EFFECTS OF ELEVATED TEMPERATURE EXPOSURE ON CEMENT-BASED COMPOSITE MATERIALS

BY

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DISSERTATION

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Concrete structures are considered to have higher degree of thermal and fire resistance than steel structures due to their non-combustible nature and low thermal conductivity. Despite concrete structures having high degree of thermal resistance, there is loss in mechanical properties and durability when they are exposed to extremely high temperatures. This research aims to improve the understanding of complex mechanisms that drive thermal degradation of cement-based composite materials. The majority of this dissertation focuses on understanding the degradation that occurs at temperatures higher than 300 °C as this temperature was reported to be critical based on previous research. Morphological, mechanical, and chemo-mechanical characterizations of cement paste samples are conducted to study changes in micro and nanostructure due to the decomposition of hydration products that could finally result in the global loss of mechanical properties after exposure to high temperatures. Specifically, relatively new advances in nanotechnology are adopted in this research, such as atomic force microscopy (AFM), static and dynamic nanoindentation, and coupled nanoindentation/scanning electron microscopy with energy dispersive x-ray analysis (SEM-EDS). Thermal degradation of calcium silicate hydrate (C-S-H) is assessed based on AFM image analysis and a statistical analysis of static and dynamic nanoindentation. Furthermore, the application of combined nanoindentation/SEM-EDS successfully overcomes the difficulty of identifying phases with statistical deconvolution based solely on mechanical data. From a combination of experimental results and existing literature, new degradation processes driving the loss of mechanical properties of cement pastes are proposed. The development of microcracks at the interface between unhydrated cement particles and paste
matrix, a change in C-S-H nanostructure, and shrinkage of C-S-H are considered as dominant factors that cause the thermal degradation of cement pastes.

This research also suggests a mitigation strategy of thermal and chemical degradation in cement-based composite materials. A detailed, experimental characterization is performed to study the effects of incorporating small dosages of nanosilica on the degradation of cement pastes exposed to various heating and cooling regimes and accelerated carbonation. Carbonation proves to be the critical cause of damage in cement paste after high temperature exposure. It is confirmed that increased thermal and chemical stability of hydration products against high temperature exposure and carbonation by incorporating nanosilica.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Concrete structures are considered to have high degree of fire and thermal resistance for their non-combustible nature and low thermal conductivity (slow rate of heat transfer) compared to steel structures. Nevertheless, there is apparent loss in mechanical properties and durability of concrete (i.e. distortion and displacement of elements, cracking, and surface spalling) when it is exposed to high temperatures, such as building or tunnel fires and some nuclear power-related postulated accident conditions [1-6]. A number of fire disasters causing enormous damage to both life and property in the past clearly underlined the vulnerability of concrete structures at high temperatures [7].

Concrete is a heterogeneous material composed of aggregates embedded in cement paste matrix. The heterogeneity of concrete constituents can result in severe thermal damage at the interface, such as the cement paste-aggregate interface (ITZ), due to the difference in behavior of the constituents under high temperatures [8, 9]. Beside this, the decomposition and dehydration of hydration products in cement paste are believed to be the primary origins of thermal degradation of concrete [10, 11], which initiate at micro and nanoscales. Although repeated attempts have been made to understand the complex mechanisms of thermal degradation of cement-based composite materials, the micro and nanostructural changes that drive the process and finally result in the global loss of mechanical properties are not well understood yet. This need, in turn, is driving the research on development of extensive knowledge on the changes in micro and nanosturcture of
cement-based composite materials and how these relate to the local and macro mechanical properties.

Recently, nanosilica is suggested widely as excellent supplementary cementitious materials (SCMs) due to its superior reactivity in comparison to other types of siliceous materials. The beneficial effects of nanosilica addition on mechanical properties of cement-based composite materials, such as strength, flexibility and permeability, were reported by many researchers [12-15]. Effects of nanosilica on the molecular, micro and nanostructure of hydration products were suggested to provide increased stability against calcium leaching [14, 15]. Incorporation of nanosilica was also reported to increase compressive strength of mortar after high temperature exposure [16]. However, the exact mechanism by which the addition of nanosilica changes the thermal stability of cement-based composite materials is not yet well understood. This lack of understanding demands a detailed, experimental investigation on the changes in micro and nanostructure of cement paste caused by the incorporation of nanosilica and effects of various heating and cooling regimes to ultimately determine how the structural changes are related to an increased thermal stability.

1.2 Objectives of research

The aim of this research is to determine the thermal degradation mechanism of cement paste that initiates at micro and nanoscales and drives loss of mechanical properties at macroscale. In order to achieve the research objective, morphological, mechanical, and chemo-mechanical characterization of cement-based composite materials at micro and nanoscales following exposure to elevated temperatures are performed. In particular, relatively new advances in nanotechnology, such as AFM, static and dynamic nanoindentation, and coupled nanoindentation/SEM-EDS, are
adopted to investigate the origins of thermal degradation of hydration products in cement paste. This research also provides a detailed, experimental investigation on the effects of incorporating small dosages of nanosilica on the degradation of cement-based composite materials in aggressive environments, e.g. various heating and cooling conditions and accelerated carbonation. The study on carbonation is included as it becomes apparent early on that carbonation plays a critical role while understanding damage due to high temperature exposure. Hence, this dissertation shed light on the effects of nanosilica on micro and nanostructure of cement paste and how it improves thermal and chemical stability of hydration products against high temperature exposure and carbonation, respectively.

### 1.3 Structure of the dissertation

This dissertation is structured as follows. Chapter 2 reviews the literature on the microstructure of concrete, behavior of concrete after exposure to elevated temperature, and decomposition processes of hydration products, such as calcium hydroxide (CH) and C-S-H, at elevated temperatures. In Chapter 3, a review on theory of nanoindentation technique for both static and dynamic nanoindentation is provided followed by an overview on the method of coupled nanoindentation/SEM-EDS.

Chapter 4 includes chemical and morphological characterization of cement paste at micro and nanoscales using x-ray diffraction (XRD), SEM and AFM. Degradation of hydration products, which could be responsible for loss of macroscopic mechanical properties, is investigated at various heating and cooling regimes.

In Chapter 5, relatively high-end nanomechanical testing, static and dynamic nanoindentation, is conducted to assess both static and dynamic responses of hydration products, such as CH, low-
density (LD) and high-density (HD) C-S-H, at nanoscale. This work is linked to the loss in global mechanical property caused by thermal damage through a process by comparing the results obtained from nanoindentation with those of compressive strength test. In addition, a novel approach for the chemo-mechanical characterization is presented which combines grid nanoindentation technique with local chemistry analyzed by SEM-EDS. Based on existing literature and experimental results, the thermal degradation mechanism of cement paste is proposed.

It is well recognized that the use of SCMs, such as silica fume (microsilica) and fly ash, improves strength and durability of concrete. Chapter 6 provides detailed discussion on how incorporating nanosilica enhances thermal and chemical stability of hydration products in cement paste samples. Also, chemo-mechanical effects of nanosilica addition on cement paste are studied through the application of coupled nanoindentation/SEM-EDS.

In Chapter 7, effects of nanosilica on the resistance against carbonation of CH and C-S-H in cement paste, which could be accelerated during cooling process after exposure to high temperatures, are described.

Finally, Chapter 8 presents the main findings of this research and recommendation for future work.
CHAPTER 2
LITERATURE REVIEW

2.1 Microstructure of concrete

Concrete is a heterogeneous material at multiple length scale. It is a mixture of cement paste and aggregate particles with a porous microstructure. When cement powder is mixed with water, hydration products are formed through a series of exothermic reactions. With time, these hydration products in cement paste form a rigid structure which is also heterogeneous and porous in nature as shown in Fig. 2.1. Mature cement paste is normally composed of 50-60% C-S-H, 20-25% CH and other chemical compounds, such as ettringite, monosulfate, and unhydrated cement particles [17]. Macroscopic properties of cement-based composite materials at high temperatures are governed by the properties of these phases, which demands detailed knowledge of the morphological and mechanical changes in each phase after exposure to elevated temperatures.

Figure 2-1 SEM images of cement paste microstructure: regions showing formation of (a) ettringite and (b) CH and C-S-H
2.2 General behavior of concrete after exposure to elevated temperatures

Many environmental factors, such as rate of temperature rise, duration of exposure at different temperature, and initial moisture content, control the response of concrete to fire. However, behavior of concrete after exposure to high temperatures is mainly influenced by its composition as both of its constituents, cement paste and aggregates, can decompose on heating. Thermal deterioration is especially critical and progressive at ITZ due to a significant difference in thermal expansion values for cement paste and aggregate. As aggregate normally occupy 65 to 75% of the concrete volume, the behavior of concrete at elevated temperatures is largely affected by the type of aggregate. The porosity of aggregates could also determine the response of concrete at elevated temperatures. Depending on the size, permeability, and moisture content of aggregates, the porous aggregates may themselves be susceptible to disruptive expansion leading to pop-outs [17]. However, the low-porosity aggregates could be free from the problems related to internal moisture movement. The mineralogy of aggregates also has an important influence on the response of concrete exposed to high temperatures. Siliceous aggregates are predominantly quartz which undergoes crystal transformation (from trigonal $\alpha$-quartz to hexagonal $\beta$-quartz) between 500 and 650 ºC leading to an approximately 6% volume increase [9]. Non-siliceous aggregates provide higher fire resistance and better spalling resistance than siliceous aggregate [18, 19]. This is mainly because non-siliceous aggregates have substantially higher heat capacity (specific heat). Most non-siliceous aggregates are stable up to about 600 ºC. At temperatures higher than 600 ºC, calcareous aggregates ($\text{CaCO}_3$), magnesite ($\text{MgCO}_3$), and dolomite ($\text{MgCO}_3/\text{CaCO}_3$) dissociate into an oxide ($\text{CaO}$ or $\text{MgO}$) and $\text{CO}_2$ following an endothermic reaction. This endothermic reaction absorbs energy supplied by fire and enhances the specific heat of concrete [19]. Khoury et al. reported that the thermal stability of aggregates increases in the following order: gravel, limestone, basalt, and
lightweight; the expansive cracking of the gravel occurs at about 350 °C, expansion of limestone and basalt without cracking occurs at temperature up to 600 °C, and lightweight aggregates are dimensionally stable even at 600 °C [20].

Compared to conventional (normal-strength) concrete, high-strength concrete with low water-to-cement ratio (w/c) behaves differently at elevated temperatures. High-strength concrete shows higher tendency to explosive spalling. The extent of explosive spalling depends on many factors, such as the loading conditions, permeability, compressive strength, and moisture content, and increases with increasing compressive stress, impermeability of concrete, and moisture content [17, 21]. The mechanisms for spalling are related to the build-up of pore pressure due to moisture release, increase in stress under steep temperature gradients, and volume change caused by phase transformation in aggregate [21, 22]. At 300 °C, the pore pressure can be as high as 8 MPa. Such a high internal pressure cannot be resisted by high-strength concrete mix with average tensile strength of about 5 MPa [23].

It is reported that addition of polymer fibers can efficiently prevent thermally induced explosive spalling [24, 25]. Polymer fibers melts at around 170 °C, whereas explosive spalling occurs between 190 and 300 °C [26]. When the fibers melt and are absorbed partially by the paste matrix, they leave a pathway for steam. This contributes to the creation of a network more permeable than the original matrix, which allows the outward migration of steam and reduces the development of pore pressure.
2.3 Decomposition of hydration products in cement paste at elevated temperatures

When cement paste is exposed to high temperatures, various hydration products gradually lose water that ultimately causes mass loss. In a well hydrated cement paste, release of water vapor resulting from the evaporation of free water and the dehydration of hydration products are nearly complete at approximately 500 °C [20, 27-31]. For example, ettringite, an important crystalline component of hydrated Portland cement, loses its stability at temperatures below 120 °C [28]. CH loses water between 400 and 500 °C, but if CO₂ is available, above 400 °C it may form the calcium carbonate (CaCO₃). In addition, decomposed CH could reform quickly while cooling down to ambient temperature [30, 32]. Decomposition of C-S-H, which is the primary hydration product and the principal binding phase, has been reported to occur within a wide temperature range due to its amorphous characteristics. It is a multi-step reaction due to the complexity of the gel structure and presence of water that is bound to a different degree and requires different amount of energy to be released [32, 33]. The results of thermogravimetric analysis (TGA), nuclear magnetic resonance (NMR), and neutron diffraction (ND) have shown that the primary temperature range at which C-S-H dehydration occurs to be 100 and 450 °C [10, 29-31]. Fordham et al. suggested that dehydration of three types of water in C-S-H occurs below 400 °C; dehydration of capillary pore water at 180 °C; interlayer water at 350 °C and absorbed water at 400 °C [34]. However, some TGA studies indicate that the temperature range corresponding to the dehydration of C-S-H is very broad, from 105 to about 1000 °C [35, 36]. Alonso et al. reported that dehydrated C-S-H forms a “new nesosilicate” with a CaO/SiO₂ ratio of approximately 2, based on ²⁹Si magic-angle spinning nuclear magnetic resonance (MAS-NMR) and XRD studies [30]. Of special note, NMR studies of cement paste exposed to high temperatures demonstrated a progressive transformation of C-S-H
to a “new nesosilicate” at temperatures above 200 °C, with complete transformation at 750 °C. Peng et al. argued that C-S-H decomposition starts at 560 °C but become significant only above 600 °C mainly based on their XRD test results [37]. Harmathy reported a secondary range of C-S-H dehydration between 650 and 800 °C followed by the primary dehydration of C-S-H between 105 and 300 °C based on their TGA results [10].
CHAPTER 3
NANOINDENTATION TECHNIQUE AND COUPLED ENERGY DISPERSIVE X-RAY ANALYSIS

3.1 Introduction

Indentation testing is a mechanical characterization method where an indenter of specific geometry is impressed into a surface of the test specimen using a known applied force. Nanoindentation is an indentation test in which the depth of penetration of the indenter is in the order of few hundred nanometer ($10^{-9}$ m). This technique can be used to calculate a wide variety of properties, such as elastic modulus, hardness, strain-hardening exponent, fracture toughness (for brittle materials), and viscoelasticity.

The technique can be applied to multi-phase materials, such as cement paste, to obtain mechanical properties of different phases present in the microstructure, however, the data analysis and interpretation is generally more complex than in the case of single-phase materials. Generally, a large number of indentations are performed on a multi-phase sample on a grid (so-called grid indentation) and the data collected is analyzed statistically to estimate the mechanical properties and volume faction of different phases present. However, it could be difficult to determine a unique solution to the statistical deconvolution if it is solely based on mechanical responses since neither the phase volume fraction nor their mechanical properties are known a priori. To address these issues, coupled nanoindentation with SEM-EDS has been applied to link mechanical response at each test location to chemical composition.
3.2 Static nanoindentation

Static nanoindentation is a depth-sensing indentation technique used for nanomechanical characterization of materials. During nanoindentation, a force is applied and removed to a sample in a controlled manner with a geometrically well-defined probe and the resulting displacement is observed to produce a load-displacement ($P-h$) plot. Analysis of the measured $P-h$ plot provides information regarding the mechanical properties of the samples, such as indentation modulus ($E$) and hardness ($H$). This analysis procedure is fundamentally based on the solution of contact between two elastic solids developed by Boussinesq and Hertz [38].

![Figure 3-1](image)

Figure 3-1 Schematic of contact between a rigid indenter and a flat specimen. $a$ is the radius of the circle of contact, and $R_i$ is the indenter radius. $h_{\text{max}}$ is the total depth of penetration, $h_a$ is the depth of the circle of contact from the specimen free surface, and $h_c$ is the contact depth which is the distance from the bottom of the contact to the contact circle [38]
A schematic of the contact between a rigid indenter and a flat specimen is shown in Fig. 3.1. Hertz [39] found that the radius of the circle of contact $a$, is related to the indenter load $P$, the indenter radius $R$, and elastic properties of the materials in contact by:

$$a^3 = \frac{3PR}{4E^*}$$  \hspace{1cm} (3.1)

where $E^*$ is combined modulus of the indenter and the specimen, which is referred to as the “reduced modulus” or “indentation modulus” of the system and is given by:

$$\frac{1}{E^*} = \frac{(1 - \nu^2)}{E} + \frac{(1 - \nu'^2)}{E'}$$  \hspace{1cm} (3.2)

where $E$ and $\nu$ are elastic modulus and Poisson’s ratio of the specimen, respectively. $E'$ and $\nu'$ are elastic modulus and Poisson’s ratio of the indenter, respectively.

In terms of the total depth of penetration $h_{max}$ beneath the specimen free surface, we can also write:

$$P = \frac{4}{3}E^*R^{1/2}h_{max}^{3/2}.$$  \hspace{1cm} (3.3)

For a conical indenter, similar equations apply where the radius of circle of contact is related to the indenter load by:

$$P = \frac{\pi}{2}a^2E^* \cot \alpha$$  \hspace{1cm} (3.4)

where $\alpha$ is the cone semi-angle as shown in Fig. 3.2 [38]. The term $acot \alpha$ is the depth of penetration, $h_c$ measured at the circle of contact. By considering the depth profile of the deformed surface within the area of contact, we can rearrange Eq. 3.4 in terms of the total depth of penetration $h_{max}$:

$$P = \frac{2}{\pi}E^* \tan \alpha h_{max}^2.$$  \hspace{1cm} (3.5)
As mentioned above, during an indentation test, the depth of penetration is recorded continuously and the contact area can be determined using known geometry of the indenter for a perfect indenter. Irregularities in the indenter geometry due to regular wear and tear can be taken into account by calibrating the tip on a material with known properties. During an indentation test, applied load and depth of penetration are measured continuously and these values are plotted on a graph to produce a $P-h$ curve such as the one shown in Fig. 3.3.
Figure 3-3 Schematic of load-displacement (P-h) curve for an instrumented nanoindentation test [40]

The contact depth \( (h_c) \) can be determined using the following equation:

\[
h_c = h_{\text{max}} - \varepsilon \frac{P_{\text{max}}}{S}
\]  

(3.6)

where \( S \) is the contact stiffness determined by calculating the slope of the curve, \( dP/dh \), upon unloading. To account for edge effects, the deflection of the surface at the contact perimeter is estimated by taking the geometric constant \( (\varepsilon) \) as 1 for a flat punch tip and 0.75 for a paraboloid of revolution. The cross-sectional area of an indentation shown in Fig. 3.4 illustrates the relationship of \( P, A, h_c \) and \( h \).
The hardness of a material is defined as:

$$H = \frac{P_{\text{max}}}{A}. \quad (3.7)$$

where $P_{\text{max}}$ is the maximum load applied during an indentation test and $A$ is the area of contact.

The reduced modulus is defined as:

$$E^* = \frac{S\sqrt{\pi}}{2\sqrt{A}}. \quad (3.8)$$

Rearranging the above equation yields:

$$A = \frac{\pi}{4} \left[ \frac{S}{E^*} \right]^2. \quad (3.9)$$

For a perfect Berkovich indenter with $\theta = 65.27^\circ$

$$A(h_c) = 3\sqrt{3}h_c^2\tan^2\theta = 2.45h_c^2 \quad (3.10)$$

where $A(h_c)$ is the contact area or the projected area of the indentation at the contact depth of $h_c$. To account for imperfect indenter geometry, a series of indents at various contact depths (varying normal loads) are performed on a sample of known elastic modulus (typically fused quartz) and
the contact area $A$ is calculated. A plot of the calculated area as a function of the contact depth is created and an 8th order polynomial called the area function is determined as:

$$A(h_c) = C_0 h_c^2 + C_1 h_c^1 + C_2 h_c^{1/2} + C_3 h_c^{1/4} + \cdots + C_8 h_c^{1/128}$$  \hspace{1cm} (3.11)

where $C_0$ for Berkovich and cube corner tips are 24.5 and 2.598, respectively.

