

Carbonation Behavior of Pure Cement Hydrates under Supercritical Carbon Dioxide Conditions – 12199

Daisuke Hirabayashi^{*}, Kayo Sawada^{**}, Youichi Enokida^{*},
Audrey Hertz^{***}, Fabien Frizon^{****}, Frédéric Charton^{***} and Fournel Brouno^{*****}

^{*} Graduate School of Engineering, Nagoya University, 1 Furo-cho, Chikusa-ku, Nagoya-shi, Aichi-ken, 464-8603, Japan

^{**} EcoTopia Science Institute, Nagoya University, 1 Furo-cho, Chikusa-ku, Nagoya-shi, Aichi-ken, 464-8603, Japan

^{***} CEA, DEN, Marcoule, DTCD/SPDE/L2ED, BP 17171, F-30207 Bagnols-sur-Ceze, France

^{****} CEA, DEN, Marcoule, DTCD/SPDE/LFSM, BP 17171, F-30207 Bagnols-sur-Ceze, France

^{*****} CEA, DEN, Marcoule, DTCD, BP 17171, F-30207 Bagnols-sur-Ceze, France

ABSTRACT

Carbonation of cement-based waste forms using a supercritical carbon dioxide (SCCO₂) is a developing technology for the waste immobilization of radioactive and non-radioactive wastes. However, the detail carbonation behaviors of cement matrices under the SCCO₂ condition are unknown, since cement matrices forms very complex phases. In this study, in order to clarify the crystal phases, we synthesized pure cement hydrate phases as each single phases; portlandite (Ca(OH)₂), ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O), and calcium silicate hydrate ($n \text{ CaO} \text{---} m \text{ SiO}_2 \text{---} x \text{ H}_2\text{O}$), using suspensions containing a stoichiometric mixture of chemical reagents, and performed carbonation experiments using an autoclave under supercritical condition for carbon dioxide. The XRD results revealed both the carbonate phases and co-product phases depending on the initial hydrate phases; gypsum for Ettringite, amorphous or crystalline silica for calcium silicate hydroxide. Thermogravimetric analysis was also performed to understand carbonation behaviors quantitatively.

INTRODUCTION

Cement is commercially used to immobilize radioactive as well as non-radioactive wastes for disposal [1]. During the processing of the wastes, the cement based composites rely on the presence of water to hydrate the cementitious materials. Normally, the cement based composites include a large amount of pore water in the micropore formed in the cement hydrates as the binder phases. This highly alkaline pore water provides protection to steel in construction concrete, but in waste encapsulation may cause problems with swelling metal corrosion, waste/matrix interactions, and migration of ions.

In order to improve the cement matrices, accelerated carbonation treatment using CO₂ has been investigated as an additional procedure. The carbonation treatment enhances the neutralization of the cement matrices and pore water. This also promotes densification of micro structures as a leaching pass of metal cations results from the carbonation of cement hydrates. A gaseous CO₂ or a liquid CO₂ was the normal source of the carbonation. However, in recent studies performed, SCCO₂ was investigated as a new source of carbonation. SCCO₂ was selected due to its specific properties of high density compared with that of gaseous CO₂ and high diffusivity compared with that of liquid CO₂. Hartmann *et al.* has demonstrated and reported on the carbonation treatment for cement forms and heavy metal immobilization using SCCO₂ [2]. So far, the application of this treatment using SCCO₂ is not only for a well-aged cement form at the final stage, but also for a cement paste at the early stage [3].

