

## Hydration of Ca A-Type Zeolite and Ca(OH)<sub>2</sub>

Motoki Uehara\* and Takahiko Sasaki

Railway Technical Research Institute, 2-8-38 Hikari-cho, Kokubunji, Tokyo 185-8540

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The hydration reaction of Ca A-type zeolite and calcium hydroxide was studied. The results revealed that an isostructural material of hydrocalumite (C-A-H) is generated at the early stage of hydration, and following that of strätlingite–vertumnite is generated. Only 0.77 nm of the C-A-H phase was observed at a humidity below 40% while part of the 0.77 nm phase swelled to 0.82 nm at a humidity of 40% or above.

Ca A-type zeolite has the properties of absorbing alkali ions and releasing Ca<sup>2+</sup> ions, bringing a greater repressing effect against an alkali-aggregate reaction compared to other admixtures. Because of this effect, Ca A-type zeolite has been put to practical use as a concrete repairing material.<sup>1</sup> Also, Ag A-type zeolite has an antimicrobial effect, and when added to concrete it is known to repress the propagation of the thiobacillus bacteria. A-type zeolite is thus seen as a high-function admixture for concrete. However, the mechanism regarding the creation of these specific functions has not been clearly studied, and it is uncertain how zeolite reacts in concrete. Furthermore, it has been noted that the initial dry shrinkage of concrete is greater by adding a small amount of zeolite.<sup>2</sup> It is thus essential to clarify the reaction mechanism of zeolite in concrete for its more practical and extensive use as a high-function admixture. Attention was paid to Ca(OH)<sub>2</sub>, which is considered to react actively with zeolite in concrete, and the hydration products from zeolite and Ca(OH)<sub>2</sub> are examined.

A synthetic Ca A-type zeolite (hereafter, abbreviated to Zeo), Na<sub>1.32</sub>Ca<sub>5.34</sub>Si<sub>11.82</sub>Al<sub>12.22</sub>O<sub>48</sub>·27.83H<sub>2</sub>O, that was ion-exchanged with Ca<sup>2+</sup>, (Nippon Chemical Co. Ltd.) and a reagent

for Ca(OH)<sub>2</sub> (hereafter, abbreviated to CH) (Kanto Chemical Co. Ltd.) was used for this experiment. This zeolite is actually used as a repair material for concrete. A Zeo and CH mixture paste was prepared by adding distilled water to the Zeo and CH mixture, varying the mass ratios from 1:5 to 5:1. Distilled water was added to make a water/solid ratio equal to 0.8. This paste was put in polypropylene bottles and immediately sealed, and kept at 20 °C. The amount of unreacted Zeo was decided by X-ray powder diffraction (XRD) using CaF<sub>2</sub> as an internal standard material. Unreacted CH was estimated from the weight loss by a Ca(OH)<sub>2</sub> → CaO+H<sub>2</sub>O↑ reaction at approximately 450 °C in dynamic TG. For the Zeo and CH hydration product, the changes in the relative amounts were calculated by comparing it to the XRD intensity of the CaF<sub>2</sub> added as an internal standard material.

Figure 1 shows XRD patterns of products hydrated for 13 days. The isostructural materials of strätlingite–vertumnite, Ca<sub>2</sub>Al(AlSi)<sub>2</sub>O<sub>2-3</sub>(OH)<sub>10-12</sub>·nH<sub>2</sub>O, and hydrocalumite (hereafter, abbreviated to Str and C-A-H respectively) were observed as hydrated products of the crystalline substance.<sup>3-6</sup> The framework of Str has a positive charge, as a third of the Ca<sup>2+</sup> sites in the CH octahedral layers is substituted for Al<sup>3+</sup>. Str has the same frame structure as C-A-H, but has a different interlayer structure. Str intercalates (SiAl)O<sub>4</sub> tetrahedral layer as an interlayer material, whereas C-A-H has anions such as SO<sub>4</sub><sup>2-</sup>, OH<sup>-</sup>, Cl<sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in the interlayer. Basal spacing is approximately 1.25 nm for Str and approximately 0.76–0.89 nm for C-A-H depending on the anion species. It is considered that the C-A-H produced in this experiment contains OH<sup>-</sup>, H<sub>2</sub>O and a small amount of CO<sub>3</sub><sup>2-</sup>, mainly in the interlayer under the present experimental conditions. Such C-A-H is also formed in concrete with no zeolite added, and is considered to affect the drying shrinkage properties of concrete.<sup>7</sup> Figure 2 shows changes in percentage of reaction of CH and Zeo with hydration time. Those values of CH and Zeo differed depending on the mixing ratio. Thus, the smaller the mixing ratio

