An *in-situ* synchrotron XAS study on the evolution of aqueous arsenic species in acid pressure leaching

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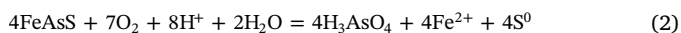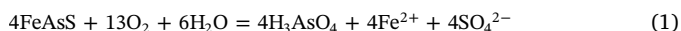## ARTICLE INFO

ABSTRACT

The evolution of oxidation state of aqueous arsenic (As) under the condition of acid pressure leaching was investigated for the first time by *in-situ* synchrotron X-ray absorption spectroscopy (XAS). At an oxygen pressure of 28 bar, the dissolved As in leaching solutions (0.5 M H_2SO_4 coexisting with arsenopyrite) existed as As(V) at room temperature. As(III) appeared increasingly with temperature rising from 100 °C and eventually, at temperatures greater than 200 °C, only As(III) was detected. The process was reversible in that the arsenic in solution was re-oxidized to As(V) during cooling. The addition of Fe^{3+} favored the presence of As(V) in solution. Higher initial ferric concentration required a higher temperature for the formation of As(III) and profoundly reduced the reduction rate of As(V) and enhanced the re-oxidation rate of As(III). Compared to pure oxygen, As(III) was more readily stabilized in leaching solutions using compressed air. The EXAFS data show that the As(V) in solution was coordinated with 4.1 oxygen atoms in the first shell with an average distance of 1.71 Å, which indicates the presence of H_3AsO_4 or its deprotonated forms. Meanwhile As(III) in solution (at 225 °C) was coordinated with 3.1 oxygen atoms in the first shell with an average distance of 1.80 Å, suggesting the presence of H_3AsO_3. It is concluded that the identified As(III) species in the leaching solution at elevated temperature has a significant impact on the reaction chemistry of acid pressure leaching for As-bearing sulfide.

1. Introduction

Many gold deposits currently being developed contain gold finely disseminated in refractory minerals such as arsenopyrite (FeAsS) (Cabri et al., 2000). To render this type of ore amenable to cyanidation, prior treatment by an intensive oxidation method is usually required to decompose the crystal structure of the host minerals and thereby liberate the gold. Acid pressure oxidation which employs temperatures above the melting point of sulfur (119 °C), and high oxygen overpressure above 700 kPa is currently widely used for this purpose (Papangelakis and Demopoulos, 1990a). The overall reactions of arsenopyrite oxidation in an autoclave can be described by the following reactions (Papangelakis and Demopoulos, 1990a; Corkhill and Vaughan, 2009).

$$4FeAsS + 13O_2 + 6H_2O = 4H_3AsO_4 + 4Fe^{2+} + 4SO_4^{2-} \qquad (1)$$

$$4FeAsS + 7O_2 + 8H^+ + 2H_2O = 4H_3AsO_4 + 4Fe^{2+} + 4S^0 \qquad (2)$$

$$4FeAsS + 11O_2 + 6H_2O = 4Fe^{2+} + 4H_3AsO_3 + 4SO_4^{2-} \qquad (3)$$

$$2H_3AsO_3 + O_2 = 2H_2AsO_4^- + 2H^+ \qquad (4)$$

$$FeAsS + 8Fe^{3+} + (4 + n)H_2O = FeAsO_4 \cdot nH_2O + 8Fe^{2+} + S^0 + 8H^+ \qquad (5)$$
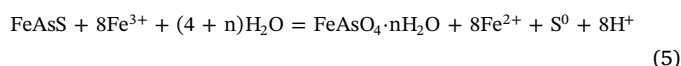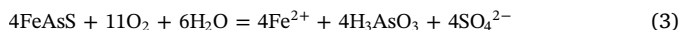
Oxidation of arsenopyrite at elevated temperature involves very complex reaction systems including several oxidation and hydrolytic reactions which occur in series and/or in parallel that release H_2SO_4, H_3AsO_3 and H_3AsO_4 (Nesbitt et al., 1995). At the same time, soluble As species may react with iron and form precipitates (Papangelakis and Demopoulos, 1990a):

