

FUNDAMENTAL STUDY ON FORMATION OF ZEOLITE FROM REACTION BETWEEN ALBITE AND PORTLANDITE

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ABSTRACT

In this paper, we investigated the products of the reaction between albite and portlandite. In these experiments, albite rock reacted with calcium hydroxide in four temperature of 20, 50, 65, 80 °C, and thermogravimetric analysis and powder x-ray diffraction were performed. XRD charts and DTG curves suggest the formation of an amorphous phase and zeolites. By comparing the relationship between Ca/ (Si + Al) ratio and the H₂O/ (Si + Al) ratio with previous studies, it seems that those products have a composition similar to C-S-H in hardened cement paste.

Keywords: aggregate, albite, C-S-H, zeolite, X-ray diffraction, Rietveld analysis

1. INTRODUCTION

With the aging of existing concrete structures, a longer life is required from an environmental and economic point of view. In order to promote the ultra-long-term operation of buildings, long-term hydration of the cement used and alteration due to interaction with aggregates needs to be considered, but the current knowledge is not sufficient. In maintenance, it is essential to evaluate both the current and future soundness of a structure. It is necessary to obtain knowledge of whether the reaction proceeds, and it is important to obtain knowledge of how this chemical change is reflected.

In a previous study [1], it was confirmed that the strength of a concrete structure that had been in service for about 50 years had significantly increased inside the concrete wall. It was also observed at the same time that the amount of amorphous phase at the corresponding location increased and the amount of portlandite crystals decreased. In addition, the analysis by SEM-EDS shows that feldspars of aggregate react with portlandite to form calcium aluminosilicate hydrate (C-(A)-S-H), which contributed to the strength increase. Already, in the 1970s, van Aardt and Visser reported that various rock-forming minerals dissolve in high pH environments with suspensions of calcium hydroxide [2]-[4]. Other studies [5]-[9] are reported, but sufficient data on the properties of hydrates have not been obtained.

In this experiment, based on a study by van Aardt and Visser, an experimental study was conducted on the reaction of portlandite with the highly alkaline and humid environment using albite rock.

2. TEST PROGRAMS

2.1 Materials and Preparation

Table 1 shows the mineral composition of the

Albite rock used in this experiment. Rocks containing about 70% albite and about 23% quartz were used. In preparing the sample, the rock was ground to 125 μm or less using a ball mill. Then 5.00 ± 0.01 g of the albite rock powdered and 5.00 ± 0.01 g of calcium hydroxide were mixed in a glove box with nitrogen gas. The mixture was poured into bottles containing 60.0 ± 0.05 mL of water, and mixed well. After these treatments, the samples were stored under four temperature environments of 20, 50, 65, and 80 °C.

2.2 Stop Hydration

The sample at a reaction temperature of 20 °C was measured at 91 days, and the samples for reaction temperatures of 50, 65, and 80 °C were measured at 14, 28, and 91 days. After the operations of stopping hydration were performed, each measurement was performed.

When the operation of stopping hydration was performed, the mixture was filtered to separate solid phase and a liquid phase. Regarding the solid phase, it was vacuum-dried with an aspirator and stopped hydration by vacuum-drying to 50 millitorrs and less using a Flovac vacuum deaerator. Then the solid phase sample was stored in a desiccator humidified to 11% RH, and each measurement was performed later. The liquid phase was separated by filtration and then sealed in a glass bottle filled with nitrogen gas, and stored in a temperature-controlled room at 20 °C.

