Research Article

Microstructural Study of Hydration of C₃S in the Presence of Calcium Nitrate Using Scanning Transmission X-Ray Microscopy (STXM)

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Calcium nitrate (CN) is used widely as an effectively inorganic setting accelerator and antifreeze admixture in concrete structures. In this paper, the multiscale investigation of CN on the hydration of C₃S was studied by scanning transmission X-ray microscopy (STXM) combined with near-edge X-ray absorption fine structure (NEXAFS), ²⁹Si MAS NMR, calorimetry, scanning electron microscope, and N₂ absorption. It was concluded that the calcium silicate hydrate (C-S-H) surrounds the unhydrated C₃S at 1-day hydrated C₃S in the presence of calcium nitrate, while portlandite is partly in transformation and is formed partly. Based on Ca L₃,2-edge NEXAFS spectra for 1-day hydrated C₃S particle, calcium nitrate does not change the structure of the asymmetrically 7-fold coordination of calcium in the C-S-H. Calcium nitrate can accelerate the hydration of C₃S to some extent and polymerization of the silicate chains within C-S-H considerably at early age, resulting in the increasing specific surface area.

1. Introduction

With the rapid speed of economic and industrial development, concrete has become the most widely used construction material. Today, many admixtures are used inside the concrete to protect it from freezing by accelerating cement hydration and depressing the freezing point of the aqueous solution [1]. The application of antifreeze admixtures is originally from Russia, and it is technologically convenient and beneficial for winter concreting.

Calcium nitrate (Ca(NO₃)₂, CN) is an effective chloride-free setting accelerator and antifreeze admixture [1–4]. Justnes and Nygaard studied the changes in the microstructure of cement paste and concrete in the presence of Ca(NO₃)₂ and concluded that Ca(NO₃)₂ can lower the amount of calcium hydroxide (CH) in hydrated cement pastes and change the morphology of CH to larger clusters, as well as increase the porosity of the OPC paste [6]. Some studies suggest that calcium nitrate may form a complex salt with aluminate phase in cement, and the accelerating efficiency of Ca(NO₃)₂ depended on the cement type, especially on belite content [4, 7]. However, it was proved by X-ray diffraction that the presence of Ca(NO₃)₂ does not affect the stability of ettringite and forms hardly the compound C₃A·Ca(NO₃)₂·10H₂O[8]. Harald and Erik proposed the mechanism for accelerating the setting of Ca(NO₃)₂: (1)
an increased concentration of Ca\(^{2+}\) leads to a faster supersaturation of the fluid for forming CH, while (2) Ca(NO\(_3\))\(_2\) decreases the concentration of SO\(_4\)\(^{2-}\), leading to slower formation of ettringite which will shorten the onset of C\(_3\)A hydration [8]. However, there are few literatures on Ca(NO\(_3\))\(_2\), obtained from the hydration of C\(_3\)S regarding its chemical and physical properties. Therefore, it is essential to investigate the effect of Ca(NO\(_3\))\(_2\) of the hydrated C\(_3\)S at its microstructure level.

Scanning transmission X-ray microscopy (STXM) is a promising technique in further understanding the structure and the properties of amorphous and crystalline materials, such as C-S-H phase [9–14]. Combined with near-edge X-ray absorption fine structure (NEXAFS), STXM provides the information on both morphology and X-ray Absorption Spectroscopy (XAS) at submicron-scale level. The object is to explore the mechanism of calcium nitrate during the hydration of C\(_3\)S as an accelerator at the molecular level. It will improve understanding of the accelerating role of calcium nitrate on the chemical information of C-S-H, bringing a state-of-the-art step closer to the development of admixtures for Portland cement and advanced concrete structures.

2. Materials and Experimental Methods

2.1. Materials. Triclinic C\(_3\)S powders were purchased from CTL Group (Skokie, IL), which were passed through sieve #325 (45 μm). The analytical reagent of Ca(NO\(_3\))\(_2\)·4H\(_2\)O was used by 2 wt% of C\(_3\)S powders, which was purchased from Sigma-Aldrich. The boiled deionized water after carbonation was used by 2 wt% of C\(_3\)S powders, which was purchased from Damao Chemical Technology.

