ABSTRACT

SHahrin, Rahnuma. Nanoindentation Investigation of FIB-Milled Microstructures to Assess Failure Properties of Cement Paste at Microscale. (Under the direction of Dr. Christopher Bobko and Dr. Mohammad Pour-Ghaz).

A mechanical test methodology using Focused Ion Beam (FIB) milled micropillars and nanoindentation is developed to investigate the failure mechanism of cement paste at the level of calcium-silicate-hydrates (C-S-H), the primary binding phase of concrete. Cement paste is a hierarchical material with different levels spanning the range from nanometers to hundreds of micrometers. C-S-H is primarily responsible for strength and other mechanical properties of cement based materials. Therefore, a fundamental understanding and quantification of the failure behavior of C-S-H at microscale is critical for understanding failure at larger scales. Current experimental techniques, however, are unable to reveal how compressive failure is initiated within the cement paste microstructure. Therefore, a need exists for the development of a robust experimental method that can characterize compressive strength and failure modes of C-S-H.

To address this need, a novel methodology - uniaxial compression of cement micropillars is developed in this thesis. Micropillar geometries are fabricated by focused ion beam milling on potential calcium silicate hydrate (C-S-H) locations identified through coupled backscatter electron imaging (BSE) and energy dispersive spectroscopy (EDS) spot analysis. Uniaxial compression testing of these pillars is performed using nanoindentation equipment. The compressive strength of C-S-H (181-715 MPa) measured from micro-compression tests is found to be consistent with values from multiscale damage and molecular dynamic models in literature. Three primary deformation mechanisms at failure were identified: axial splitting, shearing and plastic crushing of the micropillar were mainly observed. Micro-compression
experiments on C-S-H micropillars of varying diameters indicated presence of a size effect with strong increase in strength with decreasing diameter. The deformation mode at failure also exhibited size effect: the dominant failure mode changed from axial splitting to crushing as the pillar diameter was decreased. Compressive strength of C-S-H measured from cement pastes with varying w/c ratio, on the other hand, did not show any significant variation, and thus is identified as independent of composition of the cement paste. Overall, the results of this pioneering work provide valuable insight about origin of strength in cementitious materials, and can be incorporated into multiscale strength homogenization and numerical models for better predicting quasi-brittle failure of cement pastes, mortars and concrete.
Nanoindentation Investigation of FIB-Milled Microstructures to Assess Failure Properties of Cement Paste at Microscale

by
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DEDICATION

To my son Azaan, for being my greatest source of inspiration, and to my parents, Saiful Alam and Mahmuda Begum, for giving me the strength to chase my dreams.
BIOGRAPHY

Rahnuma Shahrin was born in Chittagong, Bangladesh and spent her childhood in four different cities of Bangladesh. She earned her B.Sc. in Civil Engineering from Bangladesh University of Engineering and Technology (BUET) in 2009 and graduated first in her class. After graduation, she joined the same university as a faculty of Structural Engineering and did teaching and research for four years. In 2013, she completed her M.Sc. in Civil (Structural) engineering from Bangladesh University of Engineering and Technology (BUET). She then moved to USA and started her Ph.D. in Civil Engineering at North Carolina State University in a National Science Foundation (NSF) funded research.
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Chapter 1
Introduction

1.1 General
Concrete is the single most widely used material in the world. From tower blocks to carparks – this material is used so widely in construction industry that production, transportation, and use of concrete accounts for between 5-9% of total CO₂ emissions worldwide (Metz 2005). Cement paste is the binder and key ingredient of concrete, and a hierarchical material itself with three different levels spanning the range from few nanometers to hundreds of micrometers (Constantinides and Ulm 2004). It is composed of an amorphous phase calcium-silicate-hydrate (C–S–H) that acts as a matrix and binds the inclusions of Ca(OH)₂, unhydrated cement clinkers, water and micrometer range of porosity to form cement paste (Hlobil et al. 2015). C–S–H is the glue that holds concrete together and is itself a nanomaterial. Having different properties at each length scale (from nano to macro), the properties of concrete at each scale derives from those of the next smaller scale. There is a strong evidence that the processes occurring at the small scale ultimately affect the engineering properties and performance of the bulk material. Therefore, if the fundamental mechanisms behind failure of cement can be better understood at small scale, rationally designed engineering solutions can be deployed to provide tougher materials for civil infrastructure, reducing consumption of natural resources and production of CO₂. In this context, the primary research objectives of this work are to measure failure properties of cement paste at micron length scale and to characterize the failure properties of specific C-S-H phase within cement paste using nanoindentation experiments.

Over the last decade, our vision, expectations, and abilities to control the material world have been transformed by the developments in nanotechnology and nanomechanics. With a force range of 1 µN to 500 mN and displacement range of 1 nm to 20 µm, nanoindentation is extensively being used to probe the mechanical response of materials from metals and ceramics to biological and cementitious materials. In the study of concrete and cement, grid nanoindentation testing has been successfully used to measure elastic moduli, creep and hardness properties of cement paste under complex multi-axial stress states (Constantinides
and Ulm 2004; Constantinides and Ulm 2007; Vandamme and Ulm 2009). However, investigation of failure properties of cement at this length scale is not that straightforward and hence gained less focus in nanoindentation literature.

In recent years, material scientists have introduced small-scale compression tests of micro-pillars using a customized nanoindentation system (Uchic et al. 2003). For preparing specimens suitable for such small-scale experiments, the focused ion beam (FIB) techniques are employed. Since then uniaxial compression of focused ion beam (FIB) milled micropillars using nanoindentation equipment has become an effective approach to investigate small scale strength properties (Uchic et al. 2004; Ye et al. 2010; Volkert and Lilleodden 2006; Shim et al. 2009; Korte and Clegg 2009). FIB based micro-compression tests attained greater interest and attention for various kinds of materials such as – bulk metallic glasses, shape memory alloys and single crystals. Yet, few studies have explored the application of micro-compression testing to granular and heterogeneous materials such as bones, mudstones, shales, and dental enamel- which have hierarchical microstructure like cement paste (Zhang et al. 2010; Abousleiman et al. 2016; Yilmaz et al. 2015; An et al. 2015; Dewers et al. 2010; Han et al. 2011; Luczynski et al. 2015). While one study has used FIB milled microbeams to assess tensile strength of cement (Němeček et al. 2016), uniaxial compression tests have never been performed on FIB milled cement micropillars for assessing their compressive failure behavior. In this thesis a new methodology is developed to provide a quantitative portrait of failure behavior cement paste at level-1. This study is one of the first to explore how FIB based micro-compression techniques can be applied to improve our understanding of failure of cementitious materials.

1.2 Research Needs
The following research needs and potential scope for making contributions are identified in the subsequent literature review section:

   a. Current experimental research cannot reveal how failure is generated within cement paste microstructure.
   b. Conventional nanoindentation investigations are not directly capable of measuring strength properties of cementitious materials.
c. The deformation mechanism of C-S-H phases under compressive failure load is yet to be investigated.
d. Innovative sample preparation techniques are required for making micron sized sample geometries on individual phases of cement.

1.3 Research Tasks
In accordance to the needs established in literature review and the gaps mentioned in section 1.1, the following tasks will help to achieve the research objective:

a. To develop a repeatable sample preparation method for creating cement paste micropillars using FIB milling.
b. To establish a robust experimental protocol for testing the FIB-milled sample geometries in uniaxial compression using nanoindentation system.
c. To obtain a data set of compressive strength and elastic modulus of C-S-H phase by analysis of raw data from micro-compression tests.
d. To determine the effect of w/c ratio and pillar size on compressive strength, elastic modulus, and deformation modes at failure.
e. To link the mechanical responses from experimental observations to different C-S-H packings.

1.4 Outline
The organization of this thesis consists of seven chapters.

Chapter 1: Provides a general discussion of the related background and objective of this research. The need for performing this research and its primary tasks are also summarized.

Chapter 2: Multiscale model of concrete is explained in this section. An overview of previous scanning electron microscopy (SEM) and nanoindentation investigations on cementitious materials is provided. Potential of FIB based micro-compression experiments in measuring strength, elastic modulus and effect of pillar size is also discussed using related literature.

Chapter 3: The methodological approach of this research is explained. First, an introduction to the cementitious materials studied in this research is provided with details of their preliminary surface preparation techniques. Then, the method developed for FIB milling of micropillars is explained. Detailed procedure of performing micro-compression testing using nanoindentation
system is discussed next. After that, data analysis method for assessing strength and elastic modulus results and post-test SEM imaging techniques for assessing deformation modes is discussed. Finally, specific details related to size effect analysis study is provided.

Chapter 4: This chapter investigates compressive failure behaviors of C-S-H by presenting results of micro-compression experiments on cement micropillars of a constant water to cement ratio and fixed micropillar size. Characterization of C-S-H microstructure, compressive strength and failure modes is performed by analysis of micro-compression results in terms of stress and strain as well as visual observations.

Chapter 5: This chapter focuses on investigating size effect on compressive failure of C-S-H by presenting results of micro-compression experiments on C-S-H micropillars of diameters varying between 2.5 and 0.5 μm fabricated on a constant w/c ratio cement paste. A discussion of the results is presented in the context of existing size-effect models for strength of quasi-brittle materials.

Chapter 6: Effect of cement paste composition on the failure behavior is examined in this chapter by presenting results of micro-compression experiments on C-S-H micropillars from cement pastes with varying w/c ratio. An approach considering elastic modulus obtained in the micro-compression experiments, in conjunction with prior research using grid nanoindentation, is used to propose a range of compressive strengths for cement hydration projects.

Chapter 7: The final chapter summarizes the results of this study and provides perspectives for future research endeavors.
Chapter 2
Literature Review

2.1 Introduction
In this section, a brief description is provided on the multiscale nature of concrete and its main binding phase C-S-H (Section 2.2). The mechanism, capabilities and limitations of existing nanoindentation techniques are reviewed in Section 2.3. Previous investigations on cementitious materials using various features of scanning electron microscopy (SEM) are listed in Section 2.5. Limited available literature on micro-scale measurement of cement strength is discussed in Section 2.6. The potential of FIB based micro-compression experiments in measuring strength properties is discussed in Section 2.7 using related literature. The effect of water to cement ratio on mechanical properties of C-S-H is described in Section 2.4.

2.2 Motivation for Nanoscale Experiments
Concrete is a particularly complex material because it is highly heterogeneous with multiple length scales involved. It is primarily composed of cement paste, sand, coarse aggregate and admixtures in some cases. Each of these ingredients are heterogeneous themselves at a certain level of observation and have different strength and stiffness. Therefore, the heterogeneity of concrete exists in a variety of length scales from nano to macro. It is widely recognized that many macroscopic phenomena of concrete originate from the mechanics of the underlying nano and microscale structure. All the mechanical, physical and chemical properties of the ingredients including strength, stiffness, size, shape, volume fraction, and spatial distribution can have impact on the material behavior observed at macroscale. However, measurements made at the typical scales of concrete laboratory testing are unable to reveal how failure is initiated within the microstructure of cement paste. Small scale experimental techniques are required to quantitatively assess the complex material behaviors that lead to failure in cement paste microstructure. A fundamental understanding of the failure behavior at small scale would result in better prediction and control on the macroscopic concrete properties.
2.2.1 Multiscale overview of concrete

The range of the random microstructure of concrete encompasses nine orders of magnitude in size from nanometer ($10^{-9}$m) to meters (m). Experimental methods and analytical approaches to understand strength properties of cement and concrete must respect the different material behaviors that are associated with each length scale. Figure 2.1 shows a multi-scale model framework for concrete.

Macroscopic concrete is a three phase material composed of aggregates embedded in a mortar matrix and an ITZ. Fine aggregate (sand), cement paste, entrained air bubbles in cement paste, and crushed coarse aggregates are constituents that make up the mortar. The importance of the aggregate-cement paste interfacial zone, as the third and weakest component of concrete, has been recognized for some time (Monteiro 2006; Monteiro and Mehta 1985). Together, these three phases characterize the macroscopic performance of concrete. Due to large dimension of the composite at this level, mechanical features can be obtained by standard test methods such as compressive cylinder tests.

Calcium-Silicate-Hydrates (C-S-H)\(^1\) matrix together with large Calcium Hydroxide (CH) crystals, unhydrated cement clinker, ettringite and micrometer porosity in the case of high w/c ratios, forms the cement paste, and is referred to as Level II. Scanning electron microscope (SEM) has good resolutions at this scale, and can be used to observe morphology detail of hydration products with large crystals such as CH and ettringite. Components in this level are also visible in a high-powered optical microscope but with much less resolution and depth of field compared to SEM.

Level I is the smallest material length scale that is, at present, accessible by mechanical testing. A granular composite of C-S-H aggregates and pore space comprise this face which is also called C-S-H gel. At this scale, different C-S-H packing densities, and small capillary pores greater than 10 nm characterize the behavior of the matrix (Jennings et al. 2007). According to the model proposed by Jennings, C-S-H nanoparticles are packed in two different packing densities so called Low density (LD) and High density (HD) C-S-H. The average pore volume

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\(^1\) In Cement chemistry, C=CaO, S=SiO\(_2\), H=H\(_2\)O. The atomic elements without oxides are expressed in a conventional manner. The hyphens in C-S-H indicate indefinite stoichiometry and the hydrate is sometimes referred to as “C-S-H gel”. [(Raki et al. 2010)]
of these C-S-H phases were reported 37% and 24% respectively (Jennings 2000). For low w/c ratio pastes Vandamme and colleagues identified the presence of a third type of C-S-H with higher indentation modulus and indentation hardness (Vandamme and Ulm 2009; Vandamme et al. 2010). This phase is termed either as ultra-high density (UHD) C-S-H or C-S-H/CH nanocomposite in different literature (Vandamme and Ulm 2009; Chen et al. 2010).

At Level 0, C-S-H have complicated, non-regular molecular structures. These molecules tend to organize themselves into grains which are termed as C-S-H globules. Using observations from Small Angle Neutron Scattering (SANS), Jennings (Jennings et al. 2007) termed this globules with characteristic size of 5.6 nm as the elementary block of C-S-H aggregates. Richardson used transmission electron micrographs to analyze their morphology and nano structure (Richardson 2004). He classified C-S-H aggregates as inner and outer product of hydration based on their fine-scale like and foil like morphology respectively.

![Figure 2.1: Multiscale model of concrete (Constantinides and Ulm 2007b), Level 0 drawing from (Allen et al. 2007), level I image from (Nonat 2004).](image)

Quasi-brittle failure likely initiates at the scale of Level I because at Level 0, mechanical properties within individual C-S-H globules are dominated by strength of chemical bonds.
Failure instead begins within aggregates of C-S-H, which are viewed as granular systems of C-S-H globules.

### 2.2.2 Nano scale properties of C-S-H

Calcium silicate hydrate (C-S-H) is a highly disordered nano-scale material comprised of layers of calcium and oxygen, with SiO$_2$ tetrahedra attached and interspersed by water and further Ca ions. It is formed in a dissolution-precipitation reaction involving mixtures of tricalcium silicate (Alite) and dicalcium silicate (Belite) with water. Due to the importance of C-S-H as the binder phase of Portland cement it has been widely studied over many decades. Yet, the link between composition, nano and microstructure and mechanical behavior of C–S–H remains a complex puzzle that is not resolved completely.

Grudemo (Grudemo 1955) was one of the first to propose that the C-S-H gel comprised “solid” regions of layers including some ‘chemically combined’ water with small water filled pores between these regions now widely known as gel pores. From a compositional point of view, the C-S-H gels are often characterised by their Ca/Si ratio, which is in the range from 0.7 to 2.3. The reasons behind this variation might be since C-S-H structure formed by cement hydration is highly dependent on the chemical mixtures and reaction conditions and may evolve over long periods of time.

Density results of different studies and calculations have been reviewed by Jennings in the context of the colloidal model and vary between 1.8 and 2.8 g/cm$^3$ (Jennings 2008). Much of this variability arises from the fraction of the gel pore water and other nanoscale confined or bound water that is, or is not, inferred to be included in the measurement. A widely cited result used small angle neutron scattering (SANS) and reported the density for solid crystalline C-S-H to be 2.604 g/cm$^3$ (Allen et al. 2007). In a comparatively recent work, nuclear magnetic resonance (NMR) was used to measure C-S-H density. Depending upon the degree of hydration the reported values for solid density vary in the range of 2.73 ~ 2.65 g/cm$^3$ (Muller et al. 2012).

The morphology of C-S-H continued to be the subject of active debate in the literature. From atomic force microscope (AFM) investigations Nonat, suggested a brick-type morphology of the C-S-H nanoparticle (lamellae) of dimension 60 x30 x 5nm$^3$ (Nonat 2004). Richardson identified different morphologies of C-S-H by TEM: a fine-scale homogeneous morphology
for the inner product and two distinct morphologies for outer product, a fibrillar structure and a foil-like structure that appear to correlate with the Ca/Si ratio (Richardson 2004). The foil-like structure preferentially forms below a Ca/Si ratio of about 1.5. Constantinides and Ulm identified packing density as the key factor behind two distinct C-S-H morphologies, so called, low and high density (Constantinides and Ulm 2004a). Jennigs and coworkers proposed a colloidal model of C-S-H based on results from various experimental techniques (Jennings et al. 2007). According to this model (Figure 2.2) around 5 nm sized globules of C-S-H pack together to form larger structures with lower densities, and in mature pastes there are distinct “high-density” (HD) and “low-density” (LD) morphologies of C-S-H gel depending on packing density. In a different approach, Pellenq and coworkers used bottom-up atomistic simulation to propose a molecular model of C-S-H. This model provides molecular description of interacting CaO, SiO₂, and H₂O unit and suggests that the C-S-H gel structure includes both glass-like short-range order and crystalline features of the mineral tobermorite (Pellenq et al. 2009).

Figure 2.2: Formation of C-S-H gel a) One relatively small volume fractal region of C-S-H globules. b) Same volume fractal region (shown in white) has grown into a larger, self-similar structure with a reduced packing density. c) Adjacent fractal regions have grown (Jennings et al. 2007).

2.3 Overview of Nanoindentation Investigations on Cementitious Material
While there have been a variety of available techniques for measuring physical properties and observing the microstructure, experimental investigation of mechanical properties at such
small scale is not that straightforward. In last few decades, instrumented indentation, also known as depth sensing indentation or nanoindentation has become a versatile tool to probe the mechanical response of materials from metals polymers, and ceramics to biological materials. Advances in hardware and software control currently enable accurate measurements of the continuous variation of indentation load down to micro Newtons, as a function of the indentation depth down to nanometers. Thus, instrumented indentation provides a convenient, non-destructive means to evaluate the basic mechanical response of small material volumes. The commercially available packages, with flexibility of choosing the appropriate geometry of the indenter tip, have made it an effective way of material characterization for bulk, thin film, or composite materials.

In comparison to homogenous materials, nanoindentation on heterogeneous materials have some added challenges, as it is difficult to choose to indent on a specific material phase with sufficient repeatability. To overcome this difficulty for heterogeneous materials like cement paste, researchers prefer the grid indentation technique coupled with statistical methods. In such cases, the grid size and depth of indentation are the two key parameters that need careful consideration (Ulm et al. 2007).

The initial instrumented indentation efforts reported on cementitious materials were microindentation tests. Igarashi et al. used a Vickers indenter to assess bulk properties of cement paste at a sub-millimeter to millimeter material length scale (Igarashi et al. 1996). Zhu et al. studied the mechanical properties of interfacial transition zone for reinforced concrete (Zhu and Bartos 1997; Zhu and Bartos 2000). Kholmyansky et al. discussed possible experimental methods for determination of hardness in case of fine grained concrete (Kholmyansky et al. 1994). Continuous evolution of computer technology enabled improved control over instrumented indentation testing. In two individual studies, Velez and Acker reported the initial attempts of performing nanoindentation testing on cement (Velez et al. 2001; Acker 2001). Velez studied the elastic modulus and the hardness of the major phases of Portland cements (C₃S and alite, C₂S and belite, C₃A, C₄AF) (Velez et al. 2001). Acker investigated ultra-high performance cementitious composite material, DUCTAL, and reported modulus and hardness values for portlandite (Ca(OH)₂) and the C-S-H gel with different Ca/Si ratio (Acker 2001).
Over the last decade, researchers extensively used nanoindentation as a versatile tool to investigate different mechanical properties of cement and concrete. A major portion of this research is centered on determining elastic modulus and hardness values. Constantinides and Ulm investigated the modulus and hardness values for portlandite and C-S-H gel. They used the indentation results as a basis to propose the existence of low and high density C-S-H (Constantinides and Ulm 2004b). Mondal and Shah reported individual modulus and hardness results for low, high and middle density C-S-H by using an in-situ scanning probe microscopy imaging technique of nanoindenter (Mondal et al. 2007). Zhu and his group used progressive multistep indentation tests results and interpolation to develop 2D contour maps of modulus and hardness values for cement paste (Zhu et al. 2007). Trtik and his group determined modulus and hardness results for different individual phases, with primary focus on linking physical observations of microstructure to mechanical responses (Trtik et al. 2009; Hughes and Trtik 2004). They also emphasized the importance of good surface preparation and flat topography for reduced scatter in indentation results. Detail study on surface roughness criteria for cement paste nanoindentation was performed by Miller and coworkers (Miller et al. 2008). They explained a stepwise process as well as the importance of low surface roughness to ensure repeatable and meaningful nanoindentation results.

