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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<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> 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<sub>2</sub>, but Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have little influence on the reaction behavior of  $S^{2-}$  in sodium aluminate solution, 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<sub>2</sub>) 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<sub>2</sub> 2H<sub>2</sub>O by adding fresh iron hydroxides [8]; 3) removal of  $SO_4^{2-}$  from Bayer liquor through formation of BaSO4 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<sub>2</sub> [10,11] and NaNO<sub>3</sub> [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, sulfurcontaining 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<sub>2</sub> 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<sup>2-</sup> 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 sulfurbearing 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 previous bauxite utilization. Unfortunately, the 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<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) 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 the high-sulfur bauxite during 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<sub>2</sub>S·9H<sub>2</sub>O (Xilong Chemical Co., Ltd.), Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O, Na<sub>2</sub>SO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> (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<sub>2</sub>O<sub>3</sub> 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  $(50\pm1)$  °C for 24 h.

The sodium aluminate solutions were characterized by Na<sub>2</sub>O<sub>k</sub> concentration and caustic molar ratio ( $\alpha_k$ ). The Na<sub>2</sub>O<sub>k</sub> represents caustic soda as Na<sub>2</sub>O in solution, and the  $\alpha_k$  refers to the molar ratio of Na<sub>2</sub>O<sub>k</sub> to Al<sub>2</sub>O<sub>3</sub>. 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

verify the variation of the sulfur-bearing ions, average concentrations of sulfur-bearing ions were recorded. X-ray diffraction (D/MAAX2500, Rigaku Corporation, Japan) was applied to characterizing the residues using Cu K<sub>a</sub> radiation at a scanning speed of 8 (°)/min. The contents of sodium and sulfur in residues were identified by flame photometer (AP1302, Shanghai Aopu Analytical Instruments Corporation, China) and sulfur analyzer (HDS3000, Hunan Huade Electronics Corporation, China), respectively.

### **3** Results and discussion

### **3.1 Effects of iron-containing phases on reaction** behavior of sulfur-bearing ions

The digestion of diasporic bauxite was generally conducted at 260-280 °C with the Na<sub>2</sub>O<sub>k</sub> concentration of about 230 g/L and  $\alpha_k$  of 3.0 in the alumina refineries. The main iron-containing phases involved in the digestion process were Fe (steel equipment) and iron oxides (main iron minerals in bauxite and the passivation coating of the steel equipment). In order to reveal the effects of iron-containing phases (Fe, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>) on the transformation of sulfur-bearing ions, the concentration variation of sulfur-bearing ions was investigated in sodium aluminate solution during the digestion process with adding various iron-bearing phases. Blank experiments without the addition of the iron-containing phases were also conducted for comparison. Moreover, in order to react with the sulfur-bearing ions adequately during the digestion, and the initial dosage of iron-containing phases was determined with the mole ratio of Fe to S being 1.5:1.

3.1.1 Effects of iron-containing phases on reaction behavior of  $S^{2-}$ 

When high-sulfur bauxite is treated using the Bayer process, the sulfur exists in solution predominately in the form of  $S^{2-}$ . The influence of iron-containing phases on the transformation of  $S^{2-}$  is shown in Table 1.  $SO_3^{2-}$  and  $SO_4^{2-}$  were detected in the starting solution prepared by dissolving Na<sub>2</sub>S·9H<sub>2</sub>O, which may be contributed to the oxidation of  $S^{2-}$  during the preparation.

Table 1 shows that the S<sup>2-</sup> concentration is reduced by varying degrees after digestion with adding different iron-containing phases, and the sulfur concentration in residues is increased. When adding iron, Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub> powders, the concentrations of S<sup>2-</sup> in the digested solutions correspondingly decrease by 17.33%, 6.56% and 3.28% compared with the concentration of S<sup>2-</sup> in the blank digested solution. The S<sup>2-</sup> concentration in the blank digested solution decreases slightly along with a small increase of concentrations of SO<sup>2-</sup><sub>4</sub> and SO<sup>2-</sup><sub>3</sub> compared with the starting solution, which may be caused by the oxidation of S<sup>2-</sup> during the digestion. The result shows that  $S^{2-}$  concentration decreases obviously on addition of the iron-containing phases in digestion process accompanying by an increase in  $SO_3^{2-}$  and  $SO_4^{2-}$  concentrations. Table 1 also reveals that the  $S^{2-}$ concentration variation is related to the valence of iron, i.e., the iron with the smallest valence favors the most decreased  $S^{2-}$  concentration in the digested solution.

