

MDAG.com Internet Case Study 62

MDAG-com Case Study 62 - Problems and Errors with Interpreting Humidity Cells Using Weight-Based Results (e.g., the “Oxidation-Neutralization Curve”) Rather Than Mole-Based Results

by K.A. Morin

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Abstract

For almost 170 years, the chemical units of moles have been used to delineate and interpret chemical equations by international agreement. This was not an arbitrary decision.

For decades, acid-base accounting (ABA) and geochemical kinetic tests related to water contamination and acid rock drainage (ARD) have been interpreted using mole-based data and ratios. However, for unclear reasons, weight-based interpretations have been appearing instead of mole-based ones, sometimes referred to as “oxidation-neutralization curves”.

This MDAG case study reviewed the chemical equations behind sulphide oxidation and subsequent neutralization by carbonate minerals. Interpretations of these equations, and of corresponding elemental ratios, using mole-based and weight-based approaches were compared. These comparisons showed the weight-based approach can be ambiguous, misleading, and erroneous. Then a detailed review of published weight-based interpretations of real kinetic tests illustrated how misleading and erroneous the weight-based findings can be.

Weight-based interpretations are not appropriate for geochemical kinetic tests and their corresponding ABA. Mole-based interpretations are required, which has been followed in a general sense for at least 170 years and, specifically for ARD, has been followed for decades. This was not an arbitrary decision.

1. INTRODUCTION

This MDAG case study examines the problems that arise when kinetic humidity-cell and leach-column geochemical results are interpreted on a weight basis (such as grams or milligrams) rather than on a mole basis. This weight-based approach is sometimes referred to as an “oxidation-neutralization curve”. The problems with weight-based geochemical results are not immediately apparent, but will be illustrated here.

Because oxidation and neutralization are chemical equations, they are normally expressed and interpreted using moles. This has been the accepted approach by international agreement for nearly 170 years, even earlier if the related concept of equivalents is considered. It makes no chemical sense that weight-based interpretations of geochemical kinetic tests would be used.

Section 2 of this MDAG case study presents the decades-old way of interpreting ML-ARD kinetic tests on a mole basis (Morin and Hutt, 1997 and 2001), consistent with roughly 170 years of standard chemistry. Section 3 follows the same path, but using weight instead. The comparison of the two approaches shows that weight-based interpretations can be misleading and erroneous. This fact is highlighted by real examples in Section 4. If the equations in Section 2 and 3 appear onerous, skip to Section 4 which should be mostly self-explanatory.

It is not clear why the weight-based approach is used when it offers no advantages and many disadvantages. It is clearly not consistent with principles of chemistry and geochemistry.

2. HUMIDITY-CELL INTERPRETATIONS ON A MOLE BASIS

If you are not particularly interested in the details expressed as molar-based and weight-based chemical equations, please go directly to Section 4 which should be mostly self-explanatory.

2.1 Pyrite Oxidation

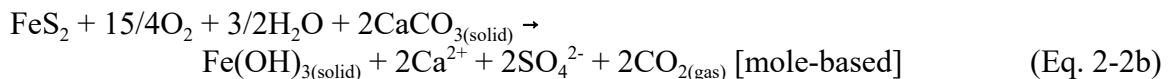
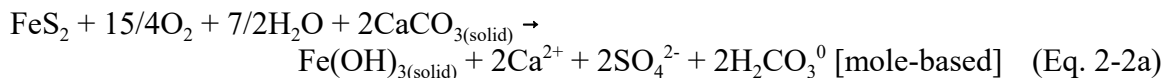
In the realm of acid rock drainage (ARD) and most other fields that include chemistry, chemical equations are typically written in terms of moles. For example, under fully oxidized conditions above pH ~ 3.5, the most common equation for full pyrite oxidation is (Price, 2009):



Equation 2-1 shows that one mole of pyrite produces 2 moles of sulphate, and 4 moles of acidity. That is easy to understand, but not so with the weight-based approach (Section 3.1). In this case, the hydronium ion, and the acidity in general, are expressed as H^+ for simplicity.

2.2 Partial Neutralization by Calcite to pH < ~6.3

When calcite (CaCO_3) is present, the partial fully-oxidized neutralization of Equation 2-1 to pH < ~6.3 is:

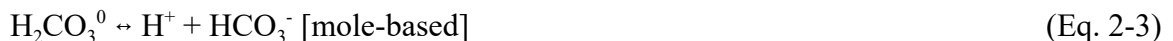


Because pH is less than 6.3, the carbon from calcite can occur as a combination of carbonic acid (H_2CO_3) (Equation 2-2a), CO_2 gas (Equation 2-2b), and CO_2 dissolved in water (similar to Equation 2-2a).

