RESEARCH ON DIGESTION BEHAVIOR OF SULFUR IN HIGH-SULFUR BAUXITE

Zhanwei Liu[1,2], Wangxing Li[3], Wenhui Ma[1,2], Zhonglin Yin[3], Guobao Wu[3]
[1]Faculty of Metallurgical and Energy Engineering, Kunming University of Science and Technology; Kunming, 650093, China
[2]State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization; Kunming, 650093, China
[3]Zhengzhou Research Institute of CHALCO; Zhengzhou, 450041, China

Keywords: High-sulfur bauxite, Digestion, Sulfur, Wet oxidation, Alumina production

Abstract

In this paper, a study was made on digestion behavior of sulfur in high-sulfur bauxite. It was investigated that the effects of temperature, time, lime dosage and initial caustic concentration on digestion behavior of sulfur. The results show that sulfur in high-sulfur bauxite goes into solution mostly in the form of S^{2-}; the digestion rates of sulfur increase at first and then decrease with the increase of lime dosage; the digestion rates of sulfur increase with the increase of temperature, initial caustic concentration and digestion time; in this experiment, the process conditions for getting higher digestion rate of alumina and lower digestion rate of sulfur are temperature 260 ℃, digestion time 60 min and lime dosage 13%, under these conditions, digestion rates of alumina and sulfur are respectively 84.16% and 40.04%. And research results reveal both S^{2-} and $S_2O_3^{2-}$ in solution can be removed completely by wet oxidation in digestion process.

Introduction

With the rapid development of alumina industry, bauxite resources are becoming scarce day by day. The production practice in recent years shows that alumina production by high-sulfur bauxite becomes actual situation which some enterprises must face up to. The reserves of diasporic high-sulfur bauxite in China are over 800 million tons, most of them are distributed in Guizhou, Chongqing and Henan[1]. It has great economic and social benefits for the sustainable development of Chinese aluminum industry to take full advantage of rich high-sulfur bauxite resources. With consideration of very low utilization ratio of high-sulfur bauxite and some other problems, the processing of high-sulfur bauxite by Bayer process has been studied[2-8].

The major hazards of the presence of sulfur in the Bayer process are as follows[9]: i. It accelerates the corrosion of equipment and result in great safety troubles. ii. It makes iron content in alumina product higher, and the quality of alumina product becomes deteriorated; iii. It brings troubles in settling separation of the red mud and spent liquor evaporation; iv. It makes alkali consumption increase.

In this paper, a study was made on the effects of temperature, time, lime dosage and initial caustic concentration on digestion behavior of sulfur in high-sulfur bauxite, and the digestion behavior of sulfur is understood, thus the theoretical basis is provided for high-efficient development and utilization of high-sulfur bauxite.

Experiments

Experimental Materials

The high-sulfur bauxite used in the experiment was taken from a certain mining area in China. Chemical and mineral components of mineral sample are shown in Table I and Table II. The X-ray diffraction pattern of mineral sample is shown in Figure 1.

Table I. Chemical Components of High-sulfur Bauxite

Chemical Components	Mass Percent (%)
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

Table II. Mineral Components of High-sulfur Bauxite

Mineral Components	Mass Percent (%)
Diaspore	67
Pyrite	4.4
Illite	11.5
Anatase	1.8
Rutile	1
Chlorite	5
Kaolinite	4

