Hydrometallurgy 179 (2018) 118–124

Contents lists available at ScienceDirect

Hydrometallurgy

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

Technical note

Sulfur removal with active carbon supplementation in digestion process

Zhanwei Liu[a,b,c,*], Wenhui Ma[a,b,c,*], Hengwei Yan[a,b,c,*], Keqiang Xie[a,b,c], Dunyong Li[a,b,c], Licong Zheng[a,b,c], Pengfei Li[a,b,c]

[a] *State Key Laboratory of Complex Nonferrous Metal Resources Cleaning Utilization in Yunnan Province, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China*

[b] *National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China*

[c] *Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China*

ARTICLE INFO

Keywords:
Sulfur removal
Active carbon
High-sulfur bauxite
Digestion process

ABSTRACT

This paper proposes a novel approach to sulfur removal with active carbon supplementation in alkali digestion process. The effects of active carbon dosage on the concentrations of different valence sulfur in sodium aluminate solution were investigated. The results demonstrated that along with increases of active carbon dosage high-valence sulfur ($S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}) concentration decreased, but the concentration of the S^{2-} increased. This suggests that active carbon reacts with high-valence sulfur to generate low-valence sulfur at digestion temperature, which is consistent with our thermodynamic calculation results. As active carbon dosage increases, sulfur digestion rate decreases while sulfur content in red mud markedly increases; the alumina digestion rate, conversely, remains fairly stable. This suggests that high-valence sulfur in the sodium aluminate solution can be converted to S^{2-} and then enter red mud by adding active carbon during the digestion process.

1. Introduction

Bauxite resources become scarce because of extensive and rapid developments of alumina industry. There are over 800 million tons of diasporic high-sulfur bauxite in China, if effective methods of removing sulfur of this bauxite are made available, it is highly valuable.

The most common sulfur-bearing minerals in high-sulfur bauxite are pyrite and its isomers as well as sulfates such as $CaSO_4$ (Yang, 1993). The most negative effects of sulfur's presence in the Bayer process are as follows (Li, 2010; Long and Dixon, 2004): 1) Na_2S can react with Fe_2O_3, and Na_2S_2 can react with $Fe(OH)_2$ forming $Na_2[FeS_2(OH)_2]\cdot 2H_2O$ which is much more soluble in sodium aluminate liquor; this increases the sulfur and iron content in alumina products. 2) $Na_2S_2O_3$ can react with.

Fe as the composition of equipment forming Na_2S, Na_2SO_3, and $Fe(OH)_2$, that destroy the steel oxide film and accelerate the corrosion of equipment. 3) The sulfur in the Bayer process is eventually converted to Na_2SO_4, which increases alkali consumption. 4) Once the content of Na_2SO_4 in spent liquor reaches a certain level, it can precipitate in the form of $Na_2CO_3\cdot 2Na_2SO_4$; the double salt can then scale the evaporator and interior digester, which impact industrial production.

To date, relatively few researchers have investigated sulfur removal in the alumina production process because high-sulfur bauxite is seldom used in alumina production outside of China. Recent years have seen a few relevant studies in China (Liu et al., 2015b; Liu et al., 2015c; Qi, 1995; Yin et al., 2009; Yin et al., 2011). The methods of sulfur removal can be mainly divided into flotation desulfurization (Bulut et al., 2004; Taguta et al., 2017), roasting desulfurization (Hu et al., 2010; Lou et al., 2016; Runkel and Sturm, 2009), bioleaching desulfurization (Blight et al., 2000; Li et al., 2016a, 2016b), electrolysis desulfurization (Gong et al., 2015; Gong et al., 2017), wet oxidation desulfurization (Dixon and Long, 2004; Liu et al., 2015a), desulfurization by precipitators (He, 1996; He et al., 2002; Li et al., 2016a, 2016b). These methods have their own advantages and disadvantages, they have not been widely applied in industry.

Large swaths of China's high-sulfur bauxite reserves are unable to be developed or utilized due to the lack of appropriate sulfur removal method for alumina production. This paper proposes a new method of sulfur removal by adding active carbon in digestion process, the active carbon can react with high-valence sulfur ($S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}) to generate low-valence sulfur (S^{2-}), then the S^{2-} reacted with iron compounds to generate Na_3FeS_3 and FeS entered red mud, so the concentration of $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, and total sulfur in liquor decreased. As discussed below, the inhibiting oxidation of S^{2-} via the proposed method was investigated to provide a theoretical and technical basis for the effective utilization of high-sulfur bauxite.

---

[*] Corresponding authors at: National Engineering Laboratory for Vacuum Metallurgy, Kunming University of Science and Technology, Kunming, Yunnan 650093, PR China.
E-mail addresses: zhanwei_liu@126.com (Z. Liu), mwhsilicon@126.com (W. Ma), hengwei_yan@126.com (H. Yan).

https://doi.org/10.1016/j.hydromet.2018.06.001
Received 10 September 2017; Received in revised form 22 May 2018; Accepted 1 June 2018

Table 1
Chemical components of high-sulfur bauxite.

Chemical components	Amount (Wt%)
Al_2O_3	63.99
SiO_2	8.12
Fe_2O_3	6.66
TiO_2	2.86
K_2O	1.23
Na_2O	0.006
CaO	0.22
MgO	2.95
S_{Total}	2.05
C_{Total}	0.42
$C_{Organic}$	0.31

2. Experiments

2.1. Experimental materials

The high-sulfur bauxite used in this experiment was obtained from Zunyi mining area in China. The chemical components of mineral samples were analyzed by XRF, as shown in Table 1. The mineral components of high-sulfur bauxite were determined by quantitative XRD, as shown in Table 2. The X-ray diffraction pattern of the mineral is shown in Fig. 2. The QEMSCAN image of the mineral is shown in Fig. 3.

