Research Article

Microstructural Study of Hydration of C_3S in the Presence of Calcium Nitrate Using Scanning Transmission X-Ray Microscopy (STXM)

Qinfei Li^{1,2,3}, Yang Wang,¹ Guoqing Geng,⁴ Heng Chen,^{1,3} Pengkun Hou,^{1,3} Xin Cheng^{1,3}, Paulo J. M. Monteiro,⁵ Shifeng Huang^{1,3} and Jae Hong Kim⁶

¹Shandong Provincial Key Laboratory of Preparation and Measurement of Building Materials, University of Jinan, Jinan, China

²State Key Laboratory of Green Building Materials, Beijing, China

³Department of Materials Science and Engineering, University of Jinan, Jinan, China

⁴Paul Scherrer Institute, Villigen, Switzerland

⁵Department of Civil and Environment Engineering, University of California, Berkeley, USA

⁶Department of Civil and Environmental Engineering, Korea Advanced Institute of Science and Technology, Republic of Korea

Correspondence should be addressed to Qinfei Li; hitqfli@gmail.com, Xin Cheng; chengxin_5027@163.com, and Shifeng Huang; huangshifeng_4886@163.com

Received 28 June 2019; Revised 21 December 2019; Accepted 20 January 2020; Published 22 April 2020

Academic Editor: Andrew R. Barron

Copyright © 2020 Qinfei Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 C_3S was studied by scanning transmission X-ray microscopy (STXM) combined with near-edge X-ray absorption fine structure (NEXAFS), ^{29}Si MAS NMR, calorimetry, scanning electron microscope, and N_2 absorption. It was concluded that the calcium silicate hydrate (C-S-H) surrounds the unhydrated C_3S at 1-day hydrated C_3S in the presence of calcium nitrate, while portlandite is partly in transformation and is formed partly. Based on Ca $L_{3,2}$ -edge NEXAFS spectra for 1-day hydrated C_3S 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 C_3S 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 ($\text{Ca}(\text{NO}_3)_2$, CN) is an effective chloride-free setting accelerator and antifreeze admixture [1–4]. $\text{Ca}(\text{NO}_3)_2$ is well known to have the ability to improve the early compressive strength [5] and accelerate the hydration

of cement [2–4]. Justnes and Nygaard studied the changes in the microstructure of cement paste and concrete in the presence of $\text{Ca}(\text{NO}_3)_2$ and concluded that $\text{Ca}(\text{NO}_3)_2$ 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 $\text{Ca}(\text{NO}_3)_2$ depended on the cement type, especially on belite content [4, 7]. However, it was proved by X-ray diffraction that the presence of $\text{Ca}(\text{NO}_3)_2$ does not affect the stability of ettringite and forms hardly the compound $\text{C}_3\text{A}\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$ ⁷. Harald and Erik proposed the mechanism for accelerating the setting of $\text{Ca}(\text{NO}_3)_2$: (1)

an increased concentration of Ca^{2+} leads to a faster supersaturation of the fluid for forming CH, while (2) $\text{Ca}(\text{NO}_3)_2$ decreases the concentration of SO_4^{2-} leading to slower formation of ettringite which will shorten the onset of C_3A hydration [8]. However, there are few literatures on $\text{Ca}(\text{NO}_3)_2$ obtained from the hydration of C_3S regarding its chemical and physical properties. Therefore, it is essential to investigate the effect of $\text{Ca}(\text{NO}_3)_2$ of the hydrated C_3S 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_3S 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_3S powders were purchased from CTL Group (Skokie, IL), which were passed through sieve #325 ($45\ \mu\text{m}$). The analytical reagent of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was used by 2 wt% of C_3S powders, which was purchased from Sigma-Aldrich. The boiled deionized water after cooling was used in the preparation of the C_3S pastes with different liquid-to-solid ratios. To avoid the carbonation of carbon dioxide into the samples, the C_3S 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].

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 calorimetry. 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_3S and hydrated C_3S with the addition of $\text{Ca}(\text{NO}_3)_2$ at 1, 3, 7, and 28 days were tested using a PANalytical X'Pert Pro diffractometer equipped with a Co X-ray tube ($\lambda = 1.79\ \text{\AA}$) and the rapid X'celerator detector. XRD was used to identify crystalline phases from a 2θ value of $5\text{--}80^\circ$ with a step of 0.02° .