2.3 Thermogravimetric analysis

Thermogravimetric analysis was performed on

Table 1 Mineral composition (wt%)

Albite	Anorthite	Quartz
69.9±0.94	3.33±0.386	23.4±0.54

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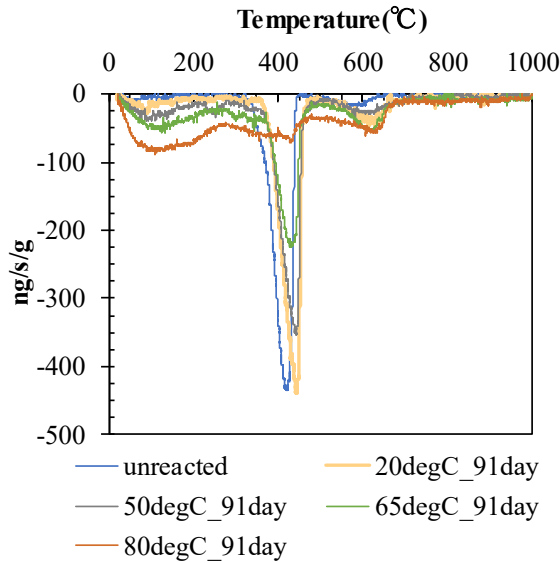


Fig. 1 DTG curve at reaction period 91days

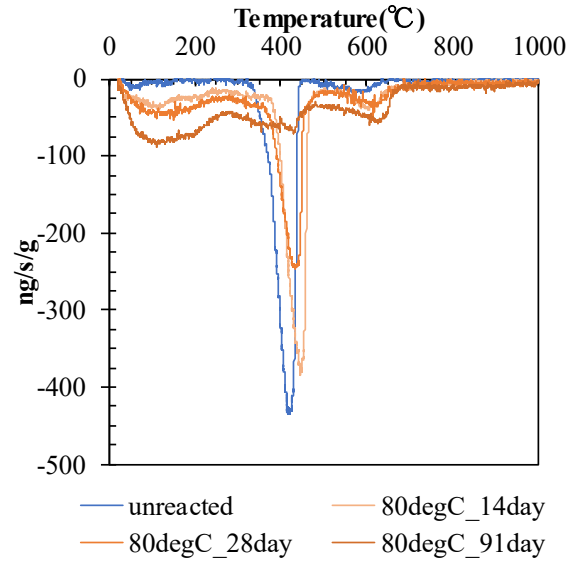


Fig. 2 DTG curve at reaction temperature 80 °C

the sample immediately after mixing the powdered feldspar and portlandite (unreacted), and on the samples after the reaction was stopped. Using TG-DTA 2010 SA, crush each sample in a nitrogen atmosphere and classify the sample to 90 μm or less. The sample weight was 20 ± 0.5 mg, the temperature was increased from room temperature to 1000 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C} / \text{min}$, and the measurement was performed in under N_2 flow. The reason for classifying it to 90 μm or less is to suppress the variation in weight loss rate due to the difference in particle size.

2.4 Powder X-ray diffraction and Rietveld analysis

In the sample unreacted and the specimen after the reaction in which the hydration was stopped, the generation of a crystalline phase and an amorphous phase was confirmed by powder X-ray diffraction. In order to suppress the variation due to the inclusion of coarse crystal, the sample was crushed to 90 μm or less as the same way of thermogravimetric analysis. A sample in which corundum ($\alpha\text{-Al}_2\text{O}_3$) is mixed at 10wt% as an internal standard sample were used for the measurement, and the test was performed under the following conditions; X-ray source Cu-K α 1, tube voltage 20 kV, tube current 5 mA, scanning range $2\theta = 2$ to 70 $^{\circ}$, step width: 0.02 $^{\circ}$, scan speed: 0.125 $^{\circ}/\text{min}$. Three measurements were performed for each specimen, and average results were used.

Rietveld analysis was performed by TOPAS ver. 6.0. In addition to $\text{Ca}(\text{OH})_2$ (Portlandite), CaCO_3 (Calcite), $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Anorthite), $\text{NaAlSi}_3\text{O}_8$ (Albite), SiO_2 (Quartz).

The mass amorphous phase was calculated from the quantitative value of the corundum according to Eq. 1.

$$A = \{100 \times (S_R - S)\} / \{S_R \times (100 - S)\} \quad (1)$$

Where, A : amount of amorphous phase (%), S : mixing ratio of $\alpha\text{-Al}_2\text{O}_3$ (%), S_R : the quantitative value of $\alpha\text{-Al}_2\text{O}_3$ (%).

