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Arsenic removal from lead-zinc smelter ash by NaOH-H_2O_2 leaching

Kunhong Gu, Wenhua Li, Junwei Han*, Wei Liu*, Wenqing Qin, Lianbing Cai

School of Minerals Processing and Bioengineering, Central South University, 410083 Changsha, Hunan, China

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ABSTRACT

The safe treatment of smelter ash with high arsenic is of great importance both for environmental protection and resource comprehensive utilization. In this study, arsenic removal from lead-zinc smelter ash by NaOH-H_2O_2 leaching was studied. The effects of different operating parameters on the leaching rate of arsenic and leaching kinetics were investigated based on thermodynamic calculation. The results indicate that NaOH concentration and H_2O_2 addition have significant effects on the leaching rate of arsenic. The optimum conditions were established as: liquid-solid ratio, 10:1; NaOH concentration, 3 mol/L; H_2O_2 concentration, 2.4%; leaching time, 2 h; and leaching temperature, 75 °C. Under these conditions, the leaching rate of arsenic was as high as 98.17%. The kinetic study reveals that the arsenic leaching process is in accordance with the diffusion-controlled type in the Avrami model, and the apparent activation energy is 16.03 kJ/mol.

1. Introduction

Smelter flue dusts are generated in the pyrometallurgical process of metal extraction from ores. In the smelting process of copper, lead and zinc, arsenic may be produced and finally enriched in smelter ash [1–3]. Arsenic and its compounds are mobile in the environment. It can be dissolved in rain, rivers or groundwater. Therefore, improper treatment of the waste ash probably causes serious environmental pollution and leads to poisoning and carcinogenesis of human organs [4–7].

The treatment of removing arsenic in waste ash has been extensively studied by many researchers in the past decades. Various technologies aim to separate arsenic from the ash. Currently used methods include various pyrometallurgical and hydrometallurgical processes. With respect to pyrometallurgical process, arsenic is removed and separated from other valuable metals by volatilization of arsenic trioxide at high temperatures [8–11]. Although roasting of the dust is easy to be operated, it has some disadvantages such as seriously environmental pollution, large investment and narrow range applicable for raw materials. As a result, most of studies focus on hydrometallurgical treatment of the dust, mainly including water leaching, acid leaching using H_2SO_4 solution and alkaline leaching using NaOH solution [12]. The different leaching rates of arsenic in water and dilute sulfuric acid from copper smelter wastes were compared by Emasmus et al. [13], indicating that sulfuric acid could strengthen the leaching efficiency. Reynolds et al. [14] used pressurized sodium hydroxide solution to extract arsenic from smelting ash and to recover arsenic by evaporation and crystallization processes with the recovery rate of 88.3%. Samuel et al. [15–18] have studied the leaching process of arsenic in sulfide system and showed that high leaching rate of arsenic might be obtained by high consumption of sulfide and alkali.

Compared with the conventional hydrometallurgical methods, this paper presents a novel method of removing arsenic from a smelter ash by NaOH-H_2O_2 alkaline oxidation leaching. This method has the advantages of easy treatment, little pollution, lower cost and higher leaching rate. The objective of this study is to explore the optimal leaching conditions for arsenic removal in alkaline oxidation system and meanwhile, to investigate the kinetics of arsenic leaching process.

2. Experimental

2.1. Materials

The powder sample of arsenic-rich ash used in this study was collected from a pyrometallurgical lead-zinc smelter in Hunan province, China. The sample was air dried, ground and sieved below −74 μm, and thoroughly mixed for analysis and subsequent experiments [19,20]. Main chemical composition of the lead-zinc smelter ash was determined by Inductive Coupled Plasma (ICP) and the result is given in Table 1. The results indicate that the arsenic content is as high as 19.15%, which is essential to remove arsenic in advance for preventing the toxic substance causing secondary pollution. X-ray diffraction (XRD) analysis of the raw materials was made on Rigaku Rapid IIR diffractometer with the result shown in Fig. 1, which indicates the sample is mainly composed of $Na_2CdCl_4(H_2O)_3$, As_2O_3, PbO_2, Sb_4O_6, and the arsenic is

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* Corresponding authors.
E-mail addresses: hanjunwei2008@163.com (J. Han), liuweipp1@126.com (W. Liu).

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Table 1
Main chemical composition of the ash raw materials (wt%).

As	Pb	Zn	Cd	Sb
19.15	15.106	1.751	5.976	3.151

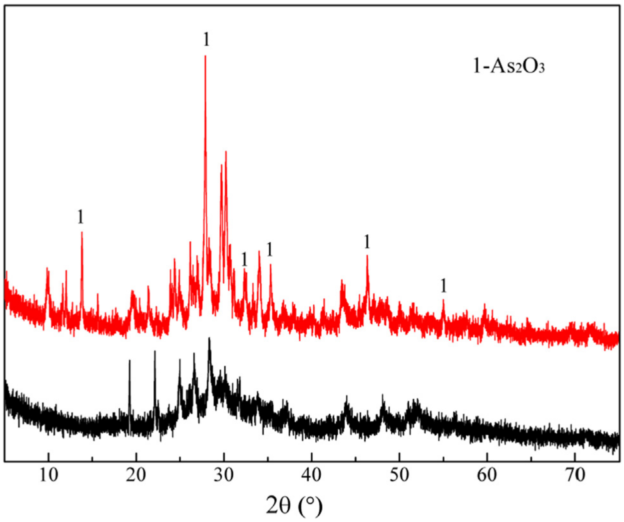

Fig. 1. XRD pattern of the raw ash and alkaline leaching residue.

mainly in the form of arsenolite (As_2O_3). In addition, NaOH and H_2O_2 reagents used in this study are of analytical grade and were bought from Sinopharm Chemical Reagent Co., Ltd, in China.

