The microstructure development during bleeding of cement paste

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The microstructure development during bleeding of cement paste: An NMR study

Yanliang Ji, Leo Pel, Zhenping Sun

ABSTRACT

NMR was applied to investigate the microstructure development of cement paste during bleeding. In this study, we have measured the void ratio and the $T_1$ relaxation, reflecting the pore structure development, at two fixed positions during the bleeding process of cement paste, whereas the void ratio was also measured over the complete sample during hydration. Here we have compared Portland and blast furnace slag cement and looked at various factors such as water-cement ratio, slag content and the use of water reducer. It was found that the void ratio at the top almost remains constant, and the void ratio at the bottom gradually decreased until it reached a constant value during bleeding. The results indicate that the finite-strain model is best suited to predict the structure development during a consolidation process. Moreover, it was found that the porosity is not totally linearly related to the distance as predicted by the consolidation model because of the existence of the transition zone.

1. Introduction

Bleeding of a fresh cement-based material is a common phenomenon, i.e., water comes out during the initial stage which can be observed as free water on top of the materials. This water is often referred to as bleeding of the cement. It often take place in cement-based materials with high fluidity such as pumping concrete, self-compacting concrete and grouting materials (i.e., for repairing flaws or cracks in an old concrete) [1–3]. During the bleeding process, the movement of the solid particles leads to uneven distribution of the cement paste which can give rise to defects on the surface if no effective measures are taken [2,4]. These defects can lead to the cement-based materials with a weak mechanical strength and high permeability, hence decreasing resistance to weathering and reducing the bonding ability to reinforcement [4–6]. Therefore, a better understanding of the microstructure development during the bleeding process is needed.

In general, for a cement paste which exhibits bleeding there are four stages that can be distinguished as shown schematically in Fig. 1. After the initial mixing in stage 1 the cement paste is considered a homogeneous suspension with solid particles distributed evenly. In the second stage, due to gravitational sedimentation of particles, there will be small amount of bleeding which results in a porosity gradient, i.e., the top of the sample is more porous then the bottom [7]. During the third stage interaction forces between solid particles causes a self-weight consolidation [7,8] and as a result water is drained out from the compressible solid skeleton as the particles reorganize themselves and driven to the surface. This stage is commonly seen as most important in determining the bleeding. In the fourth stage, the hydration of cement paste with heterogeneous porosity will become dominant, which will determine the ultimate structure and performance.

Various self-weight consolidation models have focused on predicting the extent of bleeding water. Simulations based on these models demonstrate reasonable agreement with previous experimental results [7,9–12]. In particular, these models can offer insight into the microstructure development, i.e., the void fractions as a function of the height near the surface. However, measurements of fresh cement paste such as electrical conductivity, yield stress test and hydrostatic pressure tests [5–8,13] can only provide overall information, as well as being a lack of experimental verification of the void ratio development. Nuclear Magnetic Resonance (NMR) is a nondestructive and non-invasive method for quantitatively studying the water distribution and structure of a sample. It can provide important insights into the microstructure development from fresh to hardened state [14–18], and has facilitated the scientific studies of cement-based materials such as pore structure examinations [15], cement hydration mechanism [16,17] and determination of permeability [17,18]. In this study, we...
have used NMR to measure fresh cement paste during the bleeding process where we not only focus on the bleeding water, but also on the microstructure development. We will first shortly discuss the present models on self-weight consolidation models, followed by a description of the NMR setup used in this study. The experimental results of the fresh cement paste samples prepared with ordinary Portland cement, blast furnace slag cement and different water-cement ratio as well as different amounts of slag and polycarbonate superplasticizers (PCEs), i.e., a water reducer, will be discussed next. The two types of self-weight consolidation models have been fitted with the experimental results, and the best-fit parameters for these consolidation models on microstructure development are presented. Furthermore, the pore structure development across the cement paste with bleeding during hydration was analyzed and will be discussed as well.

