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Effects of iron-containing phases on transformation of sulfur-bearing ions in sodium aluminate solution

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Abstract: Sulfides in the high-sulfur bauxite lead to serious steel equipment corrosion and alumina product degradation via the Bayer process, owing to the reactions of sulfur and iron-containing phases in the sodium aluminate solution. The effects of iron-containing phases on the transformation of sulfur-bearing ions (S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}) in sodium aluminate solution were investigated. Fe, Fe_2O_3 and Fe_3O_4 barely react with SO_3^{2-} and SO_4^{2-}, but all of them, particularly Fe, can promote the conversion of $S_2O_3^{2-}$ to SO_3^{2-} and S^{2-} in sodium aluminate solution. Fe can convert to $Fe(OH)_3^-$ in solution at elevated temperatures, and further react with S^{2-} to form FeS_2, but Fe_2O_3 and Fe_3O_4 have little influence on the reaction behavior of S^{2-} in sodium aluminate solution. Increasing temperature, duration, dosage of Fe, mole ratio of Na_2O_k to Al_2O_3 and caustic soda concentration are beneficial to the transformation of $S_2O_3^{2-}$ to SO_3^{2-} and S^{2-}. The results may contribute to the development of technologies for alleviating the equipment corrosion and reducing caustic consumption during the high-sulfur bauxite treatment by the Bayer process.

Key words: high-sulfur bauxite; sodium aluminate solution; sulfur-bearing ion; iron-containing phase; transformation

1 Introduction

More than 560 million tons of high-sulfur diasporic bauxite resources have not been effectively utilized in China [1,2]. The main sulfide mineral in the bauxite is pyrite (FeS_2) which readily reacts with alkaline solution in the Bayer process, resulting in the increase of caustic consumption, serious equipment corrosion, and Fe-contamination of alumina product [2−4]. In order to resolve such problems, many scholars have conducted researches which focused on: 1) pyrite removal from bauxite by pretreatments, such as roasting [4], flotation [5], and bio-beneficiation [6]; 2) removal of S^{2-} from Bayer liquor, such as through formation of ZnS by adding Zn(II) [3,7] or $NaFeS_2 \cdot 2H_2O$ by adding fresh iron hydroxides [8]; 3) removal of SO_4^{2-} from Bayer liquor through formation of $BaSO_4$ by adding barium compounds [9]; 4) conversion of S^{2-} to SO_4^{2-} during the Bayer digestion process by addition of oxidants, such as O_2 [10,11] and $NaNO_3$ [12]. However, inefficient desulfurization, high cost and complicated operation limit the practical application of these methods. Therefore, developing new methods to minimize the impact of sulfur-containing minerals is crucial for utilization of high-sulfur bauxite.

During the Bayer digestion process, sulfur-containing minerals in bauxite inevitably react with the alkaline solution to form S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} etc., and these sulfur-bearing ions would further react with Fe (in steel equipment), Fe_2O_3 or Fe_3O_4 (in bauxite). The adverse effects of sulfur-containing species on the alumina production process are generally believed to be caused by these various reactions. KUZNETSOV et al [13] and LI et al [14] investigated the reactions of FeS_2 in sodium aluminate solution at elevated temperatures, and proposed that the soluble iron−sulfur complex generated by sulfur and iron-containing phases was the main reason for Fe-contamination of the product. XIE et al [15−17] studied the influence of S^{2-} on corrosion of steels in sodium aluminate solution and suggested that S^{2-} could react with steel to generate iron−sulfur compounds with loose structure and thus accelerate the corrosion. XIE et al [16] also reported that the corrosion

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of steels could be decelerated by $S_2O_3^{2-}$ anion in sodium aluminate solution, while WENSLEY and CHARLTON [18] found that both S^{2-} and $S_2O_3^{2-}$ anions were the corrosion activators for steels in alkaline solution. Compared with the low-valence sulfur ions, SO_3^{2-} and SO_4^{2-} were believed to be harmless to the corrosion of steel equipment and Fe-contamination of alumina products.

In view of different impacts of various sulfur-bearing ions, the conversions of sulfur-bearing ions in aluminate solution have received considerable research attention. ABIKENOVA et al [19], and HU and CHEN [10] investigated the transformation of S^{2-} in sodium aluminate solution in the presence of oxidants, and demonstrated that the transformation process among sulfur-bearing ions, i.e., S^{2-} was first oxidized to $S_2O_3^{2-}$ and then to SO_4^{2-} or SO_3^{2-} which was finally converted to SO_4^{2-}. However, the conversion behaviors of sulfur-bearing ions during the reactions of them with iron-bearing substances were not taken into consideration.

