Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 25(2015) 640−646
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Separation and enrichment of elemental sulfur and mercury from hydrometallurgical zinc residue using sodium sulfide

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Received 3 March 2014; accepted 14 July 2014

Abstract: The separation and enrichment of mercury and the recovery of elemental sulfur from flotation sulfur concentrate in zinc pressure leaching process were carried out by sodium sulfide leaching and carbon dioxide precipitating. The results show that the leaching rate of elemental sulfur is more than 98%, and 98.13% of mercury is enriched in the residue, under the optimized conditions of sodium sulfide concentration 1.5 mol/L, liquid/solid ratio 6:1 and leaching time 30 min at room temperature. In addition, the content of mercury is enriched 5.23 times that in the leaching residue. The elemental sulfur is precipitated from leaching solution under conditions of carbon dioxide flow rate 200 mL/min and blowing time 150 min, while solution is stirred adequately. The recovery efficiency of elemental sulfur reaches 97.67%, and the purity of elemental sulfur is 99.75%, meeting the requirements of industrial first-rate product standard according to the national standard of GB/T 2449−2006 (PRC).

Key words: flotation sulfur concentrate; sodium sulfide leaching; carbon dioxide precipitating; mercury enrichment; elemental sulfur recovery

1 Introduction

The solid wastes generated in the nonferrous metal smelting process usually contain toxic heavy metals. Preservation of these wastes not only causes enormous waste of resources, but also brings huge environment pressure. Since both mercury and zinc have the affinity to sulfur, element mercury is often associated in zinc ore, especially in zinc sulfide ore. Zinc smelting is widely regarded as one of the primary anthropogenic sources of mercury emission to the atmosphere [1,2]. Hundreds of tons of mercury are emitted to the environment in the process of zinc smelting in the world every year [2,3]. In 2003, mercury emission to atmosphere reaches 187.6 t from zinc smelting in China, which accounts for 27% of anthropogenic mercury emissions to atmosphere in China [4]. At present, some studies have been conducted on mercury emission to atmosphere and its environmental impacts from zinc smelting in China [5,6].

In recent years, great changes have occurred in the zinc smelting industry in China. Some new technologies, such as pressure leaching and atmospheric oxygen enrichment leaching, have been adopted. New technology will have more applications in the zinc smelting industry in the next few years [7]. The pressure leaching process does not need roasting pretreatment of ore, which avoids sulfur dioxide flue gas producing acid process. The removal of mercury needs to be carried out both from the flue gas containing mercury [8,9] and from acidic wastewater generated in sulfuric acid production [10–12]. In the pressure leaching process, mercury and sulfur mainly remain in the leaching residue in a stable form of mercury sulfide and elemental sulfur, respectively, which may reduce the environmental impact [13]. However, the elemental sulfur in the leaching residue, due to great blending with valuable metals of mercury and zinc and so forth, needs further

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DOI: 10.1016/S1003-6326(15)63647-0

treatment to achieve comprehensive utilization. The methods of elemental sulfur recovery from hydrometallurgical residue cover flotation, hot filtration, ammonium sulfide, tetrachloroethylene and so on [14−16], but these methods still have some problems.

The purpose of this study is to firstly leach flotation sulfur concentrate derived from hydrometallurgical zinc residue with sodium sulfide, and the elemental sulfur is dissolved into the leaching solution while mercury in a stable form is enriched into the leaching residue. Then, the elemental sulfur is recovered when carbon dioxide is bubbled into the leaching solution. The sodium sulfide leaching−carbon dioxide precipitating method may make reagents recycle back into process and obtain high quality sulfur, with easy operation and simple equipments.

