Acid Mine Drainage: Measuring Metal Release Rate from an Arsenopyrite Sample

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This project was developed for implementation in an honors level quantitative analysis course. The following set of notes and comments are meant to help instructors implement or adapt pieces of this project into their own courses.

Our overall learning objectives for students:

- Perform a quantitative analysis in the context of a real-life environmental problem;
- Apply the scientific method in the development of hypotheses, design of experiments, analysis of data and justification of conclusions;
- Experience the complexities and uncertainties associated with scientific measurement, especially when working with complex systems and the natural environment, and use the outcomes of experiments to guide the development of modified procedures;
- Effectively communicate scientific results, both in writing and by oral presentation.

The project explores the dissolution of a metal sulfide mineral, arsenopyrite, and how this dissolution connects to the environmental problem described in the media as Acid Mine Drainage (AMD). In the original version of the project, students actually studied pyrite (FeS_2). Much of the research going on at the time in the lecturer's research group (Robert Hamers) was focused on pyrite, and we had a good sampling of literature articles to share with the students. Additional appeal was that students knew pyrite as "Fool's Gold", and it is also quite pretty. Pyrite is very hard, and as a result, grinding the samples to the right grain size was hard to do. The dissolution rate is also slow, so in order for students to reach measurable levels of soluble iron in solution, the reactions had to sit for 5-10 days. Arsenopyrite is not as pretty, but it does dissolve faster, and the process of the dissolution is important locally, since deposits of arsenopyrite across the state lead to arsenic contamination of well water. The unit cell of arsenopyrite is FeAsS, so a measurement of the concentration of iron should in principle be equal to the concentration of total soluble arsenic. Therefore, most of the project is focused on a spectrophotometric analysis of iron dissolution using equipment that is likely common to all chemistry departments. Arsenic analysis can also be performed provided students have access to an inductively coupled plasma instrument. Using ICP-AES, students can verify the stoichiometry of the unit crystal. High pressure liquid chromatography can be used to quantitate sulfur.

While the detail in the introductory document is very specific to Wisconsin geology, the problem of arsenic contamination in well and other bodies of water is a global health concern. Therefore these materials can be easily adapted to your region, or further generalized to address the global issue of arsenic contamination in drinking water.

Course Organization at University of Wisconsin in Madison

Our quantitative analysis course spans a 15 week semester. We list this as a 4 credit course. Students meet for lecture twice per week for 50 minutes, twice a week for four hour lab sessions, and once a week for a 50 minute discussion. A faculty member or lecturer leads the lecture sections. Teach assistants (TAs) or faculty assistants manage the labs and teach the discussion section. The lecture section is divided into lab/discussion sections of about 20 students. One TA manages one section of students and is responsible for teaching those students good laboratory practice and safety in the lab, as well as leading the discussion.

The class size averages about 100 students. For the spring semester of our honors quantitative analysis course, students are mostly second semester freshmen, many of them chemistry or engineering majors. Our course demographic changes for the fall semester and is made up mostly of upper class students looking to finish up lab requirements for their majors.

Our chemistry faculty primarily fill the lecturer role. Chemistry graduate students entering in our analytical or materials science programs serve as our teaching assistants. A laboratory director is responsible for innovating and managing the laboratory curriculum, managing and training the teaching assistants, and facilitating connections between the lecture, laboratory and discussion components of the course. We also have two stockroom staff members that prepare and dispense reagents and solutions, set up the teaching space with appropriate instrumentation, glassware, and other equipment necessary for experimentation. And finally we utilize the help of hourly student employees to help with cleaning the lab space and managing the stockroom counter where students will check out extra glassware or special equipment or reagents for a specific laboratory period.

Project Organization

We consider the project primarily a laboratory activity. Out of a fifteen week semester we dedicate 5 weeks (a total of 40 contact hours) to implementing the project labs. A sixth week of lab time is used to assess student oral presentations and provide feedback to students on the written papers they have submitted. Students find it helpful to have some experience with the following concepts before beginning the project, which we cover in lecture and in problem sets:

- Uncertainty and statistics
- Spectrophotometry
- Equilibrium
- Ionic strength/activities
- Monoprotic acids and bases
- Systematic treatment of equilibrium.

Lecture topics progress as students work on the projects and complement many of the concepts they work with in the lab, including:

- Polyprotic acids and bases
- Acid and base titrations
- Complexation chemistry
- Atomic spectroscopy.

