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Sulfur removal by adding aluminum in the bayer process of high-sulfur bauxite

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ABSTRACT

This paper proposes a novel approach to sulfur removal by adding aluminum in the bayer process of high-sulfur bauxite. The effects of aluminum dosage on the concentrations of different valence sulfur in sodium aluminate solution were investigated at length to find that high-valence sulfur ($S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}) concentration in sodium aluminate solution decreases, but the concentration of the S^{2-} in the sodium aluminate solution increases as aluminum dosage increases. This suggests that aluminum reacts with high-valence sulfur to generate low-valence sulfur at digestion temperature, which is consistent with our thermodynamic calculation results. As aluminum dosage increases, sulfur digestion rate decreases notably, and the alumina digestion rate decreases slightly, while sulfur content in red mud markedly increases. This suggests that high-valence sulfur in sodium aluminate solution can be converted to S^{2-} and then enter red mud by adding aluminum during the digestion process.

1. Introduction

Extensive and rapid developments in the alumina industry have made bauxite resources increasingly scarce. China possesses over 800 million tons of diasporic high-sulfur bauxite, mainly in Henan, Chongqing, and Guizhou provinces; this bauxite is highly valuable, provided that effective methods of removing its sulfur are made available.

Bauxite with sulfur content greater than 0.7% is called high sulfur bauxite. The nature of high sulfur bauxite is as follows: i. The higher the content of sulfur is, the deeper the buried depth of high sulfur bauxite is. The content of sulfur is between 0.8% and 7%; ii. The ore grade is high, the A/S (mass ratio of alumina to silica) of 2/3 reserves is above 7; iii. High-sulfur bauxite belongs to diasporic bauxite, the most common sulfur-bearing minerals in high-sulfur bauxite are pyrite and its isomers (marcasite and melnikovite) as well as sulfates such as $CaSO_4$ (Yang, 1993); iv. The sulfur mineral, with uneven disseminated size, has a complex embedded relationship with diasporic.

The most negative effects of sulfur's presence in the Bayer process are as follows (Li, 2010): (1) Na_2S can react with Fe_2O_3, and Na_2S_2 can react with $Fe(OH)_2$ to form $Na_2[FeS_2(OH)_2]\cdot 2H_2O$ and $Na_2[FeS_2(OH)_2]\cdot 2H_2O$, which is much more soluble in sodium aluminate solution; this increases the iron content in alumina products and deteriorates their quality. (2) $Na_2S_2O_3$ can react with Fe to form Na_2S, Na_2SO_3, and $Fe(OH)_2$, which destroy the steel oxide film and accelerate the corrosion of equipment, posing a rather significant safety risk. (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 interior digester and evaporator, creating problems during evaporation 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., 2016), 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., 2016). These methods have their own

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Table 1
Chemical components of high-sulfur bauxite (wt%).

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	S_{Total}	C_{Total}	$C_{Organic}$
66.18	7.92	7.66	2.63	1.42	0.008	0.27	2.90	2.16	0.48	0.33

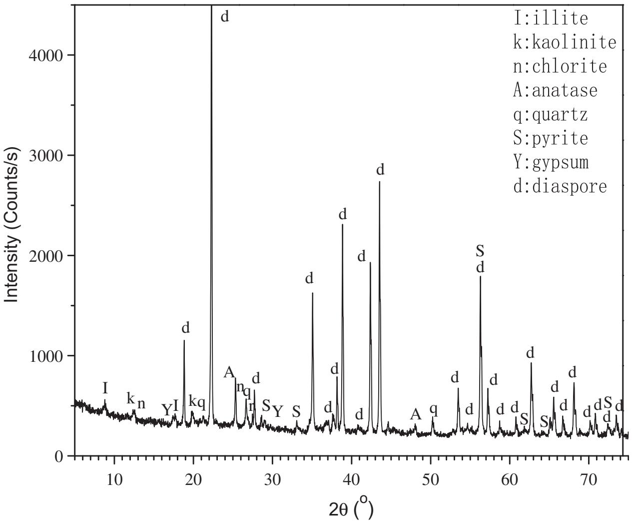

Fig. 1. X-ray diffraction pattern of high-sulfur bauxite.

