Young's modulus and creep of calcium-silicate-hydrate compacts measured by microindentation

Zhangli Hu1*, Mateusz Wyrzykowski1, Michele Griffa1, Karen Scrivener2, Pietro Lura1,3

1Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf CH-8600, Switzerland
2Laboratory of Construction Materials, EPFL, Lausanne CH-1015, Switzerland
3Institute for Building Materials, ETH Zurich, Zurich CH-8092, Switzerland

Abstract:

In this paper, compacts of synthetic calcium silicate hydrate (C-S-H) with 0.8 - 1.5 calcium-to-silicon ratio (Ca/Si) and 30 - 80% porosity were prepared by one-direction cold pressing. The Young’s modulus and the creep of C-S-H compacts were measured by microindentation. The degree of homogeneity achievable with the preparation method, the presence of cracks and their extent were investigated by scanning electron microscopy and X-ray tomography. The porosity significantly influences the Young’s modulus and the creep of the compacts, while the Ca/Si has limited influence on the Young’s modulus. The C-S-H compacts with higher Ca/Si exhibit lower creep than those with lower Ca/Si, however mainly due to the presence of portlandite at higher Ca/Si values. The calculated Young’s modulus of C-S-H solids falls into the range 21-50 GPa. The contact creep modulus of C-S-H with similar porosity as in a hardened cement paste (close to 30%) is about 180 GPa.

Keywords: synthetic C-S-H; microindentation; porosity; Ca/Si

1. Introduction

Application of indentation to cement-based materials

The development of the indentation technique started with the work of Brinell on the hardness of structural steel at the beginning of the last century [1]. In recent decades, indentation has become an efficient tool for assessing the mechanical properties, in particular hardness and Young’s modulus, of different types of materials, including construction materials [2–4]. More recently, the scope of application of the indentation technique has been broadened to quantify not only the elastic properties and the hardness but also the creep properties of cement-based materials [5,6].

At the microscale, microindentation is advantageous and widespread because of the straightforward experimental process and the simple principle for interpreting the experimental data. During the process, an indenter with a precisely designed shape is pressed into a material with a flat surface [2–4]. During the pressing, a load (P) versus penetration depth (h) curve (P-h) is built up. Sneddon [7] derived from the indentation data the now widely employed relationship between applied load, penetration depth and contact area, which relates the mechanical properties to the P-h curve.

1 Corresponding author: zhangli.hu@empa.ch, Tel +41-587656575, Fax 058 765 6935
The results of the indentation test, i.e. the indentation modulus and the hardness, reflect the properties of the material within the interaction volume directly underneath and around the indent. The interaction volume corresponding to a certain applied load is considered to extend, in the shallow sub-surface, for up to 3-4 times the indenter’s penetration depth [2]. When indentation is performed on hardened cement pastes, the material response and the mechanical properties that are measured depend on the properties and the volume fractions of different hydrated and unhydrated phases present within the interaction volume. These phases are mainly: calcium silicate hydrate (C-S-H), calcium hydroxide, ettringite, and unhydrated cement particles [8]. The response will further depend on the ratio of volume that these phases occupy in the total interaction volume. Since the interaction volume can significantly change with the range of applied load, distinct values of, e.g., indentation modulus may be obtained when probing interaction volumes of different sizes.

Therefore, to infer the mechanical properties of single phases in cementitious systems, microindentation has been carried out on monophasic materials, e.g., tricalcium silicate and C-S-H [9,10]. The conventional method for preparing monophasic materials is cold pressing of powder-like materials with a pressing die. In the literature, different procedures for the pressing were used, with different loading speeds and different magnitudes of loads [11,12]. However, publications do not usually report essential details about the specimen preparation process (especially about the pressing process). Crucially, no evidence of specimen homogeneity is usually given. Indeed, since microindentation is performed on the surface of specimens with different porosities and the results are plotted as a function of bulk porosity, it is essential to prove that the measured porosity of the bulk is the same as that of the surface. In addition, indentation results reflect the properties of the material not only at the indentation imprint but also within an “interaction volume” underneath and around the indent. The latter properties are affected by the penetration depth. No systematic studies on the effect of the penetration depth and possible respective damage are available.

Mechanical properties of C-S-H

As the phase occupying the highest volume in hydrated Portland cement, C-S-H is also the phase that most influences the mechanical properties of cementitious materials. Therefore, to understand the contribution of C-S-H to the mechanical behavior, quantification of the properties of C-S-H is key. Since cement paste is a highly heterogeneous multiphase system, measuring the macroscopic mechanical properties on cement pastes to infer those of C-S-H at the nanoscale is an ill-posed inverse problem. Possible approaches were explored in previous research: nano-/micro-indentation tests with deconvolution of probability distribution functions (PDFs) of indentation modulus and hardness [13–15], grid nano-/micro-indentation tests combined with identification of phases by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDS) [16–18] and atomic force microscopy (AFM) measurements [19,20]. However, all the listed approaches have substantial limitations, either regarding the preparation of the specimen, the interpretation of the results or both. The possibility of identifying the mechanical properties of a single phase by indentation tests has been challenged, considering that the interaction volume usually contains multiple phases. In addition, the deconvolution of the PDF of the indentation modulus is not unequivocal [21]. Even in the case of AFM, which is a promising technique for investigating the mechanical properties of cementitious materials at the nanoscale especially when equipped with peak-force tapping [22], the obtained results are highly dependent on the calibration [9,19,20]. Considering the challenges and the limitations of
measuring on cement pastes, indentation measurements on synthetic C-S-H appears to be an alternative, more straightforward approach.

The Young’s modulus values of C-S-H, obtained in different studies, are summarized in Table 1. The different literature sources have been classified based on the materials investigated and on the methods employed. According to Table 1, the estimated value for the C-S-H Young’s modulus varies within an order of magnitude, from 20 to 300 GPa. This discrepancy not only results from the different techniques used but also from the variability of the materials studied. When measuring on synthetic C-S-H, drying methods, compacting procedure and curing conditions are expected to have a significant impact on the results.

Even fewer measurements are available in the literature about the creep behavior of C-S-H. Two main approaches have been followed: using micro-/nano- indentation [10,15,23] or using macroscopic tests such as three-point bending [24]. Based on nanoindentation, the creep of C-S-H was found to evolve logarithmically in [15,23,25]. Vandamme and Ulm [15] also proposed two parameters to describe the creep properties of C-S-H: contact creep modulus $C$ (GPa) and characteristic time $\tau_i$ (s). $C$ is linked with the depth change ($\Delta h$) and the maximum load applied in the tests ($P_{\text{max}}$ (mN)) through the contact creep compliance ($L(t)$), see Eq.(1) and Eq.(2). $C$ and $\tau_i$ can be found by fitting the experimental curve with the following relationships:

$$P_{\text{max}} = \frac{2a_u \Delta h(t)}{L(t) - M_0}$$  \hspace{1cm} \text{Eq.(1)}

$$L(t) - \frac{1}{M_0} = \ln\left(\frac{C}{\tau_i} + 1\right)$$  \hspace{1cm} \text{Eq.(2)}

