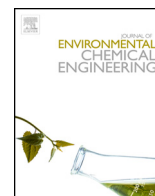




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1 Separation and recovery of arsenic from arsenic-bearing dust

2 Q1 Xueyi Guo^{a,b,*}, Jing Shi^a, Yu Yi^{a,b}, Qinghua Tian^{a,b}, Dong Li^{a,b}3 ^aSchool of Metallurgy and Environment, Central South University, Changsha, Hunan 410083, China4 ^bCleaner Metallurgical Engineering Research Center, Nonferrous Metal Industry of China, Changsha, Hunan 410083, China

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ABSTRACT

A hydrometallurgical process, including selective extraction, As-precipitation, the insoluble and sodium removal, acid dissolution and recovery of arsenic trioxide, was developed to treat arsenic-bearing dust. Arsenic was selective extracted by a mixed NaOH–Na₂S leaching system with 2.5 mol/L NaOH and 0.2 mol/L Na₂S. In this system, more than 90.0% As was extracted, while Sb and Pb were precipitated in residue as NaSb(OH)₆ and PbS. Based on the solubility of As₂O₅, a method for precipitating arsenic in the form of sodium arsenate from alkaline leachate by oxidization-precipitation was established. Then, the sodium arsenate was converted to Ca–As compound by adding exceeding CaO into sodium arsenate solution. H₃AsO₄ solution, prepared by dissolving Ca₅(AsO₄)₃OH in dilute H₂SO₄, was further reduced to HAsO₂ by H₂SO₃ and then reduction solution was concentrated and crystalized as octahedral shaped As₂O₃. This process transformed the hazardous material to valuable material and realized the resource recycling of arsenic.

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5 Introduction

6 Arsenic, a toxic element aroused major public concern, is an
7 unwanted hazardous waste generated from nonferrous pyromet-
8 allurgical industries in smelting slag, dust, anode slime and so on
9 [1,2]. The arsenic-bearing dust is one of the most important
10 secondary resources, which contains a large amount of valuable
11 metals, such as lead, antimony and indium. Therefore, separating
12 arsenic from arsenic-bearing dust to reclaim valuable metals is of
13 great environmental and economic meanings. There are some
14 studies on treating arsenic-bearing materials by pyrometallurgy
15 or hydrometallurgy [3,4]. Pyrometallurgical processes usually
16 result in secondary As pollution and have high energy consump-
17 tion [5], while hydrometallurgical processes, including removal of
18 arsenic by dilute H₂SO₄ [6], sodium-sulfide solution [7], NaOH
19 solution, mixed solution of NaHS/NaOH [8] and so on, are more
20 environmental friendly. Yu et al. [9] has studied the extraction of
21 arsenic from arsenic-containing cobalt and nickel slag by alkaline
22 leaching, which contains alkaline leaching with pressured
23 oxidation, cooling crystallization, arsenate reduction by SO₂ gas
24 and arsenic trioxide precipitation. This process can realize the
25 clean extraction of arsenic and preparation of As₂O₃, but has to
26 bear high energy consumption with high temperature and
27 pressure. What is more, many Na₂SO₄ generated in the reduction

solution need extra way to remove. Li et al. [10] reports a method
to remove arsenic from secondary zinc oxide using a mixed
NaOH–Na₂S leach, then oxidation using hydrogen peroxide and
precipitation with lime. This process transforms the hazardous
wastes into values by selective extraction of arsenic, but the
leaching efficiency of arsenic is low and arsenic is not recovered.
Therefore, it is important to find a novel technique to recover
arsenic from arsenic-bearing dust.

In this paper, an effective and environmental friendly method,
including separating arsenic from hazardous materials and
recovery of arsenic (Fig. 1), is proposed to realize a comprehensive
utilization of the arsenic-bearing dust. The influence of processing
parameters on separating arsenic from hazardous materials have
been investigated systematically in this study, such as leaching
system, leaching time, alkali concentration, temperature and Na₂S
concentration. Furthermore, the further study respect to As-
precipitation, the insoluble and sodium removal, acid dissolution
and preparation of As₂O₃ have been also studied so as to realize the
recovery of As₂O₃ from alkaline leachate.

Experimental

Materials

The arsenic-bearing dust samples obtained from blast furnace
smelting of copper dross in lead smelter, Guangxi Province, China,
were used to carry out the experimental work. Arsenic-bearing
dust were crushed, ground, and screened using a 100 mesh sieve.

* Corresponding author.

E-mail address: xyguo@csu.edu.cn (X. Guo).

