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Pyrite Oxidation in Well-Constrained Humidity Cell Tests

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ABSTRACT

Owing to its significance in the formation of acid mine drainage, the rate of pyrite oxidation has received persistent attention for many years. The vast majority of experimental rate measurements have been made under saturated (liquid) conditions (no gas phase), and a few are available for the reaction in vapor-only (humid oxygenated air) conditions. However, in field settings, either naturally occurring or associated with mineral extraction activity, liquid+vapor conditions with moist air and water present are perhaps the most common.

As part of environmental permitting programs, the mineral industry has come to rely on empirical measurements of pyrite (and other sulfide mineral) reaction rates using the Humidity Cell Test (HCT). This laboratory test exposes crushed mine rock samples to liquid+vapor water in the presence of atmospheric oxygen, provided in excess. The HCT is a standardized test method that has been evaluated for reproducibility, but limited effort has been made to assess rates, specifically pyrite, relative to existing geochemical literature.

In the present work, a series of well-constrained HCT experiments have been and are being conducted using simple mineral assemblages, with known mineral grain sizes/reactive surface area. Tests have been conducted using pyrite + quartz and pyrite + quartz + calcite. Additional testing has been conducted using two separate pyrite grain sizes. Though difficult to constrain, the proportion of liquid to vapor water in the system has also been investigated by altering the established procedure to increase the vapor relative to liquid phase (vapor-enhanced).

Results to date indicate that the rate of pyrite oxidation slows with time. Initial rates are significantly faster than in liquid-only experiments (Williamson and Rimstidt, 1994), and diminish with time. Results were consistent with trends observed in vapor-only laboratory experiments. Terminal, near steady-state rates of pyrite oxidation approached the same value for all test conditions, and were consistent with well-stirred liquid-only initial rates. Thus, hypothetical retention of reaction products that might explain the both the reduction in rate and the similarity among tests seems improbably. Terminal rates showed no relationship to rate of water supply (flushing). Rates scaled directly with pyrite reactive surface area, but sulfate production (concentration) did not scale directly with grainsize.

Keywords: pyrite oxidation, HCT, kinetics

INTRODUCTION

Owing to its significance in the formation of acid mine drainage, the rate of pyrite oxidation has received persistent attention for many years. Understanding has grown from a characterization of oxygen, temperature, sulfide mineralogy and bacterial action as reaction drivers of pyrite oxidation (Caruccio, 1968) through development of quantitative rate expressions that identify the significance of reactive surface area of pyrite. Currently, rate expressions for pyrite oxidation have been developed for water-saturated conditions (Williamson and Rimstidt, 1994) and water vapor-only conditions (Williamson, 2013). However, in field settings, either naturally occurring or associated with mineral extraction activity, liquid+vapor water conditions are the most common.

As part of environmental permitting and mine waste management programs, the mineral industry has come to rely on empirical measurements of pyrite (and other sulfide mineral) reaction rates using the Humidity Cell Test (HCT). This laboratory test exposes prepared mine rock samples to liquid+vapor water in the presence of atmospheric oxygen, both provided in excess. Initially, the HCT was thought to be an accelerated weathering test, as it was thought that the procedure removed reaction products from the test cell that would otherwise impede reaction progress (Sobek, et al, 1978). The HCT is a standardized test method (ASTM, 2012) that has been evaluated for reproducibility, but limited effort has been made to assess reaction rates relative to existing geochemical literature.

Only a few studies have tried to quantify the rate of pyrite oxidation in a two-phase water system (liquid+vapor). Of these, only a limited number of studies have been conducted for which the reactive surface area of pyrite is known or estimated. Lappakko and Antonson (2006) report rates of pyrite oxidation present in Duluth Complex rock matrices determined in an HCT; Watzlaff and Hammack (1990) made measurements in a vertical column with continual air flow and a weekly leach; and Leon, et al (2004) present results of batch-style tests with limited amounts of liquid water present in an otherwise humid environment without forced airflow. Data from other two-phase studies are reported in the literature, but reactive surface area and/or grainsize is either unknown or beyond estimation.

