NANOMECHANICAL STUDY OF CEMENT PASTES BY STATISTICAL NANOINDENTATION AND PEAKFORCE QNM

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Abstract
The study is related to the EU 7th Framework Programme CODICE (COmputationally Driven design of Innovative CEment-based materials) project. The main aim of the project is the development of a multi-scale model for the computer based simulation of mechanical and durability performance of cementitious materials.

As part of the task to study the micromechanical properties of computationally driven designs and validate the model predictions, extensive work on micro/nano-mechanical characterisation of cement-based materials has been conducted, which cover synthetic C₃S, C₂S pastes, cement pastes hydrated at different ages and pastes subjected to accelerated calcium leaching, etc. Statistical nanoindentation and micro-mechanical property mapping technique was used to study intrinsic properties of different hydrate phases and microstructures down to approximately 1 μm. A new experimental technique – Peakforce QNM was also used to examine mechanical properties of cement paste micro/nano-structures down to approximately 10 nm. The importance of proper specimen preparation is highlighted, particularly for the early-aged and leached samples due to their weak and fragile microstructure. The results obtained from the two experimental techniques are presented and advantages/limitations for each technique discussed.

1. INTRODUCTION

Micro/Nano-indentation experiment was first applied to cement-based materials in 1995/6 to assess the bond in glass fibre reinforced cement (GRC) [1-2]. The statistical (grid) nanoindentation technique was first reported in 2003/4 [3-5]. However, at the start of the EU CODICE project, almost all the work reported previously had been on well hydrated cement specimens (e.g. at least after 28 days of hydration). Little information is available on the micro-mechanical properties of the calcium silicate hydrate (C-S-H gel) at the early ages and their changes with increase in hydration age. It is well known that the C-S-H gel constitutes
the main ingredient of cementitious skeletons and determines the fundamental properties of cement-based materials. Studying and tuning the intrinsic nature and properties of the C-S-H gel through complementary action of new experimental capacities and stronger simulations schemes which explicitly pay attention to the nanoscale, could lead to better understanding of materials microstructure – properties relationship and development of better materials. These are part of the main tasks of the EU CODICE project mentioned above. As part of the CODICE project, this paper aims to study experimentally the micro/nano-mechanical properties of the C-S-H phases at early ages and their evolution with hydration age.

A major difficulty encountered in this work has been to prepare representative test specimens with a low surface roughness. This was found to be extremely difficult and impossible for the very early aged (e.g. 1 and 3 days) and degraded cement paste specimens after calcium leaching. This is mainly because, due to the big differences in stiffness/hardness among the various phases present within cement paste (e.g. E value for: anhydrous phase >130 GPa; C-S-H = 15 – 35 GPa; Pore = 0 GPa). Loss of weak hydrate phases during the grinding and polishing procedures were often observed, and also the preferential grinding and polishing of weak/soft phases usually led to high surface roughness of the test specimen prepared. Typical cases with a 1-day hydrated cement paste specimen are shown in Fig. 1. Extensive trials using various sample preparation techniques were carried out at the beginning of the CODICE project to reduce/minimise such artefacts and high roughness of the prepared specimen surface. It was found that, to obtain reliable and reproducible results, resin impregnated specimens have to be used for the early aged and calcium leached samples.

![Image](image.png)

Fig.1. Left: Loss of weak phases (i.e. ‘Pop out’) during grinding/polishing and Right: the high surface roughness observed for a typical 1-day hydrated cement paste specimen

2. EXPERIMENTALS

A commercial ordinary Portland cement (CEM 1, 52.5N) provided by Italcementi was used for this study. Cement paste prism specimens with a fixed w/c ratio of 0.4 were studied at the different hydration ages of 1, 3, 7 and 28 days. All specimens were demoulded at 1 day and then sealed in aluminium foil and stored in lab (20±3 °C) for curing. At the specified age, the paste specimen was rinsed several times using propan-2-ol to stop the hydration and then stored in a desiccator (with silica gel). Specimens for nanoindentation were prepared by cutting, embedding, resin impregnation under vacuum, grinding and polishing. Epofix resin with E = 3-4 GPa was used for impregnation in this study. The right choice of polishing pad,
duration, pressure, type and amount of lubricant for every polishing step (from 6 µm and 0.25 µm) was found also important for achieving the final surface quality required. Fig. 2 shows the typical specimens prepared for the nanoindentation testing.

A test grid consisting of at least 320 test points were used for the statistical nanoindentation study, as shown in Fig. 3. The selection of such a test grid was to cover a large and representative area and at the same time provide sufficiently fine details. At each testing point, a progressive two-step load-unload cycles with a maximum load 0.5 - 1 mN were carried out. The E modulus and hardness values at the test point were calculated using the 2nd unloading cycle, with a maximum indentation depth about 200 – 250 nm [3-6].
3. RESULTS AND DISCUSSIONS

3.1 Nanoindentation study

Statistical analysis of all the test results was carried out to extract the specific mechanical properties of each individual phase in the tested area using the deconvolution technique presented previously [5-6]. The statistical histogram plots of the E modulus results and the 4-modal Gaussian model fits for the cement paste specimens at different ages are shown in Fig. 4. For simplicity, statistical analysis was only applied to the range of results covering the hydration products (i.e. $E < 45-50$ GPa).