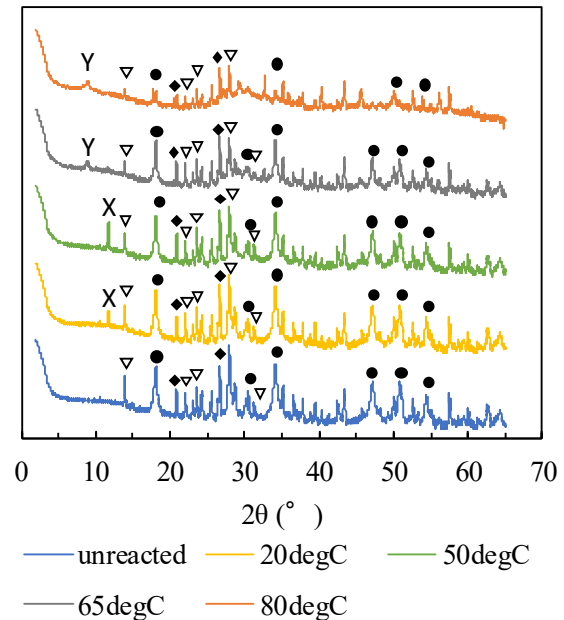


Fig. 3 XRD Charts at reaction period 91days

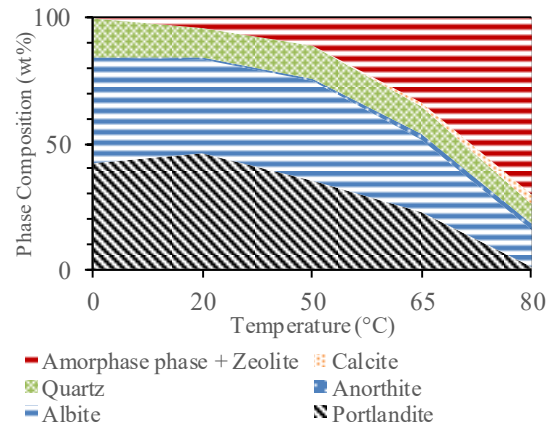


Fig. 4 Phase composition during 91 days of reaction

2.5 Analysis of liquid phase

The pH of the liquid phase of each sample was measured using a compact pH meter.

In order to quantify the solubility of Ca, Si, and Al in the liquid phase, the measurement was performed using an inductively coupled plasma mass spectrometer (ICP-MS). When preparing the sample, dilute the liquid phase about 400 times with HNO₃, and use a standard solution in the range of 0.599 to 2.03 ppm for Ca, 0.512 to 7.73 ppb for Si, and 0.487 to 52.1 ppb for Al.

3. RESULTS

3.1 Thermogravimetric analysis

Fig. 1 shows the thermogravimetric time derivative (DTG) curves obtained by thermogravimetric analysis before the reaction and at reaction period of 91 days at each reaction temperature. At the given moment of the reaction, it was observed that the peak of portlandite (400 °C to 500 °C) became smaller as the temperature increases. At 65 °C and 80 °C, the formation of calcite (550 to 750 °C) was observed. It is presumed that the formation of calcite was due to the reaction of carbon dioxide dissolved in water under high temperatures environment.

It was also observed that the peak near 100 °C increased as the reaction temperature increased. It is presumed that this peak is related to the presence of the amorphous phase.

Fig. 2 shows the DTG curves before the reaction and at the reaction temperature of 80 °C for 14, 28, and 91 days. It was observed that the peak of portlandite decreased with time, while the peak at around 100 °C, and the peak of calcite increased.

3.2 Powder X-ray diffraction and Rietveld analysis

Fig. 3 shows the XRD charts of unreacted sample and those at each reaction temperature for 91 days. The XRD charts show a value normalized by the strongest peak of the corundum (α -Al₂O₃).

