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Synchrotron X-ray Spectro-microscopy and Micro-diffraction Study on the Hydration of
Tricalcium Silicate including High-Volume Fly Ash

By

Sungchul Bae

A dissertation submitted in partial satisfaction of the

requirements for the degree of

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in

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in the

Graduate Division

of the

University of California, Berkeley

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Abstract

Synchrotron X-ray Spectro-microscopy and Micro-diffraction Study on the Hydration of Tricalcium Silicate including High-Volume Fly Ash

By

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Doctor of Philosophy in Engineering-Civil and Environmental Engineering

University of California, Berkeley

Professor Paulo J.M. Monteiro, Chair

Understanding on calcium silicate hydrates (C-S-H) formed in the hydration process of Portland cement (PC) phases and the atomic bonding structure of the C-S-H are very crucial to optimize the PC-based materials. Optimization of PC will contribute to enhance sustainability and energy efficiency of concrete structures by reducing use of PC, however, certain details of C-S-H are partially known.

The major objectives of this thesis were to elucidate a hydration process of pure triclinic tricalcium silicate (C_3S). *In situ* spectro-microscopy was carried out using C_3S solution in a wet cell to determine the morphological and structural environment changes surrounding the Ca and Si atoms in the early age hydration of C_3S . Synthesized calcium silicate hydrate (Syn-CSH) with different Ca/Si ratios was used to quantitatively evaluate the effect of silicate polymerization on the local binding structure of C-S-H.

As a secondary objective, this thesis was aimed at clarifying the effect of high-volume fly ash (HVFA) on pure C_3S and PC hydration. Synchrotron soft x-ray scanning transmission x-ray microscopy (STXM), x-ray diffraction imaging, and monochromatic scanning x-ray micro-diffraction (μ -SXRD) were utilized.

Near edge x-ray absorption fine structure (NEXAFS) analysis showed that Syn-CSH had no variation in peak positions and energy separation for Ca L_{III, II} edge for a wide range of the Ca/Si ratios. The Ca L_{III, II} edge NEXAFS of 17 days hydrated C₃S showed different local structure with anhydrous C₃S. Compared to Syn-CSH, C-S-H of C₃S was proved to have a very similar local structure around the Ca but with less crystallinity. Si K edge NEXAFS analysis on Syn-CSH showed a tendency for the peak positions of both the Si K edge and the peak induced by multiple scattering to shift to higher energy levels. The results also indicated that the distance between the two peaks increased with a decrease of the Ca/Si ratio in Syn-CSH. Silicate polymerization influenced the multiple scattering of distant shell atoms more than the binding energy of the core atoms.

In situ STXM analysis using pure C₃S solutions in a wet cell showed morphologic changes in the dissolution of the Ca and the precipitation of C-S-H on the C₃S particles in the process of hydration. Outer product (Op) layers of C₃S showed higher degree of silicate polymerization compared to core area of C₃S. The degree of silicate polymerization of Op increased during the hydration process. *Ex situ* STXM analysis on 17 days hydrated C₃S particles showed that Op layer and core area had a different degree of silicate polymerization. The results imply the Op layer reduces the hydration process of C₃S in the core area. Soft x-ray diffraction imaging showed Op and inner products of 17 days hydrated C₃S had fibrillar and an inter-globular structure with voids, respectively.

In a C₃S / HVFA matrix, the Si concentration of C₃S particle was very uniform compared to pure C₃S matrix. No clear Op layers around C₃S particles, as observed in pure C₃S, were found. C-S-H in C₃S / HVFA matrix showed very similar absorption feature with fly ash. C-S-H in the system, however, showed further lower binding energy of core Si atom and higher degree of silicate polymerization compared to Op in pure C₃S matrix. Lower binding energy of core Si atom can be due to Al substitution for Si in hydration products of C₃S, and the higher degree of silicate polymerization is assumed to be due to additional silicate provided from fly ash. ²⁹Si magic-angle spinning nuclear magnetic resonance spectroscopy confirmed that C-S-H in C₃S/ HVFA matrix have longer average chain length compared to one in pure C₃S confirming the silicate polymerization.

μ-SXRD analysis showed that the C-S-H formed in PC / HVFA system containing 50% or more of fly ash had a similar structure as C-S-H(I). Moreover, coexistence of more ordered

C-S-H (C-S-H(I)) and strätlingite ($2\text{CaO}\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$) was observed in the system containing 80% of fly ash, confirming that the amount of alumina and silicate phases provided by the fly ash is a major factor for the formation of C-S-H(I) and strätlingite in PC / HVFA system.

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CHAPTER 1

RESEARCH OBJECTIVES AND THESIS OVERVIEW

1.1 Introduction

Portland cement (PC) is one of the most common construction materials, the main binding material for concrete, and capable of bonding mineral aggregates through an exothermic hydration reaction to produce concrete. Among the hydration products created by the PC hydration process, calcium-silicate-hydrate (C-S-H), which accounts for 50 to 70 percent by volume of the fully hydrated cement matrix, is the principal reaction products as well as the primary binding phase [1]. Therefore, C-S-H is mainly responsible for the mechanical properties and the long-term durability of concrete [2]. To a great extent, the complex nanostructures of the C-S-H govern the material's macroscopic properties including strength, shrinkage behavior, and durability [3]. The structure of the C-S-H is affected by many factors, the most important of which include the curing temperature, the chemical composition and proportions of the mixture employed, and the presence of both chemical admixtures and supplementary cementitious materials (SCMs) [4].

SCMs, including fly ash, granulated blast-furnace slag, rice husk ash, and metakaolin are widely accepted as partial replacements for PC as binding phases in the production of concrete. Among these SCM substitutes, fly ash, produced during combustion of coal, has been employed in concrete mixes for many decades as a popular, low-cost mineral admixture. High-volume fly ash (HVFA) concretes containing more than 50% fly ash by mass of the cementitious material have been successfully utilized in various projects [5]. The use of these HVFA concretes permits the efficient reutilization of considerable amounts of fly ash at low cost and significantly reduces the use of PC in concrete production. Additionally, the greener HVFA concrete has technical advantages over PC concrete as well as similar or higher long-term strength and enhanced durability but has comparatively lower early-strength due to lower reactivity [6-9]. The enhanced mechanical properties and chemical resistance of concretes made with fly ash have been the topics of many studies [6-8, 10-12].

When expertise that has been acquired in utilization of fly ash is combined with our increasing environmental awareness and its economical advantages, fly ash consumption by the concrete industry is expected to rise [13]. The relatively lower early-strength of HVFA concrete can be overcome through a careful design of the concrete mixture. Although a number of studies concerning HVFA concrete have been conducted, focusing mainly on mechanical and durability properties [9, 14-16], there has been less

research on the micro- and nano-scale structures of HVFA concrete or the hydration products formed within the concrete matrix [17-19].

To develop a deep understanding of the effect of HVFA on PC system, it is necessary to have a profound knowledge of the pure PC phase systems. Tricalcium silicate (C_3S)¹, which is main phase in PC, has been often used as a model system instead of PC. Outer products (Op) of C_3S , also referred to as outer product C-S-H, play a crucial role in the bonding of C_3S with other phases; thus, the properties of Op affects the structural performance of the cementitious systems containing C_3S . Therefore, if the Op of C_3S can be analyzed separately, then it would be possible to evaluate the effect of silicate and alumina phases provided from HVFA on the C_3S hydration products. The amount of fly ash in PC / HVFA also affects the hydration products and structure of C-S-H in the system, and the C-S-H is expected to have more ordered structure compared to one produced in PC matrix. However, the actual structure of C-S-H in PC / HVFA matrix has not been determined. Although the issues stated above are very crucial to enhance the understanding of PC / HVFA systems, the characterization methods with enough resolution are very limited. Synchrotron-based soft x-ray characterization methods have supported a broad research portfolio in physics, chemistry, biology and engineering, and these methods have been applied to improve the understanding of cement chemistry [20-23]. The advanced characterization methods have potentials to provide details on characteristics of PC-based systems which are comparatively heterogeneous.

The present PhD thesis aims to address the following open challenges in order to contribute the understanding on PC-based systems.

- Develop *in situ* high-resolution imaging and spectroscopy of cement hydration products with little or no beam damage.
- Perform quantitative analysis of the changes in the local binding structure of Op in cement phase during the hydration process.
- Study the effect of Ca to Si ratio on the local binding structure of C-S-H.
- Quantify the effect of HVFA on the morphology and local binding structure in hydration products of C_3S .

¹ Cement chemistry nomenclature: C and S denote CaO and SiO₂, respectively.

- The effect of the amount of fly ash on the hydration products and the crystal structure of C-S-H in PC / HVFA system.
- Critical evaluation of the effectiveness and consistency of the advanced characterization methods used in this thesis compared to traditional characterization methods.

To tackle these challenges, the issues stated above, the present dissertation starts with the morphologic changes and hydration process of pure C_3S . Next, synthetic C-S-H and C_3S systems with and without HVFA are studied. Finally, the hydration products of PC / HVFA systems were characterized. The experimental work using synchrotron-based soft x-ray characterization methods and the related discussion presented in this thesis contributes to our understanding of the hydration products of C_3S , as well as, the effect of HVFA on hydration products of C_3S and PC system. The success of advanced characterization methods utilized here can motivate future studies on the PC hydration with different types of mineral and chemical admixtures. Consequently, those studies will contribute to optimize the admixtures for PC-based materials.

1.2 Structure of the thesis

This thesis is organized in 6 chapters. Chapter 1 gives a short description of main goals of the thesis and detailed explanation of the hydration process and experimental methods will be given in subsequent chapters.

Chapter 2 summarizes the fundamental aspects of cement phase hydration, hydration products in PC matrix, and the novel characterization methods including soft x-ray scanning transmission x-ray microscopy (STXM) and monochromatic scanning x-ray micro-diffraction (μ -SXRD) used in this research.

Chapter 3 presents experimental research using soft x-ray spectro-microscopy and diffraction imaging to analyze C-S-H and the hydration products formed in C_3S systems. Three types of synthesized C-S-H differing in Ca to Si ratios are studied to evaluate quantitative effects of silicate polymerization on the local structure of C-S-H by Ca $L_{III,II}$ edge and Si K edge near edge x-ray fine structure (NEXAFS) analysis. Additionally, an *in situ* STXM study to understand the effect of silicate polymerization in outer products of C_3S on NEXAFS during hydration in early age is also presented. This is the first time that

such experiments were conducted in cement chemistry. Obtained STXM and diffraction images of C_3S are compared with transmission electron microscopy (TEM) images.

Chapter 4 aims to determine the effect of additional silicate and alumina phase provided from HVFA on the C_3S hydration, on the formation of hydration products and on the morphology and atomic structure of C-S-H produced in C_3S hydration. Hydration products formed in C_3S / HVFA system and pozzolanic reaction were examined through synchrotron powder x-ray diffraction and thermogravimetric analysis. The effect of silicate polymerization and aluminum substitution for silicon in C-S-H of C_3S / HVFA matrix on the morphology, the binding energy of atoms in C-S-H and the silicate chain length is examined using STXM, Ca $L_{III,II}$ edge, Al K edge, Si K edge NEXAFS analysis, TEM and nuclear magnetic resonance spectroscopy.

Chapter 5 focuses on the identification and micro-structural characterization of the hydration products formed in the PC / HVFA matrix using monochromatic x-ray micro-diffraction (μ -SXRD) and scanning electron microscopy with energy dispersive spectroscopy. The results of μ -SXRD are compared to those using two different powder XRD methods to validate the effectiveness of μ -SXRD. PC pastes with up to 80% fly ash replacement were studied to differentiate C-S-H structure in a PC / HVFA system. Phase maps for HVFA samples using μ -SXRD patterns are conducted to identify and visualize the distribution of phases in the matrix.

Lastly, Chapter 6 summarizes the main results of the research and proposes new lines of investigation for future work.

CHAPTER 2

OVERVIEW OF TRICALCIUM SILICATE HYDRATION AND EXPERIMENTAL METHODS

2.1 Introduction

Calcium Silicate Hydrate (C-S-H) is the main reaction product and primary binding phase in Portland cement (PC) [24]. It accounts for 50 to 70% of the volume in a hydrated PC matrix and it contributes to macroscopic properties such as strength, shrinkage behavior, and durability of the composite material. Therefore, optimizing the properties of C-S-H has the potential to use less PC in concrete and, consequently, it can contribute a reduction of environmental impacts by reducing CO₂ generated during the manufacture of PC [25].

Understanding the properties of C-S-H is important to control the nanoporosity of the hydrated paste, but a major limitation of maximizing the potential of this material is the limited understanding of its atomic structure. The precise structure of C-S-H gels have not been fully determined, but it is known that they are partially related to those of jennite and tobermorite [26-28]. In previous research, more ordered C-S-H systems, including C-S-H (I), tobermorite, and jennite, have been proposed as models for the structure of C-S-H in hardened cement paste; however, the validity of these proposed models is still unclear [2]. Furthermore, C-S-H in a system containing high silica-rich supplementary cementitious materials (SCMs) is significantly different than C-S-H in a PC system [29]. To increase the understanding of C-S-H and other hydration products formed in a pure PC system or one with SCMs, the use of advanced characterization methods based on a synchrotron x-ray source is essential.

In this chapter, an attempt has been made to summarize some of the key studies on PC phase hydration, and the characteristics of C-S-H in a SCM system. Several advanced characterization methods used in this dissertation, such as scanning transmission x-ray microscopy (STXM) using x-ray absorption spectroscopy (XAS) and scanning x-ray micro-diffraction (μ -SXRD) will also be presented.

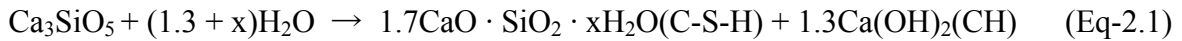
2.2 Hydration of tricalcium silicate (C₃S) with and without supplementary cementitious materials (SCMs)

PC clinker contains four main compounds: silicate phases, tricalcium silicate (C₃S) and belite (β -C₂S), tri-calcium aluminate (C₃A) and ferrite (C₄AF). In cement chemistry, C, S, A, F, and H, is often used for the chemical formulas of CaO, SiO₂, Al₂O₃, Fe₂O₃ and H₂O, respectively. The nomenclature of the individual oxides in PC is shown in Table 2.1 [1].

Table 2.1 Nomenclature used in cement chemistry

Abbreviation	Oxides
C	CaO
A	SiO ₂
S	Al ₂ O ₃
F	Fe ₂ O ₃
H	H ₂ O
$\bar{S}$, \$ or $\hat{S}$	SO ₃
$\bar{C}$ or C	CO ₂

The hydration of PC is a complex process leading to the hardening of PC matrix as various hydrated phases precipitate from solution. The chemical reaction between PC and water leads to the formation of a range of hydration products: 1) nearly amorphous or poorly crystalline C-S-H; 2) crystalline calcium hydroxide (CH); 3) ettringite, AFt phase; and 4) monosulfate, AFm phase. The macroscopic properties of a PC-based system are governed by the properties of the hydration products, and in particular, C-S-H and CH play a key role in determining the mechanical and chemical behavior and pH in a PC-based matrix. Among the PC phases in the clinker, C₃S is the dominant mineral and it constitutes about 50% to 70% of PC. It reacts with water, resulting in the formation of CH and poorly-crystalline C-S-H as shown in (Eq-2.1) [30]. The number of water molecules (x) depends on relative humidity and temperature [29].



The hydration process of C₃S is characterized by the four main periods shown in Figure 2.1: 1) initial reaction, 2) period of slow reaction, 3) acceleration period, and 4) deceleration period. The beginning and ending of these stages are still difficult to determine precisely [31]. In the initial reaction process, the exothermal rapid reaction ($\Delta G^\circ = -500 \text{ kJ/Kg}$) between C₃S and water begins immediately upon wetting. The heat is released by the wetting the cement powder and it can also be released by the dissolution of C₃S. In this period, the pH increases to over 12 due to the Ca²⁺ and OH⁻ ions released from the C₃S surface [32]. This initial reaction is normally over within 15 minutes. A period of slow reaction, also known as the induction or dormant period, can last for two to four hours after the initial reaction. The mechanism of this early induction period has been the

subject of considerable debate over the years, and many hypotheses have been proposed including the metastable barrier hypothesis and slow dissolution step hypothesis [31]. After the induction period, the Ca^{2+} concentration approaches saturation levels and the hydrolysis of C_3S consequently slows down. C-S-H is formed primarily on the surfaces of C_3S . There is general agreement that the acceleration period is related to a nucleation and growth (N+G) mechanism. Lastly, the rate of C_3S reaction slows down, reaching a steady state within 12 to 24 hours in the deceleration period.

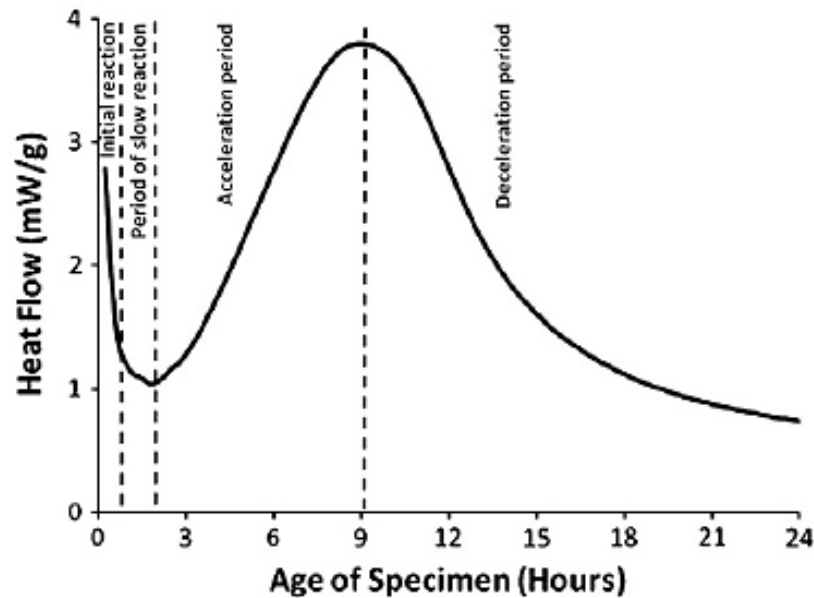


Figure 2.1 Rate of C_3S hydration as a function of time given by isothermal calorimetry measurement [31].

C-S-H gels formed during C_3S hydration are the principal hydration products and the primary binding phase in a hydrated PC matrix. In general, the molar ratio of CaO to SiO_2 (C/S) or Ca to Si ratio (Ca/Si ratio) has been used to define C-S-H. The C-S-H is often to be characterized into C-S-H (I) and C-S-H (II), for C/S ratios below and above 1.5, respectively [1]. Three types of C-S-H system have been suggested by Nonat: C-S-H(α) for $\text{C/S} < 1.0$, C-S-H(β) for $1 < \text{C/S} < 1.5$ and C-S-H(γ) for $\text{C/S} > 1.5$ [33]. The C-S-H present in hardened C_3S paste or neat PC paste has an average Ca/Si ratio of about 1.75, with a range of values a given paste ranging from 1.2 to 2.1 [24]. C-S-H (I), which has a comparatively lower Ca/Si ratio [1] can be present in pastes containing a) SCMs such as fly ash, silica fume, metakaolin, b) ground granulated blast-furnace slag (GBFS), and c) alkali-activated

slag and alkali-activated Class C fly ash systems [34]. The comparatively lower Ca/Si ratio in the PC-SCMs system is due to the increased silica content of the system, which results in an increase in the mean length of the silicate chains and the distance between the layers of C-S-H [2].

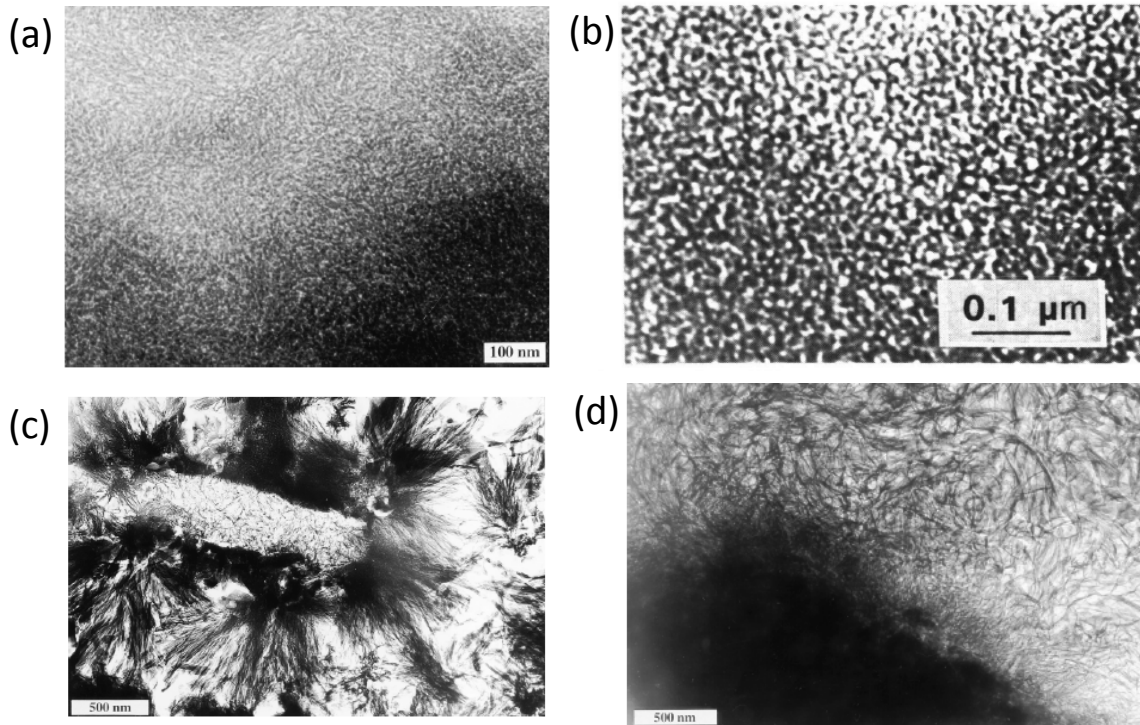


Figure 2.2 Transmission electron microscopy on inner product (Ip) and outer product (Op) of cement phase. (a) Ip in a PC paste [24], (b) Ip in C_3S paste [35], (c) fibrillar Op in PC paste [24] and (d) foil-like Op in water-activated slag paste [24].

Diverse nomenclature has been proposed for differentiating the hydration products of C_3S . The paste's microstructure can be divided into three broad regions as categorized by Taplin et al.: unhydrated material, inner product (Ip) and outer product (Op) including CH [36]. TEM analysis results of the Ip and Op of PC paste and C_3S paste are shown in Figure 2.2. The Ip and Op in C_3S are formed within the boundaries of the original C_3S grains and in the space between the original C_3S grains, respectively [35]. The Op has a fibrillar or foil-like morphology [24], depending on the types of paste. The Ip present in C_3S typically has a homogeneous and fine-grained morphology and has voids with diameters under 10nm as shown by TEM analysis [35].

To better understand the structure of hydration products, a large number of C-S-H models have been proposed based on entirely monomeric silicate anions or a ‘dreierkette’-like structure [2]. C-S-H (I) has a layer structure and shows similarities to tobermorite. The dreierkette chains present in tobermorite were described by Megaw and Kelsey [37], and its schematic diagram is shown in Figure 2.3.

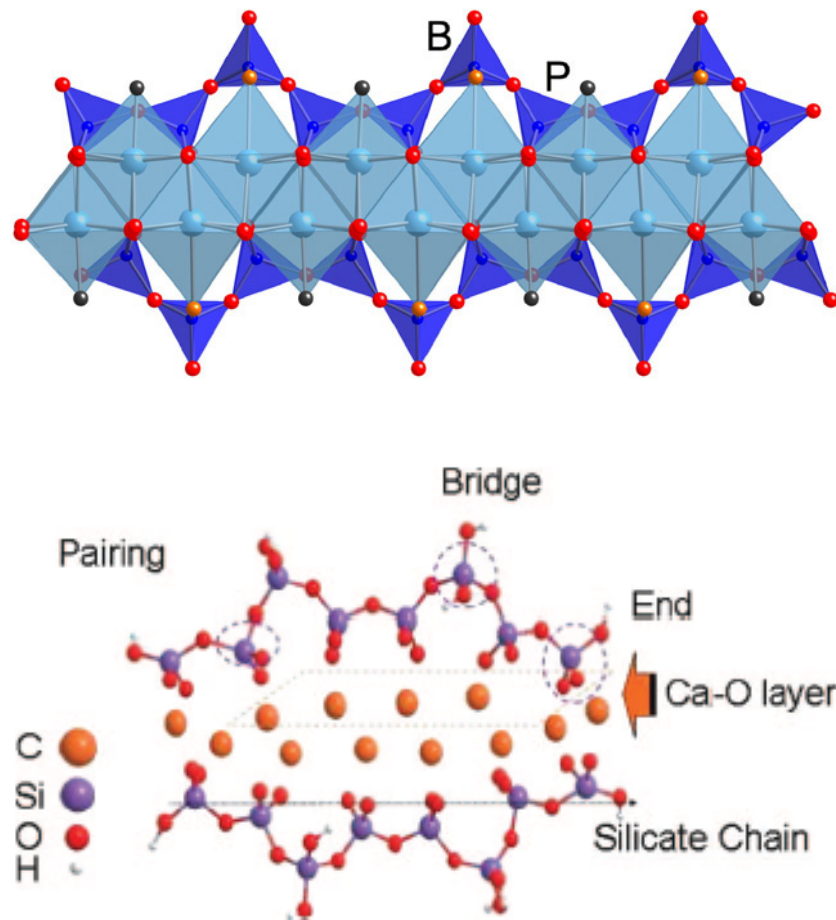


Figure 2.3 Schematic diagram showing dreierkette chains present in tobermorite (presented above), which are of infinite length. The symbol P and B denote, respectively, ‘paired’ tetrahedral and ‘bridging’ tetrahedral [2], and in C-S-H gel (presented below) [38]. In the intralayer space, there are water molecules, hydroxyls, Ca^{2+} , and ions of other elements.

Tobermorite crystal contains dreierkette linear silicate chains where the silicate tetrahedra are coordinated to Ca^{2+} ions by linking in such a way as to repeat a kinked pattern after every three tetrahedra. Two of the three tetrahedra share O-O edges with the central Ca-O part of the layer; these are linked together and are often referred to as ‘paired’ tetrahedra (P). The third tetrahedron, which shares an oxygen atom at the pyramidal apex of the Ca polyhedron, connects the two paired tetrahedra and so is called a ‘bridging’ (B) tetrahedral [2].

The C-S-H in hydrated PC is considered akin to tobermorite although it lacks some of the bridging tetrahedra. The C-S-H in cement paste is therefore referred to as a defective tobermorite structure [39]. Stacking of these layers with mainly water molecules and calcium ions form a C-S-H agglomerate. Further details of the properties and models for the C-S-H are well described elsewhere [2, 24].

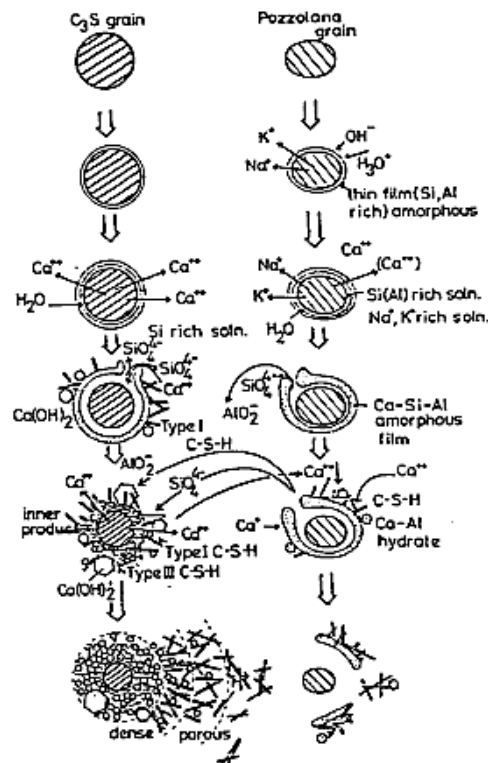
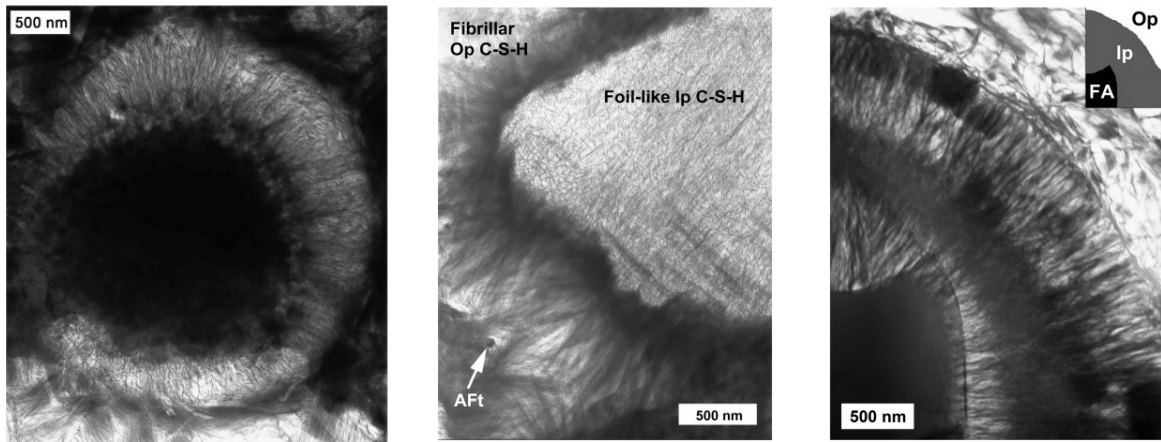


Figure 2.4 Schematic explanation of the hydration mechanism in the system pozzolan-C₃S [40].

Early hydration of C_3S is proven to be accelerated by the addition of different types of pozzolan because the surface of pozzolan acts as a precipitation site (filler effect) which is preferable to the precipitation of hydrates. Other possible mechanism of the filler effect is due to the fact that fly ash provide more space for the hydration product of PC phases [29]. The acceleration of the C_3S hydration can also be caused by the adsorption of Ca^{2+} ions by the pozzolan particle leading to a decrease in the concentration of Ca^{2+} ions in solution. This process increases the rate of dissolution of C_3S as shown in Figure 2.4 [40]. C-S-H formed by the C_3S hydration, precipitates with a the comparatively high Ca/Si ratio on the surface of C_3S particles, and as porous hydrates of low Ca/Si ratio on the surfaces of pozzolan grains [40]. This is because the dissolved Na^+ and K^+ from the pozzolan can accelerate the dissociation of water, intensify the protonic attack of water, and accelerate the dissolution of SiO_4^{4-} and AlO_2^- which then combine with Ca^{2+} and increase the thickness of the hydration layer around the pozzolan particles [40]. Transmission electron microscopy (TEM) analysis demonstrated that the layers around fly ash particles can be distinguished into Ip and Op of fly ash as shown in Figure 2.5. This study also found that for a water-activated 28-day-old sample, the Op consists of a mixture of fibrillar and foil-like [4].



(a) TEM micrograph from a water-activated paste hydrated for 28 days showing a partially hydrated PFA particle.

(b) TEM micrograph from a water-activated paste hydrated for 28 days showing fine fibrillar Op C-S-H (with a small relict of Aft) surrounding low-density foil-like Ip C-S-H.

(c) TEM micrograph from a KOH-activated paste hydrated for 28 days showing a partially hydrated PFA particle.

Figure 2.5 Transmission Electron Microscopy images of PFA particle [4]

As mentioned before, the C-S-H formed in PC with silica-rich SCMs has a tobermorite-like structure, but it may also have defects, mainly in the positions of the bridging silicon tetrahedral [29]. Moreover, the C-S-H in PC matrix with high fly ash content, compared to C-S-H in a pure PC matrix, has layer spacing of 1.1nm, a longer chain length, and a higher Al content due to the additional silicate and the substitution Al for Si in the C-S-H. As an example, the average chain length of C-S-H in PC with metakaolin (MK) system is shown in Table 2.2.

Table 2.2 Average chain length of C-S-H in PC with metakaolin (MK) system

	Average chain length	Al/Si
100% PC	2.62	0.043
80% PC + 20% MK	4.38	0.103
70% PC + 30% MK	7.24	0.149

Consequently, the C-S-H in the PC matrix containing fly ash is more crystalline. ²⁹Si magic angle spinning (MAS) nuclear magnetic resonance spectroscopy (NMR) is often used to calculate the chain length by obtaining quantitative information on the fractions of silicon present in different tetrahedral environments; Q_n (0 ≤ n ≤ 4), where Q is a silicate tetrahedron and n is the number of oxygens that bridge to adjacent tetrahedra. The average chain length with and without Al substitution for Si and the Al/Si ratios for the C-S-H can be calculated from the ²⁹Si single pulse data from Eq-2.2, Eq-2.3 and Eq-2.4, respectively [24]. NMR analysis supports the fact that the C-S-H formed in the PC matrix containing SCMs has a longer chain length compared to one in a pure PC matrix. Furthermore, it has been shown that Al substitutes for Si in C-S-H only in the bridging tetrahedra of dreierkette chains.

$$\text{Chain length } (\overline{\text{CL}}) = \frac{2}{\frac{Q^1}{(Q^1+Q^2)}} \quad (\text{Eq-2.2})$$

$$\text{Chain length } (\overline{\text{CL}}) = \frac{2}{\frac{Q^1}{(Q^1+Q^2(0\text{Al})+\frac{3}{2}Q^2(1\text{Al}))}} \quad (\text{Eq-2.3})$$

$$\text{Al/Si} = \frac{\frac{1}{2}Q^1(1\text{Al})}{(Q^1+Q^2(0\text{Al})+Q^2(1\text{Al}))} \quad (\text{E.q-2.4})$$

A successful C-S-H structural model must also account for the experimentally observed sequence of chain lengths, i.e. 2,5,8...(3n-1) where n is the integer (for individual structural units). It must also account for the fact that in Al substituted C-S-H which is expected to be formed in PC with SCMs, Al³⁺ substitutes for Si⁴⁺ only in the central tetrahedra of pentamers or in every third tetrahedron n longer chains [2]. *Ab initio* calculation confirmed the rule of tetrahedral length m=3n-1, and by analyzing the HOMO-LUMO orbitals, it was also found that aluminum atoms prefer the bridge chain site rather than the other tetrahedral, which is consistent with NMR analysis [38].

The effect of silicate polymerization and Al substitution for Si on binding energy of Si in the silicate tetrahedra will be discussed in the following section in more detail.

2.3 X-ray absorption spectroscopy

Currently, there are several types of x-ray material characterization methods including x-ray diffraction (XRD), x-ray photoelectron Spectroscopy (XPS), x-ray absorption spectroscopy (XAS), x-ray emission spectroscopy (XES), and x-ray scattering. Over the last 30 years, XAS has made major contributions to a wide variety of research topics and been used to study a wide variety of materials and phenomena, including amorphous solid and liquid systems, solid solutions, doping and ion implantation in semiconductors, local distortions in crystal lattices, organometallic compounds, metalloproteins, metal clusters, catalysts, vibrational dynamics, liquid water and aqueous solutions [41].

XAS is a technique used to determine the local geometric and electronic structure of matter in a solid, liquid, or gaseous state. It is essentially a form of electron spectroscopy that is similar to UV-visible spectroscopy, with the main difference being the higher energy and shorter wavelength of x-rays compared to the UV region of the electromagnetic spectrum. Also, the x-ray wavelength is on the same order of magnitude of the interatomic spacing in molecules. XAS has many advantages as a characterization method since it is

element specific, which means that one can focus on one element without interference from other elements present in the sample. A main feature of XAS is that, it is non-destructive and can be used for both heterogeneous and amorphous samples, including the C-S-H formed in cementitious materials. Furthermore, XAS is not limited by the state of the sample, because it is sensitive only to the local metal site structure. The sample can be prepared as a powder, a solution, or, a frozen solution for biological samples. It is not necessary to obtain single crystals of the material to examine the local structure of metal. Using XAS, the amount of a particular element, a characteristic of the chemical environment (i.e., coordination number), and the valence state (i.e., oxidation state) can be determined quantitatively [42]. It is important to emphasize that since XAS experiments require a lower x-ray dose, beam damage by XAS measurement is minor compared to electron-based characterization methods using high electron voltage [42].

X-ray absorptions are attributed to electron transitions to the lowest unoccupied molecular orbital (LUMO) at the bottom of the conduction band. They are restricted by the quantum selection rules, $\Delta L = \pm 1$, $\Delta J = 0$ or ± 1 (L: orbital quantum number, J: total angular momentum quantum number) [43]. The x-ray absorption spectral function or intensity of XAS is described according to Fermi's Golden rule as presented in Eq-2.5 [44, 45].

$$\sigma(E_{h\nu}) \sim \sum |\langle \phi_i | X | \phi_f \rangle|^2 \cdot \delta(E_i + E_{h\nu} - E_f) \dots \dots \dots (\text{Eq-2.5})$$

Where E_i , $E_{h\nu}$ and E_f indicate the energy of the initial state, the x-ray and the final state, respectively. X is the operator describing the interaction of x-rays with matter for which the dipole approximation is used. Therefore, it is necessary to find the initial and final state energies and the wave functions in order to calculate the spectral function based on finding the projected density of states (DOS) using an electronic structure calculation. As an approximation method, a multiple scattering calculation has been used to derive the equivalent spectral shape [44].

A plot of x-ray absorption versus energy shows distinct peaks, which are called absorption edges. These absorption edges occur at the incident photon energies where the absorption increases dramatically as an x-ray photon is absorbed by the atom. The name of the edge depends upon the core electron that is excited: the principal quantum numbers $n=1$

(1s), 2 ((2s, 2p with $J=1/2$ or $3/2$) and 2p), and 3 (3s, 3p, and 3d), correspond to the K, L, and M edges, respectively. For instance, excitation of a 1s electron occurs at the K edge, while excitation of a 2s or 2p electron occurs at an L edge (see Figure 2.6).

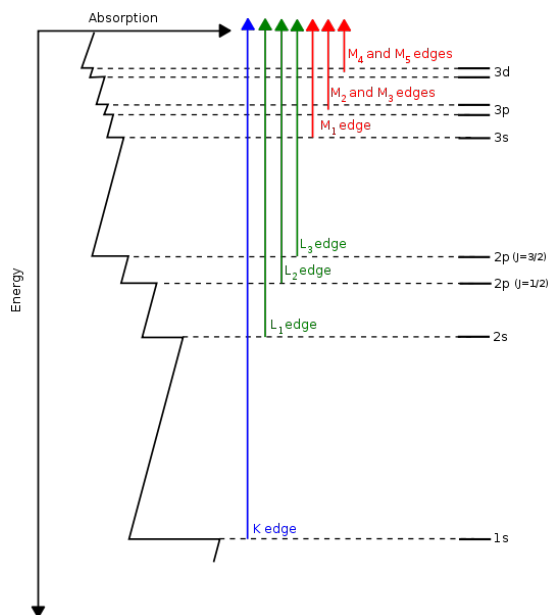


Figure 2.6 Transitions that contribute to XAS edges [46].

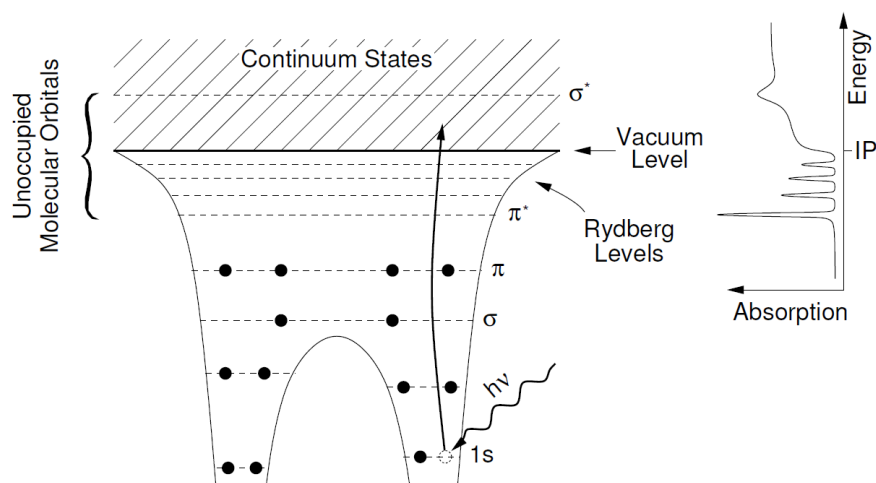


Figure 2.7 Schematic electron potential (left) and K-shell absorption spectroscopy (right) of a diatomic molecule [47].

As an example, the schematic electron potential and K edge absorption spectroscopy of a diatomic molecule is shown in Figure 2.7. The electron transition from the 1s (core) level to the unoccupied molecular orbitals caused by the x-ray photon gives rise to absorption resonances at the corresponding energy levels below and above the ionization potential. Since the photoelectron with energies above the potential receives the kinetic energy of the difference between the x-ray photon energy and the potential, the absorption fine structure is also influenced by the electron scattering processes [47].