2. Self-weight consolidation models

In this section we will shortly discuss the main self-weight consolidation models. A more detailed discussion can be found in literature [7–10]. Here we only want to focus on the main assumption and solutions in order to compare models to the experimental results. The primary assumption of self-weight consolidation models is that the water is incompressible and thus the volume of both solid particles and liquid remains unchanged. In addition, the water flow through the fresh state concrete during the bleeding is assumed to obey the Darcy’s law, i.e., a water reducer, will be discussed next. The two types of self-weight consolidation models are determined for this one-dimensional self-weight model. Their analytic solutions showed for the overall bleeding have a good agreement with results of bleeding test by Almusallam et al. [11]. Here we will only shortly discuss the analytical solutions as proposed by them.

2.1. Solutions to small strain consolidation model

Under the assumption that the strain is small (less than 10%), the ratio of effective stress $\sigma'$ to void ratio $e$ is constant and the permeability is linearly related to void ratio $e$ [9], the governing equation can be simplified as:

$$\frac{\partial e}{\partial t} = g \frac{\partial^2 e}{\partial z^2}$$

(2)

In order to take the effect of cement hydration into account during the consolidation, here $g$ is defined as a variable which changes as a function of time $t$, accordingly it can be defined as [9,10]:

$$g = g_0 \left(1 - \left(\frac{t}{t_c}\right)^m\right)$$

(3)

where $g_0$ is the finite-strain coefficient of consolidation at $t = 0$, $t_c$ is the transition time when the hydration is sufficient to stop the self-weight consolidation and $m$ is a dimensionless exponent.

The initial, upper and the bottom boundary conditions for Eq. (2) are given respectively by:

$$e(z, 0) = e_0$$

(4)

$$e(0, t) = e_0$$

(5)

$$\frac{\partial e}{\partial z} \bigg|_{z=0} = \frac{(\gamma_r - \gamma_f)}{\alpha}$$

(6)

where $e_0$ is the initial void ratio and $\alpha$ a constant. To obtain the solutions of the Eq. (2), it is convenient to convert them into normalized dimensionless forms:

$$E_{nm}(Z, T) = \frac{e(z, t)}{e(0, 0)}$$

(7)

$$Z = \frac{z}{l}$$

(8)

$$T = \frac{g_0 f}{\gamma f}$$

(9)

where $E_{nm}$ is the normalized void ratio $e$ in material coordinates. $Z$ and $T$ are the normalized dimensionless forms of $z$ and $t$, respectively and $l$ is the depth of the cement paste. Assuming a linear relationship between $e$ and $\sigma'$ one can normalize Eq. (2) giving:

$$\frac{\partial E_{nm}}{\partial T} = \frac{\partial^2 E_{nm}}{\partial Z^2} \left(1 - \left(\frac{T}{T_c}\right)^m\right)$$

(10)

Using the initial and boundary conditions given an analytic solution can be obtained for the normalized void ratio, i.e. [10]. Where A is the slope of the normalized $E-Z$ line, which need to be simulated in this study.

$$E_{nm}(Z, T) = 1 - AZ + \frac{8A}{\pi^2} \cdot \sum_{n=1,3,5} \left(\frac{1}{n^2} \sin\left(\frac{n\pi}{2}\right) \sin \left(\frac{n\pi Z}{2}\right) \cdot \exp\left[-\frac{n^2\pi^2 g_0 f}{4l^2} \left(1 - \left(\frac{1}{m + 1}\right) \left(\frac{1}{t_c}\right)^m\right)\right]\right)$$

(11)
2.2. Solutions to finite-strain consolidation model

Morris and Dux [10] showed that the normalized governing equation self-weight consolidation can be written as Eq. (13) when assuming ε and σ′ has a relationship as shown in Eq. (12):

\[ \varepsilon = (\varepsilon_0 - \varepsilon_w) \exp(-\lambda \sigma') + \varepsilon_w \]  
(12)

\[ \frac{\partial^2 E_m}{\partial T^2} = \left( \frac{\partial^2 E_m}{\partial Z^2} + N \frac{\partial E_m}{\partial Z} \right) \left( 1 - \frac{T}{T_1} \right)^m \]  
(13)

\[ N = \frac{1}{2} (\gamma_2 - \gamma_1) \]  
(14)

where λ is a constant, and ε is the void ratio corresponding to, when σ′ is infinite [10]. With associated initial, final and boundary conditions (Eqs. (4)–(6)), the solution for the normalized void ratio E_m can be obtained in this case as:

\[ E_m(Z, T) = (1 - B) \exp(-NZ) + B + \exp(-NZ_0) \exp\left(\frac{-N^2\tau_1^2}{4}\right) \times \sum_{n=1}^{\infty} (D_n \sin(\alpha_n Z) \exp(-a_n^2 \tau_1)) \]  
(15)

where B is a constant which equals to ε_0/ε_0 and α_n is the nth positive root of

\[ \tan(\alpha_n) = \frac{-2\alpha_n}{N} \]  
(16)

\[ \tau = T \left( 1 - \left( \frac{1}{m+1} \right) \left( \frac{T}{T_1} \right)^m \right) \]  
(17)

and

\[ D_n = \frac{2(1 - B)N \exp\left(\frac{N}{T_1}\right) \sin(\alpha_n)}{a_n^2 + \left( \frac{N}{T_1} \right)^2 + \frac{N}{2}} \]  
(18)

Accordingly, the total depth of bleeding water \( b_t \) at time \( t \) can be determined by:

\[ b_t = \varepsilon_i \left( 1 - \int_0^T E_m(Z, T) dZ \right) \]  
(19)

where \( \varepsilon_i \) is the void ratio at time zero. As an example in Fig. 2 we have plotted the void ratio as a function of time, i.e., the void ratio as a function of the position at various times and the void ratio as a function of time at various fixed positions in terms of material coordinates. As can be seen, as the bleeding progresses a void ratio profile develops in time and in the end an almost linear relationship is seen.

3. Experimental setup and materials

3.1. NMR set up

Nuclear magnetic resonance (NMR) is based on the principle that in an external magnetic field, H¹ nuclei have a specific resonance frequency and can be excited by a Radio Frequency (RF) field. The resonance frequency is called the Larmor frequency \( (\gamma H) \) and it is proportional to the applied magnetic field [19]:

\[ f_0 = \frac{\gamma H}{2\pi} B_0 \]  
(20)

where \( \gamma H_1/\pi \) is the gyromagnetic ratio of the H¹ nuclei (42.19 MHz/T) and B_0 is the applied magnetic field. The signal intensity S of a Hahn spin-echo sequence [20] is proportional to the amount of hydrogens and can be described by [19,20]:

\[ S(t) = \rho \exp\left( -\frac{t}{T_1} \right) \left( 1 - \exp\left( -\frac{t}{T_2} \right) \right) \]  
(21)

where \( \rho \) is the density of the hydrogen nuclei, \( T_1 \) is the spin-lattice relaxation time, \( T_2 \) is the spin-spin relaxation time and \( t_e \) is the echo time. Assuming the pores are saturated, the signal intensity S(t) will be proportional to the porosity, i.e., it will give us a direct indication of the void ratio (ε).

It has been well established [21] that the relaxation rate can be correlated with the pore size. In the so-called fast diffusion regime, both \( T_1 \) and \( T_2 \) are related to the surface-to-volume ratio of pores as:

\[ \frac{1}{T_{1,2}} = \frac{1}{T_{1,2}} + \rho \frac{S}{V} \]  
(22)

where \( T_{1,2} \) is the surface relaxivity for \( T_1 \) and \( T_2 \) relaxation respectively, which reflects a sink at the surface of the pores. As \( T_{1,2} \), for water at room temperature is in the order 3 s the first term for many porous building material with sufficient small pore can be neglected [21–23]. However complications occur as the materials under investigation, i.e., standard Portland cement and Blast furnace slag cement, contain large

Fig. 2. The simulation void ratio for the finite-strain model as a function of time in material coordinates. The parameters for the model used are \( N = 0.65, g_0 = 1.91, m = 3.59. \) (left) The normalized void ratio as a function of position every 10 min (right) The normalized void ratio at various fixed positions, i.e., \( Z = 0, 0.15, 0.22, 0.73, \) and 0.75 as a function of time.
amounts of paramagnetic ions (i.e., up to 4% Fe). The short transverse relaxation time and broad resonance linewidth of hydrogen nuclei in these materials preclude the use of standard NMR imaging techniques.

