Removal of antimony from concentrated solutions with focus on tripuhyite (FeSbO₄) synthesis, characterization and stability

Ravinder S. Multani, Thomas Feldmann, George P. Demopoulos *

Department of Mining and Materials Engineering, McGill University, 3610 University, Montreal, Quebec H3A 0C5, Canada

ARTICLE INFO

Article history:
Received 19 August 2016
Accepted 6 February 2017
Available online 10 February 2017

Keywords:
Antimony
Tripuhyite
Oxidation
Hydrogen peroxide
Leachability
Stability
Hydrothermal
Calcination

ABSTRACT

The precipitation of antimony (Sb) from acidic aqueous solutions (6 g·L⁻¹ Sb) as ferric antimonate, FeSbO₄ (tripuhyite), its further crystallization by hydrothermal or calcination treatment and the determination of its degree of stability were investigated. The precipitation was studied over the pH range 1.5–5.3 at 95 °C via the oxidation of Sb(III) and Fe(II) by drop-wise H₂O₂ addition. Among all tests, oxidation at pH 5.3 over ≈3.5 h with 10 wt% H₂O₂ was retained as best precipitation protocol. The precipitate was characterized as poorly crystalline tripuhyite (possessing high specific surface area in the order of 160–200 m²·g⁻¹). Hydrothermal treatment in pH 1 water was done at 200 °C for 12 h, while calcination at 950 °C for 12 h to increase crystallinity, the latter being more effective. A separate highly crystalline tripuhyite product was synthesized at high temperature (950 °C) by solid–state reaction of goethite and antimony pentoxide in order to serve as reference. The stability/leachability tests indicated that pseudo–equilibrium was attained by all synthesized materials in ≈15 days. Between pH 6 and 8, the untreated precipitate released 100–170 mg·L⁻¹ Sb, hydrothermally treated precipitate released ≈0.5 mg·L⁻¹ Sb, calcined precipitate released 10–35 mg·L⁻¹ Sb, and the reference tripuhyite released ≈0.5 mg·L⁻¹ Sb. The results suggested that stability was mainly a function of tripuhyite crystallinity rather than pH (over the 6–8 range tested). The hydrothermally treated precipitate demonstrated the highest stability (aside from the synthetic reference material). The relatively higher Sb release recorded by the calcined precipitate was traced to its contamination with NaSbO₃, a secondary high temperature phase. Lastly, tripuhyite produced via aqueous precipitation and hydrothermal treatment appears to offer a viable option in fixing antimony from metallurgical waste streams.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Antimony (Sb) is an element that is increasingly encountered globally and recognized as a priority pollutant by both the USEPA and EU (Wilson et al., 2004; Belzile et al., 2011; Álvarez-Ayuso et al., 2013; Resongles et al., 2013). The anthropogenic sources of antimony are primarily fossil fuel burning, mining and smelting operations, and waste incineration (Filella et al., 2009). Of these, the deportment and disposal marquently fossil fuel burning, mining and smelting operations, and waste incineration (Filella et al., 2009). Of these, the deportment and disposal of antimony and arsenic in mineral and metallurgical operations is of relevance to the present work in terms of its environmental implications. Typically, antimony is encountered as an undesirable impurity in various mineral feedstocks treated by the gold, copper, and lead extraction sectors. The processing of such feeds results in the mobilization of antimony, reporting to the air pollution control (APC) residues, slags, flue dusts, and process solutions as well as waste waters, all of which are contaminated and must be freed of antimony (Anderson, 2001). Current industrial treatment is limited to internal processing of recycled antimony waste along with wastewater treatment for environmental disposal (Multani et al., 2016). The waste sludge entering the tailing disposal site contains significant amounts of antimony; however, there is limited information in the literature on the type and stability of these antimony–carrying compounds, which raises the question whether antimony is truly ‘fixed’ at these sites.

