

## Study on New Technology for Alumina Production from High Carbonate Bauxite

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### Abstract

In the production of alumina using the Bayer process, high concentrations of sodium carbonate in the circuit will cause a series of problems such as operational instability, increased energy consumption and decrease in product output. This paper explores the utilization of high carbonate bauxite and a wet removal method to remove most of the carbonate from the ore before the digestion process. Data suggests that the removal rate of carbonate in bauxite can exceed 81.06 % which reduces the adverse effect of carbonate in ore on production process. This removal process provides a new idea for the efficient application of high carbonate bauxite.

**Keywords:** Carbonate, Bauxite, Wet removal.

### 1. Introduction

With the development of the alumina industry in China, the bauxite quality in China has decreased rapidly. It is noted that the variability of the gangue mineral type and constituent profile within the ores has increased gradually, especially as it relates to their carbonate content. In the process of alumina production, the carbonate in bauxite reacts with the alkali solution through slurry preparation, pre-desilication and high-pressure dissolution; these reactions generate sodium carbonate [1]. This sodium carbonate generation results in the increase of the sodium carbonate concentration within the process leading to a series of problems related to the refinery production. This phenomenon is observed in the smoothness of the flash steam discharge; if sodium carbonate precipitates in the digestion slurry flash process, water or washing liquor injection is used in many instances in the last few stages of flash process to ensure the continuous system operation. The water addition results in the heat balance of the leaching process being broken and the digestion steam consumption is increased.

With the increase of sodium carbonate, the viscosity of slurry and liquor in Bayer process increases resulting in the increase of power consumption related to conveying slurry and liquor as well as the deterioration of filtration performance and the production capacity of vertical plate filters, flat plate filters, and the increase of filters cleaning times. With the viscosity of sodium aluminate solution increased, the precipitation efficiency and alumina production decreases. In the evaporation process, due to the increase of sodium carbonate, the salt discharge pressure of forced circulation is increased, which leads to the increase of evaporation steam consumption and decrease of evaporative capacity; the evaporator cleaning cycle is also shortened.

There are three common ways to eliminate sodium carbonate from a production system. The first approach is evaporation crystallization to eliminate the salt in high concentration. In this process the liquor is evaporated to a high concentration to achieve the supersaturated state crystallization and eliminate the salt. This is one of the widely used methods for alumina plants; though effective,

some implications of this method are higher implementation cost and reduced evaporation capacity thus making this method unsuitable for long-term operation. If the exhaled salt causticity is not complete, it will return to the process [2-5]. The second method is the causticization of the red mud washing liquor to eliminate sodium carbonate. This method involves utilizing suitable red mud washing liquor for causticization under the required process conditions to produce sodium hydroxide from sodium carbonate. The process is simple and the operational cost is low, however, the reduction of the sodium carbonate content in Bayer process has a slow effect, and the alumina loss rate will increase correspondingly when the causticizing efficiency is pursued. It is difficult to achieve the desired effect in a short period by applying this method, and it needs to be used in combination with other carb-alkali exclusion processes [6-8]. The third method is causticizing by using barium salt to eliminate sodium carbonate. This method takes advantage of the characteristics that most salts of barium are insoluble in sodium aluminate solution to eliminate sodium carbonate. However, Ba(OH)<sub>2</sub> and BaO are expensive and the process has higher operational costs; additionally, gases and dust harmful to human health are produced in the process of calcination of BaCO<sub>3</sub> and BaSO<sub>4</sub> for regeneration, which pollutes the environment [9-11].

In this paper, a high carbonate bauxite from Guizhou, China is taken as the object. Through laboratory research, the influence of different operating conditions on the carbonate removal from high carbonate bauxite is discussed. It is thought that if most of the carbonate is removed before the bauxite enters the digestion system, it can effectively reduce the adverse effects of carbonate on the Bayer process.