3.1.2 Effects of iron-containing phases on reaction behavior of  $S_2O_3^{2-}$ 

The pyrite in bauxite will react with alkaline solution forming  $S^{2-}$  and  $S_2O_3^{2-}$  firstly in the Bayer digestion process. The  $S^{2-}$  ion can be oxidized into  $S_2O_3^{2-}$  and other high valence sulfur-bearing ions in sodium aluminate solution during the alumina production [19].  $S_2O_3^{2-}$  was found to accelerate the equipment corrosion [22]. The effects of iron-containing phases on the transformation of  $S_2O_3^{2-}$  in sodium aluminate solution were also studied. The results are shown in Table 2.

As shown in Table 2, the concentration of  $S_2O_3^{2-}$  decreases significantly in sodium aluminate solution after digestion. Compared with the starting solution, about 75% of  $S_2O_3^{2-}$  transforms to  $SO_3^{2-}$  and  $S^{2-}$  in the blank sample, possibly due to the disproportionation reaction of  $S_2O_3^{2-}$ . The transformations of  $S_2O_3^{2-}$  are enhanced by differing degrees on addition of the iron-containing phases. Besides,  $S_2O_3^{2-}$  can completely convert into  $SO_3^{2-}$  and  $S^{2-}$  on addition of iron powder, suggesting that the transformation of  $S_2O_3^{2-}$  can be accelerated obviously by iron powder, and the possible reactions can be proposed as Eqs. (1) and (2) [23].

$$Fe + S_2O_3^{2-} = FeS + SO_3^{2-}$$
 (1)

$$FeS+3OH^{-}=Fe(OH)_{3}^{-}+S^{2-}$$
(2)

In addition, the formed FeS may further react with  $OH^-$  in sodium aluminate solution during the digestion process at elevated temperature (Eq. (2)), resulting in the increase of  $SO_3^{2-}$  and  $S^{2-}$  concentrations in digested solution.

3.1.3 Effects of iron-containing phases on transformation of  $SO_3^{2-}$  or  $SO_4^{2-}$ 

In general,  $S^{2-}$  can be oxidized to  $SO_3^{2-}$  and  $SO_4^{2-}$  by  $O_2$  or other oxidants [3,12] in the Bayer process. The effects of iron-containing phases on the transformation of  $SO_3^{2-}$  and  $SO_4^{2-}$  were concerned in sodium aluminate solution, and the results are presented in Tables 3 and 4, respectively.

Table 3 indicates that  $SO_4^{2-}$  concentration has no remarkable variation and  $SO_4^{2-}$  is present in solution for all experiments. The presence of  $SO_4^{2-}$  can be attributed to the oxidation of  $SO_4^{2-}$  in sample preparation or the impurity of  $SO_4^{2-}$  in Na<sub>2</sub>SO<sub>3</sub>. In comparison with the other samples, the lower  $SO_4^{2-}$ concentration with adding iron powder may be caused by

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Table 1 Effects of iron-containing phases on reaction behavior of  $S^{2-}$  in sodium aluminate solution

Sample No.	Added phase	$Dosage/(g \cdot L^{-1})$	Concentration of sulfur-bearing ions in solution after reaction/ $(g \cdot L^{-1})$					Sulfur in
			$\mathrm{SO}_4^{2-}$	$SO_{3}^{2-}$	$S_2O_3^{2-}$	$S^{2-}$	$\mathbf{S}_{\mathrm{T}}$	residues/g
Starting solution	-	_	0.12	0.16	ND	4.65	4.93	_
Blank	-	_	0.17	0.35	ND	4.27	4.79	0.016
1	Fe	13.10	0.18	0.28	ND	3.53	3.99	0.088
2	Fe <sub>3</sub> O <sub>4</sub>	18.10	0.29	0.41	ND	3.99	4.69	0.026
3	Fe <sub>2</sub> O <sub>3</sub>	18.80	0.26	0.35	ND	4.13	4.74	0.024

 $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 232.38 g/L;  $\alpha_k$ : 3.01; temperature: 260 °C; duration: 1 h; ND: not detected

