Dielectric spectra of fresh cement paste below freezing point using an insulated electrode

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The spectra of complex dielectric constant were measured on a fresh cement paste with a water/cement ratio of 0.4 sandwiched between insulated electrodes in the frequency range 10 kHz–1 MHz and temperature range between 0 °C and − 30 °C. The bulk dielectric constant, 30–20, and conductivity, 6.14×10^{-5}–0.65×10^{-5}, in the temperature range − 10 to − 28 °C were much lower than those at room temperature, owing to the great decrease of ionic mobility caused by freezing the cement paste. The activation energy of 0.31 eV for the ionic conduction in fresh cement paste was obtained from an Arrhenius plot of conductivity at subzero temperature.

1. Introduction
There have been numerous works reported for monitoring the hydration of cement paste using a.c. electric techniques [1–6]. In many instances, cement paste has been regarded as a simple equivalent R–C circuit in parallel, and the equivalent resistance and/or capacitance were measured at a fixed frequency or narrow frequency range by a.c. bridge techniques; consequently, data on the impedance spectrum of cement paste are scarce.

Recently, McCarter et al. [7] considered a single arc and a small tail in the complex impedance plane during hydration of cement paste as indicative of bulk and electrode effects, respectively. They also considered that the low-frequency intercept of the single arc on the real impedance axis corresponded to the bulk resistance of the cement paste.

McCarter and Brousseau [8] suggested an equivalent circuit model, including double-layer capacitance and Faradic impedance, to represent the interfacial impedance. They determined the bulk resistance of cement paste and the charge transfer resistance at the cement–electrode interface from the interceptions on the real axis of two arcs in a complex impedance plane over the frequency range 10 mHz–15 MHz.

Another equivalent circuit model for an impedance spectrum proposed by Scuderi et al. [9] involved a parallel R–C circuit connected with a constant-phase element in series representing the interfacial effect between cement paste and electrode. The complex impedance spectra for the Portland cement paste with water to cement ratios, W/C = 0.3, 0.35, and 0.4, at various hydration times shows one arc in the high-frequency range and some part of a large arc in the low-frequency range arising from the bulk and interfacial effects, respectively. The bulk resistance deter-

mined from the intercept of arcs on the real impedance axis increases with time, in agreement with that of McCarter et al. [7].

A new simplified equivalent circuit model is proposed here for the dielectric spectrum of a fresh cement paste at subzero temperature, by the use of insulated electrodes from which the bulk dielectric constant and conductivity are obtained.

2. Determination of electric parameters by use of an insulated electrode
The apparent impedance of the metal–electrolyte interface is affected by both bulk and interfacial impedances due to charge transfer and accumulation at the electrode. The theories and equivalent circuits for the impedance spectrum of the interface have been analysed in detail by considering the Faradaic impedance in the literature [10–15]. Experimentally, the bulk impedance can be obtained by separating the interfacial contribution by observation of impedance spectra over a wide frequency range, provided that the responding frequency range of the bulk and interfacial process are not superposed.

The interfacial phenomena can be simplified by coating an insulating layer on the metal electrode to block the Faradaic current, allowing only the space charge polarization at the interface. Then, the equivalent circuit for the insulated electrode–electrolyte interface is simplified as in Fig. 1b, where C_i and C_{dl} are the capacitances of the insulating layer and the double layer, respectively. The Debye length [10] is defined as the distance in the electrolyte over which a small perturbation in potential or electric field decays, and is usually much less than the thickness of
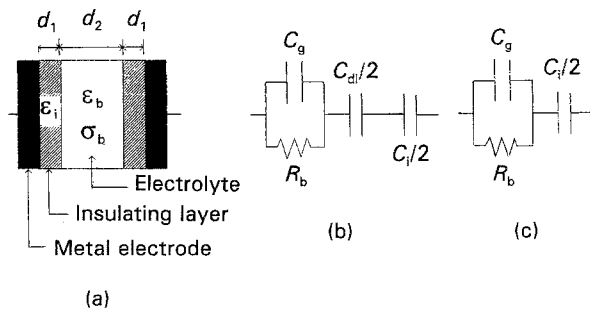
Figure 1 Insulated electrode–electrolyte interface and its simplified equivalent circuits.