The worldwide database of two-phase (presence of moist air plus liquid water) results is overwhelmingly for mine rock using the HCT. These materials often represent complex mineralogy and virtually never report reactive surface area for pyrite, although the test procedure itself does restrict the grain size of the material with which the cell is charged. Thus, it is impossible to reliably compare and contrast pyrite oxidation rates with fundamental geochemical understanding, or compare other tests on various mine rock samples. The purpose of the present study is to employ a simplifying approach to begin to study simple systems that will eventually lead to the defensible interpretation of specific reactions in humidity cell tests and support reliable predictive modeling.

METHODOLOGY

In the present work, a series of well-constrained HCT experiments have been conducted using simple mineral assemblages, with known mineral grain sizes/reactive surface area. Tests have been conducted using test cell charges comprised of pyrite (py) + quartz (qtz) and pyrite + quartz + calcite (cal). Testing has been conducted using two separate pyrite grain sizes. Though difficult to constrain or quantify, the effect proportion of liquid to vapor water in the system as well as rinsing has also been investigated by altering the established HCT procedure (ASTM, 2012) to increase the vapor relative to liquid phase (vapor-enhanced).

Approach

In contrast to the inherently more complex situation when testing poly-mineralic materials (i.e. mine rock, tailings), with a restricted but wide range in grainsize (with unknown reactive surface area), and fixed rate of water supply, the present work has taken a decidedly reductionist approach. The study has utilized a simple mineralogic composition (pyrite, calcite and quartz) with restricted grainsize, known reactive surface area. Two distinct values of reactive surface area for pyrite were examined and the rate of water supply was varied by a factor of about two. Table 1 summarizes the four tests currently being conducted, and provides a statement of test objective for each. All tests were run at 22 ± 1.5 C.

Table 1 Summary of experimental conditions.

Test Cell ID	**Cell Charge (gm)**			**Flushing Frequency**	**Test Objective**
	Pyrite	*Calcite*	*Quartz****		
HCT-1	100*	0	900	Weekly	Measure of pyrite oxidation rate at standard conditions
HCT-2	40*	200	760	Weekly	Contrasted with HCT-1, measure of pyrite oxidation rate in carbonate buffered solution, at conventional 3:1 ratio of neutralization to acid potential
HCT-3	100**	0	900	Weekly	Contrasted with HCT-1, assessment of pyrite oxidation rate at different grain size/surface area
HCT-4	100*	0	900	Bi-Weekly	Contrasted with HCT-1, assessment of pyrite oxidation rate at lower flushing frequency/rate
HCT-5	0	0	1000	Weekly	Blank

* Grain size = 0.4 mm (0.297 mm < sample < 0.5 mm) = 70 m^2/gm (Foust et al., 1980)

** Grain size = 2.4 mm (2 mm < sample < 2.83 mm) = 19 m^2/gm

*** Grain size = 0.85 mm (0.85 mm < 93.6% < 1 mm sieve)

Materials

The pure pyrite (FeS_2) used in this study was sourced in Peru, and is the same material used by Williamson and Rimstidt (1994) and Jerz and Rimstidt (2004). The sieved pyrite was washed with alcohol to remove fine-grained material as much as possible. Pure calcite ($CaCO_3$) was obtained from Ward's Scientific (optically clear; variety Iceland Spar) and was sieved to collect the 0.5 mm fraction as described above for pyrite. Silica sand (SiO_2) was purchased commercially, sourced in Wedron, Illinois, with a reported assay of 99.7% SiO_2 and less than 0.01% calcite. Mineral mixtures were loaded carefully into the test cells to avoid any gravity separation effects.

RESULTS AND DISCUSSION

Analytical Results

Analytical results for test cells' leachate over time are presented in Figures 1 to 4. Figure 1 illustrates the mass of water retained by each cell following the leach cycle. Of particular note are the results for HCT-4, which was only rinsed bi-weekly, showing the cell essentially drying out between leaching. Other cells display a loss of entrained water, but clearly maintain the presence of liquid water (not dried out) and moist vapor during the experiment.

