The study on desiliconization mechanism of sodium aluminate solution prepared from aluminum ash

Yiru Wang¹, Qiupin Zhao³*, Xiaolong Li³, Pengkuo Zhi³ and Dan Zhao³

¹ School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou, 730050, China
Email: 956142747@qq.com

Abstract. The sodium aluminate crude solution prepared by using aluminum ash often contains a certain amount of sodium silicate impurities, and needs refined desiliconization. In this paper, desilication treatment of sodium aluminate solution by adding calcium oxide during sintering and refining. Experimental results show that the amount of calcium oxide added, desiliconization time and desiliconization temperature have an important influence on desiliconization efficiency of sodium aluminate solution. The results show that the desiliconization efficiency can reach 95.80% under the optimal conditions, which satisfies the crystal decomposition of sodium aluminate solution.

1. Introduction
Aluminum ash is an industrial by-product of aluminum electrolysis and processing[1-3]. In 2008, China has listed the salt residue and scum generated in the process of crude aluminum refining as the ‘National Hazardous Waste List’[4]. Since then, aluminum ash is forbidden to accumulate outdoors to destroy the environment[5]. Many companies didn’t find a suitable method of aluminum ash increases for harmless treatment, and only built factories to pile them up[6, 7]. A large accumulation business pressure. Moreover, the presence of alumina (about 50%-80%) in aluminum ash causes waste of land and aluminum resources [8, 9].

In the process of recycling, sodium aluminate solution can be prepared by aluminum ash. However, the silicon-containing impurities in aluminum ash are considered to be the most harmful substances in the dissolution and decomposition process of sodium aluminate. The dissolution and precipitation reactions of silicon-containing impurities occur simultaneously [10, 11]. The precipitation of impurity silicon not only increases the loss of alumina during the dissolution process, but also cause a lot of scaling on the surface of the reactor, reducing the heat transfer efficiency, and also increasing the settling time of impurities in the sodium aluminate solution [12, 13].

In this paper, preparation of sodium aluminate clinker by adding calcium oxide during sintering. In this paper, sodium aluminate clinker is prepared by adding calcium oxide during sintering. And in the dissolution process, the dissolution and desilicification of sodium aluminate produce synchronously. The author analyzed the main phase composition and changes of silicon slag by XRD and optimized the desilicification conditions.

2. Experiment

2.1. Experimental materials and equipment
Aluminum ash: Jiayuguan Chengyu Metal Materials Company Limited; Sodium hydroxide (NaOH): Tianjin Binhai Kedi Chemical Reagent Co., Ltd; Calcium Oxide (CaO): Sinopharm Chemical Reagent Company Limited.

Electronic balance: HX2002T, Cixi Tiandong Weighing Apparatus Factory; High temperature box furnace: SG-XL1800, Shanghai Institute of Optics and Fine Mechanics; Constant Temperature Drying Oven: 101-1, Shanghai Dongxing Building Materials Testing Equipment Company Limited; X-ray diffraction (XRD): D/max-2400, Japanese Science Corporation (Rigaku).

2.2. Experimental process

2.2.1. Experiment on the effect of different calcium to silicon ratio (C/S) on desiliconization in sintering desiliconization process. Weigh 30 g of aluminum ash, then add 150 g of water and keep it at 40 °C for 2 h, and wash to neutral. The filter cake was dried at 100 °C for 12 h to give a solid of desalted aluminum ash. 25.20 g of desalted aluminum ash and 48.40 g of NaOH solid particles, calcium oxide (according to the multiple of the molar ratio of calcium oxide to silica, 0-6 times) was weighed and mixed, and at 750 °C for 2 h at a heating rate of 5 °C/min. 58.40 g of clinker was weighed, and added water that the quality is 5 times of clinker. After that, the clinker was activated at 100 °C for 2 h. Finally filter and dry.

