**A Simple yet Accurate Homogenization Method for Early Age Cement Pastes**

Tuan Nguyen-Sy1,2*, Trung-Kien Nguyen3, Khuong Le-Nguyen4 and Ngoc-Minh Vu5, 6

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**Abstract**

A simple and accurate method is developed to model the effective elastic properties of early age cement pastes. It uses available data of media of which the microstructures are close to that of the predicting medium. Such technique allows us to model accurately the effect of the hydration degree on the effective elastic properties. On the other hand, the hydration degree of a hydrating cement paste is predicted from the acquisition of ultrasonic velocity. The simulated results are perfectly validated against a large variety of experimental data. This simple concept provides a great potential of application in practice.

**1. Introduction**

Cementitious materials are the most used artificial materials for building and industrial applications. Therefore, a numerous number of studies have been developed to predict its mechanical and physical properties with respect to the variety of their microstructure as well as the variation of their microstructure with time. Effective mechanical and physical properties of a sample can be evaluated via direct testing (Sayers and Dahlin 1993; Boumiz et al. 1996, 1997; Sun et al. 2005; Zhang et al. 2010; Samudio 2017) or numerical simulations (Benz et al. 1999; Haecker et al. 2005). However, the experimental and numerical methods are time and budget consuming when they are employed to deal with a large variety of the microstructure of cementitious materials.

A cement paste is usually considered as a mixture of hydrate products (low and high densities C-S-H, CH, aluminates) and remaining anhydrate and water (Bernard et al. 2003). The main hydrate product, that is C-S-H, is also a porous composite itself at nanoscale. The self-consistent scheme (Hill 1965) and the Mori-Tanaka scheme (Mori and Tanaka 1973; Benveniste 1987) are usually considered to model the effective elastic properties of that mixture (Ulm et al. 2004; Sanahuja et al. 2007; Pichler et al. 2007, 2009; Ghabezloo 2010; Huang et al. 2013). They are extensions of the Eshelby’s solution that was developed for an inclusion in an infinite matrix under far-field condition (Eshelby 1957).

In the traditional approaches, theoretical homogenization methods are employed to deal with the heterogeneity of the material. Then, they are validated and calibrated against experimental or numerical data. However, the uncertainty of theoretical results is amplified from the uncertainties of many steps of the homogenization procedure: the prediction of the hydration degree versus time, the calculation of phase volume fractions at different scales, the phase morphology and the choice of an appropriate homogenization scheme, etc. Besides, many simplified assumptions are considered for the nanostructure and the microstructure of early age cement paste: CSH product is the continuous matrix phase of cement, coated morphology between low and high density CSH, perfect interfaces between the phases, the nano and micro scales are well separated, etc. Therefore, their predictive capacity has a limited satisfaction. Venkovic et al. (2013) presented an analysis of such uncertainty amplification.

Recently, new adaptive homogenization schemes are proposed to overcome such a difficulty (Nguyen-Sy et al. 2016, 2020; Nguyen-Sy 2019; Thai et al. 2020). The idea is to combine the theoretical approach with the available experimental or/and numerical data of offset media to yield an optimal homogenization scheme for the considering medium. The offset media are those of which the microstructures are close to that of the considering medium. The new homogenization scheme is flexible because it can change from one homogenization scheme to another by varying an internal parameter. The internal parameter is considered to fill the gap of the unknown microscopic properties: imperfect interface, non-ideal inclusion shape, percolation of the solid phase,
etc. More importantly, it is shown that the internal parameter can be easily calibrated using available experimental data. This technique was successfully employed for predicting the effective transport properties of rocks (Nguyen-Sy et al. 2016) and the effective elastic properties of gas hydrate material (Nguyen-Sy et al. 2019). It is also used to model the effect of water to cement ratio to elastic and viscoelastic properties of cement pastes (Nguyen-Sy et al. 2020; Thai et al. 2020).

This paper aims to use of this method for modeling the effect of the hydration degree to the elastic properties of early age and hardened cement paste. By an inverse way, it provides an advanced way to control the hydration degree of a cement paste by monitoring the ultrasonic wave velocities. This consists in considering available experimental data on an offset medium together with the adaptive homogenization scheme to predict accurately the evolution of effective properties of the considered medium at early age. The offset medium is close to the considering medium in term of cement type, hydration condition, etc. The paper is organized as following: firstly, the theoretical basis of the adaptive homogenization scheme is presented. Secondly, the developed model is applied, calibrated and validated against data of hydrating cement paste. Discussions and conclusion are given at the end of the paper.

