SYNERGISTIC EFFECT OF $C_{12}A_7$ AND CA ON ALUMINA LEACHING PROPERTY UNDER LOW CALCIUM/ALUMINUM RATIO

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Abstract

High calcium/aluminum ratio (C/A=12:7) is one of the main problems which inhibit the development of lime sinter process. Decrease the C/A of clinker is studied in this paper. $12CaO \cdot 7Al_2O_3$ ($C_{12}A_7$) and $CaO \cdot Al_2O_3$ (CA) were synthesized at 1350 °C by analytical pure reagents. The phase composition of sinters was analyzed by XRD and the alumina leaching experiments were carried out. The results show that the optimal alumina leaching ratio of $C_{12}A_7$ and CA are 93.40% and 73.18%. The leaching experiments of the mixture of $C_{12}A_7$ and CA with different proportions were carried out. The alumina leaching ratio of the mixture reaches 91.12% when the content of $C_{12}A_7$ is 40% (in mass). Above this proportion, the alumina leaching ratio increases little. The results show that the existence of $C_{12}A_7$ can promote the leaching property of CA.

Introduction

With the fast development of aluminium industry and the shortage of bauxite in China, the grade of bauxite in plants obviously decreases. There are two main problems when these bauxite are treated by Bayer process or soda-lime sintering process[1-3]. One is the lower alumina leaching, and the other is the higher cost. To treat the low grade bauxite (A/S<3, mass ratio between Al_2O_3 and SiO_2) efficiently and economically becomes one of the main problems needed to be solved. Lime sintering process, one of the efficient method to treat low grade bauxite, has many advantages, such as improving alumina leaching ratio to 85%, realizing dry sintering process or semi-dry sintering proces, decreasing the energy consumption of sintering process, and avioding the scab of rotary kiln caused by the volatilization of soda. Therefore, its application prospects is wide for low grade bauxite[4-6].

The main problem of the lime sintering process is the large amount of lime's addition. Lime will not only react with Al_2O_3 to form $12CaO \cdot 7Al_2O_3$ but also react with SiO_2 to form $2CaO \cdot SiO_2$. The theoretical Lime ratio of clinker (CaO/Al_2O_3, molar ratio is abbreviatedas C/A) is 1.71. Decrease the C/A of clinker becomes the research focus on condition that the alumina leaching ratio does not decrease. Xiao Wei [7] found that the optimal C/A of clinker was 1.4, not 1.71, and its alumina leaching ratio was 83.75% . Li Zhiying [8] studied the effect of C/A on alumina leaching ratio of lime sintering process, and found that the peak value of leaching ratio appeared when C/A was 1.4. Zhang Wu's results indicated that the optimal C/A of clinker were 1.6 and 1.4 when the A/S of clinker were 1 and 3 to 5[9]. And the leaching ratio of thses clinkers were above 90%. These studies have created favorable conditions for decreasing the addition amount of lime.

Uner the condition of low C/A, the occurrence state of Al_2O_3 changes from the single phase of $C_{12}A_7$ to the mixture phases of $C_{12}A_7$ and CA, but the alumina leachability decreases little. In order to study the alumina leaching property at low C/A, $C_{12}A_7$ and CA are synthesized by analytically pure reagents seperately, and their alumina leachability are studied and discussed.

1 Experiment

1.1 Materials

$CaCO_3$, Al_2O_3, NaOH, Na_2CO_3, all of the above reagents are analytically pure.

1.2 Equipments

Electronic balance, SFM-II planetary four head mixer, crusher, SFM-I planetary ball mill, KSL-1700X box-type high temperature sintering furnace, blower type constant temperature drying box, FY-24-A type powder tablet press machine, constant temperature water bath, mixer, condenser pipe, D/MAX-2500 X-ray diffractometer (Rigaku Japanese company).

1.3 Synthesis and analysis

$CaCO_3$ and Al_2O_3 were weighed at a certain proportion by the electronic balance. And then they were mixed by SFM-II planetary four head mixer for 2h. The mixture was put into KSL-1700X box-type high temperature sintering furnace and sintered for 2h at 1500°C, and then taken out at 350°C.