2.2.2. Experiment on the effect of different calcium to silicon ratio (C/S) on desiliconization in refined desiliconization. Weighed different weights of 1.44 g, 2.88 g, 4.26 g, 5.76 g of calcium oxide into the prepared sodium aluminate crude solution and stirring at 100 °C. Then the reaction time is 60 min, 90 min, 120 min, 150 min, 180 min, 210 min. Finally filter and dry.

2.2.3. Experiment on the effect of different temperature and time on desiliconization in refined desiliconization process. Weighed 4.26 g of calcium oxide into the crude solution. The temperature is respectively raised to 40 °C, 60 °C, 80 °C, 100 °C, 120 °C, and then reacted at each different gradient temperature for 60 min, 90 min, 120 min, 150 min, 180 min, 210 min. Finally filter and dry.

3. Results and discussion

3.1 Aluminum ash composition analysis
The raw material aluminum ash and the desalted aluminum ash composition were analyzed by XRF. The results are shown in the Table 1. Combined with the analysis of Figure 1, desalination can increase the content of alumina in aluminum ash. The main phases in the aluminum ash are Al₂O₃ and NaCl, and the alumina in the aluminum ash exists in the form of α-Al₂O₃. However, α-Al₂O₃ is difficult to directly react with the alkaline solution, so the alumina in the aluminum ash can only be treated by the process of preparing the sodium aluminate solution by alkali sintering to achieve the purpose of recycling.

| Component       | Na₂O | MgO  | Al₂O₃ | SiO₂  | CaO  | TiO₂ | Fe₂O₃ | Cl    | Others |
|-----------------|------|------|-------|-------|------|------|-------|-------|--------|
| Aluminum ash    | 19.96| 2.75 | 61.23 | 1.99  | 0.57 | 0.05 | 0.29  | 8.72  | 4.44   |
| Desalted ash    | 6.28 | 3.78 | 81.18 | 2.76  | 0.81 | 0.10 | 0.51  | 0.19  | 4.39   |
3.2 Effect of different calcium-to-silicon ratio (C/S) on desiliconization in sintering desiliconization

In this paper, calcium oxide is used as a desiliconizing agent[14]. The result is shown in Figure 3, the desiliconization efficiency and the dissolution rate of alumina both increase first and then decrease as the C/S increases. As shown in Fig. 3, even if calcium oxide is not added when C/S=0, there is still a certain desiliconization effect, which may be caused by the formation of a small amount of sodium silicon slag[15]. The main reactions to form sodium silicon slag are as follows:

$$2\text{Na}^+ + 2\text{Al(OH)}_4^- + 1.7[\text{H}_2\text{SiO}_4]^2^- \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.7\text{SiO}_2 \cdot \chi\text{H}_2\text{O} + 3.4\text{OH}^- + (4 - \chi)\text{H}_2\text{O}$$

When C/S is 1.0 to 3.0, the desiliconization rate increases sharply, mainly because the producing hydrated garnet is beneficial to desiliconization, and the characteristic peak intensity of hydrated garnet is gradually increased. When C/S is greater than 3.0, it can be found that the characteristic peak intensity of hydrated garnet is slightly weakened and the emergence of new characteristic peaks. After analysis, it is calcium fluoride and tricalcium aluminate, which affect the dissolution of alumina. So the C/S choice is 3.0. The main equations for the desiliconization reaction are as follows:

$$\text{SiO}_2 + 2\text{CaO} \rightarrow 2\text{CaO} \cdot \text{SiO}_2$$

$$2\text{CaO} \cdot \text{SiO}_2 + 2\text{NaOH} + \text{aq} \rightarrow 2\text{Ca(OH)}_2 + \text{Na}_2\text{SiO}_3 + \text{aq}$$
3Ca(OH)₂ + NaAl(OH)₄ + aq → 3CaO·Al₂O₃·6H₂O + 2NaOH + aq
3CaO·Al₂O₃·6H₂O + χNa₂SiO₃ + aq → 3CaO·Al₂O₃·χSiO₂·YH₂O + 2(1+χ)NaOH + aq

