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Computer simulation of impedance behaviour in hydrating Portland cement systems

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Computer simulation is applied to reveal the microstructural influence on the impedance behaviour of a hydrating cement paste system. Changes in two major parameters, porosity and mean pore size, have been taken into account in constructing the impedance spectrum. Simulation results show that a decrease in porosity leads to a decrease in both high-frequency resistance R_1 and high-frequency arc diameter R_2 . It has no effect on phase angle shift. A change in mean pore size has a more significant influence than a change in porosity on impedance behaviour, i.e. R_1 and R_2 of a hydrating cement paste system. It also affects the extent of phase-angle shift.

Introduction

Alternating current impedance spectroscopy appears destined to play an important role in fundamental and applied electrochemistry and materials science investigations.¹ However, this technique has been applied in cement science only in recent years.^{2–9} Useful information related to the microstructure of hydrating cement systems was obtained. Interpretation of an impedance spectrum (IS) usually requires modelling with an equivalent circuit until the electrical response of the elemental microstructure of the cement paste is well simulated. The usefulness of the analyses depends on the physical meaning of each selected reinforced concrete (RC) component in the circuit that relates to the microstructure of hydrating cement paste.

In previous work^{10–12} a simple electrical conductivity model and the corresponding equivalent circuit have been

proposed. New relations between high-frequency resistance (HFR), high-frequency arc (HFA) diameter and microstructural parameters such as porosity and mean pore size have been derived and their validity has been demonstrated by a series of experiments. An understanding of the effect of each individual microstructural variable on the IS is essential for interpretation of the data. In this Paper, a theoretical simulation of impedance behaviour of a hydrating cement paste system is described. The effects of microstructural factors, porosity and mean pore size are considered. The effects of porosity and mean pore size on the impedance behaviour of a cement paste system under a condition of constant ionic concentration in the liquid phase are demonstrated.

An equivalent circuit model for the hydrated Portland cement system

A typical IS for a cement system plotted in the imaginary against real plane is shown in Fig. 1(a). The single arc in the high-frequency range is associated with the bulk cement paste effect; a second arc in the relatively low-frequency region is due to electrode interface effects. The corresponding electrical equivalent circuit that describes the impedance behaviour of a hydrated cement paste system is shown in Fig. 1(b).^{7,8} This circuit, unlike other proposed electrical equivalent circuits,^{2–5} is derived from a simple physical model of a hydrating cement paste system. All the RC parameters have a clear physical significance.^{10–12} Frequency is denoted by ω ($\omega = 2\pi f$). R_1 is the HFR: its value can usually be determined by extrapolating the HFA to intercept the real axis at the high-frequency end. The diameter of the HFA R_2 and C_2 are solid–liquid interfacial resistance and interfacial capacitance respectively. These values can also be determined experimentally. Parameters R_{ct} and C_{dl} are related to the cement paste electrode surface effect. The

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Fig. 1. (a) Plot of an HFA in the impedance complex plane obtained for cement paste systems; (b) a corresponding equivalent circuit for hydrating cement paste

former is the charge transfer resistance due to electrochemical reaction at the cement–electrode surface: in a non-electric-polarization system, R_{ct} is usually very large. The latter is the electrode–cement system interface capacitance, or so-called double layer capacitance. The formation of C_{dl} is due to the existence of a boundary between the electrode and cement matrix in which the potential difference across the interphase results in the charge alignment at both the cement (with its electrolyte) and electrode surfaces. The interphase behaves as a capacitor. This cement–electrode capacitance effect always exists and its signal is usually picked up in the low-frequency range.