2.2. Experimental Methods

2.2.1. Isothermal Calorimetry. The samples were prepared, respectively, by 0.4 and 0.5 liquid/solid ratio. About 2 g of the fresh paste was placed into a glass Admix ampule with 20 mL, and the ampule was sealed before transferring into the chamber in the isothermal calorimeter. The data were collected continuously by isothermal calorimetry (TA Instruments, Model TAM Air) during the 36-hour hydration of the samples.

2.2.2. X-Ray Diffraction. The samples of the triclinic C\(_3\)S and hydrated C\(_3\)S with the addition of Ca(NO\(_3\))\(_2\) at 1, 3, 7, and 28 days were tested using a PANalytical X’Pert Pro diffractometer equipped with a Co X-ray tube (λ = 1.79 Å) and the rapid X’celerator detector. XRD was used to identify crystalline phases from a 2θ value of 5–80° with a step of 0.02°.

2.2.3. \(^{29}\)Si MAS NMR and N\(_2\) Absorption. The samples of C\(_3\)S pastes with calcium nitrate were prepared by 0.5 of the liquid-to-solid ratio for 1, 3, 7, and 28 days of hydration.

The hydration of the samples was stopped by isopropanol, and then, samples were dried under the vacuum oven for 3 days. The samples were ground into powders for solid-state NMR spectra (Bruker MSL-300 spectrometer). The parameters of NMR measurement followed the method of Li et al. [15]. Thereafter, the samples were crushed into fragments (≤4.75 mm) for N\(_2\) sorption measurement (Micro-meritics ASAP 2000), which is performed at the School of Municipal and Environmental Engineering, Harbin Institute of Technology.

2.2.4. Scanning Transmission X-Ray Microscopy and SEM. Scanning transmission X-ray microscopy (STXM) with near-edge X-ray absorption fine structure (NEXAFS) was performed at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) beamline 5.3.2.1 (350–2500 eV) [16]. Anhydrous triclinic C\(_3\)S powder was mixed with 0.004 g/mL Ca(NO\(_3\))\(_2\) solution with a liquid-to-solid ratio of 5.0. C\(_3\)S pastes were maintained in the CryoTube™ vials (1.8 mL) under the protection of N\(_2\) gas at room temperature and then sealed in a vacuum bag. In this paper, we followed the methods of STXM and \(^{29}\)Si MAS NMR [15].

3. Results and Discussion

3.1. Calorimetry. Figure 1 shows the isothermal calorimetry data for C\(_3\)S hydrated with calcium nitrate prepared under different liquid-to-solid ratio (L/S). Without the addition of calcium nitrate, the height of the early rate peak of C\(_3\)S paste with L/S = 0.5 increases, and the launch of the accelerating period is earlier. Commonly, the early hydration rate of C\(_3\)S
paste with L/S = 0.5 develops more quickly than that of L/S = 0.4; however, the presence of calcium nitrate is opposed due to more nucleation sites in C₃S paste. The addition of calcium nitrate has a significant accelerating effect. When calcium nitrate is absent, the accelerating effect is greater under L/S = 0.4 compared with L/S = 0.5. But the addition of calcium nitrate makes the induction period slightly eliminate. Calcium nitrate can prompt the homogeneous nucleation [17] since the high abundance of Ca²⁺ in the pore solution combined with silicate ions dissolved from C₃S. The early hydration of C₃S paste is accelerated by calcium nitrate, which provides the development of pore structure and hydration products of C₃S paste.

3.2. N₂ Sorption. According to the IUPAC classification, the hysteresis loops for all isotherms obtained from C₃S samples are not of Type IV but of Type H₃ due to no indication of a plateau at high P/P₀ in Figure 2. Each adsorption branch has the similar feature of the typical Type II without limiting adsorption at high P/P₀, and the desorption branch exhibits a different path before reaching a critical P/P₀, which implies aggregates of plate-like particles resulting in slit-shaped pores. The C₃S pastes for hydrating 3 and 7 days in Figure 2(a) have a narrower width of the hysteresis loop, while that of 28 days has the largest. However, the presence of calcium nitrate expands the hysteresis loop since hydrating for 3 days.

