ equivalent/tonne)¹</i>					
from calcite			5.0	10.0	10.0
from K-feldspar		0.9	18.0	14.4	26.1
from plagioclase (An20)		10.2	67.9	77.0	64.5
from muscovite	50.3			3.8	2.5
from biotite	3.4	118.2	33.8	3.4	10.1
from clinozoisite-epidote		41.9	4.2		8.4
from chlorite		2.4	2.4	2.4	4.8
from magnetite		56.8	11.4		5.7
Total Silicate NP	54	230	138	101	122
Total Mineralogy-Based NP (Silicate NP + Calcite NP)	54	230	143	111	132
<i>Sulphide-Based Net Potential Ratios (NP/SAP, dimensionless)</i>					
ABA-based Sobek SNPR	0.17	0.68	0.53	0.27	0.87
ABA-based Carbonate SNPR	<0.17	<0.68	<0.33	0.31	0.49
Mineralogy-based SNPR	0.80	2.30	2.14	2.22	7.93

Table 2. Calculated Neutralization Potentials and Net Potential Ratios based on acid-base accounting and mineralogy for the five humidity-cell samples

¹ Based on the stoichiometric approach explained in the text and in Morin and Hutt (2006).

² This cell became acidic relatively quickly, so its carbonate-based values seem most appropriate for predicting whether acidic conditions (pH < 6) will arise.

³ This cell had lower Sobek and mineralogy-based NPs. However, it remained near neutral to about Week 160, albeit mostly below pH 7, and the rate of sulphide oxidation was relatively low.

The other, low-NP volcanics sample (Cell 3) had a silicate NP of 138 kg/t, which was derived mostly from plagioclase, biotite, and K-feldspar. When combined with a relatively small contribution from calcite, this yielded a mineralogy-based SNPR of 2.14. Thus, it would be considered net acid neutralizing if all silicate NP were highly reactive, and its dominant calcium concentrations may be derived from dissolution of calcite, plagioclase, and/or clinozoisite-epidote. The lack of high sodium concentrations (Figure 3) suggests plagioclase was not a major contributor, although loss of sodium from solution cannot be ruled out. If plagioclase were ruled out, then the mineralogy-based SNPR would fall to around 0.4 which would be considered net acid generating. Data to Week 168, when the cell was stopped, showed that pH fell below pH 7 typical of carbonate neutralization after approximately 30 weeks. Aqueous pH then remained around 6.0-6.5, apparently reflecting silicate neutralization, until it became more acidic than the added water around Week 160. None of this accurately reflected either carbonate or silicate NP, but some subset.

Based on mineralogy, the two granodiorite samples contain roughly 5-10 kg/t of carbonate-based NP. They also contain 101-122 kg/t of silicate NP, derived mostly from plagioclase and K-feldspar. Thus, Cell 4 would remain net acid neutralizing, if a large portion of its silicate NP (primarily from plagioclase) were fully neutralizing. However, Cell 4 became acidic around pH 4.5 by Week 150 (Figure 1), after roughly 15 weeks around pH 6.0-6.5.

In contrast, granodiorite Cell 5 had less sulphide. Thus, only a small proportion of its silicate NP was needed to remain net neutralizing in the long term, as long as that NP was fully neutralizing. However, by the end of testing around Week 168, weekly rinse water from this cell had fallen to around pH 6.5, similar to temporary pH plateaus seen for Cells 3 and 4.

In summary, silicate NP values were calculated from bulk solid-phase levels of aluminosilicate minerals in the five humidity-cell samples. As a result, all except the acidic metasedimentary Cell 1 sample would be net acid neutralizing, as long as a substantial portion of this silicate NP successfully neutralized pH to above 6. However, this was not true for the high-NP Cell 2 sample, because it was acidic in early weeks. Thus, most of its silicate NP, derived from biotite, magnetite, and epidote, cannot neutralize to above pH 4. The remaining three cell samples became acidic, or trended towards more acidic pH, after Week 130. These samples contained minor carbonate, and derived most of their silicate NPs from plagioclase. Their mineralogy-based Sulphide Net Potential Ratios indicated they would not become acidic if much of their silicate NP neutralized fully, which obviously was not so.

