SCHEDULE "B-5"

RESEARCH PROJECT No. 5

Project Title: Geochemical and leaching characterization of vitrified arsenical glass

RESEARCH TEAM:

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Carol Ptacek (University of Waterloo)

PERIOD OF PERFORMANCE:

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

PROJECT DESCRIPTION:

1. Introduction

The conversion of hazardous wastes into ceramics or vitrified products has the potential to mitigate contaminant mobility and toxicity. This approach has received significant attention in the research community over recent years. Bench-scale studies have examined the potential utility of vitrification for attenuation of contaminants associated with coal fly ash (Guzmán-Carrillo et al., 2018), metallurgical slag (Guzmán-Carrillo et al., 2018; Karamanov et al., 2018), asbestos-bearing wastes (Iwaszko et al., 2018), and fly ash derived from the incineration of medical wastes (Stoch et al., 2018; Tsakalou et al., 2018). In addition, vitrification has been identified as a solution for the long-term disposal of low- and high-level nuclear wastes (*e.g.*, Kim & Kruger, 2018).

Incorporation of reagent-grade arsenic compounds into vitrified products, including arsenic trioxide (As_2O_3) and sodium arsenate (Na_3AsO_4), has been demonstrated under laboratory conditions (*e.g.*, Shi et al., 2015; Zhao et al., 2016, 2017). However, knowledge gaps exist in the scientific literature surrounding the long-term stability of vitrified arsenical glass, and the vitrification of arsenic-bearing industrial residues that are not derived from pure-phase, reagent-grade compounds.

2. Background

In 2016, Dundee Sustainable Technologies developed and implemented a pilot-scale process for the vitrification of arsenic-bearing residues (http://dundeetechnologies.com/arsenic-stabilisation). This proprietary technology is reported to produce glasses with As concentrations of up to 20%. Members of the GMOB have initiated discussions with Dundee Sustainable Technologies regarding the production of test batches of arsenical glasses using discrete samples of As_2O_3 roaster waste from the Giant Mine site. The proposed research project will examine the vitrified materials produced using Dundee's proprietary treatment process. Specifically, this project will examine the leaching characteristics, mineralogical and microstructural properties, solid-phase composition (including the association of As with the glass matrix), and the impact of roaster-waste composition on the properties of the vitrified end-product.

Previous research by Karamanov et al. (2018) focused on the vitrification of hazardous residues from ferronickel production into glass-ceramics. The authors identified that elevated concentrations of Mg-, Fe-, and Cr-oxides in the mixtures contributed to the formation of very fine, crystalline phases, including spinel, pyroxene, and magnetite, within the glass-ceramic structure. The As_2O_3 dust at the Giant Mine contains no Cr, and Fe and Mg were reported in abundances of 0.78-2.62 wt. %, and 0.13-0.37 wt. %, respectively (Dutrizak et al., 2000). Although the As_2O_3 dust at the Giant Mine contains one to two orders of magnitude lower Fe and Mg concentrations relative to the vitrified product described by Karamnov et al. (2018), the presence of Fe and Mg in the roaster waste may induce the formation of fine-grained, crystalline phases during vitrification; such phases may be susceptible to subsequent redox transformations and microbial attack, particularly if mechanical weathering of the vitrified product exposes fresh surface area for reaction.

3. Objectives

It is anticipated that long-term stabilization of As_2O_3 roaster waste through vitrification will require the complete transformation of the roaster waste and auxiliary reagents into a homogenous, vitrified product that is free of fine-grained, crystalline phases. Further, it is anticipated that the presence and abundance of chemical constituents, including oxide phases of Fe, Mg, and Sb, will impact glass stability, and elevated concentrations of these constituents may enhance the leachability and weathering of the vitrified product. The objectives of the proposed research project are to:

i. Provide insights into the leaching properties of vitrified roaster waste; and
ii. Elucidate the solid-phase associations of As within the vitrified product.

4. Methodology

Samples of vitrified slag will be obtained from Dundee Sustainable Technologies through GMOB. These vitrified materials will be characterized to determine the composition and mineralogical properties and subsamples will be subjected to leach testing protocols previously developed to assess the leachability of mine wastes and industrial wastes, and the bioavailability of contaminants contained within these materials. In addition, samples of the arsenic trioxide dust used to generate the vitrified material will be characterized through Project 1 of this proposal.

A series of leach tests and geochemical extractions will be conducted to provide insights into the leaching properties and the potential for As remobilization under differing geochemical conditions. It is anticipated that the Dundee vitrification process will yield a product comprised of ellipsoidal particles of approximately 1 cm in diameter (K. Froese, pers. comm.). All leach tests and extractions will be performed on samples of the as-received particles and on samples pulverized *via* ball mill.

