



## Effect of hydroquinone-induced iron reduction on the stability of scorodite and arsenic mobilization



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### ABSTRACT

Scorodite precipitation is widely employed for the fixation of arsenic in hydrometallurgical industries. However, its stability in reducing environment is not yet fully understood. This work investigated the effect of hydroquinone-induced Fe(III) reduction on the stability of scorodite. The results showed that  $\leq 3\%$  ( $11.3 \text{ mg L}^{-1}$ ) arsenic and  $< 4\%$  ( $11 \text{ mg L}^{-1}$ ) Fe(II) were released into solution after 72–90% of Fe(III) was reduced to Fe(II) at pH 4–8. This indicated that most of the reductive decomposition generated Fe(II) and As(V) were retained in the solid phases as secondary minerals. The XRD, ATR-FTIR, Raman, SEM-EDS and chemical analysis suggested that amorphous  $\text{FeHASO}_4 \cdot x\text{H}_2\text{O}$  was very likely the major sink for arsenic immobilization. At pH 9, the scorodite decomposed completely resulting in  $\sim 19\%$  ( $71.2 \text{ mg L}^{-1}$ ) arsenic and  $\sim 3\%$  ( $8.2 \text{ mg L}^{-1}$ ) Fe(II) release and a residual solid of Fe/As  $\sim 1.2$ . Both amorphous ferrous arsenates and Fe(II, III) (hydr)oxides were probably responsible for the retention of arsenic in this case. The solubility of scorodite in terms of dissolved arsenic concentration upon iron reduction at pH 7–9 was significantly lower than that in oxic environment under the conditions of this work.

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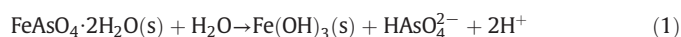
### 1. Introduction

Arsenic contamination in water environment has been recognized as a major threat for human health (Bundschuh et al., 2012; Rahman et al., 2012; Smedley and Kinniburgh, 2002). Release of arsenic to water body from anthropogenic activities is problematic in some areas proximal to mining and smelting of non-ferrous ores associated with arsenic (Vaca-Escobar et al., 2012).

In non-ferrous metallurgical industry, arsenic is usually liberated from the ores as roasting dust (mainly as  $\text{As}_2\text{O}_3$  and  $\text{As}_2\text{S}_3$ ) in pyrometallurgical operations and/or released into mineral processing solutions in hydrometallurgical operations (Riveros and Utigard, 2000; Riveros et al., 2001). In both cases arsenic must be immobilized and disposed safely to prevent polluting soils and waters. Among the available technologies, scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ) precipitation and iron-arsenate coprecipitation are widely employed in industrial practice for the immobilization of arsenic. The former product, a crystalline ferric arsenate, is a better carrier for the fixation of arsenic from roasting dusts and arsenic-rich and iron-deficient effluents. Compared with iron-arsenate coprecipitates, not only does its formation demand lower iron (Fe/As

$= 1$ ), but the product itself can be of better crystallinity, higher density and therefore greater thermodynamic stability as well (Bluteau et al., 2009; Jia et al., 2012; Majzlan et al., 2012).

The stability of scorodite during its long-term storage in the environment, which strongly depends on the redox conditions, has long been of concern. A number of studies thus far have only shown its decomposition under aerobic conditions. According to previous records scorodite is stable only in slightly acidic environments, but dissolves incongruently in circum-neutral and alkaline pH to form ferrihydrite and consequently releases arsenic to solution (Bluteau and Demopoulos, 2007; Langmuir et al., 2006), as shown by the following equation:



Influx of natural organic matter (NOM) into the tailings pond provides nutrients to the microbes. Oxygen in the subsurface tailings will be depleted due to the respiration processes and as a result, anaerobic conditions will develop. Few studies, however, have examined the stability of scorodite under anoxic conditions. Microbially-mediated iron reduction by dissimilatory Fe-reducing bacteria (DIRB) has been found to lead to the mobilization of iron oxyhydroxide-associated arsenic due to reductive dissolution of the substrate iron oxyhydroxides (Babechuk et al., 2009; Campbell et al., 2006; Fan et al., 2014;