2 Chemical reactions and thermodynamics

The elemental sulfur reacts with sodium sulfide (Na_2S) in the solution to form a polysulfide according to the following reaction [14,15]:

$$Na_2S+(x-1)S^0=Na_2S_x \tag{1}$$

Meanwhile, the soluble mercury cation (Hg^{2+}) from flotation sulfur concentrate can also react with sulfidion (S^{2-}) from the sodium sulfide solution, generating the mercuric sulfide deposit with tiny solubility product constant K_{sp} of 4.0×10^{-53}, so the element mercury is still left in the residue. The reaction is as follows:

$$Hg^{2+}+S^{2-}=HgS\downarrow \tag{2}$$

When the elemental sulfur from material is dissolved, the solution is then filtered to produce an essentially sulfur free residue. The polysulfide anion is fairly unstable, and the polysulfide-rich filtrate obtained is decomposed to recover sulfur under an acid environment when it is treated with carbon dioxide (CO_2) through the following reaction:

$$Na_2S_x+CO_2+H_2O=NaHS+NaHCO_3+(x-1)S^0 \tag{3}$$

The elemental sulfur is recovered through a second filtration of the mixture solution, and is further dried to sulfur product. The mixture solution of sodium bisulfide and bicarbonate can be regenerated to sodium sulfide by the use of lime (CaO) according to the following reaction:

$$NaHS+NaHCO_3+CaO=Na_2S+CaCO_3+H_2O \tag{4}$$

The regenerated sodium sulfide solution is recycled back into the initial leaching process, while the solid limestone ($CaCO_3$) can be decomposed by roasting to carbon dioxide and lime (CO_2 + CaO) which may be reused back into the reaction (3) and the reaction (4), respectively.

Thermodynamic analysis includes the calculations of standard Gibbs free energy ($\Delta_r G_m^\Theta$) and standard equilibrium constant (K^Θ). The reaction (1) can be simplified to the following reaction:

$$S^{2-}+(x-1)S^0=S_x^{2-} \tag{5}$$

The x of polysulfide ion (S_x^{2-}) varies from 2 to 5 [17]. Standard Gibbs free energies of formation ($\Delta_f G_m^\Theta$) of different sulfur ions at 298.15 K [17,18] are shown in Table 1. The Gibbs free energy and standard equilibrium constant for reactions of dissolving sulfur were calculated at 298.15 K and the values are shown in Table 2. The negative values of the standard Gibbs free energy, $\Delta_r G_m^\Theta$, for the reactions (8) and (9), indicate that they are all thermodynamically feasible at atmospheric pressure and temperature 298.15 K, and formations of S_4^{2-} and S_5^{2-} have higher thermodynamic probability. The large values of standard equilibrium constant, K^Θ, for the reactions (8) and (9), further suggest probability of formations of S_4^{2-} and S_5^{2-}. Based on the above thermodynamic analysis, sulfur dissolution in sodium sulfide solution can occur spontaneously at atmospheric pressure and room temperature.

Table 1 Standard Gibbs free energy of formation ($\Delta_f G_m^\Theta$) of different sulfur ions at 298.15 K

Chemical formula	Matter state	$\Delta_f G_m^\Theta$/(kJ·mol^{-1})
S	Solid	0
S^{2-}	Aqueous	85.80
S_2^{2-}	Aqueous	91.21
S_3^{2-}	Aqueous	88.28
S_4^{2-}	Aqueous	69.00
S_5^{2-}	Aqueous	65.70

Table 2 Values of standard Gibbs free energy ($\Delta_r G_m^\Theta$) and standard equilibrium constant (K^Θ) at 298.15 K for reactions of dissolving sulfur

Reaction equation		$\Delta_r G_m^\Theta$/(kJ·mol^{-1})	K^Θ
$S^{2-}+S^0=S_2^{2-}$	(6)	5.41	0.11
$S^{2-}+2S^0=S_3^{2-}$	(7)	2.48	0.37
$S^{2-}+3S^0=S_4^{2-}$	(8)	−16.80	8.77×10^2
$S^{2-}+4S^0=S_5^{2-}$	(9)	−20.10	3.32×10^3

3 Experimental

3.1 Materials

The raw material for this study is flotation sulfur concentrate from hydrometallurgical residue during the zinc pressure leaching process. The chemical