Figure 2 Spectrum of complex dielectric constant for the insulated electrode–electrolyte interface.

the insulating layer. Accordingly, the double layer capacitance, C_{dl}, connected to C_i in series can be neglected, and the equivalent circuit is further simplified as shown in Fig. 1c. The total admittance of this equivalent circuit is

$$Y = \frac{1}{Z} = 1 \bigg/ \left[\frac{2}{i\omega C_i} + \frac{1}{i\omega C_b + (1/R_b)} \right]$$ (1)

where C_b and R_b are the capacitance and resistance of bulk material, respectively, and ω is the angular frequency. Then, the spectrum of complex dielectric constant, ε^*, for the insulated electrode–electrolyte interface, known as a special case of the Maxwell–Wagner model [16], can be represented by the relation of $\varepsilon^* = (d/i\omega\varepsilon_o A)Y$ after some algebra

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}$$ (2)

$$\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2\tau^2}$$ (3)

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2}$$ (4)

where ε' and ε'' are the real and imaginary dielectric constant, respectively, and ε_s, ε_∞ and the relaxation time, τ, are

$$\varepsilon_s = \frac{\varepsilon_i d}{2d_1}$$ (5)

$$\varepsilon_\infty = \frac{\varepsilon_i \varepsilon_b d}{\varepsilon_i d_2 + \varepsilon_b(2d_1)}$$ (6)

$$\tau = \frac{\varepsilon_i d_2 + \varepsilon_b(2d_1)}{2d_1 \sigma_b} \varepsilon_o$$ (7)

where ε_i and ε_b are the dielectric constants of insulating layer and bulk material, respectively, d_i the thickness of each part as shown in Fig. 1a and σ_b the conductivity of bulk material.

Fig. 2 shows the spectra of ε' and ε'' of Equations 3 and 4, respectively. These spectra of the Debye-type dispersion reflect that the space-charge polarization caused by blocking electrodes approaches exponentially equilibrium polarization with a single relaxation time, when the direction of the applied electric field is reversed.

Thus the dielectric constant, ε_b, and conductivity, σ_b, of bulk material can be determined from Equations 5–7 with the substitutions of ε_s, ε_∞ and τ obtain-
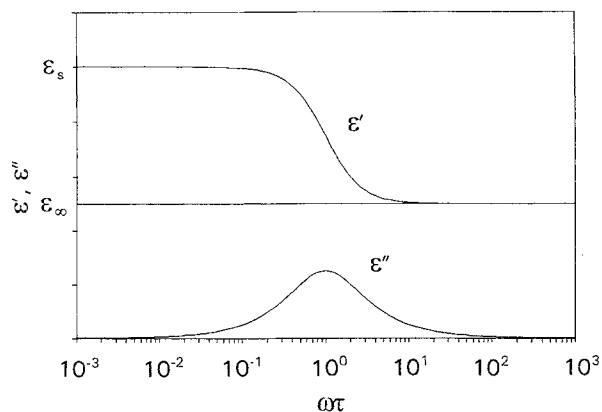
able from the spectrum of the complex dielectric constant.

3. Experimental procedure

An ordinary Portland cement (Ssangyong Co., Korea) was mixed with distilled water. The dielectric cell was a cylindrical acrylic holder with parallel electrodes of stainless steel at each side. The area of the electrode and the distance between the electrodes were $A = 1.77\ \mathrm{cm}^2$ and $d = 0.5\ \mathrm{cm}$, respectively. A polypropylene film of thickness $d_1 = 0.005\ \mathrm{cm}$ was coated on the electrodes as an insulating layer. The spectra of the complex dielectric constant for a cement paste of $W/C = 0.4$ after 2 h at room temperature mixing, were obtained in the frequency range 10 kHz–1 MHz at various temperatures between 0 and $-30\,^\circ\mathrm{C}$ using the HP 4277A LCZ meter and cryostat controlled by a personal computer. The data were obtained after the equilibrium state was attained at each temperature.

