Evaluation of micro-mechanical properties of nonlinear cementitious composite using large-displacement transient nanoindentation analysis

B S SINDU*, SAPTARSHI SASMAL and B SARAVANAN

CSIR-Structural Engineering Research Centre, CSIR Campus, Taramani, Chennai 600113, India
e-mail: sindu@serc.res.in; sindu.lsn@gmail.com

MS received 20 September 2016; revised 19 June 2017; accepted 14 July 2017; published online 10 March 2018

Abstract. Nanoindentation technique is employed for evaluation of mechanical properties of homogeneous materials at micro-level. Many engineering materials, especially cement and concrete composites, which are extensively used as building materials, exhibit phase heterogeneity and are highly porous. The presence of pores highly influences the response obtained from nanoindentation tests. In this study, mechanical properties of Calcium-Silicate-Hydrate (C-S-H), the primary binding agent in cementitious composites, are investigated using a simulated nanoindentation technique. The influence of presence of pores and its geometrical distribution on the non-linear response of C-S-H phases and the stress distribution are critically analysed.

Keywords. Nanoindentation; Calcium-Silicate-Hydrate; finite-element simulations; pores; mechanical properties.

1. Introduction

Indentation is a simple and commonly applied method to evaluate the mechanical properties of materials. Nanoindentation is a particular type of indentation that is performed to find out the material properties, especially hardness and elastic modulus, at micro- and nano-level. The technique originated from Mohs scale of mineral hardness introduced in 1812 [1]. The concept of nanoindentation test is based on contact mechanics. The analysis of the stress at the contact of two elastic solids was first developed by Hertz. The assumptions made in Hertz's theory are the following: (i) the surfaces are continuous and non-conforming, i.e., $a \ll R$ where a is the dimension of the contact area and R is the relative radius of curvature of the two bodies, (ii) the strains are small, (iii) solids can be considered as elastic half-space, i.e., $a \ll R_1$, $a \ll R_2$, and $a \ll l$, where R_1 and R_2 are the radius of curvature of the bodies and l is the significant dimension of the bodies and (iv) surfaces are frictionless.

Nanoindentation tests for determining the mechanical properties of homogeneous materials like metals, glass and ceramics are well established and are being widely used. However, application of nanoindentation technique for heterogeneous and porous materials such as cementitious composites, where it could be helpful to disclose the micromechanical properties of individual cement components, interfacial zones, fibres, aggregate, etc., is not very well established [2].

C-S-H is the primary binding agent in Portland cement. It forms the major hydration product in the hardened cement paste. Though cementitious materials are heterogeneous and the amount of presence of low density (LD) and high density (HD) C-S-H varies based on the mix proportions, the mechanical properties of both the phases remain constant because they are the intrinsic properties of the matrix. However, since cementitious materials are highly porous, there is a huge possibility that the nanoindentation is performed in the vicinity of pore. Due to the presence of pore, the mechanical response will be considerably altered. In recent years, a few attempts have been made by various researchers to apply the nanoindentation technique for evaluation of the mechanical properties of cementitious materials in form of hardened cement paste/mortar/concrete specimens. Velez *et al* [3] determined the elastic modulus and hardness of cement clinkers, viz., C_3S , C_2S , C_3A and C_4AF , by the nanoindentation technique. From their studies, it was found that the elastic modulus of these phases is between 125 and 145 GPa. It was also reported that the hardness of C_3A is around 10 GPa and that of silicates around 8–9 GPa. Constantinides *et al* [4] carried out nanoindentation tests on intact and calcium-leached cementitious material and confirmed the presence of two forms of C-S-H, i.e., LD and HD forms. Role of the HD and LD C-S-H on elastic stiffness and hardness of cement-based materials was also identified. Mondal *et al* [5] used the nanoindentation technique to determine nanoscale mechanical properties of interfacial transition zone (ITZ) in concrete. It was brought out that the ITZ in

*For correspondence

concrete is highly heterogeneous and the average modulus of ITZ is up to 70–85% of that of the matrix. Jones and Grasley [6] carried out nanoindentation tests on hardened cement pastes to determine the time-dependent mechanical properties of C-S-H phases. Taha *et al* [7] proposed a new technique in which the energy absorbed by the cracks propagating from the nanoindentation imprints was used to determine the nanoscale fracture toughness of the hardened cement paste. Aquino *et al* [8] used nanoindentation technique to develop a two-dimensional map of elastic modulus and density of cement paste, which closely resembled the BSE image obtained through SEM.