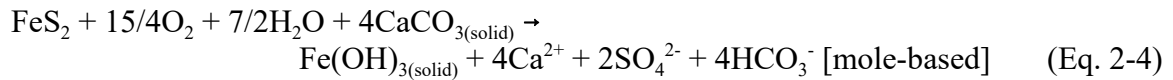
In open systems where gas can be released from the water, some CO_2 will be lost. For the moment, we will assume all carbon released from calcite remains in the water (a closed system).

2.3 Further Neutralization by Calcite to ~6.3 < pH < ~9

If neutralization continues to pH above ~6.3 up to about 9, then additional calcite is needed to neutralize the additional acidity released by dissociation of carbonic acid:



The resulting cumulative equation for this neutralization above pH ~6.3 is:



In this case, upon closed-system neutralization, one mole of pyrite fully neutralized by 4 moles of CaCO_3 will release 4 moles of aqueous calcium and 2 moles of aqueous sulphate. The molar ratios of aqueous $\text{Ca}^{2+}:\text{SO}_4^{2-}$ and of $\text{CaCO}_{3(\text{solid})}:\text{SO}_4^{2-}$ in this equation are both 4:2 or 2.0. This is discussed further in the next subsections.

In an open system, some CO_2 gas from partial neutralization (Equation 2-2) is lost from the system, which causes some aqueous H_2CO_3^0 to convert to CO_2 gas and some of this is also lost. As a result, there is less H_2CO_3^0 remaining and Equation 2-3 produces proportionally less H^+ to be further neutralized. In turn, the open-system molar ratios of $\text{Ca}^{2+}:\text{SO}_4^{2-}$ and of $\text{CaCO}_{3(\text{solid})}:\text{SO}_4^{2-}$ would be less than 4:2 or 2.0 based on Equation 2-4, but greater than 1.0.

2.4 The Net Potential Ratio (NPR) in Acid-Base Accounting and Its Relationship to Neutralization

The molar ratio of aqueous calcium to aqueous sulphate and of calcite to aqueous sulphate in the closed-system Equation 2-4 is 4:2, or 2.0. This is the reason that the common criterion for Net Potential Ratio (NPR = Effective Neutralization Potential/ Effective Acid Potential) is ideally 2.0 in acid-base accounting (ABA) (Morin and Hutt, 1997 and 2001). Effective NPR values less than 2.0 in fully oxidized closed systems indicate there is insufficient carbonate to neutralize all potential acid generation. Thus, ARD is predicted after some lag time, after NPR sequentially decreases to zero with time (Morin, 2014).

In an open system, such as field conditions or well-aerated kinetic tests, some CO_2 can be lost during initial partial neutralization as discussed in Section 2.3. As a result, the ratios of (1) aqueous calcium to aqueous sulphate and (2) calcite to sulphate can be somewhat less than 2.0 (but greater than 1.0) and remain near neutral. This is why some site-specific NPR values can be less than 2.0, but 2.0 is used as the criterion for closed systems like groundwater systems and submerged/saturated mine wastes and as a safety factor for open systems. This is discussed further in Section 2.6.

There is an important point to be made here about this link between NPR from ABA and the molar ratios from open- and closed-system neutralization by carbonate. The point is: NPR is weight based! It is Effective NP in kg CaCO_3 equivalent / Effective AP in kg CaCO_3 equivalent. However, because both numerator and denominator are mathematically converted to CaCO_3 equivalent, the NPR is the same as a molar ratio. As a result, the molar link between ABA and oxidation-neutralization (Equation 2-4) persists and remains valid with moles, but with weight (Section 3.4).

2.5 The Carbonate Molar Ratio from Humidity Cells and Its Relationship to Neutralization

In well-aerated, well-flushed, fine-grained humidity cells operated properly (Morin and Hutt, 1997 and 2001; Bouzahzah et al., 2015), the weekly measurements of aqueous calcium plus magnesium can represent the dissolution of the fast-dissolving and fast-neutralizing minerals of calcite and dolomite. Also, aqueous sulphate can represent the rate of sulphide oxidation and acid generation. In other words, humidity cells are designed to examine Equation 2-4 applied to various samples with varying mineralogy ideally without any solubility limitations.

When magnesium (or other element) occurs as a carbonate mineral, Equation 2-4 is easily adjusted to include these other “ $\text{XCO}_{3(\text{solid})}$ ”. Nevertheless, the molar ratios of carbonate minerals to aqueous sulphate and of aqueous (Ca+X) to aqueous sulphate remains the same at 2.0 using moles but not weight (Section 3.5). There are common complications to this requiring careful interpretation, as discussed in Sections 2.6 and 4 below.