Some of the studies focused specifically on characterization of C-S-H, the properties of which exhibit significant local variations. Constantinides and Ulm performed detailed investigation on nanogranular morphology of C-S-H using nanoindentation results (Constantinides and Ulm 2007a). They argued that the mechanical behavior of C-S-H is driven by the particle-to-particle contact forces at contact points rather than by the mineral properties (Constantinides and Ulm 2007a)(Constantinides and Ulm 2007a). Ulm and his group, used packing density scaling relations along with indentation modulus and hardness to investigate intrinsic anisotropy of randomly orientated C-S-H particles. Their results show that particle shape and aspect ratio do not significantly affect the nanomechanical response of C-S-H and hence it can be treated as isotropic (Ulm et al. 2007). In a separate study, the degradation of nanostiffness properties of C-S-H was discussed under elevated temperature condition. This work discussed the thermal degradation mechanism caused by significant change in packing density of C-S-H particles for exposure temperatures above 700 C. (DeJong and Ulm 2007).
Many nanoindentation studies analyzed creep properties of C-S-H. Vandamme and Ulm used cement pastes of different compositions and water cement ratios to conclude that the logarithmic creep of C–S–H is due to nano-particle sliding within C-S-H that leads to a local increase of the packing density (Vandamme and Ulm 2009). In a subsequent work, they extended their work for several loading protocols and indenter geometry and quantified the amplitude of logarithmic creep by a contact creep modulus. In another concurrent study, Pichler and Lackner used nanoindentation results for Identification of creep-compliance parameters for logarithmic creep behaviour of of C-S-H (Pichler and Lackner 2009). Němeček discussed the effect of creep deformation while determining the elastic properties of hydrated cement paste. He suggested application of long dwelling time in conjunction with cyclic loading for avoiding creep effects in elastic property measurements (Němeček 2009).

2.4 Effect of Water/Cement Ratio

Nanoindentation studies, showed that elastic modulus and hardness values of C-S-H are independent of the mix proportions. However, the water/cement ratio of cement paste influences the relative volume fractions of hydration products. Vandamme et al. (Vandamme and Ulm 2009) showed that cement-based materials prepared at high w/c ratios contain mostly LD C-S-H, whereas low w/c ratio cement pastes favor the formation of high density (HD) and ultra high-density (UHD) C-S-H (Figure 2.3). For example, for w/c ratio of 0.20 the HD C-S-H occupies 74% of hydrated phases, while for w/c ratio of 0.40 this value is about 29%.
2.5 SEM Investigations on Cementitious Material

Scanning electron microscope (SEM) has been a powerful tool for analysis of cementitious materials for several decades. For cement clinker and hydration products, it permits observation of microstructure and identification of phases, including qualitative as well as quantitative analysis of chemical compositions. The advantage of electron microscopy is all the components of the cement microstructure can be examined at a wide range of magnifications which provides information about their spatial distribution.

2.5.1 Use of BSE imaging

Backscattered electrons are electrons from the incident beam which are reflected or scattered back from the specimen by elastic scattering interactions with specimen atoms. The contrast in BSE signal is produced by the difference is atomic number among the different constituent phases of a sample. The initial users of SEM mostly utilized backscattered electron (BSE) imaging of polished cement sections to distinguish anhydrous material, calcium hydroxide, C-S-H and porosity based on their grey level intensity (Kjellsen et al. 1990; Scrivener et al. 1986). Famy and coworkers used grey level variations to further distinguish between C-S-H gels formed at different temperatures (Famy et al. 2002b). With the advancement of digital
image analysis, quantitative potential of BSE imaging was discovered. BSE imaging was shown to have significant potential of estimating the pore size distribution in concrete (Diamond 2000). Other contemporary works focused diverse applications like mass fraction estimation of the main phases in Portland cement clinker, estimation of water/cement ratio in hardened cement paste and calculation of volume fractions in the interfacial transition zone (Stutzman 2004; Sahu et al. 2004; Scrivener 2004; Campbell 1999). Some researchers used X-ray powder diffraction (XRD) and Rietveld analysis along with backscattered electron for determining amounts of different phases in anhydrous cementitious materials (Scrivener 2004; Stutzman and Leigh 2007). However, BSE imaging is still mostly used qualitatively for identification of different material phases in cementitious materials.

2.5.2 Use of EDS microanalysis

For compositional microanalysis, energy-dispersive spectroscopy (EDS), which is also known as energy-dispersive X-Ray (EDX) is an alternate approach that provides detailed information on chemistry of constituent phases. In contrast to the 2D surface information gathered through BSE imaging, X-Ray microanalysis represents a 3D interaction volume from which the X-Ray is generated. Many researchers have investigated cement pastes by using X-Ray microanalysis. Harrison and coworkers were one of the pioneers who examined the compositions of residual clinker phases by using X-Ray (Harrisson et al. 1986). Richardson and Groves used electron microprobe analysis (EMPA) to get composition for inner and outer product of C-S-H (Richardson and Groves 1993). They used cut off ratio for Ca/Si and (Al + Fe)/Ca and presence of Magnesium to distinguish this two type of C-S-H. Following a similar approach, Bonen and Diamond also analyzed cement paste and reported the present of another C-S-H phase with slightly different composition. They attributed intermixing of Ca(OH)$_2$ with C-S-H gel below the scale of SEM observation for occurrence of this phase (Bonen and Diamond 1994). Garcia and Sharp investigated the change in Ca/Si and Al/Ca and S/Ca ratio of inner and outer product C-S-H gel for various curing temperature by EDS (Escalante-Garcia and Sharp 1999). Famy and coworkers extended this approach and constructed 3D plots for Ca/Si, Al/Ca and S/Ca to quantify the C-S-H and hydrated aluminate and sulfoaluminate phases (Famy et al. 2003).

In recent past, researchers have coupled energy-dispersive spectra (SEM-EDS) analysis with micromechanical testing. Separation of cement hydration products with different stoichiometry
but very similar indentation responses at submicron scale is the advantage of such chemomechanical analysis. Based on Monte-Carlo simulation, Chen and coworkers argued that the microvolumes probed by SEM-EDS and nanoindentation are directly comparable (Chen et al. 2010). They performed EDS analysis on each of the indentation point and used the composition data to group the indentation results for different phases. Based on the Ca/Si ratio, this work reinforced the presence of a C-S-H /CH nanocomposite. In a similar methodology, indentation response of the C-S-H solid was linked to its stoichiometry via x-ray microanalysis (Krakowiak et al. 2013). In recent years, couple of researchers have used this technique to investigate hydrated phases of cement paste, specifically, C-S-H and CSH/CH nanocomposites (Bu et al. 2015; Moser et al. 2013). This coupled approach provided a promising way to study the local mechanical properties of cement paste and of its constituents by correlating them to their chemical composition.

### 2.5.3 Use of FIB sectioning

In the last decade, a special type of SEM, Focused ion beam (FIB/SEM) showed increased potential for investigations of cementitious materials. In this type of dual beam SEM, a finely focused beam of gallium ions (Ga+) can hit the sample surface and sputter a very small amount of material. The highly localized gallium ion beams allow to segment hardened cement paste, and to distinguish different phases within the solid matter (Trtik et al. 2011). Thus, the combination of an electron beam for imaging and a localized ion beams for exposing successive surfaces, provided a suitable tool for microstructural investigation of granular cementitious materials. Many applications are reported in the literature where focused ion beam nanotomography (FIB-nt) is performed on cementitious materials for serial sectioning. Because of its high resolution (15 nm), it reveals precise microstructural information at the submicrometer scale, which cannot be obtained with conventional tomography methods. The FIB-nt technique was utilized for investigation of particle size distribution and morphology of cement particles (Holzer et al. 2006; Münch et al. 2006), morphology and spatial arrangement of early hydration products (Holzer et al. 2007), surface roughness (Trtik et al. 2008) and nanoscale porosity (Trtik et al. 2009; Holzer et al. 2006) of hardened cement paste. Trtik and coworkers discussed the possibility of segmenting unhydrated cement particles from hydration products by FIB-nt of a hydrated cement paste (Trtik et al. 2008). In subsequent works, they
used the FIB-nt datasets with improved image processing technique to further distinguish between different phases of hydration products (Trtik et al. 2011).

Some of the researchers used the previously discussed approach of combing indentation results with microstructural investigations for FIB sectioning instead of EDS (Trtik et al. 2009; Lura et al. 2011). By utilizing the nano scale resolution of the ion column, FIB techniques permitted observation of deformed material underneath the indents and hence better understanding of processes which occur during micro or nanoindentation tests. Trtik and his group reported carrying out microindentation experiments on a cementious composite followed by FIB cross sectioning at selected indent points (Trtik et al. 2000; Bartos 2004). SEM micrographs collected from FIB milled trenches were used to gather information about the possible failure modes induced by the impression of diamond indenter in the surrounding material.

2.6 Limitations of Strength Measurement in Cement

Broadly, the SEM investigations literature is centered around identification of main constituent phases in cement, their pore size distribution, chemical composition, and analysis of cement microstructure and morphology. the majority of nanoindentation literature, On the other hand, focuses on measurement of Young’s modulus and hardness values of cement paste constituents. For Von-mises type of materials, a rule-of-thumb relation between (Eq. 2.1) indentation hardness \( H \) and tensile strength \( \sigma_Y \) of the material exists (Tabor 1948)

\[
H = 3\sigma_Y
\]  

(2.1)

Based on this classical relation, the indentation hardness of the metals is often used as an indicator of the strength properties. However, for cohesive materials, very different set of elastic moduli, work hardening exponent and yield strength can result in similar indentation hardness results. Hence, for granular and cohesive materials like cement paste with more complicated strength behaviors, a single indentation hardness measurement cannot be related to strength (Chen et al. 2007).

At Level II, macroscopic measurement of strength properties of cement paste is done by testing cement cubes and beams. Using micro dicing saw, Zhang et al. prepared micro-cubes (100 µm x 100 µm x100 µm) and microbeams (500 µm × 500 µm cross section) of cement paste and
loaded the cubes with a sharp indenter to measure splitting tensile strength, elastic modulus and fracture mechanisms of cement paste at a global level (Šavija et al. 2017; Zhang et al. 2017; Zhang et al. 2016). It is important to note that, theses measured properties, due to the large size of the cubes and beams, are representative of the entire paste and not of individual constituent phases.

The strength properties and failure modes of cement paste at the Level I scale have not yet been well investigated. Hlobil et al. estimated compressive strength of C-S-H matrix at Level I using coupled finite element simulations and multiscale analysis for upscaling to practical measures (Hlobil et al. 2016; Hlobil et al. 2015). This approach, however, calculates tensile strength of C-S-H globules based on their approximate packing density and used them as input parameter for compressive behavior of C-S-H matrix, which imposes intrinsic limitations on its predictions.

At Level 0, molecular dynamics simulations provided some insight about the behavior within the C-S-H globules (Pellenq et al. 2009; Selvam et al. 2009). Yet, the complex granular microstructure of C-S-H aggregates at Level I presents a system far too large for feasible atomistic computations.

In the framework of continuum micromechanics, Pichler and Hellmich and Pichler et al. calculated deviatoric strength of microscopic hydrates based on an elasto-brittle multiscale model for cementitious materials (Pichler and Hellmich 2011; Pichler et al. 2013). The corresponding model predicted uniaxial compressive strength of low-density C-S-H using parameters from finite-element reanalysis of nanoindentation results (Pichler et al. 2013; Sarris and Constantinides 2013). However, the representative volume element (RVE) considered in this model (~20 µm) for strength homogenization, is too large compared to size of individual hydrated phases observed in BSE imaging of hydrated cement paste (Famy et al. 2002a). Moreover, the input parameters used for homogenization, are not properties specific to LD C-S-H, but rather calculated as an average over all type of hydrates, including ettringite, portlandite, and C-S-H of different mass densities.

Recently, one study used microbeam bending tests to assess the tensile strength of cement hydration products (Němeček et al. 2016). However, to the author’s knowledge, no research has yet experimentally investigated uniaxial compressive failure behavior of low and high
density C-S-H, portlandite, or unhydrated clinker phases. Hence, there is a need for a robust experimental technique that can be used to obtain quantitative information about compressive failure behavior at Level I.

2.7 Coupled FIB-milling/NI-testing Approach for Strength Measurement

For strength measurement of individual phases present at the scale of Level I, it is crucial to develop localized micro-structured sample geometries on the targeted individual components of hydrated cement paste. To achieve this, an effective sample preparation technique is required that can isolate individual phases without disrupting their intrinsic properties.

A recent innovative technique in material science involves testing of FIB milled microstructures (micropillars, micro-beams and wedges) using a nanoindentation tip for measurement of strength (compressive and tensile), fracture toughness and deformation modes. Different micro-machined sample geometries can deliver different material properties, just like their more traditionally sized counterparts. Though nanoindentation systems are designed for performing depth sensing indentation experiments using sharp indenter, when outfitted with a flat or spherical indentation tip, the same platform can be used to perform conventional uniaxial compression tests at prescribed load or displacement rates (Uchic et al. 2004a; Uchic et al. 2003). Uniaxial compression testing of FIB milled micro-pillars as unconfined cylinders using nanoindentation equipment provide plastic strength properties of the tested material. The flat tip of the indenter and the attachment of the micropillar to the bulk material functions as the compression platen. In recent years, this micro-compression technique has been extensively used to investigate small scale compressive strength, failure mechanisms, elastic modulus and size effect.

2.7.1 Developing micro-structures using FIB milling

Uchic and coworkers introduced the concept of using Focused Ion Beam (FIB) technology to machine micropillars on single crystals (Uchic et al. 2003; Uchic et al. 2004b; Uchic and Dimiduk 2005). In a separate study, Fukuda and his group also discussed the applicability of FIB in machining pillar like geometries (Fukuda et al. 2004). This technique has since been applied to many other materials for making various sample geometries (Di Maio and Roberts 2005; Massl et al. 2009; Liu et al. 2013). For homogenous materials like single crystal, thin films, hard coatings, and Silicon wafers, the milling process is relatively straightforward, as
the rate at which material is removed remains same throughout the sample surface. Therefore, development of micropillars and more complex geometries like single and double cantilever beams on homogenous materials is reported in various literature (Liu et al. 2013; Riedl et al. 2012; Schaufler et al. 2012).

Different milling methods have been practiced for fabricating micropillars. The ‘ion-lathe method’ is effective but more time intensive (Uchic et al. 2004a; Uchic et al. 2003; Uchic and Dimiduk 2005). Since instrumentation time is critical issue, as an alternative approach, sequential milling of concentric rings also known as ‘annular milling method’ is widely used by researchers (Figure 2.4a). This method allows the user to change milling parameters before each milling cycle. While preparing samples for subsequent micro compression test, formation of a trench like crater has been recommend by many studies (Volkert and Lilleodden 2006; Volkert et al. 2008). Particular advantages of this trenching (Figure 2.4b) lies in (i) allowing one to image the sidewalls of the micro-sample both before and after deformation using the SEM (which is necessary for subsequent fabrication steps), (ii) avoiding the possibility of unintended contact between the indenter tip and the micro-sample, (iii) reducing the probability that sputtered material will redeposit back onto the freshly milled microsample during subsequent fabrication steps, and (iv) facilitating easy identification of the testing location with optical microscope of the nanoindenter test system during testing (Uchic and Dimiduk 2005).

Figure 2.4: Concentric rings and trench formed by annular milling on a) metallic glass ((Yang et al. 2009) b) Ni single crystal (Uchic and Dimiduk 2005).
Proper selection of milling parameters plays the key role in successful fabrication of pillar geometry. However, very few studies publish the used parameters. A brief list of the parameters used by some researchers is provided in Table 2.1. As seen from this table, most of the researchers reported using the same acceleration voltage of 30 keV, whereas, the beam current values show a wide variation. Using beam currents as high as 7 nA or higher can significantly reduce the milling time. However, excessive high currents have increased potential of introducing various damage in the micropillar structure (Shim et al. 2009; Thompson et al. 2007). Among all the possible defects, implantation of Gallium ions within the milled material possess the biggest concern in case of amorphous materials. Such implantations have the potential to affect small scale mechanical behavior. According to Thompson et al., use of lower beam currents can reduce this damage to a significant extent (Thompson et al. 2007).

Another critical aspect of preparing micropillar samples lies in deciding the appropriate aspect ratio of pillar and maintaining a constant ratio. When the aspect ratio is high, the pillar is prone to elastic buckling due to the misalignment between the pillar and the indenter (Volkert and Lilleodden 2006). Aspect ratios ranging from 2:1 to 4:1 are mostly used in recent literature to ensure compressive failure. A constant aspect ratio ensures constant relative contribution from friction and constraint from the underlying materials (Volkert et al. 2008). The tapering of FIB milled micropillars is another experimental issue that is nearly unavoidable using current FIB techniques, specially for small pillar diameters. Some papers developed analytical formula for accurate extraction of pillars’ yield strength which require determination of normal stress coefficient and the shear angle (Ye et al. 2010; Yang et al. 2009b). Another approach uses the average diameter of the pillar or the mid height diameter instead of considering the taper angle (Volkert and Lilleodden 2006).
<table>
<thead>
<tr>
<th>Authors</th>
<th>Materials</th>
<th>FIB milling conditions</th>
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<tr>
<td>Uchic et al.</td>
<td>Single-crystal Ni and Ni3Al</td>
<td>Not reported</td>
</tr>
</tbody>
</table>
|            | Single-crystal superalloy         | Accelerating voltage: 30 keV  
              Beam current: 1–7 nA for coarse milling, and 0.05–1 nA for fine milling |
|            | Single-crystal Ni                 | Not reported                                                                        |
|            | Pure Ni and Ni3Al                 | Not reported                                                                        |
| Greer et al.| Single-crystal Au                 | Not reported                                                                        |
|            | Single-crystal Au and Mo          | Not reported                                                                        |
| Volkert et al.| Single-crystal Au              | Accelerating voltage: 30 keV  
Beam current: not reported                                                                |
| Kiener et al.| Single-crystal Cu                | Accelerating voltage: 30 keV  
Beam current: 1 nA for coarse milling, and 0.1 nA for fine milling                 |
| Shan et al. | Single-crystal Ni                 | Not reported                                                                        |
| Ng et al.   | Polycrystal Al                    | Accelerating voltage: not reported  
Beam current: 20 nA for coarse milling, and 0.05 nA for fine milling                |
| Frick et al.| Single-crystal Ni                 | Not reported                                                                        |
| Norfleet et al.| Single-crystal Ni          | Not reported                                                                        |

Fewer studies applied FIB milling techniques for micro sample preparation on heterogeneous materials due to various added challenges in milling process. Micropillars geometries are reported to be made on wood materials with nonhomogeneous, composite microstructure, and on mudstone, biological exoskeleton, and dental enamel materials with granular microstructure.
like cementitious materials (Dewers et al. 2010; Han et al. 2011; Yilmaz et al. 2015; Yilmaz et al. 2013; Yilmaz et al. 2013; Zhang et al. 2010; An et al. 2015). Researchers explored the application of micro-compression and micro-bending testing of FIB-milled structures for heterogeneous shale material which exhibit hierarchical microstructure like cement paste. Abousleiman et al. tested FIB milled cantilever micro-beams in bending using nanoindenter tip, and studied tensile strength characteristics of shale (Abousleiman et al. 2016). Keller et al applied micropillar compression testing to measure Microscale uniaxial compressive strength and stiffness of shale (Keller et al. ). Very recently, FIB milling has been performed on cement for fabrication of microbeams for measurement of tensile strength (Němeček et al. 2016; Chen et al. 2015). However, FIB milled micropillars geometries have never been reported to be fabricated on cement.

2.7.2 Estimation of compressive strength

Over the last decade, uniaxial compression of (FIB)-milled micropillars using nanoindentation equipment has become an effective approach to investigate compressive failure behavior (Figure 2.5a). Strength measurement involves acquiring the load- displacement data by using the nanoindentation equipment system (Figure 2.5b). While some researchers reported using in-situ indenter which can be placed directly within the SEM, most of the micro-compression tests are performed on commercially available indentation systems. A primary obstacle using of ex-situ indenter is the difficulty of locating FIB milled structures in an optical microscope. For Hysitron Triboinder, the tip can scan the surface of the sample with the indenter tip at very low loads to find the features of the micro-milled structures (An et al. 2015; Bhushan et al. 1996). The accuracy of this method, however, is highly dependent on the quality of AFM attached to the tip and minimization of surface roughness. Alternatively, cavity or trench around the pillar approach has been widely used for locating the micromilled structure (Figure 2.4).
A closed loop trapezoidal compression loading needs to be imposed on micro-compression samples by controlling either the loading or the displacement. In both cases, a holding time of 5-15 second is preferred between the loading and unloading to remove creep effect. Uchic et al. followed the displacement controlled approach with a displacement rate of 1-5 nm/s (Uchic and Dimiduk 2005). Han et al. also used a similar approach with 5 nm/s loading rate and a prescribed maximum displacement of 120 nm (Han et al. 2011). Alternatively, the force can be controlled with a prescribed loading rate (Volkert and Lilleodden 2006; Volkert et al. 2008; Shim et al. 2009). However, it is important to note that most nanoindentation systems use voice coils as the force actuator, thus the instrument inherently become a load-controlled test system.

The extraction of stress-strain behavior from the load-displacement curve requires estimation of the pillar dimensions. Due to the increased complexities in measuring pillar dimensions after test, engineering stress and strains are used instead of true stress (Han et al. 2011). Estimation of the effective cross-sectional area needs to be done depending on the type of deformation that is observed at failure. Considering the taper in pillar sidewalls, some researchers have used average of top and bottom diameter of the pillar or the mid height diameter for estimation of effective cross-sectional area (Volkert and Lilleodden 2006). For materials that exhibit highly localized deformation, pillar dimensions should be measured in the region where the deformation typically occurs (Shim et al. 2009). For pillars that are formed on a substrate material having different properties, combined effect of the compression of the micropillar and
the indentation of the pillar into the underlying bulk material can be accounted for by applying Sneddon’s formula (Sneddon 1965). Considering the substrate compliance, the normalized engineering stress $\sigma_n$ and strain $\varepsilon_n$ for the slightly tapered pillars were calculated by Han et al. as using loading portions of the force ($F$) versus compression depth ($\delta$) curves

$$\varepsilon_n = \frac{\delta}{H}$$  \hspace{1cm} (2.2)

$$\sigma_n = \left(\frac{4}{\pi D_1 D_2} + \frac{1 - \nu^2}{D_2 H}\right) F$$  \hspace{1cm} (2.3)

Here, $\nu$ is approximated Poisson’s ratio of substrate, $H$ is the pillar height, and $D_1$ and $D_2$ are the diameters of the top and bottom face of the pillar. The elastic modulus, $E$, is extracted from the elastic portion of the normalized stress versus strain curve via least-squares linear regression (Han et al. 2011).

