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Electrochemical Behavior of Portland Cement Pastes Containing Phosphonates

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An impedance measurement technique was used to investigate the effects of aminotri(methylenephosphonic acid) (ATMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), and diethylenetriaminepenta(methylenephosphonic acid) (DTPMP) on the hydration process and setting behavior of portland cement pastes. It was demonstrated that the impedance and capacitive responses can be used to characterize setting behavior and microstructural development of the hydrating pastes containing these chemical admixtures.

The presence of a long induction period of up to 20 and more than 75 hours is revealed by the impedance curves of pastes containing ATMP, HEDP, and DTPMP at dosages of 0.05% and 0.2%, respectively. This confirms that phosphonates are efficient retarders. These compounds appear to have strong chelating or complexing capability, potentially poisoning CH and C-S-H nucleation. Stabilization of the C-S-H (metastable) film on the surface of cement grains appears to cause retarding effect. ADVANCED CEMENT BASED MATERIALS 1995, 2, 182–188

KEY WORDS: Cement hydration, Impedance behavior, Phosphonates, Super-retarders

Retarders such as sugars, casein, dextrin, glycerol, carboxymethyl cellulose, and tartaric acid are commonly used in concrete practice. Typical applications of retarders in concrete include transport and handling in hot climates, amelioration of long-term strength reduction of steam-cured concrete, and waste reduction and recycling of concrete from ready-mixed trucks. The super-retarding effect of phosphonate compounds, for example, aminotri-(methylenephosphonic acid) (ATMP), 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) and diethylenetriaminepenta-(methylenephosphonic acid) (DTPMP), on ordinary portland cement (OPC) and its constituents was first reported by Ramachandran et al. [1–3]. The phosphonate compounds appeared to be much more efficient retarders than many others. The induction period determined by conduction colorimetry [1] increases from 3 to 21 hours and the time of maximum heat development increases from 12 to 42 hours at 0.03 to 0.05% concentration (Table 1). Very few papers are available on studies related to the retardation effect of phosphonates on cement hydration [1–3].

Electrical conductivity and AC impedance methods have been used in investigations of cement paste hydration [4–16]. These methods are simple and quick. They provide useful information related to both microstructural changes and hydration processes. In this study, the electrochemical AC impedance method was applied to investigate early hydration and setting behavior of OPC paste containing phosphonates. Scanning electron microscopy (SEM) techniques were also used to supplement information obtained from impedance measurements.

Experimental Procedure

Type 10 OPC (similar to ASTM type I) was used. The chemical composition (wt%) was as follows: SiO_2 = 19.83; CaO = 61.21; Fe_2O_3 = 3.20; Al_2O_3 = 4.18; MgO = 4.09; SO_3 = 3.93; Na_2O = 0.45; and K_2O = 0.82. The phosphonate compounds were supplied by Monsanto Chemical Co., St. Louis, Missouri. The chemical nomenclature, abbreviations, and molecular structures of the phosphonates used in this study are shown in Figure 1.

The fresh OPC pastes were mixed at a water: cement ratio of 0.35 and cast into a 25.4 × 25.4 × 25.4 mm electrical cell. Stainless steel parallel electrodes with surface area of 6.45 cm^2 were used. The geometric cell constant was calculated to be 16.4 ohm · cm^{-1}. An SI 1260 impedance gain-phase analyzer from Schlum-

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TABLE 1. Comparison of the retarding effect of phosphonates in a cement paste

Compounds	Induction Period (hours)	Time of Maximum Heat Development (hours)
Reference	2.2	8.0
HEDP		
(0.03–0.05%)	3.4–10.1	12.0–30.0
ATMP		
(0.03–0.05%)	3.8–13.2	12.0–26.0
DTPMP		
(0.03–0.05%)	3.5–21.1	12.0–42.0

Data from ref. 1.

berger Technologies and a 706 scanner from Keithley Instruments were used. Impedance responses were recorded at frequencies of 1 MHz and 100, 10, and 1 kHz. These frequencies were selected to cover a wide frequency range suitable for the acquisition of impedance-hydration time data. Measurements of overall impedance (Z) and capacitance (C) were automatically recorded by the SI 1260 impedance gain-phase analyzer over a 75-hour period. SEM micrographs were obtained using a Cambridge Stereoscan S250. The specimens prepared for SEM examination were hydrated for 75 hours. Cold acetone was used to stop hydration at different intervals. Specimens were stored at −10°C to minimize further hydration.