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Wang et al., 2009). This has been considered as one of the major underlying mechanisms for the mobilization of arsenic in sediments (Postma et al., 2010; Xu et al., 2011) and the cause of elevated concentration of arsenic in groundwater (Kar et al., 2010; Percy et al., 2011). By analogue, reductive decomposition of scorodite due to iron reduction may lead to the mobilization of arsenic. In the studies on arsenic mobilization in sediments and soils where scorodite was used as a reference compound, the effect of dissimilatory Fe-reducing bacteria caused significant arsenic release from scorodite at circum-neutral pH, with the concentration of dissolved arsenic rising up to  $\sim 60 \text{ mg L}^{-1}$  (Papassiopi et al., 2003) and  $\sim 115 \text{ mg L}^{-1}$  (Cummings et al., 1999). Abiotic reduction of iron by sulfide was also found to cause significant arsenic release ( $\sim 200 \text{ mg L}^{-1}$ ) from scorodite (Lagno et al., 2010). The formation of secondary minerals, e.g. low solubility ferrous arsenate phases (Daenzer et al., 2014; Johnston and Singer, 2007) may act as a sink hence inhibiting the release of arsenic. The stability of both scorodite (Bluteau and Demopoulos, 2007; Krause and Ettel, 1988; Langmuir et al., 2006; Robins, 1990) and ferrous arsenate (Daenzer et al., 2014; Johnston and Singer, 2007) are strongly pH dependent. Hence it is necessary to investigate the influence of iron reduction on the stability of scorodite over a wide range of pH.

In this work hydroquinone was used as an iron reducing agent to assess the stability of scorodite. One of the reasons for using hydroquinone as an abiotic reducing agent was that it has been employed to study reductive transformation and the stability of iron (hydr)oxides and As(V)-bearing ferrihydrite (Anschutz and Penn, 2005; Erbs et al., 2008, 2010; Stack et al., 2004). Another consideration to use hydroquinone was that quinone/hydroquinone functional groups are widely occurring redox couples in natural organic matters (Anschutz and Penn, 2005), and can act as electron shuttles in biotic redox reaction (Fredrickson et al., 1998; Lovley et al., 1998).

Scorodite may be disposed in oxic environment or oxygen-deficient environment (e.g. tailings pond). The solubility of scorodite in oxic environment has been extensively studied whereas the latter case is not well known. It is necessary to make clear the stability of scorodite in oxygen-deficient environment and the effect of iron reduction on the scorodite stability under anoxic condition. Therefore, the objectives of this work were to investigate the stability and arsenic mobility of scorodite upon hydroquinone-induced reduction of iron at various pH values and to discuss the underlying mechanisms.

## 2. Materials and methods

### 2.1. Synthesis of scorodite and reference materials

Scorodite was synthesized via the modified precipitation method described previously (Le Berre et al., 2008). Briefly, ferric iron solution ( $7.5 \text{ g L}^{-1}$  Fe) and arsenate solution ( $10 \text{ g L}^{-1}$  As) were prepared by dissolving  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$  in de-ionized water, respectively, and adjusted to pH 0.8 using  $\text{H}_2\text{SO}_4$ . Equal volume of ferric iron and arsenate solutions (Fe/As = 1) were mixed and neutralized with NaOH solution to pH 1.2. The mixture was then heated to  $95^\circ\text{C}$  and stabilized for 12 h under mechanical stirring to convert the initially precipitated amorphous ferric arsenate to scorodite.

The ferrous arsenate references used in this work include crystalline ferrous arsenate  $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$  (identified as parasymplectite below), amorphous ferrous arsenate and the material precipitated from an Fe(II)/As(V) = 1 solution. The latter one was synthesized to simulate the reaction product formed during reductive decomposition of scorodite by hydroquinone. The experiments were performed inside a glovebox under the protection of high-purity  $\text{N}_2$  and deoxygenated de-ionized water was used. The crystalline and amorphous ferrous arsenate was synthesized by mixing equal volume of  $51 \text{ mmol L}^{-1}$  As(V) solution and  $76.6 \text{ mmol L}^{-1}$  Fe(II) solution (with the stoichiometry of Fe(II)/As(V) = 1.5) at pH 4 in a 250 mL serum bottle, followed by raising the pH of the mixture to 7 with NaOH and stabilizing for 3 days and

1 day, respectively. Magnetic stirring was applied throughout the experiments. Chemical analysis showed that the Fe(II)/As(V) molar ratio of the synthesized amorphous ferrous arsenate was 1.5. The material precipitated from an Fe(II)/As(V) = 1 solution was synthesized using the same procedure. The resultant product was digested in  $1 \text{ mol L}^{-1}$  HCl to analyze the contents of Fe(II) and As(V) and the results showed that Fe(II)/As(V) molar ratio was 1.27, hence this reference material was designated as “Fe(II)/As(V) = 1.27”.

