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CO_2 Adsorption Reactions of Synthetic Calcium Aluminum Ferrite (CAF)

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Abstract: In this study, we investigated a mechanism of carbonation reaction by CO_2 capture through synthesis of ternary (CaO-Al_2O_3-Fe_2O_3) compounds. As for the composition of the sintered calcium aluminum ferrite (SCAF), the proportions of CF-based product and CA-based product were high, at 87.3% and 64.6%, at sintering temperatures of 1000 °C and 1100 °C, respectively. In addition, in the process of both dry and wet carbonation, the carbonation reaction occurred in the synthetic SCAF regardless of the sintering temperature conditions. In particular, in the carbonation with the wet method, CAH and CAFH, which are hydrates, were produced in up to 1 h of the reaction time with CO_2, but from 3 h of reaction time, carbo compounds such as calcium carbo aluminate and calcium carbo alumino-ferrite compounds were produced. That is, with increasing reaction time, the carbo reaction becomes more active in the process. Therefore, SCAF synthesized in this study easily produced carbo compounds through carbonation reactions and formed carbonates by reaction with CO_2. Thus, it is expected that the compounds can be effectively utilized as an excellent material for CO_2 capture capable of CO_2 absorption and fixation.

Keywords: calcium aluminum ferrite; carbonation reaction; CO_2 capture

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1. Introduction

The processes of manufacturing, production, installation, and utilization of construction materials are energy intensive and use fossil fuels in most cases, and thus the construction materials sector has been classified as a typical carbon-generating sector [1,2]. Therefore, in order to curtail the energy consumption and reduce CO_2 emissions in the construction materials sector, technology development that can fundamentally address the problem of embodied carbon in the industry is required, such as improving the manufacturing process of the materials or increasing the use of alternative materials. In particular, there is a pressing need for technology development in terms of effective measures for reducing energy consumption as well as for CO_2 absorption and reduction [3]. As an alternative material to ordinary Portland cement (OPC), aimed at reduced energy consumption in the construction materials industry, granulated blast furnace slag or fly ash has been actively used, but their usage and scope of application are highly limited in practice [4]. Therefore, in addition to the efforts of CO_2 reduction by employing alternative materials or partial replacement of OPC, utilization of CO_2 capture-type materials is necessary in order to implement the principle of "Net-Zero" in the industry. Calcium aluminum ferrite (C_4AF), one of the cement clinkers, undergoes a phase change at a sintering temperature range of 700 to 1200 °C [5,6]. The phases range in composition from $2CaO{\cdot}Fe_2O_3$, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, and $6CaO{\cdot}2Al_2O_3{\cdot}Fe_2O_3$. These compounds exist as unstable solid solution series and upon cooling, they are converted to ferrite phase, which forms a more stable state [7]. There are two series of the hydrated $CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, a ternary material: one is the garnet-hydrogarnet series, which may also be referred to as the C_3AH_6-C_3FH_6 series, and this series crystallizes in the cubic system. The other is the C_4AHn-C_4FHn series, and this forms a hexagonal system. According to Equation (1), possible reactions include hydration by H_2O and the carbonation reaction by CO or CO_2. Diffusion of impurities is one of the most important phenomena in material science and understanding the diffusion profile of CO_2 into the hardened body of the ternary compound $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$ draws much research interest, with significant implications for applications. In the ternary system of $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$, a strong carbonation reaction is observed in a certain range of chemical concentrations, which allows adsorption and fixation of CO_2. Therefore, by analyzing the carbo reaction mechanism of the synthetic ternary compound $CaO\text{-}Al_2O_3\text{-}Fe_2O_3$, the applicability of the material as an OPC alternative or replacement is investigated, as well as its performance in CO_2 adsorption and reducing energy consumption and CO_2 emissions, which is expected to contribute to establishing the theory for CO_2 capture in the construction materials industry.

$$\begin{gathered}4CaO + Al_2O_3 \rightarrow 4CaO{\cdot}Al_2O_3 + CO_2 \rightarrow Ca_4Al_2O_6{\cdot}CO_3 \\ 4CaO + Fe_2O_3 \rightarrow 4CaO{\cdot}Fe_2O_3 + CO_2 \rightarrow Ca_4Fe_2O_6{\cdot}CO_3 \\ 4CaO + Al_2O_3 + Fe_2O_3 \rightarrow 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3 + CO_2 \rightarrow Ca_4Al_2Fe_2O_9{\cdot}CO_3\end{gathered} \tag{1}$$

2. Experiment

2.1. Materials

As for the materials used for synthesis of the calcium aluminum ferrite (CAF) compound, calcium oxide (CaO, CAS, Goryeong-gun, Korea; 1305-78-8), aluminum oxide (Al_2O_3, CAS; 1344-28-1), and iron(III) oxide (Fe_2O_3, CAS; 1309-37-1), all of which are of reagent grade, were used, and all samples were dried in a vacuum oven at 105 °C for 24 h to remove moisture contained in the samples.