### 3.3 Dynamic nanoindentation

During dynamic indentation test, it is assumed that linear viscoelastic conditions exist in the material. Thus, in principle, dynamic nanoindentation is similar to dynamic mechanical analysis (DMA). For a linear viscoelastic material under a sinusoidal loading in DMA, a sinusoidal strain is generated as shown in Fig. 3.5. By measuring both the amplitude of deformation at the peak sine wave and the phase lag between the stress and strain, quantities like storage and loss moduli can be calculated by:

$$\sigma = \varepsilon_0 E' \sin \omega t + \varepsilon_0 E'' \cos \omega t$$  \hspace{1cm} (3.12)

where $\sigma$ is the stress, $\varepsilon_0$ is the strain amplitude, $\omega$ is angular frequency, and $t$ is the time,

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos \varphi$$  \hspace{1cm} (3.13)

and

$$E'' = \frac{\sigma_0}{\varepsilon_0} \sin \varphi$$  \hspace{1cm} (3.14)

where $\sigma_0$ is the stress amplitude and $\varphi$ is the phase lag between the stress and the strain. $E'$ and $E''$ are storage and loss moduli, respectively. The ratio $E''/E' = \tan \varphi$ is called the loss factor and is often used as a measure of damping in a linear viscoelastic material.
Figure 3-5 Dynamic displacement and applied dynamic load. $F_d$ is the dynamic load, $F_s$ is the static load [42]

In dynamic nanoindentation, a low magnitude dynamic load is superimposed on the overall quasistatic load. The resulting signal is analyzed at the same frequency to measure displacement amplitude and phase lag. Fig. 3.6 shows a schematic illustration of the instrument used for dynamic nanoindentation test and its corresponding dynamic model [43].

Figure 3-6 (a) A schematic illustration of the testing system and the dynamic model used to describe the behavior of the system as function of frequency, (b) The dynamic model used to describe the combined frequency response of the instrument and sample [43]

The contact for dynamic test can be modeled by a single degree of freedom, damped, forced harmonic oscillator. The equation of motion for this is given by:
\[ F_d \sin \omega t = m\ddot{x} + C\dot{x} + kx \]  \hspace{1cm} (3.15)

where \( F_d \) is the amplitude of the load oscillation, \( m \) is the mass of the indenter, \( C \) is the damping coefficient of the instrument, \( k \) is the stiffness of the support spring, and \( x \) is the displacement response which is given as:

\[ x = X \sin(\omega t - \varphi). \]  \hspace{1cm} (3.16)

Solutions to the differential equation given in 3.15 are:

\[ X = \frac{F_d}{\sqrt{(k - m\omega^2)^2 + (C\omega)^2}} \]  \hspace{1cm} (3.17)

and

\[ \varphi = \tan^{-1} \frac{\omega C}{k - m\omega^2}. \]  \hspace{1cm} (3.18)

Rearranging these equations, \( k \) (stiffness) and \( C \) (damping) can be calculated by:

\[ k = \frac{F_d X}{\sqrt{1 + \tan^2 \varphi}} \frac{1}{\sqrt{1 + \tan^2 \varphi}} + m\omega^2 = \frac{F_d}{X} \cos \varphi + m\omega^2 \]  \hspace{1cm} (3.19)

and

\[ C = \frac{F_d^2}{X^2} \frac{\tan^2 \varphi}{1 + \tan^2 \varphi} \frac{1}{\omega} = \frac{F_d}{X} \sin \varphi \frac{1}{\omega}. \]  \hspace{1cm} (3.20)

When the indenter and sample, which are coupled through the geometry of the contact, undergo steady-state harmonic motion, the stiffness \( k \) and damping \( C \) are the combined stiffness and damping of the instrument and the sample as follows:

\[ k = k_i + k_s \]  \hspace{1cm} (3.21)

and

\[ C = C_i + C_s. \]  \hspace{1cm} (3.22)
The stiffness ($k_s$) and damping ($C_s$) of the sample are determined by subtracting out the instrument’s contribution ($k_i$ and $C_i$) from the combined response. During instrument calibration, stiffness, damping and mass of the instrument can be found by running dynamic calibration of the instrument in air. In the limit of linear viscoelasticity, the elastic-viscoelastic correspondence principle is valid and thus Sneddon’s stiffness equation can be used to relate the stiffness and damping to the viscoelastic properties of the sample, such as storage modulus ($E'$), loss modulus ($E''$), as calculated with the following equations:

$$E' = \frac{k_s \sqrt{\pi}}{2\sqrt{A_c}}$$ \hspace{1cm} (3.23)

and

$$E'' = \frac{\omega C_s \sqrt{\pi}}{2\sqrt{A_c}}$$ \hspace{1cm} (3.24)

where $A_c$ is the contact area. During dynamic test, a quasistatic load is simultaneously applied to the sample with the indenter and the quasistatic displacement is measured. Using the quasistatic load and displacement, the contact depth and the contact area ($A_c$) are calculated following the same procedure as described for static nanoindentation.

### 3.4 Coupled nanoindentation/scanning electron microscopy with energy dispersive x-ray analysis

A grid nanoindentation technique, based on statistical evaluation of a large number of indentations, can provide valuable information on the local mechanical properties of hydration products in cement-based composite materials. However, statistical identification of phases based solely on mechanical properties is limited. SEM and transmission electron microscopy (TEM) studies show
intermixing of hydration products in a hydrated cement paste on a submicrometer scale [44, 45]. Therefore, satisfying the length of separation (indentation depth \( \ll \) characteristics length of a phase) criterion for indentation of one phase at a time is not always possible. Thus, the mechanical phases detected even after statistical deconvolution in the frequency plots of indentation modulus and hardness are potentially a composite response of multi-phases. In order to directly correlate the mechanical properties of individual phase with a phase having a unique chemical composition, the size of the probed microvolume must be sufficiently smaller than the characteristic size, \( D \), of the chemical phase of interest as shown in Fig. 3.7(a). If, on the other hand, the probed microvolume is greater than \( D \), then a composite mechanical response will inevitably be observed as shown in Fig. 3.7(b). Furthermore, the local mechanical properties of individual phases present in a hydrated cement paste are not known a priori.

![Figure 3-7 Grid indentation on a heterogeneous system](image)

**Figure 3-7 Grid indentation on a heterogeneous system where the probed microvolume (cross-hatched regions below the indenter) is either (a) smaller or (b) larger than the characteristic length scale, \( D \), of the phase of interest [46]**
In one recent study, Portland cement paste was analyzed by grid nanoindentation coupled with SEM-EDS at each indentation point [46]. The mechanical information provided by nanoindentation was directly comparable to the chemical information provided by SEM-EDS, since finite element and Monte-Carlo simulations showed that the microvolumes probed by each method are of comparable size (approximately 2 μm). Such coupled approach provided the opportunity to determine whether the local mechanical response at each indent location is representative of a single-phase or a multi-phase response.

Figure 3-8 Multi-dimensional cube with n material characteristics (phase mechanics, chemistry, orientation) measured in independent experiments at the Nx × Ny nodal points of the grid [47]

The statistical deconvolution method to associate mechanical properties obtained from nanoindentation to local phase chemistry in cement-based composite materials is proposed in [47, 48]. In this approach, each of the j-th point on the grid is characterized by an ordered n-tuple vector $y_j$ consisting of the 5 different experimental measurements. Thus, $y_j = [E, H, C_{SI}, C_{Ca}, C_{Al}]$, where
E and H correspond to indentation modulus and indentation hardness, respectively, while C’s stand for mass fractions of the elements of interest as shown in Fig. 3.8. Each \( y_j \) is an experimental realization of the random vector \( Y \), with probability density function (p.d.f.) \( f(y_j) \). Due to the multi-phase nature of cement-based composite materials, a possible outcome of a single trial is \( y_j \) belonging to one of the \( g \) phases, such as CH and C-S-H, present within the investigated region of interest (ROI). Each phase will be associated with one and only one combination of the \( C_j \)’s and \( E \) and \( H \) on average, represented by mean vector \( \mu_i \), with \( i = 1, \ldots, g \).

The inference of mean vector \( \mu_i \) from the actual experimental data set requires assumption of the probabilistic density function of the random variable \( Y \). In this model, p.d.f. of \( Y \) is assumed to follow the Finite Mixture Model, which is a convex combination of two or more probability density functions, Eq. (3.25a) with the multivariate normal p.d.f., \( f_i \) as the component density function, Eq. (3.25b) and Eq. (3.25c):

\[
f(y_j; \Psi) = \sum_{i=0}^{g} \pi_i f_i(y_i; \theta_i), \quad 0 \leq \pi_i \leq 1 \quad (i = 0, \ldots, g), \quad \sum_{i=1}^{g} \pi_i = 1 \tag{3.25a}
\]

\[
f_i(y_j; \theta_i) = \phi(y_j; \mu_i, \Sigma_i) \tag{3.25b}
\]

\[
\phi(y_j; \mu_i, \Sigma_i) = (2\pi)^{-p/2} |\Sigma_i|^{-1/2} \exp \left\{ -\frac{1}{2} (y_j - \mu_i)^T \Sigma_i^{-1} (y_j - \mu_i) \right\} \tag{3.25c}
\]

where \( \Sigma_i \) is covariance matrix, \( \pi_i \) represents the surface fraction of a component \( i \) in the mixture, and \( \theta_i \) is a vector of unknown parameters for the \( i \)-th component density in the mixture.

Therefore, the standard deviations on each variable, as well as eventual variable correlations are captured by the covariance matrix \( \Sigma_i \). All unknown parameters of the mixture model define vector \( \Psi = (\pi_1, \ldots, \pi_g, \mu_1, \Sigma_1, \ldots, \mu_g, \Sigma_g) \) are estimated based on the maximum likelihood (ML) via the expectation maximization (EM) algorithm [49-51]. The likelihood can be written as:
$$L(\hat{\Psi}) = \prod_{j=1}^{N} f(y_j; \Psi)$$  \hspace{1cm} (3.26)

where N is the number of observations, $\hat{\Psi}$ denotes the estimate of the unknown vector $\Psi$.

The basic idea of the EM algorithm is, beginning with an initial model $\Psi$, to estimate a new model $\hat{\Psi}$, such that $f(Y; \hat{\Psi}) \geq f(y_j; \Psi)$. The new model then becomes the initial model for the next iteration and the process is repeated until some convergence threshold is reached.

On each EM iteration, the following re-estimation Eq. (3.27a), Eq. (3.27b) and Eq. (3.27c) are used which ensure a monotonic increase in likelihood value of the model:

Probability weights

$$\hat{\pi}_i = \frac{1}{N} \sum_{j=1}^{N} f_r(i; y_j, \theta_i)$$  \hspace{1cm} (3.27a)

Means

$$\hat{\mu}_i = \frac{\sum_{j=1}^{N} f_r(i; y_j, \theta_i)y_j}{\sum_{j=1}^{N} f_r(i; y_j, \theta_i)}$$  \hspace{1cm} (3.27b)

Variances (diagonal term of covariance matrix)

$$\hat{\sigma}_i^2 = \frac{\sum_{j=1}^{N} f_r(i; y_j, \theta_i)y_j^2}{\sum_{j=1}^{N} f_r(i; y_j, \theta_i)} - \hat{\mu}_i^2;$$  \hspace{1cm} (3.27c)

The a posteriori probability for $i$-th component is given by Eq. (3.28):

$$f_r(i; y_j, \theta_i) = \frac{\pi_i \phi(y_j; \mu_i, \Sigma_i)}{\sum_{l=1}^{g} \pi_l \phi(y_j; \mu_l, \Sigma_l)}.$$  \hspace{1cm} (3.28)
CHAPTER 4
DEGRADATION OF HYDRATION PRODUCTS AT VARIOUS HEATING AND COOLING REGIMES

4.1 Introduction

As reviewed briefly in Chapter 2.3, temperature ranges for the degradation of each hydration product are established through work by many researchers. However, it is not well understood yet how these changes are manifested in the micro and nanostructure of cement paste. It is generally accepted that micro and nanostructural changes are ultimately responsible for the loss of macroscopic mechanical properties; but the lack of characterization at the micro and nanoscales during and after exposure to elevated temperatures makes it difficult to establish a link between the two. Due to this research gap, several questions regarding thermal degradation of cement-based composite materials remain unanswered. For example, it is not clearly understood why (i) the compressive strength of cement paste increases upon exposure to 200 °C even though this temperature is high enough to initiate dehydration of C-S-H; (ii) loss of strength and an increase in porosity are insignificant even after exposure to temperature as high as 300 °C [1], which can result in shrinkage of C-S-H [52, 53]. In spite of the degradation of C-S-H observed at relatively low temperature, manifestation of this degradation on the micro and macroscopic level does not occur until C-S-H is exposed to much higher temperatures [1]. Therefore, further research is necessary to understand the effects of thermal exposure on the micro and nanostructure of cement paste and how it governs macroscopic degradation of the system. In this chapter, extensive experimental study is carried out to investigate the micro and nanostructural changes that occur due to exposure of cement paste to high temperatures. After exposure to temperatures up to 1000
°C, thermal damage states of the cement paste samples are studied by TGA and XRD. Also, SEM and AFM techniques are used to characterize micro and nanoscales damages in the cement paste samples. Image analysis is performed on images obtained from AFM for quantitative analysis of micro and nanostructural changes, such as the size of the hydration product features and their connectivity. As per our knowledge, this research shows for the first time an evidence based on AFM characterization and its image analysis of changes in C-S-H nanostructure after exposure to 300 °C that can be due to thermal shrinkage of C-S-H, a phenomenon indicated in the past by other researchers [52, 53]. By combining SEM and AFM characterization, we propose a degradation mechanism that initiates at micro and nanoscales and drives the process of loss of mechanical properties at macroscale.

4.2 Experimental details

Cement paste samples with w/c of 0.35 and 0.45 were prepared using Type I Portland cement (provided by Continental Cement Company) and de-ionized (DI) water. Chemical composition and physical properties of the cement provided by the manufacturer are given in Table 4.1.

**Table 4-1 Chemical composition of the cement (in % by weight)**

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.93</td>
<td>4.45</td>
<td>2.72</td>
<td>63.28</td>
<td>3.03</td>
<td>2.44</td>
<td>0.59</td>
<td>0.13</td>
<td>57.82</td>
<td>16.38</td>
<td>7.20</td>
<td>8.26</td>
</tr>
</tbody>
</table>

Cement paste was mixed in a Hobart mixer according to ASTM C305. Two different-sized samples, cylinders 2.5 cm in diameter × 5 cm in length and prisms 2.5 × 2.5 × 10 cm, were prepared. As this research focuses on understanding the changes that occur at micro and nanoscales
due to the thermal degradation of hydration products, small sample sizes were used in order to minimize the influence of thermal gradients during heat treatment. In large samples, thermal gradient can cause additional damages, such as spalling. Study of such damage is outside the scope of this research.

**Figure 4-1 Schematic diagram of the heating and cooling procedure**

After casting, samples were cured in sealed condition in laboratory environment for the first 24 hours, then demolded and stored in an environmental chamber at 25 °C and 100% R.H. for the remaining 27 days of curing. Cured samples were then exposed to different cycles of heat treatment with maximum temperatures ranging from 105 to 1000 °C at an increment of 100 °C per cycle. Fig. 4.1 presents the 10 different heating and cooling cycles employed in this research. During each cycle, a heating rate of 1 °C/min was used to reach the target temperature. Samples were held at 105 °C for 2 hour in order to promote removal of free water. After reaching the target maximum temperature, $T_m$, it was held constant for 6 hours to promote uniform temperature throughout the samples. In the final step of the cycle, samples were allowed to cool down to room temperature at a cooling rate of 1 °C/min. Samples are identified according to the heat treatment they were exposed to. For example, P25 represents the control sample without heat treatment. Similarly,
P300 stands for the paste sample that was exposed to 300 °C. Target temperatures and various characterization methods used in this chapter are summarized in Table 4.2.

### Table 4-2 Summary of heat treatment process and characterization methods used in

**Chapter 4**

<table>
<thead>
<tr>
<th>Target Temp. (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Cooling rate (°C/min)</th>
<th>TGA</th>
<th>XRD</th>
<th>SEM</th>
<th>AFM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control sample</td>
<td>-</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>105</td>
<td>-</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>300</td>
<td>1</td>
<td>1</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>-</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>-</td>
<td>✓</td>
</tr>
<tr>
<td>700</td>
<td></td>
<td></td>
<td>✓</td>
<td>-</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>900</td>
<td></td>
<td></td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

TGA and XRD were performed to identify the chemical changes the hydration products underwent due to high temperature exposure. The test samples for TGA and XRD were obtained from the inner core of cylindrical samples with w/c of 0.35. A ground paste sample (approximately 30 mg) was subjected to TGA using an SDT Q600 thermal analyzer. The temperature was programmed to rise at a constant heating rate of 10 °C/min up to 1000 °C and was held constant at 105 °C for 2 hours to promote removal of free water. The test was performed under a nitrogen flow of 50 ml/min. XRD was carried out on paste samples after exposure to various temperatures (105, 300, 500, 700, and 900 °C) using Siemens-Bruker D5000 XRD with CuKα radiation (λ=1.5406 Å). Scanned 2-theta angle from 4 to 80° was used with step size of 0.02° and scan rate of 1 °/min. JADE software suite was used to characterize the mineralogical crystalline phases.

Samples for SEM and AFM were obtained from the inner core of prism samples with w/c of 0.35 after a three-point bending test to diminish additional damage to the sample during specimen collection (specifically, cracking, which can occur during breaking of samples). Freshly fractured surface of samples were investigated using a JEOL 6060LV scanning electron microscope in
secondary electron mode. Samples for AFM were vacuum-impregnated with epoxy resin to minimize damage during polishing. The epoxy impregnation was followed by grinding and polishing. First, samples were ground with silicon carbide papers of decreasing grit sizes (320, 400, 600, and p2400 or 35, 21.8, 15.3, and 8.4 μm, respectively). They were then polished with p4000 (5-μm) silicon carbide paper, 1- and 3-μm diamond lapping film and, finally, 0.25-μm diamond paste. Glycol was used as a lubricant throughout the grinding and polishing steps. The grinding and polishing steps were performed using a Buehler EcoMet Grinder-polisher and an AutoMet Power Head at a force of 5 lbs. and a wheel speed of 50 rpm (except with the diamond lapping film). Samples were polished for 2 minutes at each step, 1 minute in the clockwise and 1 minute in the counter-clockwise directions. An Asylum MFP-3D AFM was used for imaging a polished surface of epoxy-impregnated samples at micro and nanoscales. Topographic images were acquired in tapping mode AFM using a silicon tip of radius less than 10 nm and half cone angle less than 25º along the cantilever axis. Scanning speed was varied from 0.25 to 1 Hz depending on the scan size, and image resolution was 1066×837 pixels. Varying scan sizes from 1×1 to 20×20 μm were used in this research.

