SCHEDULE "B-3"

RESEARCH PROJECT No. 3

Project Title: Sulfidation of As_2O_3 to form low-solubility As_2S_3

RESEARCH TEAM:

Tom Al (University of Ottawa)

PERIOD OF PERFORMANCE:

Start Date: July 1, 2019   End Date: June 30, 2022

PROJECT DESCRIPTION:

1. Introduction

The mineral orpiment (As_2S_3) has a much lower solubility than As_2O_3 (model calculations at 25 °C suggest 0.0025 g/L versus 11 g/L) and it is stable in anoxic water at pH < 7. Orpiment, or its amorphous form, is therefore a reasonable phase for As_2O_3 conversion and disposal. The general remedial goal would be to convert As_2O_3 to the lower solubility As_2S_3 form (reaction 1):

$$As_2O_{3\,(s)} + 3H_2S_{aq} \rightarrow As_2S_{3\,(s)} + 3H_2O \qquad\qquad [1]$$
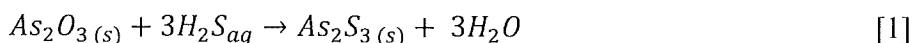
Conversion to As_2S_3 could be accomplished by entraining the As_2O_3 in a slurry, adding sulfide, perhaps as an alkali sulfide (*e.g.*, Na_2S). Upon completion of the reaction, the waste As_2S_3 could be piped deep into the mine, where it would be stable in the deep anoxic groundwater. The higher salinity and density of groundwater at depth would limit the potential for upwelling and mixing in the shallow, freshwater environment.

2. Background

In order to achieve efficient conversion of As_2O_3 dust to As_2S_3 in an aqueous slurry, the reaction rates should be rapid (*i.e.*, within minutes), and the conversion yield should be close to 100%. Based on reaction [1] and general principles of reaction kinetics, it is anticipated that the reaction rate will increase with the specific surface area and solubility of As_2O_3, and the concentration of H_2S. The solution pH is also important because the solubility minima for As_2S_3 is in the pH range < 5 (Eary, 1992). The Giant Mine dust is very fine grained, with most measurements reported by Geocon (1981) to be 100% finer than 45 μm, and one sample as low as 90.8 % finer than 45 μm. Impurities in the As_2O_3 crystals may also be a factor that affects the reaction rate. Around the time that the Giant Mine closed, the CANMET Mining and Mineral Sciences Lab conducted studies of the mineralogical composition and solubility of the As_2O_3 waste (Dutrizac et al. 2000). Four

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samples were studied by Dutrizac et al. (2002); two were recent composites (April 1997 and January 1998), and two from older material recovered from underground storage chambers 212 and 236. The As_2O_3 content in the recent composites was > 87% and the older samples from the storage chambers contained ~ 75% As_2O_3. The Sb content of the samples ranged from 0.30-2.13% and mineralogical examination determined that most of the Sb in the samples occurred in solid solution with the As_2O_3. Using electron microprobe, Poirier (2004) measured Sb_2O_3 concentrations as high as 30.8 wt. % in individual As_2O_3 grains. Dutrizac et al. (2000) conducted solubility experiments, with the results indicating that the solubility of the Giant Mine As_2O_3 dust is approximately 50% that of pure As_2O_3. The lower solubility was mainly attributed to the presence of Sb_2O_3 substitution in the dust.

Rochette et al. (2000) investigated the reduction of arsenate in the presence of sulfide. The authors determined that conditions with high S:As molar ratios promote the precipitation of As_2S_3. Further, the authors report the precipitation of orpiment from solution with a S:As ratio of 20:1 and pH of 4. The final dissolved As concentrations were in the range 0.0005 to 0.0007 mg/L.

