Considerations about statistical nanoindentation on hardened cement pastes

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ABSTRACT: Nanoindentation is an experimental technique that allows in situ measurements of the elastic properties of materials. A development of the technique is statistical nanoindentation, where hundreds of single indentation tests are carried out in a grid on a multiphase material and the indentation elastic modulus and hardness of the single phases are then extracted with statistical methods from the frequency plots. This technique has been employed by several research groups to assess the mechanical properties of different calcium-silicate hydrate (C-S-H) phases in hardened cement paste (HCP).

However, Focused Ion Beam nanotomography on HCP shows that the homogenous C-S-H regions present in HCP are too small to cause independent and separate peaks in the elastic modulus plots. Moreover, the presence of phases other than C-S-H, namely unhydrated cement, calcium hydroxide, ettringite and capillary porosity may also produce spurious peaks. Another questionable aspect is the methodology used to extract the elastic modulus of the single phases from the frequency plots by fitting with Gaussian distributions.

1 INTRODUCTION

The use of nanoindentation for the characterization of the elastic properties of materials at the nanoscale has been very popular since the publication of a pioneering paper (Oliver and Pharr (1992)). According to the theory of indentation testing, an indenter with a defined geometry is used to test the elastic properties of an infinite, homogeneous and isotropic half-space of zero surface roughness. Nanoindentation has been employed to study the mechanical properties of the clinker minerals (Velez et al (2001)) and of the different phases present in cement paste (Hughes and Trtik (2004)).

A more recent development is statistical nanoindentation, where hundreds of single indentation tests are carried out in a grid and the indentation elastic modulus and hardness are then extracted with statistical methods from the frequency plots (Constantinides and Ulm (2004), Constantinides and Ulm (2007), Constantinides et al (2006)). Using statistical nanoindentation, Constantinides and Ulm (2004) found evidence of two C-S-H phases having different mechanical properties. The two C-S-H phases have elastic moduli about 21 GPa and about 29 GPa. These two C-S-H phases correspond to the LD and HD C-S-H in a model proposed by Jennings (2000, 2008). In further publications using statistical nanoindentation, the evidence of a third C-S-H phase, ultra-high density (UHD) C-S-H was found (Vandamme et al (2010), Ulm et al (2010). The occurrence of two or more peaks in the histograms of elastic moduli in cementitious systems is reported as well by other research groups (e.g. Zhu et al (2007)).

However, several aspects of the statistical nanoindentation technique deserve a closer look (Trtik et al (2009), Lura et al (2011)), as will be shown in the following sections.
According to the principles of statistical analysis of nanoindentation results as explained by Constantinides and Ulm (2007), small indentation depths allow the determination of phase properties of single phases, while larger indentation depths lead to the response of the homogenized medium. According to these considerations, the indentation depth $h_{\text{max}}$ needs to be much smaller than the size of an average individual region of the material phase that can be considered homogeneous, $D$. How much smaller $h_{\text{max}}$ has to be with respect to $D$ depends on the mismatch in elastic modulus of the individual phases. The generally accepted rule-of-thumb in indentation testing of thin films on substrates is that $h_{\text{max}}$ has to be smaller than $D/10$. This was recently confirmed numerically and analytically by Trtik et al (2009) and by Ulm et al (2010), respectively. Investigations of elastic properties of hardened cement pastes usually employ depths between 100 and 500 nanometres. The volume of material underneath and around the indenter, of which the mechanical properties are probed, is called the interaction volume, $v$. The interaction volume of indentation is directly dependent on the indentation depth, $h_{\text{max}}$. The shape of the indenter and the microstructure of the material within the interaction volume influence the stress distribution underneath the indenter. However, even though the indentation interaction volume does not have any clear boundary, it is assumed that, for the popularly used Berkovich indenter, the mechanical response of the material stems from a domain approximately 3-4 times larger than $h_{\text{max}}$ (Constantinides and Ulm (2004)). For cement pastes, this leads to interaction volumes $v$ with linear sizes of about 1-2 $\mu$m (Trtik et al (2009), Ulm et al (2010)).

Following from the considerations above, one can say that for true peaks corresponding to the elastic moduli of the different phases to occur in the elastic modulus plot, they definitely must already occur in a plot that shows the phase composition of the interaction volumes. A simple method to verify this assumption is plotting the phase distribution of the interaction volumes in a phase diagram: for the condition to be true, the resulting set of the phase compositions of the interaction volumes must exhibit unequivocal peaks at each original phase in the phase diagram.

