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Microstructural Analysis of Young Cement Pastes Using Impedance Spectroscopy During Pore Solution Exchange

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Impedance spectra were collected in situ during the exchange of the aqueous phase with an organic solvent in young (1–28 days old) ordinary portland cement (OPC) pastes at two water-to-cement ratios (w/c = 0.35 and 0.70). The high initial values of dielectric constant (10^3–10^5) and the rapid decline upon exchange support a model of dielectric amplification where layers of calcium silicate hydrate (C-S-H) gel separate capillary pores. When the liquid in pastes of w/c = 0.35 was exchanged with isopropanol, the residual dielectric constants were typically between 10^2–10^3, indicating that C-S-H has a dielectrically amplified microstructure. After methanol exchange, however, the residual dielectric constant was much smaller, 10–100. This suggests there are two kinds of water within C-S-H gel in pastes of w/c = 0.35—that which is exchangeable by both solvents (capillary pores) and that which is exchangeable by methanol but not isopropanol (gel pores). For pastes of w/c = 0.70, differences due to solvent types were negligible. These observations suggest that the nature of C-S-H varies with w/c ratio. ADVANCED CEMENT BASED MATERIALS 1996, 4, 68–75

Many aspects of the fragile and complex microstructure of young cement paste make it prohibitive to study by conventional means, particularly if drying is required. Recently, however, impedance spectroscopy (IS) has emerged as a nondestructive technique for in situ microstructural analysis [1–7]. Data are collected over a range of frequencies, varying from hertz to megahertz, allowing for the separation of bulk and electrode polarization effects. This enables the study of both bulk conductivity, from which diffusivity and permeability can be inferred [4], and electrode (steel rebar) corrosion [8].

IS facilitates the calculation of bulk capacitance and effective dielectric constant. One striking find is the particularly high values of effective dielectric constant observed in young cement pastes [4]. These values, 10^3 to as high as 10^5, cannot be rationalized on the basis of the dielectric constants of the individual phases. Water has a dielectric constant of 80, and the other solids have much smaller values. (Our measurements on oven-dried pastes show values less than 10.) These extremely high values in paste reflect a phenomenon we are denoting as dielectric amplification.

One recently proposed model attributes the electrical properties of cement pastes, including the high dielectric constant, to a solid-liquid interface phenomenon [5–7]. However, this explanation is not consistent with the observed results. The total surface area increases as calcium silicate hydrate (C-S-H) is produced, although a drop of two orders of magnitude in dielectric effect accompanies this increase in C-S-H and its associated solid-liquid interface; there is clearly a need for a model to explain this effect.

An alternative microstructural origin for the dielectric amplification in young pastes has been proposed recently [2,4,9]. An analogy has been made to the bricklayer model (see Figure 1) of grain boundary-controlled electroceramics, where thin, resistive grain boundaries between conductive grain cores give rise to large, effective dielectric constants (ϵ_{eff}). Thus,

$$\epsilon_{eff} = \epsilon_{bl}(D/d) \tag{1}$$

where ϵ_{bl} is the dielectric constant of the boundary layer, D is the grain size, and d is the width of the boundary layer. In cement pastes, D is the size of macropores, or large capillary pores, and d is the thickness of C-S-H gel layers separating those pores. This bricklayer model will be discussed as an integral part of the following investigation.

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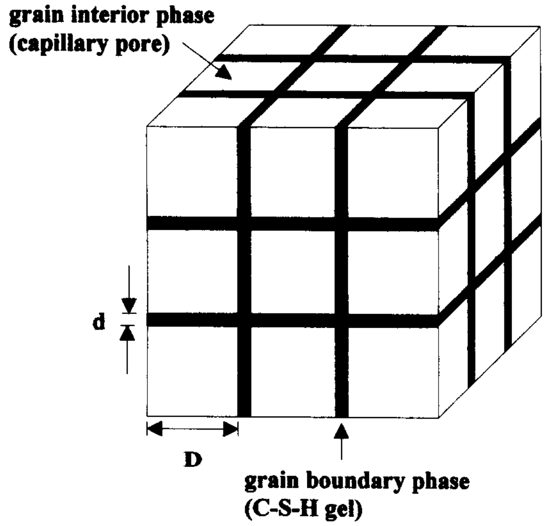

FIGURE 1. Schematic representation of the brick-layer model of grain boundary capacitors where grain cores are conductive and grain boundaries are resistive. Effective dielectric is proportional to *D*/*d* ratio.