The investigation is of particular interest to carbonation behavior of pure cement materials. Many of the cement forms and pastes contain several types of cement hydrates which are unstable under acidic conditions and under SCCO₂. The primary cement hydrates present in ordinary Portland cement (OPC) forms contain multiple phases of portlandite (Ca(OH)₂), ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O), and calcium silicate hydrate ($n \text{ CaO} \text{---} m \text{ SiO}_2 \text{---} x \text{ H}_2\text{O}$) from the clinkers consisting of calcium silicates (C₂S, C₃S), calcium aluminates (C₃A) and gypsum. In the present study, all cement hydrates are synthesized from the chemical reagents in order to obtain the mono phase of each material. X-ray diffraction was used to confirm behaviors in formation of cement hydrate and carbonate with SCCO₂. The H₂O and CO₂ contents contained in cement materials after carbonation treatment with SCCO₂ was also evaluated thermo gravimetrically using TGA.

EXPERIMENTAL

Preparation of pure cement hydrates

Portlandite:

Portlandite, Ca(OH)₂ was synthesized from calcium oxide (Aldrich, 99.9% pure) and was decarbonated by placing the sample into a ceramic crucible in a furnace for 3 hours at 900 °C. Demineralized and decarbonated water was added to reach a water/solid ratio of 50 by weight. The suspensions were stored at room temperature under nitrogen atmosphere and continuously stirred in closed polypropylene bottles for 3 days. The powder was then filtered and rinsed with isopropanol. The precipitates were subsequently dried in a glove box.

Ettringite:

Ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O was synthesized from aluminum sulfate (Aldrich, 99.9% pure) and calcium oxide (Aldrich, 99.9% pure) and was decarbonated by placing the sample into a ceramic crucible in a furnace for 3 hours at 900 °C. Demineralized and decarbonated water was added to reach a water/solid ratio of 50 by weight. The suspension was stored at room temperature under nitrogen atmosphere and continuously stirred in closed polypropylene bottles for 1 week. The suspension was then filtered and

rinsed with isopropanol followed by drying in the glove box.

Calcium Silicate Hydrate ($n/m = 0.83$):

Calcium silicate hydrates ($n \text{ CaO} \text{---} m \text{ SiO}_2 \text{---} x \text{ H}_2\text{O}$) samples, with a nominal Ca/Si atomic ratio, $n/m = 0.83$, were synthesized from silica (Degussa, Aerosil 380) and calcium oxide (Aldrich, 99.9% pure). The sample was then decarbonated by placing the sample into a ceramic crucible in a furnace for 3 hours at 900 °C. Demineralized and decarbonated water added to reach a water/solid ratio of 50 by weight. The suspensions were stored at room temperature under nitrogen atmosphere and continuously stirred in closed polypropylene bottles for 2 weeks. They were then filtered and rinsed with isopropanol. The precipitate was subsequently dried in the glove box.

Carbonation treatment of cement hydrates under SCCO_2

A stainless steel autoclave reactor works in a batch mode. The internal volume of the reactor is 1 dm³, and the maximum working conditions are 100 °C and 20 MPa. All hydrate samples were loaded in small glass vials (25 cm³) and placed in the autoclave. For each experiment, the reactor was operated according to the following procedure: after introducing a solution of reactants, the reactor was closed and CO₂ was injected at room temperature up to 5 to 6 MPa, depending on the required final pressure and temperature. Then heating (external circulation of hot water) was started. The final temperature and pressure were maintained for approximately one hour under SCCO₂ conditions in order to allow the carbonation of cement hydrate. The carbonation time was about 1 hour at the selected conditions (P, T), while the total operation time was around 2.4 hours. After ~2.4 hours, the temperature was decreased and CO₂ was vented. The reactor was then opened and the samples were collected.

Characterization methods

The morphology of the powders was studied using scanning electron microscopy. Crystalline phases were determined by X-ray diffraction on powders. The contents of H₂O and CO₂ (carbonate) contained in the sample were determined from the weight loss curves measured from room temperature to 1000 °C using TGA. The contents of H₂O were obtained from the total weight losses below 400 °C and the contents of CO₂ were calculated from the sum of weight losses between 500 °C and 800 °C derived from decarbonation.