The total impedance value of the equivalent circuit (Fig. 1) is

$$Z = R_1 + \frac{R_2 - jR_2^2 C_2 \omega}{1 + (\omega C_2 R_2)^2} + \frac{R_{ct} - jR_{ct}^2 C_{dl} \omega}{1 + (\omega C_{dl} R_{ct})^2} \quad (1)$$

and the real and imaginary terms are

$$\text{real} = R_1 + \frac{R_2}{1 + (\omega C_2 R_2)^2} + \frac{R_{ct}}{1 + (\omega C_{dl} R_{ct})^2} \quad (2)$$

$$\text{img} = - \left(\frac{R_2^2 C_2 \omega}{1 + (\omega C_2 R_2)^2} + \frac{R_{ct}^2 C_{dl} \omega}{1 + (\omega C_{dl} R_{ct})^2} \right) \quad (3)$$

From previous investigations,^{10–12} HFR R_1 and the HFA diameter R_2 are functions of ionic concentration of the pore solution and porosity of the hydrating cement paste system, and can be expressed by

$$R_1 = \kappa' \left(\frac{1}{1 - \alpha(1 - P)} \right) \left(\frac{1}{\lambda_o(1 - \beta\sqrt{[C]})[C]} \right) \quad (4)$$

$$R_2 = \frac{k_1}{\sigma_f} \left(\delta_{st} + \frac{k_2}{\sqrt{[C]}} \right) \left(\frac{1}{Pr_o} \right) \quad (5)$$

where κ' is a constant related to cell geometry, σ_f is the ionic conductivity of the interface, λ_o is the equivalent conductivity of the pore solution at infinite dilution, β is an experimental constant associated with ionic interactions and viscosity of the pore solution etc., $[C]$ is the concentration of ions in the bulk pore solution, δ_{st} is the thickness of the Stern layer, k_1 and k_2 are constants related to pore geometry and ionic strength of pore solution and temperature respectively, α is the area fraction–volume fraction ratio of the pores, P is the porosity of the cement matrix, and r_o is the mean pore size, determined from a pore-size distribution curve obtained by mercury intrusion porosimetry.

A hydrating cement paste system is very complex. Most of the constants (i.e. λ_o , β , δ_{st} , α , k_1 and k_2) in equations (4) and (5) are difficult to determine. The overall effect, however, can be determined experimentally. This is facilitated in a hydrating Portland cement paste system when the ionic concentration in the pore solution is relatively constant (at hydration times greater than 24 h). Equations (4) and (5) can then be simplified to

$$R_1 = \left(\frac{K_1}{1 - \alpha(1 - P)} \right) \quad (6)$$

$$R_2 = \frac{K_2}{Pr_o} \quad (7)$$

where K_1 and K_2 are constants. Since $R_2 C_2 = \tau_o = 1/\omega_o$, where $\omega_o = 2\pi f_o$ (f_o = apex frequency), substitution of equations (6) and (7) into equations (2) and (3) yields the real and imaginary impedance for a cement paste system

$$\text{real} = \frac{K_1}{(1 - \alpha) + \alpha P} + \frac{K_2}{Pr_o[1 + (\omega\tau_o)^2]} + \frac{R_{ct}}{1 + (\omega C_{dl} R_{ct})^2} \quad (8)$$

$$\text{img} = - \left(\frac{K_2 \omega \tau_o}{Pr_o[1 + (\omega\tau_o)^2]} + \frac{R_{ct}^2 C_{dl} \omega}{1 + (\omega C_{dl} R_{ct})^2} \right) \quad (9)$$

The modulus and phase angle are given by

$$\text{Modulus} = \sqrt{(\text{real}^2 + \text{img}^2)} \quad (10)$$

$$\text{Phase angle} = \tan^{-1} \left(\frac{\text{img}}{\text{real}} \right) \quad (11)$$

It is apparent from equations (8) and (9) that porosity and mean pore size have a direct effect on the bulk impedance behaviour of the hydrating cement paste system. K_1 and K_2 are constants related to cell geometry, chemical composition of the cement and ionic concentration of the pore solution, etc. Their values can be estimated experimentally.^{10–12}