XAS data are obtained by tuning the photon energy using a crystalline monochromator to a range where core electrons can be excited (0.1-100 keV photon energy), and can be divided into three main regions based on the binding energy (E_0) of the element of interest as illustrated in Figure 2.8:

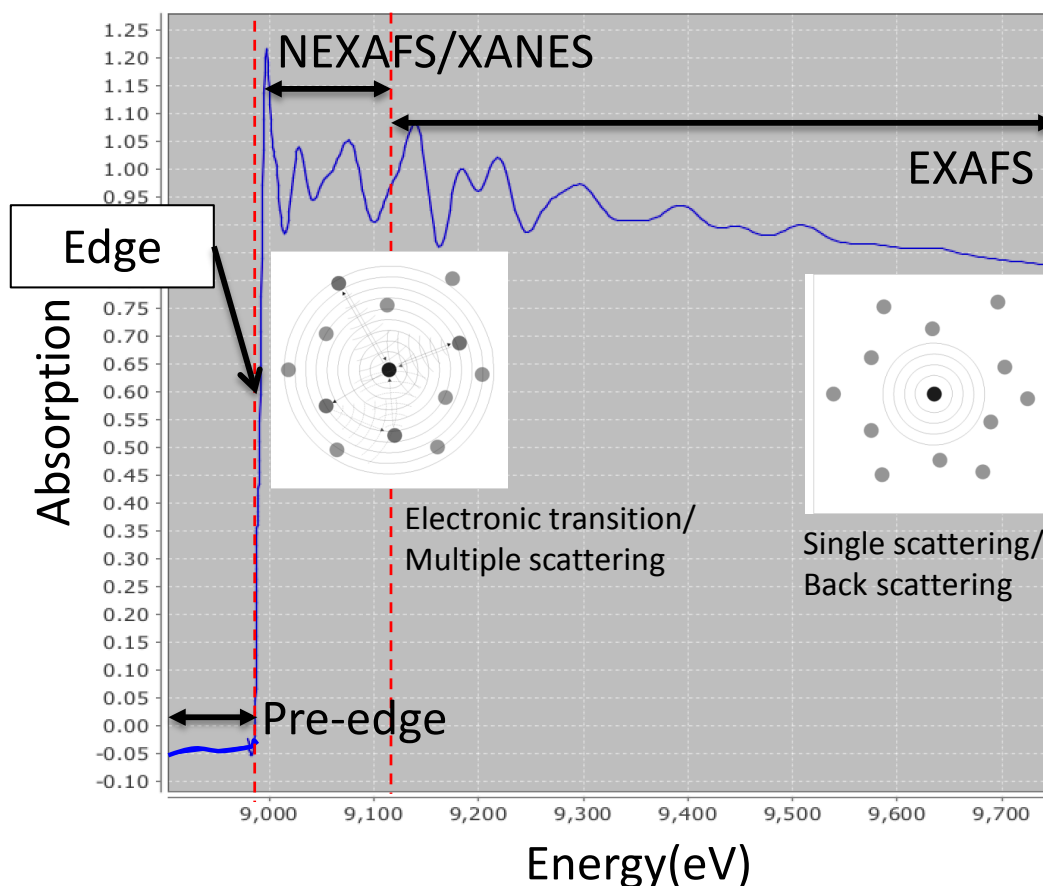


Figure 2.8 Schematics of x-ray absorption spectrum

- 1) Pre-edge and, 2) near edge x-ray absorption fine structure (NEXAFS), also known as x-ray absorption near edge structure (XANES) spectroscopy, regions refer to the absorption fine structure that is close to an absorption edge, about the first 30 eV above the actual edge. This region usually shows the largest variations in the x-ray absorption coefficient and is often dominated by intense, narrow resonances. Today, the term NEXAFS is typically used for soft x-ray absorption spectra and XANES for hard x-ray spectra.

Finally, 3) extended x-ray absorption fine structure (EXAFS) regions are the oscillating parts of the XAS that extend to about 50 to 1000 eV above the absorption edge of a particular element of a sample [48]. While NEXAFS is dominated by electronic transitions and multiple scattering of low-energy photoelectrons in the valence potential that occurred by the nearest neighbors' atoms, EXAFS is due mostly to single scattering and back scattering of a high-energy photoelectron off the atomic cores of the neighbors.

The majority of useful information from the x-ray absorption spectrum comes from both NEXAFS and EXAFS. NEXAFS is element specific and very sensitive to the bonding environment of the absorbing atom. Furthermore, it provides useful information in terms of chemical bonds and local bonding (coordination) and the oxidation state of materials. NEXAFS is an essential analytical tool in material research, and combining NEXAFS with soft x-ray microscopy adds spatial resolution and the possibility studying individual nanostructures [49].

2.3.1 Ca L edge and Si K edge NEXAFS

Calcium is a major element in the earth's crust and mantle and is an essential cation in biosystems [43]. In particular, the chemistry of Ca and its compounds is important as calcium is one of the main elements in various hydration products in PC-based materials [50]. However, Ca L edge NEXAFS using soft x-ray absorption of hydration products in PC-based materials has not been studied extensively. In particular, only a few studies have been conducted in terms of cementitious materials including C-S-H and other hydration products [22, 23, 51]. Configuration of Ca in ground state is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^0$, consisting of one single 1S state. For Ca L_{III} and L_{II} edges, the core electrons are 2p, which have dipole-allowed transition to s- and d-like final states. 2p absorption is determined by the transition probability of $2p^6 3d^0 \rightarrow 2p^5 3d^1 Ca^{2+}$. Ca is octahedron (O_h) coordination and

the actual local coordination environment of calcium compounds is shown in Figure 2.9.

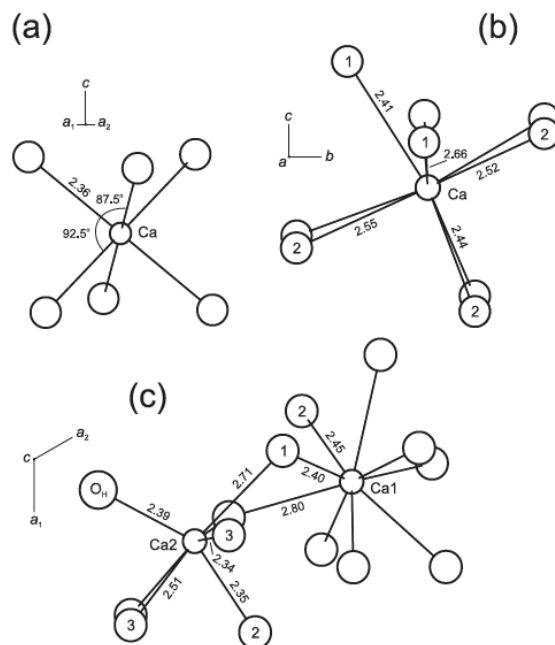


Figure 2.9 Coordination of Ca^{2+} cation in (a) calcite, (b) aragonite, and (c) hydroxylapatite (HAP) (distances are in angstroms) [43].

Examples of the Ca L edge NEXAFS of some calcium compounds are shown in Figure 2.10. Experimentally and theoretically Ca L edge NEXAFS consists of two main spin-orbit related peaks, L_{III} (a_2) and L_{II} (b_2) along with a number of smaller peaks that appear ahead of the main peaks (a_1 and b_1) occurring due to crystal field splitting [50] as shown in Figure 2.11.

The four principal peaks (a_1 , a_2 , b_1 , and b_2) are attributed to the familiar $2p_{3/2}-t_{2g}$, $2p_{3/2}-e_g$, $2p_{1/2}-t_{2g}$, and $2p_{1/2}-e_g$, respectively. The energy separation between the two main peaks in the L_{III} (peak a_1 and a_2) and L_{II} (peak b_1 and b_2) edge is a complex change of the spectrum as a non-linear function of crystal-field splitting ($10Dq$) [52] and those $10Dq$ are positive for O_h coordination (t_{2g} below e_g) [53]. More details on the Ca L edge NEXAFS of synthesized C-S-H and hydration products of the C_3S and HVFA system will be discussed in Chapter 3 and 4.

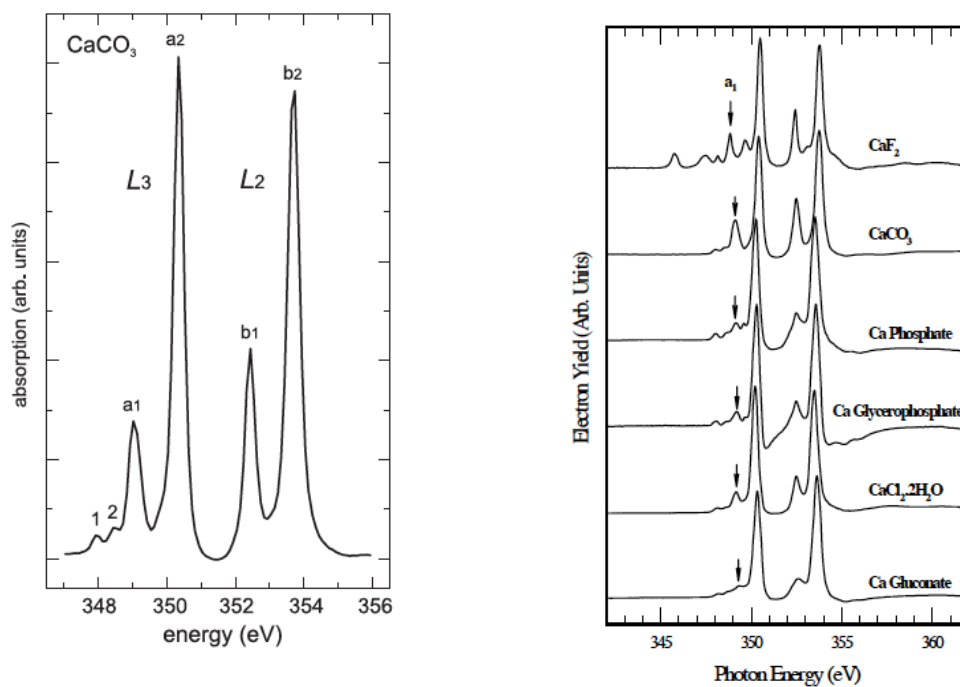


Figure 2.10 Ca L edge NEXAFS spectra of some calcium compounds. Left: calcite, right: six calcium compounds including calcite [43, 50].

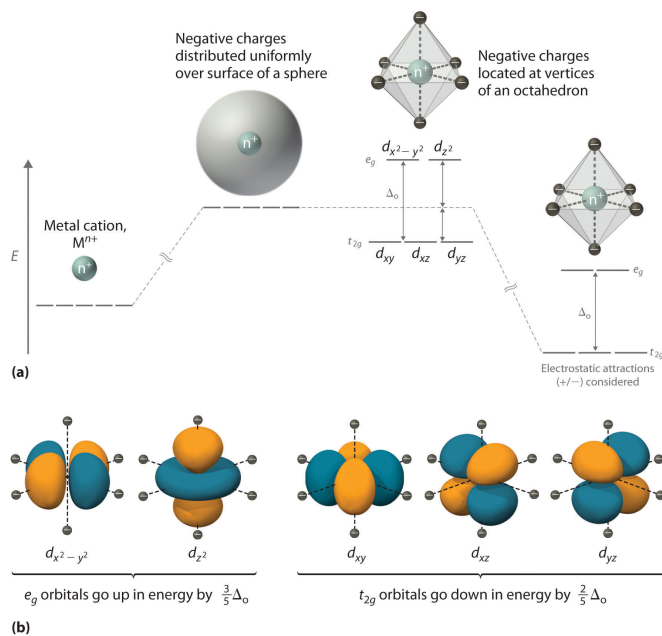


Figure 2.11 Crystal splitting in an octahedral complex. An octahedral arrangement of six negative charges around a metal ion causes the five d orbitals to split into two sets with different energies $\Delta_0 = 10Dq$ [54].

The following eight elements O, Si, Al, Fe, Ca, Na, K, and Mg, make up nearly 99% of the crust of the earth by weight, and most of the minerals crystallized from melts in the outer parts of the earth are silicates [55]. C-S-H consists mainly of Si in a PC-based system, and Si K edge NEXAFS using soft x-ray absorption of hydration products in the system has not been studied extensively. The Si K edge NEXAFS spectra of some representative silicate minerals are shown in Figure 2.12. In general, the four features, A, C, E, and G, are related to the SiO_4^{4-} cluster. Peak A is attributed to the electronic transition of Si 1s to an anti-bonding 3s-like state (a_1), and it shows very weak peak intensity since the electronic transition is forbidden by the quantum selection rule $\Delta L = \pm 1$, $\Delta J = 0$ or ± 1 [43]. Peak C, showing the highest peak intensity, is referred to the Si K- edge and it is assigned to the electron transitions of Si 1s to the anti-bonding 3p-like state (t_2). Peaks E and G are attributed to the electron transitions of Si 1s to the e and t_2 states (empty Si 3d states). Peaks D and F are attributable to the multiple scattering effects occurring beyond first coordination atoms [56].

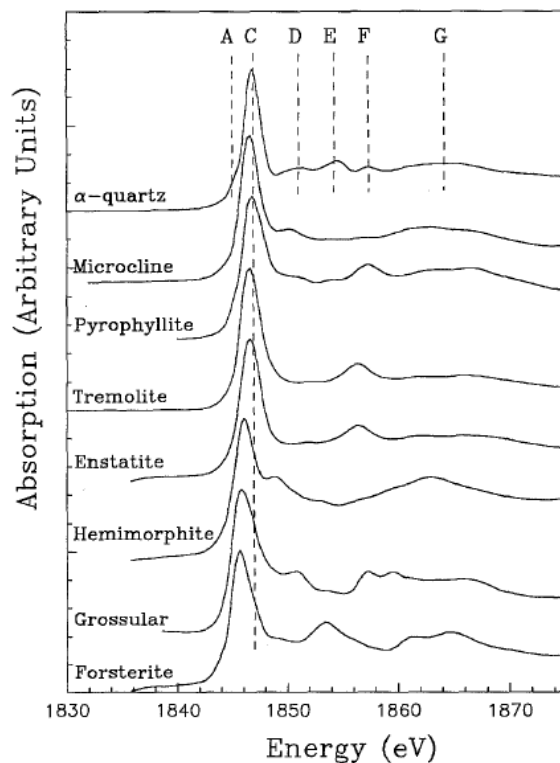


Figure 2.12 Si K edge XANES spectra of some representative silicate minerals [56]

2.3.2 Silicate polymerization and aluminum substitution for silicon in silicate and their effect on NEXAFS

Silicate anions, the basic building blocks of C-S-H, are tetrahedral SiO_4^{4-} units, and they are balanced by the presence of calcium cations in C-S-H [57]. In the process of hydration, defective sheets of silicate layers are formed through silicate polymerization. Chemical shift Si binding energy, caused by silicate polymerization, has been studied by different characterization methods, including XPS [58, 59] and XAS [56], and it is found that Ca/Si ratio decreases to correspond to the silicate polymerization in silicate minerals, resulting in increases in chain length and SiO_2 content in C-S-H [58]. The chemical shift of Si K edge NEXAFS caused by increases of silicate polymerization is presented in Figure 2.13. It is found that the Si K edge main peak (C in Figure 2.12) shifts by 1.3eV to a higher energy with an increase in the polymerization of SiO_4^{4-} clusters, from nesosilicates (Q^0) to tectosilicates (Q^4) [56].

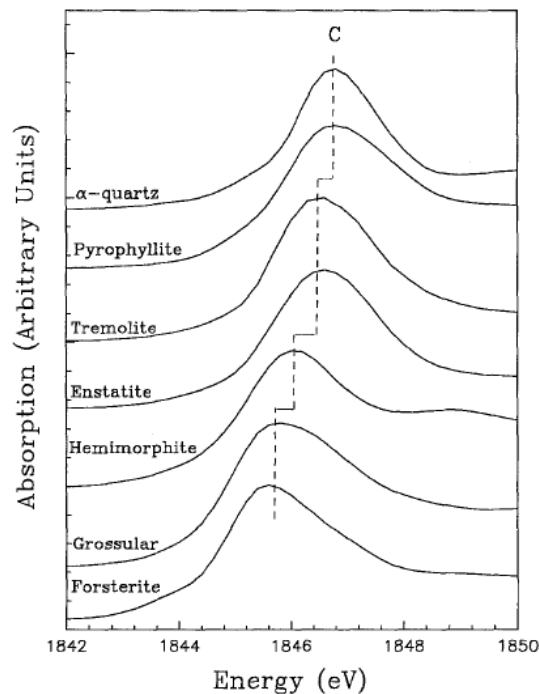


Figure 2.13 The chemical shift with regard to the Si K edge NEXAFS of silicate minerals [56].

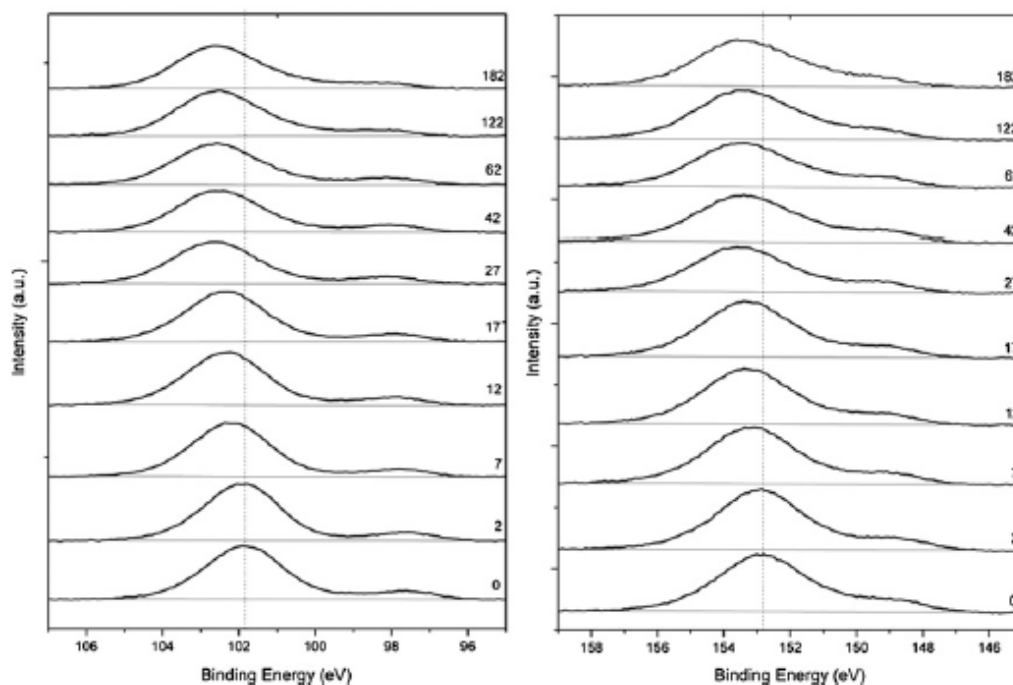


Figure 2.14 Si 2p (left) and 2s (right) XPS spectra of the C₃S thin film [58]

Recently, in a study of cement phase, the evidence a shift of Si peaks to higher energies and the subsequent decrease of the Ca–Si binding energy distance was observed by XPS analysis, indicating silicate polymerization expected upon formation of C–S–H in the process of C₃S thin film hydration. In the study, it was found that the molar Ca/Si ratio of about 1.55 evolves from that of a jennite-like material at the beginning of the experiment, to a tobermorite-like with Ca/Si ratio of 0.85 after 3 h of hydration [58].

On the other hand, Si K edge binding energy in silicate can also be affected by Al substitution for Si resulting in a shift to a lower energy level. The effect of Al substitution for Si in Si K edge NEXAFS is shown in Figure 2.15. The Si K edge shifts toward lower energy with the increase in the substitution of Al for Si because the Al–O bond is weaker than the Si–O bond and the substitution of Al for Si reduces the effective charge on Si atoms [56].

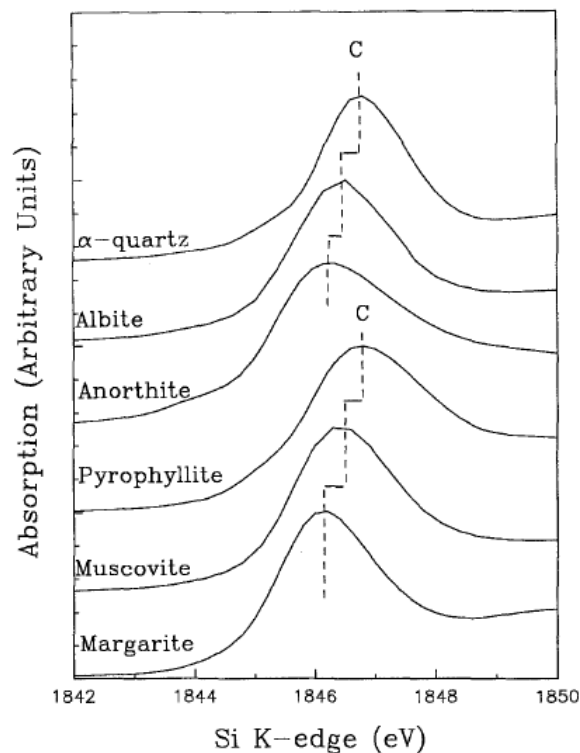


Figure 2.15 Effect of increased substitution of Al for Si in tetrahedral silicate on Si K edge NEXAFS [56]

2.4 Scanning transmission x-ray microscopy (STXM)

Over the last years, STXM, a type of the spectro-microscopy, has become an important tool in applying soft x-ray spectroscopy to many scientific disciplines. It is a microscope, thus it produces images, but its strength is in the ability to obtain high quality spectroscopy on that scale [20]. Sample preparation can be similar to that for transmission electron microscopy (TEM), but because samples can be at the full atmospheric pressure of He (or air for some x-ray energies) they can be “wet”, or fully hydrated, which is a huge advantage for biological or environmental samples.

A schematic representation of the optical elements used in the STXM set-up is shown in Figure 2.16. Coherent x-ray with a low spectra bandwidth can be obtained by a monochromators. The zone plate then selects the desired energy from the grating and focuses it onto the specimen. Since the incident x-rays include significant levels of higher-order diffracted light, an order-sorting aperture (OSA) is used to filter higher-order

diffracted light, leaving only first-order diffracted light. As a set of precise fine stages move the sample to the proper position, the focused X-ray is raster scanned across a selected area of the sample to produce an x-ray microscopic image at a given photon energy [60]. STXM resolution depends on the zone plates used. The zone plates of STXM at advanced light source (ALS) can resolve details smaller than 20 nm [20]. In STXM, x-rays are focused using a Fresnel zone plate, and the sample is mechanically scanned in the zone plate focal plane. Transmitted x-rays are detected by a single element detector and the detector signal as a function of the sample position constitutes an image. Recording images at different x-ray energies around the absorption edges of a given element allows NEXAFS to be obtained for each of the image pixels [61].

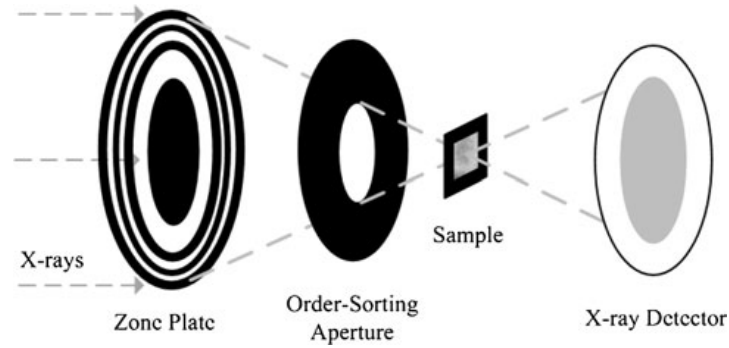


Figure 2.16 Schematic representation of the optical elements used in the STXM set-up [60].

The primary signal measured in STXM is transmitted x-ray photon intensity as a function of energy or position. A narrow, parallel monochromatic x-ray beam of intensity I_0 passing through a sample of thickness x will get reduced to intensity I according to the following expression:

$$I = I_0 e^{-\sigma(E) \cdot t} \quad (\text{Eq.-2.6})$$

where σ is the linear absorption coefficient which is the fraction of x-ray beams that is absorbed per unit thickness of the absorber, and t is the sample thickness. This expression is based on the Beer–Lambert law, which is also known as Beer’s law, Lambert–Beer law, or Beer–Lambert–Bouguer law. The x-ray absorption coefficient depends on the type of atom and the density of the material. In the data analysis, this transmitted signal collected in STXM is converted to optical density (OD) which is sensitive to sample

thickness, the density of the material, and the composition as shown in Eq-2.7.

$$\text{Optical Density (OD)} = -\ln(I/I_0) = \sigma(E) \cdot t = \mu(E) \cdot \rho \cdot t \quad (\text{Eq-2.7})$$

where μ is the mass absorption coefficient, and ρ is the density of the sample.

STXM is very versatile and it can be utilized in different modes to obtain the spectra and images of a sample. The present study measured, *single image* at a specified energy level, *image contrast map* from differential absorption of x-rays of two *single images* with a spatial resolution of 25 nm are measured. In addition, *image stacks* were collected, in which a series of images at each energy, allowing for detailed spectro-imaging. The results were combined to create a *RGB overlay maps* by singular value decomposition (SVD) based on reference spectra [62]. The main strength of SVD is the use of detailed spectral information to convert *image stacks* into chemical component maps. Since different chemical components have different NEXAFS spectra, reference spectra can be obtained from known materials and the SVD based on these reference spectra, easily convert the *image stacks* into *RGB chemical maps* [63]. *RGB chemical maps* can be used effectively to visualize and differentiate phases with different chemical compositions in a sample [64].

2.5 Monochromatic scanning x-ray micro-diffraction (μ -SXRD)

Since von Laue in 1912 and Braggs in 1913 discovered that crystalline substances act as diffraction gratings for x-ray wavelengths similar to the spacing of planes in a crystal lattice, XRD has been utilized to investigate the long range periodicity of atomic structures in crystals. XRD is a very versatile tool and its data provide information on the phase identification of an unknown crystalline material; atomic spacing; the orientation of a single crystal or grain; and the size, shape and internal stress of small crystalline regions [65, 66]. Diffraction patterns of cementitious materials provide phase, chemical, and crystal structure information data that is needed to aid in the understanding of cement performance and to aid in the selection of the optimum cement for use in concrete [67]. The microstructure of a material (the types, amounts, and distribution of its component phases) is a fundamental link between the material processing and subsequent properties. However, until recently, there has been a lack of rapid, reliable, and accurate techniques to quantify the different

phases present.

Figure 2.17 illustrates the mechanism of x-ray diffraction. The incoming beam (coming from the upper left) makes each scatterer to re-radiate a small portion of its intensity as a spherical wave. If scatterers are arranged symmetrically with a separation d , these spherical waves will be in sync (add constructively) only in the directions where their path-length difference $2d \sin \theta$ equals an integer multiple of the wavelength λ (Eq-2.8). In that case, part of the incoming beam is deflected by an angle 2θ , producing a reflection spot in the diffraction pattern [65, 68].

Crystals are regular arrays of atoms, and x-rays can be considered waves of electromagnetic radiation. Atoms scatter x-ray waves, primarily through the electrons. Just as an ocean wave striking a lighthouse produces secondary circular waves emanating from the lighthouse, so an x-ray striking an electron produces secondary spherical waves emanating from the electron. This phenomenon is known as elastic scattering, and the electron is known as the scatterer. A regular array of scatterers produces a regular array of spherical waves. Although these waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, as determined by Bragg's law.

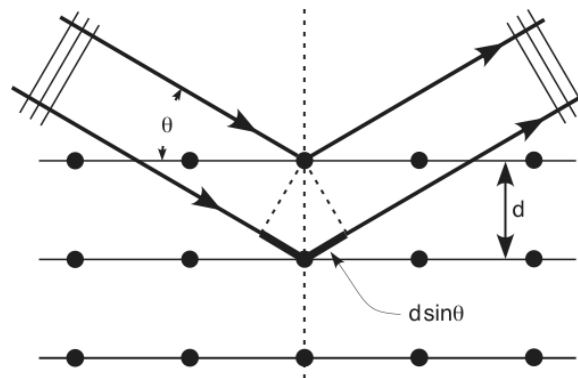


Figure 2.17 Braggs Law [68]

$$2d \sin \theta = n\lambda \quad \text{..(Eq-2.8)}$$

Compared to standard lab-based x-ray powder diffractometer, μ -SXRD is a structural analysis tool that allows for the examination of the samples in a micron- or sub-micron scale and yields greater precision in lattice parameter determination. It is often used to complement x-ray micro-spectroscopy including x-ray micro-fluorescence, extended EXAFS, and NEXAFS. This advanced technique has been widely adapted to investigate the mesoscale plastic deformation mechanisms in individual grains within a polycrystalline thin film [69], the microstructure of cerium oxide plastic [70], the elastic strains in cracks in alloys [71], and it has also been implemented in applications in the fields of biology and archeology [72, 73]. Synchrotron radiation provides ultra-bright ultraviolet light and x-rays, which are used in a wide range of analytical techniques. Beamlines that offer an x-ray beam size in micron or sub-micron dimensions are available at several synchrotron facilities including the ALS, APS, European Synchrotron Radiation Facility (ESRF), National Synchrotron Light Source (NSLS), Canadian Light Source (CLS), Swiss Light Source (SLS) and Pohang Light Source (PLS). Among those beamlines, beamline 12.3.2 at the ALS is a versatile x-ray micro-diffraction station facilities that was recently built on a superbend magnet source to deliver an x-ray spectrum ranging from 5 to 22 keV with high photon flux and rapid data collection capabilities [74, 75]. The schematics of the μ -SXRD at beamline 12.3.2 at the ALS are illustrated in Figure 2.18. Briefly, the hard x-ray beam is focused down to 1 μ m size at the sample position using a pair of elliptically-bent Kirkpatrick–Baez (KB) mirrors enclosed in a vacuum box. KB mirror improves the resolution in the nanometer scale. The sample placed on high precision stages can be raster-scanned under the microbeam while a diffraction pattern is taken at each step. Both polychromatic and monochromatic radiation modes can be conducted by μ -SXRD. A polychromatic beam is best suited for a polycrystalline sample with a grain size larger than the beam size, while monochromatic beam is best suited for polycrystalline sample with grain size smaller than the beam size. Typically, the monochromatic beam mode is suitable for cementitious material, which is polycrystalline and heterogeneous. The Laue diffraction pattern (single crystal pattern) is constructed when a polychromatic beam is used, and the Debye–Scherrer diffraction pattern (powder ring pattern) is constructed when a monochromatic beam is used [75, 76]. Examples of these patterns are presented in Figure 2.19.

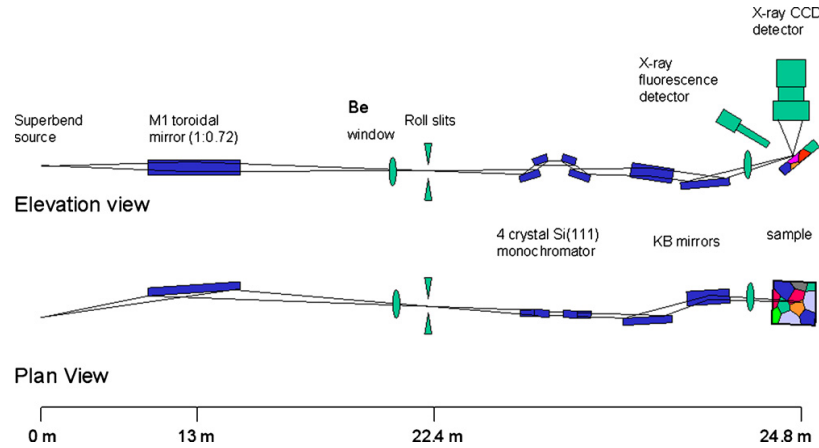


Figure 2.18 Elevation and plan view of the 12.3.2 micro-diffraction beamline at the advanced light source [75].

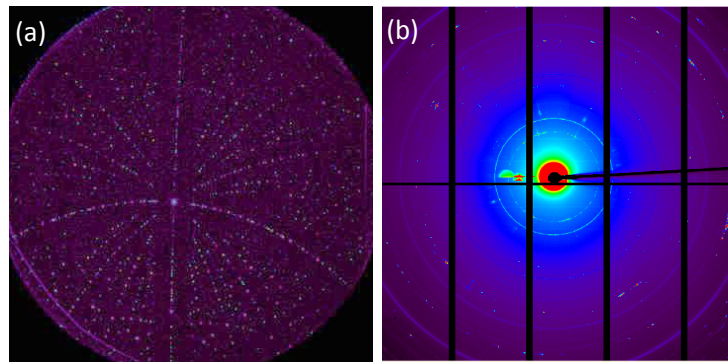


Figure 2.19 (a) Laue diffraction pattern by polychromatic (white) beam radiation [8], and (b) Debye-Scherrer diffraction pattern from a HVFA paste microstructure obtained using monochromatic beam radiation.

In addition, μ -SXRD operates in both reflection and transmission modes. Typically, thin-sectioned samples are used for measurement in the transmission mode. Each diffracted pattern can be used to index the crystalline phases in the sample. Furthermore, the arrays of the diffraction patterns collected by a MAR133 X-ray detector are analyzed to derive the distribution maps of the phases. Stress, strain and plastic deformation within the sample can also be mapped [8]. Further details of the instrument are explained by Tamura et al.,[74]. Data are analyzed with X-ray micro-diffraction analysis software (XMAS), which is used to extract quantitative information from polychromatic and monochromatic beam patterns. With XMAS, thousands of patterns can be indexed in one session, and these patterns are

converted into 2-D element mapping by individual diffraction patterns [77]. The μ -SXRD method is an effective tool in a wide range of scientific fields.

The μ -SXRD technique has been successfully applied to study the hydration products of cementitious material based systems and the corrosion of reinforcing steel bars in concrete. In a previous study, it was able to quantify the orientation and distribution of ettringite crystals $[\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}]$ (Figure 2.20) which led to the expansion and cracking of a hydrated PC matrix due to a sulfate attack [21].

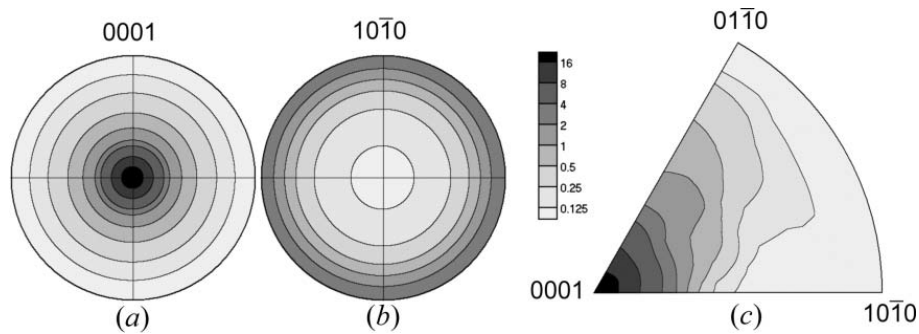


Figure 2.20 (a and b) Pole figures and (c) inverse pole figure of the fiber axis, illustrating the preferred orientation of ettringite. Equal area projection. Logarithmic contours are in multiples of a random distribution [21].

Diffraction images were analyzed using Rietveld method to obtain information on crystal textures. It was found that the c axis of the trigonal ettringite crystal, which is also the elastically stiffest direction, was preferentially oriented perpendicular to the fracture surfaces. In addition to studying the hydration products in cement based systems, corrosion products, which are formed on corrosion resistant reinforcing steel in concrete exposed to sea water, are also studied. It is possible to differentiate various crystalline phases in corrosion products, and determine their distribution in a steel–concrete interface with qualitative chemical analysis through μ XRF mapping [78]. The characteristics of C-S-H present in PC / HVFA matrix, undoubtedly the most important phase in cementitious material based systems and expecting to have more crystalline characteristic in comparison to one in pure PC system, is also studied in this dissertation. An example of an unindexed diffraction pattern from PC / HVFA paste is shown in Figure 2.19-(b). Detailed experimental results of the aforementioned HVFA study using μ -SXRD will be described in Chapter 5.

2.6 Soft x-ray diffraction imaging

Microscopes based on electrons or x-rays are a valuable tool for both biological and material science. They are, however, limited in their ability to image with nanometer-scale resolution in three dimensions non-periodic objects that are several microns in size. To fill this gap, a new beamline, stationed at ALS Beamline 9.0.1 is being developed for coherent scattering and diffraction imaging based on original work done by researchers at Stony Brook. The new beamline takes advantage of the penetrating power of x-rays while simultaneously removing the limitations imposed by lens-based optical systems [74].

Lens-less imaging uses computational techniques to reconstruct an image from diffraction data, which are the intensities and angles of x rays scattered from the sample rather than transmitted through it. In diffraction imaging, the object is retrieved from a recording of the intensity of the Fourier transform of the complex exit wave-field; that is the far-field diffraction pattern. However, since an intensity measurement only records the magnitude of the Fourier transform but not its phase, iterative algorithms have to be employed to recover the object. The details of recording and reconstructing diffraction patterns are well described elsewhere [79].

The technique also provides reconstructive imaging at spatial resolution several times better than that of lens-based x-ray imaging systems limited to a resolution of order 10nm [80]. The resolution of diffraction pattern can be expressed as shown in Eq-2.9, where d = resolution elements of width, Δx = pixel size of detector, λ = wavelength of x-ray beam, N = number of detector pixels, and z = distance between a sample and a detector [79].

$$d = \frac{\lambda z}{N \Delta x} \quad (\text{Eq-2.9})$$

For instance, for $\lambda = 1.65$ nm, $z = 160$ mm, $N = 1300$, and $\Delta x = 20$ μm , which are typical values for diffraction imaging, a theoretical maximum resolution of $d = 10$ nm is obtained. X-ray diffraction microscopy using the reconstruction method has been used successfully to image the complex-valued exit wave of an intact and unstained yeast cell

[81]. The diffraction data and reconstructed images are shown in Figure 2.21. The STXM image shows absorption effects only in grayscale whereas the diffraction images represent magnitude as well as phase in the color scale by the renderings of the complex-valued reconstructions using brightness and hue. B shows a STXM image taken of the same cell using 540 eV x-rays and a zone plate with an estimated Rayleigh resolution of 42 nm [81].

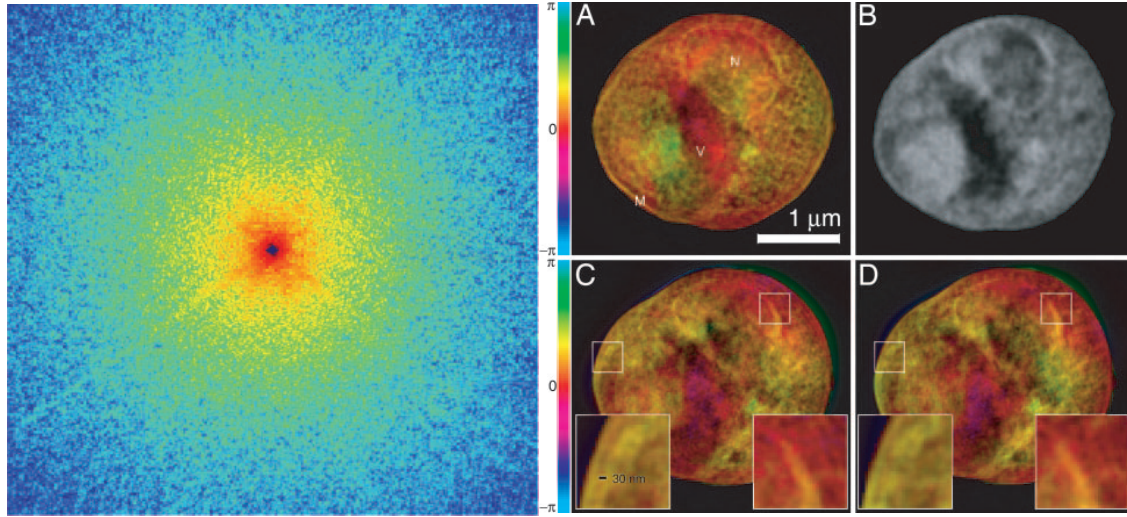


Figure 2.21 Diffraction data and images of a freeze-dried yeast cell. A was obtained by phasing the diffraction data (left), whereas C and D were obtained from reconstructions of two separate, slightly lower exposure data sets acquired with the cell tilted by 3° (C) and 4° (D) relative to A. N, V, and M denote nucleus, a storage vacuole, and the cell membrane (M), respectively [81].

One of the important features of the new technique is capability of running the reconstruction algorithms on 3D data sets by doing 3D Fast Fourier transforms instead of reconstructing each diffraction pattern in 2D and then assembling the reconstruction to yield a 3D image [79]. In the present thesis, the first trial for 2D diffraction imaging on cement phase is presented. We expect the 3D reconstruction provide morphologic details of Ip in cement phases. The results of x-ray diffraction imaging using 2D reconstruction on hydrated C₃S will be introduced in Chapter 3.

CHAPTER 3

**NEXAFS STUDY USING SOFT X-RAY SPECTRO-MICROSCOPY
AND NANOSCALE X-RAY DIFFRACTION IMAGING OF
CALCIUM SILICATE HYDRATES AND C₃S HYDRATION**

3.1 Introduction

Due to concrete's flexibility in casting and placing at construction sites, its relatively low manufacturing cost, the abundance of its raw materials, and the long-term durability of the structure, it has become the second most consumed substance on the earth, just after water [82]. However, concrete relies upon the hydration reaction of Portland cement (PC) to gain mechanical strength. The production of PC is not only energy intensive, but it also requires the decarbonation of limestone, which emits CO₂. To meet demand for concrete, the manufacture of PC is responsible for 5% of the total carbon dioxide produced by human activities, emitting 0.81 tons of carbon dioxide per ton of PC production [82-84]. The construction industry cannot simply stop using PC in concrete, so optimizing the amount of PC in concrete would be the most practical way.

In order to optimize the use of PC, we must first understand the main binding phase, calcium-silicate-hydrate (C-S-H), which is the principal reaction product and primary binding phase in PC [2]. Although a number of nano-structural and molecular models for C-S-H [2, 85] have been suggested, the actual structure is still only partially known. The hydration reaction between cement and water, which produces C-S-H, is complex, and it includes a number of different phases. The reaction between tricalcium silicate—Ca₃SiO₅ (C₃S)—and water is often used to develop techniques and theories about the hydration of cement, because it is similar but less complex [24, 86] and because it is the main and most important constituent of PC in its impure form: alite [87]. The relative simplicity of the reaction comes from the reduced variation in the hydration products formed during the C₃S reaction with water, with only calcium hydroxide (CH) and C-S-H, which are both inner (Ip) and outer (Op) product C-S-H [24]. Ip and Op refer to the C-S-H that forms in the original cement grain space and the original water fill space, respectively. The morphological distinction of the two products is clear, but there is no agreement on a mechanism to explain their formation. One theory proposes that the different products are generated by an alteration in the silicate anion structure [88] but the most popular model proposes that the two types of products are a simple result of the space available for their deposition [24]. The rate at which these two products form is also different, which has led to questions about the potential differences between the two products with regard to the effect on the structural performance of the concrete.