4. Results and discussion

4.1. Dielectric spectrum of fresh cement paste/insulated electrode system

Fig. 3a and b show, respectively, the frequency spectra of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ at various temperature for the fresh cement paste/insulated electrode system. These spectra are typical Debye-type dispersions due to the relaxation of space-charge polarization as expected in Fig. 2. The dispersion is not observed at room temperature because the space-charge polarizations oscillate without relaxation in our frequency range 10 kHz–1 MHz. By decreasing the equilibrium temperature of the cement paste, the relaxation starts to appear and shifts towards lower frequency as a result of the decrease of conductivity due to the decrement of ionic mobility, which is more pronounced between 0 and $-10\,^\circ\mathrm{C}$ due to freezing of fresh cement paste [17].

4.2. Dielectric constant and conductivity of fresh cement paste at subzero temperature

We obtain the bulk dielectric constant, ε_b, and conductivity, σ_b, of fresh cement paste by combining

TABLE I Data obtained from the spectrum of complex dielectric constant, and calculated bulk dielectric constant and conductivity for frozen fresh cement paste

Temp. (°C)	ε_∞	ε_s	$\tau(10^{-5}\,s)$	ε_i	ε_b	$\sigma_b(10^{-5}\,\Omega^{-1}\,m^{-1})$
−10.8	21.9	96.0	1.4	2.24	28.04	6.14
−15.8	20.7	94.7	2.5	2.21	26.18	3.40
−19.7	20.13	92.7	4.2	2.16	25.42	1.97
−23.0	19.4	89.3	7.3	2.08	24.50	1.09
−28.0	19.0	87.2	12.0	2.03	24.02	0.65

(a) Frequency (Hz)
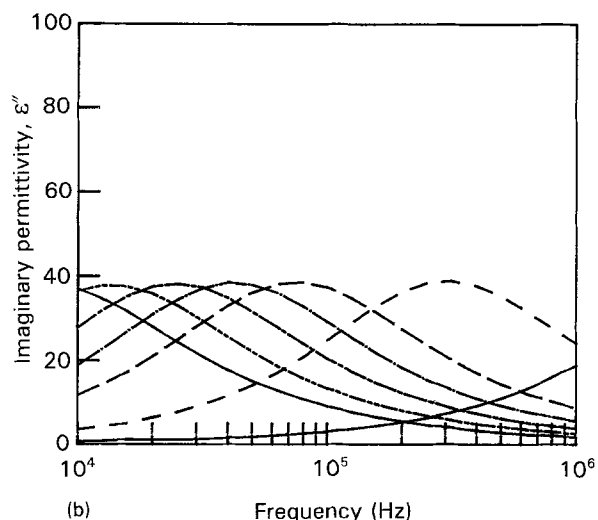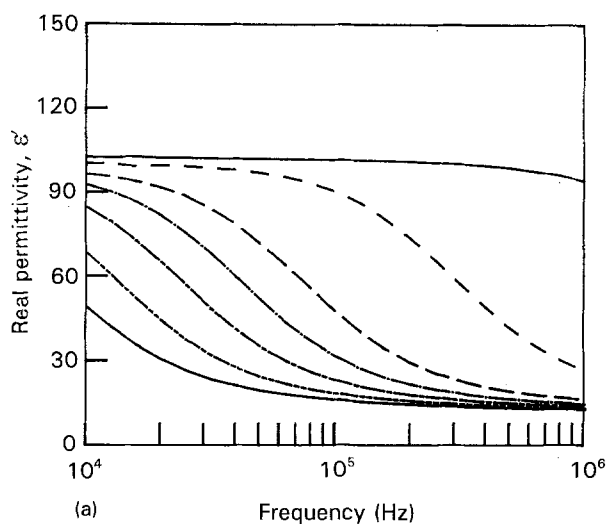
(b) Frequency (Hz)

Figure 3 Temperature dependence of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for the fresh cement paste–insulated electrode interface. W/C = 0.4; (———) 0°C, (– – –) −4.9°C, (———) −10.8°C, (–·–·–) −15.8°C, (———) −19.7°C, (————·———) −23.0°C, (———) −28.0°C.

Figure 4 Temperature dependence of $\varepsilon''\omega$ versus ε' and ε''/ω versus ε' for the fresh cement paste–insulated electrode interface. W/C = 0.4.