The specific surface area results are shown in Table 1. Since the Langmuir method is based on monolayer adsorption, the values for the Langmuir area are generally higher than those for the BET area. The specific surface area of C₃S pastes is enhanced with an increase of hydration times whether the existence of calcium nitrate is included or excluded. However, the presence of calcium nitrate can increase the specific surface area of C₃S paste. C₃S can react quickly with water to form an amorphous phase, calcium silicate hydrates (C-S-H) with many gel pores, and calcium nitrate can accelerate the hydration of C₃S resulting in the increasing specific surface area.

For comparison purposes, the pore size distributions (PSD) are of very great significance as shown in Figure 3. Pore size distributions are calculated by the Kelvin equation ranging from 2 to 50 nm. The mesopores in all samples are assessed by N₂ sorption locating primarily at around 3.5 nm, while the gel pores cannot be addressed due to pore widths < 2 nm. However, the addition of calcium nitrate makes the pore width shift slightly up to about 4 nm with the increasing hydration time. These mesopores smaller than 50 nm play an important part in drying shrinkage and creep.

3.3. STXM Analysis. As mentioned above, the development of the hydration products of C₃S paste is also affected by calcium nitrate. Figure 4 shows the XRD patterns of triclinic C₃S and hydrated C₃S pastes with calcium nitrate. In the presence of calcium nitrate, unhydrated C₃S remains slightly at 7-day hydration since the reactivity of triclinic C₃S is lower than monoclinic C₃S. The feature peaks of portlandite are occurring at 1-day hydration of C₃S pastes, while the...
The morphology of portlandite presented the plate-like crystals surrounded by unhydrated C$_3$S and C-S-H gel as shown in Figure 5.

Figure 6 presents the single image of 1 d hydrated C$_3$S taken at 340 eV (Figure 6(a)) and Ca L$_{3,2}$-edge NEXAFS spectra (Figure 6(c)) of a selected area in Figure 6(a). Based on previous studies [18], the Ca L$_{3,2}$-edge NEXAFS spectra of Ca(OH)$_2$, anhydrous C$_3$S, and pure C-S-H (in 17 d hydrated C$_3$S) were investigated, respectively, in ways of STXM with NEXAFS in Figure 6(a). Each of these spectra is unique in terms of the peak shape, positions, and the energy splitting, which has been used as a fingerprint for identifications and investigations of Ca structure. Ca L$_{3,2}$-edge NEXAFS spectra provide calcium coordination environment and characterize conveniently amorphous and crystalline Ca-containing materials.

The observed multiple peak patterns of Ca L$_{3,2}$-edge NEXAFS spectra consist of two main spin-orbit-related peaks ($a_2$ and $b_2$) corresponding, respectively, to $L_3$ and $L_2$, along with several smaller peaks ($a_1$ and $b_1$) leading to the main peaks [19] (Figure 6(a)). The experimental resolution for the spectra is approximately less than 0.1 eV. The magnitudes and symmetry of the crystal field of calcium in the first coordination sphere result in crystal field splitting, which is the origin of this multipeak pattern [20]. The peak positions and energy separation values ($\Delta L_3(a_2-a_1)$ and $\Delta L_2(b_2-b_1)$) are associated with the symmetry of Ca-O sheet in C-S-H structure.

Ca L$_{3,2}$-edge NEXAFS spectra of a selected area in Figure 6(c) show the different peak shapes, peak positions, and energy separations. Ca L$_{3,2}$-edge NEXAFS for Areas 1, 2, 6, and 8 has the splitting energy with 1.3 and 1.2 eV for $a_2-a_1$ and $b_2-b_1$ and peak intensity ratios between $a_1/a_2$ and $b_1/b_2$ in agreement with the results of anhydrous C$_3$S. Well-developed crystalline Ca(OH)$_2$ with the largest splitting energy values and peak intensity ratios [18] are shown in Figure 6(a). Moreover, Bae et al. [18] investigated the 17 d hydrated C$_3$S paste with water-to-solid ratio of 10 and concluded that the C-S-H of 17 d hydrated C$_3$S has a very similar local structure around Ca but has less crystallinity comparing to synthetic C-S-H. Ca L$_{3,2}$-edge NEXAFS spectra of C-S-H have energy separation 1.1 and 1 eV for $a_2-a_1$ and $b_2-b_1$ and the lowest peak intensity ratios [18], while the energy separation of 1.1 and 1.1 eV of Areas 3, 5, and 7 in one particle of 1 d hydrated C$_3$S with calcium nitrate has the lowest peak intensity ratios. Therefore, calcium nitrate does not change the asymmetric 7-fold coordination of calcium in the calcium silicate hydrate (C-S-H), the primary hydration product.
Figure 5: SEM images of 1-day hydration of C₃S paste with calcium nitrate.