Silicate anions, the basic building blocks for C-S-H, are tetrahedral SiO_4^{4-} units, and they are balanced by the presence of calcium cations in C-S-H [57]. In the process of hydration, defective sheets of silicate layers are formed through silicate polymerization. As described in Chapter 2, the chemical shift of Ca and Si binding energy, which occurs due to the silicate polymerization, has been studied using x-ray photoelectron spectroscopy (XPS) [58, 59] and x-ray absorption spectroscopy (XAS) [56], and it was found that a decrease in the Ca to Si molar ratio (Ca/Si ratio) corresponds to an increase in silicate polymerization of the silicate tetrahedral, also resulting in an increase of the chain length and SiO_2 content in C-S-H [58]. Energy dispersive x-ray spectroscopy (EDS) in PC paste reveals that the Ca/Si ratio of C-S-H varies from 1.2 to 2.1 with a mean value of 1.75 [24], and the ratio has been used as a representative and indirect method for estimating the degree of hydration by silicate polymerization. It has been observed that the Op of C_3S , compared to the Ip, has a lower Ca/Si ratio, which implies a higher degree of hydration by silicate polymerization [89]. This is more prominent in the case of substituting supplementary cementitious materials (SCMs) for C_3S due to the additional silicate phases from SCMs [90]. The adhesive properties of Op play a crucial role in the bonding of C_3S with other phases; thus, the structural performance of the system containing C_3S is mainly affected by the properties of Op. If the Op products of C_3S could be analyzed separately, it would then be possible to evaluate the effects of the addition of SCMs or other chemical admixtures on the bonding structures of C_3S hydration products. Electron microscopy [91-93], nuclear magnetic resonance (NMR) [92], and XPS [58] have provided valuable information on the systems of pure C_3S and C_3S with SCMs on the micro- or nano-scale. To date, however, there is no single technique that has a high enough resolution to separate the morphologies of all phases, in order for dimensions to be measurable, and that can measure the chemical composition as a point analysis or phase mapping without risking potential artifacts in the laborious sample preparation process, such as drying and ion-thinning, which can result in misleading results [89].

Scanning transmission x-ray microscopy (STXM) at the Advanced Light Source (ALS) is a type of soft x-ray spectro-microscopy that can be used simultaneously for imaging and for near edge x-ray fine structure (NEXAFS) analysis. It has been used successfully for many years in numerous applications and has recently been applied in cement research [22, 23]. It has been shown to be an effective tool for quantitating the sample composition at a relatively low beam damage with a spatial resolution of about 25

nanometers [94]. Although both Ca and Si are main elements of the PC-based systems, the NEXAFS of Ca compounds and Si minerals have not been studied extensively [50, 56], and, in particular, there is not an abundance of information available on C-S-H and hydration products of the cement phases. Newly constructed soft x-ray diffraction imaging beamline (BL) using ptychographic reconstruction techniques at the ALS [95, 96] was recently shown to be an effective method, providing a path to high resolution without the limitations imposed by an x-ray optical system, and it could possibly be complementary to NEXAFS and images obtained using STXM.

This chapter examines the potential of soft x-ray spectro-microscopy and diffraction imaging by studying synthetic C-S-Hs and the C-S-H formed in the C_3S system. Three types of C-S-H with different Ca/Si ratios were synthesized to evaluate the quantitative effects of silicate polymerization on the local structure of C-S-H by Ca $L_{III,II}$ edge and Si K edge NEXAFS analysis. In addition, to understand the effect of silicate polymerization in the Op of C_3S on NEXAFS during hydration in the early age, an *in situ* STXM study using a C_3S solution in a wet cell was also analyzed. A soft x-ray diffraction image of the hydrated C_3S particle is shown in the present study, and the obtained images were compared with TEM results. This is the first attempt to study on the cement phase hydration in terms of local structure as well as morphology using soft x-ray spectro-microscopy and diffraction imaging. This new approach could potentially trigger applications of these methods in further studies, such as explorations of the effects of SCMs and chemical admixtures on PC hydration.

3.2 Experimental procedure

3.2.1 Materials and synthesis of C-S-H with different Ca/Si ratio

The triclinic C_3S passing through sieve #325 (45 μm) was purchased from the CTL Group (Skokie, IL). For the reference measurement, purified $Ca(OH)_2$ (>95%) was used. Nano-crystalline C-S-H phases with Ca/Si ratios of 0.66, 0.95, and 1.44 were synthesized in accordance with previous research [22, 57, 97]: the precipitated $CaCO_3$ was calcinated to obtain CaO by heating it at 1000°C for 24 hours. Stoichiometric amounts of CaO and amorphous colloidal silica purchased from Cabosil were mixed with deionized water at water to solid ratio of 40. The samples were filtered after one week and mixed continuously in a falcon tube at 23°C for seven days. Following this procedure, the samples were washed

twice with pure alcohol and alcohol mixed with deionized water, dried in vacuum conditions for five days, and finally stored under an N₂ environment. All procedures of the synthesis were conducted in a globe chamber under an N₂ environment to prevent carbonation of the C-S-H phases via reaction with CO₂ in the atmosphere. Synthesized C-S-H samples were noted as Syn-CSH0.66, Syn-CSH0.95, and Syn-CSH1.44 in accordance with Ca/Si of 0.66, 0.95 and 1.44, respectively.

3.2.2 Procedure for sample preparation

Finely ground anhydrous triclinic C₃S powder was mixed with deionized water, with water to solid ratio of 10, to avoid an agglomeration of the particles due to the limitations in thickness and size for STXM and diffraction imaging. A C₃S solution produced for STXM and diffraction imaging was kept in the falcon tube with N₂ gas at 23°C and sealed in a vacuum bag. After 17 days curing, a drop of 0.1 µl from the C₃S solution was taken and placed on the center of the Si₃N₄ membrane window (window size: 1 mm x 1 mm, thickness: 50 nm) on a Si wafer frame (size: 5 mm x 5 mm, thickness: 200 µm). For the wet cell, a drop of 0.1 µm from the C₃S solution was taken and placed in the center of the Si₃N₄ membrane window, and another membrane was placed on top of it. Epoxy glue was used to seal the two membrane windows in order to minimize evaporation and leaking. The sample was hydrated at 23°C, and it was used throughout the experiment. Considering the possible beam damage from the continuous x-ray irradiation and the carbonation of the sample, different particles in the same solution were used for each measurement. A schematic of the wet cell is shown in Figure 3.1.

Before loading it in the STXM and diffraction imaging chamber, the sample was checked using an optical microscope to verify if cracks were present on the membrane window. Since the Si₃N₄ membrane window was fragile, helium gas was injected to prevent cracking while we were pumping out the residual gas in the STXM chamber. Beam damage from x-ray radiation on the sample was checked by confirming the presence of any changes in the image and the NEXAFS spectra in specific areas before and after each measurement.

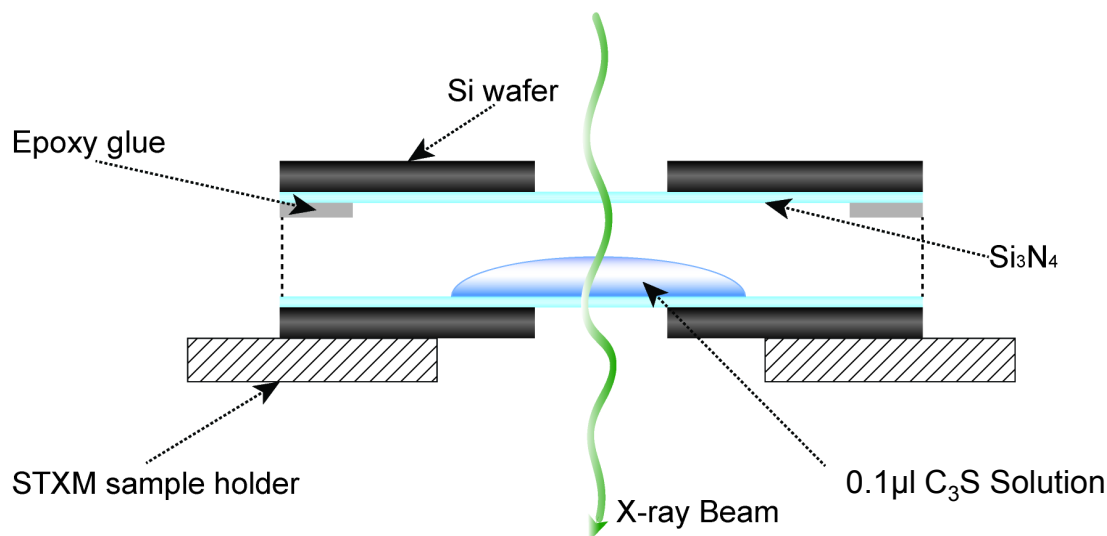


Figure 3.1 Schematic of C₃S wet cell for in –situ STXM

A powdered C₃S sample, cured for 28 days at 23°C and with a water to solid ratio of 0.4, was prepared for transmission electron microscopy (TEM). The fine powder was suspended in ethanol, 2 µl of which was deposited on a holey carbon film and dried for five minutes before examination on the TEM.

3.2.3 Scanning transmission x-ray microscopy (STXM)

STXM results were collected at the ALS at Lawrence Berkeley National Laboratory (LBNL) branch line 5.3.2.1 and 5.3.2.2 with the synchrotron storage ring operating at 1.9 GeV and 200–400 mA stored current. Counting times were of the order of a few milliseconds or less per pixel to avoid beam damage. Since both STXMs have different energy ranges (e.g., STXM 5.3.2.1: 350–2500 eV, 5.3.2.2: 250–800 eV), the images and NEXAFS spectra around the Ca L_{II,III} edge (340–360 eV), O K edge (520–560 eV) and Si K edge (1825–1890 eV) were measured by beamlines 5.3.2.2 and 5.3.2.1, respectively.

STXM is very versatile, and it can be utilized in different modes to obtain the spectra and images of the sample. The present study used a single image at a specified energy level and an image contrast map from the differential absorption of x-rays of two single-images with a spatial resolution of 25 nm. In addition, image stacks, where a series of images is collected at each energy, were collected. The results were combined to create

RGB overlay maps using singular value decomposition (SVD) based on reference spectra [62]. The main strength of SVD is the use of detailed spectral information to convert image stacks into chemical component maps. Since different chemical components have different NEXAFS spectra, the reference spectra can be obtained from known materials, and with the SVD based on these reference spectra, it can easily convert the image stacks into RGB overlay maps [63]. RGB overlay maps can be used effectively to visualize and differentiate phases with different chemical compositions in a sample [64].

The primary signal measured in STXM is the transmitted x-ray photon intensity as a function of energy or position. In the data analysis procedure, this transmitted signal collected in STXM is converted into an optical density (OD), which is sensitive to the sample thickness, the density of the material, and the composition, as shown in Eq-3.1.

$$OD = -\ln(I/I_0) = \sigma \cdot t = \mu \cdot \rho \cdot t \quad (\text{Eq-3.1})$$

where σ is the linear absorption coefficient, t is the sample thickness, μ is the mass absorption coefficient, and ρ is the density of the sample. The energy calibration of Ca, O, and Si were performed using CaCO_3 , CO_2 , and quartz as references for Ca $L_{\text{III, II}}$ and Si K edges in accordance with a previous study [22]. The normalization and background subtraction of the spectra were performed by dividing each spectrum from the sample using one of the sample-free locations. Axis2000 software [62] was utilized to align the *image stacks* and extract NEXAFS spectra from them. More details on the concepts of NEXAFS analysis and STXM are described in Chapter 2.

3.2.4 Soft x-ray diffraction imaging and transmission electron microscopy

The diffraction imaging was conducted using an apparatus at beamline 9.0.1 of the ALS, where the central cone of an undulator x-ray beam was focused by an off-axis zone-plate. An x-ray beam with 750 eV was used for diffraction imaging. The use of x-ray diffraction microscopy to measure the coherent diffraction pattern of a sample is a recently developed method, and it provides a path to high resolution without the limitations imposed by an x-ray optical system [81].

TEM imaging was performed on a Titan G^2 80–300 kV (FEI Company, Hillsboro,

OR, USA) at King Abdullah University of Science and Technology (KAUST, Saudi Arabia) operating at 300 kV and equipped with a 4k x 4k CCD camera (Gatan, Pleasanton, CA, USA) and an EDX detector, with ISIS software for imaging / x-ray analysis (Oxford Instruments, Oxford, UK). Due to the poor crystalline nature of C-S-H and the potential formation of highly crystalline Ca(OH)_2 , the selected area diffraction (SAD) aperture was used to determine the crystallinity of an area before chemical analysis. The widths of the C-S-H and pore sizes were measured from the soft x-ray diffraction and TEM images using ImageJ software developed by the National Institutes of Health.

3.3 Results and discussion

3.3.1 Ca $L_{\text{III,II}}$ edge NEXAFS analysis of synthesized C-S-H

Figure 3.2 presents the Ca $L_{\text{III,II}}$ edge NEXAFS spectra of (a) Ca(OH)_2 and anhydrous C_3S , and (b) Syn-CSH with Ca/Si ratios of 0.66, 0.95, and 1.44. Each spectrum was normalized to the incident beam intensity I_0 and had the linear pre-edge background removed.

The Ca $L_{\text{III,II}}$ edge NEXAFS of all three Syn-CSH consisted of two main spin-orbit-related peaks, $L_{\text{III}} 2P_{3/2}$ (a_3) and $L_{\text{II}} 2P_{1/2}$ (b_2), along with a number of smaller peaks, a_1 , a_2 , and b_1 , that preceded the main peaks [98]. The main peaks corresponded to excitation from $2p^6 3d^0$ to $2p^5 3d^1$ or $2p^5 4s^1$ [99]. The origin of these multi-peak patterns is due to the crystal field, which arises due to the symmetry of the atoms surrounding the Ca cation in the first coordination sphere [50]. The peak positions and energy separation values, which are correlated to the symmetry of the Ca and splitting energy, for the Ca $L_{\text{III, II}}$ edge of Ca(OH)_2 , the anhydrous C_3S , the Syn-CSH, and the selected areas in the 17 days hydrated C_3S are given in Table 3.1.

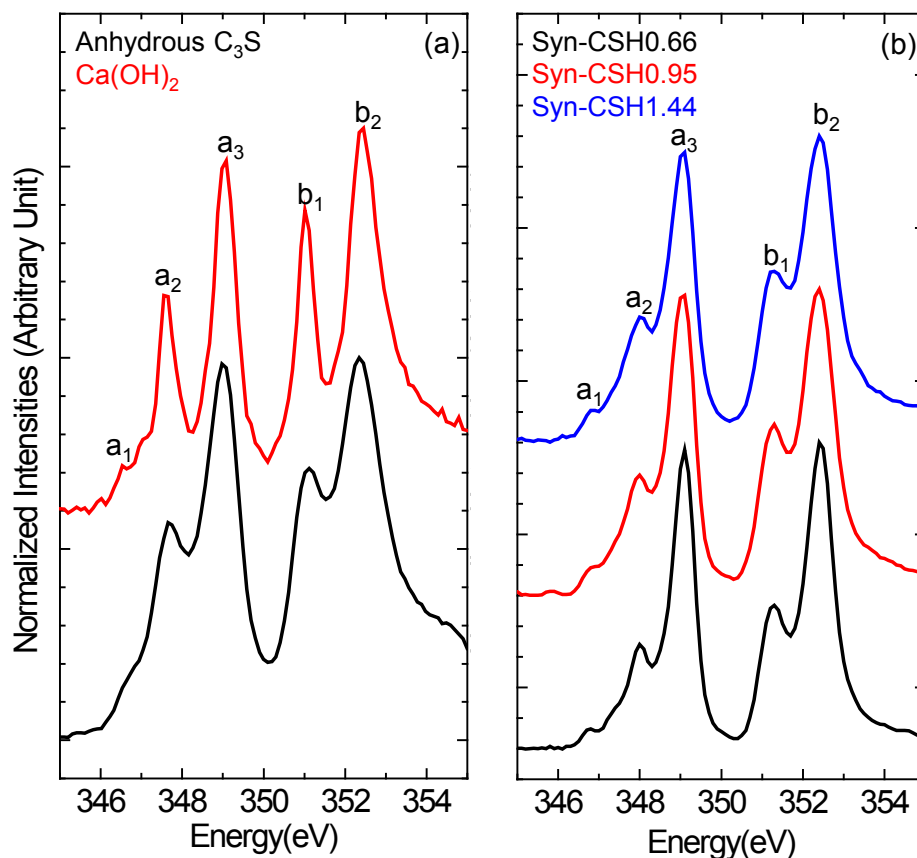


Figure 3.2 Ca L_{III,II} edge NEXAFS spectra of (a) reference of Ca(OH)₂ and anhydrous C₃S, and (b) Syn-CSH with Ca/Si ratios of 0.66, 0.95, and 1.44

The absorption feature and the peak positions of the anhydrous C₃S, with a mean coordination number of 6.21 [32], in the Ca L_{III, II} edge NEXAFS spectra were similar to those in the CaCO₃, with a coordination number of 6 [50]. The two well-resolved spectral features corresponding to the main L_{III} (349~349.1 eV) and L_{II} (352.3~352.4 eV) of all the samples were consistent with the results of other Ca phosphate compounds [50, 100, 101]. The energy separation of the anhydrous C₃S was the same as CaCO₃ [50] with 1.3 and 1.2 eV for a₃–a₂ and b₂–b₁, respectively.

On the other hand, Ca(OH)₂ showed larger splitting energy values and peak intensity ratios between a₂–a₃ and b₁–b₂ compared to those of Syn-CSH, anhydrous C₃S, and hydrated C₃S.

Table 3.1 Peak positions and splitting energy values of Ca L_{III, II} edge of Syn-CSH

Samples	Peak positions(eV)					Splitting of L _{III} and L _{II} (eV)	
	a ₁	a ₂	a ₃	b ₁	b ₂	$\Delta\text{Ca-L}_{\text{III}}(\text{a}_3\text{-a}_2)$	$\Delta\text{Ca-L}_{\text{II}}(\text{b}_2\text{-b}_1)$
Ca(OH) ₂	346.6	347.6	349.1	351	352.4	1.5	1.4
Anhydrous C ₃ S	346.7	347.7	349	351.1	352.3	1.3	1.2
Syn-CSH0.66	346.8	348	349.1	351.3	352.4	1.1	1.1
Syn-CSH0.95	347	348	349.1	351.3	352.4	1.1	1.1
Syn-CSH1.44	346.9	348	349.1	351.3	352.4	1.1	1.1

The larger splitting energy with the more pronounced intensity in the L_{III} and L_{II} splitting peaks (a₂ and b₁) is an indication of the well-developed crystalline Ca phase structure [102]. Moreover, the larger splitting energy of Ca(OH)₂ could possibly be due to the differences in the crystal field produced by ligands with different electronegativity since the splitting energy and the ratio of peak intensities are related non-linearly to the magnitude of the crystal field parameter (10 Dq) in octahedral symmetry (O_h) [50]. The larger splitting energy is consistent with the shorter Ca-O bonding length of Ca(OH)₂ compared to those of synthetic C-S-H and tobermorite [103]. The NEXAFS spectra for the three types of Syn-CSH showed no variation in terms of peak positions and splitting energies for Ca L_{III, II}, except for peak a₁, since it was not easy to find the exact peak positions due to the relatively small peak intensity.

In a previous research, XPS analysis [57] revealed that the calcium binding energies of various C-S-Hs are relatively independent of their chemical composition or structure, but at low Ca/Si ratios, the binding energies of Ca are marginally higher, as a result of both the slightly shorter Ca-O bond length between the silicate anions and the calcium ions and the decreased calcium coordination in C-S-H compounds. XAS of C-S-H with Ca/Si ratio of 0.6 and 1.5 proved that the silicate polymerization does not appear to affect to Ca K edge absorption feature of the C-S-Hs [103]. Recently, XPS analysis in early C₃S hydration also consistently confirmed that Ca binding energy does not change during the hydration process [58]. On the other hand, total x-ray scattering study found that Ca-O coordination number gradually decreases from 7 to 6 with increasing Ca/Si ratio of

synthetic C-S-H [104].

Here, no differences were observed in terms of the binding energies related to the peak positions in the Ca $L_{III,II}$ edge in the NEXAFS of Syn-CSH, but a slight difference was found in the peak intensity ratio relevant to the crystal field [50], and this ratio decreased between a_2 - a_3 and b_1 - b_2 in accordance with the Ca/Si ratios. The small decrease of the peak ratio in Syn-CSH0.66 is assumed to be due to the increase of Ca-O coordination. Although no differences with regard to the binding energy in the Ca of Syn-CSH were confirmed in the present study, the differences in the local structure of Ca between the anhydrous C_3S and the Syn-CSH with different Ca/Si were clearly observed. Therefore, the results observed in the present study suggest that the coordination of the Ca in Syn-CSH with different Ca/Si ratios is not different significantly, but the Syn-C-S-H have the smaller magnitude of the crystal field of Ca compared to anhydrous C_3S and $Ca(OH)_2$ due to the characteristic of C-S-H with comparatively higher disorder and lower crystallinity.

3.3.2 Si K edge NEXAFS analysis of synthesized C-S-H

Figure 3.3 shows the Si K edge NEXAFS spectra of three types of Syn-CSH. Peak a_1 , the main peak, is attributed to the Si K edge induced by the electronic transition from Si 1s to the anti-bonding t_2 (3p-like state) orbital. Peak a_2 is assigned to the multiple scattering effects beyond the second coordination sphere [56]. The peak positions and energy separations between the two peak positions are shown in Table 3.2. In the spectra, the Si K edge binding energies of the Syn-CSH samples increased with the decrease in the Ca/Si ratio, which corresponds to the fact that the Si K edge shifts to a higher energy and the Si 1s binding energy increases in increments according to the degree of polymerization in the silicates [58, 59]. A chemical shift with respect to the Si K edge binding energy, corresponding to the increased polymerization of the silicate tetrahedral, can be induced by an effective charge on the Si atom that increases progressively with a higher degree of Q^n . Upon hydration of the PC clinker phases, it can be observed, using XPS analysis [105], that an increment in the Si 2p binding energy of silica gel corresponds to the increased polymerization of the silicate tetrahedral. In addition, the influence of silicate polymerization in the calcium silicate wollastonite ($CaSiO_3$), upon both the Si 2p binding energy and the Si_{KLL} kinetic energy, has been shown, and it was found that these energy changes are related to the effective electrostatic force of the Si-O bonds in silicates [59].

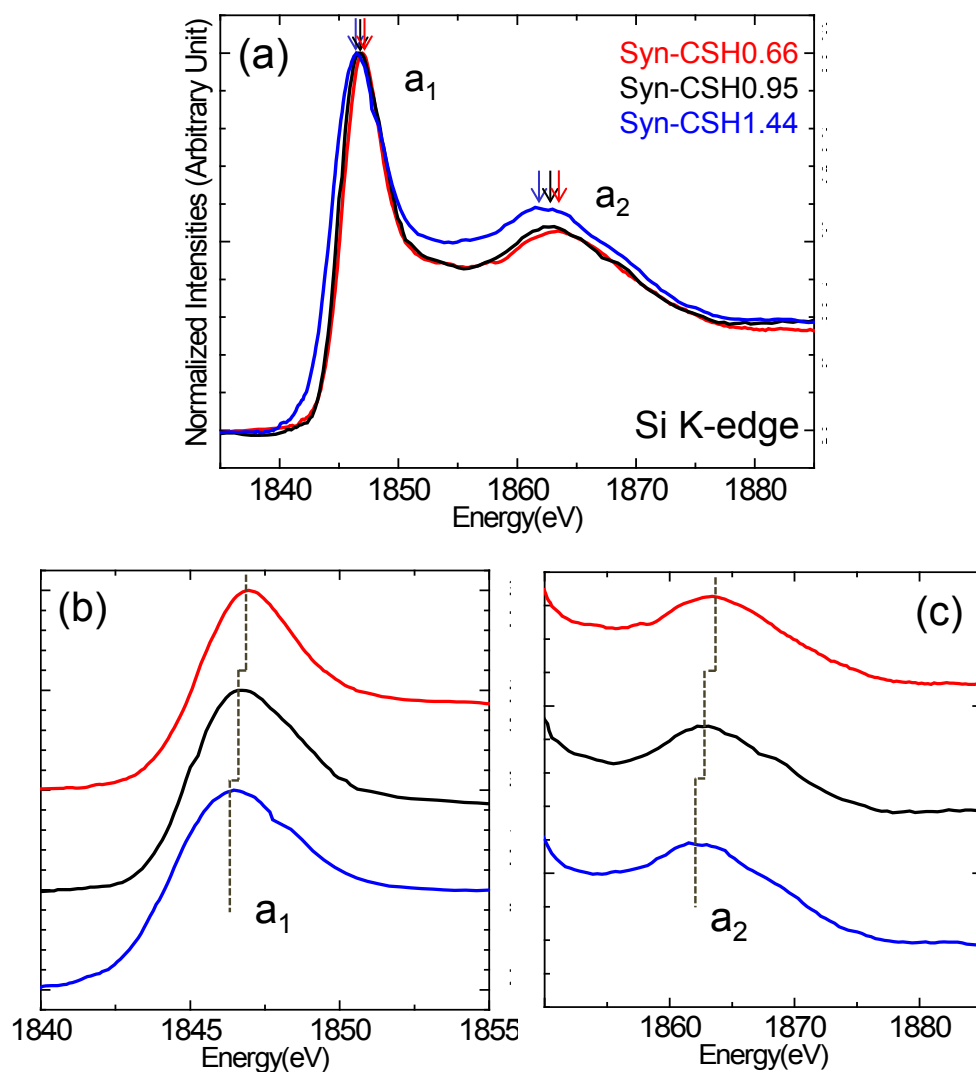


Figure 3.3 (a) Si K edge NEXAFS spectra of Syn-CSH with Ca/Si ratios of 0.66, 0.95 and 1.44. The spectra near peak position of a_1 and a_2 with extended scale are presented in (b) and (c)

Table 3.2 Peak positions and energy separation between peak positions of Si-K edge NEXAFS spectra of Syn-CSH

Samples	Peak a_1 (eV)	Peak a_2 (eV)	$\Delta a_2 - a_1$ (eV)
Syn-CSH0.66	1846.9	1863.4	16.5
Syn-CSH0.95	1846.7	1863.1	16.4
Syn-CSH1.44	1846.4	1861.5	15.1

With regard to cement phase hydration, an evaporated C_3S thin film was used to examine the effect of silicate polymerization on Si binding energy using XPS at different stages of hydration, and evidence was observed of a shift of the Si 2s and 2p peaks to higher energies, which indicates that silicate polymerization is expected upon formation of C-S-H [58]. The XPS analysis proved that the Ca/Si of evaporated C_3S thin film evolves from 1.55, that of a jennite-like material during early age hydration, to a tobermorite-like product with a ratio of 0.85 after 3 h of hydration by silicate polymerization.

When studying the Si K edge NEXAFS of several types of silicate minerals, the main focus was on the effect of silicate polymerization on the energy shift of the Si K edge main peak (peak a_1) rather than on the additional peaks (peak a_2 region). The reason for this omission is the shape of these peaks is relatively more complicated due to the crystal structure complexity of silicate minerals and the multiple factors affecting the x-ray absorption processes [56]. The Si K edge NEXAFS spectra of Syn-CSH and both the hydrated and anhydrous C_3S in the present study showed shapes that were relatively simple when compared to other silicate minerals [56]. Thus, the focus has been on not only the peak position of the Si K edge (a_1) but also the additional peak induced by multiple scatterings, a_2 , and the calculated energy separations between the two peaks, which could potentially determine an estimate for the degree of silicate polymerization.

The chemical shift values of peak a_1 and a_2 increased from 0.5 eV to 1.9 eV with the decrease in the Ca/Si ratios (1.44 to 0.66). There is a clearly observed peak position shift to a higher energy level in both the Si K edge (a_1) and the peak induced by multiple scattering (a_2), and the energy separation between the two peaks increases with the decrease of the Ca/Si ratio in Syn-CSH. Furthermore, Syn-CSH with higher Ca/Si ratio showed relatively lower peak intensity ratios between a_1 - a_2 and broader shapes due to a higher degree of disorder [106]. The results directly imply that silicate polymerization increases the multiple scattering contribution from distant coordination shell atoms more than the binding energy of 1s core electrons in Si atoms. In addition, the Syn-CSH with lower Ca/Si ratio, which results in a higher degree of silicate polymerization, have more ordered structures than ones with higher Ca/Si ratio.

3.3.3. Morphology observation of C_3S hydration using *in situ* STXM

Figure 3.4 shows the STXM image contrast map of the Ca of hydrating C_3S in the wet cell from 1 h 22 m to 7 h 46 m, which was obtained from differential absorption of x-rays, depending on the chemical composition of the sample. The images taken above the Ca $L_{III, II}$ edge were subtracted from the same images taken below the Ca absorption edge. The locations, where high concentrations of Ca in the hydration product of the C_3S particles were present, were observed as bright white areas. The image contrast map only indicates and differentiates highly concentrated locations and less concentrated locations or the thickness of particle. The difference in the intensities shown in Figure 3.4 does not provide information on the chemical speciation information of the samples [22].

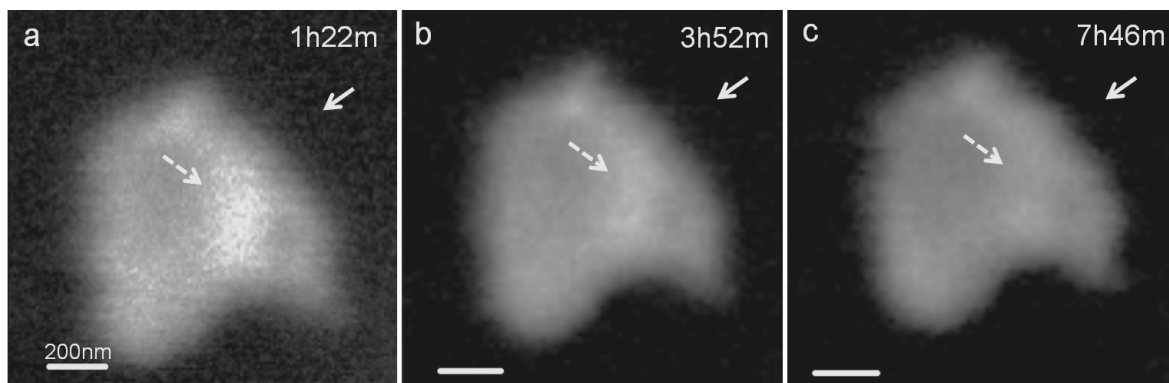


Figure 3.4 Morphology observation of a C_3S particle in the wet cell using *in situ* STXM from (a) 1 h 22 m to (c) 7 h 46 m. The Ca image contrast map was obtained by subtracting images from above to below the Ca $L_{III, II}$ edges.

Since it took 1 h to prepare the wet cell and to set the vacuum conditions in the STXM chamber for proper measurement, the first measurements were conducted at 1 h 22 m after mixing the deionized water and C_3S powder. In Figure 3.4(a), nano-particles containing Ca in the solution were observed around the C_3S particle, which are indicated by the straight-line arrows. The agglomeration of the nano-particles with the C_3S through the electrostatic force of the tetrahedral silicate anion was observed over time. The OD of the Ca in the center of the C_3S decreases, as indicated by the dotted arrows, due to the dissolution of the Ca ion and the precipitation of C-S-H on the C_3S particles in the process of C_3S hydration. Consequently, in the hydration process, the Ca ions were distributed uniformly by the dissolution of the Ca and the formation of C-S-H.

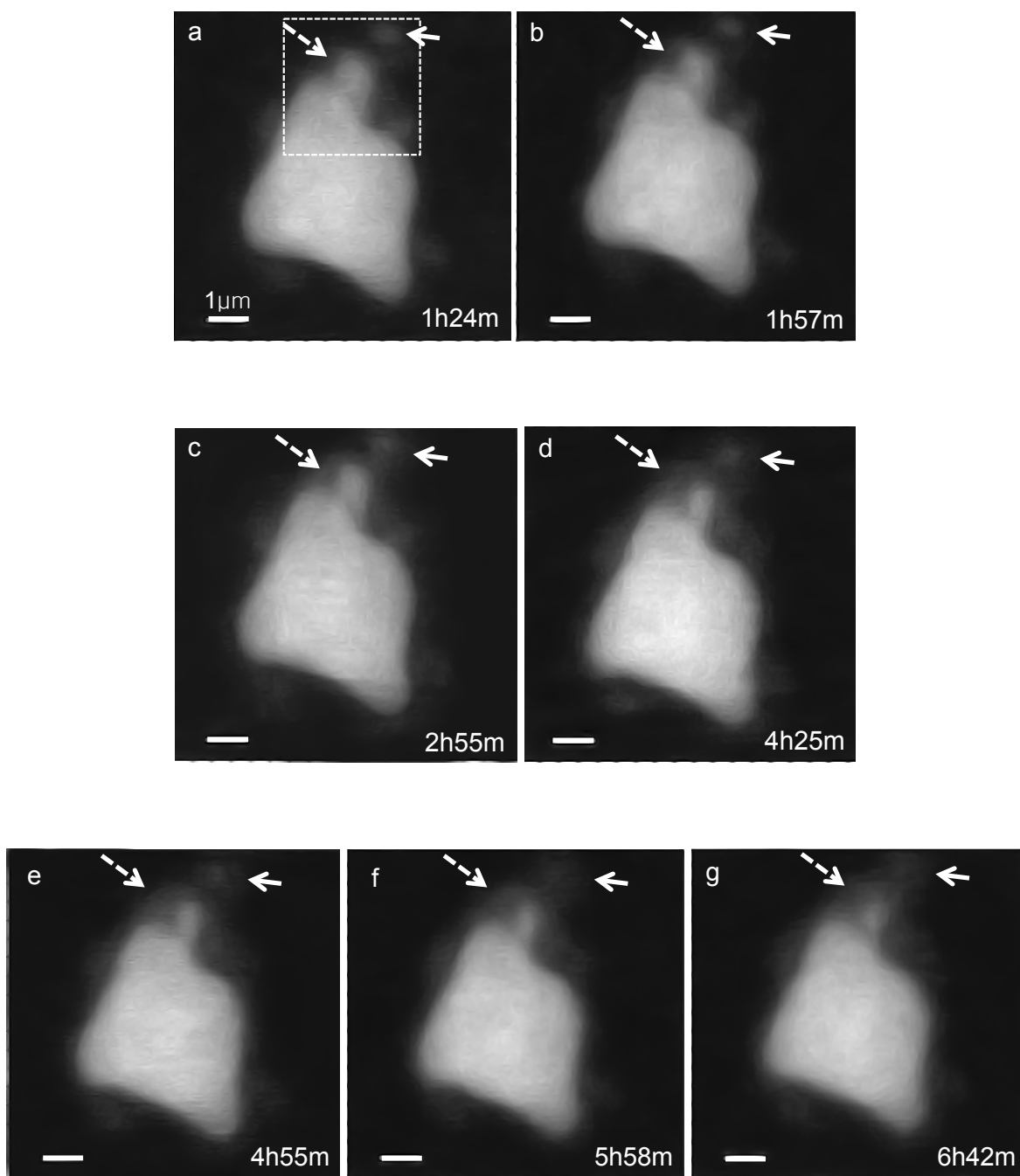


Figure 3.5 Morphology observation of a C_3S particle in a wet cell using *in situ* STXM from 1 h 24 m to 6 h 42 m. The Si elemental mapping was obtained by subtracting an image taken below Si K edge from one taken above the edge. The dotted arrows indicate a dissolving part of the C_3S particle and the lined arrows point to a part of the hydration product in C_3S .

The STXM image contrast maps of the Si of C_3S in the wet cell, from 1 h 24 m to 6 h 42 m after mixing with water, are shown in Figure 3.5. The Si elemental mapping was obtained by subtracting an image taken below Si K edge from one taken above the edge, as was the case with Ca. It is well known that C_3S reacts with water through a dissolution-precipitation process. The dotted and lined arrows indicate a dissolving part in the C_3S particle or a part of the hydration product in C_3S , respectively. From 1 h 24 m (Figure 3.5-(a)) to 6 h 42 m (Figure 3.5-(g)), it was observed that a part of the C_3S particle was dissolved by the hydration process. Furthermore, the interface of the C_3S particle is going to be hazy as a result of the formation of C-S-H. It was also observed that the area of C-S-H increased in the interface of the C_3S particle over time. Region of interest (ROI), as indicated as a square in Figure 3.5-(a), was selected in order to confirm the morphologic differences during the hydration process. The magnified Si elemental maps taken at 1h 24m and 6h 42m are shown in Figure 3.6. The dissolution of core of C_3S and precipitation of C-S-H around C_3S particle are observed more clearly. The morphologic changes during C_3S hydration validated the utility of wet cell for *in situ* STXM investigation.

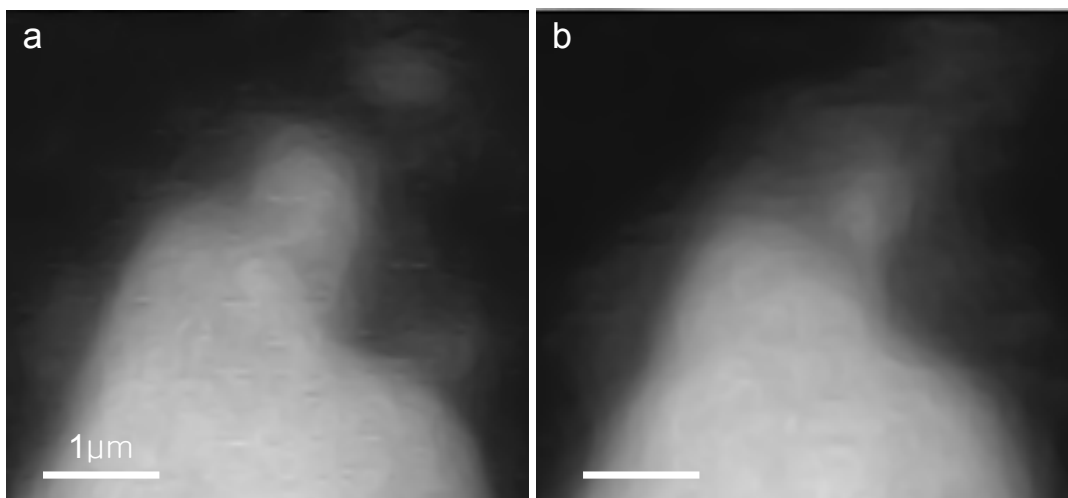


Figure 3.6 Comparison of morphology change observation of a C_3S particle in a wet cell using *in situ* STXM between (a) 1 h 24 m and (b) 6 h 42 m. ROI was presented in Figure 3.5-(a).

3.3.4 Ca $L_{III,II}$ edge NEXAFS analysis using *in situ* and *ex situ* STXM

The Ca $L_{III,II}$ edge NEXAFS spectra obtained from a line scan of the C_3S particle in the wet cell from 1 h 32 m to 7 h 42 m are shown in Figure 3.7.

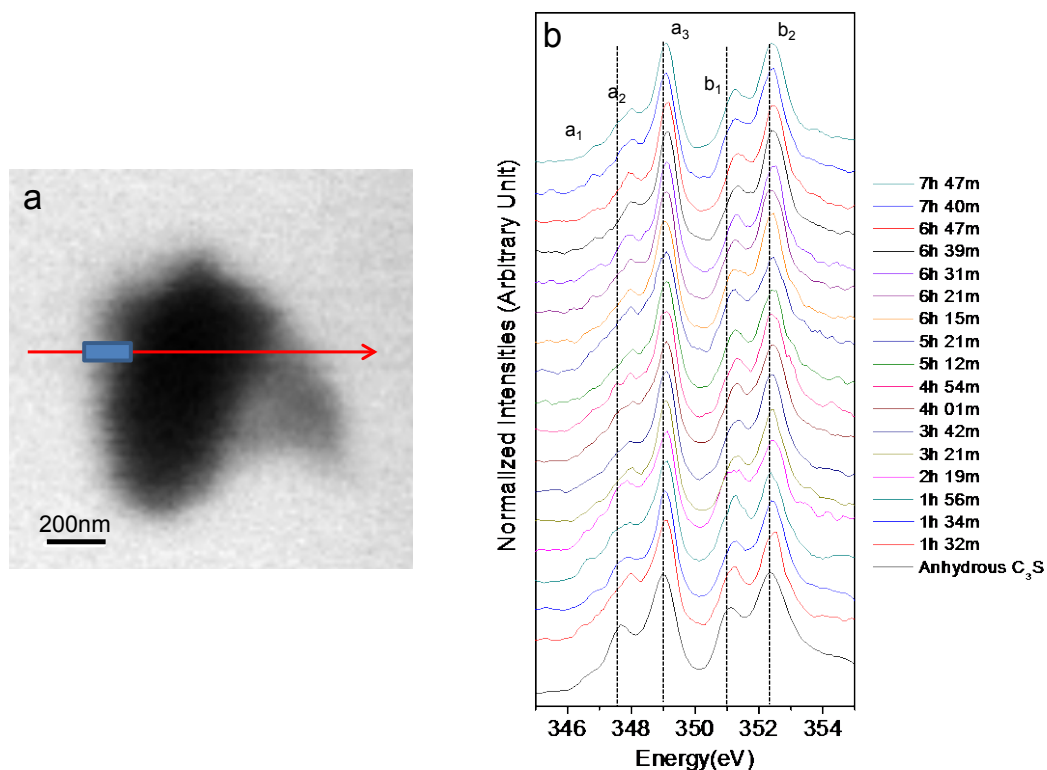


Figure 3.7 (a) Image of C_3S particle taken at 347.2 eV, and (b) NEXAFS spectra of the line scan of C_3S in the wet cell using *in situ* STXM. The image was taken at 347.2 eV. The line scan data was taken from 1 h 32 m to 7 h 47 m after mixing with water.

NEXAFS spectra using image stack, compared to line scan, show better absorption feature with low background noise. However, since the core and right area of the C_3S particle was too thick to obtain the proper amounts of transmitted x-ray beam, resulting in saturation of the OD, the area marked as a blue rectangle was selected for the Ca $L_{III,II}$ NEXAFS analysis. The particle shown in Figure 3.4 was selected for the analysis. The peak positions and splitting values of L_{III} and L_{II} are shown in Table 3.3. After 1 h 32 m, peaks a_2 and b_1 had shifted by 0.3 eV and 0.2 eV to higher energy levels, as compared to the NEXAFS spectra of the anhydrous C_3S , and they showed similar peak positions to Syn-CSH, as shown in Figure 3.2. At 1 h 56 m, the peak positions of the Ca L edge of C_3S

are exactly the same as Syn-CSH, and the positions show no significant changes, fluctuating within ± 0.1 eV from 1 h 56 m to 7 h 47 m. After 17 h 11 m, a different C_3S particle in the same solution was analyzed, as shown in Figure 3.8. Since the image stack measurement takes longer than the line scan (2~3 h for each image stack), an image stack was not used for the sample in the early age to minimize the effect of chemical changes that could occur during measurement.

