

Alkali desilicated coal fly ash as substitute of bauxite in lime-soda sintering process for aluminum production

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Abstract: By desilication treatment, the $\text{Al}_2\text{O}_3/\text{SiO}_2$ molar ratio of coal fly ash could be improved to the range of 1.63–2.0. The desilicated coal fly ash (DSCFA) was enriched in alumina extraction. A processing technology was developed for alumina extraction from the DSCFA with the lime sintering process. $\text{Ca}/(\text{SiO}_2+\text{TiO}_2)$ molar ratio, and $\text{NaO}/\text{Al}_2\text{O}_3$ molar ratio, sintering time, and temperature were the most significant parameters impacting on the aluminum extraction efficiency. The optima aluminum extraction efficiency was obtained under conditions of $\text{Ca}/(\text{SiO}_2+\text{TiO}_2)$ molar ratio of 2.0, $\text{NaO}/\text{Al}_2\text{O}_3$ molar ratio of 0.98, and sintering at 1 200 °C for 60 min. A standard industrial dissolution method was used under conditions of caustic ratio ($\alpha_k=n(\text{NaO})/n(\text{Al}_2\text{O}_3)$) of 2.0, Al_2O_3 concentration of 50 g/L, sodium hydroxide concentration (N_k) of 60.78 g/L, Na_2CO_3 concentration of 10 g/L, temperature of 85 °C, and dissolution duration of 10 min. The final aluminum extraction efficiency was 90%.

Key words: coal fly ash; alumina; desilication; lime-soda sintering; dissolution

1 Introduction

The alumina contents of coal fly ash, produced by the coal fired power plants in the northern Shanxi and Shaanxi provinces as well as southern Inner Mongolia of China, are in the range of 40%–45%. This is an unique type of coal fly ash for its high aluminum content which is the highest reported so far. With the diminishing of bauxite resource as well as the increasing of aluminum demand, industrial profitable utilization of the coal fly ash in alumina extraction has become a very important research topic[1–3].

Technologies of alumina extraction from coal fly ash can be classified into acidic, alkali, and acid-alkali methods[4–7]. The acidic method uses sulfuric acid[8], hydrochloric acid, hydrofluoric acid[9], or fly ash. The acidic method can produce organic acid to dissolve alumina from the coal aluminum oxide product with silicon-rich residue as by-product. However, it requires acid-resistant and air-tight processing equipments. In addition, alumina recovery and waste dispose are also very complex. Alkali method uses lime and/or soda

sintering with coal fly ash. LU et al[10] reported an alkali process with coal fly ash containing alumina of 26.38% and silica of 52.10% as the starting material. The fly ash was mixed with limestone, sintered at 1 260 °C, and then dissolved in sodium carbonate solution at 80 °C. The final product was ultra-fine powder with particle size of 100 nm and alumina purity of 99.9%. Alumina recovery efficiency of the process was 70%. MA[11] reported a process with coal fly ash containing silica of 48.92% and alumina of 30.97% as starting material.

The alumina was obtained through incineration. The process was simple but met problems when it was scaled up in industrial application because of the massive lime usage as well as the high energy cost. The acidic-alkali method first sinters coal fly ash with soda together, and then recovers aluminum as aluminum chloride and silica as silica gel, respectively, with diluted hydrochloric acid[12]. Similar to other two methods, the acid-alkali method also faces with some problems such as massive consumptions of strong acid and caustic base and difficulty in separation of alumina from iron and titanium impurities[13].

A process has been developed in Pingshuo

laboratory to extract alumina and silicon sequentially from the coal fly ash. Silicon was extracted and transformed into nano silica particles by alkali dissolution method. The residue left was mainly an alumina-rich alkali desilicated coal fly ash (DSCFA) by-product. This by-product can be used as a resource for alumina production. The objective of this investigation is to develop a practical method for alumina extraction from this alkali DSCFA with lime-soda sintering technology.

