Journal of Hazardous Materials 336 (2017) 168–173

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Successful sulfur recovery in low sulfurate compounds obtained from the zinc industry: Evaporation–condensation method

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HIGHLIGHTS

- Industrial residue coming from a zinc obtaining plant is used for sulfur recovery.
- An evaporation–condensation method is successfully employed for low sulfur content samples.
- The obtained sulfur has a high purity and is comparable to commercial sulfur.

ARTICLE INFO

Article history:
Received 19 January 2017
Received in revised form 19 April 2017
Accepted 20 April 2017
Available online 27 April 2017

Keywords:
Sulfur removal
Zinc industry
Sulfur recovery
Evaporation condensation method

ABSTRACT

The improvement of an evaporation–condensation method allows for successful recovery of elemental sulfur from sulfide concentrates from the zinc industry. Elemental sulfur can be obtained with this method in samples with a low (60%) sulfur content. The effects of heating temperature between 150 °C and 250 °C and heating time up to 120 min on the recovery of sulfur are also studied. Elemental sulfur obtained in this way is of high purity and therefore, there is no need for further purification. The treatment of these industrial residues would help removing sulfur from the environment.

1. Introduction

Sulfur and its derivatives are used in many chemical and industrial processes, being particularly important in the manufacture of phosphate fertilizers. Sulfur is therefore important to industrial economies, but unlike other chemicals, it is not produced intentionally as a primary product. Sulfur is derived as a by-product from operations such as petroleum refining, tar sands recovery, heavy oil and natural gas processing, and from coking and metallurgical plants [1,2]. One of the ways of obtaining sulfur is in the zinc industry.

The zinc industry has routinely achieved a high hydrometallurgical extraction of zinc (higher than 98%) [3]. Zinc is mainly recovered from primary sulfide concentrates; sulfide compounds are also obtained during this process and are usually converted into sulfuric acid. The recovery of pure sulfur is sometimes difficult.

Zinc concentrate is usually roasted as pretreatment in zinc hydrometallurgy, and the produced SO_2 is converted into sulfuric acid.

To avoid the release of SO_2 in the treatment of zinc ores, direct leaching can be performed in such a way that the sulfuric phases transform into elemental sulfur that remains in the residue after leaching. One of these processes is known as the Albion Process™.

The Albion Process™ is a combination of ultrafine grinding and oxidative leaching at atmospheric pressure. The fine grinding of the concentrate introduces a high degree of strain into the sulfide mineral lattice, increasing the number of fractures in the mineral and enabling leaching under atmospheric conditions. The feed to the Albion Process™ is a concentrate containing metals, and this process is used to oxidize the sulfide minerals in the concentrate and liberate these metals for recovery by conventional means.

The zinc sulfur concentrate is finely ground and slurried, and afterwards, it is pumped to an oxidative leaching circuit. Oxygen

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http://dx.doi.org/10.1016/j.jhazmat.2017.04.051
0304-3894/

is injected at high pressure. The acid pressure oxidation is a way to obtain metals such as Zn, Cu, Ni, Pb and precious metals from sulfates [3–15].

Different methods have been developed for sulfur recovery in pressure leaching of zinc concentrate [16–18], which are based in a floating process of the leaching residue followed by melting and filtration processes. If the flotation concentrate contains less than 70% elemental sulfur, it is difficult to obtain a melted fluid in the next stage of the fusion, which can cause difficulties in the filtration process.

The sulfide concentrates employed in this study contain approximately 60% elemental sulfur for which the melting-filter procedure is difficult to carry out. Although as a solution, the concentrate could be enriched with pure elemental sulfur until the sulfur content is high enough to obtain a melted fluid, this study will look at recovering elemental sulfur with other methods.

The aim of this work is to find a more appropriate method for the reuse of the residue of atmospheric pressure leaching of zinc concentrates with a high content of lead, with the specific goal of sulfur recovery. With that aim, the evaporation–condensation method of Watanabe et al. [19] is considered. According to this method, high-purity sulfur can be efficiently recovered from sulfurous compounds at temperatures below the boiling point of sulfur (445 °C). Sulfur has an unexpectedly high vapour pressure even in the liquid phase at temperatures near its melting point. To recover the sulfur, the float is heated to a temperature higher than sulfur's melting point (119 °C) and less than its boiling point. An inert gas is used as a carrier; the gas containing the evaporated sulfur is cooled to condense the sulfur. The cooling temperature is lower than sulfur's melting point. The Watanabe method did not show the expected results and the system was improved as explained below.