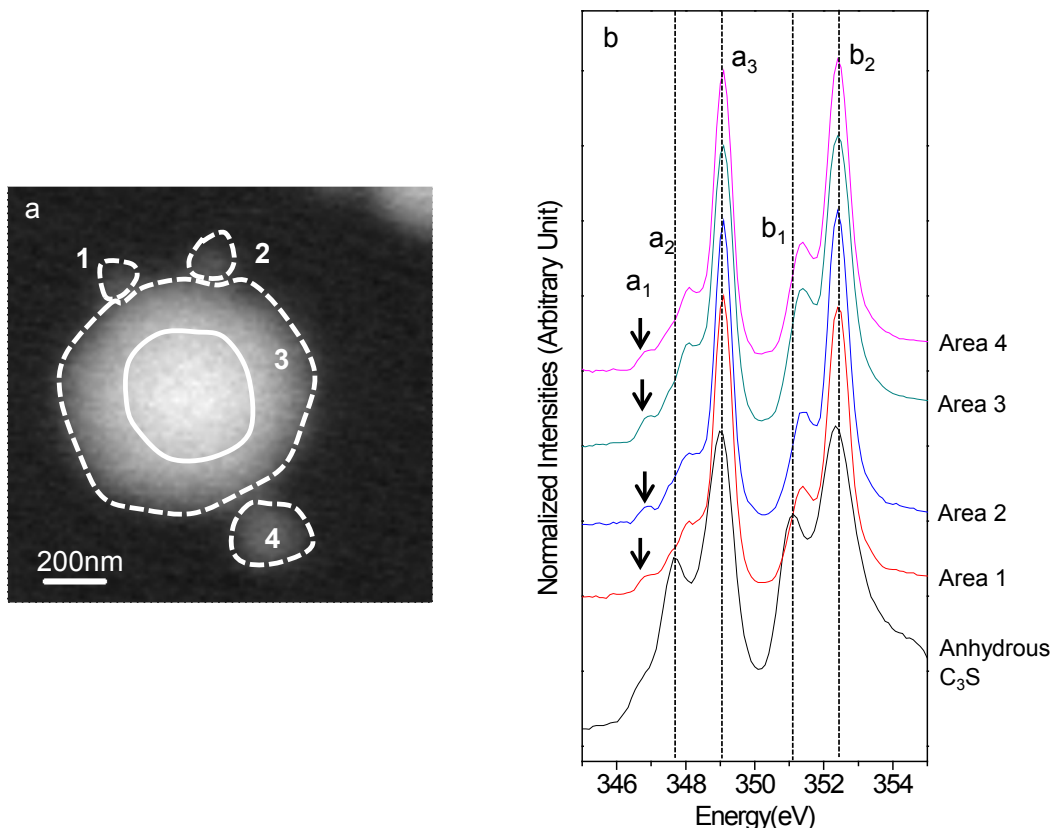


Figure 3.8 (a) STXM image contrast map of the C_3S sample in the wet cell at the Ca $L_{III,II}$ edge after 17 h 11 m, and **(b)** NEXAFS spectra of the selected areas in (a). The center of the C_3S particle, which is marked as a line circle, was excluded due to its thickness.

It is assumed that the hydration speed after 17 h was not as fast as in the early age, and an image stack (340 eV–360 eV) was conducted to obtain overall information on the whole particle, since the line scan data only provided us with localized information about the particle. The core of the particle, which is marked as the lined circle, was excluded from

Ca analysis due to its thickness. The distribution of Ca (OD) in C₃S after 17 h 11 m was very uniform compared to the image contrast after 1 h 22 m. The spectra of the analyzed area were identical to each other in terms of shape and peak positions. At 346.8 eV, peak a₁, which had a weak peak intensity in the early age, was clearly observed. The main peaks showed the same values as Syn-CSH, and peaks a₂ and b₁ showed similar values, with ± 0.1 eV variation, to Syn-CSH and the results from 1 h 32 m to 7 h 47 m.

Table 3.3 Peak positions and distance between peak positions of the Ca L_{III,II} edge NEXAFS spectra of the line-scan of C₃S in the wet cell from 1 h 32 m to 7 h 47 m. (LS: line scan)

	Peak positions(eV)					Splitting of L _{III} and L _{II} (eV)	
	a ₁	a ₂	a ₃	b ₁	b ₂	$\Delta L_{III}(a_3-a_2)$	$\Delta L_{II}(b_2-a_1)$
Anhydrous C ₃ S	346.7	347.7	349	351.1	352.3	1.3	1.2
LS1h32m	-	348	349.1	351.3	352.5	1.1	1.2
LS1h34m	-	347.9	349	351.3	352.4	1.1	1.1
LS1h56m	-	348	349.1	351.3	352.4	1.1	1.1
LS2h19m	-	348	349.1	351.4	352.4	1.1	1
LS3h21m	-	348	349.1	351.4	352.4	1	1
LS3h42m	-	348	349.1	351.4	352.4	1.1	1
LS4h01m	-	348.1	349.1	351.4	352.4	1	1
LS4h54m	-	348	349.1	351.4	352.4	1.1	1
LS5h12m	-	348.1	349.1	351.3	352.4	1	1.1
LS5h21m	-	348	349.1	351.3	352.5	1.1	1.2
LS6h15m	-	348	349.1	351.3	352.4	1	1.1
LS6h21m	-	348	349.1	351.3	352.4	1	1.1
LS6h31m	-	348	349.1	351.3	352.5	1.1	1.2
LS6h39m	-	348	349.2	351.4	352.4	1.2	1
LS6h47m	-	347.9	349.1	351.4	352.4	1.2	1
LS7h40m	-	348.1	349.1	351.3	352.5	1	1.2
LS7h47m	-	348.1	349.1	351.3	352.4	1	1.1

Figure 3.9 presents (a) a single image of the 17 days hydrated C_3S taken at 340 eV, (b) the image contrast map of Ca (349.1-340 eV), and (c) the Ca $L_{III,II}$ edge NEXAFS spectra of the selected areas in (b). The results are obtained using *ex situ* STXM since it is assumed that the hydration rate of C_3S at 17 days is very slow. The Ca image contrast map (Figure 3.9-(c)) of the 17 days hydrated C_3S shows very uniform Ca distribution, which implies that the C-S-H themselves contain uniform Ca. In the case of spectra from selected areas on the map, each spectrum showed an identical or 0.1 eV higher value with regards to peak a_3 and 0.2 to 0.3 eV smaller splitting energy values. The relative intensities of peak a_1 in the spectra are higher than the anhydrous C_3S , and it is easier to confirm the peak positions.

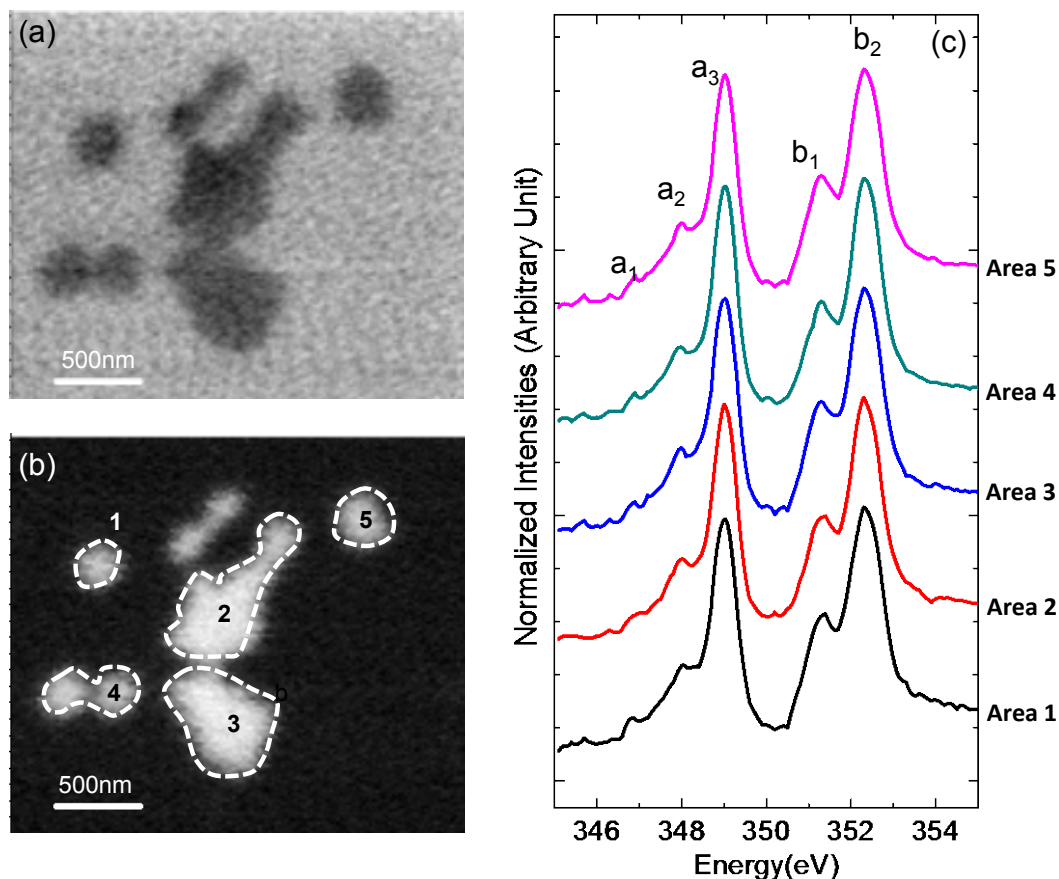


Figure 3.9 (a) Single image of 17 days cured C_3S taken at 340 eV, (b) Ca image contrast map of 17days cured C_3S , and (c) Ca $L_{III,II}$ edge NEXAFS spectra of the selected area in (b).

The absorption features of the 17 days hydrated C₃S are very similar to Syn-CSH, and the peak positions in the Ca L_{III, II} edge show similar or 0.1 eV lower values, resulting in 0.1~0.2 eV smaller splitting energy values in comparison with Syn-CSH. The small splitting energy values could be due to less crystallinity [102] in the C-S-H formed in C₃S hydration, since Syn-CSH is known to have a more ordered atomic structure than C-S-H formed in PC hydration [107]. The conclusion, based on the results of the Ca L_{III,II} edge image contrast map and the NEXAFS analysis, is that the surrounding environment of Ca in C₃S changes quickly after contact with water in the dissolution process, and it is shown to be uniform without significant changes, which is consistent with previous XPS research [58]. Furthermore, NEXAFS of the 17 days hydrated C₃S prove that the C-S-H of C₃S have less crystallinity than Syn-CSH. The peak positions and splitting value of the Ca L_{III,II} edge are given in Table 3.4.

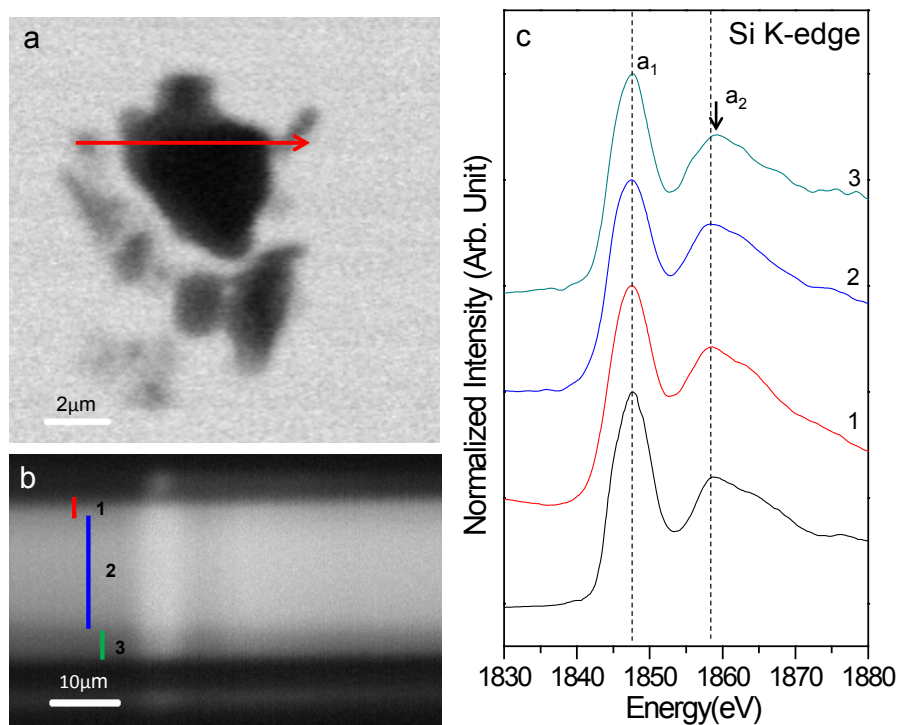
Table 3.4 Peak positions and the distance between peak positions of the Ca L_{III,II} edge NEXAFS spectra of the stack of C₃S in the wet cell after 17 h 11 m and 17 days.

Locations	Peak positions(eV)					Splitting of L _{III} and L _{II} (eV)	
	a ₁	a ₂	a ₃	b ₁	b ₂	ΔCa-L _{III} (a ₃ -a ₂)	ΔCa-L _{II} (b ₂ -b ₁)
17h11m							
Area 1,2,3,4	346.8	348.1	349.1	351.4	352.4	1	1
17days							
Area1	346.8	348	349.1	351.3	352.3	1.1	1
Area2	347	348	349	351.4	352.3	1	0.9
Area3	346.9	348	349.1	351.3	352.3	1.1	1
Area4	346.9	348	349.1	351.3	352.3	1.1	1
Area5	346.9	348	349.1	351.3	352.3	1.1	1

3.3.5 Si K edge NEXAFS analysis using *in situ* and *ex situ* STXM

Figure 3.10 shows the STXM images taken at 1840 eV, the line-scan image after 1 h 19 m, and the Si K edge NEXAFS spectra of the selected areas in the line scan of the C_3S particle in the wet cell. In the line-scan image after 1 h 19 m, the layers around the C_3S particle were observed on the right (indicated as 1 in Figure 3.10-(b), length 1.5 μm), Core (indicated as 2 in Figure 3.10-(b), length 4 μm), and left (indicated as 3 in Figure 3.10-(b), length 2 μm) of the particle.

The right and left layers around the C_3S are assumed to be Op. The same areas were selected for the line-scan analysis at 2 h 48 m and 4 h 22 m. Peak positions and the distance between peaks a_1 and a_2 are tabulated in Peak a_1 , after 1 h 19 m, showed a smaller value (0.2~0.3 eV) to that of the anhydrous C_3S . Peak a_2 , in area 3, which has a different contrast in the line-scan image after 1 h 19 m, showed a higher peak position value, which results in a larger distance (0.4 eV) between peak a_1 and a_2 . After 2 h 48 m and 4 h 22 m, both peaks a_1 and a_2 showed a tendency to increase, so that the distances of the two peaks showed values that were 0.5~0.6 eV larger.



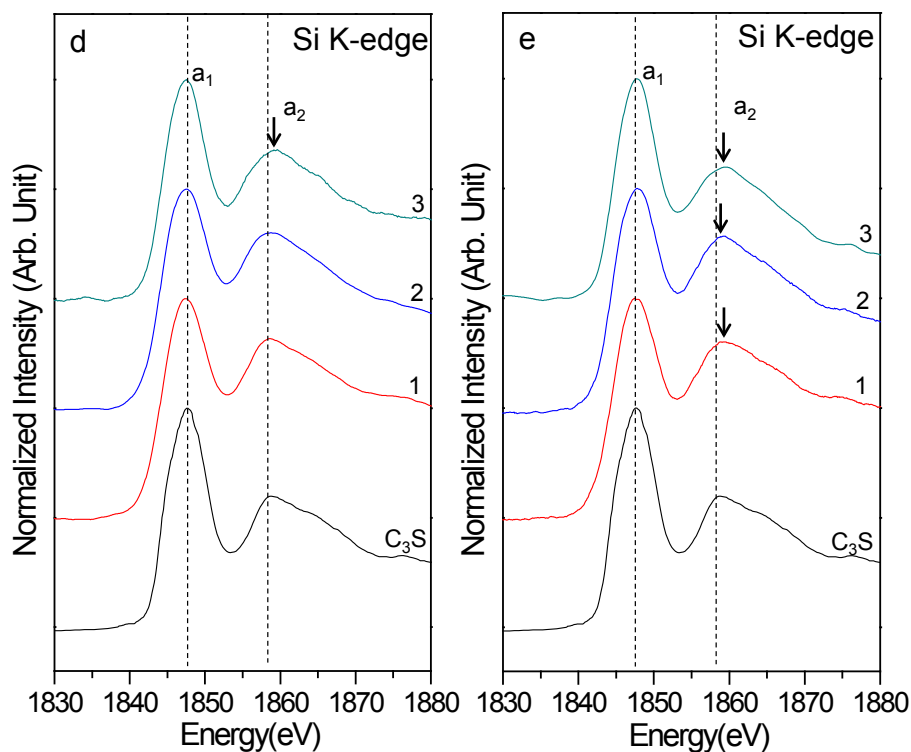


Figure 3.10 STXM images, line-scan images, and NEXAFS spectra of the selected areas in the line scan of the C_3S particle in the wet cell. (a) The STXM images of the C_3S sample in the wet cell taken at 1840 eV after 1 h 19 m; (b) the selected area in the line scan of the C_3S particle after 1 h 19 m (the same areas in the same particle were analyzed in the line scan results after 2 h 48 m and 4 h 22m); (c) the NEXAFS spectra of the selected area in (b), which were observed after 1 h 19m; (d) the NEXAFS spectra of the selected area in (b) after 2 h 48 m; and (e) the NEXAFS spectra of the selected area in (b) after 4 h 22 m.

Table 3.5 Peak positions and the distance between peak positions of the Si-K edge NEXAFS line-scan spectra of C₃S in the wet cell after 1 h 19 m, 2 h 48 m, and 4 h 22 m. (LS: line scan)

Sample	Scan Areas	Peak a ₁ (eV)	Peak a ₂ (eV)	$\Delta a_2 - a_1$ (eV)
Anhydrous C₃S	-	1847.7	1858.9	11.2
LS1h19m	1	1847.4	1858.6	11.2
	2	1847.4	1858.6	11.2
	3	1847.6	1859.2	11.6
LS2h48m	1	1847.4	1858.7	11.3
	2	1847.4	1858.6	11.2
	3	1847.6	1859.2	11.6
LS4h22m	1	1847.5	1859.3	11.8
	2	1847.4	1859.1	11.7
	3	1847.8	1859.6	11.8

As described in the previous section, peaks a₁ and a₂ are attributed to the Si K edge induced by the transition of Si 1s electrons to the anti-bonding t₂ and by the multiple scattering effects beyond the second coordination sphere [56]. Thus, it could be concluded that silicate polymerization affected the second coordination sphere of Si more than the core atoms. The tendency of a chemical shift was clearly confirmed in the hydration process, which will be shown in the following section.

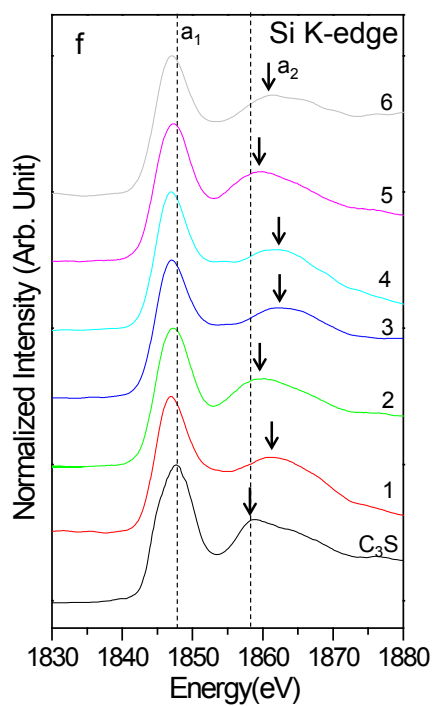
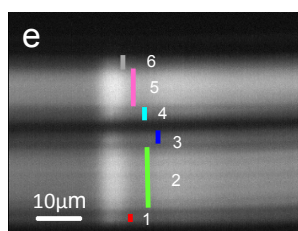
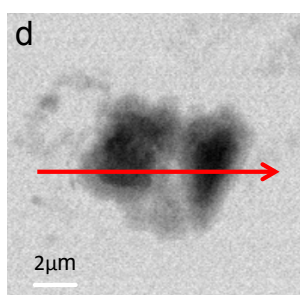
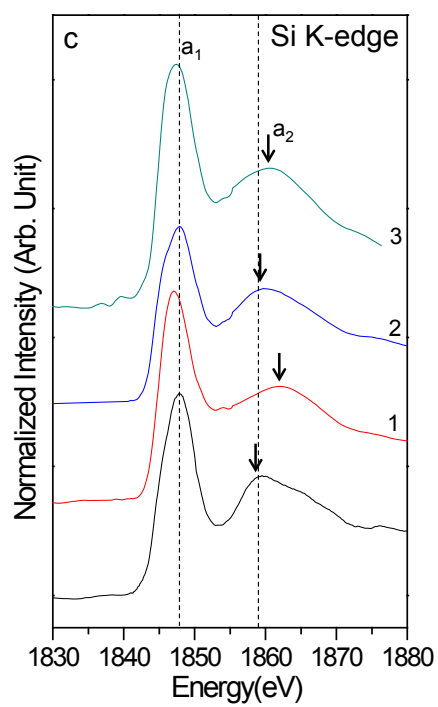
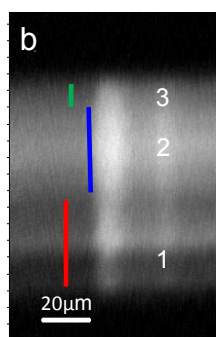
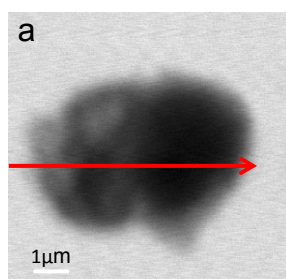
In Figure 3.11, the STXM images taken at 1840 eV, the line-scan images, and the Si K edge NEXAFS spectra of the selected areas in the line-scan image after 15 h 25 m, 17 h 13 m, 17 days, and 40 days are presented. Both the results at 17 and 40 days are obtained using *ex situ* STXM as same with Ca L edge analysis. Layers with different contrast in the images were observed in all particles. These layers were selected for line-scan analysis, and the obtained results are organized in Table 3.6.

The peak a₁ value in all spectra showed a +0.3~-0.6 eV variance compared to the anhydrous C₃S, and it does not show any obvious tendency. A possible explanation for this

is that the selected C_3S particles might have different original peak positions. However, the effects generated from the differences of particles can be excluded because the anhydrous C_3S was kept in N_2 condition to prevent carbonation, and showed identical Si K edge NEXAFS spectra when measured for different particles several times. Therefore, it is worth noting that the Op layers show a lower peak position than the core area.

With regards to C_3S hydration, the C_3S reacts with water through a dissolution-precipitation process [32, 108]. During the induction period of this hydration process, hydrated orthosilicate (monomer) is formed in cement pastes [109], which is followed by the formation of hydration products containing primarily dimeric silicates during the acceleration period. After one to three days, insertion of bridging tetrahedrals into the gaps between dimers occurs, resulting in a ‘dreierketten’ structure [110]. A possible explanation for this phenomenon is that the Si in the dissolved SiO_4 monomer has a lower binding energy than the anhydrous C_3S due to the low degree of environmental network. Except for area 2 at 15 h 25 m, the positions of peak a_1 in the Op of all other particles were still lower than that of anhydrous C_3S because the effect of silicate polymerization on the energy shift of peak a_1 is less than that of peak a_2 , as observed in the Syn-CSH results.

Through analysis of the data, it is found that peak a_2 shifted more than peak a_1 , and the distance between these two peaks increased as of the hydration progressed. Interestingly, although the peak differences in the core area (LS15h25m-2) had not changed when compared to the result after 4 h 22 m (11.7 eV), those in the Op area (LS15h25m-1,3) showed values 1.8 and 3.4 eV larger than those in the core area. The results are in good accordance with previous studies, which indicated that the Op layer, which is generated in the early ages, prevents the hydration process of C_3S in the core area. A number of the available spectroscopic results support the presence of an intermediate phase that is responsible for the isolation of the anhydrous cores of C_3S particles from the solution. However, in the present study, the intermediate phases were not observed.



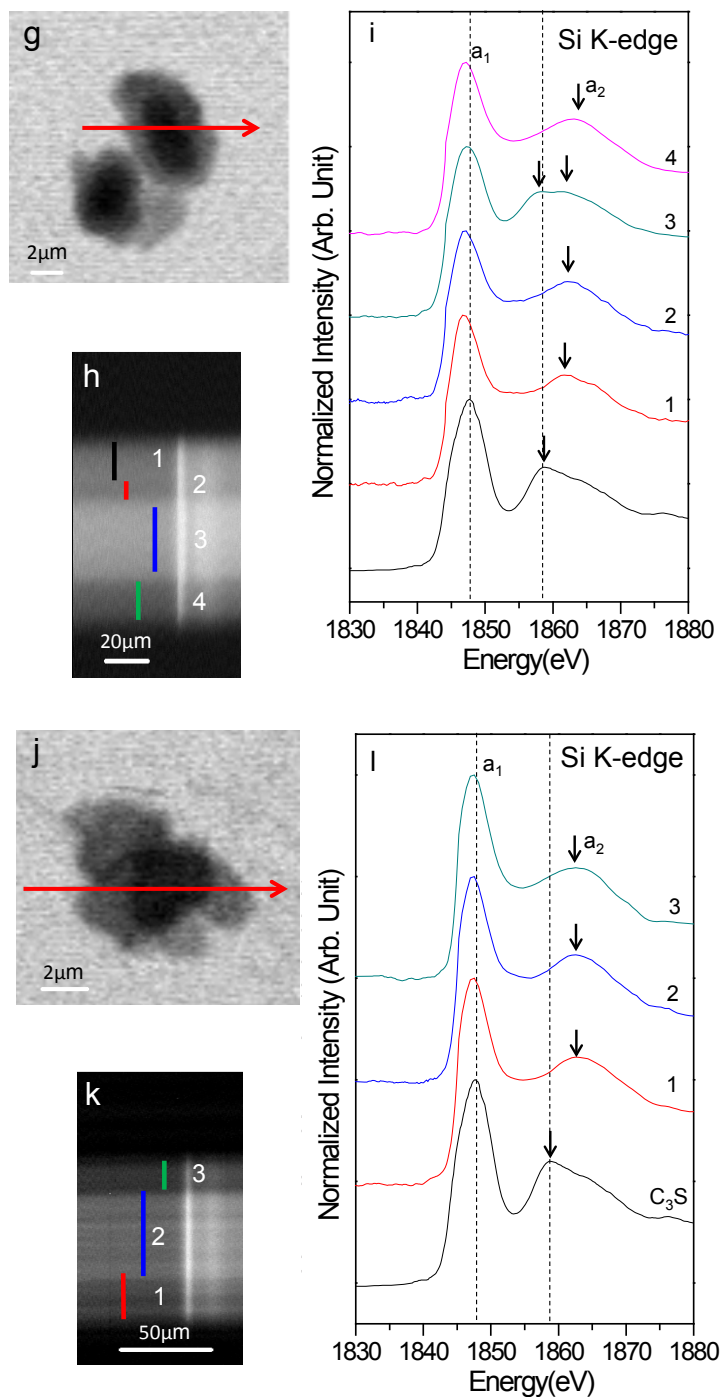


Figure 3.11 STXM images, line-scan images, and Si K edge NEXAFS spectra of the C_3S sample in the wet cell after 15 h 25 m (a, b, and c), 17 h 13 m (d, e, and f), 17 days (g, h, and i) and 40 days (j, k, and l). The layers that had different contrasts were selected for the analysis.

Table 3.6 Peak positions and the energy separation between the peak positions of the Si-K edge NEXAFS line-scan spectra of C₃S in the wet cell after 15 h 25 m, 17 h 13 m, 17 days, and 40 days. (LS: line scan)

Sample	Scan Areas	Peak a₁(eV)	Peak a₂(eV)	Δa₂-a₁(eV)
Anhydrous C₃S	-	1847.7	1858.9	11.2
	1	1847.1	1862.2	15.1
LS15h25m	2	1848	1859.7	11.7
	3	1847.5	1861	13.5
	1	1847	1861	14
	2	1847.3	1860.2	12.9
LS17h13m	3	1847.1	1862.3	15.2
	4	1847	1862.1	15.1
	5	1847.3	1860	12.7
	6	1847.1	1861.4	14.3
	1	1846.7	1861.7	15
LS17days	2	1847.2	1862.2	15
	3	1847.2	1858.4, 1861.2	11.2, 14
	4	1847.2	1863.2	16
	1	1847.6	1862.6	15
LS40days	2	1847.6	1862.6	15
	3	1847.6	1862.6	15

In the results after 17 h 13 m, the peak distance in the core area increased from 11.7 eV (LS15h13m-2) to 12.9 eV (LS17h13m-2) and 12.7 eV (LS17h13m-5) over time. The increased value is due to the increased degree of hydration in the core area or the higher degree of silicate polymerization in the Op, since the NEXAFS of the core area contain x-ray absorption information of the Op. The peak positions of Op shifted further, showing values 1.1~2.5 eV larger than the core area.

After 17 days, the layers with different contrast were clearly confirmed. Considering the fact that C-S-H is generated from the outer area of the C₃S particle, the transmitted beam through the core area in the C₃S particle should contain the information of both the core and the outer layers, as mentioned above. Consequently, in the spectra in the

core area of C_3S after 17 days, it was observed that peak a_2 contains a peak from the anhydrous C_3S (peak distance of 11.2 eV) and a peak from the hydrated C_3S (peak distance of 14 eV). Moreover, it was observed that the hydrated C_3S peak in the core area had a lower energy distance between the two peaks than the area in the Op. On the other hand, in the spectra after 40 days, no peak from the anhydrous C_3S was confirmed, and the spectra of the core and the outer product were identical, which is due to the fact that the core area of the C_3S at 40 days was fully-hydrated and had a similar degree of silicate polymerization to the Op of C_3S . To study details of the Si K edge NEXAFS of the hydrated C_3S , an image stack was conducted on the particles at 17 days in addition of line-scan analysis. Furthermore, to differentiate the morphology of the Op and core area, soft x-ray diffraction microscopy and transmission electron microscopy were used. The results will be discussed in the following paragraphs.

3.3.6 STXM analysis and soft x-ray diffraction imaging on hydrated C_3S

The STXM single image taken at 1840 eV and the Si image contrast map of the 17 day cured C_3S particles are shown in Figure 3.12(a) and (b). The Si image contrast map was obtained by subtracting an image taken from below the Si K edge from one taken above the Si K edge [22, 23]. In Figure 3.12(a), it can be observed that the hydration product layers that are assumed to be the Op in C_3S particles have a brighter OD contrast than the core area, which implies either a different thickness or chemical species. The product layer has a very uniform OD contrast, and the boundaries between these product layers are clearly distinguished. Small particles attached to the C_3S , which are marked by the dotted arrows, are confirmed to be $Ca(OH)_2$ containing no Si, which does not appear in the Si image contrast map results in Figure 3.12(b).

The peak positions (a_1 and a_2) and the energy separation between the peaks in the Si K edge spectrum, obtained from the selected area (Figure 3.12-(c)) in C_3S , are organized in Table 3.7. Before selecting areas in the figure for NEXAFS analysis, very small areas were divided and analyzed in the Op and the core area of the C_3S particle. These results are not presented in the current thesis; however, the NEXAFS spectra of the Op and core areas showed similar peak shapes and peak positions in the Op and the core area, respectively, which is indicative of a similar local structure environment in Si.

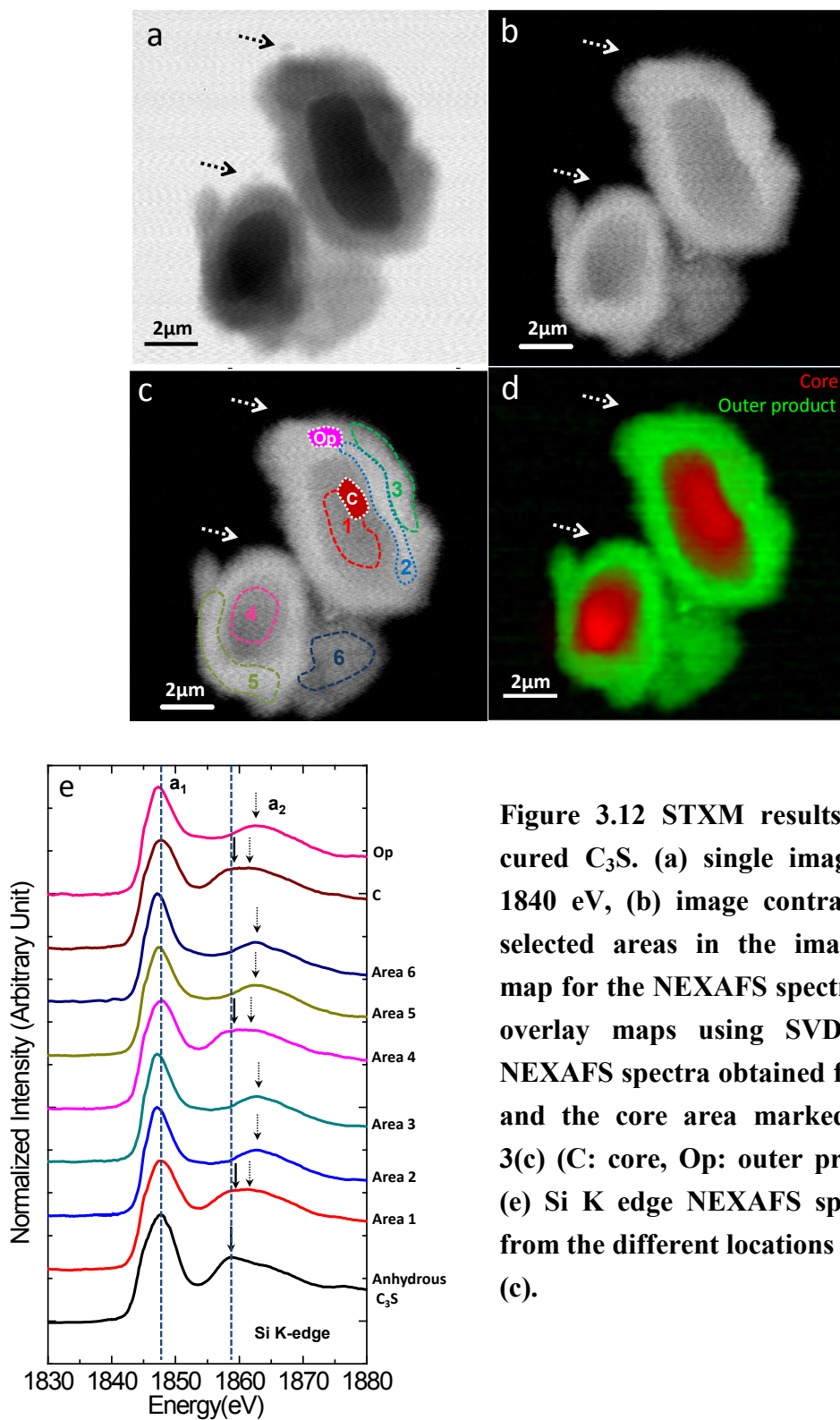


Figure 3.12 STXM results of 17 day cured C_3S . (a) single image taken at 1840 eV, (b) image contrast map, (c) selected areas in the image contrast map for the NEXAFS spectra, (d) RGB overlay maps using SVD based on NEXAFS spectra obtained from the Op and the core area marked in Figure 3(c) (C: core, Op: outer product), and (e) Si K edge NEXAFS spectra taken from the different locations indicated in (c).

Table 3.7 Peak positions and the energy separation between the peak positions of the Si K edge NEXAFS spectra of the hydrated C₃S (17 days).

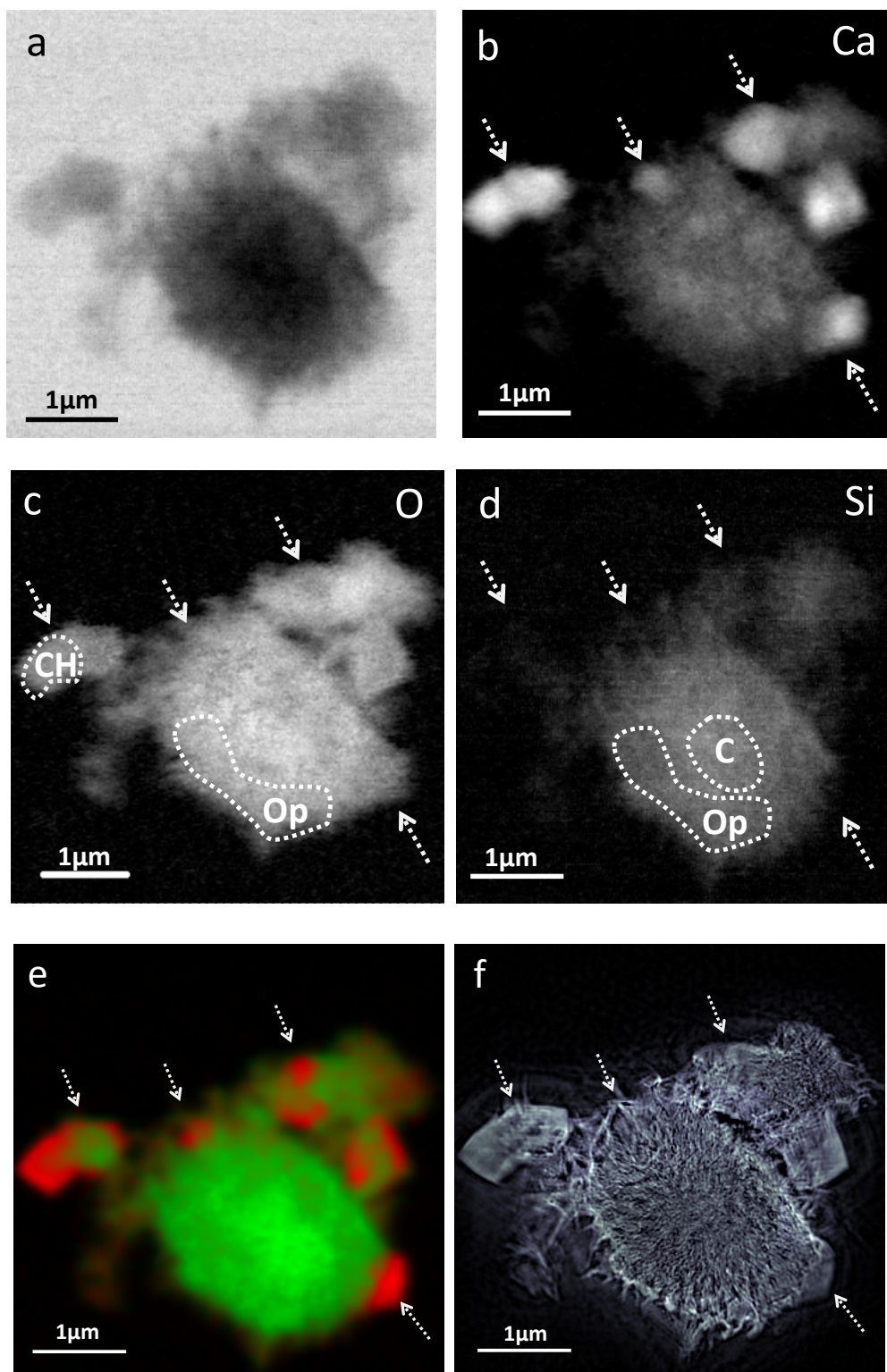
	Peak a ₁ (eV)	Peak a ₂ (eV)	$\Delta a_2 - a_1$ (eV)
Anhydrous C ₃ S	1847.7	1858.9	11.2
Area 1	1847.7	1859.7, 1861.2	12, 13.5
Area 2	1847.1	1862.7	15.6
Area 3	1847.1	1862.7	15.6
Area 4	1847.7	1858.8, 1861.2	11.6, 13.5
Area 5	1847.4	1862.4	15
Area 6	1847.1	1862.4	15.3

Since the silicate polymerization occurs in the outer area of the C₃S particle, it is still possible that there are differences in terms of the Si binding energy between the Op close to the core area and further from it. Three regions (1, 2, and 3) were selected to verify the gradational changes of the Si K edge in the Op outward from the boundary of the core area, while three areas in the separate particle (4, 5, and 6) were also selected, as shown in Figure 3.12-(c). No gradational changes in the NEXAFS spectra between region 2 and 3 were observed, and these two areas showed identical absorption features. In addition, regions 5 and 6 were shown to be very close to regions 2 and 3, considering the energy step size measurement was 0.3 eV. This means that the Op of C₃S at 17 days had a uniform chemical structure surrounding the Si, which implies a uniform degree of silicate polymerization. The main peak (a₁) in the Op showed a sharper and comparatively lower energy position (0.5~0.6 eV) compared to that of the anhydrous C₃S. This phenomenon is due to the fact that the Si in the dissolved SiO₄ monomer produced by the dissolution process of C₃S has a lower binding energy than the one in the anhydrous C₃S due to the low degree of environmental network. As confirmed in the line scan analysis, the position of peak a₁ of the Op at 17 days is lower than that of the anhydrous C₃S because the silicate polymerization affects the energy shift of peak a₁ more than that of peak a₂.

Since a signal measured in STXM is acquired from transmitted x-ray photons and the C_3S is considered spherical, the core area will contain signals penetrating through both the Op and core regions. The NEXAFS spectra of the core area (1 and 4) showed similar shapes and positions of peak a_1 compared to the anhydrous C_3S . Alternatively, peak a_2 contains two peaks with larger energy separations (+0.4~0.6 eV and +2.3 eV) than the anhydrous C_3S . These peaks showed smaller energy distances compared to those of the Op, which implies a lower degree of silicate polymerization. The results support the fact that the uniform Op layer, which is generated in the early ages, prevents the hydration process of C_3S in the core area, which results in different degrees of silicate polymerization.

RGB overlay maps, created using SVD, were used to visualize the distribution of the core and the Op in the C_3S particle based on reference spectra taken from the core area and the Op region, as shown in Figure 3.12-(c). The RGB overlay maps are shown in Figure 3.12-(d). The strength of SVD is the detailed spectral information for converting image stacks into chemical component maps. Since different chemical components have different NEXAFS spectra, SVD that is based on the reference spectra can be used to convert the image stack into chemical maps [63]. The Op is shown to be a very uniform layer around the core area, which is consistent with the Si K edge NEXAFS analysis. Furthermore, it was shown that the Op in different C_3S particles in the image have a similar degree of silicate polymerization, which implies a similar degree of hydration throughout the C_3S sample.