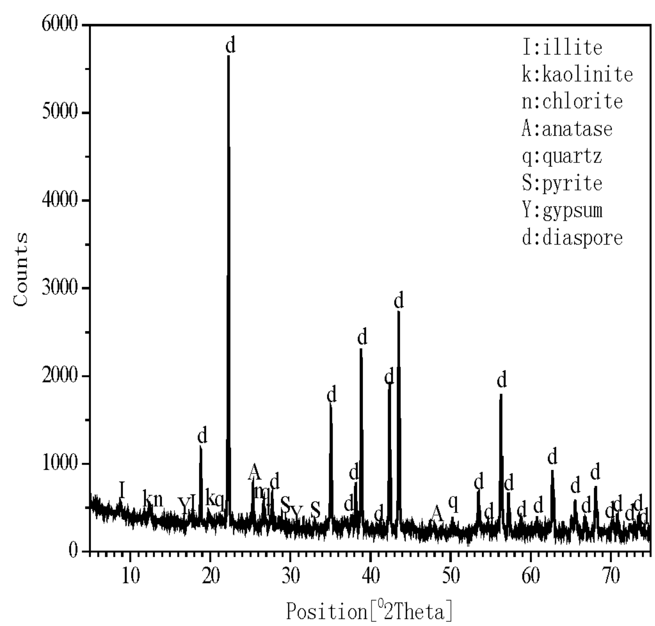

Figure 1. X-ray diffraction pattern of high-sulfur bauxite.

We can see from Table II and Figure 1 that high-sulfur bauxite belongs to diasporic bauxite, the main sulfur-bearing mineral is pyrite and the content of pyrite is 4.4%.

The alkali solution used in the experiment was taken from evaporation spent liquor of a certain alumina refinery, and its chemical components are shown in Table III.

Table III. Chemical Components of Evaporation Spent Liquor

Chemical Components	Concentration (g/L)
Na_2O_T	248.11
Al_2O_3	120.2
Na_2O_k	216
Na_2S	0.24
$Na_2S_2O_3$	4.67
Na_2SO_3	2.84
Na_2SO_4	6.58

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

The lime used in the experiment was taken from Pilot Alumina Plant of CHALCO Zhengzhou Research Institute, and the total CaO in lime is 91.05%.

Experimental Method

The digestion experiments of high-sulfur bauxite were carried out in XYF-6 digester that is heated by molten salts. The digestion temperature can be controlled within the variation range of 0.1 ℃ .The mineral sample and evaporation spent liquor according to a certain proportion were placed in a 100 ml steel bomb which was sealed in the experiment. When digester reached the specified temperature for 5 min, the steel bomb was placed in it and the digestion process was completed within the predetermined time. When the experiment was over, the sodium aluminate solution was filtered. The concentrations of 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 filtrate were analyzed by chemical analysis methods, and the dried filter cake was sampled and then analyzed by X-ray fluorescence analyzer.

The digestion rate of alumina (η_A) was calculated according to equation (1).

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

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

The digestion rate of sulfur (η_S) was calculated according to equation (2).

$$\eta_S = \frac{S_{ore} - \frac{F_{ore}}{F_{mud}} S_{mud}}{S_{ore}} \times 100\% \qquad (2)$$

S_{ore} mass percentage of sulfur in raw ore (%)
S_{mud} mass percentage of sulfur in mud (%)
F_{ore} mass percentage of iron in raw ore (%)
F_{mud} mass percentage of iron in mud (%)

Results and Discussions

The Distribution of Different Valence Sulfur in Digestion Liquor

The digestion experiment was carried out on the condition of digestion temperature 260 ℃, digestion time 60 min, lime dosage 13% and α_k (molar ratio of Na_2O_k to Al_2O_3) of digestion liquor 1.40. The concentration and the proportion of different valence sulfur in digestion liquor are shown in Table IV and Table V respectively.

Table IV. Concentration of Different Valence Sulfur in Digestion Liquor

Chemical Components	Concentration (g/L)
Na_2O_k	174
Al_2O_3	205.92
Na_2S	9.91
$Na_2S_2O_3$	0.82
Na_2SO_3	0.36
Na_2SO_4	1.45

Table V. Proportion of Different Valence Sulfur in Total Sulfur

Different Valence Sulfur	Percent (%)
Na_2S	87.4
$Na_2S_2O_3$	3.6
Na_2SO_3	2.0
Na_2SO_4	7.0

It can be seen from Table V that sulfur in high-sulfur bauxite goes into solution mostly in the form of S^{2-}, the remaining sulfurs in solution exist in the form of $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-}. Under the conditions of this experiment, the S^{2-} in digestion liquor accounts for 87.4% of total sulfur.