Han et al. considered the first point where the load dropped below 95% of the force predicted by slope of the elastic portion. Denoting that load by $F_Y$ (Figure 2.5b), the strength is estimated as,

$$\sigma_Y = \frac{4F_Y}{\pi D_1^2}$$  \hspace{1cm} (2.4)

2.7.3 Estimation of elastic modulus

For monotonic loading, the elastic modulus, $E$, is estimated from the elastic portion of the normalized stress versus strain curve via least-squares linear regression (Han et al. 2011). Many researchers have reported that this method tends to under-estimate the actual elastic modulus of the material. For comparison purposes, use of parallel nanoindentation experiments on the surface of the bulk sample is reported in some literature. Shim et al. compared the load-displacement curves from nanoindentation on a FIB milled surface with that from the elastic Hertzian solution and reported some deviations from the elastic solution (Shim et al. 2009). Yang et al. reported obtaining a young’s modulus from nanoindentation that is 30% higher than the average modulus from Micro-compression tests (Yang et al. 2009a). Uchic et al. also observed lower than expected modulus from the loading portion of micro-compression tests,
which they attributed to the lack of proper contact between the sample and tip and resulting stress localization during initial loading of the samples (Uchic and Dimiduk 2005).

Simulation of micro-compression studies suggested that lack of perfect contact between indenter tip and pillar is more pronounced at lower compression depths which reduces the elastic modulus of the loading curve. Nonetheless, better contact is achieved with increasing compression depth, and the unloading curve is not affected by this experimental issue. Hence, many researchers have performed multi-cycle loading-unloading micro-compression tests and used unloading moduli for measurement of elastic modulus (Yilmaz et al. 2015; Frick et al. 2008; Camposilvan and Anglada 2016; Greer et al. 2005). Some researchers calculated elastic modulus from a linear fit to the initial 20% of unloading curve (Yilmaz et al. 2015; Choi et al. 2012). Yilmaz et al (2015) observed gradual increase in elastic modulus from the unloading slopes of successive loading cycles, for multi-cycle tests on dental enamel micropillars. They attributed this increase in modulus to improve contact between pillar and indenter at larger compression depths and reported the elastic modulus value from the penultimate cycle as the final elastic modulus.

### 2.7.4 Investigation of size effect

The size effect is understood as dependence of the structure strength on the structure size. In recent literature, micro-compression experiments on crystalline and amorphous metals have shown the presence of size effect on both strength and elastic modulus. The ease of varying the deformation length-scale and the availability of high resolution load–displacement data makes FIB-based micro-compression well suited for studying size effects in materials. For Ni-based single crystals, Uchic et al. reported a strong dependence of yield strength on inverse of the square root of pillar diameter by testing pillars ranging in the size range of 0.5 to 40 µm in diameter (Uchic et al. 2003; Uchic et al. 2004b). Volkert and Lilleodden showed strong increase in yield strength ($\sigma_Y$) of Au as pillar diameter ($d$) decreases from 8 µm to 180 nm gradually (Volkert and Lilleodden 2006). They proposed a best fit to the yield stress data (Figure 2.6) as

$$\sigma_Y = d^{-0.61}$$  \hspace{1cm} (2.5)
Ye et al. also mentioned the size dependent deformation behavior of micropillars and normalized the yield strength results using the elastic modulus (Ye et al. 2010). Yang et al. reported another form of size dependence which is observed in case of Young’s modulus. Their work showed a spurious dependence of micropillar’s Young’s modulus on its aspect ratio (Yang et al. 2009b). It is also observed that the deformation mechanism that leads to compressive failure is also dependent on the pillar size (Volkert et al. 2008).

For the prediction of size effect in concrete, Bazant derived the size effect law (SEL) for geometrically similar structures of different sizes with initial crack using the energy balance approach of linear elastic fracture mechanics (LEFM) (Bazant and Planas 1997). The equation has the basic form

\[
\sigma_{Nu} = \frac{B f'_t}{\sqrt{1 + \frac{D}{D_0}}}
\]

Where, \(f'_t\) is tensile strength, \(D\) is the characteristic dimension of the sample (diameter for cylinders) and \(B\) and \(D_0\) are constants. According to Bazant’s proposed size effect law, structures made of brittle or quasi-brittle material, such as cement pastes, exhibit significant size effect in both tension and compression (Bazant 2005). Moreover, in such materials, compression failure begins by the formation of axial splitting cracks.
For quasi-brittle compression failure of concrete columns, Bazant suggested an asymptotic size effect law where the size effect coefficient can be expressed by power law $D^{-2/5}$ for larger sizes of cross-section (Bažant and Xiang 1997). In this asymptotic size effect law, the size effect asymptotically disappears towards a limiting small size of cross section.

For concrete cylinders, researchers have reported effect of cylinder size on compressive strength of plain concrete cylinders (Kim et al. 1999; Yi et al. 2006)(Figure 2.7). Kim et al. derived the following size effect equation (Eq. 2.7)

$$f_0 = 0.8 f'_c + \frac{0.4 f'_c}{\sqrt{1 + (h - d)/50}}$$

(2.7)

for cylindrical concrete specimen subjected to uniaxial compression loads based on Bazant’s size effect law.

![Figure 2.7: Size effect in uniaxial compression of concrete cylinders (Yi et al. 2006).](image)

Some specific size-effect considerations apply to cement, and it is possible that size effects will be observed for individual phases of cement paste from micro-compression tests results. However, the microstructure and length scales present in cement paste (discussed in Section 2.2.1) provide one set of length scale limitations on the size of the cement micropillars. To the author’s knowledge, size effect studies at the length scale of individual phases of cement paste have not been performed.
2.8 Summary

Literature reviews were mainly focused on four major areas: motivation behind small-scale experiments on cement, various SEM investigation methods for cementitious materials, capabilities and limitation of conventional nanoindentation techniques, and potential use of FIB based micro-compression studies in investigating failure mechanisms.

Major findings from this section are –

- Heterogeneity of concrete exists in a variety of length scales. To understand failure properties of concrete and cement, experimental methods must respect the differential material behavior associated with each length scale.

- Principal binding phase of cement, C-S-H, is a granular composite with varying packing densities. Previous SEM and nanoindentation studies confirmed the presence of distinct low (LD), high density (HD) and ultra-high-density C-S-H phases.

- Water to cement ratio (w/c) influences the relative volume fractions of low (LD), high density (HD) and ultra-high-density C-S-H phases in cement paste. However, their elastic modulus values are independent of mixing proportions.

- Existing nanoindentation techniques are capable of measuring volume fractions and mechanical properties such as elastic modulus, hardness and creep parameters for C-S-H. Nanoindentation results can be coupled with EDS analysis for correlating mechanical responses to distinct chemical phases. However, compressive strength cannot be measured using conventional nanoindentation techniques.

- Recent approach of uniaxial compression testing of micropillar using customized nanoindentation system provides strength measurements at micrometer and sub micrometer scale.

- FIB milling method of preparing micropillar geometries is commonly used for homogenous materials. However, successful application of this method for heterogeneous and granular materials is reported in recent studies.

- Micro-compression experiment on FIB-milled micropillars is a novel yet promising approach to investigate small scale failure properties of cement paste.
Chapter 3
Materials and Methods

3.1 Introduction
This chapter describes the methodological approach of this research, specifically developed and modified for application to cementitious materials. First, an introduction to the cementitious materials studied in this research is provided with details of their preliminary surface preparation techniques. Then, the method of micropillar fabrication using focused ion beam (FIB) milling is described in detail. Next, methodology of uniaxial compression testing of FIB milled micropillars using nanoindentation system is described. After that, analysis of indentation results for assessing individual strength and elastic modulus results and post-test SEM investigation of deformed pillars for assessing deformation modes is discussed. Finally, specific details related to size effect analysis study is provided.

3.2 Materials
3.2.1 Cement
Sample materials were carefully chosen to be representative of the basic form of cement paste. Regular type I/II cement with a water/cement (w/c) ratio of 0.42 was selected as the primary test material. The typical composition of a type I/II cement is shown in Table 3.1. According to Powers’ hydration model, w/c of 0.42 is considered adequate for complete and unimpeded hydration. No admixtures or supplementary cementitious materials were added to this paste.

The cement paste was cured under sealed condition to achieve full hydration and development of strength for three years. Specimens were cut in disk shape (Figure 3.1) and again stored in airtight containers to avoid change of mechanical properties until they were used in the FIB sample preparation process. For studying the effect of sub-stochiometric conditions (w/c<0.42) on measured mechanical properties, two samples were prepared with less amount of water (w/c 0.35 and w/c 0.3). These samples were cast in small plastic cylindrical molds of 30 mm X 50 mm size and kept sealed in airtight condition for 1 year.
Table 3.1: Bogue Composition of a typical Type I/II Portland cement.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Short Form</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite or tricalcium silicate</td>
<td>C₃S</td>
<td>61</td>
</tr>
<tr>
<td>Belite or dicalcium silicate</td>
<td>C₂S</td>
<td>16</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>C₃A</td>
<td>10</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>C₄AF</td>
<td>8</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CSH₂</td>
<td>6</td>
</tr>
</tbody>
</table>

3.2.2 Belite

Belite is impure dicalcium silicate (C₂S) which along with alite (C₃S) is responsible for formation of calcium silicate hydrate (C-S-H) in cement paste. The overall reaction of alite and belite can be described chemically (approximately) as:

\[
\begin{align*}
\text{C}_3\text{S} + 5.3 \text{H} & \rightarrow \text{C}_{1.7}\text{-S-H}_4 + 1.3 \text{CH} \\
\text{C}_2\text{S} + 4.3 \text{H} & \rightarrow \text{C}_{1.7}\text{-S-H}_4 + 0.3 \text{CH}
\end{align*}
\]

Here, H is water (H₂O) and CH is calcium hydroxide. As seen from the two equations, the primary hydration product of belite is C-S-H with a small amount of CH. This small amount of CH makes belite suitable for standard Calcium to Silicon ratio calibration in Energy Dispersive Spectroscopy (EDS) analysis. Its use as a calibration standard is described in more detail.

---

1 In cement chemistry, C=CaO, S=SiO₂, A=Al₂O₃, S=SO₃, F=Fe₂O₃, H=H₂O. The atomic elements without oxides are expressed in a conventional manner.
detail in Section 3.4.2. However, due to the slow reaction rate and strength development nature of belite, it is not used as the primary silicate in cement production.

In this study, a sample paste containing belite and distilled water was prepared with a w/c ratio ~ 0.42 (Figure 3.2) for standard calibration in EDS analysis. The sample was cast in small plastic cylindrical molds of 30 mm X 50 mm size and was kept in sealed condition for 2 months before subsequent surface preparation.

![Disk shaped belite paste sample after removing from mold.](image)

3.3 Sample preparation

3.3.1 Surface preparation

Achieving flat sample surface is important to ensure good geometry of micropillars in milling. Also, use of the nanoindentation system for micro-compression requires a flat surface with negligible slope for making proper contact between the indenter tip and the pillar top. If the sample surface is not flat enough, the pillar top will not be flat either, increasing the possibility of partial contact and eccentric loading instead of pure compression.

In this work, cylindrical or disk specimens were cut into four pieces using diamond saw in low speed settings (Figure 3.3a). These pieces were further trimmed to very thin slices of approximately 15×10×2 mm using a Buehler Isomet low speed saw specially designed for preparing microscopy specimens (Figure 3.3b). To avoid any carbonation affected region, the thin slice sample was collected from ~3 mm depth from any exposed surface. Slope of the sample surfaces were minimized by making two parallel cuts without removing the sample from the holder, and using very sharp and aligned wet saw. after slicing, the samples were air dried for 2 weeks before surface was prepared by polishing to ensure gradual drying (removal
of excess moisture) of the sample. The air drying helps to prevent rapid drying, and associated excessive cracking of the sample during vacuum application at SEM.

Figure 3.3: a) Large scale saw, and b) Buehler Isomet low speed saw used for cutting cement sample.

Special attention is required in reducing the surface roughness of the saw cut specimens, since local waviness on sample surface could also be considered as a slope. Moreover, scanning electron microscopy, particularly, backscattered electron and X-ray imaging requires highly polished surface with minimum surface roughness for examination of microstructural details. To ensure smooth and flat surface with adequate surface roughness, thin slices were polished for 40 - 45 min using a 1200-grit SiC pad (Figure 3.4) and cleaned with acetone to remove residue. During polishing, consistent pressure was applied on the samples to have consistency in polished surface. Polished samples were observed carefully with naked eye for a mirrorlike reflective surface, and then with optical microscope to ensure suitability of the sample for application of scanning electron microscopy. The optical microscope micrograph in Figure 3.5 shows the appearance of polished cement samples.

Figure 3.4: Saw cut thin cement sample on polisher machine.
3.3.2 Coating

The flat polished sample was then mounted to a SEM stub using a double sided conductive carbon tape (Figure 3.6), and wrapped by aluminum foil leaving a small rectangular opening near the center for milling. The aluminum foil is usually used to increase conductivity of non-conductive samples like cement and reduce sample charging issues in SEM. The sample was then sputter coated with a thin layer of gold-palladium (~80 nanometers). This coating makes samples more conductive by drawing away the electrons that are bombarding the sample. Without the foil/metal coating, cementitious material can build up large number of electrons on the surface that causes serious charging artifacts. The coater used is a plasma chamber with low discharge capability that radiates a target made of heavy metal with argon atoms. The coating material consists of 60% gold and 40% palladium.

3.4 Fabrication of Micropillars

The desired sample geometry for performing micro-compression experiments is cylindrical pillars of specific size that can be compressed using the nanoindentation equipment. Due to its versatility and robustness in micron-sized sample machining, focused ion beam milling
technique was used for fabricating these micropillar samples. Circular cross section was chosen for the pillars instead of rectangular to avoid any stress concentration near the corners. In Figure 3.7, a series of seven (7) micropillars milled on a w/c = 0.42 cement paste sample is shown.

![Representative SEM image showing series of micropillars milled on a 0.42 w/c ratio cement sample surface. The scratch marks around allow easy identification of the location in optical microscope.](image)

3.4.1 Introduction to the instrument

Micropillar geometries for micro-compression tests were milled using a dual beam focused ion beam system (FIB/SEM) FEI Quanta 3D FEG (Figure 3.8a). It produces focused gallium ion beams with current ranging from fractions of pico amperes to 100 nano amperes for energies between 1 and 50 keV. A finely focused beam of gallium ions (Ga+) can hit the sample surface and sputter a very small amount of material. Thus, the highly localized ion beams allow machining of micrometers or even nanometers sized structures on to surface of the bulk material (Figure 3.8b). The choice of beam current depends on the sample material and the type of features need to be milled. While high beam currents can quickly remove large amounts of material by sputtering, they tend to cause significant gallium implantation on the surface.
The main components of a typical FIB system are a focusing column containing a charged gallium ion source and lenses, a detector, gas injection needles and a sample stage (Figure 3.9). A very useful feature of the FIB system is its capability of imaging simultaneously during the milling process. When the ion beam rasters on the sample surface, it produces sputtered secondary ions as well as secondary electrons which are separately collected by two detectors to form ion image and secondary electron image respectively. In addition to these components, the FEI 3G Quanta system is also equipped with a backscatter electron (BSE) detector for capturing compositional contrast between the constituent phases of a heterogenous material and an energy dispersive spectroscopy (EDS) detector for performing quantitative chemical compositional analysis.
3.4.2 Determining location of micropillar milling

The flat, polished and coated cement samples were analyzed by scanning electron microscope (SEM) to identify potential CSH rich locations suitable for micropillar milling. The analysis was performed following a two-step methodology, using two well established techniques of electron microscopy, backscatter electron imaging (BSE) and energy dispersive spectroscopy (EDS). Application of these two techniques allows very precise identification of CSH regions, and ensures the best chance that each micropillar is fabricated within a single material phase. Each potential location was analyzed in BSE mode, as well as, in EDS. The former facilitated in avoiding clinkers and portlandite areas (areas with bright appearance from atomic number contrast) and preliminary selection of C-S-H regions (grey), whereas, the latter aided in confirming the presence of C-S-H by providing compositional information (Ca/Si ratio).
BSE Imaging

As described in Chapter 2, BSE image analysis of polished cement sections is a very effective and widely adopted method to study and visually identify different microstructural phases. Backscattered electrons are electrons from the incident beam which are reflected or scattered back from the specimen by elastic scattering interactions with specimen atoms. They are detected from greater depths compared to secondary electrons, but lower depths compared to X-rays (Figure 3.10). (Scrivener 2004)

![Figure 3.10: Signal generation depth for different type of SEM techniques. Secondary electrons (SE) are detected from close to the surface, backscatter electrons (BSE) from a somewhat greater depth and characteristic X-rays are generated throughout the interaction (Scrivener 2004).](image)

In this study, the samples were first placed inside the SEM at a 0-degree tilt position to be perpendicular to the BSE detector. Then, the sample surface was carefully analyzed in BSE mode to identify individual microscopically distinguishable phases. As seen in Figure 3.11, the four primary distinguishable phases are unhydrated clinkers, portlandite or Ca(OH)$_2$, and two types of CSH. The brightest white grains are the unhydrated clinker grains, the whitish-grey areas are portlandite, and the light and dark grey areas are the C-S-H rich regions. The distinct contrast shown by the low density (LD) and high density (HD) C-S-H regions can be clearly identified in this mode of imaging. The HD C-S-H was characterized by its darker grey color as mentioned in many literature sources (Scrivener 2004). In the cement pastes used in this study, it was mostly observed as 2~3 µm thick rims around the unreacted clinker grains. In some cases, formation of HD C-S-H was also noticed in solid chunky grain like areas likely from full hydration of an entire clinker grain. These regions were very homogenous with no
visible porosity. The LD C-S-H, on the other hand was characterized by its lighter gray color, less homogenous morphology and visible submicron range porosity.

For selection of each micropillar location, a 350 µm x 350 µm area was selected as the field of view in SEM/BSE mode, and suitable C-S-H rich areas were picked by using their characteristic color. The darker grey areas in thicker rims around clinker grains were chosen for making HD C-S-H micropillars (marked by rectangles in Figure 3.11). For better interpretation, a higher magnification image is shown in Figure 3.12a where the homogenous and dense area of HD C-S-H around the clinker grain is marked. In Figure 3.12b, two such micropillars are shown, which were fabricated inside similar dark grey rims, close to clinker grains. However, as seen in Figure 3.11a, the total area represented by darker grey, is very small compared to the overall area of the micrograph. Hence, only a few micropillars in each set of 10 could be fabricated in HD C-S-H rich regions, and, rest were fabricated on the lighter grey LD C-S-H regions, sufficiently apart from the clinker grains. Careful attention was paid to maintain a minimum distance of 50 µm between the selected location of two subsequent micropillars to ensure fabrication and micro-compression of one pillar does not affect the result of the next one.
Figure 3.11: Typical BSE image of a) w/c = 0.42 and b) w/c = 0.3 cement pastes with the individual microscopic phases distinguished by contrast.
Figure 3.12: a) BSE image of a w/c = 0.35 cement paste showing formation of HD CSH rim around partially reacted clinker b) two micropillars fabricated in dark grey areas close to clinker grains.

**EDS spectra**

The preliminary locations selected through BSE imaging were further analyzed by using Energy dispersive spectroscopy (EDS) spot analysis to ensure their composition matches with composition of CSH reported in literature (Richardson and Groves 1993b; Richardson and Groves 1993a; Richardson 2004). EDS compositional analysis was performed by measuring the energy and intensity distribution of the X-ray signal generated as the electron beam hits on the selected location of the sample surface.

The microvolume from which X-rays are generated (usually called the interaction volume) should be comparable with the volume subsequently occupied by the micropillars for the compositional information to be truly representative of the micropillar’s composition. Since
the size of the interaction volume depends on the parameters chosen for performing EDS analysis, these parameters should be calibrated beforehand for the material being analyzed. The chosen acceleration voltage should be high enough to stimulate the emission of characteristic X-rays from all the major/minor elements of interest in the specimen. A minimum voltage of 12 KeV is suggested for EDS on cement to stimulate the emission of iron which is a minor element always present in C-S-H. Also, the beam current needs to be optimized to avoid any damage to the material which is highly beam sensitive.

Monte Carlo simulation of electron trajectory was performed in Casino (Drouin et al. 2007) using a range of accelerating voltage and beam currents prior to actual EDS analyses. The simulation result (Figure 3.13) showed that for an accelerating voltage of 15 KeV and a beam current of 3.4 nA, the electron trajectories reach a maximum depth and diameter of around 2µm and of 2.5 µm respectively. The interaction volume of X-ray generation, however, is expected to be slightly less than this trajectory volume as the most deeply penetrating electrons usually do not produce X-rays. In this study, the micropillar height and diameter are chosen to be less than or equal to 2 µm and 4 µm respectively. Thus, microvolumes probed by EDS at given operating conditions are directly comparable to volume of individual micropillars.

Figure 3.13: The interaction volume probed by SEM/EDS is approximated by Monte Carlo simulation as the zone demarcated by the electron trajectories (blue lines) in the specimen.
EDS analysis can be used for either qualitative identification of elements present, or, depending upon the availability of standard material, quantitative analysis for determining detail composition. In this research, a belite paste (Ca$_2$SiO$_4$) was used as standard material for calibration of Ca/Si ratio. As mentioned earlier, the primary product of belite hydration is C-S-H (discussed in Section 3.2.2). Thus, the EDS spectra acquired from belite paste can be considered as a representative spectrum of C-S-H, and can be used as a guideline (standard) while selecting potential locations for fabricating micropillars. Multiple EDS spectrum were collected from the flat polished surface of the belite sample, And Ca/Si ratio were calculated using the area under each peak which yielded a ratio of $\sim$1.7 in each location.