Therefore, in properly operated humidity cells, an important parameter obtained from the weekly rinses is known as the Carbonate Molar Ratio (CMR):

$$\text{Carbonate Molar Ratio (CMR)} = \text{aqueous (Ca+Mg)} / \text{aqueous SO}_4 \text{ [mole-based]} \text{ (Eq. 2-5)}$$

The CMR has been used for decades in interpretations of humidity cells (e.g., Morin and Hutt, 1997). If the CMR is, for example, 1.7, then fast-neutralizing carbonate in an open system is being consumed 1.7 times faster than acidity is being generated. In turn, this sample will eventually become net acidic in an open system only if its original NPR is greater than or equal to 1.7. In this way, the molar interpretations of humidity cells (1) are relatively easily understood and (2) are directly linked to ABA through the NPR criterion being essentially mole-based also.

To be clear, Equations 2-4 and 2-5 yield a closed-system CMR of 2.0 whether calcite (CaCO_3) or dolomite ($\text{CaMg}(\text{CO}_3)_2$) neutralizes the acidity. On the other hand, a weight-based ratio will vary with mineralogy as shown in Section 3.5 and Section 4 of this MDAG case study.

2.6 Stoichiometric Dissolution of Gypsum

As an example of a soluble mineral that can affect the CMR, stoichiometric gypsum dissolution is:



In the absence of relatively little sulphide oxidation and calcium-bearing carbonate dissolution, Equation 2-6 produces one mole of calcium and one mole of sulphate, and thus a CMR value of 1.0. Because it is significantly less than typical CMR values for open-system and closed-system dissolution of carbonate, the value of 1.0 stands out. This becomes important in Sections 3.6 and 4.

3. HUMIDITY-CELL INTERPRETATIONS ON A WEIGHT BASIS

If you are not particularly interested in the details expressed as weight-based chemical equations, please go directly to Section 4 which should be mostly self-explanatory.

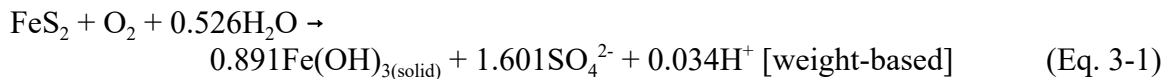
3.1 Pyrite Oxidation

As explained in Section 2.1, the molar-based equation for pyrite oxidation under well oxidized conditions above pH ~ 3.5 is (Price, 2009):



Equation 2-1 shows that one mole of pyrite produces 2 moles of sulphate, and 4 moles of acidity (expressed as H⁺). That is easy to understand.

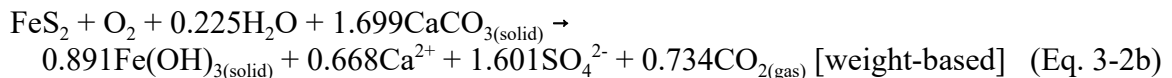
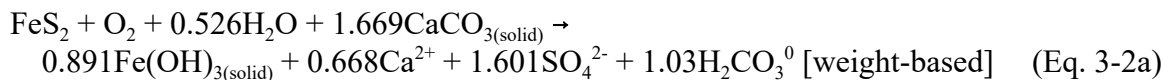
Alternatively, Equation 2-1 can be expressed by weight (grams) rather than moles:



In Equation 3-1, one gram of pyrite produces 1.601 grams of sulphate, and only 0.034 grams of acidity expressed as H⁺. In this case, weight-based generated acidity expressed as H⁺ is relatively negligible, so ARD should not be such an environmental concern! This is the first sign that weight-based interpretations can lead to incorrect conclusions.

3.2 Partial Neutralization by Calcite to pH < ~6.3

As a parallel to Section 2.2, when calcite (CaCO₃) is present, the partial neutralization of Equation 3-1 to pH < ~6.3 on a weight basis is:

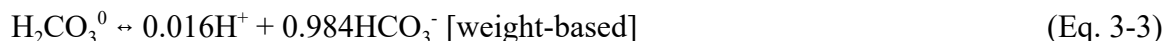


Because pH is less than 6.3, the carbon from calcite can occur as a combination of carbonic acid (H₂CO₃) (Equation 3-2a), CO₂ gas (Equation 3-2b), and CO₂ dissolved in water (similar to Equation 3-2a).

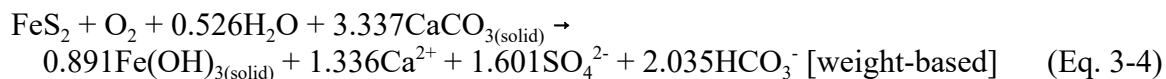
In open systems where gas can be released from the water, some CO₂ will be lost. For the moment, we will assume all carbon released from calcite remains in the water (a closed system).

