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Nanostructure and Engineering Properties of Basic and Modified Calcium-Silicate-Hydrate Systems

by
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A thesis
submitted under the supervision of
Dr. James J. Beaudoin

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To my beloved parents

ABSTRACT

The nanostructure, physical properties and mechanical performance of C-S-H, the principal component in cement-based materials, was studied. Synthetic C-S-H of variable composition was examined as a model system in comparison with that produced in the hydration of Portland cement. The current doctoral thesis is comprised of several research chapters designed to probe some of the ambiguous aspects of the C-S-H at the nano level. Several advanced analytical tools and novel approaches were utilized in order to elucidate various controversial issues in cement and concrete science. The studied topics include three areas of C-S-H investigation: nanostructural features, engineering properties and modified systems.

Nanostructural Features – The C-S-H (I) was categorized in two main classes separated at a C/S ratio of about 1.1. These exhibit distinct properties as determined by XRD, Helium Inflow, ^{29}Si NMR and ^{43}Ca NMR. New evidence was provided supporting the layered nature of the C-S-H. The role of interlayer water and calcium ions as well as silicate tetrahedra on physical properties of C-S-H analogs were evaluated. It was mainly demonstrated that the high C/S ratio C-S-H (I) can be considered as a viable model for the nanostructure of the C-S-H in hydrated cement paste.

Engineering Properties – The relation between the chemistry and mechanical performance of the phase pure C-S-H systems was investigated. The dynamic mechanical response and stress relaxation of the synthetic C-S-H as well as C-S-H in hydrated Portland cement were examined at various moisture contents. A unique oscillatory response in the storage modulus and internal friction of the C-S-H materials was identified. Viscoelastic behavior of C-S-H was associated with the sliding of the C-S-H sheets. A mechanistic model was proposed to explain the observed changes in the mechanical properties of layered C-S-H materials.

Modified Systems – Two approaches were evaluated in order prepare and characterize nanohybrid C-S-H phases: organic modification of C-S-H, and metamorphosis of C-S-H in cement paste. In situ polymerized C-S-H/polyaniline nanostructures demonstrated enhanced physical and mechanical properties attributable to the interaction of polymer molecules with the silicate structure of the inorganic host. C-S-H seeding was also employed in order to tailor the nature of the C-S-H product. It was shown that the chemical properties of C-S-H can be readily controlled depending on the stoichiometry of the seed. This offers a unique method in order to engineer the hydrated cement and concrete materials for improved sustainability.

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GLOSSARY

Abbreviations

AFM	Atomic Force Microscope
BET	Brunauer-Emmett-Teller
DMA	Dynamic Mechanical Analysis
DMTA	Dynamic Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
EDX	Energy-Dispersive X-ray
FTIR	Fourier Transform Infrared
ICDD	International Centre for Diffraction Data
IRC	Institute for Research in Construction
MAS	Magic Angle Spinning
NMR	Nuclear Magnetic Resonance
NRC	National Research Council of Canada
PMA	Poly Methacrylic Acid
PVA	Poly Vinyl Alcohol
RH	Relative Humidity
SEM	Scanning Electron Microscope
SS	Solid State
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
XRD	X-Ray Diffraction

Cement chemistry notations

A	Al_2O_3
C	CaO
C/S	CaO to SiO_2 molar ratio
C_3A	Tricalcium aluminate
C_3S	Tricalcium silicate
C-S-H	Calcium Silicate Hydrate
F	Fe_2O_3
H	H_2O
S	SiO_2
Q^n	Silicate tetrahedron sharing n bridging oxygen
w/c	Water to cement (or cementitious materials) mass ratio
$\beta\text{-C}_2\text{S}$	Beta dicalcium silicate

Variables

d	Distance between the atomic planes
E'	Storage modulus
E''	Loss modulus
$R(t)$	Hydrodynamic function
$W(t)$	Load
$\Psi(t)$	Viscoelastic function
δ	Phase lag
ε	Strain
λ	Wave length of the X-ray
θ	Angle of emitted X-ray
σ	Stress
τ_R	Hydrodynamic relaxation time
ω	Frequency

Introduction and Objectives

1.1 Introduction

Concrete is the most extensively used man-made material in the construction industry. It is made traditionally by mixing aggregate, Portland cement and water. Concrete has a relatively low cost and can be readily cast into various structural members of different shapes. It is estimated that more than 1 m³ of concrete per person is produced annually world-wide [1]. The use of chemical admixtures and pozzolanic materials in order to improve the performance and the durability of concrete has also become a common practice in the recent decades [2].

The benefit of more than a century of research and recent advancements in the field of concrete technology, has enabled engineers to design complicated structures that can resist various types of loadings including those due to earthquake [3]. The issue of concrete durability, however, has remained as one of the current challenges for materials scientists. The exposure of concrete to aggressive ions in most cases eventually leads to the deterioration of the structure. It is very difficult to predict and control many of the deleterious chemical reactions in concrete. These impose a considerable cost for the maintenance of concrete buildings and infrastructure. According to an estimate in 1997, approximately \$50 billion was required for the repair and rehabilitation of federal reinforced concrete bridges in the United States [4].

Often, it is the hydrated Portland cement (binder phase in concrete) that plays an important role in the durability related problems. The physical and chemical properties of this phase have long

been studied by cement chemists and researchers since the investigations of Le Chatelier in 1887 [5]. Yet, there remain some major issues that are not fully resolved. Examples are the state of water in the hydration products, the role of water in the shrinkage and creep phenomena, and the mechanisms of sulfate attack and alkali silica reaction. Even a basic question such as “what is the hydration mechanism of C_3S ?” remains a controversial issue in cement science and concrete technology. Calcium Silicate Hydrate (C-S-H), the principal component of the Portland cement hydration process, is a major contributor to the important properties of hardened cement paste such as strength and shrinkage [6]. The nanostructure of the C-S-H has not been fully resolved and the basis for some of the observed characteristics is still debatable. Knowledge of the material science of the nano- and micro-structure of cement-based materials can provide insight for civil engineers into the performance of concrete structures [7].

An understanding of the nature of the hydration products at the nano-scale is essential for the strategic modification of conventional systems and the development of new materials with enhanced properties. Application of nanotechnology in construction has received increased attention in recent years [8, 9] and appears to be a promising approach towards the development of new classes of cement-based materials with superior properties [10]. Figure 1-1 shows that there has been a considerable increase in the research on the nanotechnology of cement and concrete during the past few years. It appears that the key to resolve many of the debated topics in cement science lies at the nano-level. Advanced analytical tools such as ultra-high field solid state NMR and high resolution microscopic imaging techniques developed in recent years can be employed in order to re-examine controversial theories in cement and concrete science.

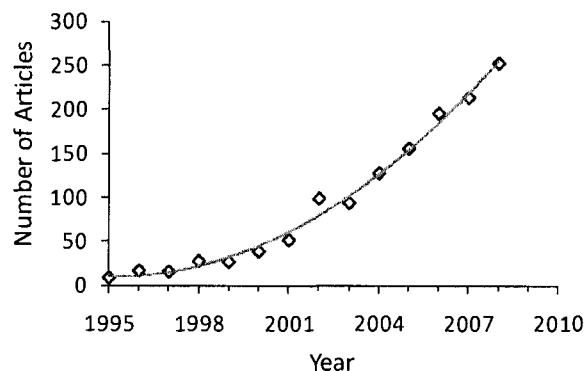


Figure 1-1. Number of articles containing “cement+concrete+nanotechnology” in the fields of chemistry, materials science, engineering and physics (source: Google Scholar, accessed August 2009).

1.2 Objectives

The current doctoral project was designed to add to the fundamental knowledge on the nature and engineering behavior of C-S-H and its analogs. Several issues in cement and concrete science were identified based on the relevant literature review (chapter 2) which merited further investigation. These debated topics were found to be mainly concerned with the nanostructure of the C-S-H, the primary binding agent in hydrated cement systems. Most of the controversies over the characteristics of C-S-H, particularly that present in hydrated cement paste, pertain to its layered nature and the role of interlayer water on physical and mechanical properties.

These debates in the cement research community are partially due to the fact that the C-S-H produced in the hydration of Portland cement is a nearly amorphous material, contains impurities and exhibits a wide range of stoichiometries. On the other hand, synthetically prepared more-ordered C-S-H systems (including C-S-H (I), tobermorite and jennite) have been proposed as models for the nanostructure of the C-S-H in hardened cement paste. The validity of using these models is still ambiguous. The current work utilizes several novel experimental methods in order to elucidate some of the new aspects of the nature of synthetic C-S-H in relation to that of the C-S-H formed in the hydrated Portland cement. The main objective of this thesis is to improve the understanding of the nanostructural features of the C-S-H. As a corollary to this, possible means of controlling and improving the performance of C-S-H-based materials are investigated.

The specific objectives of the current PhD thesis are summarized for each chapter as follows:

- Chapter 2. To identify the current debated issues related to the nanostructure and engineering properties of C-S-H materials.
- Chapter 3. To choose appropriate experimental tools in order to study the identified issues in chapter 2.
- Chapter 4. To study the changes in the basal spacing of the C-S-H of variable compositions and their significance upon the removal of interlayer water.
- Chapter 5. To examine the validity of using C-S-H (I) as a model for the layered structure of the C-S-H in hydrated cement paste.
- Chapter 6. To obtain new information about the local environment of calcium atoms in the nanostructure of various cement-based materials.
- Chapter 7. To evaluate the effect of stoichiometry of C-S-H on its chemical reactivity.

- Chapter 8. To study the relation between the chemistry and dynamic mechanical response of the C-S-H, and understand the role of adsorbed and interlayer water in this regard.
- Chapter 9. To advance the understanding of the mechanisms associated with the time-dependent deformations in C-S-H systems.
- Chapter 10. To synthesize and characterize organically-modified C-S-H nanocomposites by the *in situ* polymerization technique.
- Chapter 11. To evaluate the physical and mechanical properties of C-S-H/polyaniline nanocomposites.
- Chapter 12. To demonstrate the possibility of controlling the intrinsic properties of the hydration products of Portland cement through C-S-H seeding.

1.3 Overview

The research work of the current thesis is composed of 9 chapters. Each chapter was formatted according to the layout of a research paper and thus contains relevant sections such as abstract, introduction, experimental, results and discussion, conclusions and references. The chapters 4, 5, 8 and 9 were designed to study the change in several nanostructural characteristics of the C-S-H at various increments of drying from 11%RH condition. There is theoretically only a monolayer of water present on the surface of solid in addition to the interlayer water at this humidity level. The physical and mechanical properties of phase pure C-S-H materials having moisture contents below 11%RH were systematically studied in parallel with those of the C-S-H in hydrated Portland cement. A wide range of C/S ratio values from 0.8 to 1.5 were examined. In the other chapters, novel approaches were undertaken in order to offer new information in various fields including natural abundance ^{43}Ca MAS NMR of C-S-H, chemical reactivity of C-S-H, C-S-H/polymer nanocomposites and tailoring the nanostructural metamorphosis of C-S-H. An overview of the contents of the chapters 2 to 12 is provided as follows:

- Chapter 2. The scope of the literature review is necessarily broad and includes inorganic chemistry, polymer science, physics and civil engineering because of the multidisciplinary nature of this thesis. C-S-H, as the principal component of the hydration of Portland cement, has been the topic of significant research over the past century. An attempt has been made in the second chapter to summarize

relevant findings by other researchers. Some of the areas that are still not clearly understood have been identified. These form the topics of the next chapters.

- Chapter 3. Study of the chemistry and engineering aspects of the C-S-H necessitates application of several analytical tools. The third chapter introduces some of the important experimental instruments. A brief description of the relevant principal concepts for each technique is mentioned. The details of the experimental set-up of the tools in the current research differ based on the purpose of each investigation and are therefore included in the chapters where they are employed. The material preparation and some of the research methods are explained.
- Chapter 4. The fourth chapter employs X-ray diffractometry to examine the phase changes in various synthetic C-S-H systems upon drying from the 11%RH condition. Two methods were used for drying: a gradual increase of the temperature in a special XRD test stage; application of vacuum and heat in a drying cell. The first method allowed for monitoring the changes in X-ray spectra (mainly the basal spacing) of C-S-H samples versus temperature whereas the second method allowed for studying the same characteristics versus mass loss. Both methods provided evidence for the existence of a separating C/S ratio of about 1.1 for two types of C-S-H (I) based on their phase change behavior.
- Chapter 5. Helium inflow and ^{29}Si MAS NMR techniques are employed in order to further study the properties of the two types of C-S-H phases identified in the chapter 4. C/S ratios of 0.8 and 1.2 are selected as representative stoichiometries for these phases. Results are compared to those for the C-S-H in hydrated cement paste. It is shown that the nearly amorphous C-S-H behaves like a layered material (i.e. synthetic C-S-H).
- Chapter 6. Natural abundance ^{43}Ca ultra-high field NMR is employed in order to obtain new information about the calcium environment in cement-based materials. Various cement compounds and hydrated cement phases are investigated. It is demonstrated that the C-S-H in hydrated Portland cement has a very similar calcium structure to that of the more ordered phases such as synthetic C-S-H and tobermorite.
- Chapter 7. Chemical stability of C-S-H is an important factor in the durability of concrete structures. An innovative technique based on the Hedvall effect is developed to estimate the chemical reactivity of various C-S-H phases in the solid state. Heat

flow properties of the chemical reaction that occurs between the silver nitrate and C-S-H at the crystalline transition temperature of silver nitrate can be used to examine the extent of reaction in initial materials. It is shown that lower C/S ratio C-S-H materials are generally more reactive.

- Chapter 8. The relation between the chemistry and engineering properties of C-S-H has not been fully investigated due to the experimental limitations. Dynamic mechanical response of compacted phase pure C-S-H of variable C/S ratios is studied in this chapter. A complex behavior in the storage modulus and internal friction of C-S-H upon the removal of adsorbed and interlayer water is observed. The C-S-H in hydrated cement paste exhibits a similar response which can be readily explained by a layered model for the C-S-H with an assignment of a structural role to the interlayer water.
- Chapter 9. Time-dependent deformation of concrete is an important parameter in designing concrete structures. The stress relaxation of C-S-H is examined for various C/S ratio materials in comparison with the behavior of hydrated Portland cement paste and porous glass at several moisture contents. It is shown that interlayer water plays an important role in the viscoelastic nature of the C-S-H.
- Chapter 10. C-S-H/polyaniline nanocomposites are prepared using an *in situ* polymerization technique. The characterization of these systems supports the view that there is an intimate interaction of the polymer with the inorganic host. The results show the possibility of an enhancement in the physical and mechanical performance of the nanocomposite materials.
- Chapter 11. Preliminary investigations using XRD and DMTA are conducted on C-S-H/polyaniline nanocomposites. It appears that the aniline and polyaniline molecules can intercalate into the interlayer space of the C-S-H. The dynamic mechanical response of the nanocomposites shows improvement in the storage modulus.
- Chapter 12. The ability to control the nature of the hydration products in cement systems has always been a lofty goal. This chapter demonstrates that it is possible to tailor the nature of the C-S-H and modify its chemical composition through C-S-H seeding. Novel methods are used in order to show the dependence of the properties of the C-S-H produced in the hydration of C_3S on the C/S ratio of the C-S-H seed. This provides a unique opportunity to engineer the performance of

cement-based materials as their chemical and mechanical behavior largely depends on the C/S ratio of the C-S-H.

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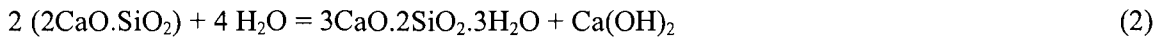
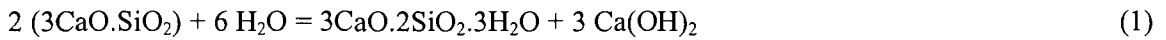
Calcium Silicate Hydrate

The literature in the area of C-S-H investigations is essentially very broad due to the central role of this hydrated phase in determining various chemical and mechanical properties of cement-based materials. An attempt has been made in this chapter to summarize some of the general research studies pertaining to the main objectives of the current thesis. A more specific literature review will be provided in the introduction section of the next chapters relevant to each individual topic.

2.1 C-S-H formation

Portland cement contains four main compounds: silicate phases; C_3S and $\beta\text{-}C_2S$, and aluminate phases; C_3A and C_4AF . In cement chemistry, mineralogical notation e.g. C, S, A, F and H is often used for the chemical formulas of CaO, SiO_2 , Al_2O_3 , Fe_2O_3 and H_2O , respectively. The chemical reaction between the calcium silicate phases of Portland cement and water results in the formation of two important components; crystalline calcium hydroxide and a nearly amorphous calcium silicate hydrate referred to as C-S-H [1]. The hyphens indicate that the stoichiometry is variable.

The hydration of C_3S and $\beta\text{-}C_2S$ clinker phases, assuming that the reactions are completed, can be approximated by the following equations [2], respectively:



The chemical formulas for the C-S-H product in these equations are approximate as the CaO/ SiO_2 ratio of the C-S-H varies within the same paste. Moreover, the molar proportion of H_2O in C-S-H can not be easily determined due to the lack of a comprehensive definition for the state of water in C-S-H. An electron micrograph of the products formed in hydrated Portland cement is shown in Figure 2-1. C-S-H forms up to about 60% of the hydration products in hardened cement paste and is primarily responsible for some of its principal properties such as strength, shrinkage, and for its durability.

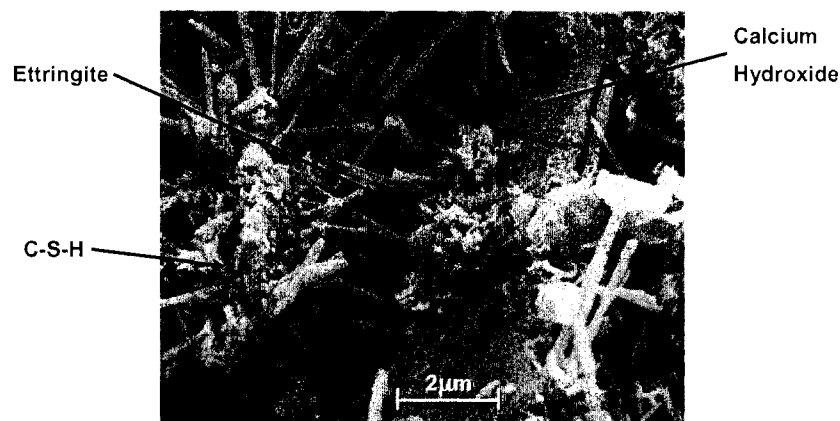


Figure 2-1. An electron microscope image of Portland cement hydration products (Courtesy of Mr. Jim Margeson, NRC-IRC).

A significant amount of the hydration products are produced within the first few days after mixing for a typical water/cement ratio of 0.3-0.6. The precipitation of the C-S-H on the surface of the anhydrous calcium silicates decreases the rate of reactions as the hydration process is then controlled by the diffusion of ions through the C-S-H layer [2]. The change in the chemistry of aqueous solution and the available reaction volume as the hydration proceeds leads to the formation of C-S-H phases of variable stoichiometry and physical characteristics. The ill-defined and variable crystalline nature of C-S-H in cement binders and incorporation of other elements such as aluminum into its structure are some of the barriers in the physical and chemical characterization of C-S-H. These have often been the main causes of the discrepancies in the research results and a major source of discussion.

2.2 Characteristics of C-S-H

C-S-H systems can be studied from various aspects as a *material*. The scope of the literature in this field is broad. The following sections provide a brief review of some of the research work relevant to the current project.

2.2.1 C/S ratio

An important stoichiometric parameter that defines a C-S-H phase is the molar ratio of CaO to SiO₂ in its structure (C/S ratio). It is possible to calculate the C/S ratio of the C-S-H produced in the hydration of calcium silicates by determining the content of calcium hydroxide [3] and unreacted materials using analytical methods such as thermo-gravimetric analysis or quantitative X-ray diffraction. The C/S ratio in calcium silicate hydrates usually covers a range from 0.7 to 2.0 with an average value of 1.75 for that in hydrated Portland cement [4].

Taylor categorized C-S-H systems into C-S-H (I) and C-S-H (II), respectively, for C/S ratios below and above the dividing value of 1.5 [1, 5, 6]. However, not many researchers were able to produce the C-S-H (II). It was shown that a C/S ratio of 1.5 is generally a maximum value in the hydrate unless extreme reaction conditions are applied [7]. Other studies distinguished various differences for the phase transition that occurs at the C/S ratio of 1.0 within the composition range of C-S-H (I) [8-12]. Nonat suggested a categorization of C-S-H systems into three types: C-S-H(α) for $C/S < 1.0$, C-S-H(β) for $1 < C/S < 1.5$ and C-S-H(γ) for $C/S > 1.5$ [13, 14]. The most significant changes that occur in the structure of C-S-H with decreasing the C/S ratio are an increase in the mean length of the silicate chains and the distance between the layers of C-S-H.

The BET surface area of the C-S-H increases noticeably when the C/S ratio is decreased below 1.0. These characteristics have been shown to affect the physico-chemical behavior of C-S-H [1, 2].

The mean C/S ratio of C-S-H varies with age and degree of hydration in hardened C_3S paste. It appears that a C-S-H product having high C/S ratio of about 3.0 forms immediately in the hydration reaction of silicate phases. The C/S ratio of this C-S-H phase decreases at later times [2]. By means of TEM analysis [15], the C/S ratio of 1 month, 3 month, 3.5 year and 26 year old C_3S paste was determined to be 1.71 ± 0.05 , 1.77 ± 0.20 , 1.74 ± 0.13 and 1.75 ± 0.05 , respectively. Although the C/S ratio does not seem to be significantly influenced by the hydration time after a few months, there are indications that the C-S-H experiences an “aging” process modifying the silicate polymerization and layering of the C-S-H sheets [1].

2.2.2 State of water in C-S-H

A minimum amount of water is required for the hydration reaction of Portland cement to go to completion and provide a reasonable workability of concrete. Excess mixing water leads to a high porosity cement paste microstructure. Subsequently, moist conditions after the setting of the cement paste are required for the hardening of the hydrated cement and controlling issues such as shrinkage. The presence of water in the pore structure also facilitates the ionic movement and transport of aggressive chemicals into the concrete. Water and concrete truly form a combination of ‘love’ and ‘hate’ [16]. The role of water in hydrated cement paste is very complex and has been always controversial. Water, as a part of the microstructure of cement paste, plays an important role in controlling some of the major characteristics such as shrinkage and mechanical properties [17].

The classification of the state of water in cement paste is generally based on the location where it is held and, the nature of its bonding with the solid structure. The latter is a function of energy required to remove that water [18]. Although several investigations have attempted to separate various forms of water in the cement paste and even in the more crystalline forms of C-S-H systems, the dividing line for the states of water is not very clear [19, 20].

Apart from the water vapor in the pores, it is suggested that water can exist in various forms e.g. capillary water (in voids larger than 5 nm), adsorbed water (held by hydrogen bonds on the surface of the hydrated particles) and interlayer water [21]. The debate about the latter i.e. water

that is associated with the nanostructure of C-S-H and is strongly held, still continues [22-24]. Implications of the state of water in the structural models for C-S-H will be discussed in section 2.4. Various techniques such as DMA and NMR have been used to differentiate the role of water in various structural locations. The dynamic mechanical response of the hydrated Portland cement in the temperature range of -140 to $+25$ °C revealed two transitions that were attributed to the water adsorbed on the internal surface of the microporous substance and capillary condensed water [25]. The study of the state of water using NMR primarily requires the application of transient techniques. Application of this method on the protons can provide information on their mobility or the state of binding [26]. The tightly bound proton in the structure is relaxed faster than free protons in the liquid as manifested by the spin-spin relaxation time (T_2). This time is of several ms for loosely bound water, $\sim 100\mu\text{s}$ for tightly bound water and about $10\mu\text{s}$ for protons in the crystalline structure [27].

It has been suggested that the C-S-H lamellae are held together by an electrostatic force [28]. In this configuration, the interlamellar space is filled with quasi-immobile water molecules and calcium ions that are bonded to the C-S-H layer by partially covalent bonds.

2.2.3 Silicate polymerization

As it will be discussed in section 2.3, the C-S-H is composed of stacking of Ca-O layers reinforced by defect silicate chains. Water molecules and calcium ions are present between the layers. The silicate tetrahedra that are flanked on both sides of the Ca-O layer, can be present in the form of dimers, dreierketten or a chain of dreierketten. Polymerization of silicates is defined by the mean length of these chains and is usually determined from the spectroscopic data obtained from a ^{29}Si MAS NMR experiment. Polymerization of C-S-H is dependent on its compositional C/S ratio. The mean silicate chain length (number of silicate tetrahedra in a chain) is normally calculated from the Q^2/Q^1 integral intensity ratio*:

$$\text{Mean Chain Length} = 2(1+Q^2/Q^1) \quad (3)$$

The chain length increases significantly from 2.6 to 9.2 as the C/S ratio decreases from about 1.44 to 0.92 in synthetic C-S-H materials (prepared through double precipitation method) [29]. Taylor calculated the C/S ratio corresponding to a specific silicate chain length in jennite and 1.4nm

* Q^1 and Q^2 are related to the population of end-chain and middle-chain silicate tetrahedra, respectively. This will be further explained in chapter 3 at the ^{29}Si NMR section.

tobermorite minerals as shown in Figure 2-2 [30]. This calculation was later generalized taking into account the amount of hydroxyl water [15].

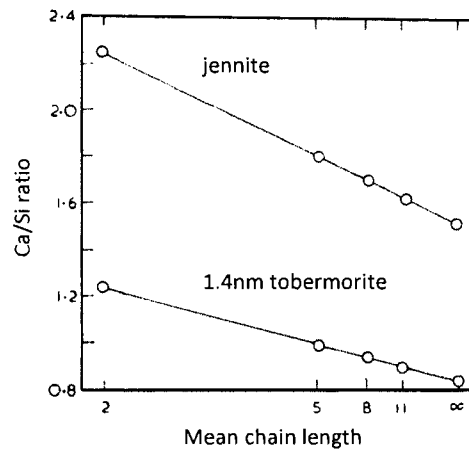


Figure 2-2. Calculated Ca/Si ratio of jennite and 1.4nm tobermorite structures modified by the omission of bridging tetrahedra plotted against chain length values (from [30]).

Incorporation of supplementary cementitious materials in hydrated cement paste results in the formation of *secondary* C-S-H, which has a relatively lower C/S ratio of about 1.0 [1, 31]. It has been shown that this type of C-S-H is more polymerized and thus has different characteristics [32]. This may also account for some of the enhanced durability aspects of the concrete using pozzolanic materials.

Polymerization of silicates is also affected by the curing conditions such as humidity level and temperature. The C-S-H in moist cured cement paste samples virtually contains all dimers, whereas pastes cured at the low relative humidity conditions (below 10% RH) have a greater degree of polymerization [33]. This effect is not that pronounced in aged samples. C-S-H samples prepared hydrothermally at temperatures above 120 °C are highly polymerized at all C/S ratios ranging from 0.3 to 2.0 [34]. The degree of hydration also affects the mean silicate chain length in addition to the volume fraction of the C-S-H produced [15]. A 10%-hydrated sample (C₃S paste) has a mean silicate chain length of about 2. This value increases linearly to about 2.5 at 85% and 5 at 100% hydration.

Young studied the hydration of C_3S at various temperatures using ^{29}Si NMR [35]. Samples were dried at 105 °C before the tests. The results indicated an increase occurs in the degree of polymerization due to the high temperature curing conditions (65 °C compared to 25 °C). Silica fume addition also resulted in an increase of the Q^2/Q^1 ratio. He did not suggest the presence of any cross-linking as no Q^3 was observed.

Yu and Kirkpatrick studied the effect of elevated temperatures up to 1000 °C on synthetic low C/S ratio C-S-H [36]. XRD results provided evidence for the formation of meta-stable and stable phases with lower basal spacing. Q^3 and even Q^4 chemical shifts were observed in various samples after heat treatment at 250 °C. It was concluded that cross-linking occurred due to the charge balance requirement after the removal of H from Si-OH groups. It was suggested that these linkages between the layers restrict the dynamic behavior of interlayer water that is entrapped in “cages” after heat treatment.

The crystallization of tobermorite from the C-S-H precursor was studied by Sato and Grutzeck [37]. C-S-H was prepared in digestion bombs at 130 °C and 180 °C. The charge was removed at various times and dried at 80 °C for 24h before conducting low-angle XRD, ^{29}Si NMR and ^{29}Si CP NMR tests. C-S-H forms after two hours followed by the appearance of the XRD peak at low angles ($\sim 7^\circ$, 2θ) after 4 hours. They identified higher field Q^3 peaks in some samples (prepared from quartz) which were attributed to the bridging tetrahedra connected between the layers by hydrogen bonds. An interesting observation was that the C-S-H samples prepared from the quartz or amorphous silica even with the same C/S ratio were different in the polymerization degree. The sample made from quartz was less polymerized and it was suggested that the initial C/S ratio of the C-S-H that was formed on the surface of quartz particles was high. They concluded that the C-S-H, C/S ratio > 1 , can be crystallized into tobermorite, while the silica rich samples did not appear to have this potential.

In their study, Wieker et al., applied ^{29}Si NMR to study the structure of various tobermorites [38]. Most of the samples were prepared at high temperatures and by the dehydration of other forms of tobermorite. Their results, indicated a high degree of polymerization with the presence of Q^3 sites even at the C/S ratio of 1.0. The decrease in the Q^1 (end groups) intensity contributed to the condensation of the single chains upon dehydration. It was also observed that the low C/S ratio sample maintains the initial basal spacing on drying possibly due to the cross-linked sites

preventing the collapse of the layers (anomalous behavior). The importance of the preparation method in the properties of tobermorite was emphasized and it was suggested that the thermal dehydration causes lengthening of the silicate chains.

2.3 Relation of C-S-H with more ordered phases

There are more than 45 known calcium (alumino) silicate hydrates of interest to cement chemists [39]. It was in the early 1950's when it became apparent that the short-range order structure of C-S-H can be related to the structure of crystalline compounds with a silicate-chain repeat distance of 0.73 nm in one direction [40]. An important advancement occurred when the crystal structure of Maddrell's salt (isostructural with β -wollastonite) was determined [41]. It was found that β -wollastonite contains infinite chains of SiO_3^{2-} repeating at the intervals of three tetrahedra termed dreierketten. The Ca-O polyhedra repeats at a distance of 0.365 nm (half of that of the silicate chain) considering the type of the silicate dreierkette's linkage to the Ca-O layer. Water molecules and calcium ions occupy the space between these layers. Among various calcium silicates, tobermorite and jennite appear to provide more structural clues about the C-S-H gel in hydrated Portland cement. Both of these minerals have a layered structure and can be synthesized. Jennite is a rare mineral and it is relatively more difficult to prepare it synthetically [42], but various forms of the tobermorite are available and can be easily produced; 0.93, 1.1 and 1.4 nm tobermorite (the prefix denotes the distance between the layers (d_{002} basal spacing) [42].

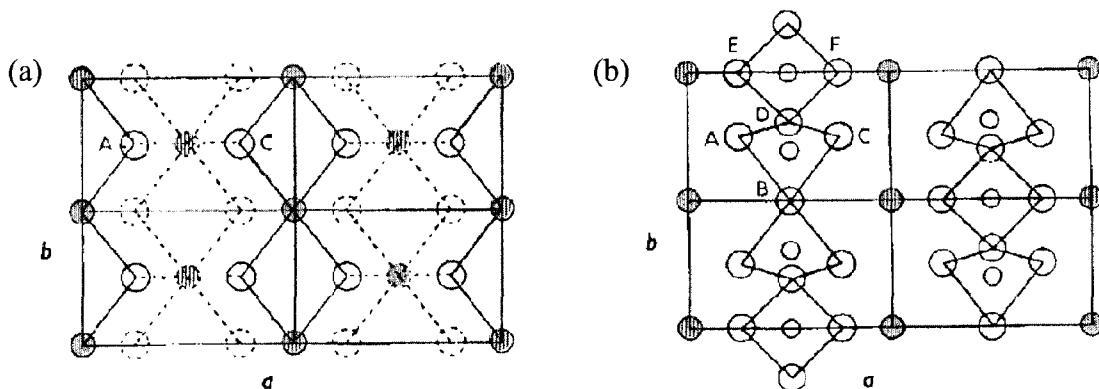


Figure 2-3. (a) Tobermorite: two central layers projected on (001)-idealized. (b) Tobermorite: upper half of layer projected on (001)-idealized (from [44]). Small circles Si, intermediate circles Ca (shaded), large circles O. Atoms and bonds shown dotted lie below middle of layer.

The structure of tobermorite (from Northern Ireland) was first described by Megaw and Kelsey (Figure 2-3) [44]. They showed that this substance was closely related to the C-S-H (I) [1]. Although their work did not clarify to what extent the hydrogen atoms in the interlayer region are

from OH groups or H₂O, they verified that its removal results in the decrease of the 002 basal spacing and allows two adjacent layers to pack together.

The crystal structure of 1.1 nm tobermorite was resolved by Hamid [45]. More recently the crystal structure of 1.4 nm tobermorite has also been resolved [46]. A tobermorite layer is formed from a sheet of calcium oxide flanked on both sides by silicate tetrahedra (schematically shown in Figure 2-4).

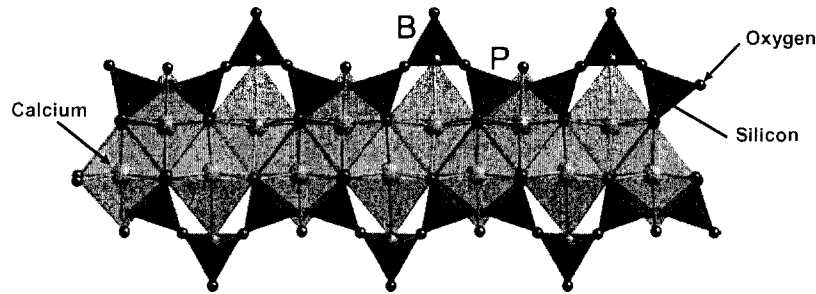


Figure 2-4. A schematic of a tobermorite layer showing a main Ca-O layer with silicate tetrahedra attached on both sides. The directly connected silicate tetrahedron is called paired (P) and the silicate tetrahedron connecting two paired tetrahedra is called a bridging tetrahedron (B) (from [39]).

The C-S-H in hydrated Portland cement is considered akin to tobermorite although it is lacking some of the bridging tetrahedra. The C-S-H in cement paste is therefore referred to as a defect tobermorite structure [47]. A stacking of these layers with mainly water molecules and calcium ions in between forms a typical C-S-H agglomerate.

2.4 Models

Any model for the C-S-H systems should be able to account for the experimentally observed physical and chemical characteristics of this material at variable stoichiometries and environmental conditions. The proposed models in the literature can be differentiated in two categories. Models that are concerned with the structural implications and those that mainly deal with the composition of the C-S-H. The structure-based models were introduced earlier in the cement research and are generally based on the surface area and adsorption-desorption data [22]. Composition-based models were developed later and advanced through the improvement and invention of experimental methods such as nuclear magnetic resonance spectroscopy. Some of the features of the most important models are discussed in this part.

2.4.1 Structure-based models

The first model for the nearly amorphous structure of hardened Portland cement paste was developed by Powers and Brownyard and is known as P-B model [48]. Their classic set of experiments in the 1940's, primarily based on mass change measurements at varying humidity and temperature, was aimed at clarifying the role of water within the structure of the cement paste. In the P-B model, water can be present in two forms; evaporable (that is water lost under D-drying conditions over the vapour pressure of dry ice at $-79\text{ }^{\circ}\text{C}$) and non-evaporable (the remaining water that can be removed by heating up to $1000\text{ }^{\circ}\text{C}$). The evaporable water was also categorized as 'gel water' (about four monolayers of water on the surface of the gels) and 'capillary water'.

The P-B model was almost generally accepted among cement researchers until Feldman and Sereda presented their model in 1968 [49] and was further explained in 1970 in a comparison with previous models [50]. Their proposed model was based on surface area and porosity measurements using nitrogen gas, and isotherms for mass, length and modulus of elasticity change at various humidity levels. The role of water in hydrated Portland cement was explained in more detail. Their evidence led to the concept of a layered model for C-S-H gel and a structural role was assigned to the water in the interlayer region.

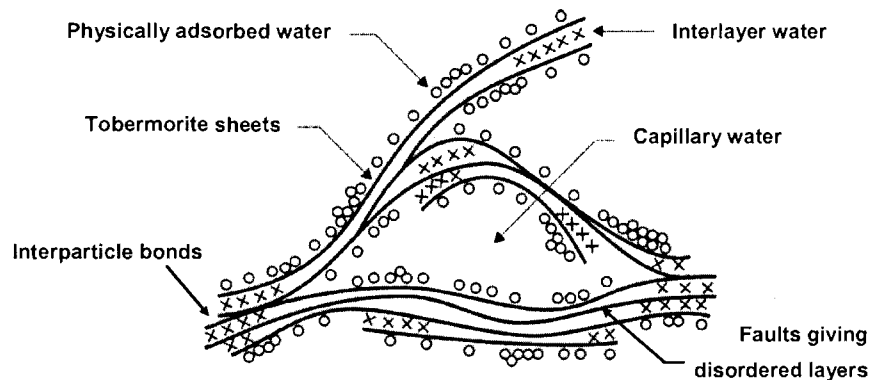


Figure 2-5. Simplified model for the hydrated Portland cement proposed by Feldman and Sereda.

The interlayer water exhibited irreversible behavior during the adsorption and desorption process. The schematic presentation of the C-S-H in the F-S model (Figure 2-5) is still used as an iconic image in the cement and concrete science text books [18]. Feldman's later work on the diffusion of helium into the C-S-H gel at various humidity conditions provided additional evidence for the layered nature of the C-S-H gel [51].

These two initial models have had their own followers. This has been the source of major long-standing debates in the cement research community. Brunauer who was involved in the development of the famous BET theory [52], was critical of the F-S model [53]. He suggested that it is possible to correctly measure the surface area and porosity of D-dried pastes by water vapor adsorption, and argued that only part of the porosity can be measured with nitrogen gas. Feldman and Sereda pointed out the shortcomings of this argument and other aspects of the P-B model. The main concerns were regarding the nature of bonding between solid particles, the mechanism of water penetration between the particles and incapability of the P-B model in explaining the irreversibility and hysteresis effects in the length and mass-change isotherms. The P-B model could not explain the experimental observations of the change in mechanical properties versus relative humidity [50, 54, 55]. The F-S model was further modified by Daimon *et al.* through the analysis of nitrogen and water vapor adsorption isotherms [56]. They added features such as inter-crystallite pores that are accessible by *narrow entrances*. They also referred to the interlayer space as intra-crystallite pore space.

The nanostructural models for the C-S-H in hydrated Portland cement are still being developed and discussed. Jennings and co-workers have conducted extensive work on various properties of C-S-H gel such as density and porosity measurements as well as mass-change isotherms, based on which structural models were proposed for the C-S-H [23, 57, 29, 58]. The main feature of their model, as shown in Figure 2-6, is that the C-S-H is made of globules of about 5nm in diameter. This does not seem plausible considering the AFM imaging results that show C-S-H particles of $5 \times 30 \times 60 \text{ nm}^3$ in size [59]. Moreover, the 5nm globule model cannot explain the fiber- or foil-like growth mechanism of C-S-H [60] as evidenced by TEM and soft X-ray imaging studies [61-63].

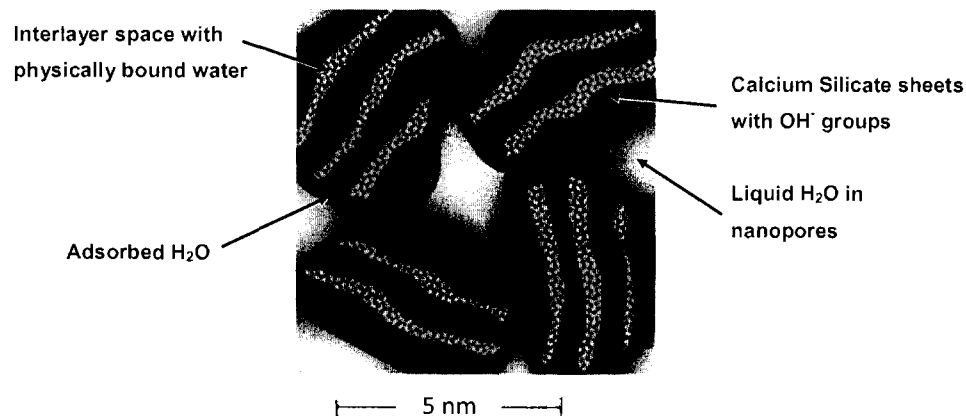


Figure 2-6. A schematic presentation of the nanoscale C-S-H phase (from [58]).

They suggested that the density of C-S-H is 2.604 g/cm^3 and its chemical formula is $(\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_{1.8}$. These results were obtained using small-angle neutron and X-ray scattering data with the assumption that the water (H_2O) in the C-S-H can be fully exchanged with heavy water (D_2O) after 24 hours of immersion. The main features of Jennings' CM-II model in 2008 [23], are noticeably different from his previous works. They are similar to the F-S model although some subtle differences still remain on the role of water in C-S-H. It is not clear from the Jennings' model if the interlayer water is a mono-layer or can be composed of several molecular layers of water. Moreover, their postulation that nanoscale spaces in the interlayer region (referred to as IGP) exist seems dubious (based on helium inflow interpretations [24]). It is suggested that IGP and the small gel pores (SGP) that form between the packed C-S-H globules are not that different in nature. The latter is a feature in the models of Feldman and Sereda, and Daimon *et al.*

2.4.2 Composition-based models

Many other researchers (mainly chemists and physicists) tried to elucidate the molecular structure of C-S-H. They looked at the silicate anions, their arrangement and other molecular bonds e.g. bonds with OH groups in the C-S-H structure. These works were generally conducted using diffraction, microscopic and spectroscopic methods and rarely were concerned with mechanical properties. Improvements in the techniques and experimental tools helped researchers to reveal more details of the nanostructure of C-S-H during the recent years.

Bernal *et al.* proposed the first dreierkette-based model for C-S-H [64]. By means of crystallographic investigation, they suggested that the hydration product of C_3S is similar to the C-S-H formed in dilute suspension, i.e. a layered fibrous structure associated with 1.1nm tobermorite. The suggestion by Taylor and Howison [65] that the generally accepted C/S ratio of about 0.8 for tobermorite can be increased by omitting the bridging tetrahedra (replaced by calcium atoms) is one of the features in many other tobermorite-based models for C-S-H [11, 29, 66-72]. In order to explain the verity of compositions, it was suggested that the C-S-H layers are separated by the so-called interlayer region, in which H_2O , Ca^{2+} and OH^- can be present. A few other studies proposed that the C-S-H has a structure related to that of jennite [73-75]. In jennite, half of the oxygen atoms from the central Ca-O part of the C-S-H layer are shared with OH^- groups, whereas in tobermorite all the oxygen atoms are shared with the infinite parallel rows of silicate chains.

Taylor proposed that C-S-H in cement paste is evidently a disordered layer structure and is a mixture of structures based on both 1.4nm tobermorite and jennite [30]. This was theoretically one of the possible ways to explain the high C/S ratio of C-S-H in cement paste (1.7 to 2.0) as dimeric 1.4nm tobermorite and jennite type structures could have a C/S ratio of about 1.25 and 2.25 at early ages, respectively. Moreover, the water to calcium ratio of the C-S-H at 11%RH lies between that of the suggested structural representatives. Richardson and Groves further explained the generalized model incorporating the features of the tobermorite-jennite composition or the tobermorite-‘solid solution’[15]. It was predicted that the very old C-S-H entirely consists of jennite-like units and that the carbonation can change them to tobermorite-like units. They further discussed this model in a reply [76] to the discussion of their work by Taylor [77]. The distinction between main layer and interlayer Ca^{2+} and the consideration of water content of C-S-H at various drying conditions were considered lacking by Taylor.

The work of Cong and Kirkpatrick shed more light on the nanostructural aspects of C-S-H [47, 70, 78]. They prepared various C-S-H phases by hydrating $\beta\text{-C}_2\text{S}$, as well as that produced in the reaction of silica fume and calcium oxide in aqueous solution. The ^{29}Si and ^{17}O MAS NMR spectroscopy studies were conducted on C-S-H (C/S= 0.6 to 1.54). The results confirmed the presence of Ca-OH and Si-OH bonds in the C-S-H, the abundance of which depends on the C/S ratio. They proposed a 1.4nm defect tobermorite structure for C-S-H, as shown in Figure 2-7, where some of the bridging tetrahedra are missing, the chains are short and they may tilt, rotate or be displaced along the b-axis. This gives a disordered structure and is responsible for the diverse C-S-H stoichiometries.

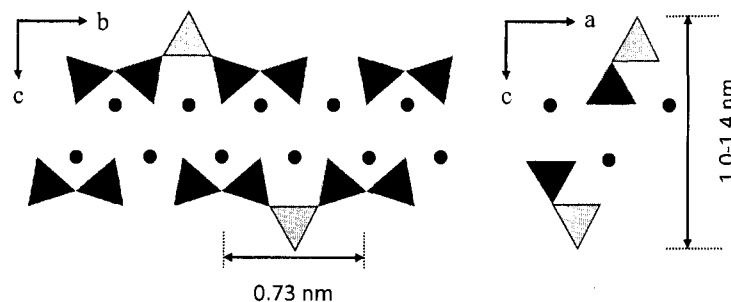


Figure 2-7. The schematic molecular structure of a single sheet of the defect tobermorite. Circles: calcium atoms located at the center of Ca-O octahedra (not shown); Triangles are silicates- light gray: bridging tetrahedra, dark gray: paired tetrahedra; OH^- attachments are not shown. (modified from [47])

2.5 Preparation of C-S-H

2.5.1 C-S-H from cement compounds

The C-S-H formed in the Portland cement hydration incorporates various elements and has a variable stoichiometry and nearly amorphous structure. Therefore, the main research in such C-S-H systems has been focused on the product of the hydration of pure C_3S or β - C_2S . The reaction product can be chemically treated to remove the $Ca(OH)_2$ and achieve almost pure C-S-H [29]. This type of C-S-H usually has an average C/S ratio of about 1.7. In some cases it is required to study the properties of low C/S ratio C-S-H systems, for which the initial preparation of C-S-H from hydrated C_3S can be decalcified. This is obtained through leaching the calcium out of C-S-H by immersing it in either distilled water or ammonium nitrate [79, 80]. The latter is more favorable as it leads to a minor loss of silicon from the structure and thus results in a nearly pure decalcification.

2.5.2 Synthetic C-S-H

C-S-H can be readily made from mixing lime and silica in an excess of water (pozzolanic reaction). The properties of such systems made at various temperatures and different C/S ratios have been intensively studied. The first of these contributions was made by Taylor [5, 81-84]. Hydrothermal conditions are often used in order to promote crystallization of the C-S-H. Curing temperatures of about 60 °C may be experienced in the formation of C-S-H systems.

Another commonly employed method for C-S-H synthesis is the double precipitation of calcium salts (most commonly $Ca(NO_3)_2$) with a soluble silicate (eg. $Na_2SiO_3 \cdot 5H_2O$). The C-S-H precipitate is washed with the lime solution. Mixing calcium hydroxide and hydrous silica in aqueous suspension can also be used to produce C-S-H [6]. In these methods, after the formation of the C-S-H the final material is filtered and washed and stored under nitrogen gas. The crystallinity of synthetic C-S-H depends on the reaction time and temperature. Pozzolanic reaction results in the formation of more crystalline C-S-H, but it is slower than the double precipitation method [85].

2.6 Mechanical properties of C-S-H

Characterization of properties such as modulus of elasticity, creep and strength has been rarely conducted systematically on synthetic or phase pure C-S-H. The hydration of calcium silicate phases of Portland cement at w/c ratios of 0.40 to 0.80 leads to the formation of a microporous material containing C-S-H and calcium hydroxide. The porosity, obviously, plays an important role in determining the mechanical properties of specimens prepared through such traditional procedures. This makes it difficult to investigate a relationship between the chemical composition of C-S-H and its mechanical characteristics.

The dependence of the mechanical properties of C-S-H with the C/S ratio has received only limited study. It was shown that the intrinsic modulus of elasticity (E_0) appears to be dependent on the C/S ratio and degree of polymerization [86]. Nanoindentation results suggested that two types of C-S-H exist in hydrated Portland cement [87]; low density and high density having a mean stiffness of about 22 and 29 GPa, respectively [88]. It was also concluded that the intrinsic elasticity of the C-S-H phase can be reduced through decalcification. This was confirmed in another study where it was shown that the elastic modulus increases at higher Ca^{2+} contents [59] with an inflection point at the concentration of about 8 mmol/L (corresponding to a C/S ratio of 1.1 [89]) suggesting a phase transition.

It is also possible to estimate the elastic properties of C-S-H through dynamic molecular modeling and free energy minimization techniques [90]. These methods were primarily used in order to evaluate the stability of the structural models of Hamid [45] and Merlino [91] for tobermorite systems. The simulated values suggest that the average Young modulus can increase from 63.5 to 89 GPa with the increase in C/S ratio from 0.83 to 1.0. The interlayer distance was found to be very important in these mechanical changes. The source of the cohesion forces in C-S-H is one of the main questions to be answered in the investigation of the mechanical properties of hydrated cement systems. Although van der Waals and capillary forces partially contribute to the cohesion of such materials [92], the major factor that keeps the layers stable appears to come from the ionic-covalent properties of chemical bonds in the interlayer. In this situation, calcium ions and water molecules are strongly localized [90].

2.7 Modified C-S-H systems

Innovation of the advanced materials with superior characteristics that can improve durability of structures and address the sustainability issues has always been of interest to the construction industry. Composite materials (one of the categories of advanced materials) benefit from the advantages each component offers. They can be engineered both at macro and micro levels. At the macro level for example fibers of centimeter range are used in concrete to improve the ductility of concrete beams and columns [93]. Significant fundamental changes, however, are not possible in the properties and behavior of cement and concrete unless the characteristics of the material are altered at the micro and nano level [94]. Carbon nanotubes, for example, have been shown to form strong bonds with cement paste and can result in micro-crack bridging [95]. In addition the nanotubes may act as nucleating agents for C-S-H formation. Here, the work on layered silicate based polymer nanocomposites, a relatively new and promising field in cement science, is reviewed.

2.7.1 Polymer/layered silicate nanocomposites

The field of clay-based polymer nanocomposite materials gained significant interest after the report of a group at Toyota on the formation of Nylon-6/Montmorillonite in 1990 [96] although the chemistry of these complexes was previously known [97]. Since then, these new range of composites have been extensively developed and characterized [98, 99, 100]. In this field, the objective has been to improve the properties of *polymers* such as modulus of elasticity, strength, heat resistance and gas impermeability. A layered silicate structure is generally used for this purpose. Montmorillonite (an aluminate silicate hydrate in which some Al atoms are replaced with Mg or Fe) is the most popular choice and often is modified organically in order to increase its interaction with polymer.

Usually, three forms of the polymer/layered silicate composites can be thermodynamically achieved [101] (Figure 2-8) :

- a. *Conventional microcomposite*: a stack of the layers of clay is mixed with the polymer matrix and the two phases are separated.
- b. *Intercalated nanocomposite*: the polymer is inserted in the interlayer region without destroying the layered crystal structure of the silicate. This type can become a flocculated nanocomposite when the hydroxylated edge-edge interaction of silicate layers occurs.

- c. *Exfoliated nanocomposite*: the individual silicate layers are separated in the polymer matrix. The average distance between the layers depends on the amount of polymer.

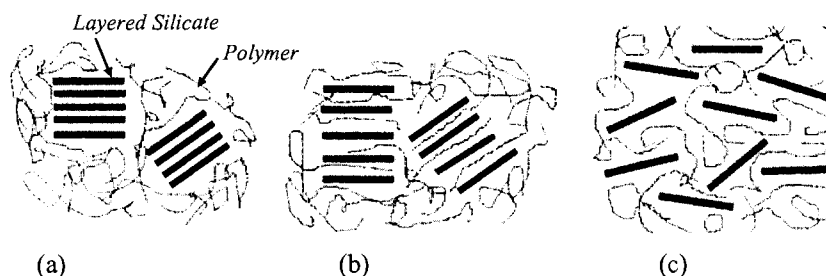


Figure 2-8. Possible composite materials through the interaction of polymer and layered silicate: (a) conventional composite, (b) intercalated nanocomposite and (c) exfoliated nanocomposite.

Several methods are available for preparing polymer/layered host nanohybrids depending on the starting materials and processing technique [102]:

- a. *Intercalation of polymer from the solution*: The layered silicate is initially swollen in the solvent. The polymer is then mixed in the solution. The exchange of interlayer solvent with the polymer results in the formation of the intercalated structure.
- b. *In situ intercalative polymerization*: Similar to the previous method, monomers are first intercalated into the galleries of the layered silicate. Polymerization is then initiated either by heat, radiation or initiator.
- c. *Melt intercalation*: The layered silicate is mixed with the molten polymer. If the materials are compatible, the polymer can crawl into the interlayer of silicate structure and form intercalated or exfoliated nanocomposites.

The type of the nanocomposite and the extent of interaction can be studied through various techniques. XRD, NMR and FTIR are among the most practically applied methods. In the intercalated specimens, there is usually an increase in the space between the layers (basal spacing) that can be detected by XRD often manifested by a low angle peak (at about 4 to 8 degrees 2θ). The absence of this peak is an indication of the exfoliated structure.

The possible chemical bonds that can be formed between the polymer and the silicate structure are investigated through NMR and FTIR. The ^{13}C , ^{29}Si and ^1H atoms have been of interest in

NMR studies of layered silicate-polymer composites [103]. The nanoscale changes in the local environment around these atoms can be detected and followed using NMR. FTIR also provides more insight about the type of chemical bonds.

2.7.2 C-S-H/polymer nanocomposites

As mentioned before, C-S-H is the principal phase in the hydration products of Portland cement. It is the primary contributor to the important properties such as strength and shrinkage. Enhancing the nanostructure of C-S-H is essential to improving its strength and durability performance. Interaction of polymers with C-S-H can be considered as one of the possibilities. In this regard, it is intended to improve the properties of C-S-H by interaction with a small amount of polymer and yet maintain the cementitious network and the functionality of the calcium silicate hydrate systems.

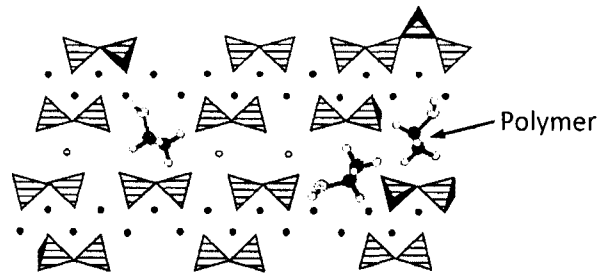


Figure 2-9. Schematic of the C-S-H/PVA nanocomposites illustrating the possible interaction of polymer molecule at defect locations. triangles: silicate tetrahedra, filled circles: calcium atoms in the Ca-O backbone, empty circles: interlayer calcium ions.

Polymer modified nano-hybrids are relatively new in cement science. The first intercalated C-S-H systems were reported by Matsuyama and Young in 1999 [104-106]. They used a range of anionic, cationic and neutral polymers such as poly(methacrylic acid), poly (4-vinyl benzyl trimethylammonium chloride) and poly (vinyl alcohol). It was claimed that the polymers intercalated into the interlayer region of C-S-H (as shown in the schematic in Figure 2-9) the extent of which depended on the C/S ratio. In some cases, an increase of about 1.5 nm (~100%) in the interlayer spacing was achieved (e.g. 1.1 g of PMA polymer/g of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ salt. C-S-H made from the double precipitation of this calcium salt and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ with C/S=1.3). It should be noted that C-S-H does not have as high a swelling capacity as that in clays (e.g. montmorillonite) where several layers of water molecules can be accommodated between the layers [107].

There have been differences of opinion over the possibility of achieving an intercalated C-S-H structure. In two separate works, Popova et al. [108] and Merlin et al. [109] examined the intercalative formation of C-S-H/polymer nanocomposites using various types of polymers. Their results showed no or negligible change occurred in the interlamellar spacing as evidenced by XRD results. ^{29}Si NMR also did not show any change in the silicate polymerization unlike a recent work that reports the increase of silicate polymerization in several types of organically-modified C-S-H systems [110]. This disagreement was attributed to the dependence of intercalation on the fabrication procedure and it was highlighted that these kinds of intercalative reactions are not facile. It was, therefore, suggested that a mesocomposite is formed in which the polymer interacts with the stacking of C-S-H lamellae and is adsorbed on the surface in the spaces between C-S-H “stacks” (Figure 2-10).