We recently demonstrated that the C-S-H gel layers do not need to be continuous, that is, completely blocking, to achieve dielectric amplification [10–12]. Pixel-based two-dimensional computer simulations in I configuration (continuous C-S-H gel layers) and T configuration (discontinuous gel layers) give rise to similar dielectric amplifications (see Figure 2). The T configuration represents features in the microstructure that protrude into the pores but do not necessarily separate adjacent pores. This is important because the capillary porosity in cement pastes remains percolated until high degrees of hydration are reached, well after significant amplification is observed [13]. The model also explains the decrease in effective dielectric constants of young pastes (after an initial peak) in spite of additional C-S-H gel, a material with a large dielectric constant. During hydration, capillary pores are continuously subdivided and consumed (*D* in eq 1 decreases) and C-S-H gel layers thicken (*d* increases), which explains why the effective dielectric constant decreases as the amount of C-S-H increases.

Similar dielectric amplification has been observed in other porous media, including porous alumina and sedimentary rocks [14–17]. Sen et al. [14,17] pointed out that dielectric amplification can be substantial for conducting spheres of radius *R* coated with insulating shells of thickness *t*. Their dielectric amplification ratios, *R*/*t*, are quite similar to the ratio, *D*/*d*, in our model.

We recently tested the model by measuring IS of young cement pastes during controlled freezing experiments [18]. At around −5°C, the large capillary pores freeze and become insulating, thereby eliminating this source of dielectric amplification. At this point, a two orders of magnitude drop in effective dielectric constant was observed, from the 10^4–10^5 range down to the 10^2–10^3 range. It was also noted that C-S-H gel must be a dielectrically amplified microstructure, because its effective dielectric constant is on the order of 10^3.

The present study also investigated the changes in dielectric constant and resistivity during solvent ex-