Equations 3 and 4

$$\varepsilon''(\omega)\omega = \frac{(\varepsilon_s - \varepsilon_\infty)\omega^2\tau}{1 + \omega^2\tau^2} = \frac{\varepsilon_s - \varepsilon'(\omega)}{\tau} \quad (8)$$

$$\frac{\varepsilon''(\omega)}{\omega} = \frac{(\varepsilon_s - \varepsilon_\infty)\tau}{1 + \omega^2\tau^2} = \tau[\varepsilon'(\omega) - \varepsilon_\infty] \quad (9)$$

Fig. 4a and b show, respectively, the plots of $\varepsilon''(\omega)\omega$ and $\varepsilon''(\omega)/\omega$ against $\varepsilon'(\omega)$ obtained from the spectra in Equations 8 and 9; both methods yield straight lines with slope $1/\tau$ and τ, respectively, intersecting the ε' axis at ε_s and ε_∞ varying with temperature. The ε_∞, ε_s, and τ obtained from Fig. 4 are listed in Table I, in which the dielectric constant of insulating layer, ε_i,
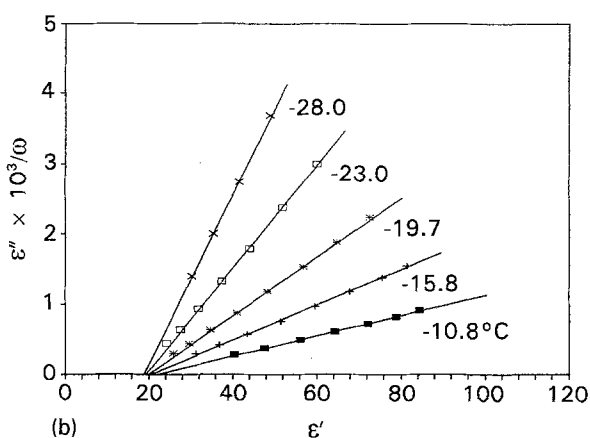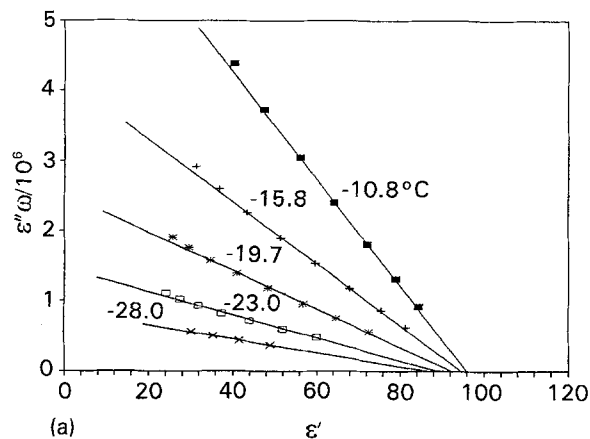
bulk conductivity, σ_b, and dielectric constant, ε_b, calculated from Equations 5–7 are also included. The ε_∞ and ε_s decrease as a result of the decrease in ε_i and ε_b with decreasing equilibrium temperature of cement paste. The relaxation time, τ, increases as the equilibrium temperature decreases, which is ascribed to the decrease of bulk conductivity, σ_b, in accordance with Equation 7.