It can be found from this discussion that nanoindentation has proven to be an efficient technique to determine the nano-mechanical properties of various components of cementitious materials [9–12]. However, carrying out nanoindentation tests (experimental) on heterogeneous and porous cementitious materials is extremely sensitive to workmanship and expertise, and involves many ambiguities and complexities. Hence, a validated numerical technique for simulating nanoindentation is an excellent way to evaluate the nano-mechanical properties of heterogeneous materials. Further, pores (capillary and gel) are developed in hydrated cement paste at different stages of hydration. The presence of these pores plays a vital role in the mechanical- and transport-properties of the hardened cement paste. If the nanoindentation is carried out in the vicinity of these pores, mechanical properties are under-predicted, and hence the whole properties of the matrix itself may be wrongly interpreted. Hence, a thorough study needs to be carried out to highlight the influence of pores on the nano-mechanical properties of cementitious materials evaluated using nanoindentation technique.

With the rapid development of finite elements (FE) analysis programs, it becomes comparatively easy to simulate the nanoindentation tests and investigate the influence of various parameters, which cannot be investigated through very expensive and complicated experiments. Sharma *et al* [13] simulated nanoindentation tests using FE to determine the mechanical properties of metals. Pelegri and Huang [14] used FE-simulated nanoindentation technique to determine the mechanical properties of two different film–substrate systems, i.e., soft film–hard substrate and hard film–soft substrate material systems and investigated its effect on pile-up and sink-in phenomena. Yan *et al* [15] investigated the numerically simulated nanoindentation technique to determine the conditions under which the Oliver–Pharr method is applicable. Sarris and Constantinides [16] used FE method to simulate the nanoindentation of Calcium-Silicate-Hydrate (C-S-H) phases. The influence of material properties (E , c and ϕ) and contact friction on the elastic stiffness and hardness of C-S-H phases was investigated. Also, the parameters influencing

the pile-up phenomenon were also identified. Asrour and Asrour [17] simulated nanoindentation test on cement paste using a visco-elastic–plastic material model. The proposed model was validated with the results obtained from experiments where load level, indentation magnitude and time of creep are the parameters. From this discussion, it can be observed that simulated nanoindentation tests on cement phases can help in understanding the mechanical behaviour of these phases better and identifying the influencing parameters of the same.

In the present study, nanoindentation test is numerically simulated in order to predict the mechanical properties of C-S-H phases. The influence of parameters like friction coefficient, the location of the pore and distribution of pores on the mechanical properties like Young's modulus, hardness and peak load has been thoroughly investigated. The present study emphasizes on the non-linear response of the C-S-H phases and stress distribution during the indentation process. Further, influence of presence of pores on load–deformation response, force-transfer mechanism and other mechanical behaviour parameters is studied. The location of pores from the indentation zone is considered as a parameter. Based on this, contours have been developed to depict the zones with expected amount of reduction of mechanical response of cement matrix due to the presence of pores. Also, the influence of the distribution of pores in the matrix on the predicted response has also been analysed. In order to simulate the distribution of pores in a more realistic way, a cement hydration model has been used to develop the microstructure of cement matrix including pores. Further, a discretization algorithm is developed to import the microstructures for computational nanoindentation using FE analysis.

2. Theoretical background

Though nanoindentation test is well established, a brief on the theoretical aspects related to the nanoindentation followed by the specific information as used in the present study is given here for ready reference. In an indentation test, a hard tip whose mechanical properties are known (generally made of a very hard material like diamond) is indented into a sample whose properties are unknown. In this procedure, load is successively applied on the indenter tip until it reaches the desired level. After performing indentation, the residual imprints in the indented material can be visualized using an Atomic Force Microscope (AFM) and the area of the indenter can be measured. Generally, indentation is done in two phases, namely the loading and unloading phases. The load–displacement characteristics obtained from the nanoindentation experiment are used to evaluate the intrinsic mechanical properties such as hardness and Young's modulus of the indented matrix.

Figure 1. Typical load versus indentation depth plot from nanoindentation.

A schematic representation of a typical load–displacement plot of nanoindentation test is shown in figure 1, where the parameter P denotes the load applied by the indenter and h is the displacement relative to the initial undeformed surface or the indentation depth. Figure 2 presents the geometry related to indentation test [18].

The contact problem with spherical indenter indenting a flat specimen was first studied by Hertz [19]. From this problem, the radius of the circle of contact is given as

$$a^3 = \frac{3PR}{4E^*} \quad (1)$$

where E^* is the combined elastic modulus of the indenter and specimen, expressed as follows:

$$\frac{1}{E^*} = \frac{(1-\nu^2)}{E} + \frac{(1-\nu'^2)}{E'} \quad (2)$$

where E and ν are the elastic modulus and Poisson's ratio of the indenter material, respectively, while E' and ν' denote the elastic modulus and Poisson's ratio of the specimen, P is the indentation load and R is the radius.