In some respects antimony is similar to arsenic, both being metalloids from Group 15 that are highly toxic, having 2 primary oxidation states in aqueous solutions (III and V) and reactive towards iron (II, III) species (Gebel, 1997; Multani et al., 2016). Recent studies on antimony/arsenic systems show that while they have many similarities, there are key differences in their co-ordination with oxygen and precipitation behaviour, resulting in different mineral morphologies and stabilities (Kossoff et al., 2015). Arsenic and its various compounds have been extensively studied in terms of removal and disposal into industrial tailings. Its removal via the co–precipitation method (initial Fe/As molar ratio > 3) which produces an amorphous ferric arsenate/ferricydrite co–precipitate is widely practiced in the industry to treat effluents (Singhania et al., 2006; Le Berre et al., 2008). At the moment, the synthetic mineral scorodite, FeAsO₄·2H₂O, along with few other minerals...
appear to be promising candidates for fixing arsenic as they have shown to release very little in select pH conditions in laboratory tests (<1 mg·L\(^{-1}\)). At pH 5) (Filippou and Demopoulos, 1997). On the other hand, antimony's environmental management is still not adequately developed within the metallurgical industry and requires extensive research as to which antimony compounds should be targeted for its safe immobilization in the supergene environment.

Based on the assessment of the available literature, only quite recently has research emerged that identifies two Fe(III,III)–Sb(III,V) minerals, namely tripuhyite, Fe\(_2\)Sb\(_4\)O\(_9\) (prominent in oxic conditions), and schafarzikite, Fe\(_3\)Sb\(_2\)O\(_6\) (prominent in anoxic conditions), as “two of the ultimate sinks for antimony in the natural environment” (Leverett et al., 2012). Tripuhyite, an analog of scorodite for antimony (bound to ferric iron), appears to fix antimony in the supergene environment, having a solubility of only a few μg·L\(^{-1}\) Sb (Selim, 2012). With such promising low antimony solubility, tripuhyite would appear to be an excellent target compound to fix antimony from mineral/metal processing–derived solutions and residues. Historically, tripuhyite has been synthesized via high temperature (800–1000 °C) solid state reactions (Tianshu and Hing, 1999; Huang and Ruiz, 2005). Very limited work has been done in terms of precipitation of tripuhyite from aqueous solutions that could be applicable to hydrometallurgical solutions. In a recent study Nag et al. (2012) reported the sonochemical precipitation using ammonia (pH 9–10) of a poorly crystalline precipitate that upon subsequent calcination treatment in air yielded crystalline FeSb\(_2\)O\(_4\). Such a process is not amenable to large scale industrial implementation. Hence, there is a need for additional work in this area.

The objective of this research is to investigate the removal of antimony from acidic aqueous solutions as tripuhyite, FeSb\(_2\)O\(_4\), and evaluate it in terms of stability and therefore a potential candidate for the fixation of antimony from mineral and metallurgical processing waste streams. In carrying out this research, the precipitation and evaluation of tripuhyite was studied drawing from our group’s experience with the analogous atmospheric scorodite precipitation system (Demopoulos, 2005). In particular, the present study’s focus is placed on three main sections: (1) FeSb\(_2\)O\(_4\) precipitation and subsequent treatment; (2) material characterization; and (3) tripuhyite precipitate stability under environmentally–relevant pH conditions.

2. Materials and methods

2.1. Synthesis (oxidation–precipitation)

The oxidative precipitation tests were conducted in a 2 L glass flat bottom stirred reactor equipped with temperature control. Reagent grade antimony(III) potassium tartrate hydrate (C\(_6\)H\(_8\)K\(_2\)O\(_4\)Sb\(_2\)·xH\(_2\)O) and iron(II) sulfate heptahydrate (FeSO\(_4\)·7H\(_2\)O) were dissolved in deionized water at equimolar ratios to obtain initial concentrations of 0.05 M. The tartrate was used as the antimony source over other reagents (i.e., SbCl\(_3\) and Sb\(_2\)O\(_3\)) since it allowed for high Sb(III) concentrations (high solubility) and maintain a strict sulfate system. The reaction temperature was set to 95 °C (±1 °C) and pH was maintained with 1 M NaOH and/or 96% H\(_2\)SO\(_4\). Hydrogen peroxide (10 wt%) was added dropwise at 100% excess by a peristaltic pump (calibrated to 1.2 mL/min) over the course of 3.5 h to oxidize Sb(III) and Fe(II).

