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Simultaneous leaching of low grade bismuthinite and pyrolusite ores in hydrochloric acid medium

Fenghua Ding, Jing Zhan *, Zhijian Wang, Liyuan Chai, Chuanfu Zhang

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

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ABSTRACT

A simultaneous leaching process to extract both bismuth and manganese by one-step leaching in hydrochloric acid solution is proposed in this paper. Thermodynamic investigations of the E_h–pH diagram of both Mn–H_2O and Bi–S–Cl–H_2O systems showed that the equilibrium potentials of MnO_2/Mn^{2+} couple were much higher than that of Bi_2S_3/Bi(III) couple. The electrochemical experiments presented the electrochemical reactions of bismuthinite and pyrolusite. Most suitable operating leach parameters were established as follows: liquid-to-solid ratio (mL/g), 5:1; initial hydrochloric acid concentration, 4 mol/L; leaching temperature, 70 °C; ore ratio (measured by the mole ratio of manganese and sulfur, $n_{(Mn)}/n_{(S)}$), 1.4/1; leaching time, 2 h; and agitation speed, 500 rpm. Leaching efficiency of 96.6% and 97.1% for bismuth and manganese were obtained, respectively, under the optimum experimental conditions.

1. Introduction

Bismuth is considered as “green and ecologically clean” metal and widely used in cosmetics and pharmaceuticals (Ha et al., 2015; Wang et al., 2007). China is the largest producer of bismuth in the world. The commercial process to extract bismuth from bismuthinite (Bi_2S_3) is the pyrometallurgical processes, which include the reductive smelting. However, the smelting process causes serious environmental pollution and large energy consumption (Yang et al., 2011). Besides, depletion of high grade bismuth ore has made low and medium grade ores to be the future raw material for the extraction of bismuth especially for the growing requirement of varistors, catalyst, gas sensors, photovoltaic cells and microwave integrated circuits. However, the aforementioned pyrometallurgical route could not economically process the low or medium-grade ore with amiable environment. Different hydrometallurgical processes for bismuthinite have been widely studied accordingly. It is known that the bismuth sulfide could not be leached directly by acid solution in the absence of oxidizing agents such as $FeCl_3$ (Senanayake and Muir, 1988), Cl_2 (Wang et al., 2001) or $NaClO_3$ (Yang et al., 2009a). Moreover, the application of these oxidizing agents during leaching process may expose many problems such as high reagent consumption, serious equipment corrosion and low recovery rate. So a more practical process need to be developed, especially for low grade bismuth ores.

Pyrolusite is main source of ore for manganese extraction (Zhang and Cheng, 2007). Higher valent oxides of manganese in pyrolusite can dissolve easily in acid solution if they are firstly reduced to lower valent manganese oxide (Vra V C Ar and Cerovi C, 2000). Hence a reductive roasting is employed in the treatment of these ores in order to make them amenable for easy processing (Cheng et al., 2009; Ghafarizadeh et al., 2011; Mishra et al., 2011; Zhang and Cheng, 2007). But this conventional process is characterized by high production costs and energy consumption, low productivity, and environmental pollution. In order to avoid the pyrometallurgical pretreatment, diversified full hydrometallurgical processes, which recovered manganese by leaching ores in the presence of reducing agents, have been developed. The proposed reducing agents include ferrous sulfate, sulfur dioxide (Senanayake, 2011), pyrite, cuprous copper, hydrogen peroxide, nitrous acid and organic reductants (Zhang and Cheng, 2007).

Previous studies on leaching MnO_2-sulfide minerals in acid medium are likely to provide an attractive alternative for commercial exploitation of pyrolusite and sulfide minerals. The simultaneous leaching of ZnS-MnO_2 (Kai et al., 2000; Wang et al., 2006a; Xiao et al., 2007; Lan, 2004), PbS-MnO_2 (Wang et al., 2003), FeS_2-MnO_2 (Li et al., 2007; Vra V C Ar and Cerovi C, 2000) and $CuFeS_2$-MnO_2 (Devi et al., 2001; Wang et al., 2006b) in acid media have been widely investigated. Among these processes, pyrite leaching of manganese has found application in industry. Manganese dioxide should also be a potential oxidizing agent for Bi_2S_3. However, literature survey show that there has been no previous report on the simultaneous leaching of Mn and Bi from low-grade bismuthinite and pyrolusite ores.

* Corresponding author.
E-mail address: zhanjing2001@hotmail.com (J. Zhan).

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Against this background, a new process to extract both manganese and bismuth simultaneously by leaching bismuthinite and pyrolusite ores is proposed in this paper. The leaching chemical reactions and the results of the leaching of a Bi_2S_3-pyrolusite combination in hydrochloric acid are addressed. This new approach would avoid pyrometallurgical pretreatment for two ores and achieve simultaneous leaching. Hence, it holds promise for wide application in exploiting pyrolusite and bismuthinite ores.

2. Experimental procedure

2.1. Materials

The low-grade bismuthinite and pyrolusite were obtained from ShiZhu Yuan Rare Metal Co., and were crushed and ground to 74 μm in the laboratory. Other reagents, including hydrochloric acid, EDTA and Potassium Permanganate were of analytical grade.

2.2. Procedures

2.2.1. Thermodynamic analysis

According to the analysis of the chemical composition of the raw material, four main elements were studied, including Bi, Mn, S and Cl using calculations based on unit activity. The calculations were performed at the temperature of 25 °C, and assuming that all of the species were at the ideal state. The E_h-pH diagrams of both Bi–S–Cl–H_2O system and Mn–H_2O system were calculated and plotted by the software Factsage 6.2, which is a commonly used thermochemical software package.

