Nanometer-Resolved Spectroscopic Study Reveals the Conversion Mechanism of CaO·Al2O3·10H2O to 2CaO·Al2O3·8H2O and 3CaO·Al2O3·6H2O at an Elevated Temperature

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Supporting Information

ABSTRACT: The main binding phases of calcium aluminate cement (CAC) concrete, CaO·Al2O3·10H2O (CAH10), and 2CaO·Al2O3·8H2O (C2AH8), slowly convert to 3CaO·Al2O3·6H2O (C3AH6) and Al(OH)3 (AH3). This reaction significantly speeds up at a temperature higher than ~30 °C, and over time leads to significant strength loss in CAC concrete. Because of the lack of direct evidence that simultaneously probes morphological and chemical/crystallographic information, intense debate remains whether the conversion is generated by a solid-state or through-solution reaction. The conversion of CAH10 at an elevated temperature is studied herein using synchrotron-radiation-based X-ray spectromicroscopy capable of acquiring near edge X-ray absorption fine structure data and ptychographic images with a resolution of ~15 nm. We show that, when stored at 60 °C, CAH10 first converts to C2AH8 by solid-state decomposition, followed by the through-solution formation of C3AH6. The C3AH6 crystallizes from both the relics of dissolved C2AH8 and from the surface of existing C3AH6 crystals. The solid-state decomposition of CAH10 occurs in multiple sites inside the CAH10 crystals; the spatial range of each decomposition site spans a few tens of nanometers, which overcomes the kinetics barrier of ion transportation in the solid-state. Our work provides the first nanoscale crystal–chemical evidence to explain the microstructure evolution of converted CAC concrete.

INTRODUCTION

The unique hydration behavior of calcium aluminate cement (CAC), such as high reactivity (even at low-curing temperatures), leads to its broad application in emergency repair, fast-track construction in cold weather, and infrastructures exposed to sulfate attack; it is also widely used to make refractory linings for high-temperature furnaces.1,2 Calcium aluminate cement contains CA (monocalcium aluminate) as the main cementing compound, with C12A7, CA2, and CA6 as the minor phases, where C=CaO, A=Al2O3, and H=H2O in the cement chemistry notation.1,3,4 The rapid hydration of CA produces CAH10 and C2AH8 + AH3 at ambient temperature and pressure condition, which contributes to the fast-strength development in the first 1–2 days after mixing with water.

The hydration route of CA is strongly temperature-dependent; see eq 1:1,5–7

\[
CA + H_2O \rightarrow \begin{cases} 
CAH_{10} & (<10 - 15 ^\circ C) \\
C_2AH_8 + AH_3 & (15 - 30 ^\circ C) \\
C_3AH_6 + AH_3 & (>30 - 60 ^\circ C)
\end{cases}
\] (1)

The low-temperature metastable hexagonal phases CAH10 and C2AH8 are kinetically stable if the curing temperature remains lower than ~15 °C and ~30 °C, respectively. However, they will inevitably convert to the stable forms, C3AH6 (cubic, with rhombic dodecahedron habit5) and AH3 (usually in the form of poorly crystalline gibbsite), over the long-term service life, especially at elevated temperatures. This occurs according to the following reaction equations:

\[
\begin{align*}
2\text{CAH}_{10} & \rightarrow \text{C}_2\text{AH}_8 + \text{AH}_3 + 9\text{H} \\
3\text{CAH}_{10} & \rightarrow \text{C}_3\text{AH}_6 + 2\text{AH}_3 + 18\text{H} \\
3\text{C}_2\text{AH}_8 & \rightarrow 2\text{C}_3\text{AH}_6 + \text{AH}_3 + 9\text{H}
\end{align*}
\] (2)

Since the products have higher densities than the initial reactants, this conversion is often accompanied by a marked increase in porosity and a significant loss of strength.1–7 To compensate for this degradation, the precursor component matrix needs to be very dense before the conversion. This

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usually requires the initial water-to-cement mass ratio (w/c) of CAC concrete to be below 0.4. Investigating the mechanism of the conversion reaction has pronounced significance both to the fundamental knowledge of cement chemistry and its engineering applications.