## 2. Test Raw Materials

### 2.1 Bauxite

The bauxite was obtained from an alumina plant in Guizhou, China., the main chemical composition of the bauxite (%) are: Al<sub>2</sub>O<sub>3</sub> 47.19, SiO<sub>2</sub> 9.25, Fe<sub>2</sub>O<sub>3</sub> 27.63, TiO<sub>2</sub> 2.13, K<sub>2</sub>O 0.72, Na<sub>2</sub>O 0.024, CaO 0.26, MgO 0.49, TC (total carbon) 0.78, TOC (total organic carbon) 0.21, TIC (total inorganic carbon) 0.57. The main mineral composition (%): diaspore 46, chlorite 16, illite 7, kaolinite 5, hematite 15, siderite 8; anatase, 1.7, rutile 0.4. The alumina content in the bauxite is 47.19 %, the total inorganic carbon content is 0.57 %, the main aluminum bearing mineral is diaspore, and the carbonate mineral is siderite. The X-ray diffraction pattern of bauxite is shown in Figure 1.

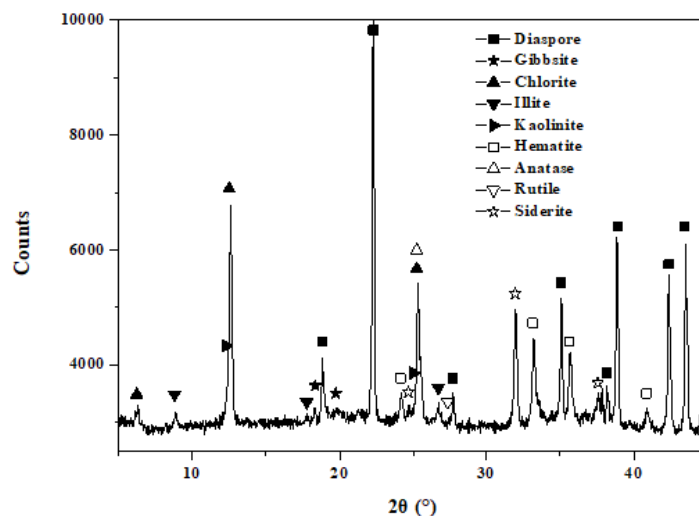


Figure 1. X-ray diffraction pattern of bauxite for the test.

## 2.2 Liquor

The cycling liquor (M-0) was obtained from an alumina plant in Guizhou, China. The other sodium aluminate liquors (M-1 to M-4) with different Na<sub>2</sub>O<sub>k</sub> concentration were obtained after dilution of the cycling liquor (M-0). The chemical compositions are shown in Table 1.

**Table 1. Chemical compositions of sodium aluminate liquors for test.**

Number	Na <sub>2</sub> O <sub>T</sub> g/L	Al <sub>2</sub> O <sub>3</sub> g/L	Na <sub>2</sub> O <sub>k</sub> g/L	Na <sub>2</sub> O <sub>c</sub> g/L	α <sub>k</sub>
M-0	289.00	140.41	250.00	39.00	2.93
M-1	57.80	28.05	50.00	7.80	2.93
M-2	115.60	56.10	100.00	15.60	2.93
M-3	173.40	84.22	150.00	23.40	2.93
M-4	231.20	112.30	200.00	31.20	2.93

## 2.3 Lime

The lime used in the experiment was obtained from an alumina plant in Guizhou, China. After grinding, it was roasted and activated. The CaO content was 95.20 %, and the effective CaO content was 91.89 %.

## 3. Test Methods

### 3.1 Wet Removal Test

The wet removal test of carbonate from bauxite was carried out in a steel bomb digester heated by glycerol. According to the requirements of the ingredients, a proportion of bauxite, sodium aluminate liquor and lime were added into the steel bomb, installed in the rotating steel bomb rack, at a predetermined temperature and immediately stirred. When the predetermined time is reached, the solution is separated from the treated solid phase, and the chemical composition of the solution is analyzed. After washing and drying, the solid phase was analyzed for chemical composition. The change of inorganic carbon content in bauxite before and after wet treatment was used to calculate the carbonate removal rate using Equation 1.

$$\text{Carbonate Removal Rate} = \frac{TIC_B/Fe_2O_{3B} - TIC_A/Fe_2O_{3A}}{TIC_B/Fe_2O_{3B}} \times 100\% \quad (1)$$

where:

$TIC_B$  Content (%) of bauxite before wet treatment

$TIC_A$  Content (%) of bauxite after wet treatment

$Fe_2O_{3B}$  Fe<sub>2</sub>O<sub>3</sub> content (%) of bauxite before wet treatment

$Fe_2O_{3A}$  Fe<sub>2</sub>O<sub>3</sub> content (%) of bauxite after wet treatment