Oliver and Pharr [18] proposed a method of analysis of nanoindentation based on analytical solutions. The load–displacement response of nanoindentation test consists of

Figure 2. Geometry of an indentation test.

an elastic–plastic loading followed by an elastic unloading. They used the elastic equations of contact with the unloading data to determine the elastic modulus and hardness of the specimen material. At any time during loading, the total displacement h is written as

$$h = h_c + h_s \quad (3)$$

where h_c is the contact depth and h_s is the displacement of the surface at the perimeter of the contact as shown in figure 2. At the peak load, P_{max} , displacement is h_{max} and the radius of contact circle is a . The projected contact area, A , is determined as a function of contact depth, h_c . For a conical or Berkovich indenter, the contact depth is given by

$$h_c = h_{max} - \varepsilon \frac{P_{max}}{S} \quad (4)$$

where $S (= dP/dh)$ is the slope of the unloading curve and ε is a factor that depends on indenter geometry. The combined elastic modulus is given by

$$E^* = \frac{1}{2} \frac{dP}{dh} \frac{\sqrt{\pi}}{\sqrt{A}} \quad (5)$$

Thus, the elastic modulus of the specimen can be found from Eq. (2) using the combined elastic modulus calculated from Eq. (5). Hardness of the material can be calculated by dividing the maximum load (P_{max}) by the projected contact area (A). For a Berkovich indenter (used in the present work), $A = 24.5h_c^2$ as given by Oliver and Pharr [18]. Specific details are provided while explaining the simulation studies as given in section 3.

3. Simulated indentation on nonlinear cementitious composite

Indentation is a highly non-linear contact problem. In order to handle this complex problem, commercially available FE package ANSYS is used. Large-displacement transient analysis in 2D FEM is carried out to solve the problem. In this study, three types of elements are used in the modelling, i.e., (a) PLANE 182, (b) CONTA 172 and (c) TARGE 169. 2D 4-node planar element PLANE 182 is used to model all the areas of indenter and matrix material. This element type is so chosen to accommodate the axisymmetric modelling function. It is capable of being used in cases of large deflection and large strain as well. The bottom surface of the indenter and the top surface of the matrix material form a contact pair in these models. It should be mentioned that PLANE 182 can be coupled with CONTA171 and TARGE169 elements to define a contact pair. CONTA 172 and TARGE 169 are known as contact pair elements. CONTA 172 is defined at material top surface, where the

Figure 3. (a) Full model and (b) part of the model near the contact area (dimensions are in nanometres).

Table 1. Material properties.

Material	Young's modulus (GPa)	Poisson's ratio	Yield strength (MPa)	Tangent modulus (MPa)
Diamond	1140	0.07	—	—
HD C-S-H	31	0.24	50	3100
LD C-S-H	21	0.24	20	2100

Table 2. Validation of the numerical model proposed in the present study.

Material	Property	Acker [20]	Constantinides <i>et al</i> [4]	Sarris and Constantinides [16]	Present work
HD C-S-H	Young's modulus (GPa)	31 ± 4	29.4 ± 2.4	38.94	31.63
LD C-S-H	Young's modulus (GPa)	20 ± 2	21.7 ± 2.2	28.37	20.31

indenter will be in contact, and the TARGE 169 is defined at indenter bottom surface, where it will be in contact with material.

3.1 Geometry of the model

The matrix dimension is assumed to be $25000 \times 25000 \text{ nm}^2$, which is large enough to remove the boundary effects. A conical indenter of tip radius 1800 nm and apex angle of 70.3° is modelled since it will have the same projected area as that of a Berkovich indenter. One half model of the matrix and the indenter are modelled for computational efficiency. Symmetric boundary conditions are applied to represent the full model. In order to acquire localized deformation of the material, the mesh density needs to be very high. However, to improve computational

Figure 4. Boundary conditions.

Figure 5. Influence of friction coefficient on (a) HD C-S-H and (b) LD C-S-H.

Figure 6. Schematic diagram of nanoindentation of matrix with a pore.

efficiency, two different sizes of meshes are used. The mesh near the contact area is made denser and that away from it is made less dense. The mesh size near the contact area is $333 \times 333 \text{ nm}^2$ and away from it is $1000 \times 1000 \text{ nm}^2$ as shown in figure 3.

3.2 Material properties

Diamond, which is used as the indenter, is modelled with linear elastic isotropic property. The HD and LD C-S-H are modelled using non-linear inelastic bilinear property. The material properties used in this model are presented in table 1.