2 Experimental

2.1 Materials

Coal fly ash raw material of this investigation was obtained from a coal fired power plant located in Shanxi Province, China. Its chemical composition is listed in Table 1.

Table 1 Chemical composition of coal fly ash raw material used in this study (mass fraction, %)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
48.20	41.24	3.37	3.31	0.20

The DSCFA was the process residue of removing the alkali soluble materials from the raw coal fly ash with 30% sodium hydroxide solution. The main component of the DSCFA was alumina in mullite, which constituted up to about 60% of total mass. The rest were silicon and sodalite.

Main chemical compositions of DSCFA and other raw materials are listed in Table 2.

Lime was purchased from a local lime manufacturer.

2.2 Analytic methods

2.2.1 SEM analysis

The morphological characteristics of raw and processed coal fly ash samples were studied with scanning electron microscope (SEM). Analytical sample was cleaned with water, ethanol, and acetone sequentially and then dried with hot air. After these pre-treatments, the prepared sample was then mounted onto a mono crystalline silicon holder, coated with gold and analyzed with an FEI Quanta 200 scanning electron microscope from FEI company, Hillsboro, Oregon, USA.

2.2.2 X-ray fluorescence (XRF) analysis

Energy dispersive X-ray fluorescence (ED-XRF) analysis was used to estimate the chemical composition of raw and processed coal fly ash samples. The sample was first ground in a mortar with a pestle, and then pressed into a 40 mm-diameter pellet before being subjected to analysis. Analytical measurement program was set up to cover the range of elements from sodium to germanium with a measurement time of 15 min per iteration. The X-ray fluorescence analyzer was from Spectro Analytical Instruments GmbH & Co. KG, Boschstrasse, Kleve, Germany. Data processing unit used was SPECTRO XEPOS from the same vendor.

2.2.3 XRD analysis

X-ray diffraction (XRD) analysis was conducted using Cu K_α radiation with 40 kV and 20 mA at a 0.2° scan rate (in 2θ). The X-ray diffractometer used was a Rigaku D/MAX-3C XRD model manufactured in Shibuya-Ku, Tokyo, Japan.

2.2.4 Chemical analysis

Silicon (represented as silicon dioxide) content in processing samples was determined by a volumetric analysis method[14]. Concentrations of the aluminum (represented as alumina) in the process samples were determined by EDTA-titrimetric analysis method[15].

2.3 Processing procedure

The starting material for the DSCFA sintering process was prepared in two forms, powder and molded cylinder. The powder sample was prepared by mixing lime, soda, and DSCFA together with C/S ($n(\text{Ca})/n(\text{SiO}_2+\text{TiO}_2)$) molar ratio equal to 2 and N/A ($n(\text{NaO})/n(\text{Al}_2\text{O}_3)$) molar ratio equal to 1. The molded sample was prepared by mixing the powder sample with a certain amount of water to form a mud, pressing it into a cylinder modeling, and drying it in an oven to remove moisture. These samples were sintered in an oven for 1 h to get the sintered DSCFA.

A standard industrial dissolution method was used to extract alumina from the sintered DSCFA. The standard dissolution solution contained 5 g/L soda and 15 g/L sodium hydroxide in water. The alumina extraction was conducted by putting one unit of the sintered DSCFA in mass in 15 units of the standard dissolution solution in mass at 85 °C and stirring at a speed of 300 r/min for 15 min.

The processing procedure is shown in Fig.1.

Table 2 Main chemical compositions of raw materials for alumina extraction process (mass fraction, %)

Materials	Al ₂ O ₃	CaO	MgO	SiO ₂	Fe ₂ O ₃	TiO ₂	Na ₂ O
Lime	5.03	55.49	2.34	1.74	0.103	0.378	0.074
DSCFA	49.2	3.53	1.37	30.26	1.11	1.48	5.95
Sodium hydroxide							60.29