Figure 6: STXM results of 1 d hydrated C₃S with calcium nitrate: (a) single image taken at 340 eV, (b) RGB overlay maps using SVD based on NEXAFS spectra of Ref. [18], (c) Ca L₂,₃-edge NEXAFS spectra of selected areas in (a).
RGB overlay maps using Singular Value Decomposition (SVD) based on NEXAFS spectra obtained previously from Ref. [18] of Ca(OH)$_2$, C-S-H, and anhydrous C$_3$S are shown in Figure 6(a). Since various chemical components have unique features for NEXAFS spectra, the reference spectra obtained from known components were used to differentiate and visualize phases in a sample [21]. It was observed in the C$_3$S particles under calcium nitrate solution that there are many magenta pixels (M = R + B = Ca(OH)$_2$+unhydrated C$_3$S) at the center in Figure 6(d) indicating that the unhydrated C$_3$S in those pixels is transforming to crystal-line Ca(OH)$_2$. There are, however, a few cyan pixels (C = G + B = C-S-H+unhydrated C$_3$S) at the boundary indicating that unhydrated C$_3$S in that pixel is transforming to C-S-H, but there are few yellow pixels (Y = R + G = Ca(OH)$_2$+C-S-H). Under the addition of calcium nitrate, the amorphous C-S-H surrounds the unhydrated C$_3$S. However, portlandite is partly in transformation in Figure 6(d), while the formation of Ca(OH)$_2$ partly occurs in Figure 5. Ca(NO$_3$)$_2$ can lower the amount of calcium hydroxide (CH) in hydrated cement pastes [6]. On the other hand, Ca$^{2+}$ is the top diffusivity of cations, while NO$_3^-$ is located at penultimate order, ranked in order of the effectiveness as accelerators [22–24]. Therefore, calcium nitrate can accelerate the hydration of C$_3$S to some extent, but it is not the most effective one, such as CaCl$_2$.

3.4. $^{29}$Si MAS NMR Analysis. $^{29}$Si MAS NMR plots for hydrated C$_3$S with different hydration times in the absence or presence of Ca(NO$_3$)$_2$ are shown in Figure 7, and the results of the associated spectral deconvolutions are presented in Table 2. The connectivity of SiO$_4$ tetrahedra, $Q^n$, is used to describe various types of monomer, dimer, trimer, and tetramer, where $n$ represents the number of bridging oxygens (Si-O-Si): $Q^0$ site is isolated SiO$_4$ tetrahedra, $Q^1$ is SiO$_4$ tetrahedra present in end units of a silicate chain, $Q^2$ is a middle group, $Q^3$ is a branching site, and $Q^4$ sites link

Figure 7: $^{29}$Si MAS NMR spectra of C$_3$S pastes as a function of hydration time in the (a) absence and in the (c) presence of calcium nitrate and deconvoluted spectrum for 28 d hydrate sample in the (b) absence and in the (d) presence of calcium nitrate.
to four other SiO$_4$ tetrahedra in a three-dimensional network. Amorphous C-S-H initially contains mainly dimeric silicate [25–27], while C$_3$S includes nine inequivalent SiO$_4$ tetrahedra ($Q^0$ sites) between -69 ppm and -75 ppm [28].

