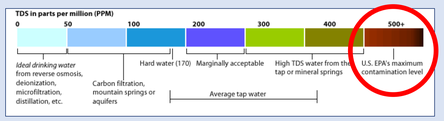
Earth Sciences
UNIVERSITY OF TORONTO

Determination of oxidation rates of pyrite and marcasite at low temperature for acid mine drainage and mineral waste solutions

Author: Char Erb, BASc.
Supervisor: Professor Daniel Gregory

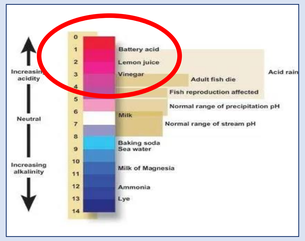
1.0 Introduction to AMD & Oxidation Rates

Acid mine drainage (AMD) is often a dangerous byproduct of mining deposits containing sulfide minerals.
Characterized by the following properties[1]:



High dissolved metal content (~200,000 mg/L or ppm) and Extremely high sulfide content (~700,000 mg/L or ppm)

Figure 1.1: Dissolved metal scale[2]



Acidic / low pH (< 3 pH)

Figure 1.3: pH scale[3]

Series of equations governing AMD generation:

- Reaction 1 (dissolved O_2): $FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H+$
- Reaction 2 (ferric iron):
  $FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H+$

AMD effects mining zones across the world, including in Canada, contaminating water sources and groundwater (Figure 1.4). These effects can be dangerous to the humans, animals, and wildlife in the areas contaminated. Oxidation rates of AMD rely on pH, temperature (T), and partial pressure of O_2, among other factors. The research presented focuses on verifying and determining the oxidation rate law effect on multiple sulfide minerals in tailings (pyrite and marcasite).

Figure 1.4: Acid Mine Drainage from Tulsequah Chief Mine, BC, (Tulsequah River)[6]

2.0 Previous Research & Analyses

- Current mitigation / industry research focuses on soil barriers, capping, treatment with lime and neutralizing chemicals
- **Gap in research: Can separating sulfide minerals from each other (e.g. pyrite and marcasite) in tailings slow down oxidation and AMD generation?**
- Oxidation rate laws developed by McKibben & Barnes (1986)[4] with additional information from McKibben et al. (2007)[5] for Fe-bearing minerals
  - R_{Fe3+} = rate law for ferric iron = $\mathbf{-10^{-9.74}(M_{Fe3+})^{0.5}(M_{H+})^{-0.5}}$
  - R_{O2} = rate law for oxygen = $\mathbf{-10^{-6.77}(M_{O2})^{0.5}}$

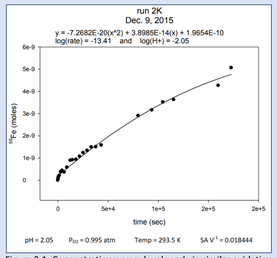


Figure 2.1: Concentration curve developed via similar oxidation experiments (Alexander van Hoorebeke, 2016)[7]

- Rate laws developed using abiotic rate law experiments which were closely replicated for this research (Section 3.0)
- Example of concentration curve used to develop oxidation rate law over experimental period[7]

3.0 Experimental Methods

Setting up the experiment

1. Crushing, grinding, and cleaning of samples
   - Size range: 45 um < x < 106 um
   - Sample cleaned with HCl to pre-leach
   - Then cleaned with concentrated TMG nitric acid and rinsed with DI to remove any dust particles
   - Rinsed with ethanol to remove any bacteria
2. Cleaning and sterilizing of apparatus
3. Prepare 2% TMG HCl solutions with gas by bubbling for 30 mins prior to experiment

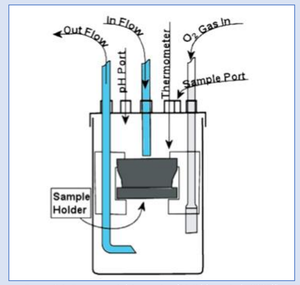
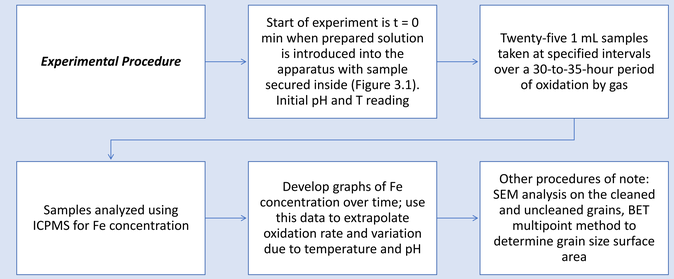