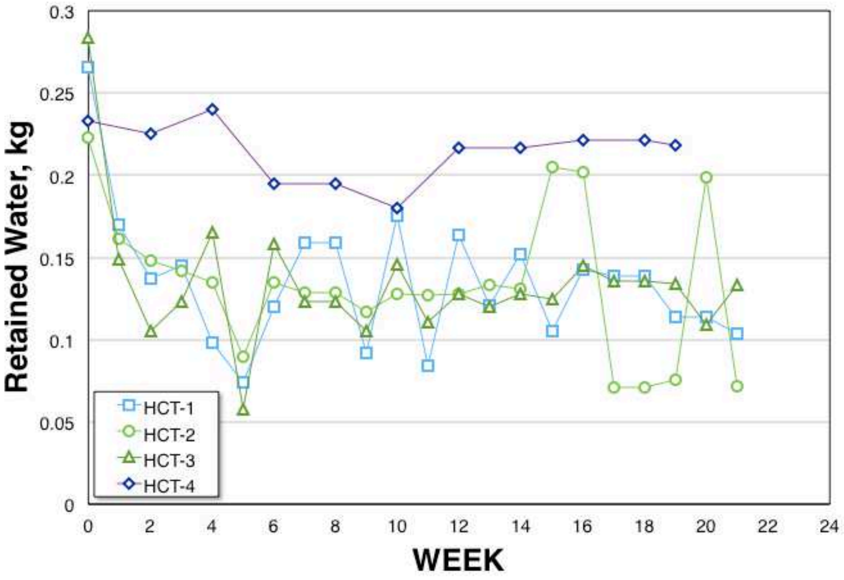


Figure 1 Cell water retention over time

Figure 2 is a graph of pH over time, and shows an expected decrease for two of three py+qtz cells. HCT-1 and HCT-4 (same pyrite grainsize, HCT-4 flushed bi-weekly) begin an immediate, but not instantaneous drop, reaching a value of 4 after 24 weeks. Oddly, HCT-3 (larger pyrite grainsize) remained generally steady for about 18 weeks, and then became more erratic, and trending toward lower values. As expected, the test containing calcite remained near neutral, but significantly below a value of about 8.2 that would be expected for qtz+cc without pyrite. The blank cell maintained a pH ranging from 5.7 to 6.3 throughout.

Figure 3 present results for sulfate, which shows an immediate and significant decrease over the first four weeks. All tests are generally steady after six weeks. Iron (Figure 4) shows an increase in tests where pH decreases. Sulfate and iron analyses for the blank cell produced were determined to be zero throughout.