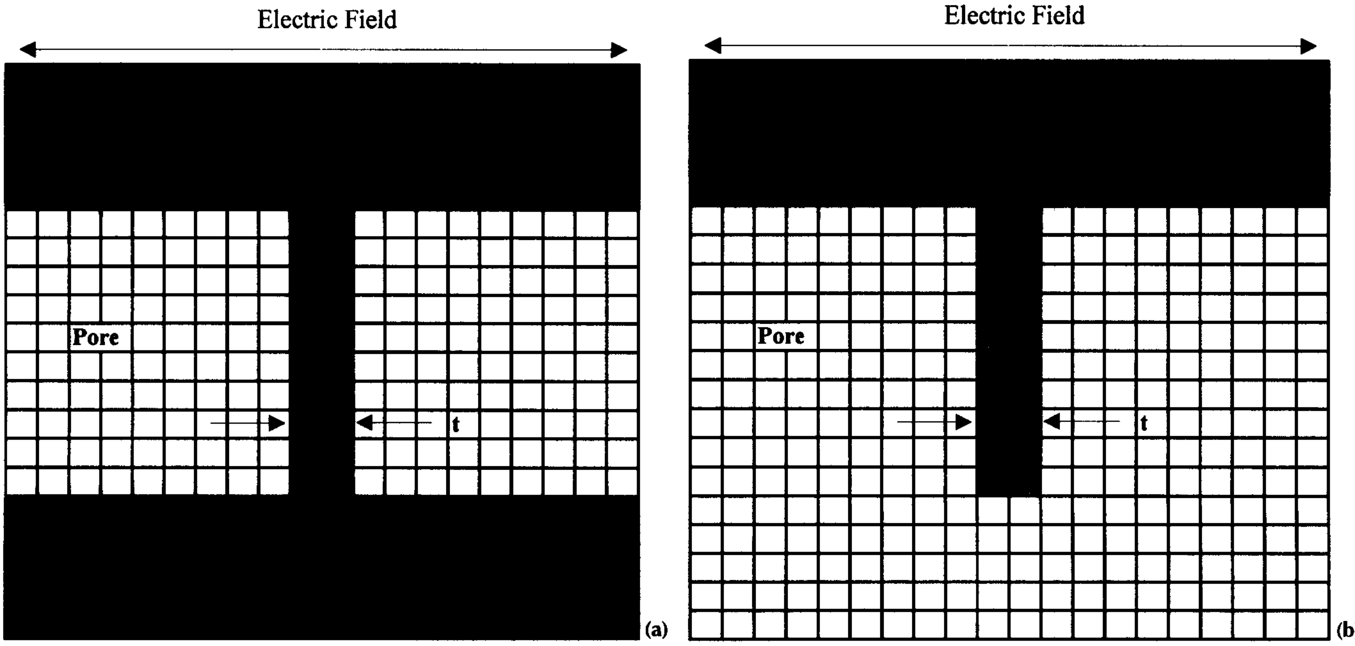

FIGURE 2. Pixel-based representation of (a) discontinuous and (b) continuous pore systems. Effective dielectric constant is large for thin C-S-H bridging layers and smaller for thick C-S-H layers.

change of young cement pastes. As in the controlled freezing studies, capillary pores become resistive when pore fluid is replaced by a low conductivity liquid, thereby eliminating them as a source of dielectric amplification. Furthermore, isopropanol (IPA) and methanol (MeOH), the liquids used in this study, have relatively low dielectric constants, 33 and 18, respectively [19]. This makes solvent exchange an ideal tool for studying dielectric amplification. Solvent exchange is also commonly used during the preparation of cement samples for mercury intrusion porosimetry and Brunauer-Emmet-Teller (BET) adsorption studies. Previously it has been used to study diffusion, drying characteristics, and pore size distributions in cement pastes [20–24]. Given the smaller size and the more polar nature of methanol versus isopropanol, it was anticipated that the range of porosity exchanged by the two solvents would be different.

Experimental

Paste specimens approximately 5 × 1.5 × 0.3-cm thick were prepared using Continental Type I ordinary portland cement (OPC). This plate-like shape was chosen to facilitate solvent exchange in a direction perpendicular to the direction of IS measurements. Steel electrodes were embedded into fresh paste for two-point IS measurements to be taken later. These electrodes extended through the entire height of the sample and were secured by the hardening of the paste itself. It is important to note that IS allows the separation of bulk and electrode effects, making this electrode placement suitable for two-point IS. Water-to-cement ratios (w/c) of 0.35 and 0.7 by weight were used. The pastes with w/c = 0.35 were hand-mixed and directly cast into pliable rubber molds on top of polystyrene sheeting. To prevent bleeding from the higher w/c pastes, these were hand-mixed in cylindrical containers and then rotated for approximately 4 h at 50 rpm prior to casting. After approximately 1 day of hydration, the samples could be separated from their molds. After demolding, the samples were rough-sanded to provide a smooth surface for solvent exchange and uniform geometrical factors for conductivity measurements. The samples were subsequently stored at 100% relative humidity during hydration; they were not immersed in water, because leaching of alkalis from the pore solution can have a significant effect on the conductivity of the paste.

Impedance scans covering 5 Hz to 13 MHz (128 individual frequencies) were made on a PC-controlled Hewlett-Packard 4192A impedance analyzer using software written in our laboratory. A commercially available software package [25] was used to fit the spectra and to derive equivalent circuit parameters. Typical spectra are shown in Figure 3 in standard Nyquist format, that is, imaginary impedance versus real impedance. These consist of a partial low-frequency electrode arc and a more complete high-frequency bulk arc. Figure 3 shows the change in the spectra during isopropanol exchange of a 1-day-old sample with w/c = 0.35.