2.2.2. Electrochemical experiments

Electrochemical experiments were performed in a typical one-compartment three-electrode glass cell on a CHI660B Microcomputer-based electrochemical system. The counter electrode was a Pt plate and the reference electrode was a Hg/Hg_2SO_4/sat. K_2SO_4 electrode (0.64 V vs. standard hydrogen electrode (SHE)). All potentials shown in the work were referred to SHE. The working electrodes were prepared by depositing a thin-layer of the bismuthinite ore ink over a titanium disk (Salgado et al., 2010). The bismuthinite ore ink was prepared by mixing the bismuthinite ore (80 wt.%), polyvinylidene fluoride (10 wt.%) and acetylene black (10 wt.%) in *N*-methyl-2-pyrrolidone. In the case of pyrolusite electrodes, the procedure was similar, with the exception that pyrolusite ore (80 wt.%) was employed. The electrodes were dried at 80 °C for 10 h, then a copper rod (1.0 mm) was inserted as conductor. After that, the working electrode was immersed into hydrochloric acid electrolyte solution (pH = 0.5). Electrochemical experiments were carried out at room temperature.

2.2.3. Leaching experiments

Bismuthinite and pyrolusite were mixed according to a certain mole ratio of manganese and sulfur ($n_{(Mn)}/n_{(S)}$). Diluted hydrochloric acid solution was added at a fixed liquid-to-solid ratio (mL/g) of 5:1. Subsequently, agitation leaching experiments were conducted in a 500 mL round-bottom glass flask placed in a temperature controlled water bath. Twenty grams of ore sample was used for each test. A stirring speed of 500 rpm was used. After selected time, the slurry was filtered and the residue was washed by diluted hydrochloric acid. Bismuth and manganese in the filtrate were estimated volumetrically using EDTA titration and Potassium Permanganate titration, respectively (Fu, 2004). Leaching efficiency were calculated based on the amount of leached metal in the liquor with respect to the original input quantity. Mineralogical analysis of bismuthinite were carried out by X-ray diffraction analysis (XRD, Rigaku, D/Max 2500; Cu/Kα radiation, 40 kV/250 mA). The samples were also characterized using scanning electron microscopy (SEM, JSM-6360LV, JEOL).

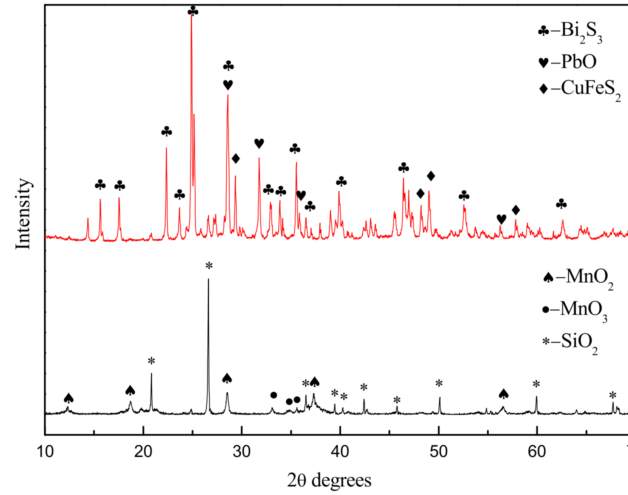

Fig. 1. XRD pattern of bismuthinite and pyrolusite ores.

Table 1
Mineral composition of bismuthinite ore.

Element or species	Bi	Fe	Cu	Pb	Zn	S	Bi_2S_3
Composition (% w/w)	25.95	23.53	4.86	3.26	0.51	27.50	28.08

3. Results and discussion

3.1. Mineralogical analysis

The XRD pattern of the bismuthinite and pyrolusite ores is shown in Fig. 1. Main chemical composition of bismuthinite is listed in Table 1, which show that the main minerals included bismuth sulfide (Bi_2S_3), chalcopyrite ($CuFeS_2$), pyrite (FeS_2), galena (PbS) and the main gangue minerals was quartz (SiO_2). The main chemical phase analysis (as listed in Table 2) of the pyrolusite sample (Fu, 2004) showed that the manganese was mainly in the form of MnO_2 and its content was up to 38.92%. Quartz and kaolinite were found as the main gangue minerals. After leaching, the XRD analysis was also employed to identify the structure and composition of the obtained leach residues. As presented in Fig. 2,

Table 2
Mineral composition of pyrolusite.

Element or species	MnO_2	SiO_2	Al_2O_3	S
Composition (% w/w)	38.92	28.20	9.27	0.013

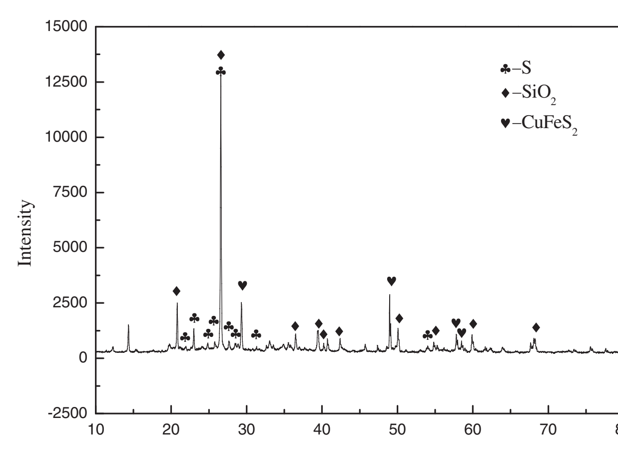

Fig. 2. XRD pattern of leach residues.