Our strategic plan for implementing the project in this course is outlined in Table 1. Since our analytical chemistry course has both lecture as well as a lab component, the described activities bridge both. It is important to make the point to students often and early on, that there are a few different, parallel experiments the groups should be working on. The first experiment to consider are the reactions that explore the impact of changing a variable on the rate of dissolution of the mineral (e.g., pH of the solution, concentration of additional Fe^{2+}, oxygen rich vs. oxygen poor environment). The second experiment student groups need to work out is exactly how they will measure soluble Fe spectrophotometrically. This involves working out the sample preparation on the aliquots from the reaction. In our curriculum, students have already done a lab illustrating Beer's Law plots using an Fe-bipyridine complex. In their case, the modifications to the experiment need to address a different concentration range and if they choose to substitute phenanthroline for the complexing agent, some changes need to be made to the buffer system. Daniel Harris includes an experiment on the phenanthroline method in the electronic manual that accompanies the Quantitative Chemical Analysis text. Details on guidelines for setting up the experiments are discussed later in this document.

Table 1: Implementation strategy for the lake study project

Schedule	How Long	Activity	Related Documents
Before the first lab day	45 minutes	Introduce the project in lecture	• Project Introduction PowerPoint • Acid Mine Drainage: Measuring Metal Release Rate from an Arsenopyrite Sample (Introduction Document) • Homework problem on predicting soluble Fe for dissolution of pyrite
First lab period	4 hours	Planning Activity	• Introductory assignment on getting started
Four lab periods	16 hours	Students conduct experiments measuring release of Fe	• Progress Report
Four to five lab periods	16-20 hours	Repeat experiments and compare results; prepare samples for ICP-AES and perhaps other instrumental techniques	• ICP-AES Instructions • The Art of Writing Science (Plaxco, K.W., *Protein Science* **Vol. 19:**2261-66 (2010)) • Final Report Details/Rubric

Students report their results in two ways: Group members write a formal report using the *ACS Style Guide (*Coghill and Garson, 2006). Group members also prepare a presentation for the rest of the class focused on results and conclusions of their research question. The formal report is typically due 7 to 10 days after the final laboratory period.

Roles Staff Members Play

Lecturer: The lecturer in our scenario primarily manages organizing and teaching lecture content for the course. They write problem sets, exams, dictate the weight of components of the course towards a student's final grade, and provide guidance on how to grade homework and exams. The more support the lecturer gives to the lab project, the happier the students! Some lecturers become quite involved in the projects and write supplemental questions related to project material for homework and exam questions. Lecturers often visit the lab to interact with students and TAs, but most lab sections may only see the lecturer in the lab for 10 or 20 minutes of each 4 hour period.

Teaching Assistants: The teaching assistant serves as the primary lab instructor. For the projects, their role is as a "thought leader". Especially during the first few days of lab work, students feel overwhelmed with the body of work ahead of them, and uncomfortable with having to develop their own procedures for measuring Fe and determining the impact of the variable on the Fe concentrations in solution. Students come to the TAs wanting to know what to do and how to do it. We instruct TAs to NOT answer those types of questions directly unless it involves a safety issue. Instead, they are asked to share how they would go about finding the answer to the question, assuming they don't know the answer themselves. A TA's response might point students to the project documents available to them, or to the literature, or perhaps the lecturer or lab director. If a student asks if a particular procedure is going to "work" (my guess would be this question ranks at the top of the "Most Frequently Asked"), a typical TA response might be, "I don't know, but you should try it and see what happens." **TAs model problem-solving skills for their students, instead of solving the problems for them.** At the beginning of each lab period, TAs will give a 5 minute debriefing to their lab class. They cover what things they should be working on, safety issues with any chemicals or procedures coming up in the lab queue, and disposal practices. Next they open the floor to allow students to address general issues, concerns, or questions before starting experiments. Once students set to work on experiments, TAs oversee experiments, addressing lab technique issues, safety, and answering individual questions as they come up.

Stockroom staff: The stockroom staff manages the inventory of chemicals, instrumentation, and special glassware. They prepare stock solutions in large quantities (such as 50 L of 1 M HCl, H_2SO_4 or NaOH) and dispense in smaller quantities to our general lab space. Staff also manage a counter, where students can request special chemicals or glassware not provided in their lab drawers. These items are "checked out" from the stockroom, and students must return them to the counter by the end of the lab period.

Laboratory Director: The lab director oversees the TAs, stockroom staff, student help, and serves as a secondary resource for students when the TAs are either very busy or stuck on a problem. The lab director grades all assignments, provides feedback and direction as students problem-solve experimental challenges, and gives guidance on developing interesting and relevant experimental questions that can be explored reasonably given the time limitations of the lab.