The Young's modulus and Poisson's ratio are obtained from the experimental data reported by Acker [20] and Constantinides *et al* [4]. The yield strength of C-S-H varies from 0.9% to 2% of elastic modulus and the tangent modulus varies from 10% to 15% of elastic modulus. The value of yield stress and tangent modulus was varied between these ranges by trial and error

method to match the experimental results shown in table 2.

3.3 Boundary conditions and loading

Symmetric boundary condition is applied around the axis of symmetry, i.e., it is restricted from moving along the lateral direction and allowed to move only in the vertical direction. The nodes in the base of the matrix are completely fixed, i.e., they cannot move in any direction as shown in figure 4. The test is carried out in displacement control mode. It is applied in two stages: loading and unloading. During the loading stage, the indenter is indented into the specimen and during unloading stage, it is brought back to its initial position. In both stages, the displacement is applied in small steps at the rate of loading of $\pm 20 \text{ nm/s}$. The maximum depth of indentation is 200 nm.

4. Results and discussion

The influence of the parameters like friction coefficient, presence of pores at different locations and their distribution on the mechanical properties of HD and LD C-S-H has been investigated.

4.1 Contact friction

The effect of contact friction between the material and the indenter on the load-displacement behaviour of HD and LD C-S-H has been investigated. Isotropic, Coulomb's friction model is used to model the contact friction in which the two contacting surfaces can carry shear stress. According to this model

$$\tau = \mu P \quad (6)$$

where τ is the shear stress, μ is the coefficient of friction and P is the contact normal pressure. The friction

Figure 7. Contour plots of vertical deformation (all units in nm).

coefficient is varied from 0 to 1 in both HD and LD C-S-H and its effect on the load–displacement behaviour is investigated. Figure 5a and b shows the influence of friction coefficient on HD and LD C-S-H, respectively.

It can be found from the plots that the friction coefficient does not play any significant role in the load–displacement response of both LD and HD C-S-H. The mechanical properties such as elastic modulus and hardness are derived from the load–displacement response and are found to be similar with different friction coefficients. Hence, in the forthcoming studies, the coefficient of friction $\mu = 0$ is used while defining the contact surfaces.

4.2 Presence of pores

The two major types of pores present in cement matrix are the gel pores and capillary pores. The gel pores are of size varying from 0.5 to 10 nm and they influence the creep and

shrinkage properties of the cement paste. The capillary pores are of size varying from 5 to 5000 nm and influence the strength and elasticity of cement paste [21]. In this study, the influence of capillary pores on the mechanical properties of C-S-H is investigated. The size of the pore is assumed to be 500 nm (average size of capillary pore). A single pore of this size is placed at different locations in LD and HD C-S-H matrix. Though, in reality, pores exist randomly in number and position, a single pore with constant diameter is considered first in order to avoid any interference effect between the pores and to omit the superposed influence of various parameters such as distribution and size of pores. Since, the computational model was considered as a symmetric model, a pore located exactly at the middle (centre of pore coinciding with the indenter tip) is not considered in this study, as it over-predicts the response on account of having only half the pore in the simulation region. However, a case has been considered where the edge of pore coincides with the

Figure 8. Contour plots of vertical stress distribution (all units in GPa).

indenter tip. This case has been mentioned as “below indenter” in the further sections. The pore is modelled by removing the matrix material and assigning no material properties. Figure 6 shows a schematic diagram of nanoindentation being carried out on a matrix with pore. The distance of the centre of pore from the centre of the matrix is denoted as x and its distance from the bottom of the matrix is denoted as y . Thus, the location of the pore is represented in the coordinate system of (x,y) . The influence of location of pores on the mechanical properties of LD and HD C-S-H is investigated. This notation is used throughout the paper while mentioning the location of the pore.

To get a clear picture of the influence of pore on the deformation pattern and stress-flow behaviour, contour plots of deformation along vertical direction, variation of stress along vertical direction and von Mises stress in LD and HD C-S-H under maximum indentation position are shown in figures 7, 8 and 9, respectively, for with pore and without pore cases.

The influence of pores on the vertical deformation can be observed from figure 7. It is found that there is no influence on vertical spread of deformation zone due to the presence of pores in both LD and HD C-S-H. Further, the horizontal spread of deformation zone is increased by 37% in both cases.

It can be seen from figure 8 that the vertical stress distribution is affected due to the presence of pore. The vertical stress zone is decreased up to 10.5% in vertical direction and increased up to 21.5% in horizontal direction due to the presence of pore in LD C-S-H. However, it is decreased up to 9.5% in vertical direction and increased up to 34.7% in horizontal direction in HD C-S-H. From these results it can be concluded that the vertical spread is affected more in LD C-S-H whereas the horizontal spread is affected more in HD C-S-H due to the presence of pore.