The clinkers were crushed and ground at the speed of 250r/min for 1h. Then they were identified by X-ray diffraction. And the conditions were: 40 kv pressure pipe, 150 mA pipe flow, Cu $K\alpha_1$ (λ=0.154056nm), 10 to 90° scanning range and 2 °/ min scanning speed.

In the end, the alumina leaching experiments were carried out and the leaching conditions were as follows: leaching temperature 85°C, leaching time 30min, liquid-solid ratio 10, Na_2CO_3 solution (Na_2O content of 80 g/L), stirring speed 300r/min. The experiment was conducted at constant temperature in a water bath. Firstly, 100 ml of Na_2CO_3 solution was accurately measured and preheated to 80°C in a flask. Then 5.00g clinkers accurately weighed were poured into the flask, stirring and leaching under atmospheric pressure. Finally, the leaching results were recorded and analyzed.

2 Results and discussions

2.1 Alumina leachability of CA

CA was formed under the contiditions of section 1.3. and the results are shown in figure 1.
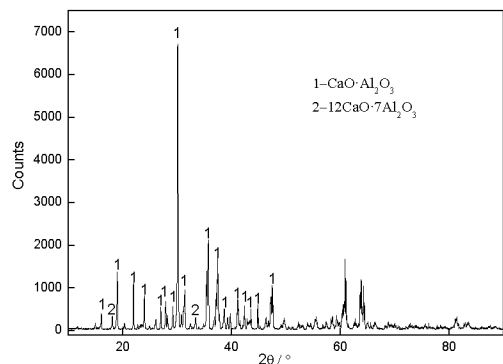

Figure 1. X-ray diffraction spectrum of CA

According to figure 1 it can be seen that the main phase of clinker is CA, and only a small amount of $C_{12}A_7$ exist in the clinker. The content of CA is above 95% as calculated by Rietveld refinement of the spectrum. CA is difficult to be formed in the serial of the compounds of calcium aluminate (CA, C_3A, $C_{12}A_7$) according the literature [10]. Therefore, $C_{12}A_7$ whose melting temperature is lower forms at first, and then it transforms into CA. The phase composition of the clinker is nearly single, so we suppose that the clinker is pure CA compound.

The leaching experiments are carried out to study the effect of leaching temperature and sodium carbonate concentration on alumina leachability of CA. The results are shown in figure 2 and figure 3.
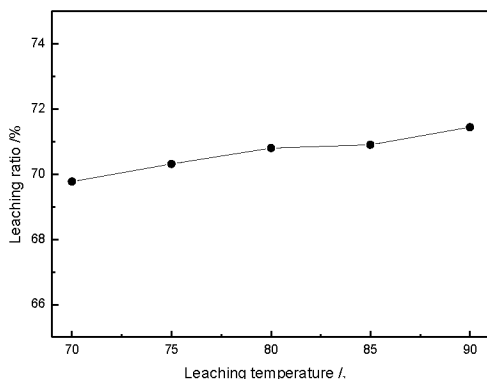

Figure 2. Leaching ratio of CA under different temperature (Conditions: leaching time 30min, L/S 10, sodium carbonate concentration 80 g/L)
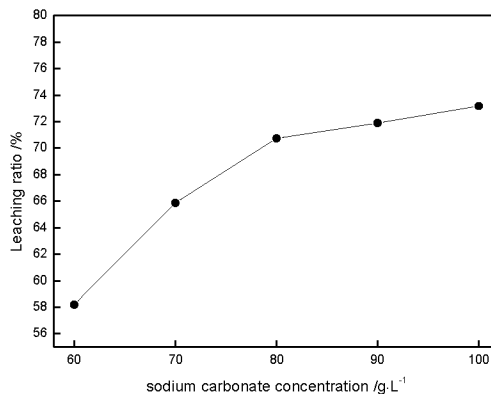

Figure 3. Leaching ratio of CA under different sodium carbonate concentration (Conditions: leaching time 30min, leaching temperature 80°C, L/S 10)

Alumina leaching ratio of CA increases slightly with the increase of leaching temperature (figure 2). But the increasing value is not obvious under these conditions. The maximum value of leaching ratio is only 71.44%.