Effect of Lime Dosage on Digestion Behavior of Sulfur in High-sulfur Bauxite

With six different lime dosage between 7% and 17%, the digestion experiment was carried out on the condition of digestion temperature 260 ℃, digestion time 60 min, and α_k of digestion liquor 1.40, using evaporation spent liquor of a certain alumina refinery. The Effect of lime dosage on digestion behavior of sulfur in high-sulfur bauxite is shown in Figure 2.

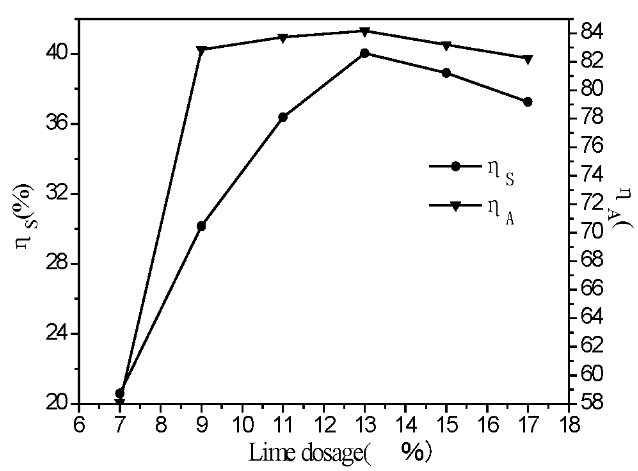

Figure 2. Effects of lime dosage on digestion rates of alumina and sulfur.

It can be seen from Figure 2 that the digestion rates of sulfur and alumina all increase at first and then decrease with the increase of lime dosage, which results from lime activation. In digestion process, high active lime can easily form hydroxy calcium titanate and calcium titanate, so the adverse effect of titanium dioxide is eliminated; low active lime goes into red mud in various form of calcium-aluminum-silicon residue, and thus the digestion rate of alumina decreases[10-11]. The lime used in the experiment is fresh lime which has high activity, so the high digestion rate of alumina is got when the lime dosage is low; and then the $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ which combine with the alumina in solution is generated with the increase of lime dosage, so the digestion rate of alumina decreases. The digestion rate of sulfur decreases when the lime dosage is above 13%, the reason was that the superfluous lime and the SO_4^{2-} in solution combine to form calium hydroaluminosulfate and the concentration of SO_4^{2-} in solution decreases. Comprehensive consideration suggests that the optimum lime dosage is 13% under these digestion conditions.

Effect of Temperature on Digestion Behavior of Sulfur in High-sulfur Bauxite

With five different digestion temperature between 200 ℃ and 270 ℃, the digestion experiment was carried out on the condition of digestion time 60 min, lime dosage 13% and α_k of digestion liquor 1.40, using evaporation spent liquor of a certain alumina refinery. The Effect of temperature on digestion behavior of sulfur in high-sulfur bauxite is shown in Figure 3.

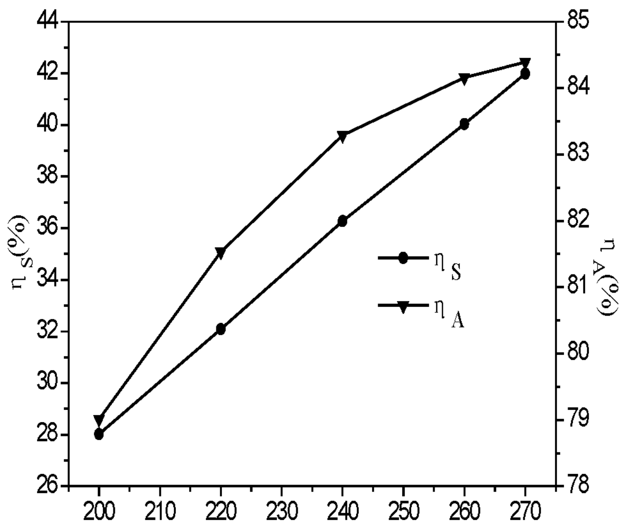

Figure 3. Effects of temperature on digestion rates of alumina and sulfur.