Results and Discussion

The impedance of the cement paste has been shown to be an inverse function of porosity, mean pore size, and ionic concentration of the pore solution. The capacitive response represents the solid-liquid interface capacitance at the test frequency [14–16]. Microstructural development in hydrating cement paste is accompanied by consumption of free water and precipitation of hy-

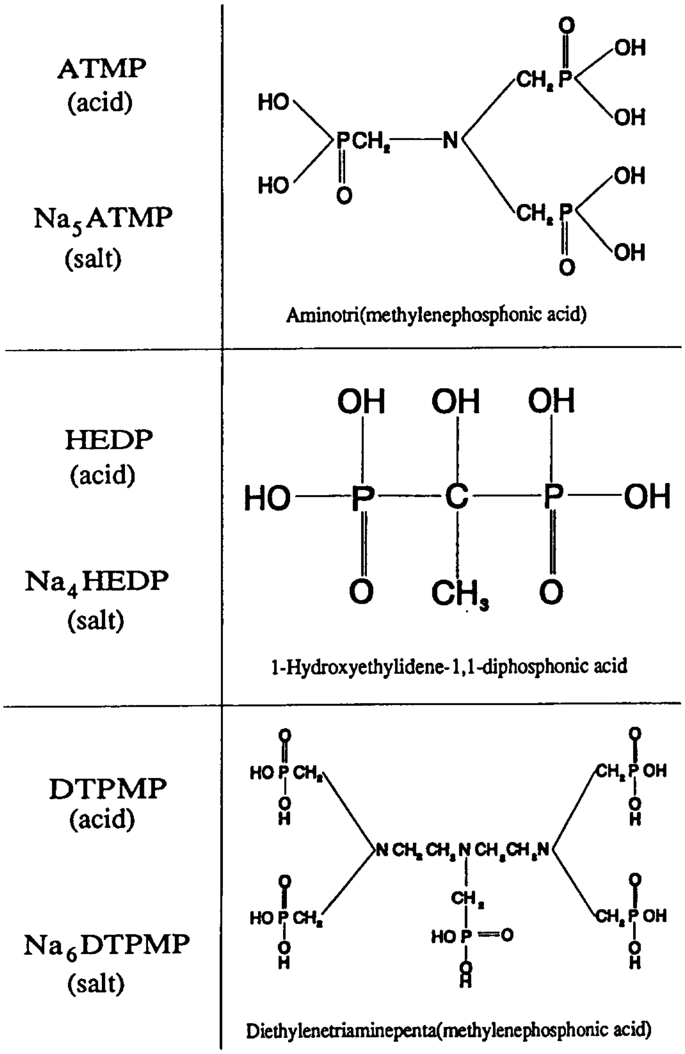

FIGURE 1. The chemical nomenclature, abbreviations, and molecular structures of the phosphonates.

dration products. This process gives rise to a denser paste that results in an increase of bulk paste impedance and a decrease of the overall solid-liquid interface capacitance. An increase of ion concentration in the pore solution leads to a decrease in paste impedance and an increase in capacitive response due to the increase in charge density per unit interface.

Hydration Behavior Characterized by Impedance Response

OPC PASTE SYSTEM: The impedance response of OPC paste is given in Figure 2. The numbers 1–4 correspond to the recording frequences 1, 10, and 100 kHz and 1 MHz, respectively. The impedance response increases with time at various rates. Three regions are distinguished in the impedance versus hydration time curve (Figure 2) representing different stages of setting and hydration behavior in the OPC system:

I. The matrix impedance is relatively constant up to approximately 3 hours, then it increases with hydration time.
II. The matrix impedance increases significantly at hydration times greater than 3 hours and reaches a maximum rate of increase, (dZ/dt) at about 28 hours.
III. The matrix impedance increases with the hydration time at a relatively small rate beyond 42 hours.

The hydration of OPC in the first few minutes mainly involves initial dissolution of CaO, $CaSO_4$, K_2O, Na_2O, SiO_2, and aluminates and iron. This is followed by the formation of a layer of metastable C-S-H(m), a high Ca:Si ratio product (normally 3) on the dissolving cement grain surface [17,18]. The average thickness of this C-S-H(m) film is usually not more than a few nanometers. It is well bonded to the substrate and inhibits further C_3S and C_2S dissolution and the diffusion of water across the film. The hydration reaction then enters a slow diffusion controlled stage referred to as the induction period. Because there is neither significant dissolution of solid phase nor precipitation in the liquid phase during this period, the ionic concentration of the liquid phase remains relatively constant resulting in approximately constant values of the matrix impedance.