The crystal structures of CAH_{10} and C_{3}AH_{6} are well established,\textsuperscript{3,4,5,6,7} however, that of C_{2}AH_{8} is still not completely defined, although it is known to be a layer-double-hydroxide (LDH) compound with Al(VI) in the main layer and Al(IV) in the interlayer space.\textsuperscript{1,2} The missing information on the C_{2}AH_{8} structure and the unclear relationship between the chemical environments of the metastable and the stable phases add to the difficulty in solving the following fundamental questions regarding the conversion reactions:

1. At temperatures above \(\sim 50\,^\circ\text{C}\), does CAH_{10} convert directly to C_{3}AH_{6} or go through an intermediate transformation phase(s), e.g. C_{2}AH_{8}?\textsuperscript{8}

2. Does the conversion happen in a through-solution mechanism\textsuperscript{9} or by a solid-state reaction?\textsuperscript{10}

Previous in situ synchrotron radiation energy-dispersive diffraction (SR-EDD) evidence showed that when CAH_{10} is stored at a constant temperature between 50–90 °C, its conversion to C_{2}AH_{8} undergoes a reaction through an intermediate C_{2}AH_{8} until C_{2}AH_{8} becomes self-nucleated, and that the conversion of CAH_{10} is governed by solid-state reaction mechanisms.\textsuperscript{11,12,13} Other research, however, suggests that a through-solution reaction is kinetically favored over a solid-state reaction as the ion transportation inside the solid is extremely slow,\textsuperscript{14} and C_{2}AH_{8} precipitates earlier than C_{3}AH_{6} due to the ease of nucleation.\textsuperscript{15}

The microstructural evolution of ordinary Portland cement (OPC) hydration has been successfully investigated in the past decades both by experiments and computational modeling.\textsuperscript{16,17,18} To apply such modeling schemes to CAC concrete, the morphological change of converted CAC hydrates at the nanometer scale needs to be clarified. In the meantime, immobilization of toxic (heavy) metals in hardened CAC is gaining increasing interest in environmental engineering practice due to its higher resistance to chemical attack and mechanical abrasion compared with OPC. Existing studies suggest that metal ions with different coordination geometries may favor the crystallization of different calcium aluminato hydrates, which would in turn alter the rate of hydration and conversion of CAC cement paste. For example, doping Zn(NO\textsubscript{3})\textsubscript{2} leads to the preferential formation of C_{2}AH_{8}, which would in turn alter the rate of hydration and conversion of CAC cement paste. For example, doping Zn(NO\textsubscript{3})\textsubscript{2} leads to the preferential formation of C_{2}AH_{8}, which would in turn alter the rate of hydration and conversion of CAC cement paste.

The present study uses synchrotron-based scanning transmission X-ray microscopy (STXM)\textsuperscript{11,19} to collect the near-edge X-ray absorption fine structure (NEXAFS) spectra at the Ca K-edge and Al K-edge,\textsuperscript{20} of the CaH_{10} conversion–reaction system. The spectroscopic information, coupled with photoemographic imaging data at resolutions of \(\sim 15\,\text{nm}\),\textsuperscript{21} allows direct chemical and morphological observations at the nanometer scale. NEXAFS spectra of the pure phases [CAH_{10}, C_{2}AH_{8}, C_{3}AH_{6}, and AH_{3} (in gibbsite form)] were first collected, followed by tracking the spatially resolved crystal chemistry evolution of CAH_{10} confined in a water bath at 60 °C. Our results provide nanoscale evidence of how CAH_{10} converts to C_{2}AH_{8} under an elevated temperature, which can be directly used in modeling the microstructural evolution of CAC concrete affected by the conversion reaction.