### 3.2 Analytical Methods

PANalytical PW2403 X-ray fluorescence spectrometer was used to analyze the contents of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, CaO and MgO in bauxite. The contents of Na<sub>2</sub>O<sub>T</sub>, Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O<sub>k</sub> in sodium aluminate solution were analyzed by chemical titration. The mineral composition of the solid phase was analyzed by Nalytical X, Pert Pro MPD X-ray diffraction

analyzer. The content of CaO in lime was determined by X-ray fluorescence spectrometry. The effective CaO content in lime was determined by titration method. The content of TC (total carbon) and TOC (total organic carbon) in bauxite and lime was determined by CS-2000 carbon-sulfur analyzer. The content of TIC (total inorganic carbon) was calculated from the difference between TC and TOC. All graphs generated for the various test results were acquired using Origin software.

#### 4. Test Results

##### 4.1 Effect of Spent Liquor Concentration on Carbonate Removal Rate

The effect of Na<sub>2</sub>O<sub>k</sub> concentration (50, 100, 150, 200, 250 g/L) of spent liquor on the removal rate of carbonate was studied under the following test conditions: lime addition of 5 %, slurry solids of 500 g/L, temperature of 90 °C and reaction time of 12 h. The change trend of TIC content in bauxite with the increase of Na<sub>2</sub>O<sub>k</sub> concentration in spent liquor is shown in Figure 2, and the change trend of carbonate removal rate in bauxite with the increase of Na<sub>2</sub>O<sub>k</sub> concentration in spent liquor is shown in Figure 3.

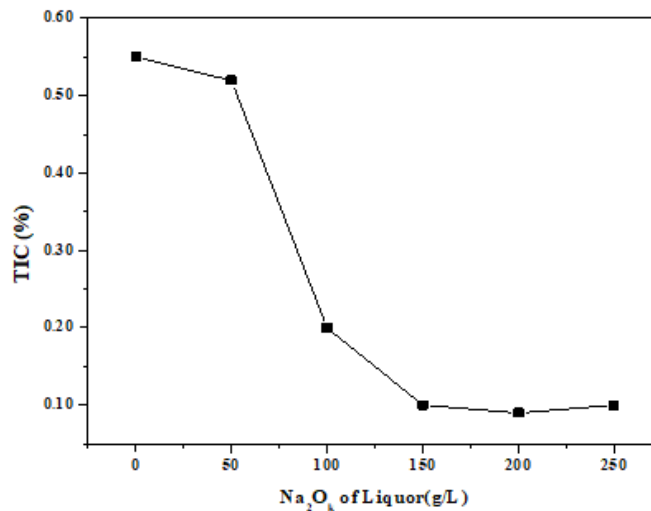


Figure 2. Relationship between TIC content in bauxite and Na<sub>2</sub>O<sub>k</sub> concentration in spent liquor.

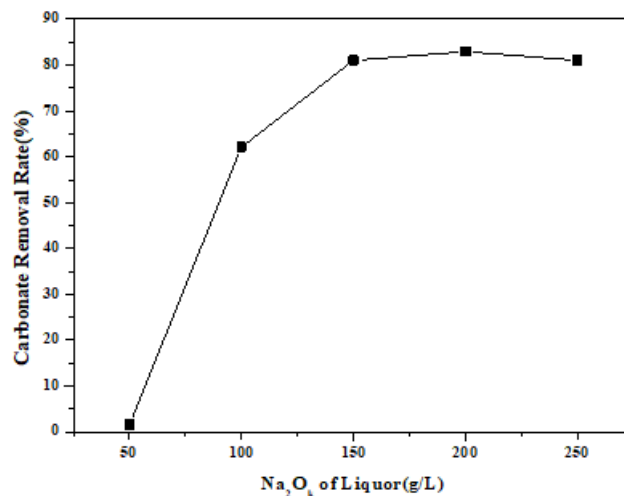


Figure 3. Relationship between carbonate removal rate and Na<sub>2</sub>O<sub>k</sub> concentration in spent liquor.

Figure 2 and Figure 3 show that under the above test conditions, with the concentration of  $\text{Na}_2\text{O}_k$  in spent liquor increasing from 50 g/L to 150 g/L, the TIC content in bauxite gradually decreases from 0.57 % to 0.10 %, and the carbonate removal rate gradually increases to 81.06 %. However, when the concentration of  $\text{Na}_2\text{O}_k$  in spent liquor is greater than 150 g/L, the TIC content in bauxite and the carbonate removal rate do not change significantly with the increase of  $\text{Na}_2\text{O}_k$  concentration in spent liquor.