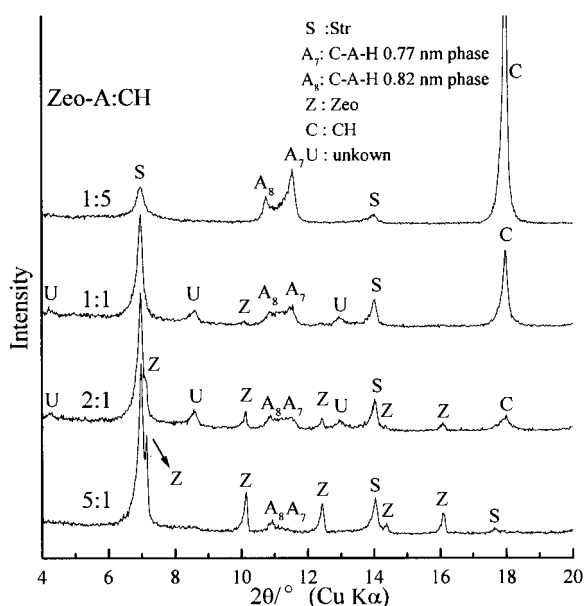


Figure 1. XRD patterns of products hydrated at 20 °C for 13 days.

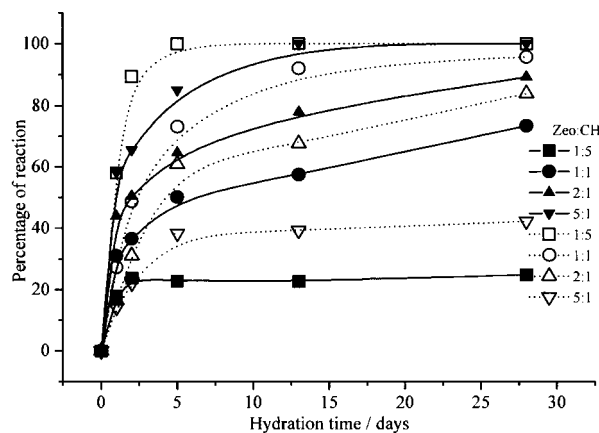


Figure 2. Changes in the percentage of reaction of CH and Zeo with hydration time. ■, ●, ▲, ▼ : CH, □, ○, △, ▽ : Zeo.

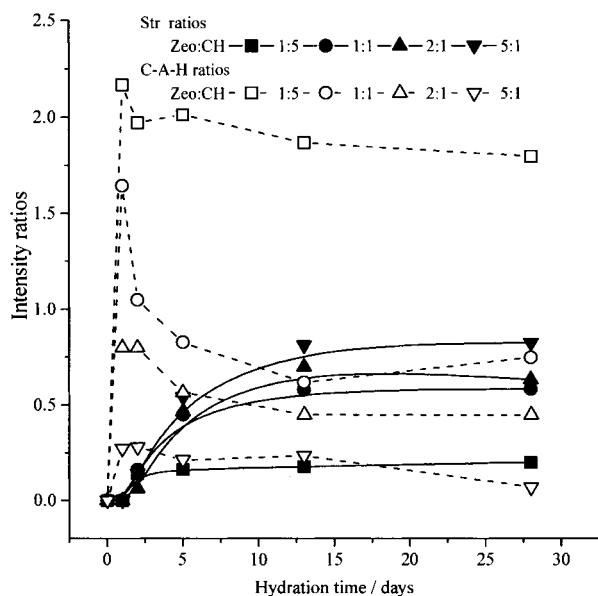


Figure 3. Changes in the intensity ratios of Str and C-A-H (001) peaks against  $\text{CaF}_2$  (311) peak intensity with hydration time.