RESULTS AND DISCUSSION

XRD Results

X-ray diffraction pattern of portlandite, ettringite and calcium silicate hydrate with carbonation treatment at 10 MPa, 65 °C are shown in Figures 1, 2, and 3, respectively. The figures also indicate patterns for each initial sample without carbonation treatment for comparison. From the patterns of initial phase, all initial samples were obtained as a single phase after the synthesis. The diffraction pattern of Calcium Silicate Hydrate ($n/m=0.83$) showed almost same pattern of C-S-H 0.8 precisely measured in Reference 4 [4].

Portlandite:

The main crystalline phase detected for carbonation at 10 MPa, 65 °C was a single phase of calcite, CaCO_3 (C). The carbonation of portlandite phase (P) is represented by the following equation:

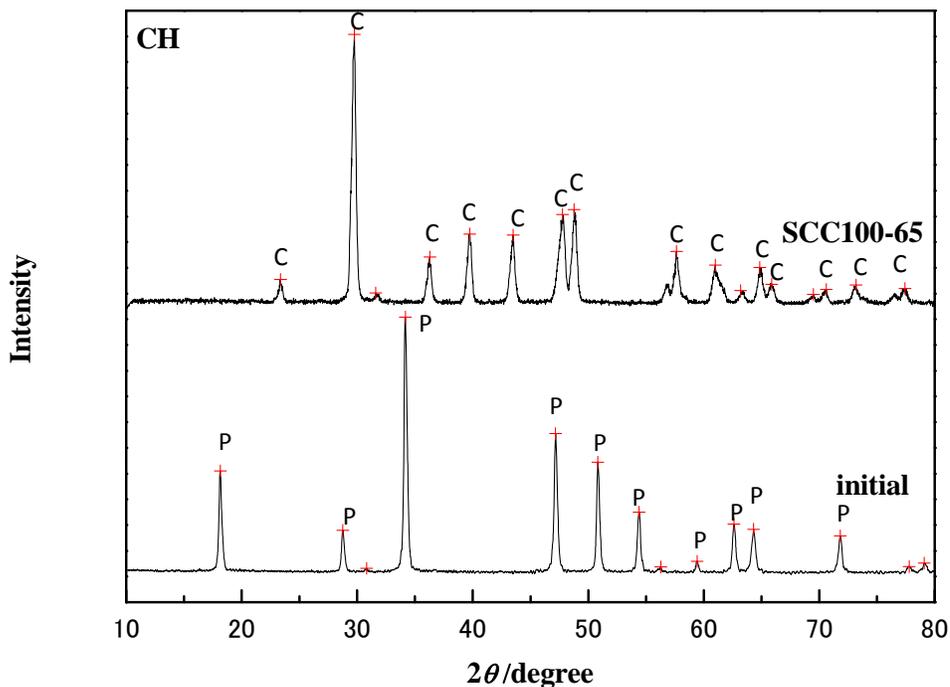
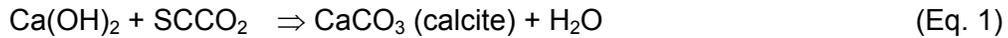


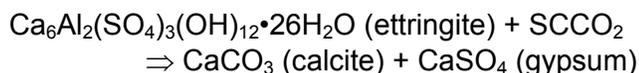
Fig. 1. XRD patterns of portlandite, Ca(OH)_2 (upper; sample treated with SCCO_2 at 100 bar, 65 °C, below; initial sample without treatment)

C...Calcium carbonate (calcite), CaCO_3

P....Portlandite, Ca(OH)_2

Ettringite:

The main crystalline phases detected after carbonation at 10 MPa, 65 °C were complex phase of calcium carbonate (C) and gypsum, CaSO_4 (G) and traces of residual ettringite phase (e). The pattern of the residual phase was very similar to the initial pattern of ettringite (E), however the diffraction peak angle of the ettringite phase (e) was slightly different from the initial pattern. This may be an analog phase of ettringite containing CO_3^{2-} [5]. The primary reaction during carbonation of ettringite with SCCO_2 was decomposition to calcium carbonate and gypsum as shown in Equation 2.



