Nano-ChemoMechanical Assessment of Rice Husk Ash Cement by Wavelength Dispersive Spectroscopy and Nanoindentation

by

Muhannad Abuhaikal

B.S., Birzeit University (2007)

Submitted to the Department of Civil and Environmental Engineering in partial fulfillment of the requirements for the degree of Master of Science in Civil and Environmental Engineering at the MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2011

© 2011 Massachusetts Institute of Technology All rights reserved

Signature of Author .............................................................
Department of Civil and Environmental Engineering May 20, 2011

Certified by ............................................................... / Franz-Josef Ulm
Professor of Civil and Environmental Engineering Thesis Supervisor

Accepted by ............................................................. / Heidi M. Nepf
Chair, Departmental Committee for Graduate Students
Nano-ChemoMechanical Assessment of Rice Husk Ash Cement by
Wavelength Dispersive Spectroscopy and Nanoindentation

by

Muhannad Abuhaikal

Submitted to the Department of Civil and Environmental Engineering
on May 20, 2011, in partial fulfillment of the
requirements for the degree of
Master of Science in Civil and Environmental Engineering

Abstract

Cement global production stands at 3 Giga tons making concrete the most consumed structural material worldwide. This massively produced material comes with a heavy environmental footprint rendering the cement industry contributing about 5% to global CO₂ emission.

Rice Husk Ash (RHA) among many other silicious materials, has the potential to partially replace cement and enhance the properties of the final product. The goal of this thesis is an investigation of the fundamental properties of RHA cement. For a set of RHA cement paste samples, we investigate at the nano-scale the effect of RHA incorporation on chemical and mechanical properties of cement. RHA is found to have high pozzolanic properties through its reaction with portlandite to form different types of calcium silicate hydrate (C-S-H). It is found that C-S-H in RHA cement has lower Ca/Si ratios compared to pure ordinary portland cement (OPC) samples prepared under the same conditions. Incorporation of RHA has minor effect on the mechanical properties of cement paste at the nano scale for low water-to-binder ratios while significant improvement in mechanical properties is found at high water-to-binder ratios.

We arrive at these conclusions as a result of a dual chemical-mechanical analysis at the nanoscale in which electron probe microanalysis (EPMA) and nanoindentations are employed.

Thesis Supervisor: Franz-Josef Ulm
Title: Professor of Civil and Environmental Engineering
Contents

I General Presentation 28

1 Introduction 29
   1.1 Industrial Context ........................................... 29
      1.1.1 Rice Production ........................................ 29
      1.1.2 Disposal ............................................... 30
   1.2 Green Concrete and Industrial Benefits ................................. 30
   1.3 Research Question ............................................. 31
   1.4 Methodology .................................................. 32
   1.5 Outline of Thesis ............................................ 32

2 Existing Knowledge 34
   2.1 Hydration .................................................... 34
   2.2 Rice Husk Ash ................................................ 36
   2.3 Summary ..................................................... 38

II Materials and Methods 40

3 Materials 41
   3.1 Raw Materials ................................................. 41
   3.2 Sample Preparation and Preservation ................................ 42
   3.3 Macroscopic Test Results: Compressive Strength and Mercury Intrusion Porosimetry ........................................... 44
4 A new Surface Preparation Technique

4.1 Polishing Procedures ........................................ 46
4.2 Roughness Assessment ....................................... 49
4.3 Summary ...................................................... 51

5 Chemical Analysis ............................................. 53

5.1 Fundamental Principles of Electron Probe Micro-Analyzer (EPMA) .......... 53
5.1.1 Specimen Beam Interactions ............................... 54
5.1.2 X-ray Detection ........................................... 56
5.1.3 Experimental Setup and Accelerating Voltage ................. 62
5.2 Nature of Hardened Cement and Spatial Distribution of Different Hydration Products ........................................ 69
5.3 History of EPMA Investigation of Cement Pastes ................. 71
5.3.1 Data Interpretation ....................................... 77
5.4 WDS data interpretation and clustering ......................... 81
5.4.1 Grid EPMA .................................................. 82
5.4.2 Cluster Analysis .......................................... 83
5.4.3 WDS data analysis and presentation ....................... 85
5.5 Summary ...................................................... 86

6 Indentation Analysis ............................................ 92

6.1 Introduction .................................................. 92
6.2 Self Similarity ................................................. 93
6.2.1 Indenter Shape and Geometric Similarity ................. 94
6.2.2 Material Behavior ....................................... 96
6.2.3 Self-Similar Scaling Relations ........................... 97
6.3 Indentation Analysis of Elastic and Strength Properties .......... 99
6.3.1 Indentation Modulus ................................... 99
6.3.2 Indentation Hardness .................................. 100
6.4 Indentation into a Heterogeneous Material ..................... 103
6.4.1 Grid Indentation Technique ............................... 103
6.4.2 Scale separability .................................................. 103
6.5 Packing Density Scaling Relations ................................. 105
  6.5.1 Indentation Modulus-Packing Density Scaling Relations ... 105
  6.5.2 Hardness-Packing Density Relations ........................... 106
6.6 Indentation Equipment ............................................... 108
  6.6.1 Calibration of Machine ......................................... 109
6.7 Statistical Analysis of Nanoindentations ......................... 112
  6.7.1 Indentation Test and Loading Profile ......................... 112
  6.7.2 Grid Indentation ................................................. 114
  6.7.3 Data Interpretation ............................................. 114
6.8 Summary .................................................................. 118

III Results and Discussion .................................................. 119
7 Chemical Analysis Results ............................................... 120
  7.1 Clinker Reference Sample ......................................... 120
  7.2 Chemical Composition of Reference Samples .................. 123
    7.2.1 Sample RHA400 ............................................... 123
    7.2.2 Sample RHA500 ............................................... 123
    7.2.3 Sample RHA600 ............................................... 128
  7.3 Chemical Composition of RHA Samples ......................... 131
    7.3.1 Sample RHA410 ............................................... 131
    7.3.2 Sample RHA420 ............................................... 131
    7.3.3 Sample RHA510 ............................................... 134
    7.3.4 Sample RHA520 ............................................... 134
    7.3.5 Sample RHA610 ............................................... 134
    7.3.6 Sample RHA620 ............................................... 141
  7.4 Summary of the Chemical Analysis .............................. 141

8 Mechanical Analysis ...................................................... 147
  8.1 Nanoindentation on Reference Samples .......................... 147
8.1.1 Properties of C-S-H Phases in Reference Samples .......................... 148
8.1.2 Solid Properties and Packing Density Distributions of Reference Samples 148
8.2 Nanoindentation on RHA Samples .............................................. 157
  8.2.1 Properties of C-S-H Phases in RHA Samples .............................. 157
  8.2.2 Solid Properties and Packing Density Distributions of RHA Samples ... 165
8.3 Chapter Summary ............................................................................. 166

9 Discussion .......................................................................................... 174
  9.1 The Effect of RHA on C-S-H Formation .......................................... 174
  9.2 The Effect of RHA on Nano-Mechanical Properties ......................... 177
  9.3 Chapter Summary ............................................................................. 181

IV Conclusions and Perspectives ......................................................... 183

10 Conclusions and Perspectives .......................................................... 184
  10.1 Summary of Main Findings ............................................................ 184
  10.2 Research Contribution ................................................................. 185
  10.3 Industrial Benefits ........................................................................ 186
  10.4 Perspectives .................................................................................. 186

11 Bibliography ....................................................................................... 188
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Major phases present in Ordinary Portland Cement (OPC) with the corresponding typical mass percentages [61].</td>
</tr>
<tr>
<td>2.2</td>
<td>Typical compositions of phases in Portland cement clinkers [61].</td>
</tr>
<tr>
<td>2.3</td>
<td>Atomic ratios for phases in Portland cement clinkers, calculated from table 2.2.</td>
</tr>
<tr>
<td>3.1</td>
<td>Chemical composition in mass percent of raw materials, OPC and RHA used in this study. Chemical analysis was provided by SIAM cement group using XRF technique.</td>
</tr>
<tr>
<td>3.2</td>
<td>Mix proportions of the 9 samples investigated in this study. The difference between samples is the water/binder ratio and the mass percentages of cement and RHA. Samples are named starting with RHA for rice husk ash project and followed by three digits, the first digit represents the w/b ratio and the last two digits represent the RHA mass percentage in the sample.</td>
</tr>
<tr>
<td>3.3</td>
<td>Porosity of select samples measured using the Mercury Intrusion Porosimetry (MIP). Porosity measurements provided by the sponsor.</td>
</tr>
<tr>
<td>5.1</td>
<td>Typical WDS spot analysis results for an OPC sample. Results are shown for 5 probes only. Elements are recorded in mass percent in addition to the yield total and location of the probe on the surface of the sample (not shown in the table).</td>
</tr>
<tr>
<td>5.2</td>
<td>Backscattering coefficients for different phases present in hardened cement paste. They are a direct function of the mean atomic number of the phase [73].</td>
</tr>
<tr>
<td>5.3</td>
<td>Direct measurement by EDS of the Ca/Si ratio in C-S-H gel in number of studies [71].</td>
</tr>
</tbody>
</table>
5.4 Direct measurements by EDS of the Ca/Si ratio in inner product (Ip) and outer product (Op) C-S-H in a number of studies .............................................. 78

6.1 Degree d of the homogeneous function and proportionality factor B for various indenter probes ................................................................. 96

6.2 Equivalent half cone angle for various pyrimidal probes ......................... 96

6.3 Indentation parameters as used in this study. ........................................... 114

6.4 The range of mechanical properties identified for each of the C-S-H phases in an investigation of a wide range of cement pastes by Vandamme and Ulm. M and H are in GPa. .................................................. 115

8.1 Summary of mechanical properties for the reference samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD is the high-density C-S-H, UHD is the ultra-high-density C-S-H and Clinker stands for un-hydrated clinker. Properties listed include volume fractions, indentation modulus M and indentation hardness H of each phase. ........................................ 152

8.2 C-S-H particle properties for the reference samples as calculated from the fitting algorithm. ................................................................. 153

8.3 Summary of packing density analysis for the reference samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H. For each phase, the table shows the mean packing density and the standard deviation. ......................... 153

8.4 Summary of mechanical properties for RHA samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H and the un-hydrated clinker. Properties listed include volume fractions, indentation modulus M, indentation hardness H of each phase. ........................................ 164

8.5 C-S-H particle properties for the reference samples as calculated from the fitting algorithm. ................................................................. 165
8.6 Summary of packing density analysis for the RHA samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H. For each phase, the table shows the mean packing density and the standard deviation. .......................... 172

9.1 Mean chemical composition in atomic % of C-S-H phases in the complete set of samples. .......................... 178

9.2 Different molar ratios in C-S-H phases in the complete set of samples. ....... 178
List of Figures

1-1 Rice production world wide in 2008 [29] ..................................... 30
1-2 Cement production world wide [68] ......................................... 31

3-1 Compressive strength of the 9 samples at different ages, ranging from 1 to 90 days. Compressive strength test was run by Siam Cement Group. .................. 44

4-1 Sample mounted on an AFM disk. AFM disk is 15 mm in diameter. ........ 47
4-2 Polishing equipment, (a) perspective view, (b) top view. ....................... 48
4-3 Schematic of the polishing equipment (a) Cross section of the Jig and the post used for polishing. (b) Top view of the polishing setup. A circular disk holder is used to allow for oscillation of the sample to prevent inclination of the surface. 49
4-4 Aluminum oxide polishing pads, range from 9μm down to 0.3μm ............... 50
4-5 Aluminum EDS maps at X750 magnification, showing (a) clean sample where the bright blue is aluninate or alumino ferrite phase recognized by the content of iron and calcium in the same location and (b) is a contaminated sample where the shiny blue is a residual aluminum oxide from polishing pads. .................. 50
4-6 AFM image of sample RHA520 over 1 μm area. Root mean square roughness (RMS) is 7.2 nm ................................................................. 51

5-1 Backscattering coefficient (η) versus atomic number. The figure shows the strong dependence of η on the atomic number [51]. ................................. 55
5-2 Schematics of the inner atomic shells. X-ray is produced by electron transitions between these shells [38]. .................................................. 57
5-3 Schematics of the energy levels of a silver atom. The energy of x-ray is equal to the difference between the initial and final energy levels in the transition process [51].

5-4 Bragg reflection: x-ray diffraction pattern of certain wavelength by a crystal of interplanar spacing $d$ [38].

5-5 Schematic of the imaginary Rowland circle geometry used to locate specimen, crystals, and detectors in EPMA [38].

5-6 Monte Carlo simulation (run on CASINO), showing the trajectories of 500 electrons accelerated at 6-15 kV with a beam radius 1$\mu$m into a C-S-H gel.

5-7 Monte Carlo simulation (run on CASINO) showing spatial energy distribution of 10,000 simulated electrons at different accelerating voltages and 1$\mu$m beam width. The material used is a Jennite based C-S-H ($C_{1.7-S-H_4}$) with 2.12 density. (a) Energy distribution for a 6 kV beam where most of the beam energy diminishes are less than 500 nm inside the surface of the sample. (b) Energy distribution for 9 kV voltage where most of beam energy diminishes at less than 900 nm inside the surface of the sample. (c) At 12 kV it reaches 1,500 nm, and (d) at 15 kV it reaches 2,200 nm.

5-8 Intensity of X-Ray emission of different elements at different accelerating voltages. Lighter elements produce higher x-ray intensities (oxygen is lighter than silicon, and silicon is lighter than calcium).

5-9 Intensity of x-ray emission of different elements at 15 kV accelerating voltage into the surface of the sample. (a) 6 keV is smaller than the ionization energy required for iron and that is why iron is not present. (b) Iron x-rays originate from half the depth from which aluminum and oxygen originate. (c) At 12 kV accelerating voltage, depth of x-ray generation for different elements is converging but iron is still excited from $\frac{2}{3}$ the depth of other elements. (d) At 15 kV, x-rays are originating from a very similar volume.

5-10 WDS results on sample RHA400 at different accelerating voltages. The plots show the Ca atomic % vs Si atomic %, and the grey scale represents the yield total after deleting all probes with yield totals below 60%.
5-11 Typical grey scale histogram of an OPC sample. The peaks in the grey scale histogram correspond to regions of similar mean atomic number i.e.; un-hydrated clinker; calcium hydroxide (CH); calcium silicate hydrate (C-S-H) and other hydration products; pores. Grey scale from 0 (black) to 255 (white) depend on the brightness and contrast of the image; but the different phases can always be discriminated in the same way.

5-12 BSE image of a clinker sample showing the 4 different phases present in a raw clinker. The difference in grey levels represents the difference in the mean atomic number. \( C_4AF \) BS coefficient (\( \eta \)) is 0.186, \( C_3S \) \( \eta = 0.172 \), \( C_2S \) \( \eta = 0.166 \), \( C_3A \) \( \eta = 0.166 \) (see table 5.2).

5-13 Spatial distribution of unhydrated clinker and hydration products in hardened ordinary portland cement paste of w/c = 0.4 (sample RHA400). White is representative of un-hydrated clinkers, light grey of portlandite, dark grey of C-S-H matrix, and the pores are black.

5-14 BSE image of sample RHA400 at X950 magnification.

5-15 BSE image and elemental concentration maps of sample RHA500 at X250 magnification showing the spatial distribution of hydration products and the unhydrated clinker. (a) BSE image in which the light grey is portlandite, white is unhydrated clinker, dark grey is the C-S-H matrix. (b) Silicon EDS intensity map: black is portlandite and unreacted clinker and \( C_4AF \), dark red is the C-S-H matrix. (c) Calcium EDS intensity map: light green is the portlandite and unreacted clinkers. (d) and (e) high concentration of aluminum and iron represent the unreacted \( C_4AF \). (f) shows higher concentration of magnesium around \( C_4AF \) grains.

5-16 A close-up at X1000 magnification on sample RHA420 showing residual RHA particles with about 10 \( \mu m \) width.
Spatial distribution of hydration products and the unhydrated clinker in sample RHA620. (a) BSE image: the light grey is portlandite, white is unhydrated clinker, dark grey is the C-S-H matrix. (b) Silicon EDS intensity map, bright red is the unreacted RHA, black is portlandite and unreacted clinker, dark red is the C-S-H matrix. (c) Calcium EDS intensity map: light green is portlandite. (d) and (e) display high concentration of aluminum and iron representative of un-reacted C4AF. (f) shows higher concentration of magnesium around C4AF grains.

Results of spot analysis carried out on C₃S pastes. The two extremes are the individual measured values; other points are means of the relevant changes. The horizontal diameter of the rings represents the uncertainty range [13].

Ca/Si ratios for 5 yr, 0.6 w/c inner hydrate. Total number of results 55, 9 with Ca/Si >4. Adapted from [50].

Use of substitutional ions (Al,S,Fe) for Si in the C-S-H matrix in the interpretation of EPMA for 5 yr, 0.6 w/c inner hydrate. Arrows denote limits within which results were accepted by Rayment and Majumdar [50].

Ternary plots of the analyses of all particles analysed. (a) data as presented on the Ca-(Al+Fe)-Si ternary field; (b) data as presented on the Ca-S-(Al+Fe) ternary field [6]. Tie lines connect the average C-S-H gel composition of amorphous ground mass particles to the theoretical compositions for calcium hydroxide (CH), ettringite, monosulfate, and ferrite.

Parametrizations of the covariance matrix Σ_k currently available in MCLUST for hierarchical clustering (HC) and expectation maximization (EM) for multi dimensional data. (‘.’ indicates availability).

Sample Bayesian Information Criterion (BIC) for different number of components calculated for the models in table 5-22. The results show that 10 components of model "VVV" has the minimum BIC, run on sample RHA600.
5-24 Clustering results of sample RHA600. The ellipses are centered on the mean values of the component while the outline covers 3 standard deviations of the assumed bivariate normal distribution. Colors and different markers represent different components identified by the clustering algorithm.

5-25 Plot of Ca vs Si of sample RHA600 showing the uncertainty of each data point. Size of the spots is proportional to the value of uncertainty. The ellipses are centered on the mean values of the component while the outline covers 3 standard deviations of the assumed bivariate normal distribution.

5-26 Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32 x 32 WDS grid spaced at 65 µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement paste. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

6-1 Load displacement curve showing the typical indentation response to the loading scheme used in this study. Curve segments show the loading at 12 mN/min and a 5 seconds hold period, followed by a 12 mN/min unloading segment under controlled load with 2 mN maximum load.

6-2 Indenter probes of different geometries.

6-3 Parameters defining the geometry of an indenter probe. z is the indentation height, and S is the cross sectional area. For an axisymmetric probe, r is the radius. Adapted from [69].

6-4 Geometric description of a conical indentation test. P is the indentation load, h the indentation depth, h_c the contact depth, A_c the projected area of contact, and a the contact radius [69].

6-5 Schematic of the grid indentation technique showing massive array of indentations on a heterogeneous material. Top: indentations with large depth (h >> D) gives the homogenized response of the material. Bottom: indentations with low depths (h << D) gives the properties of individual constituents [17].
6-6 Normalized homogenized indentation modulus $M/m_s$ versus packing density $\eta$ for a self consistent scheme. Adapted from [69]...

6-7 Scaling of the indentation hardness-to-cohesion ratio of the porous composite with the packing density $\eta$ and the solid friction coefficient $\alpha_s$ using a self consistent scheme. Adapted from [vandame]...

6-8 Nano indenter head assembly The CSM Instruments SA Nano-hardness tester (CSM Instruments Indentation Software User’s Guide)...

6-9 Mechanical Component Diagram (MCD) showing the mechanical response of sample RHA400, in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

7-1 Chemical make up of sample CLINCH P-876 displayed in the form of the compositional component diagram (CCD) and given in tabular format for two 30x30 WDS grid spaced at 50$\mu$m to cover a total area of 1.5 mm x 1.5 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate ($z$) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
7-2 Chemical make up of sample CLINCH P-876 displayed in the form of the compositional component diagram (CCD) for two 30x30 WDS grid spaced at 50µm to cover a total area of 1.5 mm x 1.5 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation.

7-3 Chemical make up of sample RHA400 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

7-4 Chemical make up of sample RHA400 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.1 for details).

7-5 Chemical make up of sample RHA500 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Chemical make up of sample RHA500 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.2 for details).

Chemical make up of sample RHA600 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

Chemical make up of sample RHA410 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.3 for details).
7-10 Chemical make up of sample RHA410 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.1 for details).

7-11 Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

7-12 Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.2 for details).

7-13 Chemical make up of sample RHA510 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
7-14 Chemical make up of sample RHA510 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.3 for details).

7-15 Chemical make up of sample RHA520 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

7-16 Chemical make up of sample RHA520 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.4 for details).

7-17 Chemical make up of sample RHA610 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
7-18 Chemical make up of sample RHA610 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.5 for details).

7-19 Chemical make up of sample RHA620 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.

7-20 Chemical make up of sample RHA620 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.6 for details).

8-1 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA400 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus (M) versus the indentation Hardness (H). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
8-2 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA500 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-3 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA600 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-4 Graphical presentation of packing density distribution for the different hydration products in sample RHA400, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.

8-5 Graphical presentation of packing density distribution for the different hydration products in sample RHA500, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.
8-6 Graphical presentation of packing density distribution for the different hydration products in sample RHA600, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.

8-7 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA410 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-8 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA420 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-9 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA510 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
8-10 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA520 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-11 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA610 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-12 Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA620 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

8-13 Graphical presentation of packing density distribution for the different hydration products in sample RHA410, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
8-14 Graphical presentation of packing density distribution for the different hydration products in sample RHA420, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6. ................................................. 167

8-15 Graphical presentation of packing density distribution for the different hydration products in sample RHA510, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6. ................................................. 168

8-16 Graphical presentation of packing density distribution for the different hydration products in sample RHA520, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6. ................................................. 169

8-17 Graphical presentation of packing density distribution for the different hydration products in sample RHA610, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6. ................................................. 170

8-18 Graphical presentation of packing density distribution for the different hydration products in sample RHA620, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6. ................................................. 171
Summary of the WDS analysis on the complete set of sample. (a) Ca/Si ratio as determined from the pure C-S-H phase. (b) The volume fraction of the residual RHA as separated by the cluster analysis. (c) Portlandite volume fraction including the mixture CH and C-S-H phase as determined from the cluster analysis.

Atomic percentage of the main elements in C-S-H phase.

Volume fractions as measured by nanoindentation clustering. Phases presented are: MP, the C-S-H phase dominated by micro pores, LD C-S-H, HD C-S-H, UHD C-S-H and UNH, the unhydrated matter including residual RHA and residual clinker.

Volume fractions of the different C-S-H phases relative to the volume fraction of the total hydrated matter.
Part I

General Presentation
Chapter 1

Introduction

1.1 Industrial Context

Rice husk ash (RHA), a by-product from the burning of rice husk, is extremely prevalent in East and South-East Asia because of the rice production in this area (figure 1-1). The rich land and tropical climate make for perfect conditions to cultivate rice in Asian countries. The husk of the rice is removed in the farming process before it is sold and consumed. It has been found beneficial to burn the rice husk in kilns of the cement industry. The rice husk ash can be used as a substitute or admixture in cement. Therefore the entire rice product is used in an efficient and environmentally friendly approach.