As shown in Figs. 2 and 3, the primary sulfur-bearing mineral is pyrite (Fig. 1). Fig. 3 also demonstrates that particle size of pyrite was 10–100 μm, pyrite was granular distribution, and goethite was disseminated distribution around pyrite. During the Bayer process of alumina production, the sulfur in high-sulfur bauxite first enters the solution in the form of S^{2-}, then the S^{2-} is gradually oxidized into various forms of $S_2O_3{}^{2-}$, $SO_3{}^{2-}$, and $SO_4{}^{2-}$.

The chemical components of the alkali solution used in the experiment are listed in Table 3.

2.2. Experimental method

Digestion experiments on high-sulfur bauxite were conducted in a XYF-6 digester, as shown in Fig. 4, which heated by molten salts.

The alkali solution, high-sulfur bauxite and active carbon were placed in a 100 mL stee1 bomb which was sealed in the experiment. The digester was heated to 533 K (260 °C) and held for 5 min, then the steel bomb was placed inside and the digestion process was run 60 min. The sodium aluminate solution was then filtered and the Al_2O_3, Na_2O_k, Na_2O_T, and different valence sulfur (S^{2-}, $S_2O_3{}^{2-}$, $SO_3{}^{2-}$, and $SO_4{}^{2-}$) in the filtrate were chemically analyzed (Wang, 1992), where the concentrations of S^{2-}, $S_2O_3{}^{2-}$ and $SO_3{}^{2-}$ in liquor are determined by iodimetry and the concentrations of $SO_4{}^{2-}$ in liquor is determined by barium sulfate gravimetric method. The dried red mud was sampled and observed with an X-ray fluorescence analyzer and carbon - sulfur analyzer.

Table 2
Mineral components of high-sulfur bauxite.

Mineral components	Amount (Wt%)
Diaspore	67
Pyrite	4.6
Illite	11.5
Anatase	1.8
Rutile	1
Chlorite	5
Kaolinite	4

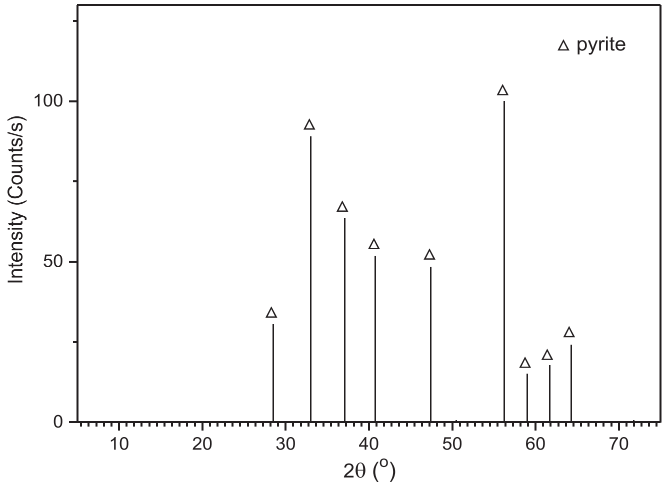

Fig. 1. X-ray diffraction pattern of pyrite.

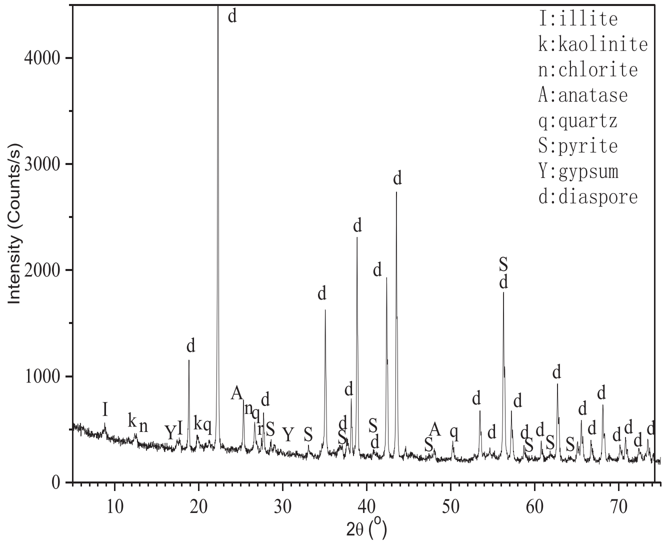

Fig. 2. X-ray diffraction pattern of high-sulfur bauxite.

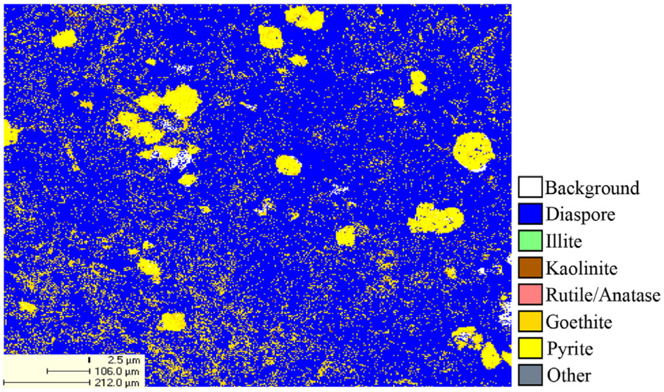

Fig. 3. QEMSCAN image of the high sulfur bauxite.

The digestion rate of alumina (η_A) was calculated as follows:

$$\eta_A = \frac{(A/S)_{ore} - (A/S)_{mud}}{(A/S)_{ore}} \times 100\% \tag{1}$$

$(A/S)_{ore}$ Mass ratio of alumina to silica in raw ore
$(A/S)_{mud}$ Mass ratio of alumina to silica in mud