**EXPERIMENTAL SECTION**

Pure CA and C_{2}AH_{8} were purchased from Mineral Research Processing Co. Pure CAH_{10} was synthesized by CA hydration in deionized (D.I.) water, according to the protocol established in previous research\textsuperscript{8} but using a water-to-CA mass ratio of 10. The hydrates were cured in polypropylene vials for 7 days at 8 ± 2 °C. Crystalline C_{2}AH_{8} with amorphous AH_{3} gel was synthesized by CA hydration in deionized water at 25 ± 2 °C and cured in polypropylene vials for 7 days. Both samples were vacuum-filtered in a N_{2}-protected glovebox. Gibbsite was synthesized by mixing 100 mL of 0.1 M aluminium nitrate hexahydrate aqueous solution with 0.25% ammonia aqueous solution up to pH 8 at 80 °C. The slurry was then loaded into a flask and heated under constant stirring at 80 °C for 4 days. After being cooled to room temperature, the material was recovered by filtration, washed with deionized water, and dried for 1 day in an oven at 120 °C. These phases were verified by a PANalytical X'Pert Pro\textsuperscript{TR} diffractometer, according to the characteristic x-ray diffraction (XRD) peak positions of each phase.\textsuperscript{6,10} The pure CAH_{10}, CAH_{8}, and gibbsite samples were used to collect reference spectra at the Ca L\_\textsubscript{3}-edge and Al K-edge. The hexagonal-shaped C_{2}AH_{8} single crystals are readily identified from amorphous AH_{3} under STXM and are used to collect the reference spectra for C_{2}AH_{8}.

The aforementioned CAH_{10}–D.I. water suspension, contained in 2 mL polypropylene vials, was rapidly heated to 60 ± 2 °C in a water bath. After being heated for the desired time durations (30 min, 1 h, and 3 h), a 0.1 μL drop of the suspension was transferred onto a 100 nm-thick-Si_{3}N_{4} window, followed by quick removal of the liquid with Kimwipes (Kimtech Science\textsuperscript{22}), as described in ref 22. The top of the sample was covered with another Si_{3}N_{4} window. Epoxy-glue was applied along the perimeter edges of the two windows in order to isolate the solid samples from the relative humidity of the experimental environment. The “sandwiched” sample was then placed in the STXM chamber for measurements.

The STXM experiments at Ca L\_\textsubscript{3}-edge were conducted at beamline S3.2.2.2, and Al K-edge at beamline S3.2.1.2, of the Advanced Light Source of the Lawrence Berkeley National Laboratory. This synchrotron radiation facility operates at 1.9 GeV and 500 mA. Beamline S3.2.2 provides X-ray beam energy in the range of 250–780 eV,\textsuperscript{23} using a zone plate with the smallest zone width of 25 nm that yields transmission images at a resolution of \(\sim 30\,\text{nm}\). Beamline S3.2.1 covers the X-ray beam energy range from 600 to 2000 eV. It is coupled with a fast CCD for ptychographic imaging at a pixel resolution \(\sim 5\,\text{nm}\), using soft X-ray beam at energy 800 eV.\textsuperscript{24} The effective resolution for this study was \(\sim 15\,\text{nm}\). For the current study, the energy scanning range is 340–360 eV (step size 0.1 eV) for the Ca L\_\textsubscript{3}-edge, and 1550–1610 eV (step size 0.2 eV) for the Al K-edge. The measured data were processed using aXis2000 software, and the spectra were normalized for comparison purposes.\textsuperscript{21} A single-value-decomposition (SVD) algorithm is imbedded in aXis2000, which allows fitting a target spectrum using linear combination of several reference spectra.