Once the parameters were finalized and the standard calibration was done, EDS analysis can be consistently used for quantitative compositional analysis. In this study, Compositional analysis of the area was done by using Oxford instruments Aztec 3.0 EDS analysis software. Areas primarily composed of Calcium, Silicon, and Oxygen with a Ca/Si ratio of 1.2 $\sim$ 2.3 were selected as potential milling locations (Richardson and Groves 1993b). EDS was used for finalizing the locations preliminarily selected by BSE imaging. An example of this process is shown in Figure 3.14 and Figure 3.15, a light grey area (selected in rectangle in Figure 3.14) is analyzed by EDS and spectrum is collected (Figure 3.15). The area was primarily composed of calcium and silicon with some trace elements of aluminium, iron, potassium, magnesium and Sulphur (Oxyzen was present but not included in quantitative analysis). The Ca/Si ratio was calculated from the area under peak for K-lines of calcium and silicon (Table 3.2).

![Figure 3.14: Location of EDS analysis selected in grey region for spectrum shown below in Figure 3.15.](image)
Figure 3.15: A representative EDS spectrum collected on a C-S-H location (Ca/Si = 1.87).

Table 3.2: Calculation of Ca/Si ratio from area under the peak.

<table>
<thead>
<tr>
<th>Spectrum 12</th>
<th>Line Type</th>
<th>Quant</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>K series</td>
<td>Yes</td>
<td>13610.1</td>
</tr>
<tr>
<td>Al</td>
<td>K series</td>
<td>Yes</td>
<td>16656.1</td>
</tr>
<tr>
<td>Al</td>
<td>L series</td>
<td>No</td>
<td>4133.4</td>
</tr>
<tr>
<td>Si</td>
<td>K series</td>
<td>Yes</td>
<td>101996.8</td>
</tr>
<tr>
<td>Si</td>
<td>L series</td>
<td>No</td>
<td>-4279</td>
</tr>
<tr>
<td>Ca</td>
<td>K series</td>
<td>Yes</td>
<td>190427.5</td>
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<tr>
<td>Ca</td>
<td>L series</td>
<td>No</td>
<td>9909.6</td>
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<tr>
<td>S</td>
<td>K series</td>
<td>Yes</td>
<td>6135.2</td>
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<tr>
<td>S</td>
<td>L series</td>
<td>No</td>
<td>2480.8</td>
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<tr>
<td>K</td>
<td>K series</td>
<td>Yes</td>
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<tr>
<td>K</td>
<td>L series</td>
<td>No</td>
<td>11378.5</td>
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<tr>
<td>Fe</td>
<td>K series</td>
<td>Yes</td>
<td>1727.6</td>
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<td>Fe</td>
<td>L series</td>
<td>No</td>
<td>783.2</td>
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<tr>
<td>Na</td>
<td>K series</td>
<td>Yes</td>
<td>984.1</td>
</tr>
</tbody>
</table>

Ca/Si = 1.866995

3.4.3 Selection of size

In this study, the goal is to characterize the material failure properties of specific phases within cement paste especially the various C-S-H aggregate phases. Thus, the length scales of these material phases present in cement paste provide one set of length scale limitations. Micropillar
samples should be much larger than the scale of a C-S-H globule (Level 0) but much smaller than the length scale where cement paste can be considered homogeneous (Level II). Thus, the size of the micropillars must be chosen based to match with characteristic size of material phases at level I, such that one single micropillar is fabricated within a single phase of the material, and does not represent a heterogenous material response. Determination of characteristic size at Level I is critical since the microstructure of cement paste shows significant variation from sample to sample, or even within different locations of the same sample. However, nanoindentation on cement studies use a characteristic length of ~2 µm based on SEM images available in literature (Vandamme 2008). Also, Sample sizes must also be tailored to the force and displacement maximums and minimums available in the nanoindenter.

Carefully considering all the conditions, cylindrical micropillars with top diameter in the range of 2-2.5 µm and height in the range of 4-5 µm was chosen as the standard sample size for studying the compressive failure behavior at Level I using the w/c 0.42 sample. Micropillars of this standard size were also fabricated on cement pastes with a w/c ratio of 0.35 and 0.3, and on hydrated belite paste for studying effect of composition. In addition, to study the effect of sample size, micropillars with three decreasing diameters and heights were fabricated on the w/c 0.42 sample. Details of all the sample sizes and associated materials are provided in Table 3.3. The aspect ratio \( H/((D_1 + D_2)/2) \) were maintained to be ~ 2 to avoid possibility of buckling during micro-compression (Zhang et al. 2006). Pillars made by annular milling methods (explained in next Section) always have a tapering in the side walls which is quantified by the taper angle \( \alpha \). Representative SEM image of a pillars explaining the terms top \( D_1 \) and bottom diameter \( D_2 \) and the height \( H \) of micropillar is shown in Figure 3.16.
Table 3.3: Details of tested micropillar samples and materials.

<table>
<thead>
<tr>
<th>Nominal Top Diameter $(D_1)$ (µm)</th>
<th>Nominal Height $(H)$ (µm)</th>
<th>w/c ratio</th>
<th>No. of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2.5</td>
<td>4-5</td>
<td>0.42</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.35</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.3</td>
<td>19</td>
</tr>
<tr>
<td>1.5</td>
<td>~3</td>
<td>0.42</td>
<td>9</td>
</tr>
<tr>
<td>1</td>
<td>~2</td>
<td>0.42</td>
<td>10</td>
</tr>
<tr>
<td>0.5</td>
<td>~1</td>
<td>0.42</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 3.16: Representative SEM image of a micropillar explaining the dimension terms.

3.4.4 Annular milling method

After selection of an area of interest through BSE imaging, and checking the composition of the area through EDS analysis, FIB milling process of micro-pillar was started. For BSE and EDS analysis, the stage and the cement sample needed to be perfectly horizontal. Whereas, the surface of the sample needed to be tilted by an angle of 52 degree to orient the surface normal to the FIB ion column for FIB milling. Once the sample is tilted, the BSE mode cannot be used anymore, and the previously chosen area for milling needs to be very carefully identified again using secondary electron (SE) and FIB imaging.
Selection of appropriate parameters for machining micropillars on a highly heterogenous and porous material like cement paste required a significant amount of trial and errors with different parameter sets and milling of more than 40 trial sample pillars. It is important to note that, the FIB system settings are calibrated on silicon, and the milling depths cannot be directly specified, rather the system needs to be frequent monitored to avoid over-milling. Hence, approximate relationships between milling time and depth of milling for cement sample was estimated by trials. Finally, parameters were optimized to minimize the side wall taper, milling time and FIB induced damage (Ga⁺ implantation) after investigating a range of beam currents, dwelling time, energy, and milling depth settings.

In annular milling method, a series of concentric annular rings with decreasing diameter were milled using a 30 keV focused Ga-ion beam with beam current gradually decreasing in 7nA to 100 pA range. The first few steps were performed with relatively high beam currents, since the goal is to quickly remove as much material from the surrounding area as possible. As the ring gets closer to the actual pillar geometry, smaller currents were chosen to minimize tapering of the pillar walls, Ga implantation within the pillar surface, and for fine-tuning the specimen into the desired cylindrical micropillar shape. The sequential annular milling method is shown in Figure 3.17. This stepwise sequence of removing materials created a 25-μm diameter trench around the micropillar, which (Figure 3.17e) provides several advantages during and after micro-compression tests. Firstly, it helps in identification of the pillars with the optical microscope of the nanoindentation system. During tests, it also ensures that the indenter tip is in contact with only pillar top and not surrounding material. Moreover, the trench increases the visibility of the pillar sidewalls in SEM and hence facilitates correct measurement of pillar dimensions and inspection of pillar geometry before and after failure.

The milling parameters used in this study, for milling pillars of different diameters, are listed in Table 3.4. The use of these parameters ensured less Ga implantation (checked by EDS) and tapering of walls, while allowing for rapid fabrication (~1.5 hour per pillar). The entire milling process was closely monitored by acquiring secondary electron images and measuring pillar diameter and height at frequent intervals. Modern FIB systems are equipped with built-in dimension measuring toolbars which can precisely measure final diameter and height of the micropillar. The process is demonstrated in Figure 3.18, where top and bottom diameters and
height of a micropillar were measured by using the dimension measuring feature in FIB. After FIB milling, the cement samples were stored in air tight SEM sample storage containers and tested within (7 -10) days.

Figure 3.17: Annular milling of micropillar shown in five steps: from milling of outer ring to fabrication of final pillar geometry.
Table 3.4: List of parameters used in FIB milling of cement micropillars.

<table>
<thead>
<tr>
<th>Nominal Top Diameter (μm)</th>
<th>Step</th>
<th>Outer Diameter (μm)</th>
<th>Inner Diameter (μm)</th>
<th>Depth (μm)</th>
<th>Beam Current (nA)</th>
<th>Current Setting</th>
<th>Dwell Time (nS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2.5</td>
<td>1.</td>
<td>25</td>
<td>14</td>
<td>2</td>
<td>7</td>
<td>Si V Hi</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>14</td>
<td>9</td>
<td>2.5</td>
<td>1</td>
<td>Si V Hi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>9</td>
<td>5</td>
<td>2</td>
<td>0.5</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>5</td>
<td>2.4</td>
<td>~1.8</td>
<td>0.1</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.</td>
<td>25</td>
<td>14</td>
<td>2</td>
<td>7</td>
<td>Si V Hi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>14</td>
<td>9</td>
<td>2</td>
<td>1</td>
<td>Si V Hi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>9</td>
<td>5</td>
<td>1</td>
<td>0.5</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>5</td>
<td>1.8</td>
<td>~1.5</td>
<td>0.1</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>1.</td>
<td>25</td>
<td>14</td>
<td>0.5</td>
<td>7</td>
<td>Si V Hi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.</td>
<td>14</td>
<td>9</td>
<td>0.8</td>
<td>1</td>
<td>Si V Hi</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.</td>
<td>9</td>
<td>5</td>
<td>0.8</td>
<td>0.5</td>
<td>Si</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.</td>
<td>5</td>
<td>0.6</td>
<td>~0.8</td>
<td>0.1</td>
<td>Si</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.18: Representative SEM image of FIB-milled micropillars showing dimension measured from high magnification image.

3.5 Micro-Compression Testing

3.5.1 Equipment and calibration

the FIB-milled micropillar samples are tested in uniaxial compression using CSM instruments nanoindentation system Ultra-Nano Hardness tester (UNHT). The instrument has a load range of 0.025 – 100 mN, a load resolution of 0.001 μN, a maximum indentation depth of 100 μm,
and a depth resolution of 0.001 nm. CSM’s proprietary data acquisition software and module are used to monitor sensors for the stage position, load control, feedback loops, and piezo signals over time. An applied voltage is converted into a tip load for acquiring force-displacement curves.

A schematic of the construction of the nanoindenter is shown in Figure 3.19a. In addition to the indenter tip (I), the indenter has a reference tip (R) that is used for surface detection. Both the indenter and the reference tips are controlled by piezo. The test set up also includes an optical microscope for visual identifications before and after the test and a sample stage (Figure 3.19b). A depth adjustment process is done before actual tests for a preliminary idea about the position of the sample surface with respect to the initial indenter position. During testing, the reference tip comes down on the sample surface at a certain offset distance from the pillar and surrounding crater. Once the reference makes contact with the sample, the indenter moves down to reach the pillar top.

Nanoindentation systems are designed for performing depth sensing indentation experiments at low loads. In order to perform micro-compression tests, the sharp indenter tip is replaced by a relatively flat tip. Use of the flat tip enables the indentation system to act as a uniaxial compression platen. The tip used in this research is a sphericoconical tip with radius of 10 µm and apex angle of 90 degree (Figure 3.19c). Due to the large radius of the inscribed sphere, the contact area of the tip is very blunt. Thus, practically the tip acts as a flat punch. Also, it does not require perfectly parallel positioning with respect to the pillar top which is an added advantage compared to the conventional flat punch tips.
It is important to note that acquisition of reliable and reproducible results from the micro-compression test is largely dependent on the instrument-tip-microscope combination calibration. To ensure concentric landing of the indenter on pillar top, the distance between optical microscope and indenter is calibrated prior to each test. Microscope-indenter distances are initially calibrated by making multiple, visually identifiable big indents on copper or epoxy sample. The distance calibration procedure is then repeated several times on polished and coated cement test samples to ensure required precision. This process is also necessary for removing residual debris of the previous broken pillar and cleaning of tip.

3.5.2 Loading protocol

A specific loading protocol is established for studying uniaxial compressive failure of the micropillars using the nanoindentation system. A schematic of the uniaxial compression test using a sphero-conical indenter is shown in Figure 3.20. The loading parameters and protocols for successful micro-compression test on cementitious material are developed after significant
trial and errors. Broadly, two types of loadings are applied in the experiments – monotonic single cycle and multiple cycle load profiles. In both cases, an initial depth offset procedure is performed on the sample surfaces before actual test. This process is required for primary referencing of the surface level with respect to the indenter tip. The depth offset process is performed sufficiently away (nearly 500 µm) from the line of pillars to prevent the pillar structures from any damage before actual test.

Figure 3.20: Schematic of uniaxial compression on the micropillar.

**Single cycle**
In single cycle micro-compression test, the applied load on the pillar is continuously increased at a constant loading rate (Figure 3.21a). Upon reaching the compressive strength of pillar material, it starts to collapse. Since, in the nanoindentation platform, the experiment process cannot be simultaneously monitored through microscopy, collapse of the micropillar structure needs to be identified from the sudden change in the load-displacement behavior captured by the data acquisition system of the software. The representative load-displacement plot of a micro-compression test is displayed in Figure 3.21b. In this plot, continuous increase of load and displacement is observed up to a point of maximum load (load = 4604 µN, displacement = 457 nm). In the next collected data point (load = 3491 µN, displacement = 1950 nm), a sudden significant increase of displacement and decrease of load is observed within a very short period. The displacement jump, also called the “pop-in”, is indicative of the collapse of the micropillar structure being tested. Moreover, the sudden load drop is caused by loss of
contact between the indenter tip and the pillar top. This phenomenon is used to mark the stopping point of each test. The unloading process should be started as soon as the signs of collapse are noticed to avoid further load application to the sample. Preserving the post-failure geometry of the micropillar helps in subsequent SEM investigation to investigate the deformation mechanism causing failure. The parameters used in the single cycle tests is listed in Table 3.5.

Table 3.5: Parameter list for single cycle tests.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Contact Load</td>
<td>9 µN</td>
</tr>
<tr>
<td>Loading Rate</td>
<td>800 µN/min</td>
</tr>
<tr>
<td>Unloading Rate</td>
<td>800 µN/min</td>
</tr>
<tr>
<td>Approach Speed</td>
<td>5000 nm/min</td>
</tr>
<tr>
<td>Approach Distance</td>
<td>5000 nm</td>
</tr>
<tr>
<td>Maximum Load</td>
<td>10000 µN</td>
</tr>
</tbody>
</table>

Single cycle tests are very useful for measuring the maximum load capacity and calculating the compressive strength of the pillar material. However, this loading protocol is not well suited for measuring the stiffness properties. The initial portion of the load-displacement diagram is often bent upwards, suggesting lack of perfect contact between micropillar top and indenter tip. This phenomenon is always very pronounced at lower strains and gets better with increasing strain level. Thus, measuring the Young’s modulus from the stress-strain behavior of the loading portion always results in underestimation of actual modulus. Therefore, an alternate experimental protocol was needed for more accurate estimation of stiffness properties where the unloading response before plastic deformation can be observed.
Multi cycle

Simulation of micro-compression experiments (Zhang et al. 2006; Schwaiger et al. 2012) reported that improper contact between micro-pillar and indenter-tip only affects the initial loading portion; with larger displacements, better contact is achieved. Thus, the unloading behavior is less affected by misalignment or improper contact and suitable for determining stiffness response. For the measurement of the pillar materials’ stiffness, many micro-compression studies (Choi et al. 2012; Yilmaz et al. 2015) suggested to use multiple cycles of loading and unloading with increasing maximum load at each cycle. In this way, the unloading slopes before failure can be used to calculate the Young’s modulus.
In the multi-cycle test method, instead of a continuously increasing loading phase, multiple trapezoidal loading segments are applied with linearly incrementing maximum load (Figure 3.22). Each trapezoid consists of a loading phase followed by a hold time at the maximum load and then an unloading phase. The maximum load of the first trapezoidal segment is chosen to be at tentatively 25 percent of the ultimate maximum load carried by the pillar. Also, instead of unloading the pillars completely to zero load, partial unloading is performed, by unloading to a certain minimum load. This unloading minimum load is chosen to be around 10 percent of the ultimate maximum load carried by the pillar, and maintained consistently in each cycle. The partial unloading helps to ensure proper contact between pillar top and the indenter tip is maintained throughout the test, once established in the first cycle. The multi-cycle test protocol is designed such that one or more trapezoidal cycles of loading-hold-unloading is completed before the material starts to deform nonlinearly.

In performing the multi-cycle tests, duration of hold time after reaching the maximum load should be carefully selected to avoid any effect of creep on the measurement of elastic properties from the unloading segment. For measurement of elastic properties unbiased by viscous effect, a holding period of 5 seconds was suggested in case of nanoindentation on cement (Vandamme 2008). For our current study, a constant hold time of 10 seconds is selected and used consistently in all the multi-cycle tests to ensure that the holding time is long enough for unloading slopes to be representative of the elastic properties. The parameters used in the multi cycle tests is listed in Table 3.6.

Table 3.6: Parameter List for Multi cycle tests on 0.42 w/c ratio cement.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1.5</th>
<th>1</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Top Diameter (µm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Peak Load in 1st cycle(µN)</td>
<td>500</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>Unload</td>
<td>200 µN</td>
<td>200</td>
<td>50</td>
</tr>
<tr>
<td>Linear Loading increment (µN/Cycle)</td>
<td>500</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>Loading Rate (µN/min)</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unloading Rate (µN/min)</td>
<td>800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hold time (seconds)</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference Contact Load (µN)</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
In summary, the monotonic single-cycle tests provide loading stiffness measurements, whereas, multi-cycle tests provide both loading and unloading stiffness measurements in the elastic regime. However, no significant change in the load-displacement behaviours was observed between these two methods (appendix A).

### 3.5.3 Use of micrograph

The nanoindentation system is equipped with an optical microscope with three different magnification objective lenses - 5X, 20X and 100X. Identification of the micropillar locations on the cement sample surface and visual inspection of the pillars before and after micro-compression was performed using optical microscope micrographs. Since the cement samples had a very large surface area (1 cm x 0.5 cm) compared to the area (2-µm diameter) of individual pillars made on them, significant amount of time would have been required on each sample to search through the surface and identify the pillar locations using the optical microscope. Hence, rectangular scratch marks (1mm x 1mm) were drawn on each sample surface using sharp tweezers prior to milling of the micropillars which could be easily identified with the naked eye, and series of pillars would be visible with the lowest (5X) magnification objective lens (Figure 3.23a). Once the general location of the pillars was known, the 25-µm trenches around the pillars were clearly visible with the next higher magnification lens (20X). Micrographs of individual pillars were collected with the highest magnification lens (100X) before and after micro-compression was applied. These
micrographs were carefully compared after each test to ensure that the micropillar was deformed and no surrounding material was in contact with the indenter tip.

Figure 3.23b shows representative optical microscope micrograph of a micropillar collected before test. The top of the FIB-milled pillar, as can be observed in Figure 3.23b, is a small circle in the center of concentric circular trenches of slightly darker color. The area outside the trenches has lighter green color from the gold palladium coating applied for increasing conductivity in SEM. The coatings in the trench area were removed as part of the milling process.

For applying micro-compression, the indenter-tip was positioned concentrically on the pillar’s top using the optical microscope, and with a positioning accuracy of ~ 1 µm. After micro-compression, the post-test micrograph of the same pillar location (Figure 3.23c) was captured and carefully compared with before-test micrograph. As can be seen, the small circle in center is not present in Figure 3.23c which indicates that the micro-pillar is totally crushed during the test. Also, no other difference is noticed between these two micrographs (Figure 3.23b and Figure 3.23c) from careful observation, which confirms that the indenter-tip did not touch any surrounding area during the test. It is important to note that, micro-pillars exhibit different deformed shapes at failure which cannot be observed in optical microscope. Hence, detail investigation of theses deformed shapes was performed using SEM imaging discussed in Section 3.6.
Figure 3.23: Optical microscope micrographs used for visual inspection of micropillars (a) Series of seven micropillars on polished and coated cement surface (b) higher magnification image showing top view of a 2-µm diameter micropillar inside a 25-µm diameter trench.

3.6 Post-test Imaging

The objective of post-test imaging is threefold, to ensure failure of the tested micropillars, to make sure load is applied only on the micropillar and indenter did not touch surrounding area of the pillar, and to identify the primary deformation mechanism causing failure. For visual evaluation of failure modes, high resolution imaging was performed on the micro-pillars after each micro-compression experiments using a Field Emission Scanning Electron Microscope – FEI Verios 460L (Figure 3.24). This particular SEM was chosen for its ability to significantly reduce chromatic abrations at high resolution and low energy imaging. It is equipped with a low energy Everhart-Thornley detector (ETD) for use in low resolution mode and a through-the-lens (TLD) detector for use in high resolution mode. The surrounding area of the pillars were imaged in low magnification using the low energy detector, whereas the micropillars were imaged at higher magnification, and in very high resolution for identifying details of deformed micropillar geometry, including position, size, and orientation of cracks. Secondary electron mode of imaging was chosen which captures electrons emitted from or very close to the surface of the materials, providing detail visual information about the sample topography.
List of the parameters used for imaging gold-palladium coated cement samples in Verios 460L is provided in Table 3.7.

![Field Emission Scanning Electron Microscope (SEM)](image)

Figure 3.24: Field Emission Scanning Electron Microscope (SEM) used for performing post-test image analysis.