1.1.1 Rice Production

Rice can be considered the leading crop produced for human consumption in the world. The leading region of the world which produces rice is Asia, especially South-East and East Asia. Rice can easily be grown in tropical regions on any type of terrain. It is well-suited to countries and regions with low labor costs and high rainfall, as it is very labor-intensive to cultivate and requires plenty of water for cultivation [72]. The plains in South-East Asia provide the perfect accommodations.

Figure 1-1 shows the amount of rice paddy cultivated which produces a significant amount of rice husk across the world. About 22% of a dried rice paddy is made up of rice husks. The current world production of rice paddy is around 648 million metric tons and hence 143 million
Figure 1-1: Rice production world wide in 2008 [29].

...tons of rice husks are produced, which produces 45 million metric tons of rice husk ash when burned [42]. China and India are the top producers of rice, but most other countries referenced in figure 1-1 are in South-East and East Asia.

1.1.2 Disposal

Disposal of rice husk ash is a serious problem in countries that cultivate large quantities of rice. Rice husk takes very long to decompose, and hence it is not appropriate for disposal in nature. Therefore the 143 million tons of rice husk produced globally begin to impact the environment if not disposed properly.

One effective method used today to get rid of rice husk is to use it to fuel kilns. Burning the rice husk is an efficient way to dispose of the rice cultivation by-product while producing other useful goods. After the kilns have been fired using rice husk, the ash still remains. As the production rate of rice husk ash is about 20% of the dried rice husk, the amount of RHA generated yearly is about 45 million tons worldwide [42] [29].

1.2 Green Concrete and Industrial Benefits

World production of cement stands at 3 Giga tons and climbing at a rate of 130 million tons/year [68] making concrete the most consumed construction material worldwide (Figure 1-2). Concrete is the preferred constructuion material for many reasons, especially due to the
easy molding at room temperature. But this massively produced material comes with a heavy environmental footprint. The average $CO_2$ emission for each ton of cement ranges from 0.65 to 0.92 ton of $CO_2$. The cement industry contributes about 5% to global $CO_2$ emissions [2].

Many industrial by-products like fly ash and silica fumes are already used as a partial replacement of cement. In addition to finding a place to dispose these environmentally damaging materials by mixing it with cement, RHA improves strength and durability of concrete. Rice husk ash, if produced properly, is mostly amorphous silica and has been used as a pozzolanic material in the cement industry. Especially in countries which cultivate large quantities of rice, the rice husk ash can reduce the environmental footprint of cement production while maintaining or improving the quality of concrete.

1.3 Research Question

Although rice husk ash has been used as a partial replacement of cement since the early 1980's, it is still not widely accepted and utilized. Many researchers already investigated the role of RHA in cement and its effect on strength development of concrete on the macro scale. Others studied the pozzolanic reaction between RHA and portlandite in synthesized materials under well controlled conditions. In this study, we aim at adding to the existing knowledge about RHA at the micro and nano scale in samples of ordinary portland cement mixed with RHA. The goal of this study is to investigate the chemical and mechanical properties of cement paste.
partially replaced by RHA. The research questions we thus want to address are: Is Rice Husk Ash (RHA) reactive? What is the role of RHA in the formation of hydration products? How does it contribute to strength and durability of concrete?

1.4 Methodology

Two primary techniques are employed in the study of rice husk ash cements: statistical nanoindentation which is used to investigate the effect of rice husk ash incorporation on the mechanical properties of hardened cement paste at the microscale. The second technique is Wavelength Dispersive Spectroscopy (WDS) which is employed for chemical investigation of the paste. Parameters of each test are designed so that both mechanical and chemical properties are extracted at the same length scale. In addition to these two primary techniques, we used scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) to aid the analysis and interpretation of our results.

1.5 Outline of Thesis

We start this study with a general presentation of the industrial context and the research question. The second chapter covers a literature review of the research that has been done in the relevant fields of cement chemistry as applied to rice husk ash cements.

In Part II, we discuss the investigated materials (chapter 3) and methods (chapters 4, 5 and 6). Chapter 4 presents an original sample preparation technique that we developed for nanoindentation, which will prove extremely helpful for electron probe microanalysis as well. Chapter 5 discusses the development of an original method of statistical electron-microprobe analysis for cementitious materials. Chapter 6 presents the method of statistical nanoindentation for cementitious materials.

In Part III, the results are presented for the chemical and mechanical investigation (chapter 7 and 8), starting with the chemical analysis of reference samples followed by a thorough investigation of rice husk ash samples. The same order is followed for the mechanical analysis in chapter 8. In chapter 9, we discuss the results of electron-probe microanalysis and nanoindentation, and make a link with macroscopic observations.
The fourth and final part summarizes the conclusions of our investigation and gives suggestions for future research.
Chapter 2

Existing Knowledge

The goal of this thesis is to study the effect of partial replacement of cement by Rice Husk Ash (RHA) on the mechanical properties and chemical composition of these pastes. In order to develop the context in which the experimental investigation was conducted, an understanding of the existing knowledge of RHA and its effect on chemistry and mechanics of cement is required. Therefore, this chapter is an attempt at summarizing the existing knowledge that is required to emphasize the importance of this research and to analyze the experimental data. First, elements of cement chemistry (incl. hydration) are reviewed in order to understand the multiscale microstructure of hardened cement paste. Second, the effect of incorporating RHA in cement paste on the composition of the hydration phases and the formation of new phases as found in the open literature is discussed.

2.1 Hydration

When mixed with water, cement sets through a complex series of hydration reactions that are still only partly understood. The different constituents of cement slowly hydrate and precipitate to form the hydration products which interlock and give to cement its strength and durability. In Portland cement, gypsum (CaSO$_4$·2H$_2$O) is added to prevent flash setting. The time it takes for cement to set varies from twenty minutes for initial set, up to 24 hours or more for the final set. The four major phases in portland cement, which react with water to form the hydration products in the hardened cement paste, are listed in table 2.1. These four phases can have some
impurities which can affect the reactivity and the properties of the hydration products. As an example of cement variability, the mass percentages listed in table 2.1 correspond to Ordinary Portland cement (OPC) Type I, and different designs of cement are available for different uses under different conditions. Abbreviations used in table 2.1, will be used throughout the thesis and they are as follows: C = CaO; S = SiO₂; A = Al₂O₃; F = Fe₂O₃; S = SO₃; H = H₂O.

The most important hydration product which forms the binding phase in cement is the Calcium Silicate Hydrate which is most commonly abbreviated as C-S-H phase. Because the silicate compounds comprise a large percentage of Portland cement (see table 2.1), the most abundant hydration product in hardened cement is C-S-H. The abbreviation C-S-H is used because of the amorphous and poorly crystalline structure of calcium silicate hydrate, and consequently the dashes indicate that no particular composition is implied [61].

Alite and Belite from table 2.1 react with water to form the following hydration products:

\[
\begin{align*}
2C₃S+10.6H & \rightarrow C₃₄S₂H₈+2.6CH \\
2C₂S+8.6H & \rightarrow C₃₄S₂H₈+0.6CH
\end{align*}
\]  

The two silicate reaction equations (2.1), represent the most important of the compound reactions. C-S-H generally comprises 50-70% of the final volume of hardened cement paste, and portlandite (CH) generally comprises 15-20% of the final volume. The exact percentages depend on several factors including the water/cement (w/c) ratio.

The hydration of Aluminate (C₃A) is a much more rapid reaction and is defined by the following set of equations:

\[
\begin{align*}
2C₃A+27H & \rightarrow C₄AH₁₉+C₂AH₈ \\
2C₃A+21H & \rightarrow C₄AH₁₃+C₂AH₈ \\
C₃A+CH+12H & \rightarrow C₄AH₁₃
\end{align*}
\]  

In addition to these reactions, ettringite can also form, if sulfates (SO₄²⁻) are present; according to the following equation:
Table 2.1: Major phases present in Ordinary Portland Cement (OPC) with the corresponding typical mass percentages [61].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Typical mass [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>(CaO)$_3$ · SiO$_2$</td>
<td>C$_3$S</td>
<td>50-70</td>
</tr>
<tr>
<td>Belite</td>
<td>(CaO)$_2$ · SiO$_2$</td>
<td>C$_2$S</td>
<td>15-30</td>
</tr>
<tr>
<td>Aluminate</td>
<td>(CaO)$_3$ · Al$_2$O$_3$</td>
<td>C$_3$A</td>
<td>5-10</td>
</tr>
<tr>
<td>Ferrite</td>
<td>(CaO)$_4$ · Al$_2$O$_3$ · Fe$_2$O$_3$</td>
<td>C4AF</td>
<td>5-15</td>
</tr>
</tbody>
</table>

\[ C_3A + 3CSH_2 + 26H \rightarrow C_6A\overline{S}_3H_{32} \quad (2.3) \]

However, once all the sulfates are consumed, the ettringite reacts with aluminates and water to form an additional aluminate product through the following reaction:

\[ 2C_3A + C_6A\overline{S}_3H_{32} + 4H \rightarrow 3C_4A\overline{S}_3H_{12} \quad (2.4) \]

Depending on the mix design of the cement paste, all of the ettringite could be consumed, but some ettringite usually remains present throughout the hydration period [61].

The final hydration reaction involves aluminoferrite and produces hydrogarnet as described by the following equation:

\[ C_4AF + 3CH + 10H \rightarrow 2C_3(A,F)H_6 \quad (2.5) \]

The hydration reactions in this section are known to be simplified and are not comprehensive of all the reactions occurring during the hydration of Portland cement. However, they do summarize the hydration of the main products present in the hardened cement paste; and therefore include the major components which will be considered in this investigation into the effect of partial replacement of cement by RHA.

2.2 Rice Husk Ash

Rice Husk Ash (RHA) is an environment-damaging by-product of the rice industry. RHA is a highly siliceous material that can be used as an admixture in concrete if the rice husk is
burned in a specific manner. The characteristics of the ash are dependent on the components, temperature and time of burning [42]. During the burning process, the carbon content is burned off, and all that remains is the silica content. The silica must be kept in a non-crystalline state in order to produce an ash with high pozzolanic activity. The high pozzolanic behavior is a necessity if RHA is intended for use as a substitute or admixture in concrete. It has been tested and found that the ideal temperature for producing such results is between 600°C and 700°C. If the rice husk is burned at too high a temperature or for too long, the silica content will become crystalline. If the rice husk is burned at too low a temperature or for too short a period of time, the rice husk ash will contain too large an amount of unburned carbon. Different methods are available for the production of active rice husk ash that is suitable for the use as a partial replacement of cement. In the batch method the rice husk is self-burned from the bottom up while the husk is piled around a chimney on a perforated slab [55]. Another method that can be used to produce an evenly burned and consistent rice husk ash, is the continuous burning method in which the rice husk passes through a rotary kiln under controlled temperature [55].

Rice husk can be turned into a useful cementitious material through incineration and milling to produce an alternative source of active silica with 95% active silica content and 40-60m²/g specific surface area [23]. The ash produced is amorphous and highly reactive when mixed with lime and water, so that RHA can react with Calcium Hydroxide (CH) to produce C-S-H of

<table>
<thead>
<tr>
<th>Phase</th>
<th>Na₂O</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SO₃</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>0.1</td>
<td>1.1</td>
<td>1.0</td>
<td>25.2</td>
<td>0.1</td>
<td>0.1</td>
<td>71.6</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>Belite</td>
<td>0.1</td>
<td>0.5</td>
<td>2.1</td>
<td>31.5</td>
<td>0.2</td>
<td>0.9</td>
<td>63.5</td>
<td>0.2</td>
<td>0.9</td>
</tr>
<tr>
<td>Aluminate</td>
<td>1.0</td>
<td>1.4</td>
<td>31.3</td>
<td>3.7</td>
<td>0.0</td>
<td>0.7</td>
<td>56.6</td>
<td>0.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Ferrite</td>
<td>0.1</td>
<td>3.0</td>
<td>21.9</td>
<td>3.6</td>
<td>0.0</td>
<td>0.2</td>
<td>47.5</td>
<td>1.6</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Table 2.2: Typical compositions of phases in Portland cement clinkers [61].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Si</th>
<th>Ca</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>10.7</td>
<td>32.3</td>
<td>0.4</td>
<td>0.2</td>
<td>0.7</td>
<td>0.1</td>
<td>55.6</td>
</tr>
<tr>
<td>Belite</td>
<td>13.0</td>
<td>28.0</td>
<td>1.0</td>
<td>0.3</td>
<td>0.3</td>
<td>0.0</td>
<td>56.7</td>
</tr>
<tr>
<td>Aluminate</td>
<td>1.6</td>
<td>24.9</td>
<td>15.1</td>
<td>1.6</td>
<td>0.8</td>
<td>0.0</td>
<td>54.7</td>
</tr>
<tr>
<td>Ferrite</td>
<td>1.6</td>
<td>22.0</td>
<td>11.1</td>
<td>6.9</td>
<td>1.9</td>
<td>0.0</td>
<td>55.6</td>
</tr>
</tbody>
</table>

Table 2.3: Atomic ratios for phases in Portland cement clinkers, calculated from table 2.2.
type C-S-H$_I$ and C-S-H$_{II}$. The reaction can be illustrated as follows: [43] [5]

$$\text{Ca(OH)}_2 + \text{SiO}_2 \rightarrow \text{C-S-H}_I + \text{C-S-H}_{II}$$

(2.6)

where

$$\text{C-S-H}_I = \text{Ca}^{(0.8-1.5)} \cdot \text{SiO}_2 \cdot (\text{H}_2\text{O})^{(1.0-2.5)}$$

(2.7)

$$\text{C-S-H}_{II} = \text{Ca}^{(1.5-2.0)} \cdot \text{SiO}_2 \cdot 2(\text{H}_2\text{O})$$

75% of the Portland cement hydration products is portlandite (CH) and C-S-H, and it has been postulated that CH is the weaker (less stable) of the two forms. Hence, the improvement in the mechanical properties of cement mixed with RHA can be attributed to the formation of more C-S-H from the reaction between CH and silica from RHA, with the nature of the reaction dependind on the reactivity of the ash [43] [74] [44].

Many studies aimed at measuring the optimum replacement of cement with RHA and the improvement of the compressive strength and permeability of concrete [10] [35] [22] [3].

2.3 Summary

This chapter presented a brief review of the existing knowledge of general cement chemistry and rice husk ash cement in particular. Most of research on rice husk ash cement involves studies of the pozzolanic reaction between synthesized portlandite and RHA under controlled conditions. Evidence is provided by several researchers that active silica provided by RHA has high pozzolanic properties. Reactivity of RHA silica depends largely on husk incineration process, which if not controlled properly, can produce crystalline silica or silica with high carbon content.

Other research shows that RHA incorporation increases compressive strength of concrete. These researchers employed macroscopic testing and in most cases used uniaxial compressive test.

The overall picture which thus emerges is that natural silica as harvested from risk husks (RHA) has the potential to replace part of the cement and to enhance concrete strength and
durability properties, provided proof can be given that natural silica, much like industrial silica fumes, entails a densification of the hydration products. The proposed research aims at contributing to this proof by means of a combined nano- and macro-characterization of natural nano-silica containing cementitious materials.
Part II

Materials and Methods
Chapter 3

Materials

In order to determine the effect of the incorporation of RHA in cement paste on the chemical and mechanical properties of cement paste partially replaced by RHA at different scales, experimental investigations are conducted at two different scales 'macroscopic investigations' and 'microscopic investigations'. Macroscopic investigations are carried out by SIAM cement group of Thailand (the sponsor of this project) at a length scale $> 10^{-3}$m, effectively testing a homogenized material at the macro scale. The results of the macroscopic investigation are detailed in the following sections. Microscopic investigation include tests on cement paste at both the microscale ($10^{-6}$-$10^{-4}$m), and nanoscale ($10^{-9}$-$10^{-7}$m), which will form the core part of this thesis. 9 cement paste samples (table 3.2) are investigated using novel nanoindentation techniques that allow a determination of the mechanical phase properties, volume fractions and packing density distributions of highly heterogeneous materials. Nanoindentation technique is employed for the mechanical assessment of the samples, while Electron Probe MicroAnalysis (EPMA) and Scanning Electron Microscopy (SEM) are used for the chemical analysis and the study of the spatial distribution of the different hydration phases present in hardened cement pastes.

3.1 Raw Materials

The goal of this study is to investigate the effect of incorporating the RHA on the properties of cement paste at the nano, micro and macro scale. For this purpose, all experiments on
Table 3.1: Chemical composition in mass percent of raw materials, OPC and RHA used in this study. Chemical analysis was provided by SIAM cement group using XRF technique.

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>LOI</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>19.89</td>
<td>4.87</td>
<td>3.68</td>
<td>65.19</td>
<td>0.79</td>
<td>2.26</td>
<td>2.08</td>
<td>0.53</td>
<td>0.23</td>
<td>0.07</td>
</tr>
<tr>
<td>RHA</td>
<td>84.26</td>
<td>0.75</td>
<td>0.48</td>
<td>1.77</td>
<td>0.29</td>
<td>9.86</td>
<td>1.53</td>
<td>0.04</td>
<td>0.62</td>
<td></td>
</tr>
</tbody>
</table>

the nano and micro scales are performed on hardened cement paste mixed with RHA only. Samples were prepared using Type I Ordinary Portland Cement (OPC) and RHA with the chemical compositions given in table 3.1. Specific surface of cement as measured by Blaine method was 3,455 cm²/g, while RHA specific surface was measured by BET N₂ method to be 139,600 cm²/g and the average particle size determined by particle size distribution (PSD) is 8 μm.

### 3.2 Sample Preparation and Preservation

Samples were prepared at different water-to-binder ratios (w/b) ranging from 0.4 to 0.6 to study the effect of RHA on the most common w/c ratios used in concrete industry. Cement pastes were prepared by SIAM cement group on May 26, 2009. Samples and mix proportions are shown in table 3.2. For each w/b ratio, a reference sample was prepared with pure OPC only, in addition to two other samples with 10% and 20% of cement mass replaced by RHA. To ensure homogeneity and consistency across the different samples, the following procedures were adopted by SIAM for sample preparation:

1. For each mixture, the powders were blended together by manual agitation in a plastic container.

2. After that, cement pastes were prepared by mixing the powders with water with a high speed mixer for 90 seconds, such that the resulting water to binder ratio (w/b) are 0.4, 0.5, 0.6.

3. The mixtures were poured into plastic molds with a diameter of 1 cm and were placed at 23°C and 95% humidity for 1 day.
Table 3.2: Mix proportions of the 9 samples investigated in this study. The difference between samples is the water/binder ratio and the mass percentages of cement and RHA. Samples are named starting with RHA for rice husk ash project and followed by three digits, the first digit represents the w/b ratio and the last two digits represent the RHA mass percentage in the sample.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample Name</th>
<th>Water/Binder</th>
<th>OPC (mass%)</th>
<th>RHA (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>RHA400</td>
<td>0.4</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>RHA410</td>
<td>0.4</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>RHA420</td>
<td>0.4</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>RHA500</td>
<td>0.5</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>RHA510</td>
<td>0.5</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>RHA520</td>
<td>0.5</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>RHA600</td>
<td>0.6</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>RHA610</td>
<td>0.6</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>9</td>
<td>RHA620</td>
<td>0.6</td>
<td>80</td>
<td>20</td>
</tr>
</tbody>
</table>

4. After removing from the molds, the specimens were kept in plastic zip bags to prevent loss of water and were stored at 23°C and 95% humidity for 60 days.

5. The samples were sent to MIT on Aug 5, 2009.

Samples were kept in sealed containers until the day of testing.

For purpose of indentation and EPMA testing, samples were preserved in sealed boxes to minimize interaction with humidity or any other possible alteration of the sample. Even with the best preservation procedures, sample can interact with CO₂ which will result in the carbonation of the sample. To solve this problem, samples were cut and polished to expose an intact surface right before testing. The sample preparation technique will be detailed in chapter 4.

A system of labeling will be used for easier reference of these samples in the rest of the thesis: Reference samples are samples RHA400, RHA500 and RHA600. Samples prepared at w/b = 0.4 are RHA400, RHA410 and RHA420 and will be referred to as RHA4 when considered as a sub group. At w/b = 0.5, the samples are denoted by RHA500, RHA510 and RHA520 and this sub group will be referred to as RHA5. At w/b = 0.6, the samples considered are RHA600, RHA610 and RHA620, and this sub group will be referred to as RHA6.
3.3 Macroscopic Test Results: Compressive Strength and Mercury Intrusion Porosimetry

Specimens were tested for the compressive strength in an unconfined uniaxial compression test by SIAM. The results of the compression tests are shown in figure 3-1. The general trend is an increase in compressive strength with increase in RHA content and reduction of w/b ratio.

Porosity measurements on select samples using Mercury Intrusion Porosimetry (MIP) on Quantachrome, Poremaster-33 machine are listed in table 3.3. There appears to be no clear trend that the addition of RHA reduces the total porosity—rather the opposite. This means that the strength increase due to RHA may not attributed to the change of the porosity as accessible by MIP. Other reasons still to be revealed need to be identified. This is one focus of the experimental program laid out next.
Table 3.3: Porosity of select samples measured using the Mercury Intrusion Porosimetry (MIP). Porosity measurements provided by the sponsor.
Chapter 4

A new Surface Preparation Technique

Nanoindentations and electron probe microanalysis (EPMA) are the primary techniques employed in the analysis of cement pastes investigated in this study. The theory and design of these tests assume a perfectly flat surface. The perfectly flat surface in this context is a surface with a roughness that is much smaller than the scale of nanoindentation or EPMA. This chapter presents a new surface preparation technique that can achieve this requirement.

4.1 Polishing Procedures

There are three primary goals of the surface preparation procedure for nanoindentation: (1) to achieve as flat a surface as possible, (2) to obtain repeatable results, and (3) to minimize the sample disturbance. The procedures described here are optimized to satisfy these three goals.

1. **Trimming and mounting:** The first step is to trim the sample to an appropriate size using a diamond drop saw. Cuts are made through the center of the sample to expose a surface. Specimens are cut into 3-4 mm thick half-disks of 10 mm diameter. The edges of the sample remaining after the use of the drop saw are removed by manually grinding both sides of the sample on a 320 grit ZirMet (Buehler). Then the sample is mounted on a stainless steel AFM specimen disk (Ted Pella) using a thin layer of cyanoacrylate as an
adhesive as shown in figure 4-1. Keeping the sample relatively short and wide compared to the specimen disk helps to prevent the sample from tilting and from creating a convex surface.

2. **Coarse grinding step.** The goal of the second step is to make the top of the sample parallel to the bottom of the specimen disk, so that there is no tilt of the surface during indentation. The sample is placed in a specially designed jig consisting of a stainless steel outer sleeve with an opening drilled through to match the diameter of the specimen disk (figure 4-2). An interior cylindrical post fits closely inside, and rests on the back of the specimen disk to apply a light weight to the sample as shown in figure 4-3. Inside the jig, the sample is ground on a TexMet P (Buehler) pad, a hard, perforated, non-woven pad mounted to a lapping wheel. The hardness of the pad assures that the highest surfaces of the sample are removed first, and the perforation gives a place for the polishing residue to collect without interfering with the polishing itself. This is important because the described polishing process does not include any cleaning of the pad during the process. The TexMet P pad is charged, every 3-5 minutes, with approximately 0.5 mL of 9 or 15 micron oil-based diamond suspension (Metadi, Buehler). A polishing fluid helps to dissipate any heat build-up, and the oil-base fluid specifically helps to prevent any further hydration and change in water-to-binder ratio. Grinding proceeds until the entire surface is ground. Because of the high precision of the diamond drop saw in creating two parallel
cuts, the grinding time is short—typically around 5 minutes. The sample and the jig are then cleaned separately, with the sample in n-decane or acetone in an ultrasonic bath for 5 minutes, and the jig is cleaned using a degreaser to get rid of the oil.