3.3 Further Neutralization by Calcite to $\sim 6.3 < \text{pH} < \sim 9$

If neutralization continues to pH above ~ 6.3 up to about 9, then additional calcite is needed to neutralize the additional acidity released by dissociation of carbonic acid:



The resulting cumulative equation for this neutralization above pH ~ 6.3 is:



In this case, upon this closed-system neutralization, one gram of pyrite fully neutralized by 3.337 g of calcite releases 1.336 g of aqueous calcium and 1.601 g of aqueous sulphate. The weight ratios of aqueous $\text{Ca}^{2+}:\text{SO}_4^{2-}$ and of $\text{CaCO}_{3(\text{solid})}:\text{SO}_4^{2-}$ in this equation are 0.83 and 2.1, respectively, compared to the molar ratio of 2.0 for both (Section 2.3). This is discussed further in the next subsections.

In an open system, some CO_2 gas from partial neutralization (Equation 3-2) is lost from the system, which causes some aqueous H_2CO_3^0 to convert to CO_2 gas and some of this is also lost. As a result, there is less H_2CO_3^0 remaining and Equation 3-3 produces proportionally less H^+ to be neutralized. In turn, the open-system weight ratios of aqueous $\text{Ca}^{2+}:\text{SO}_4^{2-}$ and of $\text{CaCO}_{3(\text{solid})}:\text{SO}_4^{2-}$ would be less than 0.83 and 2.1, respectively, based on Equation 3-4.

3.4 The Net Potential Ratio (NPR) in Acid-Base Accounting and Its Relationship to Neutralization

As explained in Section 2.4, the weight-based dissolution of calcite in kinetic tests can be represented by the weight of aqueous calcium. The weight ratio of aqueous calcium to aqueous sulphate in Equation 3-4 is 0.83, relative to the molar ratio of 2.0.

Unlike the molar ratio (Section 2.4), this weight ratio cannot be compared directly to the Net Potential Ratio ($\text{NPR} = \text{Effective Neutralization Potential} / \text{Effective Acid Potential}$) from acid-base accounting (ABA). This is because the NPR is effectively a molar ratio: two values mathematically converted to the same “mineral” (CaCO_3 equivalent).

Effective (mole-based) NPR values in closed systems less than 2.0 indicate there is insufficient calcite to neutralize all potential acid generation. However, for this weight-based approach, the NPR would have to be mathematically converted.

For example, we could say the weight-based ratio of aqueous $\text{Ca}^{2+}:\text{SO}_4^{2-}$ should be greater than 0.83 to remain near neutral. However, this would be unreliable. As shown in Section 4, the weight-based NPR criterion is not simply 0.83, but the NPR criterion varies with mineralogy and reaction rates, unlike the molar ratio. For example, if neutralization is provided by both calcite and dolomite, then the NPR criterion as a molar ratio would remain 2.0 whereas the weight-based NPR would vary with

the proportions of the two minerals and their relative reaction rates. The example in Section 4 numerically shows this.

Additionally, in an open system such as field conditions and well-aerated kinetic tests, some CO₂ can be lost during initial partial neutralization by calcite. As a result, the weight ratio of aqueous calcium to sulphate can be less than 0.83 (a molar ratio of 2.0), but still greater than 0.42 (a molar ratio of 1.0). The weight-based ratio of 0.42 will be discussed further in Sections 3.6 and 4.

3.5 The Carbonate Weight Ratio from Humidity Cells and Its Relationship to Neutralization

In well-aerated, well-flushed, fine-grained humidity cells operated properly (Morin and Hutt, 1997 and 2001; Bouzahzah et al., 2015), the weekly measurements of aqueous calcium plus magnesium can represent the dissolution of the fast-dissolving minerals of calcite and dolomite. Also, aqueous sulphate can represent the rate of sulphide oxidation and acid generation. In other words, humidity cells are designed to examine Equation 3-4 applied to various samples with varying mineralogy without any solubility limitations. The real example in Section 4 will highlight this.

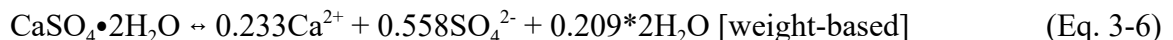
When magnesium (or other element) occurs as a carbonate mineral, Equation 3-4 is easily adjusted to include these other “XCO_{3(solid)}”. Nevertheless, the molar ratios of carbonate minerals to aqueous sulphate and of aqueous Ca+X to aqueous sulphate remains the same, but the weight ratios do not.

In properly operated humidity cells, an important parameter is the Carbonate Weight Ratio (CWR):
 Carbonate Weight Ratio (CWR) = aqueous (Ca + Mg) / (SO₄) [weight-based] (Eq. 3-5)

Here arises again the problem with weight-based interpretations: the CWR will vary with type of carbonate mineral(s) whereas the CMR (Section 2.5) will not. For example, calcite in Equation 3-4 would yield a CWR of 0.83; MgCO₃ instead in Equation 3-4 would yield a CWR of 0.51; MnCO₃ instead in Equation 3-4 would yield a CWR of 1.14; and dolomite instead in Equation 3-4 would yield a CWR of 0.67, although all four molar ratios would be 2.0.