where, $M_0$ is the indentation modulus (GPa) at the time when the maximum load is reached, determined based on the Oliver and Pharr method [26] and $a_u$ is the contact radius at the onset of unloading. The value of $C$ dominates the creep properties of the measured specimens: the higher $C$, the lower the creep. Measurements on synthetic, compacted C-S-H exhibited higher creep of C-S-H in the saturated state than at 11% RH, with contact creep modulus of 20 and 105 GPa, respectively [27]. Using microindentation, Nguyen et al. [10] measured higher creep on C-S-H with lower Ca/Si.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Ca/Si</th>
<th>Porosity</th>
<th>Method</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HD</td>
<td>26% [13]</td>
<td></td>
<td>29.2 [13], 27.4 [14], 32.8 [15]</td>
</tr>
<tr>
<td>Cement paste</td>
<td>LD</td>
<td>-</td>
<td>Nano-indentation with EDS</td>
<td>23.4 [16], 25.74 [17]</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>-</td>
<td></td>
<td>31.4 [16], 22.97 [17]</td>
</tr>
<tr>
<td></td>
<td>LS***</td>
<td>-</td>
<td>Nano-indentation with high resolution scanning probe microscopy</td>
<td>22.89 [28]</td>
</tr>
<tr>
<td>Cement paste</td>
<td>MS</td>
<td>-</td>
<td></td>
<td>31.16 [28]</td>
</tr>
<tr>
<td></td>
<td>HS</td>
<td>-</td>
<td></td>
<td>41.45 [28]</td>
</tr>
</tbody>
</table>
Employing macroscopic measurements (three-point bending with small, constant load), Alizadeh et al. investigated the stress relaxation of compacted synthetic C-S-H with 30% porosity [24]. The viscoelastic behavior of the C-S-H was reported to depend on the interlayer water content and also on the Ca/Si. It appears that the loss of interlayer water and lower Ca/Si lead to lower stress relaxation. Thereafter, an empirical model of the viscoelastic component of the stress relaxation was established in [24] using two viscoelastic relaxation times.

In this paper, both the Young’s modulus and the creep behavior of synthetic C-S-H with different porosities and Ca/Si were investigated systematically using microindentation. Scanning electron microscopy and X-ray tomography were used to verify the homogeneity of the prepared specimens. These investigations were carried out to justify the use of the global porosity in the relationship between mechanical properties and porosity of the compacts and to assess the extent of cracking in the C-S-H compacts. Different magnitudes of loads were also applied during microindentation. Statistical analysis was used to assess the relationship between the porosity (30-80%) and the Ca/Si (0.8-1.5) with the determined properties of C-S-H compacts.

2. Material and methods
2.1 C-S-H synthesis

The so-called double decomposition method [32] was employed to synthesize C-S-H in order to obtain a Ca/Si range (1.3-1.8) close to that found in cement pastes within a relatively short time when compared with other synthesis methods. For example, in the so-called direct reaction method [33], silica fume, calcium
oxide and water are mixed with a water-to-solid ratio of 45 and the mixture was shaken in a sealed vessel for longer than 3 months.

Following the process described in [32], C-S-H was synthesized/precipitated using two solutions, calcium nitrate \((\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O})\) and sodium metasilicate \((\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O})\), which supply calcium and silicon, respectively. Boiled (to remove the dissolved \(\text{CO}_2\)) and quickly cooled ultra-pure water was used to prepare these reacting solutions. During the reaction, the \(\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) solution was added drop by drop into the \(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\) solution, with a speed of 2.2 ml/min. The cylindrical reaction cell is made of poly (methyl methacrylate) with diameter of 130 mm and height of 150 mm. It was placed on a magnetic stirring system with stirring speed about 700 rpm. 10 M \(\text{NaOH}\) was added into the \(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\) solution before the reaction started to adjust the pH (the starting pH was about 13.3). In order to minimize the influence of the alkali content on the composition of the synthetic C-S-H [34], the amount of \(\text{NaOH}\) was kept the same throughout this study. After reacting for 3 hours, the suspension was filtered using a 0.45 \(\mu\)m nylon filter. After filtration, the solid was washed first using a 200 ml 1:1 mixed solutions of ethanol and water and secondly using 30 ml of pure ethanol (for reaction between 100 ml \(\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) and 100 ml \(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\)). The reaction and filtering were both carried out in a \(\text{N}_2\)-filled glove box to minimize the carbonation of the material. After synthesis and filtration, the C-S-H gel was vacuum-dried for 7 days and then stored in an evacuated desiccator until testing. For different \(\text{Ca/Si}\), different concentrations of \(\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}\) and \(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}\) solutions were used (see Table 2).

After the washing steps, residual \(\text{Ca(OH)}_2\) and \(\text{CaCO}_3\) could be found in the compacts; the corresponding amounts were determined with TGA (see Table 2 and Supplementary data in Appendix A). Therefore, it should be noted that the C-S-H compacts used through this paper are not made of pure C-S-H. At the same time, the \(\text{Ca/Si}\) of the C-S-H were determined after accounting for the \(\text{Ca(OH)}_2\) and \(\text{CaCO}_3\) contents.

### Table 2 Mixture design of synthetic C-S-H

<table>
<thead>
<tr>
<th>Label</th>
<th>Starting (\text{Ca/Si})</th>
<th>([\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}]) (M)</th>
<th>([\text{Ca(NO}_3\text{)}_2 \cdot 4\text{H}_2\text{O}]) (M)</th>
<th>([\text{NaOH}]) (M)</th>
<th>Calculated (\text{Ca/Si})</th>
<th>Residual (\text{Ca(OH)}_2) % per solids</th>
<th>Residual (\text{CaCO}_3) % per solids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Si-1.5</td>
<td>2.0</td>
<td>0.10</td>
<td>0.20</td>
<td>0.48</td>
<td>1.43-1.47</td>
<td>19.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Ca/Si-1.3</td>
<td>1.4</td>
<td>0.14</td>
<td>0.20</td>
<td>0.48</td>
<td>1.25-1.30</td>
<td>7.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Ca/Si-1.2</td>
<td>1.2</td>
<td>0.17</td>
<td>0.20</td>
<td>0.48</td>
<td>1.16-1.18</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Ca/Si-1.0</td>
<td>1.0</td>
<td>0.20</td>
<td>0.20</td>
<td>0.48</td>
<td>1.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ca/Si-0.8</td>
<td>0.8</td>
<td>0.25</td>
<td>0.20</td>
<td>0.48</td>
<td>0.8</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 2.2 Methods

#### 2.2.1 Determination of the composition of synthetic C-S-H

In order to calculate the actual \(\text{Ca/Si}\) in the C-S-H, the composition of the synthesized solids needs to be quantified. In general, with the double decomposition method, two ways are commonly used to determine the ions in the solids with the help of ion chromatography (IC): 1. dissolve the filtered and washed solids
into an acid solution (usually nitric acid or hydrochloric acid) and measure the composition in the dissolved solution; 2. analyze the composition of filtrates and back-calculate the ions in the solids using mass balance. Thereafter, thermogravimetric analysis (TGA) is typically combined with the analysis of the composition in the solids to determine the Ca/Si of the C-S-H only, excluding Ca(OH)$_2$, CaCO$_3$ and other possible phases.

In this study, the second approach was applied. The quantification of the composition in the filtrates was performed with IC. The filtrates were diluted 10, 100 and 1000 times and measurements were performed on all of them. The final result considered the four solutions (including the original, undiluted one). With the information from TGA, the calculation method to obtain the actual Ca/Si (Ca/Si$_c$ where C stands for “calculated”) was adapted from the procedure proposed in [35]. The formula used for determining the actual Ca/Si is shown in Eq. (3). The equation was derived from mass-balance calculation based on the chemical formulas of CaO, SiO$_2$, water, Ca(OH)$_2$ and C-S-H, for the latter assuming the stoichiometric formula to be (CaO)$_{Ca/Si}$ (SiO$_2$)$_x$ (H$_2$O)$_y$:

\[
Ca/Si_c = \frac{Ca/Si_I \cdot (m_{C-S-H} - m_w) - 0.81 \cdot m_{CH} + m_{C-S-H} - m_w}{0.757 \cdot m_{CH} + m_{C-S-H} - m_w}
\]

In Eq. (3), Ca/Si$_I$ is the starting Ca/Si, $m_{C-S-H}$, $m_{CH}$ and $m_w$ are the mass of C-S-H, Ca(OH)$_2$ and water in C-S-H, respectively. $m_{C-S-H}$ is equal to $1 - m_{CH} - m_{CaCO3}$. $m_w$, the mass of water in the C-S-H, determined as the weight loss from the specimens between 40 and 350 ºC in TGA [36]. The amounts of Ca(OH)$_2$ and CaCO$_3$ were quantified with TGA, see Table 2. The weight loss between 400-500 ºC in TGA was assigned to the decomposition of Ca(OH)$_2$, while the weight loss above 600 ºC was assigned to the decomposition of CaCO$_3$ [37].