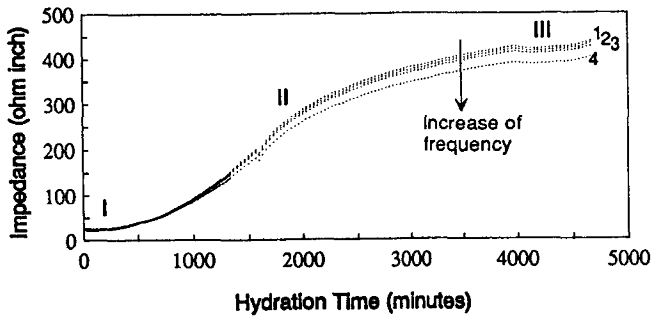

FIGURE 2. Impedance response versus hydration time for ordinary portland cement paste. The numbers 1–4 correspond to the recorded frequencies 1, 10, and 100 kHz and 1 mHz, respectively. Roman numerals I–III are explained in text.

The rapid increase of impedance after the induction period corresponds to the hydration process consisting of conversion of C-S-H (high Ca:Si ratio) to C-S-H (low Ca:Si ratio, normally 0.8–1.5) [18], which autocatalyzes the reactions of the anhydrous compounds with water and results in formation of C-S-H, calcium hydroxide, ettringite, and other minor phases. These reactions consume free water in the cement paste and promote microstructural development and setting. At advanced ages, for example, the end of acceleratory period, the hydration mechanism may change from through-solution to solid state when most of the free water has been consumed. The reactions would then take place directly on the surface of anhydrous reactants, and ionic mobility in the solution would become restricted. The impedance then seems to reach a relatively constant value dependent on the microstructural character of the hydrating paste.

PASTES CONTAINING 0.05% (BY WEIGHT) PHOSPHONATES. The impedance behavior for OPC pastes containing 0.05% (by weight of cement) ATMP, HEDP, and DTPMP is illustrated in Figure 3a–c. The numbers 1–4 correspond to the recorded frequencies of 1, 10, and 100 kHz and 1 MHz, respectively. Figure 4 shows the plot of the impedance increase rate (dZ/dt) versus hydration time at 100 kHz. The impedance-hydration time curves for pastes containing phosphonates are significantly different from that for the pure OPC paste. Differences are the following: (1) a longer induction period of more than 16 hours; (2) a smaller rate of impedance increase, dZ/dt, in the second region; and (3) no clear indication of the third stage (relatively constant values of impedance) as observed for the pure OPC paste. It is apparent from the impedance curves that even a small percent of phosphonate (0.05%) has a significant retardation effect on OPC paste hydration. From Figure 4, it is clear that OPC paste has the highest rate, that is, $dZ/dt = 7.3$ ohm/min at $5 = 28.5$ hours, whereas for phosphonates, $dZ/dt = 3.4–3.7$ ohm/min at $t = 36–41$ hours.

The impedance-hydration time curves show much larger impedance values at the very early hydration times (region I) for those pastes containing phosphonates. These large readings are only observed at relatively low frequencies, 1 kHz and 10 kHz (much less). This behavior is not observed as frequency increases.

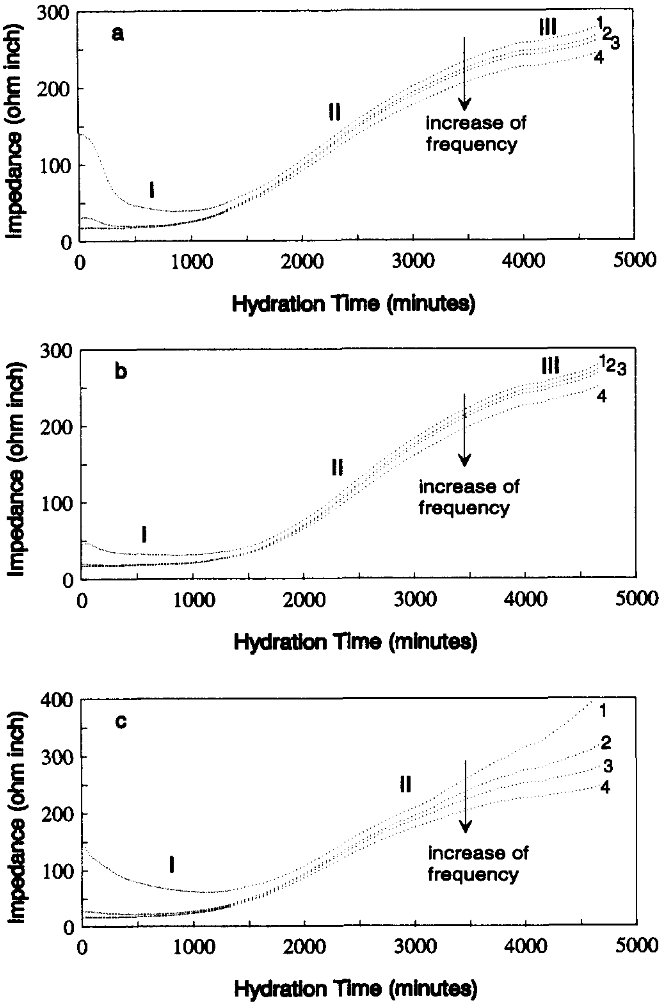

FIGURE 3. Impedance response versus hydration time for pastes containing 0.05% (by weight) phosphonates: (a) ATMP, (b) HEDP, and (c) DTPMP. The numbers 1–4 correspond to the recorded frequencies 1, 10, and 100 kHz and 1 MHz, respectively.

