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# Crystal Structure and Alumina Leaching Property of $Na_2O$ Doped $C_{12}A_7$

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## Abstract

Material of $Na_2O$ doped $12CaO•7Al_2O_3$ ($C_{12}A_7$-$Na_2O$) was prepared by the sol-gel method. And the precursor was sintered at 1623K for 3h. The phase composition and crystal structure of $C_{12}A_7$-$Na_2O$ was investigated by XRD analysis. The results indicated that $Na_2O$ would occupy the position of CaO or vacancy of $C_{12}A_7$ lattice and promote the formation of $C_{12}A_7$ when calcium/aluminum ratio ($CaO/Al_2O_3$, molar ratio) was 1.4. $Na_2O$ would promote the formation of $C_3A$ when calcium/aluminum ratio was 1.7. The lattice parameters also proved the solid solution between $C_{12}A_7$ and $Na_2O$. Alumina leaching experiments were carried out in sodium carbonate solution and the relationship between leaching ratio and doping content, calcium/aluminum ratio were established.

## Introduction

High alumina fly ash is found recently in northern China and it is characterized by the content of alumina in fly ash up to about 40%[1-5]. However, there are some problems such as large quantities of lime are consumed and leaching rate of alumina is low when alumina is extracted by lime sintering process. If these problems are solved, it not only reduces the pollution to the environment, but also eases the shortage of bauxite resources in China.

Yu Hai-yan[6]et al. find $Na_2O$ can enter into $C_{12}A_7$ ($12CaO•7Al_2O_3$) crystal lattice to form solid solution and reduce the C/A(C/A is shorted of $CaO/Al_2O_3$, molar ratio) of clinkers when $Na_2O$ is added to clinkers in the study of effect of low lime ratio on phase formation of calcium aluminate clinkers. C.Ostrowski [7]synthesizes $C_{12}A_7$ by adding less than 10% of $Na_2O$ to CA($CaO•Al_2O_3$) and also summaries a similar conclusion, which shows important research significance for reducing consumption of lime.

In addition, Wang Bo[8] also point out that adding $Na_2O$ to MgO-containing calcium aluminta slags would improve the leaching rate of alumina. Sun Huilan[9] is consistent with this opinion and puts forward that the leaching rate of alumina in $C_{12}A_7$ is related to the lattice distortion and the binding energy. But she doesn't show the influence of the relationship between them. So, in order to confirm the effect of $Na_2O$ doped $C_{12}A_7$ on crystal structure of and alumina leaching rate, $C_{12}A_7$ is synthesized by the sol-gel method[10, 11] in the article, without considering the effect of impurities such as MgO. In the pure ternary $Na_2O$-CaO-$Al_2O_3$ system, the phases are determined by XRD analysis and the article explores the effect of $Na_2O$ on parameter of cubic cell and parameter of cubic cell on alumina leaching rate.

## 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 Equipments

Electronic balance, SFM-II planetary four head mixer, crusher, SFM-I planetary ball miller, KSL-1700X box-type high temperature sintering furnace, SX-1300°C series energy-saving box-type electric furnace, blower type constant temperature drying box, FY-24-A type powder tablet press machine, KQ3200 numerical control ultrasonic cleaning machine, constant temperature water bath, mixer, condenser pipe, D/MAX-2500 X-ray diffractometer (Rigaku Japanese company).

### 1.3 Synthesis and analysis

$Ca(NO_3)_2•4H_2O$, $Al(NO_3)_3•9H_2O$ and $NaNO_3$ were weighed at a certain proportion by the electronic balance, dissolved in 150 ml of distilled water and stirred for 3h; then add a certain amount of urea and a small amount of polyethylene glycol surfactant to mixture, continue to stir for 3h at room temperature and obtain metal salt sol; metal salt sol was placed in 90°C blower type constant temperature drying box, holding for 24 h, forming metal salt gel; metal salt precursor was got by heating the metal salt gel to 350°C and insulating for 2h in the SX-1300°C series energy-saving box-type electric furnace; tablet using FY-24-A type powder tablet press machine and insulate at 1350°C for 3h in KSL-1700 box-type high temperature sintering furnace. At last, the clinkers were taken out at 400°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 $K\alpha_1$ ($\lambda$=0.154056nm), 10 to 60° 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 80°C, leaching time 2h, liquid-solid ratio 20, $Na_2CO_3$ solution ($Na_2O$ content of 80 g/L), stirring speed 300r/min. The experiment was conducted in the constant temperature water bath. 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 Effect of $Na_2O$ on phase compositions of $C_{12}A_7$

#### 2.1.1 Effect of $Na_2O$ on the phases when C/A=1.7

$12CaO•7Al_2O_3$ is the formula for calcium aluminate, which belongs to cubic, space group for I43d and lattice constant is 1.1989nm. The C/A of theory is about 1.7 according to the formula of $C_{12}A_7$. So, XRD spectrum of clinkers doped $Na_2O$ are analyzed when the C/A = 1.7 and the results are shown in figure 1.