Table 2 Effects of iron-containing phases on transformation of  $S_2O_3^{2-}$  in sodium aluminate solution

Sample	Added phase	Dosage/	C	Sulfur in				
No.	•	(g·L ¹)	$SO_4^{2-}$	$SO_{3}^{2-}$	$S_2O_3^{2-}$	S <sup>2-</sup>	$\mathbf{S}_{\mathrm{T}}$	residues/g
Starting solution	_	_	0.00	0.00	5.13	0.30	5.43	_
Blank	-	-	0.04	2.66	1.80	0.40	4.90	0.018
1	Fe	13.10	0.15	3.59	0.00	0.93	4.67	0.054
2	Fe <sub>3</sub> O <sub>4</sub>	18.10	0.12	2.83	1.29	0.64	4.88	0.024
3	Fe <sub>2</sub> O <sub>3</sub>	18.80	0.10	2.91	0.76	0.98	4.75	0.031

 $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 232.38 g/L;  $\alpha$ <sub>k</sub>: 3.01; temperature: 260 °C; duration: 1 h

Table 3 Effects of iron-containing phases on transformation of  $SO_3^{2-}$  in sodium aluminate solution

G 1			C	G 10 .				
Sample	Added phase	$Dosage/(g \cdot L^{-1})$		solution	after reaction	$n/(g \cdot L^{-1})$		Sulfur in
No.	-		$\mathrm{SO}_4^{2-}$	$SO_{3}^{2-}$	$S_2O_3^{2-}$	$S^{2-}$	$\mathbf{S}_{\mathrm{T}}$	residues/g
Starting solution	-	_	0.68	4.34	ND	ND	5.02	_
Blank	-	-	0.57	4.52	ND	ND	5.09	$0.16 \times 10^{-2}$
1	Fe	13.10	0.34	4.60	ND	ND	4.94	$0.27 \times 10^{-2}$
2	Fe <sub>3</sub> O <sub>4</sub>	18.10	0.62	4.41	ND	ND	5.03	$0.32 \times 10^{-2}$
3	Fe <sub>2</sub> O <sub>3</sub>	18.80	0.60	4.49	ND	ND	5.09	$0.38 \times 10^{-2}$

 $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 232.38 g/L;  $\alpha_k$ : 3.02; temperature: 260 °C; duration: 1 h; ND: not detected

Table 4 Effects of iron-containing phases on the transformation of  $SO_4^{2-}$  in sodium aluminate solution

Sample	Added phase	Dosage/ $(g \cdot L^{-1})$	Concentration of sulfur-bearing ions in solution after reaction/ $(g \cdot L^{-1})$					Sulfur in
No.	Ĩ		$\mathrm{SO}_4^{2-}$	$SO_{3}^{2-}$	$S_2O_3^{2-}$	S <sup>2-</sup>	ST	residues/g
Starting solution	-	_	4.61	ND	ND	ND	4.61	_
Blank	-	-	4.72	ND	ND	ND	4.72	$0.18 \times 10^{-2}$
1	Fe	13.10	4.61	ND	ND	ND	4.61	$0.21 \times 10^{-2}$
2	$Fe_3O_4$	18.10	4.77	ND	ND	ND	4.77	$0.33 \times 10^{-2}$
3	Fe <sub>2</sub> O <sub>3</sub>	18.80	4.64	ND	ND	ND	4.64	$0.33 \times 10^{-2}$

 $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 232.38 g/L;  $\alpha$ <sub>k</sub>: 3.02; temperature: 260 °C; duration: 1 h; ND: not detected

the inhibition of  $\mathrm{SO}_3^{2-}$  oxidation. The results in Table 4 demonstrate that iron-containing phases have no evident influence on the transformation of  $\mathrm{SO}_4^{2-}$  in sodium aluminate solution. Moreover, the sulfur contents in residues approximate to zero, and neither  $\mathrm{SO}_3^{2-}$  nor  $\mathrm{SO}_4^{2-}$  appears to react with iron-containing phases

during the Bayer digestion process of diasporic bauxite, which is in agreement with previous research [18].

3.1.4 Phase analysis of residues obtained from reaction

of iron-containing phases with  $S^{2-}$  or  $S_2O_3^{2-}$ As discussed above, both  $S^{2-}$  and  $S_2O_3^{2-}$  in sodium aluminate solution can react with the iron-containing phases. For better understanding the reaction mechanism, the XRD analysis of residues generated by the reaction of iron-containing phases with  $S^{2-}$  and  $S_2O_3^{2-}$  was conducted, and the results are displayed in Fig. 2.