#### 4.2 Effect of Reaction Temperature on Carbonate Removal Rate

The effect of different reaction temperatures (80 °C, 90 °C, 100 °C, 110 °C) on the removal rate of carbonate was studied under the following test conditions: lime addition of 5 %, slurry solids content of 500 g/L, reaction time of 12 h and  $\text{Na}_2\text{O}_k$  concentration of spent liquor of 150 g/L (this concentration was influenced by the results attained in section 4.1). The change trend of TIC content in bauxite with the increase of reaction temperature is shown in Figure 4, and the change trend of carbonate removal rate in bauxite with the increase of reaction temperature is shown in Figure 5.

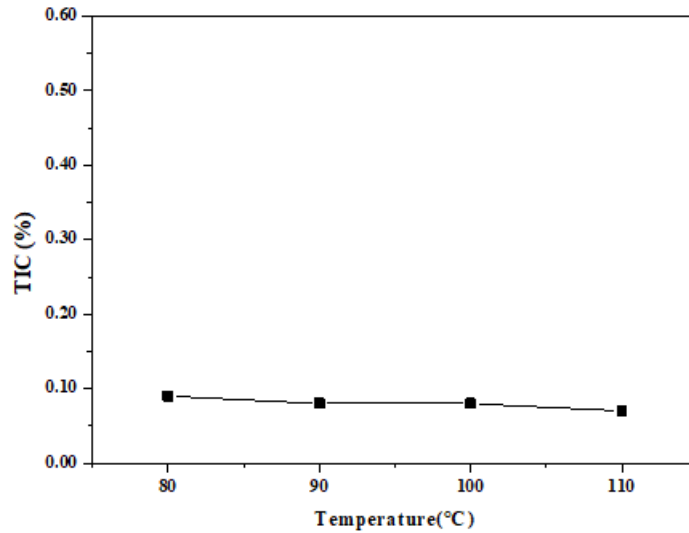


Figure 4. Relationship between TIC content in bauxite and reaction temperature.

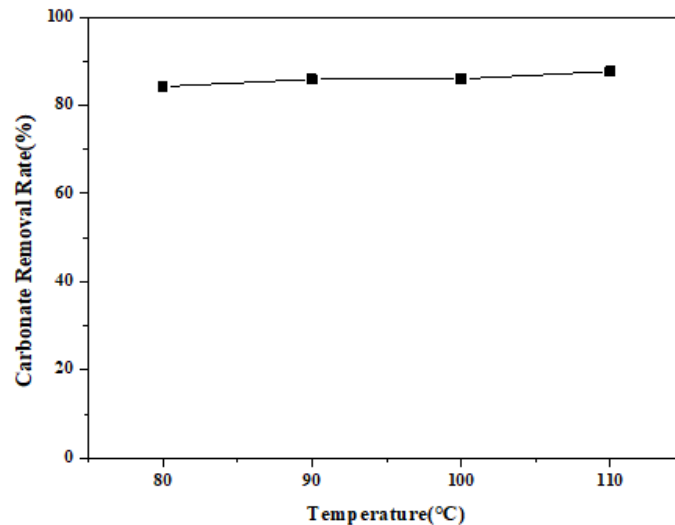


Figure 5. Relationship between carbonate removal rate and reaction temperature.

It can be seen from Figure 4 and Figure 5 that under the above test conditions, with a reaction temperature between 80 °C and 110 °C, the TIC content of bauxite is less than 0.09 % after wet treatment, and the carbonate removal rate reached more than 82.96 %. In the above test range, the reaction temperature had little effect on the carbonate removal rate of bauxite and the TIC content.

### 4.3 Effect of Reaction Time on Carbonate Removal Rate

The effect of different reaction times (2, 4, 6, 8, 10, 12, 14 h) on the removal rate of carbonate was studied under the following test conditions: lime addition of 5 %, slurry solids content of 500 g/L, temperature of 90 °C and Na<sub>2</sub>O<sub>k</sub> concentration of spent liquor was 150 g/L. The change trend of TIC content in bauxite with the prolongation of reaction time is shown in Figure 6, and the change trend of carbonate removal rate in bauxite with the prolongation of reaction time is shown in Figure 7.

