Investigating the Sulfidation and High-Temperature (100 °C – 200 °C) Dissolution of As_2O_3 Stored at the Giant Mine, NWT, Canada

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Abstract

The former Giant Mine, NWT, generated 237 000 tonnes of As_2O_3-rich dust as a by-product of gold mining. As_2O_3 is a relatively soluble form of As and is currently stored beneath the mine, posing a threat of contamination to the adjacent Great Slave Lake. This research investigates the potential for permanent remediation of the Giant Mine As_2O_3 through sulfidation. This research will contribute to the understanding of As_2O_3 solubility above 100 °C, and it explores the potential for applying high temperature-pressure dissolution as a preliminary step toward sulfidation of the As_2O_3 -rich mine waste.

Keywords: Arsenic, As_2O_3, Contamination, Giant Mine, Sulfidation

Introduction

The Giant Mine is located five kilometers north of Yellowknife, NWT, directly adjacent to Great Slave Lake and near the indigenous communities of Ndilo and Dettah. It produced over seven million troy ounces of gold during its years of operation (1948 – 2004) (Jamieson 2014). The gold-bearing arsenopyrite- and pyrite- rich ore required a roasting step prior to gold recovery using cyanidation. During roasting, arsenic-rich gases were condensed and the arsenic was captured as arsenic trioxide-rich (As_2O_3) dust, 237 000 tonnes of which were stored in mined-out stopes and purpose-built chambers in the mine. If the mine is allowed to flood, the solubility of the waste ($\approx$11 g/L at 10 °C; Dutrizac *et al.* 2000) presents a risk of arsenic contamination to Great Slave Lake. The As_2O_3-rich dust is one of Canada's largest environmental liabilities (Jamieson 2014).

This project explores sulfidation as a path to permanent remediation. The calculated arsenic concentration in anaerobic groundwater at equilibrium with $As_2S_{3(am)}$ (PHREEQC, WATEQ4f database; Parkhurst and Appelo 2013) is on the order of 0.001 g As/L, a factor of $\approx$11 000 lower than equilibrium with respect to As_2O_3. If the As_2O_3 dust can be converted to As_2S_3, it could be injected deep into the mine, allowing for reflooding without risk of contamination

to Great Slave Lake. Sulfidation is being explored with two approaches; the first involves a heterogeneous reaction system whereby sulfide, in the form of H_2S, is added to a slurry of As_2O_3. The second is a two-step method whereby As_2O_3 is first dissolved prior to sulfidation by addition of H_2S to a homogeneous aqueous solution. The rate for reaction of aqueous As(III) with H_2S, forming $As_2S_{3(am)}$ is known to be rapid, but the dissolution rate and the solubility of As_2O_3 are not well known above 100 °C, particularly for the impure As_2O_3 from the Giant Mine. Experiments were designed to define the solubility and dissolution rate for reagent-grade As_2O_3 at temperatures between 100 °C and 200 °C. The results represent a guide for subsequent experiments with the aim of determining the efficiency of aqueous extraction of As_2O_3 from the impure Giant Mine dust at temperatures between 100 °C and 200 °C.