AFM images were used for quantitative analysis to determine the characteristic size of hydration product features and their connectivity after heat treatment. Each image was prepared and analyzed carefully using ImageJ, a public domain, image processing program developed by the National Institutes of Health (NIH), USA. The following steps were taken to prepare one image for analysis. AFM images were converted to an 8-bit gray scale and then filtered to smooth extreme variations in the image using “Bandpass Filter Tool” in ImageJ. To remove high spatial frequencies (blurring the image) and low spatial frequencies (similar to subtracting a blurred image), large and small structures were filtered out with the parameter upper cutoff at 40 pixels and the lower cutoff at 3
pixels with 5% tolerance of direction. The filtered images were then binarized to segment grayscale images into features of interest (pores or hydration product) and background. Binary images were first produced by using the auto thresholding available in ImageJ [54]. The results of filtering and binarization are shown in Fig. 4.2. In a second step, manual correction was applied to carefully remove any unintentional effect of the filtering and binarization. Size of each particle (where particles are the feature of interest which can be pores or hydration product) was defined as the number of pixels covered by the particle converted to square microns and calculated using the “Analyze Particles” process available in ImageJ. Further statistical analysis was performed on the particle size data to determine particle size distribution and particle connectivity. The procedure was repeated considering both pores and hydration products as “particles” in two subsequent analyses.

![Figure 4-2 Image preparation for particle (pores or hydration product) size distribution using ImageJ: (a) AFM, (B) Bandpass filtered and (C) Binary images of the control sample](image_url)
4.3 Experimental results and discussion

4.3.1 Thermogravimetric Analysis

TGA results shown in Fig. 4.3 clearly indicate mass loss due to the dehydration of hydration products as a function of exposure temperature. Significant mass loss between room temperature and 105 °C corresponds to loss of free water and the decomposition of ettringite. Temperature was held at 105 °C for 2 hours in order to promote removal of free water, which caused steady loss in mass. Both the samples with w/c of 0.35 and 0.45 exhibit nearly identical mass loss. Between 105 °C and 400 °C, mass loss is gradual. This gradual loss in mass is believed to be related to the primary dehydration of C-S-H [10, 29-31]. The interlayer water, absorbed water, and some of the chemically bound water from C-S-H could be lost at this temperature range. Drastic mass loss between 400 and 450 °C is observed due to the decomposition of CH (Ca(OH)$_2$ → CaO + H$_2$O). Further mass loss, which occurs gradually until about 650 °C, may be related to the decomposition of C-S-H due to loss of chemically bound water (and decomposition of calcium carbonate, if present due to carbonation, despite taking strict precautionary measures). Above 650 °C, the rate of mass loss decelerates, and total mass loss is almost negligible.
As evident from the experimental data presented above and in Chapter 5, mass loss and strength loss do not correlate well throughout the temperature regime. In spite of mass loss between 105 and 200 °C, compressive strength actually increases drastically. Only a gradual reduction in strength occurs between 400 and 500 °C with significant mass loss, and a continuous decrease in strength above 600 °C occurs without any significant mass loss. The mismatch between mass loss and strength loss will be further discussed in Chapter 5.

Information on the chemical degradation of hydration products, as determined from TGA, is often insufficient to explain changes in compressive strength. Therefore, a comprehensive set of maximum heat treatment temperatures of 105, 300, 500, 700, and 900 °C was chosen for XRD, SEM, and AFM. Since the observed trends in mass loss (and compressive strength) between two samples with different w/c are comparable, w/c of 0.35 was chosen for micro and nanoscales characterizations.

Figure 4-3 Results of TGA on paste samples with w/c of 0.35 and 0.45
X-ray diffractograms for paste samples with w/c of 0.35 after exposure to various temperatures are shown in Fig. 4.4. Main phases in the control sample are identified as CH, C-S-H, brownmillerite, and β-C₂S. The peaks of CH, such as (001) crystal face, as well as (101), (102), and (110) crystal faces ($d=0.490, 0.263, 0.193$ and $0.180$ nm, respectively), dominate the x-ray diffractogram of the control sample. The weak peaks at $2\theta=29.35^\circ$ ($d=0.304$ nm) and $32.12^\circ$ ($d=0.278$ nm) for C-S-H and β-C₂S, respectively, are also identified in the control sample. Most of the peaks are persistent in samples with heat treatment at temperatures up to 300 °C. Mass loss between 105 and 300 °C, which is shown in TGA, is not reflected by any identifiable phase change in XRD. A hump related to C-S-H around $2\theta=29.35$ is persistent up to 300 °C, but disappears above 500 °C. This change at 500 °C is accompanied by an increase in intensity for peaks related to β-C₂S, which forms through C-S-H decomposition [30, 31]. A reduction in peak intensity of CH is observed at 500 °C. It confirms that mass loss observed in TGA between 400 and 450 °C corresponds to decomposition of CH, which results in the formation of CaO [30, 31]. However, peaks related to lime is not detected in XRD until the heat treatment temperature is 700 °C (Fig. 4.4(b)). Furthermore, some peaks related to CH are still identified above 500 °C probably due to reformation of CH during cooling process [30] or incomplete decomposition of CH during heat treatment. The peaks related to CaCO₃ are seen in sample treated at 700 °C, but disappears in sample treated at 900°C with increased intensity of CaO peaks in the later sample. Based on this investigation, it can be assumed that reaction of CaO formed by CH decomposition with CO₂ present in the furnace or carbonation of reformed CH could form CaCO₃. CaCO₃ is then decalcified between 700 and 900°C to reproduce CaO.
Figure 4-4 X-ray diffractograms of paste samples with \({c}/w\) of 0.35 after exposure to various temperatures: (a) Scanned 2-theta angle from 4° to 80° and (b) Zoom on dashed area in Fig. 4.4(a), key to phases: ○ Lime(CaO), ▲ Portlandite(Ca(OH)\(_2\)), ♦ \(\beta\)-C\(_2\)S, ★ C-S-H\((\text{Ca}_{1.5}\text{SiO}_{3.5}\cdot x\text{H}_2\text{O})\), ■ Calcite(CaCO\(_3\)), △ Brownmillerite(Ca\(_2\)(Al,Fe)\(_2\)O\(_5\))

4.3.3 Scanning electron microscopy

In an attempt to identify the reason behind the mismatch between strength and mass loss, rigorous SEM investigations were performed on the surface of freshly fractured samples which are heat-treated at different temperatures.

SEM micrographs in Fig. 4.5 indicate morphological changes as a function of exposure temperature at a low magnification (100X). It is obvious that surface roughness of a fractured surface increases as temperature increases. A tortuous fracture plane indicates development of weaker areas and higher degree of heterogeneity in local mechanical properties of paste.
microstructure. This could be due to non-uniform degradation of paste microstructure at high temperatures.

To identify critical changes in morphology, Fig. 4.6 compares SEM micrographs at higher resolution (3000X). As shown in Fig. 4.6(a), a dense microstructure that is composed of hydration products, such as CH (marked as CH) and C-S-H (marked as CSH), is observed in the control sample. Main hydration products, CH and C-S-H are identified based on their morphology [55]. A sample at 105 °C shows a slight increase in surface toughness compared to the control sample. However, it do not show any other changes in the microstructure and morphology, nor any sign of degradation, such as microcracks or an increase in porosity. The microstructure is dominated by well-formed C-S-H and CH, similar to the control sample. After exposure to 300 °C, the microstructure is still dominated by C-S-H and CH. In spite of the dehydration of C-S-H and associated mass loss, there is no apparent sign of damage at this temperature. This agrees with published literature where the changes in total porosity and pore size distribution are reported to be negligible after heat treatment at 300 °C [1, 56]. However, careful observation reveals an important change in the microstructure of cement paste at this temperature. Angular particles (marked as C), presumed to be unhydrated cement particles, begin to appear on the fractured surface as shown in Fig. 4.6(b). The image also shows a clear gap around the unhydrated cement particles. This observation is quite interesting and the significance will be further discussed in the following section. The appearance of microcracks is first observed on a sample heated to 500 °C as shown in Fig. 4.6(c). It seems that microcracks start propagating from the edge of the interface between the anhydrous phases and the paste matrix. The microstructure also appears to be more porous than that of the samples treated at lower temperatures.
Figure 4-5 SEM images of fractured surfaces of cement paste (a) at room temperature (control sample), (b) 105 °C, (c) 300 °C, (d) 500 °C, (e) 700 °C and (f) 900 °C with w/c of 0.35 in 100× magnification
Figure 4-6 SEM images of fractured surfaces of cement paste (a) at room temperature (control sample), (b) 105 °C, (c) 300 °C, (d) 500 °C, (e) 700 °C and (f) 900 °C with w/c of 0.35 in 3000× magnification
SEM investigation on samples exposed to 700 °C reveals more microcracks and an increase in porosity. The microcracks become wider with increasing temperatures. At 900 °C, a predominance of microcracks and porous phases are detected. Some particles (marked as M) are totally cracked as shown in Fig. 4.6(d). Another interesting change in the microstructure is observed at 900 °C. As shown in Fig. 4.7(a) and (b), large spherical voids (approx. 50 μm) appear on several areas of the fractured surface. This could have occurred as a result of particles (possibly in unhydrated phases) “popping out” of the paste; however, the exact cause of these voids could not be established.

![Figure 4-7 SEM images of fractured surfaces of cement paste with w/c of 0.35, which show development of large voids at 900 °C in (a) 30× and (b) 500× magnifications](image)

4.3.4 Atomic force microscopy imaging and image analysis

AFM is a scanning probe imaging instrument that provides spatial resolution of a fraction of a nanometer (depending on specimen type and surface roughness) with a sharpened probe, typically less than 10 nm in diameter. In this research, AFM imaging was carried out to observe morphological changes of hydration products, mainly C-S-H, at nanoscale. Polished control and
heat-treated samples at different temperatures (300, 700 and 900 °C) were characterized using AFM. Each row in Fig. 4.8 has AFM images at three different magnifications for a particular temperature. Relatively brighter (representing areas higher than the average surface in the topography image) and smoother regions (marked as C) are unhydrated cement particles and the remaining image consists of paste matrix. For quantitative analysis of changes in pore size, particle size, pore connectivity, and solid phase connectivity with exposure temperature, image analysis was performed using ImageJ. Five images of random locations on each sample with a scan size of 5 × 5-μm were used for image analysis. The image size of 5 × 5-μm was specifically chosen for image analysis since the difference in the micro and nanostructure of paste matrix with different exposure temperature is more pronounced at this resolution as shown in Fig 4.8(b). Fig. 4.9 shows examples of binary AFM images used for image analysis.
Figure 4-8 AFM images with a scan size of (a) 20 × 20-µm, (b) 5 × 5-µm and (c) 1 × 1-µm on polished surfaces of epoxy impregnated cement paste with w/c of 0.35 after exposure to various temperatures.
Figure 4-9 Two samples of binary AFM images with a scan size of 5 × 5-µm from (a) control, (b) 300 °C, (c) 700 °C and (d) 900 °C samples used for image analysis (The solid is represented by “white” and the pore space is represented by “black”)
The control sample (Fig. 4.8 top row) exhibits a continuous paste matrix. Other than the gap around the cement particles, SEM micrographs, which are presented in the previous section, do not show any evidence of C-S-H dehydration at 300 ºC. It can be observed from AFM images (Fig. 4.8 second row) that an exposure to 300 ºC changes the nanostructure of the paste matrix to more particulate, loosely packed globular structure compared to the more continuous structure of the control sample. This could be due to shrinkage of C-S-H as it loses water. This visual observation is further confirmed through the image analysis data presented in Fig. 4.10. Figs. 4.10(a) and 4.10(b) show a significant decrease in area fraction of solid with size between 10 and 100 µm², and a significant and a slight increase in area fraction of solid with size between 0.01 and 1 µm² and 1 and 10 µm², respectively. Image analysis also shows an evidence of pore coarsening. Figs. 4.10(c) and 4.10(d) show an increase in volume of pores with size between 10 and 100 µm² and decrease in volume of pores with size between 0.01 to 10 µm². The nanostructure of paste matrix continues to manifest a particulate structure with an increase in heat treatment temperature. AFM images at 700 ºC are comprised of loosely packed small globules. Some of these particles could be β-C₂S or CaO, which are known to form due to the decomposition of C-S-H and CH and are evident from the XRD analysis presented in Chapter 4.3.2 [30, 31, 57]. With further increase in temperature, globule size increases (typical sizes changed from 250 to 400 nm) and the globules are more loosely packed.
Figure 4-10 Particle size distribution of paste samples determined by image analysis using ImageJ: (a) Area fraction vs. size of pore, (b) Cumulative area fraction vs. size of pore, (c) Area fraction vs. size of cement hydration products and (d) Cumulative area fraction vs. size of cement hydration products
Once again, the qualitative information obtained through visual observation of AFM images shown in Fig. 4.8 is confirmed by the quantitative information presented in Fig. 4.10 based on image analysis. From Fig. 4.10(c), it is clear that the fraction of the solid particle with size between 0.1 and 1 µm² increases as temperature increases from 700 to 900 °C. If the diameter is calculated by assuming the particles are circular, paste matrix at 900 °C is comprised of globules with diameter between 350 to 1000 nm. Globule diameter from such calculation matches closely with the measured globule size (the difference observed is related to bin size used for Fig. 4.10) from AFM image in Fig. 4.8 after heat treatment at 900 °C and confirms an increase in globule size with increasing temperature. Higher magnification AFM images (1 × 1-μm) show that the large globules are always made up of comparatively smaller-sized spherical particles in the size range of 50 to 90 nm irrespective of temperature exposure. The implication of this observation needs further investigation.

The change in connectivity of pores and the solid matrix after heat treatment was estimated by calculating the area fraction of the top (largest) 10% of pores or particles, respectively. Fig. 4.11 shows slight increase in pore connectivity as temperature increases, whereas the drop in paste matrix connectivity is more significant. This again confirms the visual observation from Fig. 4.8 that continuous paste matrix of the control sample degrades with temperature and forms more loosely packed globular structure.
Figure 4-11 Connectivity of pores and solid matrix

4.4 Conclusions

In this chapter, the degradation of hydration products is evaluated using various characterization methods. Micro and nanoscales imaging proves to be vital in identifying critical changes that occur at the micro and nanoscales and subsequently drive thermal degradation. AFM image analysis shows that an exposure of cement paste to 300 °C changes the nanostructure to more loosely packed globular structure, which could be indicative of C-S-H shrinkage. The nanostructure of C-S-H, and the products formed due to its dehydration rearranges continuously to make the microstructure more porous after exposure to elevated temperatures.
CHAPTER 5
DETERMINATION OF GLOBAL AND LOCAL MECHANICAL PROPERTIES OF CEMENT PASTE AFTER EXPOSURE TO ELEVATED TEMPERATURES

5.1 Introduction

As mentioned in the previous chapter, it is well known that cement-based composite materials exhibit a significant reduction in mechanical properties after exposure to high temperatures. The decomposition and/or dehydration of cement hydration products are believed to be the primary origins of thermal degradation of concrete. Dias et al. argued that increases in porosity and microcracks due to decomposition of hydration products probably cause degradation in mechanical properties of cement paste [59]. Exposure to high temperatures possibly alters mechanical properties of phases present in cement paste microstructure and their phase volume. Based on statistical analysis of nanoindentation tests, DeJong and Ulm reported thermally induced change in packing density of C-S-H as the dominant mechanism that drives the thermal degradation of cement-based composite materials [52]. However, the research on this topic is still limited, and a link between thermal-induced changes in local microstructural characteristics and a global behavior of cement-based composite materials are still not fully understood. In this chapter, sophisticated nanomechanical testing, static and dynamic nanoindentation, was adopted to assess both static and dynamic responses of hydration products at nanoscale. In addition, work was performed to link loss in local mechanical properties caused by thermal damage to global behavior by comparing nanoindentation with macroscopic strength test.
5.2 Experimental details

5.2.1 Sample preparation and mechanical testing

Cement paste samples were prepared and subsequently exposed to high temperature following the method as described in Chapter 4. In order to investigate effects of degree of hydration on viscoelastic behavior of cement paste after heat treatment, samples with two different curing ages, 14 and 28 days, were prepared for dynamic nanoindentation. Target temperatures used for different characterization experiments are summarized in Table 5.1.

As part of the global mechanical testing, compressive strength was measured on cylindrical samples immediately after heat treatment. For the local mechanical testing, static nanoindentation was carried out on the control sample and heat-treated samples at 300, 400 and 700 °C. In addition, dynamic indentation was performed on the control sample and on samples i) after heat treatment at 200 and 350 °C to achieve thermal cracking without much chemical degradation, and ii) after heat treatment at 700 °C to achieve a high level of chemical decomposition. Samples for nanoindentation were prepared following the method used for AFM characterization in Chapter 4.
Table 5-1 Summary of heat treatment process and characterization methods used in Chapter 5

<table>
<thead>
<tr>
<th>Target Temp. (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Cooling rate (°C/min)</th>
<th>Compressive strength test</th>
<th>Static nanoindentation</th>
<th>Dynamic nanoindentation</th>
<th>SEM-EDS</th>
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</thead>
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<td>Control sample</td>
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</tr>
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<td></td>
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<td>✓</td>
<td>✓</td>
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<td>✓</td>
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<td>-</td>
</tr>
</tbody>
</table>

A Hysitron TI-950 Triboindenter was used for both static and dynamic nanoindentation. A threesided pyramidal Berkovich indenter tip with a total included angle of 142.35° was chosen, since it reduces the pile-up phenomena around the indented area. In static nanoindentation, a trapezoidal load function was used to make each indent, defined by a 10 s loading time to reach a maximum load of 700 μN, a 10 s holding time at the maximum load, and a 10 s unloading time, which is proposed to reduce creep and size effects. The maximum penetration depth ranged from 100 to 300 nm, which is often assumed in the literature to be smaller than the characteristic size of the phases present in the microstructure of well hydrated cement paste and larger than the characteristic size of elementary particle (the single colloidal particle or the gel pores in C-S-H) [52]. Some of the indentation test data were discarded due to a discontinuous P-h curve, which could be due to the presence of large voids at the indentation site or cracking of the sample during indentation.
Dynamic nanoindentation was performed using the same Berkovich tip which was used for static nanoindentation. A frequency sweep from 10 to 200 Hz was used to determine mechanical properties as a function of frequency. A fixed quasistatic load of 700 μN with a fixed dynamic load amplitude of 30 μN was set to achieve optimal dynamic displacement amplitude of 1-2 nm. Grid indentation was performed to determine nanomechanical properties of different phases present in a sample. 100 indents on 2 different areas on a sample (200 total indents) were made in an array in which 10 indents were made in each of the 10 rows. Spacing between each indent was 10 μm.