of each substance was, the greater the reaction ratio would become. When one of these substances was completely consumed, the reaction went no further. Figure 3 shows changes in the XRD intensities ratios of C-A-H and Str against  $\text{CaF}_2$  added in set amounts as a standard material. A large amount of C-A-H was produced as the CH ratio increased. Also, C-A-H was formed for up to 24 h after the hydration started, and then the amount produced decreased. On the other hand, Str was not formed in 24 h after the hydration, but the amount of generation increased rapidly after that. Differences in the Str formation rate for each mixing ratio turned out to be small, with a bigger Zeo mixing ratio resulting in a greater amount of the final products. Figure 4 shows the changes in the reacted Ca/Si ratio, which was estimated from the reacting weight of CH and Zeo in Figure 2, with hydration time. From Figure 4, it can be understood that the Ca ratio is especially high at an initial stage of hydration. This tendency conforms to the change in the C-A-H amount produced in Figure 3. Thus C-A-H is generated in the initial hydration stage of a small silicic ion concentration, and then Str is generated after that. Although the amount of C-A-H decreases and that of Str increases in hydration time from 5 to 13 days, Ca/Si hardly

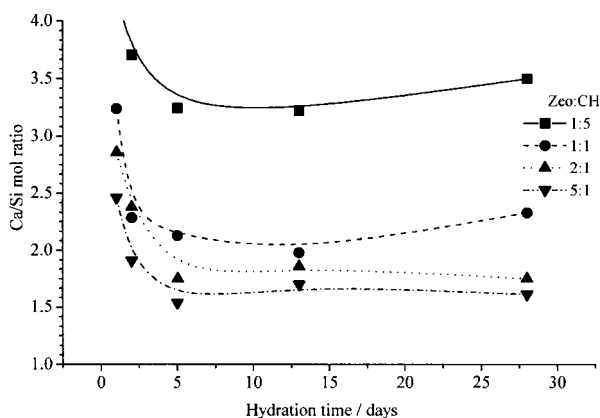


Figure 4. Changes in the reacted Ca/Si mol ratios with hydration time.

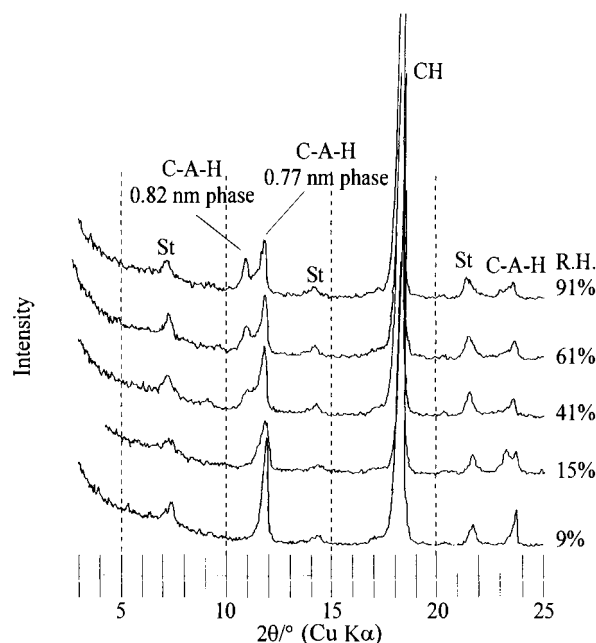


Figure 5. Relative humidity-controlled XRD patterns for products of Zeo:CH = 1:5 hydrated for 13 days.

changes. Therefore, it is considered that a part of C-A-H will be altered with anion exchange to Str.

As these materials have interlayer water, it is assumed that a large volume change will be seen as a result of hydration/dehydration of the interlayer water. Therefore, the influence of humidity on the hydrates was examined by the humidity-controlled XRD. Figure 5 shows the humidity-controlled XRD patterns of Zeo:CH = 1:5. Str was not affected by the humidity as shown in Figure 5. Only the 0.77 nm phase was observed at a low humidity on C-A-H. The 0.77 nm phase partly swelled to 0.82 nm at a humidity of 40% or above, the intensity of the 0.82 nm phase growing as the humidity increased. This reaction was reversible. Therefore, considering both this result and the fact that C-A-H is distinctively produced at an initial stage of Zeo and CH hydration reaction, it is assumed that the drying shrinkage property of the Zeo-added concrete is related to the C-A-H formation. It is noted that the 0.77 nm phase in part does not show any swelling property, which is thought to derive from the C-A-H interlayer structure, namely, the difference in amounts of anions such as  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . The quantitative correlation between the interlayer structure and the dehydration/hydration properties of C-A-H is certain to be the subject of future reports.

#### References and Notes

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