**Fig. 2** XRD patterns of residues produced by reaction of iron-containing phases with  $S^{2-}$  (a) and  $S_2O_3^{2-}$  (b): 1—Fe; 2—Fe<sub>3</sub>O<sub>4</sub>; 3—Fe<sub>2</sub>O<sub>3</sub> ( $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 232.38 g/L;  $\alpha_k$ : 3.02; temperature: 260 °C; duration: 1 h; dosage: Fe 13.10 g/L; Fe<sub>2</sub>O<sub>3</sub> 18.80 g/L; Fe<sub>3</sub>O<sub>4</sub> 18.10 g/L)

No new phases are detected using XRD analysis in the residues obtained by adding Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub>, which suggests that either Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> has little influence on the transformation of  $S^{2-}$  or  $S_2O_3^{2-}$  in sodium aluminate solution, being consistent with the results in Tables 1 and 2. Whereas, evident characteristic peaks of Fe<sub>3</sub>O<sub>4</sub> and faint characteristic peak (at about  $2\theta = 16.5^{\circ}$ ) appear in the XRD patterns of the residues obtained by adding iron powder. The possible phase at  $2\theta = 16.5^{\circ}$  may be FeS<sub>2</sub> or NaFeS<sub>2</sub>·2H<sub>2</sub>O [8], which can be formed by the ferrous or ferric compound reacting with S<sup>2-</sup> in sodium aluminate solution, respectively. The contents of sodium and sulfur were detected (in Table 5) to identify the phases in residues. In view of the low sodium contents and high sulfur contents in residues, the formation of FeS2 at  $2\theta = 16.5^{\circ}$  can be verified.

According to the previous studies [24-26], iron can

	<b>Fable 5</b>	Contents	of s	sodium	and	sulfur	in	residues
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Committee -	Mass fraction/%						
Sample	Sodium	Sulfur					
Curve 1 in Fig. 2(a)	0.23	5.08					
Curve 1 in Fig. 2(b)	0.21	3.95					

convert to  $Fe(OH)_3^-$  and  $Fe_3O_4$  in alkaline solution at elevated temperatures.  $Fe(OH)_3^-$  may react with S<sup>2-</sup> to form FeS<sub>2</sub> in sodium aluminate solution during the temperature decrease process after digestion, as discussed by LI et al [8], leading to decreased  $S^{2-}$ concentration (Table 1). On addition of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> powders, little  $Fe(OH)_3^-$  is formed in the solution. Therefore, iron powder promotes the transformation of  $S^{2-}$  into residues more greatly than  $Fe_2O_3$  or  $Fe_3O_4$ powders. It is comprehensible that iron powders can enhance the conversion of  $S_2O_3^{2-}$  to  $SO_3^{2-}$  and  $S^{2-}$ , and S2- then partly incorporates in FeS2, reducing  $S_2O_2^{2-}$ concentration and increasing  $SO_2^{2-}$ concentration (in Table 2).

### 3.2 Effects of duration and iron powder dosage on transformation of $S^{2-}$ and $S_2O_3^{2-}$

The influences of duration and iron powder dosage on the transformation of  $S^{2-}$  and  $S_2O_3^{2-}$  at different temperatures are presented in Figs. 3–5, respectively.

Figure 3(a) indicates that the main sulfur-bearing ion is  $S^{2-}$  in solution, coexisting a small amount of  $SO_3^{2-}$  and  $SO_4^{2-}$ . The concentrations of  $S_T$ ,  $S_2O_3^{2-}$ ,  $SO_4^{2-}$ ,  $SO_3^{2-}$  and  $S^{2-}$  in solution remain almost unchanged at 80 °C as a function of duration, suggesting that  $S^{2-}$  reacts weakly with iron powder in sodium aluminate solution at low temperatures. However, when the reaction temperature is increased to 260 °C (Fig. 3(b)), the concentration of  $S^{2-}$  decreases slightly with the duration prolonging. The  $S^{2-}$  concentration decreases from 4.05 to 3.52 g/L in 10 min, and then reaches 3.27 g/L at 90 min. The  $SO_3^{2-}$  concentration increases slightly and  $SO_4^{2-}$  concentration remains almost constant, i.e.,  $SO_3^{2-}$  is difficult to convert to  $SO_4^{2-}$ .