3. **Fine polishing step.** The grinding step produces a rough horizontal surface, but for indentation and WDS purposes, a flat surface is required. This surface is achieved by polishing the sample on a series of progressively finer pads. A sample set is shown in figure 4-4. In this step, the sample is manually polished on 9 down to 0.3μm aluminum oxide polishing pads. Aluminum oxide is hard enough to polish hardened cement paste samples which include hydration products with some residual un-hydrated clinkers. Although this step is operator dependent in the beginning, with some experience it is easy to recognize the quality achieved from each pad to produce repeatable results.

Aluminum oxide, silicon carbide or diamond polishing pads can be used for this final step. Aluminum oxide is appropriate for soft samples, whereas diamond is required for samples with hard inclusions. One possible problem with this method is the sample impregnation with polishing materials which in this case is aluminum oxide. To solve this problem, the sample is cleaned in an ultrasonic bath for 10 minutes in n-Decane or acetone and then cleaned with an air jet to get rid of any residual contaminations.
Figure 4-3: Schematic of the polishing equipment (a) Cross section of the Jig and the post used for polishing. (b) Top view of the polishing setup. A circular disk holder is used to allow for oscillation of the sample to prevent inclination of the surface.

It should be noted that the steps described here are only one possible solution to achieve the goals. These procedures are user dependent and the user can get better results with some experience. The same applies to the quality of the consumables used for polishing. There will always be a better polishing pad for certain type of samples and we are using these consumables only because it worked very well.

4.2 Roughness Assessment

For surface roughness assessment, Atomic Force Microscopy (AFM) was used to scan several spots on the surface of the sample with different sizes ranging from 1μm to 100μm to determine the root mean square roughness of each area. Roughness measured using an AFM can be due to roughness resulting from polishing which is our subject of analysis; or it can be a measurement of the porosity of the cement paste. For this reason, the scanned areas were chosen to have the minimum porosity to be representative of the roughness resulting from polishing alone. While it is easy to avoid large pores in the scanned area, it is well known that cement paste has a very wide range of porosity size distributions. By comparing the surface roughness of hydration products and un-hydrated clinkers in the same sample, we found that the technique provides
Figure 4-4: Aluminum oxide polishing pads, range from 9µm down to 0.3µm

Figure 4-5: Aluminum EDS maps at X750 magnification, showing (a) clean sample where the bright blue is aluminate or alumino ferrite phase recognized by the content of iron and calcium in the same location and (b) is a contaminated sample where the shiny blue is a residual aluminum oxide from polishing pads.
Figure 4-6: AFM image of sample RHA520 over 1 \( \mu m \) area. Root mean square roughness (RMS) is 7.2 nm.

A root mean square (RMS) roughness for clinkers below 5 nm, and 7 to 15 nm for hydration phases.

4.3 Summary

An original surface preparation technique is proposed to meet the requirements of both nanoindentation and EPMA analyses. The technique is divided into three general steps: The sample is first cut into an appropriate size and is mounted on an AFM disk. The purpose of this step is to expose an intact surface while an AFM disk is needed for easier handling of the sample. The second step is rough grinding on 9 \( \mu m \) diamond suspension to get a sample surface that is parallel to the AFM disk. The third step is fine polishing on a series of progressively finer
polishing pads to produce a flat surface with the minimum roughness possible. This surface preparation technique is employed for all samples investigated in this study.
Chapter 5

Chemical Analysis

Cement paste is a complex heterogeneous material, with compositional and structural heterogeneities existing on a variety of length scales. Understanding the microstructure of the primary hydration products of cement paste - the calcium silicate hydrate (C-S-H) remains a challenge in the cement research community. The main reason behind this challenge is the spatial distribution of the different phases in the hydrated cement paste, which beside C-S-H, include residual un-hydrated clinker phases, portlandite (CH) and a smaller volume fraction of AFm and AFt phases, in addition to rice husk ash. For this reason, it is necessary to employ an in-situ testing method that can characterize and quantify each of these phases individually. In this chapter, we describe how Electron Probe MicroAnalysis (EPMA) and Scanning Electron Microscopy (SEM) can be applied to the in-situ study of the composition and spatial distribution of different hydration products -including rice husk ash- at nano and micro scales. To achieve this goal, we develop an original statistical micro-chemical analysis method for cementitious materials, based on EPMA. This method is detailed in this chapter, preceded with a general discussion of EPMA method and a history of EPMA applied to cement and rice husk ash.

5.1 Fundamental Principles of Electron Probe Micro-Analyzer (EPMA)

Electron Probe Micro-Analysis (EPMA) is an analytical technique used primarily for the in-situ, non-destructive analysis to establish the chemical composition and topography of very small
areas in small solid samples. Electron probe micro-analyzer is a micro beam instrument that is capable of performing the function of a Scanning Electron Microscope (SEM) to obtain detailed and highly magnified Secondary Electron (SE) and Backscattered Electron (BSE) images, but the primary goal of using an EPMA is to establish the chemical composition of our materials. The ability of EPMA to create detailed images with high resolution at a very small spatial scale, makes it possible to analyze the complex chemical composition and spatial distribution of the different hydration phases present in hardened cement paste [71].

EPMA is a technique to chemically measure small areas of a sample. Electrons and x-rays are emitted as a result of interaction between a beam of electrons and the sample. Emitted electrons are then used to produce images of the surface of interest, while x-rays, which are a characteristic of the elements from which they are emitted, provide qualitative and quantitative measure of the elements present in the sample. The specimen-beam interactions are discussed below. Imaging capabilities of EPMA are primarily used for locating regions of interest for point analysis, which makes it an invaluable technique in materials science. Scanning electron microscope (SEM), on the other hand, is a close relative of EPMA. SEM is primarily made for imaging purposes, in which different detection modes of electrons can be used to produce topographic and compositional images. Furthermore, SEM is usually equipped with x-ray detectors enabling x-rays of selected elements to be detected and analyzed. The function of the two equipments, however, overlap considerably with different priorities.

EPMA is used for elemental quantification on the micro-scale, and for producing images of polished samples that give a great deal of microstructural details [38]. The importance of this technique stems from many reasons including easy sample preparation, high accuracy of elemental analysis, small volume of interaction (on the order of 1 micron), and the non-destructive nature of the technique in which the sample can be preserved for other tests.

5.1.1 Specimen Beam Interactions

A beam of electrons is accelerated to the surface of the sample of interest to excite electrons and x-rays which are a function of the topography and composition of the sample. These interactions cause various types of emissions, but mainly elastic and inelastic scattering and x-ray emissions.
Elastic Scattering

In elastic scattering the total kinetic energy of the collision is conserved. It mainly describes the interaction between an electron and nuclei of the specimen. It involves large deflections in which the angular deflection angle $\gamma$, derived by Rutherford, is given by [38]:

$$\tan \frac{\gamma}{2} = \frac{Z}{1.4pE}$$

(5.1)

where $Z$ is the average atomic number, $p$ is the minimum distance between the un-deflected electron path and the nucleus, and $E$ is the beam of electron’s energy. Elastic scattering is responsible for electron backscattering, in which an electron is deflected by an angle greater than $90^\circ$. Backscattered electrons are, by convention, electrons with energy greater than 50 eV. The fraction of beam electrons that are deflected along angles greater than $90^\circ$ represents the backscattering coefficient $\eta$, which is strongly dependent on the atomic number $Z$ as shown in figure 5-1. Hence, backscattering electrons provide information about the composition of the sample.
Inelastic Scattering

The energy that the beam of electrons possesses is dissipated through various types of interactions with bound electrons known as inelastic scattering. This type of scattering is responsible for the emission of secondary electrons which, by convention, possess energy less than 50 eV. During inelastic scattering, electrons receive sufficient energy to leave the surface. Similar to the backscattering coefficient $\eta$, the secondary electron coefficient, $\eta_{SE}$, represents the ratio of the number of secondary electrons produced to the number of incident electrons. The secondary electron coefficient does not vary smoothly with atomic number. As a result of their low energy, secondary electrons that are within a few nanometers from the surface are able to leave. Hence, secondary electrons provide information about the topography of a specimen.

Characteristic X-ray Emission

X-rays produced by the interaction between the beam of electrons and the sample are a characteristic of the elements from which they are emitted. X-ray emissions are produced by electron transition between the bound orbits which possess energy governed by the quantum number $n$. These orbits are usually designated as K$(n=1)$, L$(n=2)$, and M$(n=3)$ and each of these orbits contains subshells with slight energy differences (see figure 5-2). For an x-ray to be produced, the incident beam energy must exceed the critical excitation energy required to ionize the sample. Once the atom is excited by ionization of one of the core-level electrons, an outer-shell electron drops to the core state and loses energy by emission of a photon (the x-ray). Energy of the produced x-ray is equal to the difference in energy between the two electron states (core-level and the outer-level); see figure 5-2. Since x-ray emissions are characteristic of the elements from which they are emitted, they can be used to identify the composition of the specimen.

5.1.2 X-ray Detection

There are two types of x-ray detectors; energy dispersive spectrometers (EDS) characterize the emitted x-rays based on their energy, while wavelength dispersive spectrometers (WDS) sort the x-rays based on their wavelengths. In this section we will briefly discuss the two techniques and state some of their advantages and disadvantages.
Figure 5-2: Schematics of the inner atomic shells. X-ray is produced by electron transitions between these shells [38].
Figure 5-3: Schematics of the energy levels of a silver atom. The energy of x-ray is equal to the difference between the initial and final energy levels in the transition process [51].

**Energy Dispersive Spectroscopy (EDS)**

Unlike WDS, energy dispersive spectroscopy classifies x-rays based on their energy. The major component of an EDS system is a solid state detector, which can be made of lithium-drifted silicon, lithium drifted germanium, or mercuric iodide. The detector absorbs the x-ray photons and forms a charge pulse which is converted to a voltage pulse that is amplified and passed to a computer x-ray analyzer. The data is then displayed as a histogram of intensity versus voltage. This histogram provides information about all elements with x-ray emissions in the range of voltage being analyzed. Hence, one detector is sufficient to measure all elements that generate detectable radiations.

**Wavelength Dispersive Spectroscopy (WDS)**

In WDS, x-rays are classified based on their wavelengths making use of the Bragg reflection. In Bragg reflection, x-rays of a given wavelength $\lambda$ are diffracted by the atomic layers of a crystal of interplanar spacing $d$ at a certain angle of incidence $\theta$ (see Figure 5-4). The relationship
between these variables is known as Bragg’s law; and it is given by:

\[ n\lambda = 2d\sin\theta \]  

(5.2)

where \( n \) is an integer (\( n=1,2,3,.. \)) that represents the order of reflection. In WDS, the first order of reflection (\( n = 1 \)) is usually employed since it produces the most intense reflections. For \( n=1 \) and a given value of interplanar spacing \( 2d \) the wavelength range is limited. Hence, several crystals of different interplanar spacing \( 2d \) are needed to cover the whole range of x-rays. A typical WDS system can have up to five detectors which allow up to 5 elements to be measured simultaneously. Source, detectors, and analyzing crystals are usually located in the imaginary Rowland circle (see Figure 5-5). This geometry ensures that the Bragg angle is the same for all points.

Once an x-ray has been emitted and diffracted by the crystals, proportional counter is used to detect the radiation. The proportional counter consists of a tube filled in gas and a coaxial wire held at a positive potential between 1 and 2 kV. X-rays enter the detector through a window which could be thin or thick depending on the wavelength, causing the gas atoms to ionize. This ionization generates electrons and ions which are attracted to the anode wire and the cathode, respectively. The electrons cause further ionization that leads to a pulse that appears at the anode. Further analysis of the pulse follows to measure the x-rays intensities [51].

In this study, we have chosen to use the WDS method for the quantitative analysis since it has the potential of producing quantitative measurements of element concentrations; while EDS is used to generate elemental concentration maps, for which it is much faster than WDS for the same purpose.

**Quantitative Analysis of X-rays**

Two types of x-ray spectrometers can be used to collect emitted x-rays; EDS or WDS, as mentioned above. The EDS type is more suited for qualitative analysis owing to its ability to record complete spectra rapidly. This characteristic makes it the choice for element x-ray compositional maps. The WDS type can be used for the same purpose as EDS, but the most common application of WDS is for quantitative spot analysis owing to its better resolution. In
this section, we will briefly discuss quantitative analysis of x-rays collected by WDS.

The intensity of a characteristic x-ray is proportional to the mass concentration of the element of interest. Hence, for a given sample, once the x-ray intensities of each element of interest are measured, the intensities are compared to those of standards containing known values of the elements of interest. The uncorrected elemental concentrations are calculated by the following formula [51]:

$$ C'_A(sp) = \frac{I_A(sp)}{I_A(st)} C_A(st) $$  \hspace{1cm} (5.3)

where $C'_A(sp)$ is the uncorrected mass concentration of element $A$ in the specimen, and $C_A(st)$ is the mass concentration of element $A$ in the standard, $I_A(sp)$ and $I_A(st)$ are the intensities measured in the specimen and standard respectively. Several corrections are required to make sure that the WDS measurements and data analysis provide quantitative chemical data. The measured peak intensities require background and overlap corrections. The background correction eliminates background contributions to the measured peak intensities, while the overlap correction takes into account the fact that peak intensities are enhanced by overlap from a neighboring peak. In addition, uncorrected mass concentrations must be corrected for matrix
Figure 5-5: Schematic of the imaginary Rowland circle geometry used to locate specimen, crystals, and detectors in EPMA [38].
Table 5.1: Typical WDS spot analysis results for an OPC sample. Results are shown for 5 probes only. Elements are recorded in mass percent in addition to the yield total and location of the probe on the surface of the sample (not shown in the table).

<table>
<thead>
<tr>
<th>Probe No.</th>
<th>Al</th>
<th>O</th>
<th>S</th>
<th>Fe</th>
<th>Si</th>
<th>Ca</th>
<th>Mg</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.052</td>
<td>29.260</td>
<td>0.038</td>
<td>69.690</td>
<td>0.004</td>
<td>0.000</td>
<td>0.000</td>
<td>99.044</td>
</tr>
<tr>
<td>2</td>
<td>0.155</td>
<td>0.918</td>
<td>0.030</td>
<td>4.760</td>
<td>3.280</td>
<td>3.320</td>
<td>0.000</td>
<td>12.463</td>
</tr>
<tr>
<td>3</td>
<td>0.772</td>
<td>41.670</td>
<td>0.089</td>
<td>2.200</td>
<td>13.730</td>
<td>28.020</td>
<td>0.084</td>
<td>86.656</td>
</tr>
<tr>
<td>4</td>
<td>0.594</td>
<td>20.260</td>
<td>0.116</td>
<td>4.730</td>
<td>13.190</td>
<td>17.620</td>
<td>0.065</td>
<td>56.614</td>
</tr>
<tr>
<td>5</td>
<td>0.179</td>
<td>56.510</td>
<td>0.205</td>
<td>0.523</td>
<td>6.040</td>
<td>28.950</td>
<td>0.235</td>
<td>92.695</td>
</tr>
</tbody>
</table>

Effects. This correction is known as the matrix correction and is sometimes referred to as ZAF; an acronym for the different matrix effects: atomic number (Z), absorption (A), and fluorescence (F). The ZAF correction is applied iteratively since it depends on the composition of the specimen which is a priori unknown. This correction procedure is performed within a computer program that takes measured x-ray intensities, compares them to standards, computes the ZAF correction, and presents the results as mass concentrations of elements or oxides.

WDS is usually employed to generate high resolution wavelength spectra and x-ray compositional maps, but the most common application of WDS is for quantitative spot analysis. The results of WDS spot analysis is usually presented as mass concentrations of each element or as mass concentrations of the appropriate oxides. In this study, the elemental mass concentration representation will be used since it is most suited for the data analysis we envision. Table 5.1 shows a typical WDS spot analysis results of an OPC sample.

5.1.3 Experimental Setup and Accelerating Voltage

Once a flat and clean surface is obtained as detailed in chapter 4, the sample is coated with a 25 nm carbon layer to prevent charging of the sample surface when exposed to the electron beam of the WDS test. Carbon coating is required to increase the surface’s electrical and thermal conductivity, and to enhance the SE and BSE signal [38]. Carbon coating was performed through evaporation method, in which a conductive metal (carbon) is heated to its vaporization temperature in a high vacuum (~10^-2 torr) and the evaporated carbon atoms condense on the surface of the sample. The thickness of the carbon coating is a critical parameter for both imaging and chemical analysis. A too thick coating will obscure the surface details, while a too
thin layer will charge the surface and damage the sample. The thickness of coating is controlled by monitoring the color of an evaporated layer of carbon deposited on a highly polished brass surface which is blue for a 25 nm carbon coat [28]. 25 nm of carbon coating prevents charging and simultaneously is two orders of magnitude smaller than the excited depth of the electron probe. A flat surface and carbon coating are required for a quantitative WDS test, but the most important parameter that specifies the interpretation method is the accelerating voltage of the test.

To study the effect of accelerating voltage on WDS data, a publicly available Monte Carlo simulation software (CASINO) [27] was employed. With CASINO, it was possible to study the extent of electrons penetration and the spatial energy distribution inside the surface of the sample as well as the intensity and origin of the x-ray emission. Figure 5-6 shows the simulated trajectories and extent of 500 electrons penetrating inside the surface of a C-S-H gel (C1.4-S-H4) of 2.12 g/cm^3 density and 1 μm beam width. The simulation shows a significant increase of electron depth as the accelerating voltage is increased; from 500 nm at 6 kV to 2,500 nm at 15 kV. Figure 5-6 shows the extent of electron depth. The BSE are generated from about 20% of the total depth of the electrons trajectory which implies that the resolution of the BSE images, in addition to the accelerating voltage, is controlled by the width of the beam which is controlled by the aperture of the electron beam. But for EDS and WDS analysis, what matters most is the energy distribution which excites the x-rays. Figure 5-7 shows the energy distribution of the electrons inside the surface of the sample as simulated by CASINO for the same C-S-H sample. If we investigate the depth at which the beam has more than 6 keV energy for the different accelerating voltage, it appears that a 6 kV accelerating voltage activates a volume of size 100 nm, while it excites a depth of 1,500 nm at 15 kV.

The goal of this analysis is to select the appropriate accelerating voltage for our study, and thus we need to determine the depth of x-ray emission and identify how it relates to the accelerating voltage of different elements. Figure 5-8 shows the depth of x-ray origin and intensity distribution for different elements at different accelerating voltages on the C-S-H gel. From this simulation it appears that the excitation depth is directly related to the accelerating voltage. This is consistent with the found energy distribution. If the same simulation is carried out on C4AF as shown in figure 5-9, we notice the different excitation depth for the different
Figure 5-6: Monte Carlo simulation (run on CASINO), showing the trajectories of 500 electrons accelerated at 6-15 kV with a beam radius 1μm into a C-S-H gel.
Figure 5-7: Monte Carlo simulation (run on CASINO) showing spatial energy distribution of 10,000 simulated electrons at different accelerating voltages and 1μm beam width. The material used is a Jennite based C-S-H (C_{1.7}-S-H_{4}) with 2.12 density. (a) Energy distribution for a 6 kV beam where most of the beam energy diminishes are less than 500 nm inside the surface of the sample. (b) Energy distribution for 9 kV voltage where most of beam energy diminishes at less than 900 nm inside the surface of the sample. (c) At 12 kV it reaches 1,500 nm, and (d) at 15 kV it reaches 2,200 nm.
Figure 5-8: Intensity of X-Ray emission of different elements at different accelerating voltages. Lighter elements produce higher x-ray intensities (oxygen is lighter than silicon, and silicon is lighter than calcium).

Elements at the same accelerating voltage. The difference in excited depth converges to a single depth as the accelerating voltage is increased to 15kV where all elements are measured within the same interaction volume.

Wong and Buenfeld [73] verified the applicability of Monte Carlo simulations for cement-based materials, and showed that the size of interaction volume and sampling volume of backscattered electrons is a strong function of the beam energy independent of probe size. The authors also showed that the interaction volume in cement-based materials is more spherical than pearl-shaped (Figure 5-7).

To support the simulations with experimental data, a WDS test was run on an OPC sample (RHA400) at four different accelerating voltages 6, 9, 12, and 15 kV, as shown in figure 5-10. At 6kV accelerating voltage, the yield total was low for a significant fraction of the probes; and iron was not measured as the energy of the beam was smaller than the ionization energy of iron. From the same figure it also appears that the calcium content of CH is decreases as the accelerating voltage increases until it converges to 33% at 15 kV which is the realistic atomic percent of calcium in Ca(OH)$_2$ = CH.

To ensure that all elements are excited from the same interaction volume and to guarantee a high signal to noise ratio, 15kV was used throughout this study.
Figure 5-9: Intensity of x-ray emission of different elements at 15 kV accelerating voltage into the surface of the sample. (a) 6 kV is smaller than the ionization energy required for iron and that is why iron is not present. (b) Iron x-rays originate from half the depth from which aluminum and oxygen originate. (c) At 12 kV accelerating voltage, depth of x-ray generation for different elements is converging but iron is still excited from 2/3 the depth of other elements. (d) At 15 kV, x-rays are originating from a very similar volume.
Figure 5-10: WDS results on sample RHA400 at different accelerating voltages. The plots show the Ca atomic % vs Si atomic %, and the grey scale represents the yield total after deleting all probes with yield totals below 60%.
Table 5.2: Backscattering coefficients for different phases present in hardened cement paste. They are a direct function of the mean atomic number of the phase [73].

5.2 Nature of Hardened Cement and Spatial Distribution of Different Hydration Products

Backscattered electron images of a polished cement sample can be used to distinguish different hydration products based on their grey level in the image, which is a function of the mean atomic number [53] [54]. It is possible to distinguish four phases in hydrated cement paste from a BSE image, where the brightest represents un-hydrated clinker, light grey portlandite (CH), dark grey C-S-H and other hydration phases, and finally the black region of the image corresponds to pores in Figure 5-11. By means of image analysis, it is possible to resolve these four components and measure their relative proportions and spatial distribution except for pores, which are hard to separate from the dark appearance of C-S-H. Table 5.2 lists the backscattering coefficient for the prominent phases of hydrated cement, which will help through this study to resolve the spatial distribution of these phases.

The choice of magnification requires a compromise between image resolution to discriminate different phases, and a representative sampling without undue effort [45] [59]. BSE imaging and EDS elemental maps will be used to study the spatial distribution of the different hydration phases, while chemical composition will be analyzed later using WDS technique.

Figure 5-12 shows the contrast in grey scale between the four major clinker phases of ordinary portland cement which compares perfectly with intensities listed in table 5.2. It is
important to understand the levels of grey for the different phases in cement in order to successfully interpret the BSE images of our samples. Starting with one of the reference samples, a BSE image of RHA400 is shown in figure 5-13 at a magnification of X250. Portlandite in this sample is present in a wide range of sizes ranging from tens of microns down to a size that is too small to be distinguished in this figure. The same applies to the un-hydrated clinkers, except that the smaller sizes of un-hydrated clinkers are mostly C4AF. The C-S-H phase is the matrix in which all other phases are embedded and subsequently assumes a wide range of characteristic sizes.