In Figure 7, $^{29}$Si MAS NMR spectra were fitted by the Gaussian functions to obtain the Gaussian distributions centered about -75 ppm, -78 ppm, -83 ppm, and -89 ppm which are attributed, respectively, to $Q^0$, $Q^1$, $Q^2$, and $Q^3$ units [29, 30], while these multiple peaks were also deconvoluted for calculating the percentage of integral intensities of $Q^i$. There are different features of $Q^i$ units at various hydration times. As the hydration process of C$_3$S without calcium nitrate, the discrete SiO$_4$ tetrahedral ($Q^0$) in unhydrated C$_3$S transformed to dimers $Q^1$ and doubly coordinated tetrahedral $Q^2$, following the increasing $Q^3$. However, the $Q^0$ and $Q^1$ peaks keep the lowest level particularly at 28 days of the C$_3$S hydration, while the $Q^2$ fraction has been becoming a predominant level and $Q^3$ fraction comes second. As the hydration process of C$_3$S, the development of $Q^2$ fraction is anticorrelated with that of $Q^1$.

In the case of calcium nitrate, the $Q^2$ peak has been playing a dominant role in the dreierketten silicate chain structure until 3-day hydration, while the fraction for the $Q^1$ peak is increased by calcium nitrate compared to the control group. $Q^2/Q^1$ ratios of hydrated C$_3$S with calcium nitrate outweigh those of the control group, especially at an early age. The presence of calcium nitrate in the hydrated C$_3$S generates a significant increase in the $Q^2/Q^1$ ratios at an early age. Calcium nitrate is clearly indicated to accelerate the degree of polymerization of the silicate chains in C-S-H gel considerably at an early age. More $Q^2$ and $Q^3$ peaks of the calcium nitrate group make the $Q^2/Q^1$ ratios rise significantly at an early age in agreement with the above studies of the DSC analysis of hydrated C$_3$S in the presence of calcium nitrate.

### 4. Conclusions

In this study, we investigated the effect of calcium nitrate on hydration and pore structure of tricalcium silicate in ways of DSC, N$_2$ sorption, STXM with NEXAFS, and $^{29}$Si MAS NMR. Calcium nitrate can accelerate the hydration of C$_3$S to some extent and polymerization of the silicate chains within C-S-H considerably at an early age, resulting in the increased specific surface area.

At 1-day hydrated C$_3$S in the presence of calcium nitrate, amorphous C-S-H and crystalline portlandite surround the unhydrated C$_3$S. Moreover, it is indicated from STXM combined with NEXAFS that the crystal phase, Ca(OH)$_2$, is still partly in transformation at 1-day hydration of C$_3$S with calcium nitrate. As for the atomic structure of C-S-H at 1-day hydrated C$_3$S pastes, calcium nitrate does not change the asymmetric 7-fold coordination of calcium in the calcium silicate hydrate (C-S-H), the primary hydration product.

These findings definitely validate the STXM with NEXAFS spectra as a significantly powerful tool for the investigation of the microstructure of the cementitious pastes to open the possibility of studying the in situ nanostructure of cementitious materials during hydration.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that there is no conflict of interests regarding the publication of this paper.

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### Table 2: $^{29}$Si MAS NMR analysis for hydrated C$_3$S paste at 25°C for hydration period of 1, 3, 7, and 28 days.

| Samples            | $Q^0$ (%) | $Q^1$ (%) | $Q^2$ (%) | $Q^3$ (%) | $Q^2/Q^1$ |
|--------------------|-----------|-----------|-----------|-----------|-----------|
| C$_3$S-1 d         | 33.2      | 64.4      | 2.4       | —         | 0.04      |
| C$_3$S-3 d         | 20.7      | 43.2      | 30.6      | 5.5       | 0.71      |
| C$_3$S-7 d         | 11.5      | 37.2      | 43.9      | 7.4       | 1.18      |
| C$_3$S-28 d        | 11.9      | 14.4      | 53.8      | 20.0      | 3.74      |
| C$_3$S+Ca(NO$_3$)$_2$-1 d | 15.2   | 36.1      | 40.1      | 8.6       | 1.11      |
| C$_3$S+Ca(NO$_3$)$_2$-3 d | 6.5    | 34.1      | 46.5      | 12.9      | 1.37      |
| C$_3$S+Ca(NO$_3$)$_2$-7 d | 1.0    | 38.7      | 37.3      | 23.0      | 0.97      |
| C$_3$S+Ca(NO$_3$)$_2$-28 d | 3.7    | 22.3      | 52.6      | 21.4      | 2.36      |
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