Using the results from IC and TGA, the calculated Ca/Si for different systems is also listed in Table 2. The reasons for selecting the temperature ranges for C-S-H and the experimental results of TGA and IC are reported and explained in the Supplementary data in Appendix A.

2.2.2 Cold pressing and compaction tests

The specimens used for microindentation tests were compacted, vacuum-dried C-S-H powders. The dried C-S-H powders were placed in a steel die of internal dimensions Ø25 mm × 60 mm and compressed by a hydraulic press (Walter+Bai AG, Model Digicon 2000) with the maximum load of 300 kN. The loading rate was set to 10% of the final load per min. The slow pressing was used to obtain compacts as homogenous as possible. Different maximum loads (from 50 to 300 MPa) were employed according to the target porosity of the compacts. The compression process was finished by holding the maximum load constant for 10 min. The porosity of the compacts was estimated based on the apparent volume of the compacts and the volume of the solids used for the compaction. The parameters needed for the calculation are density of the solids (measured with helium pycnometer), volume (dimensions) of the compacts and mass of the solids (equal to the mass of the final compacts). Constant mass of the solids (powder) was used for all compacts. Density of the solids was 2.4 g/cm$^3$, fairly constant across different Ca/Si. The specimen used in the density measurement was also vacuum-dried, which means that only the interlayer water is present in the C-S-H [38]. The diameter of the compacts was equal to the internal diameter of the compacting steel die and the thicknesses of the compacts were measured with a Vernier caliper at three different positions.
The porosity plays a key role in the overall mechanical properties. In order to compare the effect of porosity in compacts and in cement pastes, the porosity of the synthetic C-S-H compacts covered also the range of porosities that occur in cement pastes. Therefore, an estimation of the actual porosity of the compacts was made based on $^1$H nuclear magnetic resonance (NMR) quantifications of the density of C-S-H in cement paste [39,40]. The porosity of the C-S-H, as quantified in [39,40], mainly takes into account the contribution by the pores in the C-S-H gel, including both gel pores and interlayer space. The chemical composition of the C-S-H, including the gel water, was C$_{1.35}$SH$_4$ and the density of the C-S-H including the gel water was about 1.8 g/cm$^3$ [39]. Correspondingly, the calculated gel porosity in cement pastes is about 30 to 60%, depending on the hydration degree. Based on this calculation, the target porosity of the C-S-H compacts measured in this study was in the range of 30 to 80%. Furthermore, the calculation assumed that the dried synthetic C-S-H still contains interlayer water in its structure.

2.2.3 Microindentation

In the microindentation measurement, a 4-sided pyramid Vickers diamond indenter (Young’s modulus $E_i=1140$ GPa, Poisson’s ratio $\nu_i=0.07$) was used. The main results were obtained using a maximum load of 2000 mN. For clarifying the impact of the load magnitude on the measured mechanical properties (both Young’s modulus and creep behavior), lower maximum loads, namely 1000 and 500 mN were also used for comparison. The loading rate was kept the same at all load levels, 200 mN/s. The dwell time was 60 s and an unloading step with the same speed of the loading step followed right after. The data was collected from a 5×5 array of points located around the center of the surface of the specimen (about 1/40 of the entire surface area) to eliminate the boundary effects. Indentation points were separated by at least 3 to 4 times the size of the indentation imprint. The indentation hardness $H$ (N/mm$^2$) and the indentation modulus $M$ (GPa) were measured and recorded. The indentation tests were carried out on the top surfaces of the compacts. From the loading and unloading curves of the microindentation of each specimen, the indentation modulus was determined. It was used to calculate the Young’s modulus of the tested specimen ($E_p$) with the assumption of the Poisson’s ratio ($\nu_p$). The equation used for the calculation is as follows:

$$E_p = M \left(1 - \nu_p^2\right)$$

Eq.(4)

In this study, $\nu_p$ was assumed to be the same as the Poisson’s ratio of C-S-H solids ($\nu$), 0.24 [31]. The influence of the value assumed for the Poisson’s ratio is limited: when $\nu_p$ is varied between 0.15 and 0.30, it impacts the Young’s modulus by less than ± 4%.

2.2.4 SEM

A FEI SFEG XL-30 electron microscope was applied to image the raw C-S-H powder. The coating material for the powders was iridium of about 5 nm thickness. A working distance of 1.9 mm, a spot size of 3 and an operating voltage of 2 kV were used.

A FEI Quanta 200 electron microscope was used for the SEM investigation on the compacted C-S-H before and after indentation tests. The coating material for the compacts was carbon of about 10 nm thickness. For
C-S-H compacts before indentation tests, the backscattering contrast along the depth direction of the C-S-H compacts indicated the degree of the spatial inhomogeneity of the compacts. For C-S-H compacts after indentation tests, in SEM, the indented area was visible and it was used to verify whether microcracks were evident after microindentation. For imaging the C-S-H compacts, a working distance of 10 mm, a spot size of 3 and an operating voltage of 10 kV were applied.

For investigating the homogeneity of the compacts along the depth direction, the polished sections of the C-S-H compacts with Ca/Si of 1.0 were prepared in the following way. They were first impregnated and cut in the plane perpendicular to the indentation surface (i.e. along the depth). Next, they were impregnated again and the cut surfaces were polished. More details for the specimen preparation, including the SEM image of the entire specimen, are provided in the Supplementary data in Appendix A. The considered region was selected to cover at least half of the specimen depth, see the schematic representation in Fig.1. In order to cover a relatively large region and to resolve clearly fine pores in the specimens, images with high resolution (magnification of ×5000) need to be “stitched” together. Stitching was done with MAP software with stitching overlap of 10%. The backscattering contrast along the depth of three different positions on the indentation surface (each position with area of 50 × 1000 μm²) was quantified. The three positions were selected in the center of the compacts on the pressing surface. For each respective image, we computed the average voxel value within rectangular, overlapping regions of interest (ROIs) centered at distinct positions along an axis parallel to the pressing direction. We plotted the variation of the average backscattering contrasts (pixel values) as a function of the ROI center position along such axis, i.e., as a function of depth from the specimen’s top (indented) surface. The “gray level” in the reported results is a moving average of the SEM images pixel values, computed within 100 pixel-long windows. The choice of such size for averaging window was motivated by the need of representativeness (100 pixels = 5.4 μm) compared with the length scale of the average pore size. Different sizes (50, 100 and 200 pixels) for the averaging window were also used and the averaging results compared with each other, with no significant observed difference. Thus, the computed profile of the average voxel value with depth provides information about the density spatial heterogeneity when moving away from the top surface.

Figure 1. Schematic representation of the imaging area in the C-S-H compact

2.2.5 X-ray tomography and respective 3D image analysis

X-ray tomography was performed on two compacted specimens with the two extreme Ca/Si values (0.8 and 1.5, with porosity of 58% and 67%, respectively) to investigate the possible presence of cracks due to specimen preparation. Such type of measurement can be considered as completely non-destructive, given the need of no specimen preparation and the lack of evidence of radiation damage for C-S-H. The RX Solutions (http://www.rxsolutions.fr) EasyTom XL™ instrument at Empa’s Center for X-ray Analytics was
used. The two specimens were prepared with the same cold pressing technique as described in Section 2.2.2. In order to achieve better spatial resolution in the tomographic images (in the following called “tomograms”), specimens with smaller diameter, 10 mm instead of 25 mm, were produced. The details about the X-ray tomography measurements and the cracks identified with respective 3D image analysis workflow are reported in detail in Section II of the Supplementary data in Appendix A. We report here only the key information needed to interpret the results in Section 3.2.2 below.

