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# Effect of Calcium/Aluminium Ratio on Crystal Structure and $Al_2O_3$ Leaching Property of $12CaO•7Al_2O_3$

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## Abstract

$12CaO•7Al_2O_3$ ($C_{12}A_7$) with different calcium/aluminum ratio (C/A) were synthesized by sol-gel method and high-temperature sintering method in the paper. The phase composition of sinters was analyzed by XRD and the lattice constant was calculated by celref software. Finally, the alumina leaching experiments on sinters obtained from different synthesis methods were carried out. The results show the C/A of sinter with single phase $C_{12}A_7$ is 1.7 and the range of the best alumina leaching rate is between 1.6 and 1.8 when sol-gel method is used. On the other hand, the C/A is 1.6 and the range is between 1.4 and 1.6 when high-temperature sintering method is used. And the alumina leaching rate is direct proportion to the content of $C_{12}A_7$ and is inversely to the lattice constant under a certain conditions. Compared to sol-gel method, high-temperature sintering process can reduce the optimal C/A of $C_{12}A_7$.

## Introduction

Calcium aluminate sintering process, which could extract alumina from low-grade bauxite and slag such as iron-bearing bauxite, fly ash and red mud, is another method for alumina production[1-5]. The main phases of the clinker are $C_{12}A_7$ and $2CaO·SiO_2$[6]. The method realizes the comprehensive utilization of low grade alumina-containing materials and is benefit to alleviate the contradiction of the demand of bauxite.

In addition, lime sintering process without soda carbonate could realize the dry proportioning sinter, which is difficult to be realized in lime-soda sinter process because of the problems of soda recycling and soda evaporation[7-9]. In calcium aluminate process, these problems don't exist. Because only lime is added into sinter process, and the mother liquor of carbonization recycles in the hydrometallurgy link[10]. Therefore, the energy of sinter process could decrease obviously.

But the high consumption of CaO and the low alumina leaching ratio (83%) restrict the application of this method [11, 12]. Therefore, decrease the lime proportion C/A ($CaO/Al_2O_3$, molar ratio, excluding CaO in $2CaO·SiO_2$) and improve the crystal structure and alumina leachability of $C_{12}A_7$ become the research focus.

Xiao Wei [13] found that the best C/A of $C_{12}A_7$ is not the theoretical value 1.71 but the value 1.40. Li Zhi-ying[12] also indicated that the maximum value of leaching ratio appeared when C/A was 1.40, and pointed out that this could alleviate the problem of large amount of lime. Zhang Wu's results[14] indicated that the optimal C/A was 1.40 and its alumina leaching ratio was above 90% when A/S ranged from 3 to 5. But if the A/S was 1, the optimal C/A was 1.60.

The molecular formula of $C_{12}A_7$ is $12CaO•7Al_2O_3$, but Bartl and Scheller[15] suggested that it is a continuous solid solution, and its molecular formula is $(12\text{-}x)CaO•7Al_2O_3$ (x=0~2). Christensen[16] also found that the R factor was the lowest when x was 0.7 during rietveld refinement process. If the structure of $C_{12}A_7$ of clinker was unsaturated, it is significance to decrease the lime proportion of calcium aluminate process.

Although the optimal C/A of calcium aluminate clinker is 1.4, the structure of $C_{12}A_7$ could not be determined because of the complex elements and phase composition. Therefore, the crystal structure and alumina leachability of $C_{12}A_7$ with different C/A were investigated through sol-gel method and high-temperature sintering method in this paper.

## 1 Experiment

### 1.1 Materials

$Ca(NO_3)_2•4H_2O$, $Al(NO_3)_3•9H_2O$, $NaNO_3$, $Na_2CO_3$, urea, polyethylene glycol, absolute ethyl alcohol, and concentrated nitric acid (nitrate content is 63~68%), all of the above reagents are analytically pure.

