Nanoindentation of ordinary Portland cement paste: identification of basic mechanical properties

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ABSTRACT

Necessary prerequisites for the development of multiscale models are (i) suitable homogenization schemes relating properties of the composite to properties of the constituents, e.g., matrix and inclusions, and (ii) experimental methods to identify composition at finer scales of observation and the mechanical properties of the different material phases encountered at these scales. Whereas the former have been developed since the 1950’s, the latter has only recently been established for multiscale models for concrete, starting with the identification of the elastic properties of the main clinker phases in ordinary Portland cement (OPC) and calcium-silicate-hydrates (CSH) by nanoindentation (NI). In this paper, the NI technique is extended towards identification of (i) strength and (ii) viscous properties of OPC at the micrometer range.

Introduction

Experimental methods for determination of mechanical properties (elasticity, time-dependent behavior, strength) may be classified according to load history (static or cyclic tests) and the stress distribution within the specimen (uniform or non-uniform). Among the experiments for the identification of mechanical properties of concrete characterized by a uniform stress distribution (apart from the domain of load application) are uniaxial, biaxial, and triaxial tests. Experiments with non-uniform stress distribution include the Brazilian test, pull-out tests, and 4-point bending experiments. Indentation tests rank among identification experiments inducing a non-uniform stress distribution. They have been employed in material science for the determination of the material “hardness” for over a century (Johan A. Brinell presented his spherical indentation test at the World’s Fair in Paris in 1900). Since the only prerequisite for indentation tests is a sufficiently plane sample surface, they may be conducted at small length scales of observation, leading to the so-called nanoindentation (NI) technique, developed in the 1980’s. Hereby, the loading ranges in the micronewton, the penetration depth in the nanometer level, respectively. Recently, NI has been employed for determination of intrinsic material properties at the micrometer scale of cement-based materials. A NI test is characterized by driving a tough (usually diamond-) tip into the ground and polished sample surface, while the load and penetration history, $P(t)$ [N] and $h(t)$ [m], are continuously recorded. Load-controlled NI tests usually consist of a loading, a dwelling, and an unloading phase (see Figure 1). Based on the recorded data, mechanical properties of the indented material can be computed.
Determination of elastic properties

Assuming purely elastic unloading, the indentation (plane-stress) modulus \( M = E/(1 - \nu^2) \), with \( \nu \) as Poisson’s ratio and \( E \) as Young’s modulus, is determined from the initial slope of the load-penetration curve during the unloading phase \( S = dP/dh \mid h = h_{\text{max}} \) [see Figure 1(c)] according to the so-called BASh equation (Bulychev-Alekhin-Shoroshorov equation) [11, 6]:

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

where \( A_c \) is the projected area of contact of the indenter. Conical tips are characterized by

\[
A_c = \pi h^2 c \tan^2 \theta,
\]

where \( \theta \) is the indenter half angle and \( h_c \) denotes the contact depth, i.e., the height of the (conical) indenter tip in contact with the sample. Pyramidal-shaped indenter tips might be represented by a cone such that the cross-section area of the pyramidal-shaped tip and the cone are equal [6]. Accordingly, the three-sided Berkovich tip may be represented by a cone with a half angle of \( \theta = 70.32^\circ \).

In order to avoid measuring the projected area of contact, a procedure to determine the contact depth based on the solution of the elastic contact problem was proposed in [11] as

\[
h_c = h_{\text{max}} - 2 \left( 1 - \frac{2}{\pi} \right) \frac{P_{\text{max}}}{S},
\]

with \( P_{\text{max}} \) denoting the maximum load acting at the begin of the unloading phase. Equation (1) was derived using the analytical solution (“Sneddon solution”) for the contact problem of a rigid indenter penetrating an elastic halfspace, given as [8, 5, 14]:

\[
\frac{P}{E h^2} = \frac{2}{\pi} \tan \theta \frac{1}{1 - \nu^2}
\]

and

\[
\frac{h_c}{h} = \frac{2}{\pi}.
\]

Hereby, the radial displacement of points along the surface of contact under the indenter was constrained for the derivation of Equations (4) and (5). Multiplication of the right hand side of Equation (4) with the correction term \( \beta \) [6] gives access to the so-called “modified Sneddon solution”:

\[
\frac{P}{E h^2} = \beta \frac{2}{\pi} \tan \theta \frac{1}{1 - \nu^2}.
\]