2.2. Method

2.2.1. Sintering

For investigation of the carbo reaction, the CAF compound was synthesized as follows. For firing of CAF, a fixed ratio of $CaO{:}Al_2O_3{:}Fe_2O_3 = 3{:}1{:}1$ mole was used, and firing of the materials was carried out at the temperature of 1000 °C and 1100 °C, respectively. Figure 1 presents the conditions and methods for firing of CAF compounds. As for the firing temperature (1000 °C, 1100 °C), the materials were fired for 2 h at each temperature with the heating rate at 5 °C/min, followed by furnace cooling. Dry mixing was carried out for 3 min according to the mole ratio of each sample, and then the mixed powder was diluted 10-fold in ethyl alcohol and mixed with a wet method in two steps. In step 1, mixing was performed twice at 1000 rpm for 5 min each, using a vortex mixer (Genius 3, IKA, Staufen, Germany), and in step 2, using an ultrasonic homogenizer (VCX750, Sonics, Newtown, CT, USA), mixing and dispersion of the samples were performed for 10 min. The samples in the slurry state were dried at 60 °C for 24 h in a dry oven, crushed using a ball mill, and sieved with a 100-mesh screen. Then, the samples were pressurized at 50 MPa in a 20 ø disc mold to form pellets. After firing the formed pellet samples at 1000 °C and 1100 °C for 2 h, respectively, followed by furnace cooling, the samples were taken out at ~60 °C, placed into a desiccator, and cooled to room temperature. Then, the samples were crushed using a ball mill for use in testing of material properties. To analyze the crystalline phases of the final synthesized samples, an X-ray Diffractometer (XRD; Rigaku, D/Max-2500V, Tokyo, Japan; scan range: 5~80°; acc. vol.: 40 kV, 200 mA; scan speed: 2°/min; target: Cu) was used for quantitative elemental analysis (5°/min).

2.2.2. Carbonation

The carbonation experiments were conducted in two methods: a gas–solid reaction (dry method) with direct reaction between sintered calcium aluminum ferrite (SCAF) powder with CO_2, and a gas–liquid reaction (wet method) in which SCAF powder is dispersed in water (binder: water = 1:1) to form a slurry state, and the slurry-state SCAF is reacted with CO_2. The concentration of CO_2 gas was maintained at 5% in the chamber, and the reaction time was varied from 30 min, 1 h, 3 h, up to 6 h.

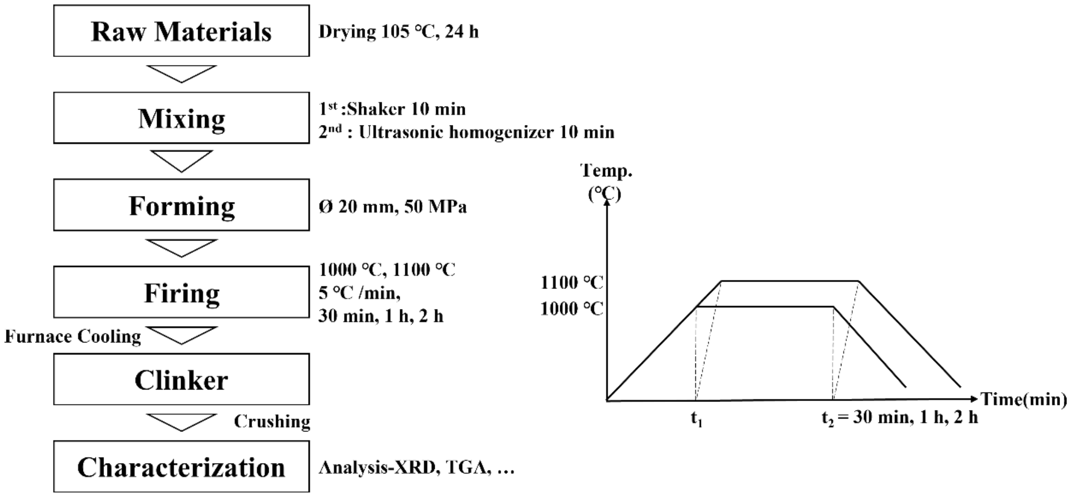


Figure 1. Schematic diagram of experimental procedures.