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \qquad (6)$$

$$Fe^{3+} + H_3AsO_4 + 2H_2O = FeAsO_4 \cdot 2H_2O + 3H^+ \qquad (7)$$
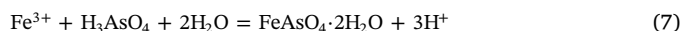
Arsenic in this form is a hazardous material and the As-containing solution needs to be treated before discharge. The fixation of arsenic from aqueous effluents is currently achieved by the precipitation of As in the form of scorodite-like compounds ($FeAsO_4 \cdot 2H_2O$) (Filippou and Demopoulo, 1997). Therefore, it is desirable that the arsenic species in

the cooling-down stage presents as As(V) which is both less toxic and less mobile.

The oxidation state and speciation of As are impacted by several environment parameters. Iron has been reported to play an important role in arsenic oxidation (Corkhill and Vaughan, 2009). At the same time, oxygen pressure also plays a vital role in pressure leaching (Papangelakis and Demopoulos, 1990b). Hug and Leupin (2003) reported that As(III) was not measurably oxidized by dissolved oxygen or dissolved Fe(III) and hydrogen on a time scale of hours at pH 3.5–7.5, but partially or completely oxidized in parallel to the oxidation of Fe(II) by oxygen in aerated solutions. Although their results were observed at ambient temperature and pressure, they indicated the presence of oxygen and iron are both important for As(III) oxidation. However, at present the impact of oxygen pressure and iron concentration on the arsenic speciation evolution in pressure leaching, in particular at elevated temperatures, is yet to be investigated.

As the nature and composition of the leaching products have a considerable impact on the downstream operations of gold recovery and waste management (Papangelakis and Demopoulos, 1990a), an understanding of the reaction mechanisms will facilitate design and optimization of pressure leaching operations. So far, the chemical speciation involved in arsenopyrite pressure leaching were mostly analyzed *ex-situ* at room temperature and ambient pressure from an autoclave leaching experiment, which cannot fully reflect the reactions and changes happening in the pressure leaching process.

For speciation studies of arsenic solubility, a range of techniques such as HPLC separation with ICPMS, HG atomic spectrometry, and electrospray MS detection have been successfully applied (*e.g.*, Gong et al., 2002; McGuire et al., 2001). These techniques provide sensitive detection to the trace level of arsenic species and play an important role in the chemical species analysis of arsenic. However, they are insufficiently able to track the chemical reactions occurring at high temperature and pressure that are typical of acid pressure leaching conditions. In contrast, XAS has been widely used to identify As speciation and oxidation state in *in-situ* solution studies in extreme sample environments (Testemale et al., 2004; Farges and Wilke, 2016). For example, James-Smith et al. (2010) studied As speciation in fluid inclusions at temperatures ranging from 25 to 200 °C, and determined the oxidation state as well as As–O bonding states of the dissolved As. However, to the best of our knowledge, there are no reports of *in-situ* XAS investigation on the mechanisms of arsenopyrite pressure leaching.

The aim of the present work was to directly reveal the evolution of As chemical speciation in solution during pressure leaching processes by *in-situ* XAS as a function of temperature. The impacts of different solution conditions such as Fe^{3+} concentration, oxygen partial pressure on the As speciation evolution were also evaluated.

2. Experimental

2.1. Starting materials

The arsenopyrite was provided by Zijin mining corporation, China. The XRD analysis of the original mineral showed arsenopyrite was the only phase detectable. The arsenopyrite was grounded to −200 mesh (less than 74 μm) before use. Sulfuric acid (AR grade) was purchased from Merck and ferric sulfate (AR grade) was purchased from Sigma. Millipore deionized water was used for solution preparation.