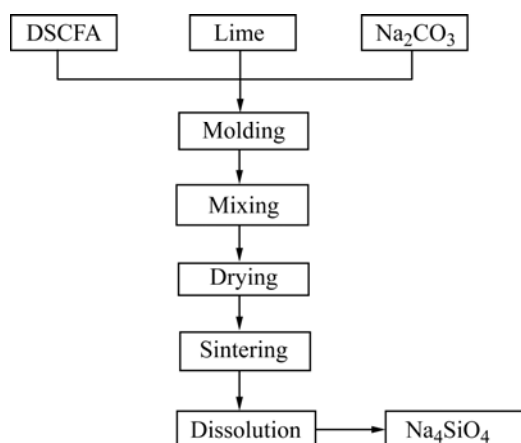


Fig.1 Processing procedure of alumina extraction from DSCFA

3 Results and discussion

3.1 Effect of sintering parameters on alumina extraction efficiency

Desilication treatment changed the phase characteristics of the coal fly ash significantly (Fig.2). Silicon content was reduced whereas sodium was introduced as a result of using sodium hydroxide.

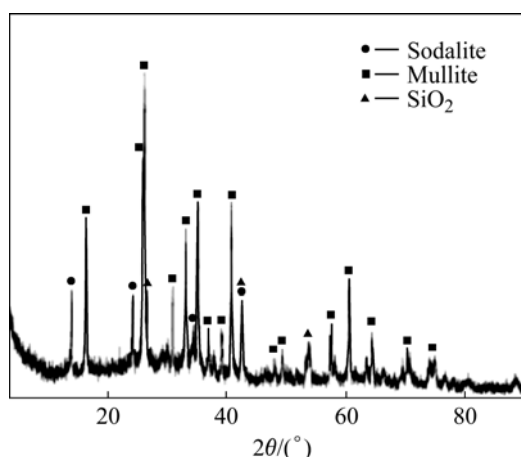


Fig.2 XRD pattern of raw DSCFA

As shown in Fig.3, sample forms had evident impacts on the alumina extraction efficiency of coal fly ash. The alumina extraction efficiency of the molded sample was much higher than that of powder sample. This was due to the small particle size of the alkali DSCFA, $D_{50} < 25 \mu\text{m}$, which made material dispense so easily. This problem can be easily resolved in industrial scale simply by recycling the dispensed dusts. However, it was not easy in laboratorial scale. In the laboratory scale, the molded starting material effectively resolved this issue and thus was used as processing starting material.

3.1.1 Effect of sintering temperature

The sintered DSCFA products can be classified into

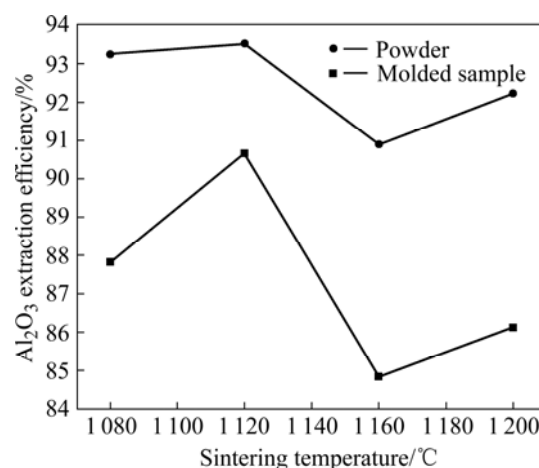


Fig.3 Effect of sample forms on alumina extraction efficiency of sintering process (C/S 2.0, N/A 1.0, sintering time 60 min, dissolution conducted under standard conditions)

three different categories, namely, under sintered, normally sintered, and over sintered based on the sintering extents. The difference among these products was resulted from the differences in the processing temperature and duration. Yellow material was produced as a result of lower sintering temperature because of the incompleteness of chemical reaction. This yellow material reduced the alumina extraction efficiency. In addition, it also added the difficulty for soluble alumina separation from insoluble materials because of the reactions between the free lime and other materials. These reactions produced significant amount of red mud, which increased the viscosity of dissolution mixture. On the other side, higher sintering temperature produced over sintered product. Glassy material was formed as a result of excessive heat treatment, which blocked aluminum oxide inside insoluble aggregates. This led to the decrease of alumina extraction efficiency[16]. As shown in Fig.4, 1 200 °C was the optimum temperature. At this temperature, the sintered material had the highest alumina extraction efficiency. Sintering below or above this temperature would produce abnormal sintered products, which led to lower alumina extraction efficiency.