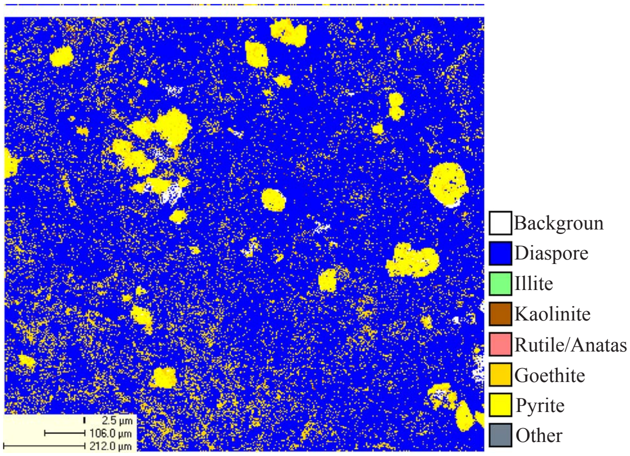

Fig. 2. QEMSCAN image of the high sulfur bauxite.

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 an appropriate bulk desulfurization method for alumina production. This paper proposes a new method of sulfur removal by adding aluminum in which aluminum is supplied to prevent S^{2-} from oxidizing into $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-} in the sodium aluminate solution, which forces S^{2-} into red mud to decrease the concentration of S^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, SO_4^{2-}, and total sulfur in the liquor. 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.

2. Experiment

2.1. Experiment materials

The high-sulfur bauxite used in this experiment was obtained from the Zunyi mining area in China. The chemical components of mineral samples are shown in Table 1. The X-ray diffraction pattern of the mineral is shown in Fig. 1. The QEMSCAN image of the mineral is shown in Fig. 2. The SEM image of the mineral is shown in Fig. 3.

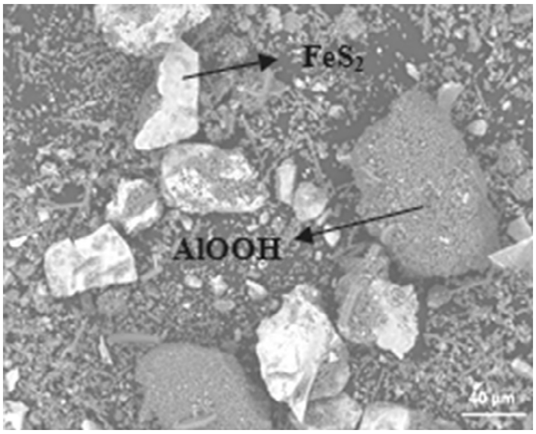

Fig. 3. SEM images of the high sulfur bauxite.

Table 2
Chemical components of evaporation spent liquor from Zunyi alumina refinery.

Chemical components	Concentration (g/L)
Na_2O_T	265.45
Al_2O_3	128.6
Na_2O_k	231
Na_2S	0.22
$Na_2S_2O_3$	4.17
Na_2SO_3	3.32
Na_2SO_4	6.62

Note: Na_2O_T—total soda (as Na_2O), Na_2O_k—caustic soda (as Na_2O).

X-ray diffraction of the prepared samples was conducted with a Bruker advanced-D8 powder diffractometer using Cu-K_α radiation operating at 40 kV and 40 mA with a Vanter-1 detector.

As shown in Table 1 the A/S of the high-sulfur bauxite is 8.36, and the total sulfur is 2.16%.

As shown in Figs. 1–3, the primary sulfur-bearing mineral is pyrite. Fig. 2 also demonstrates that pyrite has a granular aggregate distribution, with particle sizes between 10 and 100 µm, whereas the goethite is dispersed throughout the pyrite particles and diaspore matrix. It also can be seen from Fig. 3 that pyrite was wrapped on the surface of the diaspore, and there are a small number of holes on the surface. During the Bayer process of alumina production, the sulfur in high-sulfur bauxite first enters 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 alkali solution used in the experiment was taken from an evaporation spent liquor from the Zunyi alumina refinery. Its chemical components are listed in Table 2.

The lime used in the experiment was also provided by a certain Alumina Plant in China. The weight percent of total CaO in the lime is 92.65%.

2.2. Experimental method

Digestion experiments on high-sulfur bauxite were conducted in a XYF-6 digester heated by molten salts. The digestion temperature can be controlled within the variation range of 273.1 K (0.1 °C). The mineral sample and evaporation-spent liquor according in predetermined proportions were placed in a 100 ml sealed stee1 bomb. The digester was brought to the specified temperature and held for 5 min, then the steel bomb was placed inside and the digestion process was run. The sodium aluminate solution was then filtered and the Al_2O_3, Na_2O_k,