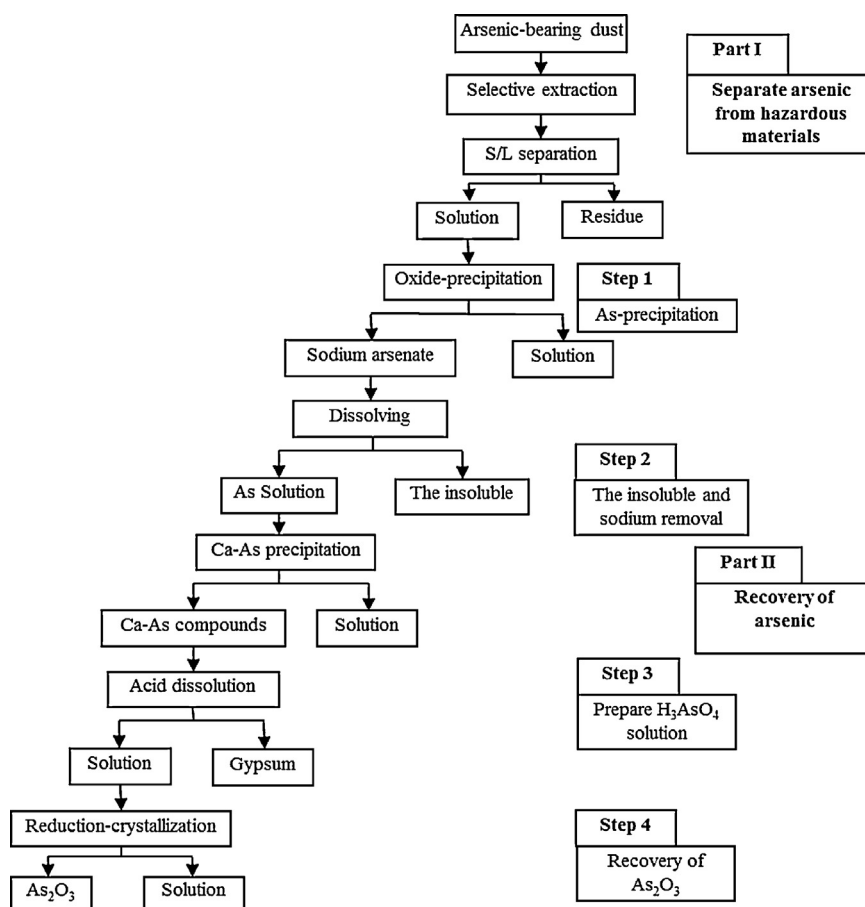


Fig. 1. Technical schematic of arsenic-bearing dust treatment.

Table 1

Chemical compositions of arsenic-bearing dust (wt%).

Element	As	Sb	Pb	Sn	Zn	Cu	Fe	S	In
Content	6.86	9.55	49.13	2.80	2.40	1.10	1.80	5.50	0.26

The chemical analysis is shown in Table 1 and the XRD presented in Fig. 2(a). The result shows that there are three main phases of $Pb_5(AsO_4)_3OH$, PbS and Sb_2O_3 .

Reagents of $NaOH$, $Na_2S \cdot 9H_2O$ and H_2O_2 (30%) were of analytical grade, manufactured by Sinopharm Chemical Reagent Co., Ltd.

Experimental procedures

Batch alkaline leaching experiments were conducted in a 500 mL four-necked round-bottomed flask with ancillary system to control the temperature and the stirring speed. All the experiments were carried out with 60 g of arsenic-bearing dust in a certain volume of leaching solution. A typical experiment was carried out as: heating the solution to about $80^\circ C$, temperature at which the flask was opened to add the dust sample. The flask was then sealed and the system was further heated to the set temperature for the experiment. At the end of the experiment, the leachate filtered for collecting the leaching residues. The residue was washed, dried and analyzed to determine the leaching ratio of As and the leachate was analyzed for Pb and Sb. Then, the alkaline leachate was used to prepare As_2O_3 by processes of oxide-precipitation, the insoluble and sodium removal, H_2SO_4 dissolution and reduction-crystallization.

Characterization

The phase of the solid sample was detected by X-ray diffraction (XRD) (The emission target of XRD was CuK_{α} , the emission power was $40\text{ kV} \times 250\text{ MA}$, the step width was 0.01° , the scanning rate was $8^\circ/\text{min}$ and 2θ was $10\sim 80^\circ$, $D/\text{max-rA}$, Rigaku Corporation of Japan). The concentration of As(III) in liquid was detected by the substoichiometric oxidation of As(III) to As(V) with potassium bromate. The total As content was detected by an atomic fluorescence spectrometry (AFS-2202E, Haiguang Corp., Beijing) coupled with a hydride generator. The other components were detected by inductively coupled plasma optical emission spectrometer (ICP-OES, Intrepid II XSP, Thermo Elemental Corporation, America).

Results and discussion

Separate arsenic from hazardous materials

Effect of leaching system on the leaching of As, Sb and Pb

The effect of the $NaOH-Na_2S$ and $NaOH$ leaching system on the leaching of As, Sb and Pb are shown in Fig. 3(a). As is seen, higher leaching efficiency of As is observed in the mixed $NaOH-Na_2S$ leaching system compared to that of $NaOH$ alone leaching system. It can be explained that arsenic is extracted as Na_3AsO_4 in $NaOH$ leaching solution but as Na_3AsO_4 and Na_3AsS_4 in mixed $NaOH-Na_2S$ leaching solution, where the solubility of Na_3AsO_4 is lower than that of Na_3AsS_4 in concentrated $NaOH$ solution [9,11]. The main reactions of this process are shown as follows:



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