Similar to the analysis presented in published literature, a commercially available peak analyzing software (Peakfit) was considered to conduct statistical analysis of the large volume of data to determine phase properties and phase volume [52, 60, 61]. However, it was realized that a combined chemo-mechanical testing using nanoindentation and energy dispersive x-ray analysis will be more appropriate for understanding thermal degradation of cement paste than use of the conventional deconvolution technique mentioned above. As mentioned in Chapter 3, relatively large microvolume (linear depth of approximately 2 μm) probed during each indentation makes it difficult to determine whether the local indentation data is a result of a single- or a multi-phase response. In addition, changes in hydration products due to exposure to elevated temperatures, such as decomposition of hydration products and formation of new phases, were not well identified by the statistical deconvolution based solely on mechanical data.
5.2.2 Coupled nanoindentation/scanning electron microscopy with energy dispersive x-ray analysis

In order to determine phase properties with more confidence using a coupled nanoscale chemomechanical testing, static nanoindentation was performed after SEM-EDS to avoid errors introduced by the local surface roughness from the indentation imprint. Therefore, samples had to be sputter coated with gold/palladium (Au/Pd) for SEM-EDS characterization before nanoindentation. The thickness of Au/Pd sputter coating was approximately 10-20 nm, which is much smaller than the average maximum indentation depth of 100-300 nm induced by a maximum load of 700 µN in paste samples with w/b of 0.45. We confirmed negligible effect of sputter coating on the result of nanoindentation by conducting nanoindentation on samples with and without sputter coating. In order to perform indentation on the exact same locations where chemical composition was analyzed by SEM-EDS, reference axes were created on the sample as the first step using nanoScratch feature of Hysitron TI-950 Triboindenter. Then EDS spot analysis was performed over a grid of 10 × 10 points, at a spacing of 10 µm in each direction, as presented in Fig. 5.1. A JEOL 6060LV SEM equipped with an Oxford Instrument ISIS EDS system (Oxford University, Oxford, UK) was used. SEM-EDS quantitative analysis was performed with an accelerating voltage of 20 kV and working distance of 10 mm. Soda lime sheet glass with a known chemical composition was used as the reference standard. The sample absorbed current was set to obtain 2500 counts/second with a measuring time of 300 s. The elements analyzed were Ca, Si, Al, Fe, and S. The iXRF Iridium Ultra software suite performed the standard ZAF (atomic number/absorption/fluorescence) corrections to determine the weight fraction of the elements in the samples.
After SEM-EDS, static nanoindentation was performed precisely on the same locations analyzed by SEM-EDS. Fig. 5.2 shows identification of the area where SEM-EDS analysis was performed on 100 locations in a grid using the optical microscope in the nanoindenter. Measured chemical composition at each data point along with the nanomechanical properties were used in a clustering analysis within the framework of Finite Mixture Models with Gaussian component density function. Details of this modeling are given in Chapter 3.4.

\[ y_j = [C_{Si}, C_{Ca}, C_{Al}] \]

Figure 5-1 SEM micrograph of cement paste sample with reference axes and the grid for EDS spot analysis
Figure 5-2 Identification of SEM-EDS analyzed location with reference axes in Hysitron TI-950 Triboindenter
5.3 Experimental results

5.3.1 Changes in global mechanical properties after exposure to high temperatures

5.3.1.1 Compressive strength

Compressive strength tests were performed before and after heat treatment at 10 different target temperatures. Test results of compressive strength with mass loss are presented in Fig. 5.3. Five distinct stages can be identified from the plot: a significant decrease in strength after exposure to 105 °C (Stage I), a drastic increase in strength between 105 and 200 °C (Stage II), a progressive decrease in strength between 200 and 500 °C (Stage III), a negligible (or less apparent) strength loss between 500 and 600 °C (Stage IV), and a progressive reduction in strength above 600 °C (Stage V). It is interesting to note that compressive strength at 300 °C is higher than that of the control sample without heat treatment for both w/c of 0.35 and 0.45. For w/c of 0.35, compressive strength at 400 °C is still higher than that of the control sample. The paste samples with w/c of 0.45 retained about 90% of their initial compressive strength after exposure to 400 °C. Test results presented here confirm the findings of Komonen [1]. However, a more gradual decrease in strength between 200 and 500 °C is observed in this research.
5.3.2 Changes in local mechanical properties after exposure to high temperatures

5.3.2.1 Static nanoindentation

Frequency distributions (number of occurrence) of indentation modulus and hardness with and without heat treatment are compared and presented in Fig. 5.4. It shows changes in both indentation modulus and hardness of paste samples with heat treatment, which indicate thermal degradation of hydration products. The main phases (LD C-S-H and HD C-S-H) in the control sample (P25) have indentation modulus ranged from 10 to 35 GPa (with median = 24.7 GPa) and indentation hardness ranged from 0.25 to 2 GPa (with median = 1.06 GPa). There is no change in local mechanical properties with heat treatment at 300 °C. C-S-H maintains their local mechanical properties with indentation modulus ranged from 10 to 35 GPa (with median = 23.05 GPa) and
indentation hardness ranged from 0.2 to 2 GPa (with median = 0.87 GPa). Following heat treatment at 400 °C, paste sample exhibits slightly lower values and broader ranges of indentation modulus and hardness, 5-35 and 0.125-1.75 GPa (with median = 22.3 and 0.79 GPa), respectively.

Figure 5-4 Frequency distributions for (a) indentation modulus and (b) indentation hardness for paste samples with w/c of 0.45 after exposure to elevated temperatures
In Fig. 5.4(a), P400 exhibits a slight increase in frequency for indentation modulus between 10 and 20 GPa, which was reported to be associated with more porous LD C-S-H. Although 100 to 450 °C is reported to be the primary temperature range at which C-S-H dehydration occurs, C-S-H seems to retain most of its local mechanical properties with a slight increase in volume fraction of LD C-S-H after exposure to 400 °C. With further heat treatment at 700 °C, both indentation modulus and hardness related to C-S-H become much lower, 0-25 and 0-1 GPa (with median = 14.4 and 0.45 GPa), respectively. Fig. 5.5 shows changes in median of indentation modulus and hardness for C-S-H with increasing temperature.

![Figure 5-5 Median of indentation modulus and hardness for C-S-H](image)

5.3.2.2 Dynamic nanoindentation

Fig. 5.6 and Fig. 5.7 show frequency distributions of storage and loss moduli, which were obtained by dynamic nanoindentation test on paste samples cured for 14 and 28 days, respectively. As expected, the results of storage modulus, the stored energy representing the elastic portion, are
comparable to indentation modulus from static indentation. There is an overall reduction in storage modulus with increasing temperature in both the samples cured for 14 and 28 days, which confirms degradation of elastic properties and material softening. It is worth noting that storage modulus of both samples cured for 14 and 28 days and exposed to 350 °C is comparable with that of the control sample. This observation is similar to the observation made based on static nanoindentation after exposure to 300 °C. The loss modulus which is the dissipated energy representing the viscous portion of the mechanical response, has different trends for samples cured for 14 and 28 days. In the 14 day samples, there is an increase in volume fraction of the phases which have loss modulus between 150 and 400 MPa after heat treatment at 200 °C. Interestingly, heat treatment at 700 °C causes a further increase in loss modulus. Loss modulus of samples cured for 28 days shows in general a decreasing trend with increasing exposure temperature. The opposite effect of heat treatment on the viscoelastic response of samples cured for different periods is interesting and demands further careful study. However, this is outside the scope of this research.
Figure 5-6 Probability distributions for (a) storage modulus and (b) loss modulus for paste samples cured for 14 days at elevated temperatures
Figure 5-7 Probability distributions for (a) storage modulus and (b) loss modulus for paste samples cured for 28 days at elevated temperatures.
5.3.2.3 Coupled nanoindentation/scanning electron microscopy with energy dispersive x-ray analysis

In order to identify phase properties through deconvolution of nanoindentation data, a matlab code was developed based on the Finite Mixture Model described in Chapter 3. During deconvolution, the matlab code varied the number of clusters in the Finite Mixture Model from 1 through 10 which corresponds to the number of phases present in the microstructure. For each cluster, the phase properties, such as indentation modulus and hardness, and concentration on chemical species, such as Ca, Si, and Al, were assumed to follow normal distribution. When the number of cluster is 1, the data analysis reports the average properties of the cement paste. Akaike information criterion (AIC) and Bayesian information criterion (BIC) were used as an indicator for the goodness of fit. As the number of clusters increases in the mixture model, the magnitude of both AIC and BIC generally decrease until they reach the optimum solution. For a specific run, once the number of clusters are set, the initial phase properties (mean, standard deviation, and phase volume fraction) were assigned using a random number generation algorithm and then 1000 iteration was performed to achieve the final solution.

During the first trial, the deconvolution process was performed for the control sample (P25) solely based on the mechanical properties. Therefore, the deconvolution process was used to determine only two phase properties, E and H, and the results are presented in Fig. 5.8. Experimental data from static nanoindentation is grouped into 4 clusters as shown in Fig. 5.8. When E is plotted as a function of H (Fig. 5.8(a)), boundaries between the 4 clusters are very clear. This is reasonable as the clustering is done based on the local mechanical properties. From the data analysis, it is observed that most of the data lies within cluster #1 and #2. Following the definition used in previous literature, cluster #1 can be called HD C-S-H and cluster #2 can be called LD C-S-H.
However, the deconvolution based solely on the mechanical properties is not satisfactory when the chemical composition of each point is considered.

**Figure 5-8** Statistical (bivariate) deconvolution of indentation data obtained on P25 with respect to the pair of observables indentation modulus (E) and hardness (H), (a) distribution of observations in the H-E plane and (b) distribution in the plane of weight % of Ca vs. weight % of Si
Fig. 5.8 (b) shows Ca concentration vs Si concentration as measured through SEM-EDS on the same location where E and H were measured through static nanoindentation. Chemical composition data is plotted using the same clustering as the one presented in Fig. 5.8 (a). Even through the mechanical properties of the clusters are well separated in Fig. 5.8 (a), the boundaries are unclear with significant overlap between the clusters in Fig 5.8 (b). Also, the Ca/Si ratio varied significantly for the clusters #1 and #2 that are thought to be HD C-S-H and LD C-S-H, respectively, without considering the chemical composition.

As a next step, local mechanical properties are coupled with the local chemistry and the deconvolution process to determine phase properties is performed using weight % of three major elements (Al, Si, and Ca) obtained at each indent location through SEM-EDS and the indentation modulus and hardness. Once again, phase properties for all five variables [Al, Si, Ca, E, H] are considered to follow normal distribution and the Finite Mixture Model is used for deconvolution. Number of cluster is varied as before. In order to compare the result of the coupled deconvolution with the mechanical property-based bivariate deconvolution presented in Fig 5.8, the data is grouped into 4 clusters and presented in Fig. 5.9. In the second case, the boundaries between the clusters in the E vs. H plot (Fig. 5.9(a)) are not as distinct as in the bivariate deconvolution (see Fig. 5.8(a)). However, the multivariate coupled chemo-mechanical deconvolution captured differences in phase chemistry a little better (see Fig. 5.9 (b)) than what is presented in Fig. 5.8(b). Obviously, there are still a lot of overlaps between the chemical compositions of the clusters. This means grouping into only 4 clusters is not enough for phase isolation and the number of cluster should be increased during the deconvolution process.
Figure 5-9 Multivariate statistical deconvolution of coupled nanoindentation/SEM-EDS data obtained on P25, (a) distribution of observations in the H-E plane and (b) distribution in the plane of weight % of Ca vs. weight % of Si.

In the third round, two specific procedures are followed to improve goodness of fit. Different phases present in the microstructure of hydrated cement paste are known to have elemental ratios, such as silicon to calcium (Si/Ca), iron plus aluminum to calcium ((Fe+Al)/Ca), and sulfur to
calcium (S/Ca), within a specific range. Therefore, [Si/Ca, (Fe+Al)/Ca, S/Ca, E, H] is used in the third round of the multivariate chemo-mechanical deconvolution. Also, the number of cluster was varied from 1 to 10. The results of deconvolution are presented in Fig. 5.10-5.11 and Table 5.2. Once again, when the cluster number is 1, the results match with the average chemical and mechanical properties of the cement paste. After each deconvolution with the number of cluster greater than 1, each deconvoluted cluster is assigned to specific phase, or a mixture of phases, based on mean Si/Ca, (Fe+Al)/Ca and S/Ca ratios as the primary identification properties and mean E and H as the secondary identification properties. In a recent study, statistically different 7 components were proposed as the optimum number of phases in cement-based composite materials [47, 48]. In this research, main hydration products, such as CH and C-S-H, begin to be separate from the rest of the data points when the number of cluster becomes equal or higher than 5. However, increasing the number of cluster to 7 helps to separate other phases with more confidence. The phase assignment is given in Table 5.2. It should be mentioned at this point that the data points which could be related to unhydrated cement particles are filtered and removed before deconvolution as they can otherwise increase error in the statistical analysis. The cement particles have distinctive properties and are small in number. In this manual identification process, any indentation points with very high indentation modulus (more than 80 GPa), Ca/Si of 2~3 and very low Al content are considered as unhydrated cement particles.

The clusters predominant after deconvolution of the indentation data from P25 and P300 can be assigned to the following phases based on primarily the Si/Ca, (Al+Fe)/Ca and S/Ca elemental ratios: C-S-H, a mixture of C-S-H with CH, and aluminate phases (AFm and/or AFt). This chemo-mechanical coupling method successfully isolated aluminum phases, which are hardly identified in statistical analysis of nanoindentation when chemical information is not considered. In sample
P25, both cluster #1 and #4 are assigned to C-S-H based on the elemental ratios. When the mean indentation moduli of cluster #1 and #4 are compared with published literature, they match well with the average properties of LD C-S-H and HD C-S-H, respectively. Therefore, Cluster #1 and #4 with mean indentation moduli of 13.43 GPa and 30.29 GPa, are listed as LD C-S-H and HD C-S-H, respectively in Table 5.2. These two clusters occupy a total of 66% of the total volume. Clusters #5 and #6 both are identified as a mixture of C-S-H and CH because of the low Si/Ca (however, not low enough to be phase pure CH), (Al+Fe)/Ca and S/Ca ratios. Both the cluster #3 and #7 are assigned to AFt/AFm phases based on high (Al+Fe)/Ca and S/Ca ratio even though they have very different mean indentation moduli and hardness. Mean mechanical properties of the cluster #7 correlate well with average properties of AFt/AFm phase reported in recent literature [47]. The mean mechanical properties of the cluster #3 is much lower. This reduction in mechanical properties can be possibly from indentation of AFt/AFm phases that are formed in pore spaces where the indented microvolume is more porous.

Upon heat treatment at 300 °C, cluster #1 is identified as a dominant phase with estimated volume fraction of 50%. This cluster is assigned to LD C-S-H considering mean Si/Ca and indentation modulus of 0.54 (Ca/Si of 1.85) and 20.82 GPa, respectively. The indentation points linked to HD C-S-H are incorporated in cluster #4, which has indentation modulus of 30.99 GPa with volume fraction of 14%. Cluster #2 is also assigned to HD C-S-H based on its elemental composition. Sum of dominant phases, cluster #1 and #6 in P25 and cluster #1 and #4 in P300 has total volume fraction of about 65%. It seems like volume fraction of HD C-S-H decreases from 38% to 30%, while LD C-S-H increases from 46% to 58% after heat treatment at 300 °C. It should be noted that the data analysis and conclusions can be strengthened further by collecting more data. In this
research, with 100 data per sample, number of data points in some of the clusters are too few to be statistically significant.

![Figure 5-10](image.png)

Figure 5-10 Multivariate statistical deconvolution of coupled nanoindentation/SEM-EDS data obtained on P25, (a) distribution of observation in the E-H plane and (b) distribution in the plane of atomic ratios (Al+Fe)/Ca vs. Si/Ca
Figure 5-11 Multivariate statistical deconvolution of coupled nanoindentation/SEM-EDS data obtained on P300, (a) distribution of observation in the E-H plane and (b) distribution in the plane of atomic ratios (Al+Fe)/Ca vs. Si/Ca
Table 5-2 Phase assignment based on Ca/Si, (Al+Fe)/Si, S/Ca, indentation modulus, indentation hardness and component weights (π) estimated in the coupled chemo-mechanical cluster analysis on P25 and P300

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cluster/phase</th>
<th>Si/Ca (Al+Fe) /Ca</th>
<th>S/Ca</th>
<th>E (GPa)</th>
<th>H (GPa)</th>
<th>π</th>
<th>Phase Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>1</td>
<td>0.42 ± 0.12</td>
<td>0.05 ± 0.04</td>
<td>0.04 ± 0.04</td>
<td>13.43 ± 6.96</td>
<td>0.17 ± 0.14</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.26 ± 0.08</td>
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<td>20.97 ± 6.95</td>
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<tr>
<td></td>
<td>3</td>
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<td>0.45 ± 0.06</td>
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<td>14.72 ± 11.32</td>
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<tr>
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<td>4</td>
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<tr>
<td></td>
<td>5</td>
<td>0.27 ± 0.16</td>
<td>0.03 ± 0.04</td>
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<td>24.09 ± 4.44</td>
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<td>0.08</td>
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<td>1</td>
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<td>30.99 ± 2.80</td>
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<td>5</td>
<td>0.34 ± 0.16</td>
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<td>40.07 ± 7.07</td>
<td>0.92 ± 0.29</td>
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</table>

5.4 Discussion

Based on our experimental work described in Chapter 4 and 5 and existing literature, an effort is made to explain changes in global mechanical properties based on the degradation of hydration products and changes in the micro and nanostructure that occur due to high temperature exposure.
Upon heating, a significant strength loss is observed at 105 °C (Stage I) mainly due to the evaporation of free water and the decomposition of ettringite. These transformations can cause an increase in the volume fraction of pores with radii about 50 nm as reported by Komonen and Penttala [1]. In spite of apparent mass loss between 105 °C and 200 °C, compressive strength increases significantly (Stage II). There are two hypotheses that can justify this mismatch. The first hypothesis ascribes the mismatch to a so-called internal autoclaving effect, which is frequently referred [62]. Above 100 °C, residual water in cement paste can be liberated as steam which, in turn, affects the surrounding phases of cement paste. Steam cannot be liberated from the sample fast enough, creating a state of high pressure inside the paste mainly due to insufficient connected porosity. The combination of high pressure and high temperature can result in a condition favorable for internal autoclaving in which remaining unhydrated cement particles can further hydrate, thereby increasing overall strength. Famy et al. showed development of another layer of inner C-S-H at 90 °C [63]. However, further hydration may not be sufficient to solely account for the observed 40-50% increase in compressive strength. It is worth noting here that in a large structure, the internal pressure buildup can actually be detrimental as it can cause surface spalling. The second hypothesis attributes the strength increase to a change in the local mechanical properties of C-S-H. Statistical nanoindentation tests reveal an increase in hardness of both LD and HD C-S-H, and a slight increase in packing density between 105 and 200 °C; though the indentation stiffness of C-S-H at this temperature range was reported to be almost constant [52]. Significant mass loss between 200 and 300 °C does not translate into a significant loss of strength and increased porosity [1]. The dehydration of C-S-H (which occurs mainly via loss of physically bound water, such as absorbed water in its gel pores and interlayer water which is more tightly bound within its interlayer spaces) occurs primarily at this temperature range [27-29, 37].
However, a hump related to C-S-H was persistent up to 300 °C in x-ray diffraction data [30, 35]. Several past publications reported the existence of interesting phenomena when cement paste is exposed to around 300 °C. Dias et al. noted that the static elastic modulus is practically unchanged between 200 and 300 °C [59]. They believed 300 °C to be a critical temperature above which strength begins to decrease rapidly. Onset of increased porosity and microcracking was presumed to initiate a decrease in strength. Komonen and Penttala [1] reported the increase in pore volume of cement paste to be significantly smaller than would be expected from mass loss for a temperature range between 200 and 300 °C and indicated a clear change in the trend at 300 °C. It seems that exposure to 300 °C causes interesting changes to the material and could be critical in understanding the thermal degradation process.