3.1.2 Effect of sintering time

As shown in Fig.5, shorter sintering time produced under sintered product. This was similar to the situation when low sintering temperature was applied. The sintering process took about 60 min at 1 200 °C to get the maximum alumina extraction efficiency. Extending sintering time produced over sintered product with high density, which also reduced the alumina extraction efficiency. Therefore, sintering duration is a crucial factor in controlling the quality of the sintered product.

3.1.3 Effect of calcium ratio

The optimum C/S value for the pre-sintering material

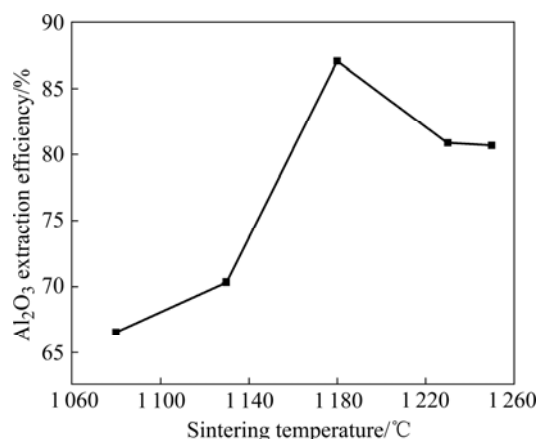


Fig.4 Effect of sintering temperature on alumina extraction efficiency (60 min, C/S 2.0, N/A 0.98, dissolution conducted under standard dissolution conditions)

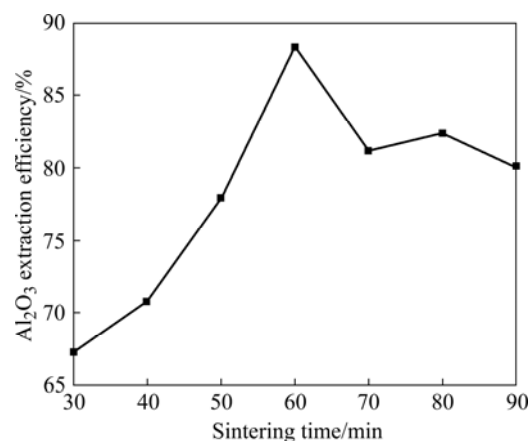


Fig.5 Effect of sintering time on alumina extraction efficiency (Sintering temperature 1 200 °C, C/S 2.0, N/A 0.98, dissolution conducted under standard conditions)

was 2.0 (Fig.6). Alumina extraction efficiency reached the maximum for the sintered product. Any deviation from this calcium ratio value would reduce alumina extraction efficiency. Low calcium ratio was in favor of the formation of insoluble $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. High calcium ratio was in favor of the formation of insoluble $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. In both cases, they led to the losses of Al_2O_3 and Na_2O .

3.1.4 Effect of alkali ratio

The alkali ratio of the pre-sintering material also had a significant impact on the sintering temperature and temperature range. Extent of solid phase reaction was affected by alkali ratio of the pre-sintering mixture.

Insoluble glassy $n\text{Na}_2\text{O} \cdot m\text{Al}_2\text{O}_3$ was produced at low alkali ratio because Na_2O was not enough to react fully with Al_2O_3 and Fe_2O_3 to form soluble $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3$. On the other hand, insoluble $n\text{Na}_2\text{O} \cdot m\text{CaO} \cdot p\text{SiO}_2$ was produced when high alkali ratio was adopted. All these insoluble materials would contribute to the losses of Na_2O and Al_2O_3 . The optimum N/A ratio was 0.98 (Fig.7).