The method presented here is a way of removing hazardous sulfur from industrial residue that are collected in industrial dumps, and therefore, chemical weathering could occur, involving the alteration of ion sulfides, and the release of dissolvable sulfides and toxic metal ions.

2. Experimental setup

Our samples were obtained from the zinc plant AZSA, (Asturiana de Zinc S.A.). The material coming from the leaching residue at atmospheric pressure and afterwards the resultant sulfur and tailing residue coming from our evaporation–condensation experiments were characterized using different techniques, in order to observe changes in composition. An elemental analysis was performed in order to determine the elemental sulfur in the minerals. The determination of metals was also carried out by mass spectrometry combined inductively coupled plasma with ICP-MS (model HP7500c of Agilent).

X-ray diffraction (PHILIPS, model XPERT PRO) was performed on the samples. Scanning electron microscopy (SEM) was performed using a conventional microscope (JEOL, model 6100) with a unit of microanalysis INCA Energy 2000.

The method considered by Watanabe et al. [19] is the only evaporation–condensation method that could be useful to extract sulfur in low sulfur content samples, to our knowledge. The examples included in [19] have an amount of sulfur as low as 44%. It was tried at first and proved to be inefficient, because a negligible amount of sulfur was obtained. To develop a suitable procedure for sulfur recovery, an improvement was made in the heating and temperature measuring system, in order to carefully control temperature and samples evaporation. The experimental set up is sketched in Fig. 1. The evaporation–condensation experiment was prepared in the following way: each 50-g sample was introduced in a sealed container in a heating reactor. Heating was accomplished

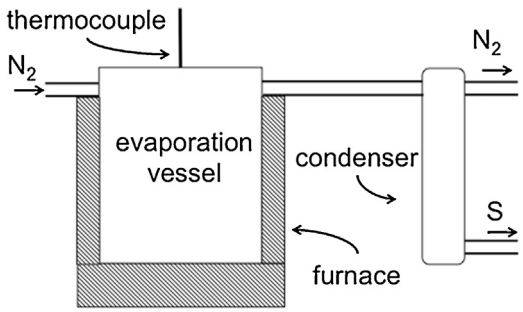

Fig. 1. Experimental set up to perform the evaporation–condensation method for sulfur extraction.

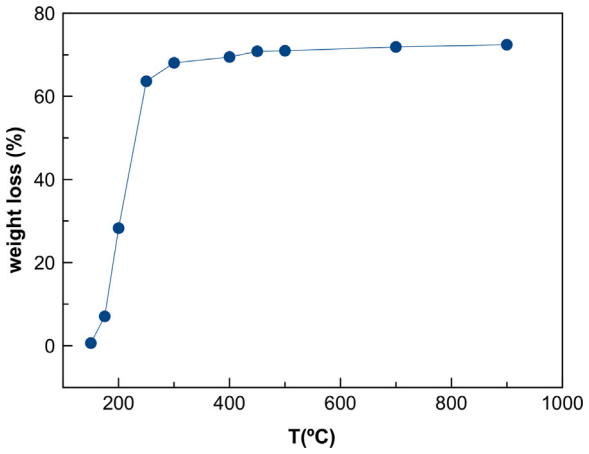

Fig. 2. Weight loss of samples with increasing temperature. Lines are guides for the eyes.

using a hotplate and a cylindrical furnace with electric heating. The temperature was carefully controlled by a k-par thermocouple located inside the heating container and connected to a digital controller, which allows the user to determine the working temperature. A flow of nitrogen (2.5 L/min) was set in a loop through the recipient with the aim of carrying the generated sulfur vapour and to set a nonoxidizing atmosphere to avoid the possible formation of sulfur oxides. The evaporated sulfur was transferred to a cooled condenser with water, where sulfur was obtained. The temperature was chosen in the range between 150 °C and 250 °C for a constant time of 120 min. The influence of time was studied also by choosing other samples, and performing the same treatment at the maximum temperature (250 °C), during time periods ranging from 30 min to 120 min. As it is explained below, this temperature range corresponds to the highest weight loss of the sample, and related to the amount of sulfur evaporated in the procedure. All measurements were repeated 5 times to check the reproductibility of the procedure, and a standard deviation of 1% was obtained.

3. Results and discussion

3.1. Characterization of the flotation concentrate

The samples coming from the leaching residue at atmospheric pressure are characterized using several techniques, with the aim of determining the amount and structure of sulfur in them. The samples had the state of dry powder and were first treated during 2 h with heat in an oxidizing atmosphere in order to determine their weight loss with temperature.

Fig. 2 shows this weight loss with increasing temperature. It can be seen that the weight loss starts to be appreciable above 150 °C