### 1.2 Synthesis of sol-gel method

$Ca(NO_3)_2•4H_2O$, $Al(NO_3)_3•9H_2O$ and $NaNO_3$ were weighed at a certain proportion by the electronic balance. And they were uniformly dissolved and stirred for 3h in 150 ml of distilled water at the room temperature. Then a certain amount of urea and a small amount of surfactant polyethylene glycol were added to the mixture and metal salts sol was obtained by continuing to stir for 3h. Let the metal sol sit for 24h in constant temperature drying oven before the metal gel was got. And the metal salt precursor was got by heating the metal salt gel to 350°C and insulating for 2h in energy-saving box-type electric furnace. Tablet and place them in corundum crucible. The sinters were gained after insulating for 3h at 1350°C. Cool and take out. Finally, the clinkers remained to be used after being crushed and grinded.

### 1.3 Synthesis of high-temperature sintering method

Analytical pure $CaCO_3$ and $Al_2O_3$ were weighed at a certain proportion and they were mixed for 2h in SFM-II planetary mixer. Then place the mixture in the graphite crucible. The graphite crucible was placed in box-type high-temperature sintering furnace (Type: KSL-1700X) and insulated for 2h at 1500°C. Finally, take out after cooling it. And the sinters remained to be used.

### 1.4 Analysis

Some sinters were analyzed by XRD and the scanning conditions included 40 kv pipe pressure, 150mA pipe flow, 10~60° scanning angle and 2°/min scanning speed.
Then the productions of sintering as the raw materials were used to carry out the leaching experiment and the experiment was

conducted in constant temperature water bath. The leaching conditions were: $Na_2CO_3$ solution (the content of $Na_2O$) 80g/L, liquid-solid ratio (L/S, ml/g) 20, leaching temperature 80°C, stirring speed 300r/min, and leaching time30min. Firstly, 100 ml of $Na_2CO_3$ solution was accurately measured and preheated to 80°C in flask. Then 5.00g clinkers accurately weighed were poured into the flask, stirring and leaching. Finally, the leaching results were recorded and analyzed.

## 2 Results and discussions

### 2.1 Phase compositions of $C_{12}A_7$ with different C/A

#### 2.1.1 Effect of the sol-gel method on phase composition

Under different C/A, the sinters synthesized by the sol-gel method are analyzed by XRD and the results are shown in figure 1. Then the diffraction intensities of the strongest peak (2θ=18.109°), the second strongest peak (2θ=33.396°) and the third strongest peak (2θ=36.692°) are shown in figure 2.

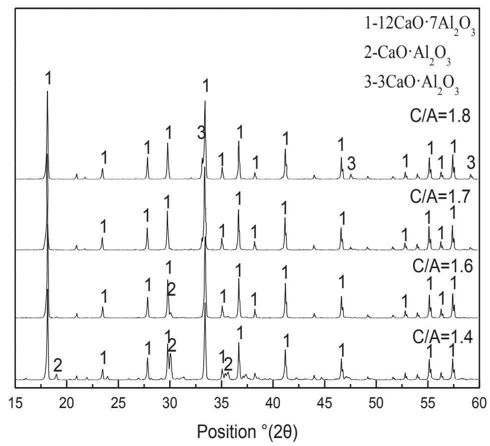


Figure 1. The X-ray diffraction spectra of sinters synthesized by the sol-gel method under different C/A

From figure 1 and figure 2, it is concluded that when C/A is 1.7, the three strong peaks of $C_{12}A_7$ almost all reach the maximum and the phase almost exists only 12CaO•7$Al_2O_3$; when C/A＜1.7, the diffraction intensities corresponding to the three strong peaks all increase with the enhancement of C/A and the phases obtained are $C_{12}A_7$ and CaO•$Al_2O_3$. The intensity of diffraction peak increases with the increase of the content of the phase in mixture, which is based on the principle of diffraction. So the content of $C_{12}A_7$ increases and the content of CaO•$Al_2O_3$ decreases with the improvement of C/A. When C/A is 1.8, the diffraction intensities of the three strong peaks are slightly lower than the ones of C/A=1.7. At the same time, a little 3CaO•$Al_2O_3$ is retrieved and the existence of CaO•$Al_2O_3$ and 3CaO•$Al_2O_3$ is related to the distribution of Ca. When the distribution of Ca is low, there is CaO•$Al_2O_3$ that contains less CaO than $C_{12}A_7$; When the distribution of Ca is high, there is 3CaO•$Al_2O_3$ that exists more CaO than $C_{12}A_7$.