In sum, understanding the reaction behaviors of the iron-containing phases and the sulfur-bearing ions as well as the transformation of the sulfur-bearing ions is essential to develop new technologies for high-sulfur bauxite utilization. Unfortunately, the previous researches paid much attention to the transformation of iron-bearing species in the sulfur-containing solutions, while the effects of iron-containing phases on transformation of the sulfur-bearing ions have been scarcely reported. In view of this, this work focused on the dependence of sulfur-bearing ion (S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}) transformation on iron-containing phases (Fe, Fe_2O_3 and Fe_3O_4) in sodium aluminate solution. We attempted to provide the fundamental basis for taking some measures to reduce the steel equipment corrosion, caustic soda loss and the product Fe-contamination during the high-sulfur bauxite treatment by the Bayer process.

2 Experimental

2.1 Materials

Sodium aluminate solutions were prepared by dissolving industrial grade aluminum hydroxide (Aluminum Corporation of China) into hot sodium hydroxide solution. Various sulfur-bearing ion solutions were obtained by adding analytical grade of $Na_2S\cdot 9H_2O$ (Xilong Chemical Co., Ltd.), $Na_2S_2O_3\cdot 5H_2O$, Na_2SO_3 or Na_2SO_4 (Sinopharm Chemical Reagent Co., Ltd.) of a defined dosage into the prepared sodium aluminate solution. Both iron powder (Kermel Chemical Reagent Corporation of Tianjing, China) and Fe_2O_3 powder (Sinopharm Chemical Reagent Co., Ltd.) were analytical grade reagents, Fe_3O_4 powder (Sinopharm Chemical Reagent Co., Ltd.) was chemically pure reagent, and no other phases were detected in these iron-containing phases (Fig. 1).

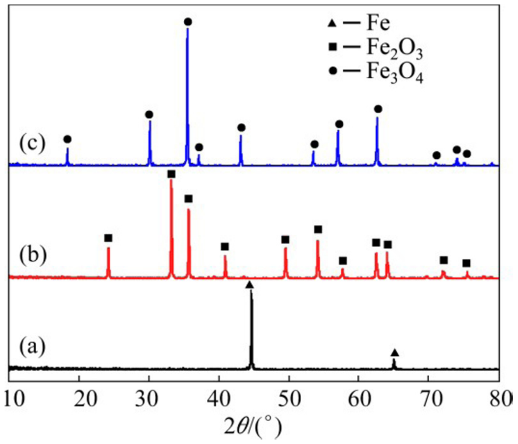

Fig. 1 XRD patterns of iron-containing phases: (a) Fe; (b) Fe_2O_3; (c) Fe_3O_4

2.2 Methodology

The digestion experiments were performed in a self-designed autoclave, in which the sealed stainless bombs (150 mL) were heated in either molten salts (>160 °C) or glycerol (<140 °C). A given mass of iron-containing substance and 100 mL sulfur-bearing sodium aluminate solution were added into a 150 mL bomb, together with four steel balls (two 18 mm-diameter and two 8 mm-diameter) for improved agitation. The sealed bomb was fixed in a rotating device (rotation speed of 120 r/min), immersed in the heating medium and was retained for fixed duration at the designated temperature. The resultant slurry obtained was filtered and washed using hot water. The filtrate was collected for sulfur-bearing ions analysis, and the residue was dried at (50±1) °C for 24 h.

The sodium aluminate solutions were characterized by Na_2O_k concentration and caustic molar ratio (α_k). The Na_2O_k represents caustic soda as Na_2O in solution, and the α_k refers to the molar ratio of Na_2O_k to Al_2O_3. The concentrations of Na_2O_k and Al_2O_3 were determined by titration [20]. The concentrations of sulfur-bearing ions were characterized by the mass concentration of element sulfur, and the total sulfur concentration (S_T) is the summation of concentrations of S^{2-}, $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} in solution. The concentrations of $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} were simultaneously analyzed by an ion chromatograph (ICS−90, Dionex, USA) and designated respectively as x_2, x_3 and x_4. The total concentration (x) of S^{2-}, $S_2O_3^{2-}$ and SO_3^{2-} was measured by titration [21]. Hence, the S^{2-} concentration (x_1) can be calculated by subtraction, i.e., $x_1=x-x_2-x_3$. Every digestion experiment was conducted at least twice to