2. The flexible homogenization scheme

Let us consider a heterogeneous medium that is a mixture of several heterogeneities. The homogenization theory is established from the local and the macroscopic relationship between the stress tensor $\sigma$ and the strain tensor $\varepsilon$ as below.

$$\sigma = C : \varepsilon; \quad \langle \sigma \rangle = \mathcal{C}^{\text{hom}} : \langle \varepsilon \rangle; \quad \varepsilon = \mathbb{A} : \langle \varepsilon \rangle$$  \hspace{1cm} (1)

where $C$ and $A$ are the fourth order local stiffness tensor and strain concentration/localization tensor, respectively; the column “:” denotes a double contraction of two tensors; the notation $\langle \cdot \rangle$ stands for a volumetric average over a representative elementary volume (REV) of the medium. The localization tensor $A$ is a function of the mechanical properties, the volume fraction and the shape of the phases as well as the interaction between them. The theory of Mori and Tanaka (1973) allows us to express $A$ by,

$$A = A^{dl}(A^{dl})^{-1}, \quad \text{with} \quad A^{dl} = \left[ I + \mathbb{P}_0 (C_{\text{inc}} - C_0) \right]^{-1}$$  \hspace{1cm} (2)

where $A^{dl}$ is the dilute localization tensor of a matrix-inclusion system that has been established by Eshelby (1957); $C_{\text{inc}}$ the elastic stiffness tensor of the inclusion; $C_0$ the elastic stiffness tensor of the reference matrix; $\mathbb{P}_0$ the Hill’s tensor that is a function of $C_0$ and the shape of the inclusion and $I$ the fourth order identity tensor. The effective stiffness tensor $\mathcal{C}^{\text{hom}}$ is related to the local stiffness tensors via the concentration tensor as in Eq. (3)

$$\mathcal{C}^{\text{hom}} = \langle A : C \rangle \quad \text{(3)}$$

For the case of isotropic matrix and random distribution of isotropic inclusions, the stiffness tensors $C_{\text{inc}}$, $C_0$, $\mathcal{C}^{\text{hom}}$ and the Hill’s tensor can be expressed in term of the bulk and shear moduli such by the following set of equations, with $a_0$ being expressed by Eq. (5).

$$C_{\text{inc}} = 3k_{\text{inc}}I + 2\mu_{\text{inc}}I; \quad C_0 = 3k_0I + 2\mu_0I$$

$$\mathcal{C}^{\text{hom}} = 3k_{\text{hom}}I + 2\mu_{\text{hom}}I \quad \text{(4)}$$

$$\mathbb{P}_0 = \frac{1}{3(k_0 + a_0)} I + \frac{1}{2(\mu_0 + b_0)} I$$

$$a_0 = \frac{4}{3} \mu_0; \quad b_0 = \frac{\mu_0(k_0 + b_0)}{6(k_0 + 2b_0)}$$  \hspace{1cm} (5)

where $I$ and $I$ are the spherical and deviatoric part of the identity tensor $I$; $I = I + I$; $k_{\text{inc}}$ and $k_0$ the bulk and shear moduli of the inclusion; $k_0$ and $\mu_0$ the bulk and shear moduli of the reference matrix. The homogenized bulk and shear moduli, $k_{\text{hom}}$ and $\mu_{\text{hom}}$, which are derived by combining Eqs. (2) to (4), can be expressed by following elegant forms.

$$k_{\text{hom}} = \left( \frac{1}{k_0 + a_0} \right)^{-1} - a_0; \quad \mu_{\text{hom}} = \left( \frac{1}{\mu_0 + b_0} \right)^{-1} - b_0$$  \hspace{1cm} (6)

Basically, the bulk and shear moduli of the reference matrix $k_0$ and $\mu_0$ are chosen on the basis of the used homogenization scheme: e.g. $k_0 = k_{\text{hom}}$ and $\mu_0 = \mu_{\text{hom}}$ for the self-consistent scheme; $k_0 = k_{\text{m}}$ and $\mu_0 = \mu_{\text{m}}$ for the Mori-Tanaka scheme (Mori-Tanaka 1963). The Voigt-Reuss bounds consider a full range of $k_0$ and $\mu_0$ from zero to infinity. The main idea of the adaptive homogenization scheme proposed by Nguyen-Sy et al. (2016) is to let the parameters $k_0$ and $\mu_0$, or equivalently the parameter $a_0$ and $b_0$, change flexibly according to the change of the microstructure.

3. Application to early age cement pastes

3.1 The model

Considering a cement paste at a certain hydration degree $\alpha$, the volume fraction of the remaining anhydrate $f_a$, the hydrate products $f_h$ and capillary pore $f_p$ are related to the hydration degree $\alpha$ by the classical Powers’ model (Powers and Brownyard 1946).

$$f_a = \frac{0.32(1-\alpha)}{w/c+0.32}; \quad f_h = \frac{0.66a}{w/c+0.32}; \quad f_p = 1 - f_a - f_h = \frac{0.36a}{w/c+0.32}$$  \hspace{1cm} (7)

It should be noted that the Powers’ model assumes a constant CSH density. The densification of CSH during
hydration is not considered, as mentioned by, for example, Muller et al. (2013) and Königsberger et al. (2016).