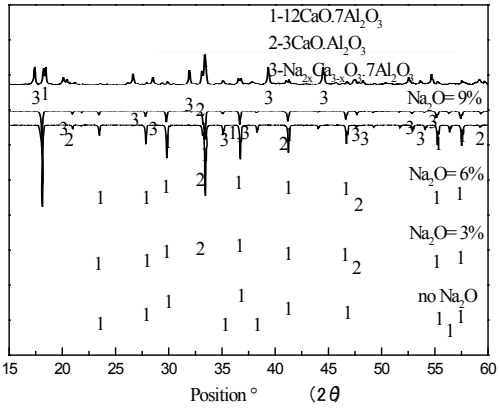


Figure 1. X-ray diffraction spectrum of clinkers with C/A=1.7 and different $Na_2O$ content

Figure 1 shows that the phase is almost all nearly $C_{12}A_7$ (standard card 70-2144) without $Na_2O$; when the content of $Na_2O$ is respectively 3% and 6%, phases, in addition to $C_{12}A_7$, also appear $C_3A$ ($3CaO•Al_2O_3$); the diffraction peaks of phases change greatly when the content of $Na_2O$ is 9%, for example the diffraction peaks of $C_{12}A_7$ increase obviously and $C_3A$ decrease significantly. What's more, there is a new phase $Na_{2x}Ca_{3-x}O_3•Al_2O_3$ synthesized and a large number of $Na_2O$ is the main reason of the existence of $Na_{2x}Ca_{3-x}O_3•Al_2O_3$.

By contrast, $C_3A$, standard card of which is 32-0148, belongs to orthorhombic and the cell data is 10.8737×10.8512×15.115 and 90×90×90, while $Na_{2x}Ca_{3-x}O_3•Al_2O_3$ also belongs to orthorhombic and the standard card of which is 26-0958, and cell data is 10.862×10.845×15.106 and 90× 90×90. So $Na_2O$ occupies the position of CaO or vacancy of $C_{12}A_7$ lattice and forms a kind of interstitial solid solution and they're both tricalcium aluminate. Dietmar Stephan [12]also has a similar view in the study of structure refinement of tricalcium aluminate doped.

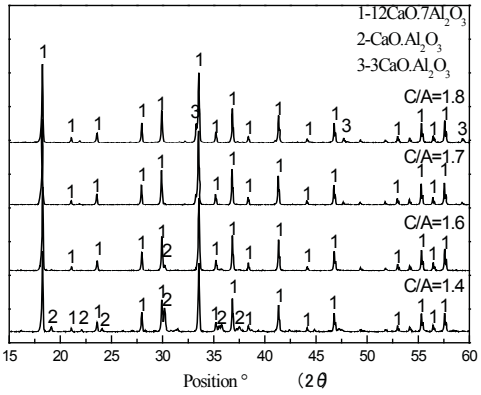


Figure 2. X-ray diffraction spectrum of clinkers with different C/A

In order to probe the effect mechanism of $Na_2O$, the results of phases in different C/A are shown in figure 2. When C/A=1.7, the phases are nearly all $C_{12}A_7$; when C/A=1.8, $C_{12}A_7$ and $C_3A$ are obtained.

Comparing figure 1 with figure 2, the phase results of clinkers with 3% and 6% of $Na_2O$ when C/A=1.7 are same to C/A=1.8. This indicates that $Na_2O$ can enter into the crystal lattice and promote the formation of $C_3A$, which, to some extent, improve the calcium aluminum ratio when C/A = 1.7.

#### 2.1.2 Effect of $Na_2O$ on the phases when C/A=1.4

$Na_2O$ can improve the calcium aluminum ratio, so when C/A=1.4, the clinkers doped $Na_2O$ are analyzed by XRD and the results are shown in figure 3.

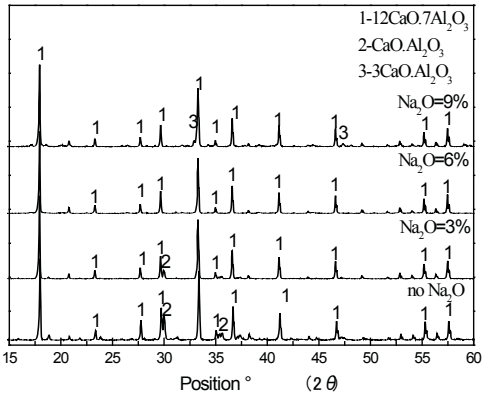


Figure 3. X-ray diffraction spectrum of clinkers with different $Na_2O$ content when C/A=1.4