It was observed that the peak of portlandite decreased as the reaction temperature increased. In particular, the peak intensity was significantly reduced at the reaction temperature of 80 °C.

Also, it was observed new peaks when 2 θ was around 11.72° (Zeolite X in **Fig. 3**, $d = 7.55$ Å) in the XRD charts at the reaction temperature of 20 °C and 50 °C, and around 8.90° (Zeolite Y in **Fig. 3**, $d = 9.93$ Å) at 65 °C and 80 °C.

From the previous studies [7], the peak positions and composition in samples, the new peaks at the reaction temperature of 20 °C and 50 °C were to be one of the zeolites, either ZSM-5, Calcined (Na_nAl_nSi_{96-n}O₁₉₂·16H₂O) or ZSM-12, Calcined (Si₅₆O₁₁₂) [10]. Also, the new one at 65 °C and 80 °C suggest that one of the zeolites, Na-X hydrated ([Na₈₈(H₂O)₂₂₀][Si₁₀₄Al₈₈O₃₈₄]) [11] was formed based on the value of 2 θ and the composition in the samples same as the case of 20 °C and 50 °C.

In addition, as the reaction temperature increases, the broad peak when 2 θ was around 28° increases, which

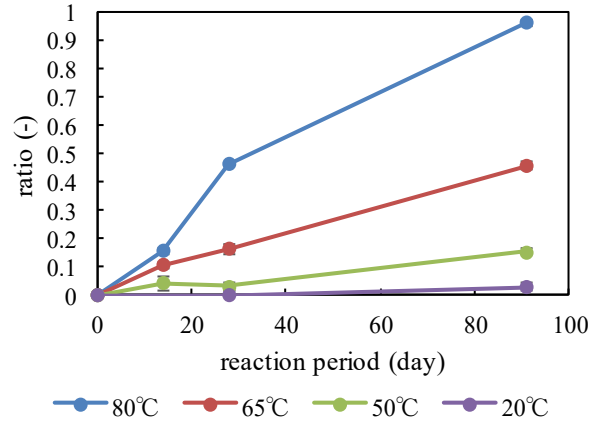


Fig. 5 Reaction rate of Portlandite

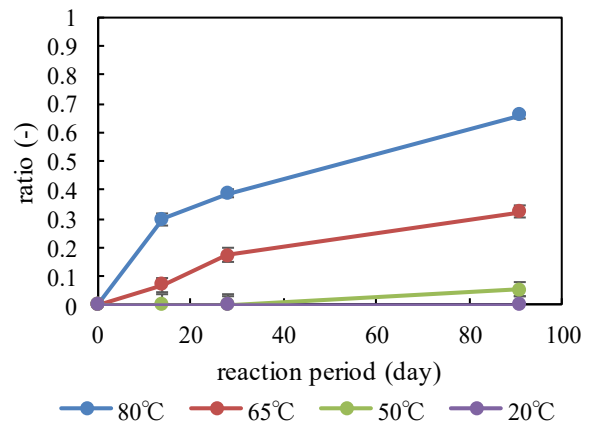


Fig. 6 Reaction rate of Albite

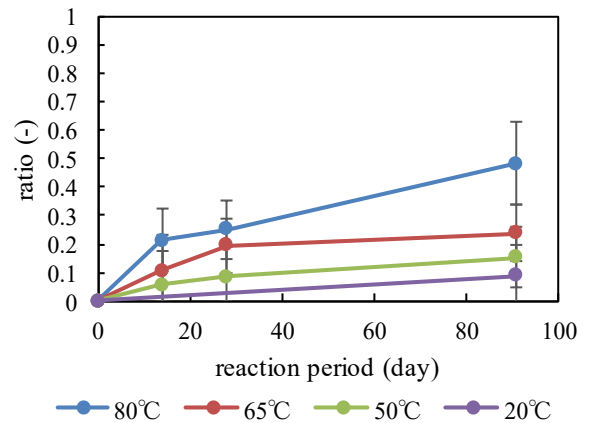


Fig. 7 Reaction rate of Quartz

suggests that the amount of amorphous phase formation increases which is consistent with the result of the thermogravimetric analysis.