X-ray tomography, based upon attenuation contrast, provides a 3D spatial distribution of values of a variable (in the following called “voxel value”) which is a proxy of the X-ray attenuation coefficient $\mu$. An effective spatial resolution of the order of about 12 $\mu$m was achieved. With the 3D image analysis workflow, voxels belonging to cracks were identified and a crack binary tomogram was created. A 3D computer graphics rendering of both the original specimen’s tomogram and the crack binary tomogram was performed. In order to avoid the external surface of the rendered specimen to cover the cracks, a high degree of transparency (90%) was set for specimen’s tomogram rendering.

### 2.2.6 Linear regression analysis

The quantitative relationships between different variables obtained by microindentation were modeled by means of multiple linear regression analysis performed using the R environment [41]. Porosity and Ca/Si were considered as the two explanatory continuous variables (regressors, $X_1$ and $X_2$, collected together in a column vector $\vec{X} = (X_1 \ X_2)$). The following response variables ($Y_j$) were considered separately: $H$, $M$, $C$ and $\tau$.

In order to unify the scales of the variables, both the explanatory and the response variables were first standardized, i.e., for each variable, the average value of the sample dataset was subtracted from the variable’s measured value and such difference was then divided by the standard deviation of the sample dataset. The statistical ensemble of values for the variables consisted of about $n = 500$ ($\vec{X}, \vec{Y}$) sets of observations collected from the total number of indentation points (500) on all specimens. Two linear regression models were used:

$$Y_j = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \epsilon_j$$

Eq.(5)

$$Y_j = \beta_3 + \beta_4 X_1 + \beta_5 X_2 + \beta_6 X_1X_2 + \epsilon_j$$

Eq.(6)

In the expressions above, the $\beta$ and $\epsilon$ are the regression coefficients and the residuals, respectively.

### 3. Results

#### 3.1 Material characterization

The C-S-H synthesized with the double decomposition method had similar morphology to that observed for the direct reaction method [33]. As shown in the SEM image in Fig.2, the dried and un-compacted synthetic C-S-H with Ca/Si = 1.2 had a foil-like structure and was highly porous. The same morphology was observed in all specimens with different Ca/Si. The grain size of the synthesized powder before compaction could not be precisely determined due to agglomeration of the particles in the synthesis process. A rough estimation based on the SEM image (not presented here) suggests particles with average size of about 2-10 $\mu$m.
3.2 C-S-H compacts before and after indentation tests

3.2.1 Compacting of C-S-H powders

After drying, the synthetic C-S-H powder was compacted with the method described in Section 2.2.2, yielding a pellet-shaped specimen with a relatively smooth top surface. The roughness of the surface was studied by means of confocal optical microscopy (see details in the Supplementary data in Appendix A). The confocal optical microscopy measurements yielded average roughness of 1.6 μm (average from two or three tested areas per each sample, each area of 120 × 90 μm²), independent from the Ca/Si and porosity. The roughness was considerably lower than the depths of the indents, e.g. the depth on the compacts with the lowest porosity (about 27%) was about 15 μm under 2000 mN load. Compaction curves were obtained from cold pressing in a die under a maximum load of 92 MPa for C-S-H with different Ca/Si, see Fig.3. The deformation of the material under controlled loading rate evolved logarithmically. The C-S-H composition appeared to have limited impact on the macroscopic deformation or densification of the specimen during compression.
Figure 3 Compaction curves of synthetic C-S-H with different Ca/Si under maximum load of 45 kN (92 MPa).

3.2.2 Homogeneity of the compacted C-S-H

Figure 4(a) and (b) shows the 3D rendering of both the specimen tomogram (in gray scale and semi-transparent) and of the crack binary tomogram (in solid blue color) of the two specimens with the extreme Ca/Si values, respectively. In both specimens, cracks with width and length larger than the tomographic spatial resolution of about 12 μm were clearly observed, especially close and directly in contact with the lateral (vertically oriented) boundary surfaces. Some cracks ran from the boundary surfaces up to 1 – 2 mm into the shallow sub-surface, typically pointing towards the specimen center (along the radial direction) but never reaching it (see especially Fig. 4(a)). Figure 4(a) shows, for a Ca/Si = 0.8 specimen, two straight cracks in contact with the top surface, extending for less than half mm into the shallow sub-surface. Except for these two straight and regular cracks, the center of each specimen was essentially crack-free. This fact suggests that the microindentation measurements would be better carried out in the center of the specimen’s top or bottom surface, although Fig. 4(b) shows for the Ca/Si = 1.5 specimen some highly porous regions (called “patches” in Fig. 4(b)) farther away from the lateral boundaries. The cracks visible on the surfaces of the compacts were most likely caused by demolding of the specimens.

Figure 5 shows a quantitative assessment of the degree of spatial inhomogeneity within 1 mm from the top surface of a C-S-H compact with Ca/Si of 1.0 and porosity of about 60%, obtained by analyzing the average pixel values of SEM images of 1-mm long regions of interest (ROIs, see Fig.1). It should be noted that 1 mm in depth covers more than half the specimen thickness. Note that Fig.5 shows the results from distinct ROIs along the depth of the same specimen. In Fig.5, the interaction depth corresponding to specimen with porosity of 60% was also marked, about 100 μm. The images used to obtain these results from different positions are shown in Section III of the Supplementary data in Appendix A. According to qualitative observation, the pore network within the C-S-H solids contains pores with size between 0.1 to 1.5 μm. Due to the complex pore network, it was practically impossible to segment the separate pores in the SEM images. Regions with smaller pixel average values (“porous patches”), compared to the overall depth, were detected at random locations in depth, possibly originating from the different original particle size of the dried raw materials. These regions are marked both in the SEM images (see Fig. S2 in the Supplementary data in Appendix A) and in depth profile plots of the moving average pixel value shown in Fig. 5.
The surface had no pronouncedly different gray level compared to the bulk volume. The averaged gray level difference between the interaction depth and the full depth was about 2%, maximum 7.3% independent of the location of the heterogeneous regions. The gray level of the heterogeneous region was about 10% lower than the average gray level of the considered volume. Except from the previously-mentioned patches, no significant variation of the gray level in the C-S-H compacts was observed. Comparing the results of the different positions, similar gray level values were observed, about 100-110.
Figure 5 Assessment of the degree of spatial inhomogeneity within 1 mm from the top surface of C-S-H compacts with Ca/Si of 1.0, (at each point along the depth, the gray level is an average from the overlapping ROI of 5.4×50 μm²): (a) position 1; (b) position 2; (c) position 3.