Now, let us consider a cement paste at an offset state with a hydration degree \( \alpha + \delta \alpha \), the volume fractions of the hydrate products \( f'_h \) can be deduced from Eq. (7) and be expressed by Eq. (8) below.

\[
f'_h = \chi f_h, \text{ with } \chi = 1 + \frac{\delta \alpha}{\alpha}
\]

(8)

The remaining anhydrate \( f'_a \) and the capillary pore \( f'_\phi \) can be expressed by Eq. (9).

\[
f'_a = \frac{\delta \alpha}{\alpha} \frac{w/c + 0.032}{w/c + 0.32} = \chi f_a; f'_\phi = \frac{\delta \alpha}{\alpha} \frac{w/c}{w/c + 0.32} = \chi f_\phi
\]

(9)

Note that the mixture of hydrate, anhydrate and capillary pore with volumes \( \chi f'_h, f'_a \) and \( f'_\phi \) with any value of \( \chi \) has identical elastic properties of the mixture of those content with the volume fractions \( f_h, f_a \) and \( f_\phi \) that is the cement paste at the hydration degree \( \alpha \). Consequently, Eq. (9) leads to the fact that the cement paste at a hydration degree \( \alpha \) can be considered as a mixture between the cement paste at a hydration degree \( \alpha + \delta \alpha \) with a volume fraction \( 1/\chi \) and additional anhydrate and porosity with volume fractions.

\[
\delta f_a = \frac{\delta \alpha}{\alpha} \frac{w/c + 0.032}{w/c + 0.32}; \delta f_\phi = \frac{\delta \alpha}{\alpha} \frac{w/c}{w/c + 0.32}
\]

(10)

Applying the homogenization scheme of Eq. (6) to that mixture, following relationships between the elastic moduli of the cement paste at the hydration degrees \( \alpha \) and \( \alpha + \delta \alpha \) can be obtained.

\[
k = \left( \frac{1}{\chi} + \frac{\delta f_\phi}{\kappa_\phi + a_0} + \frac{\delta f_a}{\kappa_a + a_0} \right)^{-1} - a_0
\]

(11)

\[
\mu = \left( \frac{1}{\mu' + a_0} + \frac{\delta f_\phi}{\mu_\phi + b_0} + \frac{\delta f_a}{\mu_a + b_0} \right)^{-1} - b_0
\]

(12)

where \( k \) and \( \mu \) are the bulk and shear moduli of the cement paste at the hydration degree \( \alpha \); \( k' \) and \( \mu' \) are the bulk and shear moduli of the cement paste at the hydration degree \( \alpha + \delta \alpha \); The volume fractions of the phases within the mixture \( 1/\chi, \delta f_\phi \) and \( \delta f_a \) are defined by Eqs. (8) and (10); the bulk and shear moduli of anhydrate are \( k_a = 112.5 \) (GPa) and \( \mu_a = 51.9 \) (GPa) (these values are computed using the Young’s modulus and the Poisson’s ratio of anhydrate given by Sanahuja et al. 2007); \( k_\phi \) = 2 (GPa) for water saturated capillary porosity. With respect to the flexible homogenization concept, the parameters \( a_0 \) and \( b_0 \) of the reference matrix are considered as calibrated parameters. Details of such calibration will be presented after.

### 3.2 Calibration

The parameters \( a_0 \) and \( b_0 \) can be calibrated by considering an ordinary Portland cement (OPC) paste of which both the ultrasonic compressional and shear wave velocities, \( V_p \) and \( V_s \), are measured together with the calorimetric measurement of the hydration degree by Boumiz et al. (1996). The bulk and shear moduli of a cement paste can be computed from its sonic velocities by following classical formulas.

\[
\mu = \rho V_p^2; \quad k = \rho V_s^2 - \frac{4}{3} \mu
\]

(13)

where the bulk density \( \rho \) of a cement paste can be computed from the water to cement ratio by Eq. (14).

\[
\rho = \frac{1 + w/c}{0.32 + w/c}
\]

(14)

It is of interest to remark that Eq. (14) can be derived by assuming a clinker density of 3.15 (g/cm\(^3\)) and neglecting the effect of the volume change due to autogeneous shrinkage.