It can be seen from Figure 3 that the digestion rates of alumina increase with the increase of temperature, increasing temperature has no obvious effect on the digestion rates of alumina when temperature is above 260 ℃; the digestion rates of sulfur increase with the increase of temperature, the digestion rate of sulfur increases about 2% when temperature increases from 260 ℃ to 270 ℃. Based on an overall consideration of the recovery of alumina, digestion rate of sulfur and alkali consumption, the optimum digestion temperature is 260 ℃ under these digestion conditions.

Effect of Initial Caustic Concentration on Digestion Behavior of Sulfur in High-sulfur Bauxite

With five different initial caustic concentration between 185 g/L and 250 g/L, the digestion experiment was carried out on the condition of digestion temperature 260 ℃, digestion time 60 min and lime dosage 13%, where the solutions were prepared from evaporation spent liquor of a certain alumina refinery. The Effect of initial caustic concentration on digestion behavior of sulfur in high-sulfur bauxite is shown in Figure 4.

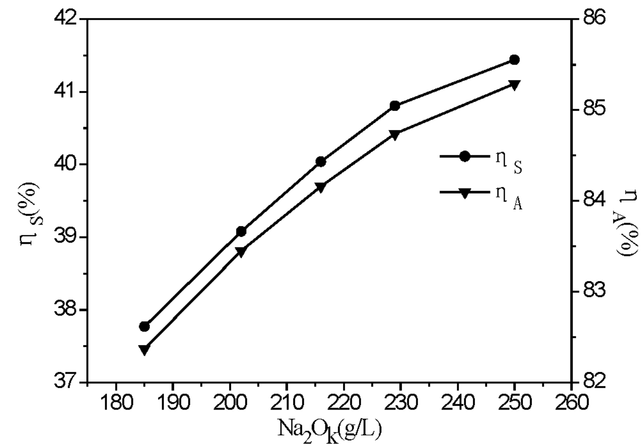

Figure 4. Effects of initial caustic concentration on digestion rates of alumina and sulfur.

It can be seen from Figure 4 that the digestion rates of alumina and sulfur increase with the increase of initial caustic concentration. Based on an overall consideration of the recovery of alumina, digestion rate of sulfur and alkali consumption, caustic concentration of solution can not too high.

Effect of Time on Digestion Behavior of Sulfur in High-sulfur Bauxite

With seven different digestion time between 5 min and 80 min, the digestion experiment was carried out on the condition of digestion temperature 260 ℃, lime dosage 13% and α_k of digestion liquor 1.40, using evaporation spent liquor of a certain alumina refinery. The Effect of time on digestion behavior of sulfur in high-sulfur bauxite is shown in Figure 5.

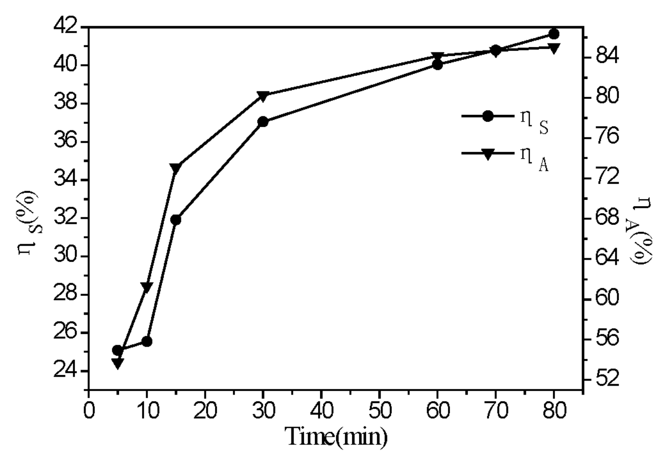

Figure 5. Effects of time on digestion rates of alumina and sulfur.

It can be seen from Figure 5 that the digestion rates of alumina and sulfur increase with the increase of digestion time; when digestion time is above 60 min, digestion rates of alumina increase slightly and more sulfur go into solution with the increase of digestion time. Comprehensive consideration suggests that the optimum digestion time is 60 min under these digestion conditions.