The influence of pore on von Mises stress distribution can be observed from figure 9. The presence of pore leads

Figure 9. Contour plots of von Mises stress distribution (all units in GPa).

to under-prediction of the stress zone up to 11.5% in vertical direction and 12.4% in horizontal direction in HD C-S-H. In LD C-S-H, the presence of pore leads to under-prediction of the stress zone by 13% in the vertical direction and 18% in the horizontal direction. Unlike the vertical stress distribution, the influence of pore on von Mises stress zone is monotonic in both directions and more in LD C-S-H. The load–displacement plots of HD and LD C-S-H with pores at two different locations are shown in figures 10–13.

Table 3 shows the peak load, Young's modulus and hardness of HD C-S-H with pores at different locations and the percentage difference of these properties with respect to HD C-S-H without pore.

It can be observed from figures 10 and 11 and table 3 that there is a huge positional dependence of pores on the mechanical properties like peak load, Young's modulus and hardness of HD C-S-H. For a pore with $r_p/r_i = 0.28$ (radius of pore by radius of indenter) located at $d/D = 0.0464$ (distance of pore from the

Figure 10. Load–displacement curve of HD C-S-H with pore at 23200 level (in legend, initial digit shows the horizontal coordinate of the pore).

surface of the matrix to the depth of the matrix), the mechanical properties are under-predicted by 35%. Further, when d/D is increased to 0.072, the results are

Table 3. Mechanical properties of HD C-S-H with pores at different locations.

	Horizontal distance from the centre of the matrix (nm)	Vertical distance from the bottom of the matrix (nm)	Peak load (mN)	Per. diff. w.r.t. no pore (%)	Young's modulus (GPa)	Per. diff. w.r.t. no pore (%)	Hardness (MPa)	Per. diff. w.r.t. no pore (%)
1000		23200	0.596	14.98	27.12	14.27	716.66	15.12
1400		23200	0.623	11.12	27.84	11.99	751.91	10.95
1550		23200	0.638	9.02	29.01	8.27	766.97	9.16
600		23400	0.545	22.26	24.24	23.35	658.17	22.05
1000		23400	0.558	20.39	25.57	19.17	670.21	20.62
1200		23400	0.582	16.94	26.80	15.28	698.67	17.25
1300		23400	0.592	15.54	26.88	15.02	712.27	15.64
1400		23400	0.608	13.23	26.58	15.96	737.27	12.68
1600		23400	0.624	11.00	29.38	7.10	745.40	11.72
1650		23400	0.629	10.23	29.15	7.84	754.17	10.68
1000		23600	0.519	26.01	22.82	27.86	627.78	25.65
1200		23600	0.549	21.68	24.01	24.08	665.38	21.19
1300		23600	0.565	19.39	25.27	20.09	681.74	19.26
1400		23600	0.586	16.38	25.75	18.60	709.74	15.94
1500		23600	0.601	14.23	26.37	16.63	728.26	13.75
1600		23600	0.613	12.57	26.74	15.46	743.07	11.99
1700		23600	0.632	9.86	28.33	10.42	761.99	9.75
1000		23840	0.447	36.19	21.72	31.33	531.56	37.04
1300		23840	0.543	22.54	23.24	26.51	660.88	21.73
1400		23840	0.568	18.89	24.85	21.42	689.09	18.38
1500		23840	0.594	15.20	25.91	18.10	720.94	14.61
1600		23840	0.623	11.16	26.87	15.05	756.80	10.37
1800		23840	0.626	10.70	27.87	11.90	755.94	10.47
1850		23840	0.635	9.43	29.48	6.79	760.53	9.92

Figure 11. Load–displacement curve of HD C-S-H with pore at 23840 level (in legend, initial digit shows the horizontal coordinate of the pore).

Figure 12. Load–displacement curve of LD C-S-H with pore at 23200 level (in legend, initial digit shows the horizontal coordinate of the pore).

Figure 13. Load–displacement curve of LD C-S-H with pore at 23840 level (in legend, initial digit shows the horizontal coordinate of the pore).

under-predicted only by 15%. A similar influence is observed when a pore is located at a constant d/D but varying horizontal distance. This shows that the position of pore has a significant influence on the mechanical properties of HD C-S-H.

The load–displacement plots of LD C-S-H with pores at different locations are shown in figures 12 and 13. It can

also be observed from these plots that as the pore comes closer to the indenter, the mechanical properties are affected more, the same as in HD C-S-H, but the region of influence is lesser in LD C-S-H compared with that of HD C-S-H.

