Effect of Lime Addition on the Predesilication and Digestion Properties of a Gibbsitic Bauxite

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Abstract

The effect of lime addition on the predesilication and digestion properties of a gibbsitic bauxite in industrial Bayer liquor at different temperatures was investigated in the present paper. Lime increases the desilication efficiency of gibbsitic bauxite during the predesilication process, which promotes the conversion of sodalite and cancrinite to hydrogarnet in the presence of $CO_3^{2^\circ}$. Lime slightly decreases the alumina digestion rate of gibbsitic bauxite at both 145 °C and 245 °C when the lime dosage is 2 wt%. However, the soda consumption during the digestion process is decreased due to lime addition, especially at the higher temperature. Lime can also promote the conversion of aluminogoethite to hematite during the digestion process, which improves the digestion property of aluminogoethitic alumina in the gibbsitic bauxite.

Introduction

As a common additive, lime is widely used in the alumina production by the Bayer process, where it performs many useful functions [1-3]. It can improve the digestion property of diasporic and beohmitic bauxites to increase the extraction of alumina [2, 4], minimize the inhibiting effect of sodium titanate on alumina extraction to increase the digestion speed [5-7], control or remove the carbonate, silica and phosphorous impurities to purify the sodium aluminate liquor [8-10]. and promote the aluminogoethite/hematite transformation to improve the settling and filtering properties of the red mud [11, 12].

In order to minimize the scaling of silicon-containing minerals on the reactor surfaces during the digestion process, the predesilication procedure is very important [13, 14]. However, the effect of lime addition on the predesilication has not been reported. Meanwhile, whether it can improve the alumina extraction of gibbsitic bauxites and its corresponding mechanism are unknown. Therefore, the effect of lime addition on the predesilication and digestion of a gibbsitic bauxite at different temperatures was studied in this paper.

Experimental procedures

The bauxite from Guinea was ground to 0.28 mm, and lime with 93.12% of reactive CaO was used in the experiments. The sodium aluminate liquor for the predesilication and digestion experiments was prepared by dissolving analytically pure sodium hydroxide and aluminum hydroxide into industrial Bayer liquor. The concentrations of Na₂O and Na₂CO₃ are 170 g/L and 15 g/L, and the molar ratio of Na₂O to Al₂O₃ is 2.90. The lime dosage is 2 wt%.

The predesilication tests were carried out in a stainless steel vessel with a nominal capacity of 500 ml. The slurry prepared by mixing bauxite into collection liquor at a solid content of 800 g/L with and without lime was added into the vessel. The sealed vessel was then put into the pre-heated oil bath followed by agitation. The slurry was predesilicated at 95 °C for 12 h, cooled and separated by centrifuging. The concentrations of Al_2O_3 and Na_2O in the liquor were analyzed by the volumetric method, and the concentration of SiO_2 was analyzed by spectrophotometry using a 722S Spectrophotometer. The solids were washed and dried for chemical analysis.

The digestion tests were carried out in bombs with a nominal capacity of 150 ml in a low pressure reactor. The reactor was heated by silicone oil with a temperature control accuracy of ± 1 °C, and the speed of each bomb is 48 rpm. The slurry mixed by the bauxite and collection liquor with and without lime was put into the bombs, sealed, and rotated. The digestions were performed at 145 °C for 1 h or at 245 °C for 0.5 h, cooled and separated by centrifuging. The solids were analyzed the same way as the predesilication tests.

The predesilication efficiency (η_{SiO2}) was calculated by the value of acid-soluble SiO₂ (S_{acid}) divided by the value of alkali-soluble SiO₂ (the total SiO₂, S_{alkali}), as given as follows:

$$\eta_{\rm SiO_2} = (S_{\rm acid}/S_{\rm alkeli}) \times 100\% \tag{1}$$

The digestion rate of Al₂O₃ was calculated by the following formula:

$$\eta_{Al_{2}O_{3}} = \frac{(A/F)_{\text{ore}} - (A/F)_{\text{nucl}}}{(A/F)_{\text{ore}}} \times 100\%$$
(2)

Where $(A/F)_{ore}$ and $(A/F)_{mud}$ denote the weight ratios of Al_2O_3 to Fe_2O_3 in the bauxite and the red mud respectively.

Emission spectral analysis was used to study the elemental composition of the bauxite. The phase compositions of the bauxite and the solids after predesilication and digestion were analyzed by X-ray diffractometer (XRD). The compositions of Al_2O_3 , SiO_2 and CaO were analyzed by X fluorescence spectrometer, while the compositions of Na_2O and Fe_2O_3 were analyzed by atomic absorption spectrometry and the volumetric method respectively.