**RESULTS AND DISCUSSION**

Ca L\_\textsubscript{3}-Edge NEXAFS Spectroscopic Study of CAH_{10}, C_{2}AH_{8}, and C_{3}AH_{6}. The Ca L\_\textsubscript{3}-edge NEXAFS spectra contain the coordination environment information on the Ca–O polyhedra in the pure phases. The interpretation here follows the theory of crystal field splitting of \(d\) compounds such as Ca\textsuperscript{2+}, which is briefly described in previous discussion of Ca-bearer minerals in cement-related systems.\textsuperscript{15,22,23} Detailed
theoretical background can be found in the literature. In summary, a typical Ca $L_{2,3}$-edge NEXAFS spectrum has two doublets due to spin-orbital coupling. Each doublet has a major ($a_2$ or $b_2$) and a minor peak ($a_1$ or $b_1$). A few leading peaks (named peak 1 and 2 herein) may also be present before the first doublet. For $d^8$ compounds, the $d$ orbitals are classified into $t_{2g}$ symmetry ($d_{xy}$, $d_{yz}$, and $d_{xz}$) and $e_g$ symmetry ($d_{z^2}$ and $d_{x^2-y^2}$). They have equal energy until they are approached by ligands (O atoms in this study), which change the energy of the $d$ orbitals depending on the coordination symmetry. As a result, the energy gap $e_g-t_{2g}$, also termed $10Dq$, is sensitive to the symmetry of the complexation. The characteristics of the spectra, i.e., the distance and relative intensity between the major and minor peaks, are greatly influenced by $10Dq$ and the coordination symmetry; therefore, they can be used as an index of the chemical environment of Ca.

The Ca–O coordination of C$_3$AH$_6$ is cubic-like as the peak 2 of the Ca $L_{2,3}$-edge NEXAFS spectrum is located between peak $a_1$ and $a_2$; see Figure 1a. In contrast, the coordination of Ca–O in CAH$_{10}$ and C$_2$AH$_8$ are octahedral-like, similar in shape to ettringite and kuzelite (also named monosulfate-AFm). As shown in Figure 1b, the atomic configuration of Ca–O polyhedron in CAH$_{10}$ is very similar to that of ettringite; a rectangle (four O atoms) and a parallelogram (four O atoms) approach the Ca from opposite directions and are aligned along the Ca–O bond axes. The Ca–O bond distances are slightly shorter than those in ettringite, which explains why the $10Dq$ value of CAH$_{10}$ is smaller than that of ettringite.
each other’s diagonals. The main peak (a$_2$ or b$_2$) positions of their Ca $L_{2,3}$-edge spectra are both $\sim$0.2 eV higher than those of kuzelite and Ca$_2$AH$_8$; see Figure 1a. The spectra of CAH$_{10}$ also has a clearly resolved b$_{10}$ peak between peak a$_2$ and b$_1$, which is not observed in ettringite, and can be used to distinguish these two phases in a Ca $K$-edge STXM study.

The atom positions of the Ca$_2$AH$_8$ have not been determined yet.$^{11}$ The results presented herein strongly imply the existence of a [Ca$_2$Al(OH)$_6$]$^+$ layer structure in Ca$_2$AH$_8$, which is highly similar to kuzelite, because they share almost identical Ca $L_{2,3}$-edge spectra. In contrast, the interlayer [SO$_4$]$^{2-}$ anion groups in kuzelite are replaced by [AlO$_4$]$^{3-}$ groups in Ca$_2$AH$_8$; see Figure 1c.$^{11}$ Therefore, in both minerals, Ca is in a 3-fold rotation site, coordinated by seven oxygen neighbors. This slightly lowers the oxidation degree of Ca compared to those in CAH$_{10}$ ettringite, and Ca$_3$AH$_8$ where the Ca–O coordination number is 8. Therefore, the main peak (a$_2$ or b$_2$) positions in Ca$_2$AH$_8$ and kuzelite are $\sim$0.2 eV lower.

**X-ray Ptychographic Image and Al K-Edge NEXAFS Study of the Conversion Reaction. Before Heat Curing and after 30 min Storage in a 60 °C Water Bath.** Compared to a transmission electron microscope, X-ray ptychographic imaging provides nanometer resolution but with much less beam damage to the samples. As shown in Figure 2a,b, prismatic CAH$_{10}$ crystals are synthesized from CA hydration at 8 °C. The crystals in the field of view are of similar size, with length 0.5–1 μm and width 150–500 nm. Particles can agglomerate up to $\sim$1 μm wide; see Figure 2a,b. After 30 min storage in a 60 ± 2 °C water bath, clear morphological changes occur to the prismatic CAH$_{10}$ as parallel gaps form along the longitudinal direction (red arrows in Figure 2c,d). Faceted particles with diameters of $\sim$700 nm are observed (black arrows in Figure 1c). On the basis of the round morphology, they are identified as Ca$_3$AH$_8$, which has the characteristic rhomb dodecahedron habit of cubic garnets.$^{8,15}$ This will be confirmed in the next section by spectroscopic evidence.

