



Ozonation leaching of a complex sulfidic antimony ore in hydrochloric acid solution



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ABSTRACT

Selective dissolution of stibnite from a complex sulfidic antimony ore containing pyrite by ozonation leaching in hydrochloric acid solution has been studied in the paper. Effects of hydrochloric acid concentration, leaching time, temperature, gas (ozone and oxygen mixture) flow rate and liquid/solid ratio on antimony extraction and iron dissolution have been examined. The results show that the leaching efficiency (%) of antimony increases with the temperature (from 35 °C to 65 °C) and hydrochloric acid concentration (from 3.0 mol/L to 4.5 mol/L). In comparison, the iron dissolution remains constant in these ranges. In addition, it is noted that the decomposition of stibnite is easier than that of pyrite. High antimony extraction (94.3%) with low iron dissolution (2.3%) is achieved under the following leaching conditions: 4.5 mol/L hydrochloric acid concentration, 2.0 L/min gas flow rate and 8:1 of the L/S ratio, leaching for 4.0 h at 65 °C. These results reveal that ozonation leaching of the complex sulfidic antimony ore in hydrochloric acid solution is a promising technology.

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1. Introduction

Most of antimony produced from antimony-bearing ores is used as flame retardants, catalysts in plastics production, pigments in paints or in production of glassware (Oorts and Smolders, 2009). China is the largest producer of antimony in the world (Yang, 2009). The most important antimony resource exploited in China is the antimony ore containing stibnite (Sb₂S₃).

Traditionally, extraction of antimony from stibnite involves a two-step pyrometallurgical process including roasting and carbothermal reduction. However, the pyrometallurgical process usually results in serious environmental pollution and high energy consumption (Wang and Lei, 2000). In 2012, a low-temperature molten salt smelting process which can directly produce antimony from its ore was proposed (Ye et al., 2012), and under the optimum conditions, the average direct recovery ratio of antimony was 84.4%. Compared with the pyrometallurgy technology, the hydrometallurgical process is considered as an environmental friendly technique which has attracted more attention due to their potential to deal with low grade complex stibnite.

Leaching of stibnite in an alkaline solution was proposed by previous researchers (Raschman and Sminčáková, 2012; Ubaldini et al., 2000; Anderson, 2003) and has been employed industrially in China, Australia and United States. The lixiviant of a mixture of sodium sulfide

and sodium hydroxide has been used by Anderson (2012). Raschman and Sminčáková (2012) reported that more than 90% antimony recovery during 60 min leaching of a stibnite ore at 19 °C using an alkaline solution containing 1% Na₂S and 1% NaOH (w/w) has been achieved. Similar antimony recovery (85%) was obtained from a refractory gold-bearing stibnite ore in 5 min with alkaline solution (20 g/L Na₂S and NaOH) at 80 °C by Ubaldini et al. (2000).

In the acidic chloride system, hydrochloric acid was used as the lixiviant in conjunction with an oxidant, such as ferric chloride, chlorine and antimony pentachloride for antimony recovery from stibnite. In the process proposed by Yang and Wu (2014), SbCl₅ was used as the oxidant to obtain the SbCl₃ solution at 85 °C. The antimony extraction from the pregnant leach solution in acidic chloride system was summarized by Du and Tang (2008).

It has been noticed that the oxidants mentioned above cause problems of equipment corrosion and low recovery of valuable elements. Previous researchers have used ozone as the oxidant in the hydrometallurgical leaching process (Carrillo Pedroza et al., 2007; Havlik et al., 1999). Ukasik and Havlik (2005) studied the tetrahedrite leaching in HCl solution using ozone as an oxidant. Li et al. (2009) introduced ozone into the leaching process of pyrite, in the sulfuric acid system and the iron dissolution was 75% under the optimum condition. Nonetheless, little information on stibnite leaching using ozone as an oxidant has been reported.

Complex sulfidic antimony ore in Hunan province (China) mainly consists of stibnite, pyrite and silica. In the past few years, researchers have paid much attention to the antimony extraction, but seldom

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focused on the dissolution of iron during leaching. Obviously, the high dissolution of pyrite may result in iron hydrolyzing in the hydrolysis process which leads to high impurity of the final antimony product (Lei et al., 2001). Thus, an improved leaching process to obtain maximal antimony extraction and minimal dissolution of iron is required. In this work, a hydrochloric acid leaching using ozone as an oxidant was applied to treat a complex sulfidic antimony ore, and the factors affecting antimony extraction and dissolution of iron have been investigated.

2. Experimental

2.1. Materials and characterization

A complex sulfidic antimony ore with high grade of stibnite and pyrite was chosen as the raw material in this work to better understand the behavior of antimony and iron in the ozonation leaching process. The ore was from the west region of Hunan province (China) and was used without any pretreatment other than crushing to a size of 100% -160 mesh (94 μm). The concentration of metal ions in solution was determined by using an Atomic Absorption Spectrophotometer (AAS, WFX-130B, RAYLEIGH, China). The elemental assays of ore and leach residue was obtained by digestion and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, PS-6, Baird, USA) and X-ray fluorescence (XRF, S0902724, Rigaku, Japan). The mineralogical composition was identified by X-Ray diffraction (XRD, S0902240, Rigaku, Japan). Analytical grade hydrochloric acid (36–38% (w/w)) was used to prepare the HCl solutions. Industrial grade oxygen was used to produce ozone for the leaching process and the mass flow of the ozone controlled by an ozonizer (OZOMJB-10B, ANQIU OZOMAX EQUIPMENT, China) was 10 g/h.