Knowing the elastic bulk and shear moduli at the hydration degrees \( \alpha \) and \( \alpha + \delta \alpha \) of a cement paste with a given water to cement ratio, Eqs. (11) and (12) can be used to calibrate the parameters \( a_0 \) and \( b_0 \) at the hydration degrees \( \alpha + \delta \alpha \). Interestingly, it is found that \( b_0 \) correlates very well with a parameter \( b' \) that is defined by [see also Eq. (5)].

\[
b' = \left( \frac{\rho k' \phi + \mu'}{\sigma(k' + 2\mu')} \right)
\]

(15)

It should be noted that the parameter \( b' \) corresponds to the Mori-Tanaka scheme in which the cement paste at the hydration degree \( \alpha + \delta \alpha \) is considered as the reference matrix of the mixture that form the cement paste at the hydration degree \( \alpha \). In other words, \( b' \) should be used in the place of \( b_0 \) if the Mori-Tanaka scheme is considered. But the calibrated results show that \( b_0 \) is smaller than \( b' \). As such, the use of the Mori-Tanaka scheme will overestimate the effective elastic properties at the hydration degree \( \alpha \).

**Figure 1** shows a good correlation between the calibrated results of \( b_0 \) and the parameter \( b' \) that was defined by Eq. (15) for two water to cement ratios, 0.35 and 0.4, and with a hydration degrees range from 0 to 0.5. Interestingly, it is found that the correlation between \( b_0 \) and \( b' \) is similar between the two cases with \( w/c = 0.35 \) and 0.4. This observation is very important because it allows us to use the calibrated results for other...
er cement pastes with other water to cement ratios. The calibration using data of Boumiz et al. (1996) was limited to the range of hydration degree from 0 to 0.5. Therefore, the calibration of $b_0$ for $\alpha > 0.5$ using data of Haecker et al. (2005) is added in Fig. 1 (the points with $b_0 > 4$ (GPa)).

In practice, the calibrated results presented in Fig. 1 can be used by the following way: starting from a cement paste at a certain hydration degree $\alpha' = \alpha + \delta \alpha$ of which the bulk and shear moduli $k'$ and $\mu'$ are known, the parameter $b'$ is computed by Eq. (15). Then the parameter $b_0$ can be calculated via the correlation with $b'$. Once $b_0$ is known, it can be used in Eqs. (11) and (12) to compute the bulk and shear moduli of the considering cement paste at the nearby hydration degree $\alpha$. The calibrated results showed that $a_0 \approx 4b_0/3$. This simplified assumption is then considered for Eqs. (11) and (12).

Once the elastic properties of a cement paste at $\alpha$ are known, they can be used to predict the elastic properties at $\alpha - \delta \alpha$ and so on. Doing so, the effective elastic properties of a cement paste can be predicted for a whole hydration range from 0 to $\alpha'$. For example, if starting from a hardened cement paste with measured elastic moduli (or sonic velocities) with $\alpha' = \alpha_{\text{max}}$, the evolution of the elastic properties of that cement paste for the whole hydration range from 0 to $\alpha_{\text{max}}$ can be predicted. It is important to remark that the increment $\delta \alpha$ must be small enough to ensure the stability of the results. A value $\delta \alpha \approx 0.01$ is appropriate for that stability condition. More precisely, changing value of $\delta \alpha$ below a threshold of 0.01 will not affect the results.

Figure 2 shows the prediction of the Young’s modulus and the Poisson’s ratio of the white cement paste with $w/c = 0.35$ that was considered by Boumiz et al. (1996). They are calculated from the predicted bulk and shear moduli [Eq. (16)] via the classical relationships of continuum mechanics for isotropic materials.

$$E = \frac{9k\mu}{3k+\mu}, \quad v = \frac{3k-2\mu}{6k+2\mu}$$  \hspace{1cm} (16)

Good agreement between both simulated Young’s modulus and Poisson’s ratio and the experimental data is obtained. Similar results for the case with $w/c = 0.4$ are shown in Fig. 3. It is important to remark that: even though the parameter $b_0$ is calibrated, the simulation using Eqs. (11) and (12) requires both the bulk and shear moduli at the starting hydration degree $\alpha'$. However, in many situations in practical application, only the compressional sonic wave velocity $V_p$ is measured. Therefore, only the term $H = k + 4\mu/3$ can be computed from $V_p$ (together with the ratio $w/c$) via the relationship in Eq. (13). Fortunately, by analyzing data given by Boumiz et al. (2016), very good correlation between the bulk and shear moduli can be found as shown in Fig. 4. That correlation is also validated on data of Sun et al. (2005) that are measured on another cement paste that is not used to establish the correlation in Fig. 4.