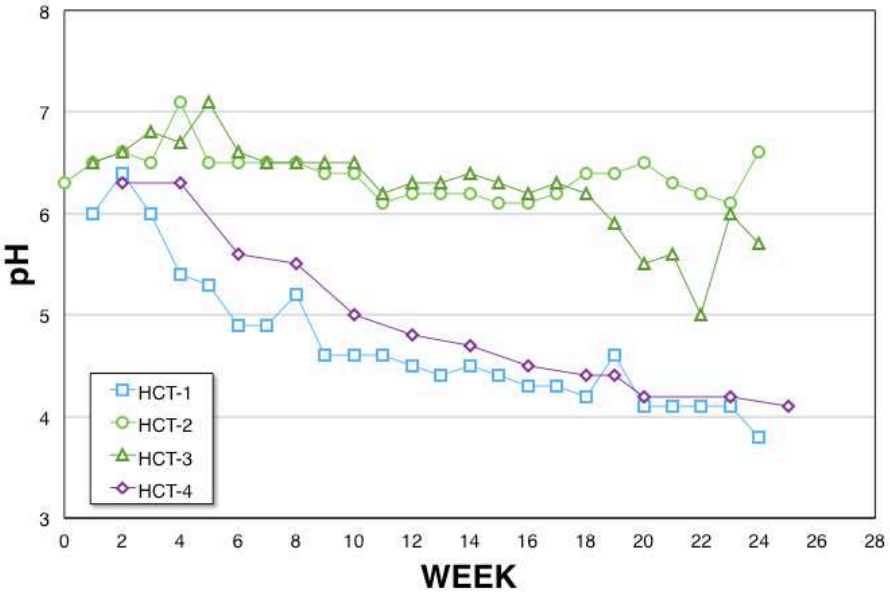


Figure 2 Leachate pH variation over time

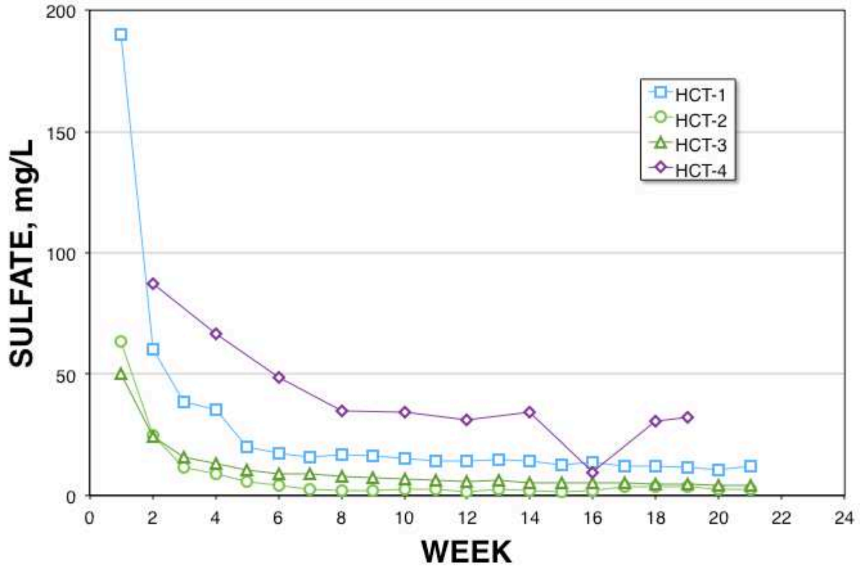


Figure 3 Leachate sulfate concentrations over time

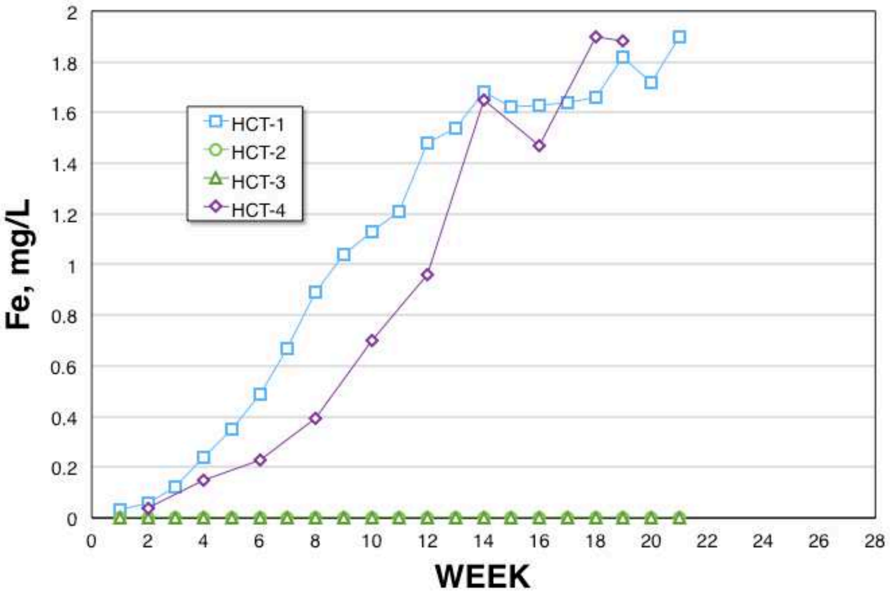


Figure 4 Leachate iron concentrations over time

Discussion

As expected, in py+qtz experiments, acidity is immediately produced by pyrite oxidation and the pH of leachate solutions begins to drop. However, despite the basic absence of acid neutralizing minerals (calcite), the pH decreases more gradually than might be expected. One py+qtz experiment, with larger grainsize pyrite, maintained near-neutral pH for about 18 weeks before it displayed a (slight) trend toward acidic conditions.

Consistent with common convention of reporting the results of HCT work, Figure 5 is a graph of the cumulative sulfate production in each test cell. In this case the sulfate production has been normalized to the mass of pyrite in the cell and not the total mass in the cell (1 kg). If the end-point of each test is used to calculate the overall rate of pyrite oxidation, the bi-weekly rinse test (HCT-4) produces less sulfate than the base case (HCT-1) and, therefore, might be interpreted to represent a slower rate of reaction. Similarly, the larger grainsize pyrite test (HCT-3) would also appear slower than the base case. However, a more appropriate basis upon which to compare rates of reaction, both between tests and with established literature is that of moles of pyrite destroyed, per meter squared, per second (mol py/m^2/s; Williamson and Rimstidt, 1994, Lappakko and Antonson, 2006), and can be calculated for each point (week) during the test.