Fig. 4 is a diagram of the phase composition at each temperature during a reaction temperature period of 91 days calculated from quantitative values obtained by Rietveld analysis. In this analysis, the peaks considered to be zeolite were quantified using dummy peaks, and

the amorphous phase and zeolite were calculated as one phase. As the reaction temperature increases, the proportion of portlandite and albite decreases compared to the unreacted sample, while the proportion of amorphous phase and zeolite increases reaching approximately 70% of the total solid-phase at 80 °C. This accounts for approximately 90% in the product phases.

Fig. 5, Fig. 6, and Fig. 7 show the reaction rates of portlandite, albite, and quartz determined by Rietveld analysis at each reaction temperature. The reaction rate was calculated by the result of Rietveld analysis corrected by DTG obtained from the thermogravimetric analysis, and the mass of each crystal before and after reaction per 1 g of the sample and the following Eq. 2.

$$\alpha(t) = \left(1 - \frac{M(t)}{M(0)}\right) \quad (2)$$

Where, $\alpha(t)$: reaction rate (-), $M(t)$: mass (g / g) in 1 g of specimen at reaction period t, $M(0)$: mass in 1 g of specimen before reaction mass (g / g).

The reaction rate of portlandite in Fig. 5 showed a tendency to increase as the reaction temperature increased, and time passed. At 80 °C, it is observed that most of the portlandite have reacted within reaction period of 91 days. At 20 °C, it was observed that the reaction slightly progressed at 91 days.

As for portlandite, the reaction rate of albite in Fig. 6 is observed to increase as the reaction temperature increases as the reaction period passed. However, it seems that the reaction did not proceed as much as portlandite at any temperature as compared with the reaction rate of that. In addition, it seems that almost no reaction occurred at 20 °C.

The reaction rate of quartz in Fig. 7 increases with the reaction time at a temperature of 80 °C, but the change is small for the samples at 65 °C and 50 °C from 28 to 91 days.

3.3 pH of liquid phase and solubility of each element

Fig. 8 shows the pH in the liquid phase at each reaction temperature. As for the sample at 80 °C for 91 days, no liquid phase remained, and all of the sample hardened, thus the measurement results up to period for 28 days are shown. It was observed that the environment was highly alkaline at any reaction temperature and period. At the reaction period of 14 days, the pH was the lowest at 80 °C, but at 91 days, it was the lowest at 50 °C and tended to decrease.

Fig. 9, 10, and 11 show the concentrations of Ca, Si, and Al in the liquid phase of each sample. It was observed that the higher the reaction temperature and the longer the reaction period, the lower the Ca concentration. At 80 °C for the period of 28 days and at 65 °C, that is significantly reduced as compared to before the reaction. Also, considering the reaction rate of portlandite in Fig. 5, Ca released from the reacted portlandite contributes to the formation of the amorphous phase or new crystals (Zeolite X, Y) in the solid phase. It was observed that the concentration of Si in the liquid phase in Fig. 10 at 80 °C was significantly higher than at other reaction temperatures. Although the