Methods

Heterogeneous Process

Sulfidation of As_2O_3 was first investigated by introducing sulfide (H_2S) to an aqueous slurry of reagent-grade As_2O_3. The experimental setup is displayed in Figure 1. Powdered As_2O_3 was added to 250 mL Pyrex® reaction vessels which were then sealed and purged with N_2. De-aerated distilled water,
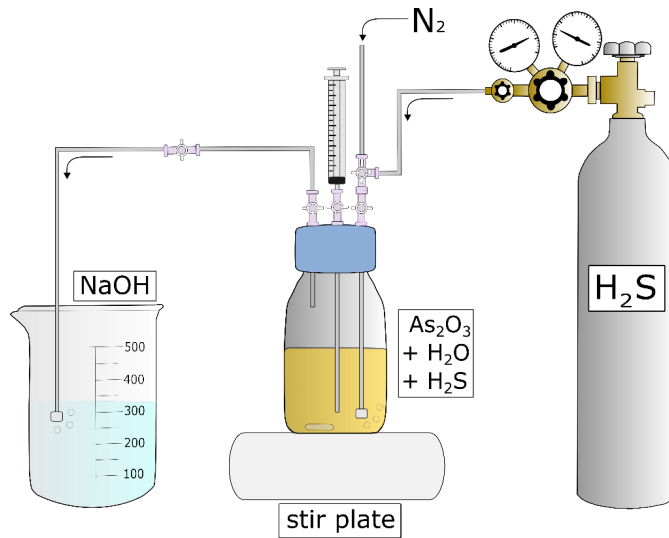
Figure 1 *Experimental setup for sulfidation of an As_2O_3 slurry with H_2S (g).*
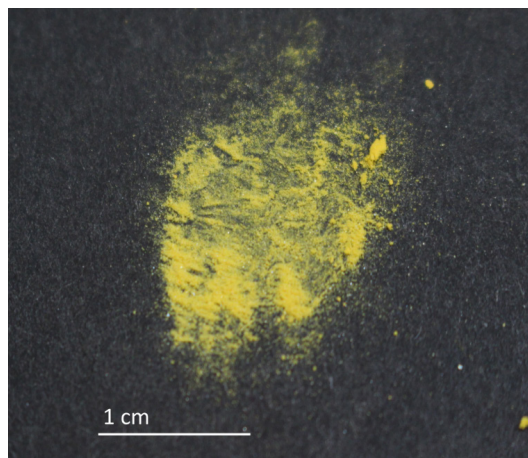

Figure 2 *Reaction product from reaction of an As_2O_3 slurry with H_2S (g).*

acidified to a pH of 4 with HCl, was added to the vessels, as As_2S_3 formation is favourable at a pH of 4 (Eary 1992). H_2S gas was then introduced through a gas dispersion tube for two hours. The solids were then separated by filtration (0.45 μm), dried, and analyzed with X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Elemental Analysis (EA).

Two-Step Process

The dissolution of the As_2O_3 was initially explored using reagent-grade As_2O_3 to determine the solubility and dissolution rate

at elevated temperatures (140 °C, 160 °C, 180 °C, 200 °C) using a CEM Discover® SP microwave. A camera installed in the microwave allowed visual determination of the time to complete dissolution (dissolution rate) for incremental masses of As_2O_3. Similarly, the camera allowed visual determination of the maximum soluble mass (solubility) at any given temperature.

The chemical composition of the Giant Mine dust (archived sample B233-P9) was determined from 10 replicates (each 30 mg) to account for heterogeneity. The replicates were dissolved in concentrated
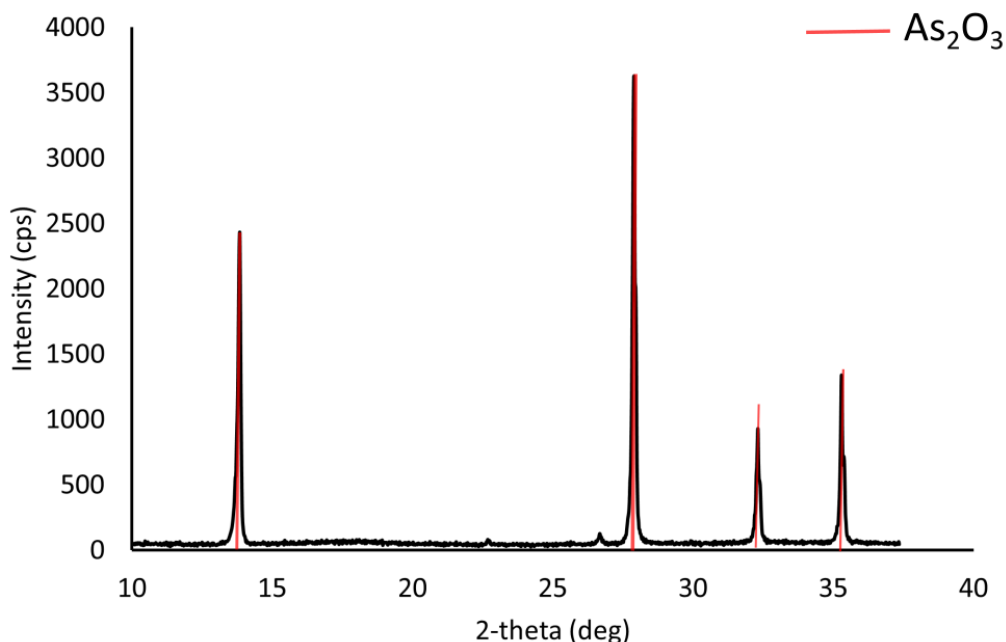
Figure 3 XRD pattern for the reaction product from heterogeneous H_2S experiments. Minor peaks observed at 22.7 and 26.7 degrees are unidentified, and not associated with As_2S_3.