In order to understand the influence better, a table (table 4) has been presented to show the percentage difference in peak load, Young's modulus and hardness of LD C-S-H with pores at different locations with respect to LD C-S-H without pore.

It can be observed from figures 12 and 13 and table 4 that the positional influence of pore on the mechanical properties of LD C-S-H is of a similar extent as in HD C-S-H.

From these investigations, it is evident that though nanoindentation technique can capture the micro-mechanical response of key phases of cement matrix very well, the accuracy significantly depends on the substrate condition, specifically, presence of pores. It is found that the presence of pores in the stress influence zone considerably alters the stress flow pattern. Smooth distribution of stress is replaced by partial stress concentration due to the presence of pores. Since nanoindentation is a highly sophisticated and sensitive technique for mechanical characterization at lower scales, it is required to understand the influence zones of pores in heterogeneous cementitious matrix so that the results obtained from such techniques can be used with a calculated scattering in results.

To meet this need, zones have been identified where the presence of pores leads to under-prediction of the mechanical characteristics and are termed as “influential zones”. Contour plots are presented showing the 20%, 15% and 10% deviation in various mechanical responses such as Young's modulus, hardness and peak load in both LD and HD C-S-H. Figures 14 and 15 show the contour plots drawn at the top of the specimen, which is very close to the indentation region. The numbers in the figure represent the distance from the tip of indentation point with respect to radius of pore in horizontal direction and distance from the tip of indentation point with respect to diameter of pore in vertical direction. It is clear from the figure that the presence of pore in the stress bulb region produced during indentation causes very high influence in the response and in all cases, viz., Young's modulus, hardness and strength (peak load), the influence of pore is qualitatively similar.

4.3 Distribution of pores

Though a single pore of spherical shape has been considered in the previous section for better understanding and to prevent interference effect, this is a more idealistic scenario. In order to understand the influence of pores in a more realistic way, C-S-H matrix with pores is modelled using a cement hydration model, CEMHYD3D [22]. In CEMHYD3D, a computational volume of size 100×100

Table 4. Mechanical properties of LD C-S-H with pores at different locations.

Horizontal distance from the centre of the matrix (nm)	Vertical distance from the bottom of the matrix (nm)	Peak load (mN)	Per. diff. w.r.t. no pore (%)	Young's modulus (GPa)	Per. diff. w.r.t. no pore (%)	Hardness (MPa)	Per. diff. w.r.t. no pore (%)
800	23200	0.351	17.07	16.41	19.19	419.79	16.68
1000	23200	0.356	15.93	17.20	15.29	422.97	16.05
1100	23200	0.360	14.80	17.29	14.85	429.30	14.79
1500	23200	0.377	10.78	18.09	10.93	449.65	10.75
1000	23400	0.336	20.47	15.06	25.85	405.93	19.43
1350	23400	0.357	15.56	15.37	24.30	434.44	13.77
1400	23400	0.360	14.85	16.27	19.88	433.89	13.88
1600	23400	0.371	12.39	16.44	19.06	448.01	11.08
1700	23400	0.384	9.27	17.43	14.18	461.85	8.33
1800	23400	0.388	8.23	18.49	8.98	463.05	8.09
1000	23600	0.312	26.26	13.63	32.88	378.16	24.94
1300	23600	0.339	19.81	15.90	21.73	405.78	19.46
1550	23600	0.361	14.78	16.36	19.44	433.86	13.89
1600	23600	0.364	13.88	16.66	17.96	437.80	13.10
1750	23600	0.383	9.43	17.22	15.19	461.90	8.32
1350	23840	0.336	20.69	13.64	32.83	413.02	18.02
1400	23840	0.343	18.94	14.05	30.83	421.43	16.35
1500	23840	0.354	16.26	16.20	20.22	425.64	15.52
1650	23840	0.369	12.72	17.17	15.48	442.32	12.21
1800	23840	0.373	11.94	18.11	10.81	442.68	12.14
1875	23840	0.387	8.51	18.39	9.44	461.78	8.34

Figure 14. Contour plots showing the positional influence of pore on the mechanical properties of HD C-S-H (20%, 15% and 10% influential zone). The numbers in the figure represent the distance from the tip of indentation point with respect to radius of pore (l/r_p) in horizontal direction and distance from the tip of indentation point with respect to diameter of pore ($l/2r_p$) in vertical direction.

Figure 15. Contour plots showing the positional influence of pore on the mechanical properties of LD C-S-H (20%, 15% and 10% influential zone). The numbers in the figure represent the distance from the tip of indentation point with respect to radius of pore (l/r_p) in horizontal direction and distance from the tip of indentation point with respect to diameter of pore ($l/2r_p$) in vertical direction.

