SCHEDULE "B-2"

RESEARCH PROJECT No. 1

Project Title: Examination of arsenic trioxide dust composition and solubility

RESEARCH TEAM:

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PERIOD OF PERFORMANCE:

Start Date: July 1, 2019 End Date: December 31, 2020

PROJECT DESCRIPTION:

1. Introduction

Arsenic trioxide (As_2O_3) dust stored underground at the Giant Mine presents a significant potential environmental and human health risk. Current plans for mitigating the potential risks of this toxic-waste material involve a frozen block method that uses thermosyphons to establish and maintain frozen conditions. This method is intended to prevent water movement through the five stopes and eleven chambers where As_2O_3 dust is currently stored. This research program is not limited to the frozen block method; instead, research activities are specifically focused on alternative strategies for As_2O_3 management and remediation. Any research into new management and remediation strategies will require detailed knowledge of the chemical, mineralogical, and physical characterization of the As_2O_3 dust stored underground at the Giant Mine site.

2. Background

Our current understanding of the characteristics of As_2O_3 dust stored underground at the Giant Mine site is largely based upon two research reports and a related article resulting from studies commissioned by SRK, the Department of Indian Affairs and Northern Development (DIAND), and Royal Oak Mines Inc. Dutrizac et al. (2000) and Riveros et al. (2000) set out to assess methods for As_2O_3 purification, and their work involved solubility measurements and mineralogical characterization on four samples. In 2003, SRK conducted a program to drill and sample the As_2O_3 in the stopes and chambers, and their work included additional mineralogical assessment on four more samples (Poirier, 2004, in SRK, 2004). These studies revealed that As_2O_3 dust from the Giant Mine contained considerable compositional variability, and while they offer valuable insight on As_2O_3 characteristics of the samples, it is unclear how representative the eight samples were of the overall material heterogeneity. Nevertheless, these studies generated important data on material properties that provide direction for the program we are proposing. A key outcome of the Dutrizac et al. (2000) study was that the antimony (Sb) content of the As_2O_3 dust strongly affects its geochemical properties and behaviour, particularly by substantially decreasing dust solubility in water. The As_2O_3 dust analyzed by Dutrizac et al. (2000) ranged between 0.30 and 2.13 wt. % Sb, and on average, the solubility was approximately half that of reagent-grade As_2O_3. Electron probe microanalysis (EMPA) also revealed discrete particles with atomic As:Sb ratios approaching 1:1. These findings are generally consistent with recent observations of As_2O_3 particles persisting in lake sediments impacted by historical baghouse stack emissions from the Giant Mine (Schuh et al., 2018, 2019). It is unclear if this relationship between Sb content and solubility is linear or contingent on other factors. In addition, it is unclear if the composition of the four samples analyzed by Dutrizac et al. (2000) are representative of the entire As_2O_3 dust inventory at the Giant Mine site. Changes in ore composition and metallurgical processes over the mine life (Silke, 2013) suggest that the As_2O_3 dust exhibits greater compositional variation than was captured by the eight samples studied by Dutrizac et al. (2000) and Poirier (2004). In addition, the dust contains a number of trace and minor amounts of mineral phases (*e.g.*, micas, iron oxides, Ca-Fe oxide, Ca-Fe arsenate; Dutrizac et al., 2000, Poirier et al., 2004) that may influence solubility and/or approaches to reprocessing.

Improving upon the current state of knowledge is critical for all future research into alternate strategies for As_2O_3 management and remediation (Riveros et al., 2001). More specifically, improving understanding of the chemical and physical characteristics and behaviour of the As_2O_3 dust, and the variability of these characteristics, will be critical to the development of new physical and chemical stabilization approaches, including the approaches described in Projects 2, 3, and 4 of this proposal. We propose to characterize additional As_2O_3 dust samples from the Giant Mine site, and to assess the impact of Sb substitution on dust solubility. The As_2O_3 dust emitted from the roaster stacks was distributed across the region and has been detected in soils and lake sediments (Bromsted et al., 2017, Schuh et al., 2018); thus, assessing the solubility and properties of these materials will also provide valuable insight on the environmental behaviour of these more diffusely distributed dust particles.

