

ACCELERATED HUMIDITY CELL TESTING USING HYDROGEN PEROXIDE, SIERRITA MINE, ARIZONA

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Introduction

The humidity cell test (HCT), as prescribed by ASTM D5744 (ASTM International, 2013), is the accepted standard kinetic test for verification of mine waste acid rock drainage (ARD) potential identified during screening-level static testing. The test is commonly required to assess the relative rates of the various ARD and metal leaching reactions that can occur, and to provide information on the formation of ARD over time (INAP, 2009). Typical test durations vary from a minimum of 20 weeks to a full year, or longer. However, even though the HCT is considered an accelerated weathering test, a year of testing can be insufficient for evaluating ARD related processes in samples that have known ARD potential. The onset of acidic conditions will generally not occur until acid-neutralizing mineral phases (e.g., calcite) are depleted or until sulfide oxidation rates greatly exceed acid neutralization rates. Time to depletion in a humidity cell can range from weeks to decades, principally dependent on the relative abundances of acid generating and neutralizing phases and their availability to the lixiviant used in the HCT protocol.

In this study, a hydrogen peroxide (H₂O₂) based lixiviant was used to induce accelerated sulfide oxidation and corresponding depletion of neutralization potential (NP) in five waste rock samples from the Freeport-McMoRan Inc. Sierrita mine near Tucson, Arizona. The samples remained at neutral pH after 60 weeks of testing using the standard method, although each of the samples were identified as potentially acid generating (PAG) during static evaluation, with net acid generation (NAG) test (AMIRA, 2002) and pH values ranging from 2.7 to 3.2. Depletion calculations for the five humidity cells indicate that depletion times are on the order of decades. Therefore, an accelerated sulfide oxidation test approach was chosen, with the following objectives:

- To verify the long term ARD potential of each sample
- To evaluate sulfide oxidation and acid neutralization rates
- To assess water quality under acidic conditions

Methodology

During the first 60 weeks of testing, the five humidity cell samples (and one blank cell) were subjected to the standard test method for laboratory weathering of solid materials using humidity cells (ASTM International, 2013), consisting of the following elements:

- Humidity cells filled with 1.0 kg of sample material passing 0.25 inch.
- Weekly leaching of samples after alternating 3-day wet and dry cycles, at 1:1 water to rock ratio (1000 ml).
- Collection of leachate for chemical analysis:
 - Weekly evaluation for indicator parameters: pH, oxidation/reduction potential, conductivity, acidity, alkalinity, iron and sulfate.
 - Analysis for an extended parameter suite, including trace metals and all constituents with applicable numeric water quality standards, at weeks 0, 1, 2, 3, 4, 5, and every 5 weeks thereafter.

All tests were conducted at Inter-Mountain Laboratories, Inc. (IML) in Sheridan, Wyoming.

The five samples comprised felsic intrusive and volcanic lithologies, including andesite, rhyolite, granite and quartz monzonite. Sulfide sulfur concentrations ranged from 0.3 to 0.9 weight percent (wt%). Reflected-light thin section petrography for the selected waste materials indicates pyrite as the predominant sulfide mineral, with occasional trace chalcopyrite. Static test results for the five samples are summarized in Table 1.

Table 1. Static Test Results

HCT ID	NAG pH	Sulfide Sulfur	Acid Generating Potential (AGP)	Acid Neutralizing Potential (ANP)	Net Neutralizing Potential (NNP)	Neutralization Potential Ratio (NPR)
-	-	wt%	$T CaCO_3/kT$	$T CaCO_3/kT$	$T CaCO_3/kT$	-
1	2.9	0.84	26.2	6.8	-19.4	0.26
2	2.9	0.55	17.3	9	-8.3	0.52
3	3.2	0.33	10.3	8.5	-1.8	0.83
4	2.7	0.51	16	11.5	-4.5	0.72
5	2.9	0.9	28.1	5.6	-22.5	0.2

After 59 weeks of testing, all five samples maintained a circumneutral pH, and showed no sign of nearing NP depletion (Figure 1).