aqua regia (90 °C for 24 hours) in a closed Savillex PTFE vial followed by analysis with Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES). The As yield from aqueous extractions of the Giant Mine dust was then tested using 250 mg of dust in 4 mL of distilled water heated to temperatures of 140 °C, 160 °C, 180 °C and 200 °C over duration of 10, 20, and 30 min in a CEM Discover® SP microwave. To allow for calculation of the yield from the aqueous extractions, a fraction of the residual solids was digested as described previously and analyzed with ICP-OES. Another fraction of the residual solids was embedded in epoxy for SEM analysis.

Results

Heterogeneous Process

As the reaction proceeded, the initially white As_2O_3 powder was transformed to a bright yellow colour (fig. 2), suggesting the formation of As_2O_3, however, subsequent XRD analyses displayed peaks of As_2O_3 with no indication of As_2O_3 (fig. 3). Any newly formed As_2O_3 was expected to be amorphous,

so the sample was further investigated by SEM/EDS analysis and only traces of sulfur were detected. The EA results indicated that the yellow powder contains approximately 1.1 wt% sulfur, whereas pure As_2S_3 contains 39 wt% sulfur.

Two-Step Process

The experiments are still underway, but the solubility measurement for reagent-grade As_2O_3 at 140 °C is plotted in figure 4a along with the solubility curve below 100 °C from Dutrizac *et al.* (2000). Data for the dissolution rate of reagent-grade As_2O_3 at 140 °C are plotted in figure 4b.

Data from the geochemical characterization of the Giant Mine dust are displayed in Table 1, indicating an As concentration of 40.4 ± 7.4 wt%. Heating the dust in water through a range of temperatures (140 to 200 °C) and over durations of 10 to 30 min yielded residues that amounted to 40.7 ± 1.5 wt% of the original mass. The SEM analyses (fig. 5) for residues obtained at 140 °C indicate the presence of As_2O_3 grains that are surrounded by mixed As, Si, Fe, and Sb phases. Residues
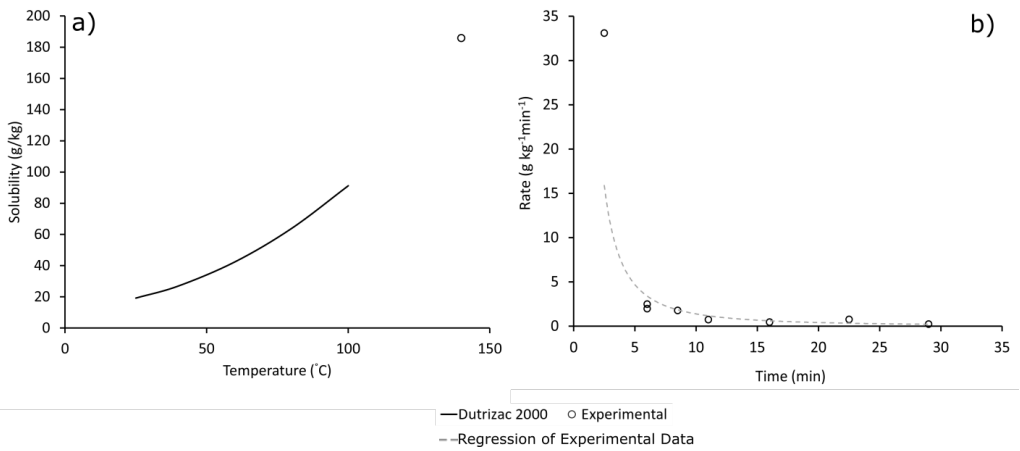
Figure 4 *a) Solubility of reagent-grade As$_2$O$_3$ up to 100 °C, determined by Dutrizac et al. (2000), and solubility determined in this study at 140 °C and 50 PSI. b) The dissolution rate of reagent-grade As$_2$O$_3$ at 140 °C and 50 PSI over time.*