3.3 Effect of different C/S changes with time on desiliconization during refined desiliconization

After desiliconization by sintering, there is still a large amount of silica in the sodium aluminate crude solution. Therefore, calcium oxide as a desiliconizing agent continues to remove silicon during the refining process to further reduce the silicon content in the sodium aluminate solution. As shown in Fig. 4. With the increase of C/S, the desiliconization effect of the sodium aluminate solution first increases and then decreases. When C/S increased from 2.5 to 7.5, the desiliconization rate increased by about 25%. The desiliconization effect was obvious. The main reason is that calcium oxide reacts with water to form calcium hydroxide, which releases a large amount of heat, accelerates the formation of hydrated garnet, and reduces the content of silica. However, when the C/S ratio is 10.0, the effect of desiliconization is deteriorated. It may be that a large amount of calcium oxide causes the concentration to increase, and the diffusion becomes slow, so that the desiliconization effect is weakened [16].

When C/S remains unchanged, with the extension of desiliconization time, the desiliconization rate shows a slight decline after a sharp rise. Therefore, it is determined that C/S is 7.5 and desiliconization time is 150 min. The reaction equation for deep desiliconization in the refining process is as follows [17]:

\[
\text{CaO + H}_2\text{O} = \text{Ca(OH)}_2
\]

\[
3\text{Ca(OH)}_2 + \text{NaAl(OH)}_4 + \text{aq} → 3\text{CaO·Al}_2\text{O}_3·6\text{H}_2\text{O} + 2\text{NaOH} + \text{aq}
\]

3.4 Effect of different temperature changes with time on desiliconization during reductive desiliconization

When the C/S is 7.5 times, the experimental results are shown in Figure 3.4. Combined with the analysis of Fig. 5, with the gradual increase of temperature, the desiliconization rate of the sodium aluminate solution first increased slightly and then decreased slightly. When the temperature rises from 40 °C to 80 °C, the desiliconization rate increases slowly, and the peak intensity of calcium oxide gradually decreases. The main reason is that the sodium aluminate solution has a higher viscosity at lower temperatures, the reaction process is slow, and the reaction is insufficient. So the desiliconization effect is not good. When the temperature is raised from 80 °C to 100 °C, the desiliconization effect is significantly improved. At 80 °C, a new characteristic peak of \( \text{Ca}_{2.93}\text{Al}_{1.97}(\text{SiO}_4)^{0.64}(\text{OH})_{9.44} \) appears. Mainly to raise the temperature, the viscosity of the system becomes smaller, and the reaction rate is accelerated to form \( \text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8 \) and \( \text{Ca}_{2.93}\text{Al}_{1.97}(\text{SiO}_4)^{0.64}(\text{OH})_{9.44} \). However, after 120 °C, it was found that the desiliconization effect in the sodium aluminate solution showed a downward trend, and the peak of \( \text{Ca}_{2.93}\text{Al}_{1.97}(\text{SiO}_4)^{0.64}(\text{OH})_{9.44} \) was weak. Mainly because \( \text{Ca}_{2.93}\text{Al}_{1.97}(\text{SiO}_4)^{0.64}(\text{OH})_{9.44} \) is easily decomposed at high temperatures. Therefore, it is advisable to choose 100 °C.
4. Conclusions
When the optimum amount of calcium oxide is C/S=3 during the sintering process, the desiliconization effect of the sintering process reaches 50.19%, and the dissolution rate of alumina increases by about 5%. Deep desiliconization is the addition of calcium oxide during the refining process. The optimum process conditions for deep desiliconization were determined as C/S=7.5, desiliconization time was 150 min, desiliconization temperature was 100 °C, desiliconization effect reached 95.80 %, and A/S reached 600, satisfying sodium aluminate dissolution. It meets the requirements for seed crystal decomposition of sodium aluminate solution.

The slag in the sintering process is mainly hydrated garnet, which replaces the unstable sodium silicon slag, reduces alkali consumption and saves production costs of alumina. The pre-desiliconization process was eliminated, which greatly saved the production time of 6-8 h.

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