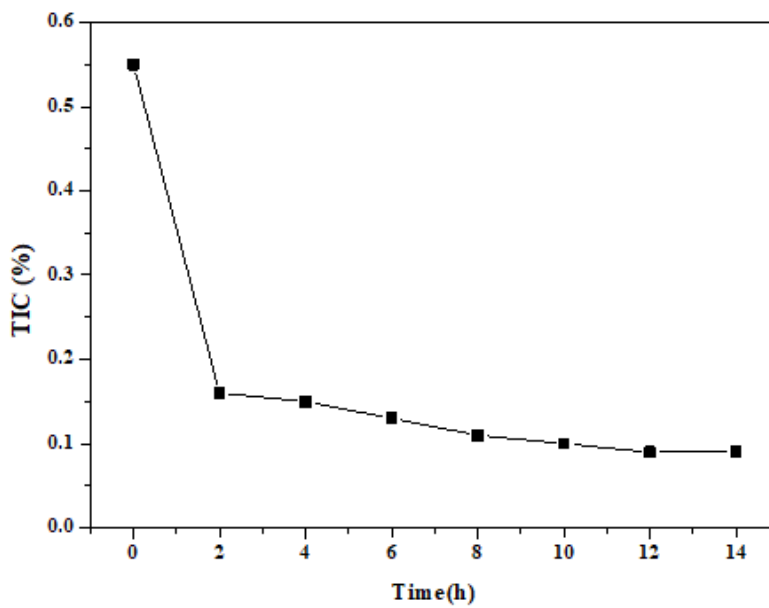


Figure 6. Relationship between TIC content in bauxite and reaction time.

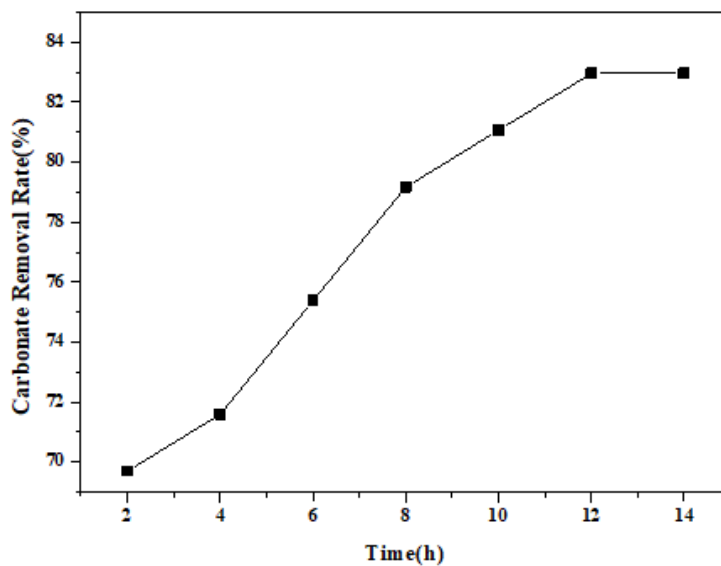


Figure 7. Relationship between carbonate removal rate and reaction time.

It can be seen from Figure 6 and Figure 7 that under the above test conditions, with the prolongation of the reaction time, the inorganic carbon content in bauxite gradually decreases with a significant drop within the first 2 h and smaller decreases between 2 and 14 h.; the carbonate removal rate gradually increased with increasing residence time up to 12 h. When the reaction time is greater than 10 h, the inorganic carbon content in bauxite is less than 0.10 %, and the carbonate removal rate can reach more than 81.06 %.

#### 4.4 Effect of Slurry Solids Content on Carbonate Removal Rate

The effect of different slurry solids content (300, 500, 700, 900 g/L) on the carbonate removal rate was studied under the following test conditions: lime addition of 5 %, reaction temperature of 90 °C, reaction time of 12 h and Na<sub>2</sub>O<sub>k</sub> concentration of spent liquor of 150 g/L. The change trend of TIC content in bauxite with the increase of slurry solid content is shown in Figure 8, the change trend of carbonate removal rate in bauxite with the increase of slurry solid content is shown in Figure 9, and the influence law of slurry solids content on Na<sub>2</sub>O<sub>C</sub> / Na<sub>2</sub>O<sub>T</sub> in sodium aluminate liquor is shown in Figure 10.