Sun et al. (2005) measured the Young’s and shear moduli of a Portland cement paste by the resonant frequency method. Their shear modulus is used to compute the bulk modulus using the correlation shown in Fig. 4, then the Young’s modulus is computed using Eq. (16). The computed Young’s modulus is compared with the measured one. Such comparison is shown in Fig. 5. Interestingly, it is observed that the correlation in Fig. 4 that was established using the bulk and shear moduli that are obtained by the ultrasonic measurement of Boumiz et al. (1996) is consistent with data obtained by Sun et al. (2005) by the resonant frequency method.

3.3 Validation

To validate the model, other data sets that were not used for the calibration of $b_0$ are used. Figure 6 shows a very good validation of the model versus data of cement pastes with high water to cement ratios, $w/c = 0.5$ and 0.6 that are measured by Boumiz et al. (1997).

Now let us consider the class G oil-well cement paste with $w/c = 0.44$ that is cured at ambient condition (Vu 2012). Only the compressional ultrasonic velocity $V_p$ is
measured together with the hydration degree (via the calorimetric method). Then only the term $H = k + 4\mu/3$ can be computed. So, a similar correlation of Portland cement paste as shown in Fig. 4 is needed for oil-well cement paste. Sayers and Dahlin (1993) have shown that the correlation between the $H$ modulus and the shear modulus of hydrating petroleum cement paste follows a very narrow trend. Indeed, using data given by Sayers and Dahlin (1993) a good correlation between the bulk and shear moduli can be obtained as shown in

![Graph showing correlation between bulk and shear moduli of white cement paste.](image1)

Fig. 3 A comparison of the model and data for a cement paste with $w/c = 0.40$ (Boumiz et al. 1996), PCCB9402 cement. The $R^2$ score between the model and data is 0.997 for the Young’s modulus and 0.985 for the Poisson’s ratio.

![Graph showing correlation between $\mu$ and $G$.](image2)

Fig. 4 Correlation between the bulk and shear moduli of the white cement paste measured by Boumiz et al. (1996).

![Graph showing comparison between modeled and measured Young’s modulus.](image3)

Fig. 5 A comparison between the modeled Young’s modulus and data measured by Sun et al. (2005).

![Graph showing validation of the model for high w/c.](image4)

Fig. 6 A validation of the model for cement pastes with high $w/c$ (Boumiz et al. 1997). The $R^2$ score between the model and data is about 0.99 for both cases.
Fig. 7. Using such correlation, both bulk and shear moduli of cement pastes can be computed from the compressional velocity $V_p$.

Now back to the petroleum cement paste that is considered by Vu (2012), the present model is used to predict the effective elastic properties. Starting from the highest hydration degree of the measured range, the bulk and shear moduli of cement paste at that state are calculated using the measured value of $V_p$. They are then used in the present model to predict the evolutions of the elastic moduli for the whole hydration range from 0 to the maximal measured hydration degree. The predicted elastic moduli are then used to predict the evolution of $V_p$ versus the hydration degree using Eq. (13). Then the evolution of $V_p$ versus time can be predicted using the measured evolution of the hydration degree versus time. A quite good validation of the present model versus experimental data is shown in Fig. 8. The discrepancy between the model and data that can be observed at one day of hydration may be due to the fact that the calibrated model on OPC cement pastes is used to predict a petroleum cement. For example the use of the Powers' law [Eq. (7)] that was derived for OPC cement paste for petroleum cement is an approximation because their compositions are different. Of course, it may also be due to the uncertainty of the experimental data.

Figure 9 shows another validation of the present model versus data of the class G petroleum cement paste with $w/c = 0.44$ cured at a large temperature range from 20°C to 90°C and atmospheric pressure condition (Samudio 2017). It is observed that the model fits quite well with data of cement pastes cured at different temperature conditions that are out of the range of temperature where the parameter $b_0$ is calibrated. $R^2$ above 0.9 score is observed for most of the cases except the one cured at 60°C. The high error observed for this case ($R^2=0.579$) may due the uncertainty of the data. Indeed, it can be observed that the sonic wave velocity measured at 36 hours for that cement paste is as small as the value measured for the cement paste cured at 40°C. This uncertainty can be also observed in Fig. 12.

3.4 Application

The present method offers two important applications: (1) prediction of the hydration degree of a hydrating cement paste using ultrasonic wave velocity acquisition; and (2) prediction of the evolution during the hydration process of the elastic properties of a cement paste using the elastic properties measured at a given hydration degree or the elastic properties of hardened cement paste. Both applications are very important in practice. For example, sonic wave velocity is usually considered for monitoring the hydration process of oil-well cement paste that is cured at several kilometers under the ground where it is not possible to use the traditional methods such as the calorimetric or the thermogravimetric methods. It is then very profitable if the hydration degree can be predicted from the measured down-hole sonic velocity. In addition, the elastic properties of a hardened cement paste can be measured in the laborato-

Fig. 7 Correlation between the dynamic bulk and shear moduli of class G cement paste using data given by Sayers and Dahlin (1993).

Fig. 8 A validation of the model versus data of class G petroleum cement pastes with $w/c = 0.44$ hydrating at ambient temperature and pressure condition (Vu 2012). The $R^2$ score between the model and data is 0.979.

Fig. 9 A validation of the model versus data of a class G cement paste cured at a large temperature range from 20°C to 90°C (Samudio 2017). The $R^2$ scores between the model and data are: 0.992 for 20°C, 0.947 for 40°C, 0.579 for 60°C and 0.986 for 90°C.
ry by traditional compression test. However, it is difficult to stop the hydration process at a certain early hydration degree then to do the compression tests for determining of the elastic properties at the stopped hydration degree. Therefore, it will be very useful if it is possible to start from the measured data of a hardened cement paste to predict the elastic properties of that cement paste for the whole hydration process.

4.1 Prediction of the hydration degree using sonic data

Figure 10 shows the hydration degree predicted by the present model using the measured ultrasonic wave velocities. It is normalized by maximal hydration degree ($\alpha_{\text{max}}$) that is measured at one day. The predicted results are compared with data measured by the calorimetric method for both cases with $w/c = 0.35$ and 0.4. The comparison is perfect for this case because these data were used to calibrate the parameter $b_2$ of the model as discussed in the calibration section. Figure 11 shows another example where the hydration degree is predicted using data measured by Sun et al. (2005). It is observed that the normalized hydration degrees obtained for $w/c = 0.35$ and 0.5 and 0.6 are almost identical. Such observation is consistent with the classical kinetic hydration analysis (Bernard et al. 2003). That consistency confirms one more time the validity of our model.

Figure 12 shows the hydration degree, predicted from measured compressional sonic velocity, of oil-well cement paste at different curing temperatures (Samudio 2017). The predicted results fit quite well with data measured by the calorimetric method. The $R^2$ score between the model and data is above 0.97 for most of the cases. An exceptional low $R^2$ of 0.85 for 60°C is similar
to that observed in Fig. 9. This may due to the uncertainty of the results as already discussed.

4.2 Prediction of the elastic properties of early age cement paste using data measured at the hardened state

Considering for example a Portland cement paste with w/c = 0.5 cured at ambient condition (Ulm et al. 2004). They assumed that the measured sample was fully hydrated (α = 1). The hardened dynamic Young’s modulus is measured by both the compressional ultrasonic wave velocity (UVP) and resonance frequency method (RF). The data given by Ulm et al. (2004) are consistent with the resonance Young’s modulus measured by Haecker et al. (2005). Those data at hardened state are used in the present model to predict the Young’s modulus of Portland cement paste with w/c = 0.5 for the whole hydration range (α = 0 to 1). Results of that prediction are shown in Fig. 13. Data at early age measured by Boumiz et al. (1996) are also plotted for comparison. A good agreement between the present model and data is obtained. Results obtained by a relevant model in literature (Sanahuja et al. 2007) are also plotted in Fig. 13 for comparison. It can be observed clearly that the model developed herein offer a better trend at early age comparing to the existent model regarding experimental observations. Similar results for the cases with w/c = 0.35, 0.4 and 0.6 are given in Fig. 14. The analytical results obtained for low w/c ratios of 0.35 and 0.4 are truncated at the maximum hydration degree (Sanahuja et al. 2007).

By a similar way, the static Young’s modulus of Portland cement paste at early age can be predicted using the measured value at the hardened state: $E_{static} = 18.6$ (GPa) (Ulm et al. 2004). Assuming that the static measurement corresponds to a drained condition, a value $k_d = 0$ is considered in Eq. (11) when computing the static Young’s modulus. Results of that prediction are shown in Fig. 15.

By an inverse way, the elastic properties of a cement paste at the hardened state can be predicted using its properties at early age. For example, data of early age Portland cement pastes measured by Boumiz et al. (1996, 1997) can be used to predict the elastic properties at hardened state. Figure 16 shows a very good fit between the Young’s modulus predicted by the model and data given by Helmuth, and Turk (1966) that are cited in Sanahuja et al. (2007).

Let us consider another example of the class G oil-well cement paste cured at ambient condition with w/c = 0.44 of which the static bulk modulus measured at drained and undrained conditions are $k_d = 8.7$ (GPa) and $k_u = 11.2$ (GPa), respectively (Ghabezloo 2010). The drained Young’s modulus of a similar cement paste at hardened state $E_d = 16.5$ (GPa) that was measured by Vu (2012) can be used together with the value $k_d = 8.7$ given by Ghabezloo (2010) to model the drained moduli at early age because the correlation shown in Fig. 7 that was derived from sonic data is not valid for the drained moduli. Using these values in the present model the drained and saturated bulk and Young’s moduli of that cement paste at early age can be computed as shown in Fig. 17. It should be noted that the parameter $k_d = 0$ is used in Eq. (11) when computing the drained bulk and Young’s moduli.