**After 60 min storage in a 60 °C water bath, the CAH$_{10}$ prisms are no longer widely observed; see Figure 3.** Instead, the main morphology is the agglomerations of thin short fibers, which are of similar size, i.e., 100–200 nm long and a few tens of nanometers thick. The contour of the fiber agglomerations is highly similar to the original CAH$_{10}$ prisms, as illustrated by the red dashed squares in Figure 3b,c. An aggregated CAH$_{10}$ prism cluster is observed in the middle of conversion to thin short fibers (red arrow in Figure 3a). The prisms have not completely disappeared, while fiber networks seem to be forming in a random orientation inside the region which was originally occupied by CAH$_{10}$ prisms. The fibers are less likely to nucleate on the CAH$_{10}$ surface in which case a specific orientation of fibers on the surface should be expected. Faceted Ca$_3$AH$_8$ particles (black arrow in Figure 3b,d), with diameter $\sim$1 μm, are also observed to be in close contact with the fiber networks on 1–2 facets; see red circles in Figure 3b,d.

The previous description of morphological changes seems to indicate a solid-state transformation from CAH$_{10}$ to the agglomerations of fibers of much smaller size relative to...
CAH_{10} prisms. To confirm this observation, a spatially resolved Al K-edge NEXAFS study was conducted in the area of Figure 3a, as shown in Figure 4. The reference spectra of pure phases (Figure 4b) are consistent with the reported work apart from the different energy calibration standards used.\textsuperscript{31,32} In general, the major absorption of the pure phases are composed of a few individual peaks, which correspond to the major 1s to 3p transition (peak 1) and the multiple scattering (MS) process from the neighboring shells (peak 2).\textsuperscript{32,33} The ratio between the intensities of the 1s \rightarrow 3p transition and the MS process can vary significantly. For example, in the spectra of gibbsite, C_{2}AH_{8}, and C_{3}AH_{6}, the MS peak is dominant, whereas in CAH_{10}, it has comparable intensity to the 1s \rightarrow 3p transition peak. A minor peak 3 is usually observed at \sim 15 eV higher than the major peaks, which can be attributed to either the MS process or a transition from 1s to 3d. Although theoretical prediction of the spectra is complex, the abundant spectral characteristics allow reliable component phase mapping.\textsuperscript{34}

To investigate the chemical information on areas with distinct morphologies, the Al K-edge NEXAFS spectra of Area_1 and Area_2 are investigated (Figure 4a,b) since they each represent a morphological type, i.e., the prisms (Area_1) and fiber agglomeration (Area_2). The spectrum of Area_1 highly resembles that of pure CAH_{10} in both peak positions and relative intensities. Area_1 is therefore assigned to a CAH_{10} prism that has not yet converted to the final product. Among all reference spectra, the spectrum of Area_2 resembles that of AH_{3} (gibbsite) most closely. The peak 3 of both Area_2 and gibbsite is at a much higher position than that of other reference phases. However, the major peak position of Area_2 is \sim 0.8 eV higher compared to that of gibbsite, which can be explained by the contribution from C_{2}AH_{8} and/or C_{3}AH_{6}. The spectrum of Area_2 clearly does not match that of CAH_{10} in either the position or the broadness of the major peak (peak 2) as well as the position of the minor peak (peak 3). Further evidence is given in the Supporting Information (SI), where single value decompositions (SVD) of the major peak of Area_2 spectrum, using the above-mentioned reference spectra, leads to a negative and insignificant coefficient for CAH_{10} spectrum, which is obviously unrealistic. The Area_2 spectrum can be satisfactorily fit using AH_{3} combined with either C_{2}AH_{8} or C_{3}AH_{6}; see SI file for details.