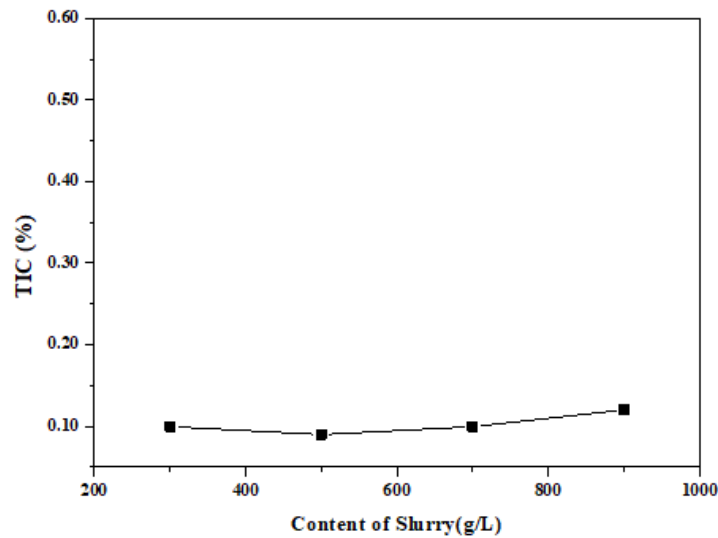


Figure 8. Relationship between TIC content in bauxite and slurry solids content.

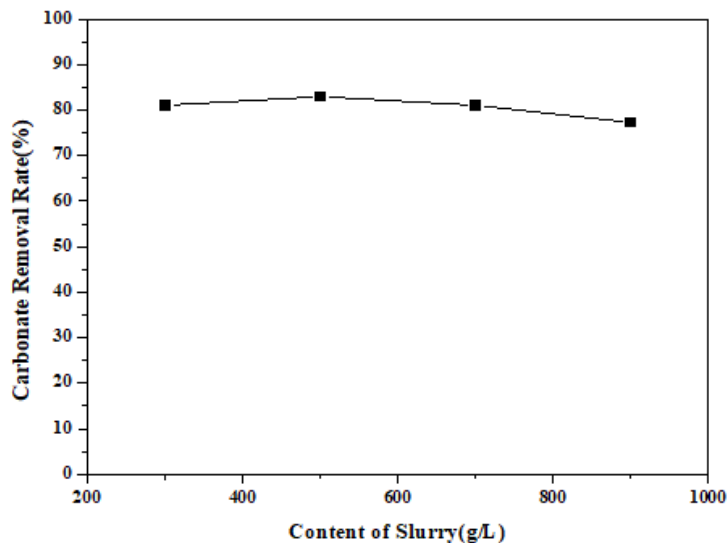
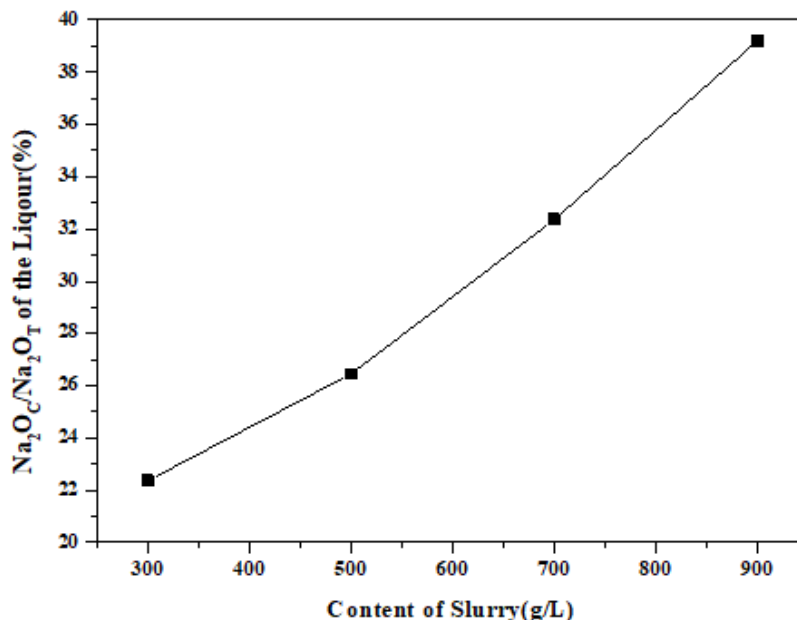


Figure 9. Relationship between carbonate removal rate and slurry solids content.

