PROPOSAL TO THE UNDERGRADUATE RESEARCH PROGRAM

by
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September 22, 2005

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An Investigation to Compare Two Dissolution Procedures for Determining the Partitioning of Heavy Metals to Amorphous Ferrihydrite

BACKGROUND

Hohn and Twidwell[1] have been investigating the effectiveness of ferrihydrite (a ferric oxyhydroxide) for adsorbing heavy metals (Cd, Cu, Ni, Zn) from wastewater (Mine Waste Technology Program, MWTP Project 35). The adsorption portion of the study has been completed and the present focus of the project is to evaluate the long-term storage stability of the metal bearing solids. The goal of the long-term stability study is to determine the relative distribution of heavy metals between three phases: a solution phase, a ferrihydrite x-ray amorphous phase and a crystalline hematite phase. From these data, conclusions can be drawn as to whether the product will be stable in an outdoor storage reservoir. Samples will soon be placed in a constant temperature water bath at 70°C and the aging process will be followed as a function of time. Therefore, samples will be available for the proposed URP study in approximately one month (in November or early December).

Ferrihydrite converts to crystalline hematite in a relatively short period of time, e.g. at pH 7 and 70 ^{o}C, ferrihydrite is partially converted to hematite in approximately one month, and is completely converted in three months. The conversion from amorphous ferrihydrite (surface area ~300 m^2/gram) to a crystalline structure results in a tremendous decrease in the solid phase surface area (to ~90 m^2/gram). The question to be answered by Project 35 is "Will the adsorbed metals remain with the crystalline phase or will they be released back into the solution phase?"

The procedure[2] that has been used by most investigators to determine the amount of ferrihydrite present is based on using a timed leach in a pH buffered oxalate solution. This solution reduces and solubilizes the ferrihydrite ferric $iron_{(in\ solid)}$ to ferrous, $Fe(II)_{(in\ solution)}$ but does not attack crystalline hematite. This procedure has been used to study the transformation rate of ferrihydrite and for studying ferrihydrite loaded with various anionic species such as arsenic, sulfate and selenium. However, it is known that some metals form solid oxalate compounds (Cd and Ni may form solid oxalate compounds), so at present it is unclear as to whether the procedure would be appropriate for determining the amount of heavy metals present in the ferrihydrite solid phase.

The EPA (Ford[3, 4]) has supported a few studies that have utilized both the oxalate and a timed hydrochloric acid leach. The hydrochloric leach has been shown to leach heavy metals but results in low iron recovery. It may be necessary, therefore, to use both the oxalate leach (for the iron content from which the amount of ferrihydrite can be determined) and the hydrochloric leach for determining the amount of heavy metals present in the amorphous ferrihydrite.

It is proposed in the present study that the two procedures be compared.

STUDY OBJECTIVES

The objectives of the proposed study will include:

- Conduct dissolution test work on similarly aged materials using both the oxalate and hydrochloric leach techniques, and
- Recommend an appropriate treatment technique to account for the iron and heavy metals associated with the ferrihydrite.

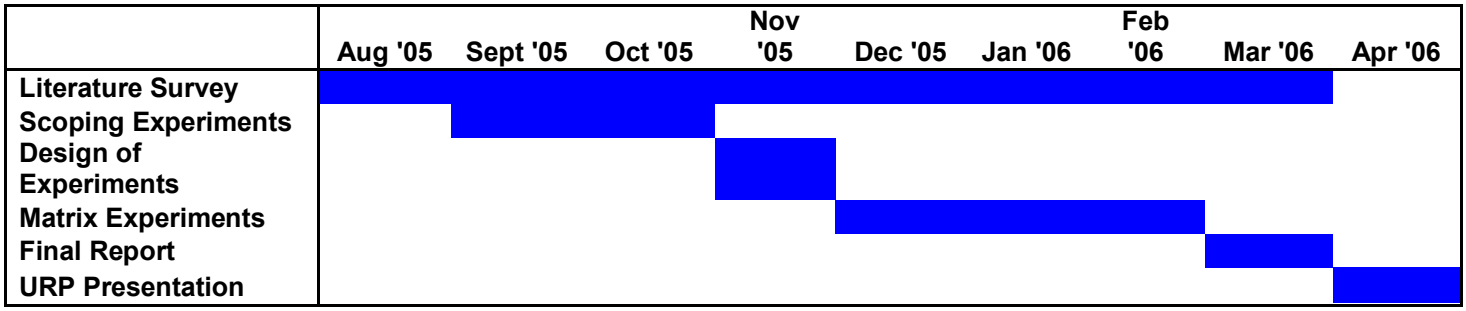
PROJECT APPROACH

The proposed study will be conducted as follows:

- Recover two sample bottles from the aging series.
- Centrifuge the samples and collect triplicate solution samples from each bottle. Preserve the solution samples according to established EPA Quality Control (QC) procedures. Have each solution analyzed for iron and heavy metal concentrations.
- Collect triplicate solid samples from each sample bottle, wash the solids three times with pH adjusted deionized water, dry at 50°C for 3 hours. Subject each dried sample to either the oxalate or hydrochloric leach (Procedures are presented in Appendix). Recover the leach solution and have analyzed for iron and heavy metals.
- Calculate the amount of ferrihydrite present and the concentration of heavy metals in the ferrihydrite. Perform a mass distribution for each heavy metal present in the solution phase, the ferrihydrite phase and the crystalline phase.

TIMELINE: *[A timeline that identifies the various components of the project and when they would be accomplished, is recommended. Consider using a graphical representation such as a Gantt chart.]*

As indicated in the Gantt Chart below, this project is divided into 6 parts. The project will be initiated in August with a literature survey in which I will use the Montana Tech Library as well as the Internet to find publications (books, papers, etc.) pertinent to this research. Most of this has already been completed by my advisor so this time is used to update his files. This will go on throughout this study except primarily in the last two months when I am finalizing both the Final Report in March and the PowerPoint Presentation for the Undergraduate Research Fair in April. The actual experimental work will initially consist of some scoping experiments in which methods and procedures are determined and the more important variables are identified along with their appropriate ranges. Afterwards, the experimental design matrix will be determined using StatEase Software. With this, each variable will have High and Low values determined and will be systematically changed such that, the total number of experiments needed will be 2^n+2 where n is the number of variables and two additional tests are performed (at the minimum) in which Medium values are used. Matrix experiments are expected to start In December and be conducted for the next 3 months.



BUDGET: The cost to the Undergraduate Research Program will be the stipend for the undergraduate student. All other costs will be borne by MWTP Project 35.

REFERENCES

1. Hohn, J., L. Twidwell, Heavy Metals *Removal by Modified Ferrihydrite Adsorption*, Montana Tech of the University of Montana, MWTP Project 35, January 2005-September 2006.

2. Schwertmann, U., R. Cornell, *Iron Oxides in the Laboratory,* VCH, New York, New York, 1991

3. Ford, R.G., *Rates of Hydrous Ferric Oxide Crystallization and Influence on Coprecipitated Arsenate*, EST, Vol 36, 2002, pp 2459-2463.

4. Ford, R.G., K.M. Kemner, P.M. Bertsch, *Influence of Sorbate-Sorbent Interactions on the Crystallization Kinetics of Nickel- and Lead- Ferrihydrite Coprecipitates,* Geochimica et Cosmochimica Acta, Vol 63, No 1, 1999, pp 39-48.