Removal of Active Forms of Sulfur by Wet Oxidation

We can know from the above that some of the sulfurs in bauxite enter into liquor with the digestion of alumina, and the active sulfur (S^{2-}, $S_2O_3^{2-}$ and S_2^{2-}) will imperil the alumina production, so the active sulfur must be removed. The technology of wet oxidation deep desulfurization has been developed, the S^{2-} and $S_2O_3^{2-}$ in sodium aluminate solution can be removed completely by wet oxidation in digestion process, so the effects of S^{2-} and $S_2O_3^{2-}$ on alumina product quality are eliminated. The experimental results of removal of sulfur by wet oxidation in digestion process are shown in Figure 6.

It can be seen from Figure 6 that when oxygen addition amount is above 9 g/L, the S^{2-} in sodium aluminate solution can be almost removed completely and the concentration of $Na_2S_2O_3$ in sodium aluminate solution decreases obviously, so the effect of S^{2-} on alumina product quality is eliminated and the corroding effect of $S_2O_3^{2-}$ on equipment is weakened; the concentration of Na_2SO_3 in sodium aluminate solution also decreases significantly and the concentration of Na_2SO_4 in sodium aluminate solution increases noticeably. It indicates that the active sulfur in sodium aluminate solution is eventually converted to inert sulfur (SO_4^{2-}). It can also be seen from Figure 6 that when oxygen addition amount is 30 g/L, the S^{2-} in sodium aluminate solution was removed completely and the $S_2O_3^{2-}$ in sodium aluminate solution was almost removed completely, but high oxygen addition amount will make cost too high.

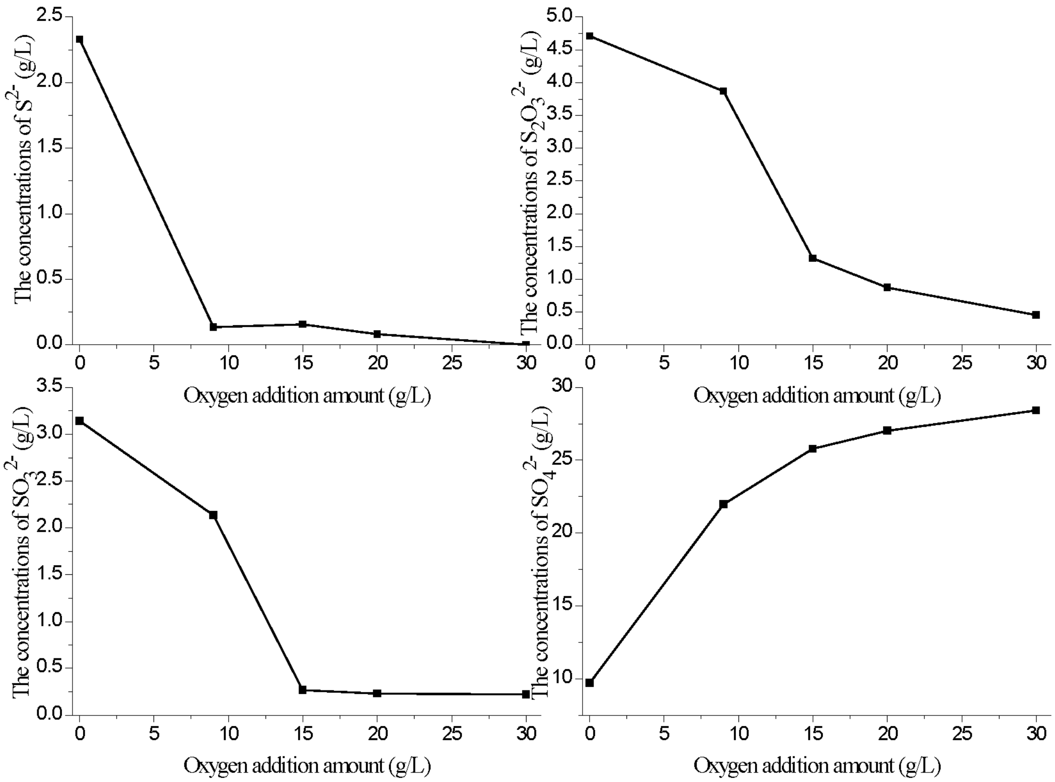

Figure 6. Effect of oxygen addition amount on desulfurization results.