Table 3.7: Optimized parameters for post-test imaging using Verios SEM.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnification</td>
<td>1500X-65000X</td>
</tr>
<tr>
<td>Accelerating voltage</td>
<td>2.00 kV</td>
</tr>
<tr>
<td>Beam current</td>
<td>13 pA</td>
</tr>
<tr>
<td>Working distance</td>
<td>6.0 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>ETD, TLD</td>
</tr>
<tr>
<td>Mode</td>
<td>Secondary electron (SE)</td>
</tr>
<tr>
<td>Tilt</td>
<td>45 degree</td>
</tr>
</tbody>
</table>

3.7 Estimation of Strength

During each test, applied load and displacement measurements were collected at 0.1 second interval, and recorded by the indentation software. A representative image of load and displacement plotted against time is shown in Figure 3.25a for a single-cycle test. As can be seen in this plot, the applied load increases from zero to 1619 µN, reaches the maximum load capacity of the pillar, and suddenly drops to 1103 µN. However, in less than a second the load again reaches back to 1619 µN. This load drop phenomenon can be attributed to the sudden
loss of contact between the indenter and the pillar top during the catastrophic collapse of the pillar. The displacement data points are also plotted against time in the same Figure 3.25a to show how the displacement increases abruptly from 180 nm to 674 nm during this load drop phenomenon, which supports the hypothesis of losing contact with the indenter.

The load vs displacement plots were also recorded in the software which helps to clearly identify the failure load of the pillar and the large displacement jump associated with it. A representative plot for single cycle method is shown in Figure 3.25b. These plots were used to estimate the compressive strength of the pillar material by using the following equation

\[ f_c = \frac{4F_Y}{\pi D_1^2} \]

(3.1)

Here, \( F_Y \) is the maximum load carried by the pillar, which is taken as the maximum load recorded before occurrence of load drop and displacement jump (Figure 3.25b), \( D_1 \) is the diameter at top of the pillar where the pillar has minimum cross-sectional area and failure is most likely to occur, and \( f_c \) is the compressive strength.
For multi-cycle tests, compressive strength was calculated from the last cycle using similar failure load ($F_y$). As can be seen from Figure 3.26, successive cycles of gradually increasing maximum load was applied, and maximum load reached in forth cycle before occurrence of displacement jump is taken as the maximum load carried by the pillar.
3.8 Estimation of Elastic Modulus

The stress-strain curves are evaluated from load-displacement data recorded by the nanoindentation software using the formula

\[ \sigma_n = \left( \frac{4}{\pi D_1 D_2} + \frac{1 - \nu^2}{D_2 H} \right) F \]  \hspace{1cm} (3.2)

\[ \epsilon_n = \frac{\delta}{H} \]  \hspace{1cm} (3.3)

Here, \( \epsilon_n \) is the engineering strain, \( \delta \) is the shortening of the micropillar measured as displacement, \( H \) is the average pillar height, \( D_1 \) and \( D_2 \) are the top and bottom diameter, and \( F \) is the applied load and \( \nu \) is the Poisson’s ratio. Also, \( \sigma_n \) is the normalized engineering stress calculated using the formula proposed by Han et al. (Han et al. 2011). This formula considers the combined effect of the compression of the micro-pillar and the indentation of the micro-pillar into the underlying bulk by using Sneddon’s (1965) concept of a perfectly rigid cylindrical punch pressed into an elastic half-space (Sneddon 1965). Thus, compliance of the underlying material was accounted for in the normalized stress calculation for measuring the corrected elastic modulus of the material.

For single-cycle tests, elastic modulus \( (E) \) was determined from the loading part of the stress-strain plot using a linear fit to the initial straight portion using the least squares linear regression formula.
A representative stress-strain diagram from a single-cycle test (Figure 3.27a) shows presence of three distinct zones - an initial curved portion bent upward, followed by a straight line (linear) portion, and finally a non-linear portion starting from ~6 percent strain. As can be seen from Figure 3.27a, the initial part of the stress-strain diagram (upto 0.01 strain) is concave upwards which indicate the initial misalignment/lack of proper contact between the micropillar and indenter.

![Stress-strain diagram](image)

Figure 3.27: a) Stress-strain behavior up to failure b) Measurement of loading elastic modulus from linear portion of stress-strain plot.

Hence, this portion was not considered, and linear fitting for elastic modulus estimation was done in the 0.01-0.05 strain range region. Yet, this method consistently provided
underestimation of the elastic modulus as compared to the literature reported values from nanoindentation experiments.

It is important to note that, nanoindentation studies use unloading slopes to calculate the modulus values, whereas, loading slopes were used in the single-cycle micro-compression tests of this study. Hence, the multi-cycle test methodology was introduced which provided means to estimate the elastic modulus from the unloading data in a fully elastic regime.

For multi-cycle tests, elastic modulus was calculated for each of the completed cycles of the stress-strain diagram. A representative stress-strain diagram is shown in Figure 3.28, where the micro-pillar has completed three loading-unloading cycles before finally collapsing in the 4th cycle. Unloading elastic modulus values were determined from a linear fit to the unloading curve. Estimated elastic modulus values from these three cycles (Table 3.8), shows significant increase in successive cycles. Such increase in modulus indicates possibility of improved contact between the indenter tip and the pillar top at larger displacements. Hence, the unloading modulus of the last cycle before collapse was chosen as the final elastic modulus.

![Figure 3.28: Representative stress-strain behavior at multi-cycle test.](image)
Table 3.8: Loading and unloading moduli measured for stress-strain plot in Figure 3.28.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$E_{\text{Loading}}$ (GPa)</th>
<th>$E_{\text{Unloading}}$ (GPa)</th>
</tr>
</thead>
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3.9 Size Effect Analysis

Drastic variation in the micropillar sizes was not feasible within length scale of Level I, that is the length scale of C-S-H aggregate. The microstructure and length scales present in cement paste (discussed in Section 2.2.1) provide one set of length scale limitations on the size of the cement micropillars. For assessing compressive behavior of C-S-H at level I, pillars should be much larger than the scale of a C-S-H globule (Level 0) but much smaller than the length scale where cement paste can be considered homogeneous (Level II). Size of agglomerations of C-S-H globules in the range of ~30 nm to few dozens of nanometers has been proposed in literature [(Jennings et al. 2007)(Vandamme 2008)]. Therefore, the minimum micropillar diameter was chosen (500 nm) such that it remains significantly larger than the length scale of Level 0. Also, Micropillar diameters larger than 2.5 µm were not chosen, since BSE imaging of cement pastes suggests an approximate ~2 µm characteristic length for C-S-H phases (especially HD C-S-H phases). Thus, increasing micropillar diameter beyond 2.5 µm would increase the chance of milling the micropillar on two or more phases and capturing a heterogenous response.

Recognizing these limitations, the size effect phenomena were studied by fabricating micropillars with decreasing diameters in the range of 2.5 µm to 0.5 µm (500 nm). Pillar sizes were also tailored to be compatible with the force and displacement maximums and minimums available in the nanoindenter. For each diameter, pillar heights were chosen accordingly to maintain a fixed aspect ratio for all sizes. FIB milling parameters used for milling smaller sized pillars and loading parameters for micro-compression testing of size effect samples are provided in Table 3.4 and Table 3.6 respectively. Geometric details of the FIB milled size effect analysis samples are provided in Table 5.2 in Chapter 5.
3.10 Summary

This chapter discussed the experimental methods used for identification of C-S-H phase in cement paste, micropillar sample preparation in FIB, and micro-compression of pillars using nanoindentation equipment. It also described the process for identification of different failure modes using SEM image analysis, and estimation of the compressive strength and elastic modulus properties using the load-displacement data acquired during micro-compression. Using these methodologies listed in this chapter, compressive failure behavior of C-S-H, including effect of micropillar size and composition of cement paste on the compressive failure will be investigated in the next three chapters.
Chapter 4
Assessment of Strength and Failure Modes

4.1 Introduction
A stochiometric cement paste with w/c 0.42 was microstructurally investigated through a combination of BSE, EDS, FIB and SE approaches and mechanically characterized through compressing a total of 35 micropillars prepared on the w/c= 0.42 sample. 3 pillars failed due to presence of pores or geometric flaws and 1 pillar was accidentally located on clinker region and were removed from the analysis. The analysis helped to develop a qualitative and quantitative portrait of about compressive failure of C-S-H, in terms of its microstructure, chemical composition, compressive strength and deformation modes at failure.

4.2 Microstructure of Stochiometric Cement Paste

4.2.1 Microstructure observations from BSE imaging
The microstructure of the cement paste was carefully analyzed using compositional contrast observed between the distinct phases present. As reported in many SEM investigation literature, the four (Yi et al. 2006) primary phases were identified: unhydrated clinkers, portlandite, and inner and outer hydration product also known as low and high-density C-S-H regions (Figure 4.1). Also, small regions of darker black color were frequently observed in different locations of the sample, which when analyzed through EDS showed presence of metals like magnesium and manganese and oxygen primarily. Thus, these regions can be considered as deposition related to impurities of cement clinkers. Unhydrated clinkers were present in relatively small volume fractions, as expected for a stochiometric (≥w/c 0.42) fully hydrated cement paste. Clinker regions were easily distinguishable with their bright white appearance. The size of the clinker grains varied widely in the range of 2-3 µm to 45-50 µm (width). Small grains were mostly of irregular shape, whereas large unreacted grains were mostly rounded in shape. In some cases, different colors and striations were observed within a single clinker grain, which might be due to possible intermixing of different clinker phases during grinding (Scrivener et al. 2004).
As expected, HD C-S-H were visible in rims around the partially reacted clinker grains (Figure 4.1), and occasionally occupying entire area of a fully reacted clinker grain. These HD C-S-H areas are primarily distinguishable from the other hydration products by their darker grey color and homogenous appearance (no intermixing of different shades). Away from the clinker, the outer product or LD C-S-H regions were found which are characterized by their lighter grey color and less homogenous appearance. When compared by Ca/Si ratio from EDS, the lighter grey regions mostly showed higher Ca/Si ratio as compared to the darker grey areas, which in most cases showed Ca/Si ratio close to 1.7. Hence, it can be anticipated that the lighter grey regions might contain more calcium compared to the darker areas (Famy et al. 2002). The portlandite or Ca(OH)$_2$ regions were visible in the form of whitish long lines spread homogenously throughout the sample. EDS analysis of these areas confirmed that these whitish areas are primarily composed of calcium and oxygen (hydrogen cannot be detected in EDS).

![Figure 4.1: Backscattered electron image of hydrated cement paste showing different phases present in a stochiometric (w/c = 0.42) paste.](image)

**4.2.2 Microstructure observations from coupled FIB milling and SE imaging**

FIB milling on selected C-S-H regions involved removing materials from a 25 µm diameter trench around the micropillar which allowed assessment of the surrounding microstructure. Secondary electron micrographs were collected from the FIB milled regions, as can be seen in
Figure 4.2, where a clinker grain was visible with clearly identifiable boundaries. Next to the clinkers, distinct differences were observed in texture of C-S-H regions. The inner product or HD C-S-H region were identified with uniform texture and no visible micro porosity. The transition between the inner and the outer product region was clearly noticeable. The outer product region has visible microporosity and non-uniform texture.

Through careful observation with high resolution SE imaging, the micro-pillars made on LD CSH, HD C-S-H or clinker region were identified to have some distinguishable features. The pillars primarily composed of LD C-S-H, frequently showed presence of micro-pores on the pillar surface and the trench around the pillar (Figure 4.3a). The LD C-S-H pillars are also distinguishable by uneven and jagged milling of the trench floors around the pillars Figure 4.3b). The HD C-S-H pillars, on the other hand showed homogenous appearance without presence of micro-porosity on or around the micropillar (Figure 4.3c). Also, the FIB-milled trench floors around the micropillar were found comparatively more even and smooth (Figure 4.3d). One micropillar was milled on unhydrated clinker region, which showed a very dense, shiny and uniform microstructure with zero microporosity (Figure 4.3e). Interestingly, the appearance of this clinker micropillar was somewhat similar to brittle metallic glass and crystal micropillars. [([Howie et al. 2012; Yang et al. 2009) However, high resolution SEM images were not captured for all the samples due to limited availability of the instrument. Moreover, some micropillars might be located on transition zones with intermixing of LD and HD C-S-
H phases or Clinker and HD C-S-H phases. Hence, micropillars were not explicitly categorized into LD and HD C-S-H based on the SEM image observations.

Figure 4.3: Distinguishable features of micropillars milled on a-b) LD C-S-H c-d) HD C-S-H and e) clinker.

### 4.3 Failure Modes

This section presents and discusses the deformed shapes of the tested micropillars under uniaxial compressive failure. Geometric details of these thirty-one (31) micropillars is provided in Table 4.1. As explained in chapter 3, the post-test images collected through scanning electron microscope were utilized for characterizing the failure modes. From the post-test images of all the 31 pillars considered in this section, it was clear that the failure mechanisms can be very broadly classified as axial splitting, shearing and plastic crushing.
failure of the micropillar. A majority of the micropillars failed through one of these three mechanisms. However, significant amount of variation was observed in the deformed geometry within each category. Moreover, in some cases, more than one mechanism might have played a simultaneous role in the failure.

The visual evaluation of failure mode, however, is somewhat limited. First, recalling that unloading of the pillars was initiated manually after failure, there remains a possibility of some pillars being more compressed than others. Second, images could only be obtained after unloading so any possible intermediate failure mechanisms could not be observed. Nonetheless, failure modes of the micropillars could be broadly categorized through this visual observation. In the next section, these categories will be demonstrated to coincide with observations from the load-displacement histories of the experiments.

4.3.1 Axial splitting

The most frequently observed failure mode was axial splitting of the micropillar which is a brittle failure mode. Failure occurred by formation of single or multiple vertical cracks, close to the pillar center. Examples of this failure mode are shown in Figure 4.4a-c. In many of these cases, half part of the pillar was found standing, with the base attached to the bulk specimen, while the other half collapsed, and further split into multiple small parts. It is interesting to note that similar failure pattern, known as columnar failure, is often reported in compressive strength testing of macroscopic concrete cylinders. Also, in macroscopic uniaxial compression testing of cement pastes, with well-lubricated interfaces between the load platens and the specimen, one single axial splitting crack is frequently observed (Fischer et al. 2014). In a few cases, cracks and splitting were found on the side walls, whereas the core portion of the pillar remained mostly intact. An example of this type of failure mode is shown in Figure 4.4d. Axial splitting type of failure might be initiated by presence of pre-existing micro-cracks, pores, or flaws in the micropillar.
Figure 4.4: a-c) Micropillars showing various type of axial splitting d) side wall cracking failure.

4.3.2 Shearing

The next category of observed failure mode can be described as shearing or diagonal splitting of the micropillars. Pillars in this category showed presence of a single diagonal crack that separated the top part of the micropillars while the bottom part remained mostly intact and attached to the base. Example of the shearing failure mode are shown in Figure 4.5. Apparently, failure occurred by localized shear deformation along the crack plane. From careful observation of the pillar surface and surrounding microstructure, these pillars are identified as partially or mostly of HD C-S-H. Hence, this type of failure pattern can be associated with the higher compressive strength of HD C-S-H phase. Also, there might be cases when the micropillar was milled on the boundary of types of C-S-H, and shear along phase boundaries of LD and HD C-S-H could have played an important role in this type of failure pattern. Similar type of diagonal shear failure was also reported for micropillars of quasi brittle bone materials [(Schwiedrzik et al. 2014) and in macroscale, compressive testing of concrete cylinders.]
4.3.3 Crushing

A minority of the pillars failed by plastic crushing of the pillar-top. Signs of damage were mainly observed near the top surface, with associated widening of the cross-section and delamination near the top in some cases (Figure 4.6). Similar failure mechanism observed in micropillar compression of quasi-brittle bone materials was reported as ‘mushrooming’ failure (Schwiedrzik et al. 2014). In contrast to the previous cases of axial splitting and shearing failure, most pillars in the plastic crushing category showed non-catastrophic failure. This particular failure mechanism was almost always observed for pillars with very solid, and uniform surface microstructure. As discussed in Section 4.2.2, HD C-S-H do not have visible micro-porosity or inhomogeneity in its microstructure, thus initiation and propagation of cracks from pre-existing flaws is less likely to occur and the material is more likely to go into plastic deformation and exhaust its full capacity.
4.3.4 Combination mode

Occasionally, failure involved a combination of crushing on the top and splitting modes (Figure 4.7). In such cases, signs of plastic crushing were visible near the top, as well as a single crack typically close to the side wall.

4.3.5 Unknown mode

For a minority of micropillars, identification of the exact failure mode with SEM image analysis was not possible, therefore, these pillars were not categorized under any primary
failure mode. Some of these pillars showed sign of explosive failure (Figure 4.8a). Apparently, boundary conditions played an important role in such explosive failure. The confinement resulting from both the friction in the top contact interface between the spheroidal tip and the micropillars, as well as the firm bond (clamping) between the bottom of the micropillars and the material substrate might have influenced a sudden bursting failure of the micropillar. However, recalling that unloading of the pillars was initiated manually after failure, there remains another possibility of these pillars being more compressed than others. In other cases, the SEM images of deformed micropillars did not reveal any obvious crack propagation direction or signs of plastic crushing (Figure 4.8b-c).

![Figure 4.8: Micropillar geometries with unknown mode of failure.](image)

### 4.3.6 Failure due to local irregularity

There were a minority of cases, where, failure clearly occurred due to some irregularity or flaw in the pillar microstructure, and not due to reaching the full compressive strength. Such cases were omitted from the calculation of strength. The most frequently observed case were excessive porosity or pre-existing weak interfaces near the bottom of micropillar (Figure 4.9).
4.4 Load-Displacement Behavior and Strength

The load-displacement behavior of the pillars tested in monotonic single-cycle test was reproducible with similar trend (Figure 4.10). Each curve consisted of three individual stages, an initial linear elastic response, followed by a relatively short nonlinear response and then failure upon reaching a critical load. Failure of a pillar was marked by sudden plateau or drop in load followed by large displacement bursts (pop-in) events. Representative load-displacement curves for the types of failure mode discussed in Section 4.3 are shown in Figure 4.10. The pillars showing axial splitting with vertical cracks, collapsed with a sudden significant drop in the load and comparatively large displacement jump, where only few data points were acquired in the failure zone (Figure 4.10a). The large load drop is probably caused by the sudden lack of contact between the indenter and pillar top as the pillar splits and collapses. For the pillars that showed presence of cracks on side walls, multiple bumps and pop-ins where noticed in the load-displacement curves (Figure 4.10b). Also, failure was less abrupt with more data points collected in the failure zone.

Very few data points were collected in the failure zone for the pillars collapsing in shearing mode. However, for the pillars failing by forming diagonal cracks in shearing mode, load drop and displacement jump were less pronounced (Figure 4.10c). In addition, strain hardening type behavior marked by sharp change in loading slope was noticed prior to failure in these pillars. For pillars showing plastic crushing failure, relatively small load drop followed by a jagged plateau and continuous acquisition of data points were noticed in the failure zone (Figure 4.10d). It is interesting to note that, the compressive strength for pillars showing in plastic crushing is also significantly high (> 500 MPa). Hence such plastic crushing could be
characteristic failure mechanism of pure HD C-S-H. The pillars that showed combined failure modes also collapsed suddenly, however, compared to the pillars showing pure splitting failure, more data points were collected in the failure zone for these pillars (Figure 4.10e).

The compressive strength ($f_c$) results of C-S-H micropillars from the 31 micropillar tests is presented in Table 4.1. The compressive strength varied in the range of 181 MPa to 715 MPa with an average compressive strength of 465 MPa and a standard deviation 147 MPa. Such variability is expected since C-S-H is a highly complex material that shows significant compositional variation with a granular aggregate morphology. Moreover, previous investigations on cement paste using standard nanoindentation methods have suggested the presence of distinct low-density (LD) and high-density (HD) C-S-H packings with different elastic modulus (Constantinides and Ulm 2007). Therefore, variations observed in compressive strength results might be also associated with the presence of these distinct C-S-H packings.

Loading elastic modulus ($E_{\text{Loading}}$) values calculated from the slope of the stress-strain curves are tabulated in Table 4.1.
Figure 4.10: Representative load-displacement curves for types of failure modes- a) axial splitting b) side wall cracking c) shearing d) crushing e) combination.
(a)  

(b)  

(c)
(d) [Graph showing Load (µN) vs. Displacement (nm)]

(e) [Graph showing Load (µN) vs. Displacement (nm)]
Table 4.1: Dimension, mechanical, and chemical properties of the tested w/c = 0.42 micropillars. Here \((D_1)\) and \((D_2)\) are top and bottom diameters, \((H)\) is the height, and \((H/((D_1 + (D_2))/2))\) is the aspect ratio of micropillars. \((Ca/Si)\) is the calcium to silicon ratio of the micropillar location.

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<th>Pillar No.</th>
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<th>(D_2) (µm)</th>
<th>(H) (µm)</th>
<th>Aspect ratio</th>
<th>Taper angle, (\alpha) (°)</th>
<th>(f_c) (MPa)</th>
<th>(E_{\text{loading}}) (GPa)</th>
<th>(Ca/Si)</th>
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Since the tests were monotonic, elastic modulus was determined from the loading part of the stress-strain plot using a linear fit to the initial straight portion (1~4-5% strain) using the method explained in Section 3.8. Unloading elastic modulus cannot be measured for the monotonic tests.

To see if the compressive strengths are related to the failure modes, average compressive strength for each of the three primary modes was also calculated (Table 4.2). The highest average compressive strength (540 MPa) was measured for micropillars failing in plastic crushing mode.

Table 4.2: Average compressive strength for the three primary failure modes.