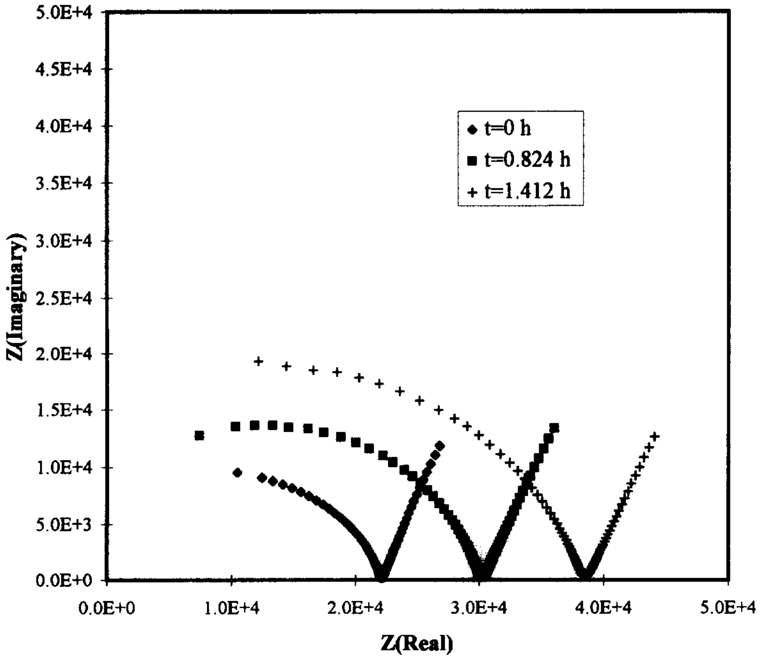

FIGURE 3. Experimental impedance spectra for 7-day-old ordinary portland cement pastes, w/c = 0.35, for different times of isopropanol exchange.

Bulk resistance of these samples is determined from the intersection of the two arcs with the real axis. From this, the conductivity σ, was calculated according to:

$$\sigma = (l/A)/R \tag{2}$$

where l is the interelectrode spacing and A is the cross-sectional area of the specimen. Capacitance (C) was approximated from:

$$C = (l/R)(2\pi\nu_{\text{top}})^{(2\theta/\pi)-1} \tag{3}$$

where ν_{top} is the frequency at the top of the arc, at which point the specimen behaves like a pure capacitor, and θ is the depression angle in degrees. OPC pastes are not pure capacitors, given the slight arc depression (see Figure 3); nevertheless, this is a reasonable approximation. Furthermore, because arc depression does not significantly change during solvent exchange, eq 3 is a reliable indicator of how effective dielectric constant changes during exchange. The effective dielectric constant was calculated from C as follows:

$$k_{\text{eff}} = Cl/\epsilon_o A \tag{4}$$

where ϵ_o is the permittivity of free space.

To correct for stray immittances associated with the cabling and sample holder, null measurements of opened (air) and short-circuited electrodes (using a brass insert) were carried out. IS spectra were subsequently corrected using the procedure given in ref 2. Occasional spectra exhibited a second bulk arc, which we associated with highly resistive layers near the electrodes. In these instances, the arc nearest the origin was taken to represent the bulk material.

Solvent exchange was accomplished by total submersion of the samples in the relevant solvent. For IS measurements, the samples were temporarily removed from the solvent bath. Spectra were obtained in a few minutes, and the samples were returned to the exchange bath. The solvent was drained and replaced at regular intervals to maintain a sufficient concentration gradient for exchange. A sealed container held the bath, sample, and electrodes at 100% vapor pressure. This prevented drying effects during the brief periods required for measurement. A schematic drawing of this setup is provided in Figure 4.

Samples used to determine weight change during exchange had the same geometries as the IS samples, but without electrodes. A number of identical samples (typically three) were measured for each experimental condition, and the results were averaged. Measurements were taken on a balance with 0.1-mg sensitivity. Before each weighing, samples were wiped with a clean, damp rag (presoaked in solvent to eliminate wicking) to remove surface liquids. Solvent baths were regularly drained and replaced (every 6 h for rapidly exchanging samples and every 24 h for slowly exchanging samples) to maintain bath composition. By accounting for the density differences of isopropanol or methanol versus water, the percentage of water exchanged was then calculated.

Volume fraction of C-S-H gel was calculated using a model developed by Jennings and Tennis [26]. This model accounts for age, w/c ratio, and cement composition in determining degree of hydration and volume fraction of reaction products.