The size of the homogenous phases in cement pastes was investigated in (Lura et al (2011)) by analyzing the 3D microstructure of cement pastes obtained with Focussed Ion Beam nanotomography (FIB-nt). FIB-nt volumes were obtained from freeze-dried and epoxy-impregnated 28-days old Portland cement paste. The water to cement ratio (w/c) of the paste was 0.3 while the curing temperature was 20°C. Several FIB-nt volumes ranging from 2'600 to 7'500 $\mu$m$^3$ with voxel size of 20 nm in all dimensions (Figure 1, left) were segmented into pores (P), hydration products (H) and unhydrated cement (U). Uniformly distributed interaction volumes of size $v$ were then probed for their phase distribution. The shape of the interaction volumes was set to cubes for simplicity reasons. In order to achieve smooth histograms, a large number of virtual interaction volumes (~100'000) was evaluated.

Figure 1. Left: example of FIB-nt volume with voxel size of 20 nm of a 28 days-old cement paste (CEM I, w/c 0.3). Right: ternary plot of Gaussian-filtered phase distribution densities in the probed interaction volumes of a FIB-nt sample (35.2 $\times$ 26.5 $\times$ 8.0 $\mu$m$^3$) of cement paste at varying interaction diameters $d$ (adapted from Lura et al (2011)).
Example of ternary plots of the Gaussian-filtered phase distribution densities for varying sizes of the interaction volumes are shown in Figure 1, right. No clear peak corresponding to the actual phases present in the sample appear for \( v > 1 \mu m^3 \), which is the typical size of interaction volumes being responsible for the determination of the elastic moduli of the different phases. Instead, for this particular volume, a peak was even formed between the phases H (hydration products) and P (porosity). Results of other datasets are shown in (Lura et al (2011)); all examined FIB-nt volumes show a consistent pattern.

These results point to the conclusion that the hydration products in cement pastes form clusters that are on average smaller than about 1 \( \mu m^3 \), or the size of the interaction volume of nanoindentation. In section 4, it will be shown that other phases (i.e. portlandite, calcite, monocarbonate, ettringite) are necessarily present in the hydration products, making it much more complicated to distinguish different phases within the C-S-H.

3 VIRTUAL STATISTICAL NANOINDENTATION EXPERIMENT

A further step in this investigation about the validity of statistical nanoindentation was reproducing a virtual statistical indentation experiment based on a FIB-nt dataset of a hardened cement paste with water to cement ratio 0.3 (Trtik et al (2009)). Cubes of 1-\( \mu m \) edge were considered as the interaction volume for each single nanoindentation experiment. This interaction volume corresponds to an indentation depth \( h_{max} \) of about 250 to 330 nm, based on the assumption that the interaction volume is 3 to 4 times larger than the indentation depth (Constantinides and Ulm (2004)). The size of the interaction volume remained the same for all the positions of the interaction volumes, thus disregarding the influence of the material microstructure on the depth of indentation. In order to avoid statistical dependency of individual interaction volumes, the 1-\( \mu m \) cubes were sampled within the microstructure of the hardened cement paste at a distance of about 2 \( \mu m \) in the three directions (a 3D grid). A dataset of 280 cubes, each representing a different indentation site, was obtained with this procedure. Once the set of the valid cubes was determined, the volume fractions of porosity, hydrates and unhydrated cement were evaluated for each cube.

The elastic modulus at each interaction volume was calculated by means of composite models (Trtik et al (2009)). A model considering a 3-phase material was employed, where the amount of the single phases present in the volume, porosity, hydrates and unhydrated cement, was used to calculate the local elastic modulus (Trtik et al (2009)). For the unhydrated cement an elastic modulus of 117.7 GPa was used, while for the hydration products the modulus was 22.4 GPa. Relative frequency plots of the elastic modulus were then constructed by assigning a bin size to the elastic modulus dataset and plotting the relative frequencies on the ordinates and the elastic modulus on the abscissas.

With the procedure described above, the elastic modulus distributions shown in Figure 2 were obtained. The dotted, thin line shows the results of one FIB-nt volume that was already presented in (Trtik et al (2009)). In this distribution, a main peak is seen at 22.5 GPa, which decreases smoothly for lower values. For higher values of the modulus, secondary peaks appear between 24 and 38 GPa. It is noticed that these multiple peaks of comparable height have been generated by the presence of unhydrated cement (with elastic modulus 117.7 GPa), hydration products (modulus 22.4 GPa) and porosity in various amounts, while no materials with elastic modulus in the range 24-38 GPa were included in the simulation. This result appears to substantiate the assumption that random peaks in the elastic modulus frequency plots may be generated by the distribution of the phases, rather than indicating the presence of a phase with a specific elastic modulus within the region of the peak (Trtik et al (2009)). Hence, peaks that are identified in the literature as belonging to LD and HD C-S-H could in reality equally reflect the presence of only one type of C-S-H next to other crystalline phases of high elastic moduli (e.g., unhydrated cement, calcium hydroxide, ettringite) within the indentation interaction volume (Trtik et al (2009)).
The continuous darker line in Figure 2 shows the results from a second FIB-nt volume, where multiple peaks appear between 10 and 22.5 GPa. This second volume contained more porosity and less unhydrated cement than the one analyzed in (Trtik et al (2009)). As a consequence, the elastic modulus shifted to values lower than the input for hydration products (22.4 GPa). Also these results confirm the conclusions of section 2: some peaks obtained with statistical nanoindentation might be the results of non-homogenous porosity distributions.