Hence, one has to be careful in interpreting the $T_2$ relaxation distribution as reflecting the pore size distribution, since internal gradients due to paramagnetic impurities or mismatch of the magnetic susceptibility can lead to dephasing. It is therefore we have chosen to use the measurement of the $T_1$ as the representation of the pore-size development during bleeding as this is not influenced by the magnetic impurities. Hence by measuring both the spin-echo signal and the $T_1$ relaxation we can get direct access to the void ratio and the pores structure changes. As we use a constant gradient during our experiments, the $T_1$ in this study was obtained using a saturation recovery sequence which has been applied in the research of building materials [20,22]. For the measurement of $T_1$ (saturation recovery) at a position about 6 s are needed to get the relaxation decay information. While for surface, i.e., at depth $d$ of a few millimeters, $T_1$ relaxation we can get direct access to the void ratio and the pores development. As we use a constant gradient during our experiments, the $T_1$ in this study was obtained using a saturation recovery sequence which has been applied in the research of building materials [20,22].

A schematic diagram of the setup used in this study is given in Fig. 2. With the help a step motor the sample can be moved through the NMR setup. The sample holder is cylindrical Perspex tube of 27 mm diameter and 90 mm high. To avoid wall effects, the cement paste sample height was limited to 75 mm. The NMR setup is equipped with gradient coils generating a constant gradient of 0.30 T/m providing a 1D resolution in the order of 1.0 mm. A webcam was placed outside of the magnet in order to obtain the bleeding water thickness. Hence after every measurement the sample is lifted outside of the NMR sensitive region with the help of the step motor as to make a picture with the webcam. As the bleeding process is quite fast in comparison to the NMR measurements it was chosen to measure the $T_1$ relaxation at two fixed positions, i.e., 16 mm (P_U) and 56 mm (P_L) from the top surface, i.e., at $Z = 0.22$ and 0.75. After 6 h when the bleeding has stopped, the void ratio was measured with Hahn spin-echo sequence over the complete sample, giving information of the pore structure development during hydration.

### 3.2. Materials

The cements used in this study (HEIDELBERG Group, ENCI B.V. Netherlands) are Ordinary Portland cement (OPC) and Blast furnace slag cement (SLC), which have specific area of 340 m²/kg and 475 m²/kg, respectively. The specific density for the cements, OPC and SLC are 3.1 and 3.0 g/cm³, respectively. The specific area of 501 m²/kg and a specific density 2.93 g/cm³. The particle size distribution of the cements and slag used in this study is shown in Fig. 6. The maximum particle size of both cements is in the order of 280 μm, and the median particle size of slag (approximately 12 μm) is smaller than that of the cements.

In this study various parameters were systematically changed of which an overview of the used mix designs and identification codes are given in Table 1. The types of cements, OPC and SLC, were used for comparison. The water-to-cement (W/C) was varied from 0.60 to 0.70, slag replacement from 0 to 60% and water reducer from 0 up to 0.5%. The water reducer (Master Gluenium 51, BASF-chemical company) used in this study is a modified polycarboxylic ether polymers (PCEs) which has a solid content of 36%. Its recommended usage range for concrete is from 0.20 to 1.0 percentage of binder materials.

### 4. Results and discussions

#### 4.1. Microstructure development of cement paste

First the microstructure development during the bleeding process of samples prepared with Portland cement and Slag cement with a water-cement ratio of 0.65 (W/C = 0.65) was measured. In Fig. 5, the results are given, i.e., Fig. 5a and b the normalized void ratio and relaxation rate representing the microstructure at two fixed positions 16 mm and 56 mm from the top surface as a function of time, which are all in natural coordinates. In Fig. 5c the measured height of the bleeding water on the top of the samples as determined by the webcam is given as a function of time.

As can be seen for both samples as the bleeding water comes out the void ratio at the top almost remains constant. In contrast the void ratio at the bottom gradually decrease until it reaches constant values, at the same time the bleeding almost stops. For both samples we see that the relaxation rate at the top of the sample is slightly smaller than at the bottom reflecting the larger pores at the top and the compaction due to the consolidation at the bottom. At the moment the bleeding almost stops we see a gradual increase in the relaxation rate indicating the development of the pore structure due to hydration. The end of the consolidation process and the beginning of the influence of the hydration can be characterized by the transition time $t_c$.

