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Batch and continuous precipitation of scorodite from dilute industrial solutions

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ABSTRACT

Enriched arsenic precipitates were obtained from dilute industrial As(III) solutions (1.1–0.1 g As/L) at 95 °C in batch and continuous reactor operations. A complete and fast oxidation of As(III) was obtained at room temperature with 20% excess of hydrogen peroxide. Arsenic removal varied from 80.5 to 94.6% and increased with the total surface area (SSA) of the seed. SSA higher than 270 m^2/g was required to promote an arsenic removal of approximately 85%. Recycling of solids was necessary to achieve high yields of arsenic removal in continuous operation. Approximately 75 to 85% As was removed in 1 h of residence time in the MSMPRR (Mixed Suspension Mixed Product Removal with Solids Recycle) reactor; the rate of crystal growth was calculated as 10^{-12} m/s. Arsenic removal was not favored by the excess of iron in the solution. TCLP (Toxicity Characterization Leaching Procedure) testing indicated that ageing plays an important role in the leachability of scorodite, which decreased from 13.6 mg As/L to 0.1 mg As/L after 8 h in a batch reactor. The decrease in As leachability was related to the decrease in the SSA (14 m^2/g to 0.9 m^2/g after 62 h in the MSMPRR) as a combination of crystal growth (1.6 µm to 5.3 µm) and densification. Scorodite was the only arsenic phase identified by X-ray diffraction and micro-Raman analyses of the precipitates.

1. Introduction

Arsenic is one of the contaminants of concern present in wastes from metallurgical and mining industries. Due to its high toxicity, environmental regulations are becoming increasingly more stringent regarding the use and disposal of As compounds. Thus, arsenic removal from industrial effluents often becomes necessary in order to comply with environmental legislation (WHO, 1993). However, it is also important that arsenic residues be disposed of in relatively stable phases in order to avoid its further release into the environment. The methods of arsenic immobilization commonly used by the mining industry are the precipitation of arsenical ferrihydrite (AsFH) at room temperature and the hydrothermal precipitation of iron arsenates. The AsFH process (here including arsenic removal by both precipitation of ferric arsenates and adsorption on iron oxihydroxides) generates large volumes of waste with low arsenic content (e.g. 3–8%). Thus, large areas for the final disposal are needed, which in turn results in additional operational costs.

Compared to the AsFH, the precipitation as crystalline scorodite ($FeAsO_4*2H_2O$) offers the advantages of combining a relatively high arsenic content and low release of As in aqueous solutions. The relatively low Fe/As molar ratio, the smaller waste volume due to its higher density, and the good capacity of sedimentation offer additional advantages for this disposal process in comparison to the conventional ferrihydrite process. Scorodite is readily produced under hydrothermal conditions (temperatures of 150 °C or higher) applied to the acid pressure oxidation of refractory gold ores. However, the relatively high capital and operational costs associated with hydrothermal operations make this option economically attractive only if it can be coupled with the extraction of a valuable product, such as gold or copper.

Due to the aforementioned advantages, there have been attempts to obtain scorodite in more benign conditions. Demopoulos and coworkers (Demopoulos et al., 1995; Demopoulos, 2005; Singhania et al., 2005, 2006) demonstrated the possibility of precipitating scorodite at atmospheric pressure conditions and temperatures below the water boiling point (95 °C). Scorodite precipitation requires previous arsenic oxidation to the pentavalent state. A number of oxidants have been investigated, such as sulfur dioxide–oxygen mixtures (Wang et al., 2000), nitric acid, sodium chlorate, ozone and hydrogen peroxide (Pettine et al., 1999), the latter being the environmentally preferred agent. Commercial applications of the atmospheric pressure scorodite precipitation are apparently hindered by the costs associated with the use of an iron source, such as $Fe_2(SO_4)_3$, and of an oxidant, such as H_2O_2. There are also the difficulties related to operations at temperatures just below the boiling point of water and to the control of supersaturation through the adjustment of pH. The precipitation should be carried out under low supersaturating conditions and with the addition of relatively large amounts of seeds in order to favor crystal growth rather than homogeneous nucleation, which leads to the formation of an amorphous ferric arsenate phase.