3.2.3 Compacted C-S-H after indentation tests

After the indentation test, the individual indents on the surface were examined with SEM, see Fig.6 (the specimens shown in insets (a), (b) and (c) were indented with loads of 500, 1000 and 2000 mN, respectively). A few visible stripes were observed, likely originating from features on the surface of the steel die/piston used to compact the specimen. The most important feature in the figure was the presence of cracks that are likely caused by the indenting process, along the indent: these are the few small cracks perpendicular to the bottom edge of the pyramid (indicated by white arrows). These cracks were found in specimens under different magnitudes of loads. As a brittle, porous material, compacted C-S-H was expected to show microcracks when indented. To the best of the authors’ knowledge, only Pelisser et al. [11] showed SEM images of compacted synthetic C-S-H after nano-indentation, where they also observed some microcracks. In order to further address this problem, the indents on specimens with different load levels were examined. As expected, the higher the load, the deeper and larger the indent area. The cracks were almost undetectable and they appeared only at the very edges of the indent area for maximum loads 1000 and 500 mN.
3.3 Mechanical properties of C-S-H compacts under different load magnitudes

To investigate the effect of the load magnitude on the properties of the materials in this study, different load levels were applied in microindentation and the corresponding mechanical properties including Young’s modulus, indentation hardness and creep properties are shown in Table 3. The contact creep moduli and the characteristic time were calculated as described in Section 2. Specimens with two extreme Ca/Si (0.8 and 1.5) and two porosities (about 30% and 45%) were used in this verification. It appears that Young’s modulus, indentation hardness and contact creep moduli were higher in measurements done with smaller loads. However, the difference was minor, especially between the results obtained using 1000 and 2000 mN. Slightly higher standard deviation was observed using 500 mN. Based on these results, a load of 2000 mN was used for the microindentation tests on the compacts covering the whole range of Ca/Si and porosities to determine both the Young’s modulus, indentation hardness and the creep properties.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Porosity</th>
<th>Loads (mN)</th>
<th>Young’s modulus (GPa)</th>
<th>Indentation hardness (GPa)</th>
<th>Contact creep modulus (GPa)</th>
<th>Characteristic time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>500</td>
<td>16.23±0.37</td>
<td>403.76±13.80</td>
<td>132.66±17.19</td>
<td>0.31±0.02</td>
</tr>
<tr>
<td>Ca/Si-0.8</td>
<td>0.31</td>
<td>1000</td>
<td>15.05±0.45</td>
<td>395.15±16.09</td>
<td>139.83±6.78</td>
<td>0.22±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td>14.61±0.41</td>
<td>372.68±11.59</td>
<td>139.37±5.55</td>
<td>0.31±0.02</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>500</td>
<td>7.82±0.64</td>
<td>226.52±27.76</td>
<td>86.14±23.11</td>
<td>0.91±1.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>6.91±0.76</td>
<td>209.57±29.07</td>
<td>94.70±11.83</td>
<td>0.20±0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td>6.87±0.89</td>
<td>200.59±30.45</td>
<td>83.74±11.26</td>
<td>0.28±0.03</td>
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<tr>
<td>Ca/Si-1.5</td>
<td>0.34</td>
<td>500</td>
<td>14.60±0.95</td>
<td>393.76±38.80</td>
<td>221.36±14.84</td>
<td>0.18±0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>14.09±0.38</td>
<td>386.63±18.78</td>
<td>207.00±6.78</td>
<td>0.19±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td>13.71±0.25</td>
<td>372.63±13.13</td>
<td>204.68±5.46</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td></td>
<td>0.46</td>
<td>500</td>
<td>12.84±0.23</td>
<td>317.75±9.45</td>
<td>174.46±4.60</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1000</td>
<td>11.97±0.60</td>
<td>307.48±24.25</td>
<td>166.83±8.42</td>
<td>0.19±0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000</td>
<td>11.66±0.16</td>
<td>295.85±6.04</td>
<td>168.51±2.96</td>
<td>0.17±0.01</td>
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</table>

3.4 Young’s modulus and indentation hardness

The Young’s modulus of the C-S-H compacts, calculated based on Eq. (4), is plotted as a function of the porosity in Fig.7. The indentation modulus of the C-S-H compacts is also plotted as a function of porosity in Fig.8. There, each marker indicates the average value over the dataset from 25 microindentation measurement points, one marker for each physical specimen. The error bar for the Young’s modulus corresponds to standard deviation computed from the specimen (25 values). The relatively small standard deviation confirms the homogeneity of the compacts within the indented surface and shallow sub-surface. As expected, the Young’s modulus of the compacts decreased with the increase of porosity. Compared with the literature [10], the results reported in Fig.7 show a smaller scatter and stronger linear relationship.
between the Young’s modulus and the calculated bulk porosity. The Ca/Si did not have a clear impact on the relationship between the porosity and the Young’s modulus, especially for compacts with Ca/Si lower than 1.4. These relationships are studied statistically by means of linear regression analysis in section 3.6.

The indentation hardness reduced from about 430 GPa to about a few GPa with the increase of the porosity of the compacts from 0.3 to 0.8, see Fig. 8. Similar to the Young’s modulus, no significant difference between C-S-H with different Ca/Si was observed.
3.5 Creep properties

The contact creep modulus $C$ and the characteristic time $\tau_i$ were obtained by fitting the $L(t)$ determined with the measured $\Delta h(t)$ and Eq.(2). Damped least square fitting (Levenberg-Marquardt algorithm) was performed. For each specimen, the data from each of the 25 indentation points were fitted individually, leading to corresponding values for $C$ and $\tau_i$. After that, for each specimen, their mean values and the standard deviations were calculated. The standard deviation is shown as error bar in the figure.

In Fig.9(a) the contact creep modulus is plotted as a function of the bulk porosity. Data from this work were compared with values in [10], also measured with microindentation. The contact creep modulus describes the deformation kinetics of the material under sustained load [25]. The contact creep modulus decreased from about 180 to 10 GPa with a porosity increase from 28 to about 80%. Not surprisingly, specimens with higher porosity showed higher creep. At equal porosity, the contact creep modulus of C-S-H with different Ca/Si did not differ significantly, especially for C-S-H with Ca/Si lower than 1.2. Specimens with Ca/Si = 1.5 showed clearly higher contact creep modulus than other systems at the same porosity, particularly when the porosity was lower than 0.6. Compared to the results reported in [10], the current study found higher contact creep modulus values.

The other creep parameter, the characteristic time $\tau_i$, is shown in Fig.9(b). The characteristic time represents the time when the response of the material becomes logarithmic [25]. Figure 7(b) shows that the characteristic time also steadily decreased with the increase of porosity and had a clear dependence on the Ca/Si. The higher the Ca/Si, the smaller the characteristic time was. The difference was especially clear at porosities smaller than 0.6. The higher the characteristic time at constant contact creep modulus, the lower the creep of the system. In other words, for Ca/Si-0.8, Ca/Si-1.0 and Ca/Si-1.2, C-S-H with higher Ca/Si appeared to creep more. Compared to the results reported in [27], the characteristic time in the current study was lower but with much less scatter. In [27], no systematic evolution of the characteristic time was observed in C-S-H compacts with different amount of Ca(OH)$_2$ mixed into the samples.

Of the few published studies dedicated to creep of C-S-H, most are on cement pastes. In [42], inner product and outer product C-S-H were examined, with porosities of 26% and 34% respectively (similar to HD and LD C-S-H). A contact creep modulus of 187.9 GPa and a characteristic time of 0.6 s were found for the inner product, while a contact creep modulus of 132.8 GPa and a characteristic time of 0.56 s for the outer product C-S-H [42]. Similar values were also obtained by Vandamme and Ulm [5], who found contact creep of $112.2 \pm 23.3$ GPa for LD C-S-H and of $182.5 \pm 43.7$ GPa for HD C-S-H. Especially when considering the large scatter of the values published in [5], the results obtained in the current study fall broadly in the same range.
3.6 Results of statistical analysis

As demonstrated in Fig. 7 and 9, the porosity had a clear impact on both the elastic and the visco-elastic properties of C-S-H compacts. On the other hand, the Ca/Si appeared to affect only the visco-elastic properties. To better assess the relationship of the elastic and visco-elastic behavior of the C-S-H on the porosity and Ca/Si, linear regression analysis was performed on the experimental data.