The research projects proposed in this document by our TERRE-NET colleagues are interdependent. For example, the precipitation of arsenic sulfides (Project 2) will depend on dissolved arsenic (As) availability, which will be controlled by As_2O_3 solubility, and could be impacted by the presence of Sb or other impurities. Similarly, the solubility of As_2O_3 dust may affect the success of the paste-backfill method (Project 3). Additional information on the chemical and physical characteristics of the As_2O_3 dust will support the overall remediation effort at the Giant Mine, and may also improve our understanding of its potential environmental behaviour and implications in the Yellowknife area.

3. Objectives

Our overarching research hypothesis is that Sb substitution for As decreases As_2O_3 solubility. We will test this hypothesis through complementary research to: (i) characterize chemical and physical properties of As_2O_3 dust from the Giant Mine; and (ii) determine how Sb substitution affects As_2O_3 solubility. The key objectives of this research are to:

i. Characterize the (geo)chemical, mineralogical, and physical characteristics of As_2O_3 dust from the Giant Mine site;

ii. Assess the variability of (geo)chemical, mineralogical, and physical characteristics of As_2O_3 dust from the Giant Mine site;
iii. Constrain how Sb substitution affects As_2O_3 solubility in both synthetic samples and dust samples collected form the Giant Mine site; and
iv. Improve our understanding of As_2O_3 dust properties to support future research into new management and disposal strategies.

4. Methodology

4.1 Sample Characterization

Sample collection
We plan to obtain as many samples as possible to ensure that the proposed research project improves understanding of the chemical and physical properties of As_2O_3 dust. These samples may include the archived "Lakefield" sample inventory, plus any additional samples that can be obtained from surface or underground at the Giant Mine. We will also sub-sample the "Lakefield" samples to facilitate further assessment of sample heterogeneity. Additional sample collection from the Giant Mine would be arranged by GMOB and associated costs are not included in our proposed project budget. Reagent-grade samples of As_2O_3 and Sb_2O_3 will also be included in the analyses and experimental work.

Additionally, tools used to characterize As_2O_3 dust will be applied to other materials generated through GMOB-funded TERRE-NET research projects, including vitrified arsenical glasses (Project 4).

Analytical Methods
We will collect complementary chemical and physical data to assess the heterogeneity of As_2O_3 dust samples. Initially, we will conduct screening tests to constrain the variability in bulk characteristics of all samples: 1) we will determine the bulk chemical composition of all samples by low-temperature digestion methods (*e.g.*, aqua regia) and detection by either inductively coupled plasma – optical emission spectroscopy (ICP–OES) or inductively coupled plasma – mass spectrometry (ICP–MS); and 2) we will characterize the bulk mineralogy of the samples with powder X-ray diffraction (XRD). The XRD will also allow us to assess whether there are low-abundance, discrete mineral phases in the dust that will need to be considered in our additional analyses. Based on these results, we will divide our samples into batches based on their composition and mineralogical properties (*e.g.*, Sb concentrations). We will select representative samples from each batch to assess in greater detail (12 samples total).
We will collect additional compositional data on these samples using an Electron Probe Microanalyzer (EPMA), and we will use XRD and scanning electron microscope (SEM) based automated mineralogy to help constrain solid-phase composition. We will use synchrotron-based X-Ray Absorption Spectroscopy (XAS) to examine As and Sb oxidation states and coordination. These data will help us to elucidate the mineralogical forms of these metalloids – particularly Sb – and may assist with interpretation of subsequent solubility experiments. Together, these methods will contribute enhanced understanding of the geochemical and mineralogical composition and variability of As_2O_3 dust.

We will measure physical characteristics including particle size and surface area by integrated Transmission Electron Microscopy (TEM) and Brunauer, Emmett and Teller (BET) specific surface area measurements. We will also assess methods to determine As_2O_3 wettability.

4.2 Solubility Experiments

The influence of Sb substitution on As_2O_3 solubility remains poorly constrained. Dutrizac et al. (2000) demonstrated that As_2O_3 samples from the Giant Mine are less soluble in water than reagent-grade As_2O_3 over a wide temperature range. These experiments did not assess the influence of Sb content on As_2O_3 solubility, nor did they evaluate the influence of other relevant geochemical variables. The proposed experiments will evaluate the influence of Sb substitution on As_2O_3 solubility using both synthetic samples and samples collected from the Giant Mine. These experiments will also investigate how temperature, pH, and ionic strength affect As_2O_3 solubility. These additional data will offer new insight into As_2O_3 dissolution during stabilization and in the environment.