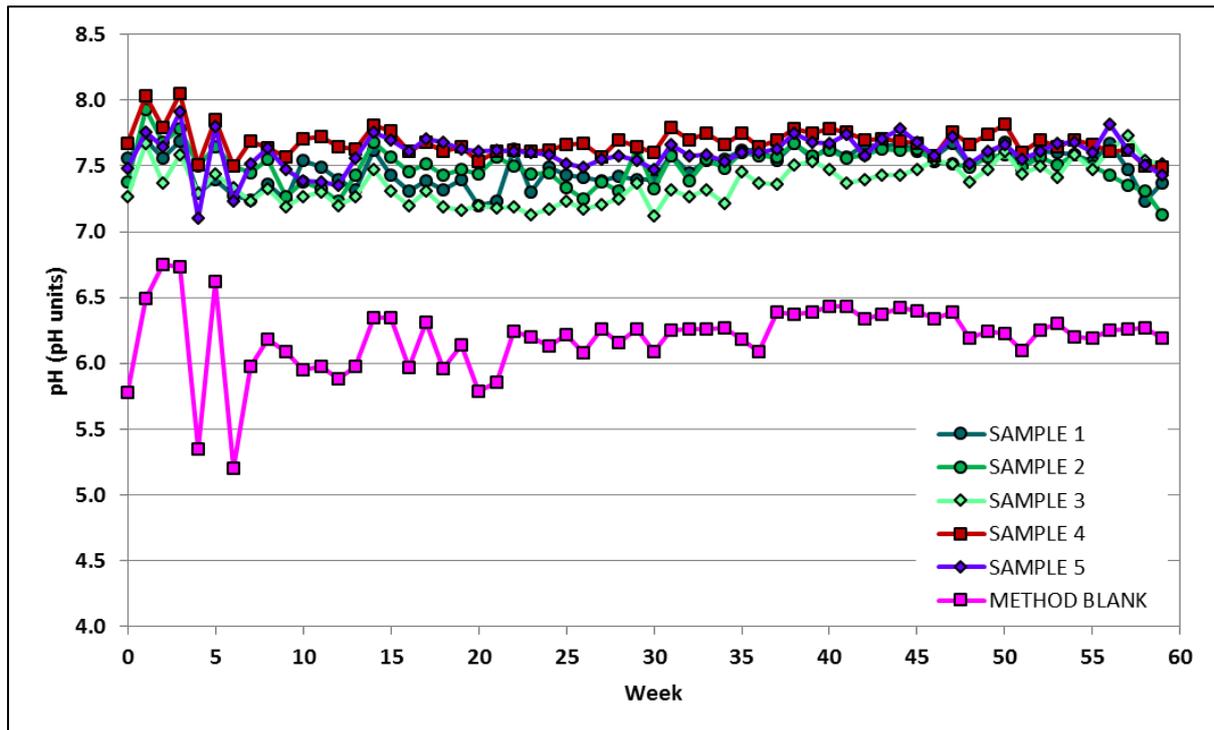


Figure 1. Leachate pH for weeks 1 to 59

To accelerate sulphide oxidation and depletion of NP, at 60 weeks, the distilled water lixiviant used for cell leaching was amended with 15% H₂O₂, following the NAG test procedure described in AMIRA (2002). The standard NAG procedure was followed because the lixiviant H₂O₂ dosage required to oxidize waste sample sulfide sulfur is difficult to calculate given that H₂O₂ is subject to rapid exothermic decomposition catalyzed by transition metals released during oxidation of sulfide minerals (Stewart et al., 2003). During application of the H₂O₂ lixiviant, IML observed temperature increases and vigorous effervescence. Although, the recommended NAG procedure dosage was initially applied, the program was designed to be adaptive based on the test results. As such, the dosage could be varied as needed if depletion of NP occurred either too rapidly or not fast enough, relative to program objectives.

Beyond the addition of H₂O₂, testing conditions were not varied except that the frequency of analysis of the extended parameter suite was increased during the early stages (extended analyses were collected in weeks 60, 61, 62, 63, 64 and 65, after which frequency was decreased to every five weeks) and a new blank was set up to account for the H₂O₂ lixiviant.

Results and Discussion

Results of the accelerated leach program through week 63 (extended suite) and 64 (short suite) are presented for pH, sulfate, calcium and predominant transition metals (plus aluminum) in Figures 2a, 2b, 2c, and 2d, respectively.

