INTERPRETATION OF MICROSTRUCTURE DEVELOPMENT OF CEMENTITIOUS MATERIALS IN EARLY AGES WITH ELECTRICAL RESISTIVITY MEASUREMENT

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Abstract

In early ages of a cement-based composite, due to progress of hydration, microstructure of the composite develops dynamically. In this study, a non-contact electrical resistivity technique is used to monitor the hydration process of cement pastes with varying water/cement (w/c) ratios. Through interpreting the resistivity measurement, the porosity development in cement-based composites can be revealed.

A modified Archie’s law and a general effective media (GEM) theory have been used to relate resistivity and porosity of cement-based composites. Archie’s law is an empirical equation while GEM has a sound theoretical background. The parameter to be determined is m in Archie’s law. The parameters to be determined are the percolation threshold of capillary pores $\Phi_c$, the percolation exponent t, and the magnification ratio M of the solid phase resistivity to the pore solution resistivity for GEM model. The parameters in the models were discussed for calculating porosity within the cement pastes. It has been found that GEM model can be used predict the porosity for a cement-based composite in mature stage once the parameters are determined.

1. INTRODUCTION

Portland cement paste is a time-dependent component of mortar and concrete, especially in early stage. Understanding of the microstructural development of pastes at early age is important in forecasting their mechanical properties. Cement-based materials have a complex hydration process and microstructure, varying in time and depending on chemical composition, admixture incorporation and temperature. Porosity describes the process of hydration, and directly relates to the fraction of the hydration products in a hydration system that governs the properties of cement-based materials. The hydration of cement-based materials leads to a continuous decrease in the amount of porosity due to the increase in
hydration products. Conventionally, porosity of concrete is measured at mature stages by the MIP method. However, MIP is difficult to conduct on cementitious material samples at early ages. Therefore, many attempts have made to develop new method to interpret porosity in early aged cement-based materials.

Electrical conduction occurs primarily due to ion transport through the pore solution in a cement-based system. It is strongly dependent on both pore solution conductivity and porosity. Electrical measurement methods have been applied to study the microstructural evolution in hydrating cement-based material systems [1, 2, 3, and 4]. However, the results from conventional electrical measurement are problematic due to the problems of the contact between electrodes and fresh cement, caused by electrochemical reactions and shrinkage gap problems.

Recently, a non-contact electrical resistivity method (NC-ERM) [5] has been developed to measure the resistivity development of fresh concrete and of the pore solution within the concrete mixes. The NC-ERM eliminates the contact problems between electrodes and surrounding materials in conventional set-ups for impedance measurement since there are no electrodes in this setup. The NC-ERM has been successfully used in the investigation of the hydration process of cement [6], Fly ash effect in cement-paste [7], alkali effect on hydration process of cement [8], and superplasticizer selection [9] in cement pastes.

The feasibility, sensitivity and effectiveness of NC-ERM for monitoring the hydration of cement-based materials have been verified in reference [6]. The degree of hydration of a concrete from resistivity measurement was interpreted based on NC-ERM[10].

The w/c ratio is one of the most important parameters in the determination of cement-based material performance, including strength and durability. In this study, the effect of w/c on cement paste was investigated. The porosity evolution ($\phi(t)$) is obtained from the modified Archie’s law and GEM model for the samples. The comparison between the two models is conducted.

2. MATERIAL AND METHODS

Paste samples are prepared using ordinary Portland cement (ASTM type I). The density of Portland cement is 3.15, the Blaine specific surface area of the cement is 3560cm$^2$/g, and the free lime content is 1.36%.

![Figure 1: Non-contact electrical resistivity set-up](image)
Three pastes P0.3, P0.35 and P0.4 with w/c ratios 0.3, 0.35 and 0.4 were prepared. Each paste sample was cast into the electrical resistivity mold (1672 cm³ in volume) with a cover preventing water within the sample from evaporation as shown in Fig.1. The measurement of the electrical resistivity was conducted over 48 hours at data recording intervals of 1 minute, under an ambient temperature of 22±2 °C.