A closer inspection of the normalized void ratio reveals that sometime a void ratio larger than 1 is observed, which especially for the Slag cement sample can be observed in the Fig. 5. In order to understand this we have given a schematic diagram in Fig. 6. With the NMR setup we always measure at the same position. In theory, as described in the Eq. (4), the fresh cement paste is considered to have a uniform structure from top to bottom after mixing with water. However, for the fresh cement paste during our experiments, the first NMR measurement is not the true $t_{s-0}$ since settling (stage 2, sediment described in the introduction part) will begin immediately upon emplacement of the paste. Therefore a gradient (G-1 indicated in Fig. 6) in the void ratio would have already developed. As the bleeding progresses the sample will shrink (the void ratio gradient G-1 was replaced by the G-2), and as a result at the top position the void-ratio will increase slightly. As a consequence, the NMR signals at $t_s$ as used for normalization can be exceeded at later times, as shown in Fig. 6, resulting in normalized values apparently greater than one.

For comparing the experimental results with the consolidation models, the material coordinate systems needs to be transformed into natural coordinate system by correcting for the compaction at the two measurement positions, i.e., at 16 and 56 mm, by:

$$E_a(0.22, T) = E_{in} \frac{16 - b_1}{75 - b_1} T$$  \hspace{1cm} (23)

$$E_a(0.75, T) = E_{in} \frac{56 - b_1}{75 - b_1} T$$  \hspace{1cm} (24)

where $E_{in}$ is the normalized void ratio in natural coordinate and $b_1$ is the total depth of bleeding. It should be noted that the bleeding depth data are obtained with the webcam method (described in Fig. 2) which has a relative error in order of 2%. As a consequence, incorporating bleeding depth data into Eqs. (23) and (24) would distort the void ratio data.

### Table 1

<table>
<thead>
<tr>
<th>No.</th>
<th>Water</th>
<th>Cement</th>
<th>Slag</th>
<th>Water reducer/%</th>
<th>Final bleeding [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC0.65</td>
<td>0.65</td>
<td>1</td>
<td></td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td>SLC0.65</td>
<td>0.65</td>
<td>1</td>
<td></td>
<td></td>
<td>4.9</td>
</tr>
<tr>
<td>WC0.60</td>
<td>0.60</td>
<td>1</td>
<td></td>
<td></td>
<td>3.1</td>
</tr>
<tr>
<td>WC0.65</td>
<td>0.65</td>
<td>1</td>
<td></td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td>WC0.70</td>
<td>0.70</td>
<td>1</td>
<td></td>
<td></td>
<td>5.5</td>
</tr>
<tr>
<td>Ref0.65</td>
<td>0.65</td>
<td>1</td>
<td></td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td>SL30</td>
<td>0.65</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
<td>2.3</td>
</tr>
<tr>
<td>SL60</td>
<td>0.65</td>
<td>0.4</td>
<td>0.6</td>
<td></td>
<td>5.7</td>
</tr>
<tr>
<td>Ref0.50</td>
<td>0.50</td>
<td>1</td>
<td>0.00</td>
<td></td>
<td>1.6</td>
</tr>
<tr>
<td>PCEs0.25</td>
<td>0.50</td>
<td>1</td>
<td>0.25</td>
<td></td>
<td>5.6</td>
</tr>
<tr>
<td>PCEs0.50</td>
<td>0.50</td>
<td>1</td>
<td>0.50</td>
<td></td>
<td>7.4</td>
</tr>
</tbody>
</table>

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which may lower the reliability of the simulation results. Additionally, the bleeding depth data are not obtained at the same time with the NMR data, because moving the sample from bottom to top (see also the setup described in Fig. 3) would cost time, i.e., in order of 5 s. Therefore the various time intervals between the simulation data (after transforming the coordinates) and NMR results will reduce the reliability of simulation models to predict the void ratio development. For the experiment performed in this study we have measured a maximum bleeding in the order of 5 mm (see Table 1). Hence this would give a correction of almost 32% for P_U, i.e., from Z = 0.22 to 0.15, and just 3% for P_L, i.e., from Z = 0.75 to 0.73. In order to see the effect of this changing coordinate system we have performed simulations, on the void ratio, which are also plotted in Fig. 2(right). From these simulations we see that the void ratios are quite different over time for the position Z = 0.15 and 0.22. However, the void ratios at position Z = 0.73 and 0.75 are closely matching over the times simulated and only differ max 0.1% of the normalized void ratio. Considering the reasons above, we can assume:

\[ E_{\text{fit}}(0.75, T) \approx E_{\text{fit}}(0.75, T) \]  