Apparatus

-Spectrophotometer capable of doing single and full-wavelength visible analysis
-Analytical balance
-Hot plate
-pH meter
-Filtering apparatus, such as a Buchner funnel, coarse filter paper with filter flask and sink aspirator
-variety of beakers, pipets, and volumetric flasks
-7 mL vials, or some means to store aliquots student sample from their reactions
-parafilm
-a means to bubble O_2 or N_2 to the solution (if oxygen rich or poor is a variable students are interested in investigating)
-15 mL plastic centerfuge tubes for submitting samples for ICP-AES analysis

Reagents

Arsenopyrite samples, purchased from Ward's Science (item number 495857--Grains are usually 1/16-3/16" in size and come in 10g packages). Our stockroom staff prepared samples in the following way:

- Grind arsenopyrite grains to smaller than 125 micron diameter. We would grind samples in about 1 gram quantities and frequently use a 125 micron sieve to separate out grains that were still too large, to be recycled back into the grinder.
- Samples falling thru the 125 micron sieve are then separated again using a 75 micron sieve. This time we discard the grain falling through the sieve and retain what's left in the sieve to package for students.
- Each group of students (3-4/group) receives one bag of ~0.8 g arsenopyrite grains. The average size is estimated to be between 75 to 125 micron diameter, i.e. 100 microns.

Ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$) aka FAS
1 M HCl
1% Hydroxylamine
2 M Sodium acetate
solid phenanthroline
0.1% Bipyridyl

Various salts of H_2SO_4 for students to use to set the pH of their reactions. They choose the final solution conditions.

First Day of Lab

Prior to lab:

- Have students complete the homework problem or group activity on predicting the concentration of dissolved Fe for a given set of experiment conditions (see Homework problem example at the end of this document).
- Students should review the project overview, "Acid Mine Drainage: Measuring Metal Release Rate of Arsenopyrite" (AMD Project Intro ASDL.docx)
- Students should review some of the literature in the references. Most helpful are reference 13 (McGuire, Edwards et. al) and 19 (Dawson and Lyle).
- Organize student groups

Handouts for first lab day activity:

- AMD Getting Started ASDL.docx

Activity description:

The goal for the planning activity is for student groups to adapt the procedures stated in the selected research articles, such that they can perform the experiments in their own lab. The questions in the Getting Started document in part guide them through some of the literature details so they can make some educated decisions on what to change. It should also inspire them to look up related literature articles (most are listed in the References section of the Introduction handout), as a way to enrich their understanding on the topic. When reviewing the proposals students submit, the grader should check that the procedure is basically correct and safe. There may be small errors in the procedure, which can be commented on. We tend to let students try what they propose even with the mistakes, provided what they propose will be safe. We value the problem-solving experience just as much as getting things working really well!

A general procedure for exploring how added ferrous ion might impact the dissolution rate might look like the following:

A. Clean the mineral sample
B. Divide out the mineral between 5 400 mL beakers (a 0.8 g sample is sufficient to have about 0.1 g in each sample. Weigh the mineral amount accurately for each reaction.
C. Prepare a 10 mg/L stock solution of FAS, and by way of serial dilution made 250 mL each of 0.01, 0.05, 0.1, 0.5 mg/L stock solution. Make all solutions with 0,1 M HCl. One sample will not have added FAS, only adding 250 mL of 0.1 M HCl to serve as a control.
D. Take 5 mL aliquots at t=0 minutes, 30 minutes, 1 hour, 2 hours, 24 hours, 48, hours, etc., until the reaction is quenched.
    a. Aliquots are stored in 7 mL glass vials (or plastic centrifuge tubes) until analysis can happen.
E. Analyze aliquots using Beer's law plot with Fe-phenanthroline per the Dawson and Lyle paper.

The grader should pay close attention that student groups do not plan to add the complexing agent directly to the reaction vessels they prepare. Groups who propose this don't understand that there are two experiments they need to work out. Make it clear to these students that they first need to take sample aliquots of the reactions they prepared for SUBSEQUENT analysis.

Leading up to the Progress Report

Relevant Handouts:

- AMD Progress Report ASDL.docx
- AMD ICP Instructions ASDL.docx

Activity Description:

We expect students will not have all the kinks worked out for the first dissolution experiment, so the timeline is designed such that students should repeat their experiment (with appropriate modifications) at least a second time. The first progress report is a chance for students to submit a preliminary set of data for evaluation and constructive feedback. After four laboratory periods students should be able to share a fairly good working curve for the spectrophotometric determination of iron, and also share if they've been able to measure any soluble iron in their dissolution experiments. Probably the most common problem we encounter is that students do not observe any soluble Fe in their aliquots. Some questions to consider/suggestions:

- Are you adjusting the pH of the aliquot so that the complex between Fe and the complexing agent can still form?
- Have you adjusted the pH too much, such that $Fe(OH)_2$ or $Fe(OH)_3$ might be a problem?
- Check the prediction on what you believe the concentration of Fe should be based on the rate of dissolution you found in the literature. Using this concentration, work through your procedure to check that you're not diluting the aliquot too much. Diluting 5 mL of a fairly

dilute Fe solution to 500 mL could definitely cause some problems with the detection limit of your method.