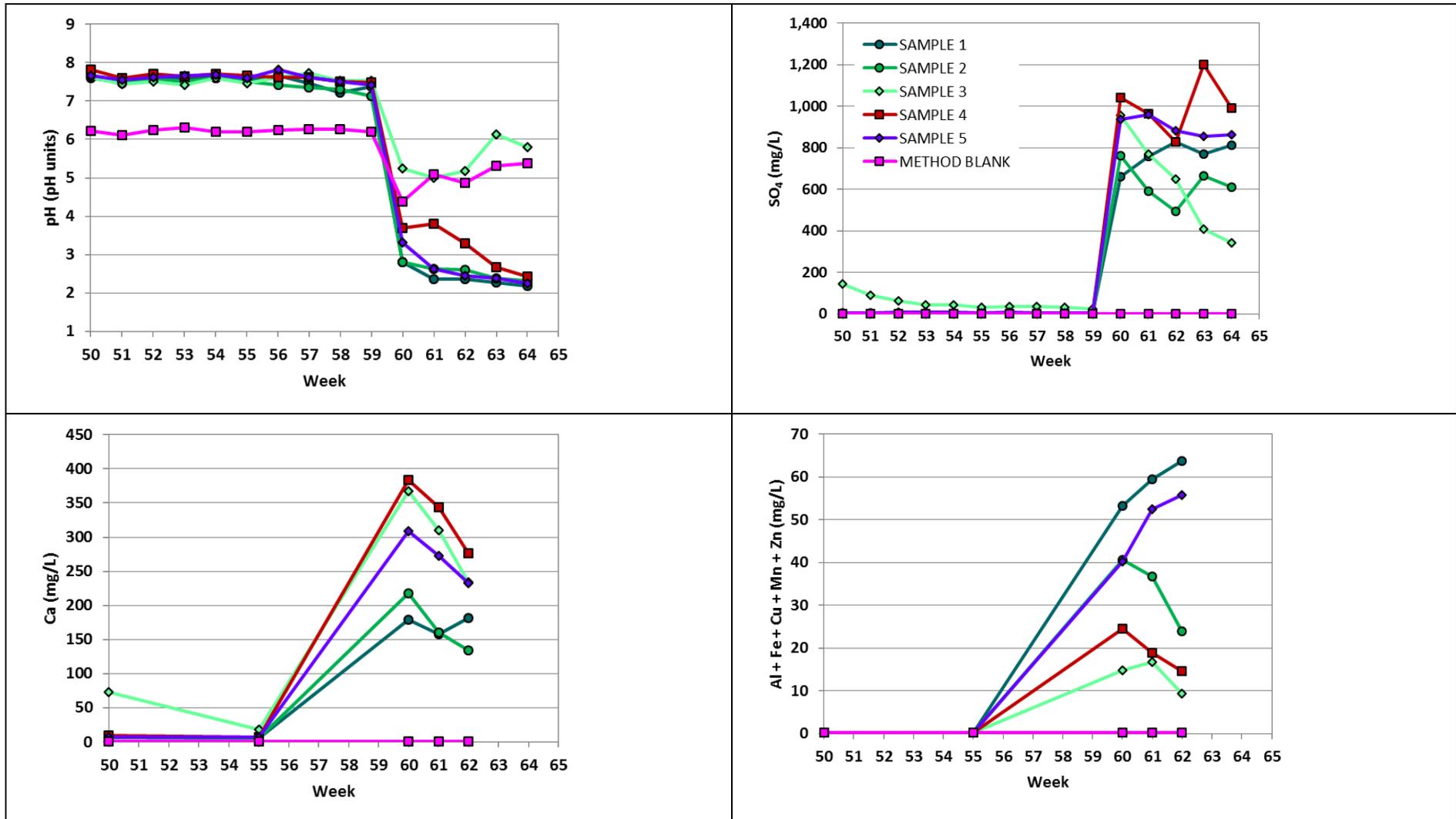
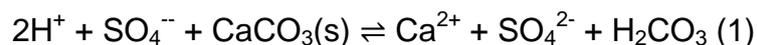


Figure 2. Leachate chemistry after five weeks of accelerated testing

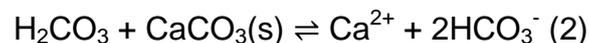
The figures indicate that all HCTs except sample 3, which had the lowest sulphide sulphur content of 0.33 wt% and highest NPR, reached acidic pH during the first leach cycle. Acidic leachate pH values are within the range of predicted static NAG pH values. The sulfate, calcium and metal concentration trends indicate that pyrite oxidation and neutralization are actively occurring. Given that the HCTs remained at circumneutral pH for 60 weeks, the sudden onset of acid generating conditions suggests that either all NP was quickly depleted or that acidic generation rates are much higher than acid neutralization rates. If the NP in acidic HCTs is completely consumed, the cells can be terminated, and a lower initial H₂O₂ dosage would have been appropriate. If not, the HCTs can provide useful information about the rates of ARD onset under accelerated test conditions, and competing oxidation and depletion rates over time.