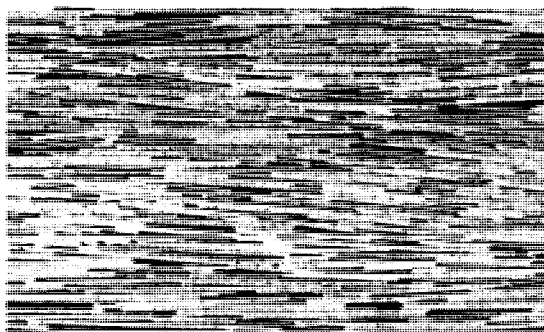


Figure 2-10. Schematic presentation of possible texture in disordered layered meso-composite material. Ill-defined regions where the separation of platelets by large distances or when they are not parallel forms major part of the voids in this model. Interlayer space is just a small fraction of the total porosity (from [108]).

In other research works, Mojumdar and Raki prepared and characterized C-S-H-poly(vinyl alcohol) and C-S-H-poly(acrylic acid) nanocomposites [111-113]. They employed the precipitation method through adding calcium nitrate to the solution of sodium silicate in which the polymer was pre-dissolved. Interpretation of their results (mainly based on an increase of about 0.2nm in the interlayer spacing as well as broadening of this peak in XRD) suggested that intermediate organizations have been developed including both intercalated and exfoliated nanocomposite materials.

A new type of covalent bonded polymer-C-S-H nanocomposite has been successfully developed in recent years [114-115]. Organic groups were covalently attached to the inorganic part of C-S-H *via* Si-C bonds (Figure 2-11). In order to achieve this linkage, modified polymers were used

containing silane functions that could be incorporated in the silicate chain of the C-S-H. The basal spacing expectedly increases due to the occurrence of these attachments in the interlayer region and is linearly correlated with the length of the alkyl chains [116].

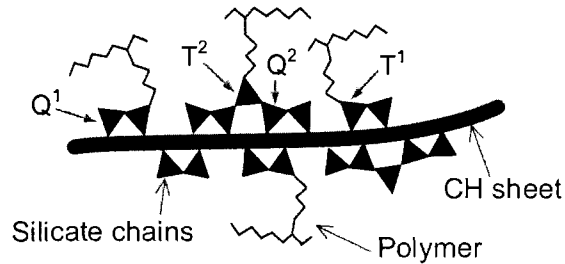


Figure 2-11. Microstructural model for the covalent bonded polymer- calcium silicate hydrate nanocomposite suggesting the linkage of organotriethoxysilane to the end chain (Q^1) and middle chain (Q^2) silicate sites. This created new silicate sites called T^1 and T^2 , respectively, detected in ^{29}Si CP-MAS NMR.

In all these works on nanohybrid hydrates, the main focus has been on the fabrication procedure and chemical characterization. None of the mechanical or durability properties of the C-S-H–Polymer nanocomposites have been reported, although a statement of the improvement in Young's modulus of elasticity (40-100%) was made with no reference [21]. If the development of this new class of materials is to be successfully applied in construction industry, it is first necessary to evaluate the physical and mechanical performance of nanohybrid C-S-H systems under load and investigate their durability in aggressive chemical environments.

2.8 Key questions

A significant amount of research has been devoted to the topic of C-S-H. Nevertheless, the nature and properties of this material have still not been completely understood. Pertinent to the current research, a summary of the important issues that have not been fully addressed yet follows:

1. Does the C-S-H that is produced in the hydration of Portland cement behave as a layered silicate?
2. What is the role of the interlayer water in the mechanical performance of C-S-H?
3. How is the stoichiometry and composition of C-S-H related to its physical and engineering characteristics?

4. Do C-S-H systems with variable stoichiometry have different durability behavior?
5. How closely is the nearly amorphous C-S-H in cement paste related to the crystalline and more-ordered phases such as C-S-H (I)?
6. Is it possible to control and modify the nature of the C-S-H binders in cement-based materials?

These questions are some of the concerns that are examined in this thesis. Details of the experimental work and the approach undertaken in order to reveal new details about the nanostructure and engineering properties of the basic and modified C-S-H systems are presented in the following chapters.

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Experimental

The experimental techniques in the investigation of the chemical, physical and mechanical properties of cement-based materials are now well established. In this chapter, some of the test methods used to study the nanostructure of C-S-H pertaining to the current research are briefly introduced. It is important to mention that often a combination of these techniques is employed in order to strengthen certain conclusions about the structure and behavior of materials since each individual technique is limited in some aspects. Detailed explanation of the experimental set-up and scientific method for each part of the current work are mentioned in the relevant chapters. The details of C-S-H synthesis, humidity conditioning, drying method and compaction technique are, however, described here as they are referred to in most chapters.

3.1 Experimental Tools

3.1.1 X-ray Diffraction

X-ray diffraction (XRD) is one of the most frequently used methods in cement chemistry [1]. It is generally used for the characterization of crystalline materials and the detection of various chemicals in a compound. The X-ray pattern of each material is a unique “fingerprint”. This technique is based on the analysis of the intensity and the angle of the diffracted X-ray beam after encountering a plane of atoms in a material.

In a crystalline material, various atoms are located in the structure in a repeating order. This can produce similar atomic planes as shown, for example, in Figure 3-1. The distance between these planes is called the d -spacing (or basal spacing). X-ray beams are diffracted partially when they hit various parallel layers. The diffracted beams can be detected easily if they are in phase. This occurs according to Bragg’s law:

$$n \lambda = 2 d \sin \theta \quad (1)$$

where λ is the wavelength of the X-ray (~ 0.15 nm for the Cu source), d is the distance between the atomic planes, θ is the angle of incidence and n is an integer.

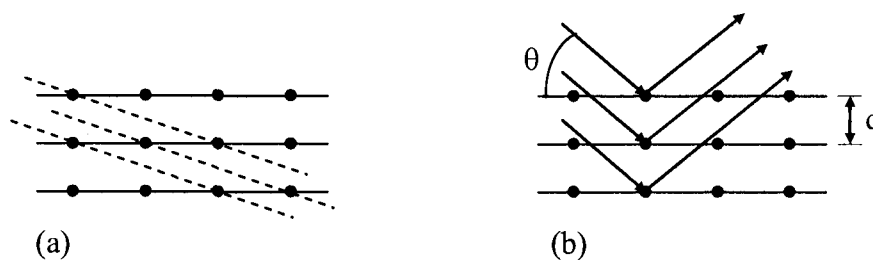


Figure 3-1. (a) Two possible atomic planes in a crystalline structure. (b) Diffraction of X-rays expressed by Bragg’s law.

In an XRD instrument that has the Bragg-Brentano geometry, the X-ray tube rotates around the sample so that the beams are emitted typically at angles from 2 to 30 degrees. Since the detector rotates at the same angle to receive the diffracted beams, only the diffraction from atomic planes parallel to the surface of the sample is detected. The intensity of the X-rays is plotted versus the 2θ (the angle between the emitted and diffracted beam).

This spectrum is then compared to known reflections in the database in order to identify the compounds in the sample. For example the XRD pattern of C-S-H (C/S=1.5) is shown in Figure 3-2 and compared to that from the ICDD database (data No. 34-0002). The peaks that are not matched at all are from the calcium hydroxide (data No. 04-0733).

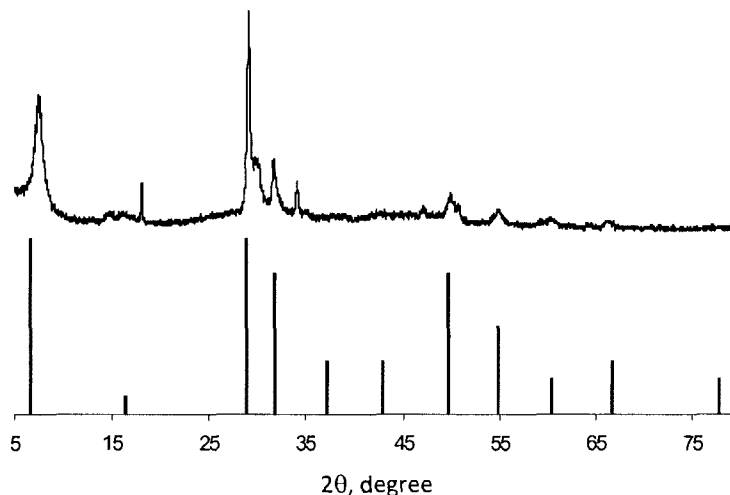


Figure 3-2. The X-ray diffraction pattern for C-S-H (C/S=1.5 on top) compared to the reference data for Calcium Silicate Hydrate (ICDD data No. 34-0002 on the bottom).

3.1.2 Thermal Methods

Most of the chemical materials are decomposed or may experience a phase transition upon heating to high temperatures. Water, for example, is evaporated at about 100 °C. Calcium hydroxide is decomposed to CaO and H₂O at about 400 °C. It is possible to measure the decrease in the mass during these transformations as well as the heat adsorbed (if the change is endothermic) or generated (when the change is exothermic). These measurements are called thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively [2]. Differential mass change measurements can be used to estimate the amount of each chemical compound. Various types of materials can also be identified based on the heat flow during the transitions. Only a few milligrams of a material is required for a simultaneous TGA-DSC test.

A typical TGA-DSC curve for the C-S-H (C/S=1.5) is shown in Figure 3-3. Analysis of the derivative mass change, for example, at the temperature range of about 400 °C shows that there is about 0.4% mass loss due to the decomposition of Ca(OH)₂ and evaporation of H₂O. Since the H₂O mass proportion in calcium hydroxide is 24%, it is calculated that 1.7% Ca(OH)₂ is present in the material. Similar calculations are possible for other components such as calcium carbonate

that decomposes at about 600 °C. Similar analyses using the DSC curve can also be conducted once it is calibrated.

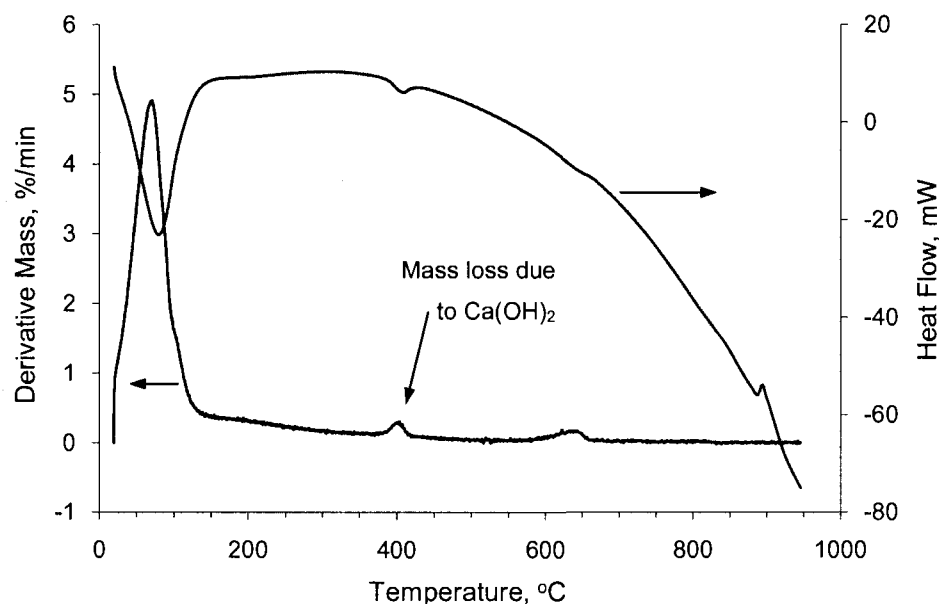


Figure 3-3. The TGA-DSC curves for C-S-H (C/S=1.5 heated from room temperature at 10 °C/min to 950 °C under nitrogen gas flow at 100 mL/min).

3.1.3 Nuclear Magnetic Resonance Spectroscopy

The concept of this technique was first discovered at 1902 [3, 4]. But, it was not until 1952 when the practical experimental technique was developed. NMR found its place in cement chemistry in the early eighties [5-7]. NMR, which is a nondestructive technique, is based on the analysis of the interaction between an oscillating radio frequency electromagnetic field with a collection of atomic nuclei in the presence of an external strong magnetic field.

In NMR, nuclei with odd mass number and half-integer spins such as ^{17}O and ^{29}Si are of most interest because of their magnetic moment. In the presence of a magnetic field the degeneracy of spin energy levels is lifted. This change of energy state in an individual nucleus results in absorbing or emitting a photon with a specific frequency. This frequency is detected and analyzed in NMR [3]. The most useful aspect of NMR in molecular structure studies is that the electrons in the vicinity of the observed nucleus shield it from the magnetic field, which results in a slightly different frequency. Therefore, depending on the neighborhood nuclei and their bonds, this interaction can be different for the same atom. Since it is difficult to measure the absolute values

of these frequencies accurately, they are always reported as chemical shifts relative to an experimentally useful standard [4].

Study of the location of the chemical shifts reveals fundamental information on the molecular structure of materials. For solid state NMR, the magic angle spinning (MAS) method is often used in order to avoid large peak broadenings caused by several nuclear interactions. This is conducted by spinning the sample at frequencies of 1-35 kHz around an axis oriented 54.7° to the magnetic field [3].

The most investigated nucleus in cement chemistry is silicon. A relatively high natural abundance of ^{29}Si (4.67%) as well as its principal structural role in the calcium silicate hydrates makes it favorable for such studies. Silicate tetrahedra are present in hydrated cement systems in various degrees of polymerization. In NMR, polymerization that results in more electron shielding makes the chemical shifts move toward values that range from -60 to -120 ppm [8]. The polymerization of a silicate tetrahedron (Q) is expressed by Q^n , where n is the number bridging oxygens per tetrahedron. If the oxygen is shared with other silicate tetrahedra, the possible Q^n sites ($n=0$ to 4) are usually observed at the following ranges shown in the Figure 3-4 [9]:

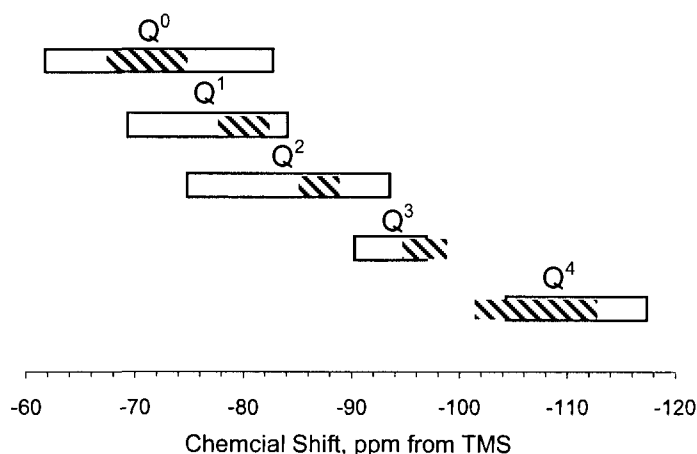


Figure 3-4. Ranges of ^{29}Si chemical shifts of Q^n units in solid silicates. The well-separated ranges are hatched [6].

In hydrated Portland cement, some Q^0 might be observed due to the unhydrated C_3S and C_2S . The commonly acquired signals are due to Q^1 (end-chain group) and Q^2 (middle-chain group) silicate sites as shown schematically in Figure 3-5. Q^3 has rarely been reported in cement paste and is

attributed to the chain branching silicate sites (between the layers) [10, 11]. Q^4 is the polymerization of the quartz and can be observed in silica fume, for example.

The structure of calcium-silicate-hydrates (including various tobermorite systems) has been widely studied by ^{29}Si NMR. The reported chemical shifts for Q^1 , Q^2 and Q^3 in C-S-H are ~ -79 to -80 , ~ -85 to -86 and near -96 ppm, respectively [6, 10, 12-15]. Various peaks have also been observed on the shoulder of Q^2 peak that are attributed to the difference in the local environment of Q^2 sites as in the bridging positions and paired groups [16, 17]. The chemical shift of bridging sites may also vary depending on the chemical attachments such as OH^- or Ca^{2+} .

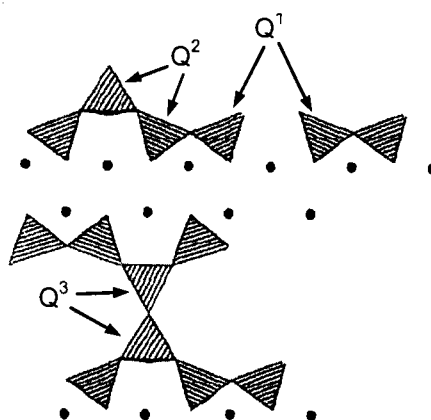


Figure 3-5. Schematic presentation of the possible silicate sites (triangles) in C-S-H. Circles are calcium atoms from the Ca-O layer.

3.1.4 Helium Inflow

Helium gas has been utilized (by Feldman and other researchers at NRC-IRC in the early 70s) as a nanostructural probe to assess the structural response of Portland cement and C_3S pastes to moisture loss [18-23]. Essentially the effects of incremental water removal from the hydrate structure on volume change are systematically and quantitatively followed utilizing helium-inflow measurements to estimate the volumes of the nanospaces vacated by water. The results obtained using the helium-inflow technique to study the Portland cement paste system correlate well with the behavior of a layered material despite its X-ray amorphous character.

The apparatus and procedure for helium-inflow measurements are described in detail in previous papers [18, 19]. In this technique, a typical helium pycnometer is employed. This tool is generally

used for solid volume measurement of specimens based on the gas laws and the assumption of helium gas as an ideal gas. All small pores of a material are instantly filled with inert helium gas allowing for the calculation of true solid volume. Knowing the mass and the apparent volume, one is then able to estimate the density and the porosity values, respectively.

In cement-based materials, a secondary phenomena occurs if the sample remains exposed to helium gas. Following the initial solid volume measurement, the helium gas (that is kept at a constant pressure of 2 atm) begins to diffuse into the very small regions of the material that are not accessible to helium at the beginning. The inflow can be monitored and the results for the adjusted volume are plotted in the form of a helium inflow/unit mass versus time curve. The inflow of helium and the characteristics of these curves are dependent on the material's pore structure and its equilibrium state with respect to water vapor. The helium inflow method has proven to be a technique capable of revealing new nanostructural characteristics, not detectable by other analytical tools [24].

3.1.5 Dynamic mechanical analysis (DMA)

Dynamic Mechanical Analysis (DMA) involves the analysis of the response of an oscillating force in sinusoidal form applied on a specimen. DMA is a widely used technique in polymer science and is often employed to study the transitions of molecular forms at various temperatures [25]. The theory of viscoelasticity in such materials implies that the steady state vibrational response involves frequency dependent moduli and that the stress and strain will not be in the same phase. The strain generally lags from the stress by an angle δ . The $\tan \delta$, which is referred to as internal friction, is a function of frequency [26]. Consider a sinusoidal load that is applied on a sample in the form of

$$\sigma = \sigma_A \sin (\omega t) \quad (2)$$

where σ is the stress at time t , σ_A is the maximum stress and ω is the frequency of the oscillation. If the stress remains within the elastic region of the material, the strain response (Figure 3-6) will be in a sinusoidal form as well and can be expressed as

$$\varepsilon = \varepsilon_A \sin (\omega t + \delta) \quad (3)$$

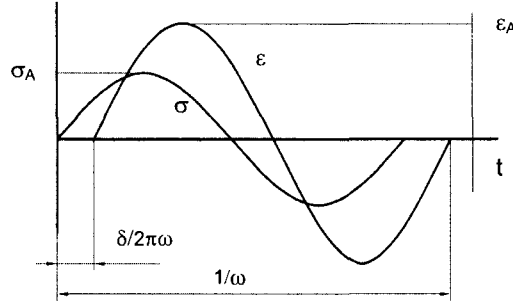


Figure 3-6. The phase shift between the stress and strain in a viscoelastic material subjected to sinusoidal oscillation.

where ε is the strain at time t , ε_A is the maximum strain (if the stress-strain remains in the linear region) and δ is the phase difference angle. All of the properties of a DMA analysis are calculated based on the maximum strain under sinusoidal stress and the angle defining the lag between the force and the response.

Equations can be derived for two types of modulus; E' : *storage modulus* and E'' : *loss modulus* [25]:

$$\begin{aligned} E' &= (\sigma_A / \varepsilon_A) \cos \delta \\ E'' &= (\sigma_A / \varepsilon_A) \sin \delta \end{aligned} \quad (4)$$

The storage modulus (also called the elastic modulus) is a measure of how elastic the material is and ideally is equivalent to Young's modulus. This may not be completely true since Young's modulus is determined from the slope of a line obtained from a range of stress-strain values, while E' represents a point at a specific stress. Loss modulus (also known as the viscous modulus) is a measure of the loss of energy due to internal friction and motions.

The tangent of the phase angle ($\tan \delta$, also called the damping angle) is an indicator of how efficiently the material loses energy (i.e. damping) to molecular rearrangements and internal friction and is independent of geometry effects.

$$\tan \delta = \varepsilon'' / \varepsilon' = E'' / E' \quad (5)$$

DMA was introduced in the seventies as a nondestructive analysis technique for cement-based materials. Radjy and colleagues first investigated states of water in cement hydration products using a temperature controlled DMA (i.e. DMTA) [27-29]. Recent applications in cement science use DMA primarily for studying the polymer modified cementitious materials. It is also possible to study other phenomena such as stress relaxation with a DMA instrument.

3.1.6 Other analytical methods

Several other techniques can be employed in cement science investigations depending on the information required about a specific chemical compound.

In order to investigate the morphology and surface characterization of materials, images at the micro and nano scales can be captured using a Scanning Electron Microscope (SEM). High-resolution images of up to about 110,000K magnification are easily obtained from various cement phases. Different crystalline shapes of materials such as long prisms of ettringite and the hexagonal form of calcium hydroxide are readily identifiable in SEM. In this technique, a focused beam of electrons strikes the surface of the material. The surface interactions result in the emission of secondary and backscattered electrons as well as X-rays. The electrons are collected and converted to the image of the surface. It is also possible to produce back-scattered images, the contrast of which depends on the atomic number. This helps differentiate regions rich in a specific atom. Elemental analysis is also possible through energy dispersive X-ray spectroscopy (EDX) that enables a qualitative estimate of the proportion of each atom in the mixture. EDX imaging allows mapping the distribution of various elements in the material.

Unknown components of a mixture of either organic or inorganic material can be detected using Fourier Transform Infrared Spectroscopy (FTIR). This technique can be applied quantitatively for gases, liquids and solids. FTIR is a powerful tool in identifying the nature of the chemical bonds of molecules. Chemical bonds vibrate at certain frequencies depending on the type of atoms and bonds. The adsorption of the energy of the infrared portion of light by a molecular bond can change the vibrational state of a chemical bond from ground level to an excited level. The energy required for this transition is unique for each bond and thus can be measured and used for the detection of various bonds in molecules. Various IR techniques have been employed to study the structure of cement-based materials [30-31].

Other methods such as BET surface area measurement, particle size distribution, can be employed in order to obtain additional information about the materials and enhance the discussion of arguments that are advanced.

3.2 Materials

Except for the C-S-H that was prepared synthetically, other materials were obtained from commercial sources. The details are mentioned in the next chapters where applicable. Here, the C-S-H preparation method, its humidity conditioning, drying and compaction are described.

3.2.1 C-S-H synthesis

All C-S-H samples were synthesized through mixing stoichiometric amounts of CaO and SiO₂ in water at room temperature. CaO was prepared from the calcination of CaCO₃ (Sigma-Aldrich) at 900 °C in a muffle furnace for 24 hours. The CaO that is freshly obtained through this method is much more reactive than the reagent-grade pure CaO. Amorphous SiO₂ (Cab-O-Sil, Grade M-5, Cabot corporation) was dried at 80 °C over night to remove surface adsorbed water. Distilled de-aired water was used for the aqueous solutions. A range of C/S ratios including 0.6, 0.8, 1.0, 1.2 and 1.5 was produced. In each preparation a water to solid mass ratio of about 10 was used. The amount of materials in each preparation is given in Table 3-1.

Table 3-1. The mass of materials used to prepare C-S-H at various C/S ratios.

C/S ratio	CaO, g	SiO ₂ , g	H ₂ O, g
0.6	16.82	30	750
0.8	22.43	30	750
1.0	28.04	30	750
1.2	33.65	30	750
1.5	42.06	30	750

The CaO and SiO₂ were first dry-mixed and shaken in high-density polyethylene bottles. The water was then added to the mixture and the bottle was additionally shaken. The hydration reaction of CaO would generally produce a significant amount of heat. Care must be taken to inspect and handle it in order to properly finish the shaking step. After the initial shaking, all the plastic bottles were mounted on rotating racks at the speed of 16 rpm. The reaction is usually

completed within the first week. The main XRD peak of C-S-H (at about 30° , 2θ) appears in the first day. A broad 002 basal spacing peak, however, is detected after a few days and is sharpened after a week. This is indicative of the evolution of the C-S-H structure to a more ordered layered material. The hydration was continued for a period of 6 months in order to complete the crystallization and ordering of C-S-H layers and obtain a well-aged material.

After this period, the samples were filtered to remove the excess water. The gel-like material (surface-wet) was then dried under vacuum for 3-4 days. During these steps maximum care was taken to avoid or minimize the exposure of the material to the atmosphere. In such conditions an undesirable carbonation may occur on the C-S-H surface due to the CO_2 in the air. After drying, the C-S-H powders were stored in glass vials purged with nitrogen gas until further use.

In order to compare the behavior of synthetic C-S-H with that in the cement paste, cylindrical ($d=31\text{mm}$) and prism samples ($12\times 100\times 250\text{mm}$) were cast from Portland cement paste (type GU i.e. type I, $w/c=0.4$). The specimens were demoulded after 24h and moist cured for 28 days. Thin circular slices of about 1mm in thickness were cut from the cement paste cylinder for helium flow measurements. Rectangular slices ($\sim 1\times 60\times 12\text{mm}$) were also cut from the prism sample for the DMA and stress relaxation experiments. The dimensions were accurately measured for final calculations. Vycor[®] porous glass plates (Corning Inc.) were cut to obtain rectangular specimens of similar dimensions as those for the cement paste slices.

The C-S-H preparations, cement paste slices and porous glass specimens were conditioned for three weeks in a vacuum desiccator over the vapor pressure of a saturated lithium chloride solution. This provides a relative humidity of about 11% at room temperature which is a desirable base for studying the stoichiometry of C-S-H [32]. There is, theoretically, only a monolayer of adsorbed water on the surface of particles at this specific humidity in addition to the interlayer water. This state was used as the starting condition for most of the experiments in the present research. A few samples of cement paste and porous glass were conditioned over the vapor pressure of water for investigation of the properties in the saturated state.

3.2.2 Characterization of materials

All C-S-H preparations were characterized using XRD, TGA-DSC, SEM and ^{29}Si MAS NMR in order to make sure that the starting materials have the typical properties of the so-called

'pozzolanic reaction' produced C-S-H (i.e. C-S-H (I)) referred to in the literature [33, 34]. Moreover, the BET surface area and the particle size distribution of these systems were measured. The main results of these basic characterizations are presented in Appendix A as a reference for the information on the C-S-H materials used in this thesis. The C-S-H preparations have a definite X-ray pattern with three main peaks at about 1.250; 0.304; 0.280 nm as reported in the literature [34]. The location of the low angle d_{002} XRD peak that occurs between 5 to 10 degrees 2θ (also referred to as 002 basal spacing) depends on the C/S ratio of the C-S-H. Based on Bragg's law this reflection can be used to calculate the mean distance between the layers of C-S-H.

The thermogravimetric curves of C-S-H (mass loss and heat flow versus temperature) are qualitatively and quantitatively similar to those reported for the C-S-H gel [35]. A relatively low mass loss was observed in the region of 400-600°C for the C-S-H (I) used in this study suggesting that the residual amount of Ca(OH)_2 is small or negligible (except for the C-S-H, C/S=1.5, that contains 1.7% free calcium hydroxide). The mass loss from the room temperature to about 110 °C is usually considered to be due to the evaporable water. Constitutional water likely contributes to the additional gradual mass loss at higher temperatures.

C-S-H that is formed in the hydration of Portland cement or calcium silicate phases, has a generally spongy and amorphous texture as shown in Figure 2-1. The synthetic C-S-H, however, is more well-ordered and depicts flaky and foil-like crystals (Appendix A). It can be inferred from the SEM images that as the C/S ratio decreases, the C-S-H flakes become smaller but more connected to each other forming a continuous network.

3.2.3 Compaction of C-S-H powder

A rigid body of the material is required for helium inflow investigation, dynamic mechanical analysis and the stress relaxation experiments. In Portland cement hydration studies, the cement paste hardens and can be cut into various shapes depending on the type of the test. It is however necessary to prepare solid samples by compressing the fine powder of materials such as calcium hydroxide and synthetic C-S-H, in order to determine the mechanical properties [36, 37]. Moreover, handling the compacted specimens for mass change measurements is much easier. In addition, it is possible to extend the range of porosity and avoid some of the limitations inherent in the use of natural rigid porous materials.

It has been shown that the compacted samples of hydrated Portland cement powders have similar properties to hardened Portland cement paste [38-40]. Essentially, the bonds between the particles in a compacted sample mimic those that form during the setting and hardening. The bridging of the surface of particles together primarily involves the formation of van der Waals's attractions. Solid-state reactions can also be postulated in this regard.

In this technique, powders are compacted in a steel mould consisting of a cylinder and two closely fitting pistons. Two types of moulds were used depending on the requirements for each experiment. The cross section of the prepared samples is shown in Figure 3-7.

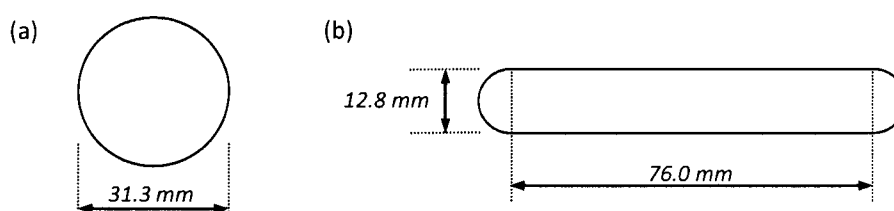


Figure 3-7. Cross-section of the compacted samples: (a) circular type for the helium inflow experiment and (b) rounded rectangle type for the DMA and stress relaxation experiments.

The mould is first mounted vertically with the bottom piston. The powder is then placed in the cylinder. The mould is then struck by a rubber hammer on its sides in order to level the surface of the powder. This is very important in achieving a uniform thickness throughout the compacted specimen. The top piston is then placed in the cylinder and the assembly is mounted in a compression machine. The pressure is increased gradually to the specified value where it is maintained for about 30 seconds before releasing. The compact is removed by pressing out the pistons.

In the compacted state the specimen may crack because of the relaxation if the density of the powder is not uniform in the sample, if the pressure exceeds a limiting value depending on the nature of the powder or if the powder is too wet. Our experimental plan required the powders to be conditioned at 11%RH at which state there is ideally only a monolayer of water of the surface of solid particles. This humidity level is favorable for making compacted powder samples. Also, the C-S-H that was produced in this study was in the form of very fine powder that could pass through a 150 μm sieve (mesh No. 100). After compaction, a length of 58.9 mm was cut from the

rectangular compacted bars to fit the specimen requirements in the DMA and stress relaxation instrument.

In this work, various types of C-S-H preparations were compressed into circular and rounded rectangle samples. It is crucial to control the porosity of the compacted specimens in order to compare the experimental results between the materials at various C/S ratios [41, 42]. A primary set of compacted samples were made from C-S-H powder at pressures ranging from 11,500 to 75,000 psi (Figure 3-8). Porosities (ranging from 25 to 70%) were calculated knowing the dimensions of the compact and the density of the powder that had been determined in a helium pycnometer.

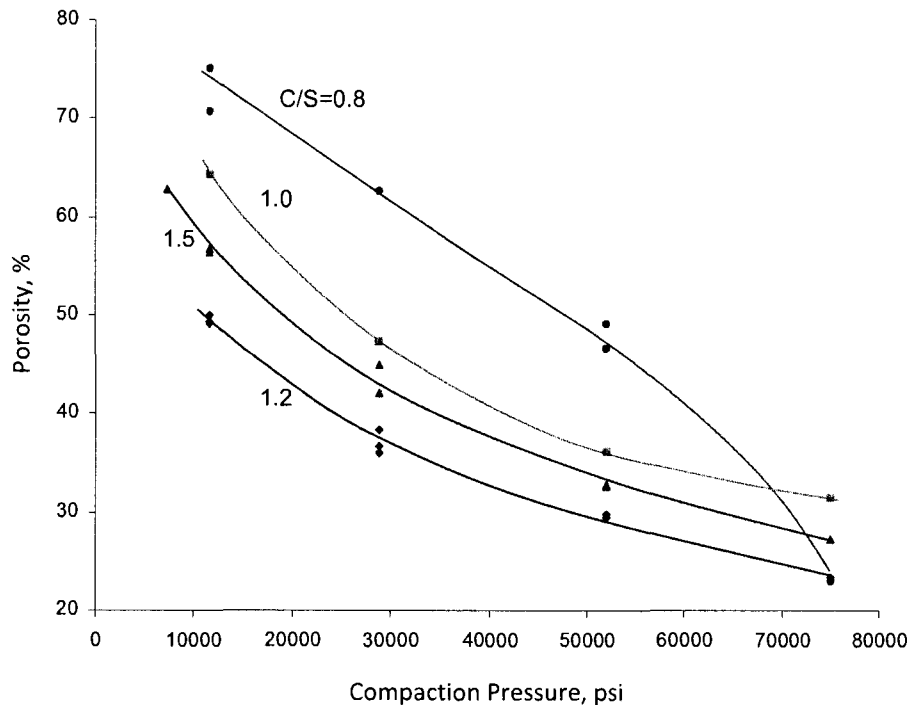


Figure 3-8. Porosity of compacted C-S-H powder (variable C/S ratios) at various compaction pressures (1psi=6.89kPa).

It is now possible to determine and adjust the compaction pressure for each powder (representing a specific C/S ratio) in order to achieve the desired porosity. A lower limit of 30% was selected as the target porosity in the stress relaxation experiment since at this state a sufficiently large fraction of the solid material would come into the play and the behavior would better represent that of the C-S-H. Also, a typical hydrated Portland cement sample ($w/c=0.40$) has a porosity of 26-30%.

The thickness of the compacts varied from 0.8 to 1.2mm. The sharp edges were smoothened using a fine sand paper in a glove box. This prevents a localized concentration of stress on the sides that may result in cracking of the sample during the test. Dimensions were measured and the samples were weighed. All compacts were then stored in the desiccator at 11%RH until used in the experiments.

3.2.4 Removal of water from C-S-H

As previously mentioned, the experimental plan was to measure the changes in various properties of C-S-H on drying the 11%RH conditioned specimens. The removal of water was achieved by the application of a combination of vacuum and heat. A special glass cell wrapped with a heating mantle was used that could be connected to a vacuum hose. The initial drying increments for the 11%RH conditioned specimens were obtained at room temperature using only vacuum. The temperature was gradually increased using the voltage adjustment (with a VARIAC W5MT3) on the heating mantle for higher mass loss levels in the samples. The temperature inside the cell under vacuum had been previously calibrated for the voltage.

In order to minimize altering the C-S-H structure, the drying temperature generally never exceeded 50 °C for most of the mass loss range and 110 °C (along with a 24h vacuum) for mass losses of about 10% at the last increment of water removal. These drying conditions can be considered as semi-equilibrium states considering the considerable amount of time spent on the water removal at each increment. It is important to increase the temperature and vacuum duration very gradually so that the moisture gradient does not cause any cracking in the specimens. Large forceps and a special steel mesh cage were designed in order to place and remove the specimens in the drying cell with maximum care. Powder samples were handled in small glass vials whereas the compacted and sliced samples were situated on a special steel net rack.

Conventional drying procedures of hydrated Portland cement cannot completely preserve the microstructure [43]. The advantage in the method utilized in the current study is that the the C-S-H microstructure was formed at low humidity (11%RH) through the compaction of the powder. No drying of a porous body is required to achieve the 11%RH state, whereas the saturated sample has to be dried to 11%RH which is the case for the hydrated paste. The latter may alter the C-S-H microstructure and possibly result in the formation of micro-cracks.

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Phase Changes of C-S-H systems

C-S-H (I) systems of variable C/S ratio were synthesized. The samples were conditioned at 11% RH before experiments. XRD experiments were conducted primarily to study the change in the 002 basal spacing of the C-S-H upon the removal of the interlayer water. Two methods were employed. 1) Samples were heated to 350°C in an in-situ X-ray diffraction stage, with scans taken every 5°C. 2) Samples were incrementally dried in a vacuum cell and the XRD spectra were acquired at various mass loss levels. The results showed that samples with a C/S ratio >1.1 exhibit an abrupt phase change, whereas there is a gradual phase change in the sample having C/S ratio of <1.1. The abrupt change of the samples with a C/S ratio >1.1 occurs at about 50-70 °C. Two forms of the C-S-H (I) were accordingly identified.

4.1 Introduction

The main binding phase in Portland cement is a poorly crystalline calcium silicate hydrate (C-S-H). It is primarily responsible for the important properties of cement-based compounds such as strength and shrinkage. The chemical and mechanical properties of C-S-H systems have been the subject of extensive studies as one would expect from a subject that can be dated back to 1824 [1] and is coupled to an industry currently producing Portland cement at a rate of approximately two billion tonnes per year [2]. Despite the large amount of literature, the structure and behavior of C-S-H has not been fully resolved and it is still of topical interest to both academic and industrial cement and concrete researchers. Improvements in the knowledge of the behavior and structure of various model C-S-H systems will help us better understand and predict the behavior of these materials when in service.

Tobermorite (a crystalline calcium silicate hydrate) and jennite (another crystalline calcium silicate hydrate with a higher calcium to silica ratio) have often been presented as crystalline analogs for the semi-crystalline C-S-H [3, 4]. Further, the C-S-H formed in the hydration of Portland cement has been linked structurally to these more ordered phases [5]. Tobermorite is a crystalline, naturally occurring calcium silicate hydrate mineral and consists of several polytypes, most notable of which are the 1.4, 1.1 and 0.9 nm tobermorite; with the numbers representing the layer thicknesses in the crystal structure. Studies of phase changes in these systems, associated with the removal of water, have shown that a phase change occurs from 1.4 to 1.1 nm tobermorite at $55 \pm 5^\circ\text{C}$ [6, 7]. Another later study reports the change to occur at 57°C [8]. Meta-stable phases have also been identified during these transitions [6]. Investigation of various phases of C-S-H is important in differentiating their chemical and physical characteristics. It is also helpful for understanding the properties of C-S-H in hydrated Portland cement. This study examines the temperature dependent phase change of several synthetic semi-crystalline calcium silicate hydrates, having various calcia to silica ratios. The mass loss associated with these phase changes was evaluated in a parallel investigation.

4.2 Experimental

Four different C-S-H (I) samples (having C/S ratios ranging from 0.8 to 1.5) were synthesized according to the method described in section 3.2. For this study the C-S-H samples were conditioned over a saturated salt solution of lithium chloride giving a starting relative humidity of 11%. There is theoretically an ideal monolayer of water on the surface of C-S-H particles in

addition to the interlayer water at this specific humidity level. Additional drying should therefore result in the removal of adsorbed and interlayer water. This is favorable for the purpose of the current study because it means that any water lost will be associated with the C-S-H rather than emptying of the pores.

The 11% RH conditioned C-S-H samples were compacted into approximately 1mm thick compacts having a porosity of about 30% according to the method mentioned in the previous chapter. These compacts were suitable for use with an Anton Paar DHS 900 domed hot stage. This stage was mounted in a Bruker D8 Discover X-ray Diffractometer with a cobalt X-ray tube and a HISTAR 2-dimensional area detector. This detector has a circular image area with a diameter of 11.5 cm that is capable of capturing a 1024 x 1024 pixel frame (or an X-ray intensity picture) of the diffraction rings. The hot stage was set to a ramp rate of 5°C per minute with X-ray frames being collected every 5°C from room temperature (~25°C) to 350°C. A 3 minute dwell time at the target temperature was employed before data collection commenced to allow the sample temperature to equilibrate. Each data set consisted of two 5 minute (300 s) frames; the first between 5 and 36° 2 θ and the second between 27 and 60° 2 θ . The two frames at each temperature were integrated to produce conventional 1-D XRD data sets and these were subsequently merged into a single data set covering the full 5-60° 2 θ range. The resulting data sets were analysed using Bruker's EVA version 12 software, and false colour contour plots were generated.

In a parallel experiment, the basal spacing of various C-S-H samples was monitored versus the mass loss of the sample at various temperatures. C-S-H powders were separately conditioned at 11% RH and subsequently placed in a vacuum cell and dried incrementally using vacuum and heat, up to temperatures of about 110 °C (for the final mass loss increments). At each drying increment, the mass loss of the individual 0.3 gram samples was measured before acquiring the XRD spectrum. The X-ray diffraction measurements for these experiments were performed with a Scintag XDS 2000 diffractometer using CuK α radiation and a graphite monochromator. A 2 θ range of 5° < 2 θ < 15°, a step size of 0.03° and a 5 second count interval was used to follow the changes in the 002 basal spacing peak. C-S-H samples were covered by Mylar film in order to prevent any humidity change during the XRD analysis.

4.3 Results and Discussion

The false color contour plots of the XRD spectra for five C-S-H samples used in this study are presented in Figure 4-1. In this way three parameters (temperature, d spacing and intensity) can be illustrated. All plots include the changes in the low angle area as it exhibited the most prominent change upon heating. This range depicts the behavior of the 002 basal spacing (the mean distance between the layers of C-S-H) with temperature. All C-S-H samples show a decrease in the basal spacing as the material undergoes higher temperature treatments. This effect can simply be explained by the removal of the water molecules and OH⁻ groups from the interlayer region [6-8]. There are, however, two distinct behavioral patterns in the XRD results of various C-S-H phases.

First, it is evident that in the samples with C/S ratio = 0.8 and 1.0 (Figure 4-1(a) and 4-1(b)) a gradual shift occurs in the d spacing of the basal peak from 1.2-1.3 to 1.0-1.1 nm over a temperature range of 30-240°C. This change is interpreted as being due to dehydration. That is, the basal spacing decreases gradually as the water is removed from the lattice. It should be noted that thermal expansion would increase the d -spacings, hence if there was no lattice dehydration any observed shift would be in the opposite direction. In all of the samples, after about 240 °C, the intensity of the low angle peak starts to drop dramatically suggesting that the layered structure of the C-S-H is disintegrated due to the removal of constitutional water. Although some of the structure must still remain due to the enduring strength of the main peak at 0.3 nm (not shown) throughout the temperature range experienced in this work.

The second behavioral pattern is observed in the samples with a C/S ratio of 1.2 and 1.5. It is clearly noticed that there is a distinct “kink” or abrupt shift in the trend of the low angle data (002 basal spacing), as opposed to a rather gradual shift observed for the C/S ratio of 0.8 and 1.0. The abrupt shift occurred at about 50-70°C, and is attributed to a phase change. This interpretation is made because the intensity (as shown in Figures 4-1(c) and 4-1(d)) sharply decreases and then increases in a slightly different position having lower d spacing. This kind of observation can only be explained by a structural re-arrangement and hence is referred to as a phase change. The phase change is more prominent for the C/S=1.2 than that for the C/S=1.5. This behavior contrasts that observed in Figures 4-1(a) and 4-1(b) which show a more gradual decrease in the intensity of the basal spacing peak as it is shifted toward lower d spacing values.

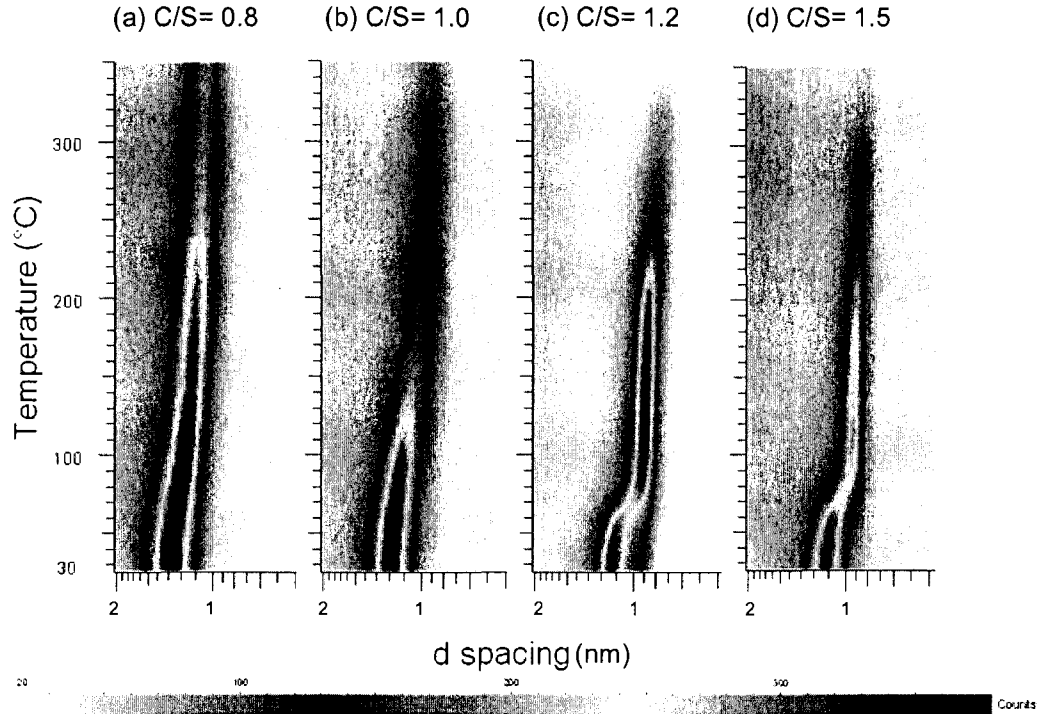


Figure 4-1. False color contour plot of temperature versus d spacing for C-S-H with a C/S ratio of 0.8 to 1.5. Only the changes in the 002 basal spacing are shown. The scale bar along the bottom of the false color plots represents peak intensity.

The 002 basal spacing values are summarized in Table 4-1 for C-S-H samples before and after heating to 250°C. The initial basal spacing of the C-S-H increases with decreasing its C/S ratio. Samples with C/S ratio = 0.8 and 1.0 appear to correspond to the 1.2 nm tobermorite, reported by Yu and Kirkpatrick [6]. The basal spacing of these samples is gradually decreased due to the dehydration as the heat treatment temperature increases.

The other C-S-H samples having C/S ratios = 1.2 and 1.5 correspond to a starting material equivalent of 1.1 nm tobermorite and dehydrate to a 0.9 nm phase with an abrupt change in the intensity and location of the basal spacing. It should also be noted that the C-S-H (C/S=1.2) has a peak appearing on the shoulder of the basal spacing peak at room temperature. This is likely to be due to existence of a mixture of phases at this stoichiometry. For the C-S-H with C/S ratios of 1.2 and 1.5 the low angle peaks are nearly eliminated at temperatures above 280 °C.

The total decrease in the basal spacing of all C-S-H samples due to the dehydration is about 0.2 nm. The diameter of a water molecule is 0.282 nm. It is therefore suggested that at most only a monolayer of water can exist between the layers of C-S-H. This is compatible with the calculations of hydraulic radius (hydrated cement system) for C-S-H that yield values of about 0.15 nm indicating that only 1 layer of water can be present between the silicate sheets [9].

Table 4-1. C-S-H basal spacing at various temperatures

C/S ratio	Basal spacing before heating, nm	Basal spacing at 250°C, nm	Total decrease in basal spacing, nm	Transition type
0.8	1.28*	1.08*	0.20	Gradual
1.0	1.19*	0.98*	0.21	Gradual
1.2	1.13 with Sh 0.99#	0.91*	0.22	Sharp
1.5	1.11*	0.94*	0.17	Sharp

* Values obtained using the centre of the Full Width Half Maximum (FWHM)

Value obtained using a single peak fit in TOPAS software. Sh=shoulder

More evidence for the existence of two C-S-H (I) phases comes from the basal spacing versus mass loss experiments. The curves in Figure 4-2 all show the decrease in the 002 basal spacing of the C-S-H as the adsorbed and interlayer water is incrementally removed from the system. For C/S ratios of 0.8 and 1.0, there is no sudden change in the rate of the basal spacing reduction, which agrees well with the in-situ XRD observations upon a continuous dehydration. However, the curves for C/S ratios of 1.2 and 1.5 show that a sharp decrease occurs in the 002 basal spacing at about 4-8% mass loss, agreeing with the in-situ XRD observations in Figure 4-1. The sudden decrease in the basal spacing for C/S = 1.5 is exhibited at mass loss levels higher than that for the C/S = 1.2. This may also be inferred from the Figure 4-1 that shows the abrupt change in the basal spacing of C/S = 1.5 samples occurs at temperatures slightly higher than those for the C/S = 1.2.

The 002 basal spacing values obtained in this mass loss experiment are somewhat different from those calculated from the results of the *in situ* XRD tests. This might be due to the difference in the setting and calibration of the instruments. Nevertheless, the results in Figure 4-2 again suggest that the 002 basal spacing of all C-S-H samples undergoes a total decrease of about 0.2 nm as observed in Table 4-1.

Taylor categorized the C-S-H into two types: C-S-H (I) and C-S-H (II), with the phase barrier existing at a C/S ratio of about ~ 1.5 [10]. Later he refined the type of these systems to C-S-H (I) having a C/S = 0.8-1.33 and C-S-H (II) with a C/S ratio = 1.5-2.0 [11]. Other studies distinguished various differences for the phase transition that occurs at a C/S ratio of about 1.0 within the composition range of C-S-H (I) [12-15]. Nonat, therefore, suggested a categorization of three kinds of C-S-H systems: C-S-H(α) for $C/S < 1.0$, C-S-H(β) for $1 < C/S < 1.5$ and C-S-H(γ) for $C/S > 1.5$ [16, 17]. It appears from the results of the XRD analysis in this chapter that a separating C/S ratio of about 1.0-1.2 (consistent with most of the other research works) can be considered for two phases of the C-S-H (I).

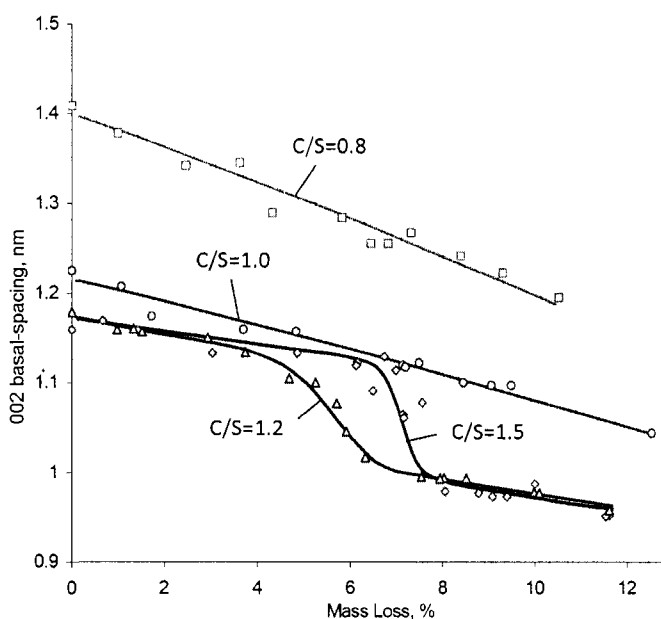


Figure 4-2. Decrease in the 002 basal spacing at various mass loss increments due to the drying of C-S-H (variable C/S ratio) from 11%RH condition.

The average C/S ratio of the C-S-H in hydrated Portland cement is at the upper limit of the high C/S ratio C-S-H (I) [18]. The C-S-H in cement paste is therefore likely to fit the second category of the C-S-H (I) exhibiting sudden phase change as the interlayer water is removed. The examination of this theory employing XRD is not possible as the C-S-H in hydrated cement paste is a nearly amorphous material and does not have a low angle basal spacing reflection. Other techniques such as ^{29}Si MAS NMR that do not require a long-range order characteristic may be able provide information regarding the type of C-S-H in hydrated cement systems. This issue is

practically important since the phase changes observed for the C-S-H (I) occur at temperature ranges than can be readily experienced in the field, for example, in mass concreting.

It is likely that the two phases identified in this chapter demonstrate different physical and mechanical properties. This will be comprehensively investigated in the next chapters. For this purpose two representative C/S ratios were selected; 0.8 and 1.2. In some experiments additional C/S ratios were examined in order to increase the certainty of the results.

4.4 Concluding remarks

Two types of C-S-H (I) were identified (based on the XRD results) stoichiometrically separated at a C/S ratio about 1.0-1.2. The C-S-H having C/S <1.1 exhibits a gradual decrease in the 002 basal spacing due to the dehydration of the system upon the removal of the interlayer water. The C-S-H with C/S >1.1, however, undergoes a sudden decrease in the 002 basal spacing at about 50-70 °C corresponding to a mass loss of about 4-8% from 11%RH conditioned C-S-H depending on its C/S ratio. This is attributed to a phase change in the high C/S ratio category.

A total decrease of about 0.2 nm was observed in all C-S-H samples as the interlayer water is removed. This indicates that not more than a monolayer of water can exist between the C-S-H sheets.

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5

The Layered Nature of C-S-H

Helium gas was used as a nanostructural probe to investigate the structural changes in C-S-H (I) (C/S=0.8 and 1.2) due to the removal of interlayer water. Changes to the 002 basal spacing were correlated with helium inflow characteristics. The ^{29}Si MAS NMR spectroscopy was conducted at various drying increments on C-S-H samples. Similarities with helium inflow and NMR experiments conducted on hydrated Portland cement and C_3S were discussed. New evidence supporting the '*layered*' nature of C-S-H in hydrated cement paste was presented. The viability of considering C-S-H (I) as a physical model for the C-S-H in hydrated Portland cement was discussed.

5.1 Introduction

The nanostructure of C-S-H has not been fully resolved. Two schools of thought have emerged in this regard. One supported the ‘layered’ model [1-4] and the other favored a ‘colloidal gel’ model [5, 7] advanced in the 1940’s. Vigorous debate over the nature of the C-S-H generated for more than 50 years still continues. The absence of direct evidence supporting the layered structure of C-S-H has been at the root of the controversy in cement science. This dichotomy of opinion is due largely to the amorphous nature of C-S-H in hydrated Portland cement products. Nanocrystalline regions have recently been identified in cement paste and the *d*-spacing of these regions observed for the first time using TEM methods [8].

Feldman and Beaudoin have utilized helium gas as a nanostructural probe to assess the structural response to moisture loss of Portland and C₃S pastes [9-15]. Essentially the effects of incremental water removal from the hydrate structure on volume change are systematically and quantitatively followed utilizing helium-inflow measurements to estimate the volumes of the nanospaces vacated by water. The results obtained using the helium-inflow technique in the study the Portland cement paste system correlate well with the behavior of a layered material despite its X-ray amorphous character.

Synthetic C-S-H (I) has been studied extensively [16, 17]. It has a definite X-ray pattern with the three strongest peaks at 1.250; 0.304; 0.280 nm [18]. The 002 basal-spacing at 1.250 nm is sensitive to changes in relative humidity and moisture content [19-21]. It is well known that in the layered silicate systems such as tobermorite or jennite, the dehydration and removal of interlayer water results in the decrease of the interlamellar distance [22-25]. For tobermorite (C/S=0.9) that is used as a structural model for C-S-H, three states of interlayer spacing were distinguished using an *in-situ* X-Ray cell at various stages of drying on heating to about 250 °C. These include 1.40, 1.10 and 0.95 nm preparations. These studies were not conducted at equilibrium conditions with respect to the amount of water in the system and the change in the 002 basal spacing has always been reported versus the ‘temperature’.

In the current chapter, the change in the nanostructural features of C-S-H systems using a more systematic approach and in semi-equilibrium states is explored. Experiments were designed to utilize the helium-inflow technique in probing the volume change sensitivity of the C-S-H (I) nanostructure to moisture change on drying. The objective of this work was to examine additional

evidence for the layered nature of C-S-H in hydrated Portland cement and C_3S pastes. The results were corroborated by XRD and ^{29}Si NMR evidence. The validity of using C-S-H (I) as a nanostructural model for Portland cement paste was discussed.

5.2 Experimental

Synthetic C-S-H was prepared at two C/S ratios of 0.8 and 1.2 according to the method described in chapter 3. These stoichiometric values are representative for two phases of C-S-H (I) identified by XRD as discussed in the previous chapter. Circular compacted specimens (~1mm thick) were prepared from the C-S-H samples for the helium inflow experiment.

The helium-inflow technique was utilized to probe the volume change sensitivity of the synthetic C-S-H nanostructure to moisture change on drying. The apparatus and procedure for helium-inflow measurements have been described elsewhere [9, 10]. The helium-inflow versus time curves, starting from the 11%RH condition, were obtained at each step following the incremental removal of water. The water was removed by vacuum alone and finally a combination of vacuum and heating at increasing temperatures for different periods of time. This was done in a separate vacuum vessel and the sample was then transferred to the helium pycnometer. Helium was allowed to flow into the sample for about two days at a constant pressure of 2 atm.