Figure 3.1: Experimental Apparatus (McKibben et al., 2007)[5]



4.0 ICPMS Concentration Curves, SEM, and Discussion

- ICPMS analysis was done on each sample taken during the experiments (over 150 preliminary data points) to find the concentration of Fe over the experiment time
- Gas combinations of 25%, 75%, and 100% O_2 with balance of Ni were used
- SEM analysis done to confirm use of concentrated nitric acid for cleaning sample grains
- Mathematical process adapted from Taylor Alexander van Hoorebeke's thesis (2016)[7] to calculate a rate law from the concentration curves using pH, T, and P_{O2} variables
  - **Rsp = 0.0013 * $[H+]^{1.443}$ * $[P_{O2}]^{0.89}$**

Concentration Rate at 100% O_2

Concentration Rate at 75% O_2

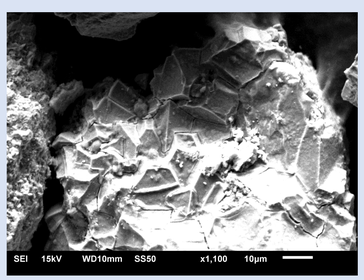


Figure 4.1: SEM Uncleaned Sample Grains (after HCl pre-leach, before nitric)

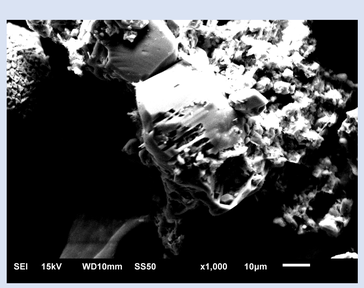


Figure 4.2: SEM Cleaned Sample Grains (after HCl pre-leach and nitric)

5.0 Conclusion & Next Steps

- From comparing trend lines, oxidation rate of pyrite in mine tailings conditions are indicated to be faster when a mix of pyrite and marcasite is used
- This indication suggests a function like a galvanic cell may be forming
- Temperature and pH dependence relationships will be investigated before completion
- From here, an oxidation rate law will be developed from the research elements
- Additional research should focus on economic deposit samples containing multiple sulfide minerals

NEXT STEPS FOR THIS THESIS:

XRD ANALYSIS TO CONFIRM AMOUNT OF PYRITE, MARCASITE, OTHER MINERALS

BET MULTI-POINT METHOD AT MCMASTER TO FIND EXACT SURFACE AREA MEASUREMENTS FOR THE SAMPLES FOR PRECISE RATE LAW

References

1. L. Warren, "Nuts and Bolts of ARD," in CME500 Course, 2021.
2. Total dissolved solids - TDS - in drinking water. Premier Water Technologies. (2017, March 15). Retrieved May 30, 2022, from https://www.premierwatermn.com/water-quality/water-contaminants/total-dissolved-solids/
3. Acidic water and (low) PH water. US Water Systems. (n.d.). Retrieved May 30, 2022, from https://www.uswatersystems.com/water-problems/acid-water-low-ph
4. McKibben, M. A., Barnes, H. L. (1986). Oxidation of pyrite in low temperature acidic solutions: Rate laws and surface textures. Geochimica Et Cosmochimica Acta, 50(7), 1509–1520. https://doi.org/10.1016/0016-7037(86)90325-x
5. McKibben, M. A., Tallant, B. A., del Angel, J. K. (2008). Kinetics of inorganic arsenopyrite oxidation in acidic aqueous solutions. Applied Geochemistry, 23(2), 121–135. https://doi.org/10.1016/j.apgeochem.2007.10.009
6. CBC/Radio Canada. (2017, April 7). 60 years later, Alaska still calling B.C. to task on a mine leak flowing through its river | CBC News. CBCnews. Retrieved May 30, 2022, from https://www.cbc.ca/news/canada/british-columbia/60-years-later-alaska-still-calling-b-c-to-task-on-a-mine-leak-flowing-through-its-river-1.4050699
7. van Hoorebeke, T. A. (2016). Oxidation Kinetics of Pyrite in Synthetic Seawater: Implications for Seafloor Mining Operations (thesis).

Acknowledgements

Thank you to my advisor Daniel Gregory for developing this project and all the help in carrying out these experiments. A special thanks to Colin Bray for his help in technical support and teaching me how to use the ICPMS equipment.