To examine the calcium carbonation reaction, XRD (X-ray Diffractometer; Rigaku, D/Max-2500V, Japan; scan range: 5~80°; acc. vol.: 40 kV, 200 mA; scan speed: 2°/min; target: Cu) analysis was used for quantitative determination of crystalline phases. In addition, for image analysis of the CO_2 reaction products, samples were applied with Pt (platinum) coating using a plasma spray, and a Field Emission Scanning Electron Microscope (FE-SEM; JEOL, JSM-6701F, Tokyo, Japan) was used. Thermogravimetry/differential thermal analysis (TG-DTA) was performed using a thermal analyzer (STA409PC Luxx, Selb, Netzsch, Germany) under the conditions of heating rate at 10 °C/min from room temperature to a maximum temperature of 1000 °C, and a nitrogen (N_2) atmosphere.

3. Result and Discussion

3.1. Characterization of the Synthetic SCAF

The study compound, SCAF, was synthesized according to the chemical equivalent ratio of each oxide, and characterization of the material was performed. Figure 2 shows the analysis results of crystalline phases of the SCAF compound according to the sintering temperature (1000 °C, 1100 °C).

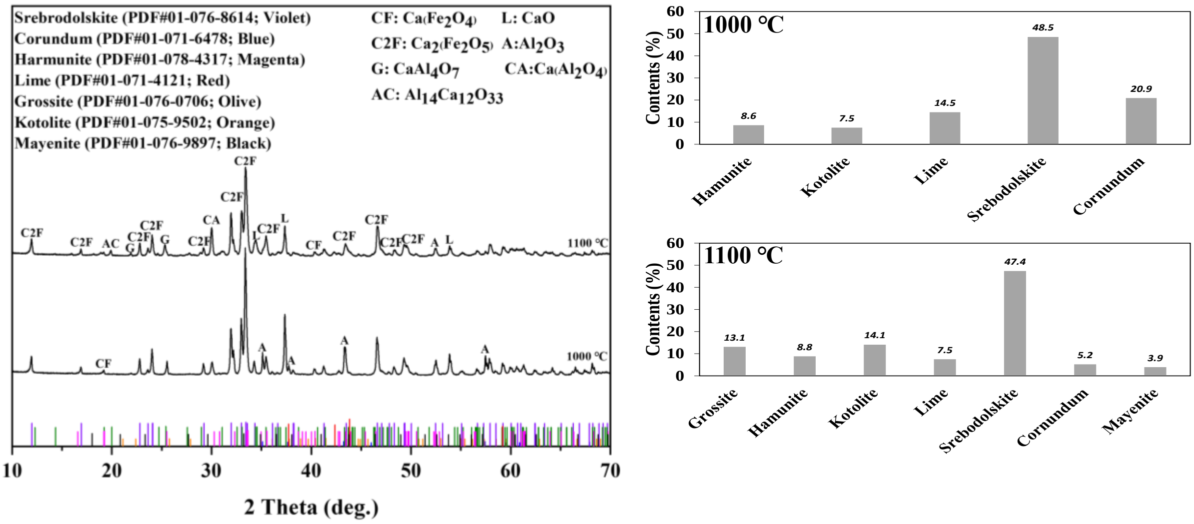


Figure 2. XRD patterns of CAF sintered at 1000 °C and 1100 °C.

After firing at 1000 °C, the composition of the products was as follows: the content of CF-based compounds was 57.1 wt.%, that of corundum was 20.9 wt.%, and the content of lime was 14.5 wt.%. As for the products after firing at 1100 °C, the content of CF-based compounds was 56.2 wt.%, and with lime and corundum were 7.5 wt.% and 5.2 wt.%, respectively.

The major difference between the two sintering temperatures is that in the case of sintering temperature at 1100 °C, 17.0 wt.% of grossite ($CaAl_4O_7$; PDF#01-076-0706) and mayenite ($Al_{14}Ca_{12}O_{33}$; PDF#01-076-9897), which are calcium-aluminum-based compounds, were produced. In the case of calcium aluminum oxide, the content was 7.5 wt.% at 1000 °C and 14.1 wt.% at 1100 °C. As a result of Rietveld-XRD analysis, at a sintering temperature of 1100 °C, CF- and CA-based compounds accounted for the highest proportion (about 87.3%) of the composition of the sintered products. At 1000 °C, the total products consisting of CF- and CA-based compounds was only 64.6%. That is, it can be seen that in the case of firing of CF/CA-based compounds, less of the residual amounts of lime and corundum, the unreacted components, were observed at the sintering temperature of 1100 °C compared to the temperature at 1000 °C.