3. Theoretical Neutralization of Aqueous Acidity by Silicate Minerals

Part of the complexity for decoding neutralization at this site is that both fast-neutralizing carbonate minerals and slow-neutralizing silicate minerals are present. For example, aqueous concentrations of calcium represent neutralization by some combination of fast-neutralizing calcite (CaCO_3) and slow-neutralizing minerals like plagioclase. Plagioclase ranges from Albite ($\text{NaAlSi}_3\text{O}_8$) to Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), with Oligoclase ($\text{Ca}_{0.2}\text{Na}_{0.8}\text{Al}_{1.2}\text{Si}_{2.8}\text{O}_8$) generally representing this site's plagioclase.

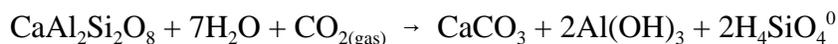
Therefore, the first step is to estimate how much of each mineral is dissolving in order to create the observed aqueous concentrations. A mass-balance spreadsheet, called "SpreadBal-2002" (Bowser and Jones, 2002), was used for this purpose. SpreadBal-2002 is a free download from the U.S. Geological Survey (<http://water.usgs.gov/software/spreadbal/>).

SpreadBal-2002 accepts a water analysis as input, and then calculates quantities of various minerals dissolved or precipitated to create the input water analysis. The input and output units are $\mu\text{moles/kg H}_2\text{O}$ (basically $\mu\text{moles/L H}_2\text{O}$ for this site). The minerals allowed to dissolve and precipitate were chosen from the SpreadBal-2002 database, based on observed mineralogy including a plagioclase Anorthite ratio of 20% (An 20) representing Oligoclase. Because formulas for minerals can vary from site to site, and even from rock unit to rock unit, the results should be taken only as general indicators and not 100% accurate estimates. For example, SpreadBal-2002 contains six varieties of biotite, all with differing stoichiometries, so biotite/chlorite was chosen because chlorite was also often identified in the cell samples (Table 3).

According to SpreadBal-2002, the water draining from the portal at this site on December 5, 2005, was created partly by dissolving silicate minerals, primarily epidote and plagioclase (An 20) (Table 3). This was driven by the calculated dissolution (oxidation) of pyrite.

There are two Spread-Bal simulations for each date in Table 3. The difference is the source of carbon found in the portal drainage for alkalinity. One source is solid-phase calcite, which is known to exist in the rock. Its dissolution neutralizes acidity and yields alkalinity to the water.

The second source is atmospheric CO_2 . This second source is important, because aluminosilicate dissolution can produce calcite at near-neutral pH. Using anorthite for simplicity, this reaction would be:



SpreadBal-2002 calculations show epidote dissolution can actually account for the formation of calcite. In any case, this secondary calcite could then dissolve later to neutralize acidity.

Table 3. Estimates of mineral dissolution/precipitation to explain observed water chemistry at the portal using SpreadBal-2002 (see text for an explanation of SpreadBal-2002)

Mineral ¹	Minerals in mg precipitated from(-), or dissolved into(+), 1 L of water ¹ at . . .			
	Portal on December 5, 2005, based on bicarbonate alkalinity ² derived only from . . .		Portal on July 4, 2006, based on bicarbonate alkalinity ² derived only from . . .	
	calcite	CO ₂	calcite	CO ₂
Plagioclase (An 20)	+154	+154	+122	+122
K-feldspar	-48	-48	-53	-53
Biotite/Chlorite	+90	+90	+98	+98
Epidote	+194	+400	+276	+459
Calcite ²	+86	NA	+77	NA
CO ₂ from air ²	NA	+38	NA	+34
Pyrite	+78	+78	+97	+97
Gibbsite as Al(OH) ₃	-137	-211	-156	-222
Quartz	-136	-201	-145	-202
Goethite as Fe(OH) ₃	-67	-86	-84	-100

¹ A positive number means that mineral dissolved into 1 L of water, and a negative number means that mineral precipitated from 1 L of water; values from SpreadBal-2002 were converted from $\mu\text{mol/kg H}_2\text{O}$ to mg/L based on mineral formulas.

² Because site waters have near-neutral pH, they contain bicarbonate alkalinity (HCO_3^-); the source of the carbon could be solid-phase calcite (CaCO_3) or CO_2 from air, so both are calculated as separate scenarios; NA means not applicable to that scenario.

This raises the issue of how much calcite at this site is a secondary product of aluminosilicate weathering, rather than a primary mineral, and thus may be replenished through time. Petrographic work found in the near-neutral cell samples:

“Fine anhedral patches, occurring with epidote”

“Fine anhedral patches occurring as selective replacement of K-feldspar and typically associated with muscovite-sericite.”