obtained at 160 °C, 180 °C, and 200 °C were similar to those obtained at 140 °C, but with fewer discrete As$_2$O$_3$ grains.

Discussion

Heterogeneous Process

The transformation of the white As$_2$O$_3$ powder to bright yellow during sulfidation suggests the formation of As$_2$O$_3$. However, the SEM and EA analyses indicate that there is very little sulfur present in the powder, suggesting an incomplete reaction. It was concluded that the reaction did not go to completion because of surface passivation by a thin layer of As$_2$O$_3$, creating a limitation on the reaction rate by diffusion through the As$_2$O$_3$ layer.

Two-Step Process

The discovery that the heterogeneous re-action approach causes passivation of the As$_2$O$_3$ surface necessitated a revised approach with an initial dissolution step prior to precipitation of As$_2$S$_{3(am)}$ by reaction of the aqueous solution with H$_2$S. The experiments designed to measure the solubility of reagent-grade As$_2$O$_3$ are intended to constrain the dissolution procedure. They are not yet complete, but results to date appear to align with the solubility curve defined by Dutrizac et al. (2000) between 25 and 100 °C (fig. 4a). Figure 4b displays the calculated dissolution rates of As$_2$O$_3$ at 140 °C between 0 and 30 min,

for which a power regression line defines the overall dissolution rate with the expression

$$R = 80.21x^{-1.764} \tag{1}$$

where R is the dissolution rate (g kg^{-1}min^{-1}) and x is time (min).

Table 1 *B233-P9 Concentrations determined from ten replicates with ICP-OES.*

Element	Mean Concentration	RSD
	mg/kg	%
As (%)	40.4	7.4
Sb	14430	9.8
Fe	90160	5.8
Al	6507	6.0
Ca	9441	8.3
Mg	5464	6.2
K	1151	6.6
Zn	1658	4.9
Na	597	597
Pb	3946	6.0
Cu	641	6.0