Depletion of Neutralization Potential

Depletion calculations were conducted to determine the extent to which the H₂O₂ lixiviant has consumed remaining sample NP for each leach cycle. NP depletion in HCTs is typically measured via a two-step process (MEND, 2009). First, the baseline or 'theoretical' NP consumption as a direct result of pyrite oxidation is measured based on sulfate production according to the following reaction:



The above is valid for solutions below the carbonic acid-bicarbonate crossover pH (~6). Above this pH, additional NP is depleted as a result of carbonic acid conversion to bicarbonate:



These reactions reasonably describe overall calcium and sulfate release in humidity cells as long as there are no other mineral phases consuming or releasing calcium and/or sulfate. However, petrographic analysis indicates that some of the waste rock samples have considerable soluble gypsum (up to 5 wt%). To help assess whether pyrite oxidation and/or gypsum dissolution are responsible for the observed sulfate concentration trends, one can look at calcium/sulfate molar ratios over time, which reveal the stoichiometry of the reactions occurring in the humidity cells (Figure 3).

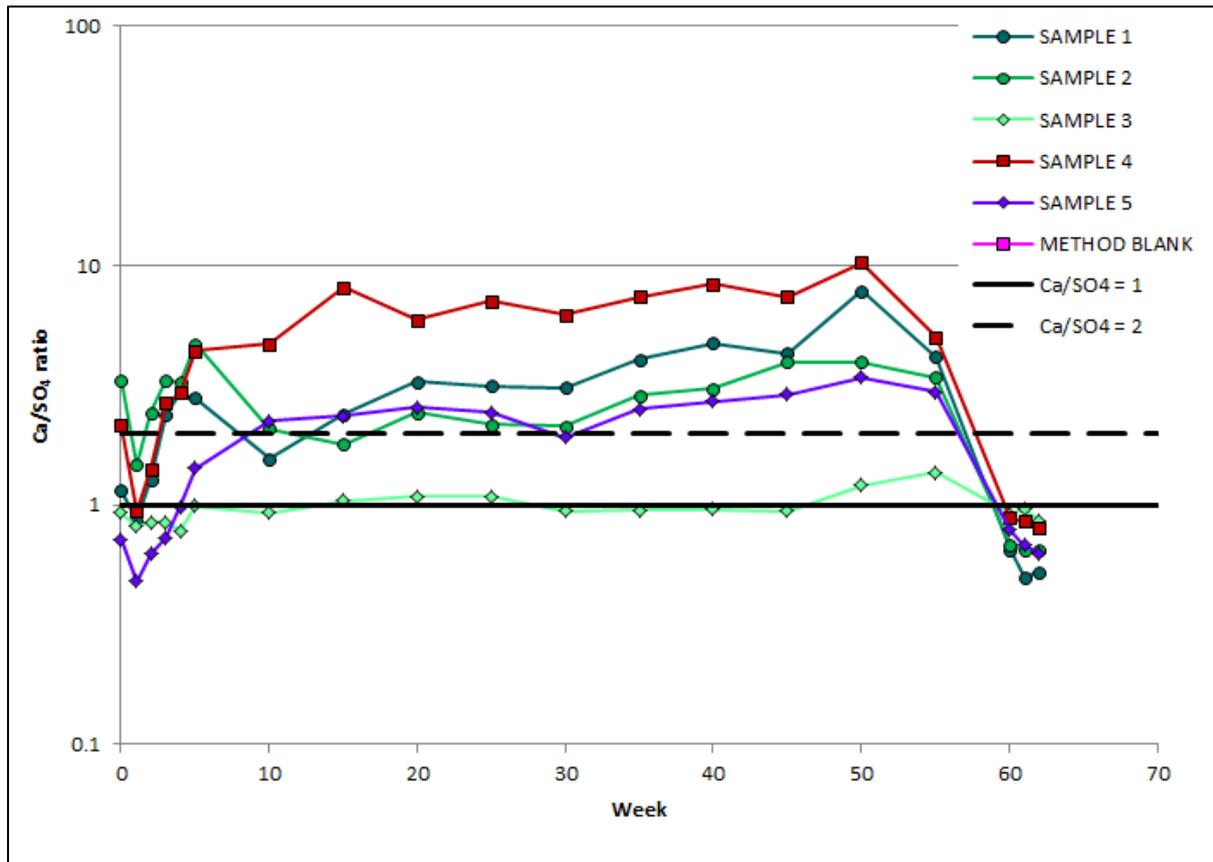


Figure 3. Molar Ca/SO₄ ratios over time

The stoichiometric ratios indicated by reactions (1) and (2), as well as for simple gypsum dissolution are as follows:

- Pyrite oxidation below pH 6: Ca/SO₄ = 1
- Pyrite oxidation above pH 6: Ca/SO₄ = 2
- Gypsum dissolution: Ca/SO₄ = 1

During the initial 60 weeks of testing, all HCTs except sample 3 plot mostly at or above the Ca/SO₄ = 2 line, consistent with pyrite oxidation under neutral conditions, although ratios are as high as 10 and there is considerable fluctuation during the flushing period. Sample 3 shows high calcium and sulfate release and a Ca/SO₄ ratio near 1 during the first 60 weeks. Transmitted-light thin section petrography indicates 5 wt% gypsum in this sample (none was detected by x-ray diffraction or petrographic analysis in the remaining four samples). The molar ratio for sample 3 is consistent with gypsum dissolution.

With the introduction of the H₂O₂ lixiviant at week 60 and the corresponding drop in leachate pH below 6 for all five samples, each HCT displays a Ca/SO₄ ratio from 0.5 to 0.8, indicating the HCTs are now releasing more molar sulfate than calcium. Four of the five samples have little or no gypsum; their molar ratios indicate a shift to sulfide oxidation at pH below 6. Furthermore, in these samples, rates of sulfide oxidation and acid production are outpacing rates of acid neutralization.

Figure 4 shows NP depletion calculations for the five HCTs. The figure illustrates how depletion can be over-estimated by incorrectly assuming that sulfate release is tied to sulfide oxidation when it is, in fact, a function of gypsum dissolution (sample 3). In the latter case, accounting for gypsum dissolution will shift the depletion line for up, as illustrated with the arrow.

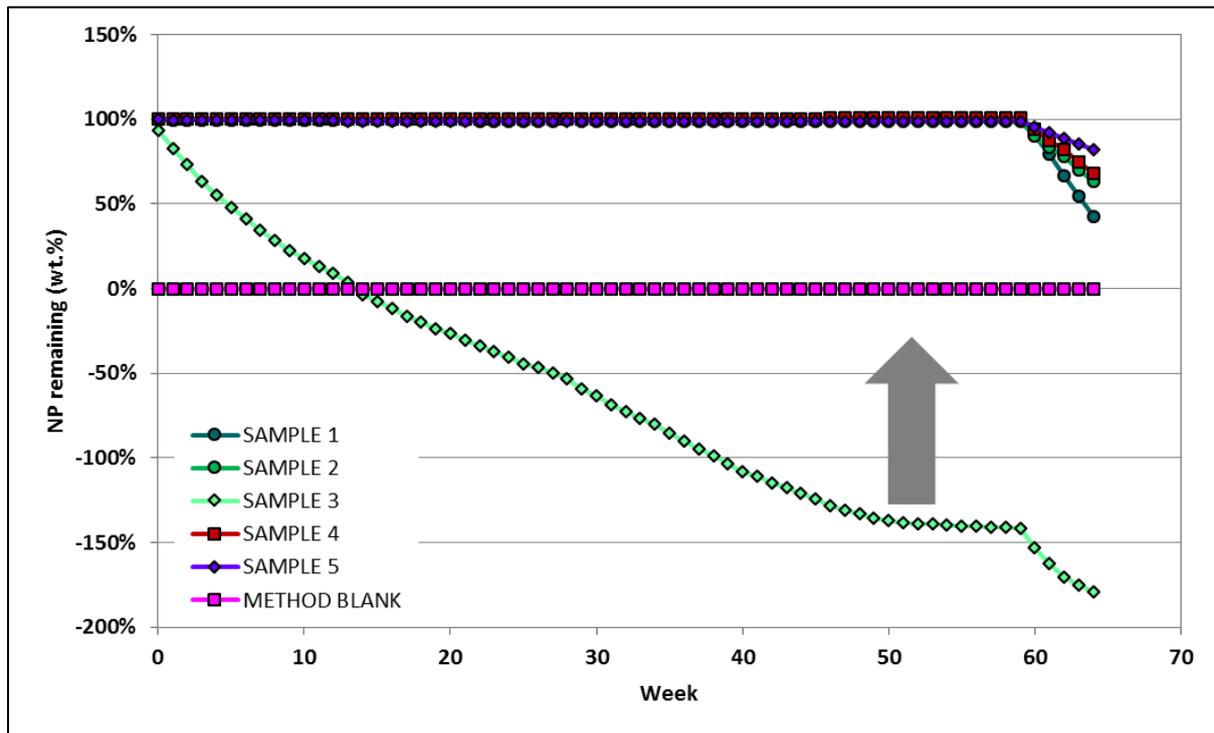
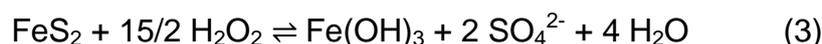