3.2. Characteristics of Carbo Reaction of SCAF

3.2.1. Analysis of Thermal Properties by Carbo Reaction of SCAF

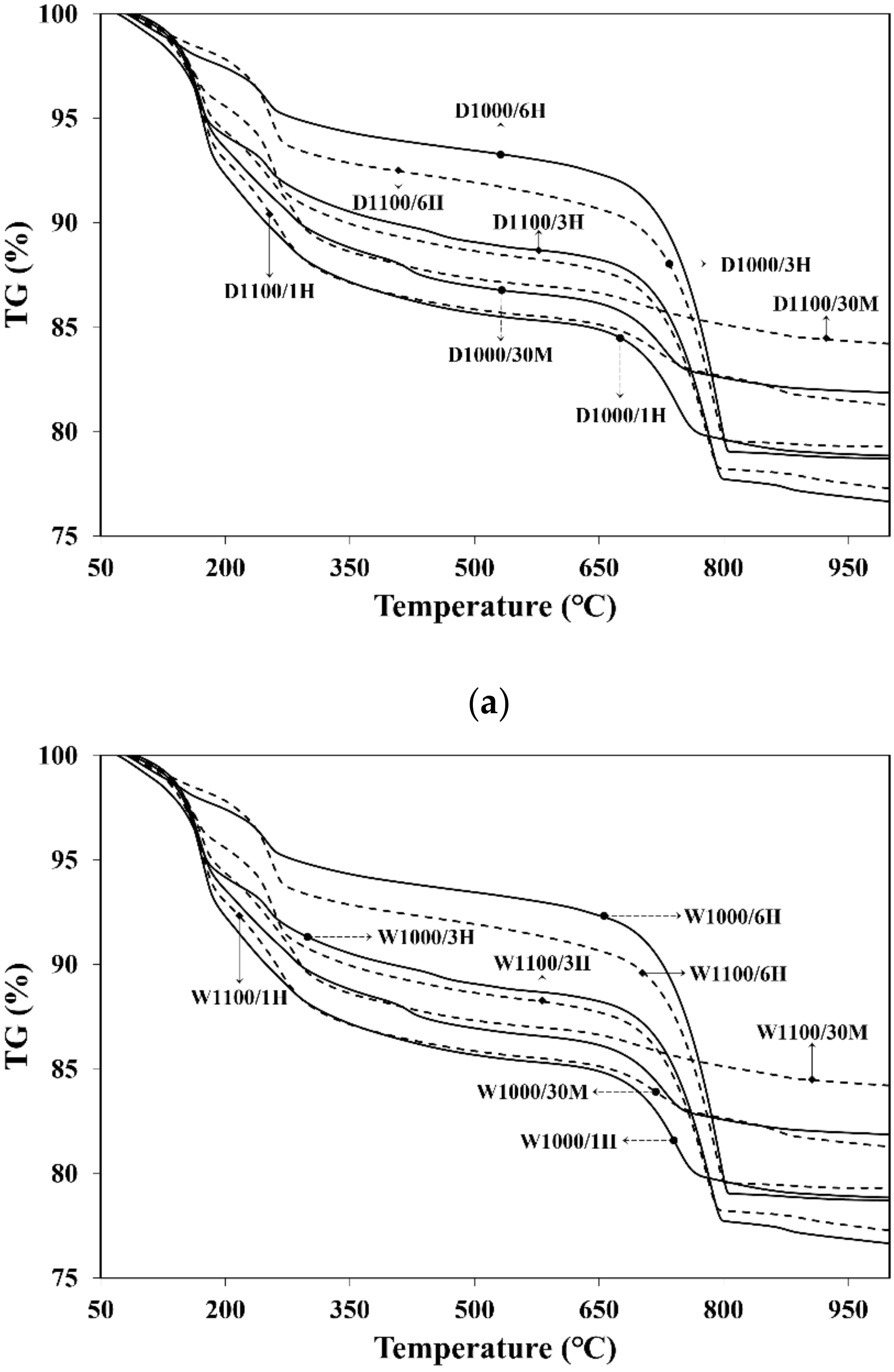
In order to investigate the reactivity of SCAF with CO_2, carbonation was conducted in two methods: a gas–solid reaction (dry method) with direct reaction between SCAF powder and CO_2, and a gas–liquid reaction (wet method) in which SCAF powder is dispersed in water (binder:water = 1:1) to form a slurry state and is reacted with CO_2. The absorption reaction time was set to 30 min, 1 h, 3 h, and 6 h, with the sampling carried out in line with the set time. In addition, thermogravimetry analysis (TGA) was performed to determine the amount of CO_2 adsorption with the reaction time. Figure 3 shows the results of thermogravimetric analysis of SCAF with different reaction times and sintering temperatures.