The effect of sodium carbonate concentration on leaching ratio of CA is obvious when it ranges between 60 g/L and 100 g/L (figure 3). The increase rate becomes slow when the concentration reaches 80 g/L. The maximum value of leaching ratio is only 73.18%.

The alumina leachability of CA is stable under the mentioned conditions, but its value is not high. This observation is similar to others in the literature [11].

2.2 Alumina leachability of $C_{12}A_7$

$C_{12}A_7$ is synthesized at 1500°C for 2h and its XRD spectrum is shown in figure 4.
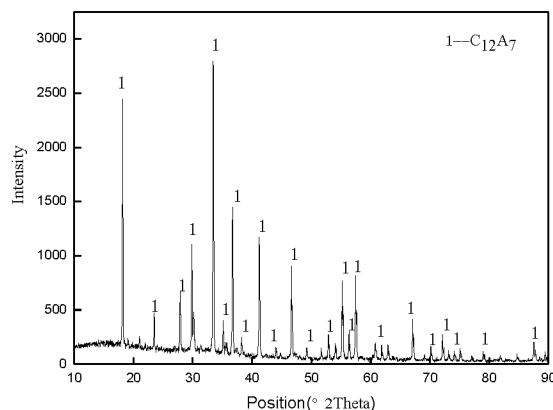

Figure 4. XRD spectrum of $C_{12}A_7$ synthesized at 1500°C

The clinker is synthesized at 1500°C using $CaCO_3$ and Al_2O_3 with the proportion of 12:7. XRD results show that the only phase

of the clinker is $C_{12}A_7$. Other calcium aluminate phases are not found in the clinker.

The alumina leaching experiments of $C_{12}A_7$ are carried out at 85 °C for 120min when the concentration of sodium carbonate ranges between $40g \cdot L^{-1}$ and $140g \cdot L^{-1}$. Results are shown in figure 5.
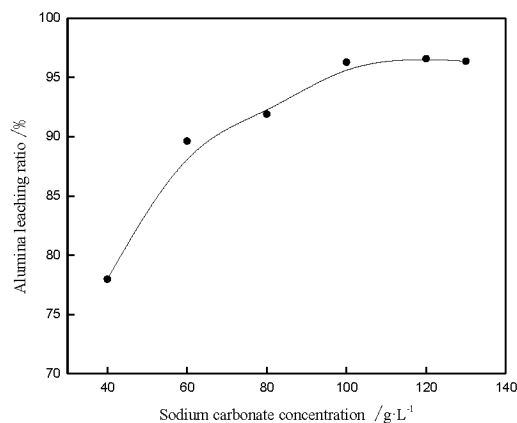

Figure 5. Effect of sodium carbonate concentration on alumina leaching ratio of $C_{12}A_7$

When the concentration of sodium carbonate concentration is lower than $40g \cdot L^{-1}$, the alumina leaching ratio is low and its value is 75% because of the lack of sodium carbonate which inhibits the extent and the speed of the reaction. Alumina leaching ratio increases from 75% to 96.28% when the sodium carbonate concentration increases from $40g \cdot L^{-1}$ to $100g \cdot L^{-1}$. After that the leaching ratio does not increase. The increase of the concentration of reactant is beneficial for the reaction, but its effect is reduced when the reaction tends towards equilibrium (the alumina leaching ratio is higher than 96% under this condition.).