- Are you actually measuring absorbance or did you accidentally capture transmittance spectra?

Once students seem to have a good grasp of the procedure using complexation and the Beer's law experiment, students should repeat the experiment one more time to collect aliquots for the ICP-AES experiment.

Other possible experiments:

Speciation and fate of sulfur after the oxidative dissolution: As the metal cations are released into solution, the fate of oxidized sulfur has been a topic of debate in the literature. Previously it was assumed the oxidized sulfur also released into solution as thiosulfate, but several studies demonstrate that sulfur remains on the mineral surface as elemental sulfur. The speciation of sulfur both in solution and remaining on the surface of the mineral sample can be determined by high-performance liquid chromatography.

A. Elemental sulfur can be extracted from the mineral surface using percholoethylene. The extract can be compared to a set of elemental sulfur standards prepared in percholorethylene. We used the same method described in MM McGuire and RJ Hamers, Environ. Sci. Technol. 2000, *34*, 4651-46-55. Students successfully measured elemental sulfur extracted from the mineral surface. The experiment is straightforward and students have a fairly easy time implementing the experimental method described in the article.
B. We adapted the procedure described by Y Zuo and H Chen, Talanta 59 (2003) 875-881. We used an Alltech Econosphere 5 μ C_{18} column (4.6 x 250 mm) and found we needed to use an injection volume of 15 microliters. We used an elution time of 20 minutes, with a flow rate of 0.8 mL/min.

Determine the dissolution rate of other metal sulfide minerals:

Our practice in lab is to allow students to explore other scientific questions if they have done sufficient work to complete the minimum requirements of the project. Students have taken their experiments in a variety of directions, but some of the most successful results have come from students trying their dissolution procedure on other metal sulfide minerals. Here are a few that worked pretty well:

A. Pyrite (FeS_2)—We originally developed this experiment using pyrite, and it does work. However, our VIS spectrophotometers are instructional grade, and students are operating at the lower end of their detection limit. We suggest students perform an experiment to determine the Method Detection Limit for the phenanthroline method, and then also suggest they let the reactions sit for at least a week. This works quite well especially when trying to measure the elemental sulfur by way of HPLC.
B. Chalcopyrite ($CuFeS_2$—Topics surrounding copper mining in Northern Wisconsin and the Upper Peninsula of Michigan frequent our local news. Since chalcopyrite is commonly found in the pure copper deposits present in these mining regions. The iron can be measured using the described phenanthroline method: Copper can be complexed with ammonia and quantitatively measured using VIS spectroscopy or detected along with iron and sulfur in the ICP-AES.

Final Paper

Relevant Handouts:

- AMD Final Report Instructions ASDL.docx
- AMD Final Paper rubric ASDL.docx
- AMD Individual grade rubric ASDL.docx

Activity Description:

Groups will submit a formal paper describing their experimental work over the course of the project. We also ask groups to prepare a short presentation focused on the results and discussion portions of the paper. Before meeting with the students, the lecturer of the course and the lab director read the student papers carefully, adding notes and suggestions to the written document. At this point we propose a current grade for the paper.

The lecturer, lab director and the section TA will meet with the student groups to first hear their oral reports and then ask questions about what they did. We then discuss the paper with students and suggest informally, ways to revise the paper to improve how the science is presented and therefore improve the grade. After this meeting, groups have one week to revise the paper and resubmit for a final grade. If they choose not to revise the paper, they can simply hand in the original paper up to one week later, and we evaluate the paper using the rubric provided.

We evaluate group members individually as well. The individual grading rubric is also included. The points distribution for the entire project is suggested in Table 2.

Table 2: Points distribution for the AMD Project

Activity	Maximum Points
Getting Started	15
Progress Report	15
Final Paper	35
Individual Assessment (Oral presentation, peer evaluation and TA evaluation)	25
Total Points	90

Appendix

Homework problem on pyrite dissolution:

This problem is related to the Project Lab you will be doing later in the semester. Consider a sample of the mineral pyrite, FeS, which has a density of 6.2 g/cm^3.

a) Assume that the sample consists of spherical particles with a diameter of 50. μm. Calculate the surface area (in m^2) of 0.25 g of the pyrite sample.

b) Suppose that the 0.25 g of the sample are allowed to react with 100.00 mL of an acidic solution. A very small amount of the mineral dissolves to form Fe^{2+}(aq) and S^{2-}(aq). If the dissolution rate is 1.1 x 10^{-9} mol m^{-2} s^{-1}, how much Fe^{2+} (in mol/L and in mg/L) is released from the mineral after 3 hours? After 5 days?