2.2. Setup for in-situ XAS measurement

Experimental setup of the *in-situ* XAS measurement at the X-ray absorption spectroscopy beamline at the Australian Synchrotron is shown in Fig. 1. The solid sample and solution was placed in a quartz capillary with an outer diameter (OD) of 1 mm and wall thickness of 0.1 mm, which was connected to a gas cylinder for pressurized air or oxygen at 28 bar. A hot air blower was positioned under the capillary
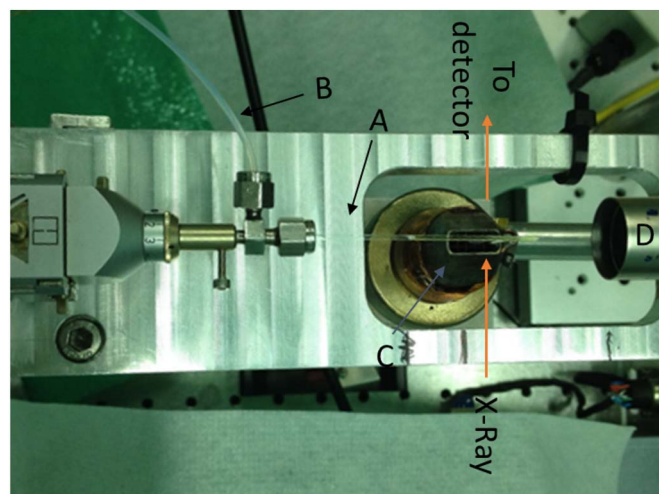

Fig. 1. Top view of the setup for *in-situ* XAS experiment (A: quartz capillary; B: gas line; C: hot air blower; D: capillary shoot-out catcher).

with an integrated thermocouple for temperature measurement. The temperature in the capillary was calibrated by the melting temperature of potassium nitrate (334 °C) and sucrose (186 °C). The position of the capillary was controlled on an XY motorized stage accurately aligned in the X-ray path.

For each leaching experiment approximately 2 mg mineral was added in the capillary with 18 μL solution, which contained 50 g/L Fe^{3+}, 10 g/L Fe^{3+} or no Fe^{3+} in 0.5 M sulfuric acid. The leaching pressure was set to 28 bar using compressed oxygen or air. In the case of air, the oxygen partial pressure was 5.88 bar. In each experiment, the system was heated from room temperature to 200–225 °C and then cooled down to room temperature. The XAS data were collected at different temperatures during the heating and cooling cycles.

2.3. XAS data acquisition and analysis

X-ray absorption spectroscopy spectra were recorded at the XAS beamline at the Australian Synchrotron. The current of the storage ring was operated in top-up mode with a beam current approximately 200 mA. The XAS beamline is a wiggler beamline equipped with a cryogenically cooled Si(111) monochromator, with an energy resolution ($\Delta E/E$) of 1.5×10^{-4}. The beam size was 0.25×0.25 mm (fully focused) at the sample. The data were collected at As K-edge in transmission mode using a set of ionization chambers. The L_3 edge of a bulk metallic Au foil was collected at the same time to calibrate the X-ray energy. XAS data calibration, normalization and peak fitting were performed using Athena software, and the EXAFS fitting was performed using Artemis software which incorporates theoretical calculated paths by FEFF 6 (Ravel and Newville, 2005). The scale factor S_0^2 was determined by fitting an arsenate standard solution and fixed at 0.73 for the analysis of the samples.

3. Results and discussion

3.1. Evolution of As solution species with temperature

The evolution of As solution species in the arsenopyrite pressure leaching solution (using oxygen) is shown in Fig. 2A *via* As K-edge X-ray Absorption Near edge structure (XANES) spectra. At room temperature, the XANES spectrum shows a single strong peak at 11874.8 eV, which indicates the presence of As(V) species (Ona-Nguema et al., 2010). With increasing temperature, the spectra showed clear changes in trend (Fig. 2A). After increasing the temperature to 80 °C, the As(V) was still predominant in the solution. However, when the temperature was