 $S_2O_3^{2-}$  concentration decreases and  $SO_3^{2-}$  concentration increases with duration at either 120 or 260 °C (Fig. 4). Increasing temperature favors the  $S_2O_3^{2-}$  conversion, e.g.,  $S_2O_3^{2-}$  concentration reduces to zero in 10 min at 260 °C along with marked increase in  $SO_3^{2-}$  concentration and slight raising of  $S^{2-}$  concentration instead of being proportional to  $SO_3^{2-}$  concentration, where the  $S_T$  concentration reduces from 5.28 to 4.17 g/L. The obvious reduction of  $S_T$  concentration and the inconspicuous variation of  $S^{2-}$  concentration are caused by the formation of FeS<sub>2</sub>.

The iron powder dosage has a significant influence on reducing the  $S^{2-}$  concentration until 8.75 g/L (mole

ratio of Fe to S being ~1), further increase in iron powder dosage does not result in further reduction of  $S^{2-}$ concentration (Fig. 5(a)). The variation of  $S_2O_3^{2-}$ concentration shows a similar trend with the effect of iron powder dosage, the critical dosage is about 4.38 g/L (mole ratio of Fe to S being ~0.5) (Fig. 5(b)). The variation tendencies of other sulfur-bearing ions with increasing the iron powder dosage in Figs. 5(a) and (b), including  $SO_3^{2-}$ ,  $SO_4^{2-}$  and  $S^{2-}$ , are coincident with the results in Figs. 3(b) and 4(b), respectively.



**Fig. 3** Effects of duration on reaction behavior of S<sup>2-</sup> in sodium aluminate solution at 80 °C (a) and 260 °C (b) ( $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 228.45 g/L;  $\alpha_k$ : 3.01; dosage of iron powder: 13.10 g/L)



**Fig. 4** Effects of duration on reaction behavior of  $S_2O_3^{2-}$  in sodium aluminate solution at 120 °C (a) and 260 °C (b) ( $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 228.45 g/L;  $\alpha_k$ : 3.01; dosage of iron powder: 13.10 g/L)



**Fig. 5** Effects of iron powder dosage on reaction of S<sup>2-</sup> (a) and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (b) in sodium aluminate solution ( $\rho$ (Na<sub>2</sub>O<sub>k</sub>): 231.55 g/L;  $\alpha_k$ : 2.98; temperature: 260 °C; duration: 1 h)

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## 3.3 Effects of $\alpha_k$ and $Na_2O_k$ concentration on transformation of $S^{2-}$ and $S_2O_3^{2-}$

As  $\alpha_k$  and Na<sub>2</sub>O<sub>k</sub> concentration are important characteristics of the sodium aluminate solution and vary in the Bayer process, their influences on the transformation of S<sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> were determined experimentally. The compositions of starting sodium aluminate solutions are listed in Table 6, and the results of the effect of  $\alpha_k$  and Na<sub>2</sub>O<sub>k</sub> concentration are presented in Figs. 6 and 7, respectively.

Table 6 Compositions of starting sodium aluminate solutions

Sample No.	$ ho(\mathrm{Na_2O_k})/(\mathrm{g}\cdot\mathrm{L}^{-1})$	$\rho(Al_2O_3)/(g\cdot L^{-1})$	$\alpha_{\rm k}$
1	232.75	263.39	1.45
2	228.48	181.79	2.07
3	222.07	151.98	2.40
4	226.34	125.75	2.96
5	226.34	107.38	3.48



**Fig. 6** Effects of  $\alpha_k$  on reaction of  $S^{2-}$  (a) and  $S_2O_3^{2-}$  (b) in sodium aluminate solution (temperature: 260 °C; duration: 1 h; dosage of iron powder: 13.10 g/L; Na<sub>2</sub>S·9H<sub>2</sub>O dosage (a): 37.50 g/L; Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O dosage (b): 19.38 g/L)

The S<sup>2-</sup> concentration reduces with increasing  $\alpha_k$ , while the S<sub>T</sub> in solution initially decreases and then remains stable (Fig. 6(a)). Figure 6(b) shows that the

 $S_2O_3^{2-}$  concentration also decreases with increasing  $\alpha_k$ , and that  $S_2O_3^{2-}$  can even completely convert to  $SO_3^{2-}$ and  $S^{2-}$  in solution at  $\alpha_k$  greater than 2.07.