It can be seen from Figure 8 and Figure 9 that under the above test conditions, with the increase of slurry solids content from 300 g/L to 900 g/L, there was a marginal increase in the TIC content in bauxite and a marginal decrease in the carbonate removal rate. The TIC content change presented in Figure 8 is statistically significant based on the equipment sensitivity of 0.01 %.



**Figure 10. Relationship between solution Na<sub>2</sub>O<sub>C</sub> / Na<sub>2</sub>O<sub>T</sub> and slurry solids content.**

As can be seen from Figure 10, under the above test conditions, with the increase of slurry solids content, Na<sub>2</sub>O<sub>C</sub> / Na<sub>2</sub>O<sub>T</sub> in the liquor increased rapidly from 22.56 % to 39.40 %. Within the scope of the condition of the slurry solids content, improving slurry solids content, more carbonate entered sodium aluminate liquor. But with the increase of slurry solid content, carbonate in the solution concentration increased which was close to its equilibrium concentration in the liquor, and carbonate removal rate fell slightly which was seen in Figure 9. Considering carbonate removal efficiency and to meet the requirements of the production organization, slurry solid content between 500 g/L and 700 g/L is more suitable.

## 5. Conclusion

The wet removal method can greatly reduce the content of carbonate in bauxite, ensuring that the content of inorganic carbon in bauxite meets the normal production requirements, thus reducing the adverse impact of high carbonate bauxite on the Bayer process.

Under the test conditions, with the increase of the concentration of Na<sub>2</sub>O<sub>k</sub> in spent liquor, the carbonate removal rate increased, but it did not change significantly when the concentration of Na<sub>2</sub>O<sub>k</sub> is greater than 150 g/L. With the prolongation of reaction time, the carbonate removal rate increases, but it has no evident changes when the reaction time is more than 12 hours. The effect of reaction temperature between 80 °C and 110 °C on the removal rate of carbonate is not obvious. With the increase of slurry solids content, the change in the carbonate removal rate was marginal. Under suitable conditions, the carbonate removal rate of bauxite can reach more than 81.06 %.

## 6. References

1. Qigui Li, Yongyi Liu, Zhonglin Yin, Reaction behavior of carbonates in digestion process of high carbon bauxite, *Light Metals* 2020, 16-20.
2. Caimei Liu et al., The influence of impurity composition in the spent liquor on the evaporating crystallization process, *Light Metals* 2006, 33-36.
3. Lili Song, Experimental study on causticization of salt discharge with evaporation, *Energy Conservation of Nonferrous Metallurgy*, 2019, 37-39.
4. Guoling Wei et al., Effect of sulfur on salt elimination from NaAlO<sub>2</sub> solution bearing Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, *Nonferrous Metals (Smelting Part)*, 2016, 26-29.
5. Hongfei Wu et al., Effects of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> seed on enhanced salt discharge of high sulfur seeded precipitation spent liquor, *Nonferrous Metals (Smelting part)*, 2018, 27-31.
6. Jianhui LIU, Study on application of red mud wash liquor causticization technology, *Nonferrous Metals (Smelting Part)*, 2005, 25-26.
7. Yingzi Guo, Baiyong Zhang, Zhiguo Li. A side-flow caustic method and device for alumina production in bayer process. Patent CN103848446A, filed Nov. 28, 2012, granted April 27 2016
8. Guohong Liu, Influence Factors of wash liquor causticization in bayer process[J], *Nonferrous Metals (Smelting Part)*, 2001, 24-26.
9. Zhiying Zhao, Junzhao Fan, Weibing Jing, Synthesis and application of barium aluminate[J], *Nonferrous Metals (Smelting Part)*, 2004, 34-36.
10. Huajun Yuan, Qinqin Li. Selection of purification process of industrial sodium aluminate solution by BaO, *Light Metals* 1995, 13-17.
11. Ruiqiao Wu, Shuhong Jiao, Ruofei Zou, Test research of barium aluminate synthesis by caustic precipitation, *Shandong Chemical Industry* 2004, 6-8.