$\times 100$ voxels is filled with cement clinkers as per the particle size distribution of cement under investigation. They are then subjected to hydration under desired conditions. A set of rules are employed to simulate the hydration behaviour. A more detailed description of simulating the hydration behaviour can be found in Sindu *et al* [23]. For this study, OPC 53-grade cement with a w/c ratio of 0.4 is subjected to hydration using the hydration model. Figure 16a and b shows the initial microstructure and the microstructure obtained after complete hydration, respectively. An area having 100×100 elements, each of size $1 \mu\text{m}$, is created in ANSYS 12.0 in order to represent a section of the microstructure obtained from CEMHYD3D. The material assignments to these elements are as per the distribution of phases in the obtained microstructure. An in-build Matlab code is used for this purpose. Though the hydrated microstructure contains many other phases like ettringite, monosulphate and portlandite, these phases are converted into HD C-S-H and the pores are kept as such.

The material properties of C-S-H and indenter are as in section 3.2. Pores are given a very soft property (with elastic modulus of 0.001 GPa and Poisson's ratio of 0.499) in order to make them behave like complete voids.

Only the pore distribution close to indentation region will affect the results. Hence, three different regions (named as case I, II and III in figure 17a, b and c, respectively) are chosen from this microstructure, which have different pore sizes and patterns, and subjected to nanoindentation. In case I, the pores are concentrated and is located a little farther from the indentation region. In case II, pores are of smaller size but located closer to indentation region. Case III is the worst scenario where many pores are concentrated in one region which is much closer to the region of indentation and just below the indenter.

Load–displacement characteristics obtained from simulated nanoindentation studies for all three cases are shown in figure 18. It can be observed from the figure that there is a considerable difference in the obtained results. It is very

Figure 16. Microstructures: (a) initial and (b) 28 days hydrated. [Colour code: black – pores, yellow – C_4AF , green – C_3A , red – C_3S , sky blue – C_2S , grey – gypsum, dark blue – portlandite, orange – C-S-H, ettringite – lime green, monosulphate – lime green.]

Figure 17. Discretized numerical model of C-S-H matrix containing pores obtained from hydration model: (a) case, (b) case II and (c) case III. [Colour code: violet – C-S-H, red – pore.]

interesting to note that though all three cases correspond to different regions of the same microstructure, the obtained results are considerably different. This is because of

different pore patterns present in each case closer to the region of indentation. The study emphasizes that the simulated nanoindentation is a good tool for understanding the

Figure 18. Load–displacement curve of C-S-H with three different pore patterns.

problems based on contact mechanics and it will help in evaluating the mechanical behaviour parameters of complex materials like cementitious composites.

5. Conclusions

In this paper, FE method was used to simulate the nanoindentation test on two major cement phases, LD and HD C-S-H. The method proposed in the present study has shown that the micro-mechanical response obtained from the numerical simulation technique adopted in the present study is well supported with the results obtained from experimental investigation. The influence of factors like contact friction, location of pores and their distribution on the mechanical properties like Young's modulus and hardness has been investigated. It has been found from the studies that friction coefficient does not affect the load–displacement behaviour of both HD and LD C-S-H. However, the presence of pores plays a vital role on its mechanical properties. It is also found out that the location of pores also causes considerable change in the response observed from nanoindentation tests. Based on the investigations, zones have been identified where the presence of pores leads to under-prediction of the peak load, Young's modulus and hardness by 20%, 15% and 10% and contour plots have been developed for both HD and LD C-S-H. Also, in order to simulate a more realistic case, multi-pore cases have been generated using cement hydration model. Three different multi-pore cases corresponding to three different locations of C-S-H matrix having different types of arrangement of pores have been considered. It has been observed that the pore pattern also plays a crucial part while carrying out nanoindentation tests. Since cementitious matrix is heterogeneous, the presence of other phases in the vicinity of the phase of interest also influences the mechanical properties obtained through nanoindentation test. Hence, attempt is being made to determine the effect of presence of various phases at the vicinity of indenting region on the mechanical properties. Also, numerical

simulations on the grid nanoindentation are also being conducted to mimic the actual experimental set-up.