Vu (2012) measured also the drained Young’s moduli together with the compressional sonic velocity of the class G cement paste with w/c = 0.44 hydrated at 3 days to 35 days. Using the measured sonic velocity, the hydration degree can be predicted by the same way as the case shown in Fig. 12. Then the measured Young’s modulus versus the hydration degree can be plotted. Doing so, the data given by Vu (2012) can be compared with the predicted Young’s modulus as shown in Fig. 17. It can be observed that the data follow very well the predicted trend.

4.3 Application of the model for mortar

Until now, the developed model is calibrated and validated for a cement paste. Now it will be extended to the case of mortar. Starting from a hydration degree $\alpha' = (\alpha + \delta\alpha)$, of which the elastic properties of mortar are

![Fig. 13 Prediction of early age dynamic Young’s modulus using data at hardened state: Portland cement paste with w/c = 0.5. The $R^2$ score between the present model and data is 0.99.](image-url)
measured. It is possible to calculate the equivalent elastic properties of the cement phase at $\alpha'$ by regarding a mortar as a mixture of cement matrix and sand inclusion through the following relationships.

\[
k_{\text{m mortar}} = \left( \frac{f_{\text{sand}}}{k_{\text{sand}} + b'} + \frac{1-f_{\text{sand}}}{k' + b'} \right)^{-1} - \frac{4}{3} \mu' \quad (17)
\]

\[
\mu_{\text{m mortar}} = \left( \frac{f_{\text{sand}}}{\mu_{\text{sand}} + b'} + \frac{1-f_{\text{sand}}}{\mu' + b'} \right)^{-1} - b' \quad (18)
\]

where $k_{\text{m mortar}}$ and $\mu_{\text{m mortar}}$ are the bulk and shear moduli of mortar; $k_{\text{sand}}$, $\mu_{\text{sand}}$ and $f_{\text{sand}}$ are the bulk and shear moduli and the volume fraction of sand within mortar; $k'$ and $\mu'$ are the bulk and shear moduli of the cement paste in mortar at $\alpha'$; and $b'$ is related to $k'$ and $\mu'$ via the formula [Eq. (15)].

Knowing $k'$ and $\mu'$ at $\alpha'$, the developed method can be used to compute the bulk and shear moduli of the cement paste in mortar for the whole hydration range from 0 to $\alpha'$. Then for each hydration degree $\alpha$ at which the bulk and shear moduli $k$ and $\mu$ of cement paste are known, the relationships in Eqs. (17) and (18) (where $k'$, $\mu'$ and $b'$ are replaced by $k$, $\mu$ and $b$, respectively) are used to compute the bulk and shear moduli of mortar. They can be then used to compute the sonic velocities as well as the Young’s modulus.

Fig. 14 Prediction of early age dynamic Young’s modulus using data at hardened state: Portland cement pastes with w/c = 0.35 (top), 0.4 (middle) and 0.6 (bottom) compared against the data of Haecker et al. (2005) and Boumiz et al. (1996). The $R^2$ scores between the model and data are 0.997 for w/c = 0.35, 0.994 for w/c = 0.4 and 0.97 for w/c = 0.6.
It should be noticed that Eqs. (17) and (18) correspond to the Mori-Tanaka scheme for the mixture of cement matrix and sand inclusions. That classical homogenization scheme is considered for cement-sand mixture because of its simplicity. The interfacial transition zones (ITZ) between cement paste matrix and sand inclusions are not considered. The consideration of ITZ at mortar or concrete levels is important in case of forward modeling, i.e. offset media is not considered for calibration (Lutz et al. 1997). However, it requires additional information about the thickness and the elastic properties of the ITZ. Readers who are interested in more advanced model for matrix-inclusion system can also be referenced to the development of Nguyen-Sy (2019). Even though the Mori-Tanaka scheme without ITZ is only appropriate for low to medium volume fraction of inclusions, it can be employed in the present situation for high volume fraction of inclusion. That is because the Mori-Tanaka scheme is used by two inverse ways: first it is used to compute elastic properties of cement matrix at $\alpha'$ using data of mortar. Second, it is used to compute mortar properties from predicted elastic properties of cement matrix for the hydration range between 0 and $\alpha'$. Doing so, the error of the Mori-
Tanaka scheme at high volume fraction of inclusion may be minimized as will be shown in the following example.