Figure 3.13 presents (a) the STXM single image taken at 1840 eV, (b) the contrast image map of Ca, (c) O, (d) the Si of C_3S particles 18 days after mixing with water, (e) the RGB overlay of species maps based on O K edge spectra from the selected area in Figure 3.13-(c), and (f) the soft x-ray diffraction image of the particles. A comparatively smaller particle than the one in Figure 3.12 was selected for analysis of Ca, O, and Si due to the limitation of the range of diffraction imaging (~5 by 5 μm) and x-ray photon penetration at low energy levels for Ca L and O K edge NEXAFS analysis.



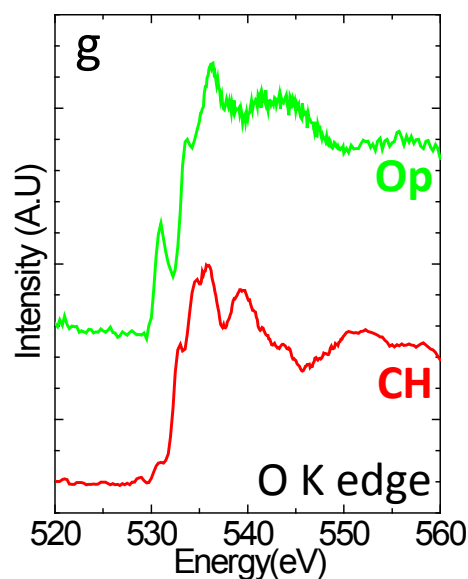


Figure 3.13 STXM and soft x-ray diffraction imaging of 17 day cured C_3S . (a) single image taken at 1840 eV, (b) image contrast map (Ca), (c) image contrast map (O), (d) image contrast map (Si) (C: core, Op: outer product), and (e) RGB overlay maps using SVD based on NEXAFS spectra obtained from the Op and core area marked in Figure 4(c) (Op: outer product, CH: $Ca(OH)_2$), (f) diffraction image, and (g) O K edge NEXAFS spectra from the selected area in (c)..

In the center of the C_3S in Figure 3.13-(a), taken at a single energy, the layers assumed to be the Op were observed to have different contrasts than the core region. On the other hand, no differences in terms of the OD were found in the image contrast maps of Ca, O, and Si, as shown in Figure 3.13 ((b),(c), and (d)).

It is assumed that the particle was fully hydrated, and thus a uniform chemical composition can be expected. The particles marked by the dotted arrows had different OD contrasts in the image contrast map of Ca and contained no Si, as shown in Figure 3.13-(d). The particles were proved to be $Ca(OH)_2$ using Ca $L_{III, II}$ edge NEXAFS analysis. The Ca $L_{III, II}$ edge NEXAFS spectra were not presented here, since the particles were too thick to obtain a proper amount of transmitted x-ray photons; however, $Ca(OH)_2$ could be still identified by checking the peak position of the spectra, since it has a different peak position than the C-S-H of C_3S .

Ca L_{III, II} edge, O K edge, and Si K edge NEXAFS analyses were conducted for the areas illustrated in Figure 3.13-(d). The NEXAFS spectra of both areas were identical to those of the Op in Figure 3.12-(e), which implies that the core region was already fully hydrated, which is consistent with the image contrast map. Based on the O K edge spectra obtained from the area illustrated in Figure 3.13(c), the RGB overlay map was created and is shown in Figure 3.13-(e). Ca(OH)₂ appears as the red region in the RGB overlay map, and while it was not readily distinguished from C₃S in the STXM image, it was clearly confirmed here. C-S-H grown on the Ca(OH)₂ particle, which is indicated by the arrows on the left and right side of the C₃S particle in the center of the image.

The STXM single image of the 40days hydrated C₃S particle and the Si K edge NEXAFS spectra of the selected areas in the particle are shown in Figure 3.14. Also, the obtained peak positions and peak distances are organized in Table 3.8. The results indicate that after 40 days of hydration, peaks a₁ and a₂ in the core area show similar or lower energy values compared to the Op region, leading to a comparatively smaller energy separation value in the core area (ST40days-2) than in the outer area (ST40days-1 and 3). Note that no peaks from the anhydrous C₃S were observed in the core area in the 40 day C₃S particle.

In summary, it was observed that Op of C₃S show higher degrees of silicate polymerization compared to the core area of C₃S particle after 17 days. While the boundaries between these products are obviously distinguished in the 17 days hydrated C₃S particles, the Op and the core area in the 40 days hydrated C₃S particles have similar degrees of hydration and no peaks from the anhydrous C₃S were observed. This can be explained by the fact that silicate polymerization has proceeded more in the core of C₃S over time.

The obtained peak positions (a₁ and a₂) of the Si K edge from 1 h 19 m to 40 days are plotted in Figure 3.15. In terms of peak a₁, in the core area of anhydrous C₃S, a gradual increase is shown. On the other hand, peak a₁ in the Op decreases until 17 days but then increases at 40 days due to the dissolution-precipitation process of C₃S.

With regards to peak a₂, both the core area and the Op show increases during the hydration process. While the peak position in the core area increases gradually, the position

in the Op shifts to a higher energy faster in the early ages (until 17 h) and then increases gradually afterward, which supports the idea that the hydration process is occurring from the outer areas of C_3S particles.

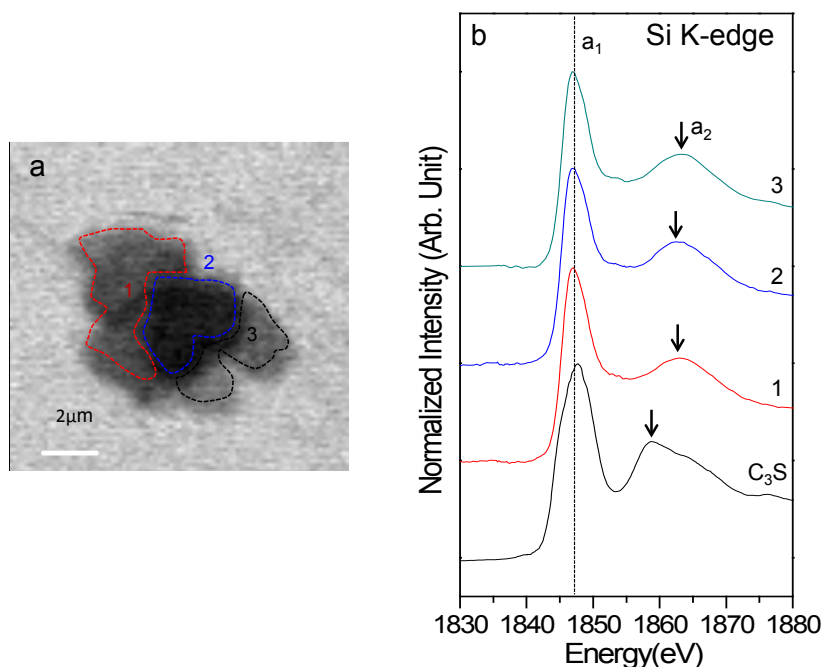


Figure 3.14 (a) STXM single image of 40 day hydrated C_3S taken at 1840 eV, and (b) Si K edge NEXAFS spectra of the selected areas in (a).

Table 3.8 Peak positions and the distance between the peak positions of the Si-K edge NEXAFS line-scan spectra of C_3S in the wet cell after 40 days. (ST: image stack)

Sample	Scan Areas	Peak a_1 (eV)	Peak a_2 (eV)	$\Delta a_2 - a_1$ (eV)
Anhydrous C_3S	-	1847.7	1858.9	11.2
	1	1847.1	1863	15.9
ST40days	2	1846.9	1862.4	15.5
	3	1846.9	1863.4	16.5

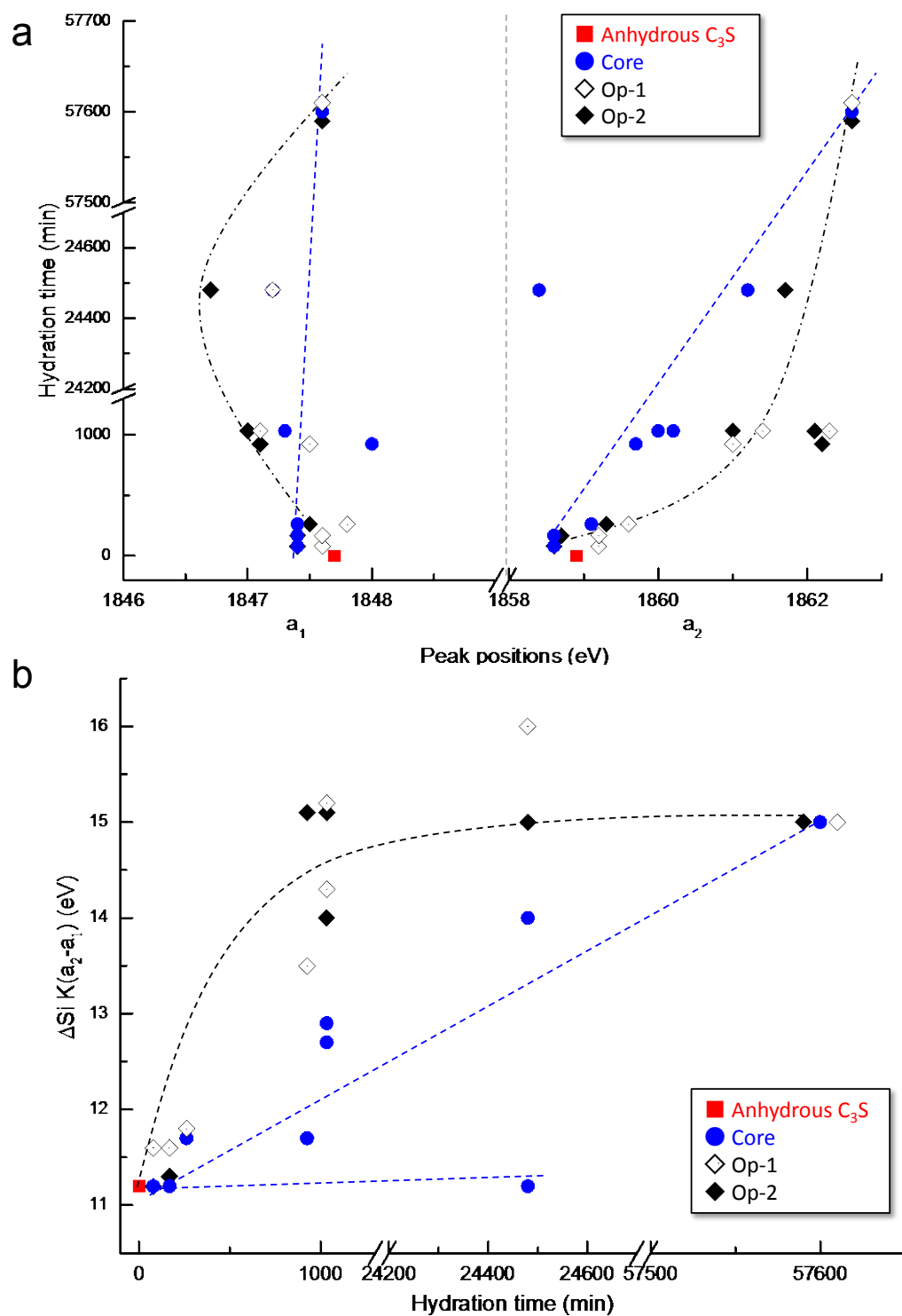


Figure 3.15 (a) Chemical shift of the Si K edge during the C_3S hydration process, and (b) the energy separation change during C_3S hydration.

3.3.7 Soft x-ray diffraction and TEM imaging on hydrated C_3S

As introduced in chapter 2, the microstructure of C_3S paste can be divided into three broad regions; anhydrous material, Ip and Op including CH as categorized by Taplin et al.[36]. Ip and Op in C_3S are respectively formed within the boundaries of the original C_3S grains and in the space between the original C_3S grains and morphology of products is affected by the amount of available space [35]. While Op varies depending on the types of paste, Ip present in C_3S typically has a homogeneous and fine-grained morphology, and voids with diameters under 10nm. However, in general, it is difficult to determine the pore size in Ip by TEM analysis since the structures likely undergo electron beam damage resulting in coarsening the morphology of Ip.

Environmental SEM imaging [91] has shown that the morphology of the Op in C_3S depends on the drying rate. Due to the necessity of a high vacuum level during diffraction imaging to reduce the scattering arising from residual gas in the chamber, the experimental conditions can be considered, according to the terms of previous research [91], as a fast dry rate. To this end, the diffraction image in Figure 3.13-f, shows the Op of C_3S to be fibrillar in nature under this fast drying rate. Furthermore, crystalline $Ca(OH)_2$, as indicated by the arrows, is easily distinguished in the diffraction image as compared to the absorption image using STXM (Figure 3.13-(a)), and it was also possible to obtain the morphologic details of fibrillar C-S-H grown on $Ca(OH)_2$ particles.

The width of the Op of 17 days cured C_3S , in the same particle shown in Figure 3.13-(f), is measured as presented in Figure 3.16-(a). Furthermore, the width of the Op in 28 days cured C_3S in TEM is shown in Figure 3.16-(c). In the images, Op that had a clear fibrillar morphology and did not overlapped with other products were selected for the size measurement. The width of the fibers has distribution of 41~59 nm in the C_3S particle of 17 days hydrated paste. They are shown to be similar size with comparatively thicker Op of C_3S shown in TEM image.

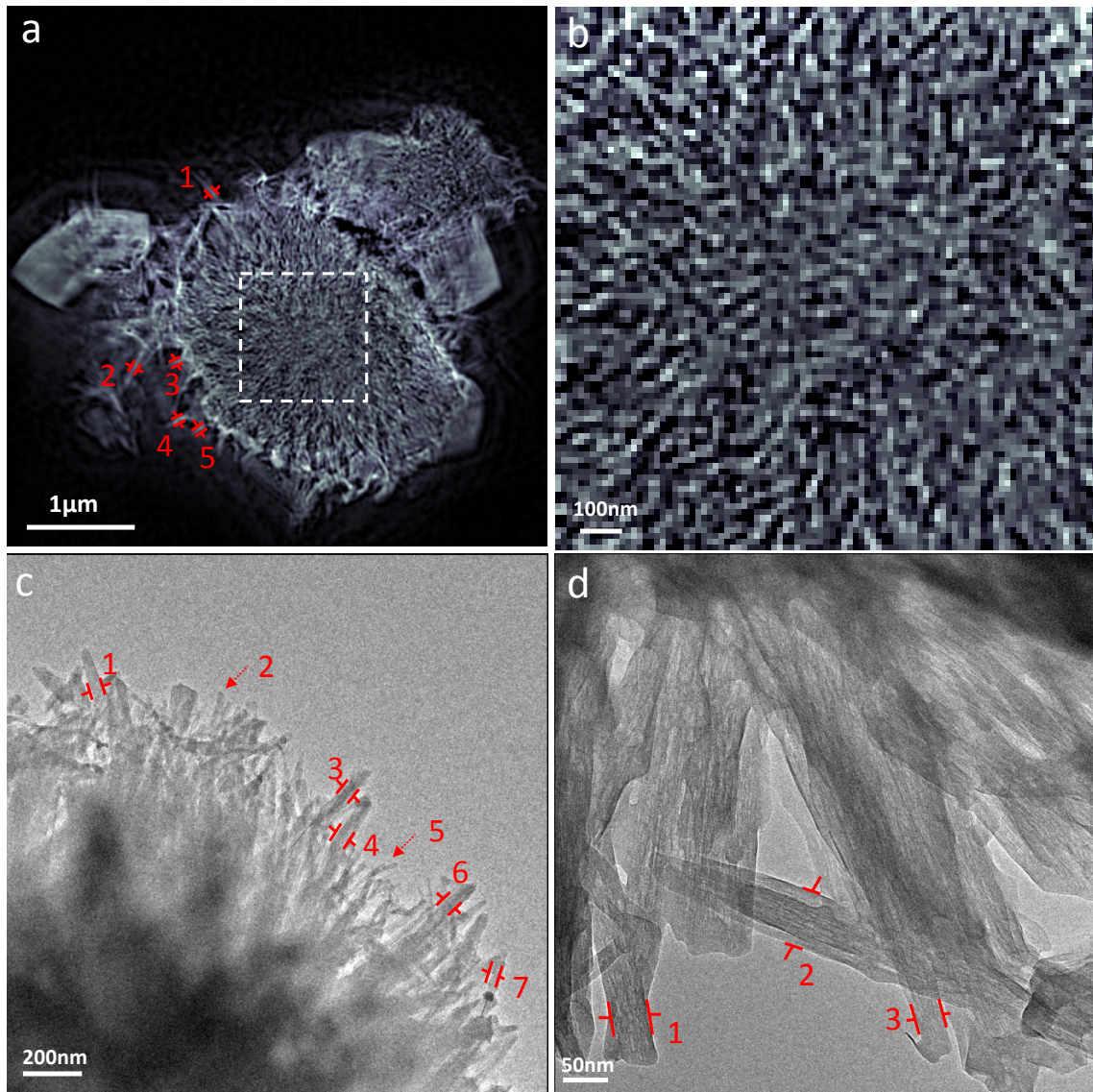


Figure 3.16 (a) Soft x-ray diffraction image of 17 day cured C_3S , and the width of the Op are 59, 42, 44, 59, and 41 nm for numbers 1 to 5, respectively; **(b)** the magnified inner product region, shown as the rectangular area in **(a)**; **(c)**, **(d)** show the TEM images of the Op for 28 day cured C_3S powder. The width of the Op are 54, 18, 53, 53, 15, and 47 nm for numbers 1 to 7 in **(c)**, respectively, and 44, 63, and 32 nm for numbers 1 to 3 in **(d)**, respectively.

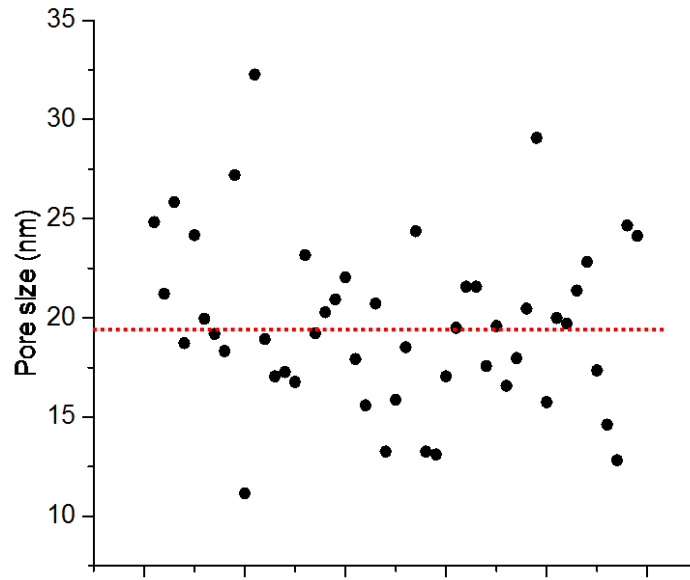


Figure 3.17 Distribution of pore size in Ip of 17 days hydrated C_3S .

To verify the details of the core area of C_3S , the core region in the diffraction image was magnified, as indicated by the dotted rectangle (Figure 3.16-(a)), and this is presented in Figure 3.16-(b). Compared with the fibrillar Op of C_3S , morphology of fully-hydrated core area of C_3S is very similar to Ip of hydrated C_3S observed by TEM in previous research [35] and it is shown to be less dense inter-globular structure with voids in average diameter of 19.7 nm (minimum of 11 to maximum of 32 nm), as shown in Figure 3.17, which is larger than that found in the previous study [35]. The larger void size of Ip could be induced by high water to solid ratio of 10 used in this thesis which provides sufficient space to expand during hydration. The x-ray beam was focus on cross section of the center in C_3S , the diffracted beam mainly contain the information in core area and Op on the same plane which is different to STXM using x-ray absorption. Therefore, the diffraction imaging can effectively show the internal structures of C_3S with less beam damage and simpler sample preparation, compared to TEM.

The TEM images presented in Figure 3.16 show that Op of C_3S has fibrillar in macro-scale and layered structure in nano-scale. The morphologies of both Ip and Op of hydrated C_3S observed by the diffraction imaging are very similar to those observed by TEM in the previous researches [24, 35, 89] proving the validity of soft x-ray diffraction imaging on morphologic observation of cement phase.

3.4 Conclusions

In the present chapter, an attempt has been made to obtain Ca $L_{III,II}$ edge and Si K edge NEXAFS reference spectra for synthesized C-S-H with different Ca/Si ratios and for anhydrous and hydrated C_3S . The spectra were compared with C-S-H formed in C_3S hydration. *In situ* STXM was used to determine the morphological and structural environment changes surrounding the Ca and Si atoms in the early age hydration of C_3S . Furthermore, as a complement to the STXM results, soft x-ray diffraction imaging was conducted and compared with the TEM results. The obtained results are summarized below.

Ca $L_{III,II}$ edge NEXAFS analysis using STXM shows that Syn-CSH, prepared with various Ca/Si ratios, had no variation in peak positions and energy separation for Ca $L_{III, II}$, but there was a slight difference in the peak intensity ratio in accordance with the Ca/Si ratios due to a different crystallinity. The Ca $L_{III, II}$ NEXAFS of 17 days hydrated C_3S show different local structure with anhydrous C_3S by the hydration process. Compared to Syn-CSH, the C-S-H of C_3S is proved to have a very similar local structure around the Ca but less crystallinity.

In the Si K edge NEXAFS of Syn-CSH, a tendency is clearly observed in which the peak positions of both the Si K edge and the peak induced by multiple scattering have shifted to higher energy levels and the distance between the two peaks increased with a decrease of the Ca/Si ratio in Syn-CSH. Silicate polymerization influenced the multiple scattering of distant shell atoms more than the binding energy of the core atoms.

In situ STXM analysis using pure C_3S solutions in a wet cell showed morphologic changes in the dissolution of the Ca and the precipitation of C-S-H on the C_3S particles in the process of hydration. The dissolution of C_3S and formation of Op layers around C_3S were clearly observed. Op layers of C_3S showed higher degree of silicate polymerization compared to core area of C_3S . The degree of silicate polymerization of Op increased during the hydration process.

RGB overlay mapping reveals that C-S-H with lower and higher degrees of silicate polymerization existed in the Op layer and in the core area, respectively, of C_3S particles after 17 days. It was proved that the Op and core area have different degrees of hydration due to silicate polymerization through Si K edge NEXAFS analysis. Furthermore, it was

observed in the RGB overlay maps that the Op layer reduces the hydration process of C_3S in the core area.

Soft x-ray diffraction imaging and TEM on 17 days hydrated C_3S showed that Op have fibrillar with laminar structure while core area have an inter-globular structure with voids. The diffraction imaging proved that core area in fully-hydrated C_3S is Ip. Soft x-ray diffraction imaging was applied to a cement-based system on a nano-scale, and this was proved to be a very effective tool for obtaining the morphology of C_3S in detail. Using the information obtained and presented here it is clear that this technique, newly applied to cement, has immense possibilities in this research area. The increase in resolution gives the diffraction imaging ability to identify clearly between Ip and Op C-S-H, presenting a major advancement from STXM. With a resolution comparative to that of TEM, but with less beam damage, further development of this techniques could led to tomography of C-S-H which contain crystalline phases.

CHAPTER 4

**SILICATE POLYMERIZATION AND ALUMINUM SUBSTITUTION
FOR SILICON ON THE HYDRATION PRODUCTS FORMED IN C_3S
SYSTEMS CONTAINING HIGH-VOLUME FLY ASH**

4.1. Introduction

High-volume fly ash (HVFA) concrete, where more than 50 wt.% of Portland cement (PC) is replaced by fly ash, has been successfully applied to reinforced concrete structure to minimize CO₂ emission due to the PC production [111]. Although HVFA concrete shows a comparatively slower rate of strength development at early age than PC concrete [9], it has various attractive properties such as enhanced workability, durability and long-term compressive strength [112]. The excellent long-term performance is due to the reaction between Ca(OH)₂ and amorphous aluminosilicate-rich ash leading crystal size refinement and pore filling in the cementitious matrix [113, 114].

In a pure PC system, calcium silicate hydrates (C-S-H) strongly, influences the physical and chemical properties of PC matrix. As discussed in previous chapters, the structure of C-S-H is affected by many factors, such as water to cement ratio, chemical composition of PC and introduction of supplementary cementitious materials (SCMs) including fly ash [115]. C-S-H in a PC-SCM system shows a relatively lower Ca to Si molar ratio (Ca/Si ratio) [2] and has a similar crystal structure to tobermorite, and it is often referred as C-S-H(I). C-S-H with a low Ca/Si ratio has a higher capacity to uptake of Al, particularly when the Al concentration in the solution increases [97]. Experimental and theoretical research showed that Al substitution for Si occurs at the bridging tetrahedral in the silicate chain of C-S-H [38, 116].

Both the silicate polymerization and the Al substitution for Si in C-S-H affect the binding energy of Si in C-S-H. The chemical shift Si binding energy, caused by the silicate polymerization, has been studied by XPS [58, 59] and XAS [56] as described in Chapter 2. In Chapter 3, Si K edge NEXAFS analysis using synthesized C-S-H clearly showed that a decrease in Ca/Si ratio leads to higher silicate polymerization of the silicate tetrahedral. Li et.al [56] observed that Si binding energy decreases when Al substitutes for Si in silicates and alumino-silicates minerals using XAS. They also reported that mainly tetrasilicates (SiO₂-Q⁴) contain Al substituted for Si.

Similarly in the HVFA system, an increase in Si binding energy is expected to happen due to many additional silicate phases provided from fly ash, leading to a higher degree of silicate polymerization in C-S-H. At the same time, however, a decrease in the Si binding energy of C-S-H is expected due to the Al substitution produced from alumina

phases in fly ash. There is a critical need to understand these mechanics in order to optimize the utilization of fly ash in concrete mixtures.

This chapter will tackle these complex mechanisms by performing a careful analysis of the effect of abundant silicate and alumina phases from HVFA on the Si binding energy in C-S-H at a nano-scale level. Scanning transmission x-ray microscopy (STXM), at Advanced Light Source (ALS) in Lawrence Berkeley National Laboratory (LBNL), can be used not only for morphology imaging with 25 nm spatial resolution, but also for NEXAFS analysis of a specific area in the x-ray image. Although, it is possible to measure the chemical shift quantitatively induced by a specific chemical environment using this method, it has not been applied extensively to cement chemistry due to the complexity and diversity of the hydration phases produced in PC-based systems [22, 23].

The present chapter aims to determine the effect of HVFA on the C_3S hydration in terms of hydration products, morphology, chemical composition and atomic structure of C-S-H. Pure C_3S , as a model system instead of PC, is used with 50% fly ash. Hydration products formed in HVFA system and the amount of $Ca(OH)_2$ consumed through pozzolanic reaction with fly ash were examined using synchrotron powder x-ray diffraction (XRD) and thermogravimetric analysis. Nuclear magnetic resonance spectroscopy (NMR) was used to confirm Al substitution in the system and to examine the degree of silicate polymerization by comparing the silicate chain length of C-S-H formed in pastes made with the neat C_3S and with C_3S / HVFA systems. Lastly, the effect of HVFA on the morphology of pure C_3S paste, and the binding energy of each atom are confirmed using Ca $L_{III,II}$ edge, Al K edge, Si K edge NEXAFS analysis and transmission electron microscopy (TEM).

4.2. Experimental procedure

4.2.1 Materials and sample preparation

Triclinic C_3S passing through #325 sieve (45 μ m) purchased from the CTL Group (Skokie, IL) and Class F fly ash were used as the raw materials. C (C_3S) and C-FA (50 wt.% of C_3S -50 wt.% of fly ash) pastes were prepared by hand-mixing the raw materials with distilled water. For all samples, water to solid ratio was kept constant at 0.5. The hand-mixed pastes were cast into PELCO[®] disc block embedding molds measuring $\phi 18 \times 3$ mm and cured at $23 \pm 1^\circ C$ under $95 \pm 5\%$ relative humidity. The pastes were de-molded at 1,

3, 7 and 28 days and treated with acetone to suspend the hydration process and kept under vacuum-drying, in carbonation-free conditions until testing.

Finely ground powder was used for XRD, thermogravimetric analysis (TGA/DTA) and TEM measurements. All samples were kept in a vacuum bag and ground just before the measurement to minimize the carbonation. The details of sample preparation for TEM, STXM, and NMR are described in following section.

For the STXM measurements, thin sectioned samples (~200 μ m thick slices) of the hardened pastes were prepared using a diamond wafering-blade saw followed by mechanical grinding and polishing. Kerosene was used instead of water to avoid any further hydration of the samples during these procedures. A small piece (~ 3 $\times$ 3mm) of the thin sectioned sample was placed on a copper grid with a single slot in the center for ion milling. The sample was ion milled by PIPSTM at the National Center for Electron Microscopy (NCEM) and kept in a box and sealed in a vacuum bag. Before loading the sample into the STXM chamber, the thin sectioned sample was checked by optical microscope to see if there was a crack on the surface of it. Helium gas was simultaneously injected to prevent cracking when the residual gas in the STXM chamber was pumped out. Beam damage on the sample from x-ray radiation was checked by confirming the presence of any changes in the image and NEXAFS spectra in specific area before and after each measurement.

4.2.2 Monochromatic synchrotron XRD

Synchrotron XRD measurement were made at beamline 12.2.2 of ALS which used a monochromatic synchrotron x-ray beam ($\lambda=0.6199$ Å) that focused on a spot size of 10 $\times$ 10 μ m. LaB₆ powder diffraction standard was used to calibrate the working distance between the sample and diffraction detector. Diffraction patterns were collected using a MAR345 image plate (3450 $\times$ 3450 pixels). The 2-dimensional raw data were converted into 1-dimensional intensity versus 2-theta scans using the Fit2D program [117]

4.2.3 Scanning transmission x-ray microscopy

STXM results were collected at the ALS branch line 5.3.2.1 and 5.3.2.2 with the synchrotron storage ring operating at 1.9 GeV and 200–400 mA stored current. Counting times were of the order of a few milliseconds or less per pixel to avoid beam damage. Since both STXMs have different x-ray photon energy ranges (e.g. STXM 5.3.2.1: 350 - 2500 eV,

5.3.2.2: 250-800 eV), images and NEXAFS spectra around Ca L_{II,III} edge (340-360 eV), Al K edge (1550-1590 eV) and Si K edge (1825-1890 eV) were measured by beamline 5.3.2.2 and 5.3.2.1 respectively. Details on the STXM and the different modes for the measurements were discussed in Chapter 2 and 3.

4.2.4 ²⁷Al and ²⁹Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy

All samples were finely ground and packed evenly into a 3.2mm zirconia rotor and sealed at the open end with a Vespel cap. The rotor was spun at 20 kHz on a Bruker Ultrashield 600WB Plus with a 14.1T magnet, operating at 156.40 MHz for ²⁷Al, with a dwell time of 7.0 μs, obtaining 1024 acquisitions, and at 119.23 MHz for ²⁹Si, with a dwell time of 7.0 μs, obtaining 4096 acquisitions. In both cases the magic angle was set to 54.734°, using KBr as a reference and for ²⁷Al MAS NMR samples were spun for no longer than 40 minutes in order to prevent dehydration of the sample and any consequent loss in peak intensity [118].

4.2.5 Transmission electron microscopy (TEM) imaging

TEM imaging was performed on a Titan G2 80–300 kV (FEI Company, Hillsboro, OR, USA) at King Abdullah University of Science and Technology (KAUST, Saudi Arabia) operating at 300kV, equipped with a 4k x 4k CCD camera (Gatan, Pleasanton, CA, USA) and an EDX detector, with ISIS software for imaging/x-ray analysis, (Oxford Instruments, Oxford, UK). The powder was suspended in ethanol, 2μl of which was deposited on a holey carbon film and dried for five minutes before examination on the TEM. The selected area diffraction (SAD) was used to determine the crystalline phases in an area of the sample before chemical analysis. Scale-bars in the TEM images were illustrated using ImageJ software developed by National Institutes of Health.

4.2.6 TGA/DTA analysis

TGA/DTA tests using ground C and C-FA 1, 3 and 28 days-aged samples were performed from room temperature to 1000°C, heated at 10°C/min. Approximately 20 to 25 mg of finely ground powder were taken in a ceramic crucible and heated in Sieko TG / DTA 6300. The flow rate of nitrogen gas was 50 ml/min.

4.3. Results and Discussion

4.3.1 XRD and thermogravimetric analysis

Figure 4.1 presents the monochromatic synchrotron powder XRD patterns of C and C-FA pastes after 1, 3, 7 and 28 days of curing. The XRD patterns appeared to be simple and contained fewer reactive crystalline quartz phases (SiO_2) in FA, anhydrous C_3S and $\text{Ca}(\text{OH})_2$ in C and C-FA.

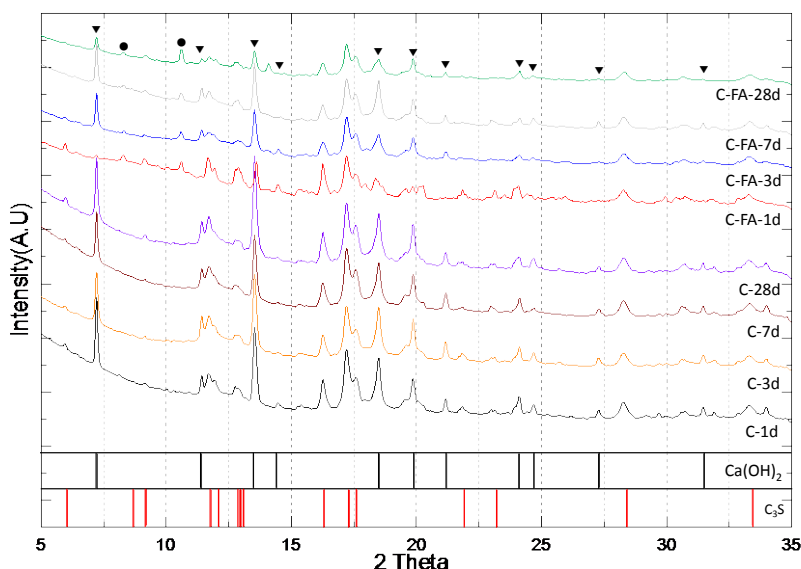


Figure 4.1 Synchrotron powder XRD patterns for C and C-FA pastes. ▼: $\text{Ca}(\text{OH})_2$, peak positions which have relative intensity above 5% in the ICDD PDF2 database reference 00-087-0674 were used. ●: Quartz (ICDD PDF2 database reference 01-078-2315)

Besides those phases, it was not possible to observe any other phases in the samples due to low peak intensities. Reference peak positions of C_3S and $\text{Ca}(\text{OH})_2$ were illustrated below the XRD patterns. For $\text{Ca}(\text{OH})_2$, the peaks, over 5% intensity compared to basal d-spacing, were selected as a reference and, for C_3S , reference XRD patterns provided from CTL were used. As expected, C-FA samples showed lower intensity of $\text{Ca}(\text{OH})_2$, compared to C, due to dilution of C_3S substituted by FA. Peak intensity of $\text{Ca}(\text{OH})_2$ in sample C increased up to 28days, however, in sample C-FA, the peak intensity of $\text{Ca}(\text{OH})_2$ decreased from 7 days to 28days due to the pozzolanic reaction between alumino-silicate phase and $\text{Ca}(\text{OH})_2$.

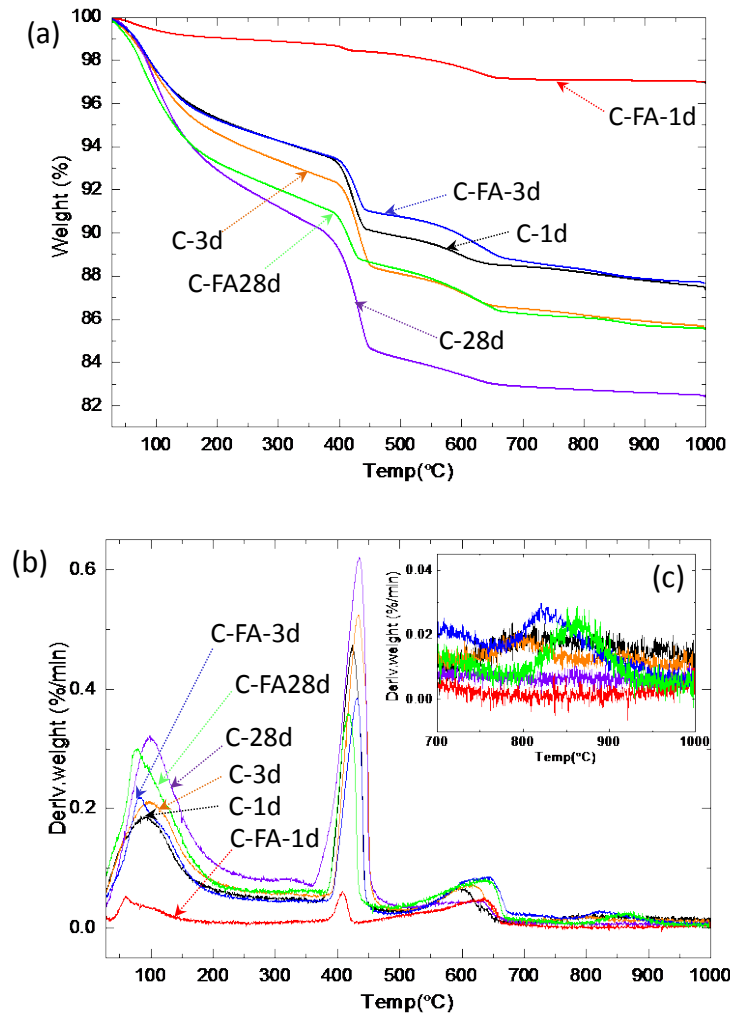


Figure 4.2 (a) TGA, (b) DTA and (c) DTA (700 ~ 1000°C) results of the C and C-FA paste samples.

To compare the amount of Ca(OH)_2 formed in each sample quantitatively, TGA/DTA analysis was carried out and the results are presented in Figure 4.2. There was a continuous loss of weight up to 350°C and this was due to evaporation of surface adsorbed water from air and dehydration of C-S-H, ettringite, and calcium aluminate hydrate [119, 120]. However, it was not possible to deconvolute each of endothermic peaks. The second mass loss, with a peak temperature of 360 to 460°C indicates the decomposition of Ca(OH)_2 formed during C_3S hydration. Finally, the mass loss attributed to the temperature around 550 to 650°C and 800 to 900°C indicates the decarbonation of CaCO_3 . In Figure 4.2-(b), C-FA-3d and C-FA-28d at 700 to 1000°C showed mass loss due to the

decarbonation of CaCO_3 since the rate of carbonation increases significantly by replacement of PC with fly ash [121].

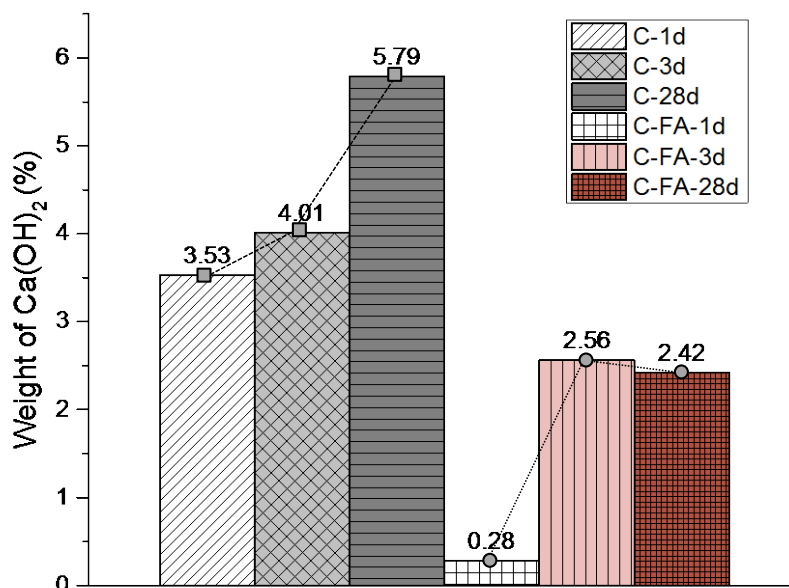


Figure 4.3 Amount of Ca(OH)_2 production as percentage of total weight in C and C-FA samples

Based on the TGA / DTA results, the amount of produced Ca(OH)_2 as percentage of total weight in C and C-FA samples were calculated as shown in Figure 4.3. The amount of Ca(OH)_2 in C pastes increased gradually up to 28 days. In comparison with a C pastes, a very small amount of Ca(OH)_2 (0.28 wt.%) was observed in C-FA-1d and it increased significantly up to 3 days. The amount of Ca(OH)_2 , however, decreased in C-FA-28d due to pozzolanic reaction which is consistent with XRD results.

The small amount of Ca(OH)_2 formation in C-FA-1d could be due to the dilution of C_3S and the pozzolanic reaction in the HVFA system. However, considering that the reactivity of Class F fly ash with low CaO content is very low in the early age and the effective water to C_3S ratio in C-FA paste is comparatively higher than in C paste which enhances C_3S hydration process, the amount of Ca(OH)_2 in C-FA-1d is too small.

In general, the introduction of fly ash accelerates the PC hydration because the

surface of the fly ash increases the number of sites that are favorable to the precipitation of hydrates. Moreover, due to the possible presence of soluble alkalis, the PC hydration reaction may also be accelerated; however, the pozzolanic and hydration reaction that takes place in HVFA systems are not independent of each other. The presence of soluble organics provided from HVFA can interfere with the surface reaction of the cement preventing nucleation and growth in PC system [122].

Another possible explanation for the small amount of Ca(OH)_2 in C-FA-1d is that pozzolans, which adsorb a large number of Ca ions at the surface of the grains, lower the Ca ionic concentration in the liquid phase and, consequently, accelerate the dissolution of C_3S . Because of the low Ca^{2+} ionic concentration in the liquid phase, the rate of the formation of hydrates is small; resulting in a small amount of Ca(OH)_2 [40].

While no other phases were observed in the XRD results, the presence of a small amount of AFm phases in the C-FA paste was confirmed in the NMR results which will be discussed more in detail in the ^{27}Al MAS NMR results. HVFA reduces the $\text{SO}_4/\text{Al}_2\text{O}_3$ ratio due to significant amounts of available Al_2O_3 , but less in SO_4 compared to PC systems, thus effectively reducing and favoring the formation of the AFm phase over the AFt phase [29, 123]. The demand on Ca(OH)_2 for the formation of the AFm phases could also account for the small amount of Ca(OH)_2 formation in C-FA-1d. Based on TGA/DTA results, it is assumed that all the AFm phases were formed in the very early ages and there was no more demand on the Ca(OH)_2 for the AFm phase formation after this early stage.