The effect of leaching temperature on leaching ratio of $C_{12}A_7$ is studied under the of leaching time 120min and sodium carbonate concentration $120g \cdot L^{-1}$. The results are shown in figure 6.
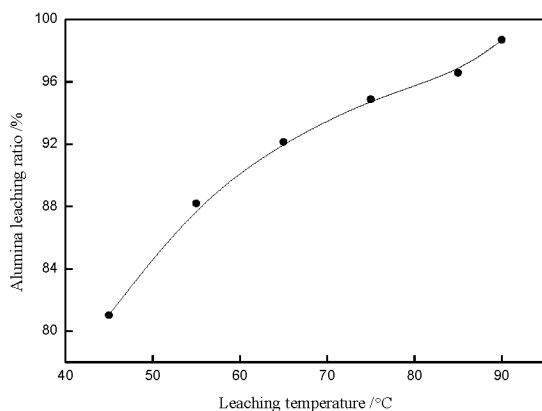

Figure 6. Effect of leaching temperature on alumina leaching ratio of $C_{12}A_7$

The alumina leaching ratio increases obviously with the increase of leaching temperature. And the best leaching ratio is 98.69% at 90°C. This indicates that the effect of temperature on leaching ratio is great. The optimal leaching conditions are leaching temperature 90°C and sodium carbonate concentration 120 $g \cdot L^{-1}$ according to figure 5 and figure 6.

2.3 Alumina leachabilty of the mixture of CA and $C_{12}A_7$

The pure compounds of CA and $C_{12}A_7$ obtained under the above conditions are mixed together with different proportion. The alumina leaching ratio of the mixture are carried out (conditions: leaching temperature 90°C, leaching time 90min, sodium carbonate concentration 100 $g \cdot L^{-1}$)and the results are shown in table 1 and figure 7.

Table 1 Alumina leaching ratio of the mixture with different proportion

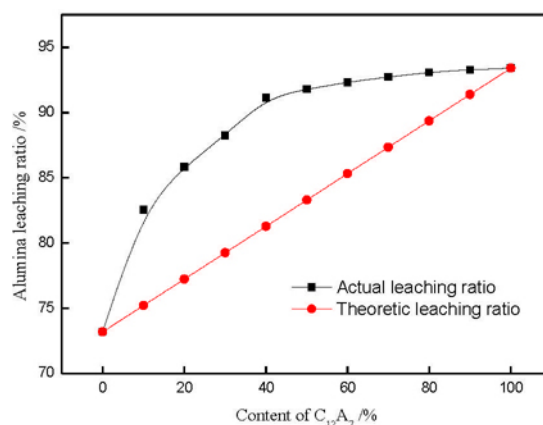| Content of $C_{12}A_7$ /%	Content of CA /%	Actual leaching ratio /%	Theoretic leaching ratio /%
0	100	73.18	73.18
10	90	82.53	75.20
20	80	85.84	77.22
30	70	88.24	79.25
40	60	91.12	81.27
50	50	91.79	83.29
60	40	92.33	85.31
70	30	92.72	87.33
80	20	93.08	89.36
90	10	93.28	91.38
100	0	93.40	93.40

Figure 7. Alumina leaching ratio of the mixture with different proportion

The actual leaching ratio is obtained from the experiments and the theoretic leaching ratio is calculated from the alumina leaching

ratio of pure CA and pure $C_{12}A_7$. Figure 7 shows that the leaching ratio of the mixture increases obviously with the increase of $C_{12}A_7$'s content. The alumina leaching ratio of the mixture whose C/A is 1.28 reaches 91.12% when the content of $C_{12}A_7$ is 40%. Compared with the theoretic leaching ratio, the actual leaching ratio is much higher. That is to say, the addition of $C_{12}A_7$ can improve the alumina leachability of CA. The mechanism of this synergistic effect may be caused by the formation of OH⁻ when $C_{12}A_7$ exists in the mixture. And the mechanism will be discused in detail according to the further experiments. Therefore, to maintain the leaching ratio up to 90% the C/A of the calcium aluminate can decrease to 1.28 from 1.71 according to the leaching results.

3 Conclusions

$C_{12}A_7$ can be leached out easily, and the best leaching ratio is 98.69%. The addition of $C_{12}A_7$ can improve the alumina leachability of CA whose leaching ratio is lower. Therefore, to maintain the leaching ratio up to 90% the C/A of the calcium aluminate can decrease to 1.28 from 1.71.

Acknowledgements

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