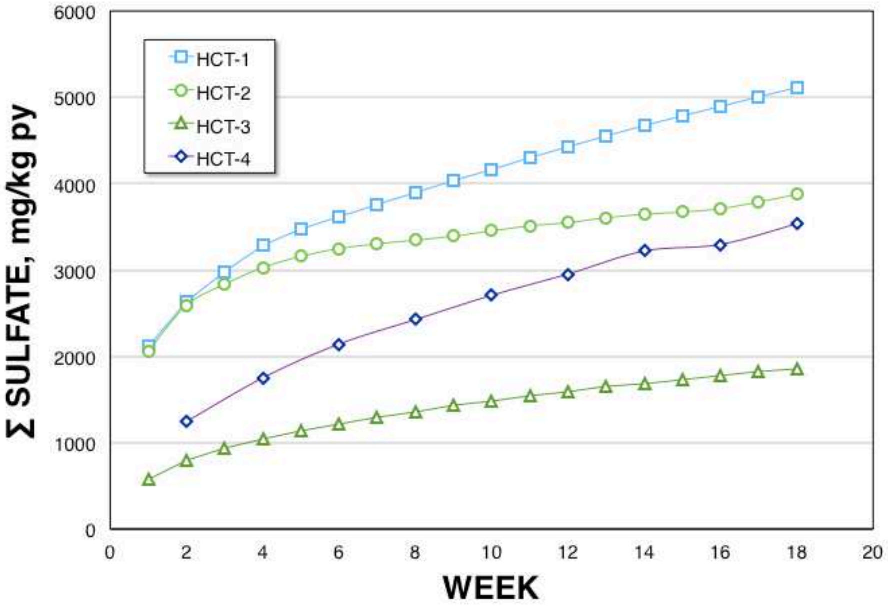


Figure 5 Cumulative sulfate production over time

When data are recast to mol py/m^2/s, calculated for each period of measurement (either one week or two), the rates of pyrite oxidation show very consistent trends. Figure 6 illustrates the pyrite oxidation rates on this basis. Owing to the simple mineralogical composition and texture of the experiments, the data plot in a remarkably smooth fashion. All but one experiment (HCT-4) shows a relatively rapid initial rate that rapidly diminishes with time. All experiments converge to essentially the same fundamental rate. Thus, the presence of calcite and bi-weekly flushing ultimately appear to have little effect on the rate of pyrite oxidation. The agreement between cells with different grainsizes, confirms that the fundamental link between rate and reactive surface area applies under HCT conditions.

The observed rapid decrease in the rate of reaction (Figure 6) is consistent with literature for the oxidation of pyrite in vapor-only conditions. Over the course of many individual experiments, Jerz and Rimstidt (2004) observed the same basic trend. Figure 7 illustrates some typical data from one of their experiments. Like the rates in the current study, the initial rate is relatively fast, and rapidly diminishes to near steady rates with time. Jerz and Rimstidt (2004) attributed this observation to the build up of an adsorbed water layer that restricted oxygen transfer to the mineral surface via diffusion. Their estimates of the amount of pyrite destroyed did not lead to a conclusion of iron precipitate armoring of the pyrite grains. Such an effect may not apply to the current results, as the HCT provides for weekly rinsing However, a similar passivation may occur in HCT work as a result of armouring by weathering products (retention of iron) or a change in electrochemical properties of the pyrite itself (Williamson and Rimstidt, 1994). Although currently unavailable, on-going microscopic analyses intend to address these possibilities.

In the present experiments, each retained iron. This is shown clearly in Figure 4 for HCT-2 and HCT-3. Although the remaining two cells discharged iron, it was less than the stoichiometric amount expected from consideration of sulfate release. Thus, armoring by iron precipitates might be anticipated. However, in comparison with literature reports for pyrite oxidation in well-stirred, liquid-only experiments, such armoring seems unlikely as reaction products are rapidly swept form the mineral surface.