Experimental procedure

Materials

Type 10 Portland cement was used. Its chemical composition (wt%) was $\text{SiO}_2 = 19.83$, $\text{CaO} = 61.21$,

$\text{Fe}_2\text{O}_3 = 3.20$, $\text{Al}_2\text{O}_3 = 4.18$, $\text{MgO} = 4.09$, $\text{SO}_3 = 3.93$, $\text{Na}_2\text{O} = 0.45$, $\text{K}_2\text{O} = 0.82$. The silica fume used was supplied by the SKW Co., Montreal. Its composition was $\text{SiO}_2 = 95.17$, $\text{CaO} = 0.23$, $\text{Fe}_2\text{O}_3 = 0.13$, $\text{Al}_2\text{O}_3 = 0.21$, $\text{MgO} = 0.15$, $\text{SO}_3 = 0.12$, $\text{Na}_2\text{O} = 0.10$, $\text{K}_2\text{O} = 0.27$.

Specimen preparation

The fresh cement paste was mixed in a conventional Hobart mixer at a water/cement + silica fume ratio of 0.35, and placed into a 1.2 cm dia. $\times$ 1.5 cm stainless steel cylindrical cell described in previous work.^{7,8} The sample was in a 100% relative humidity environment for 24 h and was then immersed in lime solution for the remainder of the test period.

Impedance measurements

Impedance data were collected using a model 1260 impedance gain-phase analyser from Schlumberger Technologies. Measurements were made logarithmically in the frequency range from 20 MHz down to 1 Hz with ten readings per decade.

Results and discussion

Impedance spectra of hydrating cement paste and paste containing silica fume

Figure 2 shows plots of impedance data in the complex plane for the hydrating cement paste at 169, 194 and 380 h. Alternating current impedance behaviour of hydrating cement-silica fume mixtures at 68, 140 and 284 h is shown in Fig. 3. Addition of silica fume significantly changes the impedance properties of the cement paste.

An HFA in the real-imaginary plot (Figs 2(a) and 3(a)) was observed and continued to grow in diameter with time. These spectra exhibit a typical HFA contributed by the bulk solid-liquid interfacial capacitance and a 'tail' or part of a second arc (at lower frequencies) corresponding to the effect of the cement system-electrode interfacial double-layer capacitance. The growth of the HFA accompanies microstructural changes during the cement hydration process. One disadvantage of the plot in the complex plane (imaginary-real or Cole-Cole or Nyquist plots¹³) is that the spacing of the frequencies along the curve is highly non-linear. A more fundamental way of plotting the impedance over a wide range of frequencies is reflected in the log modulus - log frequency or phase angle - log frequency plots, e.g. Bode plots.¹⁴ These are complementary plots where the spacing on the frequency scale is explicitly stated. Moreover, frequency plots simplify identification of the effects caused by individual RC parameters in the equivalent circuit network. For instance, six decades of frequency are shown in Figs 2(b) and 3(b). In the range log frequency < 2 , the increase in log modulus values is caused by the cement matrix-electrode surface capacitance, and the decrease of log modulus in the range

Fig. 2. Plots of experimental impedance data for hydrating cement paste at 169, 194 and 380 h: (a) imaginary-real impedance; (b) log modulus-log frequency; (c) phase angle-log frequency

> 5 is due to the cement solid-liquid interfacial capacitance. The value of log modulus (Figs 2(b) and 3(b)) increased with hydration time, as well as with the phase angle in the HFR (log frequency > 5 , Figs 2(c) and 3(c)). Compared with cement paste, the curves for cement-silica fume pastes exhibit: (a) a rapid growth of the diameter with time, (b) a rapid increase of the modulus and phase angle in the HFR and (c) less depression of the HFA at longer hydration times. All the above phenomena are due to the effect of silica fume in accelerating

Fig. 3. Plots of experimental impedance data for the hydrating cement-silica fume paste at 68, 140 and 284 h: (a) imaginary-real impedance; (b) log modulus-log frequency; (c) phase angle-log frequency

cement hydration reactions. Silica fume addition results in a reduction in the number of large pores, a smaller mean pore size and lower total porosity.