+ an ettringite phase + H₂O

...(Eq. 2)

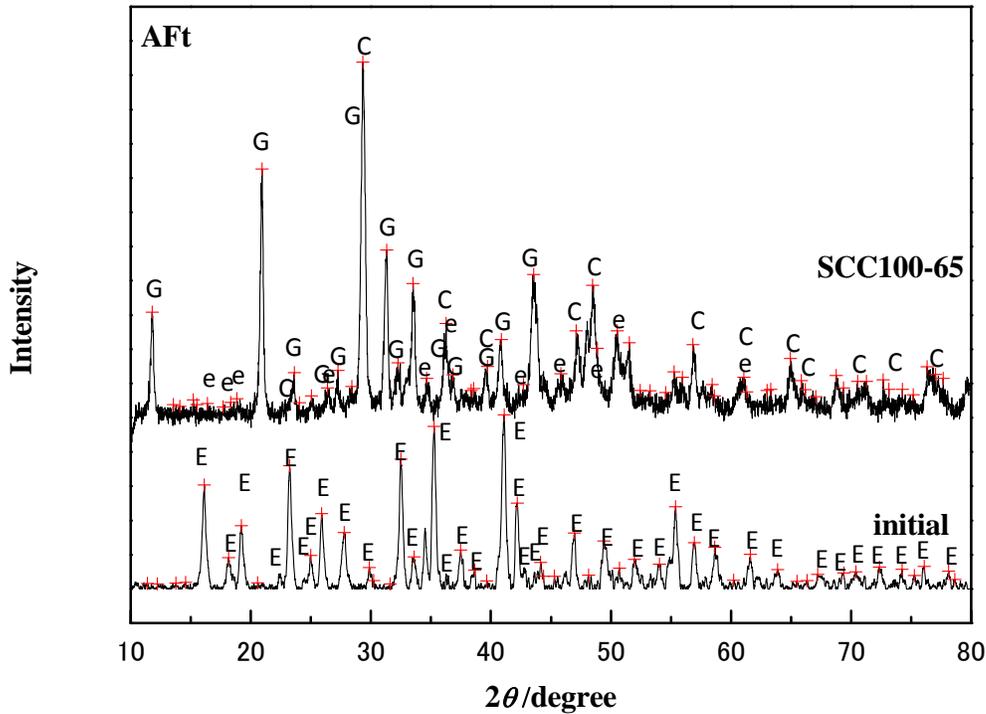
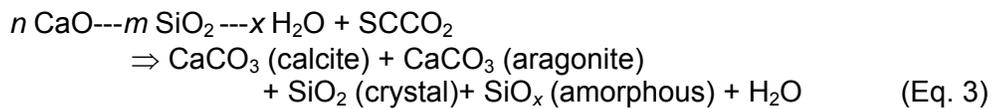


Fig. 2. XRD patterns of ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O (upper; sample treated with SCCO₂ at 100 bar, 65 °C, below; initial sample without treatment)

- C... Calcium carbonate (calcite), CaCO₃
- G... Gypsum, CaSO₄
- E... Ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O
- e... Residual ettringite phase (JCPDS data unmatched)

Calcium Silicate Hydrate ($n/m = 0.83$):

The main carbonate phases detected after carbonation at 100 bar, 65 °C were two types of polymorph of calcium carbonate; calcite (C), and aragonite (A). The silica was also detected as the crystalline products, SiO₂ (Q) and amorphous products, SiO_x (broad peak around 2θ = 25°). The calcium silicate hydrate ($n/m = 0.83$) was decomposed as following reactions with forming two types of calcium carbonate and silica under the SCCO₂ condition:



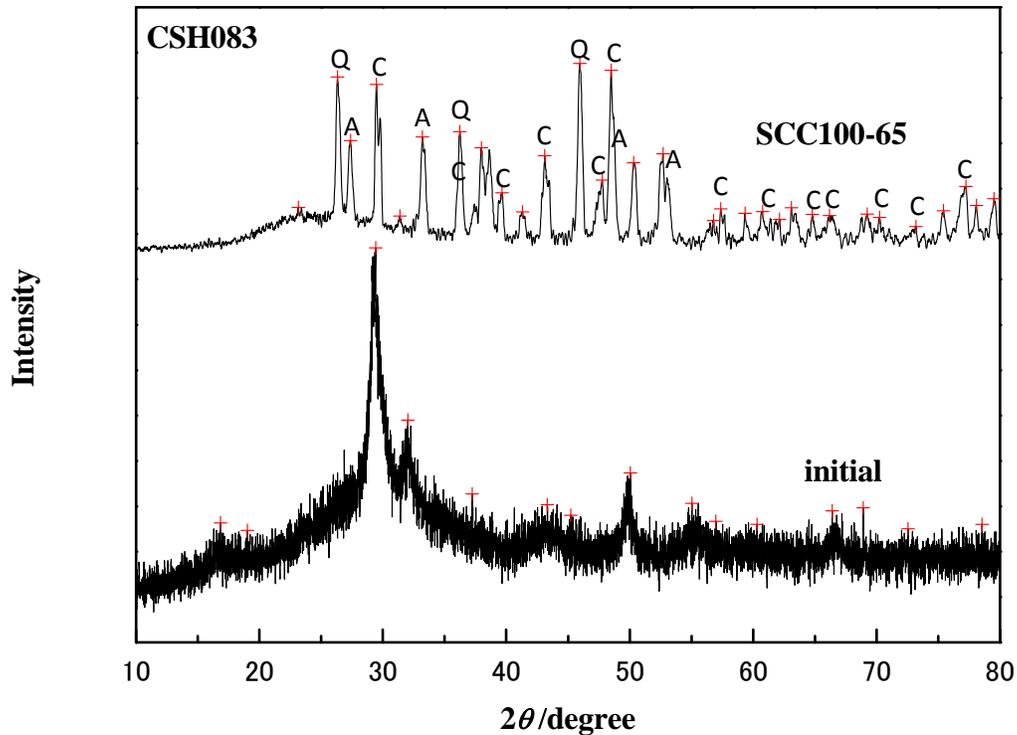


Fig. 3. XRD patterns of calcium silicate hydrate ($n/m = 0.83$), $n \text{ CaO} \text{---} m \text{ SiO}_2 \text{---} x \text{ H}_2\text{O}$ (upper; sample treated with SCCO_2 at 100 bar, 65 °C, below; initial without treatment)

- Q... Silica, SiO_2
- A... Calcium carbonate (aragonite), CaCO_3
- C... Calcium carbonate (calcite), CaCO_3

SEM results

Figure 4 contains the scanning electron micrographs of portlandite, ettringite, and calcium silicate hydrate with and without carbonation treatment at 10 MPa, 65 °C for comparison. The paragraphs below provide a description of each scanning electron micrograph contained in Figure 4.

Portlandite:

For initial portlandite sample without carbonation (Figure.4 (a)), most particle of portlandite appeared to form agglomerates of very fine particles of $\text{Ca}(\text{OH})_2$. The morphology of the sample treated with SCCO_2 (Figure 4(b)) was similar to that of initial portlandite, except that the agglomeration of carbonate sample seemed to be denser and tightly gathered. Also, the particle sizes of the agglomerations were larger than that of initial sample.

Ettringite:

In Figure 4(c), ettringite needles are seen in the initial sample without carbonation. The length of needles was typically exceeding 5 μm . However, after the treatment with SCCO_2 (Figure 4(d)), most of the needles of ettringite were decomposed and covered with dense plate-like particles of CaSO_4 over the needle-like crystal.