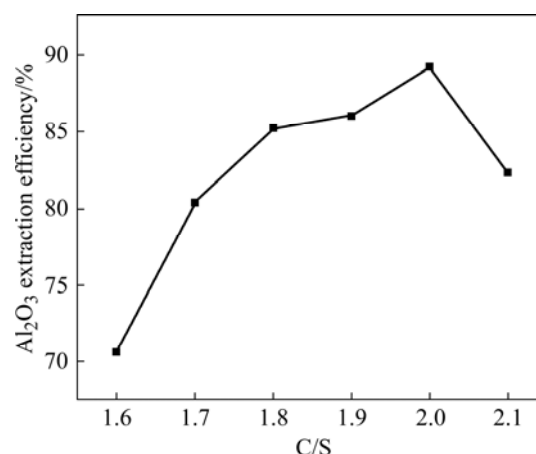


Fig.6 Effect of C/S on alumina extraction efficiency (Sintering temperature 1 200 °C, sintering time 60 min, N/A 1, dissolution conducted under standard dissolution conditions)

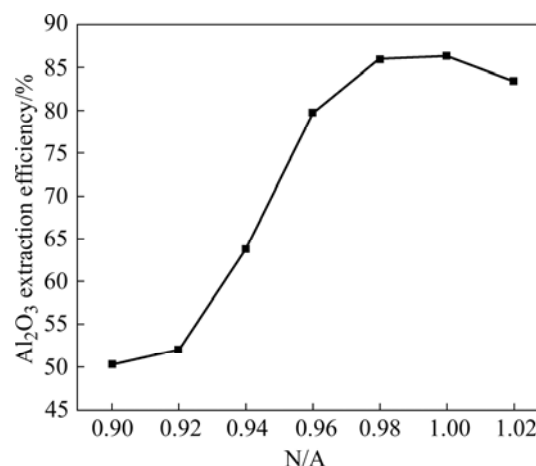


Fig.7 Effect of alkali ratio on alumina extraction efficiency (Sintering temperature 1 200 °C, sintering time 60 min, C/S 2.01, dissolution conducted under standard conditions)

3.2 Effect of dissolution conditions

By using DSCFA prepared under conditions of C/S 2.0, N/A 0.98, 1 200 °C and 60 min, dissolution conditions were studied with industrial methodology to get the optimum conditions for industrial application. Caustic ratio α_k ($n(\text{Na}_2\text{O})/n(\text{Al}_2\text{O}_3)$), temperature, time, particle size, and Na_2CO_3 concentration had been found to be the most profound parameters affecting the alumina extraction proficiency. The objective was to obtain a sodium aluminate solution that satisfies the requirements of sub-sequential carbonation processing steps to produce high quality aluminum oxide product.

The α_k value of 2.0 was used based on reference for current alumina production process with bauxite. Since particle size of DSCFA was much smaller, effect of DSCFA particular size can be ignored.

3.2.1 Effect of dissolution temperature

Temperature was the most important factor affecting alumina dissolution from the sintered DSCFA. Raising

dissolution temperature improved alumina extraction efficiency. At the same time, it also accelerated side reactions, which actually decreased the yield of alumina dissolution. As shown in Fig.8, alumina dissolution was accelerated in the temperature range of 70–80 °C. The releases of aluminum oxide and sodium oxide from the sintered mass were of exothermic