The impedance loops plotted in the real-imaginary plane (Figs 2(a) and 3(a)) are not perfect semicircles. Depression of the HFA in the impedance spectra of cement paste is explained in terms of a spread of relaxation times. Pore size and pore surface chemistry could limit the oscillation frequencies of the hydrated ions and water molecules which respond to the applied alternating current

signal. A stronger ion-ion interaction would be expected more in small pores than in large ones. Close proximity of surfaces would hinder the oscillation of hydrated ions. A broad pore-size distribution would result in a wide spread of relaxation times. A narrow pore-size distribution would result in a significantly reduced spread of relaxation times. Less depression of the HFA would then be observed.⁸

Computer simulation

The objective of the computer simulation in this work was to reveal the effect of microstructural parameters, i.e. porosity and mean pore size, on the impedance behaviour of cement systems in a qualitative way. Therefore the following simplifications and assumptions were made.

- The effect of ionic concentration of the pore solution is constant.
- The electrode effect can be separated from that of the bulk paste since the effect of microstructure, i.e. bulk arc, appears only in the HFR. The electrode effect is not discussed in this Paper.
- The dispersion angle effect was neglected in this simulation.
- The constants in equations (8) and (9), such as K_1 , K_2 and α , were estimated from experimental results.¹⁰⁻¹²

The assigned porosity values in the range 35%–20% correspond to the actual porosity values measured in a hydrating cement paste system from 3 to 28 days hydration. The mean pore size change from 0.1 to 0.01 μm also corresponds to the actual mean pore size change of a hydrating cement-silica fume paste system from 3 to 28 days hydration.

Effect of porosity on impedance behaviour

The impedance spectra at various porosity values were calculated using equations (8)–(11) and the following arbitrary values: $\alpha = 1$, $K_1 = 30 \Omega$, $K_2 = 5 \Omega \mu\text{m}$, $r_o = 0.06 \mu\text{m}$ and $\omega_o = 2 \text{ MHz}$. The values of C_{dl} and R_{ct} were assigned as $50 \mu\text{F}/\text{cm}^2$ and $30 \text{ k}\Omega/\text{cm}^2$ for all the calculations. Results are presented as imaginary-real (Fig. 4(a)), log modulus-log frequency (Fig. 4(b)) and phase angle-log frequency (Fig. 4(c)) plots. In the imaginary-real plot, only the HFA and part of the second arc are displayed. It is clearly demonstrated that the HFR R_1 and the arc diameter R_2 increase as porosity decreases. The values of R_1 and R_2 , starting with 85 Ω and 285 Ω at $P = 0.35$, increase to 150 Ω and 500 Ω respectively at $P = 0.20$. Details are listed in Table 1. The 'tails' of all impedance spectra are parallel due to constant values of C_{dl} and R_{ct} .

Figure 4(b) contains four frequency domains. In the range $\log \text{ frequency} < 1$, the increase in log modulus values is caused by the cement matrix-electrode surface capacitance C_{dl} . In the range $5 > \log \text{ frequency} > 2$, the curve with a zero slope corresponds to the cement

(a)

(b)

(c)

Fig. 4. Computer simulation of impedance spectra for hydrating cement paste systems at various porosity values (the mean pore size is fixed at $r_o = 0.05 \mu\text{m}$): (a) imaginary—real impedance; (b) log modulus—log frequency; (c) phase angle—log frequency

solid—liquid interfacial resistance or the value of the HFA diameter R_2 . The decrease of log modulus in the range $5 < \log \text{frequency} < 7$ is due to the cement solid—liquid interfacial capacitance C_2 . A constant value of modulus beyond log frequency = 7 corresponds to the HFR. The phase angle—log frequency plot is also useful in separating the effects associated with RC parameters. In Fig. 4(c), the phase-angle peak in the high frequency range $4 < \log \text{frequency} < 8$ indicates the existence of cement solid—liquid interfacial capacitance C_2 , whereas the part of a peak in the low-frequency area (log frequency < 2) is related to the cement matrix—electrode surface capacitance C_{dl} .

