STUDY ON CHEMICAL SHRINKAGE AND ELECTRICAL RESISTIVITY OF CEMENT PASTES AT EARLY AGE

Yishun Liao (1), Xiaosheng Wei (1)

(1) School of Civil Engineering and Mechanics, Huazhong University of Science and Technology, Hubei Key Laboratory of Control Structure, Wuhan 430074, China

Abstract
This paper focuses on the correlation between electrical resistivity and chemical shrinkage when these two independent techniques were used to study the hydration of Portland cement. The electrical resistivity during 3 days was measured by a non-contacting electrical resistivity apparatus. The chemical shrinkage during 28 days was measured by dilatometry described in ASTM Standard C1608-07. The experiments were conducted on the Portland cement pastes with different water to cement (W/C) ratios of 0.3, 0.4 and 0.5 cured at 20 ºC. The results obtained show that the relationship between electrical resistivity and chemical shrinkage appears to be linear after 12 h. The non-evaporable water was measured for determining the degree of hydration of the cement pastes. The evolution of chemical shrinkage and electrical resistivity can be used to determine the degree of hydration.

Key words: Chemical shrinkage; Electrical resistivity; Portland cement; Hydration; Degree of hydration; Non-evaporable water.

1. INTRODUCTION
As cement hydrates, the effect that the total volume of cement paste decreases when the water is excessive and available is called chemical shrinkage [1]. This volume change is also known as Le Chatelier’s contraction. The chemical shrinkage is occurred due to the difference of density between the hydration products and the initial reacting materials (cement and water). The hydration products occupy less volume than the cement and water.

The methods of measurement of chemical shrinkage are various. Bouasker et al [2] cites the work of Justnes et al [3] who listed three main methods to measure chemical shrinkage: dilatometry, gravimetry and pycnometry. The schematic diagrams of the three methods can be found in ref. [2]. Among these methods, the dilatometry has the advantage of simple and easy
to carry out; the gravimetry is able to record automatically; the pycnometry can make sure the measurement starts as soon as possible after mixing. However, the dilatometry is the most widely used method. The dilatometry is used in the literature [4]. The gravimetry is used in the literature [2, 5, 6]. The pycnometry is used in the literature [7]. It is noticed that the dilatometry is accepted by ASTM Standard C1608-07 [8], which is based on the method developed by Geiker [9]. The principle of this method is to measure the water amount which is absorbed from its immediate surroundings by the hydrating cement paste. The chemical shrinkage can be calculated by the water amount because the sorption is in direct proportion to the amount of hydration that has occurred [10].

For a fully hydrated paste, the ultimate chemical shrinkage is about 6.4 mL for 100 g of cement [11]. Bouasker et al [2] find that there is a quasi-linear relation between the chemical shrinkage and the degree of hydration for cement pastes and mortars. Considering this, the chemical shrinkage of cement paste is used to calculate the degree of hydration in this study. In addition, the amount of non-evaporable water was measured simultaneously. The degree of hydration is calculated as the ratio of the amount of non-evaporable water to the water necessary to reach complete hydration, which is considered to be 0.23 [1].

Besides the chemical shrinkage, heat of hydration [1], electrical resistivity or electrical conductivity [12-14] are also controlled by the hydration of cement at early age and are also capable of providing information on the process of cement hydration. Lura et al [4] measured the heat of hydration and chemical shrinkage of cement pastes simultaneously. The results showed that the relationship between the two parameters appears to be roughly linear. The purpose of this paper is to investigate the relationship between electrical resistivity and chemical shrinkage.

2. EXPERIMENTAL

2.1 Materials

Three cement pastes with water to cement (W/C) ratios of 0.3, 0.4 and 0.5 were used in this study. The cement was Portland cement and was composed of clinker and gypsum. The composition of the cement is given in Table 1 and the compressive strength at 3 days and 28 days is 22.2 MPa and 48.4 MPa, respectively. All the pastes were mixed with distilled water.

Table 1: Chemical composition of Portland cement w/%

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>f-CaO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>MgO</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>21.88</td>
<td>4.02</td>
<td>2.59</td>
<td>63.02</td>
<td>0.83</td>
<td>3.10</td>
<td>0.32</td>
<td>2.44</td>
<td>1.68</td>
</tr>
</tbody>
</table>

2.2 Methods

2.2.1. Electrical resistivity

The cement was hydrated at W/C=0.3, 0.4 and 0.5 respectively and the electrical resistivity of the paste was measured by an non-contacting electrical resistivity apparatus that
was invented by Li Z and Li W [15] and manufactured by Hong Kong Brilliant Concept Technologies. The principle of this method can be found in detail in ref. [16]. All samples were made in a room in which the temperature was maintained at 20 ± 1 °C. The pastes were mixed for 4 min in a planetary-type mixer at 45 rpm and then were casted into a ring-shaped plastic mould that was closed during the test. The electrical resistivity measurement started right after casting and the data were recorded automatically by a computer during 3 days. The sampling interval was 1 min and the operation was continuous. Each mixture was prepared and tested twice.