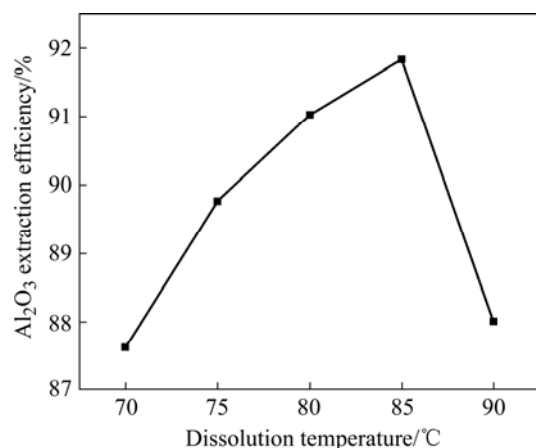
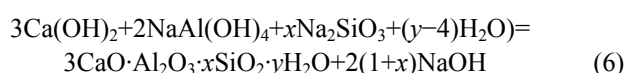
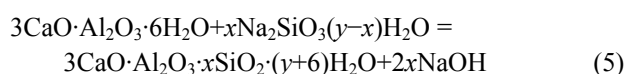
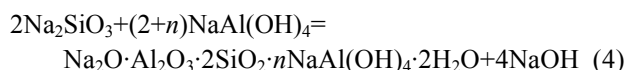
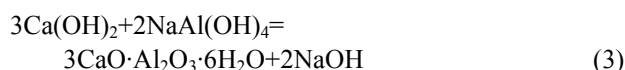
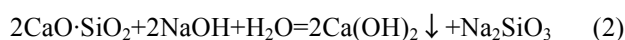
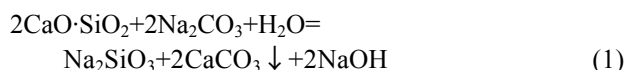


Fig.8 Effect of dissolution temperature on alumina extraction efficiency (α_k 2.0, $\rho(\text{Al}_2\text{O}_3)$ 50 g/L, sodium hydroxide concentration 60.78 g/L, DSCFA 50 g)

chemical reactions. Dissolution process was also an exothermic chemical process, which led to further rise of solution temperature. With the increase of solution temperature, decomposition of $2\text{CaO}\cdot\text{SiO}_2$ became even more significant. This was not favorable to improve alumina extraction as it also accelerated side reactions, which contributed to the loss of soluble alumina. These side reactions were attributed to the formation of calcium silicate that constituted 30% of total mass in the sintered DSCFA. The calcium silicate itself was not insoluble in water; however, it can react with sodium aluminate during dissolution process and transfer aluminum oxide into insoluble calcium aluminates [17–18]. The chemical reactions involved are listed as follows:



As a result of reactions (4) and (5), soluble Na_2O and Al_2O_3 were transformed into insoluble calcium

aluminosilicate hydrate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{SiO}_2\cdot y\text{H}_2\text{O}$) and sodium silicate hydrate ($\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot n\text{NaAl}(\text{OH})_4\cdot x\text{H}_2\text{O}$). When the two reactions became profound, they led to significant loss of alumina extraction efficiency. The optimum dissolution temperature was found to be 85 °C, as indicated in Fig.8. Alumina was not fully released from sintered ash when the temperature was below 85 °C. On the other hand, side reaction became significant above this temperature.

3.2.2 Effect of dissolution time

The dissolution time was defined as the period that started at the time when the sintered DSCFA was introduced into the mill and ended when the liquid was separated from red mud. This was the time period that dissolution solution actually contacted with the sintered DSCFA product. The longer the dissolution process, the greater the loss of the alumina extraction efficiency. This was due to the decomposition of calcium silicate as well as the side reactions. Since the particle size of the sintered DSCFA was very small, a short dissolution period actually gave the best result. The exact relationship between the dissolution time and aluminum extraction efficiency is shown in Fig.9.

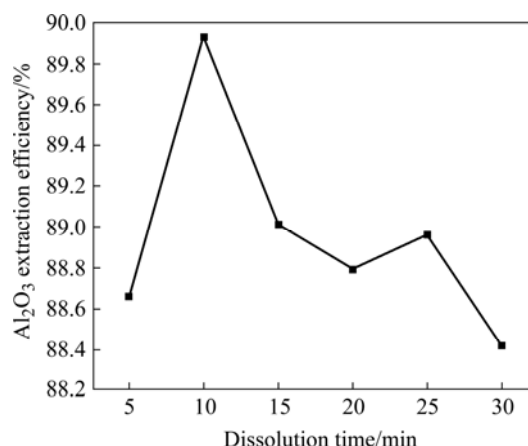


Fig.9 Effect of dissolution time on alumina extraction efficiency (α_k 2.0, $\rho(\text{Al}_2\text{O}_3)$ 50 g/L, sodium hydroxide concentration 60.78 g/L, sintered DSCFA 50 g; L/S 4.0, dissolution temperature 85 °C, without Na_2CO_3)