2.2.3. ^{29}Si MAS NMR and N_2 Absorption. The samples of C_3S pastes with calcium nitrate were prepared by 0.5 of the liquid-to-solid ratio for 1, 3, 7, and 28 days of hydration.

FIGURE 1: Isothermal calorimetry of C_3S pastes with different L/S and calcium nitrate.

The hydration of the samples was stopped by isopropanol, and then, samples were dried under the vacuum oven for 3 days. The samples were grounded 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 ($\leq 4.75\ \text{mm}$) for N_2 sorption measurement (Micromeritics 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_3S powder was mixed with 0.004 g/mL $\text{Ca}(\text{NO}_3)_2$ solution with a liquid-to-solid ratio of 5.0. C_3S pastes were maintained in the CryoTube™ vials (1.8 mL) under the protection of N_2 gas at 23°C and then sealed in a vacuum against carbonation. After 1 day of hydration, the C_3S paste was ground and dispersed with deionized water for STXM measurement. Axis 2000 software (Version 2.1) was used to analyze the data of the NEXAFS spectra collected from STXM. The morphology of the paste was also observed by the scanning electron microscope (Quattro S from Thermo Fisher Scientific).

3. Results and Discussion

3.1. Calorimetry. Figure 1 shows the isothermal calorimetry data for C_3S 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_3S paste with $\text{L/S} = 0.5$ increases, and the launch of the accelerating period is earlier. Commonly, the early hydration rate of C_3S

FIGURE 2: Physisorption isotherms for C_3S pastes with different hydration times in the (a) absence and (b) presence of calcium nitrate.

TABLE 1: Specific surface area of C_3S pastes with different hydration times (m^2/g).

Sample	C_3S 3 d	C_3S 7 d	C_3S 28 d	CN 3 d	CN 7 d	CN 28 d
BET area	9.16	11.29	33.52	15.89	25.95	38.52
Langmuir area	12.92	16.26	47.19	22.88	37.59	54.71

paste with $L/S = 0.5$ develops more quickly than that of $L/S = 0.4$; however, the presence of calcium nitrate is opposite due to more nucleation sites in C_3S 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 Ca^{2+} in the pore solution combined with silicate ions dissolved from C_3S . The early hydration of C_3S paste is accelerated by calcium nitrate, which provides the development of pore structure and hydration products of C_3S paste.

3.2. N_2 Sorption. According to the IUPAC classification, the hysteresis loops for all isotherms obtained from C_3S samples are not of Type IV but of Type H_3 due to no indication of a plateau at high P/P_0 in Figure 2. Each adsorption branch has the similar feature of the typical Type II without limiting adsorption at high P/P_0 , and the desorption branch exhibits a different path before reaching a critical P/P_0 , which implies aggregates of plate-like particles resulting in slit-shaped pores. The C_3S 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 adsorp-

tion, the values for the Langmuir area are generally higher than those for the BET area. The specific surface area of C_3S 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 C_3S paste. C_3S 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 C_3S 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 N_2 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 C_3S paste is also affected by calcium nitrate. Figure 4 shows the XRD patterns of triclinic C_3S and hydrated C_3S pastes with calcium nitrate. In the presence of calcium nitrate, unhydrated C_3S remains slightly at 7-day hydration since the reactivity of triclinic C_3S is lower than monoclinic C_3S . The feature peaks of portlandite are occurring at 1-day hydration of C_3S pastes, while the

FIGURE 3: BJH desorption PSD comparison for C_3S pastes in the (a) absence and (b) presence of calcium nitrate.

FIGURE 4: XRD patterns of triclinic C_3S and C_3S pastes with calcium nitrate.

morphology of portlandite presented the plate-like crystals surrounded by unhydrated C_3S and C-S-H gel as shown in Figure 5.

Figure 6 presents the single image of 1 d hydrated C_3S 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_3S , and pure C-S-H (in 17 d hydrated C_3S) 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 multippeak 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_3S . 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_3S paste with water-to-solid ratio of 10 and concluded that the C-S-H of 17 d hydrated C_3S 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_3S 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 C_3S paste with calcium nitrate.