References

- [1] Mohs F 1825 *Treatise on mineralogy: or, The Natural History of the Mineral Kingdom* (vol. 1). A. Constable and Company, Edinburgh, and Hurst, Robinson, and Company, London
- [2] Barbhuiya S and Nikraz H 2013 A review on the use of nanoindentation technique in characterizing cement-based materials. In: *Proceedings of the International Conference on Advanced Nanomaterials and Emerging Engineering Technologies (ICANMEET)*, IEEE, pp. 613–619
- [3] Velez K, Maximilien S, Damidot D, Fantozzi G and Sorrentino F 2001 Determination by nanoindentation of elastic modulus and hardness of pure constituents of Portland cement clinker. *Cem. Concr. Res.* 31(4): 555–561
- [4] Constantinides G, Ulm F J and Van Vliet K 2003 On the use of nanoindentation for cementitious materials. *Mater. Struct.* 36(3): 191–196
- [5] Mondal P, Shah S P and Marks L D 2009 Nanomechanical properties of interfacial transition zone in concrete. In: *Nanotechnology in construction*, vol. 3. Berlin–Heidelberg: Springer, pp. 315–320
- [6] Jones C A and Grasley Z C 2011 Short-term creep of cement paste during nanoindentation. *Cem. Concr. Compos.* 33(1): 12–18
- [7] Taha M R, Soliman E, Sheyka M, Reinhardt A and Al-Haik M 2010 Fracture toughness of hydrated cement paste using nanoindentation. In: Oh B H *et al* (Eds.) *Fracture mechanics of concrete and concrete structures—recent advances in fracture mechanics of concrete*. Seoul: Korea Concrete Institute, pp. 105–111
- [8] Aquino R J, Koleva D A, Koenders E A and Van Breugel K 2013 Characterization of Portland cement paste using MIP, nanoindentation and esem techniques. In: *Proceedings of the First International Conference on Concrete Sustainability*. Tokyo: Japan Concrete Institute, pp. 1088–1093
- [9] Xu J, Corr D J and Shah S P 2015 Nanomechanical properties of CSH gel–cement grain interface by using nanoindentation and modulus mapping. *J. Zhejiang Univ.—Sci. A* 16(1): 38–46
- [10] Yaghoobi M and Voyiadjis G Z 2014 Effect of boundary conditions on the MD simulation of nanoindentation. *Comput. Mater. Sci.* 95: 626–636
- [11] Jha K K, Suksawang N and Agarwal A 2014 A new insight into the work-of-indentation approach used in the evaluation of material's hardness from nanoindentation measurement with Berkovich indenter. *Comput. Mater. Sci.* 85: 32–37
- [12] Wilson W, Rivera-Torres J M, Sorelli L, Durán-Herrera A and Tagnit-Hamou A 2017 The micromechanical signature of high-volume natural pozzolan concrete by combined statistical nanoindentation and SEM–EDS analyses. *Cem. Concr. Res.* 91: 1–12
- [13] Sharma K, Bhasin V, Vaze K K and Ghosh A K 2011 Numerical simulation with finite element and artificial neural network of ball indentation for mechanical property estimation. *Sadhana* 36(2): 181–192

- [14] Pelegri A A and Huang X 2008 Nanoindentation on soft film–hard substrate and hard film–soft substrate material systems with finite element analysis. *Compos. Sci. Technol.* 68(1): 147–155
- [15] Yan W, Pun C L and Simon G P 2012 Conditions of applying Oliver–Pharr method to the nanoindentation of particles in composites. *Compos. Sci. Technol.* 72(10): 1147–1152
- [16] Sarris E and Constantinides G 2012 Finite element modeling of nanoindentation on C-S-H: effect of pile-up and contact friction. *Cem. Concr. Compos.* 36: 78–84
- [17] Asroun N and Asroun A 2013 The visco-elastic–plastic behavior of cement paste at nanoscale. *Int. J. Eng. Res. Technol.* 2(6): 1399–1405
- [18] Oliver W C and Pharr G M 1992 An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 7(6): 1564–1583
- [19] Hertz H 1881 On the contact of elastic solids. *J. Reine Angew. Math.* 92: 156–171, translated and reprinted in English (1896) in *Hertz's miscellaneous papers*, London: Macmillan & Co, chapter 6
- [20] Acker P 2001 Micromechanical analysis of creep and shrinkage mechanisms. In: Ulm F J, Bazant Z P and Wittmann F H (Eds.) *Creep, shrinkage and durability mechanics of concrete and other quasi-brittle materials*. Cambridge: Elsevier
- [21] Kumar R and Bhattacharjee B 2003 Porosity, pore size distribution and in situ strength of concrete. *Cem. Concr. Res.* 33(1): 155–164
- [22] Bentz D P 1997 Three dimensional computer simulation of Portland cement hydration and microstructure development. *J. Am. Ceram. Soc.* 80(1): 3–21
- [23] Sindu B S, Radha M and Saptarshi Sasmal 2016 Computational modelling of cement hydration to evaluate the mechanical and transport properties. In: *Proceedings of the Structural Engineering Convention (SEC-2016)*, CSIR-SERC, Chennai, 21st–23rd December, pp. 568–573