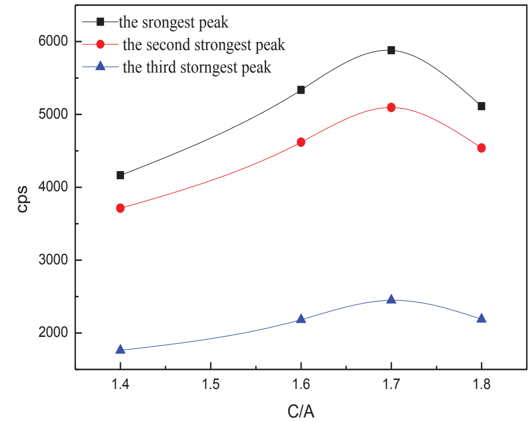


Figure 2. The diffraction intensities of the three strong peaks of $C_{12}A_7$ synthesized by sol-gel method

#### 2.1.2 Effect of high-temperature sintering method on phase composition

The sinters under different C/A are synthesized by high-temperature sintering and the X-ray diffraction spectra of the sinters are shown in figure 3. After analyzing, the diffraction intensities of the three strong peaks are shown in figure 4. The figure 3 and figure 4 show that when C/A is 1.6, the diffraction intensities of the three strong peaks of $C_{12}A_7$ all reaches the maximum and the phase is nearly only $C_{12}A_7$; When C/A is lower than 1.6, the diffraction intensities of the three strong peaks of $C_{12}A_7$ gradually enhance with the increase of C/A and the phases are $C_{12}A_7$ and CaO•$Al_2O_3$. What's more, the content of $C_{12}A_7$ constantly increases and the content of CaO•$Al_2O_3$ accordingly decreases. When C/A is higher than 1.6 (namely C/A=1.7), the intensities diffraction of the three strong of $C_{12}A_7$ are lower than the ones of C/A=1.6.

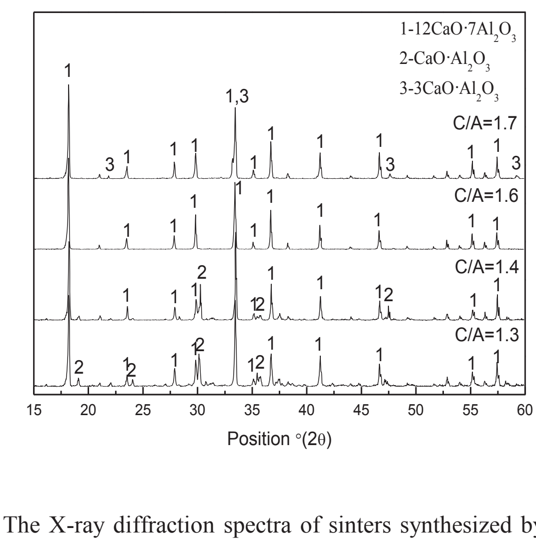


Figure 3. The X-ray diffraction spectra of sinters synthesized by high-temperature sintering method under different C/A

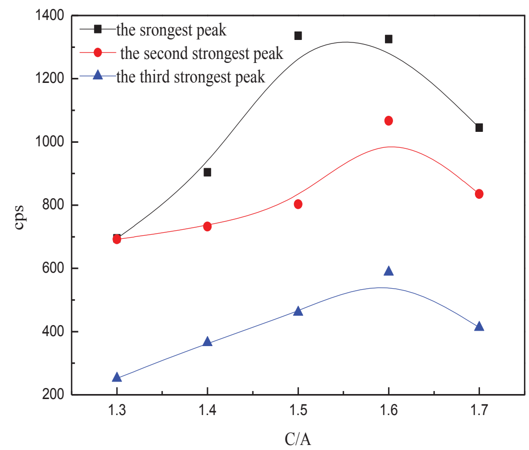


Figure 4. The diffraction intensities of the three strong of $C_{12}A_7$ synthesized by high-temperature sintering method

By comparison, the pure phase $C_{12}A_7$ can be both synthesized by the so-gel method and the high-temperature sintering method and the difference between them is the C/A of pure phase. The sol-gel method obtains the pure phase when C/A is 1.7, while the high-temperature sintering method gains the single phase when C/A is 1.6. Compared to sol-gel method, high-temperature sintering process can reduce the optimal C/A of $C_{12}A_7$.