Synthesis and characterization:
Fine-grained As_2O_3 will be synthesized in the presence of different Sb concentrations. The synthesized solids will cover a range of Sb concentrations observed in the initial As_2O_3 characterization work. The final chemical composition of these solids will be determined by measuring residual aqueous As and Sb concentrations in supernatant solutions. Low-temperature digestion and ICP-MS detection will provide confirmation of As_2O_3 compositions.

Particle size and crystal morphology of the synthetic As_2O_3 solids will be examined by TEM. Laboratory-based powder XRD will provide information on crystal structure, whereas As and Sb coordination will be examined using synchrotron-based methods. High-Energy X-Ray Diffraction (HEXD) and pair-distribution function analysis will offer insight into: (i) mechanisms of Sb substitution into the As_2O_3 structure; and (ii) changes in the crystal structure due to Sb substitution (*e.g.*, Cruz-Hernandez et al., 2018). XAS will track changes in As and Sb coordination in select samples.

Experiments:
Solubility experiments will examine the influence of composition, temperature, pH, and ionic strength on As_2O_3 solubility. We will examine the influence of compositional variation using: (i) synthetic As_2O_3 samples containing a range of relevant Sb contents; and (ii) As_2O_3 samples obtained from the Giant Mine for characterization. We will determine solubility of select As_2O_3 samples and reagent-grade controls of As_2O_3 and Sb_2O_3 over a range of temperature (4°C to 100°C), pH (*e.g.*, 4, 6, 8), and ionic strength (*e.g.*, 0.20 M, 0.02 M, 0.00 M) conditions of relevance to both stabilization methods and the stability of the As_2O_3 dust in the chambers at the Giant Mine.

We will follow similar experimental methods to those described by Dutrizac et al. (2000). Briefly, we will combine excess As_2O_3 with solution in acid-washed reaction vessels, which will be temperature controlled and continuously mixed. Preliminary experiments will be conducted to determine As_2O_3 mass and equilibration time, which will then be fixed for the experiments.

Following equilibration, solution samples will be collected from the reaction vessels for chemical analysis. We will pass these samples through 0.1 μm filter membranes into acid-washed high-density polyethylene bottles, immediately acidify them with trace-metal grade nitric acid, and refrigerate them until analysis by ICP-MS. Dissolved As and Sb concentrations from these experiments will be used to determine As_2O_3 solubility.

One Postdoctoral Fellow (PDF) and one Research Associate will be recruited to conduct the experimental and analytical aspects of the proposed research. The co-investigator team, including Dr. Joyce McBeth and Dr. Matthew Lindsay, and collaborator Dr. Heather Jamieson, will recruit suitable candidates with previous experience in the proposed research area. This approach will greatly reduce the time required to complete the experimental and analytical work. McBeth and Lindsay will co-supervise the PDF and the Research Associate at USask, and we will arrange regular interactions with Jamieson.

Two USask undergraduate students will be hired to assist in the laboratory. We have already identified an academically strong and highly-motivated third-year Geology student at USask to fill one position during the summer of 2019. McBeth will be the primary supervisor for the undergraduate students. Prior to the arrival of the PDF, the undergraduate student will work on safety planning, organizing sample acquisition, and other aspects of project set-up and planning.

This project can be started after a suitable PDF and Research Associate have been recruited. Although we have identified strong candidates to fill these role, their availability to initiate this proposed research remains somewhat uncertain. If funding is approved, we nevertheless anticipate these roles would be filled no later than July 1, 2019. There are substantial advantages to including an experienced PDF and Research Associate on this research rather than an MSc or PhD student. First, these individuals would possess the knowledge and experience to start immediately with the experimental and characterization work. Second, these individuals would not be slowed by graduate-degree requirements, including coursework, examinations, and thesis preparation. These two considerations would ensure that our challenging research objectives can be achieved in a timely manner, within a 1.5-year timeframe.