The results of linear regression models for $H$, $M$, $C$ and $\tau_i$ expressed with Eq. (5) and Eq. (6) are shown in the Supplementary data in Appendix A. The outliers were identified based on the residual analysis (function `plot.lm` in R) and they constituted 1% of all data points at most. For $H$ and $M$ in the two regression models, relatively high adjusted $R^2$ (>0.9) was found. Including the interaction between porosity and Ca/Si did not change the $R^2$ of the linear regression significantly. Both porosity and Ca/Si were statistically significant with $p<2\times10^{-16}$. However, the impact of porosity on the predicted variables was much higher than that of Ca/Si: the standardized linear regression coefficients for porosity were 12 times and 8 times (for $H$ and $M$, respectively) higher than those for Ca/Si.
Both Ca/Si and porosity appeared significant ($p<2\times10^{-16}$) with relatively high adjusted $R^2$ for $C$ in both regression cases, 0.79 and 0.81. The adjusted $R^2$ became slightly higher if the interaction between the two parameters was included. The impact of the porosity on $C$ was higher than that of the Ca/Si, as shown by the higher standardized linear regression coefficient for porosity (~47 vs. ~19). When the Ca/Si was removed from the linear regression model (so that $C$ is only a linear function of porosity), it resulted in a reduction of the adjusted $R^2$ to 0.68 (one measurement was removed as outlier based on the diagnostic of residuals). Therefore, the null hypothesis of lack of linear dependence of $C$ upon porosity + Ca/Si can be rejected with very high significance.

The same type of linear regression analysis was done for $\tau$. Both porosity and Ca/Si were again statistically highly significant in the model. However, the fit was much worse (adjusted $R^2$ equal to 0.43). The reason is partly associated to the limited data groups of Ca/Si (in fact, the Ca/Si was an ordered factor rather than a continuous variable like porosity). Removing either variable led to a serious worsening of the fit (adjusted $R^2$ reduced to below 0.30). Including the product between the two regressors had limited influence on the fit. It can be concluded that both Ca/Si and porosity influenced $\tau$.

Other analytical models for estimating the mechanical properties of C-S-H solids, taking into consideration the porosity, are shown in Section 4.5.

4. Discussion

4.1 Impact of magnitude of loads on mechanical properties

A wide range of loads was applied in previous nano- and microindentation studies of cementitious materials (from several mN to 5-10 N) [10,11,42]. Wei et al. [42], in microindentation measurements on cement pastes, found that the indentation modulus of cement pastes decreased up to 40% when the applied load increased 50 fold from 0.1 to 5 N. They also found that the higher the load, the lower the coefficient of variation. The mechanisms and properties leading to such different results with different applied load are usually identified as: (1) spatial inhomogeneity of the material (especially in the case of cement pastes) [42,43]; (2) more damage induced by higher loads [44]; (3) higher influence of the surface roughness at lower loads [43]. Wei et al. [42] explained their results by the fact that at higher loads, the interaction volume may contain more porosity. However, considering only the elastic response of the material, higher loads should induce smaller scatter but the average of a large amount of measurements is expected to remain the same. A more reasonable explanation is that the response of the material also has a plastic component and the damage induced by the indent increases with the load.

In the current study, limited differences were observed in mechanical properties of C-S-H compacts with two extreme Ca/Si obtained using different load magnitudes (Table 3). The small difference was likely only due to cracks induced during the microindentation procedure (more cracks were seen in the specimen with 2000 mN load, see Fig.6). On the other hand, 500 mN was less suitable since both elastic moduli and contact creep moduli had higher scatter and may have been affected by the surface roughness [43].

4.2 Effect of the homogeneity of cold pressed compacts
The homogeneity of the compacts in the depth and in the lateral direction is quantitatively shown in Section 3.2.2. We observed that the inhomogeneity along the pressing direction mainly consists of porous patches located at random positions (porous regions), quantitatively shown in Fig. 5. The inhomogeneity in the depth direction may be mainly due to the specimen preparation itself (i.e., the pressing protocol) and the characteristics of the synthesized powder, i.e., its particle size distribution and the mechanical and surface properties of the particles. However, it is important to remark that the degree of spatial inhomogeneity along the depth direction and within a depth corresponding to that of the microindentation volume of interest is rather small. In terms of the impact of local porosity, assuming that 10% difference in gray level is equivalent to 10% difference in porosity, it corresponds to about 2 GPa difference in the Young's modulus of the compacts. Even though the difference is relatively small, considering different initial fineness of the synthetic C-S-H powders, gentle grinding of the C-S-H powders before compaction may help improving the homogeneity of the pellets in future work.

Along the lateral direction, a smaller degree of spatial inhomogeneity of the specimens was observed (comparing results from different positions at the surface, Fig.5).

The original idea for this study included measuring the mechanical properties of C-S-H compacts with macro-level experiments (direct compressive uniaxial creep or bending tests). However, the existence of the cracks in the bulk specimen resulting most likely from the preparation protocol would have a strong impact on the macroscopic results. A different specimen preparation protocol may be necessary for obtaining crack-free specimens to be used in a macroscopic level study. It must be remarked here that in the few studies in which macroscopic mechanical tests were performed of C-S-H compacts (i.e. stress relaxation in [24] and dynamical mechanical analysis in [29]), no advanced characterization methods were employed to ensure that the compacts were crack free. In [24,29] the C-S-H was dried and compacted following procedures similar to those used in this study.

4.3 Effect of porosity on mechanical properties of C-S-H compacts

Based on the linear regression analysis performed in this study, the effect of porosity on both elastic and viscoelastic properties of the C-S-H compacts was found to be significant, as shown in Section 3.5.

On the other hand, the actual porosity of the C-S-H gel received scant attention in the literature, both in measurements on cement pastes and on synthetic C-S-H. When working on cement paste, the majority of published papers in nanoindentation identified two peaks from the deconvoluted PDF as HD and LD C-S-H without precisely determining their porosity. Generally, the considered porosity was based on the values in the colloid models proposed by Jennings [45]: HD C-S-H had porosity of about 26% and LD C-S-H of 36%. Vandamme and Ulm [15] found a third type of C-S-H in cement pastes, so-called ultrahigh density C-S-H (UHD C-S-H, Young’s modulus of 47.2 GPa, porosity of 17% [23]). This UHD C-S-H was later identified as a nanocomposite of HD C-S-H and CH by combining nanoindentation and SEM-EDS [6]. In the case of synthetic C-S-H, the material was compacted under pressure to reach porosities about 30%. However, either the porosity was not reported or the method for calculating the proposed porosity was not clearly explained in most studies. Only few publications dealt with the effect of porosity on the Young’s modulus properties of compacted synthetic C-S-H [10,46]. As expected, the Young’s modulus of the compacts decreased with an increase in porosity. However, due to the large scatter of the collected data, any relationship between
porosity and modulus had a large uncertainty. To compare the mechanical properties of C-S-H obtained from cement paste and synthetic C-S-H, regardless of the measuring technique used, it is critical to ensure that materials with comparable porosities are employed.

4.4 Effect of compositions on mechanical properties of solid C-S-H

The target Ca/Si in the synthetic C-S-H used in this study ranged from 0.8 to 2.0, with the calculated actual Ca/Si ranging from 0.8 to about 1.5. In terms of the composition, not only the Ca/Si but also the presence of Ca(OH)$_2$ in the compacts should be taken into account. To better clarify the effect of the composition on the properties of C-S-H, the contact creep modulus and the characteristic time are plotted against the indentation modulus in Fig. 10. In addition, the Young’s modulus, the contact creep modulus and characteristic time are plotted against the amount of Ca(OH)$_2$ in the C-S-H compacts in Fig. 11.

The Young’s moduli of the C-S-H compacts with different Ca/Si were almost identical, especially for the specimens with Ca/Si lower than 1.2. For Ca/Si-1.2, Ca/Si-1.3 and Ca/Si-1.5, slightly higher Young’s moduli of the C-S-H compacts were found.