2.2. Experimental procedure

A schematic diagram of the experimental setup is presented in Fig. 2. The leaching experiments were conducted in an atmospheric pressure agitation leaching device, which was equipped with temperature controller, beaker, mechanical stirrer and water bath. In the experiments, NaOH solution with required concentration and volume was first prepared and placed in the beaker. The ash sample of 25 g was mixed with NaOH solution and leached in the water bath with a temperature controller. During the leaching process, H_2O_2 was slowly dripped into the solution. At the end of each experiment, leaching residue was dried, weighed, and ground followed by digestion and chemical composition analysis. Filtrate was measured for volume using a measuring cylinder and sampled for chemical composition by ICP.

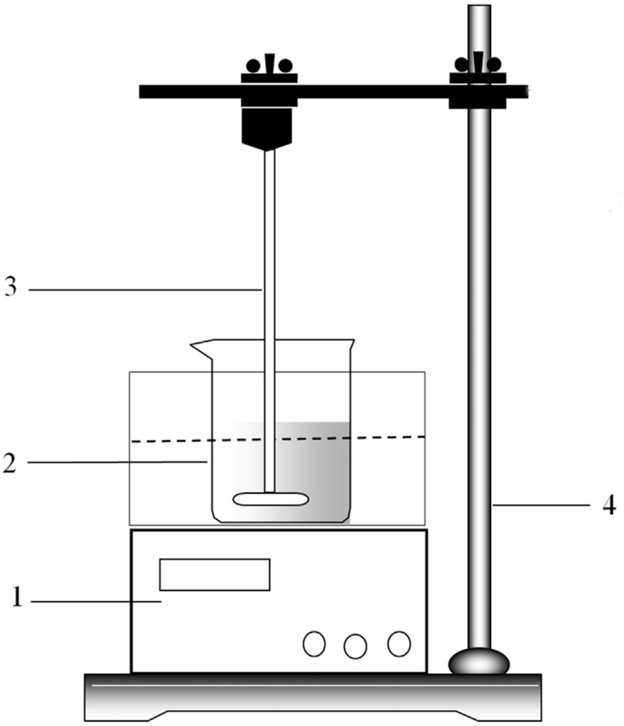

Fig. 2. Schematic diagram of the alkaline leaching setup: 1 – temperature controller; 2 – beaker; 3 – mechanical stirrer; 4 – water bath.

3. Results and discussion

3.1. Thermodynamic analysis

According to phase analysis, the arsenic in the ash exists mainly in the form of As_2O_3. The possible reaction in NaOH-H_2O_2 system is as follows:

$$As_2O_3 + 6NaOH + 2H_2O_2 = 2Na_3AsO_4 + 5H_2O \tag{1}$$

The Gibbs free energy changes for the reaction (25 °C) are calculated to be −974.864 kJ/mol, which shows that the reaction is thermodynamically feasible and the arsenic phase As_2O_3 in the ash can be leached out. In addition, Metal-H_2O systems were used as a guide in pH and potential values of the leaching situation. The E-pH diagrams of As-H_2O system at 25 °C and 85 °C were calculated by HSC Chemistry 5.0 (Fig. 3). The concentrations of related metallic ions were fixed at 1 mol/L, and both of the partial pressures of oxygen and hydrogen are at the standard atmospheric pressure of 101325 Pa. The results show that high oxidation potential and alkaline environment (pH > 11.5) are required for the transformation of As_2O_3 to AsO_4^{3+}. Besides, the E-pH diagram of As-H_2O system also indicates that increasing the potential would cause the transformation of As to As^{3+} and finally conversion to As^{5+}. The reaction of As^{5+} in aqueous solution can be regarded as a complex formation between AsO_4^{3-} and hydrogen ion. In alkaline solution, the concentration of hydrogen ion is so low that most of As^{5+} exists as monomeric [21,22].

3.2. Effect of leaching temperature

Temperature is an important factor on affecting the leaching process. A series of condition experiments were designed from 55 °C to 95 °C, to clarify the effect of temperature on the leaching rate of arsenic. Leaching experiments at various temperatures were carried out at the conditions: NaOH concentration, 3 mol/L; liquid-solid ratio, 10:1; H_2O_2 concentration, 3.6%; leaching time, 2 h. The variation of arsenic leaching rate with increasing the temperature is shown in Fig. 4. It can be seen from Fig. 4 that the leaching rate of arsenic increases significantly as the temperature increases in the range of 55–65 °C and gradually reaches up to 98.15% at 75 °C. Above 75 °C, the leaching rate has no significant variation with further increasing the temperature. According to Fant-Dutch Po rules, the reaction rate can be increased by 2–4 times when the temperature is raised by 10 °C as the diffusion rate is accelerated and Brown motion of fine particles is promoted to increase the number of effective collisions between molecules. This indicates that raising temperature within a certain range can promote the extraction of As in the ash. Therefore, considering the leaching rate and energy consumption, 75 °C was chosen as the optimal temperature, and all further experiments were carried out at 75 °C.

3.3. Effect of liquid-solid ratio

Liquid-solid ratio (L/S) is another important factor on the leaching rate of arsenic. A series of condition experiments were conducted with liquid-solid ratio from 6:1 to 14:1. Other conditions were fixed as: