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Manufacturing properties of γ-dicalcium silicate with synthetic method

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γ-dicalcium silicate(γ-C_2S) is known as a polymorphism of belite. Due to its high CO_2 fixed capacity and the low CO_2 emission production process, γ-C_2S has attracted more and more attention of researchers. For the further development of application ofγ-C_2S in building construction industry. In this study, we aim to investigate the method for synthesizing high purity of γ-C_2S. The influence of different raw materials and calcination temperatures on the purity of γ-C_2S was also evaluated. Several Ca bearing materials were selected as the calcium source, the materials which' s main component is SiO_2 were used as the silicon source. Raw materials were mixed and were calcined under different temperatures. The results reveal that the highest purity could be obtained using $Ca(OH)_2$ and SiO_2 powder as raw materials. And for the practical application, a relatively economic synthesis method using natural mineral materials- limestone and silica sand as raw materials was developed, by this method, the purity of the synthetic γ-C_2S was 77.6%.

Keyword: **Steel; γ-dicalcium silicate, Carbonation, CO_2 capture**

Introduction

Although olivine group mineral γ-C_2S has a poor hydration performance, it has a strong CO_2 fixation performance, which has attracted the attention of many researchers in recent years [1-4]. In the presence of water, γ-C_2S can react quickly with CO_2 to produce $CaCO_3$ and SiO_2 gel [5-8]. In recent years, researchers have developed fast, hard and high-strength materials by utilizing the rapid reaction of γ-C_2S with CO_2 and the cementitious ability of carbonation products, taking γ-C_2S as the main component by using the carbonization curing method. Besides, Higuchi et al. [9] added fly ash and γ-C_2S as main materials to concrete and developed a new type of concrete called CO_2-SUICOM. This new type of concrete is maintained in the exhaust treatment room full of exhaust gas at power plant, with a concentration of 15%-20%. After 28 days of curing, the strength of CO_2-SUICOM reached 21 N/mm^2, which was close to or even higher than OPC concrete. Guan et al. [4] studied that the mortar test block made with γ-C_2S could reach 60 MPa of strength within 5 hours after high-concentration of CO_2 curing. Meanwhile, the amount of CO_2 released by γ-C_2S in the manufacturing process is lower than OPC. The application of γ-C_2S was convinced to have a relatively good prospect as it could reduce low CO_2 emission compared to OPC.

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Synthetic Methods of γ-C_2S

C_2S has five crystal form, which are α, αH', αL', β and γ. For pure C_2S, crystal form of α-C_2S, αH'-C_2S, αL'-C_2S and β-C_2S can's exit steadily in constant temperature?with the trend of transforming towards γ-C_2S[10]. Therefore, γ-C_2S can be produced according to the polymorphs conversion mechanism between various crystal forms of C_2S. The polymorphs of C_2S and conversion relationship were shown in Fig. 1. Appropriate Ca ion supply material and Si supply material powder are selected and mixed in a certain proportion. Then, the mix was heated to a desired temperature to form a relatively unstable α-C_2S. Next, α-C_2S was slowly converted to γ-C_2S as it was cooled at a room temperature. Theoretically, the density of β-C_2S is 3.05 whereas γ-C_2S is 2.97 [11-12]. Therefore, in the process of transformation from β-C_2S to γ-C_2S, the volume of cement clinker ball will expand and then pulverize, which is known as "dusting phenomenon" [14-15]. Thus, the grinding energy consumption in the manufacturing process can be reduced [1].

Kriskova et al. [15] used analytical grade $CaCO_3$ and SiO_2 powder to calcine at 1450 °C for 20 hours, with a cooling speed of 1 °C/ min. The content of γ-C_2S and β-C_2S of synthetic sample is 88 ± 4% and 12 ± 4%, respectively. Liu et al. [16] mixed analytical grade $CaCO_3$ and SiO_2 powder and calcined at 1350 °C. In the synthetic samples, γ-C_2S is the dominant crystal form. Mu et al. [17] used pure $Ca(OH)_2$ and SiO_2 to be

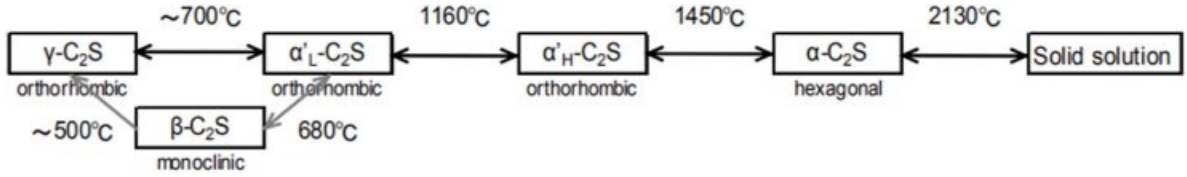

Fig. 1. Polymorphs of Dicalcium Silicate.

calcined at 1100 °C, 1200 °C, 1300 °C and 1400 °C in a mole ratio of 2:1. Results show that γ-C_2S becomes the primary component under 1300 °C, and γ-C_2S's purity can be maximized when samples were calcined under 1400 °C. It can be seen that pure chemical reagents are recommended to use with a minimum temperature of 1300 °C to achieve a higher purity.

Higuchi et al. [9] mixed SiO_2 powder with an industrial by-product powder which is $Ca(OH)_2$. After calcined at 1450 °C, the content of γ-C_2S and β-C_2S is 93.7% and 1.4%, respectively. The CO_2 emission of γ-C_2S synthesized was about 1/5 of the OPC. Guan et al. [4] used limestone and shale powder as raw materials, added a certain amount of water and molded under pressure. The samples were calcined under 1300 °C with a 95% of C_2S. Japan which has carried out relevant researches earlier has entered into the stage of mass production. Previous researchers [18] take industrial materials by-products and calcined in rotary kiln for mass production.

In this study, the influence of different materials and calcining temperatures on the purity of γ-C_2S was investigated. For the practical purposes of γ-C_2S, a relatively economic synthesis method using nature mineral materials is conducted.

γ-C_2S Synthesis Experiment

In order to investigate the effect of different raw materials on purity of γ-C_2S, analytical grade CaO powder, $Ca(OH)_2$ powder and $CaCO_3$ powder were selected to provide Ca ions. Analytical grade SiO_2 powder was used as the source of Si ions. Next, both of the ions were mixed properly with Ca/Si ratio of 2:1. The schematic diagram of calcination process was shown in Fig. 2. The rate of temperature was set at 10 °C/min, and then temperature was maintained at 1450 °C. After calcination, samples were cooled at room temperature. Then, the S1 sample synthesized by using CaO powder and SiO_2 powder, S2 synthesized by using $Ca(OH)_2$ powder and SiO_2 powder, and S3 synthesized by using $CaCO_3$ powder and SiO_2 powder, samples of γ-C_2S are obtained respectively. The analytical grade chemical reagent are manufactured by Deajung chemicals & materials co., ltd, Korea. The purity of CaO powder, $Ca(OH)_2$ powder and $CaCO_3$ powder is above 97%, 95% and 98% respectively. SiO_2 powder is extra pure. The composition of synthetic γ-C_2S samples was detected by Q-XRD.

$CaCO_3$ has a relatively lower value than $Ca(OH)_2$. In order to improve the economic efficiency of γ-C_2S in practical applications, it attempted to improve the purity of synthetic γ-C_2S in laboratory of Ssangyong cement industrial co., ltd. Analytical grade of $CaCO_3$ and SiO_2 powder were used as raw materials. The Ca/Si ratio was selected at 1.86. A certain amount of water is added to the mixed powder to transform it into a sphere. Then, the samples were calcined in a furnace. After the samples were heated at 900 °C with a temperature increase rate of 10 °C/min for 1 hour, the samples were continuously heated till up to 1450 °C, and temperature was maintained at 1450 °C for 1 hour. After cooling process, the synthetic sample- S4 was obtained. The schematic diagram of synthesis process of S4 is shown in Fig. 3. The composition of S4 was detected by Q-XRD and XRF.

As synthesis of γ-C_2S using pure chemical reagents is expensive and not conducive to mass production and practical application. Natural minerals was used as raw materials. The high purity limestone powder and silica sand powder were used and mixed with Ca/Si ratio of 1.86. Chemical composition of limestone powder and silica sand powder were shown in Table. 1 and Table. 2, respectively.

After it was added with 10% of water, the mix was pressed into the cylinder mold and dried for 3 h at 100 °C. Then, 3 groups of cylindrical samples were put in a furnace at 900 °C with a rate of 10 °C/min for 1 hour. Then, the samples were continuously heating at 1200 °C, 1300 °C, and 1400 °C of temperature for 1.5

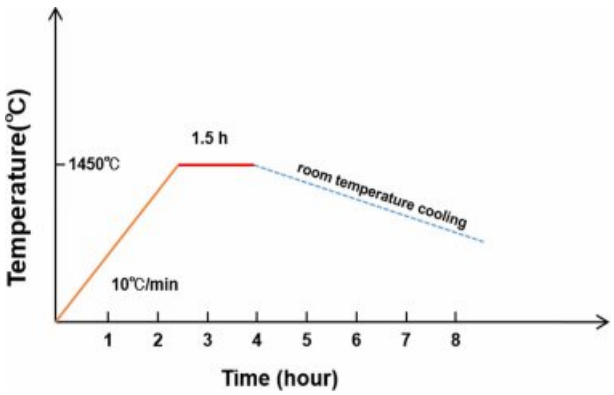

Fig. 2. The schematic diagram of calcination process of S1, S2, and S3.