As shown in Table 1, different relationships between the Ca/Si and the Young’s modulus were proposed. In the literature, the argument for which C-S-H with higher Ca/Si should have higher Young’s modulus is based on the bond order density of Ca-O and the smaller interlayer space [30]. On the other hand, the argument for C-S-H with lower Ca/Si having higher Young’s modulus is based on the longer chain length in C-S-H with lower Ca/Si (higher polymerization) and the easier packing with lower Ca/Si [11].

It should be noted that in our tests, for the higher Ca/Si of the pure C-S-H, also significantly higher content of Ca(OH)$_2$ was found in the compacts, see Table 2. The Young’s modulus of C-S-H without Ca(OH)$_2$ estimated with linear extrapolation based on the specimens with the three highest Ca/Si (all containing Ca(OH)$_2$) was similar to the measured value of specimens with the two lowest Ca/Si (containing no Ca(OH)$_2$). This result supports the hypothesis that the slight increase of the Young’s modulus of the C-S-H compacts was mainly due to the presence of Ca(OH)$_2$ rather than due to the net effect of the Ca/Si.

For creep properties, when examining the same ranges of indentation modulus, the results were consistent with [10]. In both figures, all C-S-H with different Ca/Si followed a single line when the indentation modulus was smaller than 12 GPa. A different slope was only seen for the two highest Ca/Si (see Fig. 10(a)), in which significant amounts of Ca(OH)$_2$ are present. This observation can be explained by the findings in [47,48], according to which Ca(OH)$_2$ had a much lower creep rate in microindentation compared with C-S-H. Considering instead the plot of the characteristic time in Fig. 10(b), the Ca/Si appears to have some impact on the creep behavior of C-S-H (though the scatter was considerably larger in this case). The effect of Ca/Si on viscoelastic behavior of C-S-H compacts was mostly caused by the different amount of Ca(OH)$_2$ in the specimens: the higher the amount of Ca(OH)$_2$, the lower the creep of the compacts. No intrinsic effect of the different Ca/Si in the C-S-H structure on the creep properties of C-S-H compacts could be measured by microindentation, which agrees with the C-S-H response back-calculated based on macroscopic basic creep of cement pastes in [49].
An important aspect of the studies of compacts made of synthetic C-S-H is how these materials correspond to the C-S-H in the actual cement pastes. Although similar results were reported for the Young's moduli of compacts and cement pastes in [10], the possible sources of differences should be discussed. One important source may be the moisture state of the materials. The compacts used in our tests were prepared with vacuum-dried powders. On the other hand, the cement pastes are in most cases stored at RH higher than 11% and hence the intrinsic C-S-H porosity (gel porosity) is usually saturated [40]. Hence, in our tests it was not possible to address the effect of the water content on indentation results. According to some studies, the RH has a pronounced effect on the C-S-H indentation properties in cement pastes, see e.g. [50–52]. The moisture state may be particularly important with regard to the creep behavior [50]. One of the reasons may stem from the recently proposed dissolution-precipitation mechanism of creep of C-S-H [53,54]. According to this mechanism, important contribution to the macroscopic creep of cement paste originates from stress-enhanced dissolution of C-S-H leading to deformation at the microstructural level and stress-redistribution as the C-S-H re-precipitates in new configuration. If this mechanism was indeed active, it should have a much higher effect on pastes with higher moisture content than in the relatively dry compacts tested here.

Another important difference may be due to the composition of the compacts and of the cement paste. As long as the dominating effect of porosity is similar between the compacts and the cement paste, it is not clear how the effect of Ca/Si in C-S-H determined on the compacts (little effect on elastic properties, while higher effect on creep) translates to that in the cement pastes. We believe that the dominating effect of porosity over that of Ca/Si still holds also in the pastes. Further, the effect of Ca(OH)₂ intermixed in C-S-H that according to our results leads in general to higher Young's moduli may affect the results to different extent in the pastes, see also [6].

Finally, it is not possible currently to assess how different morphologies of the elementary C-S-H particles (granular in the compacts versus more needle-like in the pastes) affect the results. More light could be shed on this aspect by means of micromechanical modelling [55,56].

The issues is complicated by the fact that among studies on mechanical properties of synthetic C-S-H, the majority of the publications did not present in-depth characterizations of the studied materials. For instance,
the actual Ca/Si and the amount of Ca(OH)$_2$ within the specimens have seldom been addressed. Furthermore, the effect of Ca/Si on the Young’s modulus of the C-S-H was examined in very few studies, and the conclusions vary significantly. In [11,29,46], higher Ca/Si resulted in lower Young’s modulus. Another study found no significant changes with different Ca/Si [18], while a recent study on synthetic C-S-H with high pressure XRD even found increasing modulus with increasing Ca/Si [30]. C-S-H with higher Ca/Si was found to have higher contact creep modulus [46], in line with the relationship between elastic modulus and the Ca/Si in [46,57].

According to some researchers, LD and HD C-S-H in cement pastes have different compositions [16,58]. Pelisser et al. [11] mentioned that the most important reason for the differences was the existence of other phases besides C-S-H within the outer product/LD C-S-H. Considering that LD C-S-H was identified with outer product C-S-H and HD C-S-H with inner product C-S-H, a TEM study [59] found no difference in Ca/Si between them. On the one hand, easier packing may occur for higher Ca/Si C-S-H since the mean chain length is shorter in the structure. Actually, for LD and HD C-S-H identified from nano-indentation, the packing density is the key for the difference [10]. In other words, the most important difference between LD and HD C-S-H is in the microstructure rather than in the composition.
Accepted version
https://doi.org/10.1016/j.cemconres.2020.106104

Figure 11 (a) Young’s modulus versus Ca(OH)$_2$ amount in C-S-H compacts, (b) contact creep modulus versus Ca(OH)$_2$ amount in C-S-H compacts, c) characteristic time versus Ca(OH)$_2$ amount in C-S-H compacts. The porosities of the compacts are 0.36 ±0.02 (circles) and 0.58±0.02 (diamonds).

4.5 Young’s modulus of the solid skeleton of C-S-H

To clarify the effect of different factors on the mechanical properties of C-S-H, including porosity and Ca/Si, different models were applied to determine the (intrinsic) elastic properties of the solid skeleton of C-S-H. We repeat here that the solid skeleton as defined in this study includes the interlayer water and the corresponding porosity. In this paper, several ways were used to achieve this purpose: 1) using empirical models to fit the relationship between the porosity and the Young’s modulus; 2) using micromechanics analytical models such as Mori-Tanaka and self-consistent schemes to do the back-estimation; 3) using microstructural models considering two-phase composites, such as two-cut Gaussian random field models (GRF).

Empirical models

Using empirical models to link the porosity with the Young’s modulus, the Young’s modulus of the solid skeleton was extrapolated to zero porosity. Some empirical models were used for similar purposes in cement-based materials (e.g., [43]): 1) linear models $E_p = E(1-kp)$, where $E_p$ is the Young’s modulus of the porous body, $p$ is the porosity and $k$ is a fitting constant [60]; 2) power law models $E_p = E(1-p)^n$, generally with $n$ between 2 and 3 [61]; 3) exponential models $E_p = Ee^{bp}$, where $b$ is a constant that depends on the shape of the embedded pores. This last equation was originally used for estimating the hardness and later extended to estimate the Young’s modulus [62]. The experimental results obtained in the present study were fitted with these three models (Fig. 12). In the power law model, the index $n$ was assumed both as the lower and the upper bound (both 2 and 3). With all the models used, reasonably good fits were obtained. When considering the porosity range from 0.3 to 0.6, the power law model seemed to give the best fit. The extrapolated elastic moduli of the solid C-S-H skeleton are listed in Table 4.
Figure 12 Numerical fits of different empirical models to the experimental Young’s modulus of C-S-H compacts and results of the two micromechanics models: Mori-Tanaka, self-consistent scheme and two-cut GRF model.