5. Potential Benefits

We expect that the characterization work can be completed within 12 months of receiving samples. We have access to all non-synchrotron methods (*i.e.*, XRD, SEM/TEM, EPMA) either at USask or Queen's University. Although synchrotron time can sometimes be difficult to obtain, there are facilities that offer a mail-in service for HEXD analysis. This approach negates the need for proposal submission and travel, and can greatly reduce project timelines. We will perform any XAS measurements using existing proposals to limit potential delays. We will begin the solubility experiments in July 2019 with expected completion by December 2020. We will prepare and submit two reports describing our research progress and findings. The first research progress report will be submitted after one year. This report will provide a status update on the characterization and experimental work, and will include an overview of preliminary findings during Year 1. The second research report will be submitted at the conclusion of the project. This report will present all research findings and include appendices with all data generated during the project. Publications are critical to PDF career development and we anticipate this proposed research will support two publications in peer-reviewed journals. These publications would present (i) sample characterization results and (ii) solubility experiment results.

Results from this study will provide comprehensive insights into the chemical, physical, and mineralogical properties of As_2O_3 dust from the Giant Mine site, which will be used to inform potential remediation scenarios (*e.g.*, sulfidation [Project 2], incorporation into cemented paste backfill [Project 3], vitrification [Project 4]). In addition, results from this study, including solubility- and leaching-experiment data, will provide valuable background data for comparison with treated materials; for instance, comparison of the leaching and solubility characteristics for As_2O_3 dust relative to vitrified arsenical glass (Project 4), can be used to substantiate the relative stability of treatment end products.

BUDGET

Project 1 will proceed over a 1.5-year timeframe. The total proposed budget for this research is $228,045, including $182,436 for direct research costs plus 25% overhead ($45,609) charged by the University of Saskatchewan (Table 1).

The budget includes PDF salary support totalling $91,000 over 1.5 years. The budget also includes $11,250 in Research Associate salary support over 1.5 years. $10,250 is allocated to salary support for two undergraduate students.

Category	Year 1	Year 2	Year 3	Total
Salaries and Benefits	$ 72,300	$ 40,200	$ -	$ 112,500
a) PhD students	$ -	$ -	$ -	$ -
b) Master's students	$ -	$ -	$ -	$ -
c) Undergraduate students	$ 4,800	$ 5,450	$ -	$ 10,250
d) Postdoctoral fellows	$ 60,000	$ 31,000	$ -	$ 91,000
e) Technical/Professional Assistants	$ 7,500	$ 3,750	$ -	$ 11,250
Equipment	$ 26,120	$ 26,120	$ -	$ 52,240
a) Purchase or rental	$ 2,400	$ 2,400	$ -	$ 4,800
b) Operation and maintenance costs	$ -	$ -	$ -	$ -
c) User Fees	$ -	$ -	$ -	$ -
d) Analytical Costs	$ 23,720	$ 23,720	$ -	$ 47,440
Materials and Supplies	$ 4,298	$ 4,298	$ -	$ 8,596
a) Laboratory supplies, reagents	$ 4,298	$ 4,298	$ -	$ 8,596
b) Machining costs	$ -	$ -	$ -	$ -
Travel	$ 4,550	$ 4,550	$ -	$ 9,100
a) Conferences and Workshops	$ 2,550	$ 2,550	$ -	$ 5,100
b) Field Work	$ 2,000	$ 2,000	$ -	$ 4,000
Dissemination	$ -	$ -	$ -	$ -
a) Publication costs	$ -	$ -	$ -	$ -
b) Communication costs (teleconference)	$ -	$ -	$ -	$ -
Subtotal	$ 107,268	$ 75,168	$ -	$ 182,436
University Overhead (25%)	$ 26,817	$ 18,792	$ -	$ 45,609
Grand Total	$ 134,085	$ 93,960	$ -	$ 228,045

BACKGROUND INTELLECTUAL PROPERTY:

(a) UW Background Intellectual Property:

None

(b) Third Party Background Intellectual Property:

None

(c) GMOB Background Intellectual Property:

None

GIANT MINE OVERSIGHT BOARD

Per: ______________________

Name: Kathleen Racher

Title: Chair of GMOB

I have the authority to bind GMOB

July 9, 2019

Date

UNIVERSITY OF WATERLOO

Per: ______________________ **Leslie J. Copp**

Name: **Director, Funding**

Title: **Agencies & Non-profit Sponsors**

University of Waterloo

I have the authority to bind the institution

July 15, 2019

Date

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