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<tr>
<th>Failure Mode</th>
<th>Average $f_c$ (MPa)</th>
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<td>Axial Splitting</td>
<td>431±169</td>
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<tr>
<td>Shearing</td>
<td>473±117</td>
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<td>Crushing</td>
<td>540±130</td>
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</table>

4.5 Effect of Ca/Si Ratio

The calcium to silicon ratio of each micropillar location was determined using EDS as explained in Section 3.4.2. The compressive strength results of tested micropillars plotted against the Ca/Si ratio of their location, yielded an approximate inverse relationship

$$f_c \sim (\text{Ca/Si ratio})^{-0.94}$$  (4.1)

within the range of Ca/Si 1.5~2.4 (Figure 4.11). Thus, from the experimental observations, the C-S-H location with lower Ca/Si ratios (1.6~1.8) showed higher probability of possessing larger compressive strength.
4.6 Discussion

The strength properties of cement paste at the scale of level-1 has not yet been well investigated. The limited available literature that has investigated strength of C-S-H at different length scales and using different frameworks, is summarized here in the context of the new experimental results. At the scale of level-0, molecular dynamics simulations predicted the shear strength of individual globules to vary in the range of 1-3 GPa for wet and dry conditions (Pellenq et al. 2009). Molecular dynamics simulation of uniaxial tension and compression performed on a C-S-H atomic structure (1-5 nm) provided ultimate tensile and compressive strength of 3.5 and 15 GPa respectively (Selvam et al. 2009). This study, however, did not consider the presence of porosity in C-S-H which would be expected to reduce these values.

Němeček et al. used microbeam bending tests to estimate tensile strength of C-S-H intermixed with other hydration products in the range of 264 to 700 MPa (Němeček et al. 2016). These beams, however, are relatively large (20 µm length) compared to the length scales of individual C-S-H phases and may reflect the response of a heterogenous composite. In addition, use of relatively high beam current in final milling step (1 nA in (Němeček et al. 2016), compared to 0.1 nA in this study) might have led to large amount of Ga+ implantation in the porous microstructure and an increase in measured tensile strength.

In the framework of continuum micromechanics, Pichler et al. calculated deviatoric strength of microscopic “hydrates” to be 69.9 MPa based on an elasto-brittle multiscale model for cementitious materials (Pichler and Hellmich 2011; Pichler et al. 2013). Using Mohr-Coulomb
parameters from finite element re-analysis of nanoindentation results, the corresponding model predicts uniaxial compressive strength of low density C-S-H as 123.5 MPa, which is slightly lower, but in the same order of magnitude with the experimental results presented here (Pichler et al. 2013; Sarris and Constantinides 2013). It is important to note that for modeling ‘hydrate foam’ in the first step of homogenization, Pichler et al. used a representative volume element (RVE) of twenty microns which is considerably larger than the average diameter of our tested micropillars. Moreover, the input parameters used for homogenization, bulk and shear modulus of “hydration products” are not properties specific to low density (LD) C-S-H, rather calculated as an average over all type of hydrates, including Ettringite, Portlandite and C-S-H of different mass densities from a “close-to-a pure-hydrate” cement paste. These two factors might have caused the differences in strength prediction.

Hlobil et al. performed multiscale damage modeling and inverse analysis to estimate compressive strength of cement paste at different length scales (Hlobil et al. 2016; Hlobil et al. 2015). They reported compressive strength of 2.5 GPa for C-S-H globules at level-0 and 528 MPa for LD CSH at level-1. This is in very good agreement with our results, particularly, with the pillars showing plastic crushing with an average compressive strength of 547 MPa. Note that in their finite element simulations, Hlobil et al. did not consider the possibility of having weaker links in the microstructure. Therefore, it is possible that the micropillars failing through plastic crushing in our study are located on volumes that do not contain any pre-existing weak interface or link in the microstructure. The micropillars showing axial splitting, on the other hand, may have some weak link or interface in the microstructure that is contributing towards early crack nucleation and reduction of strength.

In general, significant reduction in strength is expected to be observed with each increasing hierarchy level due to presence of porosity and other inclusions. Compressive strength of macroscopic cement paste lies in the range of 20-60 MPa. Thus, compressive strength for C-S-H aggregate at level-1 measured in the current study seems to be in reasonable agreement with the upper and lower limiting values from analysis and measurements at smaller and larger scales.

These observed values for elastic modulus are lower than literature reported results of LD and HD C-S-H based on conventional nanoindentation (Constantinides and Ulm 2004). Many
researchers have reported substantially smaller modulus values in micro-compression compared to standard nanoindentation (Yang et al. 2009; Yilmaz et al. 2013; Uchic et al. 2003; An et al. 2015). One possible explanation for this mismatch is the fundamental difference between the two approaches (An et al. 2015). Nanoindentation produces a complex triaxial stress state in the vicinity of the indenter, whereas, micro-compression results in uniaxial stress state. Moreover, in nanoindentation (Oliver and Pharr 2004) and also some micro-compression studies (Yilmaz et al. 2015; Frick et al. 2008), elastic modulus is calculated from unloading slope which is considered to be fully elastic. Additionally, initial non-perfect contact between the pillar and the indenter might result in misalignment in the system which lead to underestimation of the elastic modulus (Uchic and Dimiduk 2005; Zhang et al. 2006).

Finally, some material specific experimental factors could play a role. Cement is a porous material containing entrapped air and water, hence the very high vacuum pumping in FIB might damage the material, resulting in additional loss of stiffness. FIB-induced damage caused by Ga⁺ ion implantation could also affect the mechanical properties.

4.7 Summary

This chapter focused on compressive failure behaviors of 2-µm diameter C-S-H micropillars on 0.42 w/c ratio cement. BSE imaging confirmed presence of high and low-density C-S-H, portlandite, and unhydrated clinker regions in the 0.42 w/c ratio cement sample. Secondary electron images of FIB milled micropillars and surrounding trenches revealed differences in appearance of LD and HD areas. LD micropillars showed visible microporosity on the pillar surfaces and uneven milling of the surrounding trenches. HD micropillars showed very homogenous appearance without presence of micro-porosity on or around the micropillar.

From post-test SEM image analysis of 31 micropillars tested in uniaxial compression, three primary deformation modes - axial splitting, shearing and plastic crushing - were identified at failure. In a few cases, more than one deformation mode were observed, or local geometric irregularities influenced the failure. Load-displacement behavior of tested micropillars were repeatable with similar trends. Each curve consisted of three individual stages, an initial linear elastic response, followed by a relatively short nonlinear response and then upon reaching a critical load failure by sudden load drop and/or large displacement bursts events.
Loading elastic moduli varied in the 5 to 13 GPa interval, which is significantly smaller than elastic (Young’s) moduli of LD and HD C-S-H reported in nanoindentation literature. The compressive strength of C-S-H varied in the range of 181 MPa to 715 MPa, with average compressive strength of 431 ± 169 MPa for axial splitting, 473 ± 117 MPa for shearing, and 540 ± 130 MPa for plastic crushing mode of failure. The compressive strength of C-S-H measured from micro-compression tests was consistent with values from multiscale damage and molecular-dynamics models.
Chapter 5
Effect of Sample Size

5.1 Introduction
In Chapter 4, the compressive strength and primary failure modes of C-S-H were investigated with respect to a fixed size of micropillar (2-2.5 µm diameter and 4-5 µm height). However, as discussed in Chapter 2, the compressive failure of brittle and quasi-brittle materials such as concrete, bones, shales and ceramics usually exhibit strong size effect. Moreover, the micropillar compression technique has showed high potential for investigation of size effect in various materials (Section 2.4.6). The focus of this chapter, therefore, is to investigate three questions- How does the size of the micropillar sample affect compressive strength of C-S-H? Does size have any effect on elastic modulus of C-S-H? Can size change the dominant failure mode in compression?

5.2 Experimental Program
To find answer to these questions, micropillar compression tests using multi-cyclic loading protocols and post-test SEM image analysis were performed on micropillars of three smaller nominal sizes and compared to uniaxial compression results of the ~2 µm diameter micropillars of same aspect ratio. It should be noted that most of the 2 µm diameter pillars were tested in monotonic single-cycle test, whereas, the smaller sized pillars were tested in multi-cycle test. However, the compressive strength and deformation modes were not affected by monotonic versus multi-cycle loading. (discussed in appendix).

For size effect analysis, three sets of (10 micropillars) were fabricated with nominal top diameters 1.5 µm, 1 µm and 0.5 µm on 0.42 w/c ratio cement paste. Representative SEM images for the four nominal sizes considered in the size effect analysis are shown (Figure 5.1).
Figure 5.1: SEM image showing micropillar with nominal top diameter a) 2 µm b) 1.5 µm c) 1 µm and d) 0.5 µm.

Selection of these micropillar sizes for size effect analysis was based on the length scale of C-S-H at level I (discussed in Section 3.6). After careful observation from post-test SEM image analysis, the micropillars that did not collapse properly due to experimental issues were excluded from analysis. Thus, the number of samples considered for the size effect analysis from each individual size is reported in Table 5.1.
Table 5.1: No of final sample of each size considered for size effect analysis.

<table>
<thead>
<tr>
<th>Nominal Top Diameter (µm)</th>
<th>Height (µm)</th>
<th>No. of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-2.5</td>
<td>4-5</td>
<td>31</td>
</tr>
<tr>
<td>1.5</td>
<td>~3</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>~2</td>
<td>9</td>
</tr>
<tr>
<td>0.5</td>
<td>~1</td>
<td>7</td>
</tr>
</tbody>
</table>

5.3 Stress-Strain Behavior

The load-displacement curves from multi-cycle compression testing at increasing peak stress of micropillars of diameter 1.5, 1, and 0.5 µm are shown in Figure 5.2. The load-displacement behavior of the tested pillars was reproducible with similar trend. Each curve consisted of multiple individual stages in two or more cycles. In the first cycle, an initial linear elastic response in loading, followed by small increase in deformation at constant load and linear unloading response was observed. In the second cycle, the loading response consisted three stages, initially linear, followed by continuously increasing nonlinearity at higher deformations and then failure upon reaching a critical load. In a few cases, more than two cycles were completed, and failure occurred in third or fourth cycle. Failure of the pillar was marked by sudden drop in load followed by large displacement jump events. The level of load drop, and displacement jump during failure varied depending upon the different failure modes. Typically, large load drops with only few data points acquired in the failure zone were associated with pillars failing in splitting modes.
Figure 5.2: Load-displacement curve for micro-compression of a) 1.5µm b) 1 µm and c) 0.5 µm diameter pillars.
Representative stress-strain curves for each micropillar size are shown in Figure 5.3. The conversion of load-displacement to stress-strain is explained in Section 3.8. The stress-strain diagrams showed some common characteristics regardless of size. If we consider the loading segment of the first cycle, the initial part of these curves shows a continuous increase in slope with increase in strain level which gives them a concave upward shape (Figure 5.3a), usually up to ~ 0.01 strain level. This phenomenon is likely due to the lack of proper contact between the pillar top and the indenter tip, which is a commonly reported issue in the micropillar compression literature. This is followed by a linear behavior approximately up to 0.04-0.05 strain level.

In the second and subsequent loading cycles, linear behavior was observed until the previously applied peak stress was reached, followed by increasing nonlinearity and curvature until failure. Failure was observed at different strain levels for different samples. Nevertheless, the failure always occurred at 7.5 % or higher strain level and varied in the range of 7.6 to 16 % strain. Thus, C-S-H micropillars exhibited measurable nonlinear deformation before collapse, which is characteristic to quasi-brittle materials (Tandon and Faber 1993).

The unloading behaviors, on the other hand, were significantly different from loading. The multicycle micro-compression test was specifically designed to observe the unloading behavior of the material before collapse. In the figures, it is clearly visible that when micropillars are unloaded from comparatively lower level of peak stresses and strains (less than 4 %), the unloading curves was fully linear. Also, the subsequent reloading curve followed the exact same path and slope as the unloading curve. However, when unloaded from higher peak stresses and strains (> 4 %) levels, presence of a curvature was noticed in the initial part of the unloading curve (Figure 5.3a). Moreover, during the unloading and reloading segments from higher peak stress and strains (> 4 %), a narrow hysteresis loop was observed in many cases (Figure 5.3b). The width of these hysteresis loops increased with increased level of strain in successive cycles. Similar hysteresis phenomenon was also reported in case of cyclic micro-compression of ceramic micropillars (Camposilvan and Anglada 2016).

Time–dependent strain at constant stress was also observed during the 10 second hold time between loading and unloading, specifically at higher stress levels. The magnitude of strain (or deformation) continuously increased with time at a constant applied stress (load).
Moreover, with higher strain level in each successive cycle, the deformation at constant peak stress also increased significantly. For a 1.5µm pillar, example of increasing deformation during constant peak load is evident from a load and displacement versus time plot (Figure 5.4). Clearly, creep strains were developing during the holding process, and apparently continuing even in the initial part of the unloading process which could contribute to the non-linear behavior in the initial unloading parts of high strain regions of Figure 5.3.

The above discussed attributes were present in the stress-strain plot of all size group micropillars. No obvious differences were observed in the overall shape of the stress-strain curves for micropillars of different sizes. However, the concave upward bend in the initial loading curve was less pronounced with decrease in the pillar diameter. Apparently, better contact between the pillar top and the indenter is established when the pillar top diameter is significantly less than the indenter diameter. Also, as the top diameter was decreased, less variability was observed in the stress-strain behavior (in terms of initial loading slope and overall path followed) for pillars of the same size group. It can be seen in Figure 5.3c, that the stress-strain curves for 0.5 µm -diameter pillars are following same path with slightly different failure stresses. Careful examination of the stress-strain diagrams for pillar diameter of 1.5 µm, 1 µm and 0.5 µm indicated an overall increase in the failure stresses (indicated by x marks) with each decreasing pillar size.
Figure 5.3: Stress-strain curves up to failure (marked by x) for micro-compression of a) 1.5 µm b) 1 µm and c) 0.5 µm diameter pillars. 4 curves of each size are shown for clarity of image.
(a) Concave upward

(b) Hysteresis

Non-linearity at unloading

Unload

Reload
(c) Stress (MPa) vs Strain

0 0.04 0.08 0.12 0.16

0 1000

(c)
Figure 5.4: Displacement-time plot for a 1.5 µm diameter pillar (yellow one in Figure 6.3a) showing variation of displacement increase during constant peak loads.
5.4 Size-Effect for Strength

The compressive strength results from uniaxial compression of the diameter 1.5 µm, 1 µm, and 0.5 µm micropillars are presented in Table 5.2. Recalling from Chapter 4, in the ~2 µm diameter micropillars, compressive strength as small as 181 MPa was measured (Table 4.1), however, in the smallest size of micropillars (~0.5 µm diameter), compressive strength as large as 1145 MPa was recorded (Table 5.2). Thus, the results of our experiments indicate that a distinct size effect might be present when C-S-H pillars are tested in uniaxial compression.

Table 5.2: Dimension, mechanical and chemical properties of the smaller diameter micropillars. Here \((D_1)\) and \((D_2)\) are top and bottom diameters, \((H)\) is the height, and \((H/(((D_1) + (D_2))/2))\) is the aspect ratio of micropillars. \((Ca/Si)\) is the calcium to silicon ratio of the micropillar location.

<table>
<thead>
<tr>
<th>Pillar set</th>
<th>Pillar No.</th>
<th>(D_1) (µm)</th>
<th>(D_2) (µm)</th>
<th>(H) (µm)</th>
<th>Aspect ratio</th>
<th>(\alpha) (°)</th>
<th>(f_c) (MPa)</th>
<th>(E_{unloading}) (GPa)</th>
<th>(Ca/Si)</th>
</tr>
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<td>P1</td>
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<td>2.26</td>
<td>2.575</td>
<td>1.4</td>
<td>9.2</td>
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<td>20.9</td>
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<td>P3</td>
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<td>5.0</td>
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<td>25.3</td>
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<td>1.91</td>
<td>2.86</td>
<td>1.7</td>
<td>4.8</td>
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<td>2.23</td>
<td>3.33</td>
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<td>7.9</td>
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<td>0.893</td>
<td>1.4</td>
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<td>7.6</td>
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<td>17.7</td>
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<td>1.22</td>
<td>1.73</td>
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<td>1.6</td>
<td>6.3</td>
<td>475</td>
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<td>1.57</td>
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<td>31.6</td>
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<td>7.7</td>
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<td>26.406</td>
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<td>0.77</td>
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<td>4.7</td>
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<td>17.523</td>
<td>1.65</td>
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<td>0.78</td>
<td>1.25</td>
<td>1.8</td>
<td>4.5</td>
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<td>30.757</td>
<td>1.76</td>
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<tr>
<td></td>
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<td>0.72</td>
<td>1.09</td>
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<td>4.9</td>
<td>1145</td>
<td>33.724</td>
<td>1.67</td>
</tr>
<tr>
<td></td>
<td>P6</td>
<td>0.51</td>
<td>0.70</td>
<td>1.08</td>
<td>1.8</td>
<td>5.1</td>
<td>890</td>
<td>24.4</td>
<td>1.81</td>
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<td></td>
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<td>0.56</td>
<td>0.72</td>
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<td>1.8</td>
<td>4.0</td>
<td>779</td>
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<td>1.67</td>
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<td>P9</td>
<td>0.52</td>
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<td>1.7</td>
<td>5.9</td>
<td>1069</td>
<td>24.8</td>
<td>1.61</td>
</tr>
</tbody>
</table>

To better understand this phenomenon, average compressive strength for each group of micropillars was compared. As can be seen in the Table 5.3, the average compressive strength gradually increased from 465 MPa to 838 MPa, as the nominal pillar diameter was decreased.
Examination of compressive strength as a function of micropillar top diameter (Figure 5.5) also provides evidence of dramatic size effect on strength. From the plot, strong increase in strength is observed as the pillar diameter is decreased in the 2.73 to 0.5 µm range.

Table 5.3: Comparison of average failure stress.

<table>
<thead>
<tr>
<th>Top Diameter (µm)</th>
<th>No. of Sample</th>
<th>$f_c$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>31</td>
<td>465±147.6</td>
</tr>
<tr>
<td>1.5</td>
<td>8</td>
<td>660.5±286.1</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>704±178.5</td>
</tr>
<tr>
<td>0.5</td>
<td>7</td>
<td>838±244</td>
</tr>
</tbody>
</table>

To the authors knowledge, size effect studies at the length scale of C-S-H have not been performed yet. Hence direct comparison with available literature is not possible. However, in macroscale, Bazant used fracture mechanics based asymptotic equations to model size effect in concrete columns [(Bažant and Xiang 1997). For metals, size effect relations are often expressed using power equations like the Hall–Petch relation, which are based on the interaction of sample size with grain size. The Hall-Petch equation describes the relationship between strength and grain size by an inverse square root (-0.5) power.

To investigate possible relationships between compressive strength and diameter of cylindrical micropillars, linear and power equations were fitted to the experimental results. A best fitted straight line to the compressive strength data yields (Figure 5.5a)

$$f_c = -216D_1 + 963 \quad (5.1)$$

The relation suggests that when diameter $D_1 \to 0$, the compressive strengths would be ~ 964 MPa, which implies the material strength limit. However, compressive strength as high as 1145 MPa was observed in the experimental data. Hence for better representation of the experimentally observed results, a power equation is fitted to the compressive strength data. A best fit to the strength data gives (Figure 5.5b)
\[ f_c = 673.3 \times D_1^{-0.49} \]  

\[ f_c \sim D_1^{-0.49} \]

which is very close to the inverse square root dependency mentioned in the LEFM based size effect law for geometrically similar structures of quasi-brittle materials (Bazant and Planas 1997). Inverse square root size effect was also reported for uniaxial compression of concrete cylinders (Kim et al. 1999; Yi et al. 2006).

For quasi-brittle compression failure of concrete columns, Bazant suggested an asymptotic size effect law where the size effect coefficient can be expressed by power law \( D^{-2/5} \) for larger sizes of cross-section. In this asymptotic size effect law, the size effect asymptotically disappears towards a limiting small size of cross section (Bažant and Xiang 1997). Such disappearance of size effect was not observed in the present size effect study of C-S-H for the range of micropillar sizes studied. One interpretation of these results is that C-S-H might not have a critical length where size effect vanishes. C-S-H possess significantly different microstructure compared to large concrete columns with coarse and fine aggregates as inclusions, and other heterogeneities at smaller length scales.

It should be also noted that, due to the continuum mechanics conditions of scale separability between Level 0 and Level I, drastic decrease in micropillar sizes would not be acceptable. Also, due to experimental limitation, FIB milling and indentation testing of micropillar with diameters less than the smallest size investigated here (~0.5 µm) was not practical.

When explaining size effect of large concrete cylinders, Neville proposed a hypothesis according to which larger volumes are more likely to contain an element of low strength which results in low failure stress of samples with larger size (Neville 1996). In a similar analogy, Bazant used Weibull’s weakest link statistics to explain size effect in concrete. This analogy says that failure load of concrete is determined by the failure strength of the weakest link in it. Like a chain containing many links, the smaller the concrete volume the lesser probability of having a weaker link (Bazant and Planas 1997). In general, quasi-brittle failure is caused by growth of cracks which nucleate from pre-existing weaker links such as pores, flaws,
interphase or micro-cracks. When size of micropillars are decreased, the probability of a pre-existing micro-crack or other defects of a certain critical size also reduces. This statistical phenomenon might have played an important role in the size effect observed in compressive strength of C-S-H.

![Figure 5.5](image_url)

Figure 5.5: Compressive strength of micropillars plotted against top diameter. Compressive strength shows an overall increase with decrease in pillar diameter. The solid line indicates best fitted a) linear and b) power relationship.
5.5 Size-Effect for Modulus

This section focuses on the elastic (Young’s) modulus results of the smaller sized micropillars (diameter 1.5, 1 and 0.5 µm). The modulus values reported here were calculated from the fully elastic unloading slopes of the stress-strain diagrams using the method discussed in Section 3.6 for multi-cycle tests. To determine whether sample size has any influence on the measured elastic modulus, the results from micro-compression of different size micropillars are plotted against top diameter of the pillar. As can be seen in Figure 5.6, the measured modulus values vary in the range of 15 GPa to 33.7 GPa, which probably include both HD and LD type C-S-H. The measured elastic modulus range matches with range of elastic modulus (18-35 GPa) reported for C-S-H by nanoindentation investigation of cement paste (Constantinides and Ulm 2004b). Unloading moduli are not available for the 2- µm diameter micropillars on w/c 0.42 sample, since they were tested in monotonic method. However, the unloading moduli of the 2-µm diameter pillars on w/c 0.35 and 0.3 sample (discussed later in Section 6.4) also varied in the 15.5-33.7 GPa range.