“Fine anhedral patches occurring as selective replacement of K-feldspar and typically associated with muscovite-sericite or epidote-clinozoisite.”

The ongoing replenishment of calcite would explain why Sobek NP values do not seem to decrease significantly through time at some molybdenum minesites (Morin et al., 2001).

According to SpreadBal-2002, potassium feldspar (K-feldspar) may have precipitated from portal drainage (Table 3). However, portal concentrations were less than detection (2 mg/L) and thus the use of one-half the detection limit (1 mg/L) may distort the potassium balance. Similarly, iron was below detection, which affects the calculated dissolution of some aluminosilicate minerals and the precipitation of ferric oxide.

Table 3 estimated that large amounts of aluminum (gibbsite), silica (quartz), and iron (goethite) precipitated from the waters. This would explain the extensive staining and accumulation of secondary minerals observed on the walls inside the portal. Thus, the formation of these secondary minerals is consistent with SpreadBal simulations.

There must be some type of geochemical “sink” to explain the loss of sodium from the on-site portal waters, which is released by the dissolution of plagioclase. SpreadBal-2002 could not identify this sink.

For the five laboratory humidity cells, the composite average chemistries through Weeks 37 to 41, and through Weeks 101 to 105, were evaluated by SpreadBal-2002 (Tables 4 and 5). As with the portal drainage, there were some complexities, such as (1) using one-half detection for some concentrations and (2) the lack of identification of the sodium sink.

For the two cells acidic at early times (Cells 1 and 2, Table 4), there was no alkalinity and thus no estimated involvement of calcite or atmospheric CO₂. SpreadBal-2002 indicated both acidic cells experienced significant dissolution of biotite, epidote, and plagioclase for some neutralization, and pyrite for acid generation. Volcanics Cell 2 experienced dissolution of K-feldspar, due to its relatively high effluent potassium concentrations (Figure 3). In contrast, Cell 1 theoretically formed some K-feldspar, but this probably represented one or more geochemical “sinks”.

For the three remaining cells becoming acidic at later times (Table 5), epidote was the major mineral dissolving from all three samples according to SpreadBal-2002, with Cell 4 having the largest epidote dissolution of all five cells. Compared with the acidic cells (Table 4), the calculated dissolutions of plagioclase, K-feldspar, and biotite were notably smaller. Calcite dissolution was higher than plagioclase, K-feldspar, and biotite in the two granodiorite samples, but similar in the lower-pH Volcanics Cell 3. Nevertheless, calcite was not needed to explain the average weekly chemistry, with atmospheric CO₂ and additional dissolution of epidote replacing calcite dissolution.

Table 4. Estimates of mineral dissolution/precipitation to explain composite water chemistry for the two quickly-acidic humidity cells at Weeks 37-41 and Weeks 101-105 using SpreadBal-2002

<u>Mineral</u> ¹	Minerals in mg precipitated from(-), or dissolved into(+), 1 L of water ¹ at . . .			
	Metasedimentary Cell 1 averaged over Weeks 37-41/Weeks 101-105, based on bicarbonate alkalinity ² derived only from . . .		Volcanics Cell 2 averaged over Weeks 37-41/Weeks 101-105, based on bicarbonate alkalinity ² derived only from . . .	
	<u>calcite</u>	<u>CO₂</u>	<u>calcite</u>	<u>CO₂</u>
Plagioclase (An 20)	+12/+9.9	+12/+9.9	+15/+8.6	+15/+8.6
K-feldspar	-13/-12	-13/-12	+68/+23	+68/+23
Biotite/Chlorite	+37/+23	+37/+23	+43/+11	+43/+11
Epidote	+35/+7.0	+35/+7.0	+42/+18	+42/+18
Calcite ²	0/0	NA	0/0	NA
CO ₂ from air ²	NA	0/0	NA	0/0
Pyrite	+69/+33	+69/+33	+52/+15	+52/+15
Gibbsite as Al(OH) ₃	-7.7/-0.20	-7.7/-0.20	-38/-17	-38/-17
Quartz	-11/+6.5	-11/+6.5	-61/-17	-61/-17
Goethite as Fe(OH) ₃	-36/-19	-36/-19	-33/-10	-33/-10

¹ A positive number means that mineral dissolved into 1 L of water, and a negative number means that mineral precipitated from 1 L of water; values from SpreadBal-2002 were converted from $\mu\text{mol/kg H}_2\text{O}$ to mg/L based on mineral formulas.