Based on our detailed micro and nanoscale characterizations, achieved by employing both SEM and AFM as presented in Chapter 4, and coupled nanoindentation/SEM-EDS as presented in this chapter, it is clear that the micro and nanostructure of C-S-H is altered between 105 and 300 °C. This change could initiate deterioration processes; however, its manifestation in certain microscopic and macroscopic properties, such as strength loss and a change in porosity, does not occur until much higher temperatures are reached. After heat treatment at 300 °C, volume fraction of HD C-S-H decreases and volume fraction of LD C-S-H increases. An abundance of angular cement particles are easily identified in SEM images as shown in Fig. 4.6(b). An increase in the amount of visible anhydrous phase on a fractured surface could be an evidence of weak interface between anhydrous phases and the C-S-H matrix. AFM images and its image analysis at 300 °C clearly show a change in C-S-H morphology, which can be indicative of C-S-H shrinkage (Fig. 4.8). Shrinkage in C-S-H can probably change average phase properties as presented in table 5.2. Shrinkage can also explain the formation of a gap between the anhydrous phase and the C-S-H
matrix as observed in Fig. 4.6(b). Unhydrated cement particles and the inner C-S-H interface behave in a very different way during the heating and cooling process. During the heating process, C-S-H exhibits shrinkage due to moisture loss which is irreversible in nature (does not regain its original volume upon cooling as it is not gaining the moisture back) as shown in Fig. 5.12(a), whereas unhydrated cement particles expand during the heating process, and may occupy the space created by shrinkage of C-S-H. The thermal expansion of cement particles, however, is expected to be reversible. Therefore, contraction of cement particles during the cooling process is not accompanied by a regain of the original volume of C-S-H, which leaves a gap at the interface (Fig. 5.12(b)). The change in the microstructure, though it does not reduce compressive strength, could reduce flexural strength significantly as it is more sensitive to developments of flaws [1]. Also, since this process created distributed discrete flaws, it may not manifest itself in porosity measurements if a ‘flow of fluid through medium’-type measurement is made as these measurements depend on pore connectivity. At higher temperature, the rate of shrinkage of C-S-H slowly reduces as most of the water has already been lost at lower temperature. However, exposure to higher temperatures results in further expansion of unhydrated cement particles. As this expansion cannot be accounted for by accompanying shrinkage of C-S-H, stresses develop at the interface, and cause microcracks to expand into the C-S-H matrix. Microcracks within the matrix and at the interface expand/grow as cement particles contracts again during the cooling process. Compressive strength decreases continuously with increasing temperature until 500 °C (Stage III). The microstructure at this temperature becomes more porous due to the loss of water from C-S-H and the decomposition of CH. Nevertheless, compressive strength at 400 °C for the paste sample with w/c of 0.35 is still higher than that of the control sample. The paste samples with w/c of 0.45
also retain about 90% of the initial compressive strength. In addition, C-S-H maintains most of its local mechanical properties with a slight increase in the volume fraction of LD C-S-H after exposure to 400 °C.

Figure 5-12 Schematic diagrams of the degradation at the interface between unhydrated cement particles and matrix: (a) Expansion and shrinkage of unhydrated cement particles and shrinkage of C-S-H, respectively as a function of temperature and (b) Formation of a gap and propagation of micro-cracks at the interface between unhydrated cement particle and paste matrix.
No further strength loss is observed between 500 °C and 600 °C (Stage IV), which could be due to the absence of any major phase changes. Above 600 °C, compressive strength continuously decreases without noticeable mass loss (Stage V). There is only gradual mass loss of about 2 % as temperature increases to 650 °C, which could be related to the loss of chemically bound water from C-S-H (may include the decomposition of CaCO₃ as well). The complete breakdown of C-S-H due to loss of remaining chemically bound water probably leads to massive changes in morphology as seen in SEM and AFM studies and reduction in local mechanical properties. In the static nanoindentation studies, both indentation modulus and hardness related to C-S-H become much lower, ranged 0-25 and 0-1 GPa (with median = 14.4 and 0.45 GPa) after heat treatment at 700 °C. At this temperature, C-S-H completely breaks down, forms β-C₂S, and loses its binding capacity. Samples after exposure to 700 °C have very different morphology compared to samples exposed to lower temperatures. The paste matrix of samples after exposure to 700 °C is predominantly covered with microcracks and has globular structure as seen in AFM. These globules probably consist of β-C₂S and CaO. With further heat treatment up to 900 °C, strength loss is accelerated without any loss in mass. Samples have only 28.8, and 18.2 % compressive strength for w/c of 0.35 and 0.45, respectively. It seems that the globules of residual products formed by the decomposition of C-S-H continue to grow in size and rearrange as seen in the AFM study. The development of large globules may be linked to the further reduction in strength and pore-coarsening as it can create larger voids at boundaries between the globules. The development of large globules could explain pore-coarsening and an increase in volume fraction for pores with radii > 100 nm when cement paste is exposed to temperatures above 800 °C [1].
5.5 Conclusions

In this chapter, the local and global mechanical changes in cement paste are evaluated after exposure to elevated temperatures. This research shows a correlation between changes in mechanical properties of cement paste at micro/nano and global scales after heat treatment at various temperatures. Based on this work and the existing literature, the mechanism for loss of mechanical properties of cement paste is discussed, and the following conclusions are drawn:

1) The compressive strength (global) after exposure to 400 °C for the paste sample with w/c of 0.35 is higher than that of the control sample without any heat treatment. The paste samples with w/c of 0.45 also retain about 90 % of the initial compressive strength. As reported in the past, this research also confirms that the macroscopic property such as strength does not change much until higher exposure temperatures are reached. However, it is clear that the micro and nanostructure of C-S-H is altered between 105 and 300 °C.

2) The interface between unhydrated cement particles and the paste matrix could be the origin of microcracks. The opposite behaviors of the two phases at elevated temperatures; not only a difference in thermal expansion rate, but also reversible expansion of unhydrated cement particles and irreversible shrinkage of C-S-H probably result in a gap at the interface at 300 °C. This gap becomes wider, and consequently causes microcracks to expand into paste matrix as temperature increases over 300 °C.

3) Coupled nanoindentation/SEM-EDS technique with multivariate statistical deconvolution of data successfully identifies phase (or mixture of phases) properties with more confidence than statistical deconvolution of local mechanical properties only.

4) With coupled nanoindentation/SEM-EDS, it is possible to monitor changes in chemo-mechanical properties of C-S-H due to high temperature exposure. C-S-H maintains most of
its local mechanical properties, however an increase in the volume fraction of the LD C-S-H is observed after exposure to 300 and 400 °C.
CHAPTER 6
MITIGATION STRATEGIES OF THERMAL DEGRADATION IN CEMENT PASTE

6.1 Introduction

The continued importance of improving the fire- and heat-resistance of cement-based composite materials is directly related to improving its thermal stability. Several efforts have been made to enhance the thermal stability of paste matrix (and hydration products) by incorporating SCMs, which are widely used to produce high performance concrete [16, 64]. However, the use of some SCMs, such as silica fume, can increase thermally-induced explosive spalling [26, 65]. The use of sacrificial polymer fiber can successfully eliminate this problem by providing an additional pathway for moisture escape at high temperatures [24, 66]. One recent paper reported that the use of ground granulated blast furnace slag (GGBFS) can reduce surface cracks and improve strength of concrete after exposure to elevated temperatures [64]. In addition, partial replacement of cement with fly ash or slag was reported to reduce the formation of severe cracking during exposure to moist air for short periods of time after heat treatment at or above 400 °C [32, 59]. This reduction in surface cracking is thought to be a result of pozzolanic reactivity reducing the amount of CH, which can quickly reform during the cooling process.

Recently, it was proposed that the addition of nanosilica enhances properties of paste and concrete, such as strength, flexibility, durability, and permeability, due to its higher chemical reactivity and filler effects than those of other siliceous materials [12-15]. The use of nanosilica in cement paste was also reported to improve chemical stability of C-S-H as it reduces calcium leaching from C-S-H [14, 15]. NMR studies on cement paste incorporating 6% nanosilica by weight showed an
increase in the average chain length of C-S-H, making C-S-H more stable [14]. Jain et al. reported that the net Ca²⁺ ion loss from both CH and C-S-H in cement pastes, subjected to leaching in deionized water, is lower for the pastes incorporating nanosilica as compared to those containing microsilica due to the denser microstructure and modified internal structure of C-S-H with a reduced Ca/Si molar ratio [15]. Based on Fourier transform infrared spectroscopy (FTIR) studies, Sádez del Bosque et al. reported an acceleration of C₃S hydration and a decrease in percentage of jennite-like species in C-S-H by incorporating nanosilica [67]. Mondal et al. showed that volume fraction of HD C-S-H increases with the addition of nanosilica [68]. Ulm et al. reported, in a nanoindentation-based study, that the ratio of HD C-S-H to LD C-S-H changes at elevated temperatures indicating HD C-S-H could possibly have higher resistance to thermal degradation [52]. Considering the two aforementioned results, it could be assumed that the addition of nanosilica will promote thermal stability of C-S-H and may be that of cement paste as well. In recent literature, Ibrahim et al. reported that high-strength mortars, incorporating colloidal nanosilica and high-volume fly ash, have higher compressive strength than plain cement mortars after exposure to high temperatures due to the filler effect of nanosilica and higher C-S-H content [16]. However, understanding the effects of nanosilica on the thermal stability of cement-based composite materials is still very limited, and further research is needed. This chapter investigates whether the incorporation of nanosilica in cement paste increases its thermal stability and if this increased stability is due to increased thermal stability of C-S-H. Nanosilica particles with a diameter of about 30 nm were incorporated into cement paste and exposed to high temperatures up to 500 °C, followed by two different cooling regimes. Following heat treatment, compressive strength was measured, and various characterization techniques, such as XRD, SEM, TGA, and
coupled nanoindentation/SEM-EDS, were employed to study effects of incorporating nanosilica on changes in the microstructure and explain the observed changes in mechanical properties.

### 6.2 Experimental details

Besides plain cement paste samples with $w/c$ of 0.45, which was used throughout this research, paste samples incorporating nanosilica were prepared. The first series, identified as “P”, was prepared using Type I Portland cement and DI water. The second series, identified as “NS”, were prepared by replacing 5% of cement by weight with commercially available nanosilica (provided by US Research Nanomaterials, Inc.). Same Portland cement was utilized as the one used in Chapter 5 and 6. The characteristic properties of the nanosilica dispersion used are presented in Table 6.1. The nanosilica dispersion contained 25% of solid by weight dispersed in water. Accordingly, the amount of water added was adjusted to maintain the effective water-to-binder ratio ($w/b;\text{cement }+\text{ nanosilica}$) of 0.45.

**Table 6-1 Characteristic properties of nanosilica dispersion**

<table>
<thead>
<tr>
<th>Crystal structure and type</th>
<th>pH value</th>
<th>Original particle size</th>
<th>Assay SiO$_2$</th>
<th>Solvent</th>
<th>Co</th>
<th>Fe</th>
<th>SiO$_2$ Purity</th>
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<tbody>
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<td>Amorphous</td>
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<td>30 nm</td>
<td>≥25.2%</td>
<td>75% Water</td>
<td>≤0.8ppm</td>
<td>≤0.2ppm</td>
<td>99.99%</td>
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</table>

Samples were cured and subsequently exposed to high temperature following the method as described in Chapter 4. Two different paths were then followed for the cooling cycles. The first set of samples was allowed to cool down to room temperature at a cooling rate of 1 °C/min (Regime I). The second set of samples was cooled down to 50 °C at the same cooling rate of 1 °C/min and
held at that temperature for 3 days (Regime II) to study the effects of prolonged exposure to above ambient temperatures, which could be the situation in a concrete structure right after extinguishing a fire. In addition, when heat-treated cement paste samples were stored in laboratory environment for some period, they often were observed to breakdown completely with time. Therefore, it is clear that damage continued to occur well after the heat treatment. It is assumed that prolonged exposure to temperature little above ambient (prolonged heat treatment at 50 °C) after first cycle of heating and cooling could possibly enhance and accelerate this damage mechanism responsible for complete breakdown of the cement paste samples after heat treatment. Therefore, cooling Regime II was used as an accelerated test condition. Once cooled to room temperature at the end of the Regime II heat treatment, the samples were stored in desiccators filled with nitrogen gas to avoid further hydration or carbonation. Samples are identified according to the heat treatment and cooling process they were exposed to. For example, NS400 represents paste sample with nanosilica that was exposed to 400 °C, then cooled down to room temperature following cooling Regime I. Similarly, P500-prolonged stands for paste sample without nanosilica that was exposed to 500 °C, then cooled down to room temperature following the cooling Regime II. The summary of heat treatment and experiments are presented in Table 6.2.

Compressive strength test was performed on 6 paste cubes before and after each heat treatment to investigate the difference in mechanical properties between the samples with and without nanosilica. TGA, SEM and XRD were carried out; details of these procedures are given in Chapter 4. The test specimens for XRD, SEM imaging and coupled nanoindentation/SEM-EDS were obtained from the inner core of the samples after compressive strength test unless otherwise specified. TGA was performed on the ground paste specimen (approximately 30 mg), which were collected from an area close to the outer surface of the samples. Carbonation testing by means of
a phenolphthalein indicator was also employed to complement the XRD and TGA studies. 1% phenolphthalein in isopropyl alcohol solution was used to determine carbonation depth. Static nanoindentation and coupled nanoindentation/SEM-EDS were carried out following the method described in Chapter 5 to study effects of nanosilica addition on local mechanical properties and chemistry of cement paste.

Table 6-2 Summary of heat treatment process and characterization methods used in
Chapter 6

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<th>Target Temp. (°C)</th>
<th>Heating rate (°C/min)</th>
<th>Cooling rate (°C/min)</th>
<th>Compressive Strength test</th>
<th>Static nanoindentation</th>
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<th>XRD</th>
<th>SEM</th>
<th>SEM-EDS</th>
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6.3 Experimental results and discussion

6.3.1 Effects of nanosilica on thermal degradation of cement paste (Regime I)

6.3.1.1 Mechanical properties (compressive strength test and static nanoindentation)

The results of compressive strength test are given in Fig. 6.1. P25 and NS25 (control samples without heat treatment) had a comparable compressive strength after 28 days of curing. Contradictory results regarding the effect of nanosilica addition on mechanical properties of cement-based composite materials were reported by other researchers. Some researchers reported significant influence of nanosilica on the improvement of mechanical properties [13, 14, 16], whereas others reported only a negligible influence [69] and even lower compressive strength [70]. In this research, cement paste containing 5% nanosilica exhibits an 8% improvement in strength compared to plain cement paste after 28 days of curing. After exposure to 105 °C and subsequent cooling to room temperature, there is a slight reduction in strength for both samples P and NS, probably due to removal of free water and the decomposition of ettringite. However, both of the samples show an increase in strength after exposure to 200 °C and subsequent cooling. Similar results are reported for plain cement paste in Chapter 5. With heat treatment above 200 °C, compressive strength decreases gradually, however, the strength of heat-treated samples is still higher than those of samples P25 and NS25 up to 400 °C. After heat treatment at 500 °C, samples P500 and NS500 exhibit 12 and 9% reduction in strength, respectively, compared to samples P25 and NS25. Samples P and NS show very similar trends in compressive strength as a function of exposure temperature, nevertheless sample NS consistently exhibits 7-20% higher compressive strength up to 700 °C than does sample P, with the biggest difference of 20% observed at 400 °C. The difference in strength between samples P and NS diminishes after exposure to 500 °C, and sample P exhibits slightly higher compressive strength than sample NS above 800 °C. Ibrahim et
al. reported similar findings, although the difference in compressive strength between samples with and without nanosilica was more obvious in their study [16]. Mortar samples containing 5% nanosilica exhibited approximately 30% higher compressive strength than those without nanosilica after 28 days of curing. This difference was even greater, about 40%, after heat treatment at 400 °C. However, after exposure to higher temperature, 700 °C, both samples with and without nanosilica exhibited similar compressive strengths.

![Figure 6-1](attachment:image.png)

**Figure 6-1 Results of compressive strength tests on samples P and NS after 6 hour exposure to target temperatures (Compressive strength test data presented here are an average of six test samples)**

The main binding phase in cement-based composite materials, C-S-H, is reported to dehydrate primarily between 105 and 400 °C which can cause shrinkage of the matrix, increase microcracks and porosity, and consequently cause loss of strength as explained in Chapter 4 and 5. It was reported that the stability of C-S-H can be improved by the addition of nanosilica due to an increase in the silicate chain length of C-S-H and volume fraction of HD C-S-H [14, 15, 68]. This could
possibly hinder the thermal degradation of C-S-H as well, thus promoting thermal stability of the
cement paste with nanosilica. Fig. 6.2 compares the frequency distributions of indentation modulus
and hardness of cement paste samples with and without nanosilica before (control samples, P25
and NS25) and after heat treatment at 400 °C and 700 °C. The bin sizes are set at 2.5 GPa and 125
MPa for indentation modulus and hardness, respectively.
Distribution of indentation modulus shows different trends for the samples with and without
nanosilica after exposure to elevated temperatures, while a difference in indentation hardness is
not apparent as much as indentation modulus. Fig. 6.2(a) shows that incorporation of nanosilica
causes an increase in number of occurrence for indentation modulus within a range between 30
and 40 GPa, which confirms an increased volume fraction of HD C-S-H [68]. However, there are
negligible effects of nanosilica on indentation hardness as shown in Fig. 6.2(b). Both the samples
have indentation hardness ranged between 0.25-2.0 GPa (with median = 1.06 and 0.97 GPa for
samples P25 and NS25, respectively). Both P300 and NS300 retain their local mechanical
properties even after heat treatment at 300 °C. The effects of nanosilica on indentation modulus
become more obvious after exposure to 400 °C. C-S-H present in both samples NS25 and NS400
still has indentation modulus within the similar range between 10 and 40 GPa (median of 27.3 and
28.0 GPa, respectively). However, the sample P400 exhibits a slight increase in frequency of
indentation modulus between 10 and 20 GPa, which is associated with LD C-S-H probably due to
degradation of C-S-H, while C-S-H in sample NS400 retains most of its local mechanical
properties. It seems that incorporating nanosilica prevents the degradation of C-S-H after exposure
to 400 °C. With further heat treatment at 700 °C, both the samples with and without nanosilica
exhibit progressive increases in number of occurrence for indentation modulus between
Figure 6-2 Frequency distributions for cement paste samples with and without 5% nanosilica after exposure to elevated temperatures: (a) indentation modulus and hardness of P25 and NS25, (b) indentation modulus and hardness of P300 and NS300, (c) indentation modulus and hardness of P400 and NS400 and (d) indentation modulus and hardness of P700 and NS700
0 and 10 GPa and indentation hardness between 0 and 0.5 GPa, which could be indicative of significant degradation of hydration products. The changes in median of indentation modulus and hardness for C-S-H with increasing temperature are presented in Fig. 6.3.

![Figure 6-3 Median of indentation modulus and hardness for C-S-H](image)

**Figure 6-3** Median of indentation modulus and hardness for C-S-H

Surface cracks are observed after exposure to high temperatures. In general, sample P exhibits more cracks on the sample surface. In particular, edges of the samples are damaged more severely during compressive strength testing as shown in Fig. 6.4(a). During compressive strength test, both samples show spalling of the surface layer before failure. However, sample P fails immediately after significant development of cracks and spalling of the outer surface. On the contrary, the core of sample NS seems to be significantly stronger than the area near the outer surface, and it is observed that the sample is able to carry load beyond the point of surface spalling. Fig. 6.4 compares the surface cracks/spalling of both samples. The strength reported in Fig. 6.1 is calculated based on the initial cross-sectional area of the cubes even though a noticeable reduction in cross-sectional area carrying the load is observed due to spalling. Also, it should be noted that
the compressive strength test was performed in load control mode, and the failure load was determined when any sample failed to carry further load.