As a corroborative to helium inflow measurements, the XRD and ^{29}Si MAS NMR experiments were conducted on C-S-H powder samples dried incrementally from 11%RH.

The X-ray diffraction measurements were performed with a Scintag XDS 2000 diffractometer using CuK_α radiation. Scans in the range $5^\circ < 2\theta < 15^\circ$ at a step size of 0.03° with a 5 second collection time at each interval were used to follow changes in the 002 basal-spacing. C-S-H powder samples were covered by Mylar film in order to prevent any humidity change during the XRD analysis. The change in the 002 basal-spacing was determined by monitoring the location of the low angle peak. This change was confirmed by checking the position of the main reference peak of C-S-H at $2\theta = 29.1^\circ$ which did not change at various drying increments.

The ^{29}Si MAS NMR spectra were recorded at 39.6MHz on a Tecmag Apollo 200 spectrometer. Samples were packed into a 7mm Zirconia rotor and spun about the magic angle at about 4.5KHz in a probe supplied by Doty Scientific. A simple pulse pulse and acquire pulse sequence was

used. The sweep width was 10KHz and the 90-degree pulse length was 7 microseconds. A relaxation delay of 60 seconds was normally used. The final spectra took up to 48 hours to obtain. Chemical shifts are reported relative to tetramethylsilane (TMS).

5.3 Results and Discussion

Typical helium-inflow versus time curves for Portland cement paste, $w/c=0.40$, are shown in Figure 5-1 [9]. The starting condition is 11% RH. This condition corresponds to the presence of about one monolayer of adsorbed water. All the curves show a gradual increase in the helium inflow over time. The rate and the amount of inflow increases as water is removed incrementally up to a mass loss of about 5.0% and then begins to decrease.

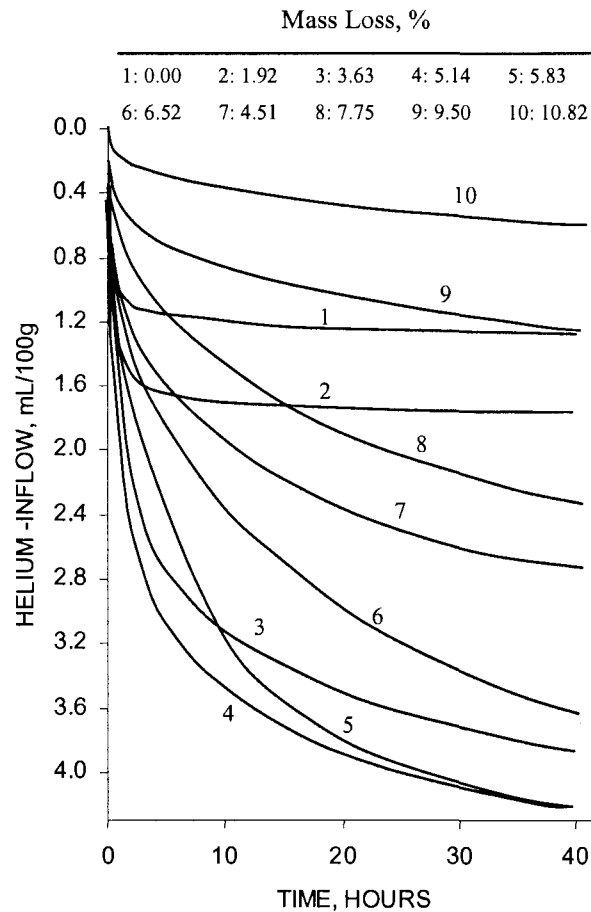


Figure 5-1. Helium-inflow into (0.4 water-cement ratio) cement paste at different moisture contents, as a function of time.

The total inflow at 40h versus mass loss is plotted in Figure 5-2. The curve exhibits a corresponding maximum at 5% mass loss. The change in the inflow behavior is attributed to the removal of interlayer water. The increase of the inflow to a maximum is the result of increased interlayer space becoming accessible to helium without significant structural reorientation of the layers themselves. The C-S-H nanostructure begins to collapse after a mass loss exceeding 5%. Further collapse occurs as the mass loss increases and the helium-inflow decreases. The helium inflow curves for hydrated C_3S (water/solid=0.50) are qualitatively and quantitatively similar having a maximum inflow at about 5% mass loss [10]. These results can not be explained by fixed-wall pore models (e.g. porous Vycor glass). The pores (mean pore size=3 nm) in this system are completely and instantaneously filled, i.e. no time dependent diffusion occurs.

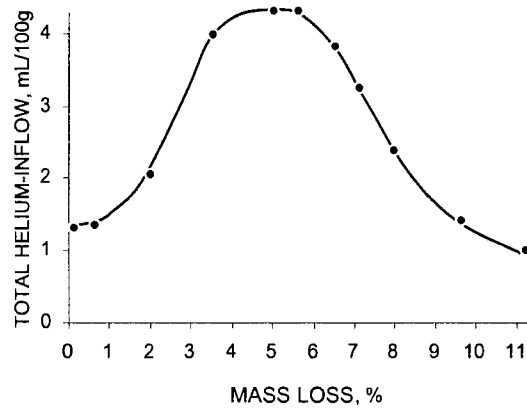


Figure 5-2. Helium-inflow at 40 hr, plotted as a function of mass loss (from 11%RH) for cement paste (W/C=0.4).

Helium-inflow versus time curves for the C-S-H (I) compacts (C/S=1.2) are presented in Figure 5-3. The correspondence between the helium-inflow curves and mass loss is remarkably similar to that observed for the cement paste (Fig. 5-1). This is further illustrated in Figure 5-4 as the helium inflow at 40 h for the C/S=1.2 increases to a maximum at 5% mass loss and then decreases. The similarity in the helium inflow characteristics of the synthetic C-S-H and the C-S-H in hydrated Portland cement is indicative of their analogous response to the removal of the water from 11%RH conditioned material. This is further explored using XRD and NMR evidence.

The changes in the 002 basal spacing of C-S-H ($C/S=1.2$) as a function of mass loss (determined in the previous chapter) are also plotted in Figure 5-4. The curve is divided into 3 regions. A gradual decrease in the 002 basal spacing occurs in the first region i.e. 1.175 to 1.120 nm. A much more rapid decrease in the basal spacing (1.120 to 1.015 nm) occurs in the mass loss region between 4.5-6.5%. This is followed by a further gradual decrease of the basal spacing to about 0.970 nm at 11.5% mass loss. The changes in the 002 basal spacing with mass loss parallel the changes in helium inflow. The beginning of the linear portion of region 2 where a sudden decrease occurs in the distance between the layers of C-S-H corresponds to the maximum in the helium-inflow versus mass change curves and the onset of nanostructural collapse.

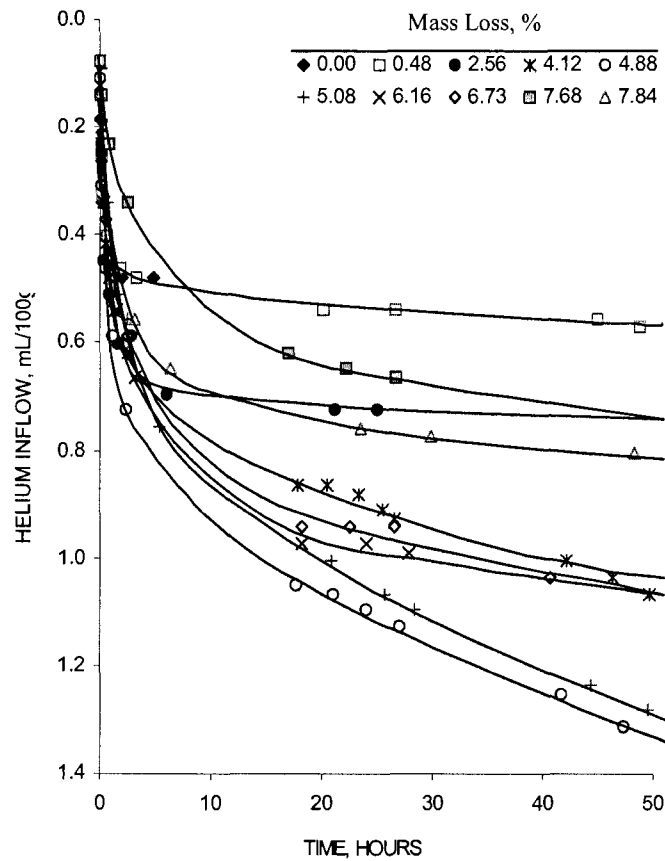


Figure 5-3. Helium inflow versus time curves for C-S-H ($C/S=1.2$) at various mass losses.

X-ray patterns of C-S-H ($C/S=1.2$) samples corresponding to the data in the three regions of the 002 basal spacing curve (Fig. 5-4) are shown in Figure 5-5. The 002 basal spacing peak for the point A (11%RH) is relatively sharp. Upon the removal of water at about 5% mass loss this peak is shifted toward higher 2θ values (i.e. lower 002 basal spacing). It is also observed that the peak

at point B is much broader and less intense than the peak for point A. This indicates that the C-S-H nanostructure is more disordered at this mass loss consistent with a structural collapse process. Additional mass loss (point C) appears to result in a realignment of the C-S-H (I) sheets.

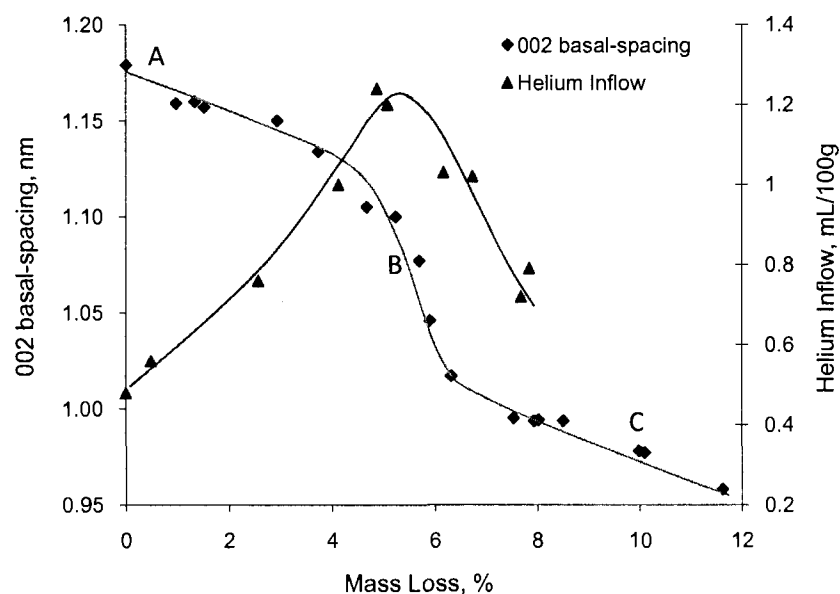


Figure 5-4. Total helium inflow (after 40hr) and 002 basal-spacing as a function of mass loss from the 11%RH condition for C-S-H (C/S=1.2).

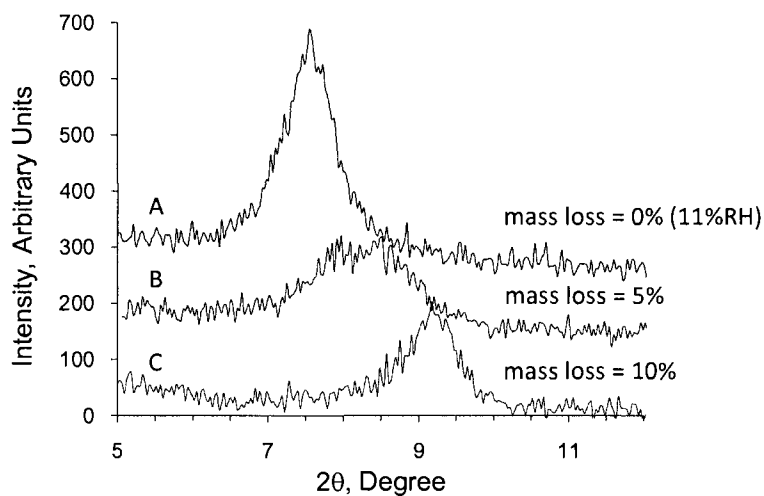


Figure 5-5. X-ray diffraction patterns at low angles for C-S-H, C/S=1.20 showing changes in 002 basal – spacing at different water contents.

It is noted that the peak for point B (Fig. 5-5) covers a wide range of basal spacing including that for the peaks of points A and C. In other words, the broadened 002 basal spacing peak of point B appears to contain reflections related to that of the points A and C. This agrees with the idea that the removal of interlayer water from C-S-H at intermediate mass loss levels results in the decrease of basal spacing of some parts of the C-S-H agglomerate to a basal spacing value similar to that for the state where all the interlayer water is removed (point C). While the basal spacing of other parts of the C-S-H agglomerate is still the same as that in the initial stage (point A), the overall pattern is broadened to reflect the existence of a wide range of 002 basal spacing values. These observations can be summarized using the schematic shown in the Figure 5-6. This model for the collapse of the C-S-H can account for the changes observed in the XRD and helium inflow data. Schematics in Figs. 5-6(b), 5-6(c) and 5-6(d) correspond to the XRD and helium inflow data for points A, B and C in Figure 5-4, respectively.

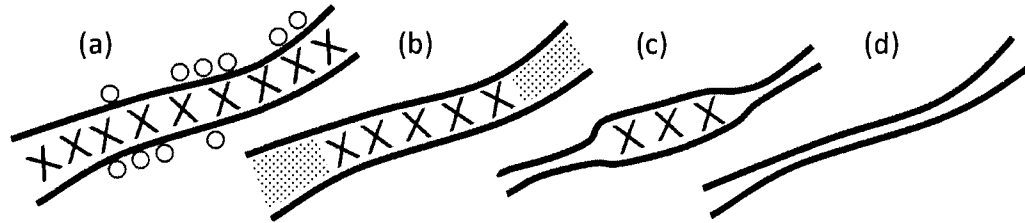


Figure 5-6. Schematic model for the removal of water from C-S-H. Circles are adsorbed water and X depicts the water between the layers of C-S-H. Dotted area is the space that is measured in the helium inflow technique. (a) starting conditions at 11%RH, (b) mass loss less than 4%, (c) mass loss between 4 and 7%, (d) mass loss more than 7%.

The helium inflow is essentially a measure of the “nano” scale spaces (including the interlayer region) that are not accessible instantly to the helium gas. Removal of water from the interlayer space is manifested by an increase in the total helium inflow due to the increase in the volume of “nano” spaces until a collapse of the structure occurs at about 5% mass loss after which the helium inflow decreases. The XRD results provide supporting evidence for the sudden decrease in the 002 basal spacing when the layers of the C-S-H collapse.

It is apparent that the correspondence of the structural collapse and helium-inflow characteristics for C-S-H (C/S=1.2) and the similarities between the helium inflow characteristics of C-S-H (C/S=1.2) and that for the hydrated Portland cement and C_3S pastes reinforce the arguments that the nearly amorphous C-S-H present in the hydrated cement pastes behaves like a layered

material [26]. The XRD experiment alone can not directly confirm this because of the nearly amorphous nature of C-S-H in hydrated products.

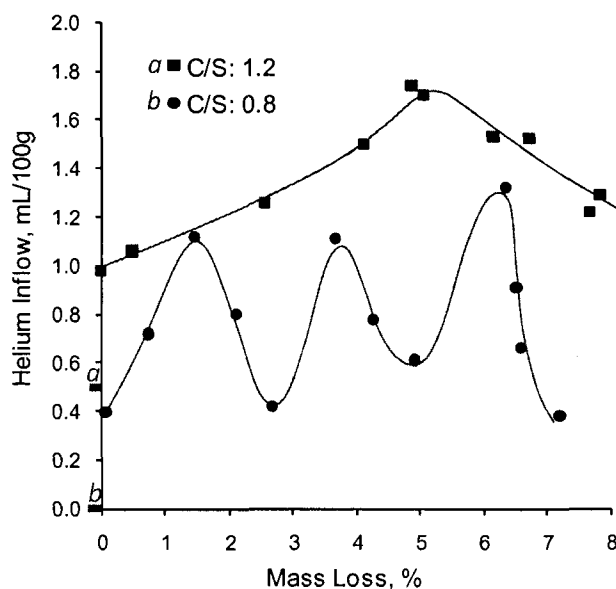


Figure 5-7. Helium inflow at 40 hours versus mass loss from 11%RH condition for C-S-H samples (C/S=0.8 and 1.2). The zero helium inflow value for each curve is marked on the y axis.

The total helium inflow measurements on the C/S=0.8 C-S-H at various drying increments from 11%RH condition is presented in Figure 5-7 in comparison to the data for the C/S=1.2 sample. The C/S=0.8 C-S-H exhibits a very different helium inflow behavior than that for the C/S=1.2 sample upon the removal of water. It is observed that the helium inflow for the low C/S ratio material has an oscillatory character *i.e.* several stages of increase and decrease occur in the helium inflow curve versus mass loss. It was discussed previously that these C/S ratios belong to two different phases of the C-S-H (I) category. As illustrated in Figure 4-2, they exhibit distinctive trends in the decrease of the 002 basal spacing as the interlayer water is removed. It is, therefore, likely that other nanostructural features of these C-S-H phases are different. The X-ray patterns for the data points at various mass loss levels of C/S=0.8 sample qualitatively demonstrates similar changes as observed for the C/S=1.2 sample in Figure 5.5. At first it may appear that the concepts such as a layered model and the collapse of the C-S-H structure due to dehydration are not able to explain the unusual helium inflow behavior of the C/S=0.8 sample. However, ^{29}Si MAS NMR spectra presented in the next section and considerations regarding the silicate tetrahedra of the C-S-H can help explain the differences in the helium inflow characteristics of the low C/S ratio C-S-H (I) phase.

5.4 Effect of Dehydration on the Silicate Polymerization

The ^{29}Si MAS NMR was employed to investigate the nanostructural changes in the silicate structure of the C-S-H preparations dried at various increments from 11%RH condition. NMR results for C-S-H (C/S=1.2) are shown in Figure 5-8. The spectra were collected at each drying increment from separate powder samples. The control ^{29}Si NMR spectrum of C-S-H with C/S ratio of 1.2 (at 11%RH) has two distinct signals at -79.6 and -85.4 ppm corresponding to Q^1 and Q^2 sites, respectively.

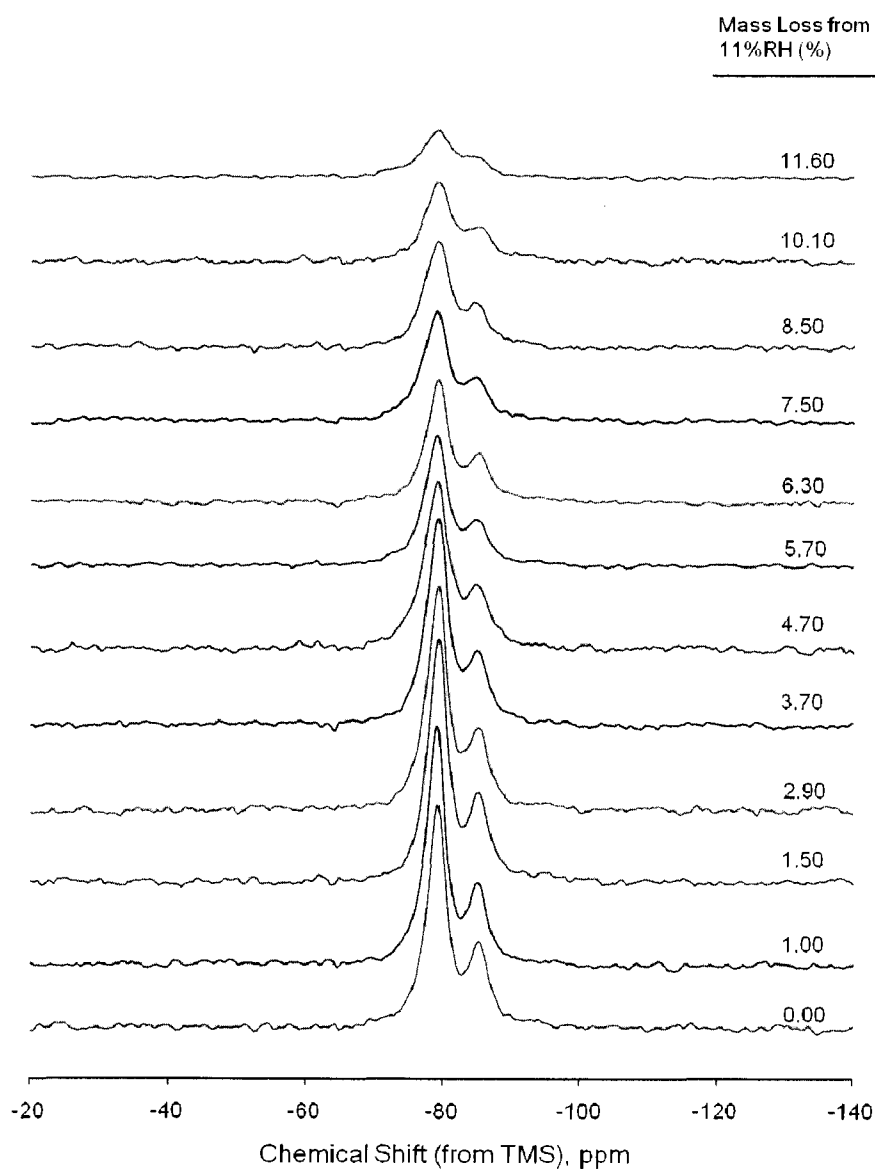


Figure 5-8. ^{29}Si NMR results for C-S-H (C/S=1.2) at various mass loss levels from the 11%RH condition.

Two major changes occur during the dehydration of C-S-H. First, both peaks are broadened as interlayer water is removed. The broadening and alteration of the peak is more significant for the Q^2 signal. Second, the relative intensity of the peaks changes as the C-S-H is dehydrated. In order to examine the latter quantitatively, the NMR spectra were deconvoluted using DMFit software [27]. Figure 5-9 shows an example of a deconvoluted spectrum. The integral intensity of the Q^1 and Q^2 signals were estimated by this method and used to calculate the Q^2/Q^1 ratio of the C-S-H (C/S=1.2) samples.

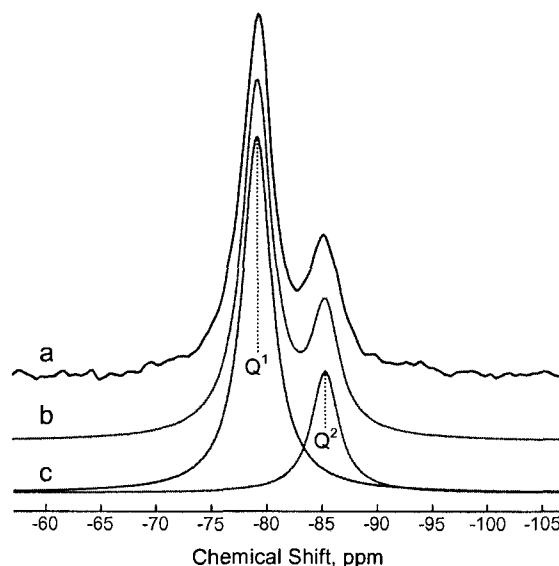


Figure 5-9. Deconvoluted ^{29}Si MAS NMR spectra of the C/S=1.2 C-S-H at 11%RH condition. a: acquired spectra, b: simulated spectra, c: deconvoluted signals for the Q^1 and Q^2 sites.

The change in the relative intensity of Q^2 to Q^1 due to the dehydration of the C-S-H from 11%RH condition (i.e. upon the removal of interlayer water) is presented in Figure 5-10. The Q^2/Q^1 ratio is often used as an indication of the degree of polymerization of the silicate tetrahedra. It is observed that the extent of silicate polymerization increases at higher mass loss levels more noticeably after a mass loss of about 5%. This mass loss is strikingly very similar to the mass loss at which the sudden decrease in the 002 basal spacing and collapse of the C-S-H layers occur according to XRD and helium inflow experiments (Fig. 5-4). Similar observations have been previously made by other researchers regarding the increase of the extent of silicate polymerization in C-S-H systems including that in the hydrated Portland cement and C_3S [23, 28], but a clear physical interpretation was not provided to explain the mechanism through which the Q^2/Q^1 ratio increases in cement systems.

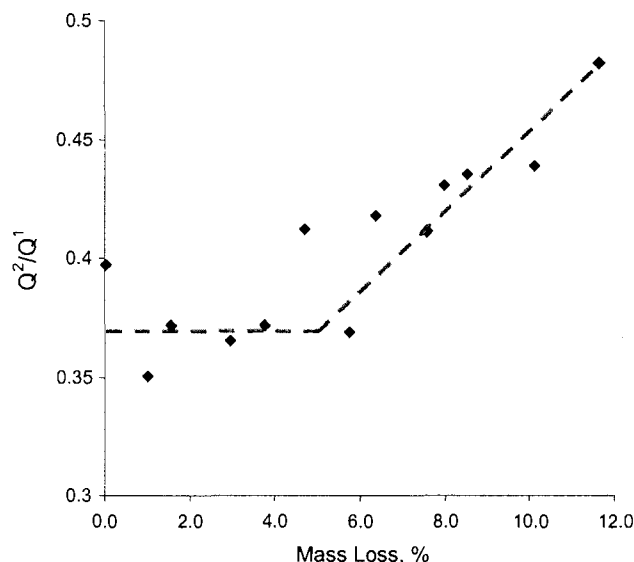


Figure 5-10. Increase of the C-S-H polymerization on the incremental removal of water from 11%RH conditioned powder.

A clearer image of the dehydration of the C-S-H emerges by putting together the evidence from the XRD, helium inflow and the ^{29}Si MAS NMR for the C/S=1.2 C-S-H. As noted before the C-S-H sheets are flanked on both sides by chains of silicate tetrahedra. The end chain and middle chain tetrahedra are referred to by Q^1 and Q^2 sites in ^{29}Si MAS NMR spectra. When they come in close proximity of each other, the silicate tetrahedra shield the adjacent silicate site from the NMR magnetic field. They may even form siloxane (Si-O-Si) bonds together [29, 30], i.e. the cross-linking of the silicate tetrahedra between the C-S-H sheets. The latter is possibly not the only mechanism as the 002 basal spacing increases upon the rehydration of the dried C-S-H. The higher shielding of the Q sites means that their signal is observed at a more negative chemical shift. For example, a silicon site initially detected as Q^1 at 11%RH would be detected as a Q^2 site after the dehydration when the C-S-H layers collapse. The broadening of the Q^2 peak (Fig. 5-8) as well as the decrease in its sharpness is another indication of the existence of a diverse range of Q^2 sites (including the shielded and cross-linked Q^1 sites) in the dried C-S-H sample.

The formation of new Q^2 sites from the condensation of previously Q^1 sites is illustrated schematically in the Figure 5-11. In a similar manner, Q^2 sites may cross-link and form Q^3 sites. The spectra in Figure 5-8 does not show the presence of detectable Q^3 sites (at about -95 ppm). This might be due the low concentration of Q^3 sites in the sample that are not identifiable at the

current resolution of the NMR data. It may also be speculated that the population of the Q^2 sites relative to the Q^1 in the interlayer region is less than that on the surface of the C-S-H agglomerates and thus it can not be expected to observe a significant cross-linking of the Q^2 sites in the dried sample.

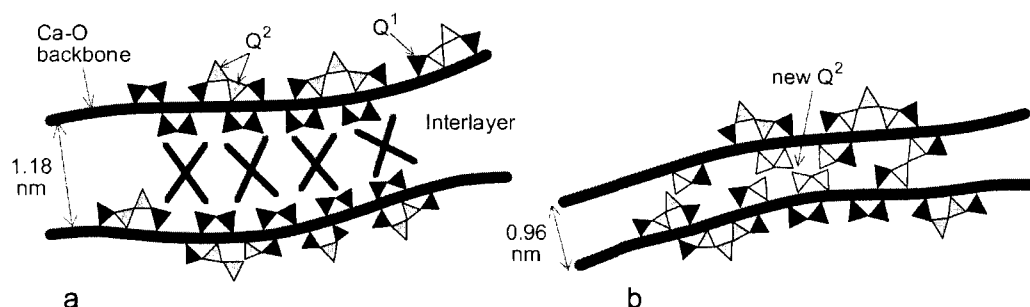


Figure 5-11. Formation of new Q^2 sites in C-S-H from the initial Q^1 sites when the interlayer water (shown by X) is removed. a: before the dehydration, b: after dehydration.

It should be noted that the increase in the extent of silicate polymerization as well as XRD and helium inflow behaviors were achieved only by drying through vacuum and heat (temperatures less than 110 °C). Therefore, the heat treatment and drying method of the C-S-H samples frequently used in various research studies has to be considered carefully in the interpretation of the observed nano- and micro-structural variations.

In a similar procedure the ^{29}Si NMR spectrum of C/S=0.8 C-S-H was acquired at various increments of drying from 11%RH conditioned samples. As shown in Figure 5-12, a main Q^2 signal is detected in all samples with Q^1 appearing as a shoulder. Moreover, another Q^2 signal (referred to as Q^2_b) is present in the C/S=0.8 sample that was not observed in the C/S=1.2 sample. The resolution of the data is not high enough to conduct a thorough deconvolution analysis. It is, therefore very difficult to follow the change in the extent of C-S-H silicate polymerization by calculating the Q^2/Q^1 ratio. However a qualitative evaluation of the spectra may be revealing.

It appears that at mass loss levels above 4%, a small signal is formed at a chemical shift of about -95 ppm. This value fits in the range of the Q^3 site. The Q^2_b signal appears to sharpen as the sample is dehydrated. The location of both Q^2 sites is slightly shifted to more negative values. These observations can be indicative of the increase in the degree of the silicate polymerization in C-S-H (C/S=0.8). The model presented in Figure 5-11 can be applied to explain the increase in

the polymerization of the silicate tetrahedra in the low C/S ratio C-S-H (I) phase. It is suggested that the Q^2 sites, initially present in the interlayer region at 11%RH, form Q^3 sites as the C-S-H layers come closer upon the removal of interlayer water. The shielding and cross-linking mechanisms described for the C/S=1.2 sample can therefore be applied.

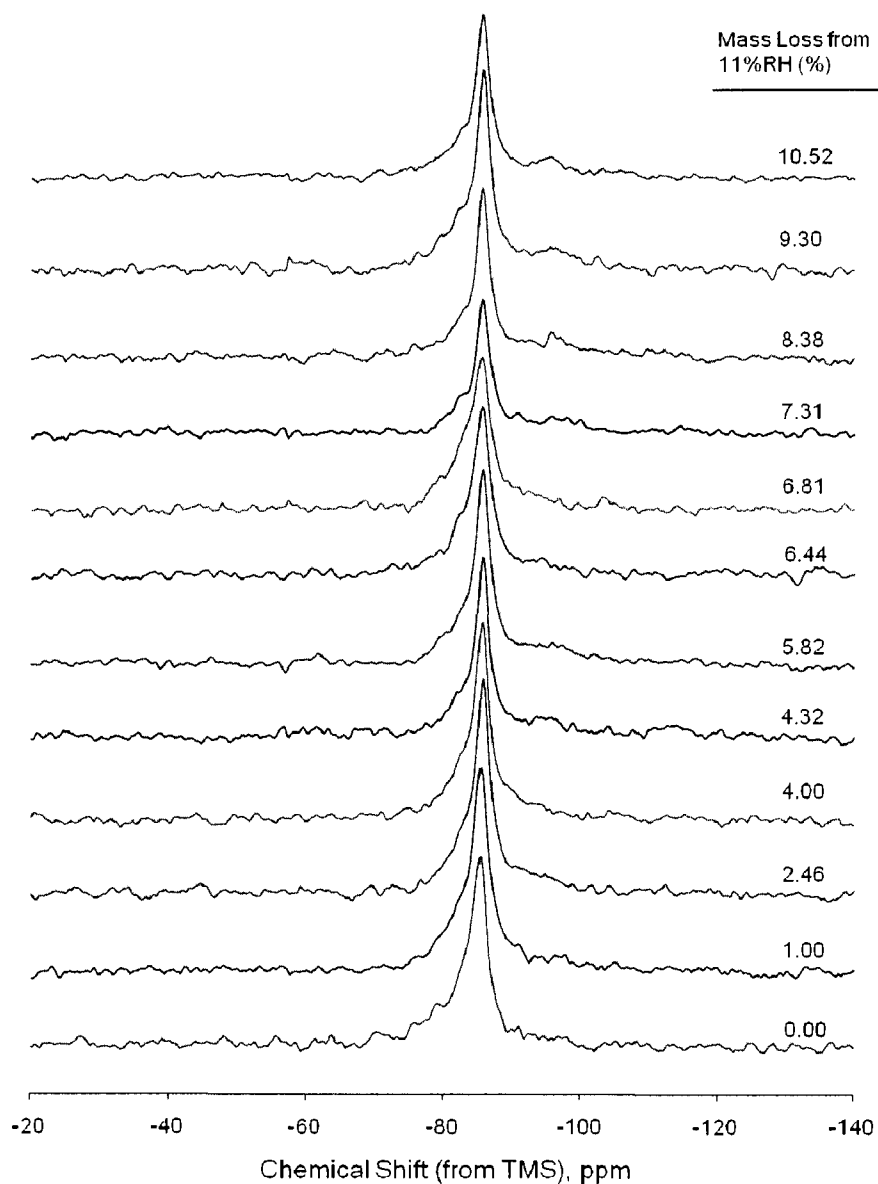


Figure 5-12. The ^{29}Si MAS NMR spectra of the C-S-H (C/S=0.8) samples at various mass loss increments from the 11%RH condition.

A physical model may now be proposed to explain the oscillatory helium inflow characteristic of the C/S=0.8 C-S-H (Fig. 5-7). According to this model, as schematically shown in Figure 5-13, a large number of Q^2 sites are present in the interlayer region. Upon the removal of water from the interlayer region, the increase in the volume of the vacated 'nano' spaces can be detected by helium inflow technique (Fig. 15-3b). After a specific mass loss when the layers are close enough together the Q^2 site in one layer can be shielded by the Q^2 site from the adjacent layer. Cross-linking can also be postulated. This is accompanied by only a gradual decrease in the basal spacing. The connection between the Q^2 sites, however, closes the 'nano' spaces accessible to helium gas resulting in a decrease of the helium inflow (Fig. 5-13c). As the mass loss increases (by removing additional water molecules) new spaces become available in the interlayer region. This results in an increase in the helium inflow. Subsequently, due to the formation of another set of Q^3 sites, the access to these spaces is limited and the helium inflow is decreased again. This process may be repeated up to several cycles. The decrease in the 002 basal spacing exhibits a constant rate throughout the whole range of mass loss. Unlike C/S=0.8, a pronounced collapse occurs in the C/S=1.2 C-S-H resulting in an increase of the extent of polymerization, abrupt decrease in the 002 basal spacing and decrease in the helium inflow. The vacated space due to further dehydration of the C/S=1.2 sample after the so-called collapse is not accessible to the helium gas.

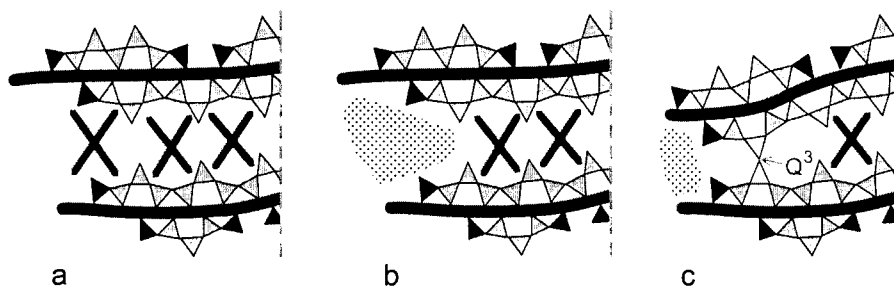


Figure 5-13. Evolution of the low C/S ratio C-S-H (I) nanostructure due to the removal of interlayer water with respect to space accessible to the diffusion of helium gas. Features are similar to those presented in Figure 5-11 except that larger number of Q^2 sites are present in the interlayer region (a); helium inflow increases as new spaces become available (shaded area) due to dehydration (b); helium inflow decreases as the access to 'nano' spaces is limited by cross-linking of Q^2 sites (c). Further dehydration creates new 'nano' spaces and results in an increase of the inflow.

5.5 Analogies with the C-S-H in hydrated cement

It was shown that the helium inflow behavior of the high C/S ratio C-S-H phase upon the removal of the interlayer water is very similar to that in the hydrated Portland cement. In both systems the total inflow reaches a maximum value and decreases after a mass loss of about 5% from 11%RH conditioned material. XRD results showed that this type of synthetic C-S-H experiences a sudden decrease in the basal spacing at a similar mass loss level. The co-occurrence of these changes was best explained by the argument that there is a collapse in the nanostructure of high C/S ratio C-S-H after a specific mass loss. Although it is not possible to conduct a similar XRD analysis on the hydrated Portland cement, the similarity of the helium inflow characteristic suggests the presence of a comparable collapse mechanism in the 'layered' nanostructure of the C-S-H in cement paste.

The NMR investigation provided more insight into this theory. The calculations using the ^{29}Si MAS NMR results (for C/S=1.2 sample) showed that there is an increase in the extent of silicate polymerization after a mass loss level similar to the critical level determined through XRD and helium inflow techniques. This was explained by the C-S-H layers coming together and forming new Q^2 sites. The changes in the silicate structure of the C-S-H in hydrated Portland cement have been previously studied using ^{29}Si NMR. Cong and Kirkpatrick showed that various room temperature preparations of C-S-H can be more polymerized if heated to 110 and 200 °C (Fig. 5-14a) [31]. No physical explanation was given in this regard. Aono *et al.* applied ^{29}Si NMR to hydrated cement paste during the drying at 50 °C [32]. The increase in the degree of polymerization was inferred from the increase in the intensity of Q^2 and simultaneous decrease in the intensity of Q^1 (Fig. 5-14b).

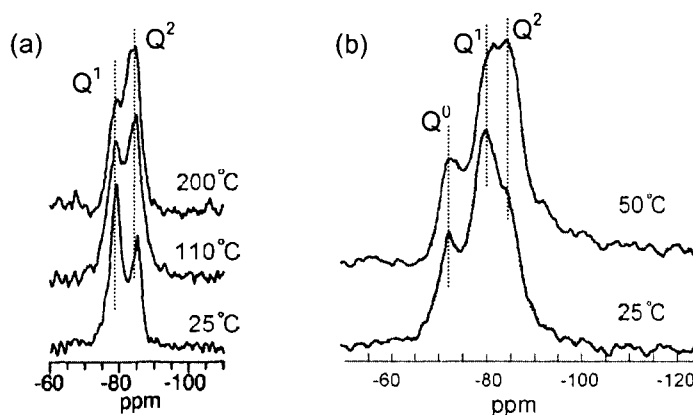


Figure 5-14. The increase in the Q^2/Q^1 ratio of the hydrated $\beta\text{-C}_2\text{S}$ (a) and ordinary Portland cement (b) due to the dehydration at high temperature treatments (modified from ref. 31 and 32).

Considering the results of helium inflow measurements and XRD, it is suggested that the increase of silicate polymerization in Portland cement systems (due to dehydration) can be readily explained through the same approach taken for the synthetic C-S-H, i.e. assigning a layered nature to the C-S-H in hydrated cement paste with the possibility of interaction between silicates in the interlayer region upon the removal of water. In fact, this is further evidence for the layered nature of the C-S-H in hydration products of Portland cement. The layered structure can effectively be used to explain the change in the helium inflow and ^{29}Si MAS NMR results of hydrated Portland cement due to dehydration.

The low C/S ratio C-S-H (I) phase does not seem to behave physically in the same manner as that in the cement paste. The helium inflow curve has an oscillatory nature and is not similar to that for the cement paste or even the high C/S ratio C-S-H (I). The 002 basal spacing of low C/S ratio C-S-H (I) decreases gradually as the interlayer water is removed. No sudden change in the interlayer spacing occurs as that in the high C/S ratio C-S-H (I). The ^{29}Si MAS NMR spectra and their evolution as the system is dehydrated are quite different from the experimental observations for the cement paste and high C/S ratio C-S-H (I). It is, therefore, suggested that although both C-S-H (I) phases ($C/S < 1.1$ and $1.1 < C/S < 1.5$) are structurally related to the C-S-H in hydrated Portland cement, the high C/S ratio C-S-H (I) has more viability to be considered as a structural model for the physical behavior of the hydrated cement systems.

5.6 Concluding remarks

Helium inflow measurements and ^{29}Si MAS NMR investigations were conducted on synthetic C-S-H (I); C/S ratios=0.8 and 1.2. The changes were examined upon the removal of water from the materials at various increments of drying from the 11%RH condition.

The results showed that the mechanism of collapse of the C-S-H layers is responsible for the variations in the helium inflow and silicate polymerization of the C-S-H corroborating the observation from the XRD analysis. Unlike the low C/S ratio C-S-H (I), the high C/S ratio C-S-H (I) ($1.1 < C/S < 1.5$) appears to demonstrate a physical behavior similar to that in the hydrated Portland cement.

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6

Ultra-High Field ^{43}Ca Solid State NMR

The natural abundance solid state ^{43}Ca MAS NMR of the cement-based materials including cement clinker phases and various C-S-H systems are reported for the first time. The results provide new insight into the nanostructure of the cementitious materials. The ^{43}Ca NMR spectra of the cement compounds are related to the variation in local environments in the vicinity of calcium atoms. It is also demonstrated that the calcium structure of the C-S-H produced in the hydration of C_3S resembles that in the more ordered layered analogs such as synthetic C-S-H and tobermorite. High C/S ratio C-S-H (I) appears to have a relatively close calcium nanostructure to that in the hydrated C_3S .

6.1 Introduction

Solid State Nuclear Magnetic Resonance is one of the major spectroscopic techniques that has been playing a significant role in nanostructural studies of cement-based materials [1]. The chemical character of cement systems greatly depends on the coordination and local environment of calcium atoms. The ^{43}Ca Solid State (SS) NMR could therefore potentially play a significant role in structural and chemical studies of these materials. Recent studies have demonstrated that this technique is impressively helpful for resolving complicated structural problems not accessible by other methods [2, 3]. The ^{43}Ca has chemical shift range of nearly 200 ppm, reflecting the sensitivity to the chemical environment of calcium [4]. Correlations between the mean Ca-O distance in the polyhedron and the chemical shift of ^{43}Ca have been reported [5, 6]. A major improvement in the interpretation and assignment of the spectra comes from the latest advancements in computational methods of NMR parameters. The most notable progress in recent years was achieved in calculations related to periodic structures such as occurs in crystalline materials. In many situations chemical shielding and quadrupolar parameters can be calculated with very high accuracy and reliability [2, 6]. Despite its advantages, the application of ^{43}Ca SS NMR in materials chemistry has been limited with just twenty original publications on the subject produced during the past 15 years [2, 3, 5-25].

The root of the problem is mainly due to the great difficulties in obtaining the spectra. The only magnetically active isotope of ^{43}Ca has a low natural abundance of only 0.135 % and is a spin 7/2 quadrupolar nuclei with a rather small magnetogyric ratio γ (absolute resonance frequency $\Xi = 6.7299$ MHz) and a moderate quadrupolar moment of -4.08 fm². The miniscule natural abundance and low resonance frequency complicated by quadrupolar interactions make ^{43}Ca SS NMR a challenging exercise. When the calcium is not in highly symmetric environment, e.g. as in cubic calcium oxide, the observed signal of the central transition is commonly broadened by the second order quadrupolar interaction drastically reducing intensity of the signals [26, 27]. An additional complication commonly encountered in solid state NMR of low- γ nuclei is rather long relaxation times. T_1 times as long as tens of seconds can be expected for the ^{43}Ca [2, 6], which complicates the accumulation of signals.

In the case of calcium silicates, the experimental difficulty is magnified by the large variety of the local structural environments calcium can be found in. In practice it leads to spreading the total intensity among multiple signals and resulting in overall low intensity. The NMR resolution of

amorphous materials such as that formed in the hydration of cement systems will be more significantly affected. The tricalcium silicate (C_3S), which is the main component of Portland-cement clinker, is known to have 29 distinct Ca sites [28]. Even if some of these sites incidentally have undistinguishable signals and completely overlap, the overall spectrum is expected to be very complicated. Great difficulties with ^{43}Ca SS NMR for cement-based materials were demonstrated once again in a recent publication [23], where attempts were made to obtain the spectra of the crystalline minerals jennite and tobermorite that are considered as model compounds for calcium silicate hydrate in cement paste. Although a high magnetic field of 21.1T was used, the authors were able to obtain very poor spectra for these two crystalline materials after about 48 hours of data acquisition.

The hydration mechanism of C_3S , and the nanostructure of C-S-H analogs are central to some of the main problems in understanding the chemistry of cement-based materials. The ^1H and ^{29}Si NMR have elucidated many aspects of the silicate structure of cement compounds and C-S-H over the past 30 years [1]. The calcium environment in cement systems, however, has not been explored using the NMR technique before. The current study employs the natural abundance ^{43}Ca SS NMR in order to investigate the nanostructure of cement-based materials from a new perspective. The ^{43}Ca NMR spectra were acquired for the first time for cement clinker compounds. Cementitious phases such as hydrated C_3S and synthetic C-S-H of variable composition were also examined.

6.2 Experimental

6.2.1 Materials

Cement clinker phases were obtained from the CTL group (Skokie, IL). These include C_3S (triclinic and monoclinic), $\beta\text{-C}_2\text{S}$ and C_3A . Regent grade CaO and $\text{Ca}(\text{OH})_2$ (from Sigma-Aldrich) were used for comparison.

A hydrated sample was prepared by mixing triclinic C_3S and distilled water ($w/\text{C}_3\text{S}=0.5$). Synthetic C-S-H materials ($\text{C}/\text{S}=0.8, 1.2$ and 1.5) were produced according to the method described in chapter 3. An $11\text{\AA}$ tobermorite sample (received from Dr. L. Mitchell, NRC-IRC) was also examined. All of the materials have a natural abundance of ^{43}Ca .

6.2.2 NMR measurements

^{43}Ca NMR measurements were performed on a Bruker Avance-II 900 MHz instrument (magnetic field of 21.14 T and Larmor frequency of 60.58 MHz). The Magic Angle Spinning (MAS) experiments were performed using Bruker single channel 7 mm low- γ probe with dry nitrogen as a carrier gas. A simple single-pulse sequence was used to acquire the spectra. The solution $\pi/2$ pulse was 9 μs and the corresponding selective solid $\pi/2$ pulse was scaled by a factor of four to 2.25 μs . All isotropic chemical shifts are referenced to a 1M solution of CaCl_2 set to 0 ppm. The choice of the reference here is different from that in the earlier works [5, 7-11] where the use of a saturated solution of CaCl_2 as the reference material resulted in a few problems [2].

Plane wave-based density functional theory calculations of nuclear magnetic shielding and electric field gradient tensors were performed using the NMR module of the CASTEP DFT code [29] that employs the Gauge Including Projector Augmented Wave (GIPAW) algorithm [30] and is a part of the Accelrys Materials Studio simulation and modeling package [31]. The Perdew Burke Ernzerhof (PBE) functional was used with the Generalized Gradient Approximation (GGA) for all calculations [32]. The convergence of calculated NMR parameters on the size of a Monkhorst-Pack k-point grid and a basis set cut-off energy were tested for all systems. The sufficient basis set cut-off energies were 550 eV and the k-point spacing was always less than 0.03 $\text{\AA}^{-1}$. Unit cell parameters and atomic coordinates were taken from the most recent published structures.

Supplementary ^{29}Si MAS NMR spectra were obtained from the cement clinker silicate phases. This test was carried out on a Bruker Avance 200 MHz instrument (magnetic field of 4.7 T and ^{29}Si Larmor frequency of 39.75 MHz) using a BL7 double resonance MAS probe and 7 mm ZrO_2 spinners at the spinning speed of 5 KHz. The spectra were acquired in a Bloch decay mode (^{29}Si $\pi/2$ pulse of 4 μs) with a high power composite pulse proton decoupling at a delay of 60s between scans.

6.3 Results and Discussion

6.3.1 Cement Compounds

The ^{43}Ca MAS spectra of several crystalline cement clinker phases are shown in Figure 6-1 in comparison to that of CaO . The spectrum of CaO (Fig. 6-1a) consists of a very narrow signal, 21

Hz wide, with the chemical shift of 136.1 ppm. The position of the signal is in a good agreement with the data reported previously [5] if corrected for the referencing [2]. It should be noted that this is the most de-shielded calcium site ever reported.

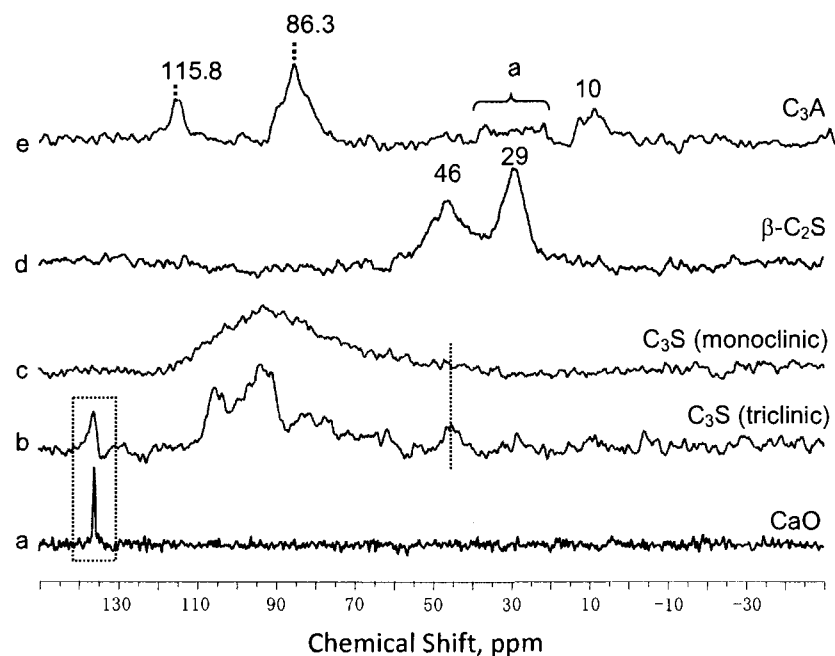


Figure 6-1. The natural abundance ^{43}Ca NMR spectra of anhydrous cement compounds and calcium oxide.

Figs. 6-1b and 6-1c present the ^{43}Ca NMR spectra of the triclinic and monoclinic C_3S samples, respectively. Although the chemical composition of these two samples is similar, their ^{43}Ca spectra show some remarkable differences in the resolution of the signals. The monoclinic C_3S exhibits a very broad and asymmetric signal in the range of 40 to 110 ppm (Fig. 6-1c). Such a broadening is commonly observed in situations where the distribution of NMR parameters such as quadrupolar constants is present. Since the crystal structure of Ca_3SiO_5 is supposed to have 29 non-equivalent sites for Ca, it wouldn't be too surprising if some small deviations from the perfect lattice produced the observed broadening in the spectrum. The NMR spectrum of the triclinic C_3S , however, has relatively well-separated ^{43}Ca signals appearing in the range between 40 to 140 ppm. At this point only the signal at 136.2 ppm can be unambiguously assigned to CaO. It is interesting that with a large number of inequivalent Ca sites in the structure of C_3S there are only a few distinct signals in the spectrum. Apparently, some calcium environments in C_3S are very similar, resulting only in a limited dispersion of the ^{43}Ca signal.

In order to confirm the structural environment diversity of the triclinic and monoclinic C_3S , the ^{29}Si MAS NMR was conducted (Fig. 6-2). It is evident that the signals of the monoclinic sample (Fig. 6-2a) are substantially broader than those for the triclinic C_3S (Fig. 6-2b). The latter is the type that is usually studied in the literature as it contains well-separated ^{29}Si signals [1]. The monoclinic C_3S has a distorted crystal lattice indicated from the NMR results (both ^{43}Ca and ^{29}Si). This is possibly due to the stabilizer (such as Mg^{2+} and Sr^{2+}) added to the C_3S at high temperatures (above 980 °C) during the formation process in order to preserve the monoclinic state [33]. Otherwise, the produced C_3S would have a triclinic structure. It should also be noted that the alite clinker phase (tricalcium silicate) in Portland cement is substantially composed of monoclinic polymorphs [33].

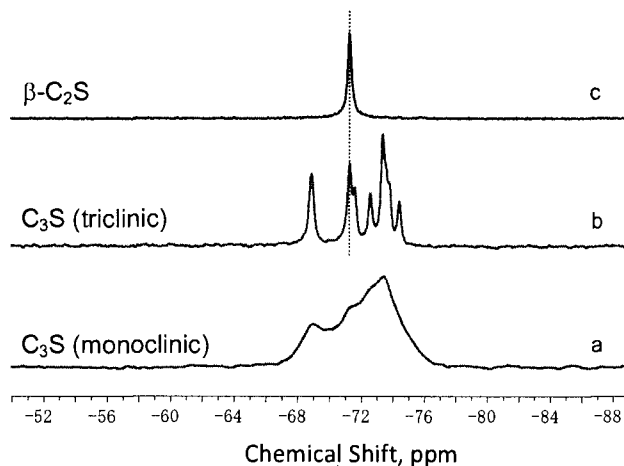


Figure 6-2. The ^{29}Si MAS NMR spectra of (a) monoclinic C_3S , (b) triclinic C_3S and (c) $\beta\text{-C}_2\text{S}$.

The distinct signals that are observed in the spectrum of $\beta\text{-C}_2\text{S}$ (Fig. 6-1d) are in agreement with the crystal structure of this compound [34]. The positions of the intensity of maximums are at about 46 and 29 ppm. These positions, however, are not the isotropic chemical shift since the signals are visibly affected by the second order quadrupolar interactions. Due to the broadening of the signals, it is difficult to produce an accurate simulation of the signals, and the isotropic shift and the quadrupolar parameters resulting from this simulation should be considered only as estimates. The isotropic chemical shifts for the first and the second signals are 53.0 and 36.0 ppm, with the C_Q 's being 2.9 and 2.6 MHz, and η 's of 0.65 and 0.9, respectively. The integrated ratio of the signal is very close to 1:1 as expected from the structure. The experimental data for both signals are in good agreement with the results of our CASTEP calculations ($\delta_{\text{Si}(1)}=55.0$ ppm,

$C_Q(1)=2.8$ MHz; $\eta(1)=0.5$ and $\delta_i(1)=37.1$ ppm, $C_Q(1)=2.4$ MHz; $\eta(2)=1.0$) and that reported elsewhere [6]. The triclinic C_3S has some impurities of C_2S indicated by a signal at about -71.3 ppm in the ^{29}Si spectrum (Fig. 6-2c compared to Fig. 6-2b). The C_2S impurity (that is roughly less than 10 mol. %) is likely to contribute to the ^{43}Ca spectral intensities of triclinic C_3S at about 46 and 29 ppm (Fig. 6-1b).

The ^{43}Ca spectrum of C_3A consists of at least three distinct signals (Fig. 6-1e). The region marked with “a” appears to show somewhat increased intensity relative to the baseline; however the signal-to-noise ratio is not sufficiently good to state this with certainty. The maximums of intensity for all three signals spun over a range of 100 ppm are found at 116, 86 and 10 ppm. It appears that all three signals are affected by the second order interaction. It is therefore necessary to fit the signals with an appropriate model to extract the spectral parameters. This is even more complicated as it is not certain if all the sites are resolved in the spectrum. In fact, the unit cell of C_3A contains six inequivalent sites for calcium [35], which can result in six distinct signals in the spectrum if all are resolved. Possible overlapping will obviously reduce the observed signals in the spectrum. Identification and assignment of signals in C_3A using first principles computations is very problematic due to the very large size of its unit cell. It is noted that there are very few reports on ^{43}Ca chemical shifts between 40 to 110 ppm. A recent work reports several experimental and calculated isotropic shifts for ^{43}Ca in the range of 40-67 ppm [6], but nothing above that. Such significant deshielding of Ca ions in C_3S and C_3A samples is very difficult to explain and requires further study.

6.3.2 Hydrated cement phases

The ^{43}Ca NMR spectra of synthetic C-S-H phases ($\text{C/S}=0.8, 1.2$ and 1.5), $11\text{\AA}$ tobermorite and hydrated triclinic C_3S are presented in Figure 6-3. Ca(OH)_2 was also examined as it is one of the main hydration products in Portland cement paste.