(25)

Hence in this study we have chosen to only fit the model the void ratio development at the low position (i.e., P_L). In order to fit the model to the NMR experimental data(all expressed in natural coordinates), the void ratio development expressed as signal intensity were all normalized with the signal intensity at the \( b_0 \). Next by varying the fitting parameters, i.e., \( t_0, g_0, m, A \) (or \( N \)) and input values such as \( l, B \) and \( e_0 \), the normalized void ratio was calculated and compared with experimental data, using least-squares procedure. The best fitting parameters as found for these experimental data are given in Table 2.

Besides, the best-fit parameters of small-strain and finite-strain consolidation models for void ratio development were also used as input for the Eq. (19) to obtain the bleeding depth data. As an example, the results in Fig. 5c show that they both reach nice agreement with the development of bleeding depth data as a function of time. It can be seen that both linear-strain and small-strain model are able to describe the bleeding over time, however they differ for the normalized void ratio as a function of time. These experimental data as measured by NMR suggests that the linear-strain model is more suitable to predict the structure development during a consolidation process for fresh cement paste up to 75 mm as studied here. Also, it can be seen that, without transforming the material coordinates into natural one, the simulation result shows a good agreement with the NMR data. This means one can use our model by inputting parameters reported in this paper to simulate the microstructure development during bleeding process without knowing the bleeding depth data first. This suggests that the simulation parameters achieved in this study have generality for applying these models.

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**Table 2** Best-fit parameters for the consolidation models on microstructure development during bleeding.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Fitting equations</th>
<th>( t_0 )[min]</th>
<th>m</th>
<th>A</th>
<th>N</th>
<th>g_0</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC_65</td>
<td>Eq. (11) small-strain</td>
<td>55.02</td>
<td>0.049</td>
<td>0.40</td>
<td>–</td>
<td>2.10</td>
<td>0.921</td>
</tr>
<tr>
<td></td>
<td>Eq. (15) finite-strain</td>
<td>3.54</td>
<td>–</td>
<td>0.61</td>
<td>1.68</td>
<td>0.932</td>
<td></td>
</tr>
<tr>
<td>SLC_65</td>
<td>Eq. (11) small-strain</td>
<td>72.33</td>
<td>0.038</td>
<td>0.48</td>
<td>2.20</td>
<td>0.904</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eq. (15) finite-strain</td>
<td>3.31</td>
<td>0.78</td>
<td>0.89</td>
<td>0.905</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WC_60</td>
<td>Eq. (11) small-strain</td>
<td>39.05</td>
<td>0.048</td>
<td>1.01</td>
<td>–</td>
<td>1.21</td>
<td>0.892</td>
</tr>
<tr>
<td></td>
<td>Eq. (15) finite-strain</td>
<td>1.60</td>
<td>–</td>
<td>0.92</td>
<td>1.34</td>
<td>0.924</td>
<td></td>
</tr>
<tr>
<td>WC_65</td>
<td>Eq. (11) small-strain</td>
<td>55.02</td>
<td>0.049</td>
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<td>–</td>
<td>2.10</td>
<td>0.921</td>
</tr>
<tr>
<td></td>
<td>Eq. (15) finite-strain</td>
<td>3.59</td>
<td>–</td>
<td>0.65</td>
<td>1.91</td>
<td>0.933</td>
<td></td>
</tr>
<tr>
<td>WC_70</td>
<td>Eq. (11) small-strain</td>
<td>78.09</td>
<td>0.043</td>
<td>0.41</td>
<td>–</td>
<td>2.02</td>
<td>0.832</td>
</tr>
<tr>
<td></td>
<td>Eq. (15) finite-strain</td>
<td>4.50</td>
<td>–</td>
<td>0.76</td>
<td>1.12</td>
<td>0.954</td>
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<td>SL_30%</td>
<td>Eq. (11) small-strain</td>
<td>21.06</td>
<td>0.044</td>
<td>0.40</td>
<td>–</td>
<td>1.61</td>
<td>0.764</td>
</tr>
<tr>
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<td>Eq. (15) finite-strain</td>
<td>0.850</td>
<td>0.26</td>
<td>0.61</td>
<td>0.831</td>
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<tr>
<td>SL_60%</td>
<td>Eq. (11) small-strain</td>
<td>74.17</td>
<td>0.050</td>
<td>0.33</td>
<td>1.70</td>
<td>0.865</td>
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<td></td>
<td>Eq. (15) finite-strain</td>
<td>0.91</td>
<td>0.61</td>
<td>2.70</td>
<td>0.987</td>
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</table>
Fig. 5. The experimental results in natural coordinates from the NMR measurements of the bleeding of fresh cement paste prepared with Portland cement and Slag cement at a water-to-cement ratio of 0.65: (a) the normalized void ratio at \( Z = 0.22 \) and 0.75 from the top of the sample. (b) the corresponding the \( T_1 \) relaxation rate reflecting the pore structure measured at \( Z = 0.22 \) and 0.75. (c) The bleeding depth as determined by the webcam and simulation models. The bleeding depth is expressed as the normalized value which has been divided by the experimental final bleeding depth value (3.6 mm for OPC0.65; 4.9 mm for SLC0.65). The solid and dashed lines represent a fit of the small and finite strain model to the data (see also Table 2).