\( ^1 \)As pointed out in [1], Equation (3) is widely used to estimate the contact depth for elastic-plastic solids. However, Equation (3) may only be applied for strength/stiffness-ratios of \( 2c/E > 0.05 \) in case of a Tresca-type material, when no “piling-up” occurs.
According to [6], \( \beta \) depends on Poisson’s ratio \( \nu \) and the indenter half angle \( \theta \). Results from a parameter study focusing on \( \beta \) as a function of indenter half angle and Poisson’s ratio [13] are in good agreement to the numerical results given in [6]. For a Berkovich indenter characterized by a half angle of \( \theta = 70.32^\circ \) and \( \nu = 0.24^2 \), \( \beta \) was obtained as 1.081. Differentiation of Equation (6) with respect to \( h \), specialized for \( h = h_{\text{max}} \), and considering \( S = dP/dh \big|_{h=h_{\text{max}}} \), Equations (5) and (2) give access to the corrected form of the BASh equation as

\[
S = \beta \frac{2}{\sqrt{\pi}} \frac{E}{1 - \nu^2} \sqrt{A_c},
\]

which is used for determination of the elastic properties of the constituents of early-age cement based materials throughout this paper. Figure 2 shows the spatial distribution of Young’s modulus \( E \) determined using Equation (7) for ordinary Portland cement (Blaine fineness: 4000 cm\(^2\)/g, medium initial radius of the clinker grains: 7 \( \mu \)m) paste characterized by a water/cement-ratio of 0.5. The NI tests were performed in a 25\( \times \)25 grid with a distance between adjacent grid points of 5 \( \mu \)m. This so-called “grid-indentation technique” [2] gives access to (i) the spatial distribution and (ii) the elastic properties, respectively, of the different material phases at the \( \mu \)m-scale of observation of cement paste. In Equation (7), \( \nu \) was set to 0.24 [16].

**Figure 2**: Young’s modulus \( E \) for material phases encountered at the cement-paste scale determined by the corrected form of the BASh equation [Equation (7)] (grid-indentation with 25\( \times \)25 indents and distance between adjacent grid points of 5 \( \mu \)m on OPC paste characterized by \( w/c=0.5 \) and a Blaine fineness of 4000 cm\(^2\)/g)

**Determination of strength properties**

While elastic material properties are determined from the unloading branch of NI tests, strength properties may be deduced from the loading branch, characterized by plastic deformations in the vicinity of the indenter tip. The hardness \( H \) [Pa] of the material is determined at the end of the loading phase with the maximum load \( P_{\text{max}} \) and its corresponding projected area of contact as

\[
H = \frac{P_{\text{max}}}{A_c}.
\]

The hardness represents the material response corresponding to the stress state under the indenter tip, characterized by predominant hydrostatic loading. Since the tip shape influences the latter, the hardness depends on the employed indenter tip (Berkovich-hardness, Vickers-hardness, ...). Hence, \( H \) is not a fundamental material property. In order to determine material parameters describing plastic material behavior, experimental data has to be analyzed in combination with analytical/numerical methods:

- In case the material strength is a linear function of the applied hydrostatic pressure, i.e., the material behavior can be described by, e.g., the Mohr-Coulomb failure criterion, the so-called “dual-indentation technique” for identification of cohesion and angle of internal friction was developed in [4]. This technique is based on the use of two different, but geometrically similar indenter tips, e.g., two conical tips with different half angles. A Berkovich- and a “Cube-Corner”-tip, characterized by \( \theta = 70.32^\circ \) and \( \theta = 42.28^\circ \), respectively, were used in [4]. Numerically obtained (employing a limit-analysis-based approach) relations for the hardness/cohesion-ratio as a function of the angle of internal friction yield two constraints for the determination of the unknown values for the cohesion and the angle of internal friction.

- For elastoplastic materials obeying the von Mises yield criterion, Tabor [15] postulated a relation between the yield strength \( f_y \) and the hardness \( H \) as: \( H \approx 2.6f_y \div 3f_y \). Recently, this relation was expanded towards inclusion of strain-hardening [1]. In [1], numerical results are given as \( (H/f_y) \) as a function of \( (f_y/E) \) for different values of the strain-hardening exponent \( n \).