The signal of calcium hydroxide (Fig. 6-3a) clearly shows the effects of the second order quadrupolar interactions in its spectrum. The isotropic chemical shift of 70.5 ppm together with the quadrupolar constant $C_Q = 2.49$ MHz and asymmetry parameter $\eta = 0.1$, agree well with previously reported experimental [10] and computational data [6]. Results of the CASTEP calculations of the chemical shift and quadrupolar parameters in the current work for Ca(OH)_2 are

similar to those previously reported [6] with a slight improvement in the observed C_Q (2.2 MHz vs 1.9 MHz in Ref. 6).

The hydrated C_3S (Fig. 6-3b) has a wide range of broad signals in the region between 20 and 70 ppm. This is not surprising as the main hydration product of C_3S is a nearly amorphous C-S-H which probably has defect calcium environments. The calcium in the C-S-H structure is located either in the main backbone (on which the silicate tetrahedra are attached) or in the interlayer region (Ca^{2+}). It is observed that one signal of relatively higher intensity with an isotropic chemical shift of 69.8 ppm is present in the spectrum. This signal can be accurately assigned to the $\text{Ca}(\text{OH})_2$ (in comparison with the spectrum in Fig 6-3a). Calcium hydroxide, the other hydration product of the C_3S in addition to C-S-H, has a crystalline structure. In order to have a better interpretation of the rest of the signals of the hydrated C_3S , the ^{43}Ca NMR spectra of the more-ordered C-S-H systems is examined as follows.

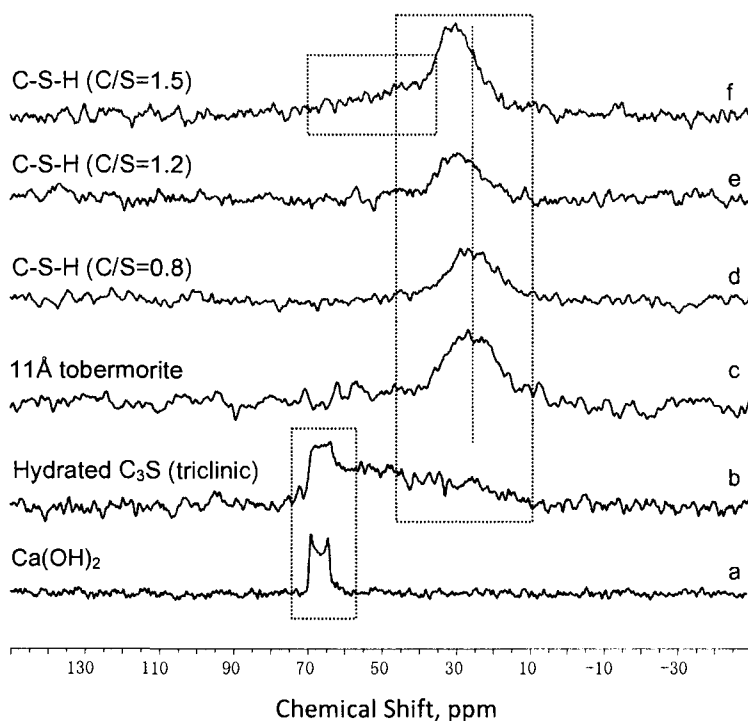


Figure 6-3. The natural abundance ^{43}Ca NMR spectra of various C-S-H systems and CH ; a: calcium hydroxide, b: hydrate triclinic C_3S , c: 11Å tobermorite, and synthetic C-S-H (d: $\text{C}/\text{S}=0.8$, e: $\text{C}/\text{S}=1.2$, f: $\text{C}/\text{S}=1.5$).

The ^{43}Ca NMR spectrum of 11Å tobermorite is shown in Figure 6-3c. It represents a featureless broad signal with the apparent maximum at about 25 ppm. This is significantly different from a maximum at about 0 ppm reported before [23] (after correcting for the difference in the chemical shift of the references). The initial attempts to perform the first principle calculations for 11Å tobermorite were unsuccessful due to the very large size of the unit cell in this material.

The ^{43}Ca NMR results of synthetic C-S-H phases (C/S ratios of 0.8, 1.2 and 1.5 are presented in Figs. 6-3d, 6-3e and 6-3f, respectively) show relatively broad signals at about 27-31 ppm very similar to that for the 11Å tobermorite. It appears that the increase in the C/S ratio results in a slight shift of the location of the main ^{43}Ca signal to more positive chemical shift values (higher frequencies). This means that the calcium atoms are being deshielded in C-S-H. It is known that the mean length of the silicate chain (flanked on Ca-O backbone) decreases as the C/S ratio increases [36]. In other words, the density of the electrons (from silicates) in the vicinity of the Ca atoms decreases. This results in less shielding of calcium environment and is thus responsible for higher observed chemical shift values as the C/S ratio increases. It is also noted that the chemical shift range of the low frequency signals in hydrated C_3S includes that of the main signals of all C/S ratio C-S-H systems. This may suggest that the nanostructure of C-S-H in hydrated cement systems is a mixture of tobermorite- and jennite-like phases as suggested before [37].

Another interesting feature is that a broad signal appears as shoulder on the main signal of the C/S=1.5 C-S-H (Fig. 6-3f) at its high frequency side. This range (although more shielded) corresponds to the region of the hydrated C_3S spectrum in which the $\text{Ca}(\text{OH})_2$ signal is located. It should be noted that at higher C/S ratios, the synthetic C-S-H contains more calcium ions in the interlayer region. Some free calcium hydroxide may even exist. Considering these points, the relatively broad signal on the shoulder of the main signal in C-S-H (C/S=1.5) spectrum is assigned to the calcium ions in the interlayer space. To test if we see all the calcium in the samples, the normalized intensities were compared and the dependence of the intensity of signals versus the delay time (saturation of the signals) was tested. Indeed, the intensity of normalized signals (to the mass of samples and number of scans) grew proportionally with the increase in the C/S ratios (not shown). Considering the analogies between the synthetic C-S-H and the C-S-H in hydrated cement paste, the ^{43}Ca NMR signals of the hydrated C_3S can be assigned to various calcium environments as shown in Figure 6-4.

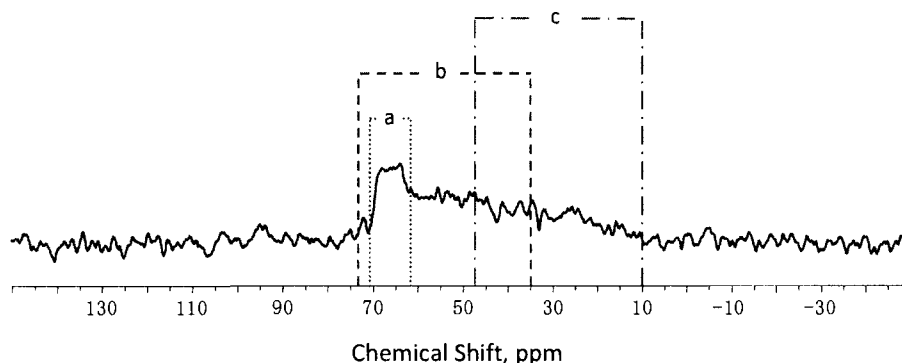


Figure 6-4. Approximate ^{43}Ca NMR chemical shift range of various species in hydrated C_3S ; (a) calcium hydroxide, (b) calcium ions in the interlayer space, and (c) calcium in the Ca-O backbone.

The minerals jennite and tobermorite are often considered as model systems for C-S-H. Recently, an attempt has been made to obtain the ^{43}Ca spectra of these minerals [23]. Although the measurements have been performed at a high magnetic field of 21T, the obtained spectra are of rather poor quality (likely due to improper experimental settings). Nevertheless, the authors drew some far reaching conclusions. More specifically, they question if jennite and tobermorite can be used at all as models for C-S-H. According to the ^{43}Ca NMR results of the current study, it is suggested that the synthetic and more-ordered C-S-H systems have similar calcium environments and can structurally be considered as models for the C-S-H produced in hydrated Portland cement.

6.4 Concluding Remarks

The natural abundance ^{43}Ca solid state NMR spectra of cement-based materials were reported for the first time. The results for the hydrated systems show that the C-S-H produced in the hydration of C_3S has similar calcium structural features to those for the well-ordered C-S-H phases such as synthetic C-S-H (I) and 11Å tobermorite. Although all synthetic C-S-H materials are structurally related to that in hydrated cement paste, the high C/S ratio C-S-H (I) appears to have a calcium environment more related to that of the amorphous C-S-H. The ^{43}Ca NMR chemical shifts of the hydrated C_3S were assigned to the calcium atoms in the Ca-O backbone and interlayer space of C-S-H in addition to that in the free calcium hydroxide.

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Chemical Reactivity of C-S-H

The Hedvall effect was used to investigate the reactivity of calcium silicate hydrates (C-S-H) with variable C/S ratios. The solid state reaction between silver nitrate and various C-S-H preparations occurring during the crystalline transition of silver nitrate was evaluated. Thermal methods as well as microscopic and XRD analyses were employed to study the nature of the reaction products and estimate the chemical reactivity of the C-S-H systems. The overall reactivity includes cationic and anionic species i.e. both calcium and silica enter into the reaction. It appears that the low C/S ratio C-S-H (I) is chemically more reactive. Silver silicate was identified as one of the reaction products.

7.1 Introduction

Two materials that are totally unreactive with each other at room temperature in the solid state may react at higher temperatures when one of them undergoes a crystalline transition. The rate and extent of these surface activated chemical reactions in the solid state that essentially depend on the structural imperfections are usually increased during and as a consequence of crystalline transformation in materials [1, 2]. The thermodynamic changes during a solid state reaction can be readily detected with a thermal analysis instrument. This is used for investigating the chemical reactivity of a solid material. This type of reaction, commonly known as the Hedvall effect, has been applied for studies of the interaction between various chemical compounds, including alkaline oxides and silver salts [3]. Ramachandran and Sereda applied this technique for the first time in cement science to study the reactivity of some cement compounds such as C_3S , β - C_2S , hydrated C_3S and $Ca(OH)_2$ [4]. They showed that C_3S was 4 times more reactive than β - C_2S . They also concluded that all the Ca in C-S-H (from hydrated C_3S), including that in the interlayer, is equally reactive.

The structure of amorphous calcium silicate hydrate (C-S-H), the main reaction product of the hydration of Portland cement, is not fully resolved [5]. Synthesized, crystalline C-S-H has been studied extensively as a model system for the C-S-H in cement paste [6-8]. Chemical stability of the cementitious materials in various environments is one of the important issues related to the sustainable development and durability. Evaluation of the chemical reactivity of different C-S-H preparations is essential for the development of more chemically stable cement-based materials.

A variation in the C/S ratio of the C-S-H results in different physical and chemical characteristics of the material [9, 10]. There are also at least two distinct types of C-S-H present in the hydration products of Portland cement [11-15]. In this study, the relative reactivities of synthetic C-S-H phases (with different C/S ratios), $Ca(OH)_2$ and hydrated C_3S were evaluated applying the Hedvall effect method. There is a reaction between each of these materials and $AgNO_3$ when their mixture is heated through the transition temperature of silver nitrate ($\sim 190^\circ C$). They quickly form a reciprocal pair at this temperature[∇]. An exothermic peak on cooling in a TGA-DSC experiment, due to the recrystallization of the unreacted silver nitrate is observed. The peak area can be calibrated so that the amount of unreacted $AgNO_3$ remaining after the reaction can be

[∇] This involves the mutual exchange between two molecules eg $BaO + CaCO_3 = CaO + BaCO_3 + Q$.

estimated. The relative reactivities of the C-S-H compounds can be evaluated by a comparison of the percentage of reacted silver nitrate with respect to the estimated C-S-H formula weight.

7.2 Experimental Procedure

7.2.1 Materials

Synthetic C-S-H samples were prepared at variable C/S ratios including 0.6, 0.8, 1.0, 1.2 and 1.5. Hydrated C_3S at a water/solid of 0.50 was also investigated. Reagent grade silver nitrate (Fisher Scientific) and calcium hydroxide (Anachemia) were used.

The C-S-H, $Ca(OH)_2$ and hydrated C_3S were ground with a mortar and pestle and dried for 5 hours under vacuum at 100 °C. All the materials along with the $AgNO_3$ were sieved through mesh No. 100. A mixture of 90% $AgNO_3$ and 10% of each of the samples by mass was placed in amber glass vials and shaken for 1 minute using a Spex mixer in order to obtain a homogenous mixture of dry reactants. It is very important that the fine particles of the materials are completely mixed together in order to have an efficient solid state reaction.

7.2.2 TGA-DSC

A 7 mg sample from the blended material was heated from ambient to 250 °C in a simultaneous (TGA-DSC) SDT Q600 T.A. instrument at 10 °C/min under the 100 mL/min flow of nitrogen gas. The sample was held at 250 °C for 10 minutes. It was then cooled at 10 °C/min to 100 °C. A TGA-DSC test was conducted on pure silver nitrate and C-S-H in a similar heating procedure. Mass change and heat flow measurements were recorded during the heat treatment and analyzed using Universal Analysis 2000 software. The test was repeated for the C-S-H- $AgNO_3$ samples in order to minimize any errors due to possible inhomogeneity of the mixtures. Results were interpreted based on the average of the two readings.

For calibration purposes, DSC was conducted on a series of samples containing mixtures of various percentages of SiO_2 (ground silica sand) and $AgNO_3$. Since there is no chemical reaction between silica and silver nitrate, the area under the exothermic peak in the cooling cycle is attributed to $AgNO_3$. A calibration curve was obtained by plotting this area versus different proportions of the silver nitrate. The DSC was also conducted on an empty crucible with a 10mg platinum wire in order to correct the baseline deviation.

7.2.3 X-Ray Diffraction

The residue after heat treatment in the TGA was collected from the crucible for XRD analysis. The X-ray diffraction measurements were performed using a Scintag XDS 2000 diffractometer and CuK_α radiation. Spectra were obtained in the range $4^\circ < 2\theta < 85^\circ$ using a step size of 0.03° at 5 sec. intervals.

7.2.4 SEM-EDS

SEM images were collected using a Hitachi S-4800 Field Emission Scanning Electron Microscope. Surface structure images were taken using a beam current of 10 mA at 3.2×10^{-16} J (2 KV). Images were acquired using an integrated frame capture with 32 frames to reduce random noise, at a working distance of 8 mm and each area of interest was captured using a series of field magnifications from 5K to 80K. Back scattered images were obtained for examining the approximate elemental distribution. Energy dispersive spectrometry (EDS) was used to determine the elemental content of areas of interest. The EDS spectra were acquired using a beam current of 10 mA at 3.2×10^{-15} J (20 KV). Spectral images and data were obtained at a working distance of 15 mm. Semi-quantitative results were based on ZAP software database reference values and are indicative of relative elemental content rather than absolute values as no reference standards were used.

7.3 Results and Discussion

The applicability of the Hedvall effect described in this study relates to the interaction of cement hydrates (C-S-H) and silver nitrate by heating the mixture from ambient to 250°C . Pure silver nitrate has two endothermic peaks in the heating cycle at 174°C and 210°C (Figure 7-1a). The first one is due to the α to β crystalline transition and the second peak is caused by the transition from solid to liquid phase [16]. On cooling, however, there is only one exothermic peak (at 202°C) indicative of the re-crystallization of silver nitrate (Figure 7-1b) [4]. There is no mass change during the heating and cooling cycles.

It appears that both endothermal events on heating merge into one single exothermal event on cooling. This is based on the observation that if reheated, the residue from the first heating-cooling cycle produces exactly the same two endothermal peaks. However, the heat equilibrium conditions are not fully satisfied as evidenced by the sum of the areas under the endothermal

peaks that is greater than the area under the exothermal peak. It is suggested that other phenomena may be involved that fulfill the requirements for equilibrium since all peaks are reproducible.

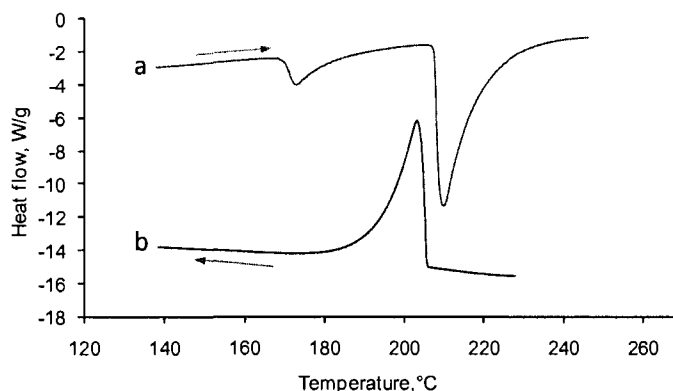


Figure 7-1. Heat flow curve of pure silver nitrate (a) on heating (b) on cooling

The calibration curve of the exothermic peak that occurs on cooling based on the heat flow in the mixture of silver nitrate and silica is shown in Figure 7-2.

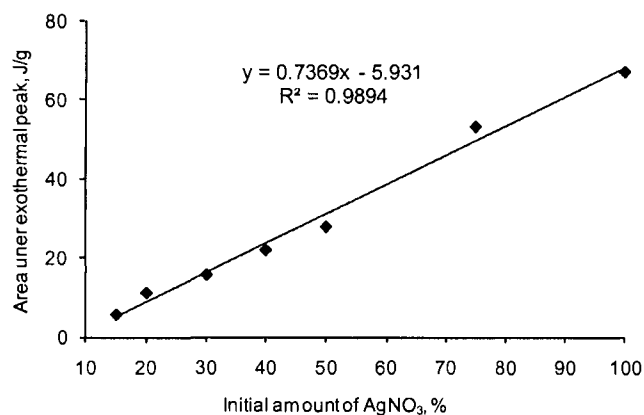


Figure 7-2. The calibration curve for the area of the exothermic peak in the curve for heat flow versus the initial amount of silver nitrate (if it remains completely unreacted).

There is a linear correlation between the area under the exothermal peak and the amount of initial silver nitrate in the mixture. This calibration curve can be used as a reference to estimate the area under the exothermic peak if the total amount of silver nitrate remains unreacted (A_0). When a reaction occurs between the test material and some of the silver nitrate, the area of the exothermic peak (A_x) representing the amount of unreacted silver nitrate will be less than A_0 . Therefore an estimate of the reacted amount of AgNO_3 (R_{AgNO_3}) can be expressed as:

$$R_{\text{AgNO}_3} = 1 - A_x/A_0 \quad (1)$$

The heat flow and mass change derivative curves obtained by TGA-DSC analysis for the mixture of reagent grade calcium hydroxide and silver nitrate are shown in Figure 7-3. On heating, there is a sharp peak in the mass-loss derivative curve at about 190 °C. It is situated at a temperature between that of the two endothermic peaks (heat flow curve) close to the initiation temperature of the second peak. It is known that the solid-state reactions happen in association with the crystallographic transformation state and at the temperatures that approximately coincide with appreciable self-diffusion of the reactants [1, 17]. This mass loss accompanies the decomposition of the reactants and the release of some gas from the system after the reaction. Possible gases can be H_2O from the decomposition of the calcium hydroxide or H_2 from unstable silver hydroxide that can be formed during the chemical reactions. However, the reaction product itself does not appear to have an obvious effect on the heat flow curve. This might be interpreted to mean that as a result of the Hedvall effect the final products consist of only a mixture of decomposed materials. It should be noted, however, that none of the starting materials (AgNO_3 and Ca(OH)_2) taken separately decompose at this temperature.

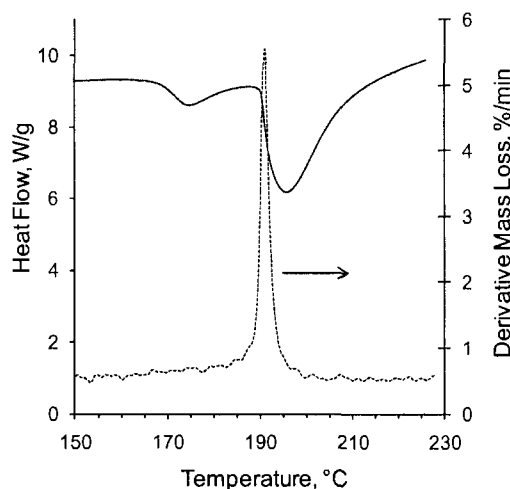


Figure 7-3. Derivative mass loss and heat flow curves for the Calcium Hydroxide-Silver Nitrate mixtures on heating.

On cooling, there is an exothermic peak (not shown) corresponding to the recrystallization of unreacted silver nitrate. Using the calibration curve, it is possible to estimate the reacted proportion of silver nitrate (R_{AgNO_3}), which is 37.8%. Therefore, assuming that two moles of AgNO_3 react with 1 mole of Ca(OH)_2 , it is estimated that 74.2% of the calcium hydroxide has reacted. Theoretically, all of the Ca(OH)_2 should react with AgNO_3 . The 25.8% of the calcium hydroxide that did not react, might possibly be due to the relatively high rate of heating since the reaction between Ca(OH)_2 and AgNO_3 might not be instantaneous [18].

The Hedvall effect results including the heat flow curve and the mass loss derivative on heating are respectively shown in Figures 7-4 and 7-5 for C-S-H samples. The two endothermic peaks on heating (Figure 7-4) are similar to that occurring in pure silver nitrate. However, there is small shift at the start of the second peak for C/S ratios of 1.2 and 1.5. Mass loss derivative curves (Figure 7-5) reveal a mass loss near the temperature of the second endothermic peak. It is noticed that there are two peaks on the mass loss derivative curve for C/S of 1.0, 1.2 and 1.5, occurring at the temperatures of about 196 °C and 208 °C, respectively. The temperature of the first peak is very close to that in the reaction between reagent grade $\text{Ca}(\text{OH})_2$ and silver nitrate (Figure 7-3). It is also known that there is some free lime and Ca^{2+} in the interlayer region in high C/S ratio C-S-H [5]. It is, therefore, suggested that the first peak is associated with minor amounts of $\text{Ca}(\text{OH})_2$. The second peak, which is also present in low C/S ratio C-S-H, is probably an indication of the association of lime within the structure of the C-S-H.

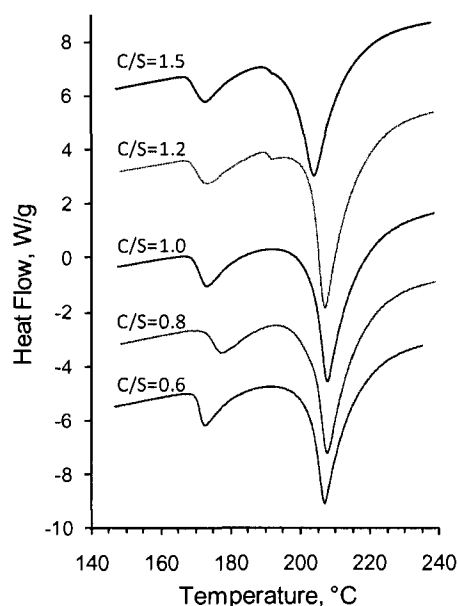


Figure 7-4. Heat flow curve on heating for C-S-H- AgNO_3 mixtures (Endothermal down).

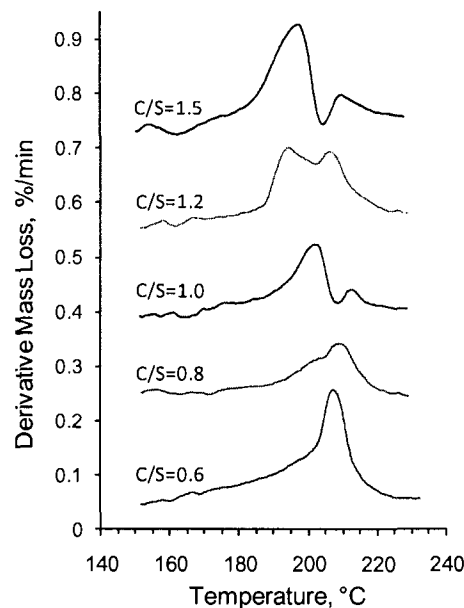


Figure 7-5. Derivative mass loss curves for mixtures of silver nitrate and C-S-H phases on the heating cycle.

In the TGA-DSC experiments the same heating cycle on pure C-S-H (not shown) did not result in any endothermic or exothermic peak within the range of temperatures utilized in the Hedvall effect study and the mass loss was trivial compared to that caused by the reaction with silver nitrate. As mentioned in the materials section, the C-S-H was initially dried at 100 °C before the Hedvall effect experiments. This treatment removes almost all the evaporable water.

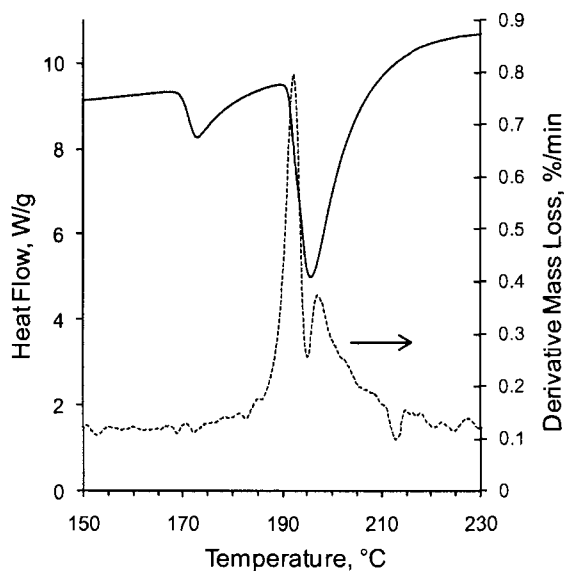


Figure 7-6. Derivative mass-loss and heat flow curves for fully hydrated C_3S subjected to a heating cycle in Hedvall effect test.

The heat flow and mass-loss derivative curves of mixtures of hydrated C_3S and silver nitrate (Figure 7-6) are very similar to those for the C-S-H–silver nitrate mixture prepared at C/S ratio of 1.5. The existence of two peaks on the mass-loss derivative curve can be considered as additional evidence for the similarity between the chemical properties of high C/S ratio synthetic C-S-H and those of naturally forming C-S-H produced in the hydration of Portland cement [19]. Also the mass-loss derivative peaks for the hydrated C_3S are sharper than those for the C-S-H formed through the reaction of CaO and SiO_2 . This is probably due to the existence of more crystalline free lime in the hydration of C_3S in addition to the calcium hydroxide within the structure of C-S-H since calcium bonds at similar structural locations are likely to take part in the reactions at a similar temperature. For C-S-H in hydrated cement paste (with variable C/S ratio) it is suggested that the various degrees of local polymerization may result in a wider range of temperature under which a solid-state reaction occurs.

The heat flow cooling curves for C-S-H samples are presented in the Figure 7-7. There is evidently a noticeable difference in the exothermic peaks of C-S-H in two groups separated at the C/S ratio of 1.0. C-S-H samples with a high C/S ratio (i.e. 1.2 and 1.5) exhibit a single peak on cooling that is an indication of the recrystallization of unreacted silver nitrate. This peak occurs at about 183 °C and is located at a similar temperature corresponding to the peak following the reaction of $Ca(OH)_2$ with $AgNO_3$. C-S-H at lower C/S (i.e. 1.0, 0.8 and 0.6), however, exhibits

two exothermic peaks at temperatures of about 191 and 165 °C. C-S-H at C/S=1.0, demonstrates intermediate behavior. A second peak exists as a shoulder on the main peak. Distinct characteristics have been observed in C-S-H systems depending on the C/S ratio with a transition occurring at the C/S ratio of 1.0-1.2 [14]. Some of these differences were presented in previous chapters.

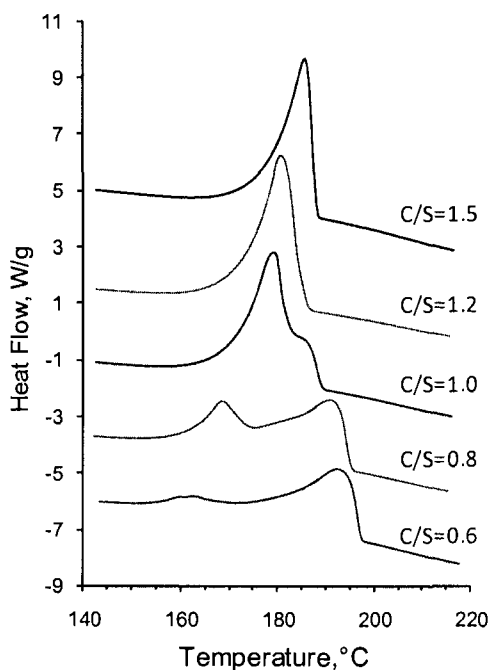


Figure 7-7. Heat flow curve on cooling for C-S-H – Silver Nitrate mixtures. The C/S ratio varies from 0.6 to 1.5 (Exothermal Up)

The formation of these two peaks suggests the possibility that two different crystalline materials are solidifying on cooling. It may also be a result of recrystallization of silver nitrate at different temperatures caused by the existence of nearby molecules in the bulk mixture of the materials with different heat capacities. In order to verify these speculations, an XRD analysis was conducted on the residue after the reaction of C-S-H (C/S=0.6) with silver nitrate. The XRD spectrum matches well with that of pure silver nitrate (Figures 7-8a and 7-8b). It is indicative of only one phase due to the masking effect of a large amount of unreacted AgNO_3 present in the residue.

In order to examine the latter possibility, a mixture of 10% silver nitrate and 90% C-S-H (C/S=0.6) was prepared for the Hedvall effect test. All the AgNO_3 was consumed in the reaction with an excessive amount of C-S-H and the residue contained some unreacted C-S-H as well as the

reaction products. XRD analysis was conducted on this residue (Figure 7-8c). This spectrum is different from that of pure C-S-H (C/S=0.6, Figure 7-8d) and has additional relatively high intensity peaks at about 31-36 degrees 2θ .

The JCPDS database was searched for possible fits. Based on the initial speculations for the reaction product, the main peaks of silver silicate (ID NO. 37-0344) with the chemical formula of Ag_2SiO_3 appeared to conform well with the unknown peaks marked in Figure 7-8c. The research work upon which this spectrum was based, employs a solid state reaction between calcium silicate or sodium silicate and silver nitrate in a heating cycle up to the temperature of 300 °C [20]. It is thus possible that silver silicate forms in the solid state reaction between C-S-H and AgNO_3 .

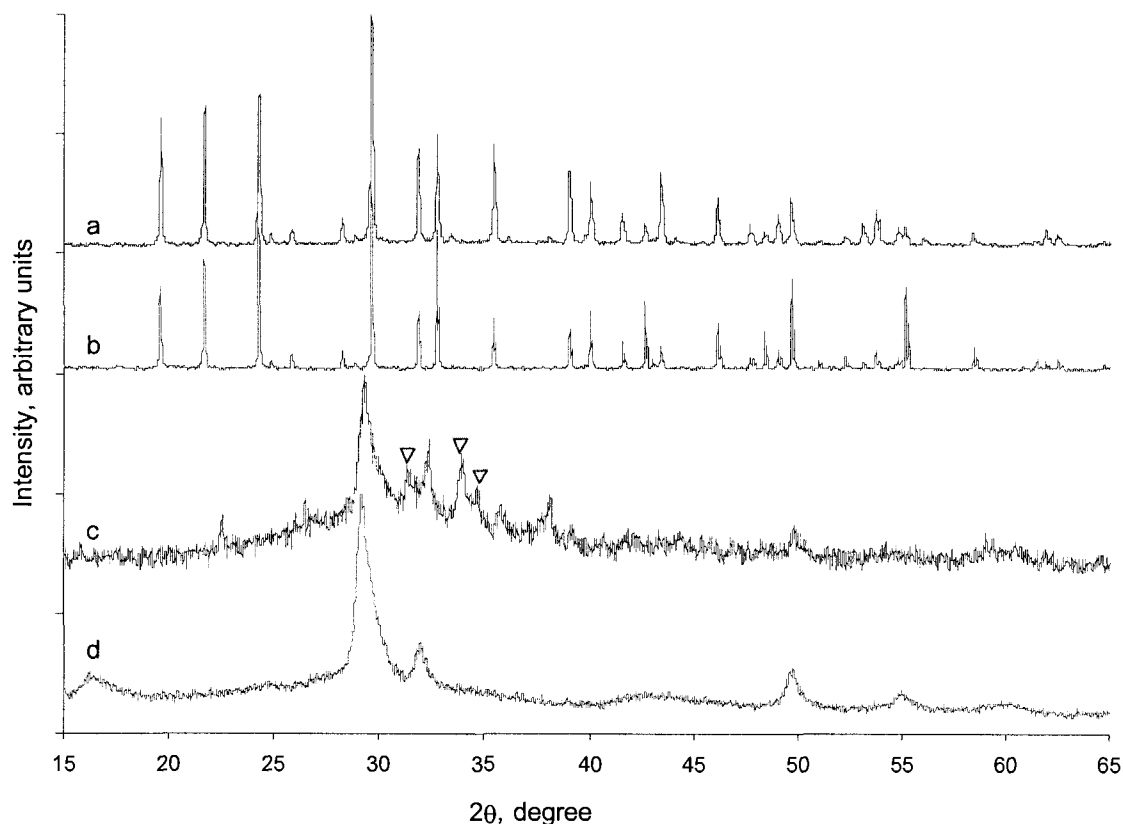


Figure 7-8. XRD analysis of (a) the residue after the Hedvall effect test between C-S-H (C/S=0.6) and silver nitrate, (b) pure silver nitrate, (c) residue after the solid state reaction between an excessive amount of C-S-H (C/S=0.6) and silver nitrate, (d) phase pure C-S-H (C/S=0.6). The ▽ Indicates additional peaks of relatively high intensity in the spectrum for (c) compared to the spectrum of pure C-S-H (d)

Further evidence for the formation of silver silicate was obtained by conducting a TGA-DSC experiment on the residue after the solid state reaction between C-S-H and silver nitrate. Heat flow curves for a second cycle of heating and cooling are presented in Figure 7-9. The heating cycle results in the appearance of shoulders on both endothermic peaks. This suggests that if a new product has formed it has a phase transformation characteristic and a melting point similar to those for the reagent grade silver nitrate. On cooling, the additional two peaks are observed again.

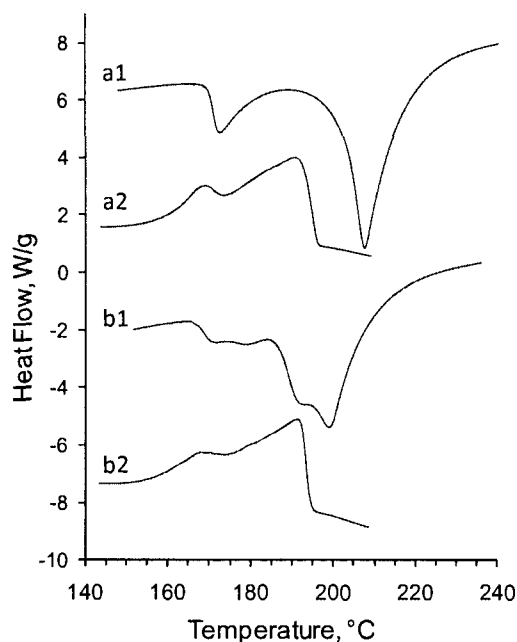


Figure 7-9. Heat flow curve of C-S-H (C/S=0.6); first cycle: (a1) on heating (a2) on cooling; second cycle: (b1) on heating (b2) on cooling.

The residue of the reaction between silver nitrate and the excessive amount of C-S-H (C/S=0.6) was heated up to 1000 °C (curve not shown). There is only one significant mass loss at temperatures between 390 and 540 °C with a peak in the derivative mass loss curve at 467 °C. A gradual mass loss that exists up to 950 °C can be attributed to the decomposition of C-S-H. The main mass loss (about 3.7%) at 467 °C seems to be related to the silver silicate as its different crystalline forms have been reported to have a decomposition temperature of 400 or 461 °C [20, 21].

Electron microscopic analysis of the residues remaining after TGA for various C/S ratio C-S-H preparations reveals three different phases. Micrographs in the Figures 7-10 and 7-11 show the normal and back-scattered imaging of the surface morphology of the residue for a C/S ratio of 0.6 and 1.5. In both cases, there is a dense background (I) in which there are large solid particles (II)

as well as smaller granular elements (III). Due to the large difference of the atomic number of Ag and other elements in this reaction, the backscattered images were proven useful. Lighter gray areas in the micrographs 7-10b and 7-11b are indicative of Ag-rich environments. EDS analysis confirmed that these particles contain only Ag. EDS results also showed that the background is composed of a mixture of Ag, Ca and Si that is likely the main reaction product. In the small granular elements that generally have angular shape, Ag and Si exist but no Ca. A high resolution SEM image of one of these particles is shown in Figure 7-12. This compound might be a crystalline form of the silver silicate evidenced by XRD and TGA results. The morphology of this particle has similarities with those micrographs for the product in the $\text{Ag}_2\text{O-SiO}_2$ system [22].

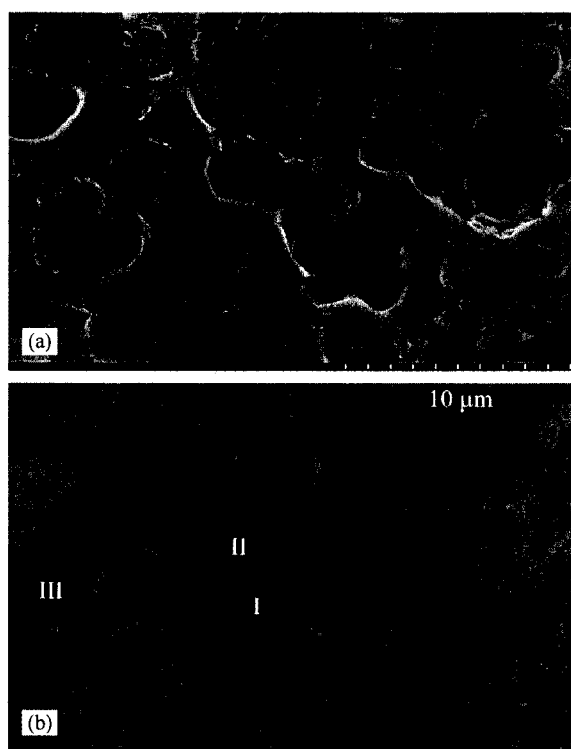


Figure 7-10. Normal (a) and back-scattered (b) micrographs of the residue after the Hedvall effect test for the mixture of C-S-H ($C/S=0.6$) and excessive silver nitrate.

The presence of two exothermic peaks in the cooling cycle of the heat flow curves for C-S-H- AgNO_3 mixtures indicate that silver nitrate recrystallizes at two different temperatures. Therefore, the area under both exothermic peaks should be taken into account in the reactivity calculations. It should also be noted that the overall reactivity of the C-S-H represents the reaction of both cationic and anionic species in the structure of C-S-H.

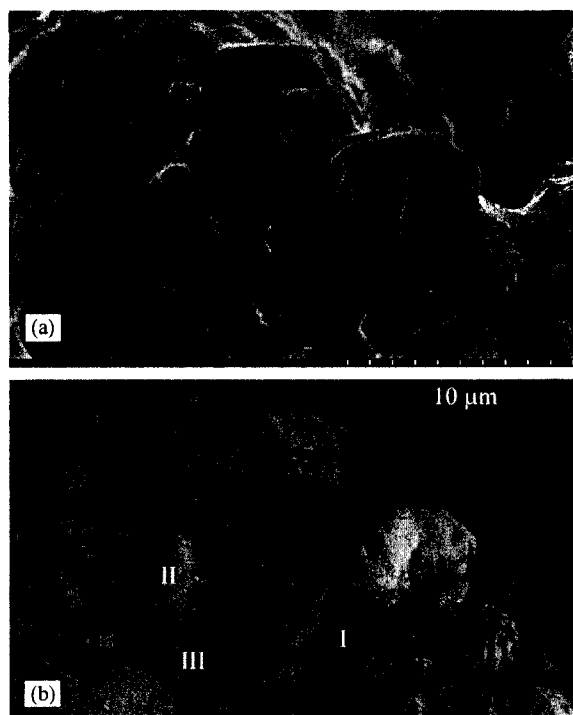


Figure 7-11. Normal (a) and back-scattered (b) micrographs of the residue after the Hedvall effect test for the mixture of C-S-H ($C/S=1.5$) and excessive silver nitrate

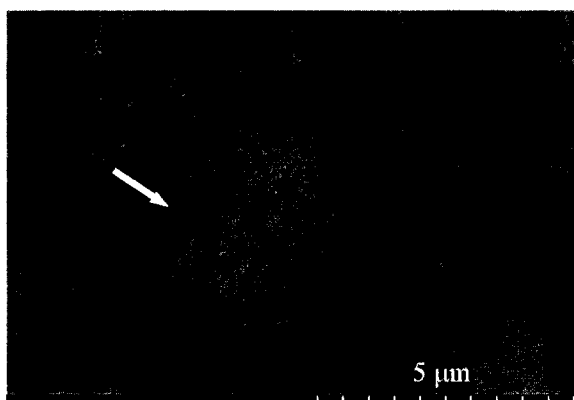


Figure 7-12. Back-scattered micrograph of the typical morphology of the reaction products containing only Ag and Si after Hedvall effect test for the mixture of C-S-H ($C/S=0.6$) and excessive silver nitrate

The area under exothermic peaks in the Hedvall effect test for various C/S ratio C-S-H materials is given in Table 7-1. There is not a considerable difference in the exothermic peak area of various C/S ratio C-S-H samples. The exothermic peak area from the calibration curve (Fig. 7-2) is about 62 J/g for all tests since the mix proportions were similar (initial amount of $\text{AgNO}_3 \approx 91\%$). Accordingly, the reacted silver nitrate (R_{AgNO_3}) can be calculated. In order to evaluate the

reactivity of C-S-H, it is required to have an estimate of its stoichiometry first. C-S-H is not a highly crystalline material and it is very difficult to precisely determine the proportion of CaO, SiO₂ and H₂O in its structure [23]. This is in part due to the fact that the water molecules at various structural locations are not well-separated in terms of their bonding energy. In this study a simple method was employed to obtain a rough chemical formula for the synthetic C-S-H preparations. The C-S-H sample was heated in a TGA instrument (at a rate of 10 °C/min under the flow of nitrogen gas) up to 100 °C. The sample was kept at the temperature for 3 hours. The temperature increase was then continued to 1000 °C and the mass loss in this part of the heating cycle was considered to be due to the removal of constitutional water in the structure of C-S-H. Using a pre-determined CaO/SiO₂ ratio, the stoichiometry can then be calculated.

This approach was considered satisfactory for the Hedvall effect test. The stoichiometric formula was expressed as $x\text{CaO} \cdot \text{SiO}_2 \cdot y\text{H}_2\text{O}$, where 'x' is the C/S ratio. The values of 'y' are given in Table 7-1. The formula weight of C-S-H was expressed as $56.1x + 60.1 + 18y$. Formula weights were used since molar weights of C-S-H are indeterminate due to the ill-formed nanostructure. Thus the number of formula weights of C-S-H in the mixture can be calculated for different C/S ratios. The reactivity of C-S-H is therefore expressed by the number of formula weights of C-S-H reacted per mole of AgNO₃.

Table 7-1. Chemical reactivity calculations for C-S-H (various C/S ratios)

C/S ratio of C-S-H	Exothermic peaks' area from the experiments* (J/g) (A _x)	R _{AgNO₃} (%)	y in xC-S-yH	Reactivity of C-S-H	Surface Area (m ² /g)
0.6	55.40	10.7	0.38	1.30	204.34
0.8	55.11	11.6	0.35	1.00	186.24
1.0	54.37	12.8	0.46	0.80	29.24
1.2	56.80	8.9	0.68	1.07	30.19
1.5	54.02	13.4	0.85	0.62	52.36

* Average value of two tests

The chemical reactivity of C-S-H determined by the Hedvall effect test, decreases as C/S ratio increases (Table 7-1) with the exception of C/S=1.2. At low C/S ratio more SiO₂ sites are available for producing silver silicate. Therefore, more silver nitrate is consumed in the solid state reaction with C-S-H of low C/S ratio. It is assumed that all C-S-H is reacted in the Hedvall effect test [4] and the amount of reacted AgNO₃ is an indication of the overall reactivity of C-S-H.

Surface area of C-S-H increases significantly at low C/S ratios (0.6 and 0.8) as shown in the Table 7-1. The chemical reactivity of a material is generally dependent on its surface area. In this study, although the chemical reactivity of C-S-H determined by the Hedvall effect is the highest corresponding to the highest surface area, the reactivity does not necessarily correlate with the surface area (eg. C/S=1.2). This may indicate that other factors such as nanostructural defects, the reactivity of the interlayer calcium ions and the structural bonds of the various elements (Ca and Si atoms) can influence the reactivity of C-S-H.

7.4 Concluding remarks

- a. The Hedvall effect test is a very quick and elegant method of evaluating the reactivity of various compounds of relevance to cement chemistry. This method can be used to determine the overall reactivity of C-S-H systems.
- b. Silver silicate is formed as a result of the solid state reaction between silver nitrate and calcium silicate hydrate.
- c. C-S-H preparations having lower C/S ratios are generally more reactive.
- d. Various factors such as the presence of interlayer calcium hydroxide, the nanostructural orientation of Ca and Si atoms as well as the surface area influence the overall chemical reactivity of C-S-H

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Dynamic Mechanical Analysis of C-S-H

The dynamic mechanical properties of compacted samples of synthetic calcium silicate hydrate (C-S-H) were determined at variable stoichiometries (C/S ratio). The stiffness and damping properties of the C-S-H systems were monitored at various increments of mass loss from 11%RH following the removal of the adsorbed and interlayer water. The changes in the storage modulus (E') and internal friction ($\tan \delta$) were discussed in terms of the state of water present in the nanostructure of C-S-H, the evolution of the silicate structure and the interaction of calcium ions in the interlayer region. Results were compared to that for the hydrated Portland cement paste and porous glass. It was shown that the C-S-H in the hydration products of Portland cement has a complicated yet analogous dynamic mechanical behavior to that of synthetic C-S-H. The response of these systems upon the removal of water was explained by a layered model for the C-S-H. A mechanistic model was proposed to describe the changes occurring at various stages in the dynamic mechanical performance of C-S-H.

8.1 Introduction

Calcium Silicate Hydrate (C-S-H), the principal product of the Portland cement hydration process, is a major contributor to the important mechanical properties of hardened cement paste such as strength and shrinkage [1]. The nanostructure and mechanical properties of this material have not been clearly understood and the link between chemical composition, microstructure and the mechanical behavior of C-S-H is still ill-defined despite many experimental and modeling studies [2].

It has been argued that the interlayer water present between the layers of C-S-H plays an important role in controlling its mechanical properties [3]. It has been shown that the removal of water molecules in the interlayer region results in significant shrinkage and reduction of the modulus of elasticity (E) of hydrated Portland cement [4, 5]. It is suggested that water molecules occupying the interlayer space can act as a “reinforcement” to the C-S-H layers [4]. Several experiments on the change in the modulus of elasticity (E) at various relative humidity levels indicate that a significant reduction in the value of E occurs when the saturated Portland cement paste is equilibrated at relative humidity levels below about 11% [3, 6]. The humidity at these levels is associated with the interlayer water in addition to a monolayer of water present on the surface of particles. There is about a 40% decrease in the modulus of elasticity in this region determined by static or dynamic methods as shown in Figure 8-1. A structural role was assigned to the interlayer water in these studies. It is inferred that reduction in stiffness in this region cannot be simply due to the microcracking as suggested by Odelson *et. al.* [7]. It has been shown that there is a hysteresis in the modulus of elasticity versus relative humidity curves of the hydrated cement paste [3-5]. The drying cycle consistently has the trend indicated in Figure 8-1 (i.e. a large decrease in E at humidity levels below 11%RH). On rewetting, the E values can increase by as much as 100%. If there was any significant amount of micro-cracking in the specimens during the first drying, the E values in the second and subsequent drying cycles would have continued to gradually decrease and thereafter would not have shown a sudden decrease as in the first drying cycle. Estimation of the changes in the stiffness of cement paste due to other phenomena involving the solid phase such as collapse of the C-S-H layers when interlayer water is removed and possible cross-linking of silicates has received little attention. There is a lack of detailed information for the variations in the elastic response of C-S-H systems in this region.

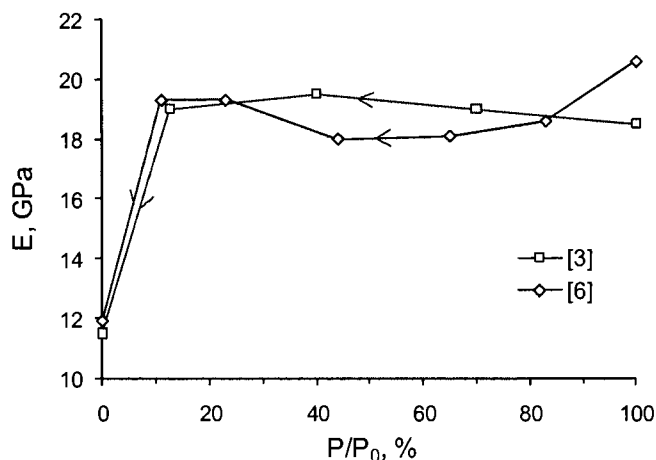


Figure 8-1. Effect of water desorption on the modulus of elasticity of Portland cement paste ($W/C=0.3$ and 0.4 from Ramachandran et al. [3] and Sellevold [6], respectively).

8.1.1 Characteristics of C-S-H in Portland cement paste

The C-S-H that forms in the hydration of Portland cement has variable stoichiometry depending on the water to cement ratio, curing conditions and use of supplementary cementitious materials [8]. It is therefore important to understand the effect of compositional changes on the different properties of C-S-H systems. These studies have been mainly conducted on the synthetic C-S-H materials due to the ease in controlling their chemical composition. Characterization of properties such as modulus of elasticity, creep and strength has been rarely conducted systematically on synthetic or phase pure C-S-H. The main parameter that controls the formation of various synthetic C-S-H structures is the starting molar ratio of CaO to SiO_2 (C/S ratio). The dependence of the mechanical properties of C-S-H on the C/S ratio has received only limited study. It was shown that the intrinsic modulus of elasticity (E_0 , zero porosity value) appears to be independent of the C/S ratio and degree of silicate polymerization [9]. The mechanical properties of the C-S-H in cement paste were also studied by a nano-indentation technique [10]. It was suggested that two types of C-S-H exist in hydrated Portland cement; low density and high density, having a volume fraction of 30 and 70%, respectively. The nanoindentation results showed that the low-density C-S-H phase has a mean stiffness of 22 GPa while the mean stiffness is 29 GPa for high-density C-S-H [11]. These two types of C-S-H identified through mechanical measurements are likely to be compositionally similar. The difference in the modulus of elasticity, therefore, is essentially due to the level of particle packing and change in the porosity at lower scales as suggested by the nanoindentation studies. It was also shown that the intrinsic modulus of elasticity of the C-S-H

phase can be reduced through decalcification (more significantly for the low density C-S-H) and this appears to be the main factor in the degradation of elastic modulus at the macroscopic level.

Plassard et al. employed nanoindentation methods (using Atomic Force Microscopy) to measure the elastic modulus of C-S-H formed on the surface of a calcite crystal in sodium silicate solution [12]. The C-S-H produced was equilibrated at various concentrations of calcium hydroxide solution in order to achieve different stoichiometries. It was shown that the elastic modulus increases at higher Ca^{2+} contents with an inflection point at a concentration of about 8 mmol/L (corresponding to a C/S ratio of 1.1 [13]) suggesting a phase transition. It was also proposed that silanol-water-silanol bonds (source of interlayer cohesion) are replaced by SiO^- - Ca^{2+} - SiO^- bonds when C/S ratio increases causing a reduction in the interlayer space and an increase of the compactness that in turn improves the modulus of elasticity.

The elastic properties of C-S-H have also been estimated through dynamic molecular modeling and free energy minimization techniques [14]. These methods were primarily used in order to evaluate the stability of the structural models of Hamid [15] and Merlino *et al.* [16] for tobermorite systems. The simulated values suggest that the average Young modulus can increase from 63.5 to 89 GPa consistent with the increase in C/S ratio from 0.83 to 1.0. The interlayer distance was found to be very important for these mechanical changes.

It has been also suggested that the attractive electrostatic forces active at short and medium ranges contribute essentially to the cohesion of C-S-H [17]. The mechanical properties of crystalline C-S-H systems were also investigated using lattice dynamic simulations [18]. Calculations indicated that the Young's modulus values (although very scattered) decrease slightly when the C/S ratio increases. High modulus values (compared to experimental results) were computed for various C-S-H systems similar to other theoretical studies [14, 18]. An increase in the mean silicate chain length in tobermorite systems was also shown to result in an increase of the modulus. A silicate structure containing defects was therefore suggested as a possible reason for the discrepancy of the theoretical and experimental results.

The source of the cohesion forces in synthetic C-S-H and C-S-H formed in cement paste has not been definitively determined. Although van der Waals and capillary forces partially contribute to the cohesion of such materials [19], the major factor that keeps the layers stable is associated with the iono-covalent properties of chemical bonds in the interlayer. In this situation, calcium ions

and water molecules are strongly localized [14].

In the current study, dynamic mechanical properties of phase pure C-S-H compacts prepared at various C/S ratios were determined. The variation in the stiffness and damping characteristics of C-S-H upon the removal of adsorbed and interlayer water is discussed. The role of water molecules on the C-S-H surface and in the interlayer region, the nanostructural changes in the silicate structure and the interactions of ions in the interlayer space on the removal of water are considered as possible mechanisms contributing to the mechanical performance of C-S-H. Results for synthetic C-S-H are compared to those for the C-S-H in hardened cement paste and porous glass. An attempt is made to relate the local order and composition of C-S-H systems to some of their macroscopic mechanical properties. Additional evidence supporting the view that the properties of synthetic layered C-S-H are analogous to those for C-S-H present in the Portland cement paste is presented and discussed. A mechanistic model is proposed for the changes in the mechanical behavior of C-S-H (variable composition) at various stages of drying. The hydrated Portland cement systems may contain a wide range of C-S-H phase compositions depending on the mixture proportions and curing conditions. It is therefore difficult to assess the contribution of each phase to the mechanical performance of hardened cement paste. The results from this study using phase pure C-S-H, however, offer new evidence to better understand the nature of the C-S-H phases and the role of water in their nanostructure. They should also help improve modeling the mechanical properties of hydrated Portland cement at the micro and nano-level.

8.2 Experimental

8.2.1 Materials

C-S-H having C/S ratios of 0.8, 1.0, 1.2 and 1.5 was synthesized according to the method previously described. This range of C/S ratio fits in the category of C-S-H (I) proposed by Taylor [8]. Two other sets of samples were prepared for comparison purposes: cement paste and porous Vycor[®] glass. Rectangular prisms (250x100x12 mm) were cast from the Portland cement paste (Lafarge Canada Type I, 2008) at a water/cement ratio of 0.4. The samples were vibrated and stored in a moist curing room for 24 hours. They were then demoulded and curing was continued for 2 months in a saturated lime solution. Thin slices (~1x12x60 mm) were cut from the cement prism using an Isomet diamond saw. The cooling agent was saturated lime solution in order to avoid calcium leaching. Vycor porous glass plates (thickness=1.3 mm, surface area=110 cm²/g, porosity~ 28%) were cut to give rectangular specimens measuring 12x60 mm. The length of the

specimens was chosen according to the standard requirements of the three point bending test [20, 21].

8.2.2 Humidity conditioning

The C-S-H powders, cement paste slices and porous glass were conditioned for three weeks in a vacuum desiccator over the vapor pressure of a saturated lithium chloride solution. This gives a relative humidity of about 11% at room temperature which is a good base for studying the stoichiometry of C-S-H [22]. There is, theoretically, only a monolayer of adsorbed water on the surface of particles at this specific humidity in addition to the interlayer water. This moisture state was used as the starting condition of the experiments. C-S-H compact bars were therefore prepared from the 11%RH conditioned powder.

8.2.3 Preparation of compacted C-S-H samples

A rigid body of the material is required for any type of investigation of mechanical properties of materials such as dynamic mechanical analysis. It is necessary to prepare solid samples by compressing the fine powder for the studies on powdered materials such as synthetic C-S-H, in order to measure the mechanical properties [23, 24]. In addition, it is possible to extend the range of porosity and avoid some of the limitations inherent in the use of natural rigid porous materials. It has been shown that the compacted specimens of powdered hydrated Portland cement have similar properties to the original hardened paste of the same sample [4, 25, 26]. The mechanical properties of compacted C-S-H powder specimens are considered analogous to those of the C-S-H in cement paste.

In order to have useful and reliable DMA data a recommended range of sample thickness has to be used according to the experimental specifications. Through a trial and error process, the mass of the C-S-H powder was varied so that the thickness of the bar resided within the limits of 0.6 to 3.0 mm suggested for each individual C-S-H compact bar (depending on its complex modulus of elasticity calculated after the initial tests). It was decided to use two grams of powder from each composition in order to satisfy the thickness requirements and simplify the procedure. Also, the length of the sample has to be 10% more than the space between the supports on both sides and the thickness should not vary more than 2% of the mean value along the length of the sample [20, 21]. Additional details for the compaction technique can be found in chapter 3.

