



Encapsulation of scorodite using crystalline polyferric sulfate precipitated from the Fe(II)-SO₄²⁻-O₂-H₂O system

Pingchao Ke, Kezhou Song, Zhihong Liu*

School of Metallurgy and Environment, Central South University, Changsha 410083, China



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ABSTRACT

Scorodite was encapsulated by precipitating a crystalline polyferric sulfate (PFS) coating layer on the surface of scorodite particles to restrain the release of arsenic. The encapsulation experiments were carried out at atmospheric pressure, 90 °C, and 1.5 pH by adding 20 g scorodite particles/L to a 0.1–0.4 mol/L ferrous sulfate solution followed by the introduction of pure oxygen to oxidize and precipitate the ferrous ions as PFS. After encapsulation the samples were characterized using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and scanning transmission electron microscopy. The results indicated that the coating was crystalline PFS, and the scorodite particles were completely encapsulated by the coating. The stability of the scorodite encapsulated with PFS was evaluated by several toxic leaching tests which use an HAC-NaAc buffer solution of 4.93 pH, a NaOH solution of 9.3 pH, a NaH₂PO₄-NaOH buffer solution of 8.6 pH, or Na₂S solutions of 7.6 and 8.1 pH and a reducing potential (E_h) within the –100 to 0 mV range as leaching solutions. The results of the leaching tests indicated that the scorodite encapsulated with PFS was highly effective at restraining the release of arsenic in both weakly acidic and alkaline solutions under both oxic and anoxic conditions.

1. Introduction

Arsenic immobilization is an important concern for arsenic-containing solutions generated from nonferrous metallurgical processes, especially the metallurgy of heavy and precious metals such as copper, lead, zinc, and gold (Riveros et al., 2001). Hence, investigations addressing this issue are necessary to solve the problem of the arsenic pollution associated with these processes. According to numerous reports, scorodite is a good carrier for arsenic immobilization due to its great stability, low operation cost, high rate of arsenic content, and good crystallinity (Hopkin, 1989; Berre Le et al., 2008; Paktunc et al., 2008; Nazari et al., 2017), and can be synthesized using both atmospheric and hydrothermal systems (Dutrizac and Jambor, 1988; Demopoulos et al., 1995; Filippou and Demopoulos, 1997; Fujita et al., 2008a; Okibe et al., 2014). However, the hydrothermal process has not been a common method for scorodite synthesis because of its large consumption of energy and resources. The atmospheric process has prominent advantages including low temperature, atmospheric pressure, high efficiency for arsenic precipitation, and large size of scorodite particles (Fujita et al., 2008b). Therefore, the atmospheric process has been a popular method for scorodite synthesis.

Moreover, the stability of scorodite is a very important indicator to

evaluate the efficacy of arsenic immobilization by precipitation as scorodite. Worldwide, the most popular method for evaluating the stability of solid waste is the Toxic Characteristic Leaching Procedure (TCLP) proposed by the United States Environmental Protection Agency (US-EPA) in 1992 (Paul, 2012), and the limit value for the leaching concentration of arsenic was regulated at 1 mg/L. In accordance with this method, many researchers have reported that scorodite had good stability in the 2.0 to 6.0 pH range, and the leaching concentration of arsenic was much smaller than 1 mg/L (Robins, 1987; Krause and Ettl, 1988). However, scorodite is not stable in alkaline conditions (Langmuir et al., 2006; Bluteau and Demopoulos, 2007). Scorodite also shows poor stability under anoxic conditions due to the presence of anaerobic bacteria commonly living in the deep regions of tailings ponds or the presence of unreacted sulfide minerals reducing Fe(III) to Fe(II) (Lagno et al., 2010; Adelman et al., 2015). On the other hand, phosphate is present in the water supply due to the use of phosphorous-containing detergents (Mohan and Pittman Jr., 2007), yet scorodite is not stable in solutions containing phosphorus due to the ionic exchange that occurs between PO₄³⁻ and AsO₄³⁻ that promotes the release of arsenic.