The results of thermogravimetric analysis can be divided into three temperature sections, and Table 1 outlines the weight loss for each section by sintering temperature. The first section shows a weight reduction due to decomposition of water, and the second section is judged to be a weight loss due to $Ca(OH)_2$. The final section shows the weight loss due to the decomposition of calcite at 700–900 °C, which is considered to be a typical characteristic of thermal decomposition of calcite produced by the reaction between SCAF and CO_2 [8,9].

Table 1. The weight lost (wt.%) with reaction time.

		1000 °C			1100 °C		
Reaction Time	**Method**	**1st Section 100~200 °C**	**2nd Section 350~500 °C**	**3rd Section 600~900 °C**	**1st Section 100~200 °C**	**2nd Section 350~500 °C**	**3rd Section 600~900 °C**
30 min	D	0.56	0.24	0.05	0.54	0.38	0.11
	W	12.22	1.81	5.22	6.32	7.27	2.82
1 h	D	0.41	0.37	0.04	0.36	0.52	0.19
	W	8.69	6.56	6.51	7.89	7.14	4.28
3 h	D	0.47	0.22	0.18	0.40	0.54	0.22
	W	6.86	5.03	12.03	4.97	7.34	11.01
6 h	D	0.43	0.47	0.02	0.37	0.93	0.02
	W	6.89	1.33	13.67	2.27	6.12	12.93

Figure 4 shows the content of calcite ($CaCO_3$) as a percentage based on the CO_2 reaction time. It can be seen that the generation of calcite increases with elapse of the reaction time, and as for the CO_2 reactivity, as shown in the XRD analysis result, more calcite generation is observed at a sintering temperature of 1000 °C than of 1100 °C. This is thought to be due to unreacted lime, in which the reaction of the unreacted CaO with CO_2 led to more calcite formation [9,10].



(**a**)

(**b**)

Figure 3. TGA carves of carbonation with (**a**) dry method and (**b**) wet method.

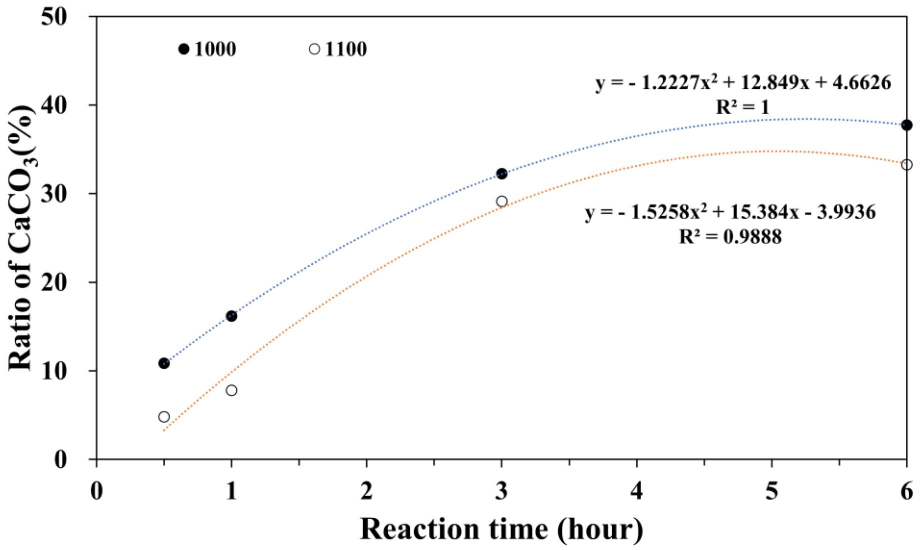
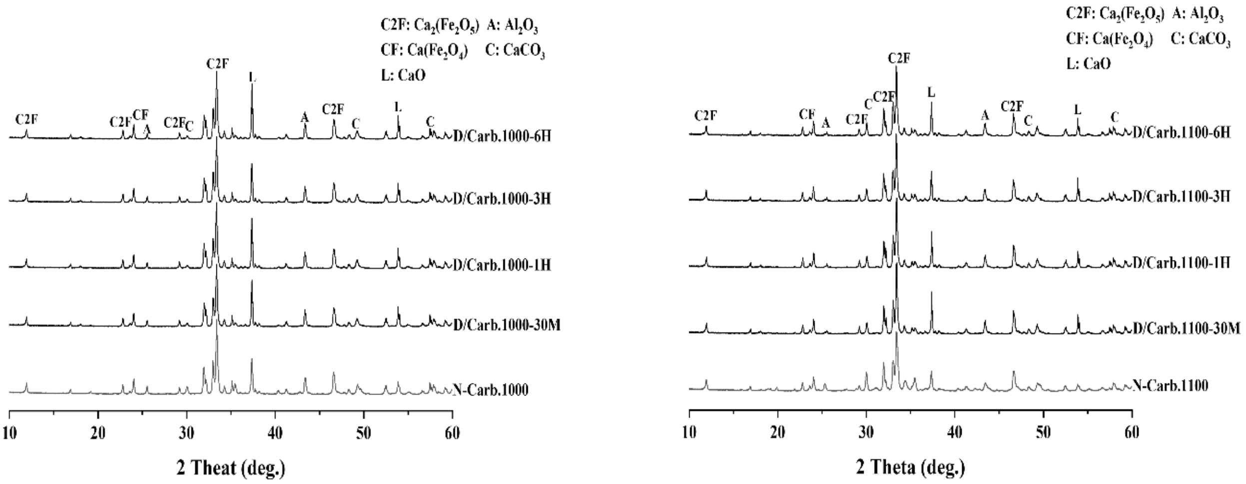