The C-S-H powders (conditioned at 11%RH) were compacted in order to make rectangular solid bodies. Four compact bars were prepared for each C/S ratio applying different compaction pressures. The porosity-pressure dependence had been determined before the experiments for each specific C/S ratio and was used as a calibration. In order to determine the porosity-pressure dependence, compacts of two grams of C-S-H (for each C/S ratio) were prepared at four different compaction pressures (80, 200, 358 and 518 MPa). The porosity of the compacted sample was determined using a helium pycnometer. The latter provides a measure of the solid volume in the sample. Porosity is calculated knowing the apparent volume and the solid volume of the compacted sample. The porosity-pressure curves can be fit with an exponential equation. The pressure required to produce a compact having a specific porosity value is obtained from the pressure-porosity curves for each C/S ratio. A separate set of samples were also prepared for the study on the effect of the removal of water on the mechanical behavior of C-S-H. For this set, a specific compaction pressure was applied for each C/S ratio C-S-H powder in order to achieve similar porosities (about 30%) in the compacted samples. The pressure applied for each C-S-H sample was 496, 517, 331 and 438 MPa, respectively, for the C/S ratio = 0.8, 1.0, 1.2 and 1.5. At the relatively low porosity level of about 30% there is a sufficiently large fraction of the solid material to better represent the behavior of the C-S-H. This volume fraction of pores is also desired since the hydrated Portland cement paste ($w/c=0.40$) and porous glass had porosity values of 26% and 28%, respectively. A length of 60 mm was cut from the middle of the rectangular compact bars to fit the specimen requirements in the DMA testing instrument. The thickness varied between 0.8 and 1.2 mm depending on the C/S ratio and the compaction pressure. It is essential to compare the mechanical properties of various C-S-H compositions, cement paste and porous glass in a similar porosity range. Porosity is an important parameter in controlling the mechanical performance of solids. The variation in the other factors influencing the mechanical characteristics of C-S-H can therefore be evaluated almost independent of their total pore volume.

8.2.4 Dynamic Mechanical Analysis (DMA)

In this technique the displacement of the sample is measured when an oscillating force is applied [27]. The stiffness of the material is calculated from the deformation under load. The elastic property obtained in DMA is called the storage modulus (E') that is analogous to the static modulus of elasticity. There is also usually a time lag between the applied force and the resulting displacement. The time lag can be measured as a phase angle between load and the displacement due to their ideally sinusoidal nature. The tangent of this angle ($\tan \delta$) represents the material's damping property or internal friction.

The DMA analysis was conducted using a Rheometrics RSA II instrument on the C-S-H, cement paste and porous glass samples starting from the 11%RH condition. The test was conducted on the same specimen after incremental drying at various mass loss levels. The removal of water was achieved by the application of a combination of vacuum and heat in a special drying cell. Maximum care was taken in the sample treatment. The combination of vacuum and heat was applied over a long period of time in order to avoid any physical damage to the samples. The initial mass loss levels were obtained only through vacuum at room temperature. The temperature was gradually increased and only exceeded 50 °C at mass loss values above about 8%. Obtaining the last couple of data points without applying higher temperatures (but below 110 °C) was inevitable. This did not affect the oscillatory nature of the E' and $\tan \delta$ vs. mass loss curves. The sample was mounted on the three point bending apparatus shown in Figure 8-2.

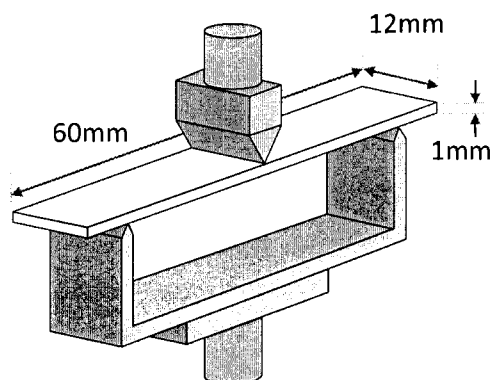


Figure 8-2. Three point bending setup for the dynamic mechanical analysis of rectangular bar specimens showing approximate dimensions.

A very low amplitude oscillation was applied on the brittle thin samples (~1 mm thick) in order to prevent any damage or microcracking. This was confirmed by a microscopic analysis after the experiment. Moreover, no decrease was observed in E' value when a trial specimen was repeatedly subjected to the same loading procedure. Samples were tested at a frequency of 0.1Hz for displacement. The original experiments were conducted in the frequency range from 0.1 to 10 Hz. It was observed that the E' and $\tan \delta$ -mass loss curves had similar features at all frequencies. The oscillatory trend in the E' and $\tan \delta$ (section 3.2) was observed at all frequencies and was independent of the moisture content. The intensity of the peaks in the curves, however, was decreased by increasing the frequency. The data for the lowest frequency (0.1 Hz) was, therefore, reported in which the variations were more distinguishable.

A strain of 0.01% (in the elastic region) was applied with an initial static load of 20 g in order to ensure a good contact between the upper fixture and the surface of the specimen throughout the dynamic loading. The induced stress was below 2 MPa which is low enough not to introduce any significant damage or micro-cracking to the sample. The initial values might be set differently for various samples depending on their response to the load. Before conducting the experiments, the calibration of the equipment was checked using the standard weights and a steel bar. The response of the sample was recorded and analyzed by the RSI orchestrator computer software.

8.3 Results and discussion

8.3.1 Dynamic mechanical properties versus porosity

The results of the E' (storage modulus), and $\tan \delta$ (internal friction) are presented in the Figure 8-3 for various C-S-H preparations ($C/S = 0.8$ to 1.5) compacted to different porosity levels. The data variation in this set of results is about $\pm 5\%$. A set of tests was also conducted on Portland cement paste and porous glass for comparison. In all C-S-H samples, the storage modulus (E' , shown in Figure 8-3a) decreases as the porosity increases as expected [9]. The regression curves are well separated based on their C/S ratio for all specimens except $C/S=0.8$ at porosity values less than 35% which exhibits lower values of E' . This does not seem to be an error as it was reproduced several times. It appears that for $C/S=0.8$, that has a very high BET surface area of about $186 \text{ m}^2/\text{g}$, the presence of water monolayer on the surface of agglomerates causes some technical problems at low porosity values. The water at these states has to be displaced when the surface of C-S-H agglomerates come into contact in the compacted samples. At porosities greater than 35% the values of E' for $C/S=0.8$ are greater than the other C/S ratios. Low C/S ratio C-S-H that can be prepared through decalcification of the cement paste [11, 28] or equilibrating the synthetic C-S-H in low lime content solutions [12] has lower stiffness compared to the starting material. This, however, is not in contradiction with our observations of high elasticity values at lower C/S ratios (at the same porosity). This may suggest that the governing factor in the decalcification of the paste is the increase in the porosity level of the solid due to the leaching of calcium out of the material. Current work utilizes careful sample preparation in order to compare the mechanical properties of various C-S-H compositions at the same porosity – an important parameter in controlling the mechanical behavior of materials. It is also possible that the decrease of strength after calcium depletion might be due to other microstructural changes in the solid body such as microcracking. Low C/S ratio C-S-H has a greater degree of polymerization and

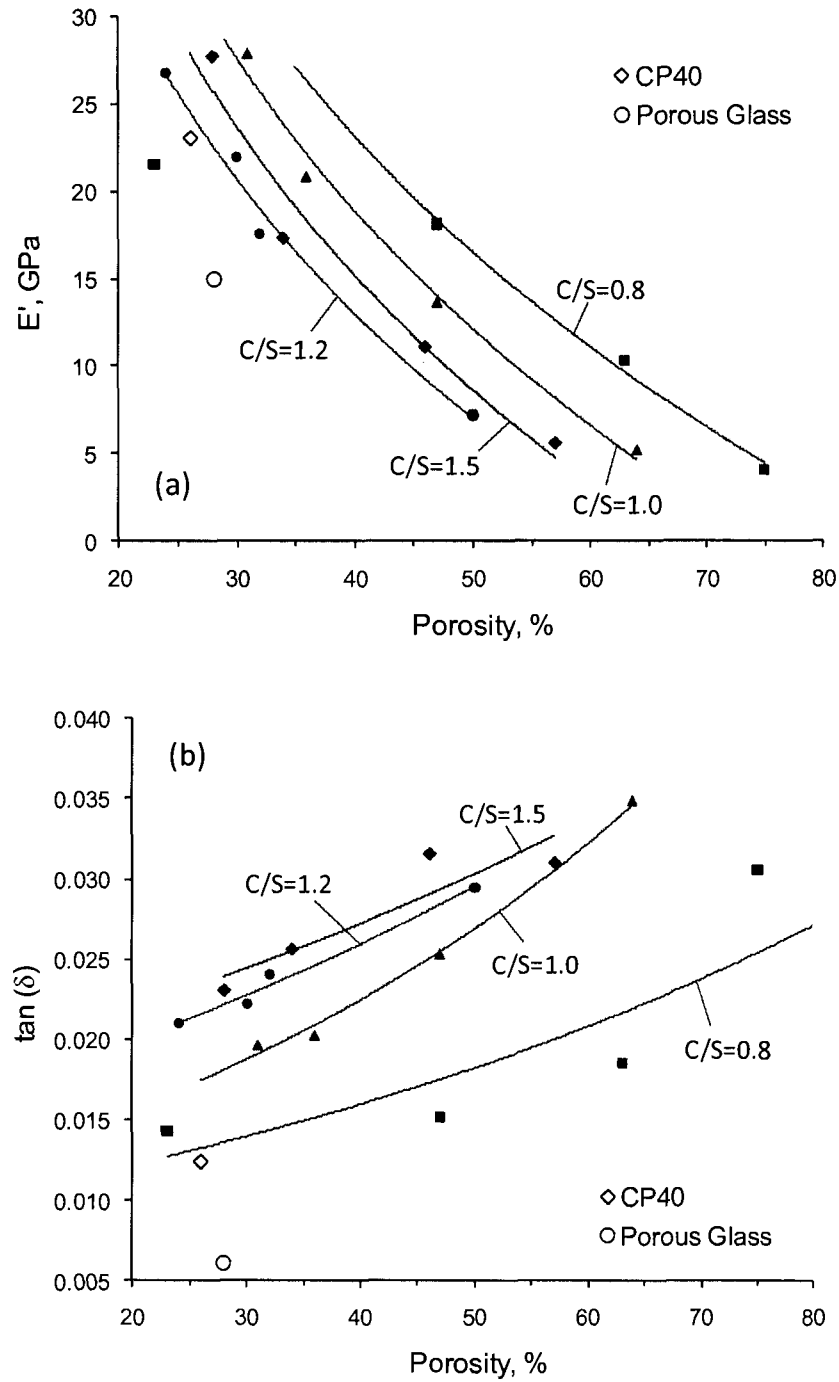


Figure 8-3. The DMA results (E' and $\tan \delta$) for C-S-H samples (various C/S ratios and different porosities) at 11%RH compared with the hydrated Portland cement (CP40) and porous Vycor® glass: (a) storage modulus, (b) internal friction.

longer silicate chains. It is suggested that the continuity of the solid phase is improved for C-S-H compacts having lower C/S ratio. Longer silicate chains may better “reinforce” the Ca-O backbone of the C-S-H sheet. This may augment the stiffness of the material. Consistent results have been recently obtained using dynamic molecular modeling of the C-S-H suggesting that the chain length of the silicate tetrahedra directly influences the modulus value [29].

Values of E' for $C/S=1.0$ are greater at all porosities than C-S-H specimens with C/S ratio greater than 1.0. The storage modulus of the $C/S=0.8$ C-S-H sample appears to be distinctly different than other samples. This may suggest that low C/S ratio C-S-H can fall in a different category. This is also supported by ^{29}Si NMR investigation and other techniques [30-34]. In general, it is suggested that the silicate polymerization of the C-S-H enhances its elastic properties.

It is possible to calculate the intrinsic storage modulus of the cement-based materials using the proposed empirical equations that correlate various mechanical properties with the porosity [35-38]. The relation proposed by Helmuth and Turk [35] can not be applied as it was developed for the saturated state. Another equation has been adopted from the studies in ceramic science [36, 37] and has been used in the investigation of cement systems [38] to relate the modulus of elasticity (E) and porosity (P) as follows:

$$E = E_0 e^{-bP} \quad (1)$$

where E_0 is the Young's modulus at zero porosity and b is a constant. An analogous equation can be used for the correlation of storage modulus (E') with porosity obtained in the current study. The following equation which is the linear form of the equation (1) was curve fitted to the data in Figure 8-3a:

$$\ln(E') = \ln(E'_0) - bP \quad (2)$$

The calculated values of E'_0 and b are as presented in Table 8-1. A relatively reasonable fitting of the equation to the data was obtained (average $R^2=0.98$) which suggests that this equation approximates well with the modulus values of compacted C-S-H samples. The zero porosity values of the storage modulus are in the order of the calculated theoretical elasticity values for C-S-H systems [14, 18]. It was observed that the E'_0 increases at lower C/S ratios similar to the behavior shown in Figure 8-3a (the value at $P=23\%$ was not considered in the calculations for $C/S=0.8$). The C-S-H having the two lower C/S ratio values ($C/S=0.8$ and 1.0) exhibits higher values of E'_0 . There is only a change in the order of E'_0 values between the $C/S=1.2$ and 1.5 . The

storage modulus of C-S-H C/S=0.8 is considerably higher than that for the other samples. Using atomistic modeling calculations, it has been shown that the modulus of elasticity of the C-S-H increases with increasing the silicate chain length (which is inversely related to the C/S ratio) [29]. The constant parameter b (that is attributed to the pore geometry and orientation under stress [38]) seems to be independent of the C/S ratio. Its average value (0.052) is less than that for the cement paste [39]. This parameter which is essentially the slope of the lines in log scale is similar for all C/S ratios, suggesting a consistent pore network in all samples.

Table 8-1. Zero porosity values of the storage modulus for C-S-H

C/S ratio	E'_0 (GPa)	b
0.8*	231.3	0.052
1	132.4	0.050
1.2	94.9	0.052
1.5	115.1	0.053

* The value at $P=23\%$ was not considered in the calculations.

The results for the internal friction of C-S-H compacts (a measure of the damping behavior of this material) are shown in Figure 8-3b versus the porosity of the specimens. For all C/S ratios, the internal friction increases with the decrease in the solid volume fraction of the specimens. The empty pore spaces in the solid body can be deformed easier under load than the solid part through which some energy is dissipated. The presence of a larger amount of pores increases the chance of the sliding of solid grains and their friction against each other. This bulk effect may be responsible for the increase of the damping at higher porosity levels.

It is also observed that the internal friction increases with C/S ratio for a given porosity (i.e. the C-S-H with C/S=0.8 has the lowest $\tan \delta$ and C-S-H with C/S=1.5 has the highest value). This can possibly be due to the effect of silicate polymerization. At higher C/S ratio, the C-S-H is less polymerized and silicate chains are shorter. Therefore, for a similar amount of moles, high C/S ratio C-S-H material may have more individual units. This may increase the sliding sites available between particles in the C-S-H compact and result in higher internal friction. It should also be mentioned that $\tan \delta$ and E' act in opposite directions in cement-based materials [40-43], i.e. when the elasticity of the specimen decreases, the damping increases and vice versa. This is consistent with the results of this study (Figure 8-3) that show the order of the $\tan \delta$ curves in

terms of their C/S ratio is almost the inverse of that for E' . It is interesting to note that the $\tan \delta$ values for C/S=1.2 and 1.5 are very close, similar to the observation for their E' values. The curve for C/S=1.0 then separates samples from the low lime content C-S-H (C/S=0.8). It appears that the C/S=0.8 falls in a different category as its DMA response is very distinct from that of other C-S-H samples.

The DMA test was also conducted on a thin slice of cement paste (W/C=0.4) and porous glass both previously conditioned at 11%RH. The results for these specimens are plotted based on their porosity for comparison with the C-S-H curves in the same graph (Figure 8-3). The E' and $\tan \delta$ values of the cement paste are almost of the same order of magnitude as for C-S-H samples although these single values are not conclusive as to any similarity with a specific C/S ratio. The main part of study with synthetic C-S-H is concerned with the role of water in its nanostructure in comparison with the cement paste and is discussed in the next section.

8.3.2 Role of adsorbed and interlayer water

The change in the dynamic mechanical properties of C-S-H as well as the cement paste and porous glass was followed on the incremental removal of water from these systems starting at the 11%RH condition. Several specimens were examined for each C/S ratio in order to study the dynamic mechanical performance of the C-S-H at various porosity levels. The current work reports only the results for the samples having the porosity value of about 30% (a relatively low value so that more solid material is present in the sample). Duplicates were also made for these samples at this porosity level. Duplicate samples do not necessarily have the same values for E' and $\tan \delta$ at a given mass loss level, but the trend used as the basis for understanding the nanostructural role of water is readily reproduced. After each drying step (using vacuum and heat treatment), the dried sample was weighed (to calculate the amount of the mass loss) and was tested quickly. The sample was then returned to the drying cell for further removal of water.

The number of data points for each curve (about 15) is relatively lower than that in an experimental set-up where the data is collected continuously. This is due to the drying procedure that was designed to monitor the changes in the E' and $\tan \delta$ at various 'mass loss' increments upon the removal of water. Each E' and $\tan \delta$ versus mass loss curve is attained using the same specimen in order to avoid inconsistencies. These are semi-equilibrium curves that require

sufficient time to obtain each mass loss level. About 7 to 10 days is required for collecting data in order to construct each E' or $\tan \delta$ – mass loss curve.

A TGA analysis at the end of the test showed a negligible amount of calcium carbonate in the rectangular samples. This confirms that the care taken was adequate to avoid any significant carbonation of the C-S-H. Moreover, the extent of carbonation would have been very limited due to the low humidity in the sample. The change in the micro- or nano-structure of the C-S-H upon the removal of water is the main point of interest in this part of the current study as it may bring insight to the nanostructural role of water in C-S-H.

The behavior of C-S-H under dynamic loading at various humidity levels is unique. There are various steps in the DMA response of C-S-H upon the removal of water. These are illustrated in the schematic shown in Figure 8-4 (stages I-IV). Tests showed reproducible oscillatory trends in the E' and $\tan \delta$. This behavior that was observed in many samples (variable porosity and chemical composition) appears to be ‘real’. The results of the E' and $\tan \delta$ measurements for C-S-H (C/S=0.8, 1.0, 1.2 and 1.5) at various mass losses from 11%RH are shown in Figure 8-5. As mentioned previously, both adsorbed water and interlayer water are present in 11%RH conditioned samples. The changes, therefore, can be discussed considering the role of water in these two states. The silicate structural changes in the C-S-H (as determined by ^{29}Si NMR and helium inflow experiments on the same materials subjected to similar drying procedure) and interlayer calcium ions are also used to account for these observations.

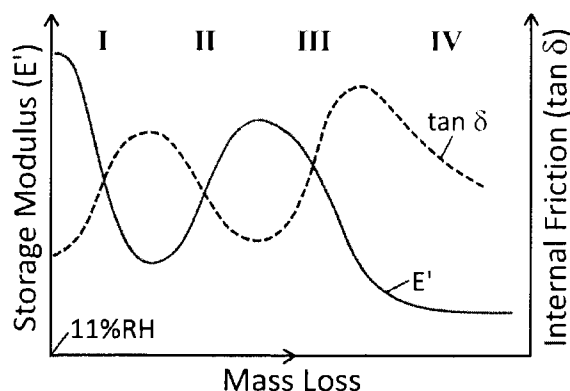


Figure 8-4. Various stages in the DMA response of the C-S-H systems upon drying from 11%RH condition.

The changes in the storage modulus of C-S-H specimens are shown in Figure 8-5a. All C/S ratio C-S-H samples depict a decrease in stiffness followed by a peak (i.e. they increase to a maximum) as they are dried to lower moisture contents. There are four distinct mass loss regions for each curve. In stage I, a significant initial decrease in E' occurs (up to about 2% mass loss from the 11%RH condition). This steep reduction in the stiffness is attributed to the loss of adsorbed water and some of the interlayer water [26]. It has been shown that the drying of hydrated Portland cement paste results in significant reduction of the dynamic modulus of elasticity which might be attributed to the microcracking [44], dehydration of calcium silicate hydrate [45], or a combination of both [46].

The DMA tests in the current work were conducted on the compacts made from 11%RH conditioned C-S-H powders. Extreme care was also taken during gradual drying. The microcracking (that might be observed when a saturated paste is dried as opposed to the starting 11%RH condition in the current study) was not observed in the C-S-H samples as confirmed by microscopic analysis. Moreover, significant micro-cracking, if present, would have resulted in a continuous decrease in the storage modulus over the entire mass loss range. The fact that the E' increases at a certain drying state suggests that the micro-cracking was not an issue. A very similar value for the E' is reproduced when the C-S-H sample is repeatedly subjected to unloading and loading at a constant moisture content. A decrease in E' should have been observed had there been significant micro-cracking. The changes therefore can be explained in terms of the dehydration of C-S-H itself. Water molecules ‘reinforce’ the silicate sheets and contribute to the stiffness of the C-S-H structure. The point of inflection on this part of the curve appears to be related qualitatively to the surface area of the C-S-H. About n monolayers of water (presented in Table 8-2) are lost at this drying level corresponding to the inflection point. The monolayer capacity of C-S-H samples and cement paste are calculated according to the following equation proposed by Powers and Brownyard [47]:

$$V_m = \frac{S \times 18 \times 10^{-3}}{10.6 \times 6.02} \quad (3)$$

where V_m is the monolayer capacity (grams per gram of dry paste) and S is the BET surface area measured using nitrogen gas (m^2/g).

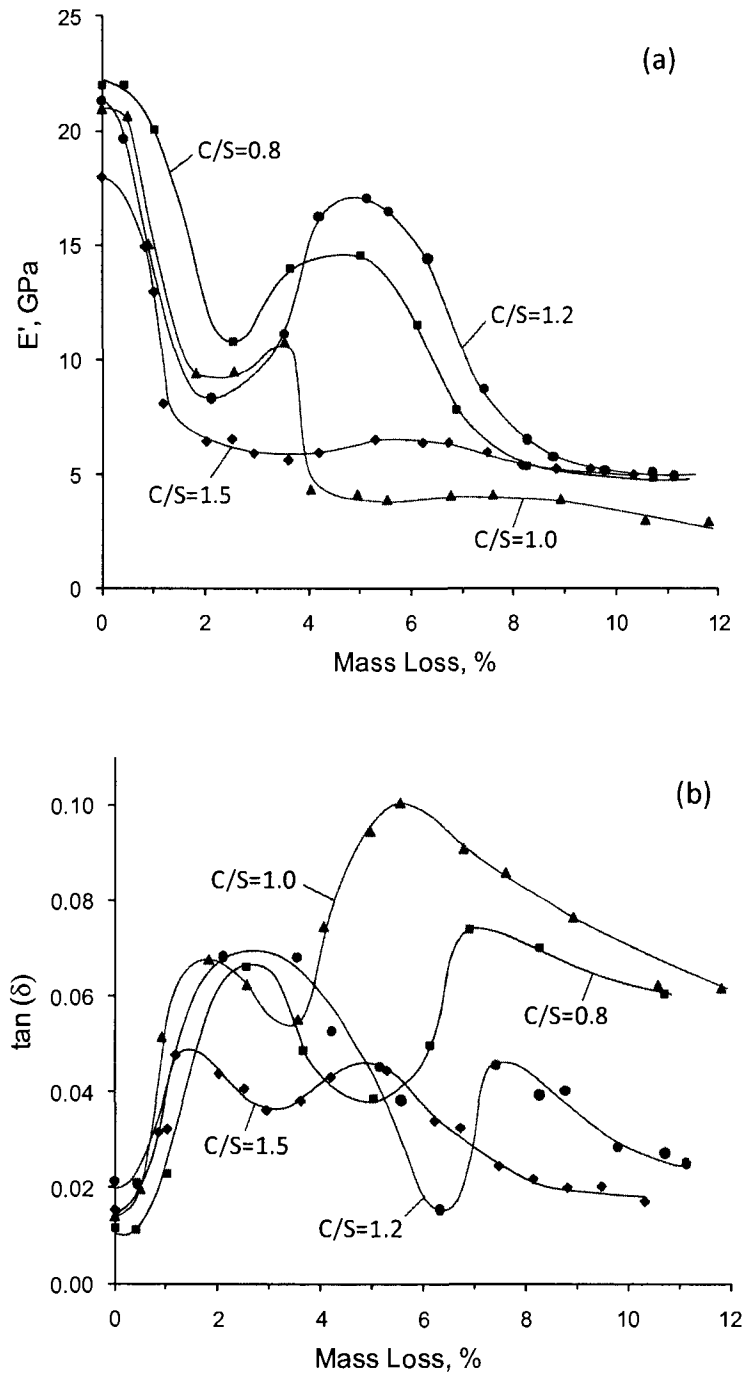


Figure 8-5. The DMA response (E' and $\tan \delta$) of C-S-H samples ($C/S=0.8$, 1.0, 1.2 and 1.5) subjected to drying starting from 11%RH condition: (a) storage modulus, (b) internal friction.

Table 8-2. Estimated monolayer capacity (V_m) of the C-S-H and cement paste samples

C/S ratio	BET Surface Area (m ² /g)	V_m (g/g)*	n
0.8	186	0.0520	0.3
1.0	29	0.0082	1.1
1.2	30	0.0084	1.2
1.5	52	0.0146	0.8
OPC (W/C=0.4)	40	0.0110	0.8

An example of continuous data collection (the dynamic mechanical properties of C-S-H versus temperature; DMTA) is presented in Figure 8-6 which confirms the adequacy of the number of data points in Figure 8-5. Observed reproducible results confirm the oscillatory variations in the dynamic mechanical properties of C-S-H systems reported here. The influence of the frequency of the applied strain can be observed as well in Figure 8-6. The increase in the frequency results in less-intensified peaks for both E' and $\tan \delta$ curves.

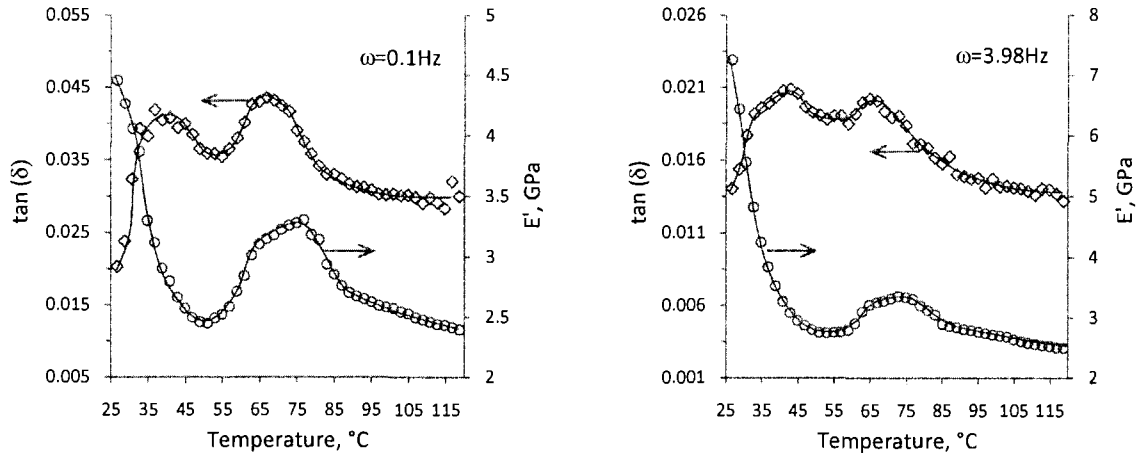


Figure 8-6. DMTA response of C-S-H (C/S=1.2) due to the gradual increase of the temperature at two frequencies; $\omega=0.1$ and 3.98 Hz.

It is suggested that the surface adsorbed water contributes to the stiffness of the C-S-H, the surface energy of which increases with the removal of this water. The inflection point in the stage I appears to occur at lower mass loss levels for higher C/S ratio. This type of C-S-H has a lower surface area and thus less capacity for adsorbing water molecules on the surface.

It is possible that some interlayer water is removed simultaneously due to the overlap of the energy by which water is held at different structural locations (i.e. adsorbed and interlayer water). The plateau at the beginning of the curves is probably only due to the adsorbed water. The overall decrease in the storage modulus as water molecules are removed from the systems is not in agreement with the computational simulation for C-S-H systems [18].

An increase in E' (stage II) begins to occur at a mass loss of about 2-3% for all C-S-H compositions. Such an increase in the stiffness of cement based materials has not previously been reported. The change in the elasticity of Portland cement paste, for example, only depicts a significant decrease for the humidity levels in this region [3, 6]. Drying of C-S-H results in an increase in the degree of polymerization and possible cross-linking of the silicate chains [48-50]. Evidence for this is based on ^{29}Si NMR observations (on the same material subjected to a similar drying procedure) where there is an increase in the Q^2/Q^1 ratio and some indication of the presence of a Q^3 peak. It is, therefore, suggested that the increase in the E' might be a result of the interaction of silicates between the layers.

The observed stiffening of C-S-H may also be explained by the role of calcium ions in the interlayer region. Partially dehydrated calcium ions interact specifically with the $\equiv\text{Si-O}^-$ groups of the short silicate chains [51]. It has been suggested that covalent bonds are created to some extent between the C-S-H sheet and the interlayer. This indicates the possibility of strong 'surface-cation-surface' ionic-covalent interactions. Calcium ions contribute to the electrostatic interaction between lamellae that is as strong as Si-O-Si chemical bonds [52]. Upon the drying of the C-S-H more calcium containing ions are dehydrated between the layers. This is likely to promote such ionic-covalent bonds and, in turn, improve the elasticity of C-S-H as observed by the increase in storage modulus in this work (Figure 8-5a). It is unlikely that the increase in the E' is related to factors that are not concerned with the chemistry of the material. For example, one may suggest that the micro-cracking and subsequent healing is responsible for the initial decrease followed by the increase in E' . The issue of micro-cracking was ruled out before. Also, healing is unlikely to occur in the phase pure C-S-H systems as there is no un-hydrated material and free lime such as is the case for the hydrated cement paste.

The observations in the variations of E' and $\tan \delta$ (Figure 8-5), therefore, appear to be related to the nanostructural changes in the C-S-H upon the removal of water. The increase in the storage modulus tends to a maximum with mass loss followed by a further decrease. The decrease (stage

III) is a result of the removal of the final quantities of interlayer water, which provide structural stability to the layered nanostructure. The decrease is analogous to what occurs on the drying of cement paste [40]. The rapid decrease in the basal spacing in this region of mass loss as observed for high C/S ratio C-S-H [53] suggests possible association of the decrease in E' with a collapse of structure mechanism. Removal of interlayer water molecules is critical to the structural integrity of the C-S-H framework.

It is difficult to compare the changes at various steps of water removal on the basis of the difference in the C/S ratio of the C-S-H. The starting point of the increase in E' (stage II) does not follow any specific order based on the C/S ratio. The initiation and occurrence of the peak at this stage, however, seems to happen at lower mass loss levels for low C/S ratio samples (C/S=0.8 and 1.0). The population of Q^2 sites is higher for low lime C-S-H samples. The possibility of cross-linking between silicates may increase at these silicate sites. This is suggested as a possible mechanism for the increase in E' . The intensity of this peak is less pronounced for C/S=1.5. There are likely to be more Ca^{2+} ions in the interlayer region that may restrict the cross-linking of silicate sites between the layers although these ions may interact with the layers and improve the cohesion of C-S-H sheets when dehydrated.

The decline in the storage modulus (stage III) occurs faster for C/S=1.0. The E' goes to a plateau (stage IV) after a mass loss of about 9% in all samples. This corresponds to a reduction of nearly 75% in the storage modulus as a result of the removal of adsorbed and interlayer water. Figure 8-5 is primarily intended to show that the C-S-H exhibits a complex dynamic mechanical response on the removal of adsorbed and interlayer water. The trend for this behavior is similar for all C-S-H preparations. The absolute values of E' and $\tan \delta$ for a given mass loss, however, cannot be conclusively compared between various C/S ratio C-S-H samples as this would involve excessive speculation. It also should be noted that the application of temperatures above 50 °C (but below 110 °C) is relevant only for the mass loss levels above 8% which has no effect on the oscillatory nature of the curves observed in the current study. Other microstructural aspects of the C-S-H such as the density may change at such relatively high temperature levels.

The changes in the $\tan \delta$ (internal friction) for C-S-H samples are presented in Figure 8-5b. The main parameter of interest in the current study that influences the $\tan \delta$ is the moisture content. The data for $\tan \delta$ was therefore compared at the same frequency (0.1 Hz). The intensity of the curves decreases at higher frequencies, but the main features showing an oscillatory trend in $\tan$

δ and the peak locations remain the same. All curves can be separated into distinct regions of mass loss consisting of four stages that represent different damping behavior upon the removal of water from various nanostructural locations. In the first stage there is a significant increase in the internal friction. This part of the curve starts off with a plateau at the beginning (corresponding to the storage modulus results observed before) that is attributed mainly to the removal of the adsorbed water. Further drying results in the partial removal of the interlayer water although the bond energy associated with the presence of interlayer water in layered silicates is greater than that for surface adsorbed water [54]. This may increase the ability of the layers to translate since water molecules are considered to restrain the C-S-H sheets. More energy is, therefore, dissipated as observed by the increase in $\tan \delta$. The stiffness of C-S-H is reduced (Figure 8-5a) during this period. The increase in the internal friction is followed by a peak at about 2% mass loss which matches well with the end of stage I in the changes of storage modulus.

The descending portion (stage II) following the peak in $\tan \delta$ is likely to be a result of the initial cross-linking between silicate layers and increase in the polymerization. Increase in the interaction of calcium ions with the lamellae can be responsible as well. Bridging of the C-S-H sheets and an increase in the number of strong bonds (either Si-O-Si or $\equiv\text{Si-O}^- - \text{Ca}^{2+}$) reduces the damping behavior of C-S-H although it improves the stiffness of the material observed before. This portion of the curve ends at the same mass loss where a peak occurs in the storage modulus for each C/S ratio C-S-H (except C/S=1.5). Stage III in the $\tan \delta$ shows an ascending behavior. This increase in damping might be due to the sliding of silicate layers as they have come closer to each other upon the removal of interlayer water. The peak observed following this stage corresponds to the end of third stage in storage modulus. The decline in damping (stage IV) after the second maximum is attributed to the removal of the remaining amount of interlayer water and possibly some constitutional water at higher mass losses. The co-occurrence of changes and simultaneous transitions in the E' and $\tan \delta$ has been previously observed in different investigations of the cement paste [41, 42]. Mechanisms responsible for these changes seem to have inverse effects on stiffness and damping.

Similar DMA tests were conducted on thin slices of hydrated Portland cement (W/C=0.4) conditioned at 11%RH. Variations in stiffness and damping of the cement paste on the removal of adsorbed and interlayer water were followed (Figure 8-7). There are several stages in the results that are analogous to the behavior of synthetic layered C-S-H as explained before.

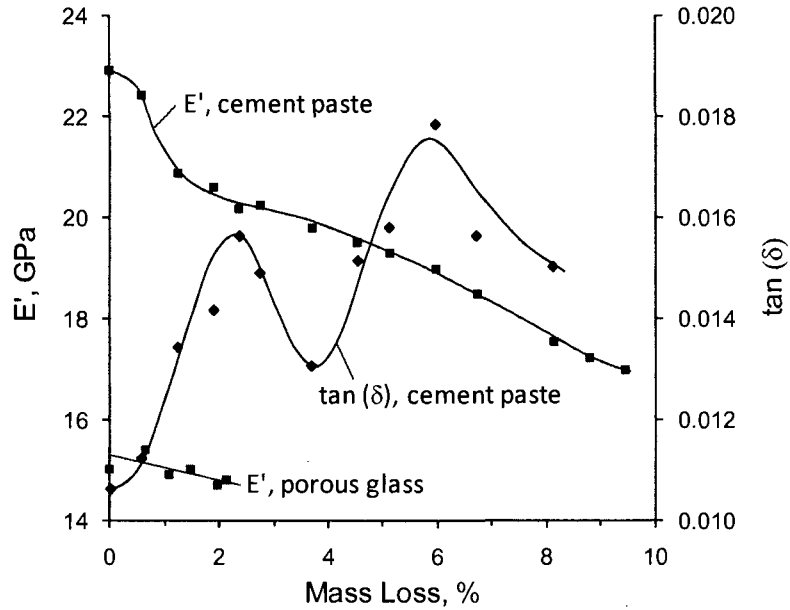


Figure 8-7. Storage modulus and internal friction in the DMA analysis of Portland cement paste (W/C=0.4) and porous Vycor[®] glass.

When the cement paste is dried, a relatively significant decrease occurs in the storage modulus simultaneously with an increase of the internal friction. This stage, as described before, is when the adsorbed water and part of the interlayer water are removed from C-S-H. The second stage of changes and the peak in E' (observed for C-S-H) are manifested by a plateau in the curve for the cement paste at about 2% mass loss. The C-S-H in cement paste is nearly amorphous and incorporates in its structure elements other than silicon such as aluminum. This may reduce the cross-linking potential and interaction of silicate sites in hydrated Portland cement that is a contributing mechanism to the increase in the stiffness of C-S-H. The first maximum and subsequent reduction of $\tan \delta$ (stage II) is, however, more pronounced. A further decrease in the storage modulus simultaneously occurring with the formation of a second maximum in the internal friction for hydrated Portland cement corresponds well with similar behavior in the synthetic C-S-H. Collapse of the silicate layers and removal of the remaining water molecules are likely to contribute to these variations. The hydrated Portland cement contains phases other than C-S-H such as calcium hydroxide. The DMA response is thus not exactly the same as that for the synthetic phase pure C-S-H. The trend in the E' and $\tan \delta$ for the cement paste was reproduced several times. In other words, the initial sharp decrease in E' followed by a short period (at about 1.5-3% mass loss) where the rate of decrease is minimal and a further gradual decrease of the E' were repeatedly obtained in the DMA experiments on several samples. The E' versus mass loss

curve for the cement paste has more subtle features than the curve for the C-S-H and does not exhibit a peak at about 4-5% mass loss. The case for the $\tan \delta$ -mass loss curve is much clearer. This reproducibility was obtained for the double peaks in the $\tan (\delta)$ -mass loss curve. These variations correspond well with those for the synthetic C-S-H. This complex behavior (specifically that for the $\tan \delta$) can be explained by considering the similar nanostructural features for the C-S-H in OPC to that of the layered synthetic C-S-H.

The similar trend in the DMA response of hardened cement paste to that in the layered semi-crystalline C-S-H is a new evidence for the layered nature of the C-S-H in hydrated Portland cement and the structural role for the water within its structure. The magnitude of the changes in the E' and $\tan \delta$ for cement paste is not as high as those for the synthetic C-S-H. There is only about a 25% reduction in the storage modulus when the sample is completely dried. The average internal friction is also about 15% of that for phase pure C-S-H. It is suggested that this is due to the fact that the C-S-H in the hydration products of Portland cement is significantly less crystalline and has a more disordered structure. The changes are therefore not very pronounced yet comparable to the behavior of more crystalline-layered phases. There are also other hydration products in the cement paste that reduce the C-S-H content and therefore diminish the variations contributed by the C-S-H phase. The complex DMA response of the cement paste upon drying was qualitatively reproduced several times using different samples.

Radjy and Richards showed that heat treatment of cement paste using temperatures up to 100 °C (that essentially results in the removal of water from various locations including interlayer water) decreases the modulus of the cement paste [43]. The range of E' and $\tan \delta$ and the extent of their variations corresponds well with the results presented here. They, however, identified only one transition [42] and suggested that changes in the internal friction are not significant and that the values are “essentially constant”. Careful examination of the results of their work (Figure 2 in Ref. [43]), however, shows a similar pattern to the results of this study (Figure 8-5b) having two maximum in the $\tan \delta$ upon drying. A parallel comparison of the results for cement paste with synthetic C-S-H in our study supports assigning physical meanings to these peaks that might seem to be experimental fluctuations at first. The reduction in modulus values decreased following the second and third drying [43]. This irreversible transition was called a “surface area” transition. It is suggested that the observed behavior is mainly due to the irreversible role of interlayer water. The cement paste treated at higher temperatures has been characterized by DMA [55, 56]. The heating of cement paste did not reveal any significant change in $\tan \delta$ and only a

gradual decrease was observed in the modulus due to the dehydration of C-S-H. It should be noted that drying in these studies was conducted dynamically as there was a continuous increase in the temperature. The work reported here, however, employs a different method of drying including several hours of vacuum and heat treatment for each data point at a constant temperature that allows us to obtain at least a semi-equilibrium humidity condition in the samples.

The change in the elasticity of porous glass on the drying from 11%RH is shown in Figure 8-7. The stiffness of porous glass is considerably less than that of the cement paste at this humidity level. The moisture content is also very low and the maximum amount of evaporable water is only about 2% of the mass at this state which is essentially adsorbed on the surface. Removal of this water slightly decreases the storage modulus value. The $\tan \delta$ values (not shown) were very scattered.

8.3.3 A mechanistic model for C-S-H

A nanostructural model is proposed to explain various steps in the change in the elasticity and internal friction of C-S-H considering that the complex dynamic mechanical response of Portland cement paste is analogous to the behavior of the layered semi-crystalline C-S-H. This model incorporates features of both physical [57, 58] and composition-based [59-61] models for C-S-H in order to explain the changes in the elasticity and damping of calcium silicate hydrates (shown schematically in Figure 8-4) with respect to the contributions from water and silicates. It is contended that the globule model [57] is not able to explain the experimental observations in this study unless a 'layered concept' is introduced with an assignment of a structural role to the interlayer water. The globule model recognizes the layered nature of the individual globules or particles. The model, as shown in Figure 8-8, considers a layered structure for the C-S-H in the hydration products of Portland cement. Water molecules can be adsorbed on the surface and be present in the interlayer space at the starting 11%RH condition (Figure 8-8a). The silicate chains (varying in length and number of defects depending on their C/S ratio) and the calcium ions in the interlayer are features of this model.

As water molecules are removed by drying from the surface of the C-S-H and partially from the interlayer space (Figure 8-8b), a significant decrease in the elasticity occurs. Layers of C-S-H are still separated at this stage and the internal friction increases during this period. Possible cross-

linking (either Si-O-Si or Si-O-Ca-O-Si bonds) as well as a slight decrease in the basal spacing occur when additional interlayer water is removed (Figure 8-8c). This is responsible for the decline in $\tan \delta$ and increase of the stiffness. Collapse of the C-S-H structure after this stage provides more sliding sites and increases the internal friction but reduces the elasticity (E'). The dehydration of the C-S-H through further removal of water molecules in the interlayer region (Figure 8-8d) decreases damping behavior and brings modulus values to a plateau.

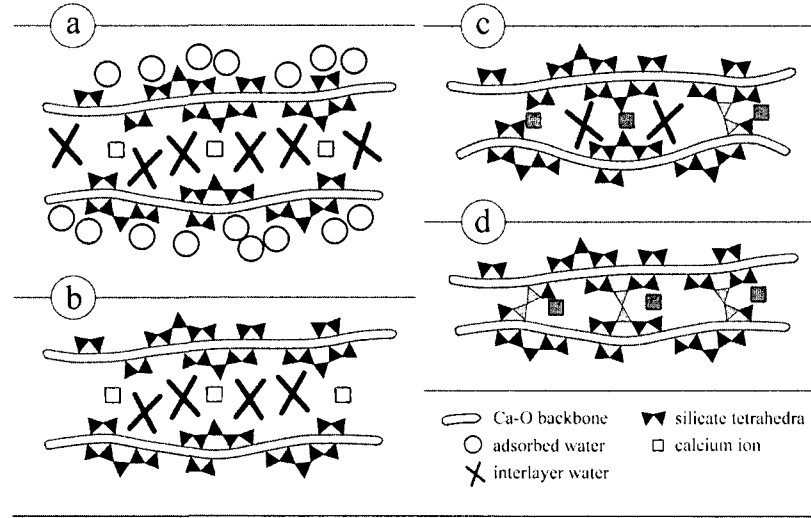


Figure 8-8. Schematic presentation of the nanostructural changes occurring on the removal of adsorbed and interlayer water in C-S-H. The interacted silicate tetrahedra and calcium ions after dehydration are shaded differently.

8.4 Conclusions

Various C-S-H compositions ($C/S=0.8$ to 1.5) and hydrated Portland cement specimens were characterized for their dynamic mechanical behavior at 11%RH condition. It was shown that the mechanical properties of C-S-H are dependent on its C/S ratio. There is a decrease in the storage modulus (E') as well as an increase in the internal friction ($\tan \delta$) as the C/S ratio of the C-S-H increases. A unique multi-stage change in the stiffness and damping of C-S-H similar to cement paste was observed as samples were conditioned to moisture contents lower than that in the 11%RH. It is suggested that adsorbed and interlayer water contribute significantly to the dynamic mechanical properties of C-S-H. Water molecules in the interlayer region act as restraints to the silicate structure. Mechanisms at the nano level such as collapse of the C-S-H structure, cross-linking of silicate sites and the interaction of dehydrated interlayer calcium ions with the silicate

structure possibly contribute to the variations in E' and $\tan \delta$ at various drying stages. The C-S-H in the hydrated Portland cement has a complicated yet analogous dynamic behavior to that of synthetic C-S-H with respect to the role of water in various nanostructural locations. The synthetic C-S-H, therefore, can be considered as a viable nanostructural model for the mechanical property studies of the C-S-H in cement paste.

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Stress relaxation of C-S-H

The origin of the time-dependent response of cement-based materials to applied stress has not been clearly resolved. The role of interlayer water in the mechanical behavior of calcium silicate hydrate (C-S-H) is still debated. In order to better understand the related mechanisms, the stress relaxation tests were conducted in the current research on thin rectangular beams of compacted synthetic C-S-H powder and hydrated Portland cement subjected to three-point loading. C-S-H of variable composition ($C/S=0.8, 1.2$ and 1.5) was studied. Specimens were prepared at various moisture content levels. A special drying procedure was applied in order to remove the adsorbed and interlayer water incrementally from C-S-H conditioned at 11%RH. It was shown that a significant part of the relaxation is attributed to the hydrodynamic component associated with the pore water. It was demonstrated that the viscoelastic performance of C-S-H depends considerably on the presence of interlayer water. It is argued that the results support the validity of the theory of sliding of C-S-H sheets as a deformation mechanism responsible for the creep and stress relaxation of cement-based materials. This concept was illustrated in a proposed model for the viscoelastic response of C-S-H.

9.1 Introduction

The time-dependent changes in the mechanical properties of concrete have been the subject of extensive research over the past century [1]. In particular, the concrete creep, i.e. the strain induced under sustained loading over time, has received significant attention due to its practical implications. Although numerous studies have been conducted in this regard, the nature of creep phenomena in cement-based systems is still not clearly resolved. There are several hypotheses proposed for the concrete creep that describe possible mechanisms for the temporal deformation of hardened concrete under load [2, 3]. None of these theories can explain all the experimental observations and it appears that multiple mechanisms may be operative. It is argued that the origin of creep is situated at the micro and nano-level within the capillary space and the calcium silicate hydrate (C-S-H) phase, respectively, referred to as the short-term and long-term creep [4].

A couple of the theories on the nature of creep that are concerned with the nanostructure of the hydrated cement paste are briefly described. The microprestress-solidification theory implies that in the ‘hindered’ adsorbed water molecule sites (including that in the C-S-H interlayer) the overstressed unstable atomic-scale bonds are locally broken and reformed [5]. This results in a quasi-dislocation of adjacent particles through a shear slip mechanism (i.e. the sliding of C-S-H sheets [4]) which contributes to the long-term creep. The theory of micro-sliding between the adjacent C-S-H sheets and the change in the orientation of hydroxylic water held on the crystalline surfaces was later supported as the main contributor to the creep behavior [6]. It was also shown that the removal of interlayer water from the hydrated cement system results in an increase of the creep capacity. Removal of the pore water before applying the load on the specimen, however, decreases the creep of concrete [3, 7]. This is consistent with the previous investigations that assign a structural role to the water situated between the layers of C-S-H [8-10]. It was, however, suggested by some researchers that no creep occurs if all the evaporable water is removed from the hydrated system [11-13].

Creep of concrete has also been described in terms of a nanogranular model of C-S-H particles [14-16]. It was suggested that the creep may involve the rearrangement of the C-S-H globules resulting in a tighter local packing, i.e. higher local density. It was also proposed that the low density (LD) C-S-H creeps more than the high density (HD) C-S-H in cement paste possibly due to the difference in the porosity levels and not the intrinsic properties of the C-S-H [15]. In a recent study, a similar conclusion was made that the mechanical properties of C-S-H phases are a

sole function of their packing density [17]. The C-S-H creep data captured by a logarithmic function employing nano indentation experiments was shown to be only dependent on the packing density of C-S-H. The logarithmic-type behavior of creep of C-S-H in hydrated cement paste at the nano scale was also confirmed in a separate study but the LD and HD C-S-H phases were not distinguished [18].

The stress relaxation of cement and concrete, a mechanical property that is closely related to the creep, has rarely been studied in the past mainly due to the experimental limitations [19]. A relatively quick method using three-point bending of thin cement paste beams that was primarily adopted in order to measure the permeability of hardened cement, was successful in the separation of the main components of the stress relaxation in saturated Portland cement paste; hydrodynamic and viscoelastic [20-23]. The pressure gradients in saturated pores under stress are alleviated through the flow of the fluid causing the hydrodynamic relaxation that diminishes at early times. The internal redistribution of water in the capillary space was identified as a factor responsible for the short-time creep [24]. Water molecules may be re-adsorbed into the fine pore structure of the paste upon unloading [25]. The solid network of the material undergoes a viscoelastic relaxation that remains active at later times.

It is well known that the stoichiometry of C-S-H in hydrated cement paste can readily be changed by various parameters such as curing conditions and use of supplementary cementitious materials [26]. It is therefore necessary to establish a relation between the chemistry of C-S-H and its mechanical characteristics in order to predict and control the performance of cement-based materials. Hardened cement paste is not an ideal material for the studies in this regard. The porosity, which has an important role in the mechanical behavior of the porous body of the solid, is obviously influenced by the mix characteristics of the cement paste. Moreover, the chemical properties of C-S-H and additional phases formed in the hydration reactions cannot be easily controlled. The mechanical characterization results therefore cannot be related independently to the stoichiometry of the C-S-H in these systems.

It has been shown that the synthetic semi-crystalline C-S-H (i.e. C-S-H(I)) can be considered as an appropriate model for the nearly amorphous C-S-H produced in the hydration of Portland cement [10, 27]. A solid body of the phase pure C-S-H (of variable C/S ratios) is required for the investigation of its mechanical performance. The current research utilizes the compaction technique in order to prepare rectangular beams from the powdered materials (synthetic C-S-H of

variable stoichiometry) at a controlled porosity value. It should be noted that the synthetic C-S-H is a fully hydrated material and the effect of the hydration of cement during the conventional creep measurements as well as other aging mechanisms [28] are eliminated. The current study reports the results of the stress relaxation of the compacted C-S-H specimens subjected to a constant strain in a three-point bending set-up at various humidity levels. Samples of hydrated Portland cement and porous glass were examined for comparison. It is primarily intended to examine the role of the interlayer water in the time-dependent deformation of C-S-H with respect to its chemical composition.

9.2 Method

9.2.1 Materials

C-S-H was synthesized at C/S ratios of 0.8, 1.2 and 1.5. Two other sets of samples were prepared for comparison: the cement paste and porous glass. The sample preparations are described in the previous chapter. The C-S-H preparations and cement paste slices were conditioned for three weeks in a vacuum desiccator over the vapor pressure of saturated lithium chloride solution i.e 11% RH. Additional samples were conditioned over the vapor pressure of water for stress relaxation experiments in the saturated state (100%RH).

Compacted specimens were prepared from the C-S-H powder conditioned at 11%RH for one month as follows. A specific compaction pressure was applied for each C/S ratio in order to achieve similar porosities of about 30% in the compacted samples where a sufficiently large fraction of the solid material would come into the play and the behavior would better represent that of the C-S-H. More details about the compaction procedure can be found in chapter 3. The thickness of the compacted C-S-H samples varied between 0.8 and 1.2 mm depending on the C/S ratio and the compaction pressure. The relatively low value of thickness allows for decreasing the time to achieve the equilibrium state at various humidity levels and avoiding major moisture gradients that may result in micro-cracking in the test specimens subjected to drying. The compacted samples were kept in a vacuum desiccator at 11%RH. The additional conditioning at this humidity resulted in about 1% mass loss in the samples. This may suggest that the monolayer of water present on the surface of particles before compaction was moved to ‘pore’ spaces after the particles come into contact in the compacted sample.

9.2.2 Experimental procedure

The starting condition for the C-S-H compacts as mentioned before was 11% relative humidity. Saturated samples were obtained by conditioning the compacted specimens at 100%RH. Lower humidity levels were achieved by the removal of water from 11%RH conditioned samples through the application of a combination of vacuum and heat. The initial drying increments were conducted at room temperature using only vacuum. The temperature was gradually increased for higher mass loss levels in the samples. These humidity levels can be viewed as quasi-equilibrium states considering the substantial amount of time spent on the water removal at each increment. It takes about one week to collect data in order to construct the whole set of data for each sample. It is important to increase the temperature and vacuum duration very gradually so that possible moisture gradients do not cause any significant micro-cracking in the specimens.

The stress relaxation test was conducted at each increment of water removal using a Rheometrics RSA III instrument. The rectangular samples were wrapped with cellophane film after drying in order to keep the humidity level constant during the test. The elasticity of cellophane wrap is negligible in comparison with the samples. This was examined using a steel plate with and without cellophane wrap. Moreover, there was no mass change in the specimens covered with the cellophane film during the relaxation test. The three-point bending method (as shown in Figure 8-2) was used for stress relaxation studies. A static load of 10g followed by a maximum strain of 0.02% was applied at the middle span of the samples. The load required to keep the strain constant was monitored up to four hours. The change in the corresponding stress was recorded by the computer. It should be mentioned that no indentation was observed on the surface of the samples caused by the supports since the contact line was wide enough on the flat specimens to distribute the load. Therefore, no correction was required in the deflection of the rectangular samples. The Hertizian indentation, however, has previously been observed in cement rods [21]. A circular cross-section essentially provides a point contact with the support and high localized stress results in measurable indentation.

A separate sample was prepared and tested for each humidity level and drying state, as the stress relaxation is only partially recoverable and the sample cannot be reused for the other humidity levels. This restriction could cause minor reproducibility errors because the compacted C-S-H samples might not be identical as their preparation was manually controlled. This is, however, not a concern for the rectangular plates of cement paste and porous glass that are more homogenous.

Several C-S-H samples were tested for the same humidity level in order to obtain reliable data when certainty was not clear.

9.3 Results and Discussion

The results for the stress values (σ_t) versus time were normalized to the initial stress (σ_0) recorded after the application of the strain. The applied strain increased gradually from zero and reached the maximum constant value after about 0.1 second, at which time the maximum stress value was obtained. The data for up to about 0.6 second is relatively noisy. This shows the equilibrium state of loading is not instant and there are some parameters affecting this period before achieving a more stable stress state. The general trend during this period, however, follows that of the later times. Some fluctuations were observed in the stress relaxation of a few samples which might be due to the experimental limitations associated with the instrument.

Porous Vycor[®] glass has been extensively used as a model system in the study of the cement-based materials [29]. The stress relaxation curves for the porous glass samples conditioned at 11 and 100% RH are shown in Figure 9-1. A dry sample was also prepared from the 11%RH conditioned porous glass by applying vacuum at 110 °C for 3 hours. This resulted in about 2% mass loss. The total stress relaxation of porous glass samples is not significant. The curves show, as expected, a decrease in the stress required in order to maintain the constant strain. The rate and the extent of this decrease are, however, different depending on the moisture content of the specimen. The maximum relaxation of about 5% is observed in the saturated specimen after about 10^3 s. The stress relaxation curve at this humidity level consists of two parts separated by an inflection point at about 2 seconds (indicated by a dashed line on the curve).

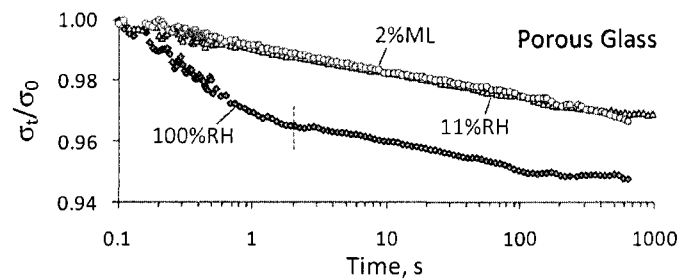


Figure 9-1. Stress relaxation curves of Vycor[®] porous glass at various humidity levels. ML: mass loss from 11%RH condition. The dashed line indicates the location of the inflection point in the 100%RH curve.