To investigate the spatial distribution of the different phases at a higher magnification, figure 5-14 shows that all phases can be intimately mixed at a sub micron scale. It shows as well that although C-S-H is the matrix into which all the other phases are embedded. CH can be considered as part of that matrix and is intimately mixed with C-S-H which will complicate the WDS analysis as discussed later.

Figure 5-15 combines BSE image and EDS elemental concentration maps of sample RHA500. This figure confirms the interpretation of BSE images for different grey levels.

Finally, figures 5-16 and 5-17 show the spatial distribution of the residual RHA at different
5.3 History of EPMA Investigation of Cement Pastes

Our investigation is far from being the first to employ EPMA in the study of cementitious materials, and it is worthwhile to study the use of this technique in the past to explore the influence of different experimental parameters and look at methods of data interpretation. The historical application of EPMA which most interests us, is its use in the determination of the Ca/Si ratio of C-S-H in cementitious material. A large number of studies have reported a wide range of value of the Ca/Si ratio based on EPMA studies, and we present a (non-exhaustive) summary of these tests in Table 5.3. We will look at the different experimental parameters and methods of data interpretation which were used as a precursor to the development of our own method.

The first three columns of Table 5.3 report the minimum, mean and maximum values of the Ca/Si ratios found in various investigations in order to make the results comparable. In some studies, all three results are reported; in others only the minimum and maximum values or the determined value are available. The number of EPMA probes of the C-S-H phase in these studies range from several carefully located point probes to several hundred distributed probes.

---

1This section is inspired by the review by James Vanzo in his master thesis [71].
Figure 5-13: Spatial distribution of unhydrated clinker and hydration products in hardened ordinary portland cement paste of w/c = 0.4 (sample RHA400). White is representative of un-hydrated clinkers, light grey of portlandite, dark grey of C-S-H matrix, and the pores are black.
Other studies found explicit differences between two types of C-S-H, typically identified as inner product (Ip) and outer product (Op) C-S-H, and the results of these studies are reported in a similar format in Table 5.4. Again, the number of probes in the studies ranged from several-wherein the authors visually identified a hydration phase as either Ip or Op C-S-H under an SEM and then determined the Ca/Si ratio of the observed spot with an EDS in order to make this distinction to several hundreds- such as the study of Richardson and Grove [52] who ran a 50x50 grid of EPMA probes spaced at 1 micron. These authors measured calcium, silicon, and other elemental percentages at these points and developed a set of criteria for distinguishing between inner and outer product C-S-H:

1. Ip C-S-H was regarded as having Mg>0 and Op C-S-H as having Mg = 0. This criterion is supported by TEM analyses of Ip and Op C-S-H and by earlier work by Taylor and Newbury [63] showing that magnesium does not migrate away from the inner product region during hydration, and therefore can be used as a chemical marker of the grain boundaries (and thus the division between Ip and Op C-S-H).

2. All values with Ca/Si > 2 were excluded to account for the effect of inclusion of portlandite
Figure 5-15: BSE image and elemental concentration maps of sample RHA500 at X250 magnification showing the spatial distribution of hydration products and the unhydrated clinker. (a) BSE image in which the light grey is portlandite, white is unhydrated clinker, dark grey is the C-S-H matrix. (b) Silicon EDS intensity map: black is portlandite and unreacted clinker and Ca, dark red is the C-S-H matrix. (c) Calcium EDS intensity map: light green is the portlandite and unreacted clinkers. (d) and (e) high concentration of aluminum and iron represent the unreacted C4AF. (f) shows higher concentration of magnesium around C4AF grains.
Figure 5-16: A close-up at X1000 magnification on sample RHA420 showing residual RHA particles with about 10 μm width.
Figure 5-17: Spatial distribution of hydration products and the unhydrated clinker in sample RHA620. (a) BSE image: the light grey is portlandite, white is unhydrated clinker, dark grey is the C-S-H matrix. (b) Silicon EDS intensity map, bright red is the unreacted RHA, black is portlandite and unreacted clinker, dark red is the C-S-H matrix. (c) Calcium EDS intensity map: light green is portlandite. (d) and (e) display high concentration of aluminum and iron representative of un-reacted C4AF. (f) shows higher concentration of magnisium around C4AF grains.
<table>
<thead>
<tr>
<th>Ca/Si ratio of C-S-H</th>
<th>Value</th>
<th>Paste</th>
<th>w/c</th>
<th>Age</th>
<th>Voltage</th>
<th>Surface</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min</td>
<td>Max</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.35</td>
<td>1.65</td>
<td>OPC</td>
<td>0.5</td>
<td>28-90d</td>
<td>12kV</td>
<td>Polished</td>
<td>64</td>
</tr>
<tr>
<td>1.5</td>
<td>1.7±0.1</td>
<td>C3S</td>
<td>0.5</td>
<td>24w</td>
<td>15kV</td>
<td>Polished</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>OPC</td>
<td>0.6</td>
<td>1-185d</td>
<td>20kV</td>
<td>Fracture</td>
<td>24</td>
</tr>
<tr>
<td>1.54</td>
<td>1.9±0.2</td>
<td>C3S</td>
<td>0.4</td>
<td>3.5y</td>
<td>?</td>
<td>Fracture</td>
<td>25</td>
</tr>
<tr>
<td>2.1</td>
<td>2.5</td>
<td>C3S</td>
<td>0.5</td>
<td>1y</td>
<td>20kV</td>
<td>Fracture</td>
<td>39</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>C3S</td>
<td>0.5</td>
<td>1y</td>
<td>20kV</td>
<td>Polished</td>
<td></td>
</tr>
<tr>
<td>1.68±0.01</td>
<td></td>
<td>C3S</td>
<td>0.5</td>
<td>9y</td>
<td>15kV</td>
<td>Polished</td>
<td>13</td>
</tr>
<tr>
<td>1.7±0.05</td>
<td></td>
<td>OPC</td>
<td>0.5</td>
<td>8d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1±0.2</td>
<td></td>
<td>OPC</td>
<td>0.7</td>
<td>2.5y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.82±0.11</td>
<td></td>
<td>Concrete</td>
<td>0.5</td>
<td>10y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.7±0.9</td>
<td></td>
<td>Concrete</td>
<td>0.55</td>
<td>10y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.97±0.26</td>
<td></td>
<td>Concrete</td>
<td>0.67</td>
<td>10y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.72</td>
<td></td>
<td>C3S</td>
<td>0.45</td>
<td>23y</td>
<td>10kV</td>
<td>Polished</td>
<td>62</td>
</tr>
<tr>
<td>1.78</td>
<td></td>
<td>C2S</td>
<td>0.45</td>
<td>23y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.86</td>
<td></td>
<td>OPC</td>
<td>0.45</td>
<td>23y</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3: Direct measurement by EDS of the Ca/Si ratio in C-S-H gel in number of studies [71].

in the probes.

3. An upper limit was placed on the (Al+Fe)/Ca ratio.

In particular, we are interested in criteria no. 2 of Richardson and Groves as it is a means of identifying C-S-H in a quantitative fashion from the composition data provided by grid EPMA, that is a large number of EPMA probes placed in a grid so as to sample a large number of representative point compositions. The issue of grid EPMA data interpretation will be revisited at the end of this section.

5.3.1 Data Interpretation

The compositional heterogeneity of cement paste is unavoidable in in-situ chemical analysis—it exists on all scales, but it can be quantitatively considered in the case of a probe which samples a mixture of two or more pure components. Chatterji [13] considered that every EPMA probe samples an excited volume composed of a certain proportion of C-S-H and CH. For such a volume the count ratio of Si to Ca x-ray photons is given by:

\[
\frac{I_{Si}}{I_{Ca}} = \frac{f_1(V_{C-S-H})}{f_2(V_{C-S-H})} + f_3(V_{CH})
\]  

(5.4)
Table 5.4: Direct measurements by EDS of the Ca/Si ratio in inner product (Ip) and outer product (Op) C-S-H in a number of studies

<table>
<thead>
<tr>
<th>Ca/Si ratio of C-S-H</th>
<th>w/c</th>
<th>Age</th>
<th>Voltage</th>
<th>Surface</th>
<th>Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min Value Max Paste w/s Age Voltage Surface Study</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ip 1.8 - 2.0 C3S 0.5 1y 20kV Etched [39]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Op 1.6±0.1 - - - C3S 0.6 1m 30kV Etched [58]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ip 2.1±0.2 - - OPC 0.3 5y 10kV Polished [49]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Op 2.7±0.6 - - OPC 0.6 5y -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ip 1.9±0.4 - - OPC 0.4 2y 15kV Polished [52]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Op 2.6±0.9 - - OPC 1.99 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ip 1.33 1.65±0.14 1.99 OPC 1.99 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Op 0.40 1.78±0.12 1.99 OPC 1.99 -</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Where I's are x-ray counts, V's are the fractional volumes of the component in the excited volume, and f's are the proportionality constants. The volume is assumed to be completely occupied by C-S-H and CH:

\[ V_{C-S-H} + V_{CH} = 1 \]  

It is apparent from Eq. (5.4) that the Ca/Si ratio of C-S-H can be ascertained directly when the volume of CH at a probe site is zero. At this point, the measured intensity of Si to Ca will be at a maximum, and so it follows that a probe of "pure C-S-H" can be identified from large number of probes of our assumed C-S-H/CH mixture by identification of the \[ \frac{f_{Si}}{f_{Ca}} \] maximum. Figure 5-18 shows a frequency plot obtained by Chatterji for 100 spot analyses of a fully hydrated C3S sample. The measured maximum of \[ \frac{f_{Si}}{f_{Ca}} \] corresponds to a Ca/Si ratio of 1.68±0.01. The author makes a further argument that the actual Ca/Si ratio will not be the \[ \frac{f_{Si}}{f_{Ca}} \] maximum but the extrapolation of the probability density function (PDF) to zero frequency due to a possible smearing of a C-S- H/CH mixture across the surface of the material as a result of the grinding and polishing procedure and missing contribution from the tail of the electron beam. In the case of the data in Figure 5-19, an extrapolation to zero frequency yields a Ca/Si ratio of 1.62. By an indirect CH extraction method, the author determined a Ca/Si ratio of 1.58 for the pure C-S-H phase, strengthening his argument for extrapolation to zero frequency as the best method for interpretation of EPMA data.
Figure 5-18: Results of spot analysis carried out on C₃S pastes. The two extremes are the individual measured values; other points are means of the relevant changes. The horizontal diameter of the rings represents the uncertainty range [13].

Figure 5-19: Ca/Si ratios for 5 yr, 0.6 w/c inner hydrate. Total number of results 55, 9 with Ca/Si >4. Adapted from [50].
Rayment and Majumdar [50] also randomly sampled many points of cement hydration products in their extensive analyses of a wide variety of portland cements. Figure 5-19 shows the distribution of Ca/Si ratios which they found from 55 EPMA probes on the "inner hydrate" of a portland cement paste. It is interesting to note the similarity between their distribution and that of Chatterji—that is, a strong peak with a long tail progressing towards higher Ca/Si (or lower Si/Ca) ratios. Rayment and Majumdar refined the analysis of the distribution by considering that silicon could be replaced in C-S-H by aluminum, sulfur, or iron. Figure 5-20 displays the resulting distribution of the Ca/(Si+Al+S+Fe) ratio for the same paste shown in Figure 5-19. The authors concluded that because of the effect of the substitutional ions the range of values representative of EPMA probes of a pure C-S-H phase were best determined by the peak in the Ca/(Si+Al+S+Fe) PDF, as indicated by the arrows on the x-axis in Figure 5-20. Values outside this range could be deemed impure, that is mixed with some other phase, most likely CH.

Rayment and Majumdar [50] applied their method of data interpretation to a number of portland cement samples with a range of w/c and found an interesting result. They note an inverse relation between Ca and w/c ratio and consider the possibility that the pure C-S-H is not really pure but is an intermix of C-S-H and microcrystalline CH due to differences in hydration for the lower w/c pastes (i.e. w/c = 0.3). However, they rejected this hypothesis on the basis that the amount of other elements (Si,Al) does not decrease proportionally to the increase in calcium.

Bonen and Diamond [6] investigated the different hydration phases by running 204 EDXA analyses on a 3-day-old ordinary portland cement paste prepared at water-to-cement ratio of 0.4 with deionized water. Location of the analyses were selected to cover the different hydration products. Then they reviewed the composition of these phases on ternary diagrams of the major elements Ca, Si, Al, Fe, and S. Figure 5-21 shows the diagrams used by the authors to visualize and analyze the data; C-S-H corresponds to the dense cluster with Ca content around 0.7 and a modest (Al+Fe) content i.e., a slight elevation above the base of the triangle. The authors then plotted the separate hydration phases on separate ternary fields for the analyses.

Bonen and Diamond found that C-S-H gel derived from in situ hydration of larger cement grains is chemically somewhat different from C-S-H gel in smaller particles making up the
groundmass of the hydrated cement paste, where the mean value for gross Ca:Si ratio observed for the solid phenograms C-S-H gel is 2.1 and the net value of the mean after subtracting mixed CH, was 1.7 to 1.8 and they found that groundmass C-S-H is in fact an intimate mixture of C-S-H and CH.

5.4 WDS data interpretation and clustering

EPMA has a long history of being applied to different materials— metal, ceramics, polymers and especially geo-materials. The application of EPMA is straight-forward when applied to homogeneous materials or materials with a heterogeneity scale that is much greater than the characteristic size of the EPMA probe on the micron scale. In this case, a single probe represents the chemical composition of a single phase. The problem could be further simplified, if the porosity scale of the tested material is much greater or much smaller than the interaction volume of the EPMA probe. Neither of these conditions apply to cement! Cement is a highly heterogeneous material over a wide range of scales from nanometers to 100’s of microns; and the porosity scale also varies over a wide range of scales. Moreover to add to the complexity of the problem, ionic substitutions are very common in cement paste.

The EPMA studies presented in section 5.3 show a range of each parameter of the EDS test,
Figure 5-21: Ternary plots of the analyses of all particles analysed. (a) data as presented on the Ca-(Al+Fe)-Si ternary field; (b) data as presented on the Ca-S-(Al+Fe) ternary field [6]. Tie lines connect the average C-S-H gel composition of amorphic ground mass particles to the theoretical compositions for calcium hydroxide (CH), ettringite, monosulfate, and ferrite.

but methods of analysis and data interpretation are more or less the same as discussed in section 5.3.1. The method developed in this section proposes a new way to interpret EPMA data that allows an improved understanding of the complex spatial distribution and the determination of the chemical composition of the primary hydration products (C-S-H, CH, AFm, AFt) using clustering techniques.

In the majority of EPMA studies of cement, EDS was employed for the chemical analysis rather than WDS. WDS was used by Vanzo and Ulm [71] for this purpose, but in this study, we will push it a step further. Instead of using a set of combinations of elements in a bivariate mixture model, we propose a multivariate model in which each element is considered individually. Complete details of the method are presented in this section preceded by a review of the clustering technique.

5.4.1 Grid EPMA

A specific location can be picked under an SEM to run an EPMA analysis and measure the chemical composition of that particular spot, like the case of some of the studies discussed in
section 5.3. That probe can represent a single phase or a mixture of two or more pure phases depending on the location of the probe. A number of these probes can be run to determine the chemical composition of certain phases within acceptable error. Another method used for EPMA analysis is to run a grid of probes without any control of the location and then study the result which will include both pure and mixture phases.

5.4.2 Cluster Analysis

Assuming a composite composition of the cement paste where each phase has a distinct chemical composition with some variations due to ionic substitutions and measurement accuracy, one can identify the properties of each phase by separating similar chemical compositions measured by a grid WDS test. For this task, we employ the MCLUST clustering algorithm [30].

Cluster analysis is an unsupervised learning technique used for classification of data. Data elements are partitioned into groups called clusters that represent proximate collections of data elements based on a distance or dissimilarity function. The strength of this technique stems from its ability to determine the number of clusters in a data set and the uncertainty of observations belonging to a cluster based on statistical criteria. In this investigation we apply this technique using the R package MCLUST [1] [31], a contributed package for normal mixture modeling and model-based clustering. It provides functions for model-based approaches assuming a variety of data models and implements maximum likelihood estimation and Bayes criteria to identify the most likely model and the number of clusters. The provided functions in MCLUST package identifies the optimal model based on Bayesian criteria (BIC) for Expectation Maximization algorithm (EM) initialized by hierarchical clustering for various parameterization of the Gaussian model [31] [33] [30].

In model-based clustering, the data are considered as a mixture density \( f(x) = \sum_{k=1}^{G} \tau_k f_k(x) \), where \( f_k(x) \) is the probability density function of the observations in group \( k \), and \( \tau_k \) is the probability that an observation belongs to the \( k \)th component ( \( \sum_k \tau_k = 1 \)). Each component is usually represented by Gaussian or normal distribution which is characterized by the mean \( \mu_k \) and the covariance matrix \( \Sigma_k \) with the probability density function:

\[
\phi(x_i; \mu_k, \Sigma_k) = \frac{\exp\{-\frac{1}{2}(x_i - \mu_k)^T \Sigma_k^{-1}(x_i - \mu_k)\}}{\sqrt{\det(2\pi \Sigma_k)}}. \quad (5.6)
\]
The likelihood for data consisting of $n$ observations assuming Gaussian mixture model with $G$ components is given by:

$$
\prod_{i=1}^{n} \sum_{k=1}^{G} \tau_k \phi(x_i; \mu_k, \Sigma_k).
$$

(5.7)

For a fixed number of components $G$, the model parameters $\tau_k$, $\mu_k$, and $\Sigma_k$ are estimated via the EM algorithm initialized by hierarchical model-based clustering. EM iterates between two steps: the expectations step (E-step), and the maximization step (M-step). In the E-step, matrix $z$ is calculated such that $z_{ik}$ is the conditional probability that reading $i$ belongs to group $k$ given the current parameter estimates. In the M-step, the maximum likelihood of the parameters is estimated given $z$. Geometric features (shape, volume, orientation) are identified by the covariance matrix $\Sigma_k$, which may be parameterized to impose constraints across components. Geometric constraints in multivariate normal mixtures can be imposed through eigenvalue decomposition of the covariance matrix $\Sigma_k$ in the following form [32]:

$$
\Sigma_k = \lambda_k D_k A_k D_k^T
$$

(5.8)

where $D_k$ is the orthogonal matrix of eigenvectors, $A_k$ is a diagonal matrix whose elements are proportional to the eigenvalues, and $\lambda_k$ is a constant of proportionality. $D_k$ governs the orientation of the $k$th mixture component, while $A_k$ identifies its shape, and $\lambda_k$ determines its volume which is proportional to $\lambda^d \det(A_k)$. These parameters ($\lambda_k, D_k, A_k$) are considered as independent sets of parameters, and can be constrained to be the same for each component or allowed to vary among components. Various model options are available in R package MCLUST. In one dimension, two models are available: $E$ for equal volume and $V$ for varying variance. In more than one dimension, the model identifiers refer to the geometric characteristics of the model. For example, EVI denotes a model in which the volumes of all clusters are equal, the shapes of the clusters are allowed to vary, and the orientation is the identity matrix. The rest of the available models are shown in table 5-22.

The best model can be identified by fitting models with different parameterization and/or number components to the data by maximum likelihood determined by the EM algorithm, and then by implementing a statistical criterion for model selection. MCLUST uses the Bayesian Information Criterion (BIC) as model selection criterion.
5.4.3 WDS data analysis and presentation

Dimensional transformation of the data set can help the clustering algorithm to accurately separate the different components, which might not be possible to achieve on the data set in the original format. In WDS clustering many forms of the data can be used as an input for the clustering algorithm, but atomic percentages prove to be the best choice to separate the different hydration phases. For that purpose, the atomic percentages of all the elements in certain probes are calculated from the mass percent measured by WDS test (for sample WDS results, see table 5.1) except for hydrogen which is ignored completely from atomic percents since it was not measured by WDS in the first place.

Once atomic ratios are calculated, it is fed to MCLUST to allocate each probe to a certain component assuming a specific number of components. For each number of components, MCLUST allocates the probes according to the Expectation Maximization algorithm (EM) and then calculates the BIC for a number of components as shown in figure 5-23 for sample RHA600. The result of this clustering is the allocation of each probe and the volume fraction of each component for the number of components that has the minimum BIC. Figure 5-24 shows clustering result for sample RHA600. In this figure, different colors represent the components.
and the ellipses are centered on the mean values of the component while the outline covers 3 standard deviations of the assumed bivariate normal distribution. Another output of MCLUST is the conditional probability \( z \) which indicates the probability of each probe to belong to each component. If a probe has high probability in two or more phases it increases the uncertainty of that probe as shown in figure 5-25.

Figure 5-26 shows a sample chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32 x 32 WDS grid spaced at 65 \( \mu \)m to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary, while different colors represent different clusters. The table in the same figure shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate \( z \) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement paste. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase. Composition of the different "poles" is marked on the figure in form of ellipses located on the chemical composition of each of the primary phases in RHA sample. Location of these poles is constant across all samples except for the C-S-H matrix which changes composition depending of the mix design of the sample.

5.5 Summary

In this chapter, we presented a method for the investigation of chemical composition of cement paste at the sub-micron scale. At this scale it becomes possible to quantitatively access the composition of the microstructure of the main hydration products (C-S-H, CH, AFm, AFt). For this purpose, we employ Wavelength Dispersive Spectrometry (WDS) which is more quantitative compared to its counterpart, Energy Dispersive Spectrometry (EDS). Effects of different parameters of WDS test were also investigated in this chapter. The main parameter of WDS test is the accelerating voltage which determines the size of interaction volume of the electron beam.

In this chapter we also investigated the nature and spatial distribution of hydration products in hardened cement paste. For this purpose, we employed a scanning electron microscope.
Figure 5-23: Sample Bayesian Information Criterion (BIC) for different number of components calculated for the models in table 5-22. The results show that 10 components of model "VVV" has the minimum BIC, run on sample RHA600.
Figure 5-24: Clustering results of sample RHA600. The ellipses are centered on the mean values of the component while the outline covers 3 standard deviations of the assumed bivariate normal distribution. Colors and different markers represent different components identified by the clustering algorithm.
Figure 5-25: Plot of Ca vs Si of sample RHA600 showing the uncertainty of each data point. Size of the spots is proportional to the value of uncertainty. The ellipses are centered on the mean values of the component while the outline covers 3 standard deviations of the assumed bivariate normal distribution.
Figure 5-26: Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32 x 32 WDS grid spaced at 65 μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement paste. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
(SEM) to collect backscattered electron (BSE) images of different locations at different magnifications of the sample surface. From BSE images, information about the spatial distribution of C-S-H, CH and un-hydrated clinkers is obtained. To investigate the spatial distribution of other products, we employed elemental concentration maps as generated by energy dispersive spectrometry (EDS).