3. RESULTS AND DISCUSSION

3.1 Bulk electrical resistivity development with time (ρ(t)-t) and the rate of bulk electrical resistivity development with time (dρ(t)/dt-t)

The bulk electrical resistivity curves with time (ρ(t)-t) of the paste mixes are plotted in Fig.2 (a). The bulk electrical resistivity and the differential of the bulk resistivity curve (dρ(t)/dt-t) of sample P0.3 are presented in Fig.2 (b). The bulk resistivity development presents the hydration process and the differential gives an assessment of the rate of hydration occurring in the system. Hydration stages of cement paste can be described by the characteristics on the electrical resistivity curve and its differential curve as shown in Fig.2 (b). The times for the characteristics occurrence and setting time were shown in Table 1.

Based on the characteristic points on the resistivity development curves, the resistivity/time response can be divided into 5 regions, designated I, II, III, IV and V, corresponding to dissolution, competition of dissolution-precipitation, setting, hardening and hardening deceleration periods[10], as shown in Fig.2 (b).

The bulk electrical resistivity developed from linear to curve shape from point L at the time of 1.53h, 2.55h and 2.98h for samples P0.3, P0.35 and P0.4, which is close to their initial setting time 2.22h, 3.31h and 4.15h (see Table 1), respectively, indicating the percolation threshold of the solid phase, when the degree of hydration is 3.13%, 5.14% and 9.47%, respectively. It is seen that the lower degree of hydration leads to percolation threshold for the lower W/C sample due to a higher initial concentration of solid particles within it. The higher the degree of hydration and longer time is needed to achieve initial setting occurrence for the higher W/C sample. It can also be seen that setting occurred before point P1 and P1 is close to the final setting times of samples P0.3, P0.35 and P0.4, which suggests that P1 indicates transition from a setting to a hardening process.

Right after P1, the rate of resistivity development (dρ(t)/dt) has a temporary decrease. It could be contributed to phases transform from AFt to AFm due to consumption of gypsum, releasing conductive ions Ca^{2+} and SO_{4}^{2-} [11,12]. When the transform reaction between the two phases is in equilibrium, the increase in the degree of cement hydration caused the resistivity rate to increase again until P2 is reached. After point P2, the increase of the bulk resistivity at a decease rate, which describes hardening deceleration occurring.

It can be seen that a higher W/C prolongs the time for the characteristics occurrence, which is attributed to a slower porosity decrease process in the sample.

In summary, from macro-point of view, fresh paste changes from fluid to solid state, from micro point of view, there are a serial of the physical and chemical reactions occurred and the consequence leads to microstructure formation and porosity decrease, the ρ(t)-t curve dynamically demonstrated these change processes, which hydration process is dominated by ions dissolution at early age and by porosity later.
(a) The electrical resistivity development of samples P0.3, P0.35 and P0.4

(b) Hydration stages

Figure 2: The electrical resistivity development and hydration stages
Table 1: Times for the characteristics points and setting occurrence (h)

<table>
<thead>
<tr>
<th>samples</th>
<th>Time occurrence for the characteristics points on the $\rho$(t)-t and $d\rho$(t)/$dt$-t curves</th>
<th>Setting time from ASTM C191</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>L</td>
</tr>
<tr>
<td>P0.3</td>
<td>0.50</td>
<td>1.53</td>
</tr>
<tr>
<td>P0.35</td>
<td>0.62</td>
<td>2.55</td>
</tr>
<tr>
<td>P0.4</td>
<td>0.68</td>
<td>2.98</td>
</tr>
</tbody>
</table>

3.2 Two-component model and Archie’s law

The bulk electrical resistivity $\rho(t)$ depends on the ionic concentration in the liquid phase, i.e. the solution electrical resistivity $\rho_0(t)$ and the volume fraction of the liquid phase, i.e. porosity $\phi$.

From the electrical modeling point of view, cement-based material can be regarded as a two-component composite material, with conductive ($V_C$) and un-conductive ($V_{UC}$) components. The solution electrical resistivity ranges from about 0.25 ~ 0.35 $\Omega$ m [13] and the solid electrical resistivity ranges from $10^5$ ~ $10^{12}$ $\Omega$ m [14]. The solid can be regarded as the non-conductive component when compared with the liquid phase. The liquid solution has partially or totally filled pores. When the saturation degree ($S_r$) (the water volume/pore volume) is 100%, the conductive-component ($V_C$) and the liquid phase volume ($V_L$) are equal to the porosity ($\phi$), when the pores are totally filled with the liquid solution.