Figure 4. Calcite generation based on reaction time.

3.2.2. Analysis of Crystalline Phase for Carbo Reaction of SCAF

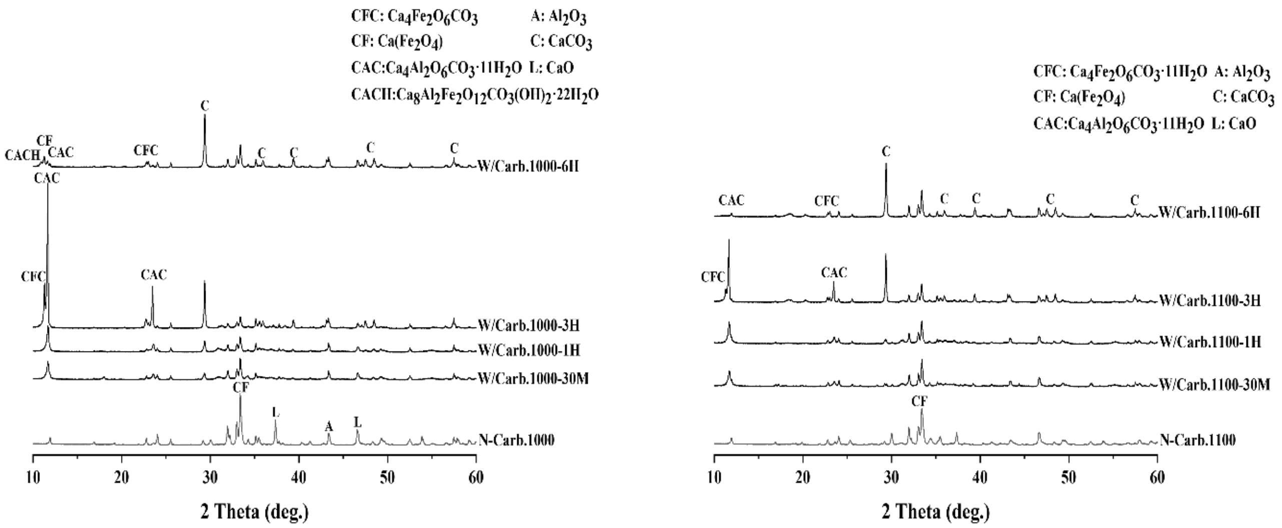
Figures 5 and 6 show the crystalline phases of SCAF formed with different carbonation reaction times and methods. In the case of carbonation with the dry method, the XRD peak pattens of the crystalline compounds produced by the carbo reaction show no significant differences with respect to the reaction time, irrespective of the sintering temperature.