Results and Discussion

Figure 5 shows how the effective dielectric constants and conductivities vary with time during isopropanol exchange. There is a rapid drop in both properties dur-

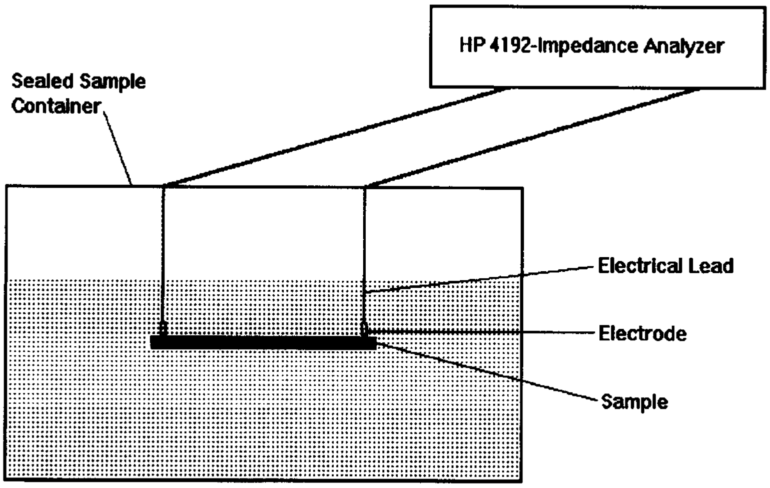

FIGURE 4. Schematic representation of sample configuration and solvent exchange apparatus.

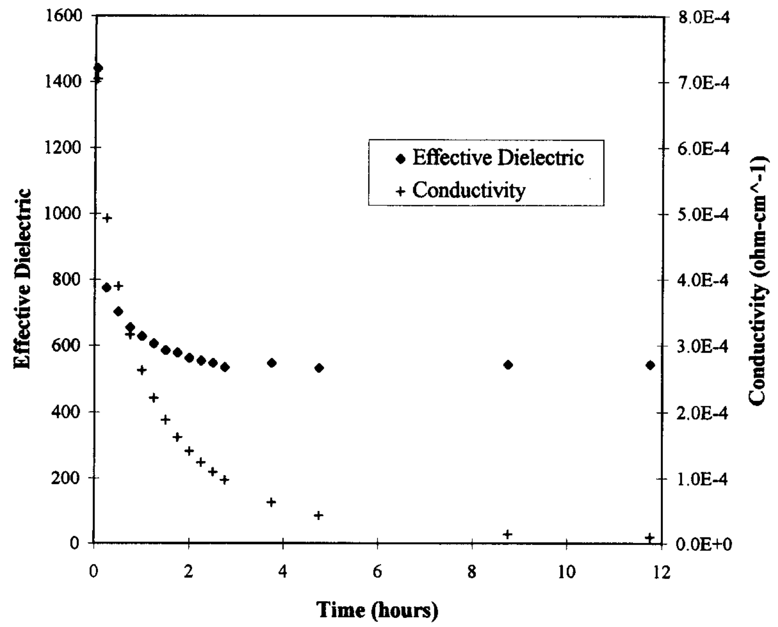

FIGURE 5. Decay of conductivity and dielectric constant during isopropanol exchange of a 1-day-old ordinary portland cement paste, w/c = 0.35.

ing the first few hours, after which the dielectric constants reach a plateau. The conductivity, in contrast, continues to decrease. It should be pointed out that the plateau value of the dielectric constant is quite high, approximately 500.

For comparison, weight change data at 1 day of hydration for the same paste of 0.35 w/c are given in Figure 6. There is a rapid rate of exchange for about the first hour, corresponding to the initial decreases in the electrical properties, followed by a more gradual process of exchange. This later exchange appears to be reflected in the conductivity but not the dielectric constant (Figure 5).

The dielectric constant data during exchange support our model of dielectric amplification. Initial large values well in excess of 10^3 fall precipitously during the first hour of exchange, when the largest, most accessible pores are being exchanged. Thereafter, the now resistive large capillary pores are eliminated as a source of dielectric amplification. The data support our contention that C-S-H gel is itself a dielectrically amplified material, shown by the relatively large dielectric constant associated with the plateau in Figure 5. For further illustration, similar exchange curves for 14- and 28-day-old pastes are plotted alongside that for the 1-day-old paste in Figure 7a. It is important to note that the magnitude of the plateau values increases with increasing time of pre-exchange hydration, a direct result of the increase of C-S-H gel in the system. Figure 7b illustrates this effect, with the plateau value of the dielectric plot-