Figure 8 illustrates the rate of reaction in the present test cells as a function of the pH, for each week. As described above, the rate drops rapidly and, in some cases, the pH decreases. The figure also shows the rate of reaction according to rate laws for liquid-only experiments (solid line; Williamson and Rimstidt, 1994) and for vapor-only rate laws for 100% relative humidity (Williamson, 2013). As shown, the present rates, over time, approach the rates for well-stirred liquid-only rates, (line for Williamson and Rimstidt, 1994 in Figure 8) where accumulation of iron precipitates is limited, to non-existent. Thus, the slowing of rates in the present test cells, despite retention of iron, does not appear to be explained by the accumulation of iron precipitates.

Lappakko and Antonson (2006) present a comparison of surface area corrected pyrite oxidation rates in their HCT cells with the rate laws of Williamson and Rimstidt (1994) and likewise conclude that there is close agreement, although the comparison is less favorable than the present cells. This difference is likely to be related to the great, but expected, difficulty in estimating reactive surface area for their clearly more complex test cell charges (rock).

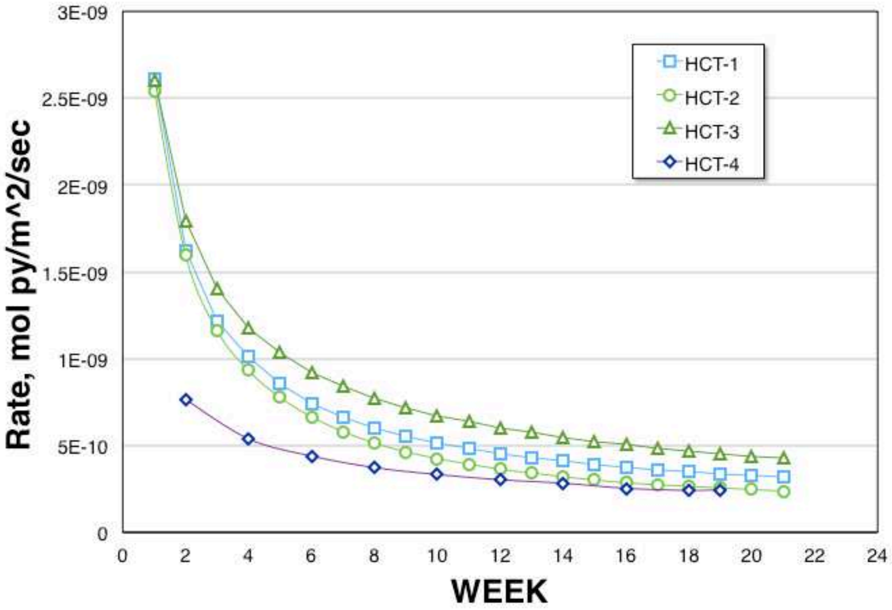
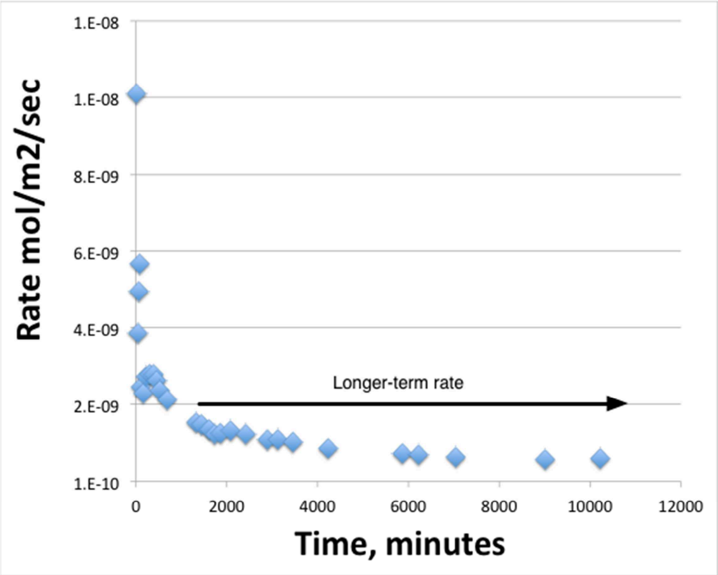


Figure 6 Rate of pyrite oxidation over time



Jerz and Rimstidt (2004)