A brief review of EPMA history on cement and methods of data interpretation is also discussed in this chapter. Finally, an original method for WDS data presentation and interpretation is developed. This method employs statistical analysis tools to separate and determine chemical composition and volume fractions of the different hydration products. We will use this technique extensively in our investigation of rice husk ash doped cement pastes.
Chapter 6

Indentation Analysis

The second pillar of our investigation of rice husk ash cement pastes is nanoindentation analysis. The application of indentation analysis to cement paste samples is enabled by an extensive development of the grid nanoindentation technique for cementitious materials in previous work by Constantinides and Ulm [19], Vandamme and Ulm [69] and Gathier and Ulm [37]. This Chapter is heavily based on the work of these authors. Herein we present the aspects of indentation analysis, which will serve us in the investigation of our reference and rice husk ash materials. We begin with a general presentation of the indentation technique and the theory behind it, starting with the self-similarity of the technique. Then we discuss the methods of extracting elastic and strength properties using indentation data and the generalization of these methods for heterogeneous materials. We then discuss the machinery which was used, and finally present a method of statistical indentation techniques for cementitious materials, similar to the method of statistical EPMA for cementitious materials presented in the previous Chapter. In the last section we present a method for data interpretation first applied by Vanzo and Ulm [71]; and in this study a different statistical software is employed.

6.1 Introduction

The aim of indentation tests is to extract the elastic and hardness properties of materials. An indentation test consists of pushing an indenter of known geometry and mechanical properties orthogonally into the surface of the material of interest. During the indentation test, the
load $P$ applied to the indenter tip and the depth $h$ of the indenter with respect to indented surface are continuously recorded, as shown in Figure 6-1. The resulting $P$-$h$ curve defines the characteristic mechanical properties of the material and is used to extract the elastic, strength and creep properties of the indented material. The indentation data has been traditionally summarized in two parameters; the indentation modulus $M$ and indentation hardness $H$. Using contact mechanics theories, the indentation modulus is related to the elastic properties of the material, while the indentation hardness to the strength properties.

### 6.2 Self Similarity

Self similarity is one of the important features of the indentation test that allows linking measured parameters to material properties\(^1\). A time-developing phenomenon is referred to as self-similar if the spatial distributions of its properties at different times can be obtained from one another by a self similarity transformation [4]. Self-similarity in this context implies that

\(^1\)Inspired by the presentation of M. Vandamme [69].
the displacement fields at any load $P$ can be inferred from the displacement fields at a different load $P_0$. Self similarity depends on three criteria [9]. First, the constitutive relation must be a homogeneous function of the stress or strain. Second, the shape of the indenter probe must be described by a homogeneous function with degree greater than or equal to 1. Finally, the loading at any point must be increasing during the contact process. The following section details the above conditions.

6.2.1 Indenter Shape and Geometric Similarity

The most common indenter probes are shown in Figure 6-2. In practice the pyramidal indenters, such as the Berkovich, Vickers, and Cube-Corner probes, are the most used indenter shapes. Their sharp geometries allow for the testing of volumes of materials smaller than what other geometries can probe. However, this sharp geometry generates stress concentrations so that the material is solicited plastically even at low load magnitudes. For any given probe within a Cartesian coordinate system, $O(x_1, x_2, x_3)$, where the probe tip is at the origin, and $x_3$ going into the depth of the indenter, the height $z$ of the surface of the probe verifies:

$$z(\lambda x_1, \lambda x_2) = \lambda^d z(x_1, x_2) \quad \text{with } \lambda > 0$$

(6.1)

where $d$ is the degree of the homogeneous function. For axisymmetric problems, eq. (6.1) simplifies to

$$z(r) = Br^d$$

(6.2)

where $r$ is the radius of the probe at a given height $z$, and $B$ is a proportionality factor that represents the height at $r = 1$ (Figure 6-3). The degree $d$ and the proportionality factor $B$ for the probes shown in Figure 6-2 are provided in Table 6.1.

Two objects that can be transformed into each other by dilation or contraction are geometrically similar. Applied to the considered indenter geometries in Figure 6-2, all flat indenters are geometrically similar. In contrast, all pyramidal indenter probes are invariant when contracted or dilated. That is, pyramidal and conical indenters are similar to themselves, and said to be geometrically self-similar. Making use of this geometric self similarity, the non-axisymmetric pyramidal probes are often approximated by axisymmetric cones of same degree $d = 1$, which
Figure 6-2: Indenter probes of different geometries.

Figure 6-3: Parameters defining the geometry of an indenter probe. $z$ is the indentation height, and $S$ is the cross sectional area. For an axisymmetric probe, $r$ is the radius. Adapted from [69].
<table>
<thead>
<tr>
<th>Probe type</th>
<th>d</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flat punch</td>
<td>→ ∞</td>
<td>1/(a^n)</td>
</tr>
<tr>
<td>Spherical</td>
<td>2</td>
<td>1/2R</td>
</tr>
<tr>
<td>Conical</td>
<td>1</td>
<td>cot θ</td>
</tr>
<tr>
<td>Pyramidal</td>
<td>1</td>
<td>cot θ_eq</td>
</tr>
</tbody>
</table>

Table 6.1: Degree d of the homogeneous function and proportionality factor B for various indenter probes

<table>
<thead>
<tr>
<th>Probe Type</th>
<th>Equivalent half-cone angle, θ_eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkovich</td>
<td>70.32°</td>
</tr>
<tr>
<td>Vickers</td>
<td>70.32°</td>
</tr>
<tr>
<td>Cube Corner</td>
<td>42.28°</td>
</tr>
</tbody>
</table>

Table 6.2: Equivalent half cone angle for various pyramidal probes

greatly simplify analysis of the indentation experiment. This approximation is obtained by the implementation of an equivalent half cone angle, θ_eq, whose cone gives the same projected contact area for a given depth as the original indenter. The equivalent half-cone angles of common pyramidal probes are provided in Table 6.2.

6.2.2 Material Behavior

The self similarity of an indentation experiment requires that the constitutive relations of the indented material be homogeneous with respect to the resulting strains (or strain rates) or stresses. This means that the operator of constitutive relations $F$, and thus the stress tensor $\sigma(\varepsilon)$, must scale as:

$$F(\lambda \varepsilon) = \lambda^\kappa F(\varepsilon)$$  \hspace{1cm} (6.3)

where $\varepsilon$ is the strain tensor, and $\kappa$ the degree of the homogeneous constitutive function $F$. Linear and nonlinear-elasticity satisfy this requirement provided that [8]:

$$\sigma = C(\varepsilon) : \varepsilon$$  \hspace{1cm} (6.4)

$$C(\lambda \varepsilon) = \lambda^{\kappa-1} C(\varepsilon)$$  \hspace{1cm} (6.5)

where $C(\varepsilon)$ is the secant stiffness tensor. $\kappa = 1$ corresponds to the case of linear elasticity. Eq (6.3) is also satisfied for the case of a rigid plastic limit behavior, for which the stress derives
from the dissipation (or support) function $\sigma : \varepsilon = \pi(d)$ [26]:

$$\sigma = \frac{\partial \pi}{\partial d}(d)$$

(6.6)

where $\pi(d)$ is a homogeneous function of degree 1 with respect to the strain rate $d$, such that:

$$\pi(\lambda d) = \lambda \pi(d)$$

(6.7)

Hence, the yield design solution applied to indentation analysis satisfy self-similarity condition with $\kappa = 0$.

But not all materials satisfy self-similarity condition (6.3). One example of such materials is a linear-elastic perfectly-plastic material, for which $\kappa = 1$ within the elastic domain, and $\kappa = 0$ at the limit of the elastic domain, corresponding to the strength limit. Hence, there is no unique value of parameter $\kappa$ for which condition (6.3) holds for all strain levels eventually present in the indentation test. Therefore, indentation testing performed on linear-elastic, perfectly-plastic materials are not self-similar. In general, whenever the material response of the indented half-space is not governed uniformly by the same class of material behavior characterized by the parameter $\kappa$, the non-homogeneous stress distribution within the indented half-space may imply the loss of self-similarity of the indentation test.

### 6.2.3 Self-Similar Scaling Relations

Provided that conditions (6.1) and (6.3) are satisfied, the loading phase of an indentation test possesses self-similarity. That is, given a known indentation response represented by load $P_0$, indentation depth $h_0$, contact depth $(h_c)_0$, and projected area of contact $(A_c)_0$ (see Figure 6-4), the indentation response $(P, h, h_c, A_c)$ is obtained from a similarity transformation [7]:

$$\frac{P}{P_0} = \left( \frac{h}{h_0} \right)^{2+\kappa(d-1)}$$

(6.8)

For example, for the case of an elastic material ($\kappa = 1$), $P \propto h$ for flat punch, and $P \propto h^{3/2}$ for a spherical indenter. For conical and pyramidal indenters ($d = 1$), $P \propto h^2$ irrespective of the material behavior. This provides a strong argument in favor of using the Berkovich indenter,
as self-similarity will prevail irrespective of the constitutive relations.

Another relation obtained from the self-similarity of the indentation test is [7]:

\[
\frac{h}{h_0} = \left( \frac{A_c}{(A_c)_0} \right)^{\frac{d}{d-1}}
\] (6.9)

A combination of the previous two scaling relations readily shows that the average pressure below the indenter, i.e. the indentation hardness \( H = P/A_c \), scales as:

\[
\frac{H}{H_0} = \left( \frac{h}{h_0} \right)^{\frac{\kappa(d-1)}{d}}
\] (6.10)

As a result, the hardness \( H \) is constant throughout the loading process and does not depend on the applied load for any rigid plastic behavior \( (\kappa = 0) \) or for any pyramidal or conical indenter \( (d = 1) \).

Finally, given that \( A_c = \pi a^2 \), where \( a \) is the contact radius, eq. (6.9) can be written as:

\[
\frac{a^d}{h} = \text{cst.}
\] (6.11)

For axisymmetric probes, for which the contact radius \( a \) and the contact depth \( h_c \) are linked
by \( h_c = Ba^d \), an equivalent expression is given by:

\[
\frac{h_c}{h} = \text{cst}
\]  

(6.12)

Hence, provided self-similarity of the indentation test, the contact height-to-indentation depth ratio, \( h_c/h \), does not depend on the indentation load. This result is of critical importance for indentation analysis and forms the basis of indirect methods of determining the projected area of contact \( A_c \).

### 6.3 Indentation Analysis of Elastic and Strength Properties

#### 6.3.1 Indentation Modulus

The indentation modulus \( M \) of an indentation test is given by:

\[
S = \frac{2}{\sqrt{\pi}} M \sqrt{A_c}
\]  

(6.13)

where \( S = dP/dh \) is the measured initial slope of the unloading branch of the \( P-h \) curve (see Figure 6-1), and \( A_c \) the projected area of contact between the indenter tip and the indented material (see Figure 6-4). This definition of indentation modulus was introduced by Bulychev, Alekhin and Shorshorov, and hence eq. (6.13) is called BASh formula [11]. The application of this solution is challenging since the indentation modulus is measured from the unloading portion of an indentation test, after the plastic domain of the material has already been solicited. However, recent developments have shown that the initial part of the indentation curve measures the elastic properties of the probed material (e.g. [16], [14]).

Another important parameter in the BASh formula is the area of contact \( A_c \). While elastic indentation solutions provide a direct means to determine the contact area \( A_c \) from the contact depth-to-indentation depth relation, \( h_c/h \), (the Galin-Sneddon solution [34], [57], the contact area for other material behaviors, such as elasto-plastic materials, is a priori an unknown of the contact problem. To solve this problem, indirect methods have been developed to determine the contact area in terms of the maximum indentation depth measured in the indentation experiment. One of these methods is the Oliver and Pharr method [47]. Making use of the
self-similarity of the indentation problem, where the contact depth-to-indentation depth ratio is constant, Oliver and Pharr found that:

$$\frac{hc}{h_{\text{max}}} = 1 - \frac{P_{\text{max}}}{E S h_{\text{max}}}$$  \hspace{1cm} (6.14)

where \( \varepsilon = 3/4 \). The contact area is linked to the contact radius \( a \) by:

$$A_c = \pi a^2$$  \hspace{1cm} (6.15)

The contact radius is then determined from the contact depth by Eq. (6.2). Hence, we have sufficient parameters \((A_c, S)\), which can be obtained from an indentation test, to determine the indentation modulus.

In this context, it is worth introducing the link between the indentation modulus and meaningful mechanical properties of the indented material. For the case of isotropic materials, such as cement, the indentation modulus can be linked to the plane-stress modulus through the following formula [56], [34]:

$$M = \frac{E}{1 - v^2}$$  \hspace{1cm} (6.16)

where \( E \) is the Young’s modulus, and \( v \) the Poisson’s ratio of the indented isotropic material.

### 6.3.2 Indentation Hardness

The indentation hardness \( H \) is defined as the average pressure below the indenter:

$$H = \frac{P}{A_c}$$  \hspace{1cm} (6.17)

where \( P \) is the maximum load applied to the indenter and \( A_c \) is the projected area of contact between the indenter tip and the indented material, determined by the Oliver and Pharr method. Hardness is often related to strength properties of materials. For metals, Tabor suggested a rule-of-thumb relation between hardness \( H \) and tensile strength [60]:

$$\frac{H}{\sigma_y} \approx 3$$  \hspace{1cm} (6.18)
However, indentation hardness is not a material property and its physical meaning is still subject to debate [15]. The main limitation to using indentation hardness to back-calculate plastic or strength properties is the non-uniqueness of the solution of the reverse analysis. In fact, for cohesive materials with work-hardening, very different material properties (yield strength-to-Young's modulus ratio and work-hardening exponent) can yield identical indentation hardness values, and even identical loading curves. For the case of cohesive-frictional elasto-plastic material, Ganneau et al. [36] developed a dual indentation approach which allows the determination of cohesion and friction of a Mohr-Coulomb solid from the dependence of the hardness-to-cohesion ratio on the cone angle $\theta$:

$$\frac{H}{C} = \Pi_H(\mu, \theta)$$  \hspace{1cm} (6.19)

where $\mu = \tan \phi$ is the Coulomb friction coefficient. Recent developments by Cariou and Ulm [12] and Gathier and Ulm [37] provide a similar solution for porous cohesive-frictional material whose particle strength behavior is governed by the Drucker-Prager strength model. In particular, the method of Gathier and Ulm provides a means for establishing the relations between measured hardness $H$, porosity (expressed as one minus the packing density $\eta$), and the solid’s cohesion and friction properties ($c^s, \alpha$). The scaling relations follow the form [37]:

$$H = h^s(c^s, \alpha) \times \Pi_H(\alpha, \eta)$$  \hspace{1cm} (6.20)

where $\Pi_H(\alpha, \eta)$ is a dimensionless function to be developed, and $h^s(c^s, \alpha) = \lim_{\eta \to 1} H$ is the asymptotic hardness of cohesive-frictional solid that is governed by a Drucker-Prager strength criterion. This asymptotic value relates to the solid’s cohesion $c^s$, and friction coefficient $\alpha$, by the function [69]:

$$h^s = c^s \times A(1 + B\alpha + (C\alpha)^3 + (D\alpha)^{10})$$  \hspace{1cm} (6.21)
in which:

\[
\begin{align*}
A &= 4.76438 \\
B &= 2.5934 \\
C &= 2.8160 \\
D &= 1.6777
\end{align*}
\]

The dimensionless function \( \Pi_H(\alpha, \eta) \) depends on the packing density \( \eta \) and the friction coefficient \( \alpha \), and is given by the following expression:

\[
\Pi_H(\alpha, \eta) = \Pi_1(\eta) + \alpha(1 - \eta)\Pi_2(\alpha, \eta)
\]

where \( \Pi_1(\eta) \) and \( \Pi_2(\alpha, \eta) \) are given by:

\[
\Pi_1(\eta) = \frac{\sqrt{2(2\eta - 1)} - (2\eta - 1)}{\sqrt{2} - 1} (1 + g(1 - \eta) + h(1 - \eta)^2 + j(1 - \eta)^3)
\]

\[
\Pi_2(\alpha, \eta) = \frac{2\eta - 1}{2}(k + m(1 - \eta) + p(1 - \eta)\alpha + q\alpha^3)
\]

with fitted parameters:

\[
\begin{align*}
g &= -5.3678 \\
k &= 6.7374 \\
h &= 12.1933 \\
m &= -39.5893 \\
j &= -10.3071 \\
p &= 34.3216 \\
q &= -21.2053
\end{align*}
\]

The previous relations are valid for a porous composite composed of a granular material.
6.4 Indentation into a Heterogeneous Material

6.4.1 Grid Indentation Technique

The application of the indentation technique to a heterogeneous material is challenging as it is difficult to choose to indent on a specific material phase with sufficient repeatability. To address this challenge, Ulm and co-workers [17] [65] [18] [66] [20] [21] developed the so-called grid indentation technique, which consists of performing a large number of indentations over the surface of heterogeneous material of interest. Provided the adequate choices for the indentation depth and grid size, each indentation experiment could be considered as statistically independent, and statistical techniques may be applied to analyze the results.

The grid indentation concept can be illustrated by considering the following thought-experiment of two materials of different mechanical properties as shown in Figure 6-5. A random indentation on the sample surface provides access to the properties of either of the phases given that the indentation depth is much smaller than the characteristic size of the two phases. In contrast, a much deeper indentation depth compared to the characteristic size of the phases provides access to the homogenized response of the two phases. This thought-experiment shows how the classical indentation test can be applied to heterogeneous materials provided an adequate choice of indentation depth. This requires a large array of indentations followed by statistical analysis of the data to separate the mechanical properties of individual phases.

6.4.2 Scale separability

The grid indentation technique introduces a new length scale to the problem, the grid size must be chosen properly to achieve statistical independence in the sampling process. The grid size $L$ must be much larger than the imprint of the indentation test. To avoid sampling effects, a large number $N$ of tests is necessary. Furthermore, to obtain the properties of individual phases, the indentation depth $h$ must be much smaller than the length scale of individual phases. These conditions can be summarized as:

$$h << D << L\sqrt{N}$$  \hspace{2cm} (6.27)
Figure 6-5: Schematic of the grid indentation technique showing massive array of indentations on a heterogeneous material. Top: indentations with large depth (h >> D) gives the homogenized response of the material. Bottom: indentations with low depths (h << D) gives the properties of individual constituents [17].
In addition, because the analysis of the indentation tests evokes continuum mechanics theory, the indentation test must conform to the scale separability condition of continuum mechanics:

\[
d << l << h
\] (6.28)

where \( l \) is the characteristic size of the representative elementary volume, which must be larger than the characteristic size of the largest heterogeneity \( d \) contained in the representative elementary volume (rev), and smaller than the indentation depth \( h \).

### 6.5 Packing Density Scaling Relations

A variety of imaging techniques have provided ample evidence that the C-S-H matrix is composed of elementary nano-particles whose smallest dimension is on the order of 5 nm. The space not occupied by solid particles forms the gel porosity, which is fundamental for the understanding of the link between C-S-H microstructure and mechanical properties. C-S-H microstructure refers to the morphology and assembly of C-S-H solid particles.

#### 6.5.1 Indentation Modulus-Packing Density Scaling Relations

Recall the indentation modulus \( M \) determined from an indentation test by means of BASH formula (eq. 6.13):

\[
M \overset{\text{def}}{=} S \frac{\sqrt{\pi}}{2\sqrt{A_c}}
\] (6.29)

were \( S = (dp/dh)_{h=h_{max}} \) is the initial contact stiffness measured during unloading, and \( A_c \) the projected area of contact between the indenter tip and the indented material determined with the Oliver and Pharr method. The indentation modulus is representative of the elasticity content of the indented material as discussed in section 6.3.1. For a two phase material (pore and solid), the indentation modulus \( M \) thus is representative of the elastic properties of the material. In particular, the indentation modulus \( M \) depends on the elastic properties of the solid \((m_s, \nu_s)\), which we consider constant for the rev subjected to the indentation load, and the microstructure (porosity \( \phi \), or alternative packing density, \( \eta = 1 - \phi \)). The following dimensionless relation
summarizes the above conditions:
\[
\frac{M}{m_s} = \Pi_M(\nu_s, \phi) \quad (6.30)
\]

where \(\Pi_M\) will be defined based on the chosen morphology to characterize the microstructure of the solid-pore composite. Based on experimental evidence found by Constantinides and Ulm [19], the morphology deemed most relevant to our material is a granular morphology with spherical particles. The polycrystal scheme, developed independently by Hershy [41] and Kroner [46], is best suited to model the nanogranular morphology. In this model, it is impossible to determine one dominating matrix phase among all phases present in the composite. In this case, \(\Pi_M\) in eq. 6.30 becomes [19]:

\[
\Pi_M^{SC} = \frac{M^{SC}}{m_s} = \mathcal{M}^{SC} \frac{9\eta \gamma_s + 4M^{SC} + 3\gamma_s)(3\gamma_s + 4)}{4(4M^{SC} + 3\gamma_s)(3\gamma_s + 1)} \quad (6.31)
\]

where \(M^{SC}\) is the composite indentation modulus, \(\gamma_s = 2(1 + \nu_s)/3(1 - 2\nu_s) > 0\), and \(\mathcal{M}^{SC}\) is the composite shear-to-solid shear moduli ratio:

\[
\mathcal{M}^{SC} = \frac{1}{2} - \frac{5}{4}\phi - \frac{3}{16}\gamma_s(3 - \phi) + \frac{1}{16}\sqrt{144(1 - \gamma_s) - 480(1 - \phi) + 400(1 - \phi)^2 + 408\gamma_s(1 - \phi) - 120\gamma_s(1 - \phi)^2 + 9\gamma_s^2(3 - \phi)^2} \quad (6.32)
\]

Relation 6.31 is plotted in Figure 6-6. The figure shows that the change in poisson’s ratio has a little effect on the relation. We also notice that the spherical granular morphology is characterized by a percolation threshold at \(\eta_0 = 1/2\); that is, a packing density below which the granular composite has no stiffness.

### 6.5.2 Hardness-Packing Density Relations

Recall the indentation hardness determined from an indentation test:

\[
H = \frac{P}{A_c} \quad (6.33)
\]
Figure 6-6: Normalized homogenized indentation modulus $M/m_s$ versus packing density $\eta$ for a self consistent scheme. Adapted from [69].

As discussed in section 6.3.2, the hardness is representative of the strength properties of the material. Thus, the indentation hardness of a two phase composite system consisting of a solid and pores depends on three parameters: the strength properties of the solid phase (the cohesion $c_s$ and the friction coefficient $\alpha_s$), the microstructure described by the packing density or equivalently the porosity $\phi = 1 - \eta$, and the geometry of the indenter probe $\theta$. The above parameters can be summarized by the following formula:

$$\frac{H}{h_s} = \Pi_H$$

(6.34)

where $h_s$ is the asymptotic hardness of a cohesive-frictional solid phase that obeys the Drucker-Prager criterion. $h_s$ is independent of the morphology and assumed to be an intrinsic value of the solid. It is given by eq. 6.20. In return, function $\Pi_H(\alpha_s, \eta)$ is given by Eqs. (6.23) - (6.26).

Figure 6-7 presents a sampling of results for the the polycrystal morphology in terms of relationships between packing density and hardness-to-cohesion ratios for various friction coefficients. The fitting function links the measured indentation hardness $H$, the solid hardness $h_s$, and...
the solid friction angle $\alpha$, and the packing density $\eta$ for cement paste indentation tests.