A simple two-component model is proposed, as a parallel model, in Equation (1) and Equation (2). The system is time-dependent and the conductive component becomes less with increase of the curing time as shown in Fig.3.

\[
\frac{1}{R} = \frac{a}{R_C} + \frac{b}{R_{UC}}
\]

(1)

\[
\frac{1}{\rho} = \frac{C_V C_C}{\rho_C} + \frac{C_V UC}{\rho_{UC}} = \frac{V_C}{\rho_C} = \frac{V_L}{\rho_{UC}} = \phi^m
\]

(2)

Archie [15] investigated the relationship between the resistivity and porosity of rocks saturated with conducting water. Archie’s law, Equation (2), can be applied to cement paste for a saturation degree of 100%. Because $\rho$, $\rho_0$, $\phi$ and $m$ are time dependent for cement-based materials, Equation (2) can be expressed as Equation (3) and Equation (4).

\[
. \rho(t) = \rho_0(t)\phi(t)^{-m(t)}
\]

(3)

\[
\phi(t) = (\rho(t) / \rho_0(t))^{(-1/m(t))}
\]

(4)

Where $m$ (t) is a modified Archie’s law fitting parameter, related to tortuosity of hydration system.

Equation (3) means that the bulk electrical resistivity $\rho(t)$ is a combination of electrical resistivity $\rho_0(t)$ of the pore solution and porosity $\phi(t)$. There is an increase in $\rho(t)$ with increase in $\rho_0(t)$ and a decrease in $\phi(t)$.
The parameter \( m \) used in Archie’s equation is a measure of the cementation of the material, and for the changing pore system of Portland cement, the value of \( m \) is expected to vary with the degree of hydration. Therefore, a two-\( m \) value method [7] is proposed to determine change of the \( m \) value.

Based on Equation (3), a logarithmic relation exists between \( m(t) \) and \( \rho(t) \). Thus, \( m(t) \) is assumed as a function of \( \rho(t) \) in Equation (5)

\[
m(t) = m_1 + \frac{\ln \rho(t) - \ln \rho_1}{\ln \rho_2 - \ln \rho_1} (m_2 - m_1)
\]

The results of \( m \) for samples P0.3, P0.35 and P0.4 are 1.72~3.68, 1.55~3.58 and 1.49~3.49, respectively. For a fluid state, \( m_1 \) is about 1.49~1.72, and \( m_2 \) is between 3.49~3.68 in the hardened state. It is reasonable from the cementation concept, as lower W/C sample has higher tortuosity and the hardened paste has a higher tortuosity than that of its fresh state.

The porosity development curve (\( \phi(t) \)) can be then calculated as shown in Fig.4. From the curves in Fig. 4, it can be seen that there is a larger drop during setting period than the hardening period. That is reasonable as the hydration during the setting period is controlled by chemical reaction, whereas in the hardening period it is a diffusion control process.
3.3 Two-phase composites and GEM equation

Cement paste can be treated as a composite of a conductive pore phase dispersed in a resistive matrix consisting of unreacted cement grains and product phases. An effective media equation, general effective medium (GEM) quantitatively fits electrical resistivity as a function of the volume fraction data for a two-phase composite [16], which is based on both Bruggeman’s theory [17] and the percolation theory [18]. The GEM equation can be written as [16]:

$$
\sigma_l^{1/t} + \frac{f}{1-f} \sigma_l^{1/t} = \frac{f}{1-f} \sigma_h^{1/t} + \frac{1-f}{1-f} \sigma_h^{1/t} + \frac{1-f}{1-f} \sigma_l^{1/t}
$$

where,
- $\sigma_l$ — the conductivity of the low-conductivity phase.
- $\sigma_h$ — the conductivity of the high-conductivity phase
- $\sigma$ — the conductivity of composite
- $f$ — the volume fraction of the low-conductivity phase
- $f_c$ — the critical volume fraction of the low-conductivity phase, equal to which the low-conductivity phase is isolated by the other phase
$t$ — exponent for the percolation and GEM equation