² Because near-neutral cells contain bicarbonate alkalinity (HCO_3^-), the source of the carbon could be solid-phase calcite (CaCO_3) or CO_2 from air, so both are calculated as separate scenarios; however, for these acidic cells, alkalinity is zero, so calcite and CO_2 do not play a role in neutralization; NA means not applicable to that scenario; results from Weeks 37-41 are on the left side of the “/” and Weeks 101-105 on the right.

Table 5. Estimates of mineral dissolution/precipitation to explain composite water chemistry for the three humidity cells still near neutral at Weeks 37-41 and Weeks 101-105 using SpreadBal-2002

Mineral ¹	Minerals in mg precipitated from(-), or dissolved into(+), 1 L of water ¹ at . . .					
	Volcanics Cell 3 averaged over Weeks 37-41/Weeks 101-105, based on bicarbonate alkalinity ² derived only from . . .		Granodiorite Cell 4 averaged over Weeks 37-41/Weeks 101-105, based on bicarbonate alkalinity ² derived only from . . .		Granodiorite Cell 5 averaged over Weeks 37-41/Weeks 101-105, based on bicarbonate alkalinity ² derived only from . . .	
	calcite	CO ₂	calcite	CO ₂	calcite	CO ₂
Plagioclase (An 20)	+5.3/+3.3	+5.3/+3.3	+4.6/+3.3	+4.6/+3.3	+4.5/+3.3	+4.5/+3.3
K-feldspar	+4.7/+1.0	+4.7/+1.0	+4.2/+1.4	+4.2/1.4	+3.0/+1.2	+3.0/+1.2
Biotite/ Chlorite	+2.2/+1.1	+2.2/+1.1	+1.2/ +0.40	+1.2/ +0.40	+2.2/ +0.80	+2.2/ +0.80
Epidote	+38/+26	+48/+31	+148/+91	+179/+107	+36/+32	+86/+62
Calcite ²	+4.2/+2.1	NA	+13/+6.9	NA	+21/+13	NA
CO ₂ from air ²	NA	+1.8/+0.92	NA	+5.9/+3.0	NA	+9.1/+5.5
Pyrite	+8.5/+5.2	+8.5/+5.2	+33/+21	+33/+21	+8.5/+5.3	+8.5/+5.3
Gibbsite as Al(OH) ₃	-17/-11	-21/-13	-56/-34	-67/-40	-15/-13	-33/-24
Quartz	-16/-8.1	-19/-9.7	-50/-29	-60/-35	-13/-10	-29/-20
Goethite as Fe(OH) ₃	-7.5/-4.8	-8.4/-5.2	-28/-18	-31/-19	-7.4/-5.4	-12/-8.1

¹ A positive number means that mineral dissolved into 1 L of water, and a negative number means that mineral precipitated from 1 L of water; values from SpreadBal-2002 were converted from $\mu\text{mol/kg H}_2\text{O}$ to mg/L based on mineral formulas.

² Because these near-neutral cells contain bicarbonate alkalinity (HCO_3^-), the source of the carbon could be solid-phase calcite (CaCO_3) or CO_2 from air, so both are calculated as separate scenarios; NA means not applicable to that scenario; results from Weeks 37-41 are on the left side of the “/” and Weeks 101-105 on the right.

Each mineral that dissolved and precipitated in SpreadBal-2002 simulations for the portal (Table 3) and humidity cells (Tables 4 and 5) can be associated with a certain amount of either acidity neutralization or acidity generation (Section 2, and Morin and Hutt, 2006). The amount depends on the stoichiometry of the mineral, the amount of mineral dissolved or precipitated, and the fate of various reaction products. Based on this, the amount of neutralization by the reacting silicate minerals, minus the amount of acidity by the sulphide assumed to be all pyrite, provides a mineralogy-based net alkalinity (Table 6).

For the acidic cells, this approach correctly yielded negative values for mineralogy-based net alkalinity, for both Weeks 37-41 and Weeks 101-105 (Table 6). This was consistent with the lack of measured alkalinity. The mineralogy-based partial neutralizations were typically higher than measured neutralizations, but within 20%. The exception was Cell 1 at Weeks 101-105, where measured neutralization was about one-half of the calculated mineralogy-based neutralization. Nevertheless, the partial neutralization in the two acidic cells could generally be explained by SpreadBal-2002 calculations considering the generalizations.