3.6 Stoichiometric Dissolution of Gypsum

As an example of a soluble mineral that can affect the CWR, stoichiometric gypsum dissolution by weight is:



In the absence of any sulphide oxidation and calcium-bearing carbonate dissolution, one gram of gypsum produces 0.233 g of calcium and 0.558 g of sulphate, and thus a CWR value of 0.42. Because it is significantly less than typical CWR values for open-system and closed-system dissolution of carbonate, this lower value of 0.417 stands out. This becomes important in Section 4.

4. PUBLISHED EXAMPLES OF WEIGHT-BASED KINETIC-TEST RESULTS AND PROBLEMS WITH THEIR INTERPRETATIONS

For unclear reasons, weight-based interpretations of kinetic tests using humidity cells and leach columns are becoming more common. In some cases, graphical plots are called “oxidation-neutralization curves”. As explained below and in Figure 1, they can be misleading or erroneous. There are reasons why chemical equations and interpretations have used moles by international agreement for almost 170 years.

One published reference on weight-based interpretations of kinetic tests (cells and columns) is Benzaazoua et al. (2004). In that paper, five samples of net-acid-generating tailings were tested in well-rinsed humidity cells and in leach columns to (1) evaluate kinetically the acid-generation potential and (2) compare the two types of kinetic tests.

The mineralogy of these tailings was relatively simple. An unpublished study indicated the tailings were mostly comprised of quartz, with small amounts of albite and “orthose” [sic], and traces of micas, chlorite, epidote, and amphibolites. They also contained various amounts of sulphides (4.2-10.4%S) as mostly pyrite. They also contained carbonate minerals as mostly dolomite and calcite, creating non-Sobek, “modified” Neutralization Potentials of 115-180 kg CaCO₃ equivalent/tonne.

All five samples remained near neutral pH (roughly pH 7 to 8) for the duration of testing (up to 400 days). The authors attributed the neutralization to carbonate dissolution.

The authors’ Figure 10 plotted the running sequential “cumulative” total of sulphate production in mg SO₄/kg of sample against the running sequential total “cumulative” total of Ca+Mg+Mn in mg/kg for each kinetic test. As time passed, the cumulative amounts increased, thus displaying an “oxidation-neutralization slope”. This approach is generalized in Figure 1 below.

Strangely, the humidity cells produced significantly higher accumulated Ca+Mg+Mn and sulphate in mg/kg than the columns, which the authors interpreted as the cells being accelerated. However, aqueous concentrations of sulphate (initially thousands of mg/L) were similar at the beginning of both cells and columns, but decreased significantly with time in the cells while remaining more constant in the columns. As explained below, the authors did not recognize solubility effects by using weight-based values, and in reality these cells cannot be verified as accelerated.

The slopes of these plots were summarized in their Table 6, where cells produced weight-based slopes (which is the CWR of Equation 3-5 above) of 0.37 to 0.41, and columns produced weight-based slopes of 0.33 to 0.36 with one at 0.40. The weight-based pre-test analyses of sulphur and Ca+Mg+Mn were then plotted and, if plotting above the slope (above the CWR), were declared net acid neutralizing (Figure 1). This concept is similar to using the CMR (Section 2.5), but is wrong.

There are so many misunderstandings and errors hidden in this weight-based approach. For students learning to interpret kinetic tests, it would be worthwhile to try to identify these problems before reading the explanations below.