2.2.2. Chemical shrinkage

In this study, chemical shrinkage measurements are carried out by dilatometry. The test procedure was according to Procedure A described in ASTM Standard C1608-07. About 10 g of freshly mixed cement paste were inserted in the small glass vials. The height of the paste in the vial was less than 10 mm. Consolidating the paste in the vial by tapping the vial and then adding de-aerated water carefully by syringe to fill the glass vial to the top. After that, the vial was closed with a rubber stopper, through which inserted a graduated glass pipette with graduations of 0.01 mL and a capacity of 1 mL (see Fig. 1). A drop of paraffin oil was placed in the top of pipette to avoid water evaporation during the testing period. The vial was immersed in a water bath at 20 °C. The water level in the graduated pipette was recorded periodically during 28 days. The measurements were performed on two replicate specimens.

Figure 1: Illustration of the experimental setup for measuring chemical shrinkage and the microstructure of cement pastes

2.2.3. Degree of hydration

The degree of hydration of the cement paste is calculated from the measurement of the quantity of non-evaporable water. In this study, the amount of non-evaporable water was defined as the mass loss recorded between 105 °C and 950 °C.

All the samples were immersed into ethanol to stop hydration and then were
crushed for the measurement of non-evaporable water. The samples were first dried in a drying oven on forced convection at 105 °C for 2 h and then ignited in a muffle furnace at 950 °C for 3 h. The amount of non-evaporable water is computed as:

$$ m_{wp} = \frac{m_1 - m_2}{m_2} - \text{LOI} $$

(1)

Where, \( m_{wp} \) is the amount of non-evaporable water (%); \( m_1 \) is the mass of cement paste dried at 105 °C (g); \( m_2 \) is the mass of cement paste ignited at 950 °C (g); \( \text{LOI} \) is the loss of ignition of cement (%). The ratio of \( m_{wp} \) to 0.23 is considered to be the degree of hydration of the cement paste.

3. RESULTS AND DISCUSSION

3.1. The evolution of chemical shrinkage

The chemical shrinkage of the cement pastes with W/C=0.3, 0.4 and 0.5 is plotted versus the hydration time in Fig.2. It can be seen that the chemical shrinkage increases sharply at early age of hydration and then increases slowly. The experimental results show that the value of chemical shrinkage at 3 days is 63.5%, 63.9% and 64.2% of the value at 28 days for the cement pastes with W/C=0.3, 0.4 and 0.5 respectively. The value of chemical shrinkage at 7 days is 78.4%, 80.1% and 79.4% of the value at 28 days respectively.

The chemical shrinkage of cement is depended on the hydration of cement. As the progress of hydration, the chemical shrinkage increases gradually. At the early period of hydration, the reaction between cement and water occurred immediately after mixing. As a result, the evolution of chemical shrinkage increases sharply. That was approved by Beltzung and Wittmann [7], who studied the evolution of chemical shrinkage during the first 8 h after
the time the water and the cement are in contact.

3.2. The evolution of electrical resistivity

The electrical resistivity development up to 3 days for the cement paste with W/C=0.3, 0.4 and 0.5 are shown in Fig. 3. It can be seen that the electrical resistivity development with time is similar for the different W/C ratios; however, the electrical resistivity values are significantly different. The electrical resistivity curve of cement paste with a low W/C ratio is always above those with a high W/C ratio.

![Figure 3: The evolution of electrical resistivity of cement paste during 3 days](image)

3.3. Relationship between chemical shrinkage and electrical resistivity

Fig. 4 shows the evolution of chemical shrinkage and electrical resistivity as a function of hydration time. It can be seen that the trend of the two curves are similar after 1 day.

![Figure 4: The evolution of chemical shrinkage and electrical resistivity of cement paste (W/C=0.4)](image)
Figure 5: Derivative of electrical resistivity and chemical shrinkage curves of cement paste (W/C=0.4)

Fig. 5 shows the evolution of the rate of chemical shrinkage and the rate of electrical resistivity as a function of specimen age. It can be seen that the decreasing stages of the two derivative curves are almost coincide with each other. That means the increasing rate of chemical shrinkage and electrical resistivity is approximately similar.