FIGURE 6: STXM results of 1 d hydrated C_3S with calcium nitrate: (a) single image taken at 340 eV, (b) RGB overlay maps using SVD based on NEXAFS spectra of Ref. [18], (c) $Ca\ L_{3,2}$ -edge NEXAFS spectra of selected areas in (a).

FIGURE 7: ^{29}Si MAS NMR spectra of C_3S 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.

RGB overlay maps using Singular Value Decomposition (SVD) based on NEXAFS spectra obtained previously from Ref. [18] of $\text{Ca}(\text{OH})_2$, C-S-H, and anhydrous C_3S 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_3S particles under calcium nitrate solution that there are many magenta pixels ($M = R + B = \text{Ca}(\text{OH})_2 + \text{unhydrated } \text{C}_3\text{S}$) at the center in Figure 6(d) indicating that the unhydrated C_3S in those pixels is transforming to crystalline $\text{Ca}(\text{OH})_2$. There are, however, a few cyan pixels ($C = G + B = \text{C-S-H} + \text{unhydrated } \text{C}_3\text{S}$) at the boundary indicating that unhydrated C_3S in that pixel is transforming to C-S-H, but there are few yellow pixels ($Y = R + G = \text{Ca}(\text{OH})_2 + \text{C-S-H}$). Under the addition of calcium nitrate, the amorphous C-S-H surrounds the unhydrated C_3S . However, portlandite is partly in transformation in Figure 6(d), while the formation

of $\text{Ca}(\text{OH})_2$ partly occurs in Figure 5. $\text{Ca}(\text{NO}_3)_2$ 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_3S 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_3S with different hydration times in the absence or presence of $\text{Ca}(\text{NO}_3)_2$ 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

TABLE 2: ^{29}Si MAS NMR analysis for hydrated C_3S paste at 25°C for hydration period of 1, 3, 7, and 28 days.

Samples	Percentage of integral intensities of Q^n (%)				Q^2/Q^1
	Q^0 -74 ppm	Q^1 -78 ppm	Q^2 -83 ppm	Q^3 -89 ppm	
C_3S_1 d	33.2	64.4	2.4	—	0.04
C_3S_3 d	20.7	43.2	30.6	5.5	0.71
C_3S_7 d	11.5	37.2	43.9	7.4	1.18
C_3S_{28} d	11.9	14.4	53.8	20.0	3.74
$\text{C}_3\text{S}+\text{Ca}(\text{NO}_3)_2$ 1 d	15.2	36.1	40.1	8.6	1.11
$\text{C}_3\text{S}+\text{Ca}(\text{NO}_3)_2$ 3 d	6.5	34.1	46.5	12.9	1.37
$\text{C}_3\text{S}+\text{Ca}(\text{NO}_3)_2$ 7 d	1.0	38.7	37.3	23.0	0.97
$\text{C}_3\text{S}+\text{Ca}(\text{NO}_3)_2$ 28 d	3.7	22.3	52.6	21.4	2.36

to four other SiO_4 tetrahedra in a three-dimensional network. Amorphous C-S-H initially contains mainly dimeric silicate [25–27], while C_3S 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 center 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^n . There are different features of Q^n units at various hydration times. As the hydration process of C_3S without calcium nitrate, the discrete SiO_4 tetrahedral (Q^0) in unhydrated C_3S 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_3S hydration, while the Q^2 fraction has been becoming a predominant level and Q^3 fraction comes second. As the hydration process of C_3S , 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^3 peak is increased by calcium nitrate compared to the control group. Q^2/Q^1 ratios of hydrated C_3S with calcium nitrate outweigh those of the control group, especially at an early age. The presence of calcium nitrate in the hydrated C_3S 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_3S 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_3S 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_3S in the presence of calcium nitrate, amorphous C-S-H and crystalline portlandite surround the unhydrated C_3S . Moreover, it is indicated from STXM combined with NEXAFS that the crystal phase, $\text{Ca}(\text{OH})_2$, is still partly in transformation at 1-day hydration of C_3S with calcium nitrate. As for the atomic structure of C-S-H at 1-day hydrated C_3S 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.