On the other hand, in the case of carbonation of SCAF with the wet method, in addition to the formation of new products, there are differences in terms of peak intensity compared to the products of carbonation with the dry method, and regardless of the sintering temperature of SCAF, after 3 h of carbonation reaction time, formation of a large amount of hydrates can be seen due to the reaction of CAF compound with CO_2. The products of the carbonation reaction include CAC($Ca_4Al_2O_6CO_3{\cdot}11H_2O$) and CACH($Ca_4Al_2O_6CO_3{\cdot}11H_2O$), which are calcium carbo aluminate compounds, and CAFC($Ca_4A_{12}Fe_2O_{12}CO_3(OH)_2{\cdot}22H_2O$), which is a calcium carbo alumino-ferrite compound. In particular, a strong peak intensity is observed at 3 h of the carbonation reaction, and at 6 h, the peak of the calcite gradually increases, and it can also be observed that the peaks of CAC and CFC crystalline compounds, which are calcium carbo compounds, increase with the reaction time [11,12].



(**a**) (**b**)

Figure 5. XRD patterns for carbonation with dry method. (**a**) 1000 °C; (**b**) 1100 °C.



(**a**) (**b**)

Figure 6. XRD patterns carbonation with wet method. (**a**) 1000 °C; (**b**) 1100 °C.

Therefore, it can be seen that SCAF reacts with CO_2 to produce calcite and calcium carbo aluminate and/or calcium carbo ferrite compounds, and the carbo reaction becomes more active over reaction time.