It is reported that C_{2}AH_{8} crystallizes in the beginning of CAH_{10} conversion reaction.\textsuperscript{6} Considering the shape of the short fibers, they are more likely C_{2}AH_{8} (hexagonal crystal shape), rather than C_{3}AH_{6} (cubic crystal shape). Reported research has also confirmed that the AH_{3} formed from the conversion of CAH_{10} often exists as an amorphous gel that cannot be detected by XRD.\textsuperscript{5,6,13,14} Therefore, Area_2 is most probably composed of aggregated short fibers of C_{2}AH_{8} intermixed with AH_{3} gel. The coexistence of C_{2}AH_{8} and AH_{3} gel is consistent with the reaction formula; see eq 2.

We then investigated a much thicker region; see Area_3 in Figure 4a. As shown in Figure 4c, the spectrum of Area_3 can be well fitted by the linear combination of the reference spectra of Area_1 (CAH_{10}) and Area_2 (C_{2}AH_{8} + AH_{3} gel), which confirms that Area_3 contains residual CAH_{10} and the conversion products, i.e., C_{2}AH_{8} + AH_{3} gel. From a quantitative analysis point of view, the prepeak and postpeak baseline intensities of two reference spectra components in Figure 4c, i.e., CAH_{10} (red curve) and C_{2}AH_{8} + AH_{3} gel (green curve), are almost identical. Previous literature demonstrates that the difference between the prepeak and postpeak baseline intensity is linearly proportional to the amount of attenuation created.
due to the absorption edge of Al. Therefore, in Area_3, the amount of Al from CAH_{10} and C_{2}AH_{8} + AH_{3} gel is roughly the same. It should be noted that Area_2 may also contain residue CAH_{10}; however, we chose this visually thin area with uniquely distinguished morphology (agglomerated fibers) so that the chance of CAH_{10} be mixed in Area_2 is significantly low.

By applying the same fitting strategy to the whole studied region, a phase mapping is displayed in Figure 4d with red representing CAH_{10} and green representing C_{2}AH_{8} + AH_{3} gel. The prismatic morphology is mainly assigned to CAH_{10} (white circles in Figure 4d), and the region of short fibers (blue circles in Figure 4d) is mainly assigned to C_{2}AH_{8} + AH_{3}, with contributions of CAH_{10} spectrum in the thick areas. Coupled with the morphological observation that the short fibers agglomerate in the contour of the original CAH_{10} prism, the spectroscopic evidence leads to the hypothesis that CAH_{10} converts to C_{2}AH_{8} fibers and AH_{3} gel through internal decomposition, i.e., C_{2}AH_{8} + AH_{3} gel form within the region which was originally occupied by CAH_{10} prisms. In such case, the conversion reaction happens in a solid-state route, and the external bulk water is not needed to transport dissolved ions.

At 60 °C, this nanoscale ion transportation is rapid enough to decompose a large crystal of CAH_{10} to crystalline Ca-rich regions (C_{2}AH_{8}) and amorphous Al-rich regions (AH_{3} gel) within an hour of incubation. After 180 min storage in a 60 °C water bath, with storage at 60 ± 2 °C for 180 min, we observe an enrichment of the faceted C_{3}AH_{6} dodecahedral crystals (Figure 5); however, their sizes are not significantly larger, compared with water bath for 30 and 60 min. The proximity of adjacent C_{3}AH_{6} facets indicates that C_{3}AH_{6} may crystallize on the facets of existing C_{3}AH_{6} crystals, as indicated by the red circles in Figure 5a,b.