For the near-neutral cells that became acidic later, the mineralogy-based neutralization typically overestimated the measurement-based neutralization (Table 6). However, this was often within 20% for Cells 4 and 5, but 40-100% for Cell 3. Overall, discrepancies between calculated and measured neutralizations were lower for the calcite-based scenario than the CO₂-based scenario, although the differences were often less than 10% and thus may not be significant.

The calculated and measured alkalinity values were relatively low for the three near-neutral cells before becoming acidic, and often agreed within 5 mg CaCO₃/L for the same scenarios. Like total neutralization, discrepancies between the calculated and measured alkalinities were typically less for the calcite-based scenario than the CO₂-based scenario, but often by only a few mg/L.

Therefore, the USGS SpreadBal-2002 software, and subsequent conversions for neutralization, showed that silicate neutralization played a major role in the partial to full neutralization in these five humidity cells. The calculations could not decisively confirm whether calcite was needed at all for neutralization, but slightly better agreement was obtained when calcite was included.

In summary, the USGS SpreadBal-2002 software estimated the amounts of silicate minerals dissolving and precipitating to explain water chemistries seen at the on-site portal of the 1066 Adit and in the selected weeks of the five laboratory humidity cells. Epidote, plagioclase, calcite, and biotite were often calculated as major dissolving components to create the observed water chemistries, with substantial precipitation of quartz, ferric oxides, and aluminum oxides also needed to explain the observed chemistries. Subsequent conversions to neutralization potentials and alkalinities showed that silicate neutralization played a major role in the partial (below pH 6) to full neutralization (above pH 6) in these humidity cells. This work also showed that calcite was not needed to explain the water chemistry, with atmospheric CO₂ potentially supplying the carbon for alkalinity. However, slightly better agreement was obtained when calcite was included.

Table 6. Calculated alkalinities and net alkalinities based on mineralogy and on measured average humidity-cell data from Weeks 37-41 and Weeks 101-105			
<u>Cell</u>	<u>Parameter (mg CaCO₃ equivalent/L)</u>	Carbonate Alkalinity at Weeks 37-41/101-105 Derived from . . .	
		<u>calcite</u>	<u>atmospheric CO₂</u>
Acidic Metasedimentary Cell 1	Neutralization by Epidote	15/3.0	15/3.0
	Neutralization by Biotite/Chlorite	13/7.7	13/7.7
	Mineralogy-Based Total Neutralization ¹	28/11	28/11
	Mineralogy-Based Total Acidity Generation ²	116/56	116/56
	Mineralogy-Based Net Alkalinity ³	-88/-45	-88/-45
	Measured Total Neutralization ⁴	25/4.6	25/4.6
	Measured Aqueous Alkalinity ⁵	0	0
Acidic Volcanics Cell 2	Neutralization by Epidote	18/7.5	18/7.5
	Neutralization by Biotite/Chlorite	15/3.6	15/3.6
	Neutralization by K-feldspar	12/4.1	12/4.1
	Mineralogy-Based Total Neutralization ¹	48/17	48/17
	Mineralogy-Based Total Acidity Generation ²	86/25	86/25
	Mineralogy-Based Net Alkalinity ³	-39/-8.0	-39/-8.0
	Measured Total Neutralization ⁴	45/14	45/14
	Measured Aqueous Alkalinity ⁵	0	0
Near-Neutral Volcanics Cell 3	Neutralization by Epidote	16/11	20/13
	Neutralization by Calcite	2.1/1.1	NA
	Neutralization by Plagioclase	1.2/0.75	1.2/0.75
	Mineralogy-Based Total Neutralization ¹	21/13	23/14
	Mineralogy-Based Total Acidity Generation ²	14/8.6	14/8.6
	Mineralogy-Based Net Alkalinity ³	6.6/4.6	8.7/5.6
	Measured Total Neutralization ⁴	15/7.1	15/7.1
	Measured Aqueous Alkalinity ⁵	4.2/2.1	4.2/2.1