Figure 2. Elastic modulus frequency plots calculated taking into account hydration products, porosity and unhydrated cement. Results of calculations on two different FIB-nt volumes are shown, one from reference (Trtik et al (2009)) and a new volume. Bin size was 1 GPa.

4 PHASES IN PORTLAND CEMENT PASTES

In cement paste, a number of phases other than C-S-H and unhydrated cement are present. For example, Lothenbach et al. (2008) reported for a mature Portland cement paste with w/c 0.4 a composition of about 50% C-S-H, 20% portlandite, 10% ettringite, 12% monocarbonate, 1% calcite, 3% unhydrated cement and 4% porosity by volume. This means that purely on a statistical basis, even if an indenter were small enough to probe individual phases of a cement paste, about 50% of the time the indenter should be probing phases other than C-S-H.

Portlandite (calcium hydroxide, CH) occurs in the structure of HCP as 1-10 nm crystals within C-S-H, as thin elongated platelets of 10-100 nm in thickness and as large domains of high geometrical complexity of several of µm (Skalny et al (2001)). Portlandite crystals have a higher elastic modulus compared to C-S-H and moreover their elastic modulus depends on the direction of loading, ranging from 22.6 to 99.4 GPa (Laugesen (2005)). Depending on their orientation in the paste, they may show different elastic properties when indented. It is therefore questionable whether a peak around 40 GPa in the elastic modulus plots should be interpreted as portlandite (Constantinides and Ulm (2007)). Similar considerations are valid for ettringite: depending on the orientation of the crystals and the direction of loading, the elastic modulus of ettringite varies from 20 to 40 GPa (Speziale et al (2008)).

Calcite is present in the majority of modern Portland cements and makes up to 5% of cement mass. A small amount of calcite will be present in the hydrated cement paste, for which an elastic modulus of 79.6 GPa (Haecker et al (2005)) is reported. More important, a substantial amount of monocarbonate is expected to be formed (Lothenbach et al (2008)), which should have elastic properties similar to CH (Haecker et al (2005)).

Depending on their size distribution, the minor components of hardened cement pastes may create new peaks in the elastic modulus frequency plots or influence size and position of the peaks attributed to C-S-H (see sections 2 and 3).
As the expression “statistical nanoindentation” implies, the key to the determination of phase properties is the identification of the statistical distribution of the elastic modulus of the single phases. It is noticed that whereas in the following only the distribution of the elastic moduli is addressed, our reasoning is more general and can also be extended to hardness distributions and to coupled distributions of hardness and elastic modulus (Vandamme et al (2010)). The identification of peaks supposedly belonging to single phases is achieved by means of deconvolution of the elastic moduli density functions into sets of Gaussian functions (Vandamme et al (2010)).

For each Gaussian function, three free parameters are available, e.g. the mean value $\mu$, the half width $h$ and the height $f$ amounting to the fraction of its specific phase. In case of three Gaussians (LD and HD C-S-H, unhydrated clinker) and without assuming any prior knowledge of the phases, this results in a 9-dimensional space where the optimum is expected to be found by mean squares error minimization (Eq. 3 in Vandamme et al (2010)). This means finding the global optimum of a strongly non-linear function based on a set of numerical values in an n-dimensional space. Neither Vandamme et al (2010) nor any other reference about statistical nanoindentation gives any quantitative information about the algorithm for the optimum search they have been using. Such functions may produce a large number of local optima. Due to the high dimensionality of the parameter space, it is possible that an optimization process may converge to any one of those local optima. If so, then different results may be obtained by selecting different starting conditions.

Figure 3, upper corner, left, shows a recently published deconvolution (see Figure 1 in Ulm et al (2010)) of statistical nanoindentation data into four Gaussians denoting (from lowest to highest elastic modulus) low, high and ultra-high density (or LD, HD and UHD) C-S-H, and clinker. The original data was carefully extracted from the figure, whereas small errors cannot be completely excluded. The reader is referred to (Lura et al (2011)) for a discussion of the limitations of this procedure. The reconstructed fit of four Gaussians corresponding to the values chosen by Ulm et al. (2010) achieves a $r^2$ of 0.9239.