To solve this problem, many researchers proposed the use of special materials such as sodium silicate gel and aluminum phosphate to

* Corresponding author.

E-mail address: zhliu@csu.edu.cn (Z. Liu).

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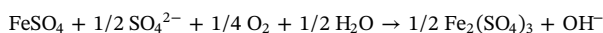
encapsulate scorodite. The results of leaching indicated that aluminum phosphate appeared effective at controlling the release of arsenic by more than one order of magnitude, however sodium silicate gel strengthened the release of arsenic due to the ion exchange between SiO_4^{2-} and AsO_4^{3-} (Lagno et al., 2010; Adelman et al., 2015). All the encapsulation methods reported were based on the idea that an inert material was used to coat the surface of scorodite to prevent the physical contact between the scorodite particles and surrounding environment. However, these approaches brought new challenges for the encapsulation material.

Herein, we propose a new idea to improve the stability of scorodite: (1) a special material was employed to encapsulate scorodite to block the diffusion of invasive ions and release of arsenic during leaching (Jenna et al., 2017; Mukhopadhyay et al., 2017); (2) the equilibrium of the scorodite dissolution was broken, and a new equilibrium was established by the coexistence of scorodite and iron compounds to restrain the release of arsenic (Zhu and Merkel, 2001; Krause and Ettel, 1989). Thus, we found an effective material, crystalline polyferric sulfate (PFS), to encapsulate scorodite.

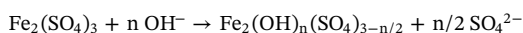
Polyferric sulfate is a well-known flocculation agent, and is typically used for wastewater treatment (Zouboulis et al., 2008). The chemical formula of PFS is described as $[\text{Fe}_2(\text{OH})_n(\text{SO}_4)_{3-n/2}]_m$, where $n < 2$. When PFS comes in contact with water, $[\text{Fe}_2(\text{OH})_3]^{3+}$, $[\text{Fe}_2(\text{OH})_2]^{4+}$, $[\text{Fe}^3(\text{OH})_6]^{3+}$, and other complex hydroxyl ions form. These ions are able to decrease the chemical oxygen demand (COD), biochemical oxygen demand (BOD), and turbidity of water, as well as the amount of heavy metal ions in water through hydrolysis, adsorption, gathering, and bridging processes (Zhang et al., 2017). Moreover, PFS is less sensitive to temperature and pH, and exhibits efficiency in a wide pH range of 4–11. Two methods can be typically used to synthesize PFS (Chang and Wang, 2002). First, PFS was synthesized by adding a ferric sulfate solution to a sodium hydroxide or sodium bicarbonate solution under high-speed stirring. Second, the synthesis of PFS commences with the oxidation of ferrous sulfate to ferric sulfate in highly acidic conditions. In general, the oxidizing agents used were nitric acid, hydrogen peroxide, sodium/potassium chlorate, oxygen, or oxygen-enriched air (Fan et al., 2002).

In our study, the second method was employed to synthesize PFS, and pure oxygen was introduced for oxidizing ferrous sulfate. The reaction followed these three steps (Li et al., 1997):

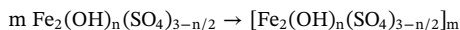
oxidation



hydrolysis



and polymerization



On the other hand, encapsulating scorodite is also an important aspect. Usually scorodite can be encapsulated by immediately adding it to the encapsulating materials such as sodium silicate gel or by precipitating an encapsulation layer such as aluminum phosphate (Lagno et al., 2010; Adelman et al., 2015). In this study, considering the filtering performance of encapsulation products, we opted to precipitate crystalline PFS on the surface of scorodite. Therefore, scorodite particles were added to the ferrous sulfate solution. A high temperature of 90 °C was required during the encapsulation to ensure the precipitation of crystalline instead of amorphous PFS on the surface of scorodite.

This study proposed a method of encapsulating scorodite via the precipitation of crystalline PFS from the $\text{Fe}(\text{II})\text{-SO}_4^{2-}\text{-O}_2\text{-H}_2\text{O}$ system on the surface of scorodite to restrain the release of arsenic under both weak acidic and alkaline conditions.