For a cement-based system, the Eq (6) can be written as,

$$
\phi = \frac{[(1 - \phi_c)\rho_0^{1/t} + \phi_c\rho^{1/t}]\left(\rho_s^{1/t} - \rho_0^{1/t}\right)}{\rho^{1/t}\left(\rho_s^{1/t} - \rho_0^{1/t}\right)}
$$

(7)

where, $\Phi$—volume fraction of the pore solution phase $(1-f)$, porosity
$
\rho_0$—pore solution resistivity
$
\rho_s$—solid phase resistivity
$
\rho$— bulk resistivity
$
\Phi_c$ —critical volume fraction of the pore solution phase $(1-f_c)$, percolation threshold

The conductivity of the solid phase in a cement-based system is considered as non-zero [19], although it is very tiny with comparison of the pore solution conductivity in GEM Equation.

Parameter $M$, the ratio of the solid phase resistivity to the pore solution resistivity ($\rho_s/\rho_0$) is introduced to show the magnification coefficient between the solid phase resistivity and the pore solution resistivity. The formation factor $F(\rho/\rho_0)$, shows the ratio of bulk resistivity to the pore solution resistivity. Eq (7) can be written as:

$$
\phi = \left[\left(1 - \phi_c\right)F^{-1/t} + \phi_c\right] \frac{M^{1/t} - F^{1/t}}{M^{1/t} - 1}
$$

(8)

Take $M = 400$ ($M$ is determined diffusion test show pore solution conductivity is higher by a factor of 400 than C-S-H gel.), $t = 2$, $\phi_c = 0.18$ (independent of w/c) [19], the porosity development of samples P0.3, P0.35 and P0.4 can be calculated as shown in Fig.5. It can be seen that there is a larger drop during setting period which is similar to the observation in Fig.4, but much deeper drop in porosity.

![Figure 5: The porosity development based on the GEM model](image)
3.4 Comparison of Archie’s law and GEM

Cement paste hydration is a time-dependent process, the parameters in the models related to conductive phase shape, fraction, and distribution in the system, such as cementitious factor \( m \) and shape factor \( t \) should be variable with hydration time, because they reflect tortuosity information in a hydration system.

In modified Archie’s model, solid phase conductivity is considered as zero with comparison to the pore solution conductivity, which is reasonable for cement-based systems. Cementitious factor parameter \( m \) is time-dependent and has been determined by Eq. (5).

In GEM, the solid phase conductivity is considered as non-zero and \( M \) is determined from diffusion tests, showing that pore solution conductivity is higher by a factor of 400 than C-S-H gel.

As we known, the solid phase in a cement paste also contains other hydration products and unhydrated cement, \( M \) value then needs to be determined by a suitable method. Additionally, parameter \( t \) should be time-dependent [20] which is not like in a stable two-phase composite, such as metal oxides or graphite in a poly matrix.

In fact, Archie’s law can be derived from the GEM equation. When \( M \rightarrow \infty \), and zero percolation threshold, \( \Phi_c = 0 \). Thus, Eq. (8) can be written as:

\[
\phi = F^{-1/m} = \left( \frac{\rho}{\rho_0} \right)^{-1/t}
\]  

This equation is similar to the Archie’s law as Eq. (2), where \( t = m \). Both Archie’s law and the GEM theory consider tortuosity effect, the higher \( m \) or \( t \) means the more tortuous the solid phase networking in a system.

It was mentioned that \( \Phi_c \) should be considered in Archie’s law[19] for this model to be applied to a cementitious system in a more reasonable way, although it has good fitting results obtained. It is the most important thing for GEM theory to be applied in a cementitious system that \( t \) should be obtained as a time-dependent parameter, which have left more topics for further study.

4. CONCLUSION

The bulk electrical resistivity development curve as S-shaped growth demonstrates hydration stages of cement pastes. A high \( w/c \) ratio delays each hydration stage of cement paste. Initial setting occurs close to point \( L \) and final setting before the first peak of the differential electrical resistivity curve.

The porosity development curve is calculated based on the non-contact electrical resistivity measurement according to two Archie’s law and GEM theory. Determination of \( t \) as a time-dependent parameter for the GEM theory used in a cementitious system is necessary.

ACKNOWLEDGEMENTS

The financial support from the Hong Kong Research Grant Council under grant number HKUST 6272/03E is gratefully acknowledged.

REFERENCES