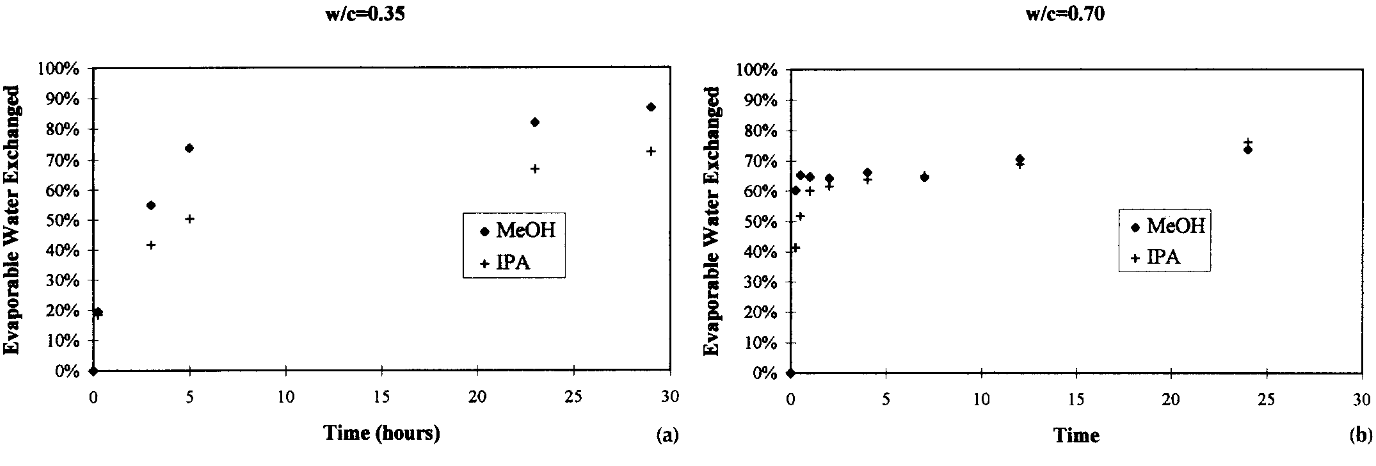

FIGURE 6. Percent of evaporable water exchanged by isopropanol (IPA) and methanol (MeOH) for a 1-day-old ordinary portland cement paste with (a) w/c = 0.35 and (b) w/c = 0.70.