![Image](a) P400 NS400 (b) P400 NS400

**Figure 6-4** Comparison of surface cracking and spalling: (a) surface cracking after heat treatment and (b) surface spalling occurred during compressive strength test

6.3.1.2 Coupled nanoindentation/scanning electron microscopy with energy dispersive x-ray analysis

Results of the multivariate chemo-mechanical deconvolution are presented in Fig. 6.5-6.6 and Table 6.3. Statistically different 7 phases are clustered in both samples NS25 and NS300. It is clear that most phases are a mixture of 2 or more hydration products. In sample NS25, the indentation points linked to C-S-H intermixing with CH are incorporated in clusters #5 and #6, which have mean indentation modulus of 20.43 GPa and 28.87 GPa with volume fraction of 30% and 24%, respectively. Cluster #1 is characterized by very high mean Si/Ca (low Ca/Si) of 0.63, which could be due to the presence nanosilica intermixed with C-S-H. Aluminate phases are well identified as cluster #2 with indentation modulus of 29.09 GPa. After heat treatment, in sample NS300, cluster #4 is recognized as the primary phase with estimated volume fraction of 43%. It is assigned to HD C-S-H considering Si/Ca and indentation modulus, 0.49 (Ca/Si of 2.04) and 28.78 GPa,
respectively. Second dominant cluster #2 is allocated to LD C-S-H intermixing with CH due to its low Si/Ca of 0.29 and medium indentation modulus of 22.58 GPa. Clusters #3 and #5 are also assigned to C-S-H intermixing with CH considering chemical compositions.

C-S-H and C-S-H intermixing with CH phases in samples P25, NS25, P300 and NS300 are presented in Table 6.3. Samples P25 and NS25 have comparable volume fraction of C-S-H about 83% with similar proportion for HD C-S-H and LD C-S-H. This estimation is not exact as C-S-H is intermixed with CH in most cases and the volume fraction of CH is known to be different in the P25 and NS25 sample. With heat treatment at 300 °C, volume fraction of HD C-S-H in sample without nanosilica (P300) decreases from 38% to 30%, while sample with nanosilica does not have reduction in volume fraction of HD C-S-H. It is interesting to note that incorporation of nanosilica actually increases volume fraction of HD C-S-H upon heating from 35% to 56% and the volume fraction of NS almost disappears. Further study could be performed to validate if heat treatment at 300 °C encourages further reaction of remaining nanosilica particles that causes increase in HD C-S-H.
Figure 6-5 Multivariate statistical deconvolution of coupled nanoindentation/SEM-EDS data obtained on NS25, (a) distribution of observation in the E-H plane and (b) distribution in the plane of atomic ratios (Al+Fe)/Ca vs. Si/Ca
Figure 6-6 Multivariate statistical deconvolution of coupled nanoindentation/SEM-EDS data obtained on NS300, (a) distribution of observation in the E-H plane and (b) distribution in the plane of atomic ratios (Al+Fe)/Ca vs. Si/Ca
Table 6-3 Phase assignment based on Ca/Si, (Al+Fe)/Si, S/Ca, indentation modulus, indentation hardness and component weights (π) estimated in the coupled chemo-mechanical cluster analysis on NS25 and NS300

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cluster/phase</th>
<th>Si/Ca</th>
<th>(Al+Fe)/Ca</th>
<th>S/Ca</th>
<th>E (GPa)</th>
<th>H (GPa)</th>
<th>Π</th>
<th>Phase Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.63 ± 0.14</td>
<td>0.03 ± 0.04</td>
<td>0.02 ± 0.04</td>
<td>24.27 ± 1.48</td>
<td>1.36 ± 0.25</td>
<td>0.08</td>
<td>HD C-S-H + NS</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.16 ± 0.09</td>
<td>0.41 ± 0.04</td>
<td>0.01 ± 0.03</td>
<td>29.09 ± 6.68</td>
<td>1.03 ± 0.11</td>
<td>0.02</td>
<td>AFm/Af</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49 ± 0.13</td>
<td>0.08 ± 0.06</td>
<td>0.04 ± 0.04</td>
<td>11.00 ± 7.99</td>
<td>0.33 ± 0.12</td>
<td>0.15</td>
<td>LD C-S-H (porous)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>0.47 ± 0.07</td>
<td>0.07 ± 0.05</td>
<td>0.05 ± 0.04</td>
<td>49.70 ± 7.64</td>
<td>1.74 ± 0.62</td>
<td>0.03</td>
<td>HD C-S-H + CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.39 ± 0.15</td>
<td>0.04 ± 0.04</td>
<td>0.04 ± 0.04</td>
<td>20.43 ± 8.04</td>
<td>0.79 ± 0.37</td>
<td>0.3</td>
<td>LD C-S-H + CH</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>0.43 ± 0.11</td>
<td>0.05 ± 0.04</td>
<td>0.04 ± 0.04</td>
<td>28.87 ± 9.58</td>
<td>0.67 ± 0.23</td>
<td>0.24</td>
<td>HD C-S-H + CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.57 ± 0.17</td>
<td>0.04 ± 0.04</td>
<td>0.03 ± 0.04</td>
<td>19.68 ± 7.41</td>
<td>0.52 ± 0.24</td>
<td>0.17</td>
<td>LD C-S-H + NS</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>0.38 ± 0.12</td>
<td>0.19 ± 0.15</td>
<td>0.05 ± 0.03</td>
<td>41.24 ± 3.23</td>
<td>1.71 ± 0.28</td>
<td>0.06</td>
<td>AFm/Af + C-S-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.29 ± 0.14</td>
<td>0.05 ± 0.05</td>
<td>0.03 ± 0.04</td>
<td>22.58 ± 6.25</td>
<td>0.90 ± 0.43</td>
<td>0.23</td>
<td>LD C-S-H + CH</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.32 ± 0.21</td>
<td>0.05 ± 0.04</td>
<td>0.03 ± 0.04</td>
<td>48.99 ± 5.43</td>
<td>1.40 ± 0.23</td>
<td>0.13</td>
<td>HD C-S-H + CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49 ± 0.06</td>
<td>0.06 ± 0.04</td>
<td>0.05 ± 0.03</td>
<td>28.78 ± 6.49</td>
<td>1.05 ± 0.39</td>
<td>0.43</td>
<td>HD C-S-H</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>0.45 ± 0.09</td>
<td>0.08 ± 0.04</td>
<td>0.04 ± 0.04</td>
<td>20.28 ± 1.58</td>
<td>0.56 ± 0.12</td>
<td>0.1</td>
<td>LD C-S-H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.14 ± 0.06</td>
<td>0.24 ± 0.04</td>
<td>0.16 ± 0.04</td>
<td>20.59 ± 6.21</td>
<td>0.60 ± 0.22</td>
<td>0.03</td>
<td>AFm/Af</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>14.18 ± 0.03</td>
<td>5.30 ± 0.03</td>
<td>0.21 ± 0.03</td>
<td>18.73 ± 0.03</td>
<td>0.72 ± 0.03</td>
<td>0.01</td>
<td>NS</td>
</tr>
</tbody>
</table>
Table 6-4 C-S-H (intermixture with CH) phases in samples P25, NS25, P300 and NS300

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>Ca/Si</th>
<th>M (GPa)</th>
<th>H (GPa)</th>
<th>Π</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>HD C-S-H</td>
<td>2.13</td>
<td>37.65 ± 4.80</td>
<td>1.08 ± 0.51</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>HD C-S-H + CH</td>
<td>3.33</td>
<td>30.29 ± 8.65</td>
<td>1.25 ± 0.32</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H</td>
<td>2.38</td>
<td>13.43 ± 6.96</td>
<td>0.17 ± 0.14</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H + CH</td>
<td>3.7</td>
<td>24.09 ± 4.44</td>
<td>0.57 ± 0.34</td>
<td>0.13</td>
</tr>
<tr>
<td>NS25</td>
<td>HD C-S-H + NS</td>
<td>1.59</td>
<td>24.27 ± 1.48</td>
<td>1.36 ± 0.25</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>HD C-S-H + CH</td>
<td>2.13</td>
<td>49.70 ± 7.64</td>
<td>1.74 ± 0.62</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H</td>
<td>1.75</td>
<td>19.68 ± 7.41</td>
<td>0.52 ± 0.24</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H + CH</td>
<td>2.56</td>
<td>20.43 ± 8.04</td>
<td>0.79 ± 0.37</td>
<td>0.3</td>
</tr>
<tr>
<td>P300</td>
<td>HD C-S-H</td>
<td>1.75</td>
<td>30.99 ± 2.80</td>
<td>1.39 ± 0.13</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>HD C-S-H</td>
<td>1.85</td>
<td>42.79 ± 5.80</td>
<td>1.91 ± 0.30</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>HD C-S-H + CH</td>
<td>2.08</td>
<td>40.07 ± 7.07</td>
<td>0.92 ± 0.29</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H</td>
<td>1.85</td>
<td>20.82 ± 5.02</td>
<td>0.72 ± 0.23</td>
<td>0.5</td>
</tr>
<tr>
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<td>LD C-S-H + CH</td>
<td>2.94</td>
<td>18.32 ± 2.96</td>
<td>0.41 ± 0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>NS300</td>
<td>HD C-S-H</td>
<td>2.04</td>
<td>28.78 ± 6.49</td>
<td>1.05 ± 0.39</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>HD C-S-H + CH</td>
<td>3.12</td>
<td>48.99 ± 5.43</td>
<td>1.40 ± 0.23</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H</td>
<td>2.22</td>
<td>20.28 ± 1.58</td>
<td>0.56 ± 0.12</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>LD C-S-H + CH</td>
<td>3.45</td>
<td>22.58 ± 6.25</td>
<td>0.90 ± 0.43</td>
<td>0.23</td>
</tr>
</tbody>
</table>

6.3.1.3 X-ray diffraction

XRD studies were performed in order to investigate the effects of nanosilica addition on the changes in chemical composition following heat treatment. Samples P and NS treated at 400 ºC (P400 and NS400), are selected as they exhibit the biggest difference in compressive strength. X-ray diffractograms of control samples (P25 and NS25) and heat-treated samples (P400 and NS400) are shown in Fig. 6.7, with the main peaks identified. Typical reflections associated with ettringite, CH, C-S-H, and β-C$_2$S are found in both samples P25 and NS25. There is a distinction between the intensities of peaks related to CH. Though quantitative analysis of XRD was not conducted, the CH peaks are less intense in the sample NS25 which indicates the effects of pozzolanic reaction of nanosilica with CH to produce C-S-H. However, the presence of CH peak in sample NS25 shows that 5% replacement of cement with nanosilica is not enough to achieve complete
conversion of CH to C-S-H through pozzolanic reaction. Also, the main peaks for $\beta$-C$_2$S at 2$\theta$=32.136 and 32.593 are more intense in sample NS25 than those in sample P25. It can indicate that sample NS25 contains a larger amount of unhydrated cement particles, potentially because incorporating nanosilica can decrease the degree of hydration of cement at 28 days compared to the plain paste sample [14, 71].

The main phases identified from XRD in samples P400 and NS400 are comparable. Peaks related to ettringite are identified in both samples only prior to heating but disappear after heat treatment at 400 °C. Intensity of peaks related to $\beta$-C$_2$S decreases for both samples, with this effect being more obvious in the sample NS. The decrease in the amount of $\beta$-C$_2$S could indicate further...

Figure 6-7 X-ray diffractograms of the control samples (P25 and NS25) and the heated samples (P400 and NS400), Key to phases: ● Ettringite, ▲ Portlandite (Ca(OH)$_2$), ■ Larnite ($\beta$-C$_2$S), ★ C-S-H(Ca$_{1.5}$SiO$_{3.5}$•xH$_2$O), ♦ Calcite (CaCO$_3$)
hydration of unhydrated cement particles during the initial part of the heat treatment. This explains the higher compressive strengths of samples P400 and NS400 than those of samples P25 and NS25, respectively, even with decomposition of hydration products occurring during the latter part of the heat treatment. Though the hump related to C-S-H is still identified after exposure to 400 °C in both samples, the existence of C-S-H cannot be confirmed due to the chance of overlap with main peaks of CaCO₃ (2θ=29.405°) and β-C₂S (2θ=32.05°). However, the decomposition of CaCO₃ in samples P25 and NS25, which takes place between 600 and 750 °C, is barely visible in TGA results, indicating negligible carbonation in the samples. Results of TGA are further discussed in the next section. The formation of new C-S-H and then dehydration of C-S-H seem to occur between 105 and 400 °C. As a result, the compressive strength increases at 200 °C then gradually decreases at temperatures above 200 °C. However, compressive strengths are still higher than those of samples P25 and NS25 up to 400 °C.

As mentioned in the previous paragraph, incorporation of 5% nanosilica in cement paste does not convert all CH to C-S-H via pozzolanic reaction. It was reported elsewhere that as the dosage of nanosilica increases from 5% to 7.5%, the compressive strength of mortars after exposure to high temperatures increases [16]. In order to increase thermal stability of the system by incorporating nanosilica, future research should be devoted to determine the optimum nanosilica content to best achieve this purpose.
6.3.2 Effects of nanosilica on thermal degradation of cement paste with prolonged heating at 50 °C (Regime II)

6.3.2.1 Compressive strength

Since samples with nanosilica have higher strength after heat treatment than samples without, prolonged heat treatment is used for this section for the following reasons: (i) in practice, the temperature of the core can be higher than ambient temperature for a while even after the fire is extinguished, and (ii) temperatures higher than ambient temperature can promote carbonation. For these reasons, it is thought that prolonged exposure to temperatures above ambient may even amplify the difference observed between samples with and without nanosilica and aid in fully understanding the mechanism. Therefore, samples were first heated to target temperatures between 105 to 500 °C, then, while cooling down, held at 50 °C for 3 days (referred to as prolonged heat treatment) before cooled down to room temperature. Compressive strengths before and after prolonged heat treatment are compared (comparison between Regimes I and II) in Fig. 6.8. Prolonged heat treatment at 50 °C on P25, NS25, P105, and NS105, results in a 10-20% increase in strength. It seems that prolonged heat treatment with these samples work in a manner similar to high temperature curing and promoted further hydration of unhydrated cement particles. As increasing temperature from 200 to 400 °C, the gradual loss of strength is observed, but both samples P and NS still maintain higher strength than the control samples even after prolonged heat treatment. When the same test is conducted on samples P500 and NS500, the drastic difference in mechanical properties is observed. Sample P500-prolonged completely breaks down into small pieces as shown in Fig. 6.9(a), while sample NS500-prolonged is still intact enough to maintain almost 80% of its initial strength. Although an increase in surface crack is detected even on sample NS500-prolonged, it does not seem to propagate into the core of the sample as shown in Fig. 6.9(b).
Figure 6-8 Results of compressive strength test on samples: (a) without nanosilica and (b) with nanosilica exposed to 50 °C for 3 days after 6 hours exposure to target temperatures

Figure 6-9 Samples (two examples) after prolonged heat treatment at 50 °C for 3 days after 6 hours exposure to 500 °C: (a) paste samples without nanosilica (P500-prolonged) and (b) paste samples with nanosilica (NS500-prolonged)

6.3.2.2 Scanning electron microscopy and x-ray diffraction

In order to understand the reason behind the drastic difference observed between samples P500-prolonged and NS500-prolonged and use this information to finally explain how nanosilica addition can increase thermal stability of cement-based composite materials, SEM, XRD (as detailed in this section) and TGA (as detailed in the next section) were performed. SEM was performed on the broken surface, which was obtained after compressive strength test of samples P500, NS500, P500-prolonged (compressive strength test could not be performed in this case), and
NS500-prolonged to investigate changes in morphology as a consequence of prolonged heat treatment. After heat treatment at 500 °C, paste matrix of both samples P and NS is rather porous due to the dehydration of CH and C-S-H and is covered with microcracks as shown in Fig. 6.10. These microstructural changes explain the strength loss for both samples P and NS as reported in the previous section. Similar findings were reported earlier by Handoo et al. in 2002 for concrete samples exposed to 500 °C [72].

Figure 6-10 SEM images of broken surfaces of samples: (a) without nanosilica (P500) and (b) with nanosilica (NS500) after 6 hours exposure to 500 °C

Further SEM investigations on the samples with prolonged heat treatment reveal the difference between the samples with and without nanosilica. Scanning electron micrograph shows growth of crystals similar to trigonal calcium carbonate crystals on the broken surface of sample P500-prolonged, as shown in Fig. 6.11(a), while sample NS500-prolonged shows only the presence of microcracks but no crystal growth. In addition, microcracks which develop on the broken surface of sample P500-prolonged are easily identified even at low magnification as shown in Fig. 6.12. Based on the observed microcracks in Fig. 6.12, it seems, if one would further extend the period of prolonged heat treatment, the samples would presumably break down into even smaller pieces.
Figure 6-11 SEM images of broken surfaces of samples: (a) without nanosilica (P500-prolonged) and (b) with nanosilica (NS500-prolonged) with prolonged heat treatment at 50 °C for 3 days after 6 hours exposure to 500 °C

In order to investigate changes in the chemical composition after prolonged heat treatment, XRD was carried out on samples P500 and P500-prolonged. Specimens were collected from an area near the outer surface. The results are shown in Fig. 6.13, where main peaks are identified. Main phases
in samples P500 and P500-prolonged are comparable. The distinction between them is only in the intensity of the peak at $2\theta=29.405$ related to calcite (CaCO$_3$). It seems that sample P500-prolonged has higher calcite content than sample P500. This speculation is further verified by TGA results as discussed in the next section. Carbonation test using a phenolphthalein indicator was performed on both samples P500-prolonged and NS500-prolonged to complement the XRD test results. Carbonation on the broken surface of sample P500-prolonged is very clear as shown in Fig. 6.14. Carbonation depth of sample P500-prolonged is found to be more than 5 mm, whereas carbonation of sample NS500-prolonged is barely visible. It is important to mention here that the experiments were performed immediately after prolonged heat treatment to minimize any carbonation of samples during storage. Another interesting point is that even after heat treatment at 500 °C and subsequent prolonged heat treatment at 50 °C, the reflection peaks of CH are well identified, indicating reformation of CH during the cooling process.
Figure 6-13 X-ray diffractograms of samples P500 and P500-prolonged, Key to phases: ▲ Portlandite (Ca(OH)$_2$), ■ Larnite ($\beta$-C$_2$S), ♦ Calcite (CaCO$_3$)

Figure 6-14 Carbonation test using phenolphthalein indicator on (a) a broken surface of the sample P500-prolonged and (b) a cross section of the sample NS500-prolonged
6.3.2.3 Thermogravimetric analysis