4.3.2 STXM imaging and NEXAFS analysis

The results of Ca $\text{L}_{\text{III, II}}$ edge STXM analysis are presented in Figure 4.4. Due to low x-ray photon energy (340~360eV) for Ca $\text{L}_{\text{III, II}}$ edge NEXAFS analysis, only the areas that were thin enough for x-ray beam penetration and had a uniform Ca distribution in the image contrast map were selected as shown in Figure 4.4-(b), (d). Ca $\text{L}_{\text{III, II}}$ edge NEXAFS spectra obtained from the region of interest (ROI) and anhydrous C_3S are shown in Figure 4.4-(e). Each spectrum has been normalized to incident beam intensity (I_0) and a linear pre-edge background was removed.

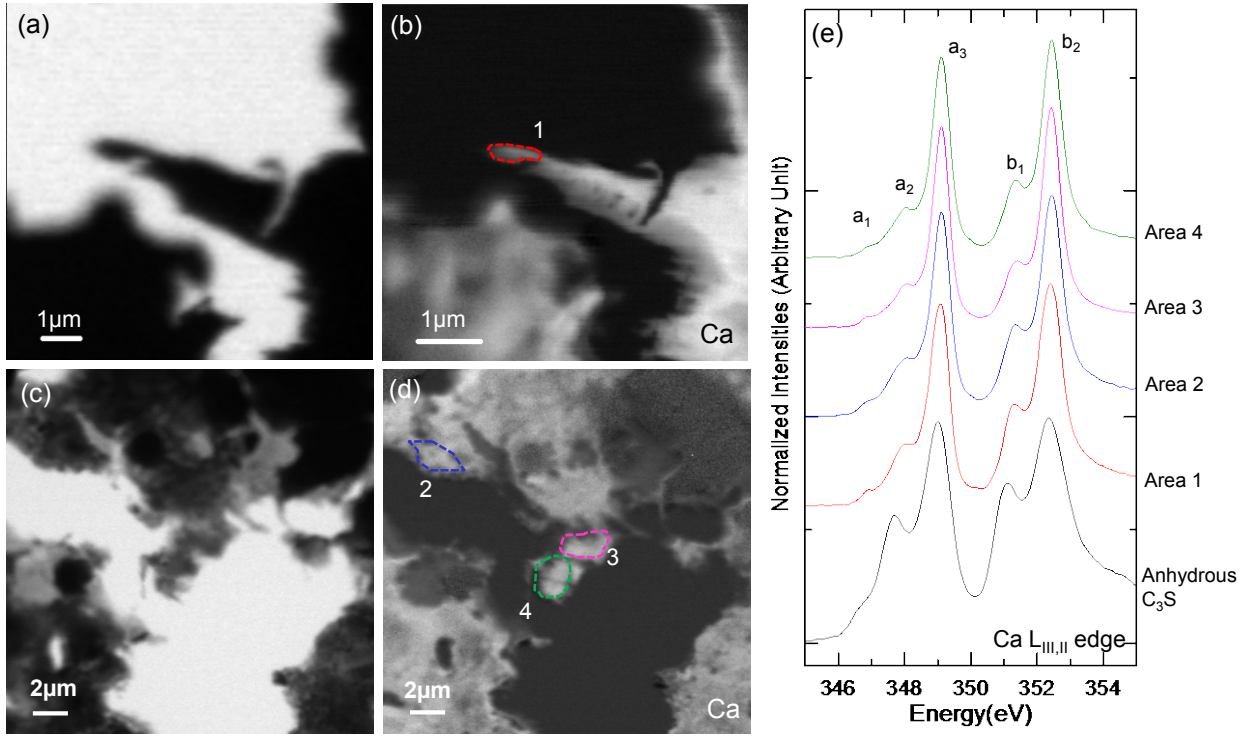


Figure 4.4 (a) Single image of C-28d taken at 349 eV (b) Ca image contrast map of C-28d (349eV - 340eV) (c) Single image of C-FA-28d taken at 340 eV (d) Ca image contrast map of C-FA-28d (349eV - 340eV) (e) Ca $L_{III,II}$ edge NEXAFS spectra of anhydrous C_3S extracted from ROI specified in (b) and (d).

As discussed in Chapter 2 and 3, Ca $L_{III, II}$ edge NEXAFS of calcium compounds including C-S-H consists of two main spin-orbit related peaks, $L_{III} 2P_{3/2}$ (a_3) and $L_{II} 2P_{1/2}$ (b_2), along with a number of smaller peaks, a_1 , a_2 , b_1 that precede the main peaks [98]. These multi-peak patterns are induced due to the crystal field, arising from the symmetry of the atoms surrounding the Ca cation in the first coordination sphere [50]. The peak positions and energy separation values are correlated to the symmetry of Ca and the magnitude of the crystal field parameter ($10Dq$) [50]. The values of the anhydrous C_3S , ROIs in C-28d and C-FA-28d are given in Table 4.1.

Table 4.1 Ca L edge peak positions and splitting energy

Samples	Area	Peak positions (eV)					Splitting of L _{III} and L _{II} (eV)	
		a ₁	a ₂	a ₃	b ₁	b ₂	$\Delta\text{Ca-L}_{\text{III}}(\text{a}_3\text{-a}_2)$	$\Delta\text{Ca-L}_{\text{II}}(\text{b}_2\text{-b}_1)$
Anhydrous C ₃ S		346.7	347.7	349	351.1	352.3	1.3	1.2
C-28d	Area 1	346.9	348	349.1	351.4	352.4	1.1	1
	Area 2	346.8	348	349.1	351.3	352.4	1.1	1.1
	Area 3	346.9	348	349.1	351.3	352.4	1.1	1.1
	Area 4	346.8	348	349.1	351.3	352.4	1.1	1.1

In Figure 4.4-(e), the absorption feature (peak intensity ratio) and peak positions of anhydrous C₃S differ from those areas in C-28d and C-FA-28d, implying that C-S-H formation by hydration process resulted in the change of Ca L_{III,II} edge NEXAFS. Based on peak intensity ratio and energy separation values, it can be demonstrated that anhydrous C₃S with triclinic crystal structure lose crystallinity in the dissolution process and transform to nearly-amorphous C-S-H in the precipitation process of C₃S hydration. While there were differences with regards to the Ca L_{III,II} edge NEXAFS between anhydrous C₃S and C-S-H formed in each sample, the hydration product in C-28d showed very similar peak positions compared to on in C-FA-28d; splitting energy values and absorption feature indicating no significant effect of additional silicate and Al substitution in HVFA on Ca L_{III,II} edge NEXAFS of the hydration products.

Figure 4.5 presents the single image, Si and Al image contrast map of C-28d and C-FA-28d. The brighter areas in the image contrast map indicates a high concentration of each element [23]. As discussed in Chapter 3, the morphology of the hydrated C₃S particle can be divided into anhydrous area, inner product (Ip) and outer product (Op) [36] and the Op plays an important role as a binder between phases in a PC system and it affects most to the mechanical and chemical properties. In Figure 4.5-(b), the hydrated C₃S particle in C-28d, containing no fly ash, had a core area and Si-rich Op layer which was brighter than the core area and the exact boundary between those areas was clearly resolved. The differences in Si concentration were induced by the different degrees of silicate polymerization since the Op layer reduces the hydration of the core area as observed in Chapter 3. It is worth noting that Op had a uniform Si concentration implying a similar degree with regards to silicate polymerization. In the Si and Al image contrast map of

C-FA-28d (Figure 4.5-(d) and (e)), fly ash particles had a high amount of Si and Al concentration as expected. Compared to C_3S particle in C-28d, the particles, assumed to be C_3S , showed very uniform Si concentration without any Op layers in the particles. To confirm the different degree of silicate polymerization between the core area and the Op of the C_3S particle in C-28d sample, the area indicated by dotted square that has clear Op layers and comparatively less thickness in Figure 4.5-(a)-1 was chosen for Si K edge NEXAFS analysis.

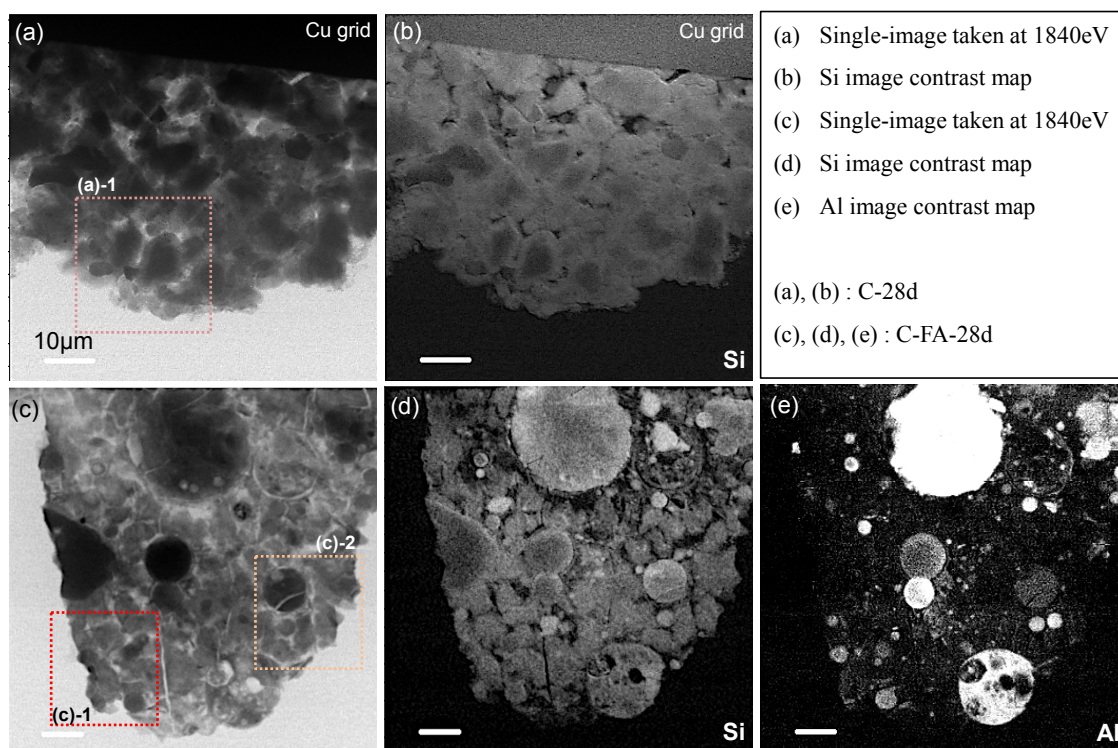


Figure 4.5 Single image, Si and Al image contrast map of C-28 and C-FA-28d samples. Brighter area in image contrast map ((b), (d) and (e)) contains higher amounts of each element. The dotted square areas with index in (a) and (c) were magnified and focused for NEXAFS analysis.

The results of the single imaging, Si image contrast map and Si K edge NEXAFS analysis of the selected area are shown in Figure 4.6. Si contrast image map was obtained by subtracting an image taken below the Si K edge from one taken above Si K edge [22, 23].

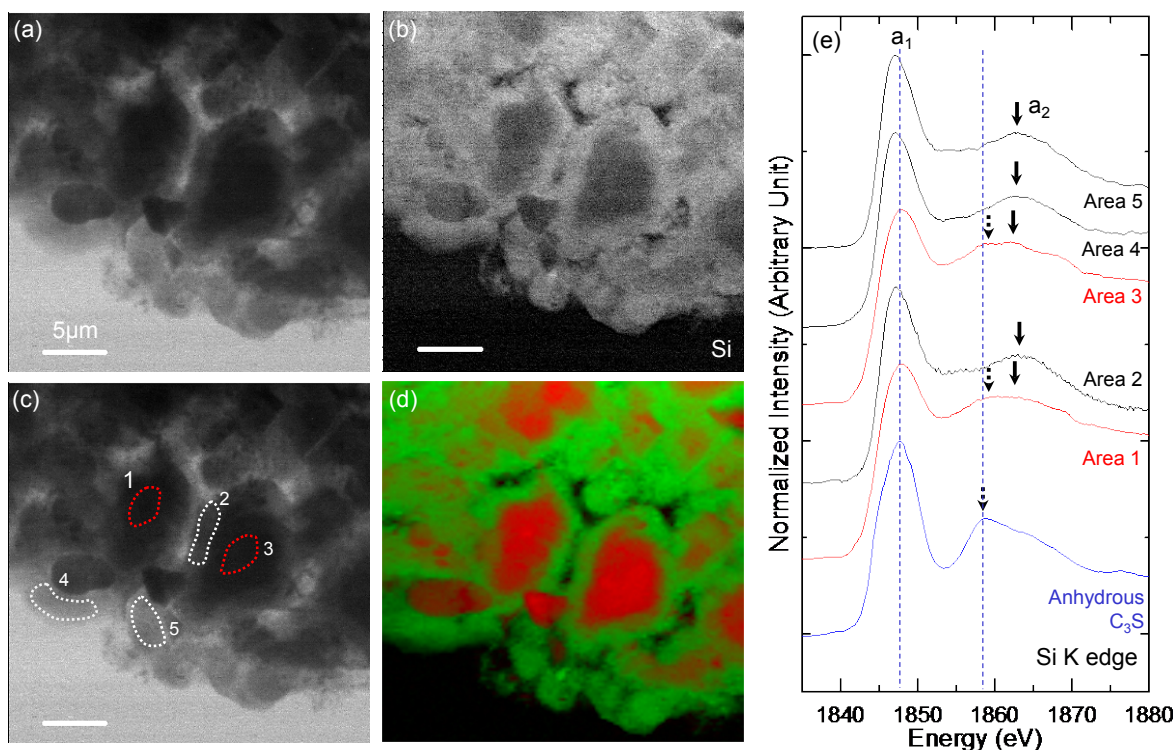


Figure 4.6 The results of single imaging, Si K edge NEXAFS spectra in selected areas and RGB mapping of C-28d (a) Single image taken at 1840eV, (b) Si image contrast map (c) Areas selected for Si NEXAFS analysis 1,3: core area, 2,4,5: Op layer.(d) RGB overlay maps conducted by using spectra obtained from Area 1 (appearing in red) and 2 (appearing in green) shown in (e)

In the Si contrast map (Figure 4.6-(b)), the Op layers of C₃S particle were clearly observed. The indicated areas in Figure 4.6-(c) were selected for Si NEXAFS analysis. Figure 4.6-(e) shows the Si K edge NEXAFS spectra of the selected areas in C-28d. Peak a₁, the main peak, is attributed to Si K edge induced by the electronic transition from Si 1s to the anti-bonding t₂ (3p-like state) orbital. Peak a₂ is assigned to the multiple scattering effects beyond the second coordination sphere [56]. In Chapter 3, it was observed that both peak positions shift to a higher energy level and the energy separation between the two peaks increases with the decrease of the Ca/Si ratio of synthesized C-S-H which implies that silicate polymerization increases the multiple scattering contribution from distant coordination shell atoms more than the binding energy of 1s core electrons in Si atoms. Furthermore, it was found that Op in 17 days hydrated C₃S particles has a higher Si K edge peak position and degree of silicate polymerization compared to the core area of the

particle.

The main peak (a_1) in the Op (areas 2, 4 and 5) present in C_3S of C-28d showed a comparatively lower energy position compared to that of anhydrous C_3S due to a dissolution process of C_3S as observed in Chapter 3. Moreover, the absorption features of peak a_1 in Op were sharper with smaller full width half maximum (FWHM). The core areas of C_3S particle (areas 1 and 3), on the other hand, showed a similar or higher peak position value than anhydrous C_3S . Furthermore, the absorption feature in peak a_1 of core areas was similar to one in anhydrous C_3S . Peak a_1 showed larger FWHM since the core area of C_3S would contain x-ray signals that penetrated both the Op and core regions of C_3S .

Peak a_2 in the Op (areas 2, 4 and 5) showed higher peak shift values (+3.6~4.1eV) compared to anhydrous C_3S . The peak a_2 has further shifted to a higher energy value compared to peak a_1 which implies that silicate polymerization increases the multiple scattering contribution from distant coordination shell atoms more than the binding energy of 1s core electrons in Si atoms. All the results obtained from C-28 were very consistent with one of 17days hydrated C_3S discussed in Chapter 3. Note that the core areas (area 1 and 3) contain two peaks in the region of peak a_2 with larger energy separation compared to anhydrous C_3S . Those two peaks of a_2 in the core area are assumed to be induced by both Op and anhydrous C_3S . The presence of anhydrous C_3S in the core area supports the fact that the uniform Op layer, which is generated at the early ages, reduces the hydration of C_3S in the core area. RGB overlay map by SVD was conducted to visualize the distribution of Op and the core area, by using NEXAFS spectra obtained from area 1 (core area) and Area 4 (Op). As shown in Figure 4.6-(d), Op layers formed around C_3S particles, which have uniform degree of silicate polymerization, were more clearly distinguished from core areas. RGB overlay mapping was proved to be very effective to differentiate the Op and core area in C-28d.

Figure 4.7 shows the results of single image, image contrast map of Si and Al, and Si K edge and Al K edge NEXAFS analysis of selected area of C-FA-28d (Figure 4.5-(c)-1). NEXAFS spectra (Figure 4.7-(e)) are obtained from the areas indicated in Figure 4.7-(a). As observed in the Si image contrast map in low magnification (Figure 4.5-(d)), Si concentration of C_3S particles in C-FA-28 is very uniform compared to C-28d and no clear Op layers around C_3S particles as observed in C-28d are found. Fly ash particles and the

hydrated C_3S particles were selected for Si and Al K edge NEXAFS analysis to confirm the degree of hydration of C_3S particles in C-FA system and to compare with those in the neat C_3S system. Based on the NEXAFS results, it is possible to determine the effect of additional silicate and alumina phases provided from fly ash particles in the system. For the selected areas for the Si and Al K edge NEXAFS analysis, the results are shown in Figure 4.7-(a), (e) and (f), respectively.

The absorption features of hydrated C_3S (Areas 1, 2, 3 and 4) are very similar to those of FA obtained from the selected area in the fly ash particles and Op of C-28d (Figure 4.6-(e)). The peak a_1 in these areas shows lower values (0.6 ~ 0.9eV) than for anhydrous C_3S . Moreover, comparing with the Op of C_3S in C-28d (Area 5 in Figure 4.6-(c)), the positions of peak a_1 in the selected areas of C-FA-28d show lower peak position values (0 ~ 0.3eV). Positions of peak a_2 in the areas of hydrated C_3S in C-FA-28d are higher (0.2 ~ 1.2eV) than those obtained in the Op of C_3S in C-28d.

Unlike for sample C-28d, no peak a_2 from anhydrous C_3S (1858.9eV) are present which implies that the C_3S particles in C-FA-28d have a higher degree of silicate polymerization and the entire area of each particle has a uniform degree of hydration. In addition, Al K edge NEXAFS analysis indicates that the hydrated C_3S areas in C-FA-28d contain comparatively lower intensity of Al compared to FA. The presence of Al in hydrated C_3S in sample C-FA-28d is assumed to be due to Al supplied from fly ash particles. RGB overlay map by using NEXAFS spectra obtained from fly ash and Area 2 are shown in Figure 4.7-(d). It is proved that hydrated C_3S with uniform degree of silicate polymerization are distributed in C-FA-28d which is consistent with the results of NEXAFS analysis.

The other area in C-FA-28d was selected for each analysis and the results are shown in Figure 4.8. All results were very consistent with those of the previous selected area shown in Figure 4.7.

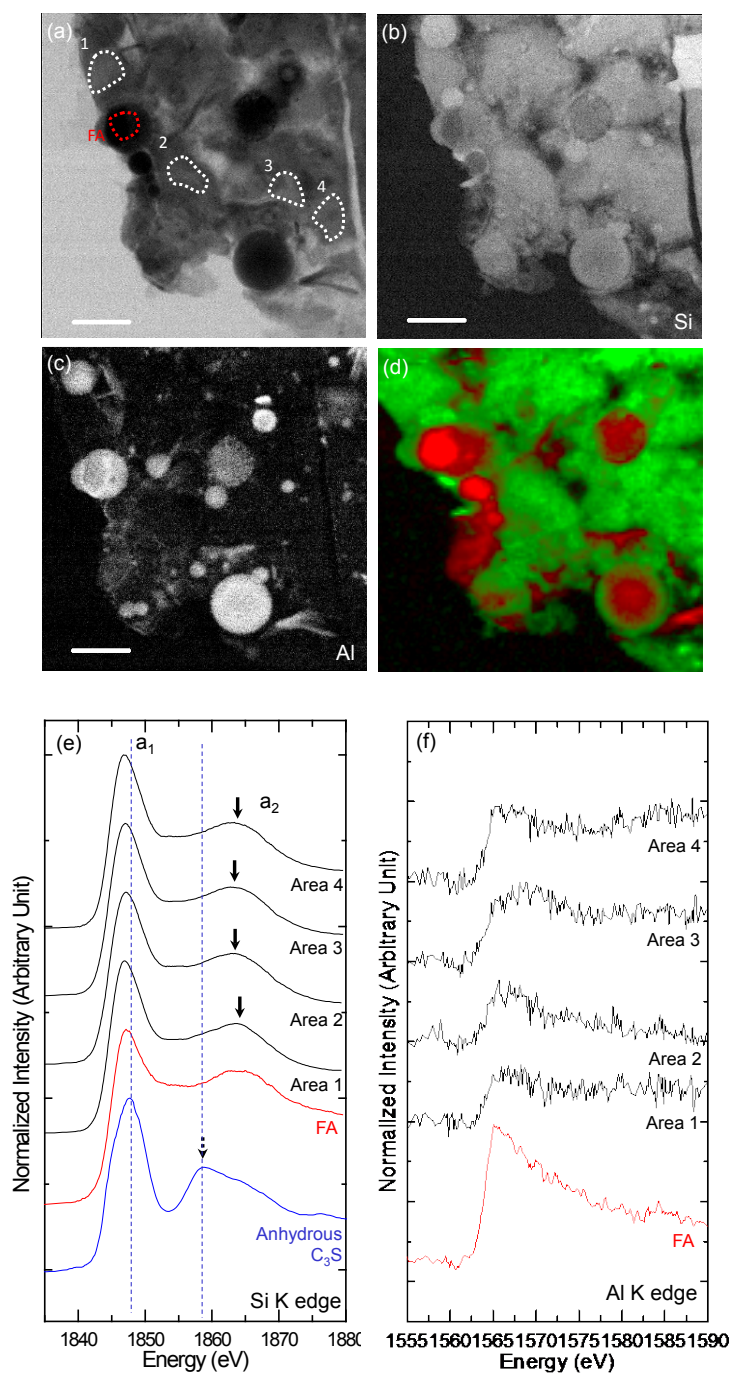


Figure 4.7 The results of single imaging, Si K edge NEXAFS spectra in selected areas and RGB mapping of C-FA-28d (a) Single image taken at 1840eV, (b) Si image contrast map (c) Areas selected for Si NEXAFS analysis FA: fly ash (d) RGB overlay maps conducted by using spectra obtained from FA (red) and Area 2 (green) shown in (e)

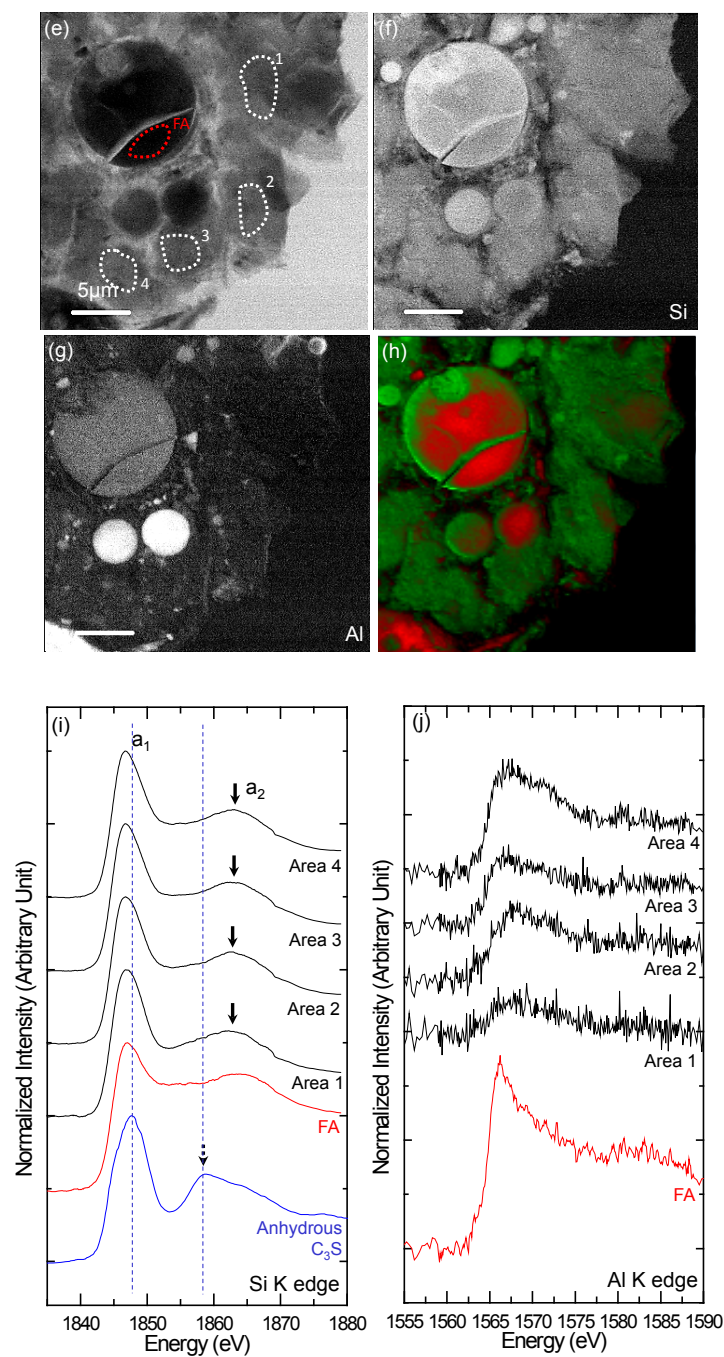


Figure 4.8 The results of single imaging, Si K edge NEXAFS spectra in selected areas and RGB mapping of C-FA-28d (a) Single image taken at 1840eV, (b) Si image contrast map (c) Areas selected for Si NEXAFS analysis FA: fly ash (d) RGB overlay maps conducted by using spectra obtained from FA (red) and Area 2 (green) shown in (e).

Hydrated C_3S (Area 1, 2, 3 and 4) showed very similar absorption features compared to FA and peak a_1 in the areas showed lower value than one of anhydrous C_3S and Op of C_3S (Area 5 in -(c)). Positions of peak a_2 in the areas of hydrated C_3S were higher (0.2 ~ 0.9eV) than in the Op of C_3S and presence of anhydrous C_3S in peak a_2 was not observed. All measured peak positions (a_1 and a_2) and energy separation values (a_2-a_1), measured in the selected area for C-28 and C-FA-28d, are organized in Table 4.2 and plotted in Figure 4.9.

Table 4.2 Si K edge peak positions and energy separation values

Samples	Areas	Peak a_1 (eV)	Peak a_2 (eV)	$\Delta Si-K(a_2-a_1)$ (eV)
Anhydrous C_3S		1847.7	1858.9	11.2
C-28d	Area 1	1848.1	1860.4	12.3
	Area 2	1847.2	1863.0	15.8
	Area 3	1847.8	1859, 1862.1	11.1, 14.3
	Area 4	1847.1	1862.6	15.5
	Area 5	1847.1	1862.5	15.4
C-FA-28d-1	FA	1847.1	1865	17.9
	Area 1	1846.9	1863.7	16.8
	Area 2	1847.1	1862.7	15.6
	Area 3	1847	1862.7	15.7
	Area 4	1846.8	1863.3	16.5
C-FA-28d-2	FA	1846.9	1863.3	16.4
	Area 1	1847.0	1863.4	16.4
	Area 2	1846.8	1862.7	15.9
	Area 3	1846.7	1862.7	16
	Area 4	1846.7	1863.1	16.4

The Op of hydrated C_3S in C-28d showed lower peak a_1 and higher peak a_2 values compared to anhydrous C_3S . Furthermore, the core area contains anhydrous C_3S and hydration product with lower degrees of hydration. In addition, the energy separation between those peaks increased from core to outer products. On the other hand, hydrated C_3S in C-FA-28d showed very uniform peak position values and lower peak a_1 and higher peak a_2 values compared to Op of C_3S in C-28d. Relatively lower peak a_1 values could be due to Al substitution for Si in hydration products of C_3S . Moreover, higher peak a_2 value is

assumed to be due to higher degrees of silicate polymerization induced by additional silicate provided from abundant fly ash in the HVFA system. Furthermore, the higher effective w/c ratio for HVFA system could be one possible reason for the enhanced hydration of the cement phases in HVFA pastes [113]. More details on the morphology of hydration products, and Al substitution for Si and silicate polymerization in HVFA systems were determined by TEM and NMR analysis.

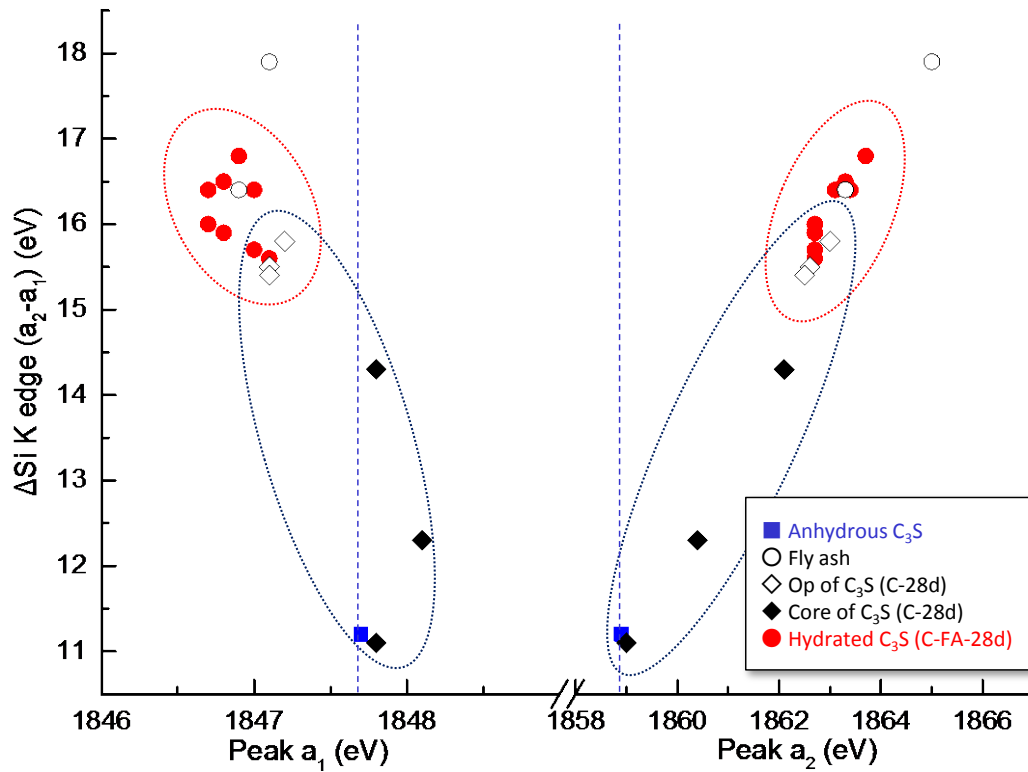


Figure 4.9 Relationship between peak positions (a_1 and a_2) and energy separation values (a_2-a_1) in the selected area of C-28 and C-FA-28d

4.3.3 ^{27}Al MAS NMR analysis

^{27}Al MAS NMR spectroscopy has disadvantages in that the spectra can be difficult to interpret, due to ^{27}Al being effected by quadrupolar interactions, which leads to a field-dependent shift in resonance position and a broadening of the peaks [124]. Unlike ^{29}Si MAS NMR where high quality spectra require a large amount of acquisition time, ^{27}Al has a spin nuclei of $I=5/2$, and a natural abundance of 99.99%, which makes the acquisition time for the spectrum far less than that of silicon. This means even with limits on duration being imposed good quality spectra can still be obtained.

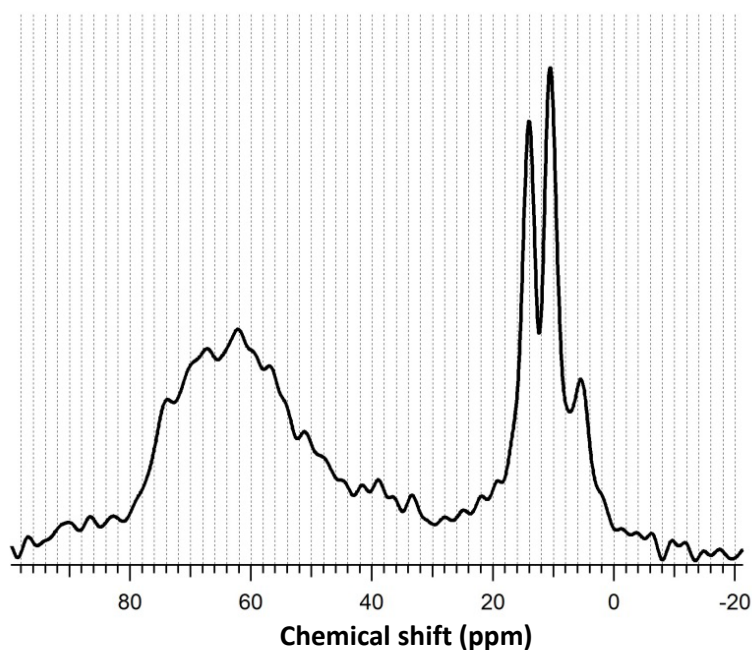


Figure 4.10 ^{27}Al NMR of C-FA-28d

In the work performed before with this equipment it has been reported that a large aluminum background exists in the probe [125]. For this reason a rotor containing only C_3S , which should have no aluminum signal, was run using the same acquisition set-up as the other samples. The principle here was that any signal obtained would be the relevant background signal and could be removed. However, it was found that no signal was present and as such no background removal was necessary.

MAS NMR has become very useful in cement research, as Al^{3+} is a common guest ion in cement clinker and as such is incorporated in to the C-S-H structure. The technique is

used to differentiate tetrahedral (Al^{IV}) and octahedral (Al^{VI}) coordination with their different ^{27}Al isotropic chemical shifts; Al^{IV} being in the range of 100-50 ppm and Al^{VI} in the 20-10 ppm range [126]. The first work performed on this subject showed a single peak for that of alite, corresponding to Al^{IV} . This demonstrated that the guest ions of aluminum in alite will substitute for tetrahedral rather than octahedral coordinated silicon. The same study performed on belite also showed a peak in the same range attributed to Al^{IV} ; however, it also had a peak at 10 ppm, in the range of Al^{VI} coordination. As the structure of belite does not have the vacancies for octahedral Ca this peak was assigned to unrelated aluminate phases. The quadrupolar nucleus of ^{27}Al means spectra tend to be characterized by broad peaks, but also that quadrupolar coupling parameters can help to identify structurally different aluminum sites [127]. Skibsted et al., [126, 128, 129] further developed the work of Muller et al., on monitoring the hydration of aluminate cements and applied ^{27}Al NMR spectroscopy to the study of the calcium aluminate phases in cements. It was found that the peaks were often very broad and overlapping, but it still could be determined that peaks for Al^{VI} in AFt were found at around 13ppm and AFm around 8ppm in hydrated pastes, along with a tetrahedral peak for aluminium in C-S-H at around 66ppm.

In this research, several sharp aluminium environments were present, in the octahedrally coordinated range, between 0 and 20 ppm. The three distinguishable peaks have been attributed to: AFt phase at $\approx 14\text{ppm}$ [124, 130], AFm at $\approx 10.5\text{ppm}$ [127] and a third peak at $\approx 5.6\text{ppm}$. Chemical shifts of $\approx 9\text{ ppm}$ have been reported in studies for hydrotalcite-type phases [131-133] and for monosulfate [134]. The peak at 9ppm is thought to be a convolution of resonances from an AFm phase [127] and a Mg-Al LDH phase [132], as NMR alone cannot determine which it is or in what ratio appears. The peak at $\approx 4\text{ppm}$ could be due to the presence of one of two compounds. The first is the third aluminates hydrate (TAH) phase, observed in the range of 3-5 ppm [134]. A third octahedral peak has been previously observed in hardened PC pastes, which could not be assigned to any of the well-known aluminate species [135]. This study also showed a peak around 40 ppm, attributed to Al^{IV} [130], which has previously been observed in water activated samples contacting fly ash [136]. Tetrahedrally coordinated aluminium is generally observed in the range of 50 to 80 ppm as can be seen here. The broad peak overlaps and almost hides the 40 ppm peak, showing a highly discordant Al environment. This signal includes Al in anhydrous material, as well as Al in the C-S-H, substituting into bridging sites for Si ions.

4.3.4 ^{29}Si MAS NMR analysis

The ^{29}Si MAS NMR results for anhydrous C_3S , C-28d, and C-FA-28d are shown in Figure 4.11. The NMR spectrum of anhydrous C_3S has a number of resonances in the range of -68 to -76 ppm all with chemical shifts typical of an orthosilicate (Q^0) [137, 138], and the multiple resonances are due to a number of isolated silicate anion environments [138].

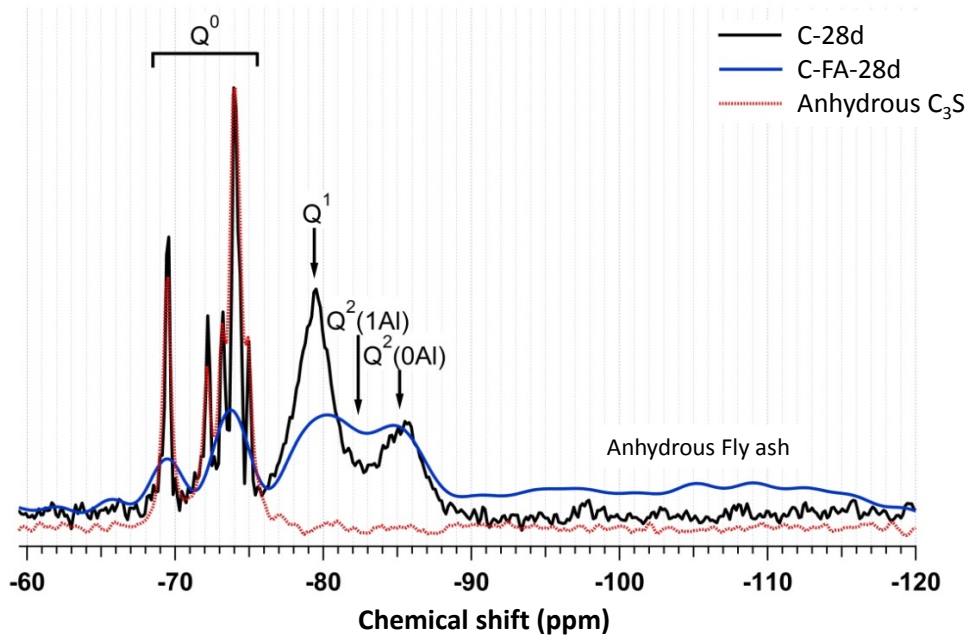


Figure 4.11 ^{29}Si NMR of anhydrous C_3S , C-28d, and C-FA-28d pastes.

The spectrum in C-28d has peaks in the range of -79 and -86 ppm in addition to peak induced by Q^0 , and these peaks are due respectively to chain end- (Q^1) and middle-chain ($\text{Q}^2(0\text{Al})$) unit present in C-S-H occurring in C_3S hydration [92, 137]. Comparing the C-FA-28d blend with hydrated C-28d, the first noticeable effect of the addition of fly ash is the lack of order in the blended paste which implies reduction of anhydrous C_3S . Recall that the reduction of the anhydrous core region of C_3S in C-FA-28d is also confirmed by STXM analysis. The spectrum is evident for the far broader, overlapping peaks. There is now also the introduction of a third hydrate peak at around -82 ppm attributed to $\text{Q}^2(1\text{Al})$; the exact peak position is difficult to read from the spectra due to the breadth of the peaks and overlapping. However, it can be assumed that the peak is $\text{Q}^2(1\text{Al})$ which most commonly lies around -82 ppm and indicates Al substituting for Si in the bridging tetrahedra. The C-FA-28d spectrum also shows an expected peak at -109 ppm

designating a three-dimensional frame work (Q^4) of the anhydrous fly ash, confirming that the fly ash is not fully reacted at 28 days due to low reactivity. The C-FA-28d spectrum also showed a peak at around -95 ppm, which is indicative of chain branching sites (Q^3), arising from either a continuous range of $Q^n(mAl)_4$ species in the glassy phase of the fly ash [139] or a carbonation of the C-S-H phase. As thermogravimetric analysis results show carbonation in the C-FA-28d paste, it has been assumed in this study that the -95 ppm peak is Q^3 rather than Q^4 with Al substitution, which would result in a downward shift of a peak.

As C_3S does not have the Voigt shape, characteristic of the hydrated peaks, it is not possible to perform simultaneous fitting. There are methods for fitting the C_3S peaks to quantify the amount of C_3S from NMR data using a number of Gaussian and/or Lorentzian shaped peaks. However, the chemical shifts for this method remain unpublished and as such an alternative method has been used [140, 141]. For this reason all peaks below -75 ppm, being anhydrous C_3S have been excluded from peak fitting and only calculations not involving anhydrous data have been performed.

The polymerization of the silicate probably occurred through the addition of monomer to form linkages between dimeric groups, which were thereby converted into pentamer, octamer and longer chains in the ($m=3n-1$, m :chain length and n : integer) series [24, 32]. Contents of Q^1 and Q^2 and maximum mean chain length

The deconvoluted ^{29}Si NMR spectra for the fitting of C-28d and C-FA-28d are presented in Figure 4.12 and Figure 4.13, respectively. Based on the relative intensity of each peak by deconvoluting each spectrum shown in Table 4.3, the silicate chain length and Al/Si ratio in C-28d and C-FA-28d are calculated using Eq-2.3, Eq-2.3 and Eq-2.4. While C-28d shows the average chain length of 2.54 which is consistent with the results that 50 to 70% hydrated C_3S has a mean chain length of 2.4 to 2.6 [142], C-FA-28d show 4 times longer average chain length (10.27) compared to C-28d confirming the silicate polymerization expected to occur in the HVFA system. Using the Al/Si ratio which is 0.257, it can be assumed that the chain length in C-FA-28d is most likely undecamer ($m=11$), and Al is substituted for Si in at least two of the three of bridging tetrahedral in undecamer ($Al/Si=0.22$).