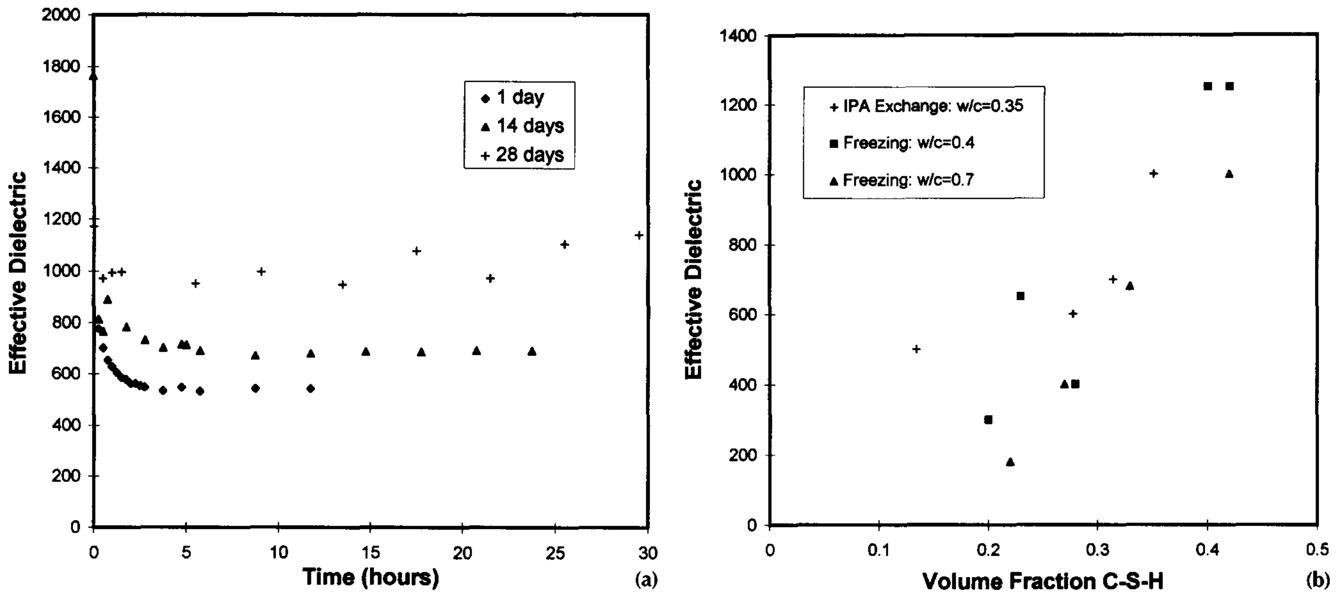

FIGURE 7. (a) Effective dielectric constant versus time of isopropanol (IPA) exchange in ordinary portland cement pastes of varying ages with w/c = 0.35. Initial values (not plotted) of effective dielectric were 9320, 1740, and 1180 for 1, 14, and 28 days, respectively. (b) Dielectric constant plotted versus volume fraction of C-S-H gel. Values were calculated after either freezing or solvent exchange had been completed.

ted versus volume fraction of C-S-H; clearly, C-S-H gel and dielectric behavior are directly related. The behavior of relative dielectric constant versus C-S-H volume fraction determined by solvent exchange also correlates well to behavior found in the controlled freezing studies, shown in Figure 7b [18]. We have speculated that the small deviation at low volume fraction is a result of the destructive nature of the freezing experiments. Also, linear extrapolation of the data in Figure 7b to 100% C-S-H yields a value for dielectric constant of approximately 3000. It is interesting to note that Coverdale et al. required a value of 3000 to fit computer simulations to experimentally measured values for paste [10–12].

A comparison of two 7-day-old OPC pastes, w/c = 0.35 and 0.70, during isopropanol exchange is shown in Figure 8. The initial value of the paste with w/c = 0.70 was nearly 6000, whereas that of the paste with w/c = 0.35 was smaller, 1500. This behavior can be predicted on the basis of the model for geometric dielectric amplification. In the paste with high w/c, there is a more open C-S-H structure and larger pores. This contributes to a higher dielectric amplification, because *D*/*d* is larger. After exchange, when pores have been made resistive, the plateau should be indicative of the volume fraction of C-S-H gel. After exchange, the low w/c paste has nearly twice the dielectric constant of the high w/c paste, consistent with a larger volume fraction of C-S-H gel in the low w/c specimen.

Figure 9 illustrates marked differences in dielectric effect during exchange of the two solvents of 1-day-old pastes at the two w/c ratios, 0.35 and 0.70. This correlates with the weight change data in Figure 6a. Isopropanol exchange at w/c = 0.35 results in a plateau value of 500–600, whereas methanol exchange results in a plateau value of nearly 100. At 5 h, there is 50% more porosity exchanged by methanol than by isopropanol. There is very little difference in behavior for the two

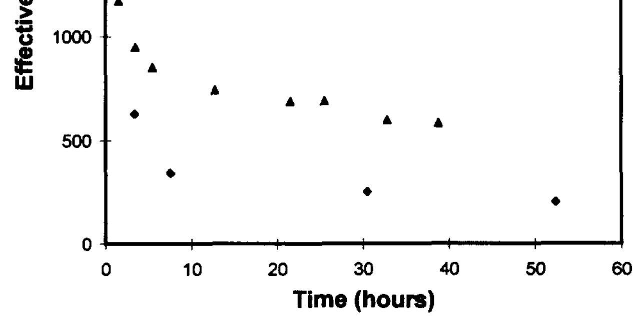

FIGURE 8. Comparison of effective dielectric constant versus isopropanol exchange time for pastes with w/c = 0.35 and 0.70. The initial values were 1500 and 6000, respectively.