### 6.6 Indentation Equipment

Nanoindentation experiments for this study were performed using a nano-hardness tester from CSM Instruments SA (Peseux, Switzerland) located in the Department of Civil and Environmental Engineering at MIT. The force is applied electromagnetically by passing a current through a coil mechanically connected to the tip. The displacement is measured via the change in voltage of a parallel plate capacitor. The indentation depth is measured with respect to the thermal calibration ring. The indenter is supplied with an optical microscope so that the surface may be visually identified before being indented. The sample and the indenter are housed in a sealed box to minimize temperature drifts and the mechanical and acoustic noise. The apparatus is capable of applying a maximum load of 300 mN (resolution 40 nN). The maximum displacement is 20 $\mu$m (resolution 0.04 $\mu$m).
6.6.1 Calibration of Machine

Several calibrations are required to ensure that the measured load and displacement provide meaningful results that can be related to the indented material only.

Shape Area Function

In indentation testing, projected area of contact is an important parameter that need to be known to make sure that the data analysis provides meaningful results. The projected area of contact as a function of indentation depth $A_c(h_c)$, necessary to calculate indentation properties ($M$ and $H$), is obtained from Oliver and Pharr method (section 6.3.1), which provides an estimate of the contact depth $h_c$ and, hence, the function $A_c(h_c)$ can be precisely determined.

In theory, for perfectly sharp Berkovich tip, the area function is well defined. In reality, however, the Berkovich indenter has some level of bluntness, usually a radius of curvature greater than 30 nm. This bluntness can have significant effects on the results, especially for shallow indentations. For this reason, the area function $A_c(h_c)$ must be carefully calibrated. $A_c(h_c)$ can be determined by atomic force microscopy (AFM) or scanning electron microscopy [17]; however, these are time consuming methods. Instead, $A_c(h_c)$ is usually determined indirectly by indentation on a
material whose mechanical properties are well-known (e.g., fused silica, which has an indentation modulus $M = 72$ GPa). $A_c$ can then be determined by the BASH formula (Eq. 6.29) and $h_c$ with the Oliver and Pharr method. A function is fit to the measured $h_c$ and $A_c$ values of the form:

$$A_c(h_c) = C_1 h_c^2 + C_1 h_c + C_1 h_c^{1/2} + C_1 h_c^{1/4} + \ldots$$

(6.35)

where $C_1$ is usually fixed to the area-to-depth constant of the perfectly sharp indenter ($C_1 = 24.58$ for a Berkovich indenter) and $\{C_i\}_{i>1}$ are the factors that capture the bluntness of the tip.

A well-polished fused silica sample was used for the area calibration where a set of 160 indents was run on the sample at 16 different loads ranging from 1 mN to 200 mN to cover a penetration depth range from 70 nm to 1,200 nm. Loads were selected such that the range penetration depths covers the penetration depths of the several phases present in the hardened cement paste at 2 mN maximum load as will be discussed in section 6.7.

**Electronic-Mechanical Interface**

The interface between mechanical parts and electronics must be well defined and calibrated frequently, in particular, the load versus applied current and the depth versus change in capacitance. The load applied to the specimen is proportional to the current passed into the loading coil. The proportionality factor is calibrated every two years by hanging weights of precisely known mass on the indenter and measure the current necessary to bring the indenter back to its initial position. On the other hand, the displacement of the indenter is measured by a change in capacitance in a parallel plate capacitor. The proportionality factor between change in depth and change in capacitance must be calibrated every two years by indentation on a calibrated piezoelectric crystal with a spherical indenter.

**Frame Compliance**

The frame of the indenter deforms in response to the load applied to the sample. Hence, the measured indentation depth is a linear combination of the real displacement in the sample ($h$)
and the movement of the frame \((h_{frame})\):

\[
h_{meas} = h + h_{frame}
\]  

(6.36)

The frame compliance can be modeled as a linear spring of compliance \(C_f\):

\[
h_{frame} = PC_f
\]

(6.37)

where \(P\) is the applied load. Due to the specific design of the CSM indenter, the frame compliance is fixed, \(C_f = 0.1 \text{ nm/mN}\), and requires no calibration.

**Thermal Drift**

Thermal drift is the variation in depth measurements in an indentation test resulting from thermal expansion or contraction of the sample or indentation apparatus during an indentation test. The CSM indenter is designed such that it does not require thermal drift correction. This is because the depth is measured in reference to a thermal ring that sits on the sample surface, and hence, acts as a floating reference. This means that the movement of the reference ring will be the same as the thermal drift of the sample, and this can be easily removed from the measured displacement (see figure 6-8).

**Pre-Test Calibration**

Prior to each grid indentation test, the indenter is depth-calibrated to locate the surface of the sample and reduce the test time. Depth calibration is a semi automated process that starts with upward movement of the sample until it comes into contact with the reference ring (Figure 6-8) which will remain in contact with the surface of the sample during the entire test. Then, the indenter tip approaches the sample at a high speed (100 mm/min) and plunges into the surface of the sample until the speed is reduced by a "delta slope factor" (usually 25% for cement paste). Then the depth is recorded to estimate the location of the surface in the z-direction. During this process, the user defines the approximate range within which the surface of the sample is expected to be located. During the indentation test, the indenter will descend rapidly until it reaches this range; once in this range, the tip will start to move at user defined lower
speed as it approaches the surface. For this reason, the definition of this range is an important step in setting up the indentation test: Making the window too large will greatly increase the time of the grid test; making it too small entails the risk of having the indenter tip plunge into the sample without ever realizing that it has. This range is about 5\( \mu \text{m} \) above the surface of the sample in our test and the approach speed was 2,000 nm/min.

### 6.7 Statistical Analysis of Nanoindentations

In this section we present the statistical nanoindentation analysis method on cementitious materials. This method was originally developed by Constantinides and Ulm [19] and subsequently refined by Vandamme and Ulm [69]. Our presentation is inspired by the work of Vanzo and Ulm [71]. The goal of this method is to extract the mechanical properties of the different phases of hardened cement paste in a way similar to the statistical analysis of chemical composition presented in chapter 5. For a heterogeneous material like cement, we must carefully design the indentation test to sample the properties on a meaningful scale and capture, at the same time, the heterogeneous response of the material.

#### 6.7.1 Indentation Test and Loading Profile

A single indentation test is designed to determine the mechanical properties of the individual hydration products. We recall the scale separability condition which will allow us to apply the indentation analysis developed in this chapter to a solid-pore composite.

\[
d << l << h
\]

(6.38)

\( l \) is the scale of the \( \text{rev} \) from which mechanical properties are extracted, \( h \) defines the scale of mechanical solicitation of the indentation test, and \( d \) defines the scale of the solid or pore in the solid-pore composite. We also need to consider that the volume of material solicited by the indentation test must be small enough not to be influenced by heterogeneities on a larger scale, which in this case is the scale of the microstructure of C-S-H gel. Constantinides and Ulm [19] referenced the thin-film analogy to ensure that the measured elastic properties do not diverge.
by more than 10% from the intrinsic elastic properties of the phase:

\[
\frac{h}{D} \leq \frac{1}{10}
\]  

(6.39)

We can combine criteria (6.39) and (6.38) to define a range of acceptable interaction length scales for indentation of cementitious materials:

\[
d_0 << h_{\text{max}} << d_I/10
\]  

(6.40)

where \(d_0 \simeq 5\, \text{nm}\) is the size of the C-S-H particles, and \(d_I\) is the characteristic size of the C-S-H microstructure. Ulm et al. [67] showed the existence of homogeneous material regions extending beyond 3\(\mu\)m in cementitious materials. From this information, we determine that an appropriate depth scale of indentation is:

\[
h_{\text{max}} \simeq 200\, \text{nm}
\]  

(6.41)

However, the indentation test is load controlled. Vandamme and Ulm [69] found that:

\[
P_{\text{max}} = 2mN
\]  

(6.42)

satisfies criterion (6.41) well from trial and error on cement paste. Another advantage of this load is the similarity of the excited volume (1.5\(\mu\)m [70]) of the indentation and the interaction volume of the WDS test.

Finally, the loading profile is additionally defined by the duration of the loading phase \(\tau_L\), the holding phase \(\tau_H\), and the unloading phase \(\tau_U\). The holding phase is of particular importance as it must be long enough to ensure that the measured stiffness is representative of the elastic properties of the indented material but short enough that the measured hardness is representative only of the strength. Vandamme and Ulm [70] found by convergence that an appropriate loading profile is defined by \(\tau_L = \tau_U = 10\, \text{s}\) and \(\tau_H = 5\, \text{s}\).

The complete parameters of the indentation test are given in table 6.3.
Table 6.3: Indentation parameters as used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Load</td>
<td>2 mN</td>
</tr>
<tr>
<td>Loading Rate</td>
<td>12 mN/min</td>
</tr>
<tr>
<td>Holding Time at Max. Load</td>
<td>5 s</td>
</tr>
<tr>
<td>Unloading Rate</td>
<td>12 mN/min</td>
</tr>
<tr>
<td>Surface Seek Speed</td>
<td>2000 nm/min</td>
</tr>
<tr>
<td>Delta Slope Factor</td>
<td>25%</td>
</tr>
<tr>
<td>Data Acquisition Frequency</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>

6.7.2 Grid Indentation

For this experimental investigation, two different grid geometries were employed, a 30x30 indents covering an area of 2 mm by 2 mm at 69 μm spacing between indents or three grids with 20x20 indents each of these grids cover the area of 0.4 mm by 0.4 mm at 20 μm spacing. Spacing of 20 μm is a sufficient distance to exclude interaction effects between indents, and at the same time, covers a representative area of the sample.

6.7.3 Data Interpretation

Statistical Analysis

Grid indentation tests provide a bivariate data set \((M, H)\) with 900-1,200 entries. Our method of analyzing this data differs from that used to analyze similar data by Constantiniides and Ulm [19] and Vandamme and Ulm [69]. The first used a deconvolution technique in which they manually fit a number of probability density functions (PDF) to the experimental frequency plot (a normalized histogram) of each measured parameter separately. Vandamme and Ulm automized the process in an effort to make the deconvolution results independent of the operator. In the deconvolution technique, the two variables are linked only by the volume fractions, and the authors used the cumulative distribution function (CDF) instead of the PDF to fit the data.

Here we use the MCLUST cluster analysis algorithm presented in section 5.4.2 which keeps the bivariate data set completely coupled. This method is identical to the method used by Vanzo and Ulm [71] except for the employed algorithm.

The analysis with MCLUST is identical to the clustering of EPMA data presented in section 114.
Table 6.4: The range of mechanical properties identified for each of the C-S-H phases in an investigation of a wide range of cement pastes by Vandamme and Ulm. M and H are in GPa.

<table>
<thead>
<tr>
<th></th>
<th>LD C-S-H</th>
<th></th>
<th>HD C-S-H</th>
<th></th>
<th>UHD C-S-H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_{LD}$</td>
<td>$H_{LD}$</td>
<td>$\eta_{LD}$</td>
<td>$M_{HD}$</td>
<td>$H_{HD}$</td>
<td>$\eta_{HD}$</td>
</tr>
<tr>
<td>16-26</td>
<td>0.27-0.88</td>
<td>0.62-0.71</td>
<td>27-40</td>
<td>0.74-1.45</td>
<td>0.69-0.82</td>
</tr>
</tbody>
</table>

5.4.2. The only difference is that we are using a bivariate data set ($M$ and $H$) while in WDS analysis we use a multivariate data set (Si, Al, Fe and Ca).

For indentation on hydrated cement paste, we expect the component model to reflect the mechanical properties of the C-S-H phases determined in the literature [19] [69]. We can compare the mechanical component model with the work of Vandamme and Ulm [69] as a reference. The authors studied a wide range of cement pastes and reported the values of indentation modulus, indentation hardness and the C-S-H packing density which they obtained for low-density (LD), high-density (HD) and ultra-high-density (UHD) C-S-H. The values they found are reported in table 6.4. All phases with indentation modulus higher than 65 GPa and indentation hardness higher than 3 GPa can be identified as un-reacted clinker materials [48].

Clustering results will be presented as shown in figure 6-9 in the form of a Mechanical Component Diagram (MCD) showing the mechanical response of the sample, in addition to a table listing the mechanical properties of each component. Displayed in the plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.

**Determination of C-S-H Microstructure by Indentation**

The grid indentation technique discussed in section 6.7.2 entails performing a large number of indentations $N$ on the surface of a cement sample. As a results, a large number of these indentations $N'$ will be performed on the C-S-H phase. Thus, given that the C-S-H phases are a mix of C-S-H solid and pores, it is possible to determine the microstructure properties of

---

2 This section is inspired by the presentation of Vandamme [69].
Figure 6-9: Mechanical Component Diagram (MCD) showing the mechanical response of sample RHA400, in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
the C-S-H phase (C-S-H solid properties and the packing density). Using the theory developed in this chapter, requires the solid to be isotropic, which for C-S-H is unlikely at the scale of a particle. However, since C-S-H is amorphous as a whole, in which particles are expected to show little order from one to another, we associate with the C-S-H crystal an isotropic mechanical equivalent which we call the C-S-H solid.

Making use of the indentation moduli \( \{M_i\}_{i=1..N'} \) and indentation hardness \( \{H_i\}_{i=1..N'} \) for the hydration phases, the microstructure properties (indentation modulus \( m_s \), Poisson’s ratio \( \nu_s \), indentation hardness \( h_s \) and friction coefficient \( \alpha_s \) of the solid phase, packing density \( \eta_0 \) at percolation, as well as a set of \( \{\eta_i\}_{i=1..N} \) of local packing densities) are determined by minimizing the sum of quadratic error between model predictions and the experiment:

\[
\min_{\left(\{m_s, \nu_s, h_s, \alpha_s, \eta_0\}, \{\eta_i\}_{i=1..N'}\right)} \sum_{i=1}^{N'} \left[ \left(1 - \frac{m_s \Pi_M(\nu_s, \eta_i, \eta_0)}{M_i}\right)^2 + \left(1 - \frac{h_s \Pi_H(\alpha_s, \eta_i, \eta_0)}{H_i}\right)^2 \right] \tag{6.43}
\]

Fixing some parameters helps in simplifying the minimization process:

- Given a nanogranular morphology, the percolation threshold is 0.5 (see Figure 6-6).

- The asymptotic indentation modulus of the quasi-isotropic solid particles is fixed at \( m_s = 65 \) GPa, derived from MD simulations and confirmed from extrapolation of nanoindentation results.

- Given the negligible effect of Poisson’s ratio on the indentation modulus - packing density scaling relations for any morphology, the particular value of \( \nu_s = 0.2 \) simplifies the dimensionless \( M - \eta \) scaling relation:

\[
\frac{M}{m_s} = \Pi_M(\nu_s = 1/5, \eta_i, \eta_0 = 1/2) = 2\eta - 1 \geq 0 \tag{6.44}
\]

Assuming that the same discussion applies for strength properties, the dimensionless relations \( \Pi_M(\nu_s = 1/5, \eta_i, \eta_0 = 1/2) \) and \( \Pi_H(\alpha_s = 1/5, \eta_i, \eta_0 = 1/2) \) given by equations (6.44 and 6.23), will be used to solve the two solid strength properties \( (h_s, \alpha_s) \) and \( N' \) packing density.
values from:

$$\min_{(m_s, v_s, h_s, \alpha_s, \eta_0)} \sum_{i=1}^{N'} \left[ \left( 1 - \frac{m_s \Pi_M(v_s = 1/5, \eta_1, \eta_0 = 1/2)}{M_i} \right)^2 + \left( 1 - \frac{h_s \Pi_H(\alpha_s = 1/5, \eta_1, \eta_0 = 1/2)}{H_i} \right)^2 \right]$$

(6.45)

where $m_s = 65$ GPa.

Finally, filtering the indentations performed on the hydration products out of a grid indentations must be considered. Given that the indentation modulus $m_s$ of the C-S-H solid is considered to be an upper bound of all C-S-H phases, this is achieved through elimination of un-hydrated clinker after clustering.

### 6.8 Summary

In this chapter, we presented a brief review of the grid nanoindentation technique for cementitious materials as developed in previous work by Constantinides and Ulm [19], Vandamme and Ulm [69] and Gathier and Ulm [37].

We now dispose of two complementary methods for the assessment of the chemo-mechanical signature of cementitious materials at the sub-micron scale: a statistical WDS technique for the chemical make-up, a statistical grid indentation technique for mechanical properties. The methods will be employed in the next part to our RHA-containing samples.
Part III

Results and Discussion
Chapter 7

Chemical Analysis Results

This part of the thesis presents the chemical and mechanical analysis on the complete set of cement paste samples discussed in chapter 3. This chapter presents the results of our EPMA analysis which shows the effect of RHA on the chemical composition of the different hydration phases, especially that of C-S-H. The next chapter presents the nanoindentation results, which show that the w/b ratio has a bigger impact on the mechanical response at the nano scale compared to the incorporation of RHA, which increases the hardness of the paste at that scale. Finally, the last chapter of this part discusses the results.

7.1 Clinker Reference Sample

In order to properly understand the chemical composition of cement paste samples, we start with the chemical composition of un-hydrated clinker in an OPC sample. Figure 7-1 shows the compositional component diagram (CCD) of the clinker sample where phase 1 is C$_3$S, phase 2 C$_2$S, whereas phase 4 is C$_3$A and phase 5 C$_4$AF. The other phases are mixtures between the main clinker phases. Chemical composition of clinker as shown in figure 7-1 compares very well to the values available in literature as detailed in table 2.3 except for Aluminate which is partially mixed with Ferrite as can be clearly noticed in a plot of Fe vs Si in figure 7-2.

The remainder of this section presents the results of the statistical EPMA analysis on our samples (see chapter 3), starting with the reference OPC samples prepared at different w/b ratios (0.4, 0.5 and 0.6) without any RHA. Then, in the following section, we investigate
Figure 7-1: Chemical make up of sample CLINCH P-876 displayed in the form of the compositional component diagram (CCD) and given in tabular format for two 30x30 WDS grid spaced at 50μm to cover a total area of 1.5 mm x 1.5 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-2: Chemical make up of sample CLINCH P-876 displayed in the form of the compositional component diagram (CCD) for two 30x30 WDS grid spaced at 50μm to cover a total area of 1.5 mm x 1.5 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation.
the effect of RHA on the chemical composition of the different hydration phases, and in the microstructure of the paste in general.

7.2 Chemical Composition of Reference Samples

The compositional component diagram (CCD) of the reference samples are shown in figures 7-3 to 7-8. These figures include the WDS data presented in different plots focusing on calcium, silicon and aluminum in addition to a table for each sample summarizing the numerical results of the clustering. The reason behind the selection of these elements and other details are discussed in section 5.4.3. Following is a description of each sample.

7.2.1 Sample RHA400

Sample RHA400 is the pure OPC sample with water-to-binder ratio of 0.4. As illustrated in figures 7-3 and 7-4, the main hydration phase (C-S-H) is phase number 4 with, 26.1% volume fraction. This volume fraction is not the precise volume fraction of all the C-S-H present in the sample, rather, it just represents the pure C-S-H phase ignoring all mixture phases. Phase 9 is very close to pure portlandite (CH); but it is still mixed with some C-S-H. Phases 1 and 3 are mixtures between CH and C-S-H. Phase 7 is mostly C₄AF. Phases 5 and 6 are the AFm phase mixed with C-S-H. Phase 9 represents the un-hydrated C₃S and C₂S phases. Phase 2 is mostly a mixture between CH and C-S-H but mixed with AFm.

7.2.2 Sample RHA500

Sample RHA500 is the pure OPC sample with water-to-binder ratio of 0.5. As illustrated in figures 7-5 and 7-6, the main hydration phase (C-S-H) is phase number 1, with 16.3% volume fraction, representing the pure C-S-H phase ignoring C-S-H in mixture phases. Phase 4 is very close to pure portlandite (CH) but intermixed with some C-S-H. Phases 5 is a mixture between CH and C-S-H. Phase 9 is mostly C₄AF. Phases 2 and 3 are the AFm phases mixed with C-S-H. Phase 6 represents the un-hydrated C₃S and C₂S phases. Phases 7 and 8 are mostly a mixture between CH and C-S-H, but mixed with AFm.
Figure 7-3: Chemical make up of sample RHA400 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-4: Chemical make up of sample RHA400 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.1 for details).
Figure 7-5: Chemical make up of sample RHA500 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-6: Chemical make up of sample RHA500 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.2 for details).
7.2.3 Sample RHA600

Sample RHA600 is the pure OPC sample with water-to-binder ratio of 0.6. As illustrated in figures 7-7 and 7-8, the main hydration phase (C-S-H) is phase number 1, with 27.1% volume fraction, representing the pure C-S-H phase ignoring C-S-H in mixture phases. Phase 6 is very close to pure portlandite (CH) but intermixed with some C-S-H. Phases 5 is a mixture between CH and C-S-H. Phase 10 is mostly C₄AF. Phase 9 is the AFm phase mixed with C-S-H. Phase 8 represents the un-hydrated C₃S and C₂S phases. Phases 1, 2 and 3 are mostly a mixture between CH and C-S-H but mixed with AFm. Phase 7 is a mixture between AFm and C-S-H.
Figure 7-7: Chemical make up of sample RHA600 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-8: Chemical make up of sample RHA600 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.2.3 for details).
7.3 Chemical Composition of RHA Samples

This section presents the WDS result on samples where cement is partially replaced by RHA. The compositional component diagrams (CCD) of these samples are shown in figures 7-9 to 7-20. These figures include the WDS data presented in different plots focusing on calcium, silicon and aluminum in addition to a table for each sample summarizing the numerical results of the clustering. The reason behind the selection of these elements and other details are discussed in section 5.4.3. The RHA inclusion in these samples is recognized by the long tail of the C-S-H phase pointing towards 33% atomic silicon content which is the percentage expected for pure SiO$_2$ forming the majority of RHA. Following is a description of each sample.

7.3.1 Sample RHA410

Sample RHA410 has 10% of solid mass as RHA prepared at water-to-binder ratio of 0.4. As illustrated in figures 7-9 and 7-10, the main hydration phase (C-S-H) is phase number 1, with 25.2% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the mixture phases. There is no distinct phase for pure portlandite (CH) as a result of low volume fraction of portlandite which must have disappeared after reacting with RHA to form C-S-H. Phases 9 and 4 are mixtures between CH and C-S-H. Phase 7 is most likely C$_4$AF. Phases 5 and 6 are the AFm phase mixed with C-S-H. Phase 10 represents the un-hydrated C$_3$S Phase. Phase 3 is mostly a mixture between CH and C-S-H but mixed with AFm; and finally, Phase 8 is a mixture between RHA and C-S-H. There is no separate RHA phase due to the small volume fraction of residual RHA.

7.3.2 Sample RHA420

Sample RHA420 has 20% of solid mass as RHA prepared at water-to-binder ratio of 0.4. As illustrated in figures 7-11 and 7-12, the main hydration phase (C-S-H) is phase number 4, with 10.1% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the mixture phases. There is no distinct phase for pure portlandite phase (CH) in the sample. Phase 4 is a mixture between CH and C-S-H. Phase 9 is most likely C$_4$AF. Phases 1 and 3 are AFm phases mixed with C-S-H. Phases 2 and 10 represent un-hydrated C$_3$S and C$_2$S mixed
Figure 7-9: Chemical make up of sample RHA410 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-10: Chemical make up of sample RHA410 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.1 for details).
with C-S-H. Phases 1 and 3 are mixtures between C-S-H and AFm. Phases 6 and 8 are mixtures between RHA, CH and C-S-H. Phase 7 is almost pure RHA.