Acknowledgments

Funding for this project was provided by the National Natural Science Foundation of China (No. 51802112 and No. 51761145023) and the Shandong Provincial Natural Science Foundation (ZR2019BEM034). Supports from the 111 Project of International Corporation on Advanced Cement-Based Materials (No. D17001) and the Taishan Scholars Program and Science and Technology Innovation Support Plan for Young Researchers in Institutes of Higher Education in Shandong (2019KJA017) are greatly appreciated. The funding is also supported by the Opening Project of State Key Laboratory of Green Building Materials and Case-by-Case Project for Top Outstanding Talents of Jinan.

STXM data were acquired at beamline BL5.3.2.1 and BL5.3.2.2 at the Advanced Light Source, supported by the Director of the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy, under Contract No. DE-AC02-05CH11231.

References

- [1] V. S. Ramachandran, *Concrete Admixtures Handbook - Properties, Science, and Technology*, William Andrew Publishing/Noyes, 2nd edition, 1996.
- [2] C. Korhonen, "New developments in cold-weather concreting," in *Cold Regions Engineering*, pp. 531–537, American Society of Civil Engineers, 2002.
- [3] F. Karagöl, R. Demirboğa, M. A. Kaygusuz, M. M. Yadollahi, and R. Polat, "The influence of calcium nitrate as antifreeze admixture on the compressive strength of concrete exposed to low temperatures," *Cold Regions Science and Technology*, vol. 89, pp. 30–35, 2013.
- [4] H. Justnes and E. C. Nygaard, "Technical calcium nitrate as set accelerator for cement at low temperatures," *Cement and Concrete Research*, vol. 25, no. 8, pp. 1766–1774, 1995.
- [5] B. Abdelrazig, D. Bonner, D. Nowell, J. Dransfield, and P. Egan, "Effects of accelerating admixtures on cement hydration. Admixtures for concrete: improvement of properties," in *Proceedings of the International Symposium Held by Rilem (The International Union of Testing and Research Laboratories for Materials and Structures)*, Barcelona, 1990.
- [6] J. Harald and C. N. Erik, "Changes in the microstructure of cement paste and concrete due to calcium nitrate addition," *Special Publication*, vol. 173, pp. 657–672, 1997.
- [7] H. Justnes and E. C. Nygaard, "Technical nitrate as set accelerator for cement," *Nordic Concrete Research*, vol. 13, no. 2, 1993.
- [8] H. Justnes and E. C. Nygaard, "Setting accelerator calcium nitrate fundamentals, performance and applications," *Special Publication*, vol. 171, pp. 325–338, 1997.
- [9] J. Ha, S. Chae, K. W. Chou, T. Tyliczszak, and P. J. M. Monteiro, "Effect of polymers on the nanostructure and on the carbonation of calcium silicate hydrates: a scanning transmission X-ray microscopy study," *Journal of Materials Science*, vol. 47, no. 2, pp. 976–989, 2012.
- [10] J. Ha, S. Chae, K. W. Chou, T. Tyliczszak, and P. J. M. Monteiro, "Scanning transmission X-ray microscopic study of carbonated calcium silicate hydrate," *Transportation Research Record: Journal of the Transportation Research Board*, vol. 2142, no. 1, pp. 83–88, 2010.
- [11] S. R. Chae, J. Moon, S. Yoon et al., "Advanced nanoscale characterization of cement based materials using X-ray synchrotron radiation: a review," *International Journal of Concrete Structures and Materials*, vol. 7, no. 2, pp. 95–110, 2013.
- [12] P. J. M. Monteiro, L. Clodic, F. Battocchio et al., "Incorporating carbon sequestration materials in civil infrastructure: a micro and nano-structural analysis," *Cement and Concrete Composites*, vol. 40, pp. 14–20, 2013.
- [13] D. Hernández-Cruz, C. W. Hargis, S. Bae et al., "Multiscale characterization of chemical-mechanical interactions between polymer fibers and cementitious matrix," *Cement and Concrete Composites*, vol. 48, pp. 9–18, 2014.