Results and Discussion

The bauxite

The oxide intensity of the bauxite analyzed by emission spectral analysis is listed in Table I. The dominant elements in the bauxite are Al, Fe, Si and Ti, while the amounts of other elements such as Cr, P, Zr, S, K, Ca, Mn and Na are relatively low. As presented in Table II, the contents of Al_2O_3 and Fe_2O_3 in the bauxite are relatively high, and the content of SiO_2 is low. The calculated ratio of Al_2O_3 to SiO_2 is 15.83, which indicates the bauxite is an ore with good quality.

Table I. Oxide intensity of the bauxite by emission spectral analysis (wt%)

Oxide	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	Cr ₂ O ₃	P ₂ O ₅
Intensity	51.885	41.755	2.823	2.762	0.251	0.138
Oxide	ZrO ₂	SO3	K ₂ O	CaO	MnO	Na ₂ O
Intensity	0.094	0.077	0.071	0.048	0.045	0.042

Table II. Chemical composition of the bauxite (wt%)

Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	TiO ₂	CaO	LOI
40.22	30.48	2.54	2.17	0.06	24.02

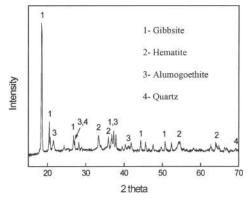


Figure 1. XRD pattern of the bauxite

According to Figure 1 and Table III, the minerals of the bauxite are comprised of gibbsite, alumogoethite, hematite, kaolin, quartz and minor boehmite. The aluminum-containing minerals are gibbsite, alumogoethite and boehmite, while the silicon-containing minerals are kaolin and quartz. Aluminogoethite ($Fe_{(1-x)}Al_xOOH$ (x=0-0.33)) present in the bauxite can be converted to hematite, which offers a possibility to extract the goethitic alumina [11, 12].

Table III. Constitution of main minerals in the bauxite (wt%)

Gibbsite	Alumogoethite	Hematite	Kaolin	Quartz	Boehmite
54.6	18.8	16.7	3.3	1.1	0.3

On predesilication

The silicon-containing minerals have different forms in the bauxites and their reaction abilities with sodium aluminate liquor are different. The main silicon-containing minerals in the bauxite are kaolin and quartz. Kaolin, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, can react with the caustic liquor at low temperatures (70-95 °C). Quartz is difficult to be dissolved at a low temperature, but it can react with the caustic liquor at high temperatures, which causes losses of

caustic alkali and alumina. When the gibbsite is digested at regular pressure, quartz is not harmful to the alumina production.

The mineralogy of desilication products (DSP) formed during the reaction of pure kaolin and lime in synthetic Bayer liquors indicates that: the kaolin reacts with Bayer liquors to form a product of sodium silicon aluminium hydrate hydroxysodalite (HS, $3[Na_2O \cdot Al_2O_3 \cdot 2SiO_2] \cdot 2NaOH \cdot aH_2O)$ in the conventional Bayer process, while it reacts to form the alternate desilication products containing calcium, the cancrinite (Ca-CAN, $3[Na_2O \cdot Al_2O_3 \cdot 1.8SiO_2] \cdot 1.42CaCO_3 \cdot 2.4H_2O)$ and/or hydrogamet (HG, $Ca_3Al_2(SiO_4)_n(OH)_{(124n)}$ where n < 0.8) in the presence of lime, as shown in Eq. (3) to Eq. (5) [8, 15].

$$\begin{array}{c} 3[\operatorname{Na}_2 O \cdot \operatorname{Al}_2 O_3 \cdot 2\operatorname{SiO}_2] \cdot 2\operatorname{Na}OH \cdot \operatorname{aH}_2 O \qquad (3) \\ \text{Bayer liquor } + \longrightarrow 3[\operatorname{Na}_2 O \cdot \operatorname{Al}_2 O_3 \cdot 1.8 \operatorname{SiO}_2] \cdot 1.42 \operatorname{CaCO}_3 \cdot 2.4 \operatorname{H}_2 O \qquad (4) \\ \lim_{k \to \infty} \mathbb{C} & \mathbb{C} & \mathbb{C} & \mathbb{C} \\ \end{array}$$

$$Ca_{3}Al_{2}(SiO_{4})_{n}(OH)_{(12-4n)}$$
(5)

The predesilication results of the bauxite with and without lime addition are listed in Table IV. The concentration of SiO_2 in the desilicated liquor is decreased due to lime addition, and accordingly the predesilication efficiency of the bauxite is increased by 18.02%. Meanwhile, the amount of Na₂O in the desilicated solid with lime is lower than that without lime, indicating that the addition of lime during predesilication can promote the transformation of HS or Ca-CAN to HG in the presence of $CO_3^{2^2}$.