\(^2\)In [3], this value was suggested for CSH.
behavior, the viscous material response during the dwelling phase of the NI test may be employed to quantify the creep behavior of cement-based materials at the m-scale. The NI data is characterized by a pronounced increase of the penetration depth during the loading phase of the NI test. With Young’s modulus determined according to Equation (7), the loading phase of the NI test can be plotted in terms of the dimensionless quantity $\Pi_p = \frac{P(t)}{Eb(t)^2}$ (see Figure 3). The experimental data indicates a progressive switch from spherical to conical indentation. The initial contact of the indenter tip is characterized by spherical indentation due to the small (but ever present) bluntness of the indenter tip. The initially large values for $\Pi_p$ reflect this type of loading situation. With increasing penetration depth, however, the experiment is characterized by conical indentation, with $\Pi_p$ reaching a constant value. The observed horizontal asymptote indicates that, for the employed loading rate of $P=100$ $\mu$m/s (see Figure 3), the loading phase of the NI test is characterized by mainly elastoplastic material response. Viscoelastic-plastic material response, on the other hand, would result in monotonically decreasing values for $\Pi_p$ during the loading phase of the NI test [13, 12]. When the value for $\Pi_p$, representing the horizontal asymptote is scaled by the respective value corresponding to the elastic solution, $\Pi_p/\Pi_p^0$, with $\Pi_p^0 = \beta 2/\pi \tan \theta/(1-\nu^2)$ [see Equation (6)], the elastoplastic scaling relation $G_0(c/E)$ [13] gives access to the cohesion/stiffness-ratio $c/E$ of the tested material (see Figure 3) and, thus, to the cohesion $c$. Figure 4 shows the result from 20×20 indents performed on OPC paste, with $w/c=0.3$, comparing the material hardness $H$ according to Equation (8) with the cohesion $c$ determined from the loading phase of the NI test by means of the scaling relation $G_0$. Based on the obtained results, $c/E$ at the investigated observation scale is in the range $1/100 – 1/200$. The obtained strength properties characterize plastic material failure due to predominant hydrostatic loading under the indenter tip. Hence, they may not be used to extrapolate material properties describing material failure under mainly deviatoric loading, such as, e.g., the uniaxial tensile- or compressive strength.

Determination of viscous properties

Whereas the loading branch is characterized by mainly elastoplastic material response and unloading is predominated by elastic behavior, the viscous material response during the dwelling phase of the NI test may be employed to quantify the creep behavior of cement-based materials at the $\mu$m-scale. The NI data is characterized by a pronounced increase of the penetration depth during the dwelling phase [see Figure 1(c)], particularly during the first minute after load application. Recently, analytical solutions for conical indentation of the viscoelastic halfspace characterized by the Maxwell model, the Kelvin-Voigt model, and the three-parameter model were derived in [16]. In [12], this approach is extended towards (i) a logarithmic-type creep model [10, 9] and (ii) plastic deformations modelled by the Tresca criterion. The logarithmic-type model is characterized by a creep compliance proportional to $\ln(1 + t/\tau^\nu)$, where $\tau^\nu$ denotes the characteristic time of the creep process, showing the best agreement with experimental data. Whereas elastic material behavior is considered for hydrostatic loading, the viscoelastic deviatoric creep compliance function

$$J^{dev}(t) = \frac{1}{\mu} + J^{v, dev} \ln \left(1 + \frac{t}{\tau_v^{dev}}\right)$$

is employed [12]. Hereby, $\mu = E/(1+\nu)$ [Pa] denotes the shear modulus given by the unloading branch of the NI data, and $J^{v, dev}$ [Pa$^{-1}$] and $\tau_v^{dev}$ [s] the creep compliance parameters to identify. In case of a step load $P(t) = H(t)P_{max}$ applied to a

3 According to [9], the two mechanisms leading to logarithmic creep in crystalline solids are either (i) work hardening: dislocations move forward under the applied stress by overcoming potential barriers, while successively raising the height of the potential barriers or (ii) exhaustion: while neglecting work hardening the barriers to dislocation motion do not have equal activation energies; those with relatively small activation energies are overcome faster than those with relatively large activation energies; if each barrier which is overcome contributes an equal increment of strain, the total strain increases linearly with the increasing activation energy, where the latter is a logarithmic function of time.