Figure 7 Rate of pyrite oxidation over time in vapour-only experiments

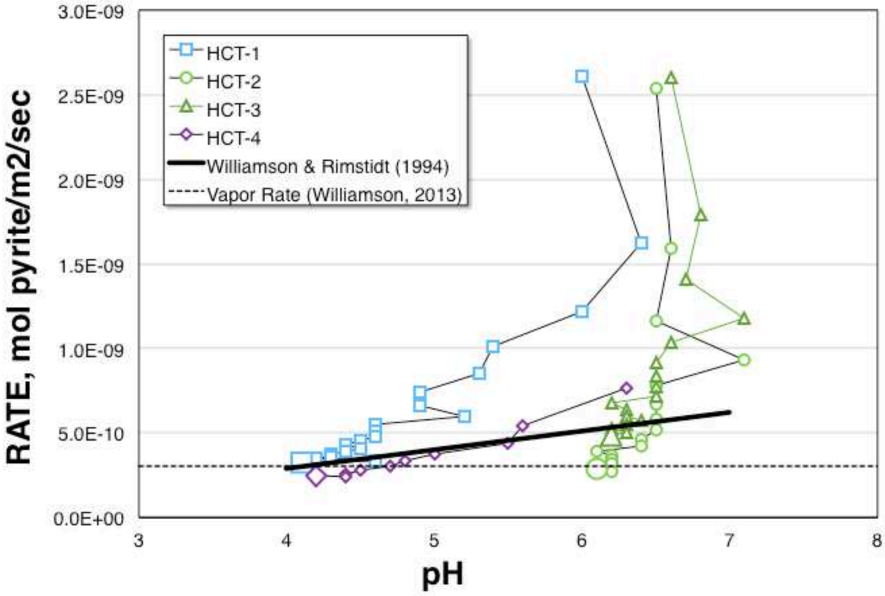


Figure 8 Rate of pyrite oxidation over time

CONCLUSION

The rate of pyrite oxidation in HCT liquid+vapor conditions, with routine flushing, is in close agreement with literature rates of reaction in liquid-only conditions and for vapor-only 100%

relative humidity. Although there is some thought that HCTs might retard the rate of reaction due to the retention of reaction products, it did not appear to be appreciable in the present test cells. There was only very limited difference in observed rate when pH was buffered by the presence of calcite, or for cells with pyrite of different reactive surface area, or indeed the rate of flushing.

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REFERENCES

ASTM (2012) Standard Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell. *American Society for Testing and Materials.* Method D5744 – 12.

Caruccio 1968 An evaluation of factors affecting acid mine drainage production and ground water interactions in selected areas of western Pennsylvania. In *Proceedings of the Second Symposium on Coal Mine Drainage Research.* Bituminous Coal Research Inc. Monroeville, Pennsylvania.

Hammack, R. W. and G. R. Watzlaf (1990). The effect of oxygen on pyrite oxidation. Proceedings of the 1990 Mining and Reclamation Conference and Exhibition.

Jerz, J. and J. D. Rimstidt (2004). Pyrite oxidation in moist air. *Geochimica et Cosmochimica Acta*, **68**: 701-714.

Lapakko, K. and D. A. Antonson (2006). Pyrite oxidation rates from humidity cell testing of greenstone rock. *Seventh International Conference on Acid Rock Drainage*, St. Louis, Missouri, USA, American Society of Mining and Reclamation.

León, E. A., et al. (2004). Weathering of sulphide minerals at circum-neutral-pH in semi-arid/arid environments: influence of water content. *SuperSoil 2004: 3rd Australian New Zealand Soils Conference*, University of Sydney, Australia.

Sobek, A. A., et al. (1978). Field and Laboratory Methods Applicable to Overburdens and Minesoils. Cincinnati, *U.S. Environmental Protection Agency*. EPA-600/2-78-054

Williamson, M.A. (2013) Pyrite oxidation in two phase liquid+vapor conditions. *Geological Society of America Annual Meeting Programs with Abstracts.*

Williamson, M.A. and J.D. Rimstidt, J.D. (1994) The kinetics and electrochemical rate-determining step of pyrite oxidation. *Geochim. Cosmochim. Acta.* **58**: 5443-5454.