In the figure, when there is no $Na_2O$ and the content of $Na_2O$ is 3%, the phases are $C_{12}A_7$ and CA. The difference is that the diffraction peaks of CA in clinkers without $Na_2O$ is higher than the ones doped 3% of $Na_2O$; when the content of $Na_2O$ increases to 6%, the phase is almost $C_{12}A_7$; When the content of $Na_2O$ is

9%, the phases are $C_{12}A_7$ and $C_3A$. There is no phase found containing $Na_2O$ with 3~9% of $Na_2O$ doped from the phase analysis results. However, there is a trend that C/A increases with the enhancement of $Na_2O$. From figure 2, $C_{12}A_7$ and CA are gained when C/A=1.4 and 1.6; When C/A=1.7, the phases are nearly all $C_{12}A_7$; when C/A=1.8, $C_{12}A_7$ and $C_3A$ are obtained. Comparing figure 2 with figure 3, the phase results with the increase of C/A are consistent with the improvement of $Na_2O$ doped, which further illustrates that $Na_2O$ can improve the calcium aluminum ratio and it to a certain extent, can ease the problem of large dosage of lime in the production of alumina. It is of great significance to the practical production of alumina.

2.2 Effect of $Na_2O$ on lattice parameters of $C_{12}A_7$

The lattice constant and unit cell volume of $C_{12}A_7$ in different clinkers are calculated by celref software with C/A = 1.4 and C/A = 1.7, as shown in table 1 and table 2. The lattice constant and the cell volume of $C_{12}A_7$ without $Na_2O$ are less than $C_{12}A_7$ standard card and the main reason is that the missing of CaO leads to volume shrinkage, spacing distance d value decreasing and lattice constant reducing; however, the lattice constant and the cell volume of $C_{12}A_7$ with $Na_2O$ are more than $C_{12}A_7$ standard card which illustrates $Na_2O$ can enter into cell gap of $C_{12}A_7$ and causes the increase of cell volume, spacing distance and lattice constant.

Table 1. Lattice parameters of $C_{12}A_7$ in clinkers doped different $Na_2O$ with C/A=1.4

| | No $Na_2O$ | $Na_2O$ =3% | $Na_2O$ =6% | $Na_2O$ =9% | $C_{12}A_7$ standard card |
|---|---|---|---|---|---|
| Lattice constant a/Å | 11.9684 | 11.9914 | 11.9932 | 11.9935 | 11.9890 |
| cell volume V/Å$^3$ | 1714.39 | 1714.29 | 1725.06 | 1725.19 | 1723.25 |

Table 2. Lattice parameters of $C_{12}A_7$ in clinkers doped different $Na_2O$ with C/A=1.7

| | No $Na_2O$ | $Na_2O$ =3% | $Na_2O$ =6% | $Na_2O$ =9% | $C_{12}A_7$ standard card |
|---|---|---|---|---|---|
| Lattice constant a/Å | 11.9744 | 12.0066 | 12.0021 | 11.9647 | 11.9890 |
| cell volume V/Å$^3$ | 1716.96 | 1730.85 | 1728.91 | 1712.80 | 1723.25 |

2.3 Effect of $Na_2O$ on alumina leaching rate of $C_{12}A_7$

Alumina leaching experiment is carried out for $Na_2O$ doped clinkers. The leaching condition is shown in section 1.3 and the leaching results are shown in figure 4 and 5.

When C/A = 1.4, the leaching rate of clinkers without $Na_2O$ is 95.90%; adding 3% of $Na_2O$, $C_{12}A_7$ is more easily synthesized and the leaching rate is 99.03%, which is improved by 3.13%. Along with the increase of the content of $Na_2O$, the leaching rate is slightly reduced. When the content of $Na_2O$ reaches 9%, the leaching rate is lower than the ones without $Na_2O$. This shows that when the content of $Na_2O$ is over a certain range, promote the synthesis of $C_{12}A_7$ and alumina leaching rate can be improved greatly; when the content of $Na_2O$ is more than 9%, promote the synthesis of $C_3A$ and alumina leaching rate is lower than the clinkers without $Na_2O$.

When C/A = 1.7, the leaching rate continues to reduce with the increase of $Na_2O$ and the main reason is the synthesis of $C_3A$ that isn't beneficial to the digestion of alumina.