Fig. 3. Synthesis process of S4.

Table 1. The chemical composition of limestone powder

CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	K_2O	SO_3	P_2O_5
54.29	0.69	1.50	0.30	1.11	0.08	0.02	0.02

Table 2. The chemical composition of silica sand powder

CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	K_2O	SO_3	P_2O_3
0.15	10.21	80.49	1.94	0.19	2.66	0.32	0.21

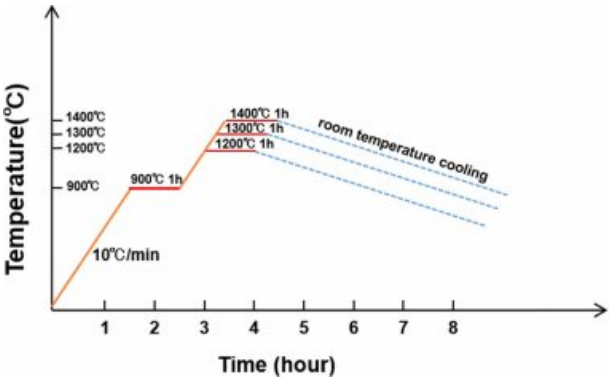

Fig. 4. The schematic diagram of calcination process of S5, S6, and S7.

hour, and after cooling process, S5, S6, and S7 were obtained, respectively. The schematic diagram of synthesis process of synthetic samples using nature materials is shown in Fig. 4. The composition of S5, S6, and S7 was detected by Q-XRD.

Result and Discussion

The purity of synthesis γ-C_2S samples are shown in Table. 3. For the S1, S2, S3, result shows that under the same experimental conditions, maximum purity of γ-C_2S samples synthesized by using $Ca(OH)_2$ powder is 94.9%. Besides, samples synthesized by using $CaCO_3$ powder shows a relatively high purity which is 77.7%. Synthetic samples using CaO powder has the lowest purity, which is caused by the low activity of CaO.

The purity of synthetic γ-C_2S sample- S4 by using $CaCO_3$ powder is 90.4%. Comparing with the S3, although the calcination temperature was deceased, the purity was improved. This was due to the Ca/SiO ratio which is 1.86 that controlled the formation of free CaO. In additional, the presence of water reduced the distance between the powder particles and increase the contact area. Furthermore, calcining at 900 °C for 1 hour made the $CaCO_3$ powder to be fully decarbonized then the synthesis reaction was enhanced.

For the synthetic samples using limestone and silica sand powders -S5, S6 and S7, with the increase of temperature, the formation of high purity γ-C_2S was improved which can enhanced the reaction degree. The purity of γ-C_2S synthesized at 1400 °C is 77.6% which is the highest. Besides, γ-C_2S synthesized at 1200 °C contains a large number of impurities such as unreacted CaO with a main product of β-C_2S. The purity of samples synthesized at 1300 °C temperature is 69.1%. From the perspective of economy, it is more suitable for practical application.

Table 3. Purity of synthesis γ-C_2S samples by using analytical grade materials (wei. %).

Sample	Raw materials	Calcination temperature	Purity of synthesis γ-C_2S sample
S1	analytical grade CaO and SiO_2 powder	1450 ºC for 1.5 h	65.4
S2	analytical grade $Ca(OH)_2$ and SiO_2 powder	1450 ºC for 1.5 h	94.9
S3	analytical grade $CaCO_3$ and SiO_2 powder	1450 ºC for 1.5 h	77.7
S4	analytical grade $CaCO_3$ and SiO_2 powder	Step 1 : 900 ºC for 1 h Step 2 : 1450 ºC for 1 h	90.4
S5	limestone powder and silica sand powder	Step 1 : 900 ºC for 1 h Step 2 : 1200 ºC for 1 h	< 20
S6	limestone powder and silica sand powder	Step 1 : 900 ºC for 1 h Step 2 : 1300 ºC for 1 h	61.9
S7	limestone powder and silica sand powder	Step 1 : 900 ºC for 1 h Step 2 : 1400 ºC for 1 h	77.6

Conclusions

In this study, the influence of different materials and synthetic methods on the purity of γ-C_2S was explored. The main conclusions are as follow:

Under laboratory conditions, synthesize γ-C_2S by using $Ca(OH)_2$ as calcium resource can obtain synthetic γ-C_2S with the highest purity.

Selecting Ca/Si ratio at 1.86, addition of water and fully decarbonization can enhance the purity of synthetic γ-C_2S by using $CaCO_3$ powders.

Using natural mineral materials and heat at relatively high temperature can obtain γ-C_2S with relativity high purity. This synthesis method using the economical materials as raw materials which provided an idea for mass amount manufacturing of γ-C_2S, and prepared the conditions for future practical applications.

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