Calcium Silicate Hydrate ($n/m = 0.83$):

The microstructure of initial calcium silicate hydrate (Figure 4(e)) shows foil-like morphology typically observed for calcium silicate hydrate ($\text{Ca}/\text{Si} = 0.83$) in cement based systems [6]. After the carbonation (Figure 4(f)), the foil-like structures had completely disappeared and defined crystalline silica (SiO_2), which has block like morphology, appeared on the dense agglomeration of small particles of CaCO_3 .

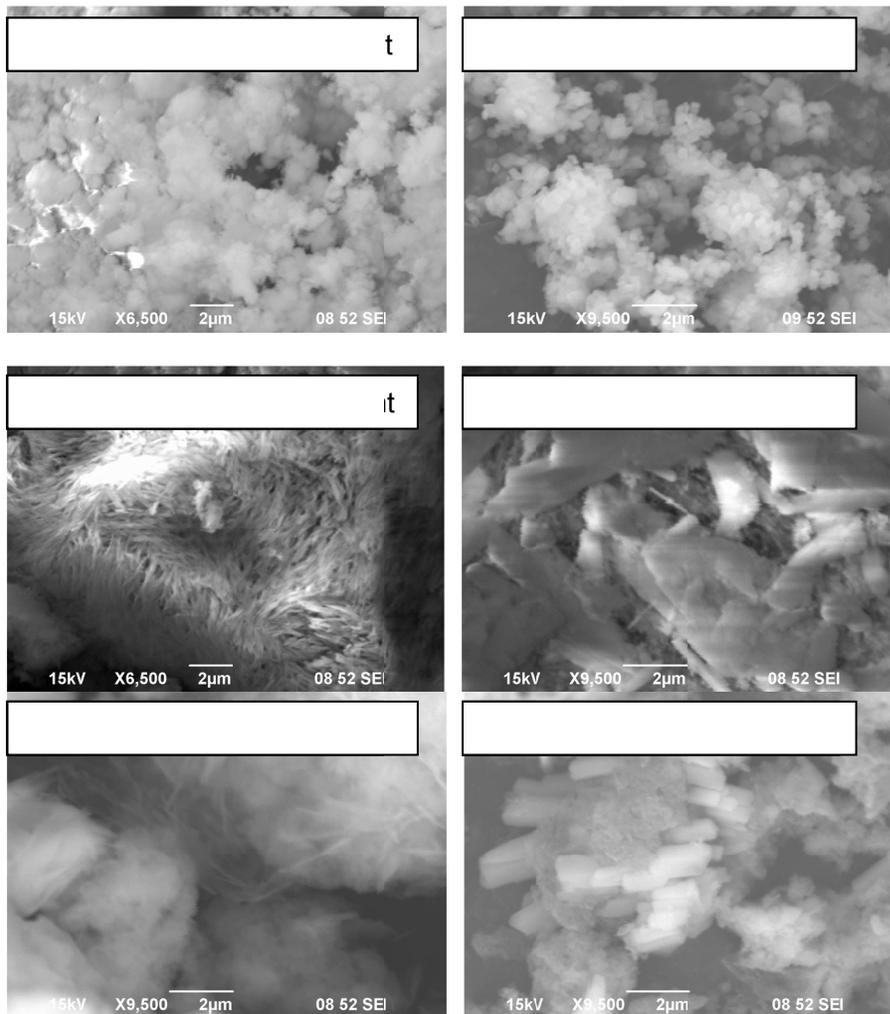


Fig.4. SEM photos of samples with and without treated with SCCO_2 at 100 bar, 65 $^{\circ}\text{C}$.

Thermogravimetric analysis

Thermogravimetric analysis was carried out to estimate moisture (H₂O) and carbonate (CO₂) contents contained in the sample for several carbonation conditions with SCCO₂. Table I summarizes the tested conditions.