3. Objectives

The overall objective of this research is to investigate sulfidation in aqueous media as a possible remediation strategy for the As_2O_3 dust stored underground at the Giant Mine. This objective will involve three key milestones:

i. Determine the rate of reaction between aqueous H_2S and solid As_2O_3 under conditions of variable pH (*i.e.*, 4 to 7) and variable S:As ratio (*e.g.*, 2:1 to 20:1);
ii. Characterize the solid product from the reaction to identify the products and check for incomplete reaction (*e.g.*, armouring of the As_2O_3 with As_2S_3 coatings); and
iii. Investigate the stability of the product in aqueous systems representative of the Giant Mine water.

4. Methodology

4.1 Sulfidation

The rate of reactions will be assessed as a function of the initial pH and the initial ratio of sulfide to As (S:As; Table 2). Batch reactions will be conducted with the following steps:

1. A known mass of solid will be added to a reaction vessel;
2. The vessel will be sealed and purged with N_2 gas to remove O_2;
3. A deaerated Na_2S solution will be titrated with HCl to one of the initial pH values indicated in Figure 1, and then a known volume/concentration will be added to the reaction vessel (time = 0);
4. The vessel will be stirred continuously and the aqueous solution will be sampled periodically to measure the total sulfide concentration and pH versus time.

Table 2. Proposed experimental design. Shaded cells indicate experiments conducted in triplicate. Three different solid phases will be used in separate batch reactions; a limited subset of experiments are planned with reagent-grade As_2O_3 and reagent-grade Sb_2O_3 to test the rates for the pure-phase end members and the full set of experiments will be conducted for the As_2O_3 dust from the Giant Mine. For the Giant Mine samples, reproducibility will be tested by conducting experiments in triplicate for one S:As ratio at each initial pH (shaded cells in Table 2).

Initial Solution pH															
4				5				6				7			
S:As Ratio				S:As Ratio				S:As Ratio				S:As Ratio			
2:1	5:1	10:1	20:1	2:1	5:1	10:1	20:1	2:1	5:1	10:1	20:1	2:1	5:1	10:1	20:1

The sulfide ion (S^{2-}) is the reaction-progress variable and concentrations will be determined using either a sulfide-specific ion selective electrode (ISE) in the high range (> 0.8 mg/L) or colourimetry (methylene blue) in the low concentration range. All experiments will be conducted at ambient laboratory temperature (21 ± 2 °C).

The reactions will be considered complete when there is no significant change in aqueous sulfide concentration over five consecutive measurements. At this point, solution samples will be collected from the reaction vessel and prepared for a full inorganic chemical analysis, including As and Sb (ICP-OES and ICP-MS).

4.2 Solid-phase Characterization

The solid product from sulfidation will be dried anaerobically and the mineralogical composition will be characterized using XRD, SEM, and TEM. A subsample of the solids will be digested in aqua regia and analyzed by ICP-OES and ICP-MS.

4.3 Stability of the Solid (As_2S_3) Product

The success of a sulfidation treatment process will be dependent on the stability of the product in the environment where it is disposed. We suggest that isolation of the product in a deep region of the mine workings would be optimal for several reasons:

- The deep mine water (2000' level) has high salinity, with sodium and chloride concentrations of approximately 1.5 and 6 g/L, respectively (Clark, 2001). Solutions of this composition have high density relative to the near-surface freshwater and would tend to remain at depth, not mixing with the shallow groundwater.
- The deep saline groundwater has chemical and isotopic characteristics consistent with deep brines at the Con Mine and elsewhere in the Canadian Shield that have been interpreted to represent ancient (Devonian) evaporated seawater (Bottomley et al., 2005). This means these saline waters must have been stable at depth for several hundred million years.
- Long-term stability of the As_2S_3-containing product requires anoxic conditions to prevent oxidative dissolution. Disposal at great depth in the mine, where it is isolated from the shallow groundwater flow system, would prevent contact with dissolved oxygen.

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Although deep disposal of the sulfidation product should assure long-term stability, it is still necessary to understand the stability of the material in aqueous systems similar to the Giant Mine water.