4 $h(t)$ denotes the Heaviside step function.
conical indenter, the deviatoric creep law [Equation (9)] gives the penetration history as [12]

\[ h^2(t) = \frac{N(t)P_{\text{max}}}{\beta} \frac{\pi}{2 \tan \theta} \frac{1 - \nu^2}{E} \left( 1 + \frac{1}{2(1 - \nu)} \mu J^{\nu, \text{dev}} \ln \left( \frac{t + \tau^{\nu, \text{dev}}}{\tau^{\nu, \text{dev}}} \right) \right) \left[ G_0 + G_{\text{LOG}}(1 - G_0) \right]^{-1} , \]

(10)

where \( G_0(c/E) \) denotes the elastoplastic scaling relation described in the previous section (see Figure 3) and \( g_{\text{LOG}}(\nu, c/E, J^{\nu, \text{dev}}, \tau^{\nu, \text{dev}}) \) is an interpolation function, which accomplishes the transition between elastoplastic (short-term) response and viscoelastic (long-term) response (see Figure 5) [12]. The unknown deviatoric creep parameters \( J^{\nu, \text{dev}} \) and \( \tau^{\nu, \text{dev}} \) are determined employing a least-square fitting method. Hereby, the error between the measured penetration history in the dwelling phase, \( h^2_{\exp}(t) \), and \( h^2(t) \) for a step load according to Equation (10) is minimized:

\[ R(J^{\nu, \text{dev}}, \tau^{\nu, \text{dev}}) = \sum_n \left[ h^2_{\exp}(t_n) - h^2(t_n, J^{\nu, \text{dev}}, \tau^{\nu, \text{dev}}) \right]^2 , \]

(11)

where \( n \) denotes the number of data points in the dwelling phase considered in the minimization scheme. Figure 6 shows the distribution of \( R \) obtained for an NI test on OPC as a function of \( J^{\nu, \text{dev}} \) and \( \tau^{\nu, \text{dev}} \), indicating a clear minimum. Thus, the proposed parameter-identification scheme leads to a unique solution for \( J^{\nu, \text{dev}} \) and \( \tau^{\nu, \text{dev}} \).

An experimental study was conducted in order to identify the influence of the Blaine fineness \( \phi \) on the finer-scale creep properties. Hereby, the three test series\(^5\) were characterized by \( \phi=3000, 3890, \) and \( 4850 \) cm\(^2\)/g, respectively, \( w/c=0.4 \), and a relative humidity in the test chamber of \( h_{\exp}=50 \% \). The respective results are shown in Figures 7 to 9. The grid indentation, with \( 20 \times 20=400 \) tests for each series, gives access to the spatial distribution of mechanical properties. Hereby, the specimen with \( \phi=3000 \) cm\(^2\)/g is characterized by a coarser microstructure with some anhydrous clinker grains, the specimen with \( \phi=3890 \) and \( 4850 \) cm\(^2\)/g by a finer and more homogeneous microstructure. Whereas the frequency distributions of \( E \) show two (or three) maxima in the range 15–35 GPa, corresponding to different types of CSH [3] [low-density (LD) and high-density (HD) CSH] and portlandite, the frequency distributions of \( 1/J^{\text{dev}}_{\text{CSH}} \) are characterized by one pronounced peak. Hereby, this peak value amounts to \( \approx 22.5 \) GPa for \( \phi=3000 \) cm\(^2\)/g, \( \approx 27.5 \) GPa for \( \phi=3890 \) cm\(^2\)/g, and \( \approx 32.5 \) GPa for \( 4850 \) cm\(^2\)/g. The corresponding values for \( J^{\text{dev}}_{\text{CSH}} \) are \( 0.044, 0.036, \) and \( 0.031 \) GPa\(^{-1}\).

Concluding remarks

- The reasonable duration of the dwelling phase of a nanoindentation (NI) test is limited by the so-called machine drift of the NI-testing rig, \( \dot{h}_{\text{rig}} \). This drift is mainly caused by creep of the 3-axis piezo scanner [7]\(^6\), which is part of the measuring head holding the indenter tip. It is determined prior to the actual NI test by putting the indenter tip on the sample surface, applying a small force, e.g., \( 2 \) \( \mu \)N and recording the deformation rate – ideally until a steady state is reached. However, for materials with low viscosity (i.e., high compliance), the compliance of the indented specimen may spuriously be interpreted as machine drift when employing the mentioned procedure. For the NI tests on ordinary Portland cement (OPC) pastes presented in this paper, \( | \dot{h}_{\text{rig}} | \) ranges from 0.01 to 0.1 nm/s. Once \( | \dot{h}_{\text{rig}} | \) is in the range of the penetration rate, the test data loses its relevance. For cement-based materials and the employed NI-testing equipment, a reasonable duration of the dwelling phase was found to be around 2 – 3 minutes. On the other hand, the average value of the penetration rate at the begin of the dwelling phase was approximately 30 nm/s for the conducted NI tests.