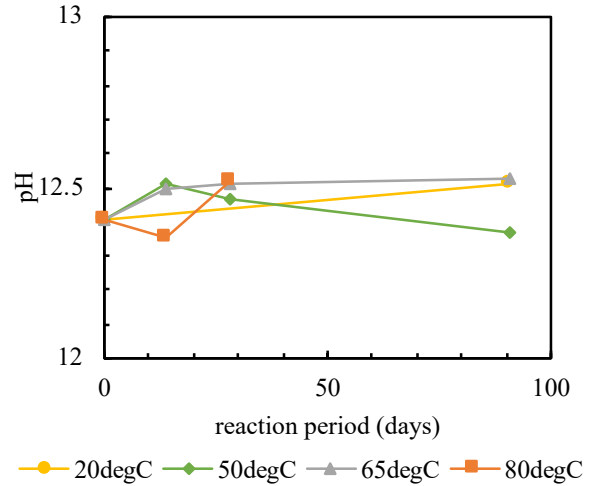


Fig. 8 pH in liquid phase

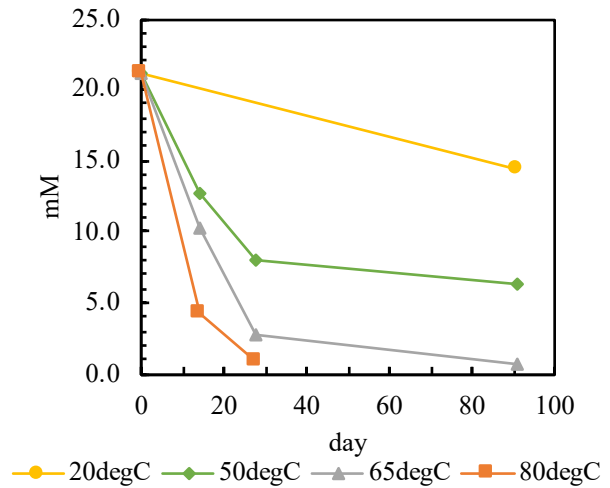


Fig. 9 Ca in liquid phase

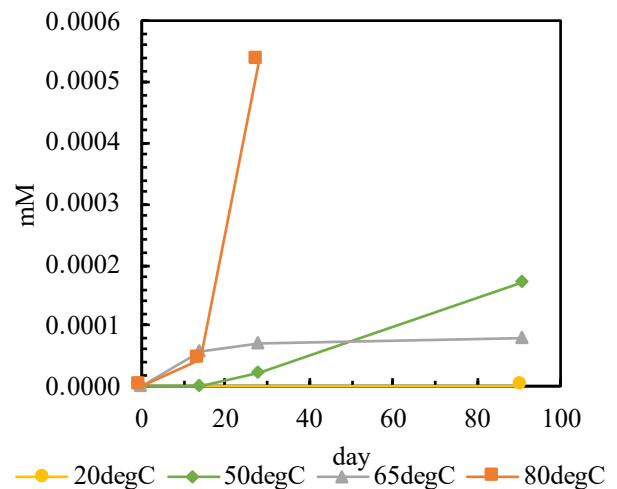


Fig. 10 Si in liquid phase

concentration of Si at 20 °C is remarkably small, the reaction rate of quartz at 20 °C in Fig. 7 suggests that the released Si is present in the solid phase. Also, the concentration was reversed between the period of 28 and 91 days at 50 °C and 80 °C, and it was observed that the concentration was higher at 50 °C than at 65 °C for 91 days.

The concentration of Al in the liquid phase in Fig. 11 at 80 °C was significantly increased same as that of Si. At other temperatures of 20, 50, 65 °C, Al is seemed to be scarcely present in the liquid phase. Also, the reaction rate of the albite at 20 and 50 °C in Fig. 6 suggests that Al was not released to the liquid phase because albite did not react. In addition, the reaction rate of albite at 65 °C is from 20 to 30%, indicating that released Al exists in the solid phase.

4. DISCUSSION

From the results of thermogravimetric analysis and XRD/ Rietveld analysis, it was confirmed that portlandite, albite, and quartz reacted to produce amorphous phase and supposedly crystalline zeolite.