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The pioneering work of Demopoulos and co-workers at McGill University on scorodite precipitation at ambient pressure were mainly focused on concentrated solutions, the obvious niche for this process' application. Previous publications usually describe arsenic precipitation under batch conditions and from solutions prepared with reagent grade chemicals. In batch tests, arsenic concentration decreases over time. In a continuous operation, under steady-state conditions, the arsenic concentration remains constant within the reaction vessel, thus allowing for a more favorable supersaturation control, which in turn favors scorodite production. Solution composition may also affect the kinetics and efficiency of arsenic removal. The present work investigates the precipitation of arsenic from relatively dilute aqueous solutions (1.1 g/L As) leaving the gas washing tower of the oxidative roasting of a refractory gold ore. Arsenic is currently being removed as arsenical ferryhydrite (3–6% As) and disposed of as toxic wastes in constructed tailings dams (Caldeira et al., 2005; Caetano et al., 2006). The expansion of the roasting plant, coupled with the consequent need for larger waste disposal areas, gave way to the search for process alternatives, including scorodite precipitation. The present work was aimed at establishing operational conditions for scorodite precipitation from solutions 100 to 10 times more diluted than those usually described in the literature. Firstly, the conditions for As(III) and Fe(II) oxidation were established and the effect of the initial arsenic concentration was evaluated in tests carried out in batch systems. The effect of seed concentration was also studied but with the focus on surface area. At a subsequent stage, scorodite precipitation was investigated in a continuous system. In addition to the better control of process variables, the continuous system represents better actual industrial operations. The relative leachability of the precipitates was compared through standard leaching tests (TCLP), as an indication of a potential arsenic release into the environment. The broader aim was to assess the possibility of obtaining a more stable waste with greater arsenic content than that currently produced by the ferryhydrite process. Expected benefits include the reduction of the waste volume and the associated costs of disposal.

2. Experimental procedure

An industrial solution containing 1.1 g/L As ($As_{total}=1.1$ g/L; As(III) = 0.96 g/L; $Fe_{total}=0.15$ g/L, Fe(II) = 0.13 g/L; pH = 2.3; $(SO_4^{2-})_{total}=2.85$ g/L; Cu = 7.6 mg/L; Ni = 0.51 mg/L; Mn = 25.1 mg/L) and Fe/As molar ratio equal to 0.2 was used as the feed solution. In order to reach a Fe/As mean ratio = 1, iron (II) sulfate or ferric chloride was added. The oxidation experiments were performed in a 2 L stirred reactor for 60 min, with the addition of 20% stoichiometric excess of hydrogen peroxide (1.75 mol/L) to assure the total oxidation of Fe(II) and As(III). The pH was previously adjusted at 1.2 (Caldeira et al., 2005) with the addition of concentrated H_2SO_4, in order to avoid the precipitation of the amorphous arsenate in the subsequent stage of scorodite precipitation or when the oxidation was carried out above room temperature. The preparation of the seed materials was carried out in a 2L PARR autoclave using concentrated ferric sulfate and sodium arsenate (Fe/As molar ratio of 1:1) solutions prepared with reagent grade chemicals. The initial arsenic concentration was 33 g/L or 25 g/L, and the pH of 1.3 or 1.5, respectively, adjusted with the addition of sulfuric acid. The temperature was kept at 150 °C, and the reaction time was of 2 h (Papangelakis and Demopoulos, 1990; Swash and Monhemius, 1994).