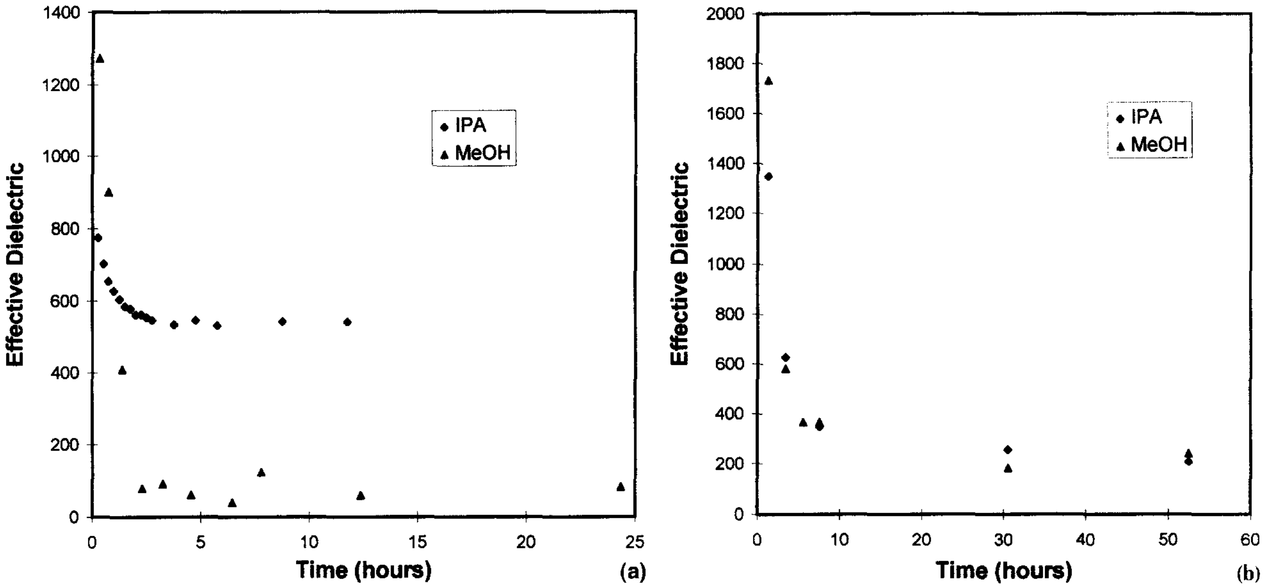

FIGURE 9. (a) Effective dielectric constant of a 1-day-old paste with w/c = 0.70 during solvent exchange. (b) Effective dielectric constant of a 1-day-old paste with w/c = 0.35 during solvent exchange. IPA = isopropanol; MeOH = methanol.

solvents at w/c = 0.7, in keeping with the weight change measurements of Figure 6b.

Behavioral differences for solvents suggest that isopropanol exchanges the large capillary pores and some fraction of the gel pores, as witnessed by the continued decline in conductivity (see Figure 5), but methanol is much more aggressive. It not only exchanges the large capillary pores responsible for dielectric amplification of paste but also the appropriate level of fine gel pores responsible for the dielectric amplification of C-S-H gel. In other words, there is a fundamental difference in microstructure between the two w/c ratios. For low w/c, there exists a microstructural element open to methanol but closed to isopropanol; for high w/c, this second microstructural element does not seem to exist. Jennings and Tennis [26] have argued for the existence of two types of C-S-H gel based upon BET surface area measurements using H_2O and N_2. Similarly, Diamond [27] has proposed that C-S-H gel consists of high-density hydrated phenograin regions and low-density groundmass regions. The present results substantiate the concept that C-S-H is not a uniform microstructure.

Conclusions

Solvent exchange studies of young OPC pastes support a mechanism of dielectric amplification based upon large capillary pores in addition to layers of C-S-H gel, which do not necessarily completely bridge the pores. Furthermore, the dielectric properties of isopropanol-exchanged pastes indicate that C-S-H gel is itself a dielectrically amplified microstructure, where gel pores and C-S-H layers account for the dielectric amplification. There appear to be two kinds of C-S-H gel formed in OPC pastes of w/c = 0.35—that which is exchangeable by both solvents (capillary porosity) and that which can be exchanged by methanol but not isopropanol (gel porosity). However, in OPC pastes of w/c = 0.70, only one type of C-S-H gel, exchangeable by both solvents, is present. The combination of IS and solvent exchange appears to be a powerful means of probing both the capillary and gel porosity in cement pastes.

Acknowledgments

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