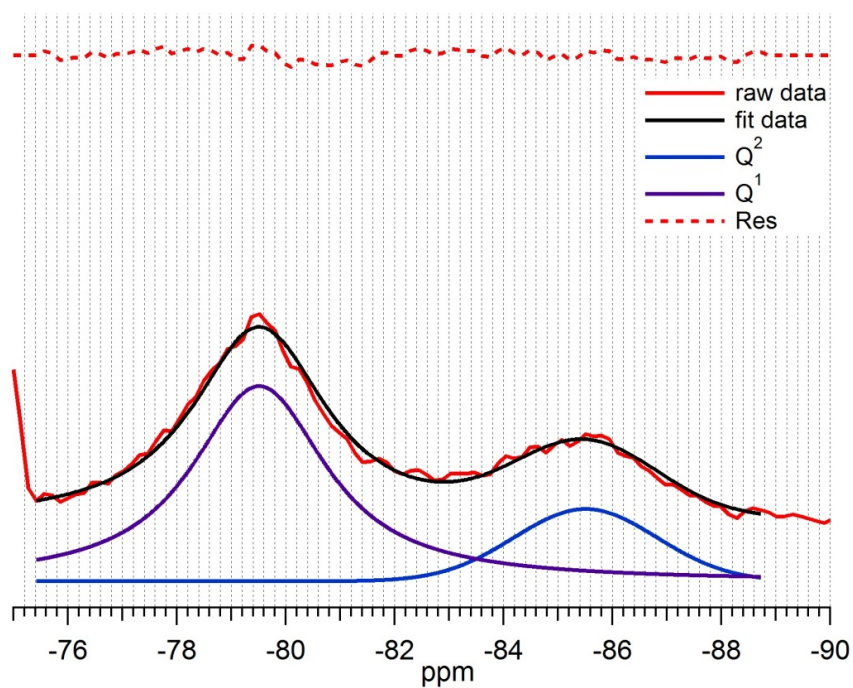


Figure 4.12 ^{29}Si NMR deconvolution for C-28d (-75 to -90 ppm).

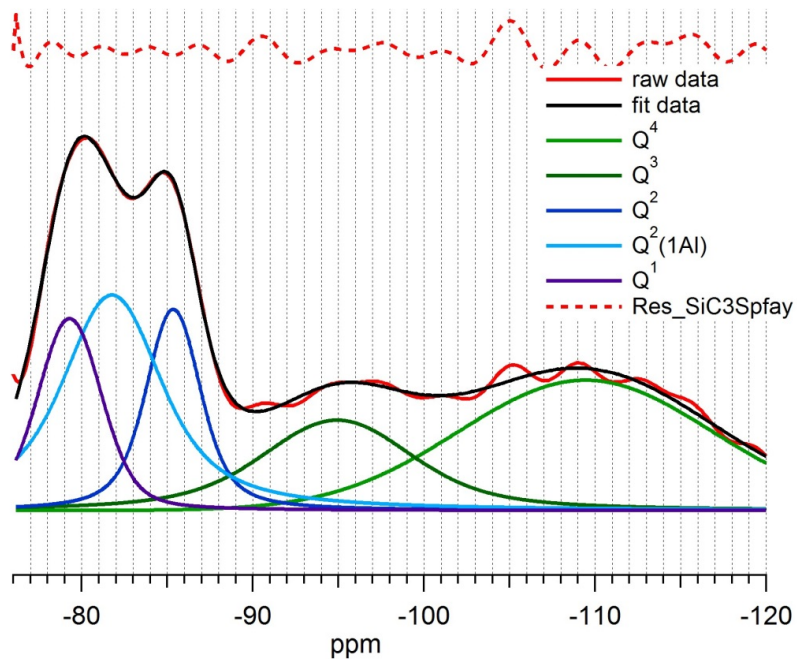


Figure 4.13 ^{29}Si NMR deconvolution for C-FA-28d (-75 to -120 ppm).

Table 4.3 Deconvolution results of both C-28d and C-FA-28d

Sample	Peak	Shift	Intensity (%)	MCL	%B	Al/Si
C-28d	Q ¹	-79.51	78.9	2.54	-	-
	Q ² (1Al)	-	-			
	Q ²	-85.51	21.1			
C-FA-28d	Q ¹	-79.30	12.95	10.27	76.3	0.257
	Q ² (1Al)	-81.77	27.20			
	Q ²	-85.35	12.69			
	Q ³	-94.93	15.88			
	Q ⁴	-109.45	31.29			

4.3.5 Morphologic imaging of C-FA-28d paste using TEM

TEM images of Op in hydrated C₃S observed in C-FA-28d are shown in Figure 4.14, Figure 4.15, and Figure 4.16. The images show the fully reacted particles, fine Op and coarse Op in hydrated C₃S particles. As we expected based on STXM and NMR results, no anhydrous C₃S was observed in the images. Fine C-S-H, large Ca(OH)₂ crystals intermixed with the C-S-H, nano Ca(OH)₂ crystals intermixed with C-S-H, and some small fully reacted grains were observed as shown in Figure 4.17. The presence of intermixed nano Ca(OH)₂ with C-S-H was confirmed using selected area electron diffraction (SAED) (see Figure 4.17-(b)).

The limited EDX chemical analysis was performed on the sample at rough calculation gives a Ca/Si ratio of 1.13, and Al/Si ratio of 0.22 and Mg/Ca ratio of 0.096 and S/Ca ratio of 0.004. Ca/Si ratio 1.13 is much lower than the Op of hydrated pure C₃S which is in the range of 1.5 to 1.9 [24, 93, 143]. These values indicate intermixing of many phases such as Ca(OH)₂, AFm, Aft, and the possible tricalcium aluminate hydrate (TAH) phases as suggested in ²⁷Al MAS NMR results.

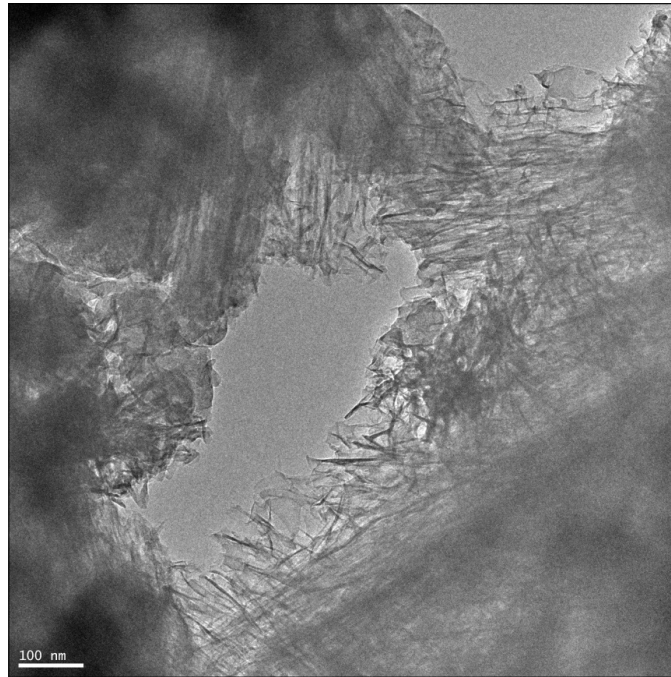


Figure 4.14 TEM image of Op C-S-H in C_3S of C-FA-28d paste. (Scale bar=100 nm)

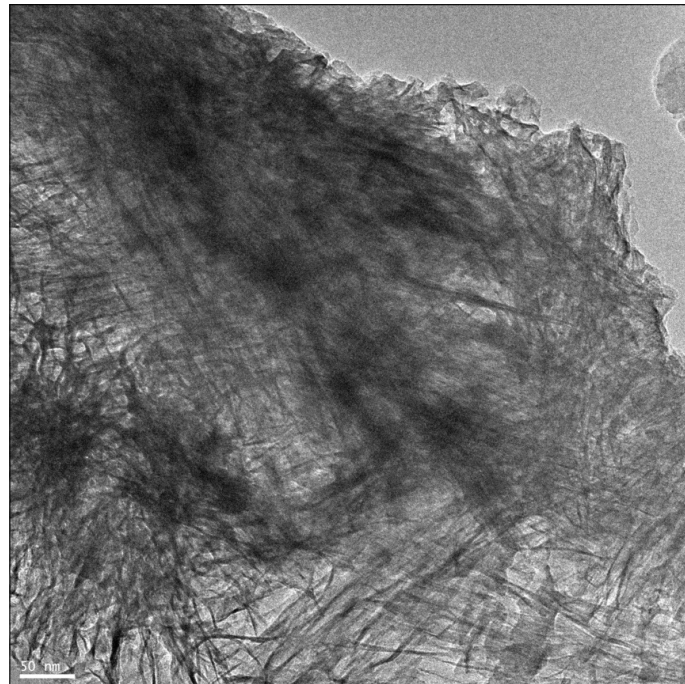


Figure 4.15 TEM image of Op C-S-H in C_3S of C-FA-28d paste. TEM image showing fully reacted particles, fine outer product C-S-H and coarse Op. (Scale bar=50 nm)

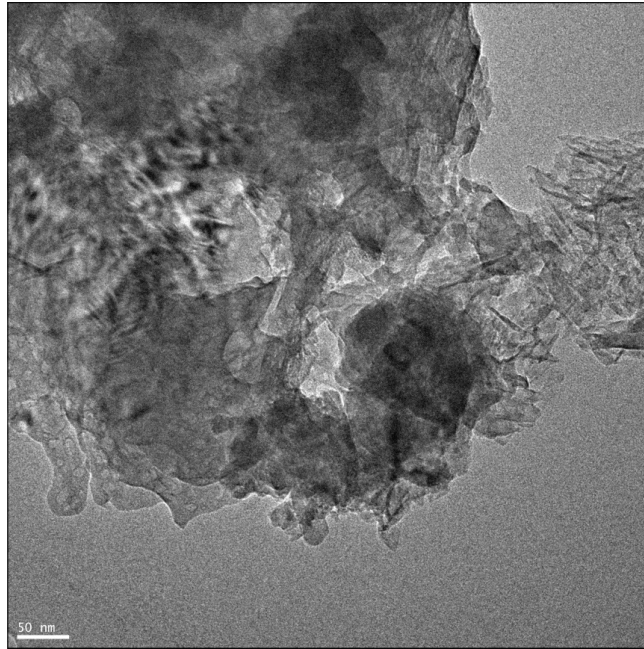


Figure 4.16 TEM image of Op C-S-H in C_3S of C-FA-28d paste. TEM micrograph showing large CH crystal intermixed with C-S-H. (Scale bar=50 nm)

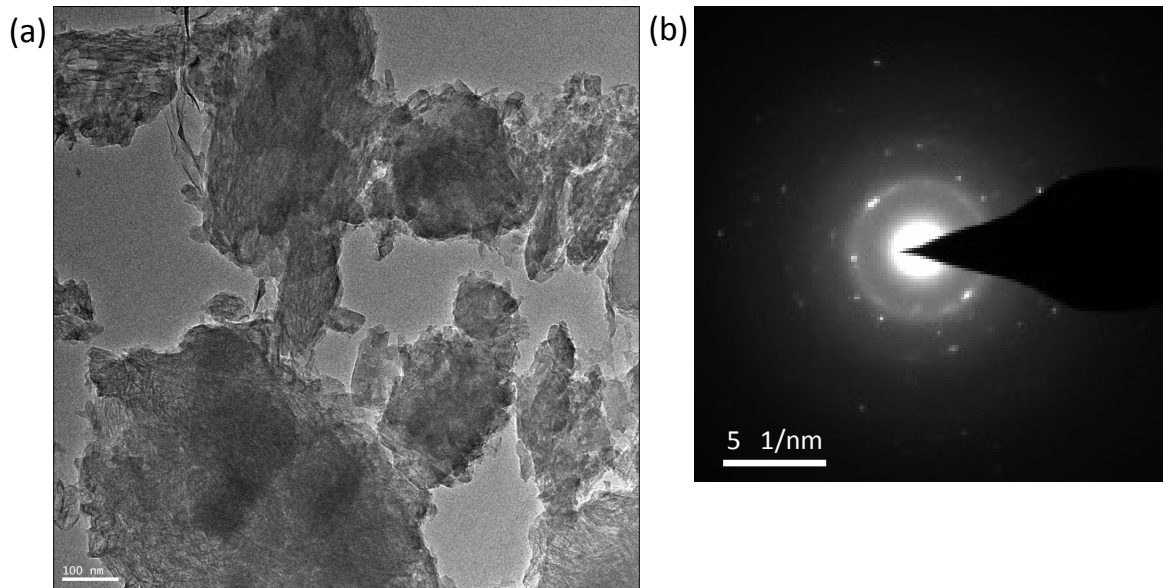


Figure 4.17 (a) TEM image of Op C-S-H in C_3S of C-FA-28d paste. (b) Selected area diffraction (SAD) image pattern of $Ca(OH)_2$. TEM images showing fine outer product C-S-H; the SAD image of the sample shows a crystalline phase present assumed to be nanocrystalline $Ca(OH)_2$ intermixed with the C-S-H phase.

4.4 Conclusions

This chapter studied the effect of HVFA on pure triclinic C_3S hydration in terms of hydration products, morphology, chemical composition and atomic structure of C-S-H using STXM, synchrotron powder XRD and thermogravimetric analysis, and NMR. Obtained results are summarized below.

XRD found that C-FA samples show lower intensity of $Ca(OH)_2$, compared to sample C, due to dilution of C_3S substituted by FA. Peak intensity of $Ca(OH)_2$ in sample C increases up to 28days, however, in C-FA, the peak intensity of $Ca(OH)_2$ decreases from 7 days to 28days due to the pozzolanic reaction by consumption of $Ca(OH)_2$. In addition, TGA/DTA analysis also confirmed $Ca(OH)_2$ consumption.

STXM results showed that Si concentration in the C_3S particles present in sample C-FA-28 was very uniform compared to C-28d and no clear Op layers around C_3S particles, as observed in C-28d, were found. Hydrated C_3S in C-FA-28d show very uniform peak position values and further lower peak a_1 and higher peak a_2 values in Si K edge NEXAFS compared to Op of C_3S in C-28d. Relatively lower peak a_1 value could be due to Al substitution for Si in hydration products of C_3S , and the higher peak a_2 value was assumed to be due to a higher degree of silicate polymerization induced by additional silicate provided from abundant fly ash in the HVFA system.

^{29}Si MAS NMR analysis proved that C-FA-28d show four times longer average chain length compared to C-28d confirming the silicate polymerization expected to occur in the HVFA system, and it was also found that the silicate chain in C-FA-28d is most likely undecamer. Al is substituted for Si in at least two of three of bridging tetrahedral in undecamer.

TEM-EDX analysis showed the fully reacted particles, fine Op and coarse Op exist in C-FA-28d. No anhydrous C_3S were observed in the images of C-FA-28d which is consistent with STXM and NMR results. Fine C-S-H, large $Ca(OH)_2$ crystals intermixed with the C-S-H nano $Ca(OH)_2$ crystals intermixed with C-S-H and some small fully reacted grains were observed in C-FA-28d.

CHAPTER 5

**CHARACTERIZATION OF MORPHOLOGY AND HYDRATION
PRODUCTS OF HIGH-VOLUME FLY ASH PASTES BY
MONOCHROMATIC SCANNING X-RAY MICRO-DIFFRACTION**

5.1 Introduction

The use of supplementary cementitious materials (SCMs), such as fly ash, granulated blast-furnace slag, rice husk ash, or metakaolin as substitution for portland cement (PC) is a widely accepted practice: it produces durable concrete and the resulting cementitious materials have a lower carbon footprint. Fly ash, a popular, low-cost SCM generated during combustion of coal for energy production, has been used as mineral admixture in concrete for many decades. Although class F fly ash possesses little to no cementitious value, when used as a SCM in PC concrete, the highly amorphous silica and alumina rich ash reacts with the portlandite $[\text{Ca}(\text{OH})_2]$ and water in the cement matrix to form additional calcium-silicate-hydrate (C-S-H) and calcium-aluminate-silicate hydrate (C-A-S-H) phases through a pozzolanic reaction [113, 144]. Enhanced mechanical properties and chemical resistance of concretes with fly ash have been the topics of many studies [6-8, 10-12]. When the gained expertise on utilization of fly ash is combined with the increased environmental awareness and economical advantages, fly ash consumption by the concrete sector is expected to rise [13].

Currently, the global availability of fly ash is around 800 million metric tons annually [111]. Considering the significant increase in the use of coal for power production in China and India since 2004, the global availability of fly ash is predicted to increase. In 2010, the U.S. fly ash production was around 68 million tons annually, of which 62% was being dumped into landfill sites and the ocean. Only the remaining 38% was utilized in a variety of applications, including pozzolanic cement and concrete production [145]. Unfortunately the European Union (EU 15) shows similar numbers, whereby in 2008, Europe (EU 15) generated 40 million tons of coal fly ash, but the re-utilization rate was only 45% [146]; the remaining ash was treated as a waste product. Fly ash contains large levels of leachable toxic trace elements (e.g. As, Cd, Cu, Hg, Ni, Pb, B and Zn, etc.) so the un-recycled excess fly ash may contaminate soils, ocean, and water reservoirs, presenting a severe threat to human health and ecosystems.

Traditionally, fly ash substitution in structural concrete is limited to 15-25 wt% [113]. Within the last decade, concretes containing more than 50% fly ash by mass of the cementitious material -- referred as high-volume fly ash (HVFA) concretes -- have been successfully used in various projects [5]. Re-utilizing fly ash in HVFA concrete allows efficient consumption of considerable amounts of fly ash at a low cost that significantly

reduces the PC usage in concrete. In addition, the greener HVFA concrete has technical advantages over a portland cement concrete with similar 28-day strength. Among those are the higher long-term strength and modulus of elasticity, lower drying shrinkage and creep, and excellent durability [6-9]. An excellent choice for mass concrete applications, HVFA concrete is characterized by its enhanced workability, reduced bleeding, and lower evolution of heat of hydration. The main shortcoming of HVFA concrete has been the slow rate of the pozzolanic reaction which may result in lower early-age strength [9]; however this can be overcome through a careful design of the concrete mixture. Although a number of studies concerning HVFA concrete have been conducted, and mainly focused on mechanical properties (e.g., early and long-term strength, corrosion resistivity, durability, rheological behavior, etc.) [9, 14-16], studies on the structure of the HVFA concrete on micro- or nano-scale and on the formed hydration products in the concrete matrix are limited [17-19].

Previous research has shown that the reaction products of the alkali-activated slag systems contain C-S-H(I) which has lower Ca/Si ratio and that C-S-H(I) is produced in alkali-activated class C fly ash systems [34]. In a hardened PC matrix, the Ca/Si of the C-S-H ranges from 1.2 to 2.1 with a mean value around 1.75 [147]. However, in HVFA systems, additional C-S-H and C-A-S-H gels formed slowly through the pozzolanic reactions between the amorphous aluminosilicate rich ash and portlandite. The newly formed gel tends to have a lower Ca/Si due to increased silica content of the overall system by polymerization of SiO_4 tetrahedra. Due to the low Ca/Si ratio, it is possible that the additional C-S-H from the pozzolanic reaction products in the HVFA paste might have a similar C-S-H(I) structure as in alkali-activated slag and class C fly ash systems. This remains undetermined, however, as the characteristics of the C-S-H in HVFA systems has not yet been fully investigated.

In the previous chapters, the focus was laid on C_3S system with and without HVFA. The present chapter examines the C-S-H and hydration products formed in PC / HVFA paste which is more close to real system. X-ray diffraction (XRD) using monochromatic synchrotron scanning x-ray micro-diffraction ($\mu\text{-SXR}$ D) was performed and the results are compared with those of laboratory based and synchrotron powder XRD methods. Elemental mapping via x-ray micro-fluorescence ($\mu\text{-XRF}$) is used to identify the cement matrix where C-S-H is present. This technique provided a differentiation between fly ash and the cement

matrix. . Based on μ -SXRD data, mapping of main phases existing in PC / HVFA paste was also conducted. Scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS) was used for imaging and obtaining elementary compositions of the hydration products in PC / HVFA system on a micro-scale. These results allow a better visualization of the microstructure of the PC / HVFA paste system, thus providing a deeper understanding of the formed hydration products and facilitating the understanding on the mechanical behavior of HVFA concrete. Such understanding can contribute to the practical application of HVFA concrete in the field.

5.2 Experimental procedure

5.2.1 Materials and sample preparation

Table 5.1 lists the oxide compositions of ASTM cement Type I/II (PC) and class F fly ash (FA) used in this study. To identify the main crystalline phases in the raw materials, standard laboratory-based bulk powder XRD measurements were conducted.

Table 5.1 Oxide compositions of the raw materials

Oxide Compositions (weight %)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	MnO	L.O.I.
PC : Type I/II Cement	20.44	3.97	4.07	62.90	2.42	0.37	0.43	0.16	0.23	0.32	4.69
FA : Class F Fly Ash	62.00	18.90	4.90	5.98	1.99	2.41	1.14	0.26	1.09	0.04	1.30

Four different PC-FA pastes were prepared by hand-mixing the raw materials with distilled water. Weight ratios of PC to FA within the pastes were as follow: 100:0, 80:20, 50:50, and 20:80; the pastes were labeled as PC100FA0, PC80FA20, PC50FA50, and PC20FA80 respectively. For all samples, water-to-binder ratios were kept constant at 0.4 (g/g). The hand-mixed pastes were cast into cylindrical molds measuring $\phi 2.54\text{cm} \times 2.54\text{cm}$ and cured at $23 \pm 1^\circ\text{C}$ with 100% relative humidity for six months. The 6-months old pastes were treated with acetone to suspend the hydration process and kept under the vacuum-drying, in carbonation-free conditions until testing.

For the μ -SXRD and the SEM with EDS measurements, thin sectioned samples ($\sim 200\mu\text{m}$ thick slices) of the hardened pastes were prepared with a diamond wafering blade saw followed by mechanical grinding and polishing. During these procedures, kerosene was used instead of water to avoid any further hydration of the samples. For the SEM measurements, a 20 nm-thick carbon coat was applied to the polished samples in a vacuum coating machine to prevent charging during microscopic investigations.

5.2.2 Characterization methods

Three different types of x-ray diffractometers were used to identify the hydration products in the samples:

(a) standard laboratory-based bulk powder XRD, PANalytical X'Pert Pro diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$);

(b) beamline 12.2.2 of Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory (LBNL) which used a monochromatic synchrotron x-ray beam ($\lambda=0.6199 \text{ \AA}$) that focused on a spot size of $10 \times 10 \mu\text{m}$. LaB_6 powder diffraction standard was used to calibrate the working distance between the sample and diffraction detector. Diffraction patterns were collected using a MAR345 image plate (3450×3450 pixels). The obtained 2-dimensional raw data were converted into 1-dimensional intensity versus 2-theta scans using Fit2D [117].; and

(c) μ -SXRD experiments carried out at beamline 12.3.2 of ALS (LBNL). The μ -SXRD is a tool based at synchrotron facilities capable of phase identification and characterization of materials at the micron- and submicron-scale. The μ -SXRD can measure local variations in orientation, elastic strain, and plastic deformation between grains and within individual grains, enabling understanding of mechanical properties at this critical length scale. In addition, because local characteristics such as texture and elastic strain within individual devices can be measured, the μ -SXRD offers an experimental counterpart to computer simulations [76]. More details on the instrument are described in chapter 2

In general, PC-based systems are highly complex and heterogeneous making spatially resolved characterization a challenge. Using monochromatic μ -SXRD in transmission mode on non-destroyed thin sectioned samples (thickness $\sim 200\mu\text{m}$) allows for identification of small amounts of phases embedded in a heterogeneous matrix [148]. The

beamline 12.3.3 has capabilities of operating under polychromatic (5-22 keV) or monochromatic radiation. Monochromatic mode (beamsize~ $2 \times 20 \mu\text{m}$) is preferred for samples with an average grain size much smaller than the beam[77]. Utilizing monochromatic beam results in standard powder diffraction patterns (Debye-Scherrer rings). This study focused on nanocrystalline C-S-H; therefore, the μ -SXRD experiments were conducted with a monochromatic beam (10 keV/ $\lambda = 1.24 \text{ \AA}$) selected from a pink beam using a 4-bounce Si(111) monochromator that focused on a spot size of 2 (v) x 20 (h) μm using a pair of Kirkpatrick-Baez mirrors. Diffraction data were collected using a Pilatus 1-M detector. More details on the experimental set-up of ALS beamline 12.3.2 can be found in Ref.[75].

Beamline 12.3.2 is also capable of collecting fluorescence signals through a VORTEX Si-drift detector that can be used to locate areas enriched with elements heavier than Ca ($Z > 20$). In the present study, micro X-ray Fluorescence (μ -XRF) was employed to obtain Fe and Cr elemental maps. These maps allowed excluding the areas containing large fly ash particles and an area of interest of $0.1 \times 0.1 \text{ mm}$ was located on each sample. Using a scan step size of 0.01 mm in each direction, 100 x-ray diffraction patterns (10×10 in x and y directions) were collected using the monochromatic x-ray beam. These patterns were analyzed and integrated using an in-house written x-ray micro diffraction analysis software (XMAS) [77].

The results obtained from the μ -SXRD were compared with those obtained from powder XRD methods. In each case a different wavelength was used. To effectively compare the XRD patterns, the x-axis was chosen as d -spacing on the plots.

The morphological observations and chemical analysis of the samples were performed using a ZEISS EVO®MA10 equipped with an EDS detector at an accelerating voltage of 15 to 18 kV. The working distance was set between 6 to 9.5 mm for backscattered electron imaging (BEI) and 10 to 15 mm for EDS analysis. For investigations of the microstructural morphology, 12k and 30k magnification images were taken.

To obtain high quality images at these magnifications a probe current between 100 pA and 200 pA was selected. The EDS analysis in spot mode was used to investigate the PC100FA0 and PC50FA50 samples. The spot locations are represented on the respective

SEM micrographs with a “+” sign. In the PC100FA0 sample, the Ca/Si atomic ratio in and around a hydrated cement particle was measured. In the PC50FA50 sample, the Ca/Si, Ca/(Si+Al) and Al/Si ratios were measured on a profile from the center of a fly ash particle to the outer hydration product regions and into the paste matrix in two different directions. In addition, element mapping for the reacted fly ash sample was conducted showing distributions of Ca, Si, Al, S, Mg and Na.

5.3. Results and Discussion

5.3.1 XRD analysis

The standard laboratory based bulk powder XRD (lab-XRD) patterns of raw materials are shown in Figure 5.1. Quartz (SiO_2), alite (Ca_3SiO_5), belite (Ca_2SiO_4) and calcium aluminoferrite ($\text{Ca}_2\text{Al}_2\text{Fe}_2\text{O}_5$) phases were identified in FA and PC. Figure 5.2 presents lab-XRD patterns for each sample after six months of curing.

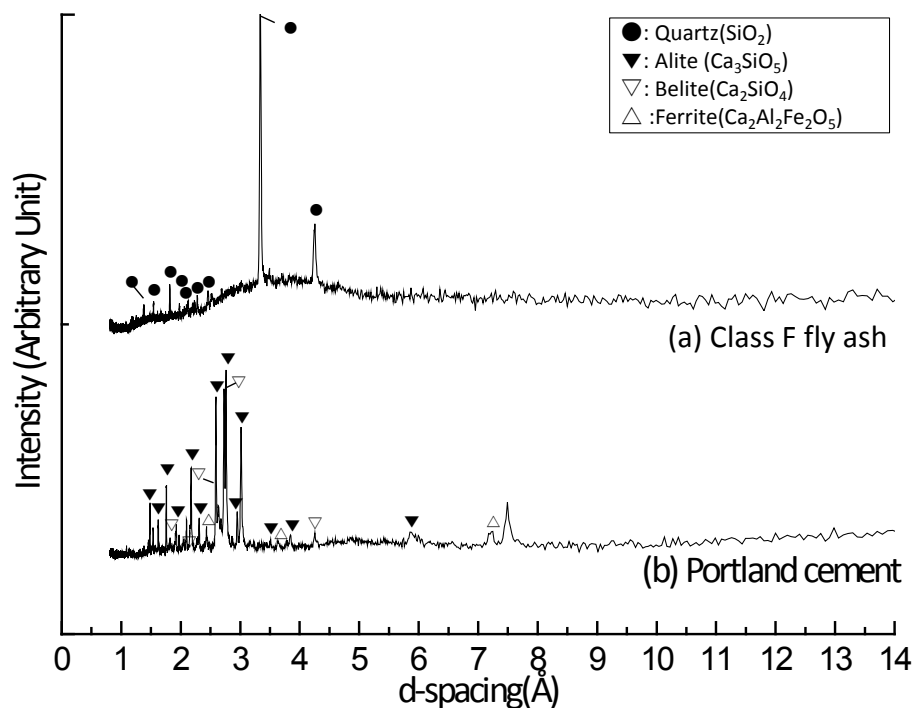


Figure 5.1. Standard laboratory bulk powder XRD patterns of raw materials

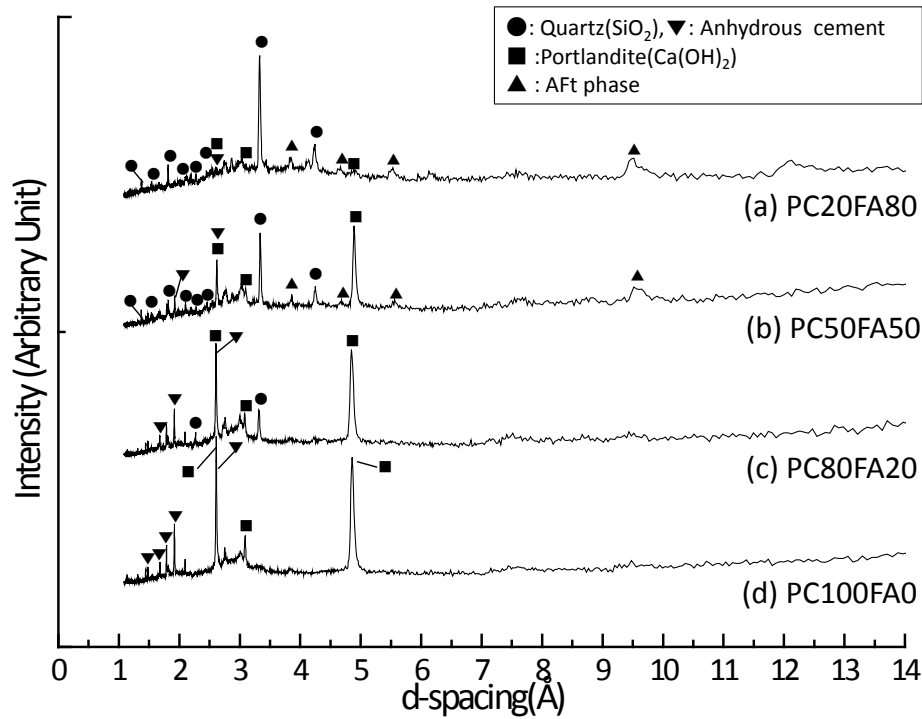


Figure 5.2. Standard laboratory bulk powder XRD patterns of HVFA samples

In PC100FA0, strong peaks from anhydrous PC phases and portlandite were detected. It is also confirmed that the XRD peaks from both phases decrease with incremental substitution of fly ash in the each sample, especially, the peaks from portlandite in PC20FA80, which decreased significantly due to the dilution of portland cement by fly ash and the pozzolanic reaction with silicate phases in the HVFA system. In both PC50FA50 and PC20FA80, strong peaks for quartz, an unreacted crystalline phase found in fly ash were identified. Because quartz has a lower reactivity than the glassy phase in fly ash particles [149], its presence would be expected even in the absence of other anhydrous phases. In the same two HVFA samples, PC50FA50 and PC20FA80, peaks attributed to one of the AFt phases [ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$); d -spacing(d)=5.61 and 9.7Å] were observed. However, in the low-volume fly ash sample, PC80FA20 and PC100FA0 no peaks from any of the ettringite phases were recorded. Figure 5.3 presents the monochromatic synchrotron XRD (sync-XRD) patterns of each sample after six months of curing.

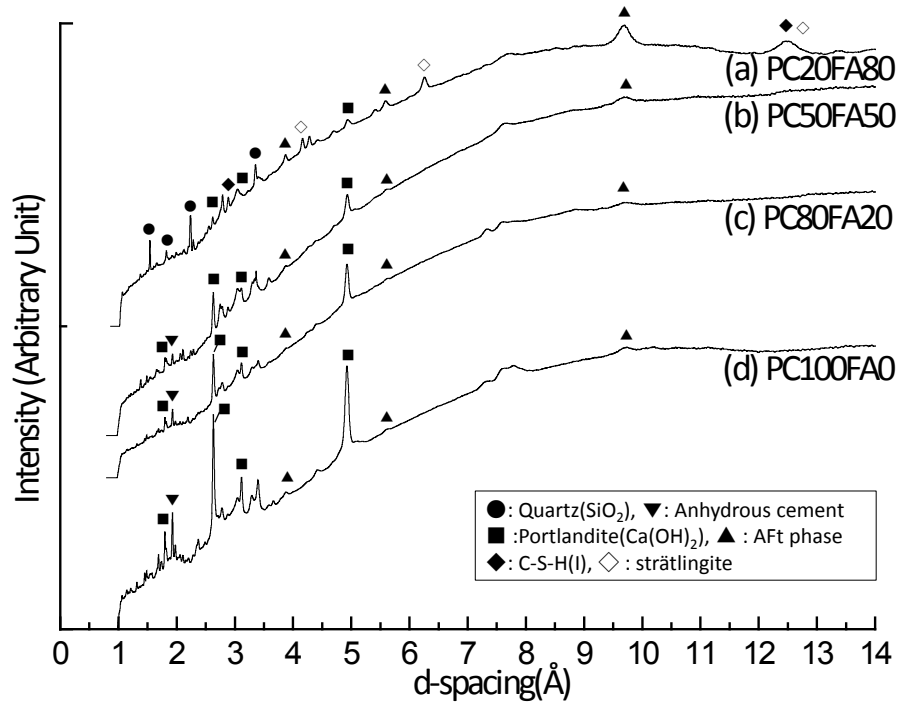


Figure 5.3. Synchrotron powder x-ray diffraction patterns for HVFA samples.

In the sync-XRD data of PC100FA0, very strong peaks from anhydrous PC particles and portlandite were detected. The peak intensity of portlandite gradually decreased with incremental substitution of fly ash into the samples. Portlandite peaks were especially weak in samples PC50FA50 and PC20FA80, which is consistent with the lab-XRD results. The agreement in the rapid reduction of the portlandite peak intensities verifies the consumption of portlandite due to pozzolanic reaction. On the sync-XRD patterns, the diffraction peaks attributed to ettringite ($d=3.87$, 5.61 and $9.7\text{\AA}$) were observed in all samples; whereas, the lab-XRD measurement showed evidence of ettringite only in PC50FA50 and PC20FA80. In C20FA80, ettringite peaks showed higher relative intensities than those in other samples. Peaks assumed to come from C-S-H(I) or strätlingite ($2\text{CaO}\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O}$) peaks ($d=12.5\text{\AA}$) were detected only in PC20FA80. However, PC20FA80 also had peaks attributed to C-S-H(I) ($d = 3.04\text{\AA}$) and strätlingite ($d = 4.18\text{\AA}$ and $6.28\text{\AA}$) besides the peak at $d=12.5\text{\AA}$.

The sync-XRD technique has become a useful tool for a wide range of structural investigations in various fields of research (including cement chemistry) because it uses powerful x-ray sources that are thousands to millions of times more intense than lab-XRD. The present study found that even though the amount of samples ($\sim 0.006\text{mg}$) for the sync-XRD measurement was much smaller than the powder sample for lab-XRD ($\sim 5\text{g}$) it showed clearer peak profiles with less noise than lab-XRD: even though the amount of sample for sync-XRD measurement is relatively small, it is enough to obtain overall information of existing phases in the samples. In addition, powder XRD methods using ground powder sample are not sensitive to poorly crystalline phases such as C-S-H(I) or calcium aluminate silicate hydrates phases, e.g. strätlingite, due to the high background caused by the presence of amorphous phases in the sample. Therefore, the existence of C-S-H(I) and strätlingite in any other samples besides PC20FA80 could not be verified when studied both powder XRD methods. To prove the existence of C-S-H(I) and strätlingite in HVFA samples and differentiate those phases better, the μ -SXRD method using in situ thin sectioned samples is advantageous.

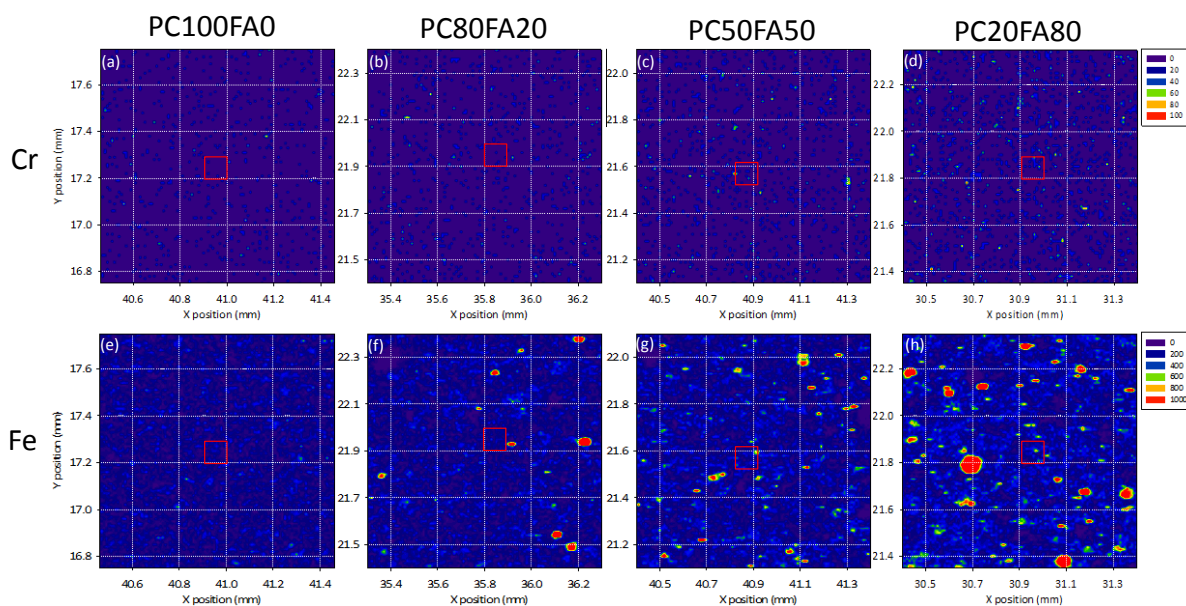


Figure 5.4. μ -XRF maps ($1\text{mm} \times 1\text{mm}$) of the HVFA samples. Top row shows the Cr-maps (a-d), while the bottom row shows the Fe-maps (e-h) for PC100FA0, PC80FA20, PC50FA50, and PC20FA80 respectively. Marked red squares represent the areas ($100\ \mu\text{m} \times 100\ \mu\text{m}$) investigated with monochromatic scanning x-ray micro-diffraction.

To exclude the area that contains large fly ash particles, before initiating the μ -SXRD experiment, element mapping based on x-ray fluorescence (μ -XRF) for Fe and Cr was conducted to visualize and understand the chemical distribution in the hardened paste. The μ -XRF results of the samples are shown in Figure 5.4, where the red squares represent the scanned areas.

Automatically integrated 100 μ -SXRD patterns of each sample are given in Figure 5.5. The results of μ -SXRD showed pure crystalline patterns with less noise compared to the lab-XRD patterns. Peak intensity of portlandite decreased significantly by substitution of fly ash (PC100FA0 to PC80FA20), showing similar peak intensities in the samples containing fly ash. The reduction in noise makes it possible to identify strong peaks of ettringite ($d = 3.87, 4.7, 5.61, \text{ and } 9.7\text{\AA}$) with similar peak intensity in all samples. Moreover, C-S-H(I) ($d = 3.04 \text{ and } 12.5\text{\AA}$) and strätlingite ($d=4.18, 6.28\text{\AA} \text{ and } 12.5\text{\AA}$) were identified only in PC20FA80 one hundred individual μ -SXRD patterns for all samples were analyzed.

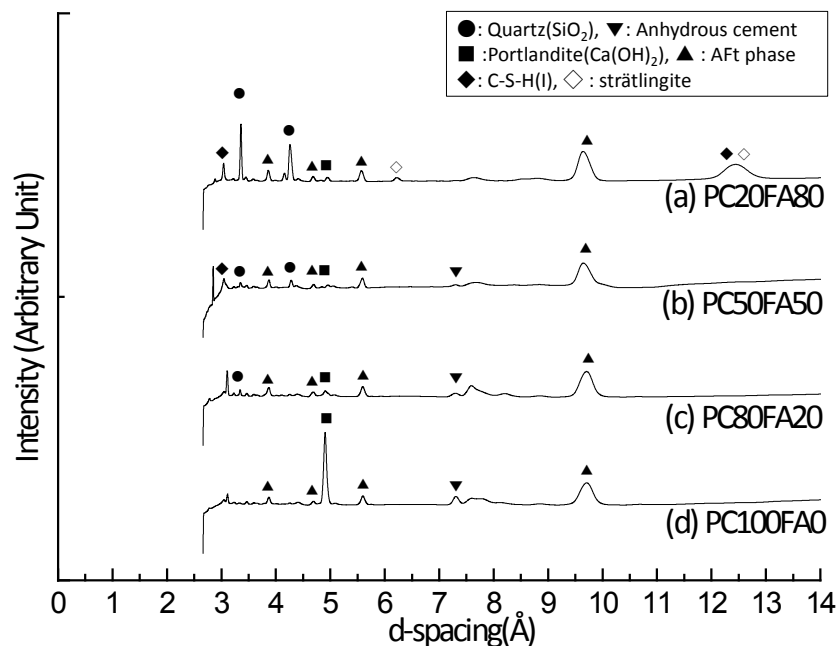


Figure 5.5. Integrated monochromatic scanning x-ray micro-diffraction patterns collected over the area marked with red boxes in Figure 5.4.