This observation is consistent with a previous study on porous glass [30]. The first part of the stress relaxation is due to the release of pore water pressure (hydrodynamic). The second part is attributed to the solid body of the glass that exhibits a relatively small viscoelastic behavior.

At the 11%RH condition, there is ideally only a monolayer of water present on the surface of the solid body of the porous glass. The porous glass sample at this relative humidity, therefore, does not exhibit hydrodynamic relaxation associated with the pore water and it only shows a gradual decrease in the stress at a constant rate (in log scale). The dry specimen (2% mass loss from 11%RH) demonstrates a very similar relaxation behavior to that of the 11%RH conditioned sample. It is also noted that the rate of decrease in the stress after the inflection point for the saturated sample is similar to that for the specimens at the 11%RH and dry conditions. It appears that the viscoelastic response of porous glass is not dependent on its moisture content. These observations were repeatedly made and may suggest that the monolayer of water does not have a major contribution to the stress relaxation of porous glass. It is also possible that the effect is so small that it can not be captured accurately by the current experimental setup. The latter seems more plausible as it has been suggested that the water molecules (available at 11%RH) attack the strained siloxane bonds of porous glass resulting in the viscoelastic relaxation [30].

The stress relaxation curves of compacted samples of synthetic C-S-H (C/S ratios=0.8, 1.2 and 1.5) at various humidity levels are shown in Figure 9-2. In all samples, the saturated specimen (100%RH) experiences a relatively higher relaxation at the initial times. The shape of the curve and the rate of decrease in the stress are different at this moisture content from those at 11%RH and below. This is due to the hydrodynamic component that is active at initial times. This part is eliminated after about 20 seconds at which time an inflection occurs in the stress relaxation curve in all the saturated C-S-H samples. The observation of the similar time for the end of hydrodynamic relaxation suggests that the C-S-H test samples have a comparable pore structure. All specimens had a similar total porosity of about 30%. The remainder of the relaxation behavior is attributed to the viscoelastic component of the C-S-H phase.

The other curves for all C-S-H samples (at 11%RH and lower moisture contents) show a different relaxation response than that of the 100%RH condition. The hydrodynamic component that results in a remarkable alleviation of the stress at the initial times for the saturated samples appears to be eliminated in these specimens. This is due to the absence of 'pore water' at such low humidity levels.

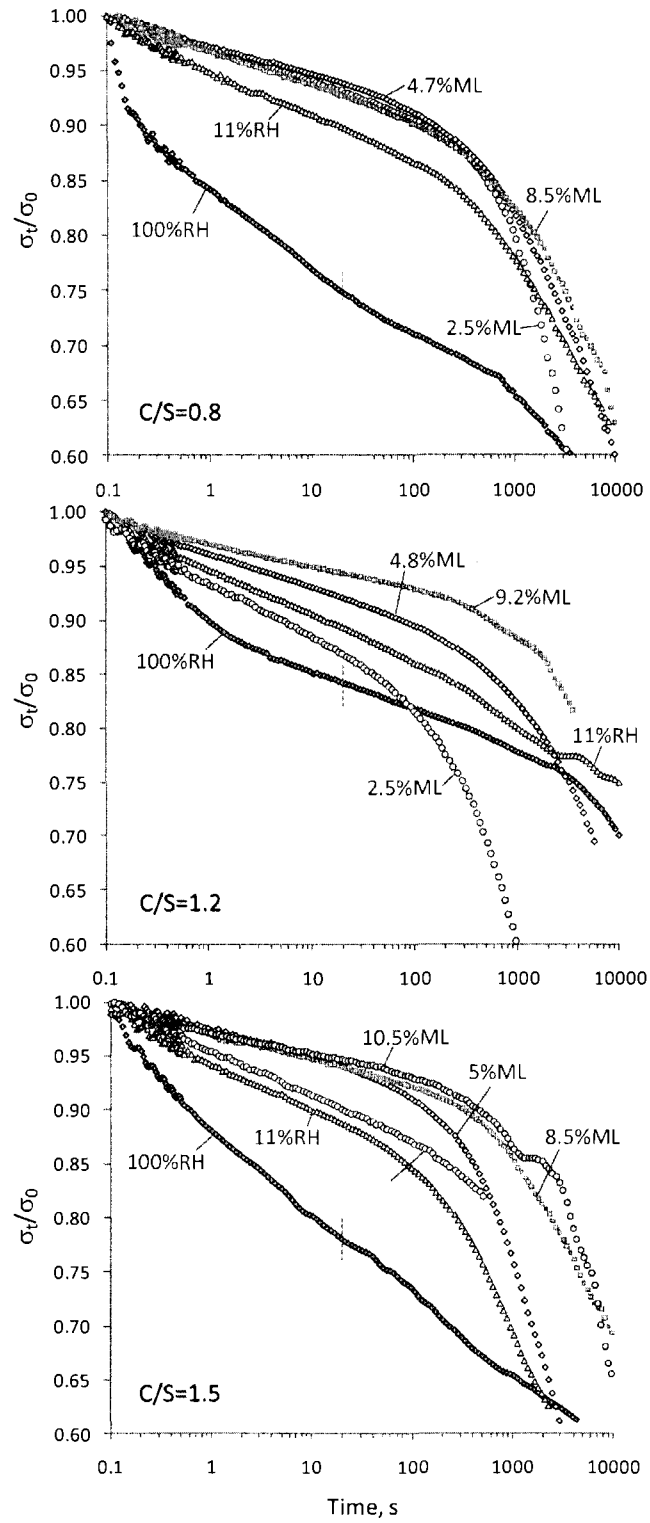


Figure 9-2. Stress relaxation curves for the C-S-H samples of variable stoichiometries at various moisture contents. The compacted specimens were prepared from the C-S-H powder conditioned at 11%RH.

The deformation of the pore structure under stress does not lead to an increase in the water pressure as in the saturated condition. The stress is directly transferred to the solid structure of the compacted C-S-H. A dominant viscoelastic response is therefore observed in all the ‘dry’ specimens from the beginning. It is however likely that water may exist in entrapped spaces. The water at these structural locations can not be readily removed and may slightly contribute to a negligible hydrodynamic relaxation that would be dissipated at a longer period of time compared to that for the pore water. Some of the relaxation curves in the ‘dry’ (11%RH and below) state contain a subtle concave-up portion at the beginning within the first 100s. This is likely associated with a hydrodynamic component other than that related to the bulk pore water.

It is noted (in Figure 9-2) that the drying of specimens conditioned at 11%RH changes the viscoelastic response of the C-S-H generally resulting in a lower stress relaxation at initial times more noticeably in the $C/S=1.2$ and 1.5 samples. At later times the relaxation curves may intercept with each other resulting in different total stress relaxation values not fully correlated with the mass loss level. The water molecules removed through drying of the 11%RH equilibrated samples are essentially located between the sheets of the layered synthetic C-S-H. It is therefore suggested that the interlayer water has a major role in the time-dependent viscoelastic deformation of the C-S-H. In order to examine this, a few 11%RH conditioned compacted C-S-H samples were completely dried and equilibrated again to the 11%RH condition. The first drying results in the removal of the interlayer water but water molecules cannot fully re-enter the interlayer region in the wetting at 11%RH [31]. The stress relaxation of the C-S-H specimens subjected to this regime (not shown) was significantly lower than that in the control specimens. It is suggested accordingly that the presence of the interlayer water facilitates the time-dependent deformation of C-S-H under load. The mechanism of viscoelastic behavior of C-S-H may therefore be attributable to the sliding and translation of the C-S-H sheets as hypothesized before [4, 6]. In order to verify this, X-ray diffraction was conducted before and after the stress relaxation test on representative C-S-H samples at various moisture content levels. Synthetic C-S-H has a basal spacing reflection (d_{002}) unlike the C-S-H in the hydrated Portland cement. The test results, however, did not show any significant change in the location (2θ) and the intensity of the 002 basal spacing peak of the compacted C-S-H samples subjected to stress. Theoretically, it is possible that the layers slide parallel to each other without affecting the reflection of the X-ray. The XRD investigation also suggests that the C-S-H layers are not compressed under stress. Analytical methods for short-range order investigation such as NMR might be able to provide

more evidence in this regard if mechanisms such as breaking of silicate and hydrogen bonds (consistent with previous theories [5]) apply.

It has been previously shown that the mechanical properties of C-S-H are significantly influenced by the interlayer water [10]. It was also suggested that the removal of water molecules from the interlayer region may also lead to nanostructural changes primarily related to the silicate tetrahedra and the calcium ions situated between the C-S-H sheets. These changes modify the mechanical response of C-S-H at various steps resulting in an oscillatory dynamic mechanical behavior. This might be responsible for some of the inconsistencies in the order of the stress relaxation curves versus mass loss on drying of C-S-H below 11%RH. It is also noticed that the stress relaxation of the C-S-H samples having the lowest C/S ratio (C/S=0.8) does not vary substantially as the interlayer water is removed. It appears that for this C/S ratio all the curves corresponding to the moisture contents below 11%RH are qualitatively similar. At higher C/S ratios (1.2 and 1.5), however, the stress relaxation curves are well-separated for various increments of drying. This may suggest that interlayer water and possibly ionic species such as Ca^{2+} have a more significant structural role in high C/S ratio C-S-H. The difference in the mechanical properties of C-S-H samples separated at a C/S ratio of about 1.1 has been previously observed [10].

In order to compare the viscoelastic behavior of C-S-H of variable compositions together and also between the 'dry' states and the saturated condition, it is necessary to separate the hydrodynamic and viscoelastic components of the stress relaxation curve for samples at 100%RH. Extensive work by Scherer's group at Princeton has led to developing and solving the stress relaxation equations for the hydrated Portland cement [20-23]. These equations are applicable only at the saturated state. An analytical solution for the load (W , which is directly related to the stress) as a function of time for a rectangular cross section beam can be expressed as:

$$W(t) = W(0) R(t) \Psi_{VE}(t) \quad (1)$$

where $R(t)$ is the hydrodynamic and $\Psi_{VE}(t)$ is the viscoelastic relaxation function. The hydrodynamic component can be described by the following equation:

$$R(t) = 1 - A + A S_1(\theta) S_2(\kappa\theta) \quad (2)$$

where A is the material parameter, S_1 and S_2 are functions reflecting the rate of the hydrodynamic relaxation, θ is the reduced time ($\theta = t/\tau_R$, in which τ_R is hydrodynamic relaxation time) and κ is the square of the aspect ratio ($\kappa = a^2/b^2$, for a sample with thickness $2a$ and width $2b$). The S functions that are roots of the Bessel function are given approximately by:

$$\begin{aligned} S_1(\theta) &\approx \exp\left[-\left(\frac{6}{\sqrt{\pi}}\right)\left(\frac{\theta^{0.5} - \theta^{2.5}}{1 - \theta^{0.551}}\right)\right] \\ S_2(\theta) &\approx \exp\left[-\left(\frac{2}{\sqrt{\pi}}\right)\left(\frac{\theta^{0.5} - \theta^{2.094}}{1 - \theta^{0.670}}\right)\right] \end{aligned} \quad (3)$$

The viscoelastic part of the relaxation can be described by the following expression:

$$\Psi_{VE}(t) = \frac{\exp\left[-\left(\frac{t}{\tau_2}\right)^{b_2}\right]}{1 - \exp\left[-\left(\frac{t}{\tau_1}\right)^{b_1}\right] + \exp\left[-\left(\frac{t}{\tau_2}\right)^{b_2}\right]} \quad (4)$$

where τ_1 and τ_2 are viscoelastic relaxation times. Through the curve fitting of the equation 1 to the experimental data of the load (or stress) versus time, the free parameters are obtained. These include theoretical load at zero time ($W(0)$), material property (A), hydrodynamic relaxation time (τ_R), viscoelastic relaxation times (τ_1 and τ_2) and their powers (b_1 and b_2). The two components of the stress relaxation can then be easily separated. As mentioned, the data for the stress ($\sigma(t)$) can be used in which case the free parameter of $\sigma(0)$ is used instead of $W(0)$.

The extracted viscoelastic component of the C-S-H samples conditioned at 100%RH is shown in Figure 9-3. It is observed that the total viscoelastic relaxation of the saturated specimen ($\sigma(t)/\sigma(0)$ at 10^4 s), for the same C/S ratio, is less than the stress relaxation of most of the specimens dried below 11%RH. This could also be concluded indirectly from the unprocessed stress relaxation results (Figure 9-2) where the stress relaxation curve of the 100%RH conditioned specimen is intercepted by almost all the other curves for samples having lower moisture contents. This may suggest that the removal of interlayer water modifies the viscoelastic nature of the C-S-H and results in an increase of the total stress relaxation. The increase in the creep compliance (analogous to the stress relaxation) upon drying has been previously reported for the Portland cement paste [6]. It should also be noted that the 100%RH curve for porous glass

(Figure 9-1) does not intercept with the curves for samples at 11%RH and dried conditions. The viscoelastic component of the porous glass appears to be independent of the moisture content (essentially related to the water adsorbed on the surface of solid phase and that in the pores).

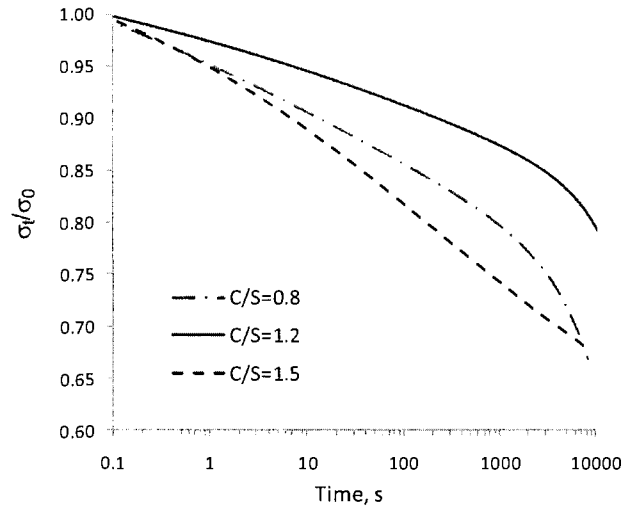


Figure 9-3. The viscoelastic component of the stress relaxation extracted through curve fitting of the data for the 100%RH conditioned C-S-H samples having various C/S ratios.

This observation supports the suggestion that the variations in the viscoelastic properties of C-S-H are attributable to the role interlayer water. The difference in the surface energy of the C-S-H (compared between the 100%RH and the 'dried' states) might be additionally responsible for partial changes in the viscoelasticity of the C-S-H. It is not clear from the results of the current study if the viscoelasticity of the C-S-H is dependent on its chemical composition. It would be necessary to examine a larger number of specimens covering a wider range of C/S ratio to confirm this. The dynamic modulus of elasticity was shown previously to be dependent on the C/S ratio of the C-S-H [10].

The stress relaxation curves of the Portland cement paste ($w/c=0.4$) are shown in Figure 9-4. The general trend in terms of the order of the curves for the samples in the saturated state to the 11%RH condition and below seems to be similar to those for the synthetic C-S-H. The saturated cement paste exhibits a distinct behavior, as mentioned for the compacted C-S-H samples, due to the hydrodynamic component of the stress relaxation. The inflection point in the curve seems to occur at about 20 seconds, analogous to that for the synthetic C-S-H, but much earlier than the values previously reported for the stress relaxation of the cement paste [20-23]. This difference is

possibly due to the fact that the hydrodynamic relaxation time is directly related to the square of the thickness [23]. The average thickness of the rectangular cement paste specimens tested in the current study was about 1 mm. In comparison to the results for the synthetic C-S-H (Fig. 9-2), the cement paste exhibits a noticeably lower stress relaxation. This is likely due to the difference between the degree of crystallinity of the C-S-H in the cement paste and that in the synthetic C-S-H. The relatively well-ordered and semi-crystalline structure of the synthetic C-S-H may provide more sites (analogous to “creep sites”) contributing to the stress relaxation. It is suggested that these sites are associated with the interlayer region of C-S-H.

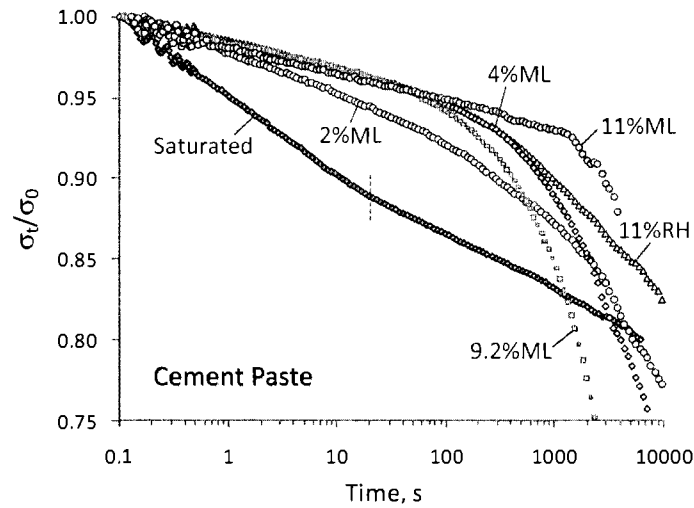


Figure 9-4. Stress relaxation of the Portland cement paste ($w/c=0.4$) at various humidity levels.

Comparison of the stress relaxation curves at 11%RH and subsequent incremental drying does not provide conclusive information on the role of interlayer water. It is well-known that the C-S-H in the hydrated cement paste is a nearly amorphous material [26]. The silicate structure is modified by the incorporation of other elements such as aluminum. Several types of cations may exist in the interlayer region. These parameters increase the complexity of the C-S-H structure and are likely to be responsible for the variations different from those for the synthetic C-S-H in the stress relaxation upon drying. It is, however, clear that the relaxation curves of ‘dry’ specimens intercept with the curve of the saturated one (similar to the observation for synthetic C-S-H in Fig. 9-2). This may be indicative of an increase in the viscoelastic deformation of C-S-H in cement paste when interlayer water is removed, analogous to the test results for the synthetic C-S-H.

It is interesting to notice that there is a considerable stress relaxation in the dry cement paste (Fig. 9-4) and C-S-H samples (Fig. 9-2) after the removal of final increments of water (about 10% mass loss from 11%RH condition achieved by 24 hour vacuum drying at 110 °C at the end of a typical drying regime). This may imply that even the completely dry solid structure of the C-S-H undergoes time-dependent deformations under load. Although water has a significant contribution to the stress relaxation of the C-S-H, it appears that the stress relaxation does occur in the dry state. This is contradictory to some research that suggests there is no creep behavior in the cement paste if the evaporable water is removed [11-13].

9.4 A model for stress relaxation and creep

The stress relaxation of C-S-H samples consists of hydrodynamic and viscoelastic components. The hydrodynamic component depends on the pore structure characteristics of the sample and the saturation level of the pores. The viscoelastic component of the stress relaxation appears to be dependent on the nanostructural features of the C-S-H. Interlayer water is suggested to contribute significantly to the viscoelasticity of the C-S-H and thus its time-dependent mechanical properties such as stress relaxation and creep. Several models have been proposed for the creep of concrete [2, 3]. A combination of mechanisms appear to account for the temporal deformation of cement-based materials. The following model is developed based on the ideas advanced in the current study with a focus on the role of interlayer water.

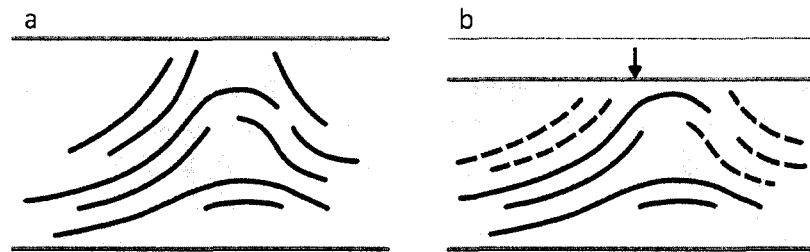


Figure 9-5. Proposed model for the viscoelastic behavior of the C-S-H. a: C-S-H layers are shown by solid lines. The nanostructural features are based on the Feldman-Sereda model for C-S-H [49]. b: The time-dependent deformation of C-S-H under load through the translation and sliding of the layers (shown by dashed lines).

The schematic in the Figure 9-5a presents a simplified model of the C-S-H. The agglomerates of C-S-H layers are formed from the stacking of several sheets of C-S-H, the details of which were discussed by Feldman and Sereda [32]. A monolayer of water is ideally situated in the interlayer

region in addition to the OH^- groups and Ca^{2+} ions (not shown). Under load (Fig. 9-5b) the stress is applied to the solid pore network. The deformation of the pore network results in an increase of the water pressure in the pores which is alleviated later by the flow of water. This accounts for the hydrodynamic relaxation. There is an elastic deformation in the C-S-H solid phase. It is suggested that under stress the C-S-H agglomerates exhibit a viscoelastic deformation exhibited over time. The C-S-H sheets translate against each other. A progressive breaking and formation of hydroxyl bonds in the interlayer region may also be postulated [5, 6]. The sliding of the C-S-H layers is proposed as the mechanism responsible for the viscoelastic behavior of C-S-H. Water molecules “reinforce” the C-S-H sheets. It is suggested that their removal increases the total stress relaxation of the C-S-H. Viscoelasticity of C-S-H is readily modified by the change in the moisture content associated with the interlayer water. Cross-linking of silicate tetrahedra and the interaction of calcium ions with the silicate tetrahedra are likely to be responsible for some of the inconsistent variations of the stress relaxation upon the removal of interlayer water. Further studies are required in order to elucidate the effect of these parameters. The development of a more comprehensive model that can explain all the experimental observations is subject to advanced corroborative research utilizing tools such as silicon and proton NMR.

9.5 Concluding Remarks

The stress relaxation behavior of phase pure C-S-H ($\text{C/S}=0.8, 1.2$ and 1.5), hydrated Portland cement and porous glass was studied using a three-point bending method. The samples were tested at various moisture contents obtained by conditioning them at 100%RH and 11%RH as well as removing water in several drying increments from 11%RH.

It was shown that the hydrodynamic component (present at the 100%RH condition) has a significant contribution to the stress relaxation during the initial times (up to 20s). At later times when the pore water pressure is alleviated, the viscoelastic part of the stress relaxation becomes dominant. The stress relaxation curves of the samples at 11%RH and lower humidity levels apparently do not exhibit a hydrodynamic relaxation and are primarily of a viscoelastic nature. The viscoelastic component of porous glass is similar at all humidity levels and does not appear to be dependent on the moisture content. In cement-based systems, however, the viscoelastic response of C-S-H is altered (generally in the form of a relative decrease at the initial times and an increase at later times) as the water is removed from the interlayer region. The total stress relaxation of ‘dry’ specimens (C-S-H and cement paste) is greater than that for the samples

conditioned at 100%RH. This is not the case for porous glass. It is suggested that the interlayer water plays an important role in the time-dependent deformation of cement-based materials. The viscoelastic behavior of C-S-H is attributed to the sliding of the C-S-H sheets which results in the deformation of C-S-H agglomerates under stress. The siloxane bonds may be broken and reformed due to the translation of the C-S-H layers. Removal of water from interlayer spaces modifies the viscoelastic behavior of C-S-H resulting in a higher total relaxation compared to that for the saturated conditions. Understanding the details of the sliding mechanism of C-S-H layers possibly taking into account the interaction of silicate tetrahedra and cations in the interlayer region at various moisture contents requires additional study utilizing methods such as NMR.

9.6 References

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C-S-H/Polyaniline Nanocomposites

Synthesis and characterization of a new cement-based polymer nanocomposite is reported. Calcium silicate hydrate (C-S-H) was prepared in the presence of aniline monomer followed by *in situ* polymerization in order to increase the degree of interaction between inorganic and organic phases. Two stoichiometrically different C-S-H systems were used. The properties of the C-S-H/polyaniline materials were studied using several analytical techniques including SEM, XRD, TGA, ^{29}Si MAS NMR and FTIR. It is suggested that the *in situ* polymerization can effectively be employed for producing a C-S-H/Polymer nanocomposite. The extent of molecular interaction with the polymer depends on the chemical composition of the C-S-H. Production of a new range of polymer modified cement-based systems having improved environmental stability and mechanical performance is promising.

10.1 Introduction

Application of nanotechnology in cement and concrete science has shown early promise for improving the properties and performance of concrete materials [1]. The preparation of inorganic/organic nanocomposites is a possible approach in order to achieve this goal. The advancements are primarily obtained through the polymer-modification of the calcium silicate hydrate (C-S-H) phase. Enhanced engineering properties and improvement in the durability characteristics are key objectives in the preparation of cement-based nanocomposites. Several mechanisms have been suggested for the interaction of various organic molecules with the inorganic C-S-H systems. These include: surface adsorption/grafting at the defect sites in the C-S-H silicate chain [2-4]; intercalation into the interlayer galleries of the C-S-H [5-9]; covalent bonding of silylated co-polymers on the C-S-H surface [10-12]. The observed differences in the nature and extent of the C-S-H/polymer interaction are most likely due to the preparation method and type of the polymer.

The main ideas for the synthesis of polymer-layered silicate nanocomposites have been originally developed in clay science [13]. Clay minerals such as montmorillonite, unlike C-S-H, have a very high swelling capacity [14] which makes it relatively easy for the polymer molecules to intercalate into the gallery regions. Thus, the methods applied in clay science that result in the formation of polymer intercalated nanocomposites have to be used cautiously in cement science. Generally, in the studies of organically modified C-S-H systems, a small amount of the polymer is added either to pre-formed C-S-H or during the C-S-H synthesis. Polymer molecules are relatively large in size, which makes them very difficult to fully interact with the inorganic C-S-H materials that can accommodate only about a monolayer of water between their sheets [15].

In the current work, the *in situ* polymerization technique is employed. This allows for the initial interaction of monomers with the C-S-H and makes the subsequent polymerization more effective. Polyaniline (PAn) was chosen as the organic moiety. Its monomer, aniline, is relatively small and can be readily polymerized by introducing an oxidant to the system [16]. Polyaniline is a popular conductive polymer that has excellent environmental stability [17]. It has been used successfully in the preparation of intercalated clay-based nanocomposites [16-19]. In this work, C-S-H was investigated for its capability to host the aniline and polyaniline guest molecules. Several analytical tools were employed in order to elucidate various aspects of the interaction of C-S-H with the aniline and polyaniline.

10.2 Method

10.2.1 Materials

C-S-H was prepared by mixing the stoichiometric amounts of calcium oxide and silica in excess water as described before. Two compositionally different C-S-H materials were studied having C/S ratios=0.8 and 1.2. These representative stoichiometries were selected based on the chemical and physical differences observed for two categories of C-S-H obtained above and below a C/S ratio of about 1.1 [20, 21]. C-S-H/aniline samples were prepared in a similar method to that for the phase pure C-S-H except that the water contained aniline monomer. 2mL of aniline (Sigma-Aldrich) was dissolved in the 75mL water in a beaker using a magnetic stirrer. Aniline has an oily appearance in water. Thus it needs to be carefully mixed in order to obtain a well-dispersed aqueous solution. This solution was added to the dry mix of the CaO and SiO₂ (C/S ratios=0.8 and 1.2). In clay science, the addition of aniline to the layered silicate is generally conducted under low pH conditions using HCl [16, 19]. This is not favorable in cement-based materials as it may result in the decalcification of the C-S-H.

All the bottles were mounted on a rotating rack (speed=16rpm) and the reactions were continued for 50 days. The gel-like materials were then filtered and washed several times with water. The phase pure C-S-H and C-S-H/aniline preparations were dried under vacuum for 4 days at room temperature. In order to polymerize the aniline monomers, ammonium persulfate (Sigma-Aldrich) was used as an external oxidant. Each dried C-S-H/aniline preparation (0.5g) was first mixed in 100 mL of water using a magnetic stirrer. While stirring the suspension solution, 0.228g of ammonium persulfate was added. The stirring was continued for 24 hours at room temperature. The final material was filtered, washed several times, and dried under vacuum at room temperature for 4 days. The filtered C-S-H/polyaniline (C/S=1.2) had a light orange-pinkish color whereas the other nanocomposite sample (C/S=0.8) was nearly white. A similar color difference was observed for the original C-S-H/aniline samples. The difference in the color of the produced materials is an indication of the different extent of interaction of C-S-H (depending on its stoichiometry) with organic molecules.

Pure polyaniline was separately produced by adding ammonium persulfate to the aqueous solution of the aniline. All the materials were stored in nitrogen purged glass vials after drying until used in various experiments.

10.2.2 Characterization

The morphological changes due to the interaction of C-S-H precursor with polyaniline were investigated using a scanning electron microscope. Micrographs were acquired from the uncoated specimens using a Hitachi S-4800 instrument. An accelerating voltage of 1.2 kV and an emission current of 7 μ A were applied at a working distance of about 3 mm to obtain images having relatively greater resolution and more details of the surface features than those obtained with higher accelerating voltage and working distance as demonstrated previously [22]. The SEM pictures reported in the current work were all acquired at 40K magnification.

The changes in the d_{002} basal spacing of the samples were monitored using the X-ray diffraction technique. The XRD spectra were obtained using a Scintag XDS 2000 diffractometer using $\text{CuK}\alpha$ radiation (wavelength=0.15405 nm) and a graphite monochromator. A diffraction angle range of $2\theta = 5$ to 15° was used at a step size of 0.03° and a 7 second count interval with an accelerating voltage of 45kV and current of 35mA. The noise level in the spectra was reduced by replacing the curves with a moving average of 5 data points.

Simultaneous thermogravimetric and differential scanning calorimetry (TGA-DSC) were performed using a TA Instruments SDT Q-600. About 10mg of the sample was heated from ambient to 1000 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$ under the flow of nitrogen gas (10mL/min). The derivative mass loss and heat flow was analyzed using Universal Analysis 2000 software.

The ^{29}Si MAS NMR spectra were recorded using a Bruker Avance 200 instrument operating at a ^{29}Si resonance frequency of 39.73 MHz. A magic angle spinning (MAS) rate of 4kHz was employed using a 7 mm MAS $^1\text{H}/\text{X}$ Bruker probe. High-power proton decoupling (50 kHz) was employed during spectra acquisition. The relaxation delay between 4 μs ($\pi/4$) r.f. pulses was 60 s which was found sufficient for obtaining quantitative spectra. A total number of 1420 scans were acquired for each spectrum. The ^{29}Si NMR chemical shifts were referenced to external tetramethylsilane at 0.0 ppm.

The Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet spectrometer (Model Nexus 870) equipped with an MTEC photoacoustic cell (Model 300). The test was conducted on the powder materials placed in a 10mm diameter stainless steel pan. 100 scans were collected for each sample. The background was corrected using the carbon black standard

reference sample. Helium was used as the purge gas (flow rate = 5mL/s). Results were analyzed using OMNIC software (Nicolet Instruments).

10.3 Results and discussion

10.3.1 Scanning Electron Microscopy (SEM)

The micrographs acquired from the surface of the polymer modified C-S-H samples are compared in Figure 10-1 with those obtained from the control samples. It is observed that the C-S-H has a flaky morphology. The size of the C-S-H flakes depends on the C/S ratio. Low lime C-S-H (Fig. 1-a) has smaller but densely connected flakes compared to C-S-H having C/S=1.2 (Fig. 10-1c). The relatively high surface area of the C-S-H (C/S=0.8) can easily be noticed. This is qualitatively consistent with the nitrogen BET surface area measurements for this sample, 186 m²/g. The high content lime C-S-H (C/S=1.2) seems to have thicker and larger flakes, and thus lower BET surface area, 30 m²/g.

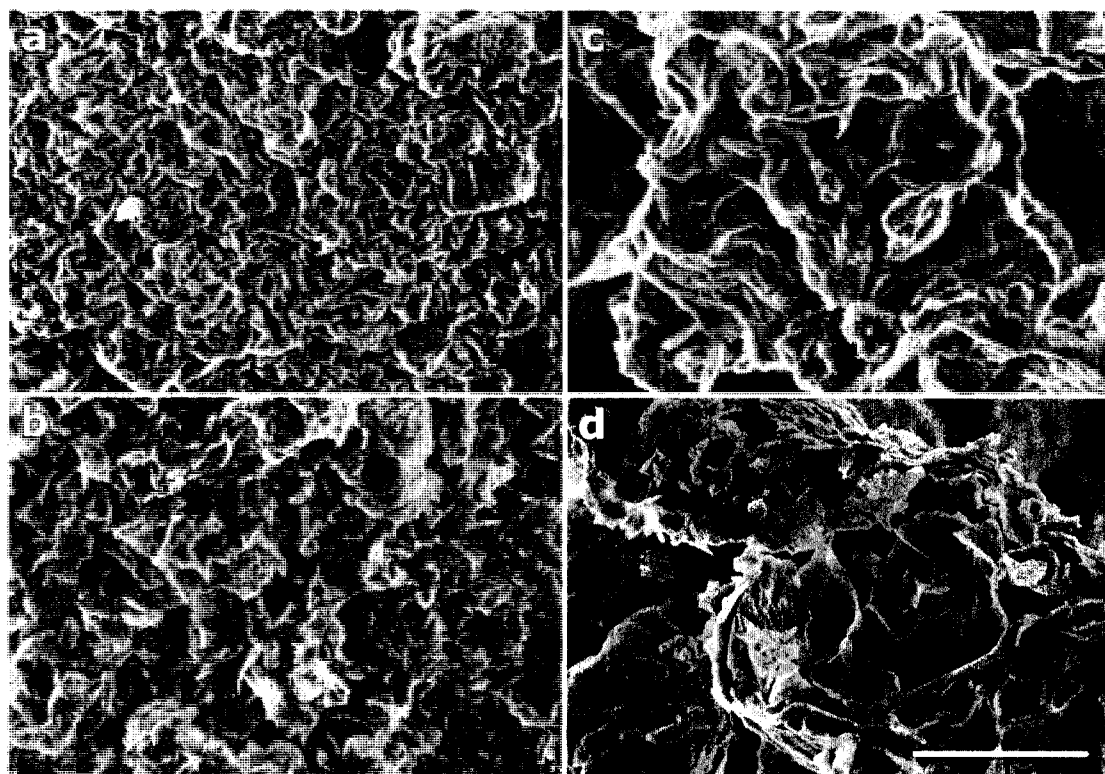


Figure 10-1. The representative SEM images of a) C-S-H (C/S=0.8), b) C-S-H/polyaniline (C/S=0.8), c) C-S-H (C/S=1.2), d) C-S-H/polyaniline (C/S=1.2) captured at 40K magnification. The white scale bar indicates 1 μm.

The morphology of the C-S-H is altered following the interaction with the polyaniline (Figs. 10-1b and 10-1d) although the main structural features are maintained. It appears that the C-S-H (C/S=0.8) nanocomposite has thinner flakes and a less dense structure. The SEM is not conclusive as to any significant change in the morphology of the polymer modified C-S-H (C/S=1.2). This might be explained by assuming that the poly/aniline molecules are interacted at the defect sites. The number of defect locations (i.e. missing bridging tetrahedra) is relatively larger at higher C/S ratio C-S-H [5]. The interaction of polyaniline molecules on the surface at these defect sites, therefore, may not significantly change the morphology of the C-S-H (C/S=1.2) as much as that in the 0.8 C/S ratio C-S-H. Particles having a morphology similar to that of the pure polyaniline (shown in Figure 10-2) were not found in either of C-S-H/polyaniline preparations. This may suggest that the polymer is intimately interacted with the nanostructure of the C-S-H and is not freely present in the samples. Moreover, the elemental analysis using energy dispersive X-ray technique (EDX) did not provide any evidence for the existence of regions containing only carbon atoms (the primary detectable atom in the polyaniline). Si and Ca atoms were present in all particles indicative of the absence of separately formed pure polyaniline (that would contain only detectable C atom) in the nanocomposite.

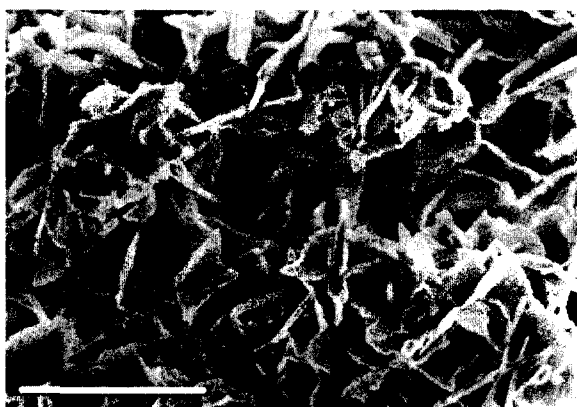


Figure 10-2. The SEM micrograph of the pure polyaniline prepared by the polymerization of aniline monomer using ammonium persulfate as an oxidant at room temperature. The white scale bar indicates 1 μm .

10.3.2 X-Ray Diffraction (XRD)

The main purpose of the XRD analysis was to examine the change in the distance between the layers of C-S-H due to the possible interaction with aniline and polyaniline. The XRD spectra of the samples are shown in Figure 10-3. Only the region from $2\theta=5$ to 12 degrees, where d_{002} basal spacing reflection occurs, is selected. The XRD peaks shown are somewhat broad indicative of

the semi-crystalline nature of the synthetic C-S-H. There is a clear distinction between the basal spacing of the two phase pure C-S-H samples (Figs. 10-3a and 10-3d). The mean distance between the C-S-H sheets decreases as C/S ratio increases from about 1.17nm (C/S=0.8) to 0.97nm (C/S=1.2). This difference is possibly due to the existence of a larger number of bridging tetrahedra and Si-OH groups in the silicate chain of low C/S ratio C-S-H. The interlayer water occupies a similar space of about one water molecule thick in both C-S-H systems and the total decrease in the basal spacing upon the removal of interlayer water from various C-S-H systems is essentially similar [15]. The semi-crystalline structure of the C-S-H is preserved in the aniline solution as supported by the existence of low angle basal spacing reflection (Figs. 10-3b and 10-3e). The basal spacing does not seem to be affected compared to the control samples when the C-S-H is formed in the presence of aniline monomers. It can, however, be noticed that this peak is broadened. It is suggested that the monomer molecules, considering their size of about 0.2nm [16], are possibly partially intercalated into the interlayer regions of C-S-H. This may result in an uneven change in the basal spacing that is manifested by X-Ray diffraction over a wider range of 2θ ; i.e. a broader peak.

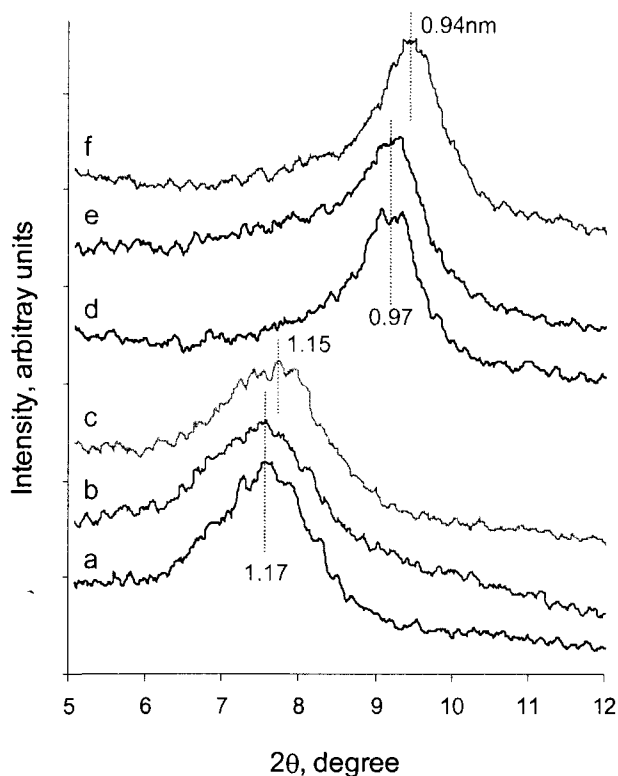


Figure 10-3. The XRD spectra showing the d_{002} basal reflection of a) C-S-H (C/S=0.8), b) C-S-H/aniline (C/S=0.8), c) C-S-H/polyaniline (C/S=0.8), d) C-S-H (C/S=1.2), e) C-S-H/aniline (C/S=1.2), f) C-S-H/polyaniline (C/S=1.2)

The XRD spectra of the samples after the polymerization of aniline are shown in Figures 10-3c and 10-3f. It is unexpectedly observed that the basal spacing of the C-S-H is slightly decreased to about 1.15nm and 0.94nm for C/S=0.8 and 1.2, respectively. The broadness of the peaks is similar to the C-S-H/aniline preparations. Other researchers have only reported either an increase [5-7] or no change [23, 24] in the distance between the layers of C-S-H when organically modified. It may be suggested that the aniline monomers situated initially at the end of interlayer galleries are removed to form the polyaniline during the polymerization process. This would slightly decrease the basal spacing. Another possible explanation is that the orientation and alignment of the rings in the polymer is different from that in the monomer molecules. The polyaniline may situate between the C-S-H layers in a way that the benzene ring is oriented parallel to the sheets. The monomer molecules, however, are most likely arranged randomly in various directions which results in higher basal spacing compared to that in the case of C-S-H/polyaniline samples after polymerization.

10.3.3 Thermogravimetric Analysis (TGA)

The derivative of the mass loss curves for C-S-H/polyaniline samples obtained through TGA are shown in Figure 10-4. The first peak, located between ambient temperature and about 250 °C, is associated with the removal of free, adsorbed and interlayer water. It is also possible that the unreacted aniline monomers contribute to the mass loss in this region. In both samples, this peak is followed by a smaller and broader peak (240 - 460 °C) that is possibly due to the removal of constitutional water from the C-S-H crystal structure as reported earlier [25]. These two peaks are present in the control samples as well as C-S-H/aniline preparations (not shown).

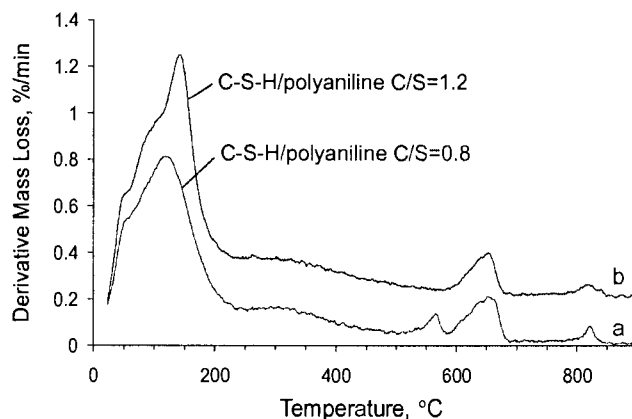


Figure 10-4. The derivative of the mass loss curves in TGA experiment for C-S-H/polyaniline nanocomposites; a) C/S=0.8, b) C/S=1.2.

After these events there is no significant mass loss in all samples up to about 800 °C except for the C-S-H/polyaniline materials (Figure 10-4). The derivative mass loss for the high lime C-S-H nanocomposite (Fig. 10-4b) has a peak between 580 and 640 °C. This mass loss, that is about 0.94% of the solid mass, is attributed to the thermal decomposition of the polyaniline in the sample [26, 27]. This event is accompanied by an exothermal peak in the heat flow curves from differential thermal analysis (not shown). It should also be mentioned that there is no mass loss in this region for the C-S-H/aniline preparations.

The TGA result for the low lime sample (C/S=0.8) contains a similar peak to that in the derivative mass loss of C-S-H/polyaniline (C/S=1.2) in the range of 580-640 °C. However, there is an additional smaller peak between 450 and 580 °C. It is suggested that this extra peak is also associated with the polyaniline decomposition. It is likely that the polyaniline in this sample is formed in two different structural locations of C-S-H (e.g. grafted on the surface or partially intercalated in the interlayer regions). The bond energy between the polymer and the inorganic base is possibly different between these locations. The mass loss at lower temperatures is likely associated with the polyaniline that is physically adsorbed on the surface of C-S-H and therefore requires less energy for the decomposition. Higher temperature mass loss, on the other hand, can be attributed to the presence of stronger bonds between polyaniline and C-S-H (such as those related to the defect sites and interlayer regions). It is also possible that the polymer chain length and therefore its molecular weight depends on the local environment in which the aniline monomer was polymerized [28, 29]. Therefore, the energy required to decompose the polyaniline is different for two distinct polyaniline materials manifested by a shift to lower temperatures. The total mass loss in the solid phase is about 1.58% for the low lime nanocomposite preparation (C/S=0.8). The polymer content for this sample is almost 50% more than that for the high lime C-S-H/polyaniline sample. This is possibly because of the higher surface area of the C-S-H (C/S=0.8) that provides more sites for the interaction with the polymer. The nitrogen BET surface area of the C-S-H is about 186 and 30 m²/g for C/S=0.8 and 1.2, respectively. An estimate shows that the polyaniline loading was about 20% of the surface monolayer coverage in C/S=0.8 C-S-H/polyaniline preparation, or about 40% of the available intercalation volume. In the C/S=1.2 C-S-H/polyaniline preparation, the estimated polyaniline loading was even higher, at about 60% of the monolayer coverage, or 120% of the estimated intercalation capacity.

There is a final mass loss in both samples at about 810 °C, which is due to the transformation of C-S-H to β -wollastonite [30].

10.3.4 ^{29}Si MAS NMR Spectroscopy

Silicon NMR is a powerful technique for probing the nanostructure of the layered silicate hydrates including C-S-H [31]. It has also been employed in order to provide evidence for the interaction of organic substances with C-S-H [32]. The ^{29}Si MAS NMR spectra obtained for various C-S-H systems are shown in Figure 10-5. The spectra of high C/S ratio preparations (C/S=1.2) contain two peaks at about -79.3 and -84.9 ppm. These peaks correspond to Q^1 (end chain silicate tetrahedra) and Q^2 (middle chain and bridging silicate tetrahedra), respectively [31]. It is observed that the relative intensity of Q^2 to Q^1 , which serves as an indication of the silicate polymerization, changes when the C-S-H is organically modified.

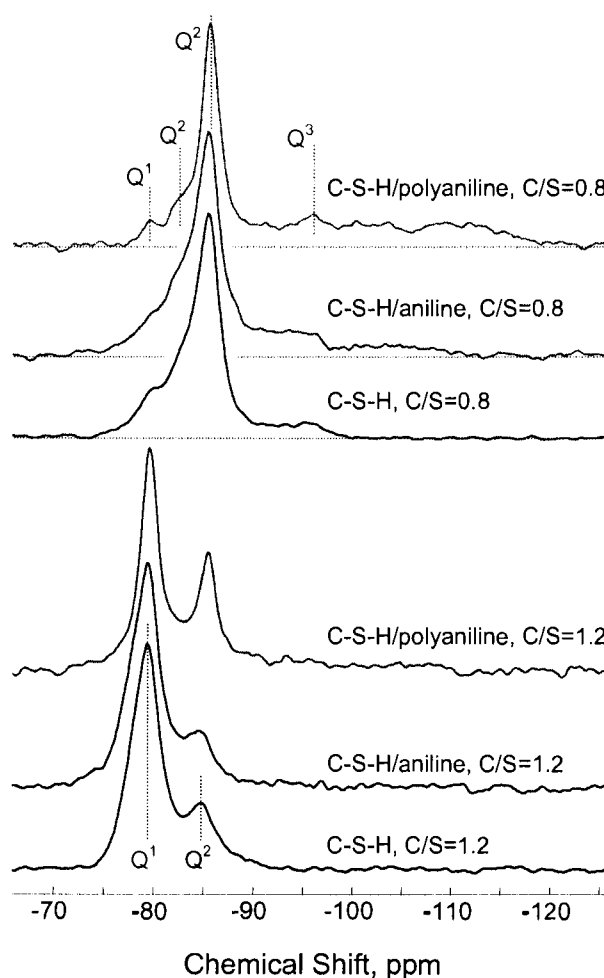


Figure 10-5. The ^{29}Si MAS NMR spectra of the phase pure and organically modified C-S-H systems.

In order to examine the extent of silicate polymerization in these materials quantitatively, the spectra were deconvoluted using DMfit software [33]. The integral intensity of the simulated Q^1 and Q^2 peaks by Lorentzian lines (not shown) are presented in Table 10-1. It is noted that the

Q^2/Q^1 ratio increases from 0.21 for the pristine phase pure sample to 0.63 in the polymer-modified C-S-H ($C/S=1.2$). The increase in the silicate polymerization of modified C-S-H system is attributed to the shielding effect of organic materials adsorbed at defect locations on the surface of the C-S-H as suggested previously for several other organically modified C-S-H nanocomposites [32]. Some decalcification of the C-S-H during the polymerization (caused by the immersion in excess water and relatively low pH of the solution) as examined using EDX may partially be responsible for the increase in the silicate polymerization of the C-S-H [34]. However, similar increase in the degree of silicate polymerization of C-S-H-polymer nanostructures has been previously reported [32] even when the reagents are not interacted in an aqueous solution.

Table 10-1. Integral intensity (%) of the deconvoluted peaks in the ^{29}Si MAS NMR spectra using Lorentzian lines.

	Sample	Q^1	Q^2	Q^3	Q^4	Q^2/Q^1
$C/S=1.2$	C-S-H	82.6	17.4	—	—	0.21
	C-S-H/aniline	87.4	12.6	—	—	0.14
	C-S-H/polyaniline	61.3	38.7	—	—	0.63
$C/S=0.8$	C-S-H	8.6	86.6	4.8	—	10.1
	C-S-H/aniline	3.1	75.9	11.4	9.6	24.7
	C-S-H/polyaniline	1.7	48.9	28.8	20.6	28.1

The deconvolution of the spectra for the low C/S ratio C-S-H systems ($C/S=0.8$) suggests that in addition to the relatively small Q^1 peak at -79.8 ppm three other peaks exist having more negative chemical shift values. Contrary to the C-S-H ($C/S=1.2$), two peaks at about -83.4 and -85.6 ppm are identified for the $C/S=0.8$ C-S-H samples in the region for Q^2 sites (Fig. 10-5). Both of these peaks are attributed to the Q^2 sites at different silicate structural locations [35]. Their combined integral intensities were thus considered in calculating the extent of silicate polymerization. As shown in Table 10-1, the Q^2/Q^1 ratio increases from 10.1 in the control C-S-H($C/S=0.8$) to 24.7 and 28.1 in the C-S-H/aniline and /polyaniline preparations, respectively. The peak at -95.4 ppm is assigned to the Q^3 site. This peak that does not exist in the high C/S ratio systems ($C/S=1.2$) is due to the cross-linking of some of the silicate tetrahedra between the C-S-H sheets [36]. The integral intensity of Q^3 is increased while it is broadened when the C-S-H is organically modified. Simultaneously, the integral intensity of Q^2 is decreased. It is interesting to note that an additional

very broad peak in the chemical shift range of -100 to -120 ppm is formed in aniline and polyaniline preparations having C/S=0.8. The existence of a peak in this area that represents Q^4 sites [37] has not been reported previously for polymer-modified C-S-H systems. This is indicative of a significant increase in the silicate polymerization of the C-S-H structure. The schematic shown in Figure 10-6 presents a model for possible interaction of the polymer molecules with the C-S-H resulting in an increase of the silicate polymerization. The formation of Q^4 sites may also imply that the structural integrity and mechanical performance of the polymer-modified C-S-H nanocomposites would be increased.

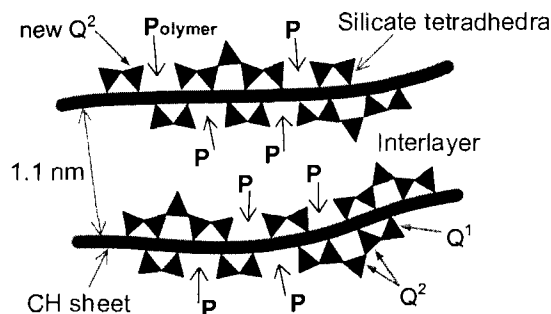


Figure 10-6. Schematic of the polymer-modified C-S-H nanostructure.

10.3.5 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the phase pure and organically modified C-S-H systems are shown in Figure 10-7. The characteristic set of bands in the range of 750-1250 cm^{-1} in all samples is due to stretching vibrations of Si-O bonds in the C-S-H [38-40]. The location of the main high intensity band in this region is indicated in Table 10-2 for various C-S-H materials. This band is associated with the Q^2 silicon sites [39, 40]. The average frequency for this vibration is about 967 and 957 cm^{-1} for the C-S-H systems having a C/S=0.8 and 1.2, respectively. The somewhat higher vibration frequency of this band for lower C/S ratio material is an indication of higher level of polymerization in the C-S-H [39]. It is also observed that the location of this band is slightly shifted toward higher frequencies when the C-S-H is interacted with aniline and subsequent formation of polyaniline, again suggesting the increase in the polymerization of the silicate structure. The intensity of the bands at higher frequencies on the left shoulder of the main Q^2 band also increases. It is also noted that a high frequency band appears at about 1210 cm^{-1} in the C-S-H/polyaniline sample (C/S=0.8, Figure 6-c). This band is most likely due to the existence of Q^3 silicate sites [40]. These results are consistent with the observations from the ^{29}Si MAS NMR

(discussed in the previous section) indicating that the interaction of C-S-H with organic molecules increases the polymerization extent of the silicate tetrahedra. Samples having $C/S=1.2$ contain double bands at 790 and 815 cm^{-1} that are assigned to the Si-O stretching of the Q^1 tetrahedra. These bands are not present for $C/S=0.8$ materials.

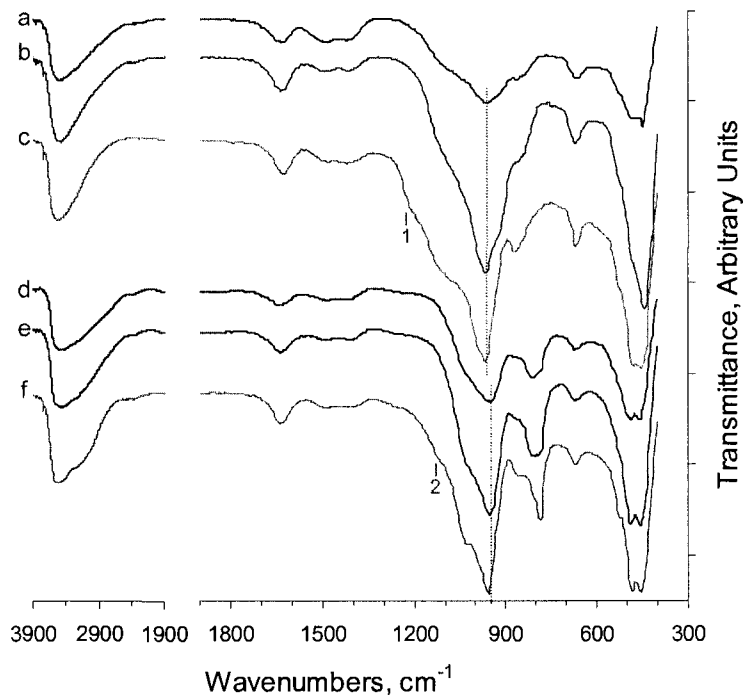


Figure 10-7. The FTIR spectra of a) C-S-H ($C/S=0.8$), b) C-S-H/aniline ($C/S=0.8$), c) C-S-H/polyaniline ($C/S=0.8$), d) C-S-H ($C/S=1.2$), e) C-S-H/aniline ($C/S=1.2$), f) C-S-H/polyaniline ($C/S=1.2$). The location of the main band in C-S-H is identified by the dotted line. Bands marked as 1 and 2 are associated with the Si-O (in Q^3 and possibly Q^4 sites) and polyaniline, respectively.

The FTIR spectrum of pure polyaniline (not shown) contains a main band at about 1110 cm^{-1} due to the vibration of C-N groups [17, 41]. This band appears on the shoulder of the primary band of the C-S-H/polyaniline sample ($C/S=1.2$, Figure 10-7f) which is easily identified when compared with the spectra of the C-S-H and C-S-H/aniline (Figs. 10-7d and 10-7e). For $C/S=0.8$ preparations this band overlaps the band in the phase pure C-S-H sample. However, it appears that its relative intensity increases in the polymerized systems. This may be indicative of an interaction between polyaniline and the surface of C-S-H. The presence of other bands of polyaniline in the C-S-H-polymer materials can not be distinguished due to their low intensity and overlap with the bands from C-S-H. Nevertheless, the absorption bands at about 3400-3200 cm^{-1} and 2300-2800 cm^{-1} , could be attributed to the interaction of NH and NH^+ groups present in polyaniline chains with the C-S-H surface [42].

Table 10-2. The frequency (cm^{-1}) of the main FTIR band for the C-S-H.

	C/S=0.8	C/S=1.2
C-S-H	964	957
C-S-H/aniline	968	957
C-S-H/polyaniline	968	960

The set of bands in the region from 400-750 cm^{-1} is characteristic of Si-O-Si deformation. These bands are well-defined in the C/S=1.2 samples. The stretching bands due to the water are located at 1650 and 3550 cm^{-1} [38]. The Ca-OH vibration results in the formation of a band at 3750 cm^{-1} . This band becomes sharper in the organically modified C-S-H samples. The remaining bands at about 870, 1430 and 1500 cm^{-1} are associated with the carbonates [40].