- [14] S. Yoon, J. Ha, S. R. Chae, D. A. Kilcoyne, and P. J. M. Monteiro, "X-ray spectromicroscopic study of interactions between NaCl and calcium silicate hydrates," *Magazine of Concrete Research*, vol. 66, no. 3, pp. 141–149, 2014.
- [15] Q. Li, Y. Ge, G. Geng, S. Bae, and P. J. M. Monteiro, "CaCl₂-accelerated hydration of tricalcium silicate: a STXM study combined with ²⁹Si MAS NMR," *Journal of Nanomaterials*, vol. 2015, Article ID 215371, 10 pages, 2015.
- [16] A. L. D. Kilcoyne, T. Tyliczszak, W. F. Steele et al., "Interferometer-controlled scanning transmission X-ray microscopes at the advanced light source," *Journal of Synchrotron Radiation*, vol. 10, no. 2, pp. 125–136, 2003.
- [17] L. Nicoleau, "Accelerated growth of calcium silicate hydrates: experiments and simulations," *Cement and Concrete Research*, vol. 41, no. 12, pp. 1339–1348, 2011.
- [18] S. Bae, R. Taylor, D. Hernández-Cruz, S. Yoon, D. Kilcoyne, and P. J. M. Monteiro, "Soft X-ray spectromicroscopic investigation of synthetic C-S-H and C₃S hydration products," *Journal of the American Ceramic Society*, vol. 98, no. 9, pp. 2914–2920, 2015.
- [19] F. M. F. de Groot, J. C. Fuggle, B. T. Thole, and G. A. Sawatzky, "2px-ray absorption of 3d transition-metal compounds: an atomic multiplet description including the crystal field," *Physical Review B: Condensed Matter*, vol. 42, no. 9, pp. 5459–5468, 1990.
- [20] S. J. Naftel, T. K. Sham, Y. M. Yiu, and B. W. Yates, "Calcium L-edge XANES study of some calcium compounds," *Journal of Synchrotron Radiation*, vol. 8, no. 2, pp. 255–257, 2001.
- [21] Z. Yangquanwei, S. Neethirajan, and C. Karunakaran, "Cytogenetic analysis of quinoa chromosomes using nanoscale imaging and spectroscopy techniques," *Nanoscale Research Letters*, vol. 8, no. 1, p. 463, 2013.
- [22] D. L. Kantro, "Tricalcium silicate hydration in the presence of various salts," *Journal of Testing and Evaluation*, vol. 3, pp. 312–321, 1975.
- [23] D. D. Double, P. C. Hewlett, K. S. W. Sing, and J. F. Raffle, "New Developments in Understanding the Chemistry of Cement Hydration [and Discussion]," *Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences*, vol. 310, no. 1511, pp. 53–66, 1983.
- [24] C. R. Wilding, A. Walter, and D. D. Double, "A classification of inorganic and organic admixtures by conduction calorimetry," *Cement and Concrete Research*, vol. 14, no. 2, pp. 185–194, 1984.
- [25] J. J. Beaudoin, L. Raki, and R. Alizadeh, "A ²⁹Si MAS NMR study of modified C-S-H nanostructures," *Cement and Concrete Composites*, vol. 31, no. 8, pp. 585–590, 2009.
- [26] M. Chloup-Bondant and O. Evrard, "Tricalcium aluminate and silicate hydration. Effect of limestone and calcium sulfate," in *Nuclear Magnetic Resonance Spectroscopy of Cement-Based Materials*, P. Colombet, H. Zanni, A.-R. Grimmer, and P. Sozzani, Eds., pp. 295–308, Springer, Berlin, Heidelberg, 1998.
- [27] S. A. Rodger, G. W. Groves, N. J. Clayden, and C. M. Dobson, "Hydration of tricalcium silicate followed by ²⁹Si NMR with cross-polarization," *Journal of the American Ceramic Society*, vol. 71, no. 2, pp. 91–96, 1988.
- [28] M. Magi, E. Lippmaa, A. Samoson, G. Engelhardt, and A. R. Grimmer, "Solid-state high-resolution silicon-29 chemical shifts in silicates," *The Journal of Physical Chemistry*, vol. 88, no. 8, pp. 1518–1522, 1984.

- [29] C. E. Tambelli, J. F. Schneider, N. P. Hasparyk, and P. J. M. Monteiro, "Study of the structure of alkali-silica reaction gel by high-resolution NMR spectroscopy," *Journal of Non-Crystalline Solids*, vol. 352, no. 32–35, pp. 3429–3436, 2006.
- [30] R. J. Myers, S. A. Bernal, R. San Nicolas, and J. L. Provis, "Generalized structural description of calcium–sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model," *Langmuir*, vol. 29, no. 17, pp. 5294–5306, 2013.