Here, the composition of the amorphous phase and zeolite will be examined. For the calculation of Ca, it is assumed that the difference between the reduced amount of portlandite before the reaction and the amount of Ca in the liquid phase is Ca contained in amorphous phase and zeolite. Similarly, for the amount of Si, the difference between the reduced amount of albite and quartz and the amount of that in the liquid phase is the amount of Si contained in the amorphous phase and zeolite. And about the amount of Al, the difference between the reduced amount of Al before the reaction and the amount of in the liquid phase is the amount of Al contained in the amorphous phase and zeolite. The difference between the amount of dehydration from crystals determined by Rietveld analysis and the amount of dehydration obtained by thermogravimetric analysis was determined as the amount of H₂O in the amorphous phase and zeolite. Fig. 12 is a graph plotting the relationship between the Ca/ (Si + Al) ratio and the H₂O/ (Si + Al) ratio at each reaction temperature. The solid line shows the relationship between the Ca/ Si ratio and the H₂O/ Si ratio of C-S-H dried at 0% RH and 11% RH synthesized from C₃S paste reported by a previous study [10], in addition, the dashed line shows the relationship of C-S-H dried at 0% RH by a previous study of Richardson.[11]. It seems that the the state at 11% RH is approached as time passes at 65 °C and 80 °C. From these, the reaction between albite and portlandite produces an amorphous phase with a composition similar to C-A-S-H in the cement paste, and among them, it is seemed that zeolite, ZSM-5, Calcined (Na_nAl_nSi_{96-n}O₁₉₂ · 16H₂O) are formed as highly crystalline substances. Even at 50 °C, it is likely to show similar trends at 65 and 80 °C over a longer reaction period, as it is close from 28 to 91 days. At 20 °C and 50 °C, H₂O / (Si + Al) is larger compared to H₂O / (Si + Al) at 65 °C and 80 °C. It is presumed that the amount of bound water in the solid phase was larger than that of Si and Al

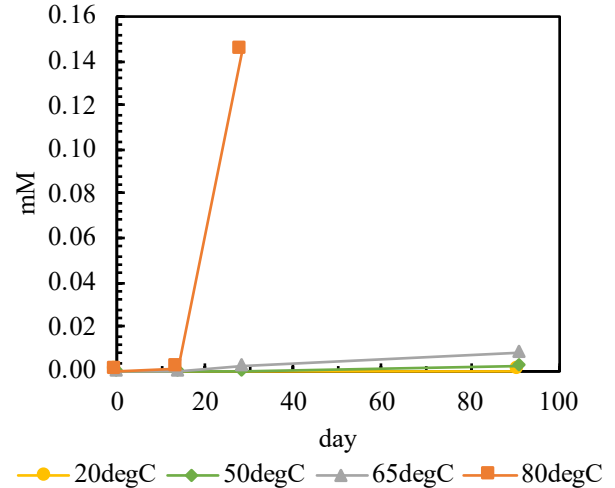


Fig. 11 Al in liquid phase

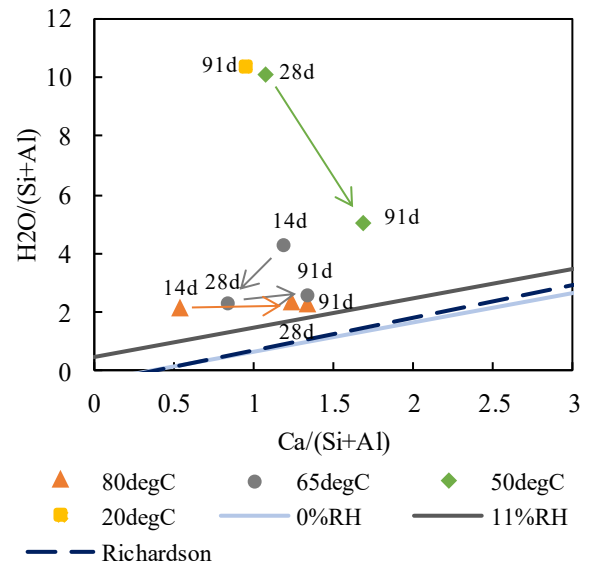


Fig. 12 The relationship between Ca/ (Si + Al) and H₂O/ (Si + Al)

(The reaction period x days is expressed as "x d".)

because the reaction proceeded greatly.