In order to estimate the stability of curve fitting on such kind of data, an optimization procedure has been established. Due to the highly nonlinear characteristic of the least squares objective function (i.e., Equation 3 in (Vandamme et al (2010)), a downhill simplex algorithm achieving a tracking with an N-polytope (N: number of free dimensions) has been used (Nelder and Mead (1965)). In our example data aiming at the optimization of four Gaussians, this simplex is a 12-polytope. The outstanding advantage of the used algorithm is the flexible size of the N-polytope which is continuously being adjusted according to the local curvature of the objective function. The algorithm is fast and finds a single optimum within ~1.5 seconds on an Intel XEON 5430. The optimization was repeatedly applied on various initial simplices which have been randomly determined. Thereby, thousands of local optima could be found.

The optimization procedure was further extended in order to enforce equivalent half widths $h_i$ for the Gaussians. This modification is interesting because it is remarkable that the clinker phases show much wider Gaussians compared to the narrower C-S-H phase distribution in the discussed diagram (Ulm et al (2010)) as well as in other deconvolved results from statistical nanoindentation (Vandamme et al (2010)). In fact, clinker has low porosity and is composed of phases which have similar elastic modulus; on the contrary, hydration products are composed of multiple phases of very different moduli and have large and inhomogenous porosity. In addition, due to the high modulus and hardness of clinker, the interaction volume should be smaller than in the case of hydration products (Ulm et al (2010)). According to these considerations, one would expect to obtain narrower Gaussians for the clinker and broader for the hydration products, while the opposite is the case. In addition, the average values of elastic
moduli of clinker found by statistical nanoindentation on cement paste (Ulm et al (2010), Vandamme et al (2010)) are much lower than the values found by indenting the clinker (Velez et al (2001)).

A total of 9'788 local optima have been identified, almost all of them with \( r^2 \) above 0.9239, which was estimated for the fit by Ulm et al (2010) (Figure 3, upper corner). The highest \( r^2 \) found was 0.9614 for an optimization with 4 Gaussians, shown in Figure 1, upper right corner. Others are shown in (Lura et al (2011)). It is noticed that there are many different ways of curve fitting for achieving \( r^2 \) far above the one published by Ulm et al (2010), which however yield completely different distribution characteristics. We notice that the observation that many better fits are possible with totally different characteristics from the fit in (Ulm et al (2010)) does not represent a definitive statement against this fit. However, this observation shows that this fit is based on a model postulating three types of C-S-H with distinct elastic moduli (LD, HD and UHD C-S-H), rather than being an independent proof for this model. Two further optimizations obtained by lowering the number of Gaussians are presented in Figure 3, below. They show that fits superior to the published one could also be achieved by using only 3 (\( r^2 = 0.9430 \)) or even only 2 (\( r^2 = 0.9314 \)) Gaussians. Importantly, the last two cases show that fitting the results of the cement paste investigated in (Ulm et al (2010)) with four Gaussians (i.e., three types of C-S-H and unhydrated clinker) is only one of the available possibilities. Our results show that the same statistical nanoindentation results can be fitted by a different number of Gaussian peaks (i.e., material phases), still obtaining similar or better \( r^2 \). As a consequence, the statistical nanoindentation datasets as presented in (Ulm et al (2010)) could be also used for supporting the presence in the investigated hardened cement pastes of only one, or only two, C-S-H types.

![Figure 3](image-url)

Figure 3. Upper corner, left: Reproduction of statistical nanoindentation results (binned histogram of indentation moduli) as published in (Ulm et al (2010)). Other figures: alternative fits using 4, 3 or 2 Gaussians, all achieving a better \( r^2 \). Adapted from (Lura et al (2011)).
CONCLUSIONS

In this paper, different aspects of the statistical nanoindentation technique were addressed, in particular the influence of the microstructure on the statistical nanoindentation results (sections 2-4) and the procedure for fitting the statistical nanoindentation plots (section 5).

The results of the virtual experiments presented in sections 2 and 3 indicate that, in cement pastes, interactions volumes of 1 $\mu$m$^3$ and larger contain a mixture of different phases. As a result, statistical nanoindentation is not able to assess the elastic properties of single phases.

The large variety of possible Gaussian fits (section 5) indicates that statistical nanoindentation data of the quality that is currently being published cannot be used to prove any model about C-S-H, such as the one proposed by Jennings (2000). Our results show that the published deconvolution of the nanoindentation data is rather itself based on model assumptions about bimodality or trimodality of elastic moduli of C-S-H.

REFERENCES