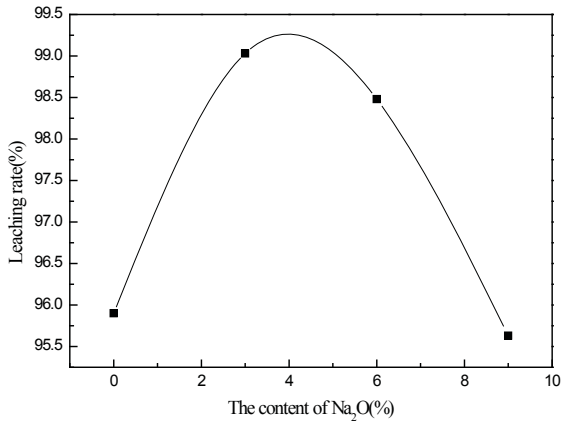


Figure 4. The alumina leaching rate of clinkers with different $Na_2O$ when C/A=1.4

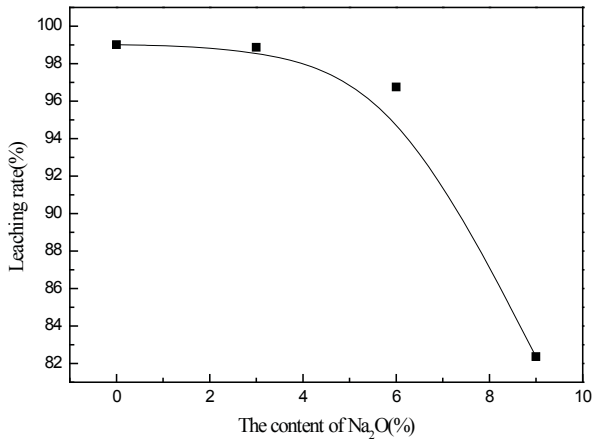


Figure 5. The alumina leaching rate of clinkers with different $Na_2O$ when C/A=1.7

**3 Conclusions**

(1) $Na_2O$ can enter into crystal lattice of $C_{12}A_7$ and form a replacement or interstitial solid solution, improving the calcium aluminum ratio.

(2) When C/A = 1.4, $Na_2O$ can occupy the position of CaO or vacancy of $C_{12}A_7$ lattice and promote the formation of $C_{12}A_7$; When C/A = 1.7, $Na_2O$ can promote the formation of $C_3A$.

(3)The lattice constant can be improved by proper $Na_2O$.

(4) When C/A = 1.4, a certain content of $Na_2O$ will, to some extent, improve alumina leaching rate; when C/A = 1.7, $Na_2O$ can decrease alumina leaching rate.

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**References**

[1] A. Shemi, et al. "Alternative Techniques for Extracting Alumina from Coal Fly Ash," Minerals Engineering, 34(2012): 30-37.

[2] Qin Jin-guo. "Technology Sevelopment on Fully Resource Utilization of High Alumina Fly Ash," Light Metals, (9)(2012): 3-7,14.(in Chinese)

[3] Qi Li-qiang, Yuan Yong-tao. "Characteristics and the Behavior in Electrostatic Precipitators of High-alumina Coal Fly Ash from the Jungar Power Plant, Inner Mongolia, China," Journal of Hazardous Materials, 192(1)(2011): 222-225.

[4] Eva Selic, Jan-Dirk Herbell. "Utilization of Fly Ash from Coal-fired Power Plants in China," Journal of Zhejiang University(Science A), 9(5)(2008): 681-687.

[5] Sun Jian-Qiu, et al., "Sol-gel Preparation of Porous $C_{12}A_7$-Cl Crystals," The Chinese Journal of Nonferrous Metals, 14(z1)(2004): 91-97.

[6] Yu Hai-yan, et al., "Effect of $Na_2O$ on Formation of Calcium Aluminates in $CaO$-$Al_2O_3$-$SiO_2$ System". Transactions of Nonferrous Metals Society of China, 22(12)(2012): 3108-3112.

[7] C.Ostrowski, J.Żelazny. "Solid Solutions of Calcium Aluminates $C_3A$, $C_{12}A_7$ and CA with Sodium Oxide," Journal of Thermal Analysis and Calorimetry, 75(3)(2004): 867-885.

[8] Wang Bo, et al., "Effect of $Na_2O$ on Alumina Leaching Property and Phase Transformation of MgO-containing Calcium Aluminate Slags" Transactions of Nonferrous Metals Society of China, 21(12)(2011): 2752-2757.

[9] Sun Hui-lan, et al., "Effect of $Na_2O$ on Alumina Leaching and Self-disintegrating Property of Calcium Aluminate Slag," Light Metals,(2010):29-32.

[10] Ren Sun-xia, Dan Yang. "Application of Sol-gel Methods to Preparation of Nano-structured Particles," China Powder Science and Technology, (1)(2006): 48-50.

[11] Sun Jian-qiu, et al., "Sol-gel Preparation of Porous $C_{12}A_7$-Cl Crystals," Acta Physico-Chimica Sinica, (03)(2010): 795-798.

[12] Dietmar Stephan, Sebastian Wistuba. "Crystal Structure Refinement and Hydration Behaviour of Doped Tricalcium Aluminate," Cement and Concrete Research, 36(11)(2006): 2011-2020.