The stability of the As_2S_3 reaction product will be studied using batch kinetic reactions, and possibly also flow-through kinetic reactions using an approach similar to that described by Lengke and Tempel (2001). The experiments will be conducted with simulated mine-water compositions based on data from Clark (2001). The principal experimental variables will be pH and dissolved oxygen concentration, and the rate of oxidative dissolution will be monitored with dissolved As and SO_4^{2-} as the reaction progress variables. However, because the arsenic-trioxide dust from the Giant Mine contains minor and trace mineral phases that will react during sulfidation to form products other than As_2S_3, the stability of these other phases during oxidation must be considered. To this end, the overall major, minor, and trace-element geochemistry of the experimental solutions will be monitored. Following the oxidative dissolution experiments, the solid-phase residue will be characterized by XRD, SEM-EDS, and possibly TEM-EDS.

5. Potential Benefits

This research will test the potential for transforming the soluble As_2O_3 waste at the Giant Mine to a low-solubility solid that would be stable in the deep regions of the flooded mine workings. Although this type of treatment would require the removal of the waste from the present storage areas, storage of a stable product deep in the flooded mine would represent a permanent solution for As_2O_3 remediation, with the real possibility that the mine could safely be allowed to flood.

BUDGET

The total proposed budget for this three-year research program is $150,500, including $107,500 for direct research costs plus 40% overhead ($43,000) charged by the University of Ottawa (Table 3). The program will support two MSc students.

Category	Year 1	Year 2	Year 3	Total
Salaries and Benefits	$ 21,000	$ 21,000	$ 21,000	$ 63,000
a) PhD students	$ -	$ -	$ -	$ -
b) Master's students	$ 21,000	$ 21,000	$ 21,000	$ 63,000
c) Undergraduate students	$ -	$ -	$ -	$ -
d) Postdoctoral fellows	$ -	$ -	$ -	$ -
e) Technical/Professional Assistants	$ -	$ -	$ -	$ -
Equipment	$ 4,000	$ 4,000	$ 4,000	$ 12,000
a) Purchase or rental	$ -	$ -	$ -	$ -
b) Operation and maintenance costs	$ -	$ -	$ -	$ -
c) User Fees	$ 2,500	$ 2,500	$ 2,500	$ 7,500
d) Analytical Costs	$ 1,500	$ 1,500	$ 1,500	$ 4,500
Materials and Supplies	$ 7,000	$ 7,000	$ 7,000	$ 21,000
a) Laboratory supplies, reagents	$ 5,000	$ 5,000	$ 5,000	$ 15,000
b) Machining costs	$ 2,000	$ 2,000	$ 2,000	$ 6,000
Travel	$ 2,500	$ 2,500	$ 2,500	$ 7,500
a) Conferences and Workshops	$ 2,500	$ 2,500	$ 2,500	$ 7,500
b) Field Work	$ -	$ -	$ -	$ -
Dissemination	$ -	$ 2,000	$ 2,000	$ 4,000
a) Publication costs	$ -	$ 2,000	$ 2,000	$ 4,000
b) Communication costs (teleconference)	$ -	$ -	$ -	$ -
Subtotal	$ 34,500	$ 36,500	$ 36,500	$ 107,500
University Overhead (40%)	$ 13,800	$ 14,600	$ 14,600	$ 43,000
Grand Total	$ 48,300	$ 51,100	$ 51,100	$ 150,500

BACKGROUND INTELLECTUAL PROPERTY:

(a) UW Background Intellectual Property:

None

(b) Third Party Background Intellectual Property:

None

(a) GMOB Background Intellectual Property:

None

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Acknowledgement and Consent of Principal Investigator

I, having read this Agreement, hereby agree to comply with all the terms and conditions contained herein and further agree to ensure that all participants who are involved in the Research Project are informed of their obligations under the provisions of this Agreement.

By: _____   Date: _____ July 10, 2019
Name: David Blowes,
Title: Professor