![Figure 5.6: Elastic (Young’s) modulus of micropillars plotted against top diameter.](image)

Thus, uniaxial compression tests performed on micropillars of C-S-H with diameters between 2 µm and 0.5 µm did not reveal any significant size effect on modulus. This absence of size effect on elastic modulus may be attributed to the fact that strength and elasticity of composite materials are derived from different mechanisms. The physical reason of size effect on strength is mostly hypothesized to be related to the presence of pre-existing flaws or weaker links such
as pores or micro-cracks. Under increasing loads, these flaws or weaker links can grow, interact, or nucleate new cracks and thereby significantly reducing the failure stress of the entire cross-section or volume (Nemat-Nasser and Horii 1982; Pichler and Hellmich 2011). In elasticity, on the other hand, the micromechanics-based homogenization schemes suggest that the stiffness contribution of pores, flaws or any other weaker phase with low stiffness should be homogenized over the entire microstructure representative elementary volume (REV) (Miled et al. 2011; Constantinides and Ulm 2004a). Hence, the overall elasticity of the composite is not significantly affected by the negligible volume fraction of weak links with low stiffness.

5.6 Comparison of Failure Modes
The different failure modes observed for the uniaxial compression of 2 µm-diameter micropillars was discussed in detail in Section 4.3. The most frequently observed modes included axial splitting, plastic crushing and shearing failure. Similar deformation modes were observed in case of the smaller size samples as well, however, the relative occurrence of these three primary modes changed significantly with decrease in pillar size.

SEM images analysis of the eight (8) deformed 1.5 µm-diameter micropillars showed presence of plastic crushing, axial splitting, and shearing failure. The most dominant failure mode was plastic crushing of the top part of the pillar with widening of the top cross section (Figure 5.7a). The pillars showing such crushing failure almost always had signs of bulging and chipping of small portions from the top part. In literature, similar failure of the top of the pillar leading to localized cracking and delamination is called “mushrooming”. [(Schwiedrzik et al. 2014). Only one (1) of the deformed pillars failed thorough axial splitting, with vertical cracks passing close to the center (Figure 5.7b). The micropillar, however had existing microcracks and porosity on the walls, which, from post-test images, were found to be in the vicinity of the splitting line. Hence, presence of these flaws most likely contributed to the axial splitting failure mode. Another micropillar showed signs of ductile shearing failure with a single crack oriented in the diagonal direction (Figure 5.7c). In this case, failure most likely occurred in the plane of maximum shear stress. Unlike the pillars in splitting and crushing failure, the pillar showing shear failure had the top nearly intact with only one lateral crack across the top (see
Figure 5.7c). It is worth mentioning here, that the pillar showing shear failure also exhibited the highest compressive strength (1110 MPa) of this set.

![Figure 5.7: Appearance of 1.5 µm diameter pillars after failure by a) axial splitting b) crushing and c) shearing.](image)

SEM images analysis of the nine (9) deformed 1.0 µm-diameter micropillars also showed presence of plastic crushing, shearing, axial splitting and side wall splitting. Like the 1.5 µm-diameter pillars, the most frequently observed deformation mode in the 1 µm pillars was plastic crushing. As discussed in Section 4.3 and previously in this section, the 2 µm-diameter and 1.5 µm-diameter pillars that failed by plastic crushing failure, showed signs of crushing damage like delamination and localized cracks mostly near the top part of the pillar. However, the 1 µm-diameter micropillars showing plastic crushing collapsed in a slightly different way. In these pillars, the crushing failure mode involved collapse of the entire height of the sample (Figure 5.8a). Two of the pillars in this group failed by the development of diagonal shear planes with presence of localized microcracks on the top (Figure 5.8b).
Only one of the 1 µm-diameter pillars, pillar number 8 (Table 5.2), failed by formation of vertical cracks and axial splitting. As shown in the post-test SEM micrograph (Figure 5.8c), the pillar was clearly located at the interface between high and low-density C-S-H and, failed by splitting into half right through the boundary line. Apparently, the transition zone of two different type C-S-H acted as a weak link or weak interface that can nucleate cracks. Another of the 1 µm-diameter pillars, pillar number 9 with very high compressive strength (Table 5.2), exhibited a less common mode of failure by forming a single shallow crack on the side wall, and experienced non-catastrophic failure (Figure 5.8d). Such deformation modes are not usually seen in micro-compression of quasi-brittle material. Nevertheless, they are frequently observed for brittle crystals micropillars and known as side splitting [(Howie et al. 2012).

![Image](attachment://a.png)  ![Image](attachment://b.png)  ![Image](attachment://c.png)  ![Image](attachment://d.png)

Figure 5.8: Appearance of 1 µm diameter pillars after failure by a) crushing and b) shearing c) axial splitting and d) side splitting.

SEM image analysis of the smallest size micropillars with diameter 0.5 µm revealed only two failure modes; crushing and shearing. Only one pillar collapsed in shearing (Figure 5.9a), and interestingly, none of the pillars exhibited axial splitting. Among the pillars showing plastic
crushing, one pillar failed by crushing of top part (Figure 5.9b), while rest of the five pillars exhibited crushing of the entire sample similar to failure observed in majority of the 1 µm-diameter pillars.

![Figure 5.9](image)

Figure 5.9: Appearance of 0.5 µm diameter pillars after failure by a) shearing b) crushing of top c) and crushing of entire pillar. Most of the pillars of 0.5 diameter showed crushing of entire pillar like c.

In summary (Table 5.4), for the 2 µm diameter pillars, 45% of the pillars failed by axial splitting, 19% by plastic crushing, and 13% by shearing. Hence the most frequently observed failure mode was axial splitting. As the pillar top diameter is decreased, the percentage of axial splitting failure reduced to 12.5% for 1.5 µm, 11% for 1 µm and 0% for 0.5 µm pillars. For the pillars collapsing in diagonal shearing failure, no obvious differences in the overall percentage was noticed. On the other hand, the percentage of plastic crushing showed overall increase with the decrease in pillar size. As the pillar diameter is decreased from ~2 µm to 0.5 µm, plastic crushing failure increased from 19% to 86%. Also, there was certain variation in the type of the crushing failure observed when the pillar size was decreased. for the pillars with diameter 1.5 or larger, the crushing affected at the top of the pillar with localized cracking and
delamination, however, for most of the 1.0 and 0.5 µm pillars showing crushing failure, entire sample was collapsed. However, since the tests were not displacement controlled, height of the micropillar might have played a role on the extent of crushing. Thus, the results of uniaxial compression experiments on four different size micropillars indicated a sample size effect on the primary deformation mode at failure. The primary failure mode changed from axial splitting to plastic crushing with decrease in sample size.

Table 5.4: Percentage of dominant failure modes observed in different size micropillars.

<table>
<thead>
<tr>
<th>Top Diameter (µm)</th>
<th>Axial Splitting</th>
<th>Shearing</th>
<th>Crushing</th>
<th>Combined</th>
<th>Unknown</th>
<th>Side Splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>2~2.5</td>
<td>0.45</td>
<td>0.13</td>
<td>0.19</td>
<td>0.10</td>
<td>0.13</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>0.125</td>
<td>0.125</td>
<td>0.75</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>0.5</td>
<td>0.11</td>
<td>0.22</td>
<td>0.45</td>
<td>0.11</td>
<td>--</td>
<td>0.11</td>
</tr>
<tr>
<td>5.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.7 Discussions

5.7.1 Effect of weak link on strength and deformation mode

In the overall size effect study, there were some special scenarios where the observed uniaxial compressive strength of a sample micropillar was noticeably less than the other samples of the same set. Such outliers, when correlated to their post-test imaging results, showed presence of some local irregularities or unusual features which possibly acted as weaker links and initiated in premature failure of the sample. For a few representative cases, SEM images collected before and after micro-compression are shown in Figure 5.10. The first example micropillar shown in Figure 5.10a had few large pores and a visible microcrack on the surface, and failed at 350 MPa which is the lowest of the 1.5 µm set, with average strength of 660MPa. Post-test images (Figure 5.10b) confirmed, that the sample failed by formation of vertical cracks through that microcrack. The next micropillar (Figure 5.10c) was located in a very porous area, with some big (relative to micropillar dimensions) pores at the bottom. Post-test images of the pillar revealed an unusual failure mode where the pillar separated from the base along the pores (Figure 5.10d). Since this failure was not proper “compressive failure”, the result was not included in the analysis. The third example of an outlier-type micropillar was the 1 µm-diameter micropillar discussed at the end of the previous section, located at the transition zone.
of two types of C-S-H (Figure 5.10e). Post-test images showed that the pillar collapsed by spitting into half by forming a single crack through the transition zone (Figure 5.10f). The micropillar showed a compressive strength of 475 MPa, which is significantly less than the other micropillars of the 1 µm-diameter set. It is important to note that these kinds of multiphases and other local irregularities could be viewed as a preexisting flaw or weak link. In general, these irregularities were less prevalent at the smaller sizes and thus, might be contributing to the observations of stronger materials at smaller sizes.

5.7.2 Modeling perspective

As discussed in Section 2.7.4, Bazant used fracture mechanics-based scaling law to model size effect in quasi-brittle materials (Bazant and Planas 1997). This scaling law represents a gradual transition from the LEFM to strength or plasticity theory. For larger sizes, LEFM dominates with an inverse square root (-0.5) relationship between nominal strength and size. As the size becomes very small and approaches zero, plasticity dominates, and the curve reaches a constant value representing strength or plasticity theories.

In the size effect study of C-S-H micropillars, the experimental results of compressive strength indicated presence of a similar inverse square root scaling, which corresponds to LEFM theory. Because the variation in size is limited at larger and smaller scales by microstructural features, observations of failure modes are required to understand if a transition to plasticity occurs for C-S-H phases of decreasing size. In the SEM investigation of failure modes, 45 percent of the 2–2.5-µm micropillars showed failure through axial splitting. Together, the strength and failure mode results reveal that for larger sizes of micropillars, micro-cracks, pores, interphases or other discontinuities act as the preexisting crack. The observed splitting failure is probably associated with interaction, merging and growth of these cracks. Hence, the observed behavior of strength and deformation is in line with the scaling theory of quasi-brittle failure.

However, for the smallest size of micropillars tested (0.5-µm diameter), none of the pillars exhibited axial splitting and with 86 percent of the 0.5 µm pillars showing plastic crushing. As failures were almost exclusively by crushing, it is evident that plasticity played the dominant role in failure when reaching the smallest sample sizes. Overall, the gradual reduction in the percentage of splitting failures (Table 5.4) hints towards a shift in the underlying mechanism of failure with decrease in micropillar size. For the intermediate sizes, damage associated with
fracture (cracking) and plasticity both play a simultaneous role in deformation. Existing literature on compressive failure also suggests that two modes of failure can operate simultaneously, and as sample size is reduced it can transition from cracking to yielding (Kendall 1978). Hence, it might be argued that for C-S-H micropillar, for a size in between
1.0 and 0.5 µm, and probably close to 0.5 µm, the dominant deformation mechanism changes from damage (micro-cracking) to plasticity.

Together, the observed scaling relationship and investigation of failure modes provide an experimental basis for modeling strength and deformation behavior. Based on the observed trends, the tested pillar sizes, between 0.5 µm and 2.5 µm, represent the transition between LEFM and plasticity failure theories, as described by Bazant’s scaling law of quasi-brittle failure. Plasticity or strength-based theories can be effectively utilized for modeling the failure behavior of C-S-H aggregates at length scales (REV) smaller than 0.5 µm. The measured compressive strength of $f_c = 838 \pm 244$ MPa can be taken as the plastic strength. On the other hand, for larger length scales beyond ~2.5 µm, fracture mechanics-based concepts and inverse square root relationship should provide adequately accurate results.

### 5.7.3 Estimation of fracture toughness from observed failure behavior

Two different approaches can be used based on the observed experimental results for deriving approximate fracture toughness of the C-S-H material.

In the first approach, the experimentally observed relation between compressive strength and micropillar diameter can be compared to the LEFM size effect relation (Bazant 2004)

$$\sigma_N = \sqrt{\frac{E G_f}{D g(\alpha)}}$$  \hspace{1cm} (5.3)

Here, $\sigma_N$ is the nominal strength (compressive strength $f_c$, in our case), $g(\alpha)$ is the dimensionless energy release function that characterizes the effect of structure geometry, $\alpha = \frac{a}{D} =$ relative length of crack, $D$ is the characteristic dimension of the structure (diameter of micropillar in our case), and $\sqrt{\frac{E G_f}{}} = K_c$ (the mode I fracture toughness of the material). Comparing equation 5.3 with equation 5.2a, we derive

$$\frac{K_c}{\sqrt{g(\alpha)}} = 673.3 \text{ MPa } \sqrt{\mu m}$$

$$= 0.77 \text{ MPa } \sqrt{m}$$
This gives an approximate idea about the fracture toughness of the material. By knowing the magnitude of the $g(\alpha)$, more accurate prediction about the fracture toughness can be made.

In an alternate approach, fracture toughness of a material can be estimated using the LEFM, formula (Van Mier 2012),

$$K_I = f(\varepsilon)\sigma\sqrt{\pi a}$$

Here, $K_I$ is the stress intensity factor, $\sigma$ is the failure stress, $a$ is the initial crack length and $f(\varepsilon)$ is the geometric correction factor.

To estimate the fracture toughness therefore requires knowledge of an initial crack length. In general, this initial crack length may be quite difficult to identify even from pre-loading images of each pillar. Additional studies with controlled crack lengths are suggested. At least one easily identifiable example, however, was found in the current dataset. For the pillar geometry of Figure 5.11 (P7 of diameter 1.5 µm set in Table 5.2), the geometric correction factor is 1.08 and the initial crack length can be taken as 500 nm which is the dimension of the large pore seen near the pillar bottom. Using the failure stress 350 MPa of this pillar, a critical stress intensity factor ($K_I$) of 0.47 MPa√m is obtained which gives a rough estimate of the fracture toughness $K_c$.

It is interesting to note that the estimated fracture toughness values, lie in the same order of magnitude of the fracture toughness for concrete (0.2-1.4 MPa√m). Hence, it can be concluded that unlike compressive strength, the fracture toughness of C-S-H does not show significant increase from the fracture toughness of macroscopic concrete. Due to limitations of the experimental observations, detail investigation of fracture toughness was not performed in this thesis. However, significant potential lies for future work by performing controlled crack fracture experiments on micropillar and micro-beam geometries of C-S-H.
5.8 Summary

Uniaxial micro-compression experiments were conducted on C-S-H micropillars of diameters varying between 2.5 and 0.5 µm fabricated on a 0.42 w/c ratio cement paste. The experimental results indicated presence of a strong size effect on compressive strength and failure mode of C-S-H. The stress-strain curves for different diameter pillars were reproducible with similar trends but with different failure stresses. The average compressive strength of C-S-H increased from 465 MPa to 838 MPa with decrease in pillar diameter in the ~2 µm to 0.5µm range. The overall size effect on strength can be modeled by a power relationship with an inverse square root dependency between strength and pillar diameter. The unloading elastic moduli, however, did not exhibit any strong size effect as the pillar size was decreased in the diameter range of 1.5 to 0.5 µm. The deformation mode at failure was also found to show size effect: the primary failure mode changed from axial splitting to crushing as the pillar diameter was decreased.

The most likely explanation for the observed size effect on both strength and deformation mode is based on the presence of pre-existing weak links (pores, micro-cracks, interphase) in C-S-H microstructure. As the micropillar size is decreased, the probability of containing a pre-existing weak link also decreases. Hence, the axial splitting failure which is frequently initiated by such weak areas became less dominant in smaller micropillars. Similarly, the smaller micropillars has lesser probability of having a weaker link and hence exhibited relatively higher compressive strength.
Chapter 6
Effect of Mixing Proportions on Strength, Modulus, and Deformation

6.1 Introduction
In Chapter 4 and Chapter 5, the compressive strength and deformation modes of C-S-H were characterized by testing micropillars milled on a cement paste with a single water/cement ratio (w/c = 0.42). Thus, any possible effect arising from changes in cement paste mixing proportions (water to cement ratio) was carefully avoided. As discussed earlier, (in Chapter 2), literature suggests that elastic modulus and hardness values of C-S-H are independent of the mix proportions. However, water/cement ratio of cement paste influences the volumetric proportions of the two types of C-S-H and unhydrated clinkers in the paste. Samples with substochiometric conditions (w/c < 0.42) were found to contains higher percentage of HD C-S-H compared to the stochiometric samples. However, effect of changes in mixing proportions on compressive strength of C-S-H remains still unexplored. In this regard, the focus of this chapter is to investigate the following questions.

1) Is compressive strength an intrinsic property of C-S-H, or does it change when w/c ratio is decreased?

2) Do the relative proportions of high and low strength results change as the w/c ratio is decreased?

3) What is the elastic modulus range of C-S-H for different w/c ratio materials?

4) Does a variation in w/c ratio have any effect on the primary failure mode?

6.2 Experimental Program
To find answer to above questions, 2 µm-diameter micropillars milled on cement pastes with w/c ratio of 0.35 and 0.30 (using the sample preparation methods discussed in Section 3.2.1) were tested in micro-compression (using the test protocol discussed in Section 3.5.2) and
compared with results of 2 µm-diameter micropillars on w/c ration of 0.42 samples (as reported on Chapter 4).

The very different microstructure of the stochiometric (w/c ratio ≥ 0.42) and the substochiometric cement pastes is visible from the BSE images shown in Figure 6.1. The stochiometric paste is almost fully hydrated with negligible amount of unhydrated clinker particles. The clinker particles are mostly big chunks of ~20 µm characteristic size. The hydration products contain mostly LD C-S-H regions (lighter grey) except for a few darker grey HD C-S-H regions around the clinkers. The two substochiometric pastes, on the other hand, contain larger amounts of clinker grains with sizes varying widely from 1-2 µm to 35-40 µm. The hydration products contain relatively higher volume fraction of dark grey HD-C-S-H compared to the 0.42 w/c ratio sample, however the boundaries between low and high density C-S-H areas are not as obvious as they are in the 0.42 w/c ratio sample.

Careful observations revealed additional differences between the 0.35 w/c ratio and the 0.30 w/c ratio samples. The 0.30 w/c ratio samples showed presence of a higher volume fraction of clinker grains as compared to the 0.35 w/c ratio sample. However, the size of individual clinker grains was smaller. Moreover, very small clinker grains (~1-2 µm) were evenly dispersed in the hydration products which made isolation of clinker free C-S-H regions extremely challenging.

20 micropillars were milled on the 0.35 w/c ratio samples and 19 micropillars were milled on the 0.30 w/c ratio samples. Representative images of micropillars on each sample are shown in Figure 6.2. After micro-compression and post-test SEM observation, 16 micropillars from each category were selected for final analysis. The micropillars which either did not collapse in the proper way (due to eccentricity, geometric irregularity, etc.) were excluded from the analysis. Also, one micropillar was identified to be on unhydrated clinker region, (from post-test SEM image) and was excluded as well.
50 percent of the 0.35 w/c ratio micropillars were tested in monotonic single cycle method, and rest of the w/c 0.35 pillars and all the 0.30 w/c ratio paste were tested in multicycle method. The
two methods, however, do not have any difference in terms of measurement of strength and failure modes (discussed in appendix A). Hence, the compressive strength results from both methods can be directly compared. The elastic modulus results from only the multi-cycle method are included in analysis.

![Representative image of micropillars on a) w/c 0.42 b) w/c 0.35 and c) w/c 0.30 sample.](image)

### 6.3 Strength and Modulus Results

The elastic (Young’s) modulus results for the tested micropillars were calculated from the unloading modulus of the multi-cycle stress-strain diagram using the method discussed in Section 3.8. The strength results for all the 32 tests, and the elastic modulus results for 8 tests on w/c 0.35 sample and 16 tests on 0.3 sample, are shown in Table 6.1

The compressive strength versus elastic modulus for the two substochiometric samples is plotted in Figure 6.3. The plots suggest a positive correlation between the strength and elastic stiffness properties of C-S-H. A best fitted power equation yields

\[ E \sim f_c^{0.42} \]  \hspace{1cm} (6.1)

And, for the w/c 0.30 cement paste

\[ E \sim f_c^{0.8} \]  \hspace{1cm} (6.2)

It is important to mention that, square root dependency between elastic modulus and compressive strength have been observed in the macroscale for uniaxial compressive cylinder test of regular concrete. For normal strength concrete, ACI proposed an equation for the
estimation of elastic modulus of concrete where modulus of elasticity of concrete is proportional to the square root of compressive strength of concrete. Studies have also showed that the exponent of $f_c$ changes for high strength concrete (Lim and Zollinger 2003; Tomosawa and Noguchi 1993).

As can be seen in Table 6.1, the measured elastic modulus results varied in the 14.9 to 33.7 GPa range with one outlier at 42.7 GPa. However, 14 out of 24 elastic modulus results in table 6.X, are in the range of 17-21 GPa, which matches the elastic modulus results reported for LD C-S-H from different nanoindentation studies (Acker 2001; Constantinides and Ulm 2004; Vandamme et al. 2010). Also, the micropillars with elastic modulus results greater than 24 MPa mostly exhibited compressive strengths higher than 600 MPa. It is interesting to note that, for a w/c ratio 0.30 sample, a nanoindentation modulus ($M$) of 21.9±4.9 GPa for LD C-S-H was reported in literature (Vandamme et al. 2010). Where,

$$M = \frac{E}{1 - \nu^2}$$  \hspace{1cm} (6.3)

Using the Poisson ratio of $\nu = 0.24$ for C-S-H, equation 6.3 yields an elastic modulus ($E$) range of 16~25 GPa.

Elastic modulus is not as sensitive to the presence of weaker links or flaws as strength, nonetheless, elastic modulus results might serve as a basis for distinguishing the pillar results into two types of C-S-H (LD versus HD C-S-H). Plugging the upper bound elastic modulus 25 GPa in the relationship developed between elastic modulus and strength of w/c 0.3 ratio sample, a corresponding compressive strength value of 607 MPa is obtained (Figure 6.3b). Thus, the elastic modulus results support a hypothesis of marking ~600 MPa as the lower bound of compressive strength for HD C-S-H.