10.4 Concluding Remarks

C-S-H based polymer modified nanostructures were prepared by the *in situ* polymerization method. Two different C-S-H systems (C/S=0.8 and 1.2) were investigated. C-S-H was produced in the presence of aniline monomers subsequently polymerized by an oxidant. There are several indications, obtained using a variety of analytical methods, that suggest the organic phases are intimately interacted with the nanostructure of C-S-H. It is observed that the C-S-H/polyaniline samples have a higher level of silicate polymerization, the extent of which depends on the stoichiometry of the C-S-H. It is therefore possible to engineer various types of cement-based nanocomposite systems by varying the chemical composition of the inorganic host. The interaction of polyaniline with the C-S-H may be improved through various methods such as conducting the reactions at temperatures higher than ambient, increasing the concentration of the monomer in the solution or increasing the hydration and polymerization times. The experimental characterization provided indirect evidence for possible enhancement of the mechanical performance and durability of the C-S-H-polymer nanohybrids. The more detailed measurements in this regard are the subject of a separate study.

10.5 References

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Physical and Mechanical Stability of C-S-H Nanocomposites

This chapter presents the results of preliminary investigations on the mechanical and durability performance of C-S-H/polymer nanocomposites (C/S=0.8 and 1.2). The C-S-H/polyaniline preparation method presented in chapter 10 was slightly modified. XRD and DMA experiments were conducted in order to evaluate the physical and mechanical stability of polymer-modified C-S-H systems. Changes in the 002 basal spacing, storage modulus (E') and internal friction ($\tan \delta$) of the C-S-H/aniline and /polyaniline nanocomposites were examined upon the removal of the interlayer water. It was shown that the interaction of polyaniline with the C-S-H reduces the amount of decrease in the 002 basal spacing. Initial DMA response of the C-S-H/polyaniline samples appears to be improved.

11.1 Introduction

The main objective in the recent attempts to produce organically-modified C-S-H nanocomposites has been to enhance the mechanical and durability characteristics of cement-based materials [1-4]. The main focus of these studies has been on various preparation techniques and use of different organic moieties [2-13]. Although a direct measurement has not been conducted on the C-S-H/polymer nanohybrids, it has been suggested that the modulus of elasticity of C-S-H can be increased by as much as 40-100% [3]. Durability of these novel systems may also be improved as the polymer molecules can limit the access of aggressive ions to the nanostructure of C-S-H specially the interlayer region [4].

The durability of C-S-H based materials is largely dependent on the extent of interaction of aggressive ions with its nanostructure. The accessibility and exchange of ions in the interlayer region also plays an important role in the stability of layered calcium silicate hydrates. The lack of experimental evidence for the mechanical and durability performance of C-S-H/polymer nanostructures is partially due to the fact that materials are prepared in the powder form which is not a suitable state for most engineering investigations. A link between the chemistry of organically-modified materials and their engineering performance has been lacking in most cases.

In the current work, the change in the 002 basal spacing of phase pure and organically-modified C-S-H preparations (C/S ratios = 0.8 and 1.2) are examined due to the removal of the interlayer water. This may provide clues about the stability of the layered structure of C-S-H nanocomposites. For engineering investigations, a compaction technique is used to form solid bodies from the C-S-H and C-S-H/polyaniline materials. The DMA response of the compacted samples is evaluated at various increments of drying from the 11%RH condition.

11.2 Experimental

The preparation of materials (phase pure and polymer-modified C-S-H) was similar to that explained in the chapter 10. Briefly, C-S-H, C-S-H/aniline and C-S-H/polyaniline systems were synthesized having C/S ratios = 0.8 and 1.2. A longer period of hydration was, however, used in this study (90 days) in order to obtain well-aged and more crystalline materials. Polymerization of the monomers was also allowed to continue for 3 days as opposed to 1 day in the previous work. This may increase the interaction of the polymer molecules with the C-S-H. Moreover, the aniline monomers that are supposedly intercalated in the interlayer space are not easily polymerized due

to the limited access of the initiator to this region. An extended period of polymerization may therefore be proven useful. The materials were equilibrated at 11%RH before the experiments. For mechanical measurements, the powder materials were compacted (according to the method mentioned in chapter 3) in order to obtain rectangular prisms of C-S-H and C-S-H/polyaniline systems. The compaction pressure was adjusted so that the total porosity level of the specimens would be about 30%. This is an important aspect in comparing the mechanical properties of solids as they are greatly controlled by the porosity of the material. The thickness of the samples varied between 0.8 and 1.2 mm depending on the type of the material. The length and width of all specimens were 58.9 and 12.97 mm, respectively. The compacted samples were conditioned at 11%RH for an additional 1 week.

Two sets of experiments were conducted: XRD and DMA. Various types of phase changes due to the dehydration of the C-S-H systems were demonstrated based on XRD results in chapter 4. These include a sudden decrease in the basal spacing of high C/S ratio C-S-H (I) (after about 4-7% mass loss from the 11%RH condition) as opposed to a gradual decrease in the basal spacing of low C/S ratio C-S-H (I). If intercalated in the interlayer space of the C-S-H, the monomer or polymer molecules may restrict the change in the basal spacing of C-S-H upon the removal of interlayer water. This can be examined using XRD analysis of the samples before and after drying. The X-ray diffraction spectra of the samples were acquired using a Scintag XDS 2000 diffractometer (CuK_α radiation). A 2θ range of $5^\circ < 2\theta < 13^\circ$, a step size of 0.03° and a 3 second count interval was used to follow the changes in the d_{002} peak. Samples were covered by Mylar film in order to avoid the change in the moisture content of the samples during the test. This layer did not produce any reflection in the 2θ range studied in the current work. Samples were examined at two humidity conditions: 11%RH, and dried under vacuum at 110°C for 3 hours.

The dynamic mechanical response of the compacted C-S-H and C-S-H/polyaniline rectangular samples were evaluated at various temperatures using a Rheometrics RSA II instrument in three-point bending method. An initial static force of 3g was first applied on the specimen. The temperature was increased from 30 to 200°C (rate= $2^\circ\text{C}/\text{min}$). Measurements were made at 2°C increments. At each increment a frequency range of 0.1 to 10 Hz using an oscillating strain level of 0.01% was applied. The storage modulus (E') and internal friction ($\tan \delta$) of samples were recorded at each temperature and frequency.

11.3 Results and Discussion

11.3.1 X-Ray Diffraction

The XRD spectra of the phase pure C-S-H systems as well as C-S-H/aniline and C-S-H/polyaniline nanocomposites at 11%RH and after drying are shown in Figure 11-1. The 2θ values for the x axis were converted to d spacing (in nm) using Bragg's law.

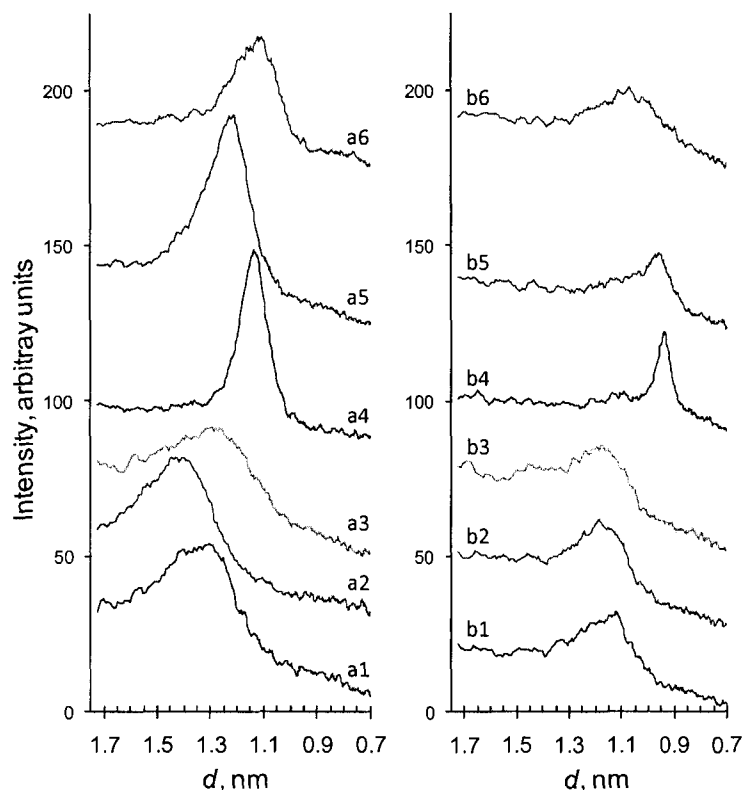


Figure 11-1. The XRD spectra of phase pure and polymer-modified C-S-H systems at 11%RH (series a) and after the removal of interlayer water using vacuum drying at 110 °C for 3 hours (series b). Samples are: 1: C-S-H (C/S=0.8), 2: C-S-H/aniline (C/S=0.8), 3: C-S-H/polyaniline (C/S=0.8), 4: C-S-H (C/S=1.2), 5: C-S-H/aniline (C/S=1.2), 6: C-S-H/polyaniline (C/S=1.2).

The location of the 002 basal spacing peak was considered as the basis for discussions. The d_{002} values for various C-S-H systems are presented in Table 11-1 at two humidity conditions. The decrease in the basal spacing of the C-S-H due to drying is also calculated in the same table. The results for the first series (a) of the samples show marked increased in the 002 basal spacing values of the C-S-H systems from those for the analogous systems prepared for the study in

chapter 10 (Fig. 10-3). This clearly shows the effect of the hydration time and aging on the distance between the layers of the C-S-H. Incorporation of calcium ions in the interlayer space and change in the extent of the silicate polymerization may be responsible for the increase in the basal spacing of the C-S-H systems at extended reaction periods.

Table 11-1. The decrease in the basal spacing of the phase pure and polymer-modified C-S-H systems due to the removal of interlayer water.

		d_{002} basal spacing, nm		
		11%RH	Dried	Total decrease
C/S=0.8	C-S-H	1.325	1.130	0.20
	C-S-H/aniline	1.420	1.185	0.24
	C-S-H/polyaniline	1.285	1.170	0.12
C/S=1.2	C-S-H	1.130	0.935	0.20
	C-S-H/aniline	1.220	0.960	0.26
	C-S-H/polyaniline	1.110	1.075	0.04

It is also noticed (in comparison with results presented in Fig. 10-3) that significant changes occur in the basal spacing of the C-S-H interacted with aniline and polyaniline if longer reaction and polymerization times are allowed. There is about a 0.1 nm increase in the basal spacing of the C-S-H (both C/S ratios) when synthesized in the presence of the aniline monomers in the aqueous solution. This may be attributed to the intercalation of the aniline monomers in the interlayer space. There is, however, a decrease of about 0.14 and 0.11 nm in the basal spacing after polymerization of the C-S-H/aniline samples having C/S=0.8 and 1.2, respectively. It is suggested that the polymerization of the aniline changes the orientation of the aniline molecules as discussed in the previous chapter resulting in a decrease of the basal spacing. Organically modified C-S-H materials (both C/S ratios) have a broader basal spacing reflection than the phase pure C-S-H which again supports the interaction of the aniline and polyaniline in the interlayer region of the C-S-H.

The XRD spectra of the samples were obtained after drying (series b in Fig 11-1) in order to examine the possibility of intercalation of the aniline and polyaniline in the interlayer space. Upon the removal of the interlayer water, C-S-H undergoes a phase change manifested by a

decrease in the basal spacing. It is shown in Table 11-1 that the level of decrease in the basal spacing is altered systematically in the organically modified C-S-H nanocomposites. C-S-H/aniline and C-S-H/polyaniline preparations exhibit, respectively, higher, and lower decrease in the basal spacing than that in the phase pure C-S-H samples upon the removal of interlayer water.

The evidently lower decrease in the basal spacing of the C-S-H/polyaniline samples is possibly due to the restraining effect of the polyaniline molecules present in the interlayer region. This has two main implications. First, the presence of the polyaniline in the interlayer space is likely to restrict the access of the aggressive ions to the nanostructure of the C-S-H. This improves the durability of the modified C-S-H materials. Second, the phenomena such as shrinkage and creep that are related to the layered nature of the C-S-H may be modified. The collapse of the C-S-H layers upon the removal of water and the length change associated with is likely altered.

11.3.2 Dynamic Mechanical Analysis of C-S-H/Polyaniline Nanocomposites

Dynamic mechanical properties of the cement-based materials can be monitored over a wide range of temperatures. Applying temperatures higher than ambient would essentially result in the removal of the water molecules. These include the adsorbed, interlayer and constitutional water in the 11%RH conditioned C-S-H systems. It was shown in chapter 8 that the DMTA method provides similar results to that of DMA conducted at various mass loss increments in the C-S-H upon the removal of water. It also results in a more continuous set of data with a larger number of data points. The main oscillatory features of the E' and $\tan \delta$ curves for C-S-H obtained in DMTA and DMA techniques are qualitatively the same.

The DMTA results for the phase pure C-S-H prepared in this section are shown in Figure 11-2. It should be noted that the C-S-H studied in the chapters 10 and 11 has a much lower reaction time (compared to that in the previous chapters) in order to be consistent with the aniline- and polyaniline-modified samples. Only the results obtained at the frequency of 0.25Hz are presented. Unlike the study in chapter 8, the data obtained at the frequency of 0.1Hz were very noisy. It should be noted that, as mentioned previously, the sensitivity of the DMTA data decreases as the frequency increases resulting in relatively low intensity peaks in the E' and $\tan \delta$ curves.

The results for the C-S-H (C/S=1.2) show qualitatively similar features to those in Figure 8-6. The location of the peaks in the E' and $\tan \delta$ curves, however, appears to be shifted toward higher

temperatures. The only difference in the C-S-H materials preparation is the reaction time. This observation is again indicative of the aging of the cement-based materials even though the chemical reactions are completed. A broad peak is also observed in the E' curve (Fig. 11-2) at about 145 °C. This response is possibly due to the removal of the constitutional water in C-S-H. It is also noted that the decrease in the E' from the 11%RH condition to that before the occurrence of the peak in the 'young' C-S-H curve (Fig. 11-2) is almost twice as much as the analogous decrease in the E' value of the well-aged C-S-H (Fig. 8-6). The internal friction of this sample is also higher than that for the young C-S-H. These observations are compatible with the interpretations advanced in chapter 8 regarding the dynamic mechanical response of various types of C-S-H.

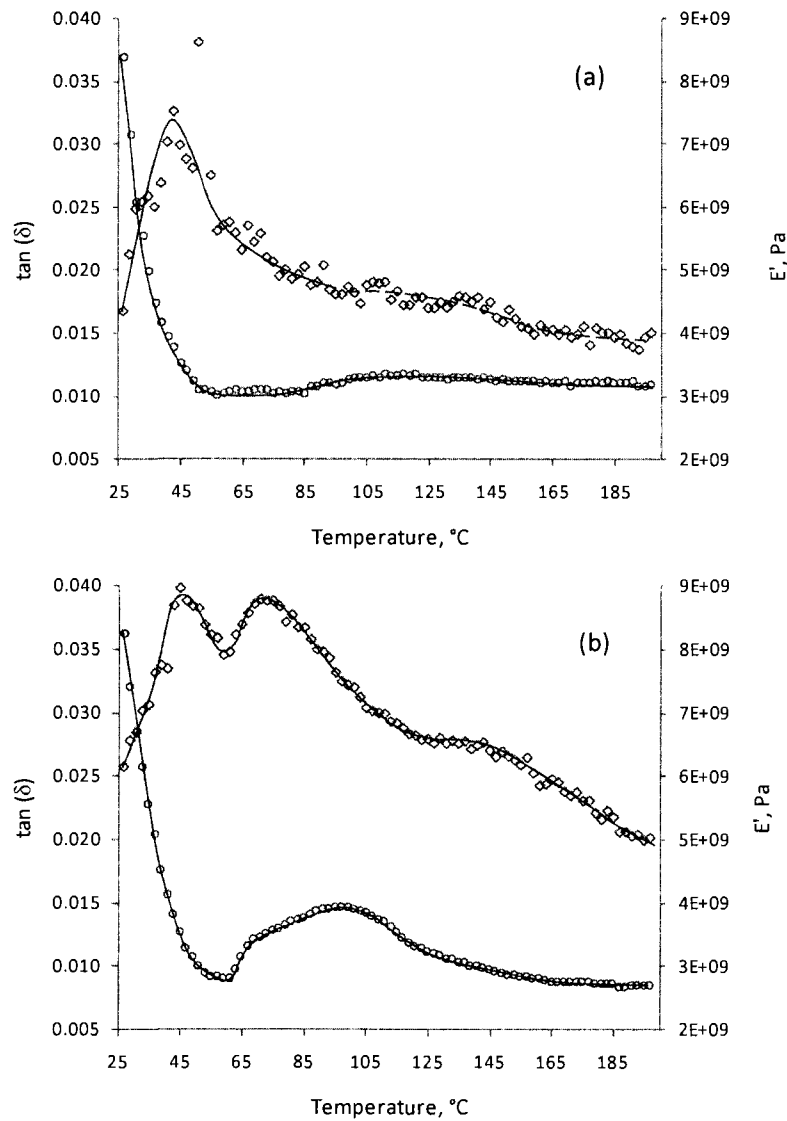


Figure 11-2. DMTA response of phase pure C-S-H ($\omega=0.25$ Hz); a: C/S=0.8, b: C/S=1.2.

The E' and $\tan \delta$ curves of the C-S-H (C/S=0.8) do not exhibit the typical double-peak in the $\tan \delta$ curve as observed in Figure 8-5. The E' curve experiences only a very subtle increase (a very broad peak) from 85 to 185 °C as opposed to a distinct peak. The data for E' is also relatively scattered compared to that for C/S=1.2 C-S-H. The dependence of the mechanical properties of C-S-H on its 'age' seems very important and merits a detailed study which is beyond the scope of the current chapter.

The DMTA results of the compacted C-S-H/polyaniline specimens are shown in Figure 11-3. The E' and $\tan \delta$ values of these samples at 11%RH are compared to those from the phase pure specimens in Table 11-2. It is noted that the initial modulus of the polymer-modified samples (at 11%RH) is higher than that for the control C-S-H. This may suggest that the interaction of polymer with the nanostructure of the C-S-H may increase its elastic properties. This conclusion is yet to be validated using a larger number of specimens over a wide range of porosity levels in the compacted specimens. The $\tan \delta$ values obtained at 11%RH show that the internal friction of the polymer-modified C-S-H is decreased compared to that for the phase pure C-S-H (more noticeably in C/S=1.2 specimens). The first peak formed in the $\tan \delta$ response appears to be sharper.

Table 11-2. Storage modulus (E') of the phase pure and polyaniline-modified C-S-H samples at 11%RH condition and at the end of the stage I of the E' curves.

		E' (GPa)			$\tan (\delta)$
		11%RH	At the end of Stage I	Decrease in E' (%)	11%RH
C/S=0.8	C-S-H	8.38	3.09	63.1	0.017
	C-S-H/polyaniline	9.39	2.37	74.8	0.015
C/S=1.2	C-S-H	8.24	2.82	65.8	0.026
	C-S-H/polyaniline	9.38	2.41	74.3	0.010

The increase in the extent of silicate polymerization was shown (chapter 8) to result in an increase of the storage modulus and decrease of internal friction of C-S-H. It was also shown (in chapter 10) that degree of silicate polymerization of the C-S-H (Q^2/Q^1 ratio determined using ^{29}Si NMR) increases in the organically modified C-S-H materials. These separate conclusions together can explain the increase in the E' and decrease in the $\tan \delta$ of the C-S-H/polyaniline samples.

The polyaniline-modified C-S-H, however, does not seem to have thermally stable elastic capacity. As presented in Table 11-2, the decrease in the storage modulus of the C-S-H/polyaniline systems (both C/S ratios) is higher than that for the phase pure C-S-H when exposed to temperatures above ambient.

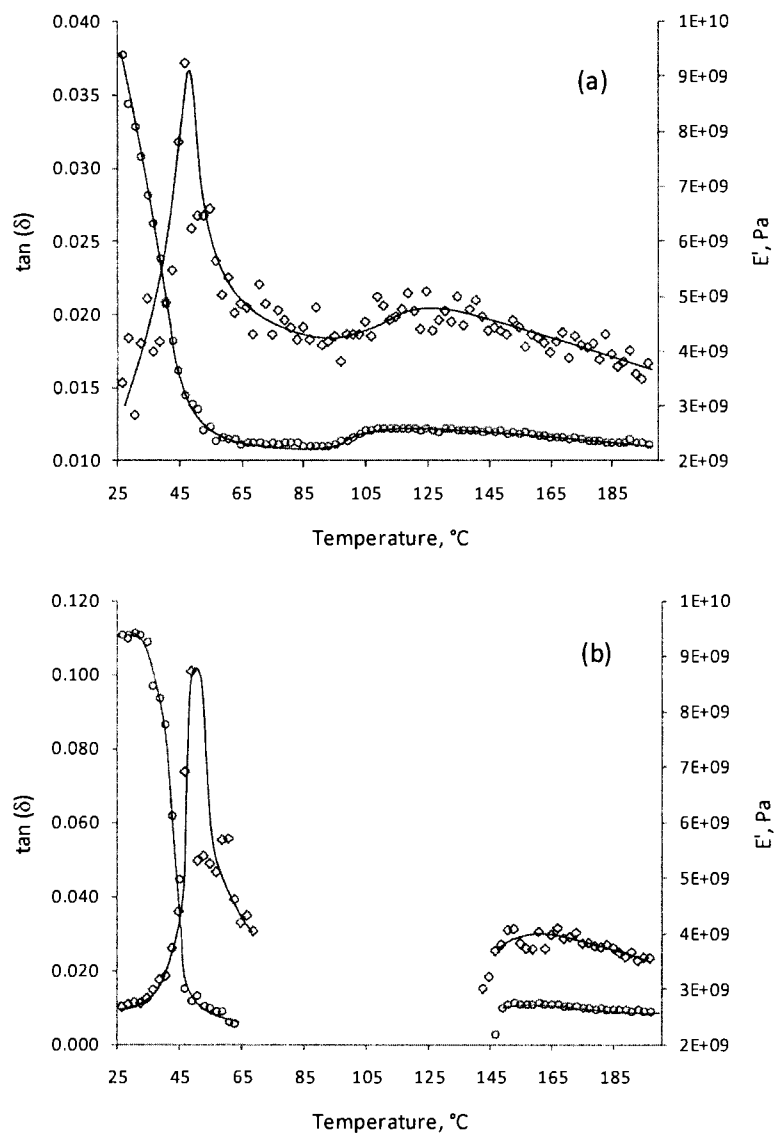


Figure 11-3. DMTA response of polyaniline-modified C-S-H. a: C/S=0.8, b: C/S=1.2.

The E' and $\tan \delta$ curves for the C/S=0.8 sample (Fig. 11-3) are qualitatively similar to that for the phase pure C-S-H obtained from ambient to 200 °C. Although very scattered, a second broad peak appears in the $\tan \delta$ curve from about 95 to 185 °C (Fig. 11-3a). The C/S=1.2 C-S-H

nanocomposite, however, exhibits unusual behavior between 65 and 145 °C. The compacted specimen undergoes a very large relaxation at about 65 °C and loses its contact with the upper fixture in the DMA instrument. No data could therefore be recorded during this stage. At about 185 °C the specimen regains its rigidity and makes contact with the upper fixture. This behavior was reproduced several times for compacted C-S-H/polyaniline duplicates (C/S=1.2). The source of this un-expected response is not clear. It may be related to the difference in the coefficient of the thermal expansion of the polyaniline and C-S-H. But, even if this is the case, it would be difficult to explain the increase in the rigidity of the sample after 145 °C. Further research is required to understand the details of the thermo-mechanical response of C-S-H/polymer nanocomposites.

11.4 Concluding remarks

The preliminary physical and mechanical investigations were conducted on the properties of the C-S-H/polyaniline nanocomposites (C/S=0.8 and 1.2). The XRD and DMTA results provided interesting information about the stability of the organically-modified C-S-H systems. It was shown that the interaction of polyaniline with the C-S-H decreases the change in the 002 basal spacing of the C-S-H when it is dehydrated. The storage modulus of the C-S-H/polyaniline nanomaterials appears to be improved in both studied C-S-H chemical compositions. However, the mechanical stability of these systems upon the removal of interlayer water was not enhanced in comparison to the phase pure C-S-H. Further investigations are required to examine the mechanical properties of C-S-H/polymer nanocomposites over a wide range of porosity levels. Experiments such as helium inflow may provide additional evidence about the C-S-H-polymer interaction mechanism.

11.5 References

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C-S-H Seeding

The early age hydration of tricalcium silicate, the main chemical compound in Portland cement, was studied in the presence of synthetic calcium silicate hydrate (C-S-H) addition having C/S ratios=0.8 and 1.2. Isothermal conduction calorimetry, scanning electron microscopy, differential scanning calorimetry and ^{29}Si MAS NMR were employed in order to investigate events occurring during various stages of the hydration. The results that were analyzed using novel methods in cement chemistry showed that the addition of seeds of synthetic C-S-H significantly accelerated the hydration of C_3S . The extent of the acceleration was dependent on the amount and chemical composition of the C-S-H seeds. It was suggested that the synthetic C-S-H significantly increased the rate and degree of dissolution of the C_3S particles. It was also found that the nucleation and silicate polymerization of the C-S-H that formed during the hydration of the C_3S phase was promoted. Direct evidence of the seeding effect was provided. The properties of the resulting C-S-H hydration products seemed to be dependent on the lime to silica ratio of the synthetic C-S-H. It was suggested that the silicate polymerization and chemical composition of the hydration products of silicate phases may be manipulated through C-S-H seeding. As the chemical and mechanical properties of C-S-H are largely controlled by its C/S ratio, this method should provide a unique tool for tailoring the nanostructure of the hydration products of Portland cement through the addition of selective C-S-H seeds for optimum engineering and durability performance.

12.1 Introduction

Tricalcium silicate (C_3S) is arguably the most important clinker phase in Portland cement [1]. Its hydration greatly influences the setting and hardening of the cement paste. The main product of the reaction of C_3S with water is calcium silicate hydrate (C-S-H), a nearly amorphous material, which primarily contributes to the strength and volume stability of cement-based materials [2]. Numerous studies have been conducted to understand various steps and mechanisms in the hydration of C_3S [2, 3]. These mainly include the application of conduction calorimetry, thermogravimetric analysis, quantitative X-ray diffraction and nuclear magnetic resonance spectroscopy [4]. It is known that as soon as the C_3S comes into contact with water a significant amount of heat is generated due to the dissolution of species such as Ca^{2+} and OH^- ions in the aqueous phase [5, 6]. This stage is called the pre-induction period. During the next few hours (dormant or induction period) the rate of hydration is negligible. This period is followed by an acceleration in the hydration process. The heat of hydration diminishes after about ten hours during the deceleration stage. There are several hypotheses for the mechanisms responsible for these stages [2, 7], that can be employed to describe the hydration of C_3S systems in various environments. The hydration kinetics of C_3S can be altered through the addition of various chemicals. The occurrence and duration of the hydration stages can be readily tailored by controlling the type and amount of these admixtures and additives. Calcium chloride, for example, accelerates the hydration process, shortening the dormant period and generating more heat at a higher rate during the acceleratory stage [5]. Fine minerals such as calcium carbonate may act as nucleation sites for the formation and growth of the C-S-H, essentially promoting the hydration of C_3S [8]. The extent of nucleation and acceleration often depends on the surface area of the fine particles added [9, 10]. In most cases, however, it is not very clear if there is any chemical interaction between these additives and the hydration products.

Analogous to the nucleation and growth of crystals in nature, pre-formed calcium-silicate-hydrate may promote the development of the C-S-H produced from the hydration of silicate phases in cement. Several studies have shown that addition of silicate hydrates (including the pre-formed C-S-H) accelerates the formation of C-S-H produced in the hydration of C_3S [11-14] or Portland cement [15, 16] as evidenced mainly by conduction calorimetry results. The mechanical and durability characteristics of the hydrated cement system may also be improved through this method [15, 16]. The term “seeding” is often used for the modification of the hydration process using pre-hydrated silicates. Dehydration of C-S-H prior to use as a seeding agent reduces its acceleration effect [12, 13]. The mechanism of hydration and nucleation in these studies has not

been fully investigated, as analytical techniques other than the conduction calorimetry were not employed for examining the early age hydration products. Moreover, nearly amorphous C-S-H materials were often used, the stoichiometry of which was not discussed in relation to the hydration process. The discrepancies in the extent of hydration acceleration observed between previous seeding studies are likely due to the difference in the chemical composition and physical properties of the C-S-H materials used as seeds for promoting the hydration of cement systems.

In the current study, the hydration of tricalcium silicate in the presence of synthetic C-S-H addition ($C/S=0.8$ and 1.2) was investigated at early ages. In addition to isothermal conduction calorimetry, experimental methods such as differential scanning calorimetry, scanning electron microscopy and quantitative ^{29}Si MAS NMR were employed in order to examine the hydration products and understand pertinent mechanisms controlling various stages of the hydration of C_3S and C_3S -C-S-H systems. Unlike the previous C-S-H seeding studies [12-16], the influence of the stoichiometry of the seed particles on the nature of the C-S-H product was investigated in the current research. The ^{29}Si MAS NMR measurements and the isothermal conduction calorimetry results were analyzed using quantitative NMR and derivative conduction calorimetry methods that are novel in cement research. The NMR analysis is described in this chapter, while the calorimetric approach has been presented elsewhere [17].

12.2 Method

The C_3S clinker was obtained from the CTL Group (Skokie, IL). It was calcined at 900°C for 24 hours in order to remove any carbonate impurities, ground in a ball mill using isopropanol, dried under vacuum and stored in a vacuum desiccator until used. The C_3S powder had a nitrogen BET surface area of about $2.4\text{ m}^2/\text{g}$. Synthetic C-S-H (C/S ratios = 0.8 and 1.2) was prepared using the stoichiometric amounts of CaO and SiO_2 [18]. These representative stoichiometries were selected from the category of C-S-H (I) (having $C/S < 1.5$) [2] based on the chemical and physical differences observed for two types of C-S-H obtained above and below a C/S ratio of about 1.1 [19, 20]. The nitrogen BET surface area of the C-S-H was 186 and $30\text{ m}^2/\text{g}$ for the C/S ratio = 0.8 and 1.2 , respectively. Other characteristics such as basal spacing (d_{002}), silicate polymerization and density are also affected by the C/S ratio of the C-S-H. The typical morphology of the C-S-H materials is shown in Figure 12-1. Quantities of each C-S-H were added to the C_3S to produce samples for experimental investigations. Pure C_3S was also retained for use as a control.

Six test samples of 4 grams of C_3S with 5, 10 and 20% additions of each C-S-H material and a seventh control sample of 4 grams of pure C_3S were prepared for isothermal conduction calorimetry. Water (Accusolv, Anachemia Inc.) was added to the dry mix in plastic vials at a w/C_3S ratio=0.8 and mixed outside the calorimeter for 30 seconds using a micro spatula. The 0.8 w/C_3S ratio was used in order to obtain the desirable workability for mixing the samples especially when a high proportion of C-S-H was added.

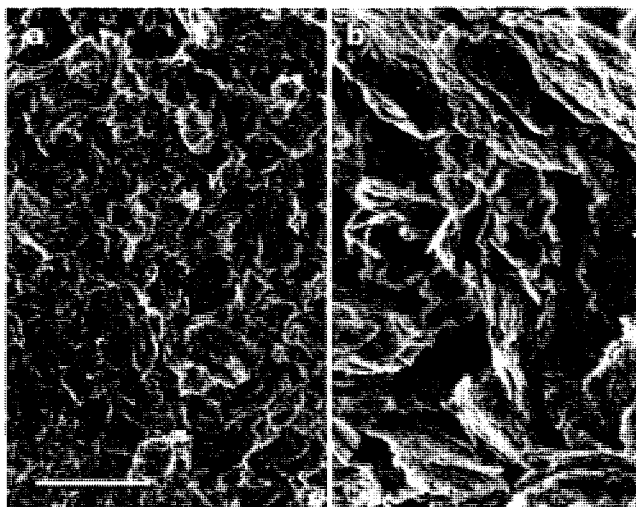


Figure 12-1. The Morphology of the synthetic C-S-H (a: $C/S=0.8$, b: $C/S=1.2$) used as seeding agents during the hydration of C_3S . The white scale bar indicates $1\mu m$. (40K magnification)

Each plastic vial was placed in the calorimeter 30 seconds after mixing. The heat of the hydration of the cement systems (C_3S and C_3S -C-S-H) was immediately monitored in a Tam Air Isothermal Calorimeter (model 3114, Thermometric AB). Glass beads (3mm diameter, having equal heat capacity to each sample) were used in the reference channels of the instrument. Data for the heat evolution was recorded (typical uncertainty= ± 0.002 mW/g) at 30-second intervals at a constant temperature of $24^\circ C$. The heat capacity of the synthetic C-S-H was assumed to be about 1.3 J/g- $^\circ K$ in the calculations. This is a low average value obtained from the literature [21] since the C-S-H seeds were relatively dry as they were subjected to vacuum for 4 days prior to use. The accurate determination of this value is very difficult for hydrated cement systems where the state of water is not very clear. The choice of the heat capacity may slightly affect the absolute values of the heat of hydration, but it does not change the location and relative intensity of the peaks. A derivative analysis was performed on the isothermal conduction calorimetry data in order to better identify the subtle changes in the rate of heat development that might be associated with different hydration phenomena.

Samples of C_3S having 20% C-S-H addition were used for DSC investigation, SEM analysis and NMR measurements. The high addition percentage was used in order to augment the effects of the hydration mechanisms involved and to better detect minor changes in the samples during the hydration. A small sample was taken from these specimens at various hydration times (marked in Fig.12- 2). These samples were first immersed in excess isopropanol for 24 hours in order to stop the hydration process and then dried under vacuum for another 24 hours. This procedure has been successfully used in SEM studies of the hydration of cement and tricalcium silicate although it may slightly affect the morphology of the hydration products [22]. The dried samples were kept in a vacuum desiccator until examined.

Differential scanning calorimetry (DSC) was conducted on the samples obtained at various hydration times using a TA Instruments SDT Q-600. About 10mg of the sample was heated from ambient to 1050 °C at a rate of 10 °C/min under the flow of nitrogen gas (10mL/min). The heat flow was analyzed using Universal Analysis 2000 software.

Scanning electron micrographs were acquired from the uncoated specimens using a Hitachi S-4800 field emission gun SEM instrument. An accelerating voltage of 1.2 KV and an emission current of 4 μ A were applied at a working distance of about 3 mm to obtain images having greater resolution and more detail than those that are possible at higher accelerating voltages [23].

The ^{29}Si MAS NMR measurements were carried out on a Bruker Avance 200 instrument (magnetic field of 4.7 T and ^{29}Si Larmor frequency of 39.75 MHz) using a BL7 double resonance MAS probe and 7 mm ZrO_2 spinners. All NMR measurements were performed at room temperature at the spinning speed of 5000 Hz. The spectra were acquired in a Bloch decay mode (^{29}Si $\pi/2$ pulse of 4 μ s) with a high power composite pulse proton decoupling. The delay between the scans was set at 60s. This was sufficient for complete relaxation of all the signals and quantitative measurements. Between 1000 and 1500 scans were commonly acquired in order to obtain a sufficiently high signal-to-noise ratio. Fitting and deconvolution/integration of the spectra were performed using the DMFit simulation program [24]. In quantitative measurements the absolute intensity in the spectra was normalized to the total number of scans acquired. The signal of tetrakis(trimethylsilyl)silane was used as the external reference (-9.9 ppm relative to TMS).

12.3 Results and Discussion

12.3.1 Isothermal Conduction Calorimetry

One of the primary techniques for studying the hydration kinetics of cement-based systems is the measurement and analysis of the heat developed (Q) after the contact of the material with water. The rate of heat development (dQ/dt) in the hydration of C_3S -C-S-H systems and the control C_3S sample investigated in the current study are shown in Figure 12-2[†]. It is observed that the addition of synthetic C-S-H noticeably modifies the rate of heat generated at various stages of the hydration, the extent of which depends on the composition and the amount of C-S-H added. A derivative analysis of the curves in Figure 12-2 was also conducted (see curves in Fig. 12-3) in order to better identify the subtle changes in the rate of heat development that might be associated with different phenomena. This kind of analysis has been successfully applied in the studies of the hydration of C_3S and Portland cement systems [17, 22, 23].

The pre-induction period lasts less than an hour for all samples. This stage ends slightly earlier when the synthetic C-S-H is added. The end of pre-induction period (i.e. the time at which the rate of heat development is a minimum and $d^2Q/dt^2=0$) occurs at about 53, 45, 40 and 36 minutes for the control C_3S , and 5, 10 and 20% C-S-H additions, respectively. This time does not seem to be dependent on the type of C-S-H. The total heat of hydration (i.e. the area under the rate of heat development curve) evolved during this stage is higher for samples containing C-S-H addition than that for the control C_3S . It was, however, not possible to measure the amount of heat produced in this period quantitatively as its rate exceeded the capacity of the instrument. In most of the hydration studies of modified C_3S systems using calorimetry [11-16], the pre-induction period has not been investigated in detail possibly due to the experimental limitations.

In a separate study (not reported) using a less reactive C_3S sample, it was observed that the heat generated during the pre-induction stage increased significantly for C_3S in the presence of C-S-H. This effect was much more pronounced in the case of low lime C-S-H ($C/S=0.8$). It can, therefore, be argued that the early reactions occurring at this stage such as the dissolution of ions from the C_3S grain into the aqueous phase (responsible for the initial heat development) are promoted due to the presence of the synthetic C-S-H seeds. It is also likely that the “barrier layer” that has been suggested to form on the C_3S surface and is responsible for the beginning of the dormant period [12] becomes less effective in the presence of synthetic C-S-H. Ions such as Ca^{2+}

[†] The data for the first 20m was not plotted in order to enhance clarity.

and OH^- hypothetically migrate toward the synthetic C-S-H (that has a high surface area which makes it very suitable as a nucleation site) and are adsorbed on its surface where they nucleate and grow to form the C-S-H product instead of forming an early-stage product on the surface of tricalcium silicate.

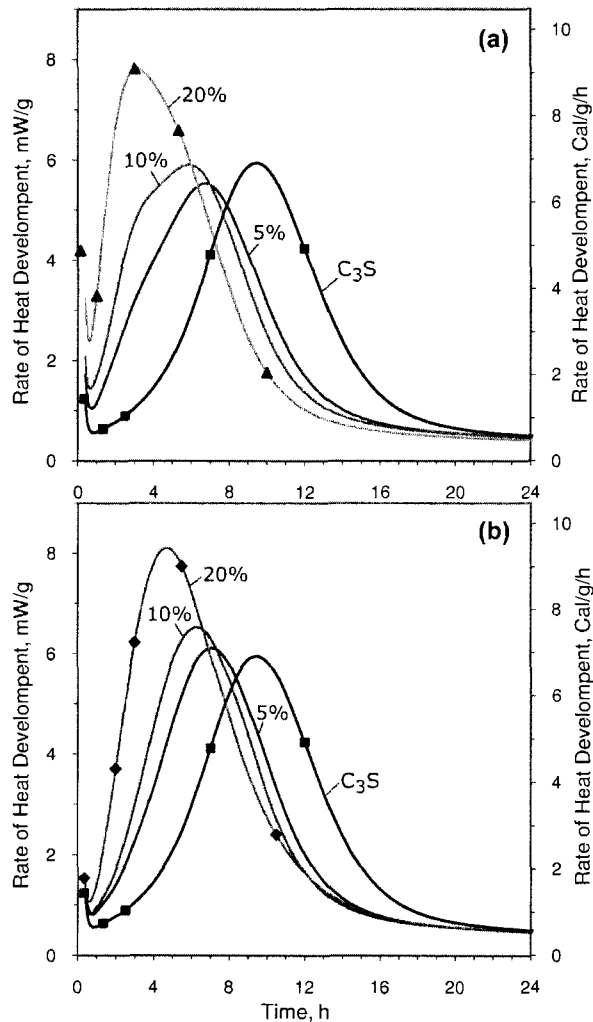


Figure 12-2. Rate of heat development recorded by isothermal conduction calorimetry for C₃S–C-S-H systems containing various amounts (per mass of C₃S) of synthetic C-S-H addition compared with that for the control C₃S. a: addition of C-S-H (C/S=0.8), b: addition of C-S-H (C/S=1.2). Markers indicate the time at which samples were taken for other analyses.

Direct evidence from SEM (section 12.3.2) supports this theory. Formation of hydration products (precipitated from the solution) on the surface of the C-S-H seed decreases the concentration of ions in the solution phase and accelerates their dissolution from the C₃S into the aqueous phase even during the pre-induction period (refer to Figs. 12-4a1 and 12-4b1 for direct evidence of

additional dissolution). More heat is then generated during the pre-induction stage due to the suggested mechanisms for dissolution and precipitation. This theory is consistent with the previous observations suggesting that the addition of fine particles such as silica fume and calcium carbonate has similar effects in terms of the length of the pre-induction period and the increased rate of heat development [9, 25-27].

The induction or dormant period can not be identified as such (Fig. 12-2). The heat flow data for the samples experiences only a brief minimum value after the end of pre-induction period in the rate of heat development curves of seeded samples. Immediately after the occurrence of the minimum value, the rate of heat development increases at a rate that seems to vary according to the amount and surface area of the C-S-H seed present in the sample. This effect is better demonstrated in Figure 12-3. It has been shown that the induction period is extended when there is a high concentration of dissolved Ca^{2+} and OH^- ions in the aqueous solution [28]. The depletion of Ca^{2+} and OH^- ions from the aqueous solution can accelerate the hydration of C_3S [29]. It is therefore suggested that the synthetic C-S-H which acts as a nucleation site for the growth of the C-S-H product adsorbs the ions in the aqueous solution. This in turn shortens the “induction period”. A decrease in the length of the dormant stage has been observed previously when C_3S and Portland cement are hydrated in the presence of various silicate hydrate systems [12-15]. The end of this period was also observed to occur faster in seeded samples consistent with the interpretations advanced in the current study.

The acceleratory stage leads to a peak after the dormant period followed by the deceleratory stage. This peak occurs at earlier times (presented in Table 12-1) for the C_3S -C-S-H mixes compared to the control C_3S where rate of heat development reaches a maximum value at about 9.5 hours. This maximum, for the control sample, is preceded by a smaller peak appearing on the shoulder immediately after the end of induction period. It has been demonstrated that the time between the end of the induction period and the start of the deceleration in hydration process is composed of two separate stages [22, 23]. Immediately after the end of the induction period surface reactions predominate, while afterwards bulk nucleation and growth are more significant. The calculation of the derivative of the heat flow curves (obtained using high resolution calorimeters such as that in the current work) can assist in separating the two processes.

Table 12-1. Time (hours) at which the maximum value in the peak of the rate of heat development curve occurs. This time is 9.5h for the control C_3S .

	Amount of C-S-H Addition		
	5%	10%	20%
$C_3S+C-S-H$ (C/S=0.8)	6.7	5.9	3.1
$C_3S+C-S-H$ (C/S=1.2)	7.1	6.3	4.7

The derivative of the rate of heat development curves are shown in Figures 12-3a and 12-3b for samples containing synthetic C-S-H addition, C/S=0.8 and 1.2, respectively. The acceleratory stage for the control C_3S sample (corresponding the part of the curves in Fig. 12-3 where $d^2Q/dt^2 > 0$) can be divided into two regions; One region of near constant derivative heat flow starting at about 1.2h and the second region between 2.5 and 9.5h where a peak is observed. The first event is attributed to the initial hydration reactions including the nucleation of C-S-H on the surface of C_3S . The second event that has a relatively higher rate is likely due to the bulk growth of the C-S-H [22, 23].

The existence of these two events is more distinct in the C_3S -C-S-H systems. The intensity and location of the peaks associated with these events appear to be influenced by the type and amount of C-S-H seed. A comparison between the derivative heat flow curves for the control sample, increasing amounts of 0.8 C/S ratio C-S-H (Figure 12-3a) and increasing amounts of 1.2 C/S ratio C-S-H (Figure 12-3b) suggests that different processes may be in play during the hydration of the samples with the two different types of synthetic C-S-H. In the 0.8 C/S ratio blends, the main hydration peak from the control sample becomes attenuated with increasing synthetic C-S-H content. This is observed as a shift from being the main positive peak for the control sample to being a secondary maximum with a value less than zero in the samples with higher synthetic C-S-H content.

Instead, the maximum heat flow occurs in an early peak that increases in size with increasing synthetic C-S-H content. Previous work has shown that increasing surface area of C_3S produces such an effect [22], which was attributed to surface hydration reactions, as opposed to bulk ones. The high surface area of this type of synthetic C-S-H provides a massive number of sites for the formation of initial C-S-H substances. This promotes the nucleation of C-S-H and accelerates the

rate of heat development during the acceleratory stage observed by the increase in the intensity of the peak associated with the first event in Figure 12-3a.

This effect is not dominant in the 1.2 C/S ratio blends, where only a single peak is observed during the initial stages of the hydration reaction. This result suggests that bulk hydration product reactions are the primary mechanism in these samples. Although there is a significant difference in the surface area between the 0.8 C/S ratio and 1.2 C/S ratio samples, both materials had surface areas that are much higher than those that produced the early, surface area related hydration peak in C_3S alone [22]. Instead, the differences in hydration behavior may be due to structural differences in the synthetic C-S-Hs. This point is developed further in the next sections.

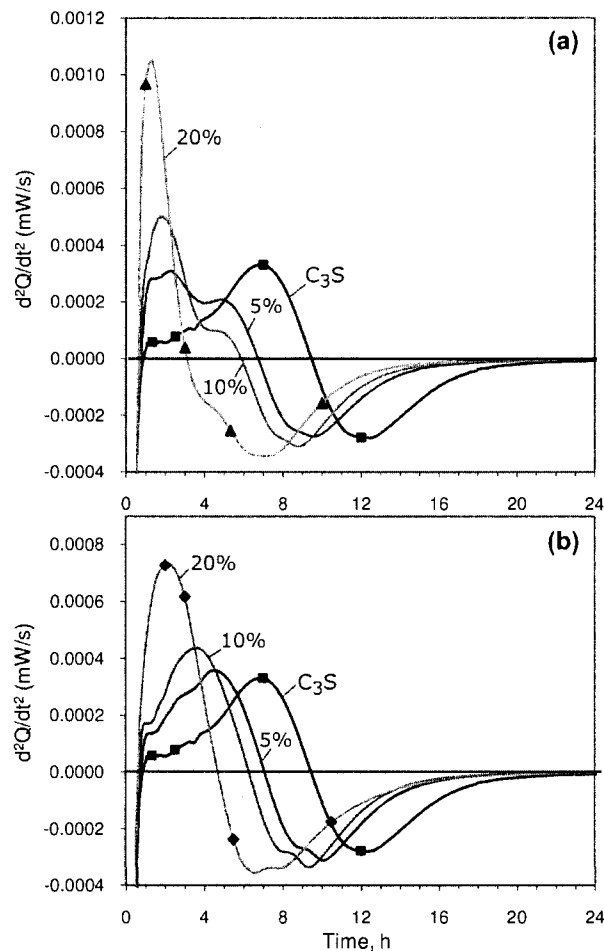


Figure 12-3. The derivative analysis of the rate of heat development curves in Fig. 12-2 for various amounts of C-S-H addition to C_3S ; a: C/S=0.8, b: C/S=1.2.

The deceleratory period in the hydration of C_3S -C-S-H is initiated at earlier times for the $C/S=0.8$ sample compared to the $C/S=1.2$ and control sample. The total heat developed in the hydration reactions (i.e. the area under the curves in Fig. 12-2) is higher when the synthetic C-S-H is added. This suggests that more C_3S is consumed in the hydration reactions when C-S-H is used for seeding. The degree of hydration is therefore likely to be higher in the modified systems. Despite the significant differences during the acceleratory stage, the slope of the rate of heat development curves during the deceleratory stage (as shown by the derivative analysis in Figure 12-3 between 6 to 12 hours) is similar for all samples. It also appears that two events occur during the deceleratory stage (indicated by double peaks in the region where $d^2Q/dt^2 < 0$) in the seeded samples whereas control C_3S has only one peak. This behavior, which is more distinct for the $C/S=1.2$ sample, may support the existence of two mechanisms in the formation of hydration products: conventional C-S-H on the surface of C_3S and the C-S-H on the surface of seeds. It is suggested that these two events in the conduction calorimetry have different rates during their acceleration and deceleration stages. The calculation of this rate (i.e. their derivative analysis as shown in Fig. 12-3) will therefore produce curves with double peaks in both stages of the hydration. There is also a slight increase in the rate of heat development reduction (inferred from the intensity of the peaks in the deceleratory stage) when C-S-H is added to the C_3S suggesting a quicker completion of the reactions.

12.3.2 Scanning Electron Microscopy

The results of the SEM examination of the control C_3S and $C_3S+20\%$ C-S-H ($C/S=0.8$) samples are shown in Figure 12- 4. The surface of the control C_3S (Fig. 12-4a1) is intact after 20 minutes of hydration during the pre-induction stage. It has a relatively smooth surface similar to that in the unhydrated C_3S . Few etch pits appear on the surface after 1h20min of hydration (Fig. 12-4a2). Formation of these etch pits has been previously reported to occur at the end of induction period [22, 23]. Small C-S-H hydration products can be observed on the surface of C_3S at this time (that is at the beginning of the acceleratory period). After 2.5h of contact with water, most of the surface of the C_3S is covered with etch pits and the C-S-H particles have grown larger (Fig. 12-4a3). The surface of the C_3S grain is fully covered by C-S-H products at later times (Fig. 12-4a4) and thus the morphological changes of the C_3S surface cannot be further monitored.

The presence of synthetic C-S-H ($C/S=0.8$) results in noticeable differences in the appearance of the C_3S grains during the hydration (shown in Fig. 12-4b). The surface of the C_3S is covered by small etch pits after only about 10min (Fig. 12-4b1). This is indicative of a significant dissolution

of the C_3S during the pre-induction period, which is consistent with the intense release of the hydration heat at this stage for the seeded systems. The heat of wetting is therefore not the dominant factor controlling the heat of hydration before the dormant period in the blended samples.

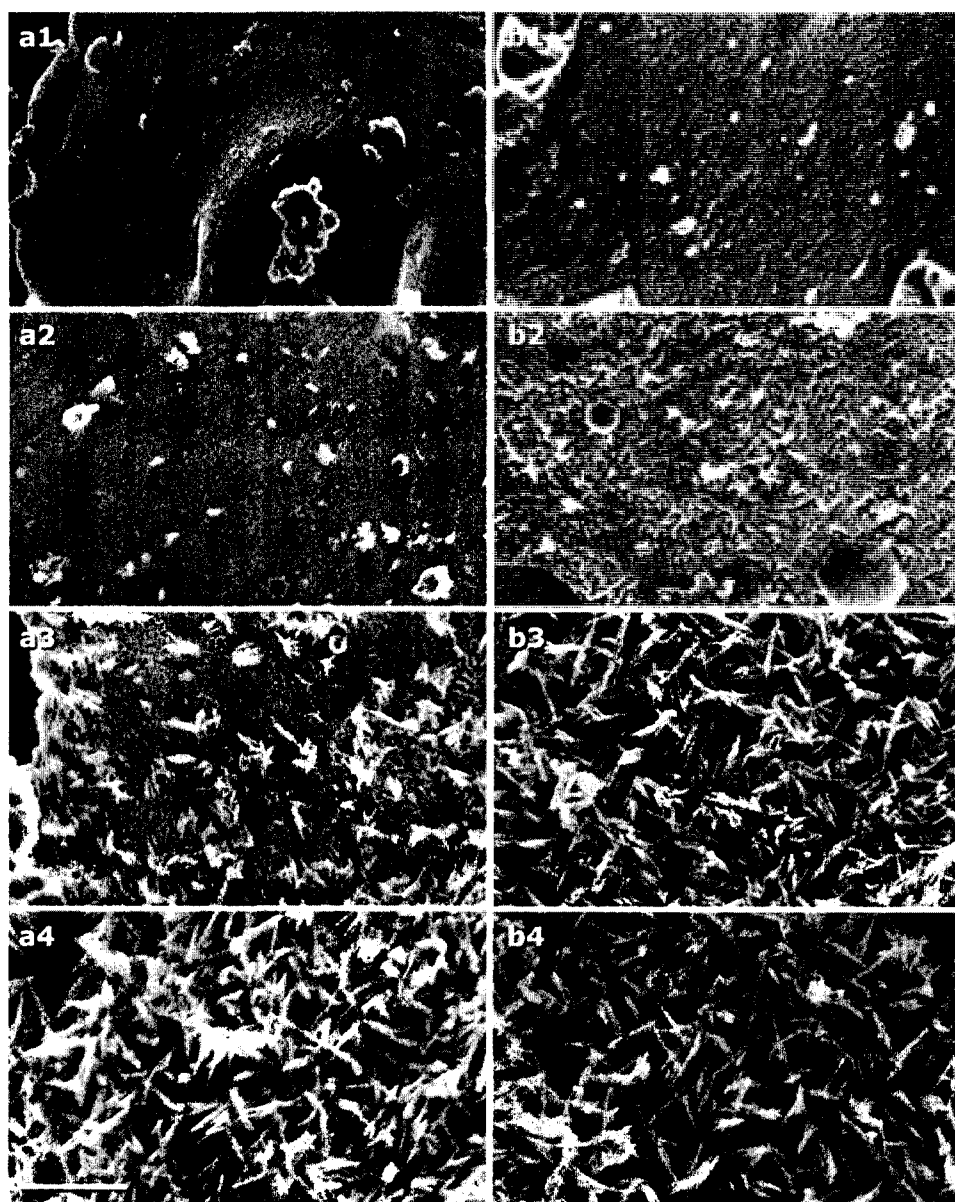


Figure 12-4. SEM micrographs of the evolution of the surface of C_3S at various hydration times. Series a (control sample); a1:20min, a2:1h20min, a3:2h30min, a4:7h. Series b (C_3S in the presence of synthetic C-S-H ($C/S=0.8$)); b1:10min, b2:1h, b3: 3h. b4:10h. The white scale bar indicates 500nm. (80K magnification)

In a separate study, it was observed that the amount of heat generated in the hydration of β -C₂S–C-S-H systems during the pre-induction stage is much less than that in the corresponding C₃S–C-S-H system. It is therefore unlikely that the wetting effect is a governing factor for the initial release of heat as soon as material comes into contact with water. Dissolution of ions from the unhydrated grains into the solution is suggested to be responsible for the heat of hydration before the dormant period. After 1h, the surface of the C₃S is extensively covered with etch pits (Fig. 12-4b2). Small C-S-H hydration products and Ca(OH)₂ crystals (identified by their distinct morphology [2]) also appear on the surface. The surface of the control C₃S sample (Fig. 12-4a2) is relatively intact at a similar hydration time. The surface of the C-S-H seed does not seem to be affected during the hydration up to this stage (not shown). Changes at the nucleation sites, if any, cannot be observed probably due the limitation of the SEM imaging resolution.

The surface of C₃S particles is covered by C-S-H after 3 hours of hydration (Fig. 12-4b3). This corresponds to the location of the maximum in the rate of heat development curve. A larger number of C-S-H particles forms on the surface of the C₃S after this time (Fig. 12-4b4). Their population, however, is not as high as that in the control C₃S sample (Fig. 12-4a4). This qualitative observation that was made in several spots may suggest that the C-S-H products can form at other sites.

Examining the surface of the C-S-H seed at this time (identifiable by its distinct morphology in Fig. 12-5a) reveals interesting features. In comparison with the surface of the pristine C-S-H (C/S=0.8) in Figure 12-1a, it is observed that small needle-like particles are formed on the surface of the synthetic C-S-H after 3 hours. These structures appear to be the C-S-H phases produced from the hydration of C₃S, but nucleated on the surface of the seeds rather than on the C₃S itself.

These particles grow larger at later times and finally cover the surface of the synthetic C-S-H. This may also be responsible for the relatively lower population of the C-S-H products on the surface of C₃S in these samples. This provides direct visual evidence for the nucleation of hydration products on the surface of fine particles. The formation of C-S-H on the surface of the synthetic C-S-H may help to explain the marked increase in the peak intensity associated with the initial reactions observed in Figure 12-3a for this sample. This also supports the theory that the dissolved ions migrate toward the surface of the C-S-H seed.