Figure 4. Calculated NP depletion rates

The depletion rates indicate that, under the accelerated conditions generated by the H_2O_2 , full depletion of NP will occur between weeks 70 and 80 for four of the five samples, and longer for sample 3 (between weeks 100 and 110). Furthermore, the depletion calculations indicate that the onset of ARD is not dependent on complete removal of NP in the accelerated test. This is discussed in more detail in the acid production and consumption section.

Peroxide Efficiency

H_2O_2 oxidizes pyrite according to the following reaction (Weber et al. 2005):



Reaction stoichiometry implies that 7.5 moles of H_2O_2 are required to oxidize one mole of pyrite (or two moles of sulfur). With a density of 1.45 g/cm^3 for H_2O_2 , a 1000 mL, 15% H_2O_2 lixiviant is sufficient to oxidize 100 grams of pyrite (10 wt%) or 53 grams of sulfur (5.3 wt%) in a 1 kg sample mass, assuming that sulfide sulfur represents the only oxidizable species. Initial sulfide sulfur concentrations in the five HCT samples ranged from 0.3 to 0.9 wt% (Table 1). Sulfide sulfur depletion percentages are given in Figure 5.

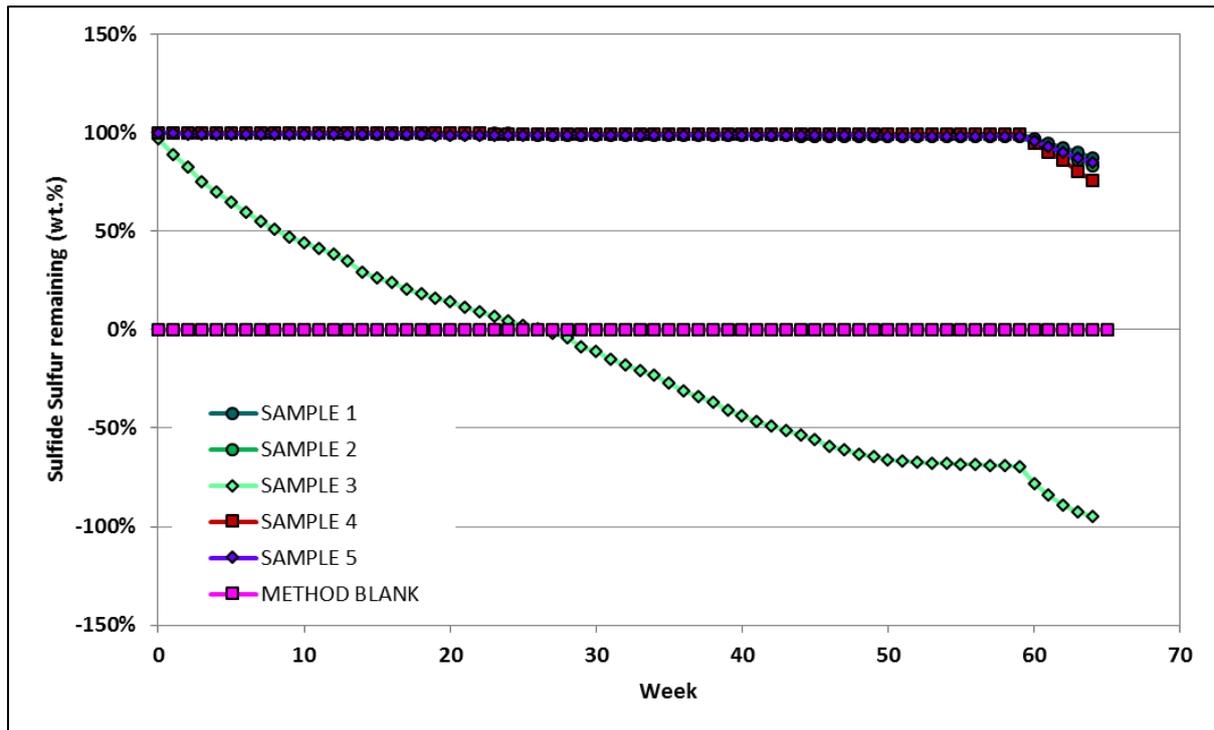


Figure 5. Sulfide sulfur depletion

After five leach cycles, the H_2O_2 lixiviant removed 13 to 24% of the initial pyritic sulfur, representing a total of 0.23 to 0.65 g pyrite per leach cycle. This represents 0.2 to 0.6% efficiency, indicating that 99.4 to 99.8% of the H_2O_2 is not involved in the sulfide oxidation reaction. Peroxide reactivity is likely limited by the available surface area of sulfide minerals in the waste rock sample.

Acid Production and Consumption Rates

It is useful to measure acid production and consumption rates so that the accelerated laboratory tests might be scaled to long term field conditions. Weekly sulfate production rates can be converted to sulfide oxidation rates, using the following simple rate law for mineral dissolution:

$$r_k = A_S k_+ \left(1 - \frac{Q}{K}\right)$$

The rate law (Bethke, 2008) gives the sulfide oxidation rate, r_k (mol/sec) in terms of the mineral surface area (A_S , m^2), rate constant (k_+ , $mol/m^2 \cdot sec$) and distance from saturation ($1 - Q/K$). Additionally, pyrite oxidation rate studies indicate that oxygen, pH and iron (a proxy for acidophilic bacteria) act as significant catalysts to the overall rate (Singer and Stumm, 1970).