Upon completion of the precipitation test, the hot slurry was filtered and subsequently washed and dried before being further treated or tested/characterized. In the wash cycle procedure, the filter cake was repulsed in 1 L de-ionized water and agitated/mixed for 3 h, after which the slurry was pressure filtered again. Following the completion of wash cycles (5–6), the final filter cake was dried for 24 h at 50 °C. The dried precipitate (typically ≈24 g) was ground by mortar and pestle and separated into 3 equal parts (≈8 g); where 1 part (untreated) was retained for stability testing, 1 part was treated hydrothermally, and the remaining part treated by calcination.

2.2. Thermal treatments (hydrothermal and calcination)

Hydrothermal treatment of the precipitate was conducted in a non-agitated Parr pressure autoclave of 100 mL capacity equipped with a Teflon container (autonomous pressure). The dried precipitate was added into 50 mL acidified (with H\(_2\)SO\(_4\)) deionized water (pH 1) placed in the Teflon container which was then transferred into the pressure vessel for treatment. Solution pH 1 was chosen in order to accelerate the dissolution of any amorphous material and facilitate recrystallization into higher crystalline tripuhyite. The temperature was 200 °C and the duration was 12 h. Calcination of the dried precipitate powder was conducted in a Thermo Scientific box furnace. The powder (8 g) was placed in a ceramic bowl, it was then calcined in the furnace in the presence of stagnant air at 950 °C for 12 h. The hydrothermally and calcined products were also subjected to the same wash cycle procedure mentioned previously, where the only differences were the filtration times (4–5 h for the hydrothermal product and <5 min for the calcined product; the difference was due to material particle size). The product filter cakes were also dried for 24 h at 50 °C and subjected to stability testing.

2.3. Solid state reference material synthesis

Crystalline tripuhyite reference material was synthesized using a modification of the high temperature solid–state method previously reported by Martinelli et al. (2002) in which reagent grade goethite (α–FeOOH) and antimony pentoxide (Sb\(_2\)O\(_5\)) were substituted for hematite (Fe\(_2\)O\(_3\)) and antimony trioxide (Sb\(_2\)O\(_3\)), respectively. Initial tests employing Fe\(_2\)O\(_3\) and Sb\(_2\)O\(_3\), as mentioned in the original paper, resulted in incomplete reaction with mixed phase product, hence the substitution with α–FeOOH and Sb\(_2\)O\(_3\). The synthetic material was made under the same conditions as the calcined precipitate; however, the starting powder (15.67 g) was an equimolar mixture of reagent grade goethite (α–FeOOH) (5.67 g) and antimony pentoxide (Sb\(_2\)O\(_3\)) (10 g). After calcination, the powders were lightly ground by mortar and pestle to break down agglomerates.

2.4. Stability/leachability tests

Representative powder samples of the different products (after washing/filtration and drying) were subjected to stability testing at 22 °C to quantify the amount of antimony released along with other ions (iron, sodium, sulfur, and calcium). Dried powder samples (1 g) were placed in Erlenmeyer flasks containing deionized water (100 mL), after which the solution pH (5, 6, and 7) was adjusted with 5 mM nitric acid or 1 mM lime solution (base); the pH was kept stable around ±0.5 of the target value. For high pH solutions (8 and 9), 20 mM lime solution was used to maintain pH if 1 mM was found to be insufficient. The flasks for the stability tests were sealed with Parafilm tape and placed on a shaker table (100 rpm) and were opened only during sampling periods. Solution pH was monitored and aliquots were taken periodically (filtered with 0.22 μm syringe filters) to determine elemental concentrations. For each tested powder, a separate solution was monitored for natural pH drift and antimony release, where no pH adjustment was done.

2.5. Characterization methods

Solution samples were analyzed with a Thermo Scientific iCAP 6500 ICP–OES CID Spectrometer. Ferrous (Fe(II)) titration for both filtrate and slurry samples was carried out as per procedure outlined in Daenzer et al. (2014). Powder characterization for phase identification (X-ray diffraction) was performed with a Bruker Discover D8 – 2D Diffractometer using Co Kα radiation. The diffractometer scan rate was set to approximately 3.5°/20 min, with the total acquisition time of 30 min (1 h for poorly crystalline samples). The 2θ range was between 12.8 and