The results obtained from TGA for the control samples (P25 and NS25) and heat-treated samples at 500 °C without and with prolonged heat treatment (P500, NS500, P500-prolonged and NS500-prolonged, respectively) are presented in Fig. 6.15, where percent mass loss and the derivative of mass loss (DTG) are depicted. There is a similar trend of mass loss for control samples as shown in Fig. 6.15(a). Both of the samples exhibit drastic mass loss between room temperature and 105 °C which corresponds mainly to loss of free water and the decomposition of ettringite. During the test, temperature was held constant at 105 °C for 2 hours to promote removal of free water, which caused a steady loss in mass. Gradual mass loss between 105 and 400 °C was reported to be related to the primary dehydration of C-S-H [10]. Physically bound water, such as interlayer water and part of chemically bound water from C-S-H, could be lost in this temperature range. A negligible difference in mass loss between the two samples is observed in this temperature range. Furthermore, mass loss around 450 °C, attributes to the decomposition of CH, is more obvious in sample P25 than sample NS25 (4.38 and 3.01 % mass loss, respectively), due, in part, to pozzolanic activity of nanosilica consuming CH in sample NS25.
Figure 6-15 Results of TGA on (a) samples P25 and NS25, (b) samples P500 and NS500 and (c) samples P500-prolonged and NS500-prolonged
Table 6-5 Thermogravimetric data and the estimation of CH and CaCO$_3$ content

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight loss (%) related to the decomposition of</th>
<th>Ca(OH)$_2$ content (%)</th>
<th>CaCO$_3$ content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca(OH)$_2$ (400-500 ºC for P25 and NS25, 350-450 ºC for the rest)</td>
<td>CaCO$_3$</td>
</tr>
<tr>
<td>P25</td>
<td>4.38</td>
<td>0.41</td>
<td>18.01</td>
</tr>
<tr>
<td>NS25</td>
<td>3.01</td>
<td>0.41</td>
<td>12.35</td>
</tr>
<tr>
<td>P500</td>
<td>4.33</td>
<td>0.51</td>
<td>17.80</td>
</tr>
<tr>
<td>NS500</td>
<td>2.99</td>
<td>0.39</td>
<td>12.29</td>
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<tr>
<td>P500-prolonged</td>
<td>3.57</td>
<td>2.48</td>
<td>14.67</td>
</tr>
<tr>
<td>NS500-prolonged</td>
<td>3.11</td>
<td>0.41</td>
<td>12.79</td>
</tr>
</tbody>
</table>

The decomposition of CaCO$_3$ which occurs between 600 and 700 ºC is barely detectable in both samples P25 and NS25. The amounts of CH and CaCO$_3$ were estimated using Eq (6.1) and Eq (6.2) and summarized in Table 6.5:

$$\text{CH} (\%) = \text{WL}_{\text{CH}} (\%) \times \frac{\text{MW}_{\text{CH}}}{\text{MW}_{\text{H}_2\text{O}}} \quad (6.1)$$

where $\text{WL}_{\text{CH}}$ corresponds to the weight loss in percentage associated with CH decomposition, and $\text{MW}_{\text{CH}}$ and $\text{MW}_{\text{H}_2\text{O}}$ are the molecular weights of CH (74.01 g/mol) and water (18 g/mol), respectively,

$$\text{CaCO}_3 (\%) = \text{WL}_{\text{CaCO}_3} (\%) \times \frac{\text{MW}_{\text{CaCO}_3}}{\text{MW}_{\text{CO}_2}} \quad (6.2)$$

where $\text{WL}_{\text{CaCO}_3}$ corresponds to the weight loss in percentage associated with CaCO$_3$ decomposition, and $\text{MW}_{\text{CaCO}_3}$ and $\text{MW}_{\text{CO}_2}$ are the molecular weights of CaCO$_3$ (100 g/mol) and CO$_2$ (44 g/mol), respectively.
When TGA is performed on samples P500 and NS500, significant mass loss is observed in both samples between 350 and 450 °C, as shown in Fig. 6.15(b). This mass loss is related to the decomposition of reformed CH, which could have poorly recrystallized compared to the original crystalline CH, hence the shift in the degradation temperature range. Although prior heat treatment at 500 °C should have caused dehydroxylation of CH, the CH content before and after heat treatment at 500 °C is nearly constant as shown in Table 6.5. When the temperature is raised to 500 °C, CH loses its chemically bound water and changes into very reactive CaO. During the cooling process, CaO undergoes a reaction with moisture in the air which causes the CH to reform. In this research, TGA was conducted within 30 minutes after the cooling process commenced. This provides confirmation that CH reforms rapidly after heat treatment. It was reported that the reformation of CH is expansive and accompanied by a 44% volume increase due to the difference in density of CaO and CH, consequently leading to destruction of the structure of cement paste [32]. This expansive reformation of CH could promote development of the microcracks that easily detected on sample P500, while sample NS500 exhibits fewer microcracks likely due to less reformation of CH. This explains the higher compressive strength observed in samples with nanosilica, as the level of damage in samples due to reformation of CH is related to amount of initial CH present in the sample.

After prolonged heat treatment of samples P500 and NS500, both the samples exhibit similar levels of mass loss between 350 and 450 °C as shown in Fig. 6.15(c). There is reduction in the CH content for sample P500 from 17.8% to 14.67%, while sample NS500 has near identical CH content even after prolonged heat treatment as shown in Table 6.5. In Fig. 6.15(c), TGA curve of sample P500-prolonged shows another important mass loss of 2.48% between 600 and 700 °C, attributable to the decomposition of CaCO₃, while sample NS500-prolonged experiences rather small, gradual
mass loss in this temperature range. This is indicative of progressive carbonation only in sample P500-prolonged during prolonged heat treatment. It is important to note here that TGA was performed immediately after prolonged heat treatment. Therefore, the mechanism of total loss in mechanical properties of paste samples after prolonged heat treatment seems to be due to carbonation. Thermal decomposition of hydration products leads to an increase in microcracks and porosity during exposure to temperature higher than 400 °C. During the cooling process, the dehydrated CH rapidly reforms, resulting in further development of microcracks and making the samples more susceptible to carbonation. The carbonation of hydration products under atmospheric conditions is slow due to the low partial pressure of CO₂ (which is approximately 0.03% air by volume), and the slow rate of diffusion of CO₂ into the matrix. However, during prolonged heat treatment, the diffusion of CO₂ could be promoted due to the development of surface microcracks. CaCO₃ could then form either due to carbonation of C-S-H or carbonation of CH. It was reported that CO₂ can simultaneously react with C-S-H and CH, although carbonation of CH might be initially more rapid than that of the C-S-H [73-75]. As mentioned earlier, nanosilica is reported to increase chemical stability of C-S-H and hence can arguably exhibit higher resistance against carbonation as well. The temperature for prolonged heat treatment is chosen to be 50 °C as the formation of CaCO₃ is most favorable at this temperature, and any difference between samples with and without nanosilica will be more prominent [76]. In this research, CH seems to be the main source of Ca²⁺ ion for carbonation. The reduction in CH content of sample P500 after prolonged heat treatment is 3.13%. This, by reaction with CO₂ in the unsealed furnace, can produce 4.22% CaCO₃ out of a total 5.63% CaCO₃ present in sample P500-prolonged. If we considered the initial CaCO₃ content to be 1.17% that exists in sample P500 before prolonged heat treatment, most of CaCO₃ (about 95%) formed in sample P500-prolonged
comes from the carbonation of CH. Also, the formation of aragonite and vaterite, which is reported to be a reliable indication of C-S-H carbonation [77, 78], is not detected in our XRD studies as shown in Fig. 6.13. The volume of CaCO$_3$ formed is about 12% greater than the volume of CH, which could result in further cracking and significant loss in mechanical properties of the paste samples. Thus, the damage exhibits in sample P500-prolonged in Fig. 6.9(a) can be justified by dual effects of expansive reformation of CH during the cooling process and accelerated carbonation of CH during prolonged heat treatment. Prolonged heat treatment amplifies the effects of nanosilica addition; however, the damage is still mainly governed by the amount of CH available in the system. Higher pozzolanic reactivity of nanosilica, due to its high specific surface area, than the other siliceous mateirials could be responsible for the reduction in microcracks of sample NS500-prolonged as less CH is available for reformation during heating and the subsequent cooling process. Thus, the level of diffusion of CO$_2$ into the matrix is not great enough to cause as much carbonation of hydration products as in the paste without nanosilica.

6.4 Conclusions

In this chapter, the effects of high temperature exposures and subsequent cooling down to room temperature following two different processes on global (compressive strength) and local (static nanoindentation) mechanical properties, and phase composition of cement paste incorporating nanosilica are studied. This research has shown that the cement paste incorporating 5% nanosilica exhibits enhanced thermal stability. The main findings of this chapter are summarized below:

1) Paste samples incorporating nanosilica show 8% higher compressive strength at room temperature than paste samples without nanosilica. This difference becomes more obvious
when the samples are exposed to 400 °C at which the greatest difference (nanosilica-containing pastes show 20% higher compressive strength than pastes without nanosilica) in compressive strength is observed.

2) Incorporating nanosilica improves local mechanical properties of cement paste. The results of coupled nanoindentation/SEM-EDS and static nanoindentation indicate that there is a decrease in volume fraction of HD C-S-H in the sample without nanosilica after heat treatment at 300 °C and 400 °C, while sample with nanosilica does not have reduction in volume fraction of HD C-S-H.

3) TGA results show that CH, which decomposes during the heating process, rapidly reforms during the cooling process.

4) Expansive reformation of CH during the cooling process, and accelerated carbonation of CH during prolonged exposure to above ambient temperature (50 °C) could result in significant loss in mechanical properties of paste samples without nanosilica.

5) The reduction in compressive strength in paste samples after heating and cooling and total loss of mechanical properties after prolonged heat treatment seem to be mainly governed by the initial CH content.

6) Carbonation is a main cause of damage in cement paste after high temperature exposure. This could be of great importance in identifying damage that can continue to occur after a fire.
CHAPTER 7
EFFECTS OF NANOSILICA ON RESISTANCE AGAINST CARBONATION OF HYDRATION PRODUCTS

7.1 Introduction

As discussed in Chapter 6, stress development due to carbonation of hydration products during cooling process (after exposure to high temperatures) can cause a significant loss in mechanical properties of cement paste. Carbonation of concrete reduces the alkalinity of the pore solution in cement paste, and thus causes the depassivation of steel reinforcement, and could result in severe deterioration of concrete [79, 80]. It was reported that carbonation can be a self-arresting process as CaCO$_3$ precipitates in the pore spaces reducing permeability [81, 82]. However, decalcification of C-S-H can cause shrinkage particularly in aggressive carbonating environments where reaction with CH is arrested due to the formation of a protective CaCO$_3$ layer.

Carbonation of concrete can be affected by several parameters, such as its surrounding environment (relative humidity, concentration of atmospheric CO$_2$), the permeability and the calcium (carbonatable) content of cement paste [83, 84]. Both CH and C-S-H are main carbonatable constituents in cement paste. Although carbonation of CH might be initially more rapid than that of C-S-H, a polymorph of CaCO$_3$ - vaterite, can soon start forming preferentially on the surface of CH because of the similarities of their symmetries and the positive surface charge of vaterite [73, 75, 85]. Once the carbonation of CH is hindered, due to the formation of vaterite on the CH surface, carbonation of C-S-H could be accelerated.

The effects of replacing OPC with SCMs are difficult to predict and thus there are conflicting views on it. It was reported that the rate of carbonation increases in the long run as cement is
replaced by SCMs due to a decrease in the amount of carbonatable constituent through pozzolanic reaction [86, 87]. Another research group emphasized the changes in pore size distribution toward smaller pores, due to the long term pozzolanic reaction. Therefore, diffusion of CO$_2$ and carbonation will diminish [88]. Yet another research group had a neutral view on the effects of SCMs on carbonation as it may differ according to the exact structure and environment of the paste, such as $w/b$ and replacement level [73, 89]. This disagreement on the effects of SCMs on carbonation could be due to difference in permeability or $w/b$ between the samples tested by different groups.

One could argue that the reduction in carbonation of hydration products observed after heat treatment in samples with nanosilica is due to the reduction in permeability as a result of better particle packing and pozzolanic activity, not really due to any increase in chemical stability against calcium leaching [14, 15] or resistance to carbonation of hydration products. However, the effects of nonosilica on the carbonation of C-S-H have rarely been studied. In this research, an accelerated carbonation test was performed on both bulk and powdered cement paste samples, incorporating micro and nanosilica to investigate more fundamental effects of SCMs on the carbonation.

### 7.2 Experimental details

Besides plain cement paste samples (P) and paste samples incorporating nanosilica (NS) with $w/b$ of 0.45, which are used in the previous chapters, paste samples incorporating microsilica (MS) were prepared following the method as described in Chapter 4. Microsilica and nanosilica were used as 5% replacement (by mass) of cement. Table 7.1 summarizes the chemical composition of microsilica used. Cement paste was mixed and formed into cylinder molds having dimensions of
5 cm-diameter × 7.5 cm-length. Cured samples were then used for pore solution extraction, accelerated carbonation test, TGA and SEM-EDS.

Table 7-1 Chemical composition of microsilica (in % by weight)

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>Total Alkalis (Na₂O)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.0</td>
<td>0.7</td>
<td>0.5</td>
<td>0.7</td>
<td>0.7</td>
<td>-</td>
<td>0.9</td>
<td>0.4</td>
<td>1.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Pore solution extraction was carried out using a high-pressure steel die; details of this procedure are given elsewhere [90]. Extracted pore solution was neutralized and sealed to minimize any carbonation. The pH of pore solution was measured using a digital pH meter, and the concentrations of alkali ions (K, Ca, and Na) in the pore solution were measured using inductively coupled plasma spectroscopy (ICP).

The evolution of carbonation in concrete is extremely slow in normal environments due to a very low concentration of CO₂: from 0.03% to 1%. Thus, an accelerated carbonation test was performed inside a chamber with a CO₂ concentration of 5%, RH of 55±5%, and temperature of 22±2 ºC. For the bulk cylinder samples, top and bottom sides were sealed with epoxy to ensure radial CO₂ diffusion during the carbonation test. In addition, powdered samples were prepared to study the effects of SCMs addition on carbonation of cement paste, irrespective of a difference in permeability. Samples were powdered using a mortar and pestle and then sieved by a sieve (#100, 150 μm mesh). An accelerated carbonation test was carried out at various durations; 10 hours for powdered samples and 7, 14 and 21 days for bulk samples.

At the end of the desired exposure period, using a diamond saw (IsoMet, Buehler, Lake Bluff, USA), a 10 mm cube was cut from the surface which is directly exposed to the environment with
high CO$_2$ concentration, and ground to form powder. TGA was carried out on the powdered sample by the same instrument and method described in Chapter 4. Mass loss and the derivative of mass loss (DTG) were used to estimate changes in the amount of carbonatable constituents (mainly CH and C-S-H) and CaCO$_3$ present in each sample. The amount of CH and CaCO$_3$ were calculated using Eq (6.1) and (6.2), respectively. CH was calculated from the dehydroxylation at 380-480 °C. The amount of CaCO$_3$ was calculated based on the decarbonation at 550-780 °C. Although loss in mass between 780 and 990 °C could also be associate with the decomposition of CaCO$_3$ [91]. This region is not considered in this chapter, because all samples had a similar amount of mass loss (approximately 2%) between 780 and 990 °C regardless of the extent of carbonation. Further detail is presented and discussed in the next section.

After the accelerated carbonation, the amounts of CaCO$_3$ formed by carbonation of CH were estimated based on the reduction in the amount CH using Eq (7.1):

$$\text{CaCO}_3(\%)_{\text{fromCH}} = [\text{CH}(\%)_{\text{beforeAC}} - \text{CH}(\%)_{\text{afterAC}}] \times \frac{\text{MW}_{\text{CaCO}_3}}{\text{MW}_{\text{CH}}} \quad (7.1)$$

where CaCO$_3(\%)_{\text{fromCH}}$ refers to the amount of CaCO$_3$ formed due to carbonation of CH, and MW$_{\text{CaCO}_3}$ and MW$_{\text{CH}}$ are the molecular weights of CaCO$_3$ (100 g/mol) and CH (74.01 g/mol), respectively.

The amount of CaCO$_3$ formed by carbonation of other phase (mainly C-S-H) was calculated using Eq (7.2):

$$\text{CaCO}_3(\%)_{\text{fromCSH}} = \text{CaCO}_3(\%)_{\text{afterAC}} - \text{CaCO}_3(\%)_{\text{beforeAC}} - \text{CaCO}_3(\%)_{\text{fromCH}} \quad (7.2)$$

where CaCO$_3(\%)_{\text{fromCSH}}$ refers to the amount of CaCO$_3$ formed due to carbonation of other phases (mainly C-S-H).
It is worth noting that the temperature ranges for the decomposition of each phase were visually determined based on TGA/DTG, and it was assumed that mass loss between 550 and 780 °C is related to emission of CO₂ only. Hence, the amount of CaCO₃ could be overestimated if C-S-H continued to dehydrate above 550 °C.

SEM characterization was performed on the surface of bulk samples after 14 days of accelerated carbonation. A diamond saw was used to cut 20 mm cubic samples, which were then epoxy-impregnated and polished; details of this procedure are given in Chapter 4. Two different locations in each sample, 1 mm and 10 mm away from the exposed surface, were analyzed by SEM-EDS to study the changes in the chemical composition of hydration products as a function of carbonation. Details of this procedure are given in Chapter 6.

The backscattered electron (BSE) images were used for quantitative analysis of porosity. The BSE images (1276 × 830 pixels) were acquired at 500× magnification. In order to study changes in porosity due to carbonation, eight different depths (0, 0.5, 1, 2, 3, 4, 5, and 10 mm) from the exposed surface were characterized. Taking account of statistical variations in the results of image analysis, five different locations in each depth were randomly chosen and analyzed; details of this procedure is given in Chapter 4.