Fig. 6. A schematic representation of the influence of bleeding on the measurement of the void ratio at the two measurement positions. The void ratio with a gradient (G-1) is measured at time \( 0 (t_0) \); the void ratio with a gradient (G-2) is measured at time \( t \) (before \( t_0 \)).
4.2. Influence factor on the consolidation process

The bleeding can be influenced by various factors such as water-cement ratio, slag content and the use of water reducer, which will be discussed in this section.

4.2.1. Water-to-cement ratio

Here, we have investigated the influence of the water-to-cement ratio on the consolidation process. That is we have measured the consolidation process for Portland cement samples with different water-to-cement ratio, i.e., 0.60, 0.65 and 0.70. In Fig. 7 the result are shown for the measured normalized void ratio and $T_1$ relaxation rate of the cement paste sample with water-to-cement ratio of 0.60, 0.65 and 0.70. As can be seen in first order the bleeding process as a function of time is almost independent from the water-to-cement ratio. Only if we look closer we see that final void ratio for W/C = 0.70 is smallest, which is also reflected in the greater extent of bleeding measured of 5.5 mm. Moreover we see that the smallest $T_1$ relaxation rate is measured reflecting the larger pores formed. That is with increased W/C ratio the pores formed are larger and the void ratio increases, resulting in large bleeding extent.

4.2.2. Slag replacement

We have also looked at the influence of the addition of slag powders into the cement as it will change the particle distribution and initial hydration [24–26]. As a result, the particle movements and water transportation during the bleeding will be influenced. In Fig. 8 the result are shown for the normalized void ratio and $T_1$ relaxation rate of a Portland cement paste sample with different slag replacement from 0% up to 60% at a fixed water-to-cement ratio of 0.65. A clear difference

Fig. 7. Normalized void ratio(a) and $T_1$ relaxation rate as a function of time (b) as measured for two positions, i.e., $Z = 0.22$ (top) and $Z = 0.75$ (bottom) for Portland cements samples with water-to-cement ratio of 0.60, 0.65 and 0.70 in natural coordinates. In order to normalize the void ratio, the signal at both top and low location was divided by signals intensity at the $t_0$. The NMR signal will be proportional for the moisture content in arbitrary units. The final bleeding extent was 3.1, 3.6 and 5.5 mm. The lines represent best fits based on the finite strain model (see also Table 2).
can be seen. A 30% slag replacement results in a more homogeneous structure as can be seen from the void ratio. The slag powder used in this study has a high specific surface area. Compared with the WC0.65, the solid particle surface for SL30 is 14% larger, which may result in more water being absorbed at the surface. The slag powders also have a larger fraction of smaller particle size (see Fig. 4), which may help to form a more close-packed structure [24, 27]. As a result less water can be transferred. In contrast to 30% slag replacement, a 60% slag replacement once more results in a void ratio decrease and promoting of bleeding. This is probably due to the fact that the retarding effect [25, 27, 28] of slag powders on initial hydration will start to dominate when the slag replacement is increased up to 60%.