Ferrihydrite was synthesized according to the conventional procedure (Schwertmann and Cornell, 2000). Briefly, the Fe(III) solution was prepared by dissolving  $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$  in de-ionized water. The pH of the solution was rapidly brought to  $\sim 7.5$  using  $1 \text{ mol L}^{-1}$  NaOH solution. The slurry was maintained at constant pH for 24 h with mechanical stirring vigorously. For the preparation of arsenate adsorbed ferrihydrite, the above-mentioned ferrihydrite slurry was added into an arsenate solution and the mixture ( $280 \text{ mg L}^{-1}$  Fe,  $75 \text{ mg L}^{-1}$  As, Fe/As = 5, pH  $\sim 7.5$ ) was allowed to equilibrate for 24 h with mechanical stirring. The ferrihydrite samples with and without adsorbed arsenate were separated by centrifuging, washed three times with de-ionized water and freeze-dried for characterization.

### 2.2. Abiotic iron reduction of scorodite

The experiments were performed in the anaerobic chamber at  $30^\circ\text{C}$  under the protection of high-purity  $\text{N}_2$ . All solutions were prepared by using oxygen-free de-ionized water. Equal volume (100 mL) of hydroquinone ( $\text{QH}_2$ ) solutions and scorodite slurries ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}/\text{QH}_2$  molar ratio of 0.02), both pre-adjusted to desired pHs (4, 5, 6, 7, 8, 9) with HCl and/or NaOH solutions, were mixed in serum bottles with magnetic stirring. The solid/liquid (S/L) ratio of 1:900 used in this study was comparable to the S/L ratio (1:500–1:2000) employed in previous works on the reductive dissolution of As(V)-ferrihydrite (Erbs et al., 2008, 2010). The concentrations of total iron and arsenic in each system were 280 and  $375 \text{ mg L}^{-1}$ , respectively. The pHs of the mixtures were maintained constant over the course of reaction using  $0.1 \text{ mol L}^{-1}$  NaOH or HCl solutions. Aliquots of the mixture were collected at regular time intervals and filtered through  $0.22\text{-}\mu\text{m}$  membrane filters. To minimize the possible oxidation of reduced Fe(II) caused by frequent sampling, the sampling interval was set to 1–4 weeks after the first 48 h. The filtrates were analyzed to determine the concentrations of total arsenic, As(III), total iron and Fe(II) in the aqueous phase. The residual solids were dissolved in  $6 \text{ mol L}^{-1}$  HCl and analyzed for total iron and Fe(II) concentrations. The percentage of Fe reduced was calculated by the following equation:

$$R = \frac{\text{Fe(II)}_{\text{aq}} + \text{Fe(II)}_{\text{s}}}{\text{Fe(T)}} \times 100 (\%) \quad (2)$$

where R represents the percentage of Fe reduced;  $\text{Fe(II)}_{\text{aq}}$  represents the concentration of dissolved Fe(II);  $\text{Fe(II)}_{\text{s}}$  represents the concentration of solid Fe(II);  $\text{Fe(T)}$  represents the concentration of total Fe in each system.

All tests were conducted in duplicates and the averages were reported. At the end of the reaction (i.e. 125 days), the sampled slurries ( $<0.5 \text{ mL}$  each time) were filtered with syringe filter, blew out the entrained solution among the particles with high purity nitrogen gas (in glovebox) followed by three times of washing with oxygen-free de-ionized water and ethanol to remove the residual hydroquinone and the organic reaction products. This procedure maximized washing away of residual solution and minimized washing away of As and Fe in secondary minerals. The concentrations of As and Fe in the washing solutions were measured and found to be negligible for As and Fe in the bulk solids. Then the solid phases were dried naturally in the glovebox under the protection of high-purity  $\text{N}_2$ , transferred to serum bottles with a butyl rubber stopper and a screw-cap lid and stored in fridge for characterization.

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