Table IV. Predesilication results of the bauxite with and without lime addition

Lime (%)	Liquor Concentration(g/L)			Solid Composition(%)				η _{SiO2}
	Na ₂ O	Al ₂ O ₃	SiO ₂	Al ₂ O ₃	SiO ₂	Na ₂ O	S _{acid}	(%)
0	160.8	125.2	0.79	39.98	2.57	0.19	0.97	37.74
2	160.2	124.4	0.74	38.57	2.29	0.16	1.02	44.54

On digestion

The compositions of dominant oxides in the red mud after digestion at different temperatures with and without lime are listed in Table V. The corresponding digestion rates of Al_2O_3 are calculated according to Formula (2) and shown in Figure 2. Lime slightly decreases the alumina digestion rate of gibbsitic bauxite at

both 145 °C and 245 °C when the lime dosage is 2 wt%, but the decrease is not obvious. However, the digestion rates at 245 °C are higher than those at 145 °C.

Table V. Chemical composition of the red mud after digestion with and without lime at different temperatures (wt%)

Temperature(°C)	Lime(%)	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	Na ₂ O
145	0	65.01	12.94	4.24	1.08
145	2	63.04	13.27	4.19	0.91
245	0	67.77	9.87	4.24	2.71
245	2	64.29	9.80	4.06	2.01

Figure 3 and Figure 4 show the XRD patterns of the red mud after digestion. All the mud is mainly comprised of hematite and alumogoethite, although the intensities of the peaks are different. Table VI shows the intensities of hematite and alumogoethite at their characteristic peaks obtained from the XRD patterns, and A/H represents the corresponding intensity ratio of alumogoethite to hematite.

The conversion of alumogoethite to hematite makes the aluminum in the alumogoethite digestible into the liquor, hence increasing the digestion rate of Al_2O_3 . As presented in Table VI, the A/H values at 245 °C are much lower than those at 145 °C, indicating that the conversion amount of alumogoethite to hematite at 245 °C is much larger than that at 145 °C, which results in the higher digestion rate at 245°C.

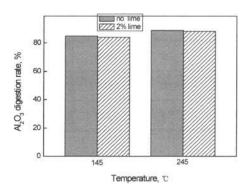


Figure 2. Al₂O₃ digestion rates with and without lime addition at different temperatures

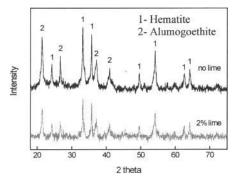


Figure 3. XRD patterns of the red mud after digestion at 145 °C

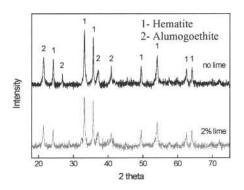


Figure 4. XRD patterns of the red mud after digestion at 245 °C

Table VI. Intensities of alumogoethite and hematite at their characteristic peaks in the red mud determined by XRD

Temperature(°C)	Lime(%)	Alumogoethite (2θ=21.45)	Hematite (2θ=33.17)	A/H
145	0	1979	2356	0.84
145	2	1806	2324	0.78
245	0	1676	3348	0.50
245	2	1290	3184	0.41

The A/H value with lime addition at the same digestion temperature is lower than that without lime addition, indicating that the conversion amount of alumogoethite to hematite with lime addition is larger than that without lime addition. Meanwhile, at higher temperatures, lime addition has a more significant effect on the alumogoethite/ hematite conversion. However, this is not consistent with the digestion results. The reason is that although the conversion of alumogoethite to hematite can increase the digestion rate of Al_2O_3 , the desilication products carry Al_2O_3 away from the digested liquor, which enters into the red mud and results in the lost of alumina. The desilication during digestion with lime addition reacts more completely than those without lime addition. The alumogoethite/hematite conversion and the desilication trade off, thus there is no obvious change in the digestion rate of Al_2O_3 .

Meanwhile, the amounts of Na₂O in the red mud with lime both at 145 °C and 245 °C are lower than those without lime by 15.74% and 25.83% respectively. It shows that the addition of lime during digestion can improve the transformation of HS or Ca-CAN to HG, especially at higher temperatures. Therefore, the formation of soda-free HG minimizes the soda lost in the red mud.

Conclusions

The bauxite studied in this paper is comprised of gibbsite, alumogoethite, hematite, kaolin, quartz and minor boehmite. Lime increases the desilication efficiency of gibbsitic bauxite during the predesilication process by promoting the transformation of sodalite and cancrinite to hydrogarnet in the presence of CO_3^{2-} . Lime hardly affects the alumina digestion rate of gibbsitic bauxite at both 145 °C and 245 °C when the lime dosage is 2 wt%. The desilication reactions during digestion promoted by lime addition lead to the loss of Al₂O₃ entering into the red mud; however, the conversion of aluminogoethite to hematite promoted by lime addition increases the extraction amount of aluminogoethitic Al₂O₃ entering into the digested liquor. The Al₂O₃ digestion rate at 245 °C is higher than that at 145 °C mainly because of the more conversion of aluminogoethite to hematite at the high temperature. The soda consumption during the digestion process is decreased due to lime addition, especially at the higher temperature.

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