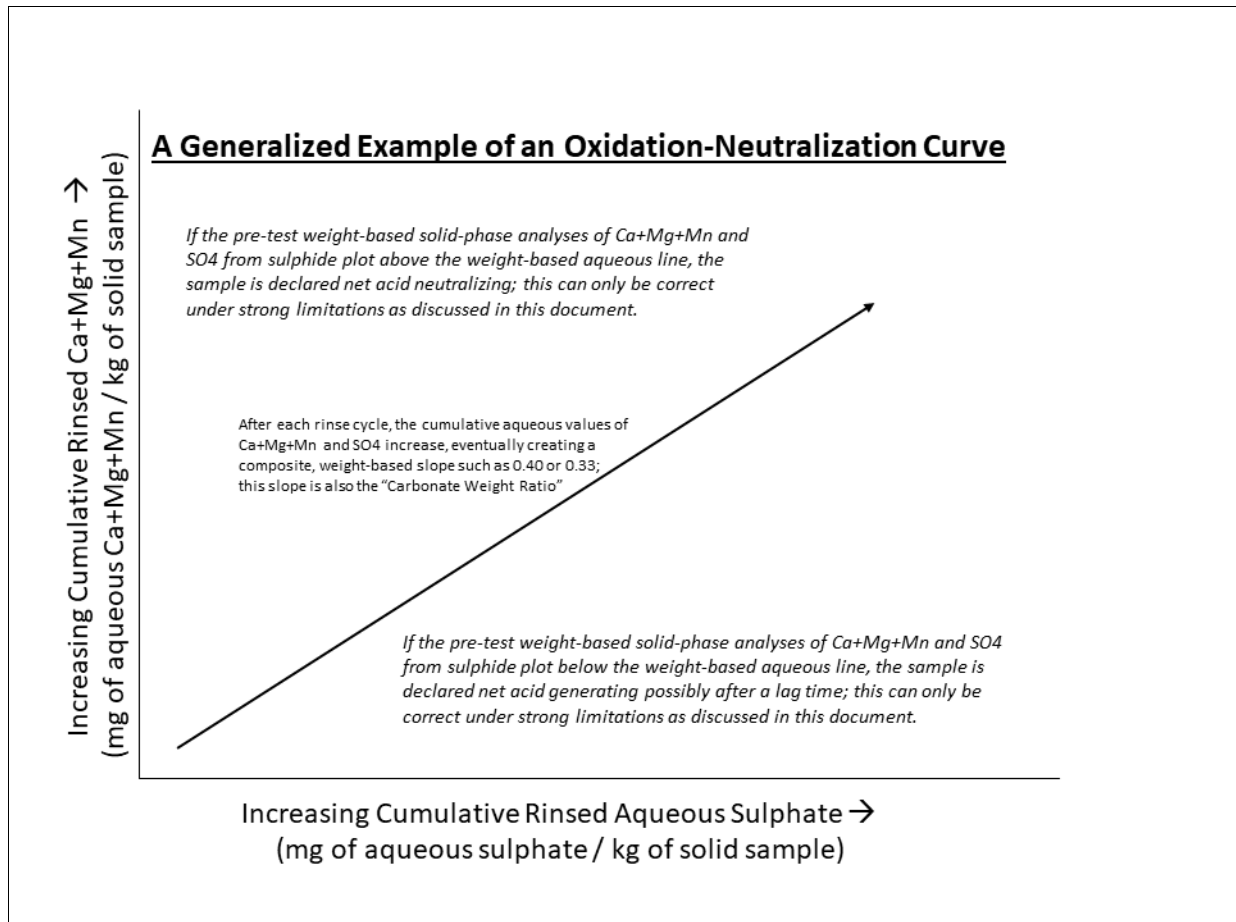


Figure 1. A generalized example of an oxidation-neutralization curve used in weight-based interpretations of geochemical kinetic tests; this approach was used by Benzaazoua et al. (2004).

Issue 1) Did the results of the humidity cells reflect ongoing sulphide oxidation and subsequent neutralization by carbonate minerals as the authors explained?

No.

The authors stated, “It should also be noticed that the evolution of sulfates in the leachates through time follows closely that of calcium for both test types.” This implies a correlation of sulphide oxidation and acid neutralization by carbonate minerals. However, there are alternate explanations.

As explained in Sections 2.6 and 3.6 above, the simple stoichiometric dissolution of gypsum provides one mole of calcium and one mole of sulphate, for a Carbonate Molar Ratio (CMR, Section 2.5) of 1.0. This is notably less than CMR values for open-system and closed-system neutralization with CMR values up to 2.0. The initial aqueous concentrations from the cells of up to 3000 mg/L were typical of secondary-mineral dissolution and not active oxidation-neutralization.

Stoichiometric dissolution of gypsum (Section 3.6) would produce a slope and Carbonate Weight Ratio of 0.42. Open-system and closed-system neutralization would produce significantly higher CWR values, up to 0.84 depending on mineralogy. As explained above and in the authors’ Table 6, CWR values for the cells were 0.37 to 0.41. These values are close to the weight-based CWR of 0.42 for gypsum dissolution, and notably lower than active oxidation-neutralization.

Benzaazoua et al. (2004) minimized this issue by saying, “Gypsum is present in some samples, as seen by the sulfates analysis in the prior section.” Their Table 2 showed every sample contained sulphate, mostly around 1wt% gypsum or higher. Such levels could take a long time to rinse out of cells and columns.

Issue 2: Did the cells show any signs of oxidation-neutralization rather than the observed gypsum dissolution?

Perhaps, but there are insufficient data from that study, and the cells were not operated until rates generally stabilized according to the decades-old recommendation.

The authors’ Figure 5 shows aqueous concentrations of sulphate from the cells displayed an erratic but gradual trend from thousands of mg/L to below 1000 mg/L. Recommendations have existed for decades that cells continue until concentrations generally stabilize (e.g., Morin and Hutt 1997; Price, 2009), but these authors did not do this.