2.2. Experimental procedure

The leaching experiments were carried out in a beaker (500 mL) heated by a thermostatted water bath (DF-101B, YUHUA, China) equipped with a magnetic stirrer and a digital controller unit. Ozonizer provided a constant amount of ozone during the whole experiment and the gas (a mixture of ozone and oxygen) flow rate was controlled by a gas flowmeter.

As a leaching agent, 400 mL of hydrochloric acid as the required mole ratio diluted with distilled water was added to the beaker. A continuous stirring speed of 400 rpm was maintained using a Teflon coated magnetic stirrer bar. When the temperature reached the set value, about 40 g of the complex sulfidic antimony ore was added, and the ozone was pumped into the solution. A condenser was used to prevent evaporation during the experiment. After the leaching treatment, the slurry was withdrawn from the reactor and vacuum filtered. The volume of the filtered pregnant solution was measured by a measuring cylinder, and 5 mL of the liquor sample was collected to assay antimony and iron by AAS. The filter cake was washed twice with 400 mL distilled water, and then dried at 80 °C for 24 h. The dried filter cake was analyzed by XRD.

3. Results and discussion

3.1. Assays and characterization

The chemical composition of the ore is listed in Table 1. The XRD analysis in Fig. 1 shows stibnite, pyrite and quartz as the major mineral phases.

Table 1

The chemical compositions of the complex sulfidic antimony ore.

Component	Sb ₂ S ₃	FeS ₂	SiO ₂	As ₂ O ₃	MgO	Al ₂ O ₃	CaO	Others
% (w/w)	58.57	24.41	12.43	3.04	0.22	0.43	0.41	0.49

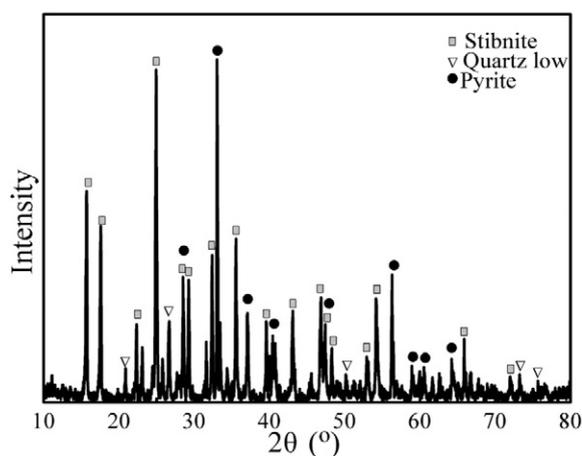


Fig. 1. XRD scans of the complex sulfidic antimony ore.

3.2. Antimony and iron extraction

3.2.1. Effects of temperature

Fig. 2 shows the effect of temperature on the extraction of antimony and dissolution of iron. The results indicate that antimony extraction increases rapidly from 18.0% at 35 °C to the maximum of 99.0% at 65 °C, and then gradually decreases from 95.8% at 80 °C to 88.2% at 95 °C. The iron dissolution slightly increases from 2.5% at 35 °C to 2.7% at 65 °C. It increases in the temperature range of 65 °C to 95 °C, and reaches 6.2% at 95 °C.

This decrease of the antimony extraction in the temperature range of 65–95 °C would be due to the volatilization of HCl. The ozone solubility in solution decreases with the increase in temperature (Tian et al., 2012; Wang et al., 2009) and causes a decrease of leaching efficiency. In addition, the decomposition of ozone (O₃) in water increases drastically with increasing temperature (Knud et al., 1991), and the most important decomposition product is hydroxyl radical. The standard hydrogen electrode potential of hydroxyl radical is 2.80 V (Guedes et al., 2003) which is higher than 2.07 V of ozone (Ukasik and Havlik, 2005), indicating that the decomposition of O₃ favors the leaching process by shifting the oxidative potential of the solutions to more oxidizing conditions. However, decomposition of O₃ means that the concentration of O₃ will decrease in the solution and this will lower the kinetics of the leach process. So, the antimony extraction increases first and then decreases in the temperature range of 35 °C to 95 °C.

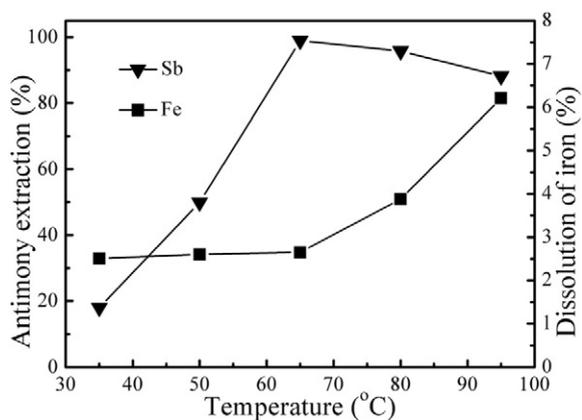


Fig. 2. Effects of temperature on extraction of antimony and dissolution of iron from the complex sulfidic antimony ore. The operating conditions: 4.5 mol/L HCl, 2.0 L/min gas flow rate, L/S ratio of 10 mL/g, and 5.0 h.

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