Additionally, it is interesting to recall that for micropillars of smaller sizes on w/c 0.42 paste (Table 5.2), the elastic moduli varied in the range of 15.5-33.7 GPa. Thus, no obvious differences in the range of elastic moduli of C-S-H was noticed for micropillars of different w/c ratio and different size.
Table 6.1: Compressive strength and elastic modulus results for 0.35 and 0.30 w/c ratio sample.

<table>
<thead>
<tr>
<th>w/c ratio</th>
<th>Failure mode</th>
<th>Pillar Id</th>
<th>Strength (MPa)</th>
<th>Elastic Modulus, $E_{\text{unloading}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35</td>
<td>Axial splitting</td>
<td>1-2</td>
<td>484</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1-5</td>
<td>505</td>
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<td>1-6</td>
<td>419</td>
<td>--</td>
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<tr>
<td></td>
<td></td>
<td>1-10</td>
<td>560</td>
<td>22.9</td>
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<td>696</td>
<td>24.2</td>
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<td>331</td>
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<td>354</td>
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<td>Shearing</td>
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<td>397</td>
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<tr>
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<td></td>
<td>2-6</td>
<td>439</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>Shearing</td>
<td>1-1</td>
<td>498</td>
<td>17.6</td>
</tr>
<tr>
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<td></td>
<td>1-3</td>
<td>431</td>
<td>17.1</td>
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<tr>
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<td></td>
<td>1-9</td>
<td>484</td>
<td>20.7</td>
</tr>
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<td>1-2</td>
<td>412</td>
<td>18.1</td>
</tr>
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<td></td>
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<td>33.6</td>
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<td>42.7</td>
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<td>20.7</td>
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<tr>
<td></td>
<td>Local</td>
<td>1-7</td>
<td>840</td>
<td>28</td>
</tr>
</tbody>
</table>
6.4 Comparison of Strength Results for Different w/c Ratios and Different Phases of C-S-H

Comparison between the compressive strength results of micro-compression on the substochiometric pastes (0.3 w/c ratio and 0.35 w/c ratio) with those on the stochiometric paste (0.42 w/c ratio), did not reveal significant differences in average strength measured with decreased w/c ratio (Figure 6.4). The range of measured results of compressive strength for the three cement pastes lied in the same order of magnitude. For the w/c 0.42 samples, the strengths varied in the range of 181-715 MPa, and, for 0.35 w/c ratio and 0.3 w/c ratio sample, the results varied in the range of 240-1205 MPa and 388-976 MPa respectively. Thus, the experimental results suggest that compressive strength of C-S-H measured at this length scale is an intrinsic property of the material which does not depend on the water content of the paste.
Notably, majority of the strength results (77 percent of the 0.42 w/c ratio sample, 81 percent of the 0.35 w/c ratio sample, and 81 percent of the 0.30 w/c ratio sample) lied in the range of 180-600 MPa. These individual observations are consistent with the hypothesis that 180-600 MPa might be considered as the compressive strength range of LD C-S-H, and the values above the mentioned range as the range for HD C-S-H. It is difficult, however, to determine the upper limit of the compressive strength of HD C-S-H due to limited amount of available data. Nonetheless, most of the observed results in this category lied in the 600-750 MPa range. It is also important to note that some micropillars might have been comprised of intermixing of LD and HD C-S-H or HD C-S-H and clinker phases and therefore represented a composite response.

Although the compressive strength range was in the same order of magnitude for all three samples, there are some interesting observations and patterns. The lowest compressive strength measured in each sample gradually increased with decrease of w/c ratio. As can be seen in the Figure 6.4, for the 0.42 w/c ratio sample, the lowest measured strength was 181 MPa, which is less than the 240 MPa and 388 MPa measured in the 0.35 and 0.3 w/c ratio samples respectively. Also, 26 percent of 0.42 w/c ratio results were less than 350 MPa compared to only 13 percent of 0.35 w/c ratio sample and 0 percent of the 0.3 w/c ratio sample. These relatively lower strength points possibly correspond to the LD C-S-H regions with higher levels of microporosity.

The average compressive strength measured for the micropillars on the three w/c ratio materials is shown in Table 6.2. The slight increase in the strength of the substochiometric samples might be due to the presence of some unusually high strength results on these two samples, coupled with the reduction in microporosity. On the 0.35 sample, one micropillar showed compressive strength of 1205 MPa, while on the w/c 0.3 sample two micropillars showed compressive strength of 976 MPa and 840 MPa. The exceptionally high strengths might result from presence of unhydrated clinker phase within the micropillar with HD C-S-H, since HD C-S-H packings are always found adjacent to unhydrated clinker particles. Alternatively, these high strength possessing micropillars might also be located on the ultra-high density C-S-H/CH phase, reported in some nanoindentation on cement studies (Zanjani-Zadeh 2013)(Vandamme 2008).
One of the micropillars with unusually high strength (976 MPa) exhibited an elastic modulus of 42.7 GPa (Table 6.1), which is an outlier in modulus results. This elastic modulus is also higher than the range of elastic moduli reported for HD C-S-H from nanoindentation (Constantinides and Ulm 2007) but less than that for clinkers, and in the same order for the UHD C-S-H/CH nanocomposite phase. Thus, either of the two hypotheses about the micropillar (being partially on clinkers, or representing a UHD C-S-H phase) might be true.

![Graph showing compressive strength results for different w/c ratio.](image)

**Figure 6.4:** Compressive strength results for different w/c ratio.

**Table 6.2:** Average compressive strength for each w/c ratio sample.

<table>
<thead>
<tr>
<th>w/c ratio</th>
<th>0.42</th>
<th>0.35</th>
<th>0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of Sample</td>
<td>31</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$f_c$ (MPa)</td>
<td>465±</td>
<td>506±</td>
<td>527±</td>
</tr>
<tr>
<td></td>
<td>148</td>
<td>216</td>
<td>162</td>
</tr>
</tbody>
</table>

### 6.5 Comparison of Failure Modes

The primary failure modes observed in the w/c 0.42 sample micropillars were discussed previously (in Chapter 4 for 2-µm diameter samples, and in Chapter 5 for smaller diameter samples). In this section, the failure modes observed in the micropillars on the two substoichiometric pastes is described, and compared with the previously observed failure modes.
SEM image analysis of the 16 micropillars on the w/c 0.35 sample primarily showed presence of the similar primary failure modes- axial splitting, shearing, and plastic crushing. The most frequently observed mechanism was splitting failure of the micropillar with formation of columnar vertical cracks. Notably, in a majority of the pillars showing axial splitting, half part of the pillar was found standing, while the other half collapsed, and further split into multiple small parts (Figure 6.5a). Similar failure patterns were also dominant in the failure of the 2-µm diameter micropillars on w/c 0.42 sample (Section 4.3.1). In two micropillars, failure occurred along inclined planes, resembling the shear failure mode (Figure 6.5b). Lateral cracks were noticed on the pillar top in one of the two micropillars like the ones noticed in the shearing failure of w/c 0.42 samples. Plastic crushing and failure of the entire pillar was observed in three micropillars (Figure 6.5c). Only in one micropillar (with unusually high strength), crushing of the top leading to localized cracking, bulging and delamination was observed (Figure 6.5d). There was one observation, where failure occurred at a certain depth from the top by horizontal crack forming and separating from the rest of the pillar (Figure 6.5e). This type of highly localized failure might result from presence of the boundary between two different phases within the micropillar.
Similar failure modes were also observed in the 16 micropillars of w/c 0.3 sample. A majority of the samples collapsed in axial splitting and vertical crack forming (Figure 6.6a). In some of these pillars, evidence of interaction and merging of microcracks were observed on the surfaces (Figure 6.6b). A minority of the samples failed in shear by forming diagonal crack (Figure 6.6c). Plastic crushing of the top (Figure 6.6d) and the entire pillar (Figure 6.6e) was also noticed in few micropillars. Notably, crushing of top was almost always observed for pillars with very solid, and uniform surface microstructure. One pillar showed signs of localized failure in one corner of the top (Figure 6.6f). Similar failure is sometimes noticed in uniaxial...
compression of concrete cylinders with unbonded cap (ASTM 2001). This pillar also separated from the base during failure which might be due to presence of some porosity near the base.

The percentage of pillars failing in different modes for each w/c ratio materials is compared in Table 6.3. As can be seen from here, the 45 percent of the w/c 0.42 pillars, 50 percent of the w/c 0.35 pillars and 38 percent of the w/c 0.30 pillars failed by axial splitting. Hence, the most dominant failure mode was axial splitting for all the three w/c ratio. The percentage of pillars failing in shearing mode by forming diagonal crack did not show any significant change as well. However, there was certain increase in the percentage of pillars showing plastic crushing failure with decrease in w/c ratio. As discussed before, plastic crushing failure is noticed to be associated with pillars with higher compressive strength. Thus, the increased percentage of plastic crushing failure might be related to the presence of more HD C-S-H pillars in the substochiometric samples. It is important to mention that there were a few observations in each w/c ratio group, where failure mode was not clear from the deformed geometry, and were categorized as unknown. Also, a few observations for the substochiometric samples showed very localized failure and were classified separately under local failure. Nonetheless, the overall experimental results provide evidence that 1) the primary failure mode of C-S-H is axial splitting independent of the mix proportions 2) the relative proportion of three major failure modes remains mostly unaffected by the change in mix proportions. Hence, from the overall observation, it can be concluded, that like the compressive strength, failure mode is also an intrinsic property of C-S-H which does not depend on mix proportions of the cement paste.

Table 6.3: Percentage of different failure modes observed in different w/c ratio samples.

<table>
<thead>
<tr>
<th>Failure Mode</th>
<th>Water to cement (w/c) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td>Axial splitting</td>
<td>0.45</td>
</tr>
<tr>
<td>Shearing</td>
<td>0.13</td>
</tr>
<tr>
<td>Crushing</td>
<td>0.19</td>
</tr>
<tr>
<td>Combined</td>
<td>0.10</td>
</tr>
<tr>
<td>Unknown</td>
<td>0.13</td>
</tr>
<tr>
<td>Local failure</td>
<td>--</td>
</tr>
</tbody>
</table>
Summary

Uniaxial micro-compression experiments were performed on C-S-H micropillars from cement pastes with varying w/c ratio. The range of measured results of compressive strength for the three cement pastes lied in the same order of magnitude, with an average compressive strength of 465 MPa, 506 MPa, and 527 MPa for C-S-H micropillars of 0.42, 0.35 and 0.3 w/c ratio cement pastes. Thus, the micro-compression results suggest that compressive strength of C-S-H do not depend on the composition of the mixture and is an intrinsic property of the material at the measured length scale.
The unloading elastic modulus results from the 0.3 w/c ratio samples, varied mostly in the 15 to 33 GPa range, and matched well with the elastic modulus range of C-S-H (16 to 34 GPa) reported from nanoindentation on 0.3 w/c ratio cement paste (Vandamme et al. 2010). Based on micro-compression results, approximate relationship between elastic modulus and compressive strength of C-S-H has been proposed. Coupling this observed relationship between strength and modulus, with the literature reported bounds of elastic modulus for LD C-S-H, 180-600 MPa is identified as the compressive strength range of LD C-S-H, and the values above the mentioned range as the range for HD C-S-H. Most of the observed results for HD C-S-H category lied in the 600-750 MPa range. However, due to limited amount of available data in HD C-S-H, an upper bound compressive strength of HD C-S-H was not proposed.

A few unusually high strength results (840 to 1205 MPa) were also observed on the two substochiometric samples. Such high strength might result from partial presence of clinkers with HD C-S-H in the micropillar or from presence of an ultra-high-density C-S-H/CH phase.

The relative proportion of the observed primary failure modes- axial splitting, shearing and crushing, did not show any significant change for variation in w/c ratio. Moreover, axial splitting was the most dominant failure mode for each w/c ratio sample. Therefore, experimental observations provide evidence that like the compressive strength, failure mode is also an intrinsic property of C-S-H which does not depend on mix proportions.
Chapter 7
Conclusions

The overall goal of this research was to understand the compressive failure behavior of C-S-H, the main hydration product of cement paste, at the micrometer scale. This chapter presents a summary of this understanding and key scientific findings, as obtained through a comprehensive implementation and analysis of micro-compression experiments on C-S-H pillars. Based on the findings, some future research suggestions are proposed.

7.1 Summary and Key Findings

In this thesis, the potential of a new, unproven technique – uniaxial compression of micropillar, was explored to study failure of cementitious materials at microscale. In this effort, FIB milling techniques and parameters were tailored and optimized for developing a repeatable micropillar sample preparation process applicable to cement paste, and other heterogeneous materials with granular microstructure. A novel testing protocol for uniaxial compression of cement micropillars using nanoindentation system was developed and refined for successful and replicable test data. Applying these novel sample preparation and experimental technique, stress-strain behavior and microscopic failure information was acquired for compressive failure of C-S-H. The study revealed the following scientific findings:

- High (HD) and low-density (LD) C-S-H, portlandite (Ca(OH)$_2$), and small amount of unhydrated clinker phases were present in the 0.42 w/c ratio cement sample. The clinker particles were mostly chunks of ~20 µm characteristic size. FIB milling of micropillars and trenches in C-S-H regions provided access to observe the C-S-H microstructure. LD C-S-H areas showed presence of micro-porosity, micro-cracks and uneven surface milling, whereas, HD C-S-H areas showed dense, homogenous microstructure without visible porosity.

- The load-displacement or (stress-strain) behavior of C-S-H in uniaxial micro-compression was reproducible with similar trends. When monotonically loaded until failure, the load-displacement curve consisted of three individual stages, a linear elastic response (up to 4 - 5% strain), followed by a nonlinear response and then failure upon
reaching a critical load marked by sudden load drop and displacement jump. Failure was observed in the range of 7.6 to 16% strain.

- Failure mostly occurred by one of the three primary deformation mechanisms: axial splitting, plastic crushing and shearing. Occasionally, more than one deformation modes were observed, or local geometric irregularities influenced the failure.

- Compressive strength of C-S-H varies in the range of 181 MPa to 715 MPa, with average compressive strength of 431 MPa for axial splitting, 473 MPa for shearing, and 540 MPa for plastic crushing mode of failure. The reported range includes both HD and LD type C-S-H. The measured strength from micro-compression tests is consistent with values from multiscale damage and molecular-dynamics models in literature.

- Initial non-perfect contact between the pillar and the indenter leads to underestimation of the loading elastic modulus. However, better contact is achieved at increased deformation, hence, elastic modulus from unloading slopes are not affected by the initial lack of contact. Therefore, while monotonic tests cannot reliably measure elastic modulus, analysis of the unloading branches of multi-cycle tests provides a good assessment of elastic modulus.

- Micro-compression experiments on C-S-H micropillars of varying diameters indicated presence of a strong size effect. Significant increase in strength was noticed as the pillar diameter was decreased in the 2.5 to 0.5 µm range. Average compressive strength of 465 MPa, 660 MPa, 704 MPa, and 838 MPa was observed respectively for ~2 µm, 1.5 µm, 1 µm, and 0.5 µm diameter pillars. The observed relationship between strength and pillar diameter ($D$) can be modeled by an inverse square root dependency ($D^{-0.49}$). The deformation mode at failure also exhibited size effect: the dominant failure mode changed from axial splitting to crushing as the pillar diameter was decreased.

- Presence of pre-existing micro-cracks, porosity or boundary of distinct phases can contribute to failure at significantly lower stress.

- The observed size effect phenomenon can be explained based on the presence of pre-existing weak links (pores, micro-cracks, interphase) in C-S-H microstructure. As the micropillar size is decreased, the probability of containing a pre-existing weak link decreases, hence, smaller pillars fail at relatively higher stress.
• Compressive strength of C-S-H measured from same sized (~2 µm) micropillars on cement pastes with varying w/c ratio did not show any significant difference. Hence, it can be concluded that compressive strength of C-S-H is an intrinsic property at this length scale and does not depend upon composition of the mixture. From experimental results on different w/c ratio cement pastes, 180-600 MPa is identified as the compressive strength range of LD C-S-H, and the values above the mentioned range as the range for HD C-S-H. For the selected size of micropillar, axial splitting is the dominant failure mode for each w/c ratio sample.

• The unloading elastic modulus of C-S-H do not depend on the micropillar size or w/c ratio of the cement paste. It varies in the 15 to 33 GPa range in all cases, and matched well with the elastic modulus range reported in nanoindentation literature.

7.2 Future Work

The findings in the research of compressive failure of C-S-H in cement paste has led to the identification of research questions and opportunities for further extension. Following are some research ideas based on the works described in this dissertation.

Further research beyond this dissertation could allow for fabrication of micropillars on other products of cement hydration, such as portlandite, ettringite and monosulphate phases, as well as unhydrated clinkers. Investigation of compressive strength, elastic modulus, and deformation mechanisms for these phases could provide an even more complete picture of the microscale behavior of cement paste. In addition, micropillars of C-S-H from hydration of pure alite and belite pastes without impurities could provide insight on whether the measured properties of C-S-H are affected by the presence of impurities in commercial cement.

A few unusually high strength micropillars were noticed for the two substochiometric paste studied (0.35 and 0.3 w/c ratio) indicating possibility of an ultra-high-density (UHD) C-S-H/CH nanocomposite phase. Future research can explore cement pastes in the 0.15-0.3 range to prove or disprove the hypothesis of increased compressive strength being related to this UHD phase.

Presence of time dependent strains were noticed at multi-cycle tests during holding at constant larger applied stresses, and also during unloading from higher level of strains. Further research
might assess the creep deformation of C-S-H at different applied stress and strain levels and investigate the possible viscoelastic behavior of C-S-H.

In the current research, FIB milling was exclusively applied to fabricate pillar geometries on cement paste. Following the recent advancements in material science, this methodology can be extended to fabricate other micro-machined sample geometries such as microbeams, and micro-wedge-splitting samples of cement paste to measure different material properties. Notched beams and the wedge-splitting tests are classic methods of measuring fracture toughness through well-controlled tension across a crack. Microbeams of cement paste have been recently studied to investigate tensile properties of C-S-H, but only a few tests were reported so far. Meanwhile, wedge geometries have not yet been attempted on cement paste. Nonetheless, both sample geometries can be fabricated by FIB milling and tested using nanoindenter to study fracture properties of C-S-H. Additionally, some researchers have used nanoindenters installed within electron microscopes to apply loads and simultaneously image the failure mechanisms.

Experimental findings on compressive failure of C-S-H can be incorporated in different modeling approaches. Comparison with numerical simulations of micro-compression experiments can help clarify the occurrence of the different failure modes. Finite element analysis studying failure of metallic alloys have been reported in literature. However, for cementitious materials additional challenges arise in selection of a proper material model. Once the microstructure of C-S-H is adequately incorporated in the model, micro-compression simulations can be performed to compare the strength, stiffness and deformation modes with the results observed in experiments.

Until now, the strength homogenization models developed for prediction of macroscopic compressive strength lacked compressive strength of C-S-H as a basic input data. Researchers have used nanoindentation reported elastic properties and packing densities of C-S-H for approximating strength of C-S-H and predicting compressive strength of cement paste using the micromechanical models (Pichler and Hellmich 2011). Alternatively, strength of C-S-H was estimated by downscaling from experimental data on cement paste and then incorporated into micromechanical model (Hlobil et al. 2016). The experimentally measured compressive strength of C-S-H at the length scale of ~2 μm can now be incorporated as the basic input data.
into continuum micromechanics based multiscale strength homogenization models for upscaling and better predicting quasi-brittle failure strength of cement pastes, mortars and concrete.


Metz, B. (2005). *Carbon dioxide capture and storage: special report of the intergovernmental panel on climate change*. Cambridge University Press,


Two different loading protocols were used—monotonic single cycle and multi-cycle load profiles, with the multi-cycle expected to give more reliable results for elastic modulus (discussed in Section 3.5.2). In single cycle micro-compression test, the applied load on the pillar was continuously increased at a constant loading rate until failure occurs. In the multi-cycle test method, instead of a continuously increasing loading phase, multiple trapezoidal loading segments were applied with linearly incrementing maximum load. Each trapezoid consisted of a loading phase, followed by a hold time at the maximum load, and then an unloading phase. Here, we check that the compressive strengths obtained from each method can be directly compared.

In the 0.35 w/c ratio sample, 8 tests were performed in monotonic single-cycle method and 8 in multi-cycle method. Representative load versus displacement plots from both type of tests is shown in Figure A.1. The load-displacement plots in single-cycle and multi-cycle tests did not show any difference in overall behavior in terms of trends, loading slope and displacement jump and load drop observed at failure. In the multi-cycle tests, the unloading and reloading segments in each successive cycle joined the loading curve of the previous cycle and continued with the same loading slope. Thus, the load-displacement plots of single and multi-cycle tests did not reveal any obvious difference in overall shape and failure behavior.

The compressive strength results for all 16 tests is shown in table A.1. As can be seen here, the for monotonic single cycle and multi-cycle tests average strength was 471±86 MPa and 450±140 MPa respectively. Thus, the strength results measured from the two methods did not show significant difference.
Figure A.1: Load displacement plots for micro-compression on 0.35 w/c ratio sample. (left side plots) Monotonic single-cycle (right side plots) Multi-cycle test

fc = 505 MPa
fc = 486 MPa
fc = 457 MPa
fc = 452 MPa
fc = 484 MPa
Table A.1: Comparison of compressive strength results from pillars on 0.35 w/c ratio sample

<table>
<thead>
<tr>
<th>Testing Method</th>
<th>Pillar Id</th>
<th>Strength (MPa)</th>
<th>Average Compressive Strength (MPa)</th>
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</thead>
<tbody>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>471±86(^1)</td>
</tr>
<tr>
<td>Multi-Cycle</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>450±140</td>
</tr>
</tbody>
</table>

\(^1\) The outlier strength result of pillar 1-7 (1205 MPa) is not considered in average calculation.