As shown in Fig.4, the 1st peak from the left at $E = 15 - 18$ GPa represents the loose-packed, or LP C-S-H phase, while the two peaks in the middle are for the low-density, or LD C-S-H phase at $E \approx 24$ GPa and the high-density, or HD C-S-H phase at $E \approx 31$ GPa. The 4th
peak at $E \approx 39$ GPa is mainly for CH and possibly other higher density C-S-H phases. These mean $E$ values are in good agreement with the reported $E$ values for those phases in well-aged cement paste specimens [3-6]. Furthermore, the $E$ values for the specific phases do not seem to change with the hydration age. However, it appears that the relative volume of the different phases determined from the area under the fitted curves changes with hydration age. As shown in Fig.5, the LD C-S-H phase decreased gradually with hydration age while the HD C-S-H phase increased with age, indicating a densification process of the microstructures.

![Graph showing relative volume percentage of LD and HD C-S-H phases vs hydration age](image)

Fig.5. Relative volume percentage of LD and HD C-S-H phases of the total hydration products determined from the statistical nanoindentation test

### 3.2 Nanomechanical study by PeakForce QNM

Atomic Force Microscope (AFM) based techniques have been developed for imaging surface profile and phases of different compositions since 1980s. Recent advances have also enabled the mapping of mechanical properties at the nano-metre scale. PeakForce QNM is such a technique developed by Veeco/Bruker based on the peak force tapping mode of AFM [7]. Fig.6 shows schematically the operation principle of the technique for measuring mechanical properties at the nano-scale.

Generally, the forces applied to the sample are precisely controlled, which is similar to the common nanoindentation testing. However, the forces applied in the PeakForce QNM are usually in 100 – 400 nN range, much smaller than in the nanoindentation test (around 0.5 – 1 mN). A suitable probe (i.e. cantilever) with the right stiffness range for the material to be measured is chosen in order to limit the indentation depth to several nano-meters in most cases, which both maintains resolution and prevents damage to the tip of probe or sample. As a result, one of the major advantages of the PeakForce QNM is that it allows much smaller indent size to be used, compared to the nanoindentation technique. Also, due to its high frequency in the testing cycles, a test scan over an area of, e.g. 50x50 µm, with huge number of test points (typically a few hundred thousands) can be done within 1-2 hours, which is several orders of magnitude faster than in the nanoindentation technique (typically less than
10 test points per hour). The modulus of elasticity of each test point is determined using the unloading force-displacement curve (i.e. the green line in Fig.6), similar to that used in the nanoindentation test.

The PeakForce QNM, however, does have its own limitations. Firstly, current modulus measurement range is limited to a maximum of about 50 GPa by the probe choice. This makes it unsuitable to study un-hydrated phases in cement pastes. Secondly, regular calibrations and checks are often necessary to determine the probe tip radius or if the probe needs to be replaced. Furthermore, a constant operator attention is required throughout the testing period to choose and adjust the necessary testing parameters. Also, as expected, surface quality of the test specimen is perhaps even more critical to the measured results, compared to the case of the nanoindentation testing.

Fig.6. Schematic of the operation principle of the PeakForce QNM for measuring the mechanical properties at the nano-scale [7].

The PeakForce QNM study of a 500x500 nm area of 1-day hydrated specimen (Left: Map of E modulus of the test area; Right: Histogram plot of the E modulus results)

Fig.7. Results of PeakForce QNM study of a 500x500 nm area of 1-day hydrated specimen
A preliminary investigation was carried out to study the nanomechanical properties 1-day hydrated cement paste using the PeakForce QNM. Fig. 7 shows results of nanomechanical property measurements carried out in a hydrated area of 500 nm by 500 nm next to an unhydrated clinker particle. The results from the PeakForce QNM appear to support the E values obtained from the statistical nanoindentation test. For example, for the 500x500 nm area studied the E modulus are between 15 to 35 GPa with a peak value at around 24-25 GPa, which is consistent with the range of E values for the C-S-H phases extracted from the statistical nanoindentation study. Limited tests in relatively larger areas (e.g. 50x50 and 20x20 µm) using PeakForce QNM also revealed possible peaks of E values at 10-15 GPa and ~40 GPa, thus confirming the presence of LP C-S-H phase and CH phase as well.

4. CONCLUSIONS

– Resin impregnation were found to be essential for preparing specimen for nanoindentation testing, in order to allow the weak and porous phases in specimens at early hydration ages to be properly studied.
– The results of mechanical properties of the individual hydrated phases obtained for the cement paste specimens are in reasonable agreement with those previously published. The E values for the individual hydrate phases were found to be almost unchanged with the hydration age. The relative volume content of the C-S-H phases, however, shifted significantly from LD to HD phases with increase in hydration age.
– PeakForce QNM technique has been applied, for the first time, to study hydrated cement paste. Compared to the nanoindentation technique, the AFM based PeakForce QNM technique allows tests to be carried out at even smaller scale (down to about 10nm across) and at much faster rate.
– Preliminary PeakForce QNM results, consisted of a huge number of test points (millions), of the selected hydrated specimens show very good agreement with those determined from the statistically nanoindentation tests, both in terms of the range of E values and the histogram peaks for the individual phases.

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REFERENCES