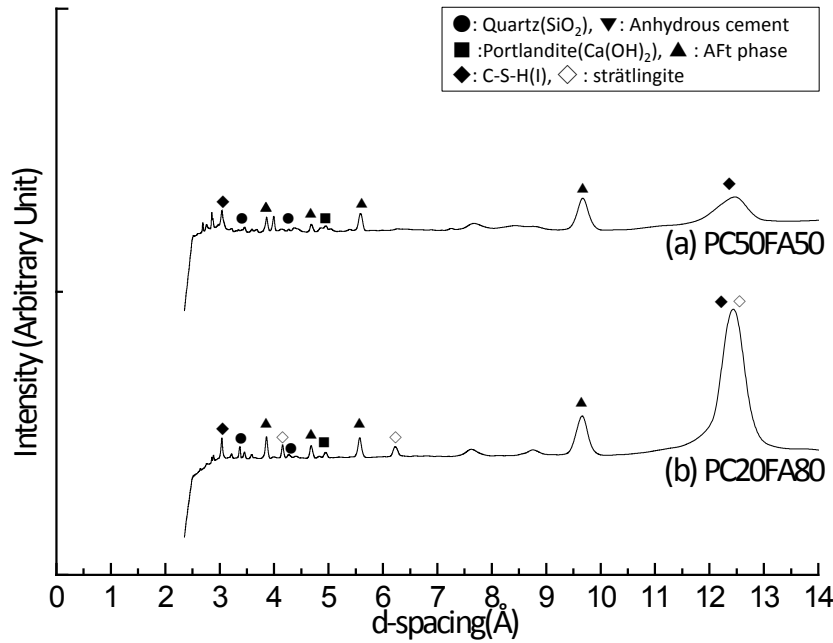


Figure 5.6. Selected individual monochromatic scanning x-ray micro-diffraction patterns among one hundred patterns collected over the chosen spots marked in Figure 5.4.

Figure 5.6 presents patterns for the samples PC50FA50 and PC20FA80, which showed the strongest signals of C-S-H(I) and strätlingite. In PC80FA20, no patterns containing C-S-H(I) or strätlingite peaks were found. In PC50FA50, only C-S-H(I) was observed as shown in Figure 5.6-(a); in PC20FA80, both C-S-H(I) and strätlingite peaks were observed. Because both C-S-H(I) and strätlingite have the same basal d -spacing ($d=12.5\text{\AA}$), this overlapped peak shows exceptional high intensity in Figure 5.6-(b).

In PC, calcium aluminate silicate hydrates (C-A-S-H) gel and strätlingite are normally formed by the reaction between silicate anions and hydrated calcium aluminates. Strätlingite also can be produced in addition to synthesized pure Al substituted C-S-H when C-S-H(I), which has a high Ca/Si ratio, is used [97]. Midgley et al. [150] observed that a small amount of strätlingite formation in old high alumina cement systems. High calcium-class C fly ash [151], microsilica [152], and high alumina cement containing granulated blast furnace slag [153] have been also reported to favor the formation of strätlingite which reacts with high alumina phases in the systems [154]. The production of strätlingite in HVFA paste was identified only in PC20FA80 which contains the highest

amount of alumina and silicate phases in the system and is believed to be the same mechanism involving high alumina phases as described above. It is possible that a portion of C-S-H(I) with high Ca/Si formed in PC20FA80 is transformed to strätlingite in the HVFA system, however in PC50FA50, it is assumed that the amount of the alumina and silicate phase is not sufficient to produce strätlingite.

The role of C-A-S-H gels and strätlingite on mechanical properties in high alumina systems is under debate. It has demonstrated that the formation of strätlingite from a reaction between hexagonal calcium alumina phases (i.e. $\text{CaAlH}_{10}\text{O}_9$, $\text{Ca}_2\text{Al}_2\text{O}_{13}\text{H}_{16}$) and silica in the system might be responsible for the strength recovery after conversion since it has a relatively higher strength than those calcium alumina phases [150, 154]. According to Bumrongjaroen [155], however, the formation of C-A-S-H gel and strätlingite would indirectly impede the formation of C-S-H of the system since the pozzolanic reaction and C-A-S-H gel formation compete for the silicate anions in high alumina system and the calcium cations in pore solution of concrete thus reducing the amount of C-S-H as binder in the system that could induce the degradation of mechanical properties of HVFA system.

Furthermore, Rayment and Majumdar [153] have demonstrated that very strong diffraction peaks associated with hydrogarnet ($\text{Ca}_3\text{Al}_2(\text{OH})_{12}$) exist in high alumina cement paste systems, reporting that conversion of hexagonal calcium alumina phases described above to hydrogarnet and $\text{Al}_2\text{H}_6\text{O}_6$ in high alumina cement systems could be an important reason for the degradation of mechanical properties of high alumina cement systems. However, no hydrogarnet was detected in any of the XRD experiments on HVFA samples reported herein. This indicates that additional sources of silicate from fly ash in the HVFA paste increased the strätlingite formation from those calcium alumina phases since silica has been shown to be effective in reducing hydrogarnet formation [153].

In general, HVFA concrete shows lower compressive strength in early ages [156] because it contains small amounts of PC which is the main material to produce C-S-H for strength development. However, it shows comparatively higher compressive strength than normal concrete in the long term ages due to the pozzolanic reaction resulting in additional C-S-H which has more ordered-structure than the one from PC hydration process [107]. In addition, one could argue that the formation of strätlingite and the reduction of hydrogarnet formation might affect the long-term strength behavior of HVFA concrete since cement

pastes containing major quantities of strätlingite shows higher compressive strength and low porosity than the one containing hydrogarnet mostly [157]. Therefore, given the results obtained by the XRD analysis, it can be concluded that the C-S-H produced by the pozzolanic reaction has a similar crystal structure as the C-S-H(I) and those C-S-H(I) and strätlingite coexist in high alumina HVFA paste. Furthermore, the amount of fly ash is a key factor for the formation of C-S-H(I) and strätlingite in the HVFA system. The identified phases and combined information on all of the phases from the three different XRD measurements is tabulated in Table 5.2 and Table 5.3, respectively.

Phase mapping based on the μ -SXRD data was used to better understand distribution of the phase in the scanned area of the sample. As described above, thin-sectioned samples were utilized individual non overlapping peaks indicative of specific phases were selected for phase mapping. The distribution of each phase is shown with relative intensity differences to the background; it does not present the absolute amount of these phases.

Table 5.2. Identified phases in the samples. (O: Identified. - : Unidentified)

Phases	Fly Ash	Portland Cement	PC100FA0	PC80FA20	PC50FA50	PC20FA80
Quartz	O	-	-	O	O	O
Tri-calcium Silicate	-	O	O	O	O	O
Di-calcium silicate	-	O	O	O	-	-
Tri-calcium aluminate	-	O	O	-	-	-
C-S-H(I)	-	-	-	-	O	O
Strätlingite	-	-	-	-	-	O
Aft Phase (Ettringite)	-	-	O	O	O	O
Portlandite	-	-	O	O	O	O

Table 5.3. Information on the main phases identified in the samples, with their most important lattice planes, *d*-spacing and ICDD PDF2 database reference number.

Phases	Chemical Formula	<i>hkl</i>	<i>d</i> -spacing (Å)	References (ICDD PDF2 #)
Quartz	SiO ₂	100, 011, 110, 102, 200, 201, 112, 121, 203	4.25, 3.34, 2.46, 2.28, 2.12, 1.98, 1.82, 1.54, 1.37	01-078-2315
Tri-calcium Silicate	Ca ₃ SiO ₅	110,11-2, 31-1, 22-1, 40-1, 003, 22-2, 221, 40-4, 22-4, 62-2, 22-5, 224	5.95, 3.89, 3.55, 3.05, 3.03, 2.78, 2.76, 2.61, 2.19, 1.94, 1.77, 1.63, 1.54	00-049-0442
Di-calcium silicate	Ca ₂ SiO ₄	120, 131, 112, 222	4.32, 2.75, 2.73, 1.91	00-049-1672
Tri-calcium aluminate	Ca ₃ Al ₂ O ₆	020, 130, 211	7.25, 3.63, 2.41	00-042-1469
C-S-H(I)	CaO?SiO ₂ ?H ₂ O	—	12.5, 3.04	Taylor[1]
Strätlingite	Ca ₂ Al ₂ SiO ₇ ·8H ₂ O	001, 002, 003	12.5, 6.28 4.18	00-029-0285
Aft Phase (Ettringite)	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ 26H ₂ O	100, 110, 104, 114	9.72, 5.61, 4.69, 3.87	00-041-1451
Portlandite	Ca(OH) ₂	001, 100, 101, 102	4.91, 3.11, 2.63, 1.92	01-087-0674

The phase mapping results of PC20FA80 are given in Figure 5.7, including both C-S-H(I) and strätlingite phases in the μ -SXRD. Based on the mapping results of each phases, we combined into one image the distribution of (1) quartz, C-S-H(I) and strätlingite, (2) alite and ettringite and (3) all of the phases in one map, see Figure 5.8.

Note that C-S-H(I) exists in the vicinity of strätlingite in the system. This supports the claim that a part of C-S-H(I) transforms to strätlingite in PC20FA80. The detailed morphology and chemical composition of the sample were revealed by SEM and EDS analysis.

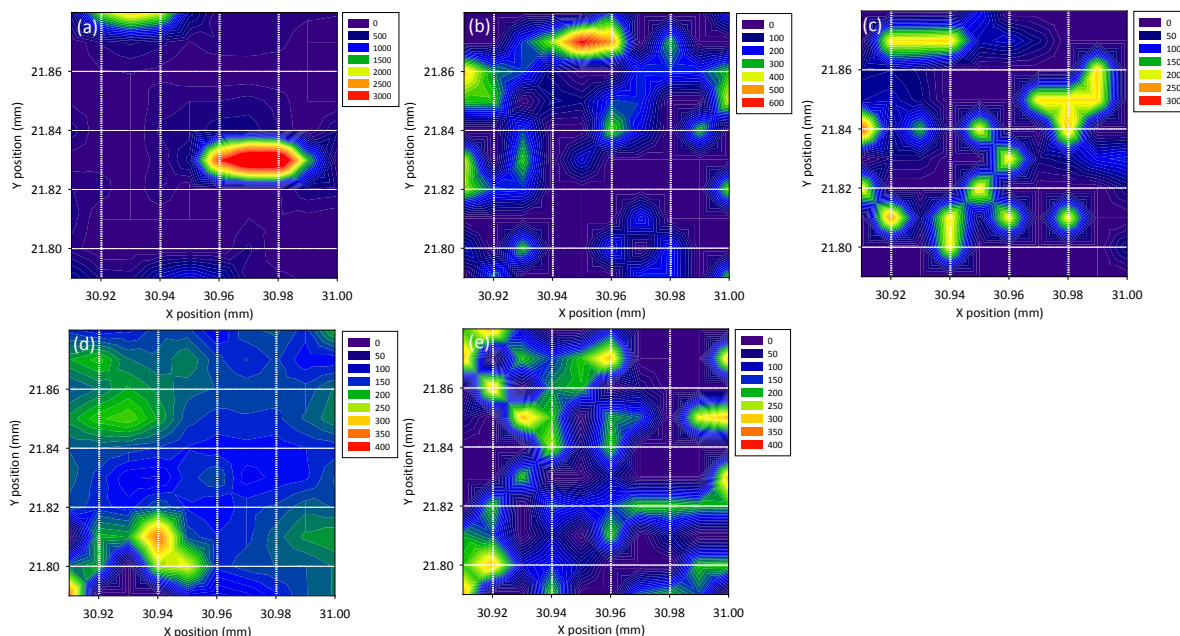


Figure 5.7. Monochromatic scanning x-ray micro-diffraction maps of the $100\ \mu\text{m} \times 100\ \mu\text{m}$ area marked in red on Figure 4 for PC20FA80: (a) Quartz ($d=3.34\text{\AA}$), (b) C-S-H(I) or Strätlingite ($d=12.5\text{\AA}$), (c) Strätlingite ($d=6.28\text{\AA}$), (d) Ettringite ($d=9.72\text{\AA}$) and (e) Alite ($d=5.95\text{\AA}$). The scan step is $10\ \mu\text{m}$ in x and y direction

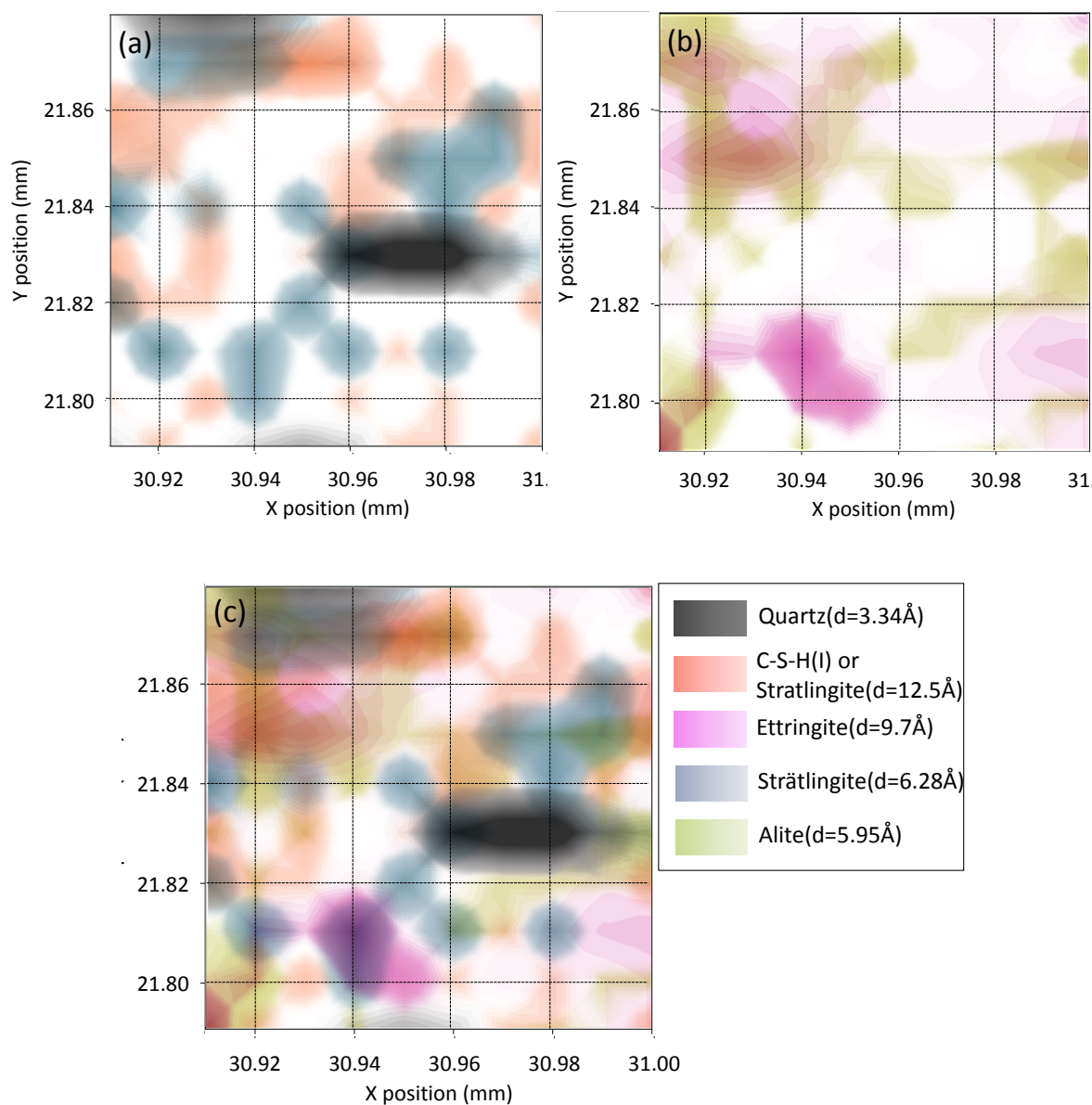


Figure 5.8 Monochromatic scanning x-ray micro-diffraction mapping results in PC20FA80 (a)Quartz ($d=3.34\text{\AA}$), C-S-H(I) or Strätlingite ($d=12.5\text{\AA}$) and Strätlingite ($d=6.28\text{\AA}$), (b)Alite ($d=5.95\text{\AA}$) and Ettringite ($d=9.72\text{\AA}$), (c) All of the phases

5.3.2 Backscattered electron (BSE) imaging

BSE imaging was used to examine the morphology and chemical composition of the HVFA samples. The BSE imaging results of the PC50FA50 and PC20FA80 (aged six months) are shown in Figure 5.9. A large number of unreacted fly ash particles in addition to fully reacted fly ash particles still remained in PC50FA50, see Figure 5.9-(a). Fly ash particles are marked by a dotted rectangle in Figure 5.9-(b) and (c).

As shown in Chapter 2, layers around fly ash particles can be distinguished into inner (Ip) and outer products (Op) of fly ash [4]. This study also found that for a water-activated 28-day-old sample, the outer product C-S-H consists of a mixture of fibrillar and foil-like. Ogawa et al. [40] observed using SEM analysis that a Si- and Al- rich amorphous layer can be formed on the surfaces of pozzolan by dissolution of SiO_4^{4-} and AlO_2^- which combine with Ca^{2+} in the system of C_3S -pozzolan. The vacant space in the inner product region is generated due to osmotic pressure caused by the difference of concentration of alkali ions between inside and outside of fly ash particles. This study focused on those fly ash particles in the HVFA matrix, that have different hydration product layers. As shown in Figure 5.9-(b-e), two different types of reaction product layers around fly ash particles were observed in PC50FA50 and PC20FA80. The Ip shows hair-like morphology and grows outward from the core of fly ash particle. The Op, however, has more of a foil-like morphology and are similar to the hydration products in the paste matrix region. Partially dissolved parts of fly ash particles and the vacant space between the Ip and the core of fly ash particles were also clearly identified, see the red circles in Figure 5.9-(e). The image indicates that the dissolved area is transforming to the Ip. Note the vacant space not only in the Ip region but also between Op region and paste matrix. It is possible that these vacant layers in the Ip or between the Op and the paste matrix might affect the mechanical properties (e.g. early and long-term strength) and the shrinkage behavior of HVFA concrete. Furthermore, assuming additional C-S-H for the Op of the fly ash is a key phase for its strength development. Conversely, at the same time this additional C-S-H may prevent the full-reaction of fly ash because it has a higher density than the Ip [4].

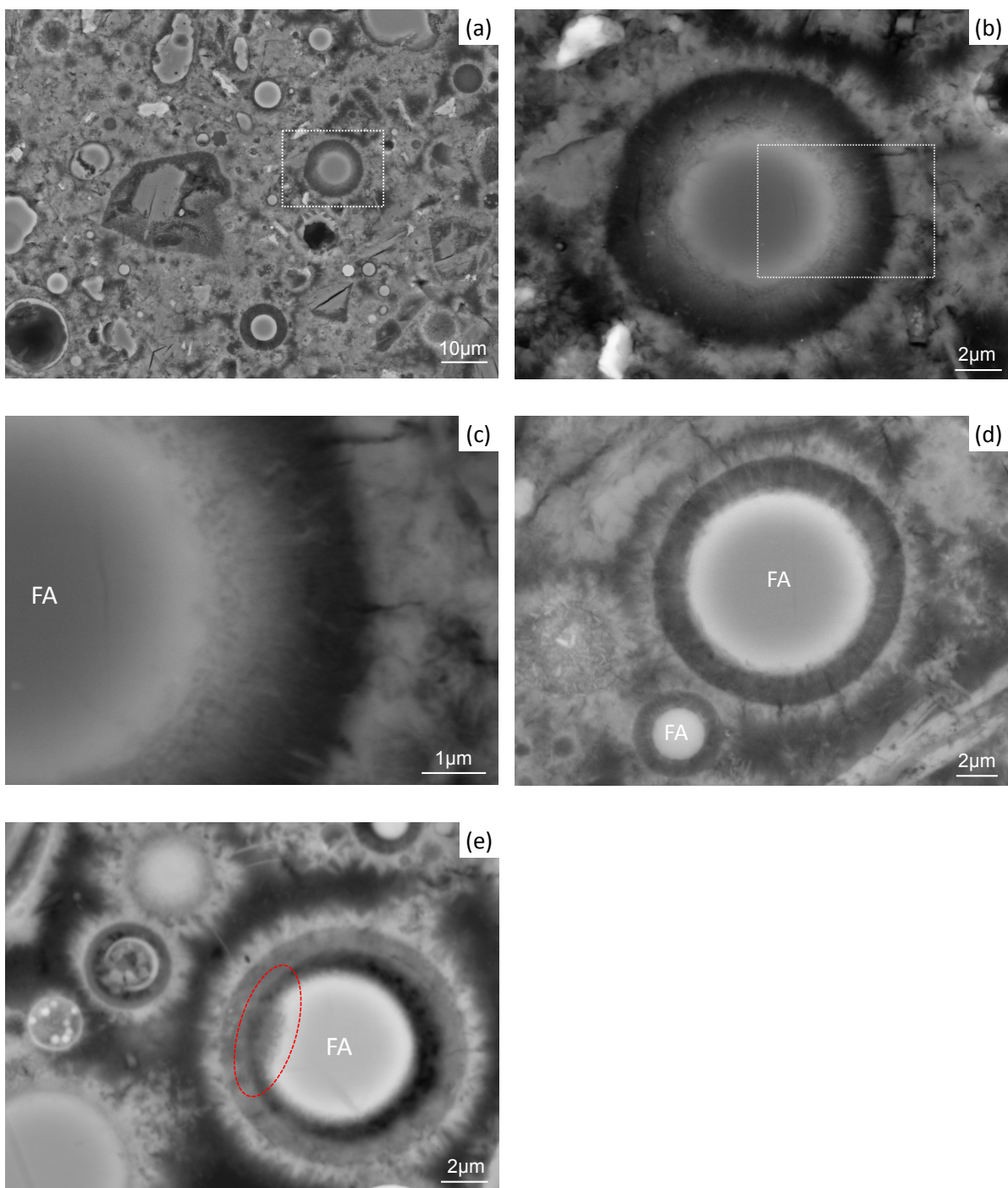


Figure 5.9. Backscattered electron images of PC50FA50 (a-d) and PC20FA80 (e).

5.3.3 Chemical composition analysis by EDS

The EDS measurement locations in the BSE image of PC100FA0 and its results are displayed in Figure 5.10 and Figure 5.11 respectively.

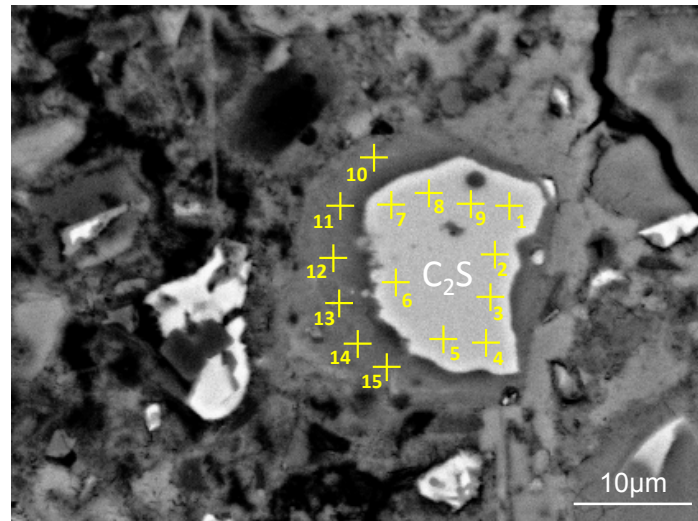


Figure 5.10. EDS analysis spots in backscattered electron image of PC100FA0.

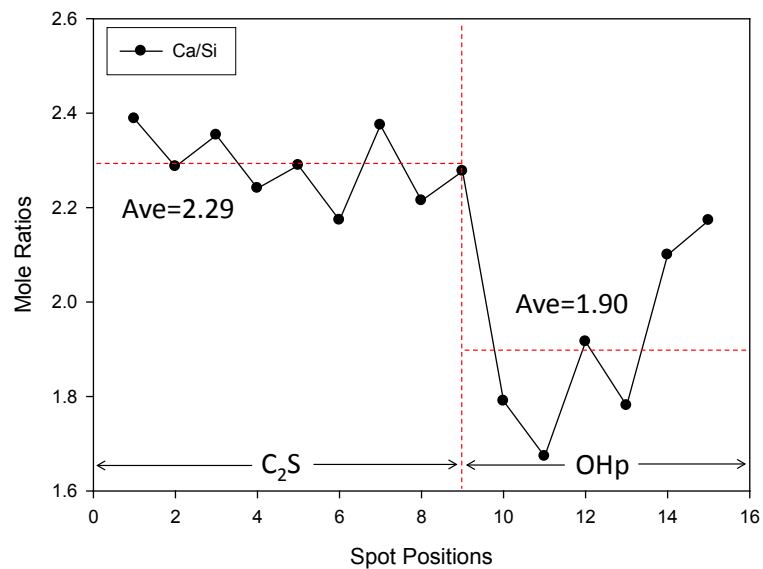


Figure 5.11. Results of EDS spot analysis (Ca/Si mole ratios) of PC100FA0.
 *C₂S:belite, OHp: outer hydration product

The results show that the average value of Ca/Si for the measuring points from 1 to 5 is 2.29, its range is 2.17 to 2.39 and the anhydrous particle is likely to be belite. The average value of the Ca/Si ratio of C-S-H around belite is 1.9, and its range is 1.67 to 2.17, which is in agreement with the Ca/Si ratio range of hydration product in a pure PC paste system [147] .

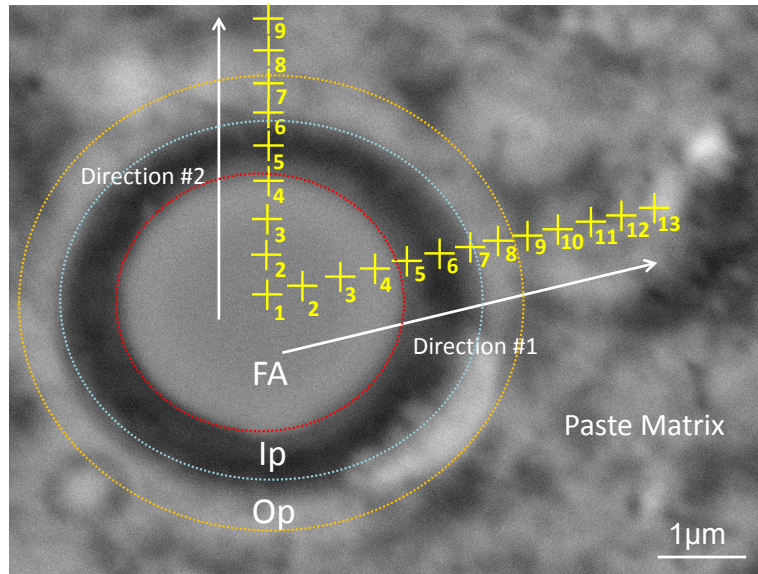
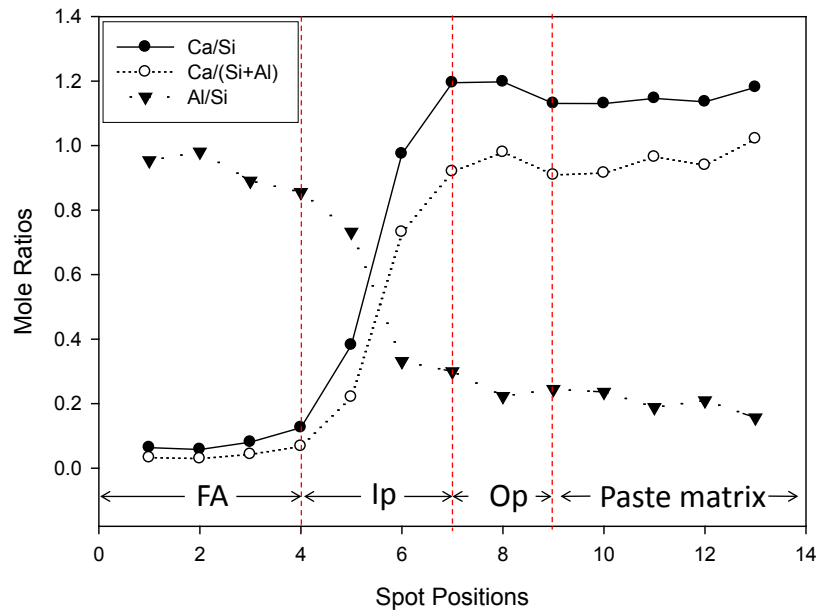
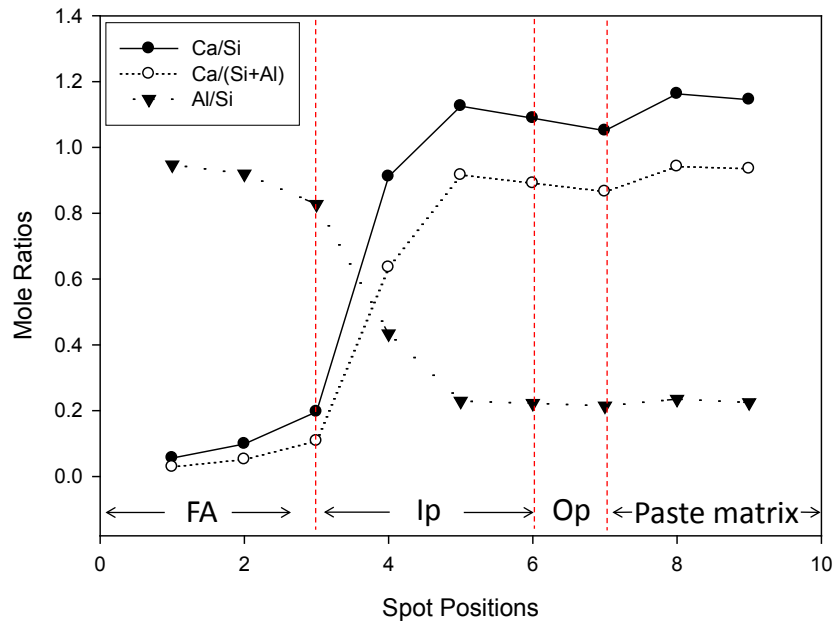


Figure 5.12. EDS analysis spots and directions for a reacted fly ash particle in PC50FA50

Profiles of EDS spot analyze in two different directions within PC50FA50 and molar ratio plots are shown in Figure 5.12 and Figure 5.13, respectively. As shown in Figure 5.13-(a), in both directions, the Ca/Si ratios change rapidly in the inner product region, leveling out to a constant 1.0~1.2 in the outer hydration product region and the paste matrix. These values are lower than the ones measured in hydration products in PC100FA0. It is known that the Ca/Si ratio of C-S-H changes with the portlandite concentration of the equilibrium solution [97]. The lower Ca/Si ratios of reacted HVFA paste could be due to availability of Si and Al cations from dissolution of the fly ash particles and the lower supply of Ca cations because of the replacement of PC and the decrease of portlandite solubility due to pozzolanic reaction [17].



(a) Direction #1



(b) Direction #2

Figure 5.13. Results of EDS spot analysis (Ca/Si, Ca/(Si+Al), Al/Si mole ratios)
***FA:fly ash, Ip: inner products, Op: outer product**

In the present study, $\text{Ca}/(\text{Si}+\text{Al})$ ratios show similar trends compared to the Ca/Si ratios. In both directions, the $\text{Ca}/(\text{Si}+\text{Al})$ ratios change in the inner product region, leveling out to a range of 0.9 ~ 1.0 in the outer hydration product and paste matrix regions. This result implies that (a) excessive aluminum supply from fly ash glass phases is substituted for Si of the C-S-H that formed around fly ash particles or (b) it is used for the production of calcium aluminate silicate hydrate phase. The maximum value of Al/Si ratio is 0.19 in the case of natural tobermorite 1.4nm and jennite [158, 159]. In this study, Al/Si varies in the range of 0.15~0.24, with a higher maximum value compared to the natural calcium silicate hydrates minerals described above.

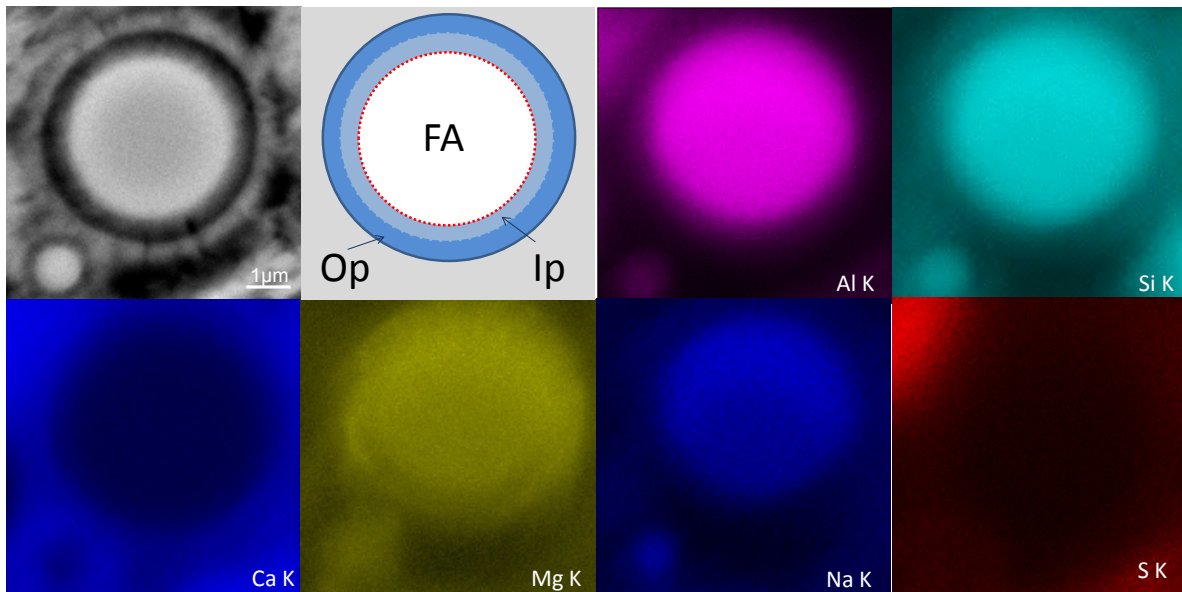


Figure 5.14. Results of EDS elemental mapping of a dissolved fly ash in PC50FA50. Ip: Inner product, Op: Outer product. The mapping area was selected in Figure 5.9-(d)

The element mapping results of PC50FA50 by SEM-EDS are shown in Figure 5.14. The mapping area selected is from Figure 5.9-(d), which shows that fly ash particles contain higher amounts of Si and Al compared to the paste matrix region. In the paste matrix region, a homogenous Ca distribution was observed. The inner product region around fly ash is Al-rich; the outer product region, however, is Si-rich, which is in good agreement with spot analysis results. The Si-rich outer product acts as a barrier, prohibiting alkali ions in the fly ash particle from dissolving into the paste matrix: this prevents the hydration process between alkali ions and Ca ions. Besides Ca, Al, and Si, note that the

outer product regions contains higher amounts of Na and Mg ions than the paste matrix. The S-rich region in the figure was shown by EDS analysis to be ettringite.

5.4 Conclusions

Even though a significant amount of research has been devoted to the topic of the properties of HVFA concrete on the macro scale, the nature and properties in the micro/nanoscale of this system are still not completely understood. To properly understand the mechanisms of chemical reaction and the characteristics of HVFA concrete, information on the micro/nanostructure of HVFA concrete is crucial. To clarify the role of hydration products and microstructure of HVFA paste system, four different samples, cured for six months, with different fly ash substitution ratios have been characterized using standard laboratory bulk powder x-ray diffraction, synchrotron powder x-ray diffraction, monochromatic scanning x-ray micro-diffraction, and scanning electron microscopy with energy dispersive x-ray analysis. The obtained results are summarized below.

Monochromatic scanning x-ray micro-diffraction analysis has revealed that ordered C-S-H(I) and strätlingite coexist in HVFA paste, which is not observed in pure PC paste or paste containing lower amounts of fly ash. The results of μ -SXRD-based phase mapping clearly show the distribution of the phases in the HVFA sample, implying that the mapping technique is applicable to comparatively complicated cementitious material research.

The BEI imaging and EDS analysis, confirm that C-S-H(I) created in HVFA paste has a lower and constant Ca/Si ratio value compared to the C-S-H phase in pure PC paste. Furthermore, the Ip and Op in fly ash particles are being produced in concentric rims. Those two different types of products have a different morphology and the chemical composition is changing rapidly in the inner product region. The Op around fly ash particle is Si rich and it is assumed that those Op prevent the hydration process between Ca ions existing in matrix and alkali ions dissolving from fly ash particles which might affect the mechanical properties of HVFA concrete.

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6. Conclusions and future work

The major result from the research performed for the present dissertation has been determination of morphology and atomic bonding structure on pure triclinic tricalcium silicate (C_3S) pastes, systems containing C_3S with high-volume fly ash (HVFA), and systems containing Portland cement (PC) with HVFA. To elucidate the chemical changes of hydration products in C_3S hydration and the effects of HVFA on the reaction products, different types of advanced characterization methods were employed: near edge x-ray absorption fine structure (NEXAFS) analysis using scanning transmission x-ray microscopy (STXM), soft x-ray diffraction imaging, and monochromatic micro-diffraction (μ -SXRD). This final chapter provides a summary on the main results of this research and gives suggestions for future work.

NEXAFS analysis showed that synthesized calcium silicate hydrate (Syn-CSH) had no variation in peak positions and energy separation for Ca $L_{III, II}$ in accordance with the Ca/Si ratios. The Ca $L_{III, II}$ NEXAFS analysis for a 17 days hydrated C_3S sample showed different local structure compared to anhydrous C_3S . The C-S-H from a C_3S paste had a similar local structure around Ca as the Syn-CSH, but with a lower crystallinity. Si K edge NEXAFS analysis of the Syn-CSH indicated a tendency that the peak positions of both the Si K edge and the peak induced by multiple scattering have shifted to higher energy levels and that the distance between the two peaks increased with a decrease of the Ca/Si ratio in the Syn-CSH. Silicate polymerization influenced the multiple scattering of distant shell atoms more than the binding energy of the core atoms.

In situ STXM analysis using pure C_3S solutions in a wet cell showed morphologic changes in the dissolution of the Ca and the precipitation of C-S-H on the C_3S particles in the process of hydration. The dissolution of C_3S and formation of Op layers around C_3S were clearly observed. Op layers of C_3S showed higher degree of silicate polymerization compared to core area of C_3S . The degree of silicate polymerization of Op increased during the hydration process.

For the 17 days cured C_3S particles, *ex situ* STXM analysis showed that Op layer and core area had a different degree of silicate polymerization. The results imply the Op layer reduces the hydration process of C_3S in the core area. Soft x-ray diffraction imaging and transmission electron microscopy (TEM) analysis of the 17 days hydrated C_3S showed

that Op had a fibrillar with laminar structure while the core area an inter-globular structure with voids. Soft x-ray diffraction imaging also showed that the core area in fully-hydrated C_3S is inner product (Ip).

With regard to the C_3S / HVFA system, XRD and thermogravimetric analysis showed that C_3S with HVFA samples contained lower intensity of $Ca(OH)_2$, compared to pure C_3S , due to dilution of C_3S substituted by fly ash. Moreover, $Ca(OH)_2$ consumption by pozzolanic reaction in C_3S with HVFA system was also confirmed.

STXM results showed that Si concentration of C_3S particles in C_3S / HVFA matrix was very uniform compared to pure C_3S system. No clear Op layers around C_3S particles, as observed in pure C_3S paste, were found in C_3S / HVFA paste. Compared to Op of C_3S in pure C_3S matrix, C-S-H of C_3S in C_3S / HVFA matrix showed very similar absorption features, but further lower peak a_1 position and higher peak a_2 position in Si K edge NEXAFS. Chemical shift of peak a_1 to lower energy could be due to Al substitution for Si in hydration products of C_3S , and the shift of peak a_2 to higher energy was assumed to be due to increased degree of silicate polymerization induced by additional silicate provided from abundant fly ash in HVFA system.

^{29}Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy proved that C-S-H in C_3S with HVFA matrix have longer average chain length compared to one in pure C_3S matrix, confirming the silicate polymerization expected to occur in the HVFA system. Electron microscopy imaged the fully reacted particles, fine Op and coarse Op in hydrated C_3S particles. Fine C-S-H, large $Ca(OH)_2$ crystals intermixed with the C-S-H, nano $Ca(OH)_2$ crystals intermixed with C-S-H, and some small fully reacted grains were observed in C_3S with HVFA matrix. However, no anhydrous C_3S was observed in the image which is consistent with STXM and NMR results.

In PC with HVFA system, more ordered C-S-H(I) and strätlingite ($2CaO \cdot SiO_2 \cdot Al_2O_3 \cdot 8H_2O$) coexisted in PC with 80% of fly ash, which was not observed in pure PC paste or paste containing lower amounts of fly ash. The results of μ -SXRD-based phase mapping clearly showed the distribution of the phases in the HVFA sample. The BEI imaging and EDS analysis, confirm that C-S-H(I) created in HVFA paste had a lower and constant Ca/Si ratio value compared to the C-S-H phase in pure PC paste. Ip and Op in fly

ash particles were being produced in concentric rims and those products had a different morphology. It was also observed that the chemical composition is changing rapidly in the Ip region. The Op around fly ash particle was Si rich and it was assumed that the Op reduces the hydration process between Ca ions existing in matrix and alkali ions dissolving from fly ash particles.

The obtained results in this thesis showed that spectro-microscopy, soft x-ray diffraction imaging, and micro-diffraction are very effective tools for obtaining the invaluable morphologic and chemical information of cement phase hydration products with and without HVFA. Based on the results of this dissertation, following future projects will be suggested.

- The present research studied Class F fly ash and it would be important to perform similar work for different types of supplementary cementitious materials including Class C fly ash and blast furnace slag.
- Spectro-microscopy should be a powerful tool to characterize the products formed in a deteriorated concrete: iron oxides for corrosion of reinforced concrete, expansive sodium silicate gels from alkali-aggregate reaction, ettringite formation from a sulfate attack.
- Improve the diffraction imaging methods to obtain spatial resolutions in the order of a few nano-meter. The technique should also allow for high-resolution three-dimensional tomography of cement pastes. The tomography will provide details of Ip of hydrated cement phases.

Now that the wet cell for *in situ* STXM has been developed, it will be possible to study the followings:

- *In situ* investigation on the hydration process of other PC phases.
- *In situ* hydration reactions of calcium aluminates and the modifications caused by the presence of gypsum.
- Monitoring of the interactions between organic admixtures, such as superplasticizers and polymers, on the early hydration of cementitious materials.
- *In situ* reactions related to the alkali-activation of fly ash or blast furnace slag, as well as, the formation of alumino-silicate based geopolymers.

- The C, Ca, Si, and Al edges will be of particular interest for these projects.

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