The sulfide oxidation rate can be calculated directly from the long term sulfate production rate, by assuming that two moles of sulfate are generated from dissolution of one mole of pyrite. Mineral surface areas can be calculated by

multiplying sulfide sulfur concentrations by bulk surface areas (the latter obtained from HCT grain size distributions).

Average calculated sulfide oxidation rate constants for the five HCTs range from $1.5e^{-7}$ to $1.3e^{-5}$ mol/m²·sec (depending on whether one assumes that the oxidation occurs primarily during the two hour leach cycle, or over the course of an entire test week). The rate constant is significantly higher than published rate values (e.g., Nordstrom and Alpers, 2004) for the microbially mediated oxidation of pyrite by ferric iron ($1e^{-8}$ to $2e^{-8}$ mol/m²·sec), reflecting the efficacy of the peroxide accelerant.

In similar fashion, NP depletion rates can be calculated using weekly calcium production rates, based on the stoichiometry of reaction 1. Final calculated rate constants are an order of magnitude lower than those calculated for sulfide oxidation, and range from $8.3e^{-8}$ to $9.7e^{-6}$ mol/m² sec. This explains why the HCTs go acidic immediately, prior to NP depletion; acid consumption is unable to keep pace with acid production.

Once acid production and consumption rates have been calculated for non-accelerated and accelerated sulfide oxidation, they can be contrasted to rates observed in the field (e.g., Nordstrom and Alpers, 1999), so that weekly HCT loading rates can be adjusted to long term field scale loading rates, for purposes of estimating long term water quality.

Conclusions

A hydrogen peroxide based lixiviant was used to induce accelerated sulfide oxidation and corresponding NP depletion in five waste rock humidity cell samples from the Sierrita mine near Tucson, Arizona. Acidic conditions were quickly observed in the cells as sulfide oxidation rates overwhelmed NP depletion rates.

The use of peroxide in kinetic testing offers the following benefits:

- Provides an opportunity to observe the geochemical behavior of waste materials under acidic conditions in humidity cells that remain neutral under standard HCT test conditions.
- Provides a more realistic estimate of 'worst-case' water quality than a simple NAG test, given the more realistic water to rock ratio (1:1) and grain size distribution of the HCT.
- Allows for the development of more realistic long term water quality estimates in samples in a realistic test timeframe.

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