Table I: Carbonation conditions with SCCO₂

| | Temperature | Pressure | Density |
|------------|-------------|----------|-------------------|
| | °C | MPa | kg/m ³ |
| SCC-100-65 | 65 | 10 | 270 |
| SCC-150-38 | 38 | 15 | 810 |
| SCC-150-65 | 65 | 15 | 500 |
| SCC-300-65 | 65 | 30 | 810 |

Table II, III, IV show H₂O and CO₂ content calculated from the TGA results of portlandite, ettringite and calcium silicate hydrate, respectively. The H₂O contents were normalized to theoretical water content of pure hydrates crystal, and the CO₂ contents were represented as a molar ratio of CO₂ to CaO contained in the pure hydrates.

Portlandite:

The TGA results (Table II), in the case of portlandite, show almost theoretical (stoichiometric) values of H₂O and CO₂ contents following equation (Eq.1). The weight loss occurred around 500°C for initial samples and around 600 °C for carbonated samples. Here, Ca(OH)₂ contains one molar of bonded water in the crystal structure and reacts with CO₂ to form calcium carbonate during carbonation.

Table II: Moisture and carbonate contents in portlandite, Ca(OH)₂ (F.W. = 74.09) calculated from TGA data.

| | H ₂ O content | CO ₂ content |
|------------|--------------------------------------|------------------------------|
| | mol-H ₂ O/mol-portlandite | mol-CO ₂ /mol-CaO |
| Initial | 1.00 | 0.00 |
| SCC-100-65 | 0.00 | 0.99 |
| SCC-150-38 | 0.00 | 0.96 |
| SCC-150-65 | 0.00 | 0.98 |
| SCC-300-65 | 0.00 | 0.98 |

Ettringite:

Ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂•26H₂O contains several type of waters and is composed of crystal columns of Ca₆[Al₂(OH)₁₂ • 24H₂O]⁶⁺. The columns are made up of Ca and Al polyhedra, which coordinate to H₂O (Ca only), and OH (Al and Ca). The sulfate of crystal columns contains coordinated water molecules. Therefore, the weight loss curves show

several step-like reductions below 400 °C. The experimental results in Table III indicate 12 ~ 13 molecules of H₂O molecules and/or OH⁻ ions were decomposed after carbonation. On the other hand, as the result of carbonation, ettringite reacted with 0.86 to ~ 0.87 molar of CO₂ per one CaO molecule. Measured CO₂ contents were a little smaller stoichiometric values to form CaCO₃ (CO₂/CaO = 1) as the carbonation product, which indicates one part of CaO forms CaCO₃ and another part of CaO remained as sulfate or hydroxide form in the ettringite phase without decomposition. This could be mean that a part of ettringite phase potentially remains even after the carbonation with SCCO₂.

Table III: Moisture and carbonate contents in ettringite, Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O (F.W. = 1255) calculated from TGA data

| | H ₂ O content | CO ₂ content |
|------------|-------------------------------------|------------------------------|
| | mol-H ₂ O/mol-ettringite | mol-CO ₂ /mol-CaO |
| Initial | 33.2 | 0.00 |
| SCC-100-65 | 18.9 | 0.86 |
| SCC-150-38 | 18.9 | 0.86 |
| SCC-150-65 | 20.2 | 0.87 |
| SCC-300-65 | 19.5 | 0.86 |

Calcium Silicate Hydrate (*n/m* = 0.83):

The results of calcium silicate hydrates are summarized in Table IV. The contents of H₂O and CO₂ show a strong dependence to the conditions under which they were subjected to carbonation with SCCO₂: Initial calcium silicate hydrate includes 0.70 g of water in 1.0 g of calcium silicate powders. However, the H₂O content is reduced at higher temperatures and at higher pressures. On the other hand, the CO₂ contents after the carbonation increased at higher temperatures and at higher pressures. Especially, after carbonation in the case at 30 MPa, 65 °C, CaO in calcium silicate hydrate was completely converted to CaCO₃, furthermore almost all the H₂O was dried up with SCCO₂.