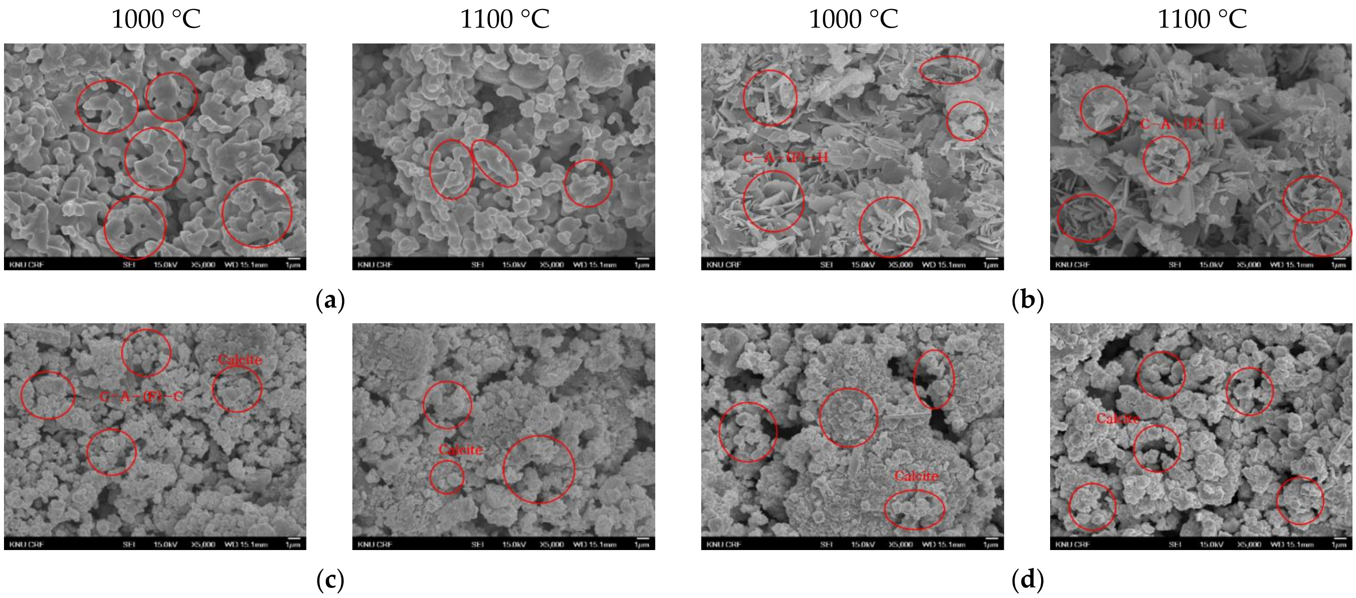
3.2.3. Image Analysis of SCAF

Figure 7 shows the results of the SEM analysis according to the carbonation reaction time and sintering temperature. As a result of the analysis of SCAF compounds fired at sintering temperatures of 1000 °C and 1100 °C, (a) is the CAF compound in the powder state before hydration, and (b), (c), and (d) show the state of hydrates after reaction times of 1 h, 3 h, and 6 h of carbonation with the wet method. In the case of (a), the synthetic CAF compound in the powder state before hydration, a typical crystal state of CAF compound is observed in glassy form. However, in (b), the crystal after 1 h of hydration, a needle shape is observed, but also the crystals of calcium aluminate hydrate (C-A-H) and calcium aluminate-ferrite hydrate in a plate shape can be seen. In the case of (c), which is hydrate after 3 h of hydration with the transition to calcium carbo aluminate (CAC) compounds, calcium carbo ferrite (CFC) compounds, and $CaCO_3$ crystals, the hexahydrate is observed [13]. The same pattern can be seen in (d), the result after 6 h of hydration, and a large amount of $CaCO_3$ crystals can be observed.

On the other hand, the results of SCAF fired at 1100 °C were similar to those of SCAF fired at 1000 °C. In the synthesis of SCAF, conditions of sintering temperature of 1000 °C or 1100 °C are considered to not be significant in the production of compounds.

In the case of carbonation with the wet method, CAH and CAFH, the hydrates, were formed up to the reaction time of 1 h, but after 3 h of reaction time, carbo compounds, which are calcium carbo aluminate and calcium carbo alumino-ferrite compounds, were produced by carbonation.

The calcium aluminate ferrite compound ($4CaO\ Al_2O_3 \cdot Fe_2O_3$-$C_4AF$), one of the representative clinker minerals in the cement industry, is the interstitial phase and accounts for about 10% of cement composition. When Fe_2O_3 is added to the CaO-Al_2O_3 system to form the ternary system of CaO-Al_2O_3-Fe_2O_3, C2F is first generated around the temperature of 800 °C, and Al_2O_3 is combined at 1100 to 1200 °C to form C_4AF. As such, the calcium aluminate ferrite compound is formed at a temperature lower than the cement sintering temperature of 1450 °C. If the SCAF compound, the synthetic product of this study, is synthesized at 1000 °C or 1100 °C and then used as partial replacement of the OPC clinker, an energy-saving effect can be expected because the material is fired at a temperature lower than the cement sintering temperature by the amount of SCAF replacement. Furthermore, the SCAF compound with CO_2 capture performance can be utilized to implement the effect of CO_2 capture when used as an OPC clinker replacement.



(**a**)

(**b**)

(**c**)

(**d**)

Figure 7. Scanning electron micrographs (×5000) of carbonation sintered at 1000 °C and 1100 °C. (**a**) OH; (**b**) 1H; (**c**) 3H; (**d**) 6H.

4. Conclusions

In order to investigate the carbonation reaction, SCAF was synthesized in this study with a ternary system of CaO-Al_2O_3-Fe_2O_3, and the mechanism of the carbonation reaction of SCAF was analyzed.

(1) As a result of Rietveld-XRD analysis by firing CAF compounds at sintering temperatures of 1000 °C and 1100 °C, CF- and CA-based products (about 87.3%) accounted for the major proportion at 1100 °C, and at 1000 °C, CF- and CA-based products accounted for 64.6% in total.

(2) In the carbonation of SCAF with the wet method, the peak intensity of the products by carbonation was larger than that in the dry carbonation, and regardless of the synthesis temperature of the CAF compound, from 3 h of the reaction time, as hydration products from reactions of the CAF compound with CO_2, formation of CAC($Ca_4Al_2O_6CO_3 \cdot 11H_2O$) and CACH($Ca_4Al_2O_6CO_3 \cdot 11H_2O$), which are the calcium carbo aluminate compounds, and CFC($Ca_4Al_2Fe_2O_{12}CO_3(OH)_2 \cdot 22H_2O$), the calcium carbo alumino-ferrite compound, was confirmed.

(3) In the case of carbonation with the wet method, CAH and CAFH, which are hydrates, are produced in up to 1 h of reaction time, but from 3 h of reaction time, calcium carbo aluminate and calcium carbo alumino-ferrite compounds, which are carbo compounds, are formed by carbonation.

(4) Irrespective of the SCAF synthesis temperature, SCAF reacts with CO_2 to produce calcite and calcium carbo compounds, and the carbonation reaction becomes more active over time.

Therefore, it is expected that the SCAF compound synthesized in this study can be utilized as an excellent material for CO_2 capture capable of absorption and fixation of CO_2, because with the material, carbo compounds are easily formed by the carbonation reaction and carbonate is produced by reaction with CO_2.

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