7.3.3 Sample RHA510

Sample RHA510 has 10% of solid mass as RHA prepared at a water-to-binder ratio of 0.5. As illustrated in figures 7-13 and 7-14, the main hydration phase (C-S-H) is phase number 1, with 25.3% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the mixture phases. There is no distinct phase for pure portlandite (CH) as a result of low volume fraction of portlandite which disappeared after reacting with RHA to form C-S-H. There is no separate RHA phase due to the small volume fraction of the residual RHA. Phase 7 is a mixture between C₄AF and C-S-H. Phases 2 and 6 are mixtures between C-S-H and AFm. Phase 3 represents the un-hydrated C₃S and C₂S mixed with C-S-H. Phases 4 and 8 are mixed CH and C-S-H. Phase 5 is a mixture between RHA and C-S-H. Phase 7 is a mixture between C-S-H and C₄AF.

7.3.4 Sample RHA520

Sample RHA520 has 20% of solid mass as RHA prepared at a water-to-binder ratio of 0.5. As illustrated in figures 7-15 and 7-16, the main hydration phase (C-S-H) is phase number 5, with 20.23% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the mixture phases. There is no distinct phase for pure portlandite (CH) as a result of low volume fraction of portlandite which disappeared after reacting with RHA to form C-S-H. There is no separate RHA phase due to the small volume fraction of residual RHA. Phase 1 is a mixture between AFm and C-S-H. Phases 2, 4 and 7 are mixtures between CH and C-S-H. Phases 3 and 9 are mixtures between C₄AF and AFm. Phases 6 and 10 are mixtures between C-S-H and residual RHA.

7.3.5 Sample RHA610

Sample RHA610 has 10% of solid mass as RHA prepared at water-to-binder ratio of 0.6. As illustrated in figures 7-17 and 7-18, the main hydration phase (C-S-H) is phase number 1, with 31.54% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the
Figure 7-11: Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-12: Chemical make up of sample RHA420 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.2 for details).
Figure 7-13: Chemical make up of sample RHA510 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-14: Chemical make up of sample RHA510 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.3 for details).
Figure 7-15: Chemical makeup of sample RHA520 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-16: Chemical make up of sample RHA520 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.4 for details).
mixture phases. There is a distinct CH phase, phase 4. Compared to all other RHA containing samples, this sample has a CH phase due to high w/b ratio which forms more CH. There is no separate RHA phase due to the small volume fraction of the residual RHA. Phase 3 is residual C₃S and C₂S. Phase 2 is a mixture between C-S-H and AFm. Phase 5 is a mixture between CH and C-S-H. Phase 6 is a mixture between AFm and C₄AF. Phase 7 is C-S-H mixed with AFm. Phase 8 is a mixture of RHA, C-S-H and CH.

7.3.6 Sample RHA620

Sample RHA620 has 20% of solid mass as RHA prepared at water-to-binder ratio of 0.6. As illustrated in figures 7-19 and 7-20, the main hydration phase (C-S-H) is phase number 1, with 25.8% volume fraction, representing the pure C-S-H phase ignoring the amount of C-S-H in the mixture phases. There is no distinct phase for pure portlandite (CH) as a result of low volume fraction of portlandite which disappeared after reacting with RHA to form C-S-H. There is no separate RHA phase due to the small volume fraction of the residual RHA. Phase 2 is a mixture between C₄AF and AFm. Phase 3 is a mixture between C-S-H and AFm. Phase 4 is a mixture between C-S-H and RHA. Phase 5 is a mixture between CH, C-S-H and RHA. Phase 6 is the residual C₂S and C₃S. Phase 7 is a mixture between C-S-H and CH.

7.4 Summary of the Chemical Analysis

In this chapter we presented the results of our chemical analysis of the complete set of samples. Results are presented in form of Chemical Component Diagrams (CCD) accompanied with details of each component in tabular form. Also presented in this chapter, is the detailed description of each component in each sample.

In all samples, C-S-H phase was recognized as the matrix which in most cases exhibits the highest volume fraction of the hydration products. In all samples, C-S-H was the only pole with heavy density which made it easy to identify this phase. No other phase in hardened cement could be distinguished and discriminated like C-S-H except for some un-reacted C₃S in samples RHA4 as a result of low w/b ratio of 0.4. The low w/b ratio prevented the complete hydration of C₃S, but as w/b ratio was increased in samples RHA5 and RHA6, the residual C₃S phase
Figure 7-17: Chemical make up of sample RHA610 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-18: Chemical make up of sample RHA610 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.5 for details).
Figure 7-19: Chemical make up of sample RHA620 displayed in the form of the compositional component diagram (CCD) and given in tabular format for a 32x32 WDS grid spaced at 65μm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. The table shows the atomic percent of each element in each phase in addition to the yield total (Total), allocation rate (z) and volume fraction of each cluster. Each cluster is representative of a chemically distinct phase within the hardened cement. The number of unique clusters is identified via Bayesian statistics, and the cluster volume fraction is determined from the number of probes comprising that phase.
Figure 7-20: Chemical make up of sample RHA620 displayed in the form of the compositional component diagram (CCD) for a 32x32 WDS grid spaced at 65µm to cover a total area of 2 mm x 2 mm. In CCD, numbering of phases is arbitrary and different colors represent different clusters. Each cluster is representative of a chemically distinct phase within the hardened cement. Different plots are generated to simplify the process of phase separation (see section 7.3.6 for details).
was too small to be recognized as a separate phase.
Chapter 8

Mechanical Analysis

This chapter presents the results of statistical nanoindentation. The method was presented in chapter 6. We start with the OPC samples prepared at different w/b ratios (0.4, 0.5 and 0.6). Then the results for the RHA samples are presented. Results will be reported in form of mechanical component diagram (MCD) accompanied by a table listing all properties as identified by the clustering algorithm. Packing density results will be presented in the form of packing density frequency plot, as discussed in section 6.7.3.

8.1 Nanoindentation on Reference Samples

This section presents the results of the nanoindentation analysis on the reference samples RHA400, RHA500 and RHA600 (see chapter 3 for details of sample composition). Results discussed here for the mechanical signature of pure OPC samples with different w/b ratios are shown in form of Mechanical Component Diagram (MCD) in figures 8-1 to 8-3. These plots display the raw data of indentation Modulus (M) versus the indentation Hardness (H), as well as the clustering results as fitted with the MCLUST cluster analysis algorithm. The properties of each component are listed in a numerical form in the tables attached to these figures. The hydration phases are identified by clustering algorithm as the phases that have an indentation modulus and indentation hardness below the modulus and hardness of C-S-H particles as defined in [48], i.e. $M < m_s = 65$ GPa and $H < h_s = 3$ GPa.
8.1.1 Properties of C-S-H Phases in Reference Samples

Detailed results of the clustering analysis are presented in the mechanical component diagrams (MCD) in figures 8-1 to 8-3 and listed in table 8.1. Along with other phases, the clustering provides mean values of the indentation modulus $M$, indentation hardness $H$ and volume fractions of the three identified C-S-H phases (Low-Density C-S-H (LD), High-Density C-S-H (HD) and Ultra-High-Density C-S-H (UHD)). $M$ and $H$ of these phases do not depend on the water-to-binder ratio; unlike volume fractions which depend on w/b ratio. Average properties of these phases are as follows:

- for LD C-S-H: $M_{LD} = 20.32 \pm 5.57$ GPa, $H_{LD} = 0.68 \pm 0.20$ GPa.
- for HD C-S-H: $M_{HD} = 31.84 \pm 6.68$ GPa, $H_{HD} = 1.19 \pm 0.29$ GPa.
- for UHD C-S-H: $M_{UHD} = 41.39 \pm 9.67$ GPa, $H_{UHD} = 1.84 \pm 0.50$ GPa.

The indentation modulus results compare fairly well with the findings of Vandamme and Ulm [69] for which the following values were reported: $M_{LD} = 23.3$ GPa, $H_{LD} = 0.6$ GPa, $M_{HD} = 30.6$ GPa, $H_{HD} = 0.86$ GPa and for UHD C-S-H $M_{UHD} = 43.2$ GPa, $H_{UHD} = 1.5$ GPa. While values of the indentation modulus are very similar, the indentation hardness values of our samples are around 20% higher than the one reported by Vandamme and Ulm.

In addition to the three identified C-S-H phases, a weak phase is identified in samples with high w/b ratio. This phase has an indentation modulus $M < 15$ GPa and indentation hardness $H < 0.25$ GPa. This phase is shown in table 8.1 as phase MP as it is believed to be dominated by micro pores (MP), typically of a size on the order of the indentation depth $h$; and thus at the limit of the scale separability condition, eq. (6.41)

8.1.2 Solid Properties and Packing Density Distributions of Reference Samples

The microstructure assessment technique provides packing density distributions and particle properties of the C-S-H phases within the hydrated matter (see section 6.7.3).
Figure 8-1: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA400 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus \( (M) \) versus the indentation Hardness \( (H) \). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-2: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA500 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus (M) versus the indentation Hardness (H). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-3: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA600 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus \((M)\) versus the indentation Hardness \((H)\). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Table 8.1: Summary of mechanical properties for the reference samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD is the high-density C-S-H, UHD is the ultra-high-density C-S-H and Clinker stands for un-hydrated clinker. Properties listed include volume fractions, indentation modulus $M$ and indentation hardness $H$ of each phase.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>MP</th>
<th>LD</th>
<th>HD</th>
<th>UHD</th>
<th>Clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA400</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>14.91</td>
<td>51.27</td>
<td>13.86</td>
<td>16.07</td>
</tr>
<tr>
<td></td>
<td>$M$ [GPa]</td>
<td>-</td>
<td>18.62</td>
<td>29.27</td>
<td>41.53</td>
<td>119.48</td>
</tr>
<tr>
<td></td>
<td>$sd(M)$</td>
<td>-</td>
<td>4.44</td>
<td>6.40</td>
<td>7.80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$H$[GPa]</td>
<td>-</td>
<td>0.56</td>
<td>1.05</td>
<td>1.81</td>
<td>9.91</td>
</tr>
<tr>
<td></td>
<td>$sd(H)$</td>
<td>-</td>
<td>0.17</td>
<td>0.28</td>
<td>0.48</td>
<td>-</td>
</tr>
<tr>
<td>RHA500</td>
<td>Vol. Frac. %</td>
<td>24.54</td>
<td>39.39</td>
<td>14.10</td>
<td>16.81</td>
<td>5.17</td>
</tr>
<tr>
<td></td>
<td>$M$ [GPa]</td>
<td>11.04</td>
<td>21.38</td>
<td>34.24</td>
<td>41.24</td>
<td>99.55</td>
</tr>
<tr>
<td></td>
<td>$sd(M)$</td>
<td>4.14</td>
<td>5.97</td>
<td>5.15</td>
<td>11.54</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$H$[GPa]</td>
<td>0.33</td>
<td>0.79</td>
<td>1.23</td>
<td>1.86</td>
<td>7.72</td>
</tr>
<tr>
<td></td>
<td>$sd(H)$</td>
<td>0.17</td>
<td>0.25</td>
<td>0.19</td>
<td>0.52</td>
<td>-</td>
</tr>
<tr>
<td>RHA600</td>
<td>Vol. Frac. %</td>
<td>60.29</td>
<td>25.45</td>
<td>11.74</td>
<td>0.00</td>
<td>2.51</td>
</tr>
<tr>
<td></td>
<td>$M$ [GPa]</td>
<td>11.28</td>
<td>20.96</td>
<td>32.01</td>
<td>-</td>
<td>76.50</td>
</tr>
<tr>
<td></td>
<td>$sd(M)$</td>
<td>0.50</td>
<td>6.30</td>
<td>8.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$H$[GPa]</td>
<td>0.32</td>
<td>0.70</td>
<td>1.29</td>
<td>-</td>
<td>5.09</td>
</tr>
<tr>
<td></td>
<td>$sd(H)$</td>
<td>0.10</td>
<td>0.19</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

C-S-H Particle Properties

The C-S-H particle properties of the reference samples, back-calculated with the microstructure assessment technique (see section 6.7.3) are listed in table 8.2. The hardness of the C-S-H solid, $h_s = 4.12$ GPa $\pm 1.32\%$, shows very little variability in between samples. This implies that the hardness of the C-S-H solid $h_s$ is independent of the water-to-binder ratio. Vandamme and Ulm [69] found that the hardness of the C-S-H solid in 48 cement pastes prepared at w/c ratios ranging from 0.15 to 0.4 to be $h_s = 2.99$ GPa $\pm 6.4\%$ which is 25% lower than the value calculated here. This difference can be a result of the significantly different w/b ratios or the different technique used for the evaluation of the C-S-H solid properties.

In contrast to $h_s$, the cohesion $c_s = 0.54\pm 0.52\%$ and the friction coefficient $\alpha_s = 0.20\pm 0.43\%$ show greater variability; but there is no trend with the w/b ratio.

Packing Density Distributions

Although the phase properties do not change with the w/b ratio, the packing density distributions change dramatically, as can be observed in figures 8-4 to 8-6. The general trend is a shift...
Table 8.2: C-S-H particle properties for the reference samples as calculated from the fitting algorithm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$c_s$ [GPa]</th>
<th>$sd(c_s)$</th>
<th>$\alpha_s$</th>
<th>$sd(\alpha_s)$</th>
<th>$h_s$ [GPa]</th>
<th>$sd(h_s)$</th>
<th>$\eta$</th>
<th>$sd(\eta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA400</td>
<td>0.52</td>
<td>0.0102</td>
<td>0.21</td>
<td>0.0079</td>
<td>4.08</td>
<td>0.0229</td>
<td>0.73</td>
<td>0.061</td>
</tr>
<tr>
<td>RHA500</td>
<td>0.62</td>
<td>0.0033</td>
<td>0.12</td>
<td>0.0027</td>
<td>3.94</td>
<td>0.0071</td>
<td>0.69</td>
<td>0.0963</td>
</tr>
<tr>
<td>RHA600</td>
<td>0.46</td>
<td>0.0020</td>
<td>0.28</td>
<td>0.0022</td>
<td>4.33</td>
<td>0.0097</td>
<td>0.63</td>
<td>0.0658</td>
</tr>
</tbody>
</table>

Table 8.3: Summary of packing density analysis for the reference samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H. For each phase, the table shows the mean packing density and the standard deviation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Packing density</th>
<th>MP</th>
<th>LD</th>
<th>HD</th>
<th>UHD</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA400</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>14.91</td>
<td>51.27</td>
<td>13.86</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>-</td>
<td>0.63</td>
<td>0.73</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>$sd$</td>
<td>-</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>RHA500</td>
<td>Vol. Frac. %</td>
<td>24.54</td>
<td>39.39</td>
<td>14.10</td>
<td>16.81</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>0.57</td>
<td>0.68</td>
<td>0.77</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>$sd$</td>
<td>0.03</td>
<td>0.04</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>RHA600</td>
<td>Vol. Frac. %</td>
<td>60.29</td>
<td>25.45</td>
<td>11.74</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>$\eta$</td>
<td>&lt; 0.6</td>
<td>0.67</td>
<td>0.76</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$sd$</td>
<td>&gt; 0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

to lower packing density with increasing w/b ratio. This translates into an overall lower mean packing for high w/b ratio samples, as shown in table 8.3.

The changes in packing density distributions are a consequence of the changes in volume fractions of the three C-S-H phases within the hydrated matter (see table 8.1). Decreasing the w/b ratio favors denser phases.
Figure 8-4: Graphical presentation of packing density distribution for the different hydration products in sample RHA400, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.
Figure 8-5: Graphical presentation of packing density distribution for the different hydration products in sample RHA500, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.
Figure 8-6: Graphical presentation of packing density distribution for the different hydration products in sample RHA600, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.1 and 8.3.
8.2 Nanoindentation on RHA Samples

This section presents the results of the nanoindentation analysis on RHA samples (RHA410, RHA420, RHA510, RHA520, RHA610 and RHA620); (see chapter 3 for details of sample composition). Results discussed here for the mechanical signature of RHA samples with different w/b ratios are shown in form of Mechanical Component Diagram (MCD) in figures 8-7 to 8-12. These plots display the raw data of indentation Modulus ($M$) versus the indentation Hardness ($H$), as well as the clustering results as fitted with the MCLUST cluster analysis algorithm. The properties of each component are listed in a numerical form in the tables attached to these figures. The hydration phases are identified as the phases that have an indentation modulus and indentation hardness below the modulus and hardness of C-S-H particles as defined in [48], i.e. $M \leq m_s = 65$ GPa and $H \leq h_s = 3$ GPa.

8.2.1 Properties of C-S-H Phases in RHA Samples

Detailed results of the clustering analysis are presented in the mechanical component diagrams (MCD) in figures 8-7 to 8-12 and listed in table 8.1. Along with other phases, the clustering provides mean values of the indentation modulus $M$, indentation hardness $H$ and volume fractions of the three identified C-S-H phases (Low-Density C-S-H (LD), High-Density C-S-H (HD) and Ultra-High-Density C-S-H (UHD)). The mean values of $M$ and $H$ of these phases are found to not depend on the water-to-binder ratio; unlike the volume fractions which display a clear trend in function of the w/b ratio. Average properties of these phases are as follows:

- for LD C-S-H: $M_{LD} = 19.22 \pm 4.01$ GPa, $H_{LD} = 0.59 \pm 0.15$ GPa.
- for HD C-S-H: $M_{HD} = 26.93 \pm 5.82$ GPa, $H_{HD} = 0.94 \pm 0.23$ GPa.
- for UHD C-S-H: $M_{UHD} = 38.72 \pm 9.60$ GPa, $H_{UHD} = 1.84 \pm 0.51$ GPa.

The mean value of mechanical properties of the three C-S-H phases in RHA samples are similar to those found in the reference samples.

In contrast to the reference samples, in RHA samples, the MP C-S-H phase is identified only in samples RHA610 and RHA620; and is not present in samples RHA510 and RHA520. This phase is listed in table 8.4 as phase MP.
Figure 8-7: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA410 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus \( M \) versus the indentation Hardness \( H \). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-8: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA420 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-9: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA510 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-10: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA520 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus (M) versus the indentation Hardness (H). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-11: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA610 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
Figure 8-12: Mechanical Component Diagram (MCD) showing the nanomechanical response of sample RHA620 in addition to a table listing the mechanical properties of each component. Displayed in this plot is the indentation Modulus ($M$) versus the indentation Hardness ($H$). Components are numbered in ascending order according to the mean indentation modulus. The allocation of each experimental point is indicated by its color as shown in the legend. The ellipses are centered on the mean values of the component while the outline covers a 95% confidence interval of the assumed bivariate normal distribution.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Parameter</th>
<th>MP</th>
<th>LD</th>
<th>HD</th>
<th>UHD</th>
<th>RHA</th>
<th>Clinker</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA410</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>22.72</td>
<td>47.76</td>
<td>12.78</td>
<td>6.16</td>
<td>10.59</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>-</td>
<td>20.40</td>
<td>28.78</td>
<td>42.27</td>
<td>52.94</td>
<td>127.94</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>-</td>
<td>4.92</td>
<td>6.99</td>
<td>11.66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>-</td>
<td>0.66</td>
<td>1.00</td>
<td>1.89</td>
<td>4.64</td>
<td>9.98</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>-</td>
<td>0.19</td>
<td>0.26</td>
<td>0.48</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA420</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>44.84</td>
<td>29.59</td>
<td>9.35</td>
<td>9.26</td>
<td>6.96</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>-</td>
<td>22.81</td>
<td>30.33</td>
<td>39.22</td>
<td>49.33</td>
<td>124.29</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>-</td>
<td>4.90</td>
<td>5.77</td>
<td>7.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>-</td>
<td>0.67</td>
<td>1.00</td>
<td>1.61</td>
<td>3.82</td>
<td>10.01</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>-</td>
<td>0.16</td>
<td>0.21</td>
<td>0.34</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA510</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>45.41</td>
<td>33.23</td>
<td>12.53</td>
<td>-</td>
<td>8.82</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>-</td>
<td>18.39</td>
<td>27.10</td>
<td>38.76</td>
<td>-</td>
<td>80.62</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>-</td>
<td>4.41</td>
<td>5.25</td>
<td>7.97</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>-</td>
<td>0.55</td>
<td>0.95</td>
<td>1.97</td>
<td>-</td>
<td>6.88</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>-</td>
<td>0.16</td>
<td>0.22</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA520</td>
<td>Vol. Frac. %</td>
<td>0.00</td>
<td>44.02</td>
<td>35.64</td>
<td>10.17</td>
<td>5.50</td>
<td>4.67</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>-</td>
<td>17.59</td>
<td>25.27</td>
<td>38.70</td>
<td>42.05</td>
<td>108.83</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>-</td>
<td>4.64</td>
<td>6.66</td>
<td>9.12</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>-</td>
<td>0.52</td>
<td>0.87</td>
<td>1.70</td>
<td>5.00</td>
<td>8.13</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>-</td>
<td>0.16</td>
<td>0.26</td>
<td>0.55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA610</td>
<td>Vol. Frac. %</td>
<td>20.59</td>
<td>25.94</td>
<td>29.58</td>
<td>18.62</td>
<td>-</td>
<td>5.27</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>13.20</td>
<td>19.31</td>
<td>25.12</td>
<td>38.92</td>
<td>-</td>
<td>93.30</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>3.52</td>
<td>2.49</td>
<td>4.88</td>
<td>11.87</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>0.46</td>
<td>0.60</td>
<td>0.91</td>
<td>1.81</td>
<td>-</td>
<td>8.47</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>0.19</td>
<td>0.13</td>
<td>0.24</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RHA620</td>
<td>Vol. Frac. %</td>
<td>19.49</td>
<td>38.85</td>
<td>27.07</td>
<td>6.48</td>
<td>-</td>
<td>8.11</td>
</tr>
<tr>
<td></td>
<td>M [GPa]</td>
<td>11.99</td>
<td>16.81</td>
<td>24.98</td>
<td>35.84</td>
<td>-</td>
<td>78.58</td>
</tr>
<tr>
<td></td>
<td>sd(M)</td>
<td>1.85</td>
<td>2.69</td>
<td>5.33</td>
<td>9.43</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>H [GPa]</td>
<td>0.33</td>
<td>0.51</td>
<td>0.88</td>
<td>2.03</td>
<td>-</td>
<td>6.80</td>
</tr>
<tr>
<td></td>
<td>sd(H)</td>
<td>0.08</td>
<td>0.11</td>
<td>0.22</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 8.4: Summary of mechanical properties for RHA samples. MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H and the un-hydrated clinker. Properties listed include volume fractions, indentation modulus M, indentation hardness H of each phase.
Table 8.5: C-S-H particle properties for the reference samples as calculated from the fitting algorithm.

### 8.2.2 Solid Properties and Packing Density Distributions of RHA Samples

The microstructure assessment technique provides the particle properties and packing density distributions of the three C-S-H phases (see section 6.7.3).

#### C-S-H Particle Properties

The C-S-H particle properties of the RHA samples, back-calculated with the microstructure assessment technique (see section 6.7.3) are listed in table 8.5. The hardness, $h_s$, of the C-S-H solid in samples RHA410 and RHA420 is similar to the particle hardness of the reference samples listed in 8.2. In return, the particle hardness in samples RHA510, RHA520, RHA610 and RHA620 is 25% higher than the particle hardness of the reference samples prepared at the same w/b ratio.