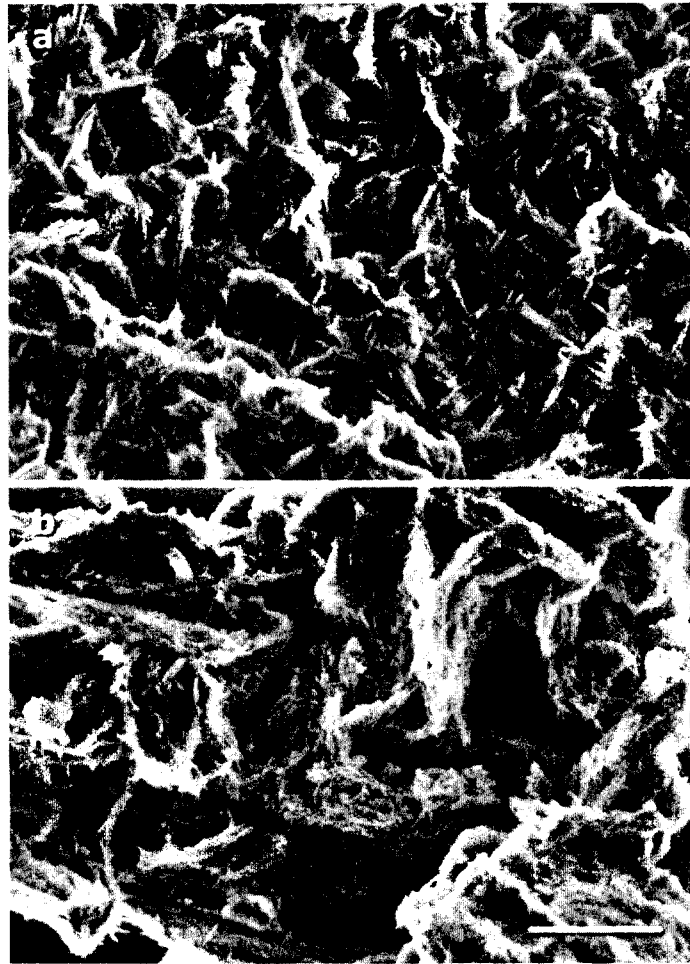


Figure 12-5. SEM image of the surface of synthetic C-S-H seeds (a: C/S=0.8, b: C/S=1.2) after 3 hours of the hydration of C_3S showing the nucleation of needle-like C-S-H products. The white scale bar indicates 500nm. (80K magnification)

Similar changes in the morphology of C_3S occur (not shown) in the presence of synthetic C-S-H (C/S=1.2), but at a slower rate possibly due to the difference in the surface area of the C-S-H seeds as mentioned before. At 20min of hydration no visible change was detected on the surface of C_3S and C-S-H. The etch pits and initial C-S-H products appear on the surface of the C_3S after about 2h. The formation of C-S-H on the surface of the synthetic C-S-H is clearly observed after 3h as shown in Fig. 12-5b. The needle-like structure of the initial C-S-H products on the surface of the seed are easily observed in contrast with the appearance of the pristine C-S-H seed in Figure 12-1b. The growth of C-S-H on the surface of synthetic C-S-H (C/S=1.2) at later times is not as extensive as that in the case of C/S=0.8. The morphology of synthetic C-S-H (C/S=1.2) is still detectable at later hydration times as it is not fully covered by the hydration products. The observed lower rate of formation on the surface of the synthetic C-S-H corresponds well to the

results of Figure 12-3b, which shows more prominent effects on the bulk growth of the C-S-H. It should be noted that the C-S-H formed on the surface of synthetic C-S-H must be considered in a separate category distinct from the ‘inner’ and ‘outer’ products postulated in the hydration of conventional silicate phases [30]. The mechanism of nucleation and growth of this type of C-S-H is apparently different from that forming on the surface of the C_3S . The C-S-H that is precipitated on the surface of the C_3S affects the rate of the dissolution of the covered C_3S grain and the diffusion of ions. This mechanism, however, is not applicable to the C-S-H forming on the surface of the seed particles. The chemistry of the C-S-H materials at these locations is, therefore, likely to be different from the C-S-H growing on the surface of C_3S . The Energy Dispersive X-Ray (EDX) analysis was not helpful regarding the chemical analysis of the hydration products as the accuracy of this qualitative method was not high enough to conduct measurements on the small nucleated C-S-H particles (about 100 nm in length in Fig. 12-5). Moreover, a specific depth of the sample is affected by EDX. This includes a layer of the hydration products as well as the original grains. The thickness of this layer can not be measured. The proportion of each phase analyzed by EDX is therefore not determinable. The qualitative results using this method thus can not be accurately compared. Other approaches were carried out using DSC and NMR techniques (as described in the next sections) in order to better understand and explain the stoichiometry of the C-S-H phases formed during the hydration of C_3S seeded with the synthetic C-S-H materials.

12.3.3 Differential Scanning Calorimetry

The DSC technique has been extensively applied in the investigation of calcium silicate systems in cement chemistry [31]. C-S-H and C_3S both exhibit thermal behavior due to the crystalline conversion and transition at high temperatures between 800 and 1000 °C. This behavior was explored for the C_3S -C-S-H systems in the current study. The results for the thermal analysis of the control and modified samples with 20% C-S-H addition at selected hydration times are shown in Figure 12-6. Two endothermal peaks are observed for the control C_3S sample (Fig 12-6a) at 921 and 972 °C indicating the presence of unreacted C_3S . These peaks are observed for hydration times of up to 30 hours (not shown). The pure C_3S undergoes two endothermic events at these temperatures due to the crystalline transitions from triclinic to monoclinic and monoclinic to trigonal forms, respectively [31].

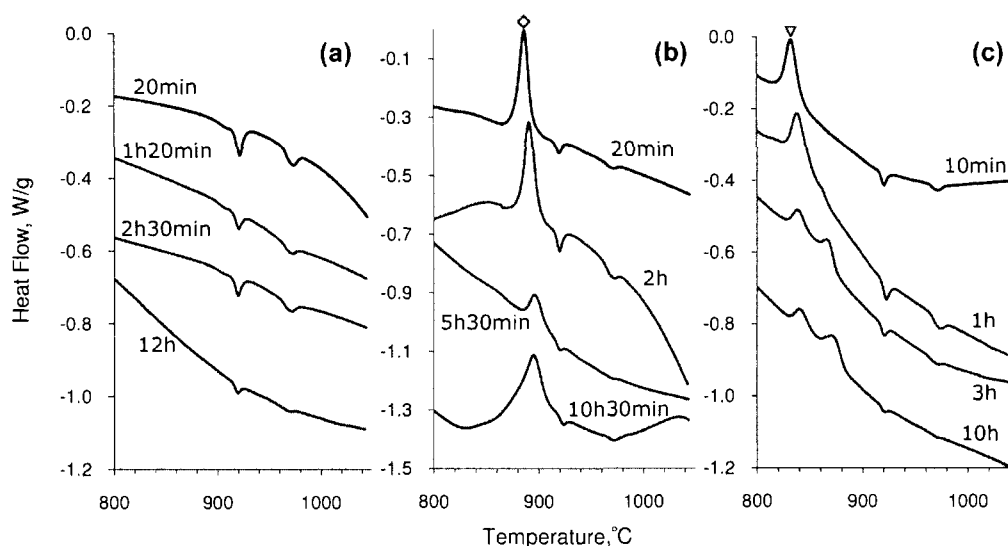


Figure 12-6. DSC curves of the hydrated samples at various times. a: C_3S , b: $C_3S+20\%C-S-H(C/S=1.2)$, c: $C_3S+20\%C-S-H(C/S=0.8)$. The curves are offset along the y-axis for clarity. Markers in Figure 12-6b and 12-6c indicate the exothermal conversion of synthetic C-S-H seed to β -wollastonite at temperatures depending on the lime to silica ratio of the C-S-H; ◇: $C/S=1.2$, ▽: $C/S=0.8$.

The systems containing synthetic C-S-H experience additional thermal events at temperatures between 800 and 900 °C. In addition to the peaks for the unhydrated C_3S , Fig 12-6b shows an exothermal peak exists in the $C_3S+20\%C-S-H(C/S=1.2)$ sample at about 886 °C, the location of which is gradually shifted to about 898 °C after 30 hours of hydration. This peak is due to the phase pure synthetic C-S-H initially added to the mixture. The C-S-H has a sharp exothermal peak due to the conversion to β -wollastonite [32, 33]. The temperature at which this peak occurs depends on the C/S ratio of the C-S-H and varies from 830 to 900 °C as the C/S ratio increases [32]. It is also observed that this peak is broadened at later hydration times.

The DSC curves for the C_3S with C-S-H ($C/S=0.8$) addition are shown in Figure 12-6c. The exothermic peak at 832 °C after 10min of hydration is from the synthetic C-S-H. The location of this peak is also shifted to higher temperatures (about 839 °C) at later hydration times suggesting a change in the thermal behavior of synthetic C-S-H addition. In this system, however, a new peak starts to appear after one hour of hydration at about 865 °C. The relative intensity of this peak increases with time. The peaks from the crystalline transformation of C_3S are present in the seeded systems during these events.

The C-S-H produced in the hydration of the control C_3S sample does not depict any exothermal event (Figure 12-6a) at the hydration times examined in this study. This might be due the

amorphous nature of the C-S-H from the hydration of silicate phases. At later times, however, a relatively small exothermal peak may appear at about 840-867 °C [34]. Synthetic C-S-H is a semi-crystalline material and has a high temperature exothermal behavior (as shown in Figs. 12-6b and 12-6c) due to the conversion to β -wollastonite [32, 33]. The broadening of this exothermal peak in Fig. 12-6b and the formation of the new exothermal peak in Figure 12-6c as the hydration process is advanced may, therefore, be due to another C-S-H phase that has more ordered structure than that in the control sample and is apparently different in nature from the C-S-H produced in the hydration of pure C_3S . It is suggested that the C-S-H that nucleated and grew on the surface of the C-S-H seed is responsible for the changes in the exothermal events observed in Figures 12-6b and 12-6c. This type of C-S-H is likely to have a more developed nanostructure than that forming on the surface of C_3S and, unlike it, can be converted to β -wollastonite. XRD analysis was conducted on the seeded systems in order to obtain additional support for the crystallinity of the new hydration products. The results, however, did not provide any conclusive information in this regard. The location and sharpness of the XRD peaks (primarily due to the semi-crystalline seed) did not change after the nucleation of the C-S-H product on the surface of the seed.

As mentioned, the new exothermal peak (in Fig. 12-6c) occurs at temperatures higher than that for the peak associated with the conversion of synthetic C-S-H ($C/S=0.8$) to β -wollastonite. In the C_3S -C-S-H ($C/S=1.2$) system (Fig. 12-6b) this peak is obscured due to the broadening of the exothermal peak of the C-S-H seed as hydration progresses. In both seeded samples, a shift is observed in the location of the exothermic peak of synthetic C-S-H to higher temperatures at later times. It has been shown previously that the location of this exothermal event is dependent on the stoichiometry of the C-S-H. A higher C/S ratio C-S-H exhibits the exothermal conversion to β -wollastonite at higher temperatures [32]. It is, therefore, suggested that in each seeded system, the C/S ratio of the new semi-crystalline C-S-H phase forming on the surface of the C-S-H seeds is proportionally higher than the C/S ratio of the seed itself. It should also be noted that the average C/S ratio in hydrated silicate phases of Portland cement is about 1.75 [35]. It is suggested, accordingly, that the chemical composition of the C-S-H product can be modified through the addition of various types of C-S-H seeds having selected C/S ratios. This may provide a unique tool for engineering the properties of the cement-based materials.

12.3.4 ^{29}Si MAS NMR

Nuclear magnetic resonance (NMR) spectroscopy is a powerful technique that has proven very useful in a wide range of applications in cement chemistry [36, 37]. In the current study, the ^{29}Si MAS NMR was conducted on control and seeded C_3S samples (having 20% addition of C-S-H, $\text{C/S}=0.8$ and 1.2) in order to investigate the extent of polymerization in the hydration products after 1 week of hydration. The ^{29}Si MAS NMR spectra of the samples are shown in Figure 12-7. They all have similar features in terms of the chemical shift of the peaks. The first set of signals from -68 to -75 ppm labeled Q^0 are due to the isolated (uncondensed) silicate tetrahedra at various locations in the crystal structure of unhydrated C_3S [38]. The two broad signals located at about -79 and -84 ppm are referred to as Q^1 and Q^2 , respectively. These two signals are due to the silicon atoms in the silicate chain of the C-S-H [39]. Q^1 corresponds to the end chain silicate tetrahedra and the Q^2 is from the middle chain or bridging tetrahedra. Both synthetic C-S-H and the C-S-H product have Q^1 and Q^2 signals, which overlap in the spectra shown in Figures 12-7b and 12-7c. It is therefore desirable to separate the contribution from each of these phases in the spectra in order to evaluate the silicate structure of the hydration products in the seeded systems. This can be accomplished by comparing the absolute concentration of the silicon atoms in the starting and hydrated materials in a specific Q site.

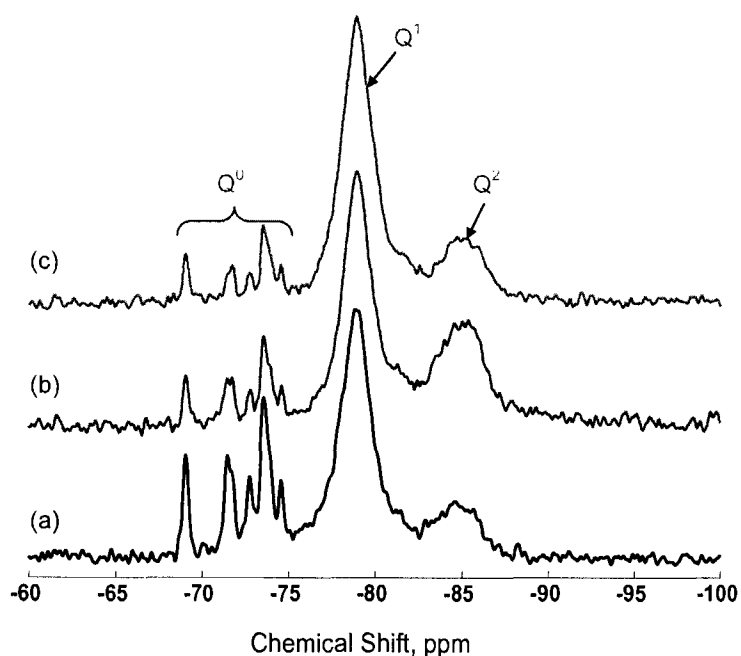


Figure 12-7. ^{29}Si MAS NMR spectra of the C_3S -C-S-H systems hydrated for 1 week; a: control C_3S , b: $\text{C}_3\text{S}+20\%\text{C-S-H}(\text{C/S}=0.8)$, c: $\text{C}_3\text{S}+20\%\text{C-S-H}(\text{C/S}=1.2)$.

Quantitative ^{29}Si MAS NMR analysis of the absolute concentration of Si atoms in different environments was accordingly conducted on the hydrated samples as well as the initial pure phases. Na Y zeolite ($\text{Si}/\text{Al}=2.9$) was used as the reference material. The spectra were deconvoluted in order to calculate the integral intensity of each peak employing Lorentzian lines using DMFit software [24]. The values of the integral intensity of Q^0 , Q^1 and Q^2 sites for various samples are presented in Table 12-2. The integral area under the spectrum for the reference zeolite sample was calibrated for the number of scans and the mass of silicon atoms in the sample. It is therefore possible to calculate the mass of silicon atoms associated with various Q sites based on their integral intensity normalized for the number of scans. The mass of a specific chemical compound can then be determined knowing the mass percentage of Si in its molecular weight.

Table 12-2. Integral intensity of the Q sites, degree of hydration and silicate polymerization in the C_3S and C_3S -C-S-H samples after 1 week of hydration based on quantitative ^{29}Si MAS NMR.

	Integral Intensity, %			Degree of Hydration, %	Silicate Polymerization (Q^2/Q^1)		
	Q^0	Q^1	Q^2		Total C-S-H	C-S-H Seed	C-S-H Hydration Product
C_3S	24.1	61.5	14.4	75	0.23	---	0.23
$\text{C}_3\text{S}+20\%\text{C-S-H}$ (C/S=0.8)	10.0	53.6	36.4	91	0.68	3.55	0.29
$\text{C}_3\text{S}+20\%\text{C-S-H}$ (C/S=1.2)	8.3	72.4	19.3	90	0.27	0.32	0.25

The amount of unreacted C_3S was calculated according to this procedure based on the integral intensity (i.e. the area under the spectrum) of the Q^0 sites and assuming that C_3S has a chemical formula of Ca_3SiO_5 [2]. The degree of hydration can then be determined knowing the amount of initial C_3S in the mixture. A more convenient approach using only the integral intensity measurement of Q^0 could be applied had the C_3S not been mixed with C-S-H seeds [37]. Similarly, the Q^1 and Q^2 peaks associated solely with the hydration process can be determined for the blended samples by subtracting the signal produced by the synthetic phases. The normalized area under each peak (Q^1 and Q^2) was initially determined for the phase pure C-S-H samples (C/S=0.8 and 1.2) using ^{29}Si MAS NMR. A factor of the normalized area (for the percentage of C-S-H addition and total mass of the sample) was then subtracted from the area of the

corresponding signal (Q^1 and Q^2) in the NMR spectra in Figure 12-7. The remaining value is, therefore, due to the C-S-H that is produced in the hydration of C_3S . The extent of the silicate polymerization in the hydration products (Q^2/Q^1 ratio) can then be simply expressed as the ratio of the calculated areas for Q^1 and Q^2 sites for the new C-S-H. The summary of the results calculated based on the quantitative ^{29}Si MAS NMR analysis is presented in Table 12-2.

It is shown that the degree of hydration is significantly higher when synthetic C-S-H is added to the C_3S (Table 12-2). The increase of the degree of hydration has been observed previously for similar seeded systems [13]. The observations from conduction calorimetry and SEM are consistent with these results. It seems that the C-S-H seeds accelerate the dissolution of the C_3S particles during the initial hydration times before setting. A significant amount of hydration products are formed on the surface of the added synthetic C-S-H. It is suggested that the formation of the hydration products on the surface of synthetic C-S-H rather than the surface of the C_3S increases the amount of exposed C_3S surface as compared to the control samples, allowing a greater rate of C_3S dissolution and increased hydration activity during the hydration process.

The Q^2/Q^1 ratio is directly related to the mean silicate chain length and the extent of the condensation of silicate in layered silicate systems [4, 37]. The degree of polymerization values calculated for the samples have some interesting aspects. The synthetic C-S-H is more polymerized at lower C/S ratios. It is known that the decrease in the C/S ratio of the C-S-H results in an increase in the degree of silicate polymerization (i.e. relatively longer silicate chains with only few defects due to the omitted bridging tetrahedra). The Q^1 signal appears as a shoulder of the Q^2 signal in low C/S ratio C-S-H systems whereas in high C/S ratio C-S-H the Q^1 and Q^2 signals are well-separated. The Q^2/Q^1 ratio is quantified after the deconvolution of the peaks in the spectrum. The relatively high Q^2/Q^1 values have been previously reported [39] similar to the value of 3.55 for the C/S=0.8 C-S-H. At higher C/S ratio C-S-H systems (including the C-S-H that forms in the hydration of cement phases) the silicate chains primarily consist of dimers and the Q^2/Q^1 ratio is thus lower than that for the low C/S ratio C-S-H. As shown in Table 12-2, the Q^2/Q^1 ratio of the C-S-H that is produced in the hydration of C_3S is lower than that in the synthetic C-S-H indicative of shorter silicate chains containing a greater number of defect sites. This ratio, however, increases for the C-S-H produced in the presence of synthetic C-S-H. The effect is slightly higher when low C/S ratio C-S-H is used for seeding compared to the case of C-S-H having C/S=1.2. It should be noted that the estimated silicate polymerization of the C-S-H

product is the average value for the C-S-H that is formed on the surface of C-S-H seeds as well as the C-S-H that is precipitated on the surface of C_3S grains. The C-S-H forming on the surface of C_3S is likely to have a similar silicate polymerization degree to that in the control sample. The extent of polymerization of the C-S-H grown on the surface of seeds is, therefore, higher than what is presented in Table 12-2. As this effect is related to the chemical composition of the C-S-H, it is suggested that the C-S-H produced in the hydration of C_3S interacts chemically with the C-S-H seed and may have a similar nanostructure to that of the seed particle. This is consistent with the DSC results showing the dependence of the exothermal behavior of C-S-H product on the C/S ratio of the C-S-H seed.

This observation can be plausibly explained by the nucleation and growth model described by Gartner [40]. According to this model schematically shown in Figure 12-8, the new C-S-H grows at the end of the initial nucleated C-S-H sheets (or from the C-S-H seeds in the current work) and therefore develops a similar structure to that of the sheets on which it is nucleating. It is reasonable to assume that the C-S-H growing through this mechanism may also have a similar silicate structure to that of the C-S-H seed (i.e. mimicking the nanostructural features of the nucleation site). This behavior can explain the dependence of the Q^2/Q^1 ratio in the C-S-H product to the C/S ratio of the C-S-H seed. One can expect that the silicate polymerization and chemical composition of the hydration products of silicate phases can easily be manipulated through C-S-H seeding if a wider range of C/S ratio is employed. This effect that was also observed in the DSC results has important practical implications as the chemical and mechanical properties of C-S-H are largely controlled by its C/S ratio [19, 20]. It may, therefore, be possible to employ C-S-H seeding in order to produce cement-based systems having a specific durability and engineering performance.

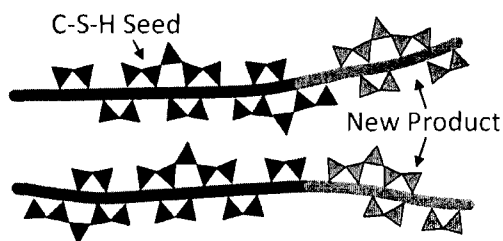


Figure 12-8. Nucleation of the C-S-H product at the end of C-S-H seed layers compatible with Gartner's model for nucleation and growth of C-S-H.

12.4 Concluding remarks

The mechanism of C-S-H seeding in cement systems employing advanced analytical tools such as quantitative ^{29}Si MAS NMR was studied for the first time. C-S-H seeding was shown to be very effective in accelerating the hydration of C_3S . The location of the maximum rate of heat development (after the dormant period) was shifted to earlier times by as much as 6 hours when synthetic C-S-H was added to the C_3S . The dissolution of C_3S into the aqueous solution and the rate of heat development due to the formation of C-S-H were significantly increased. It was shown (by the direct evidence using SEM analysis) that, in modified systems, the C-S-H produced in the hydration of C_3S nucleates and grows on the surface of the synthetic C-S-H. The extent of the silicate polymerization of the C-S-H product was measured through quantitative NMR calculations. It was found that the Q^2/Q^1 ratio of the C-S-H product can be modified depending on the stoichiometry and silicate polymerization of the C-S-H seeds. This was corroborated by the DSC results suggesting the formation of a C-S-H phase having exothermal behavior at high temperatures. Further experimental investigations including spatially resolved techniques and chemical analysis of the pore solution are still required to better understand the mechanism and chemistry of C-S-H seeding.

It should, therefore, be possible to tailor the properties of the hydration products in cement-based materials through a controlled metamorphosis method by modifying the hydration process in order to produce a specific C/S ratio C-S-H. The stoichiometry of the C-S-H (as expressed by its C/S ratio) primarily influences its chemical and mechanical properties. Cementitious systems can thus be engineered by controlling the type and the amount of synthetic C-S-H in order to obtain a specific mechanical performance or chemical stability. This should provide a unique opportunity to tailor the properties of concrete materials in the future. Moreover, the nucleation of C-S-H on the surface of seeds is suggested to result in the formation of a more homogenous and well distributed hydration material compared to the control C_3S where C-S-H essentially precipitates on the surface of C_3S particles. The better distribution of hydration products through C-S-H seeding is likely to improve mechanical properties and durability characteristics of the hydrated cement system such as strength and permeability.

12.5 References

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Summary and Future Work

The detailed discussion and specific conclusions for each part of the current thesis were presented in the relevant chapters. The most important achievements are the *identification of two C-S-H (I) phases, the link between the chemistry and engineering performance of C-S-H systems, and the possibility of controlling the nature of the hydration products in cement paste*. Here, the main findings of various parts of this study are summarized. Recommendations have been made for future research work in order to advance the knowledge of C-S-H systems.

13.1 Summary

This project was designed to improve the current understanding about the nanostructure and engineering properties of basic and modified C-S-H systems. Some of the main controversial issues in cement science were identified. A comprehensive research study was planned in order to examine the key features of the C-S-H systems at the nano level. Chapters 4 to 12 presented new evidence for a number of chemical and mechanical aspects of the phase pure as well as hybrid C-S-H (I) materials. Several advanced analytical tools were employed in order to corroborate the observations in each section. The fundamental achievements of the current work are mentioned briefly as follows:

Chapter 4

The change in the 002 basal spacing of the C-S-H (I) samples at various drying increments from the 11%RH condition was evaluated using XRD. The dehydration of C-S-H resulted in a decrease of the distance between the C-S-H layers. The rate and the trend of this decrease were shown to be dependent on the chemical composition of the C-S-H. It was demonstrated that a separating C/S ratio of about 1.1 exists, below which the C-S-H exhibits a gradual decrease in the 002 basal spacing due to dehydration. High C/S ratio C-S-H phases, however, experienced a sudden decrease in the distance between the C-S-H layers as the interlayer water was removed at about 4-7% mass loss from the 11%RH condition. The existence of two C-S-H (I) categories was also verified using *in situ* X-ray methods.

Chapter 5

Nanostructural investigations using helium inflow and ^{29}Si MAS NMR were conducted on C-S-H (I) having two representative C/S ratios of 0.8 and 1.2. The helium inflow, which is a measure of the volume of 'nano' spaces accessible to delayed diffusion of helium gas, offered additional evidence on the different properties of two types of C-S-H (I). The total helium inflow of high C/S ratio C-S-H (I) increased as the interlayer water was removed. This was followed by a decrease after about 5% mass loss in 11%RH conditioned sample. This moisture content strikingly coincided with that observed for the sudden change in the 002 basal spacing of high C/S ratio C-S-H (I). Furthermore, the ^{29}Si MAS NMR results for this type of C-S-H showed that at a similar mass loss level the silicate polymerization (i.e.

Q^2/Q^1 ratio) is increased. The experimental observations were best explained by proposing a collapse mechanism of the layered nanostructure of high C/S ratio C-S-H (I).

The C-S-H in hydrated Portland cement exhibits similar helium inflow and ^{29}Si NMR characteristics when dehydrated. The analogous behavior of C-S-H in cement paste to that of synthetic C-S-H was considered as new evidence supporting the layered nature of the C-S-H, a basic question debated in the cement research community for more than 50 years. The low C/S ratio C-S-H, however, did not appear to be an appropriate physical model for the C-S-H in hydrated cement systems. This type of C-S-H (I) went through a gradual decrease in the 002 basal spacing and demonstrated an oscillatory helium inflow behavior upon the removal of interlayer water. The ^{29}Si MAS NMR suggested the cross-linking of silicate sites in C-S-H phases as the C-S-H layers come closer together due to dehydration.

Chapter 6

The solid state ^{43}Ca NMR was employed for the first time in the nanostructural investigation of cement-based materials. New information was provided about the calcium environment in cement clinker phases as well as hydrated systems. The results on the calcium structure of anhydrous cement compounds were consistent with their X-ray crystallographic information. It was shown that the C-S-H in cement paste has a similar calcium environment to that of synthetic C-S-H systems such as C-S-H (I) and $11\text{\AA}$ tobermorite. The signals in the ^{43}Ca NMR spectra of the hydrated C_3S were assigned to various calcium-bearing species including $\text{Ca}(\text{OH})_2$, Ca^{2+} ions in the interlayer region, and Ca atoms in the Ca-O backbone of the C-S-H.

Chapter 7

The Hedvall effect which is related to the solid state reactions was employed to study the chemical reaction between the C-S-H (I) phases and silver nitrate. The amount of unreacted silver nitrate after the heat treatment of a mixture of C-S-H and AgNO_3 was calculated from the heat flow curves. This value was used to estimate the relative chemical reactivity of the C-S-H systems. It was shown that the low C/S ratio C-S-H (I) is chemically more reactive. Both cationic and anionic species were found to be responsible in the overall reactivity of C-S-H phases. Silver silicate was identified as a crystalline reaction product between C-S-H and silver nitrate.

Chapter 8

The relation between the chemical composition of C-S-H (I) and its dynamic mechanical properties was investigated. Preparing solid specimens through the compaction of C-S-H powder was the key to establish this link. It was shown that the storage modulus of C-S-H increases with decreasing the C/S ratio while the internal friction decreases with this change in the stoichiometry. The DMA response of C-S-H samples of variable stoichiometries (both synthetically prepared and that in the hydrated cement paste) was examined upon the removal of interlayer water from 11%RH condition. A unique oscillatory behavior was identified in the E' and $\tan \delta$ curves of all C-S-H systems. This response was easily explained by a layered model for C-S-H and assignment of a structural role to interlayer water, silicate tetrahedra and calcium ions in the interlayer. These observations were considered as new mechanical evidence for the layered nature of the C-S-H in hydrated Portland cement.

Chapter 9

The stress relaxation of compacted synthetic C-S-H specimens was studied in analogy with that in the cement paste. It was shown that the removal of interlayer water modifies the viscoelastic nature of the C-S-H (more noticeable at high C/S ratios). This suggested that the interlayer water has an important role in the time-dependent deformations of cement-based materials. It was also demonstrated that the dehydrated C-S-H exhibits a viscoelastic response. A model was proposed for the stress relaxation and creep behavior of C-S-H, the main feature being the sliding of the C-S-H layers under load.

Chapter 10

A new class of polymer-modified C-S-H nanocomposites was prepared through the *in situ* polymerization of aniline monomers. Two C-S-H chemical compositions were considered. The results of various analytical tools supported the existence of intimate interaction of the polyaniline with the nanostructure of C-S-H. It was shown that the extent of silicate polymerization of organically-modified C-S-H increases relative to the phase pure C-S-H. The chemical properties of C-S-H/polymer systems appeared to be influenced by the stoichiometry of the inorganic C-S-H host.

Chapter 11

Preliminary experiments were conducted in order to make an assessment of the physical stability and mechanical performance of the C-S-H/polyaniline nanocomposites. XRD was utilized to evaluate the change in the 002 basal spacing of C-S-H, C-S-H/aniline and C-S-H/polyaniline systems (C/S ratios = 0.8 and 1.2). It was shown that the amount of decrease in the 002 basal spacing of C-S-H is limited for polymer-modified systems supporting the possibility of the intercalation of polymer molecules in the interlayer region. DMTA results indicated there is an improvement in the storage modulus of C-S-H/polyaniline samples. The dehydration of these systems, however, resulted in a larger decrease in the storage modulus.

Chapter 12

Synthetic C-S-H was employed as a seeding agent in the hydration of C_3S . The accelerated hydration of C_3S -C-S-H systems was studied using novel techniques such as quantitative ^{29}Si MAS NMR. Data obtained from isothermal conduction calorimetry, SEM and DSC were used to support conclusions based on NMR results. Two types of C-S-H were identified – one that emanates on the surface of C_3S grains and one that nucleates on the synthetic C-S-H particles. It was demonstrated that the C-S-H product that forms on the synthetic C-S-H surfaces results in a nanostructural metamorphosis. In other words, the degree of silicate polymerization and C/S ratio of the nucleated C-S-H on the seed is controlled by the stoichiometry of the C-S-H seed. A model for the growth and interaction of the nucleated C-S-H with the seeds was presented suggesting that the C-S-H product nucleates at the end of the crystalline C-S-H layers. It was shown that it is possible to engineer the nature of C-S-H in cement-based materials through C-S-H seeding. This was considered central to strategies pertaining to the tailoring of C-S-H formation for the enhancement of durability and engineering performance.

13.2 Recommendations for future work

Despite a great deal of research on the nature and properties of C-S-H, various aspects of the characteristics and behavior this material still remain ambiguous. Working with phase pure synthetic C-S-H systems is advantageous as their chemical composition can be readily controlled. The advancements in experimental methods provide an opportunity to re-examine and elucidate some of the debated issues in cement and concrete science. A couple of relevant fields that merit detailed investigation in the future are suggested as follows:

1. The methods developed in the current thesis regarding the study of the changes in various nanostructural features of C-S-H upon the incremental removal of water from the 11%RH condition can be employed in conjunction with other experimental tools in order to understand new aspects of the behavior of C-S-H and the role of cationic and anionic species in its nanostructure. For example, high resolution ^1H NMR, TEM imaging and AC impedance spectroscopy may be proven useful.
2. The C-S-H in cement paste is generally considered as a defect tobermorite/jennite-like material. The evidence is primarily based on the ^{29}Si NMR results. It is necessary to probe the calcium environment in the Ca-O backbone of the C-S-H using ultra high field ^{43}Ca NMR in order to better understand the relation between the nanostructure of this material with that of more ordered phases. It may also be possible to estimate the 'length' of the C-S-H layers (analogous to the calculations regarding the silicate chain length) in various C-S-H phases. No information has been provided in this regard yet.
3. The aging of the C-S-H appears to be an important parameter in the development of its mechanical properties. It is proposed that a complete set of C-S-H (I) samples be synthesized utilizing various hydration periods. The engineering performance of C-S-H can thus be studied as this material undergoes ageing using various methods such as DMA and nanoindentation. This has important practical implications for the service life design of concrete structures.
4. The current thesis includes the preliminary results on the durability and mechanical properties of C-S-H/polymer systems. It is important to understand in more detail the performance of this novel organically modified C-S-H materials. It is suggested that compacted specimens having a wider range of porosity be prepared. The results of mechanical measurements on these samples will provide a better idea about the engineering aspects of C-S-H/polymer nanocomposites. The helium inflow technique

may also reveal new information about the durability aspects of these materials. This can be assessed by the study of the change in the accessibility to the 'nano' spaces in C-S-H at various humidity levels.

5. C-S-H seeding was introduced as an effective method to induce the metamorphosis of the hydration products in Portland cement paste. This has opened up several opportunities for pursuing various aspects of modified C-S-H materials. Different types of C-S-H seeds (e.g. variable composition and surface area) can be employed. The C-S-H seeding effect can be explored in parallel with the effect of chemical admixtures such as retarders in order to investigate the possibility of controlling the delay of cement hydration. The durability and mechanical characteristics of C-S-H seeded paste needs to be evaluated.
6. Quantitative ^{29}Si NMR was developed in the current work. This powerful tool can be utilized in the nanostructural studies pertaining to the hydration mechanisms in many of the cement-based materials. The formation and development of various silicate-bearing species can be quantitatively monitored employing the method described in this thesis.
7. The current doctoral project investigated various nanostructural and mechanical properties of C-S-H systems upon the removal of water. It should be interesting to conduct similar studies on the rehydration of the dried C-S-H materials and study the change of various properties as water molecules possibly enter the nanostructural locations including the interlayer region. Such investigation should provide insight into the nature of C-S-H binders in hydrated cement systems.

Particle size distribution

The particle size distribution of the C-S-H samples of variable composition is presented in Figure A-1. The samples were tested 'as prepared' without any additional grinding or sieving. The experiment was conducted in a Malvern Mastersizer 2000 instrument.

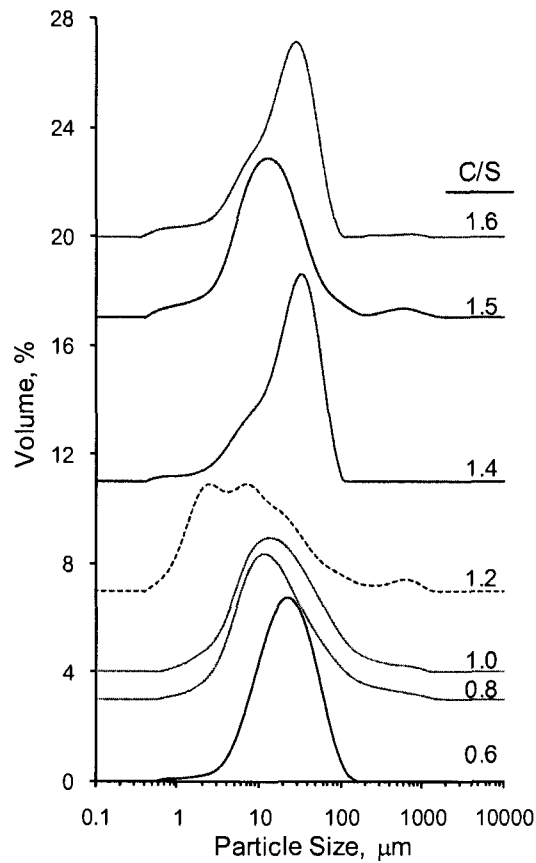


Figure A-1. Particle size distribution of the synthetic C-S-H as prepared. The curves are offset along the y-axis for clarity.

X-ray diffraction

The XRD patterns of the synthetic C-S-H samples of variable stoichiometry are shown in Figure A-2. The test was carried out in a Scintag XDS 2000 with the experimental settings as mentioned in chapter 4.

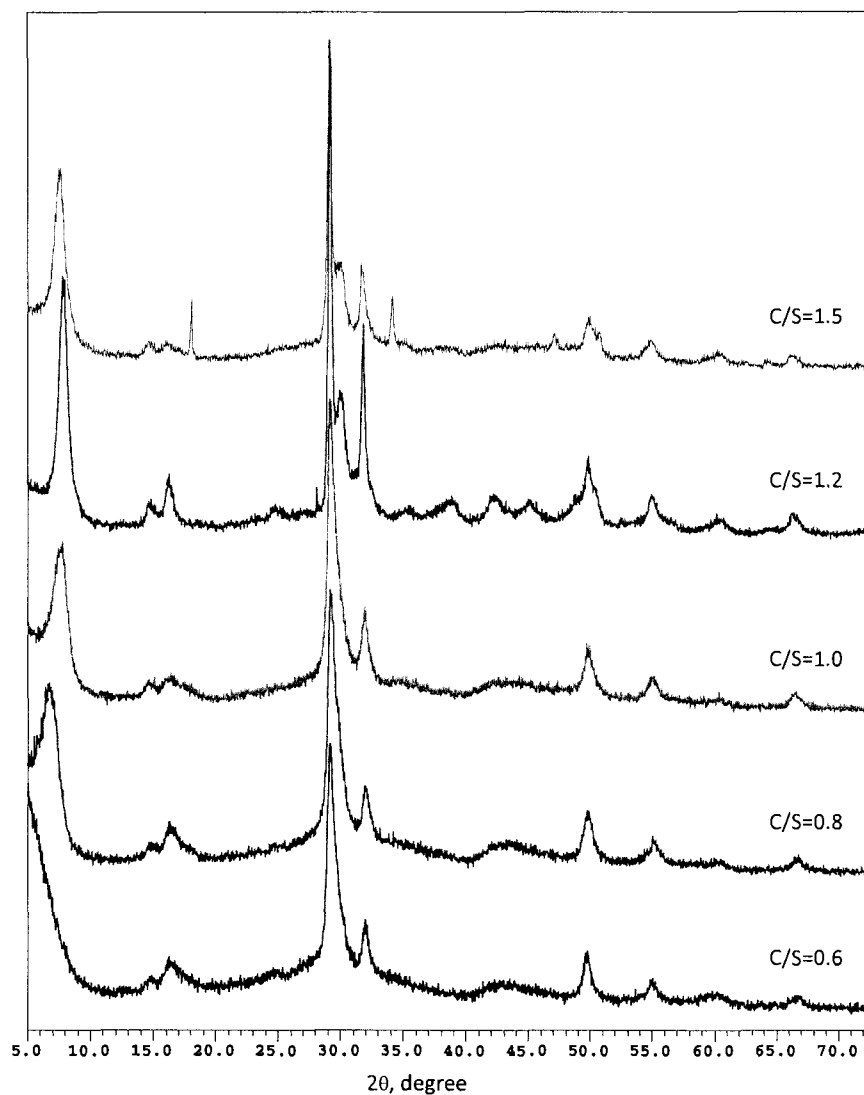


Figure A-2. The XRD patterns for the C-S-H (I) samples (C/S=0.6-1.5).

Scanning electron microscopy

The SEM images of the synthesized C-S-H (I) materials are illustrated in Figures A-3 for C/S ratios of 0.6 to 1.5. Pictures were acquired at a 50K magnification from the surface of C-S-H agglomerates on a Hitachi 4800 field emission instrument at a working distance of 3mm. An accelerating voltage of 1.2KV and emission current of 7 μ A were used. It should be noted that a complete imaging at various magnification levels and observation sites is required in order to develop a better feel about the morphology of the C-S-H.

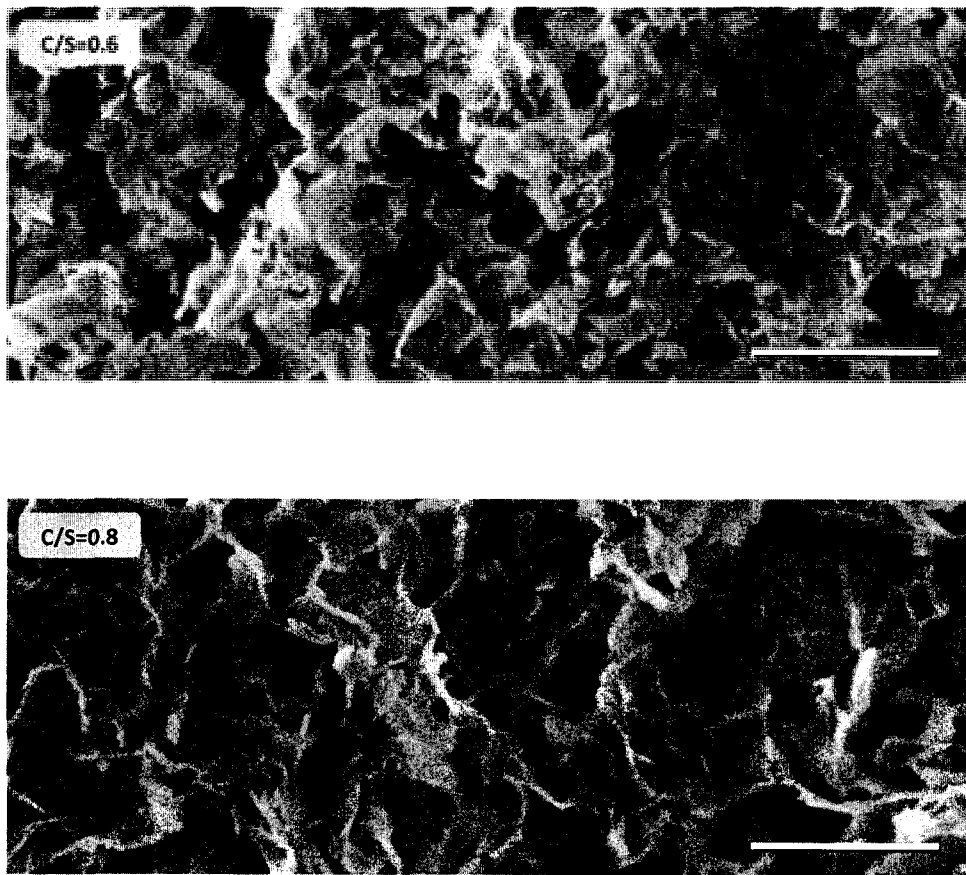


Figure A-3. The SEM micrographs of the C-S-H samples. The scale bar indicates 500nm on all images.

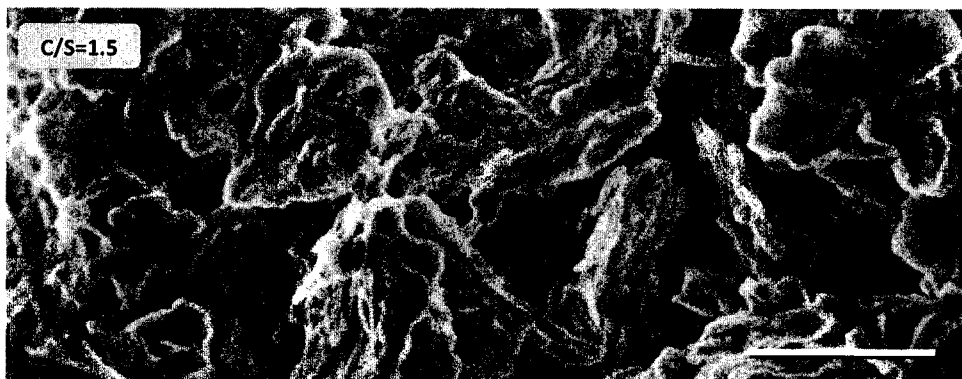
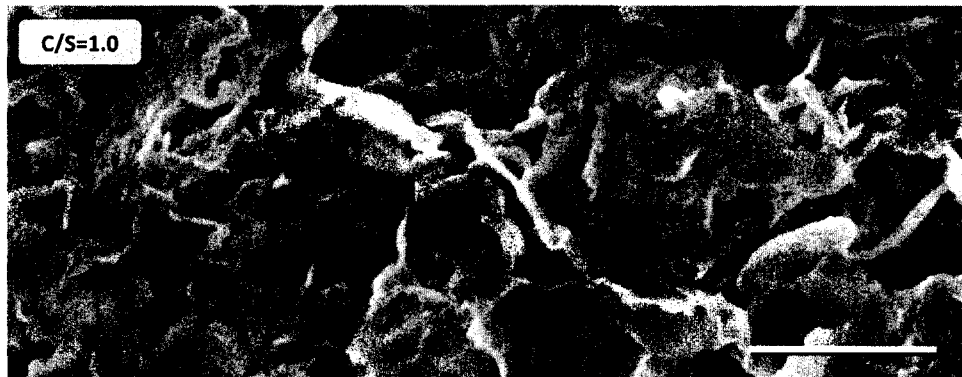


Figure A-3 (cont.). The SEM micrographs of the C-S-H samples. The scale bar indicates 500nm on all images.

Differential scanning calorimetry

The heat flow data for the synthetic C-S-H samples ($C/S=0.6-1.5$) determined through DSC experiment are presented in the Figure A-4. The temperature was varied from ambient to 1050 °C (10 °C/min) under the flow of nitrogen gas (100mL/min). A 1 hour isothermal condition at 80 °C was applied in order to separate out the contribution from free water.

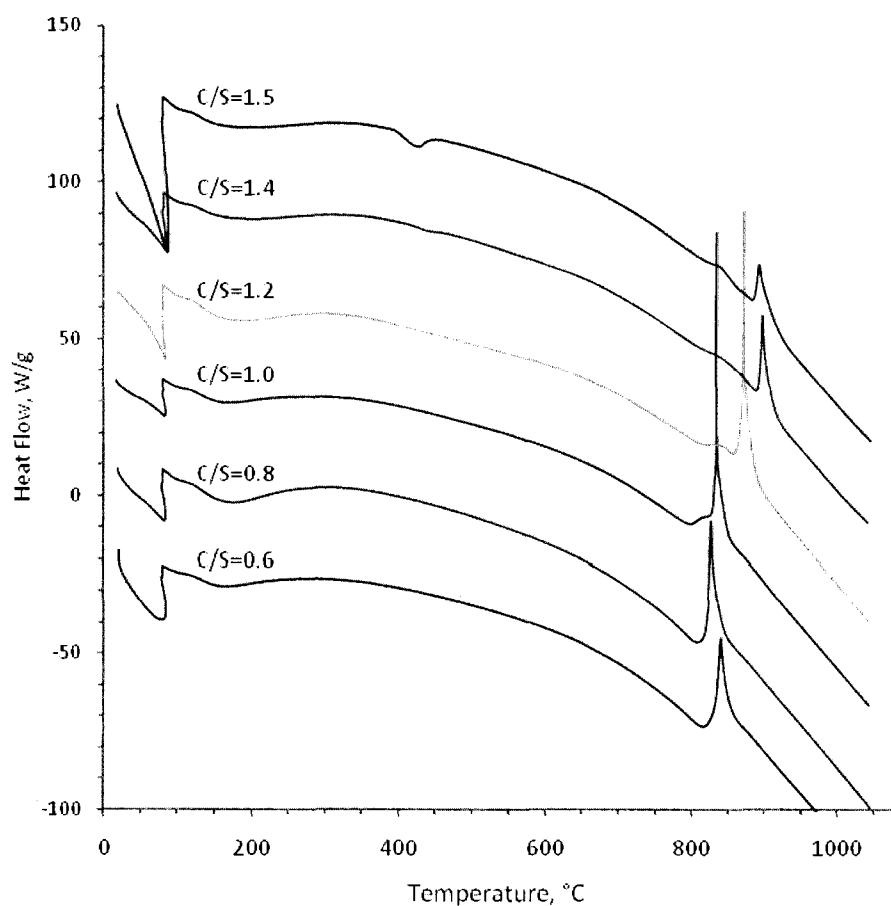


Figure A-4. The heat flow curves for various C-S-H preparations.

^{29}Si NMR spectroscopy

The ^{29}Si MAS NMR spectra of the C-S-H preparations ($\text{C/S}=0.6\text{--}1.5$) are presented in Figure A-5. A Bruker Avance 200 MHz instrument was used for the experiments. Settings are the same as those mentioned in chapter 12.

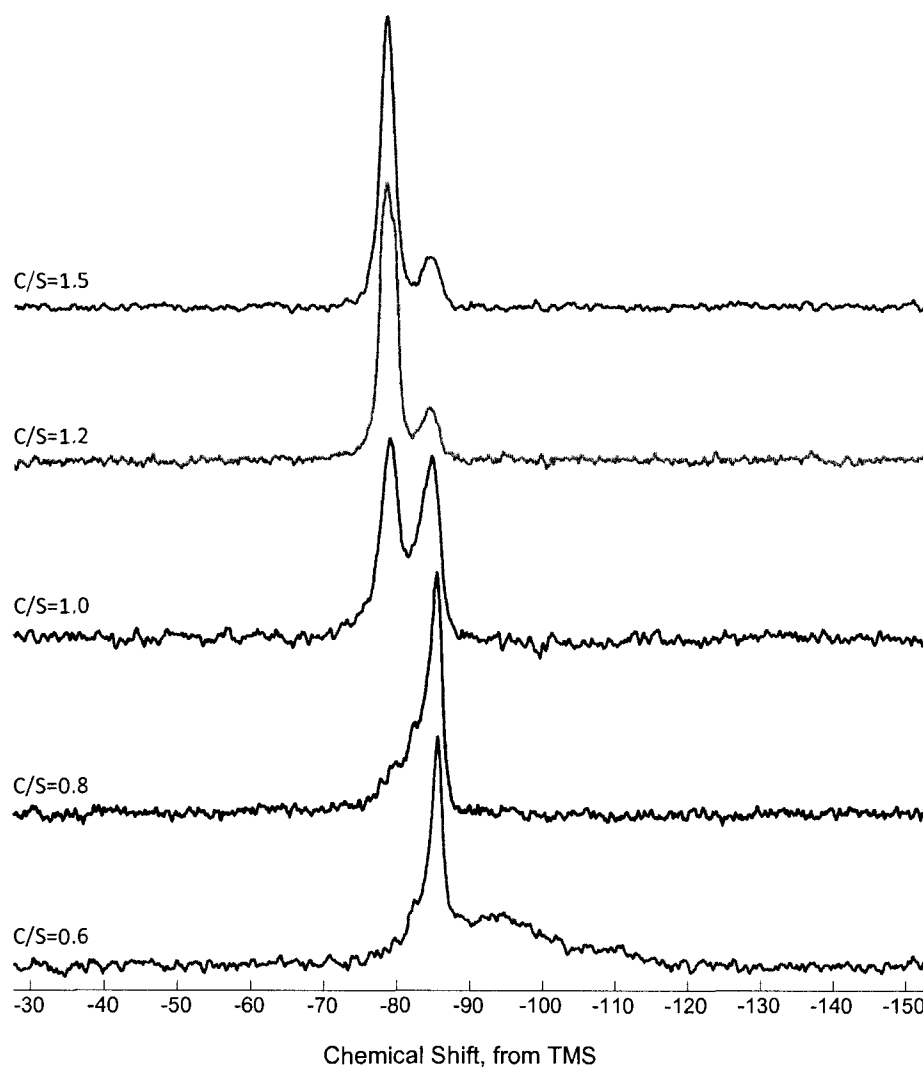


Figure A-5. The ^{29}Si MAS NMR spectra of the synthetic C-S-H samples.

Rouhollah Alizadeh received his B.Sc. and M.Sc. degrees in Civil Engineering both from the University of Tehran in 2001 and 2004, respectively. His M.Sc. thesis was entitled “Effect of curing condition on the chloride diffusion into concrete in Persian Gulf region”. He was admitted to the PhD program in Civil Engineering at the University of Ottawa in 2006. The cement and concrete nano-science has been at the core of his research during the past few years. He has made the following contributions during the course of his doctoral research:

Peer-Reviewed Journal Publications:

1. Alizadeh R., Beaudoin J.J., Raki L., Terskikh V. (submitted 2009) “C-S-H/Polyaniline nanocomposites prepared by in situ polymerization,” *Materials Characterization*, pp. 1-30.
2. Raki L., Beaudoin J.J., Alizadeh R., Makar J., Sato T. (submitted 2009) “Nanotechnology in cement and concrete science,” *Materials*, pp. 1-29.
3. Alizadeh R., Beaudoin J.J., Raki L. (submitted 2009) “Dynamic mechanical analysis of calcium silicate hydrates,” *Materials and Structures*, pp. 1-43.
4. Beaudoin J.J., Patarachao B., Raki L., Alizadeh R., (submitted 2009) “The Adsorption of Methylene Blue Dye by C-S-H,” *Cement and Concrete Composites*, pp. 1-24.
5. Mitchel L., Alizadeh R., Whitfield P., Beaudoin J.J. (submitted 2009) “Phase changes in semi-crystalline synthetic calcium-silicate-hydrate.” *Cement and Concrete Composites*, 1-14.
6. Beaudoin J.J., Raki L., Alizadeh R., Mitchel L. (2010) “Dimensional change and elastic behavior of layered silicates and Portland cement paste,” *Cement and Concrete Composites*, 32 [1] 25-33.
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16. Beaudoin J.J., Alizadeh R. (2007) "Detection of nanostructural anomalies in hydrated cement systems," *Cement and Concrete Composites*, 29 [2] 63–69.
17. Alizadeh R., Beaudoin J.J., Raki L. (2007) "C-S-H (I) - A Nanostructural model for the removal of water from hydrated cement paste?" *Journal of the American Ceramic Society*, 90 [2] 670–672.
18. Beaudoin J.J., Alizadeh R. (2007) "A discussion of the paper 'A multi-technique investigation of the nanoporosity of cement paste' by Hamlin M. Jennings et al.'," *Cement and Concrete Research* 37 [9] 1373.

Journal Papers under Preparation:

1. Alizadeh R., Beaudoin J.J., Raki L. "Stress relaxation of the calcium silicate hydrate," pp. 1-30.
2. Moudrakovski I., Alizadeh R., Beaudoin J.J. "Natural abundance ultra-high field ^{43}Ca solid state NMR in cement-based materials," pp.1-19.
3. Alizadeh R., Beaudoin J.J., Raki L. "Physical and mechanical stability of C-S-H/polyaniline nanohybrids."
4. Alizadeh R., Beaudoin J.J., Ramachandran V.S., Raki L. "Reactivity of cement compounds – Hedvall effect," pp. 1-18.
5. Alizadeh R., Beaudoin J.J., Raki L. "The layered nature of calcium-silicate-hydrate."

Conference Contributions:

1. Alizadeh R., Beaudoin J.J., Raki L. "Nanostructural Metamorphosis and Engineering Behavior of C-S-H in Hydrating Cement Systems" (*Invited Lecture*) *International Summit on Cement Hydration Kinetics*, Québec City, Canada, July 27-29, 2009.
2. Raki L, Beaudoin J.J., Alizadeh R. "Nanotechnology application for sustainable cement-based products," *Nanotechnology in Construction*, Proceedings of NICOM3: *3rd International Symposium on Nanotechnology in Construction*, Prague, Czech Republic, 119-124, May 31-June 2, 2009.
3. Beaudoin J.J., Raki L., Alizadeh R. "Nano-cement and concrete science," (Keynote Lecture) *CSCE Annual General Conference*, St John's, NL, May 27-30, 2009.
4. Alizadeh R., Beaudoin J.J., Raki L. "Hydration of C₃S– C-S-H systems" *American Concrete Institute Spring Convention*, San Antonio, US, March 2009.
5. Alizadeh R., Beaudoin J.J., Raki L. "Nanotechnology Research in Concrete Science," *The 12th GSAED Interdisciplinary Conference*, Ottawa, Canada, February 2009.
6. Beaudoin J.J., Raki L, Alizadeh R. "A ²⁹Si NMR Study of Calcium Silicate Hydrate Nanohybrids" *CCEDS-II: Sustainability of Civil Engineering Structures*, Hamilton, Canada, 1-24, May 2008.
7. Alizadeh R., Beaudoin J.J., Raki L. "The role of interlayer water on drying of Calcium-Silicate-Hydrate" *American Concrete Institute Spring Convention*, Los Angeles, US, April 2008.
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