### 7.3 Experimental results and discussion

#### 7.3.1 Thermogravimetric analysis

The results obtained from TGA before and after accelerated carbonation are presented in Fig. 7.1, where mass loss (in percentage) and the DTG are depicted. The DTG curves show that the dehydration of CH is occurring within a temperature range between 380 and 480 °C. Decomposition of CaCO₃ is observed to occur within a broad range of temperatures between 550
and 990 °C. The DTG curves of all three samples have small hump between 780 and 990 °C irrespective of the degree for accelerated carbonation. It is generally reported that decalcification of well-crystallized calcite occurs between 780 and 990 °C [91]. As mass loss at this temperature range is consistent between all samples, it is assumed that mass loss is due to decomposition of preexisting CaCO₃ in cement. Thus the temperature range between 780 and 990 °C is excluded from the estimation of CaCO₃ formed due to accelerated carbonation. Furthermore, nature of the DTG curves within the temperature range between 550 and 780 °C seems to show two distinct behaviors, possibly due to the decomposition of various polymorphs of CaCO₃. Thiery et al. reported that vaterite and aragonite could decompose at lower temperatures than the well-crystallized calcite, for example between 680 and 780 °C [91]. They also proposed that mass loss at further lower temperature (between 550 and 680 °C) is associated with the decomposition of amorphous CaCO₃. Formation of aragonite and amorphous carbonates was reported to be indicative of carbonation of C-S-H [77, 92].
Figure 7-1 Results of TGA and DTG on samples (a) P, (b) MS and (c) NS
Table 7.2 TGA data and the estimation of the extent of carbonation of CH and other phases (mainly C-S-H)

<table>
<thead>
<tr>
<th>Accelerated carbonation</th>
<th>Sample type</th>
<th>Mass loss (380-480 °C)</th>
<th>Mass loss (550-680 °C)</th>
<th>Mass loss (680-780 °C)</th>
<th>Mass loss (780-990 °C)</th>
<th>%CH from TGA</th>
<th>%CC from TGA</th>
<th>Expected % of CC from carbonating CH</th>
<th>Expected % of CC from carbonating other phases (mainly C-S-H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (No carbonation)</td>
<td>P</td>
<td>4.42</td>
<td>0.82</td>
<td>0.55</td>
<td>2.15</td>
<td>18.15</td>
<td>3.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>3.49</td>
<td>0.83</td>
<td>0.49</td>
<td>2.13</td>
<td>14.33</td>
<td>3.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>3.04</td>
<td>0.87</td>
<td>0.53</td>
<td>2.11</td>
<td>12.47</td>
<td>3.19</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7 days (Bulk)</td>
<td>P</td>
<td>3.21</td>
<td>2.99</td>
<td>3.44</td>
<td>2.06</td>
<td>13.21</td>
<td>14.58</td>
<td>6.67</td>
<td>4.79</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>2.89</td>
<td>3.07</td>
<td>2.16</td>
<td>1.77</td>
<td>11.88</td>
<td>11.88</td>
<td>3.30</td>
<td>5.57</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>2.66</td>
<td>2.74</td>
<td>0.98</td>
<td>1.72</td>
<td>10.93</td>
<td>8.46</td>
<td>2.08</td>
<td>3.19</td>
</tr>
<tr>
<td>14 days (Bulk)</td>
<td>P</td>
<td>2.59</td>
<td>3.88</td>
<td>5.64</td>
<td>1.94</td>
<td>10.64</td>
<td>21.61</td>
<td>10.13</td>
<td>8.36</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>2.79</td>
<td>3.31</td>
<td>2.95</td>
<td>2.01</td>
<td>11.47</td>
<td>14.21</td>
<td>3.87</td>
<td>7.34</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>2.38</td>
<td>3.38</td>
<td>2.59</td>
<td>1.79</td>
<td>9.77</td>
<td>13.53</td>
<td>3.65</td>
<td>6.70</td>
</tr>
<tr>
<td>21 days (Bulk)</td>
<td>P</td>
<td>2.46</td>
<td>3.96</td>
<td>6.53</td>
<td>2.09</td>
<td>10.10</td>
<td>23.83</td>
<td>10.86</td>
<td>9.85</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>2.64</td>
<td>3.78</td>
<td>3.86</td>
<td>1.97</td>
<td>10.83</td>
<td>17.35</td>
<td>4.72</td>
<td>9.63</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>2.26</td>
<td>3.85</td>
<td>3.42</td>
<td>1.83</td>
<td>9.30</td>
<td>16.50</td>
<td>4.28</td>
<td>9.03</td>
</tr>
<tr>
<td>10 hours (Powdered)</td>
<td>P</td>
<td>2.48</td>
<td>3.53</td>
<td>7.92</td>
<td>2.15</td>
<td>10.19</td>
<td>25.99</td>
<td>10.74</td>
<td>12.13</td>
</tr>
<tr>
<td></td>
<td>MS</td>
<td>2.29</td>
<td>3.53</td>
<td>6.23</td>
<td>2.26</td>
<td>9.41</td>
<td>22.16</td>
<td>6.64</td>
<td>12.52</td>
</tr>
<tr>
<td></td>
<td>NS</td>
<td>2.17</td>
<td>3.64</td>
<td>5.13</td>
<td>2.25</td>
<td>8.92</td>
<td>19.91</td>
<td>4.80</td>
<td>11.92</td>
</tr>
</tbody>
</table>

Table 7.2 summarizes mass loss during TGA due to dehydration or decomposition of various phases. Concentration of CH and CaCO₃ in various samples are calculated based on the Eq. (1) and (2) and reported in the table. In addition, amounts of CaCO₃ expected to form due to carbonation of CH and C-S-H are calculated based on Eq. (3) and (4). It is worth reiterating here that all samples for TGA were prepared in a N₂-filled glove bag to prevent any carbonation during grinding. However, approximately 3% CaCO₃ is initially present in all three samples. Before accelerated carbonation, samples NS and MS have a lower amount of CH than sample P due to pozzolanic reaction. The least amount of CH is present in sample NS probably because of higher pozzolanic reactivity of nanosilica than microsilica (14.33% CH in MS and 12.47% CH in NS).
For ease of comparison between samples, Fig. 7.2 and Fig. 7.3 compare the most critical results graphically.

![Graph showing percentage of CH and CaCO₃](image)

**Figure 7-2 % amount of CH and CaCO₃ determined by TGA**

Fig. 7.2 shows the changes in the amount of CH and CaCO₃ in both bulk and powdered samples due to accelerated carbonation. It is clear that for all samples the amount of CH decreases and the amount of CaCO₃ increase with progressive carbonation. The amount of CH remaining after 21 days of accelerated carbonation is about 10%, which is about the same for all three bulk samples. This indicates the highest degree of CH carbonation in the control sample (sample P) as the initial CH content before accelerated carbonation is highest in sample P. The extent of CH carbonation seems to be related to the initial amount of CH present. It is interesting to note that the major decrease in CH concentration occurs within the first 14 days of accelerated carbonation. The CH content for all samples does not decrease much beyond 14 days even though the concentration of CaCO₃ increases significantly in all samples. From Fig. 7.2, it is clear that bulk sample P has the highest amount of total CaCO₃, regardless of the duration of accelerated carbonation. The rate of
carbonation of bulk samples seems to be highest for sample P and lowest for sample NS. Furthermore, the rate seems to be higher during the first 7 or 14 days, then slow down. The CaCO$_3$ content in bulk samples NS and MS after 14 and 21 days of accelerated carbonation seems to be comparable, however, bulk sample NS always shows the least amount of CaCO$_3$. It should be mentioned here that the data obtained from only 10 hours of accelerated carbonation exposure of powdered samples shows much greater carbonation than even after 21 days exposure of bulk samples. This is reasonable as powdered samples have much higher surface area and access to CO$_2$ does not depend on permeability of bulk samples. Therefore, the data from carbonation of powder samples are used in both the Fig. 7.2 and 7.3 as the last data point. Once again, powdered sample NS has the least total amount of CaCO$_3$, 19.19%, while 25.99% and 22.16% of CaCO$_3$ are identified in powered samples P and MS, respectively.

Figure 7-3 % amount of CaCO$_3$ formed by carbonation of CH and other phases (mainly C-S-H)
Fig. 7.3 shows the amount of CaCO$_3$ formed due to carbonation of CH and other phases (mainly C-S-H) after accelerated carbonation. At 7 days, 6.67% of CaCO$_3$ in bulk sample P is formed due to carbonation of CH which is more than twice as much as those in bulk samples MS and NS, 3.3% and 2.08 %, respectively. C-S-H carbonates the least in bulk sample NS, which forms only 3.19% CaCO$_3$. At 14 days, bulk sample P has 10.13% CaCO$_3$ formed due to CH carbonation. This is more than 4% increase over 7 days. In comparison, at 14 days, 3.87% and 3.65% CaCO$_3$ are formed due to CH carbonation in bulk samples MS and NS, which is only a small increase over 7 days (0.57% and 1.57% for bulk samples MS and NS, respectively). Bulk sample NS has 6.7% CaCO$_3$ formed due to C-S-H carbonation, which is still the least amount. As mentioned earlier, carbonation of CH seems to be almost complete at 14 days. The increase in the amount of CaCO$_3$ formed due to CH carbonation is less than 1% in all three samples after 21 days of accelerated carbonation. The carbonation of CH can be hindered due to the formation of a protective CaCO$_3$ layer on the surface of CH, particularly in an aggressive carbonating environment such as the one present in accelerated carbonation test. At 21 days, bulk samples MS and NS have a comparable amount of CaCO$_3$ from C-S-H carbonation, however the amount is slightly lower in bulk sample NS. Powdered sample NS also has the least amount of carbonation of CH as well as C-S-H after 10 hours exposure to accelerated carbonation.

The results clearly show that incorporating nanosilica reduces carbonation of both bulk and powdered samples. Thus, the reduction in permeability by incorporating nanosilica is not the only reason to cause the decrease in carbonation of the paste.
7.3.2 Pore solution analysis

The pH and alkali ion contents in the pore solution extracted from all three types of samples before accelerated carbonation are presented in Fig. 7.4. The concentration of alkali ions controls the pH of the solutions as expected. It was reported that the alkali content of pore solution plays an important role in the kinetics of carbonation [93]; i.e. higher alkali content can accelerate the step in which the CO₂ combines with OH⁻ from the pore solution to form CO₃²⁻ which ultimately reacts with CH or C-S-H to form CaCO₃. When 5% cement is replaced with microsilica or nanosilica, both the pH and alkali ions’ content decrease progressively. It can partially justify the reason that samples MS and NS have less total carbonation than sample P. The difference in pH and total alkali is more between samples P and MS than between samples MS and NS. This compares well with the difference in the total CaCO₃ between samples P and MS and between samples MS and NS. However, the degree of C-S-H carbonation is a little higher in sample MS and a little lower in sample NS compared to sample P, which seem to occur due to the difference in the initial carbonatable CH in the sample, rather than the difference in pH. Furthermore, incorporation of microsilica and nanosilica alters the nature of C-S-H which could play a role as well.

![Figure 7-4 pH value and alkali concentration in the pore solution](image)

**Figure 7-4** pH value and alkali concentration in the pore solution
7.3.3 Scanning electron microscopy imaging in back scattered mode and image analysis

Fig. 7.5 shows BSE images of paste samples near the exposed surface after 14 days of accelerated carbonation. The unhydrated cement particles appear as bright particles, CH slightly darker, other hydrated products further dark, and epoxy filled pore spaces as black. It is apparent that the exposed surface of sample P is more porous after 14 days of accelerated carbonation than those of samples MS and NS. Densified carbonation front due to precipitation of CaCO$_3$ in the pore spaces is not observed in our SEM study. TGA results presented earlier show that sample P has the most carbonation from CH followed by sample MS and NS after 14 days of accelerated carbonation. Carbonation of CH could cause a densification of matrix and a decrease in porosity as open pores can get filled with CaCO$_3$, which has higher volume than the initial CH [81, 82]. However, results of our image analysis clearly show an increase in porosity near the surface as a function of carbonation.

For quantitative analysis of changes in porosity in all three samples, P, MS and NS, due to accelerated carbonation, image analysis was performed using Image J; the results are presented in Fig. 7.6. As carbonation proceeds from the exposed surface toward the core, the porosity changes. It is clear that the exposed surface is more porous for all three samples, however, the porosity in sample P is much greater than those of samples MS and NS. Sample P has 17.14% porosity within the first 500 micron of the exposed surface, while the porosity is 12.82% and only 6.95% for samples MS and NS, respectively. In addition, porosity drops to the level observed in bulk paste (core region, 10 mm away from the exposed surface) within a very short distance for NS sample (only 0.5 mm) and it takes longer for samples MS and P, 2 mm and 4 mm, respectively. Decalcification of C-S-H, due to carbonation, can cause shrinkage of cement paste [94].
Figure 7-5 Backscattered electron (BSE) images of samples (a) P, (b) MS and (c) NS near the exposed surface after 14 days of accelerated carbonation.
It seems that the higher extent of decalcification of C-S-H in samples P and MS could make them more porous than sample NS near the exposed surface. The results presented here also highlight a possible difference in nature and extent of carbonation of different phases during accelerated carbonation tests often used in the laboratory, compared to carbonation due to a mild long term exposure.

Figure 7-6 Binary SEM-BSE images of samples (a) P, (b) MS and (c) NS at 500× magnification used for image analysis
Figure 7-6 (cont.)
Figure 7-7 Changes in area fraction of void from exposed surface to inner core
7.3.4 Scanning electron microscopy with energy dispersive x-ray analysis

Fig. 7.8 shows plots of the (Al+Fe)/Ca ratio versus the Si/Ca ratio from EDS analysis performed near the exposed surface (within 1 mm from the exposed surface) and on bulk paste (core region, 10 mm away from surface) after 14 days of accelerated carbonation. It shows the clustered data of HD C-S-H, which formed mainly within the original cement particle boundaries, and the scattered LD C-S-H along the lines, which is an intimate intermixture of C-S-H with other phases, such as AFm or CH. Figs. 7.8(a) and (b) show formation of a phase with a very high Si/Ca ratio, between 0.6 and 0.8, due to carbonation near the exposed area of samples P and MS. It could indicate more apparent decalcification of C-S-H due to carbonation in samples P and MS at the surface region. In comparison, sample NS (Fig. 7.8(c)) in general shows higher Si/Ca ratio (lower Ca/Si ratio) in an area away from the exposed surface (core region which is not affected due to carbonation) than samples P and MS. This confirms a decrease in Ca/Si ratio due to pozzolanic reaction by incorporating nanosilica. EDS analysis on an area 1 mm away from the exposed surface does not show a change in the Ca/Si ratio in NS sample. This is consistent with the microstructural observation presented in Fig. 7.5 and the porosity data presented in Fig. 7.7.
Figure 7-8 Al/Ca vs Si/Ca ratios for samples (a) P, (b) MS and (c) NS after 14 days of accelerated carbonation.
7.4 Conclusions

In this chapter, the effects of incorporating microsilica and nanosilica on the carbonation of cement paste are studied. The comparison of the results obtained by TGA, SEM-EDS, and BSE image analysis on bulk and powdered pastes leads to the conclusions presented below.

1) The incorporating small dosages of microsilica or nanosilica reduces the total carbonation of both bulk and powdered cement paste samples. This confirms that the reduction in the extent of carbonation in microsilica and nanosilica cement paste is not only due to the reduction in permeability.

2) The reduction in pH and alkali content by incorporating microsilica and nanosilica could reduce the extent of total carbonation.

3) The rate of CH carbonation is faster in all samples for the first 7 and 14 days.

4) The reduction in the initial CH content due to high pozzolanic reactivity of nanosilica could result in the reduction in CH carbonation.

5) Incorporating nanosilica causes a small reduction in C-S-H carbonation. This could be possibly due to reduction in pH of the pore solution and an increase in chemical stability of hydration products.

6) Incorporation of microsilica and nanosilica reduces the carbonation depth.
CHAPTER 8
CONCLUSIONS AND FUTURE WORK

This research examines the behavior of cement-based composite materials at elevated temperatures. With a goal of improving the understanding of thermal degradation mechanism of cement-based composite materials, relatively new advances in nanotechnology, such as AFM and static and dynamic nanoindentation, are employed to investigate the changes in micro and nanostructure of cement paste at elevated temperatures. Furthermore, chemo-mechanical characterization, which combines mechanical properties obtained by grid nanoindentation with local phase chemistry by SEM-EDS, was used and overcame the limitation of statistical deconvolution based solely on the mechanical data obtained by grid nanoindentation. This research also provides insight on the effects of nanosilica on cement paste micro and nanostructure and how it improves thermal and chemical stability of hydration products against high temperature exposure and carbonation. This final chapter summarizes the conclusions made in the course of this research.

8.1 Conclusions

Micro and nanostructural changes of cement paste are ultimately responsible for the loss of macroscopic mechanical properties, though the lack of characterization at the micro and nanoscales at elevated temperatures makes it difficult to establish a link between the two. From a detailed, morphological characterization of cement paste after heat treatment, the degradation mechanism that initiates at micro and nanoscales driving the loss of mechanical properties at global scale is proposed.
Moreover, a correlation between thermal-induced changes in local mechanical characteristics and global behavior of cement-based composite materials is still not fully understood. From a micromechanics combined with local chemical analysis, we link the loss in local mechanical properties caused by thermal damage to global behavior.

In an attempt to mitigate thermal and chemical degradation of cement paste against high temperature exposure and carbonation, effects of nanosilica on cement paste micro and nanostructure and how it improves thermal and chemical stability of hydration products are discussed in this research.

The main conclusions made in the course of this research are summarized below:

1) The interface between unhydrated cement particles and paste matrix is considered as the origin of microcracks. The opposite behaviors of the two phases at elevated temperatures; not only difference in thermal expansion rate, but also reversible expansion of unhydrated cement particle and irreversible shrinkage of C-S-H probably result in a gap at the interface at 300 °C. This gap becomes wider, and consequently causes microcracks to expand into paste matrix as temperature increases over 300 °C.

2) AFM image analysis shows that an exposure of cement paste to 300 °C changes the nanostructure to a more loosely packed globular structure, which could be indicative of C-S-H shrinkage. The nanostructure of C-S-H continues to rearrange with high temperature exposure making the microstructure more porous.

3) Cement paste samples retain most of their compressive strength after heat treatment at 400 °C. However, it is clear that the micro and nanostructure of C-S-H is altered after exposure to 300 and 400 °C as observed in AFM and nanoindentation studies. In coupled
nanoindentation/SEM-EDS, volume fraction of HD C-S-H decreases from 38% to 30%, while LD C-S-H increases from 46% to 58% after heat treatment at 300 °C.

4) Coupled nanoindentation/SEM-EDS technique with multivariate statistical deconvolution of data successfully identifies phase (or mixture of phases) properties with more confidence than statistical deconvolution of local mechanical properties only.

5) Expansive reformation of CH during cooling process, and accelerated carbonation of hydration products during prolonged exposure to above ambient temperature (50 °C) could result in significant loss in mechanical properties of cement paste.

6) Incorporating nanosilica effectively enhances the mechanical properties (compressive strength and indentation modulus) of cement paste after exposure to elevated temperatures. The results of static nanoindentation and coupled nanoindentation/SEM-EDS indicate that there is a decrease in volume fraction of HD C-S-H in sample without nanosilica after heat treatment at 300 °C and 400 °C, while sample with nanosilica does not have reduction in volume fraction of HD C-S-H. The effect becomes more obvious when the paste samples are exposed to prolonged heat treatment.

7) Carbonation proves to be a main cause of damage in cement paste after high temperature exposure if the samples are maintained in above ambient temperature for long times. Similar damage occurs at a slower rate if ambient temperature is maintained. This could be important for damage that can continue to occur after a fire.

8) The incorporating microsilica or nanosilica reduces the total carbonation of both bulk and powdered cement paste samples. This confirms that the reduction in the extent of carbonation in microsilica and nanosilica cement paste is not only due to the reduction in permeability.
The reduction in pH and alkali content by incorporating microsilica and nanosilica could reduce the extent of total carbonation.

9) The CH carbonation is almost completed within the first 7 and 14 days irrespective of incorporation of microsilica or nanosilica. The reduction in the initial CH content due to high pozzolanic reactivity of nanosilica could result in the reduction in carbonation of CH. Incorporating nanosilica causes a small reduction in C-S-H carbonation. This could be possibly due to the reduction in pH of the pore solution and an increase in chemical stability of hydration products. Incorporation of both the microsilica and nanosilica reduces the carbonation depth.

8.2 Recommendations for Future Research

In coupled nanoindentation/SEM-EDS with 100 data per sample, it was possible to isolate phases or intermixture of two phases from complex heterogeneous mixtures with other hydration products and unhydrated cement particle. However, with 100 data per sample, number of data points in some of the clusters are too few to be statistically significant. The data analysis and conclusions can be strengthened further by collecting more data.

Furthermore, it will be necessary to investigate effects of nanosilica on thermal degradation of mortar and concrete samples and verify if the advantage of nanosilica addition observed for cement paste is also extended to mortar and concrete. Also, better understanding of effects incorporating nanosilica on interfacial transition zone between paste matrix and aggregates will be necessary.
REFERENCES


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