On the other hand, the cohesion $c_s = 0.45 \text{ GPa} \pm 0.54\%$ and the friction coefficient $\alpha_s = 0.31 \pm 0.56\%$ show greater variability, but in general exhibit an increase with the decrease of w/b ratio in RHA samples. This is consistent with the hardness model (Eq. ??), that is $h^s = c^s \times F(\alpha)$.

#### Packing Density Distributions

Similar to the reference samples, packing density distributions are mostly affected by w/b ratio as observed in figures 8-13 to 8-18. The changes in packing density distributions are a consequence of the changes in volume fractions of the three C-S-H phases within the hydrated matter (see table 8.6). In return, the RHA content does not affect significantly the packing density distributions.
Figure 8-13: Graphical presentation of packing density distribution for the different hydration products in sample RHA410, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.

Otherwise said, the w/b ratio determines the particle density distribution, while RHA content affect the particle properties.

8.3 Chapter Summary

This chapter presented the results of the statistical nanoindentation analysis on the complete set of RHA samples. The first section of this chapter presented results of statistical nanoindentation analysis on the reference samples. Mechanical properties and packing density distributions of the main three C-S-H phases (LD, HD and UHD C-S-H) are comparable to values found in the literature. Mechanical properties of C-S-H solid particles in the reference samples are
Figure 8-14: Graphical presentation of packing density distribution for the different hydration products in sample RHA420, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
Figure 8-15: Graphical presentation of packing density distribution for the different hydration products in sample RHA510, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
Figure 8-16: Graphical presentation of packing density distribution for the different hydration products in sample RHA520, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
Figure 8-17: Graphical presentation of packing density distribution for the different hydration products in sample RHA610, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
Figure 8-18: Graphical presentation of packing density distribution for the different hydration products in sample RHA620, as calculated from the fitting algorithm discussed in section 6.7.3. Only hydration products as identified in the clustering analysis are considered in this fitting. Phase numbers in this plot represent the same phase numbers in the corresponding MCD plot. Properties of each phase are listed in tables 8.4 and 8.6.
### Table 8.6: Summary of packing density analysis for the RHA samples.

MP is a phase dominated by micro pores, LD is the low-density C-S-H, HD in the high-density C-S-H, UHD is the ultra-high-density C-S-H. For each phase, the table shows the mean packing density and the standard deviation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Vol. Frac. %</th>
<th>Packing density</th>
<th>MP</th>
<th>LD</th>
<th>HD</th>
<th>UHD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Vol. Frac. %</td>
<td>η</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA410</td>
<td>0.00</td>
<td>0.64</td>
<td>0.73</td>
<td>0.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA420</td>
<td>0.00</td>
<td>0.67</td>
<td>0.74</td>
<td>0.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA510</td>
<td>0.00</td>
<td>0.64</td>
<td>0.71</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA520</td>
<td>0.00</td>
<td>0.63</td>
<td>0.70</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA610</td>
<td>20.59</td>
<td>0.64</td>
<td>0.70</td>
<td>0.81</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RHA620</td>
<td>19.49</td>
<td>0.63</td>
<td>0.69</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.01</td>
<td>0.02</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
independent of w/b ratio. In return, packing density distributions changed dramatically with the change in w/b ratio. This change in packing density distributions was mainly a result of the change in the volume fractions of the main three C-S-H phases.

In the second section of this chapter, we presented the statistical nanoindentation analysis on RHA samples. Mechanical properties of C-S-H phases in RHA samples are similar to C-S-H phases in the reference samples. Although C-S-H solid properties did not change across different w/b ratios in the reference samples, it increased in RHA samples with high w/b ratio.

The next chapter is devoted to reconciling this particular nanoindentation signature of RHA materials with the chemical results presented in chapter 7 to ultimately answer the question about the nano-chemo-mechanical nature of C-S-H in RHA materials.
Chapter 9

Discussion

Before starting the discussion of our results, we remind ourselves of the primary research question that we set out to answer: Is Rice Husk Ash (RHA) reactive, does it produce- or contribute to the formation of hydration products? And how does RHA alter the microstructure of cement paste. To answer these questions, 9 cement paste samples were investigated using Wavelength Dispersive Spectrometry (WDS) combined with a statistical analysis tool to assess the chemical composition of these samples; and novel nanoindentation techniques that allow a determination of the mechanical phase properties, volume fractions and packing density distributions of highly heterogeneous materials.

9.1 The Effect of RHA on C-S-H Formation

The WDS results in chapter 7 show that C-S-H, in most samples, is the dominant phase of all hydration products.

For the reference samples, a strong C-S-H pole surrounded by several mixture phases was found (Figures 7-3 to 7-8). The main mixture phase in terms of volume fraction in these samples is a CH–C-S-H mixture. In addition to the strong C-S-H pole and the CH–C-S-H mixture there were other mixture phases that include C₄AF, C₃S and AF₃m.

In samples with RHA, the chemical composition as measured with WDS is similar to that of the reference samples with the addition of a new pole; the RHA. Incorporation of RHA has two primary effects on the composition of cement paste: the first is the decrease in Ca/Si molar
ratio of the C-S-H phase. This change in Ca/Si of C-S-H can be attributed to the reaction of RHA with micro crystalline CH present inside the C-S-H matrix to form more pure C-S-H of a lower Ca/Si ratio. This interpretation is consistent with the second observation of RHA, which is the consumption of portlandite. Figure 9-1(a) shows the relation between Ca/Si molar ratio and the original volume fraction of RHA. The figure shows a perfectly linear relationship between these two parameters at all w/b ratios. The decrease of Ca/Si as RHA increases can be attributed to either the formation of pure C-S-H once all CH has reacted to form C-S-H, or to a solid mixture between RHA and C-S-H at the submicron scale, in which the Ca/Si decreases as a result of probing the physical mixture by WDS (see section 5.1.3). The volume fractions of RHA in figure 9-1(a) were calculated from the original mix design assuming that the total volume would comprise cement, water and RHA.

The volume fraction of portlandite increases as the w/b ratio increases. Yet, it drastically decreases as the RHA content increases. For this reason, portlandite can only be recognized as a separate phase in samples with both high w/b ratio and low RHA content. Although portlandite (CH) is present in large crystals in most samples, it is not recognized as a separate phase except in samples RHA500 and RHA600 in which the high w/b ratio enables the formation of large CH crystals. The reason CH is not recognized as a separate phase in RHA samples is the small volume fraction of the large crystals while most of CH is found in small characteristic sizes.

The same reasoning applies to the volume fraction of CH and C-S-H mixture phase, which is large in the reference samples. Figure 9-1(b) shows the volume fraction of CH and CH-C-S-H mixture as calculated from the cluster analysis. Volume fraction of CH shown in this figure were calculated by separating all phases with Ca/Si ratio greater than that of C3S which has the highest calcium content, if not mixed with CH.

The approximate volume fraction of residual RHA is shown in figure 9-1(c). The figure shows a perfectly linear relation between the original RHA volume fraction and the residual RHA in hardened cement paste while showing an inverse relation between the w/b ratio and residual RHA. As the separation of RHA is a very complicated process, the volume fractions were approximated by separating all the probes with Ca/Si ratio lower than that of the main hydration product of each sample.

Chemical composition and molar ratios of the C-S-H phases in the complete set of samples
Figure 9-1: Summary of the WDS analysis on the complete set of sample. (a) Ca/Si ratio as determined from the pure C-S-H phase. (b) The volume fraction of the residual RHA as separated by the cluster analysis. (c) Portlandite volume fraction including the mixture CH and C-S-H phase as determined from the cluster analysis.
are listed in tables 9.1 and 9.2. Table 9.1 shows that atomic percentage of elements Fe, S and Mg do not change across the entire set of samples. On the other hand, Al atomic percent tends to increase as RHA content increases. Al does not change across the reference samples, but shows a different behavior in RHA samples at different w/b ratios (Figure 9-2(a)). Another interesting observation is that the decrease in Ca/Si in samples prepared at w/b = 0.4 is a result of a slight increase in Si content with significant drop in Ca content. This observation is completely different in samples with w/b ratio of 0.5 and 0.6 in which the Ca content is constant and the drop in Ca/Si is a result of an increase in Si content alone (Figures 9-2(b) and 9-2(c)). These observations lead us to conclude that RHA is "more effective" at higher w/b ratios.

A closer look at the Al and Fe atomic percentages shows that the content of these two elements either increase or staye constant, which implies a pozzolanic reaction. If the reduction in Ca/Si ratio was a result of probing a physically mixed CH and C-S-H, then Al and Fe content should decrease since RHA has an atomic percentage of 0.33% Al and 0.14% Fe.

### 9.2 The Effect of RHA on Nano-Mechanical Properties

Nanoindentation results in chapter 8 show that the mechanical properties of the three C-S-H phases (LD, HD, UHD C-S-H) in the reference samples are similar to those found in the literature:
Table 9.1: Mean chemical composition in atomic % of C-S-H phases in the complete set of samples.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>S</th>
<th>Ca</th>
<th>Mg</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA400</td>
<td>8.94</td>
<td>0.98</td>
<td>0.27</td>
<td>0.62</td>
<td>19.55</td>
<td>0.26</td>
<td>69.37</td>
</tr>
<tr>
<td>RHA410</td>
<td>10.07</td>
<td>1.07</td>
<td>0.30</td>
<td>0.56</td>
<td>18.36</td>
<td>0.23</td>
<td>69.41</td>
</tr>
<tr>
<td>RHA420</td>
<td>10.49</td>
<td>1.02</td>
<td>0.21</td>
<td>0.47</td>
<td>15.71</td>
<td>0.22</td>
<td>71.87</td>
</tr>
<tr>
<td>RHA500</td>
<td>9.15</td>
<td>1.03</td>
<td>0.31</td>
<td>0.63</td>
<td>19.18</td>
<td>0.28</td>
<td>69.43</td>
</tr>
<tr>
<td>RHA510</td>
<td>11.23</td>
<td>1.33</td>
<td>0.30</td>
<td>0.44</td>
<td>19.95</td>
<td>0.28</td>
<td>66.47</td>
</tr>
<tr>
<td>RHA520</td>
<td>12.80</td>
<td>1.38</td>
<td>0.24</td>
<td>0.50</td>
<td>19.18</td>
<td>0.19</td>
<td>65.72</td>
</tr>
<tr>
<td>RHA600</td>
<td>9.06</td>
<td>1.02</td>
<td>0.28</td>
<td>0.46</td>
<td>17.86</td>
<td>0.28</td>
<td>71.04</td>
</tr>
<tr>
<td>RHA610</td>
<td>10.25</td>
<td>1.29</td>
<td>0.32</td>
<td>0.47</td>
<td>17.92</td>
<td>0.25</td>
<td>69.50</td>
</tr>
<tr>
<td>RHA620</td>
<td>11.39</td>
<td>1.29</td>
<td>0.31</td>
<td>0.41</td>
<td>17.94</td>
<td>0.23</td>
<td>68.44</td>
</tr>
</tbody>
</table>

Table 9.2: Different molar ratios in C-S-H phases in the complete set of samples.

<table>
<thead>
<tr>
<th></th>
<th>Al/Si</th>
<th>Ca/Si</th>
<th>Fe/Si</th>
<th>S/Si</th>
<th>Mg/Ca</th>
<th>O/Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>RHA400</td>
<td>0.110</td>
<td>2.186</td>
<td>0.030</td>
<td>0.069</td>
<td>0.013</td>
<td>7.75</td>
</tr>
<tr>
<td>RHA410</td>
<td>0.106</td>
<td>1.823</td>
<td>0.029</td>
<td>0.056</td>
<td>0.013</td>
<td>6.89</td>
</tr>
<tr>
<td>RHA420</td>
<td>0.098</td>
<td>1.497</td>
<td>0.020</td>
<td>0.045</td>
<td>0.014</td>
<td>6.85</td>
</tr>
<tr>
<td>RHA500</td>
<td>0.113</td>
<td>2.097</td>
<td>0.033</td>
<td>0.068</td>
<td>0.015</td>
<td>7.59</td>
</tr>
<tr>
<td>RHA510</td>
<td>0.118</td>
<td>1.776</td>
<td>0.026</td>
<td>0.040</td>
<td>0.014</td>
<td>5.92</td>
</tr>
<tr>
<td>RHA520</td>
<td>0.108</td>
<td>1.499</td>
<td>0.018</td>
<td>0.039</td>
<td>0.010</td>
<td>5.14</td>
</tr>
<tr>
<td>RHA600</td>
<td>0.113</td>
<td>1.972</td>
<td>0.031</td>
<td>0.051</td>
<td>0.016</td>
<td>7.85</td>
</tr>
<tr>
<td>RHA610</td>
<td>0.126</td>
<td>1.748</td>
<td>0.031</td>
<td>0.046</td>
<td>0.014</td>
<td>6.78</td>
</tr>
<tr>
<td>RHA620</td>
<td>0.113</td>
<td>1.575</td>
<td>0.027</td>
<td>0.036</td>
<td>0.013</td>
<td>6.01</td>
</tr>
</tbody>
</table>
- for LD C-S-H: $M_{LD} = 20.32 \pm 5.57$ GPa, $H_{LD} = 0.68 \pm 0.20$ GPa.
- for HD C-S-H: $M_{HD} = 31.84 \pm 6.68$ GPa, $H_{HD} = 1.19 \pm 0.29$ GPa.
- for UHD C-S-H: $M_{UHD} = 41.39 \pm 9.67$ GPa, $H_{UHD} = 1.84 \pm 0.50$ GPa.

These results are also comparable to the mechanical properties of the C-S-H phases in RHA samples:

- for LD C-S-H: $M_{LD} = 19.22 \pm 4.01$ GPa, $H_{LD} = 0.59 \pm 0.15$ GPa.
- for HD C-S-H: $M_{HD} = 26.93 \pm 5.82$ GPa, $H_{HD} = 0.94 \pm 0.23$ GPa.
- for UHD C-S-H: $M_{UHD} = 38.72 \pm 9.60$ GPa, $H_{UHD} = 1.84 \pm 0.51$ GPa.

In addition to the C-S-H phases detailed above, a new phase was identified with very low mechanical properties. This phase is believed to be dominated by micro pores and is referred to as MP C-S-H. MP C-S-H is prevalent in samples with high w/b ratios.

Although the phase properties do not change when modifying the w/b ratio, the packing density distributions change dramatically. The changes in packing density distributions are a consequence of the changes in volume fractions of the three C-S-H phases within the hydrated matter (see figure 9-3). Lower w/b ratios favor the formation of denser phases. MP C-S-H phase disappears or reduce drastically in samples with 20% RHA content, which indicates densification of hydration phases at the micro scale.

The properties of the C-S-H solid in the reference samples is independent of w/b ratio. Solid cohesion $c_s$ and angle of friction $\alpha_s$ show a substantial variability, but exhibit no trend with w/b ratio or RHA content. For samples RHA400, RHA410, RHA420, RHA500 and RHA600, the solid hardness is $h_s \approx 4$ GPa while for samples RHA510, RHA520, RHA610, RHA620, the solid hardness $h_s \approx 4.4 - 5.3$ GPa. This is consistent with the change in Ca/Si ratio found in the samples: as Ca/S-ratio decreases, the particle hardness increases. Here we identify a handshake between chemical and mechanical properties, that may ultimately explain the observed macroscopic strength growth (see section 3.3).

Finally, a new phase is present in RHA samples with indentation modulus $M = 42.05 \pm 11.23$ and indentation hardness $H = 5.00 \pm 2.16$. This phase is clearly shown as phase 4 in sample
Figure 9-3: Volume fractions as measured by nanoindentation clustering. Phases presented are:
MP, the C-S-H phase dominated by micro pores, LD C-S-H, HD C-S-H, UHD C-S-H and UNH, the unhydrated matter including residual RHA and residual clinker.

Figure 9-4: Volume fractions of the different C-S-H phases relative to the volume fraction of the total hydrated matter.
RHA520 and mixed with other phases in sample RHA420 while only a trace of this phase is present in sample RHA620. The mechanical properties of RHA as extracted from these phases are not accurate as these phases generally represent a mixture between RHA and C-S-H. The accurate modulus and hardness of RHA cannot be calculated directly from these tests but is expected to have the mechanical properties of the upper bound of these mixture phases i.e., $M \approx 60 \text{ GPa}$ and $H \approx 10 \text{ GPa}$.

Increase in hardness of the hydration phases with the increase in RHA indicates that we are indenting a physically mixed RHA and C-S-H phase. At the same time, the formation of denser hydration phases and disappearance of MP C-S-H, indicates a pozzolanic reaction. To answer the question of whether the decrease in Ca/Si ratio is due to the physical mixing of RHA and C-S-H or due to the pozzolanic reaction, other tests like X-Ray Diffraction (XRD) are required.

### 9.3 Chapter Summary

This chapter presented a discussion of the results of both statistical EPMA and statistical nanoindentations. WDS test, indicate the formation of new C-S-H phase with lower Ca/Si ratio as the RHA content increases. The formation of this new C-S-H is accompanied by the consumption of CH. Changes in the composition of C-S-H along with the consumption of CH indicates a pozzolanic reaction.

Mechanical properties of the C-S-H phases are independent of RHA and w/b ratio, but the volume fractions of these phases vary with w/b ratio and RHA content. Lower w/b ratio and higher RHA content favor the formation of denser phases. Effect of w/b ratio on the packing density is much larger than the effect of RHA. C-S-H solid hardness was found to be larger in samples with high RHA content and high w/b ratio.

Both, WDS and nanoindentation techniques, provided evidence that RHA has the effect of a pozzolan and simultaneously indicates that RHA can simply be physically mixed with C-S-H. It is thus most likely that the pozzolanic reaction leads to the formation of more C-S-H solid that primarily fill the micropores. This is most likely the reason of the observed macroscopic strength increase. In fact, as micro pores are filled with new C-S-H products, stress concentration are
reduced in the microstructure. In return, the lower Ca/Si ratio of the C-S-H phases which comes along with higher particle hardness indicates a physical mixture between RHA and C-S-H. The C-S-H that fills the micropores thus has a higher strength which further contributes to the observed strength increase.
Part IV

Conclusions and Perspectives
Chapter 10

Conclusions and Perspectives

10.1 Summary of Main Findings

The primary goal of this study is to understand the effect of rice husk ash (RHA) on the chemistry and mechanics of cement paste. Thus, a dual chemical and mechanical investigation was conducted on a set of samples with different RHA contents. These samples were prepared at different water:binder ratios to cover the most common ratios used in the industry. The following summarizes the main findings:

1. Chemical analysis: Chemical analysis shows that the incorporation of RHA in cement paste has two related effects on the chemistry of the paste. The first effect is the consumption of portlandite, where the volume fraction of portlandite in the hardened cement paste is reduced as the volume fraction of RHA increases. This first effect can be related to the second, which is the decrease of the Ca/Si ratio of the main hydration product (C-S-H). This decrease of Ca/Si can be a result of a pozzolanic reaction between microcrystalline portlandite and RHA silica. The reason behind the second effect could not be verified using WDS; but most likely that the particle in RHA materials is a physical mixture of C-S-H and RHA at nanoscales.

2. Mechanical investigation: Mechanical analysis shows that both, the increase in RHA content and decrease in w/b ratio favor the formation of denser C-S-H phases. This densification entails a higher mean packing density of the C-S-H phases. Mechanical analysis
also shows that the C-S-H solid hardness $h_s$ increases for higher w/b ratio and higher RHA content. Given the high value of hardness of RHA, this supports the suggestion that the nano particl of RHA materials is a physical mixture of C-S-H and RHA at nanoscale. Further more, the increase in particle hardness indicates that RHA incorporation is more effective at higher w/b ratios. In general, the effect of w/b ratio on the nano-mechanical properties is much higher than that of the RHA content.

3. The observable macroscopic strength increase is attributable to the combination of two phenomena, particularly at high w/b ratio: (1) the filling of micropores by additional hydration products due to pozzolanic reaction; and (2) higher particle properties due to the physical mixture of C-S-H and RHA at nanoscale.

10.2 Research Contribution

The general contribution of this study is the contribution to experimental nano-chemomechanics of cementitious materials applied to complex systems made of rice husk ash. Along the way, several original method developments were achieved:

1. **Development of a new surface preparation technique:** A smooth, flat, and level surface is crucial for meaningful nanoindentation and EPMA test. The theory and design of these test assumes a flat half-space with minimum roughness. This was the motivation for the development of this polishing technique.

2. **Development of a new statistical electron-probe microanalysis (EPMA):** This is not the first study in which a statistical EPMA analysis is employed. Vanzo and Ulm [71] developed a similar method for the analysis of carbonated cement. The main difference between our method and Vanzo’s is the use of multivariate mixture analysis instead of a bivariate analysis in which Vanzo combined several elements to create a bivariate data set. In our method instead, we treated each of the chemical elements as an individual variable in a set of four main dimensions (Si, Ca, Al, and Fe).
10.3 Industrial Benefits

Previous studies on RHA cement focussed on the chemical analysis of the pozzolanic reaction in which portlandite reacts with the active silica provided by RHA to form more C-S-H gel. Other researchers focussed on the macroscopic testing of cement and concrete mixed with RHA. Macroscopic testing was generally achieved with uni-axial compressive strength testing conducted on samples with various RHA content and w/b ratios.

Through this study, we provide a deeper understanding of the behavior of RHA in cement at different replacement ratios, while studying the effect of w/b ratios as well. This study combines the macroscopic strength development and an intensive study of the microscopic properties of RHA cements. The deeper understanding can help optimize the use of RHA and build a wider acceptance of concrete that utilizes RHA.

10.4 Perspectives

Nanoindentation and EPMA allow access to the properties of cement paste and of the cement paste phases at a very small scale. The application of these methods to determine the effect of RHA incorporation on the properties of cement paste led to a general understanding of RHA cement. But to get more precise and detailed understanding, we need to employ other methods and techniques:

1. **Chemo-Mechanical Coupled Analysis**: Running both nanoindentation and WDS analysis on the same location can provide more information about the mechanical properties of the cement paste phases. This technique can help to determine the mechanical properties of each phase separately and only then the mechanical response of C-S-H phase can be separated from any mixture with other phases.

2. **X-Ray Diffraction**: This technique can be employed to quantify volume fractions of portlandite and residual Clinkers in cement paste and to study the possible crystalline residual RHA. It may also help to shed light on the chemo-physical nature of the fundamental building block of RHA cement-based materials; and could answer the question whether this particle is a nano-sized physical mixture of RHA and C-S-H, or a stand alone
C-S-H phase.

3. **Multiphase Packing Density Analysis:** In our study, we "identified" mechanically the C-S-H phases by extracting -through clustering- phases with nanoindentation properties, $M < 65$ GPa and $H < 3$ GPa. In addition, we assumed that the C-S-H particle was a single particle phase of well defined properties. Here some refinements will be necessary in order to pin down the mixture nature of the elementary building block of RHA materials. This refinement should consider the possibility of at least two solid phases, C-S-H and RHA. Some algorithmic development will also be needed to fully characterize the particle properties without fixing the solid stiffness to 65 GPa.

While these developments hold the promise to refine our results, they will be essential for fine tuning mix design proportions for improved efficiency of RHA-doped cement-based materials; a material of great promise for a sustainable development of construction materials industry in large parts of this world.
Bibliography


194