Figure 6: Chemical shrinkage as a function of electrical resistivity for cement pastes with different W/C ratios

Chemical shrinkage as a function of electrical resistivity for cement pastes with different W/C ratios is shown in Fig. 6. It is noticed that the relationship between electrical resistivity and chemical shrinkage appears to be roughly linear for the three cement pastes. However, the slopes are different. The slope of the chemical shrinkage versus electrical resistivity line for the paste with a high W/C ratio is larger than that with a low W/C ratio. The linear equations for the three cement pastes are as follows:

\[ CS = 0.0012p + 0.0068 \]  \hspace{1cm} (at W/C=0.3)  \hspace{1cm} (2)

\[ CS = 0.0023p + 0.0074 \]  \hspace{1cm} (at W/C=0.4)  \hspace{1cm} (3)
Where, $CS$ is the chemical shrinkage (mL/g cement); $\rho$ is the electrical resistivity ($\Omega \cdot m$). The coefficient of correlation ($r$) for Eq. (2), (3) and (4) is 0.9984, 0.9984 and 0.9977, respectively.

According to Eq. (2), (3) and (4), we can infer the chemical shrinkage of cement pastes from the electrical resistivity. For example, the experimental results show that the electrical resistivity of the cement paste with W/C=0.3, 0.4 and 0.5 at 3 days is 21.16, 11.23 and 5.80 $\Omega \cdot m$, respectively. Thus, the chemical shrinkage at 3 days can be calculated as 0.0320, 0.0332 and 0.0369 mL/g cement, which is similar to the experimental results—0.0310, 0.0328 and 0.0374 mL/g cement. The uncertainty is calculated to be less than 5%.

3.4. Degree of hydration

Both chemical shrinkage and non-evaporable water are used to calculate the degree of hydration of cement pastes with different W/C ratios. The result of degree of hydration versus hydration age is listed in Table 2. It can be seen that the result from chemical shrinkage are similar and slightly less than that from non-evaporable water in most circumstance.

<table>
<thead>
<tr>
<th>Age (d)</th>
<th>W/C=0.3</th>
<th></th>
<th></th>
<th>W/C=0.4</th>
<th></th>
<th></th>
<th>W/C=0.5</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CS$^a$</td>
<td>NEW$^b$</td>
<td>CS</td>
<td>NEW</td>
<td>CS</td>
<td>NEW</td>
<td>CS</td>
<td>NEW</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>17.69</td>
<td>19.17</td>
<td>14.23</td>
<td>18.70</td>
<td>15.86</td>
<td>16.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>31.23</td>
<td>37.04</td>
<td>29.68</td>
<td>37.35</td>
<td>32.93</td>
<td>39.87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>41.92</td>
<td>49.70</td>
<td>43.78</td>
<td>52.61</td>
<td>48.98</td>
<td>56.30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48.45</td>
<td>55.74</td>
<td>51.25</td>
<td>61.13</td>
<td>58.41</td>
<td>64.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>59.76</td>
<td>60.39</td>
<td>64.32</td>
<td>71.09</td>
<td>72.19</td>
<td>76.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>69.58</td>
<td>66.48</td>
<td>72.77</td>
<td>77.65</td>
<td>82.18</td>
<td>84.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>79.85</td>
<td>69.87</td>
<td>80.26</td>
<td>82.57</td>
<td>90.91</td>
<td>88.91</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) CS = chemical shrinkage. In this case, the degree of hydration was calculated from the ratio of chemical shrinkage at different specimen age to 0.064 mL/g cement, the ultimate chemical shrinkage for a fully hydrated paste.

b) NEW = non-evaporable water. In this case, the degree of hydration was calculated from the ratio of non-evaporable water at different specimen age to 0.23, the total weight fraction of non-evaporable water for a fully hydrated paste.

The degree of hydration ($\alpha$) of cement pastes is given by

$$\alpha = \frac{CS}{0.064}$$

Using Eq. (2), (3), (4), and (5), we have
Using Eq. (6), (7) and (8), we can calculate the degree of hydration by electrical resistivity for cement paste with a certain W/C ratio.

4. CONCLUSIONS

a) As cement hydrates, the chemical shrinkage increases sharply at the early age and then increases slowly. The value of chemical shrinkage at 3 days and 7 days is more than 60% and 80% of the value at 28 days, respectively.

b) During the hydration age except for the first day, the relationship between electrical resistivity and chemical shrinkage appears to be linear for the Portland cement pastes with different W/C ratios.

c) The degree of hydration of cement pastes with different W/C ratios can be estimated by the evolution of chemical shrinkage and electrical resistivity.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from National Natural Science Foundation of China (NSFC) under Grant No. 51178202.

REFERENCES