2. Experimental

2.1. Preparation of scorodite

Scorodite particles were prepared in a 1 L cylindrical quartz reactor following a method we previously proposed (Ke et al., 2017). Arsenic trioxide was dissolved and oxidized by hydrogen peroxide in an aqueous solution to prepare a 0.4 mol/L arsenic acid solution, then the pH was adjusted to 1.50 ± 0.05 by adding 0.8 mol/L sodium hydroxide solution, dropwise. A 0.4 mol/L ferrous sulfate solution was prepared and the pH was adjusted to 1.5 ± 0.5 using a sulfuric acid solution. Subsequently, the ferrous sulfate solution was added to the arsenic acid solution using a low-speed constant flow pump, while controlling the arsenic to iron molar ratio to be 1:1. During the preparation, pure oxygen gas was introduced into the solution at a continuous 1 L/min rate using a cylindrical bubble stone 8.0 cm in diameter and 1.5 cm high. The temperature inside the reactor was maintained at 90 °C for 7 h. The slurry was stirred at 250 rpm using an impeller. Thereafter, the sample slurry was passed through a 4 μm pore polytetrafluoroethylene (PTFE) membrane, washed with distilled water three times, then dried at 60 ± 1 °C for 24 h. The dried solid was pulverized in a mortar for encapsulation, characterization, and testing.

2.2. Encapsulation of scorodite

Pure PFS should be synthesized before encapsulating scorodite, because it should be confirmed that the precipitate synthesized from the $\text{Fe}(\text{II})\text{-SO}_4^{2-}\text{-O}_2\text{-H}_2\text{O}$ system was indeed PFS. Therefore PFS should be analyzed and compared with the scorodite coated with PFS. On the other hand, to evaluate the adsorption capacity of PFS for arsenic, pure PFS samples also should be synthesized as adsorbent.

The PFS samples were prepared by oxidizing ferrous to ferric ions and then precipitating them. The apparatus used in our experiment is illustrated in Fig. 1. Before the reaction, 0.1, 0.2, 0.3, 0.4, 0.8, and 1.0 mol/L ferrous sulfate solutions were prepared and their pH was adjusted to 1.5 ± 0.05 using sulfuric acid. Subsequently, 250 mL ferrous sulfate solution and 1 g PFS seeds synthesized following the general method reported by Zouboulis et al. (2008) were mixed into a 1 L cylindrical quartz reactor, and then the mixture was preheated to 90 °C using a thermostatic water bath. The temperature was calibrated using two thermometers of which one was immersed into the reaction mixture, and the other into the water bath. The impeller was driven at a 250 rpm speed using a motor to ensure that the solid and liquid mixed adequately. Furthermore, high purity oxygen was introduced via a

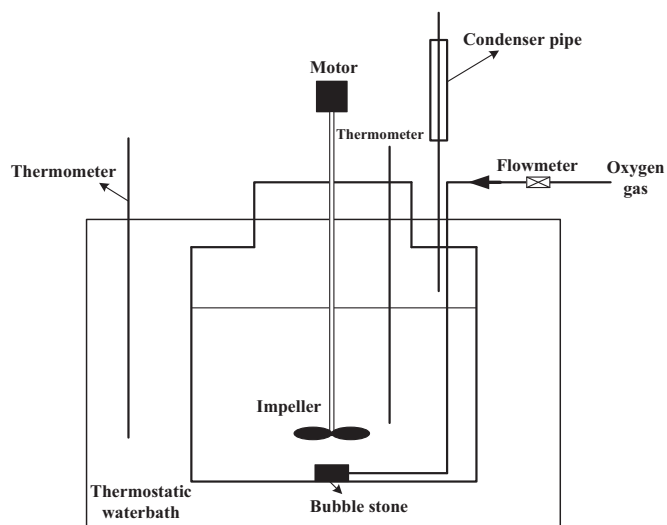


Fig. 1. Experimental apparatus for the preparation of PFS.

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