**Fig.** 7 Effects of Na<sub>2</sub>O<sub>k</sub> concentration on reaction of S<sup>2-</sup> (a) and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> (b) in sodium aluminate solution ( $\alpha_k$ : 2.97; temperature: 260 °C; duration: 1 h; dosage of iron powder: 13.10 g/L; Na<sub>2</sub>S·9H<sub>2</sub>O dosage (a): 37.50 g/L; Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O dosage (b): 19.38 g/L)

It is also demonstrated that higher  $Na_2O_k$  concentration can expedite the reaction of  $S^{2-}$  with iron powder (Fig. 7(a)) with the  $Na_2O_k$  concentration ranging from 170 to 300 g/L,  $S_2O_3^{2-}$  can be completely transformed and its concentration declines to zero (Fig. 7(b)).

In summary, higher  $\alpha_k$  or concentrated Na<sub>2</sub>O<sub>k</sub>, corresponding to greater free sodium hydroxide concentration, is conducive to the reaction of S<sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> with iron powder due to increased formation of Fe(OH)<sub>3</sub><sup>-</sup> [26]. In addition, the variations of SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations with  $\alpha_k$  or Na<sub>2</sub>O<sub>k</sub> concentration exhibit the similar tendency to those with the increasing duration discussed in section 3.2.

#### 4 Conclusions

1) Fe promotes the transformation of  $S^{2-}$  into

residues, nevertheless, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have minimal effects on the reaction of S<sup>2-</sup> at 260 °C. The ironcontaining phases including Fe, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, can promote S<sub>2</sub>O<sub>3</sub><sup>2-</sup> transformation to SO<sub>3</sub><sup>2-</sup> and S<sup>2-</sup>, but have little influences on the transformation of SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup> in sodium aluminate solution.

2) The  $Fe(OH)_3^-$  formed by iron powder at elevated temperatures may react with S<sup>2-</sup> in sodium aluminate to generate FeS<sub>2</sub> after digestion, resulting in the S<sup>2-</sup> concentration decrease in solution.

3) Increasing the temperature, duration, dosage of iron powder,  $\alpha_k$  and  $Na_2O_k$  concentration accelerates the transformation of S<sup>2-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup> in solution in the presence of iron powder.

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### 含铁物质对含硫离子在 铝酸钠溶液中转化的影响

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**摘 要:**用拜耳法处理高硫铝土矿时,矿石中的硫化物会与含铁物质在铝酸钠溶液中反应,进而导致严重的设备腐蚀和氧化铝产品降级。本文作者研究含铁物质对含硫离子( $S^{2-}$ ,  $S_2O_3^{2-}$ ,  $SO_3^{2-}$ 和 $SO_4^{2-}$ )在铝酸钠溶液中转化的影响。研究结果表明:铁粉、Fe<sub>2</sub>O<sub>3</sub>和 Fe<sub>3</sub>O<sub>4</sub>均难以与 $SO_3^{2-}$ 和 $SO_4^{2-}$ 反应,而且所有含铁物质,特别是铁粉,均能促进 $S_2O_3^{2-}$ 转化为 $SO_3^{2-}$ 和 $S^{2-}$ ;在高温条件下铁粉与铝酸钠溶液反应生成Fe(OH)<sub>3</sub>,进而可与 $S^{2-}$ 反应生成FeS<sub>2</sub>,但 Fe<sub>2</sub>O<sub>3</sub>和 Fe<sub>3</sub>O<sub>4</sub>对 $S^{2-}$ 的反应影响很小;升高温度、延长反应时间、增加铁粉添加量、提高溶液中 Na<sub>2</sub>O<sub>k</sub>与 Al<sub>2</sub>O<sub>3</sub>的摩尔比和苛碱浓度均有利于 $S_2O_3^{2-}$ 向 $SO_3^{2-}$ 和 $S^{2-}$ 转化。本研究结果有助于在拜耳法处理高硫铝土矿过程中开发减缓设备腐蚀和降低碱耗的技术。

关键词: 高硫铝土矿; 铝酸钠溶液; 含硫离子; 含铁物质; 转化

(Edited by Wei-ping CHEN)