It is possible that later sulphate values did represent active oxidation rather than gypsum dissolution. However, these cannot be seen on the cumulative oxidation-neutralization curves similar to Figure 1. This is because the relatively large initial values overwhelmed the later, smaller values, and thus the initial gypsum dissolution dominated the entire slope and the overall CWR for the lengths of the tests.

Humidity cells are traditionally interpreted by time series, so that variations in weekly results can

be seen. This can show, for example, that trends during early times are very different from later times. The cumulative slope as used in the weigh-based approach of Figure 1 cannot provide this variability reliably or clearly.

Issue 3: Did solid-phase measurements of Ca+Mg+Mn represent only carbonate minerals as required by this approach?

Sort of in this particular study by Benzaazoua et al. (2004), but not accurately.

The weight-based oxidation-neutralization approach compares initial solid-phase Ca+Mg+Mn in mg/kg to acid-generating solid-phase sulphide in mg SO₄/kg (Figure 1), rather than correctly comparing molar carbonate to molar sulphide that reflects the Net Potential Ratio from acid-base accounting (Sections 2.4 and 3.4). Therefore, this weight-based approach is sort of reliable if and only if most Ca+Mg+Mn is found in carbonate minerals. This appears generally the case for this particular study (Benzaazoua et al., 2004), but this is rare and is difficult to document reliably when comparing at least two methods for mineralogical characterization.

If there are other minerals containing significant amounts of solid-phase Ca+Mg+Mn, then this approach can incorrectly indicate the sample will remain near neutral when it may actually become acidic (Figure 1). The reason is because all the solid-phase Ca+Mg+Mn is incorrectly assumed to be neutralizing carbonate. This can lead to catastrophic error in ARD prediction.

Moreover, there is a significant problem again with weight-based values.

- For example, let's say the NP of a sample is composed of one mole CaCO₃, one mole MgCO₃, and one mole MnCO₃. This is three moles of neutralization, and 299.3 g of pre-test solid-phase Ca+Mg+Mn.
- Let's say NP is one mole CaCO₃, zero moles MgCO₃, and two moles MnCO₃. This is still three moles of neutralization, but 330.0 g of pre-test solid-phase Ca+Mg+Mn.
- Let's say NP is one mole CaCO₃, two moles MgCO₃, and zero moles MnCO₃, which is also equivalent to one mole calcite and one mole dolomite. This is still three moles of neutralization, but 268.7 g of pre-test solid-phase Ca+Mg+Mn.

In these three examples, there are exactly three moles of solid-phase carbonate neutralization, but 269 to 330 g of solid-phase Ca+Mg+Mn. The weight-based approach is strongly dependent on mineralogy, and changes significantly as mineralogy changes even if molar amounts remain the same.

So what did the weight-based values of Ca+Mg+Mn tell us about neutralization in this study? I don't know, because the weight-based data is ambiguous and difficult to interpret.

Issue 4: What about the columns?

Columns and cells cannot be compared, because they are designed to test for two different conditions. If they are operated properly (which surprisingly not often the case), humidity cells are

specifically designed to be highly diluted, thoroughly aerated, relatively fine-grained tests, to obtain as much as possible unit-weight (or unit-surface-area) reaction rates unhindered by mineral solubility. On the other hand, columns can be designed in many ways, but usually simulate the conditions of partially flushed, variable grain size, short flowpaths (the length of the column unless recirculated), and not necessarily full aerated. Some believe the comparison of results from these two properly-operated kinetic tests are indications of scale effects, but that is wrong.

In this study by Benzaazoua et al. (2004), Column BH96-11 produced a slope of 0.40 and released the lowest monthly amount of Mg and SO₄, and an average monthly amount of Ca (authors' Figure 4). Normal gypsum saturation is around 1500-2000 mg/L when Ca is around 300-500 mg/L, which is about what Column BH96-11 released. Therefore, normal gypsum saturation was likely occurring in Column BH96-11, and, as expected, it produced a weight-based slope and CWR of 0.4 (and a Carbonate Molar Ratio around 1.0). Sections 2.6 and 3.6 explained a CWR around 0.4 is typical of stoichiometric gypsum saturation.

The other column slopes are a lower and tightly clustered around 0.33 to 0.36. They also produced more sulphate in the monthly leachates than BH96-11, without any clear signs of decreasing with time like the cells. All this month-to-month stability suggests some type of mineral saturation is at work, which columns are normally designed to simulate.

How could the other columns release more sulphate in mg/L than gypsum-saturated BH96-11? There are several potential explanations, such as aqueous complexation of calcium, polymerization/nanoparticles of calcium, and oxidation of reduced aqueous sulphur species to sulphate after the leachates left the columns. I cannot tell from the available data, and apparently no one checked during the testing.