Micromechanics models

The Young’s modulus of the solid C-S-H can be also back-calculated by using analytical micromechanics models, such as Mori-Tanaka and self-consistent scheme [14]. The former one is an effective median approximation while the latter one is an effective field approximation [63]. Both Mori-Tanaka and self-consistent schemes are based on Eshelby’s elasticity solution. One typical difference between them is the solid percolation threshold: for Mori-Tanaka, the percolation threshold is 0, while for the self-consistent scheme, the percolation threshold is 0.5 [14]. Therefore, in the back-calculation, the Mori-Tanaka scheme was applied to elastic moduli of C-S-H compacts in the whole porosity range; while the self-consistent scheme was applied only to elastic moduli of C-S-H compacts with porosity lower than 0.5 (hence, solid packing density >0.5). The detailed description of this method is provided in the Supplementary data in Appendix A. The obtained results using both schemes are listed in Table 4 and Figure 12.

Microstructural models

With the assumption of a two-phase porous body, the Young’s modulus of the solid C-S-H can be also back calculated with the known porosity. Different kinds of microstructural models can be used to do the back-calculation. The most important advantage of this type of model is that the morphology of the generated model is closer to the real microstructure. In this study, the three dimensional two-cut GRF model was used, see Eq.(7), since it gave accurate predictions in a recent study on creep of blended cementitious materials [56]. The calculated Young’s modulus of the C-S-H solid skeleton is plotted in Fig.13.

\[
\frac{E_p}{E} = \left(\frac{1-p-p_0}{1-p_0}\right)^m
\]

Eq.(7)

where \(p_0\) and \(m\) are fit parameters. The fitting values obtained in [56] for these two parameters were used: \(p_0 = -0.064\) and \(m = 2.09\).

Two clusters of Young’s modulus values were identified and marked as black and red ovals in the figure. It has to be remarked that the applicability of the two-cut GRF model was limited only to a certain porosity range [56]; for too high porosity values (higher than about 75%), the model became unreliable. Therefore, the values within the red oval were expected to give a better estimation of the Young’s modulus of the solid skeleton of C-S-H and are reported in Table 4.

As shown in Table 4, the different approaches yielded elastic moduli of the C-S-H solid skeleton ranging from 21 to 50 GPa. Based on the same set of data, different values could be obtained with different fitting approaches. Even larger differences might be found when using different experimental methods and analysis processes at the same time. Using Molecular Dynamics simulation, Fu et al. calculated a value about 61 GPa [64]. Obtaining the Young’s modulus of HD and LD C-S-H with nano-indentation and calculating the solid C-S-H with Mori Tanaka and self-consistent scheme, Constantinides and Ulm proposed 59.7 GPa for the Young’s modulus of solid C-S-H [14]. Using AFM measurement, 80 GPa was suggested by Jones et al.
for C-S-H [19]. Applying the same models from the current study on the nano-indentation results in [23], a Young’s modulus of 42-49 GPa for solid C-S-H would be obtained.

Considering only the C-S-H with Ca/Si of lower than 1.2, in which almost no Ca(OH)₂ was present, the calculated elastic moduli of the solid skeleton of the C-S-H are 20.5±1.2 GPa, 26.7±1.2 GPa, 42.7±3.9 GPa, 45.2±2.5 GPa, respectively by fitting the linear, power (n=2), power (n=3) and exponential models. These values were a little lower than the ones obtained by taking C-S-H with the entire range of Ca/Si into consideration, which could be explained by the absence of (stiffer) Ca(OH)₂ in compacts with Ca/Si lower than 1.2. The small observed difference could be explained by the similar Young’s modulus of CH (about 40 GPa [2]) and C-S-H and by the small amount (in any case less than 20%-mass) of Ca(OH)₂. The size of CH crystal observed with SEM is about 1 μm², while the indent size is larger than 1000 μm², even with 500 mN load. Therefore, the measured modulus was a homogenized modulus, to which Ca(OH)₂ had a small, but measurable, contribution.

Table 4 Calculated Young’s modulus of the C-S-H solid skeleton using different methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Linear model</th>
<th>Power law model n=2</th>
<th>Power law model n=3</th>
<th>Exponential model</th>
<th>Mori-Tanaka scheme</th>
<th>Self-consistent scheme</th>
<th>Two-cut GRF model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus of solid C-S-H (GPa)</td>
<td>21.6±1.2</td>
<td>28.1±1.3</td>
<td>44.5±3.1</td>
<td>50.3±2.7</td>
<td>41.7</td>
<td>31.7</td>
<td>25.3</td>
</tr>
</tbody>
</table>

5. Conclusions
In this study, C-S-H was synthesized and one-direction cold pressed into cylindrical pellets. Both the degree of heterogeneity and the damage (cracking) during pressing of the pellets and microindentation tests were investigated in depth. SEM showed that, while the pellets had some degree of local inhomogeneity, likely arising from the initial particle size of the pressed powders, the compacts were rather uniform in both pressing and lateral directions (no more than 10 % in gray level difference). X-ray microtomography revealed the presence of cracks due to sample preparation, because of which macroscopic measurements of elastic properties and creep could not be performed. The mechanical properties obtained by microindentation were almost independent of the load magnitude. A limited amount of cracks was observed around the indent only at the higher loads.

The Young’s modulus and the creep properties of C-S-H composites were investigated systematically and the Young’s modulus of the solid C-S-H was estimated by different methods. The effect of the porosity (30-80%), Ca/Si (0.8-1.5) and amount of Ca(OH)\textsubscript{2} (0-20%) in synthetic C-S-H compacts was clarified with comprehensive material characterization. The following conclusions can be drawn:

1. C-S-H with different compositions has similar compression curves under the same load. The deformation of synthetic C-S-H powders has a logarithmic evolution in time during indentation process. The C-S-H compacts showed a mesoscopic homogenous behavior, with a wide pore size distribution and largest pores smaller than about 1-2 μm. The specimens prepared with this method were reasonably homogenized and suitable for microindentation.

2. The Young’s modulus of C-S-H compacts is dominated by their porosity, while the composition of the C-S-H has considerably (about 1 order of magnitude) lower influence. Using different models to calculate the Young’s modulus of the solid skeleton of the C-S-H, different values, ranging from 21 to 50 GPa, were found.

3. By fitting the indentation creep curves of the C-S-H compacts, the contact creep modulus and the characteristic time were obtained. With higher porosity, lower contact creep modulus and lower characteristic time were found, corresponding to larger creep. Slightly different contact creep modulus was found for C-S-H with different Ca/Si. For C-S-H with lower Ca/Si without Ca(OH)\textsubscript{2} in the compacts, similar contact creep modulus was observed.

4. The effect of the amount of Ca(OH)\textsubscript{2} on the Young’s modulus of C-S-H was not significant, while the effect on creep cannot be neglected. The small influence of Ca(OH)\textsubscript{2} on the Young’s modulus was likely due to the similar elastic moduli of C-S-H solid and Ca(OH)\textsubscript{2}. On the other hand, the much more significant impact on creep is likely due to the fact that Ca(OH)\textsubscript{2} creeps at much lower rate than C-S-H. These findings call for more careful characterization of the composition of C-S-H to determine its elastic and viscoelastic behavior.

Acknowledgement

The authors would like to thank Dr. Jirawan Siramanont for helping with synthesizing C-S-H, Emmanuelle Boehm-Courjault for SEM measurements and Franco Zunino for density measurement with helium pycnometry. The fruitful discussion on AFM measurements with Dr. Josef Kaufmann is highly appreciated. We would like to thank Mahdieh Shakoori Oskooie for her help with performing the first feasibility/ test X-ray tomography measurements on our specimens.
Accepted version
https://doi.org/10.1016/j.cemconres.2020.106104

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