Table IV: Moisture and carbonate contents in calcium silicate hydrate (*n/m* = 0.83), *n* CaO---*m* SiO₂---*x* H₂O calculated from TGA data

| | H ₂ O content | CO ₂ content |
|------------|---|------------------------------|
| | g-H ₂ O/g-CSH0.83 [†] | mol-CO ₂ /mol-CaO |
| Initial | 0.70 | 0.00 |
| SCC-100-65 | 0.36 | 0.51 |
| SCC-150-38 | 0.53 | 0.68 |
| SCC-150-65 | 0.27 | 0.77 |
| SCC-300-65 | 0.03 | 1.01 |

[†]Calcium silicate hydrate (*n/m*=0.83)

CONCLUSIONS

According to the experimental results, it was found that the major reaction was formation of calcium carbonate (CaCO₃) in all cases. However, the behaviors of H₂O and CO₂ content

were quietly different: Portlandite was most reactive for carbonation under SCCO₂ conditions, and the CO₂ content per one molar CaO was ranged from 0.96 ~ 0.98. In the case of Ettringite, the experiment indicates partial decomposition of ettringite phase during carbonation. Ettringite was comparatively stable even under the SCCO₂ conditions. Therefore, a part of ettringite remained and formed similar phases after the ettringite carbonation. The CO₂ content for ettringite showed almost constant values around 0.86 ~ 0.87. In the case of calcium silicate hydrate, the carbonation behavior was significantly influenced by the condition of SCCO₂. The CO₂ content for the calcium silicate hydrate had values that ranged from 0.51 ~ 1.01.

The co-products of the carbonation were gypsum (CaSO₄) for ettringite, silica gel (SiO_x) and silica (SiO₂) for calcium silicate hydrate, which also contributed to the densification of the particles. The production of co-products enhanced the change to their morphology after the carbonation.

REFERENCES

1. C.D. HILLS, R.E.H. SWEENEY, N.R. BUENFILD, "Microstructural study of carbonated cement-solidified synthetic heavy metal waste.", *Waste Management*, **19**, 5, (1999), pp. 325-331.
2. T HARTMAN, P PAVIET-HARTMAMM, J.B RUBIN, M.R FITZSIMMONS, K.E SICKAFUS, "The effect of supercritical carbon dioxide treatment on the leachability and structure of cemented radioactive waste-forms.", *Waste Management*, **19**, 5, (1999), pp. 355-361.
3. K.KAMIYA, D. HIRABAYASHI, K. SAWADA, Y. ENOKIDA, "Temperature Effect of Curing on Crystal Phase in Cement for the Treatment with Supercritical Carbon Dioxide.", Proceedings of NUWCEM 2011, International Conference, Avignon, France (October, 2011)
4. G. RENAUDIN, J. RUSSIAS, F. LEROUX, F. FRIZON, C. CAU-DIT-COUMES, "Structural characterization of C-S-H and C-A-S-H samples—Part I: Long-range order investigated by Rietveld analyses.", *Journal of Solid State Chemistry*, **182**, 12, (2009), pp. 3312-3319.
5. H.F.W. TAYLOR, "Crystal structures of some double hydroxide minerals.", *Mineralogical Magazine*, **39**, 304, (1973), pp. 377-389.
6. S.C.B. MYENI, S.J. TRAINA, T.J.LOGAN, "Ettringite Solubility and Geochemistry of the Ca(OH)₂ – Al₂(SO₄)₃ – H₂O System at 1 atm Pressure and 298K.", *Chemical Geology*, **148**, (1998), pp. 1-19.

ACKNOWLEDGEMENTS

This research work was achieved in a collaboration project between two laboratories in CEA (DEN, Marcoule site, DTCD/SPDE/L2ED and LFSM) and the Nuclear Chemical Engineering Research Laboratories in Nagoya University.