Following the oxidation of Fe(II) and As(III) and seeds production, the experiments of batch precipitation were carried out in a stirred reactor containing 1 L of solution. The temperature was maintained at 95 °C while the Fe/As molar ratio was within a range of 0.9 to 1.2. After a reaction time of 2 h, the solids were vacuum filtered and the solution was diluted using 50 µL of concentrated nitric acid to prevent the formation of amorphous solid material. A comparative study of scorodite and gypsum seeds (reagent grade calcium sulfate) was also carried out. The effects of the initial arsenic concentration and sulfate concentration on arsenic removal have been evaluated as well.

In the continuous system, the precipitation was carried out with the recycling of solids in a set-up designated as *Mixed Suspension Mixed Product Removal with Recycling* — MSMPRR. The tests were carried out in duplicate with samples of the industrial solution used in batch tests. In order to achieve steady-state conditions, the experiments were carried out during at least eight residence times (8 h). The temperature was kept constant at 95 °C by hot oil circulation within the reactor jacket. The industrial solution containing 40 g/L of scorodite seed was added to the reactor (1 L) at a continuous controlled mass flow (approximately 1 L/h) using a previously calibrated peristaltic pump. The heating and stirring systems were turned on, and the time zero of the experiments was defined upon reaching 95 °C. At 15-minute intervals, the pulp was collected and vacuum filtered. The solids were then mixed with fresh oxidized solution (1 g/L As) and returned to the reactor, maintaining the solid/liquid ratio of approximately 35% under steady-state conditions. During the tests, samples were taken from the slurry leaving the reactor at regular periods of time (approximately 50 mL/h). The pulp was vacuum filtered, and the solution acidity was adjusted using 50 µL of concentrated nitric acid to prevent the formation of amorphous material prior to the chemical analyses.

The As_{total} and Fe_{total} concentrations were determined by atomic absorption spectrometry (Perkin Elmer AAnalyst 300), with the air/acetylene flame (wavelength of 328.1 nm and 248.3 nm for As_{total} and Fe_{total}, respectively). Sulfate concentration was determined by turbidimetry (Micronal model B382) according to the procedure described in the Standard Methods for the Examination of Water and Wastewater (Standard Methods, 1998). The scorodite seed produced in autoclave, and the products obtained in the precipitation tests, were dried at 40 °C for 24 h and characterized by X-ray diffraction analyses (Philips model PW1710), scanning electron microscopy (MEV) (JEOL model JSM-6360L VI coupled with an energy dispersive spectrometer-EDS), and Micro-Raman spectroscopy (Jobin Yvon/Horiba model LabRam HR 800). The latter included a He–Ne laser with 632.8 nm wavelength and power output of 20 mW as the excitation source with a liquid nitrogen cooler CCD. In order to obtain the MEV images, the samples were covered with a carbon layer to assure the electron conduction and heat dissipation. The particle size distribution and the BET specific surface area (SSA) were determined by laser scattering (Cilas 1064) and nitrogen adsorption (Quantachrome, model Nova 1000), respectively. Leaching tests were carried out in order to examine the leachability of the precipitates, according to the Toxicity Characterization Leaching Procedure-TCLP tests (EPA, 1992). The determination of arsenic and iron concentrations in the extract was carried out using an ELAN ® 9000 ICP-MS instrument (Perkin Elmer SCIEX).

3. Results and discussion

3.1. Batch precipitation

Efficient precipitation and stability of arsenic wastes require prior oxidation of the arsenic and iron species to As(V) and Fe(III). Oxygen alone is not effective in oxidizing As(III) in acidic solutions. Various oxidizers have been investigated, hydrogen peroxide being the best choice to date. The original studies of Tozawa and Nishimura (1984) indicated slow oxidation rates of As(III) by hydrogen peroxide at room temperature and acidic solutions. The results demonstrated the need of high temperatures and large excess of hydrogen peroxide to achieve adequate yields. Pettine et al. (1999) also concluded that the undissociated $As(OH)_3$ does not react with hydrogen peroxide and the oxidation rate increases with the increase of pH. Debekaussen et al. (2001) investigated a number of parameters affecting As(III) oxidation and demonstrated that with a combination of slow addition