Cell	Parameter (mg CaCO ₃ equivalent/L)	Carbonate Alkalinity at Weeks 37-41/101-105 Derived from . . .	
		calcite	atmospheric CO ₂
Near-Neutral Granodiorite Cell 4	Neutralization by Epidote	62/38	75/45
	Neutralization by Calcite	6.7/3.5	NA
	Neutralization by Plagioclase	1.0/0.75	1.0/0.75
	Mineralogy-Based Total Neutralization ¹	71/43	77/46
	Mineralogy-Based Total Acidity Generation ²	56/36	56/36
	Mineralogy-Based Net Alkalinity ³	15/7.1	22/11
	Measured Total Neutralization ⁴	64/39	64/39
	Measured Aqueous Alkalinity ⁵	13/6.9	13/6.9
Near-Neutral Granodiorite Cell 5	Neutralization by Epidote	15/14	36/26
	Neutralization by Calcite	10/6.3	NA
	Neutralization by Plagioclase	1.0/0.75	1.0/0.75
	Mineralogy-Based Total Neutralization ¹	28/21	39/27
	Mineralogy-Based Total Acidity Generation ²	14/8.9	14/8.9
	Mineralogy-Based Net Alkalinity ³	14/12	24/18
	Measured Total Neutralization ⁴	32/19	32/19
	Measured Aqueous Alkalinity ⁵	21/13	21/13
¹ Based on the sum of calculated neutralization by epidote, calcite, and other relevant minerals minus the acidity produced by the precipitation of secondary minerals.			
² Based on the acidity produced by oxidized pyrite; all sulphides were assumed to be pyrite for this calculation.			
³ Mineralogy-Based Net Alkalinity = Mineralogy-Based Total Alkalinity minus Mineralogy-Based Total Acidity Generation.			
⁴ Measured Total Neutralization = Measured Sulphate minus Measured Acidity plus Measured Aqueous Alkalinity; for comparison to Mineralogy-Based Total Neutralization.			
⁵ Average alkalinity measured in cell effluents from Week 37 to Week 41 / from Week 101 to Week 105; for comparison to Mineralogy-Based Net Alkalinity.			

4. Theoretical Rates of Neutralization by Silicate Minerals

The preceding sections examined neutralization based on bulk amounts of solid-phase minerals. This section looks at theoretical kinetic rates of neutralization by various aluminosilicate minerals. An aluminosilicate mineral at a low solid-phase concentration could have a relatively fast reaction rate, despite its bulk amount, and thus account for much of the weekly neutralization observed in the humidity cells.

A major problem here is that reaction rates are often dependent on pH. The pH around the reacting mineral grains could be very different from the composite pH of water draining from laboratory humidity cells and the full-scale portal (e.g., Li et al., 2006). Thus, identifying the micro-scale pH at which the silicate minerals is actually dissolving, and the corresponding theoretical neutralization rate, is not possible. In turn, this means that using near-neutral pH to calculate reaction rates could underestimate actual silicate neutralization rates if micro-scale pH were acidic.

In order to calculate neutralization rates by aluminosilicate minerals, the pH-dependent dissolution rates of minerals from Palandri and Kharaka (2004) were compiled into a spreadsheet. Silicate neutralization was calculated by applying a time-based aqueous rate (Table 7), instead of a bulk solid-phase level as done in the previous sections. This rate was expressed in units of mg CaCO₃ equivalent / kg of sample / week, for comparison with measured rates of neutralization (sulphate production minus residual acidity) for near-neutral periods in the humidity cells. Measured rates were calculated without including alkalinity as a rough estimate of silicate-only neutralization, and with alkalinity as a rough estimate including calcite neutralization.

The silicate neutralization rate was generally similar to that of measured neutralization, with and without alkalinity, in the near-neutral volcanics Cell 3. For Granodiorite Cell 4, with the highest rate of sulphide oxidation, its neutralization rates with and without alkalinity exceeded the silicate rate substantially. For Granodiorite Cell 5, the measured rate without alkalinity was similar to the calculated silicate rate, but the measured rate including alkalinity to approximate calcite contributions was much greater. Again, micro-scale pH around the silicate grains might be more acidic than the composite effluent pH, especially in Cell 4 with the highest oxidation rate, which would lead to higher silicate neutralization rates than calculated here. However, such a small-scale pH cannot be estimated from available information.

In summary, theoretical rates of neutralization by aluminosilicate minerals in the near-neutral humidity cells were similar to, or substantially less than, the measured neutralization rates. The substantially larger measured rates apparently reflect (1) the additional contribution of calcite and/or (2) the possibility of micro-scale acidic conditions (pH < 6) around the aluminosilicate mineral grains that would cause them to react faster. However, such a small-scale pH cannot be estimated from available information.