As a starting point, let's say there was some active oxidation in these columns and that MgCO₃ controlled the neutralization in these columns (not including BH96-11). With a molar ratio Mg/SO₄ of 1, the weight-based ratio would be 0.25 [(1 mole Mg * 24.31) / (1 mole SO₄ * 96.06) = 0.25]. That theoretical slope of 0.25 is lower than 0.33 to 0.36 detected in these columns over the entire test length, and thus the higher slopes may indicate active oxidation-neutralization with a Carbonate Molar Ratio perhaps around 1.5.

However, next, let's instead say dolomite controlled the neutralization. In this case, [(0.5 moles Ca * 40.08) + (0.5 moles Mg * 24.31)] / (1 mole SO₄ * 96.06) = 0.34. This value of 0.34 for the cumulative slope and CWR with dolomite falls within the range of 0.33-0.36 for those columns. Benzaazoua et al. (2004) said these tailings samples contained "carbonates, which are represented mainly by dolomite and calcite". However, this calculated value of 0.34 is a Carbonate Molar Ratio of 1.0 with dolomite, and thus indicates solubility-limited results rather than mostly oxidation-neutralization.

Therefore, the results of the columns may or may not indicate some significant active oxidation-neutralization. A reliable explanation is not provided by the weight-based data.

Issue 5: Important Requirements for the Weight-Based Oxidation-Neutralization Approach to Provide Reasonable Results

This MDAG case study has shown that weight-based interpretations of kinetic tests like humidity cells and leach columns are fraught with ambiguity and error. There is a reason why chemical interpretations with chemical equations have been based on moles rather than weight for nearly 170 years.

If reliable weight-based interpretations are desired for kinetic tests as summarized in Figure 1, there are some restrictive requirements that must be met. Benzaazoua et al. (2004) simply explained their weight-based approach is “based on certain assumptions”, but these major, unjustified assumptions were not mentioned. They are:

- Whatever reaction is occurring during the times of highest aqueous concentrations (and with the greatest effect on the oxidation-neutralization slope and CWR) must continue throughout the test. This is rarely the case.
- The only reaction occurring is oxidation of sulphides followed directly by neutralization with carbonate minerals with no solubility limitations. This is rarely the case.
- The site-specific molar-based Net Potential Ratio (NPR) from acid-base accounting (ABA) is not important to the study. Weight-based values numerically break the link between kinetic testing and ABA. This breakage of the link is rarely desired or needed, and should be avoided. Also, solid-phase pre-test weights of Ca+Mg+Mn now represent pre-test Neutralization Potential, rather than the pre-test analyses with acid titrations and/or of carbonate.
- The only solid-phase minerals and compounds containing calcium, magnesium, and manganese are fast-reacting and fast-neutralizing carbonate minerals. This is rarely the case. Moreover, this is difficult to prove, due to nugget effects in small samples and large uncertainties often revealed by inter-method mineralogic comparisons.

An easier and more reliable solution is to simply use molar units and carbonate measurements (Section 2), as has been done for over a century in general and for decades with geochemical kinetic tests.

As a final note, it is very important to remember that aqueous concentrations and ratios from kinetic tests cannot show anything reliable about what is happening inside the kinetic test when significant amounts of secondary minerals are forming, dissolving, and/or at saturation. Equilibrium and meta-equilibrium are “path independent”, so internal reactions, dissolution, and precipitation cannot be distinguished and separated when they are operative.

5. CONCLUSION

For almost 170 years, the chemical units of moles have been used to delineate and interpret chemical equations by international agreement. This was not an arbitrary decision.

This MDAG case study examines the problems that arise when humidity-cell and leach-column geochemical results are interpreted on a weight basis (such as grams or milligrams) rather than on a mole basis. This weight-based approach is sometimes referred to as an “oxidation-neutralization curve”. The problems with weight-based geochemical results are not immediately apparent, but were illustrated here.

Section 2 of this MDAG case study presented the decades-old way of interpreting ARD kinetic tests and corresponding ABA data on a mole basis, and Section 3 followed the same path using weight instead. The comparison of the two approaches showed that weight-based interpretations can be misleading and erroneous.

Section 4 summarized published weight-based data and interpretations from real humidity cells and leach columns. This showed the extent to which misleading and erroneous interpretations can be obtained from the weight-based data.

It is not clear why the weight-based approach is used when it offers no advantages and many disadvantages. It is clearly not consistent with principles of chemistry and geochemistry.

Weight-based interpretations are not appropriate for geochemical kinetic tests and their corresponding ABA. Mole-based interpretations are required, which has been followed in general for at least 170 years and, specifically for ARD, has been followed for decades. This was not an arbitrary decision.

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