The Giant Mine dust that was used for the aqueous extraction experiments (B233-P9) was generated in the early years of the Giant
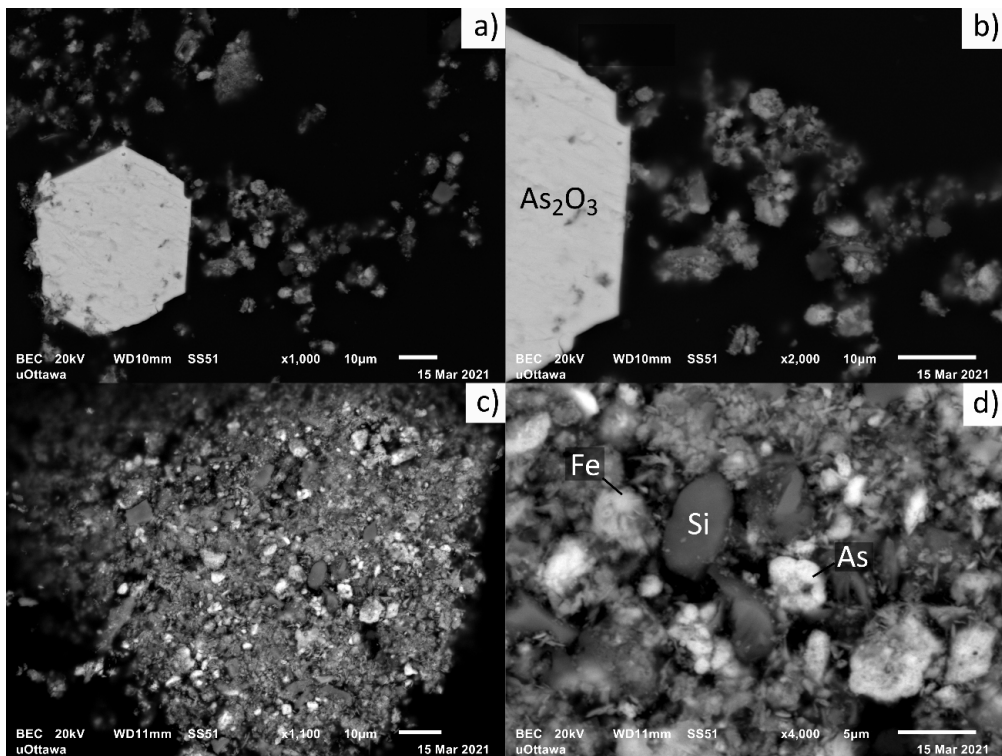
Figure 5 Sample B233-P9. 1a) Residue remaining after heating to 140 °C and 50 PSI for 30 min. 1b) Higher magnification image of 1a). 2a) Residue remaining after heating to 200 °C and 50 PSI for 30 min. 2b) Higher magnification image of 2a). Labels indicate dominant element, but each grain is a mixed phase consisting of As, Sb, Fe, and Si.

Mine's operation (1952–1956) when the roasting operation was relatively inefficient. This sample has low As and high Sb content compared to the material generated in the later years of the Mine operation. The chemical composition of the dust determined in this study (Table 1) is consistent with previous analyses by SGS Lakefield Research Ltd (2004). During the aqueous extraction experiments, 59.3% ± 1.5% of the sample mass dissolved, independent of temperature and extraction duration. This suggests that the Giant Mine dust contains a fraction, approximately 60 wt%, which is relatively soluble, with the remainder being recalcitrant. The recalcitrant nature likely relates to the elevated Sb content as Dutrizac *et al*. (2000) noted that the Sb impurity in the As_2O_3 causes a reduction in the solubility. SEM analyses reveal that Sb is ubiquitous in the residual grains. Further research is planned to investigate the characteristics of the residue.

Conclusion

Sulfidation of As_2O_3 has been investigated in i) a heterogeneous reaction system, and ii) a two-step approach with dissolution of the As_2O_3 followed by sulfidation. The research conducted to date leads to the following conclusions.

- In heterogeneous experiments, where $As_2O_{3(s)}$ is reacted with H_2S in aqueous solution, the reaction does not go to completion because of surface passivation by a thin layer of As_2S_3.
- Experiments designed to constrain the dissolution conditions for the As_2O_3 have extended the upper limit of temperature for the solubility curve from 100 °C to 140 °C and have provided data on the dissolution rate at 140 °C (eq 1).

- Aqueous extraction experiments with the Giant Mine dust at temperatures between 100 and 200 °C indicate that the material contains a fraction that is amenable to aqueous extraction (approximately 60 wt%) with the remainder being relatively recalcitrant.
- The recalcitrant fraction contains Sb-rich As_2O_3, and additional work is required to explore methods to stabilize this residue.

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