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Interaction of sulfur with iron compounds in sodium aluminate solutions

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Abstract: Reaction behaviors of sulfur and iron compounds in sodium aluminate solutions were investigated. The results show that iron compounds can remarkably remove the S^{2-} but cannot get rid of $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} in sodium aluminate solutions. The removal efficiency of S^{2-} using ferrous compound and ferric compound can reach 86.10% and 92.70% respectively when the iron compounds were added with a molar ratio of 2:1 compared with the sulfur in liquors at 100 °C. Moreover, several same compounds are formed in those two desulfurization processes with ferrous or ferric compounds, including erdite, hematite, amorphous ferrous sulfide, polymerized sulfur-iron compounds and ferric sulfate. The major difference between these two processes is that the erdite generated from ferrous compounds at the initial reaction stage will convert to a sodium-free product FeS_2 at the subsequent stage.

Key words: high-sulfur bauxite; sodium aluminate; iron compounds; desulfurization; mechanism

1 Introduction

The constraint on sustainable development of alumina industry in China by bauxite resources has become increasingly obvious because of the large industrial production capacity of alumina, the exhausted high-grade quality bauxite resources in China and the restrictive export policies of foreign bauxite [1]. The reserve of high sulfur-containing diasporic bauxite has reached 560 million tons in China and is expected to rise greatly to 2 billion tons in the future, which is mainly located in Guizhou Province and Chongqing Municipality. In addition, more than 60% of the high sulfur-containing diasporic bauxite in Guizhou Province is high-grade quality bauxite and it is suitable for the Bayer process [2,3]. During the high temperature digestion of Bayer process, the sulfur minerals can completely or partially react with the aluminate solutions, as a result, the sulfur enters into and accumulates in the Bayer liquor mainly in the form of S^{2-}[4], which will obviously increase the caustic soda consumption and iron content in the alumina product and seriously corrode the steel equipment. Unfortunately, the current methods for sulfur removal could not treat high sulfur-containing diasporic bauxite effectively and economically, which results in the rarely using of high sulfur bauxite in alumina production [5,6]. However, it is worth noting that the disadvantages of high sulfur bauxite mentioned above involve the reaction behaviors of sulfur species and iron compounds in sodium aluminate solutions, and it would be of great significance to investigate the behaviors of sulfur compounds and iron compounds in sodium aluminate solutions.

Up to now, considerable studies have been proceeding, such as decomposition of sulfur or iron minerals in bauxite, increase of iron content in alumina product resulting from the more soluble sulfur-iron compounds, and corrosion of steel equipment. Pyrite in high sulfur bauxite can easily react with alkali liquors during the Bayer process [7]. The iron−hydroxyl complexes are generated firstly by the reaction of Fe^{2+} on the pyrite surface with OH^- in sodium aluminate solution, then the complexes detach from the surface of pyrite, and the sulfur enters into the solution mainly in the form of S^{2-} with a small quantity of $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} [8]. At the same time, the iron content in aluminate solutions increases sharply with the accumulation of S^{2-}. KUZNETSOV et al [9] and HE [10] held that iron would combine with oxygen or hydroxyl to generate coordination

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complexes in aluminate solutions at high temperature, and then the S^{2-} in solutions would substitute the oxygen or hydroxyl and form a more soluble $Na_2FeS_2(OH)_2 \cdot 2H_2O$, which results in the increase of iron content in solutions and subsequent contamination of alumina product. Additionally, the formation of $Na_2FeS_2(OH)_2 \cdot 2H_2O$ would destroy the passive film on the surface of steel equipments and accelerate the corrosion of low alloy steel [11]. Recently, LI et al [12] have found that the sulfur could be removed by the addition of specific iron compounds, thus the problem of caustic soda consumption and alumina product contamination could be solved simultaneously. But the further research has not been reported. In this work, the reaction behavior of iron complexes and sulfur compounds in aluminate solutions were investigated, a new idea and an important fundamental basis of removing sulfur from aluminate solutions were provided and an effective protocol to utilize high sulfur bauxite was developed.

2 Experimental

2.1 Materials

Sodium aluminate solutions were prepared by dissolving industrial aluminum trihydroxide in hot solutions of industrial sodium hydroxide. The ferric compound and ferrous compound were respectively synthesized by the sedimentation of ferric chloride solution and ferrous chloride solution with the sodium hydroxide solution at 25 °C. The sulfur compounds were dissolved in sodium aluminate solutions to prepare sodium aluminate solutions to a certain sulfur concentration as element S. Sodium thiosulfate (AR purity) and sodium sulfite (AR purity) and sodium sulfate (AR purity) were purchased from Kermel Chemical Reagent Corporation of Tianjin, China. Sodium sulfide nonahydrate which contains small amounts of high valence state sulfur compounds was purchased from Xilong Chemical Corporation Limited (Guangdong, China).

2.2 Experimental procedure

The experiments were carried out in the DY−8 low pressure reaction kettles (Central South University Machinery Factory) in which stainless bombs (150 mL) sealed were immersed and rotated in glycerol with the temperature precision of 1 °C. The sulfur-containing aluminate solutions and ferric compound or ferrous compound as well as several stainless balls for agitation were added to the bomb and remained in the low pressure reaction kettle for 1 h at 100 °C. Then the bombs were cooled rapidly in cold water to room temperature, and the slurry was subsequently filtered and washed with hot water. The residue was dried at 50 °C for more than 24 h. The concentrations of S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} in the filtrate were analyzed by titration method [13] and the concentration of SO_4^{2-} in the filtrate was determined by ion chromatography (Dionex China Limited). The concentration of iron impurities (labeled as Fe_2O_3) in solutions was determined by atomic absorption spectrometry. The phases of residues were further characterized by XRD analyzer D/MAX2500X (Rigaku Corporation, Japan), X-ray photoelectron spectrometer ESCALAB MK-II (Vaccum Generator Corporation, UK) and FT-IR 6700 spectrometer (Nicolet Corporation, USA), respectively.

3 Results and discussion

3.1 Interaction of sulfur and iron compounds in sodium aluminate solutions

The sulfur enters the sodium aluminate solutions and exists as S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} due to the redox reaction, and the amounts of sulfur species vary greatly with different production processes during the alumina production. The reactions of ferrous compound and ferric compound (the molar ratio of Fe to S represents the dosage of iron compound, $n(Fe)/n(S)$) with aluminate solutions with a sulfur concentration of 5 g/L (as element S) were firstly proceeded in order to examine the desulfurization efficiencies of iron compounds. The results are given in Tables 1 and 2.

Table 1 Removal efficiency of sulfur compounds using ferrous compound

$n(Fe)/n(S)$	$\rho(S^{2-})/(g \cdot L^{-1})$	$\rho(S_2O_3^{2-})/(g \cdot L^{-1})$	$\rho(SO_3^{2-})/(g \cdot L^{-1})$	$\rho(SO_4^{2-})/(g \cdot L^{-1})$	Removal ratio of S^{2-}/%
0	4.25	1.31	0.70	0.76	0
0.5:1	2.89	2.33	0.37	0.24	32.00
1:1	2.52	1.75	0.26	0.02	40.70
2:1	0.31	1.63	0.57	0.87	92.70
3:1	0.12	1.16	0.78	1.24	97.18
4:1	0.63	1.05	0.39	0.73	85.17

Reaction conditions: temperature 100 °C; reaction time 1 h; sodium aluminate solution: $\rho(Na_2O)$=165 g/L; α_k=1.41