To investigate the chemistry of areas with distinct morphologies, Al K-edge NEXAFS spectra of Area_1 (round crystal), Area_2 (fibillar crystal), and Area_3 (fibers intermixed with featureless phase) were collected; see Figure 5a,b. Apart from these crystalline morphologies, areas exist that lack crystalline features; see Area_3, N_1, and N_2 in Figure 5a.
It is clearly confirmed by comparing the spectra Area_1 and C2AH6 that the particles are C2AH6. The spectrum of fibrous phases (Area_2) resembles the spectrum of the fibrous area in Figure 4a, which is confirmed to be a mixture of C2AH6 and AH3 gel. The major peak position (peak 2) in the spectrum of Area_2 (Figure 4c) matches that of C2AH6 yet the former is much broader. This broadness can be explained by the contributions from remnant C2AH6 + AH3 that exhibits the fibrous feature. As shown in Figure 5d, the spectrum of Area_3 can be well-fitted using a linear combination of the spectra of (C2AH6 + AH3) and C2AH6 at a mass ratio of ∼2:1. We investigate two other poorly crystalline areas, N_1 and N_2, which exhibit featureless morphologies that were similar to Area_3, with residue of fibrous features; see the enlarged images of N_1 and N_2 in Figure 5e. The spectra of N_1 and N_2 also resemble that of Area_3 in Figure 5c; i.e., there is clear contribution from C2AH6 spectrum to their major peak broadness. Therefore, the featureless areas in Area_3, N_1 and N_2 are most likely poorly crystalline C2AH8 precursors, intermixed with remnant crystalline region of C2AH6. This is consistent with previous findings that C2AH8 provides a nucleation site for C3AH6.

The C2AH8 crystallized to individual particles with a unique dodecahedral shape, which are distinct to the prismatic or fibrous shapes of the metastable phases. This initial crystallization implies a through-solution, rather than a solid-state reaction path. As shown in Figures 2, 3, and 5, the existing C2AH8 and C3AH6 crystals seem to act as preferred nucleation sites for C2AH6. Therefore, the formation of C2AH6 may be self-accelerated when nucleation is factored into the rate-control process. It should also be noticed that C2AH8 does not grow to macrocrystals throughout the heating duration in this study, and the number of C2AH8 crystals soon decreases after ∼1 h of thermal storage. This explains why the maximum diffraction signal of C2AH8 remains low compared with that of C2AH6 as shown by the SR-EDD study. In real CAC concrete infrastructure, the rate of conversion may differ from the current study due to the difference of reaction conditions. Therefore, the percentage and morphology of C2AH10, C2AH8, and C3AH6 in a converted infrastructure are functions of the local temperature, local ion concentration, and spatial availability for crystal growth.

## CONCLUSION

The current study used nanometer resolved Ca K-edge and Al K-edge NEXAFS spectroscopy to investigate the conversion reaction of CAH10 at an elevated temperature (60 °C). Our results provide solid evidence that solves the decades-long debate regarding conversion reaction mechanisms. The results are summarized as follows:

1. Although the atomic positions of C2AH8 are not completely solved, we provide spectroscopic evidence to prove that the local environment of Ca in the layer structure [(Ca3Al(OH)6)2] of C2AH8 highly resembles that of kuzelite. The Ca K-edge spectra reported here can be used as reference spectra for future study at Ca K-edge.
2. After storage in a 60 °C water bath for 60 min, the prismatic CAH10 decomposed to thin fibers of C2AH8 and amorphous AH3 in a solid-state route through short-range ion transportation within a few tens of nanometers.
3. Upon extended incubation for 180 min under 60 °C, the C2AH8 destabilizes to form C3AH6 in a through-solution route. Existing C2AH8 and C3AH6 crystals may act as preferred nucleation sites for C2AH8 crystalization.

Understanding the mechanism of the conversion reaction in CAC is fundamentally important to innovate and implement control strategies at the reaction stage. Future work may include quantitatively correlating the solid-state decomposition rate of CAH10 with the external conditions, such as the relative humidity and curing temperature. In the application of immobilizing heavy metals, the internal condition of CAH10, such as the changing coordination geometries of the incorporated metallic ions, may alter the kinetics and path of the conversion reaction. This study presents a coupled morphological and spectroscopic tool to reveal such process at the nanoscale.

## ASSOCIATED CONTENT

### Supporting Information

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A single value decomposition (SVD) of the Area_2 spectrum in Figure 4 (PDF)

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Notes

The authors declare no competing financial interest.

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