Table 7. Calculated theoretical rates of neutralization by silicate minerals in the five humidity-cell samples at near-neutral pH				
<u>Cell</u>	Measured Neutralization Rate (mg CaCO ₃ equivalent / kg of sample / week) ¹		Silicate-Based Neutralization Rate (mg CaCO ₃ equivalent / kg of sample / week) ²	Main Silicate Mineral(s) Accounting for the <u>Neutralization</u>
	<u>with Alkalinity</u>	<u>without Alkalinity</u>		
Volcanics Cell 3	6.3/3.4	4.6/2.4	5.2	Epidote, plagioclase
Granodiorite Cell 4	26/19	21/15	2.4	Plagioclase, K- feldspar, chlorite
Granodiorite Cell 5	13/8.8	4.6/3.0	5.2	Epidote, plagioclase, biotite
¹ Measured Neutralization = Measured Sulphate minus Measured Acidity; first value in a cell is the average rate from Weeks 37-41 and the second is from Weeks 101-105; in the first column, Measured Alkalinity is included as a rough estimate of calcite contribution.				
² All silicate rates were calculated at pH 7 for comparison; a change of one pH unit caused predicted rates to change generally by less than 20%.				

5. References

- Bowser, C.J., and B.F. Jones. 2002. Mineralogical controls on the composition of natural waters dominated by silicate hydrolysis. *American Journal of Science*, 302, p. 582-662.
- Eary, L.E., and M.A. Williamson. 2006. Simulations of the neutralizing capacity of silicate rocks in acid mine drainage environments. IN: R.I. Barnhisel, ed., *Proceedings of the 7th International Conference on Acid Rock Drainage (ICARD)*, p.564-577, March 26-30, 2006, St. Louis, MO, USA.
- Jambor, J.L., J.E. Dutrizac, and M. Raudsepp. 2006. Comparison of measured and mineralogically predicted values of the Sobek Neutralization Potential for intrusive rocks. IN: R.I. Barnhisel, ed., *Proceedings of the 7th International Conference on Acid Rock Drainage (ICARD)*, p.820-832, March 26-30, 2006, St. Louis, MO, USA.
- Li, L., C.A. Peters, and M.A. Celia. 2006. Upscaling geochemical reaction rates using pore-scale network modelling. *Advances in Water Resources*, 29, p. 1351-1370.
- Morin, K.A., and N.M. Hutt. 2008a. Field Study of Unavailable Neutralization Potential in Acidic Rock. MDAG Internet Case Study #31, www.mdag.com/case_studies/cs31.html
- Morin, K.A., and N.M. Hutt. 2008b. Case Studies of Unavailable Neutralization Potential in Acid-Base-Accounting Datasets. MDAG Internet Case Study #30, www.mdag.com/case_studies/cs30.html
- Morin, K.A., and N.M. Hutt. 2006. Conversion of Minerals into Neutralization Potentials with Units of CaCO₃ Equivalent. Internet Case Study 20 at www.mdag.com.
- Morin, K.A., and N.M. Hutt. 2001. *Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies - Digital Edition*. MDAG Publishing, Vancouver, Canada. ISBN 0-9682039-1-4.
- Morin, K.A., and N.M. Hutt. 1997. *Environmental Geochemistry of Minesite Drainage: Practical Theory and Case Studies*. MDAG Publishing, Vancouver, Canada. ISBN 0-9682039-0-6.
- Morin, K.A., N.M. Hutt, W.A. Price, and V. Coffin. 2001. Violation of common ABA prediction rules by molybdenum-related minesites in British Columbia. IN: *Proceedings of Securing the Future, International Conference on Mining and the Environment*, Skellefteå, Sweden, June 25-July 1, Volume 2, p. 566-575. The Swedish Mining Association.
- Palandri, J.L., and Y.K. Kharaka. 2004. A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling. U.S. Geological Survey Open File Report 2004-1068, 70 p.
- Sobek, A.A., W.A. Schuller, J.R. Freeman, and R.M. Smith. 1978. Field and Laboratory Methods Applicable to Overburdens and Minesoils. Report EPA-600/2-78-054, U.S. National

Technical Information Report PB-280 495. 403 p.

White, A.F., M.S. Schulz, J.B. Lowenstern, D.V. Vivit, and T.D. Bullen. 2005. The ubiquitous nature of accessory calcite in granitoid rocks: Implications for weathering, solute evolution, and petrogenesis. *Geochemica et Cosmochimica Acta*, 69, p. 1455-1471.