5. CONCLUSION

In this experiment, the following findings were obtained:

- 1) From thermogravimetric analysis and powder X-ray diffraction, it was confirmed that when the albite rock and portlandite were reacted in a humid environment, the amount of each crystal was reduced and the formation of amorphous was confirmed. It is presumed that ZSM-5, Calcined (Na_nAl_nSi_{96-n}O₁₉₂ · 16H₂O) or ZSM-12, Calcined (Si₅₆O₁₁₂) was formed as a highly crystalline substance at 20 °C and 50 °C. At 65 °C and 80 °C, formation of Na-X hydrated (| Na₈₈ (H₂O)₂₂₀ | [Si₁₀₄Al₈₈O₃₈₄]) was suggested.
- 2) It was observed that the reaction rates of calcium

hydroxide, albite, and quartz increased as the reaction temperature increased, and increased with the reaction period.

- 3) About the concentrations of Ca, Si, and Al in the liquid phase, it was confirmed that the concentration of Ca decreased as the reaction temperature increased and decreased with time. In the case of Si and Al, the opposite tendency to that of Ca was obtained.
- 4) From the relationship between the Ca / (Si + Al) ratio and the H₂O/ (Si + Al) ratio reported in previous studies, the composition of amorphous and zeolite in the solid phase is thought to approach the line obtained from the previous studies.

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REFERENCES

- [1] Jiri Rymes et al: Long-term Material Properties of a Thick Concrete Wall Exposed to Ordinary Environmental Conditions in a Nuclear Reactor Building: the Contribution of Cement Hydrates and Feldspar Interaction, *Journal of Advanced Concrete Technology* Vol. 17, 195-215, 2019
- [2] J. H. P. van Aardt and S. Visser: Formation of hydrogarnets : Calcium hydroxide attack on clay and feldspars, *Cement and Concrete Research*, Vol. 7, pp. 39-44, 1977
- [3] J. H. P. van Aardt and S. Visser: Reaction of Ca(OH)₂ and of Ca(OH)₂ + CaSO₄.2H₂O at various temperatures with feldspars in aggregates used for concrete making, *Cement and Concrete Research*, Vol. 8, pp. 677-682, 1978
- [4] J. H. P. van Aardt and S. Visser: Calcium hydroxide attack on feldspars and clays: Possible relevance to cement-aggregate reactions, *Cement and Concrete Research*, Vol. 7, pp. 643-648, 1977
- [5] Constantiner D, Diamond S: Alkali release from feldspars into pore solutions, *Cement and Concrete Research*, Vol. 33, pp. 549-554, 2003
- [6] Locati F, et al.: Na₂O, K₂O, SiO₂ and Al₂O₃ release from potassic and calcic-sodic feldspars into alkaline solutions, *Cement and Concrete Research*, Vol. 40, pp. 1189-1196, 2010
- [7] Lothenbach B, Bernard E, Mäder U: Zeolite formation in the presence of cement hydrates and albite. *Phys. Chem. Earth*, Vol. 99 pp.77-94, 2017
- [8] S J Way and W F Cole : Calcium hydroxide attack on rocks, *Cement and Concrete Research*, Vol. 12, pp. 611-617, 1982
- [9] Jeffrey J. Chem, et al. : Solubility and structure of calcium silicate hydrate, *Cement and Concrete Research*, Vol. 34, pp.1499-1519, 2004
- [10] M.M.J. Treacy and J.B. Higgins, "Collection of Simulated XRD Powder Patterns for Zeolites", published on behalf of the Structure Commission of the International Zeolite Association Fourth Revised Edition, 2001, pp. 228-239,
- [11] S. Mintova, "VERIFIED SYNTHESSES OF ZEOLITIC MATERIALS", published on behalf of the Synthesis Commission of the International Zeolite Association, 2016, pp. 224,
- [12] Suda, Y., Saeki, T. and Saito, T : Relation between Chemical Composition and Physical Properties of C-S-H Generated from Cementitious Mterials, *Journal Advanced Concrete Technology*, Vol. 13, pp. 275-290, 2015
- [13] Richardson, I. G. : Model structure for C-(A)-S-H (I), *Acta Crystallographica Section B, Structural Science, Crystal Engineering and Materials*, Vol. 70, pp. 903-923, 2014