This project will utilize a six-step, non-sequential aqueous-extraction protocol modified after Langman et al. (2017) and references therein: 1) Milli-Q water to target water-soluble As; 2) 0.1 M calcium chloride to target exchangeable and/or weakly-sorbed As; 3) 1 M sodium acetate to target less-readily exchangeable and/or sorbed phases; 4) 0.2 M oxalic acid and 0.2 M ammonium oxalate (pH 3) to target amorphous, reducible phases; 5) 0.5 M hydrochloric acid to target amorphous to crystalline reducible phases; and 6) 30% w/v hydrogen peroxide (adjusted to pH 2 using nitric acid) and 1 M ammonium acetate to target oxidizable phases (*e.g.*, sulfides). In addition, and pending discussions and approvals from Crown-Indigenous Relations and Northern Affairs Canada, leach tests will be conducted using composite groundwater samples collected from the dewatering sump in the underground mine workings at the Giant Mine site as the leachate. Extractants and leachates will be analyzed using ICP–OES, ICP–MS, and ion chromatography (IC).

Optical microscopy and X-ray diffraction will be used to assess the amorphous nature of the vitrified product, and to identify potential crystalline constituents. Scanning electron microscopy – energy dispersive X-ray spectroscopy will be used to provide solid-phase stoichiometric associations. Synchrotron-based X-ray absorption spectroscopy will be used to elucidate As bonding, speciation, and coordination in the vitrified product. Finally, Fourier-transform infrared spectroscopy will be used to observe structural changes resultant of the vitrification process.

Three years of partial funding for a PDF are requested through this project. The PDF will be recruited to conduct the experimental and analytical aspects of the proposed research. The PDF will be assisted by research hydrogeochemists at the University of Waterloo.

5. Potential Benefits

The proposed research activities will inform on the potential utility of vitrification of As_2O_3 from the Giant Mine site to serve as a long-term remediation strategy. This project will provide insights into the solid-phase association of As and other contaminants associated with the roaster waste within the vitrified product. Further, this project will provide insights into potential for remobilization of As and other contaminants from the vitrified product, and will identify potential geochemical incompatibilities for long-term disposal of vitrified arsenical glasses.

BUDGET

The total proposed budget for this research is \$270,400, including \$208,000 for direct research costs plus 30% overhead (\$62,400) charged by the University of Waterloo (Table 5).

The budget includes PDF salary support totalling \$120,000 over three years. The remainder of the PDF salary will be secured from other sources for work on other projects within the Groundwater Geochemistry & Remediation Research Group at the University of Waterloo.

Category	Year 1	Year 2	Year 3	Total
Salaries and Benefits	$ 45,000	$ 45,000	$ 45,000	$ 135,000
a) PhD students	$ -	$ -	$ -	$ -
b) Master's students	$ -	$ -	$ -	$ -
c) Undergraduate students	$ -	$ -	$ -	$ -
d) Postdoctoral fellows	$ 40,000	$ 40,000	$ 40,000	$ 120,000
e) Technical/Professional Assistants	$ 5,000	$ 5,000	$ 5,000	$ 15,000
Equipment	$ 8,000	$ 18,000	$ 18,000	$ 44,000
a) Purchase or rental	$ 2,000	$ 2,000	$ 2,000	$ 6,000
b) Operation and maintenance costs	$ 500	$ 500	$ 500	$ 1,500
c) User Fees	$ 500	$ 500	$ 500	$ 1,500
d) Analytical Costs	$ 5,000	$ 15,000	$ 15,000	$ 35,000
Materials and Supplies	$ 10,000	$ 5,000	$ 5,000	$ 20,000
a) Laboratory supplies, reagents	$ 10,000	$ 5,000	$ 5,000	$ 20,000
b) Machining costs	$ -	$ -	$ -	$ -
Travel	$ -	$ 4,000	$ 4,000	$ 8,000
a) Conferences and Workshops	$ -	$ 2,500	$ 2,500	$ 5,000
b) Field Work	$ -	$ 1,500	$ 1,500	$ 3,000
Dissemination	$ -	$ 500	$ 500	$ 1,000
a) Publication costs	$ -	$ 500	$ 500	$ 1,000
b) Communication costs (teleconference)	$ -	$ -	$ -	$ -
Subtotal	$ 63,000	$ 72,500	$ 72,500	$ 208,000
University Overhead (30%)	$ 18,900	$ 21,750	$ 21,750	$ 62,400
Grand Total	$ 81,900	$ 94,250	$ 94,250	$ 270,400

BACKGROUND INTELLECTUAL PROPERTY:

(a) UW Background Intellectual Property:

None

(b) Third Party Background Intellectual Property:

None

(a) GMOB Background Intellectual Property:

None

GIANT MINE OVERSIGHT BOARD

Per: ______________________

Name: Kathleen Racher

Title: Chair, GMOB

I have the authority to bind GMOB

August 23, 2019

Date

UNIVERSITY OF WATERLOO

Per: ______________________

Name: Leslie J. Copp

Title: Director, Funding Agencies & Non-profit Sponsors, University of Waterloo

I have the authority to bind the Institution

Aug 13, 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: ______________________

Name: David Blowes,

Title: Professor

Date: August 9, 2019