4.2.3. PCEs dosage

Water reducer, e.g., PCEs, can greatly improve the effectiveness of cement dispersion by not only initiating the electrostatic dispersion but also generating steric hindrances due to its side chains [29–31]. Besides, it is also known that PCEs can release the water from flocculation, delay early hydration and alter the chemical composition and physical property of the pore solution. In Fig. 9 the results are given for Portland cement paste with W/C = 0.5 with different dosages, i.e., 0%, 0.25% and 0.50% (by the cement weight). The final bleeding extent was 3.6, 2.3 and 5.7 mm. The lines represent best fits based on the finite strain model (see also Table 2).

Fig. 8. Normalized void ratio (a) and T1 relaxation rate as a function of time (b) as measured for two positions, i.e., Z = 0.22 (top) and Z = 0.75 (bottom) for Portland cements samples with water-to-cement ratio of 0.65 and slag replacement of 30 and 60% in natural coordinates. In order to normalize the void ratio, the signal at both top and low location was divided by signals intensity at the t0. The final bleeding extent was 3.6, 2.3 and 5.7 mm. The lines represent best fits based on the finite strain model (see also Table 2).
possible reason is that the PCEs reduce the yield stress [30,32] of the sample so that the skeleton system cannot withstand the self-weight of the paste resulting in an extension of the sedimentation process. Moreover, it can be observed that adding PCEs delays not only the consolidation process in time but also the hydration process as can be seen from the relaxation data. The consolidation process in this case can no longer be described by the consolidation models reported in this study.

4.3. Influence on the hydration

In Fig. 10, the typical NMR profiles are given after bleeding, i.e., during the hydration time, as measured from 6 h to 72 h for the four influence factors considered in this study, i.e., W/C ratio, slag replacement and PCEs dosage. As can be seen the signal of the bleeding water on top of the samples is suppressed in this measurements. This is due to the repetition time of 500 ms used in these measurements. As a result of this the signal of free water with $T_1$ in the order of 3 s will be suppressed [33]. Especially for the measurement with PCEs_0.25% which has the largest bleeding still a peak of free water is measured on top of the sample. As expected, the void ratio profiles of samples generally decrease as the function of hydration time from 6 h to 72 h. As can be seen, the experimental results indicated the porosity is not completely linearly related to the distance as predicted by the consolidation model (see e.g., Fig. 2).

Indeed the part close to the bleeding surface, i.e., a transition zone, shows an opposite trend, i.e., an increasing porosity with distance. The existence of transition zone was found by Han and Wang [4] to be correlated with uneven distributed gypsum during the bleeding process and would therefore lead to more SO2–4 existing in this part and facilitating the formation of hydration products such as ettringite (AFt) and calcium hydroxide (CH). As can be seen the final porosity
distribution, i.e., the porosity as a function of distance is correlated to the bleeding. That is for the sample with PCEs which shows the largest the bleeding also the largest porosity gradient is measured, whereas for the reference sample (Ref_50) which shows almost no bleeding and the end almost no porosity gradients is seen.

5. Conclusions

This study used NMR to investigate the microstructure development during both bleeding and hydration process. It was found that the NMR data can provide direct insights into the mechanism of the consolidation behaviour of cements pastes. It is seen that as the bleeding water comes out the void ratio at the top almost remains constant, and the void ratio at the bottom gradually decrease until it reaches a constant value. The results suggest that the finite-strain model is more suitable to predict that structure development during a consolidation process for fresh cement paste, except in the case of the use of PCEs. However, the depth of cement paste in this study is kept at a height of 75 mm which may not be sufficient to ensure whether the consolidation models are adequate for prediction of structure development in a deep sample. Further research concerning the validation of consolidation models with cement paste samples with large heights is needed. Moreover, the porosity is not completely linearly related to the distance as predicted by the consolidation model because of the existence of transition zone.

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References