Fig. 5 shows plots of bulk conductivity and dielectric constant against the equilibrium temperature of cement paste given in Table I. The cement paste 2 h after mixing is in the induction period in which the hydration reactions do not occur for several hours [18], hence it can be regarded as fresh cement paste. The bulk dielectric constant of fresh cement paste, ε_b, decreases from 28.04 to 24.02 as the temperature decreases from −10°C to −30°C, which is shown to be much less than that at room temperature and in the
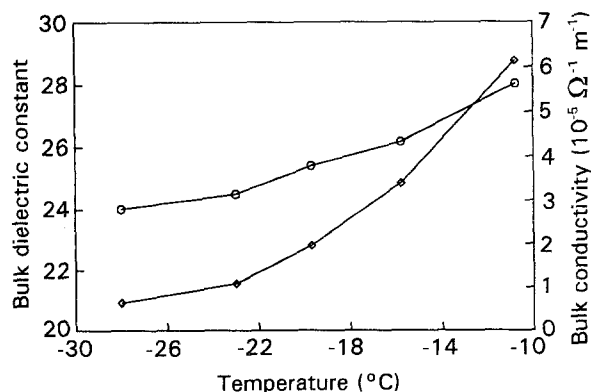
Figure 5 The change of (◇) bulk conductivity and (○) dielectric constant with the equilibrium temperature of cement paste given in Table I.
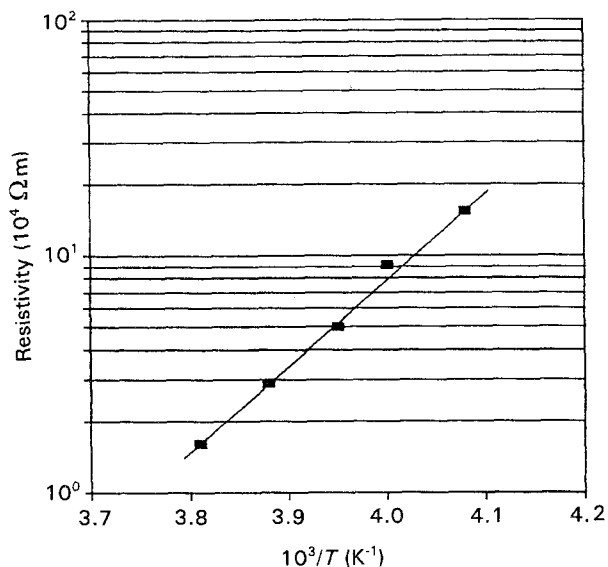

Figure 6 Arrhenius plot for the resistivity of the frozen cement paste. W/C = 0.4

similar frequency range, $10^4–10^5$, reported by other workers [4–6]. The space-charge polarization by blocking near the electrode and cement grains does not follow the high-frequency oscillating electric field due to decreased ion conductivity caused by freezing. Hence, the low dielectric constant, ε_b, of 24–28 is attributed to the contribution from background polarization of bound charges such as permanent and induced dipoles. Thus the decrease of ε_b with decreasing temperature is attributed to the decrease of polarizability of bound charges.

The bulk conductivity, σ_b, of the order of 10^{-5} $\Omega^{-1}m^{-1}$, at subzero temperature observed in the present work is much less than $10^{-1}–10^1\,\Omega^{-1}m^{-1}$, that at room temperature and in the similar frequency range reported by other workers [4–6]. This suggests that the ions, such as Ca^{2+} and OH^- [19], dissolved in water are locally bound by freezing in the temperature range -10 to $-28\,°C$.

Fig. 6 is the Arrhenius plot of the resistivity of frozen fresh cement paste, $\log \rho_b = \log(1/\sigma_b)$ against inverse equilibrium temperature, using the data in Table I. The straight line indicates that the ionic conduction in the frozen cement paste is governed by a single activation process

$$\sigma_b = A\exp(-E/kT) \qquad (10)$$

where A is a pre-exponential and E is the activation energy of a particular conduction process, T the temperature (K), and k Boltzmann's constant $(8.63 \times 10^{-5}\,eV\,K^{-1})$. The activation energy of $0.31\,eV$ for the ionic conduction process in the frozen cement paste was obtained from the slope of the straight line in Fig. 6.

5. Conclusion

The spectra for the dielectric constant of a fresh cement paste/insulated electrode system in the frequency range 10 kHz–1 MHz and the temperature range between 0 and $-30\,°C$, showed a Debye-type dispersion due to the relaxation of space-charge polarization. The dispersion was not observed at room temperature and starts to appear and shifts towards lower frequency with decreasing equilibrium temperature of the cement paste, as a result of the decrease in conductivity due to the decrease in the ionic mobility, as anticipated.

The bulk dielectric constant, 24.02–28.04, and conductivity, $\simeq 10^{-5}\,\Omega^{-1}m^{-1}$, of fresh cement paste in the temperature range between -10 and $-30\,°C$, were determined from the spectra of the complex dielectric constant for an insulated electrode system. The values are much lower than those at room temperature, which is ascribed to the great decrease of ionic mobility by freezing of the cement paste at subzero temperature.

The activation energy obtained from the Arrhenius plot of conductivity was 0.31 eV for the ionic conduction process in the frozen fresh cement paste. The results indicate that the use of an insulated electrode can simplify the interfacial process by excluding the interfacial effect due to Faradaic impedance, and is a useful method to determine the bulk dielectric constant and conductivity of cement paste.

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