Let us consider the case of B35 mortar measured by Boumiz et al. (1996). The elastic properties of sand within that mortar are $E_{\text{sand}} = 45$ (GPa) and $\nu_{\text{sand}} = 0.3$ (Bernard et al. 2003) that correspond to $k_{\text{sand}} = 37.5$ (GPa) and $\mu_{\text{sand}} = 17.3$ (GPa). The value $k_{\text{sand}}$ is equal to the bulk modulus of quartz crystal but the value of $\mu_{\text{sand}}$ is about two time smaller than the shear modu-

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**Fig. 18** Compressional and shear ultrasonic velocities of a mortar: a comparison between the present model and data given for mortar B35 by Boumiz et al. (1997). R² scores are 0.99 for $V_p$ and 0.97 for $V_s$.

**Fig. 19** Modeling Young's modulus of a mortar: a comparison between the present model and data given by Boumiz et al. (1997), mortar B35. R² score between the model and data is 0.98.

**Fig. 20** Effect of low w/c to the parameter $b_0$, calibrated using data given by Boumiz et al. (1997).
lus of quartz crystal. It may because a sand grain embedding within a cement paste is bounded by an imperfect interface. However, analyzing the interface effect is out of the scope of the present paper. For instance, the values $k_{\text{sand}} = 37.5$ (GPa) and $\mu_{\text{sand}} = 17.3$ (GPa) that are given by Bernard et al. (2003) are considered to model the considering B35 mortar. Figures 18 and 19 shows a perfect fit between the results of the model and experimental data of Boumiz et al. (1996) for both sonic velocities versus time and Young’s modulus versus hydration degree.

In addition, it is possible to predict the elastic properties of mortar made of ordinary Portland cement paste by a more generic way considering the known elastic properties of hardening Portland cement paste that are shown in Figs. 13 and 14. Such generic model requires a more advanced model than the simple Mori-Tanaka model to consider accurately the contribution of the sand inclusion in the mortar mixture (Nguyen-Sy 2019).

4. Discussion

In previous sections, the developed model are calibrated and validated versus data of cement paste with medium to high water to cement ratios ($w/c \geq 0.35$). For low water to cement ratio, experimental studies have shown a significant increase of the strength and elastic moduli because of a fundamental change of the hydrate morphology. Precisely, low water to cement ratio leads to an increase of the ratio between CaO and SiO2 (Živica 2009) and the formation of C-S-H/CH nano-composite (Chen et al. 2010). Such effect causes a smaller parameter $b_0$ for the case with low w/c comparing with the case of medium to high w/c at a given value of $b'$ as shown in Fig. 20. In this figure the parameter $b_0$ that is calibrated for C3S cement paste with different water to cement ratio range from 0.3 to 0.6 (data given by Boumiz et al. 1997) is also plotted. Interestingly, it is found that the parameter $b_0$ of the ordinary Portland cement paste with low w/c is in line with the parameter $b_0$ of C3S cement paste. This observation can be explained by the fact that: the hydrate product of C3S cement paste, with any water to cement ratio, contains only C-S-H and CH. Therefore, it may form a similar C-S-H/CH nano-composite as the case of an ordinary Portland cement paste with low w/c. However, proving this assumption is out of the scope of the present paper. The observation shown in Fig. 20 suggests that the parameter $b_0$ that is calibrated on C3S cement paste should be used for modeling ordinary Portland cement paste with low water to cement ratio.

5. Conclusions

A quite simple and accurate model is developed, calibrated and validated for modeling the effective elastic properties of hydrating cement paste. It is a flexible homogenization scheme that is developed based on the classical homogenization theory in combination with available experimental data. Only one model parameter, that is the parameter $b_0$, need to be calibrated. It is observed that the parameter $b_0$ correlated very well with an equivalent parameter $b'$ that is defined within the Mori-Tanaka theory. More importantly, the parameter $b_0$ that is calibrated on data of Portland cement paste at a ratio $w/c$ of 0.35 and 0.4 can be employed for Portland cement paste with other water to cement ratios as well as oil-well cement cured at different temperature conditions. The case of a cement paste with a low $w/c$ ratio is also discussed in detail.

The proposed model is validated against a large variety of relevant experimental data available in literature and it has been proved that our model is significantly more accurate than existent models exist in literature those were developed to predict the elastic properties of early age cement paste.

In practical application, this model can be used for two main purposes: first, it can be used to predict the hydration degree from monitored compressional (or/and shear) sonic wave velocity. Such application is very important in situation where the traditional calorimetric or thermogravimetric methods could not be considered. For example, an oil-well cement paste hydrated in the borehole at several kilometers under the ground. Second, this model can be employed to predict the elastic properties of hydrating cement paste by using measured data of that cement paste at the hardened state. By an inverse way, it can be considered to predict the hardened properties from early age properties.

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