Conclusions

High-sulfur bauxite belongs to diasporic bauxite, the main sulfur-bearing mineral is pyrite. The sulfur in high-sulfur bauxite goes into solution mostly in the form of S^{2-}, the remaining sulfur exist in the form of $S_2O_3^{2-}$, SO_3^{2-} and SO_4^{2-} in solution. Under the conditions of this experiment, the S^{2-} is 87.4% in proportion to total sulfur in digestion liquor.

The digestion rates of sulfur increase at first and then decrease with the increase of lime dosage. The digestion rates of sulfur increase with the increase of temperature, initial caustic concentration and digestion time.

The digestion result of high-sulfur bauxite is good, that is to say, there are higher digestion rate of alumina and lower digestion rate of sulfur. The general principle is that the digestion rate of sulfur must be as low as possible on the premise of getting higher digestion rate of alumina.

For the digestion of high-sulfur bauxite in Guizhou using evaporation spent liquor of a certain alumina refinery, the process conditions for getting higher digestion rate of alumina and lower digestion rate of sulfur are that temperature is 260 ℃, digestion time is 60 min and lime dosage is 13%. Under this condition, digestion rate of alumina is 84.16% and digestion rate of sulfur is 40.04%.

The S^{2-} and $S_2O_3^{2-}$ in sodium aluminate solution can be removed completely by wet oxidation in digestion process, so the effects of S^{2-} and $S_2O_3^{2-}$ on alumina product quality are eliminated.

Acknowledgements

Z.W. Liu would like to express her thanks to her former colleagues in Zhengzhou Research Institute of Chalco, especially Dr. W.X. Li.

References

1.B.Q. He and L. Luo, "Discussion on the New De-sulfuration Method of Chinese High Sulfur Bauxite," *Light Metals*, (12) (1996), 3-5.

2.Chongyu Yang, *The Process Technology of Alumina*, (China, NY: Metallurgical Industry Press, 1993).

3.T. He and Z.Y. Li, "Optimal Condition Analysis of Guizhou High-sulfur Bauxite Leaching Process," *Nonferrous Metals*, 60 (2) (2008), 68-70.

4.R.D. He et al., "Research on Leaching Function of Guizhou High-Sulfur Bauxit," *Journal of Guizhou University of Technology(Natural Science Edition)*, 34 (3) (2005), 63-65.

5.N.B. Zhang, H.S. Jiang and X.X. Wu, "Research on Disposing of Sulfur of High Grade Bauxite Containing Sulfur in Guizhou," *Light Metals*, (7) (2007), 7-10.

6.Y.Y. Wang et al., "Developmental Trend of Leaching Technology for Domestic Bauxite," *World Nonferrous Metals*, (1) (2006), 25-27.

7.T.A. Zhang et al., "Enhancing the Digestion Efficiency of Diaspore Ore Pulp by Sweetening Technique," *Journal of Northeastern University(Natural Science)*, 26 (7) (2005), 667-669.

8.Y.Z. Cao, F.Z. Dong, and S. zhang, "The Influence of Lime Activation on the Digesting Efficiency of Alumina," *Light Metals*, (5) (2007), 21-23.

9.Wangxing Li, *Theory and Technics of Alumina Production*, (China, NY: Central South University Press, 2010).

10.L. Cheng and Y. Li, "The Effect of Lime on High Pressure Digestion of Bauxite," *Journal of Guizhou Institute of Technology*, 25 (1) (1996), 44-47.

11.H.J. Chen, "The Effect of Lime on High Pressure Digestion in Bayer Process," *Nonferrous Metals Industry*, (5) (2004), 54.