Another source of measuring errors is the so-called thermal drift. It is associated with thermal dilation of test rig and specimen. The thermal-drift error can be minimized by (i) setting up the NI test equipment in a temperature-controlled environment and (ii) storing the specimen in the test rig (which is hooded) prior to testing.

- Viscous material response influences the unloading slope and, thus, the determination of elastic properties [1]. This effect can even cause “outbulging” in the load-penetration diagram, characterized by increasing penetration depth for decreasing loading of the indenter tip. Two measures minimize the described deviation from purely elastic unloading: (i) A sufficiently long dwelling phase. When the creep response subsides, i.e., the creep potential is consumed to a great part, unloading is not influenced either. (ii) Fast unloading – for the theoretical situation of infinitely fast unloading, only elastic material response occurs. The two measures are also visible when deriving a criterion for a suitable duration of the unloading time, \( \tau_u \), in order to exclude viscoelastic behavior during the unloading branch [16]. For a finite unloading period following a step load, this criterion reads for the logarithmic-type model [12]

\[ \tau_u \ll \frac{2(1 - \nu)}{\beta \mu J^{\nu, \text{dev}}} \left( t_u + \tau^{\nu, \text{dev}} \right) , \]

(12)

with \( t_u \) denoting the time instant at the beginning of the unloading phase. Hence, for the load history considered in the performed NI tests, characterized by a duration of the dwelling phase of 100 s, and \( \mu = E/[2(1 + \nu)] = 20/[2(1 + 0.24)] = 8 \) GPa, \( \tau_u = 1 \) s \( \ll 2(1 - 0.24)(101 + 0.1)/(1.0818 \times 0.037) = 480 \) s, thus, satisfying condition (12).

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\(^5\)These test series were characterized by a maximum load of \( 1000 \) \( \mu \)N and a duration of loading, dwelling, and unloading phase of 1, 100, and 1 s, respectively.

\(^6\)Whereas a capacitive transducer is employed for load application, a 3-axis piezo scanner is adopted for 3D imaging of the sample surface, as well as for the (final) approach of the indenter tip to the sample surface before NI testing.
References


Figure 4: (a) Young’s modulus $E$ according to Equation (7), (b) Hardness $H$ according to Equation (8), and (c) cohesion $c$ according to Figure 3 for material phases encountered at the cement-paste scale (grid-indentation with $20 \times 20$ indents and distance between adjacent grid points of 5 $\mu$m on OPC paste characterized by $w/c=0.3$ and a Blaine fineness of $4000 \text{ cm}^2/\text{g}$).
Figure 5: Interpolation function $g_{LOG}(\nu, c/E, J^{v,dev}, \tau^{v,dev})$ for different values of $\Pi_\mu = \mu J^{v,dev}$, $\nu=0.24$, and $\Pi_c = c/E = 1/100$.

Figure 6: Distribution of $\mathcal{R}$ as a function of $J^{v,dev}$ and $\tau^{v,dev}$ [see Equation (11)] showing uniqueness of the solution obtained by the proposed parameter-identification scheme.
Figure 7: (a) Young’s modulus $E$ according to Equation (7) and (b) creep parameter $J^{v, dev}$ obtained from backcalculation of the dwelling phase (grid-indentation with $20 \times 20$ indents and distance between adjacent grid points of 5 $\mu m$ on OPC paste characterized by $w/c=0.4$ and a Blaine fineness of 3000 $cm^2/g$)

Figure 8: (a) Young’s modulus $E$ according to Equation (7) and (b) creep parameter $J^{v, dev}$ obtained from backcalculation of the dwelling phase (grid-indentation with $20 \times 20$ indents and distance between adjacent grid points of 5 $\mu m$ on OPC paste characterized by $w/c=0.4$ and a Blaine fineness of 3890 $cm^2/g$)
Figure 9: (a) Young’s modulus $E$ according to Equation (7) and (b) creep parameter $J^{v,dev}$ obtained from backcalculation of the dwelling phase (grid-indentation with $20 \times 20$ indents and distance between adjacent grid points of $5 \, \mu m$ on OPC paste characterized by $w/c=0.4$ and a Blaine fineness of $4850 \, cm^2/g$).

$$E \,[GPa]$$

$$\frac{1}{J^{v,dev}} \,[GPa]$$