Table 1. RC parameters obtained by computer simulation at various porosity values

Porosity: %	$R_1: \Omega$	$R_2: \Omega$	$C_2: \text{F}$
35	85	285	1.75×10^{-9}
30	100	333	1.50×10^{-9}
25	120	400	1.25×10^{-9}
20	150	500	1.00×10^{-9}

In the four calculated cases in Fig. 4(b) the parallel upward movement of the curves as porosity decreases indicates an increase of both R_1 and R_2 . It is interesting that the change of porosity alone does not affect the shift of the phase angle as the curves are superimposed in the high-frequency range. This result is compared below with the case where the mean pore size varies.

Effect of mean pore size on impedance behaviour

Theoretical simulations of the effect of mean pore size on the impedance spectrum at a constant porosity were conducted by assigning the following arbitrary values: $\alpha = 1$, $K_1 = 30 \Omega$, $K_2 = 5 \Omega \mu\text{m}$, $P = 0.25$, $\omega_o = 2 \text{ MHz}$, $C_{dl} = 50 \mu\text{F}$ and $R_{ct} = 30 \text{ k}\Omega$. All three plots are shown in Fig. 5, i.e. imaginary—real impedance, log modulus—log frequency and phase angle—log frequency, where $r_o = 0.1, 0.05$ and $0.01 \mu\text{m}$. The simulated RC parameters are given in Table 2.

The effect of mean pore size on the impedance spectrum is much greater than that of porosity. The imaginary—real impedance plot (Fig. 5(a)) shows that the diameter of the HFA increases significantly from 200Ω to 2000Ω as the mean pore size changes from $0.1 \mu\text{m}$ to $0.01 \mu\text{m}$. The effect of mean pore size can also explain the experimental observation that the HFA diameter is larger for the silica fume—cement paste system than for the ordinary Portland cement (OPC) paste. The silica fume—cement system has a smaller mean pore size than the OPC system.⁷ A significant increase in the modulus corresponds to an increase in the HFA, as indicated in Fig. 5(b). The phase angle—log frequency plot (Fig. 5(c)) is also affected by the mean pore size. Total porosity alone does not affect the extent of phase-angle shift. The simulation appears to explain observed behaviour.

In a hydrating OPC system, both porosity and mean pore size (as well as ionic concentration in the liquid phase) change with hydration time. Therefore, a change in the IS would not be linear. Variation of ionic

Table 2. RC parameters for cement paste obtained by computer simulation at various mean pore size values

Mean pore size μm	$R_1: \Omega$	$R_2: \Omega$	$C_2: \text{F}$
0.10	100	200	2.50×10^{-9}
0.05	100	400	1.25×10^{-9}
0.01	100	2000	2.50×10^{-10}

Fig. 5. Computer simulation of impedance spectra for hydrating cement paste systems with pore structure characterized by various values of mean pore size r_0 (porosity = 0.25): (a) imaginary—real impedance; (b) log modulus—log frequency; (c) phase angle—log frequency

concentration in the liquid phase would also make the impedance behaviour of hydrating cement paste more complicated. Changes in IS with ionic concentration in the pore solution will be dealt with in a further paper.

Conclusions

1. The effect of varying porosity on impedance behaviour of a hydrating cement paste system has been demonstrated by computer simulation. Varying porosity leads to changes in both HFR R_1 and HFA diameter R_2 , but has no effect on the shift of phase angle.

2. A change in mean pore size has a greater influence than a change in total porosity on the impedance behaviour of hydrating cement paste systems. It affects both the HFA diameter and the shift of phase angle.

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