3.2.3 Effect of sodium carbonate concentration

The industrial dissolution solution contains a certain amount of sodium carbonate. Its effect on the alumina extraction efficiency is shown in Fig.10. Sodium carbonate played important roles in accelerating the decomposition of $2\text{CaO}\cdot\text{SiO}_2$, inhibiting the expansion of red mud, and enhancing the separation of red mud from liquid. The higher the concentration of sodium carbonate, the more the decomposition of $2\text{CaO}\cdot\text{SiO}_2$. However, when sodium carbonate concentration reached a certain value, it accelerated the transformation of $\text{Ca}(\text{OH})_2$ to CaCO_3 , which inhibited the formation of calcium aluminosilicate hydrate and sodium silicate hydrate. This

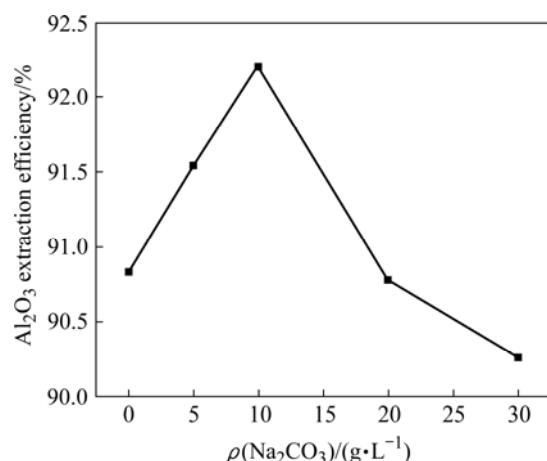


Fig.10 Effect of Na_2CO_3 concentration on alumina extraction efficiency (α_k 2.0, $\rho(\text{Al}_2\text{O}_3)$ 50 g/L, sodium hydroxide concentration 60.78 g/L, sintered desilicated ash 50 g, L/S 4.0, dissolution temperature 85 °C, dissolution time 10 min)

resulted in the declination of alumina extraction efficiency due to these side reactions. The optimum sodium carbonate concentration was 10 g/L at which the alumina extraction efficiency reached the maximum.

3.3 Mechanism of alumina extraction from desilicated ash

Coal fly ash is a mixture of silicon and aluminum materials with silicates as the major components. It is formed at high temperature under a quick flowing condition during coal burning process. The surface tension of glassy material formed during coal burning process makes it aggregate together very easily to form sphere clogs. When being cooled, these sphere clogs transformed into porous glassy body. Alkali desilication process released silicon from these clogs by destroying the glassy structure with sodium hydroxide, while most aluminum components like mullite were kept intact[19].

Fig.11(a) shows XRD pattern of the sintered desilicated coal fly ash. Fig.11(b) shows XRD pattern of red mud obtained from dissolution process.

NaAlO_2 is the major component of the sintered DSCFA. $2\text{CaO}\cdot\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot\text{Fe}_2\text{O}_3$ are the minor components. The soluble aluminum materials are dissolved. It also produced insoluble residues called red mud. Calcium silicate and calcium carbonate are the major components of red mud.

This was confirmed by XRD analysis in Fig.11(b) that $2\text{CaO}\cdot\text{SiO}_2$ and CaCO_3 were found to co-exist in the red mud. SEM analysis of the sintered ash and red mud also gave similar explanation, as shown in Fig.12.