2.2 Lattice parameters of $C_{12}A_7$ with different C/A

The crystal structure of $C_{12}A_7$ is cubic[17], and its space group is I43d. And the lattice parameters of it are 11.989×11.989×11.989, 90×90×90. Sun Huilan[18] points out alumina leaching rate is associated with lattice distortion when the effect of $Na_2O$ on alumina leaching rate is researched. So the lattice constants of $C_{12}A_7$ synthesized by the two methods are calculated by celref software. And the results are shown in figure 5.

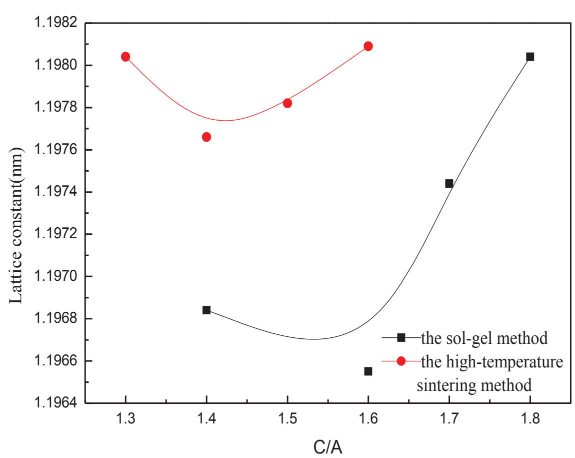


Figure 5. The variety of lattice constant under the two synthesized methods

From the figure, it is known that the lattice constant firstly increases and then decreases with the increase of C/A. And the difference is that the inflection point in sol-gel method is at the point of C/A=1.4 and the one in high-temperature sintering method is at the point of C/A=1.6. In addition, the lattice constant of $C_{12}A_7$ got by sol-gel method is lower than the one gained by high-temperature sintering method. On the whole, the lattice constant curve of $C_{12}A_7$ got by sol-gel method is shifted to the upper left corner to get the one of high-temperature sintering method.

2.3 Alumina leaching rate of $C_{12}A_7$ with different C/A

The alumina leaching experiments are carried out and the raw materials are the sinters synthesized by the sol-gel method and high-temperature sintering method under different C/A. The experiment condition is shown in section 1.3 and the results are shown in figure 6.

By comparing the two curve, the curve of alumina leaching rate got by the high-temperature sintering is similar to the one gained by the sol-gel method. And it can be got by offsetting the curve gained by the sol-gel method to the upper right corner.

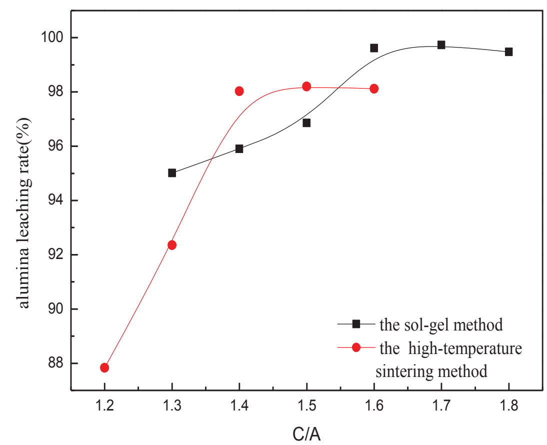


Figure 6. The vary of alumina leaching rate under different synthesized methods

## 3 Conclusions

(1) The pure phase $C_{12}A_7$ can be got when C/A is 1.7 in the sol-gel method while the single phase $C_{12}A_7$ can also obtained when C/A is 1.6 in the high-temperature sintering method.

(2) In the sol-gel method, when C/A is 1.6 the lattice constant of $C_{12}A_7$ reaches the minimum; when C/A is 1.4 it arrives to the minimum in the high-temperature sintering method. And the minimum of the former is less than the latter.

(3) When C/A ranges from 1.6 to 1.8, the alumina leaching rate arrives to the maximum in the sol-gel method; when C/A ranges from 1.4 to 1.6, the alumina leaching rate achieves the maximum in the high-temperature sintering method. And the maximum value of the former is higher than that of the latter.

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