SEM image of sintered ash exhibited mainly as clogs. They were formed by reactions of sodium hydroxide, silicon, and aluminum oxide in the sintering process. These clogs were irregular in shapes. However,

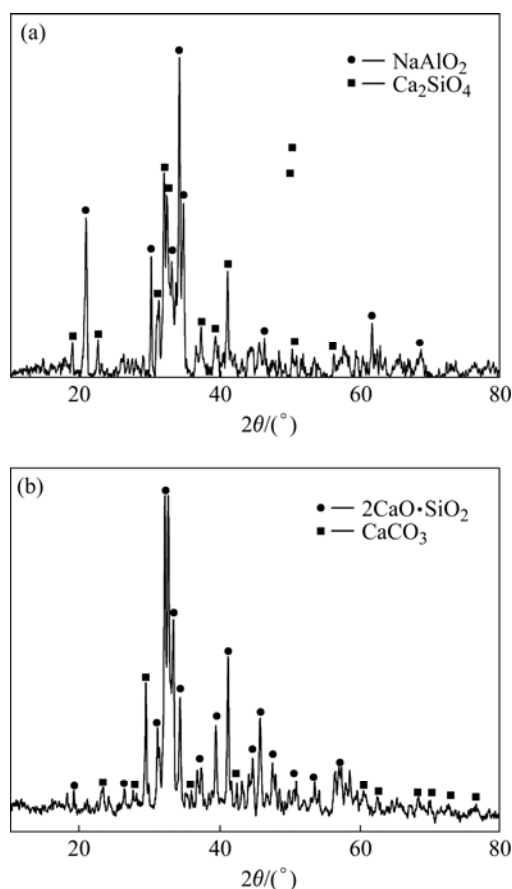


Fig.11 XRD patterns of sintered DSCFA: (a) Sintered DSCFA; (b) Red mud from dissolution of sintered DSCFA

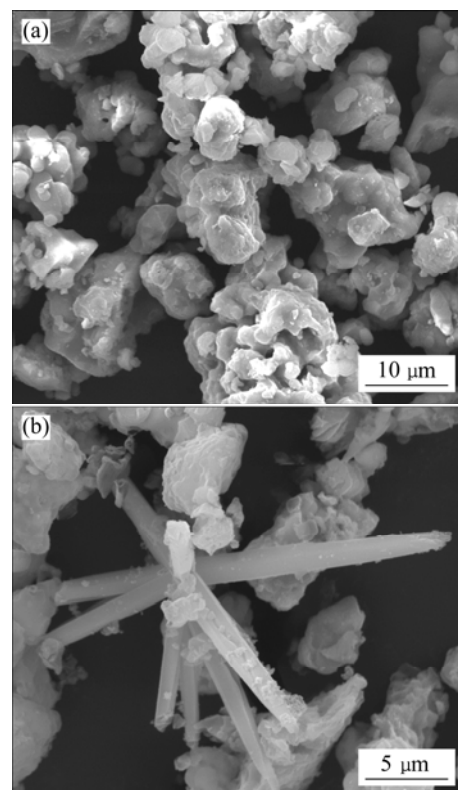


Fig.12 SEM images of sintered DSCFA: (a) Sintered DSCFA; (b) Red mud from dissolution of sintered DSCFA

needle crystal was found in the SEM image of red mud, as shown in Fig.12(b). This was the evidence of existence of CaCO_3 in the red mud.

Process of alumina extraction from the DSCFA was very similar with the process of alumina extraction from bauxite.

4 Conclusions

1) Desilicated coal fly ash can be used as a bauxite substitute in the lime-soda sintering process for alumina production.

2) Cylindroid shaped sintering material was better than powder in alumina extraction efficiency.

3) Optimum conditions for desilicated ash sintering were C/S 2.0, N/A 0.98, 1 200 °C and 60 min.

4) Optimum conditions for sintered ash dissolution were α_k of 2.0, $\rho(\text{Al}_2\text{O}_3)$ of 50 g/L, $\rho(\text{sodium hydroxide})$ of 60.78 g/L, $\rho(\text{Na}_2\text{CO}_3)$ of 10 g/L and at 85 °C for 10 min.

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