The difference of impedance recorded at high frequencies (1 MHz or 100 kHz) and low frequency (1 kHz) may be a result of surface adsorption phenomena.

PASTES CONTAINING 0.2% (BY WEIGHT) PHOSPHONATES. The impedance behavior of OPC pastes containing 0.2% (by weight) ATMP, HEDP, and DTPMP was studied. Stronger retardation is obtained with a higher dosage of phosphonates as indicated in Figure 5a–c. The numbers 1–3 in the figure correspond to the recorded frequencies of 1, 10, and 100 kHz, respectively. Data recorded at 1 MHz coincide with those at 100 kHz. The impedance values of all three pastes remained constant within the time period (more than 75 hours). The curve recorded at 1 kHz, however, decreased at early hydration times for the paste systems containing ATMP and HEDP. None of these pastes had set at 75 hours hydration time as indicated by Vicat tests. SEM examination of these unset pastes (Figure 6a–c) revealed that only very few isolated crystals appeared on the surface of the unhydrated cement particles (compared to OPC pastes at 10-minute and 2-hour hydration shown in Figure 6d and e). The energy dispersive X-ray analysis (EDXA) failed to identify the composition of crystals due to strong influences of the substrate (unhydrated cement). One possible argument to explain the super-retarding effect appears to be the strong chelating or complexing capability of the phosphonate compounds resulting in poisoning of CH and C-S-H nucleation and stabilization of the C-S-H(m) film during OPC hydration [1]. The complexes may also form at early ages with the aluminate phases.

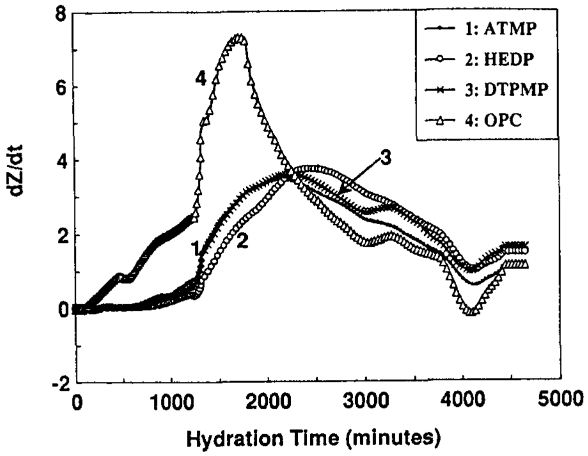

FIGURE 4. Plot of the impedance increase rate versus hydration time at a frequency of 100 kHz for paste and pastes containing 0.05% (by weight) phosphonates.

Setting Behavior and Capacitive Response

The capacitance curves recorded at a frequency of 1 KHz for the pure OPC paste and pastes containing 0.05% phosphonates are given in Figure 7. A peak at approximately 2 hours hydration is clearly observed for the pure OPC paste. Similar peaks were also observed in the pastes containing 0.05% phosphonate but at much longer hydration times. The times corresponding to the maximum in the capacitance curves are approximately 10, 7, and 12 hours for pastes containing 0.05% ATMP, HEDP, and DTPMP, respectively. Beyond the maximum point, the capacitance decreases rapidly (except in the paste containing 0.05% HEDP for which a shoulder was observed). The decrease of matrix capacitive response with hydration time usually corresponds to an increase of matrix impedance due to the setting of the paste (Figures 2 and

3a–c). The development of microstructure results in formation of an increased amount of C-S-H and other hydration products [18]. This is generally accompanied by an increase in internal surface area and leads to a lower value of charge density per unit solid-liquid interface. It appears that the rapid decline of capacitance is a descriptor of the onset of the setting process of a hydrating cement paste. The observed trend of capacitance decrease is similar to that reported by McCarter [6,19,20], who characterized the hydrating OPC paste system by means of dielectric property measurement.

The capacitance behavior is also significantly affected by the concentration of phosphonates. A plot of capacitance versus hydration time for pastes containing 0.2% phosphonate is given in Figure 8. The capacitance of the pastes containing phosphonate increases with early hydration time (ATMP, HEDP) and then remains at the maximum value for more than 75 hours. This indicates that the pastes had not set.

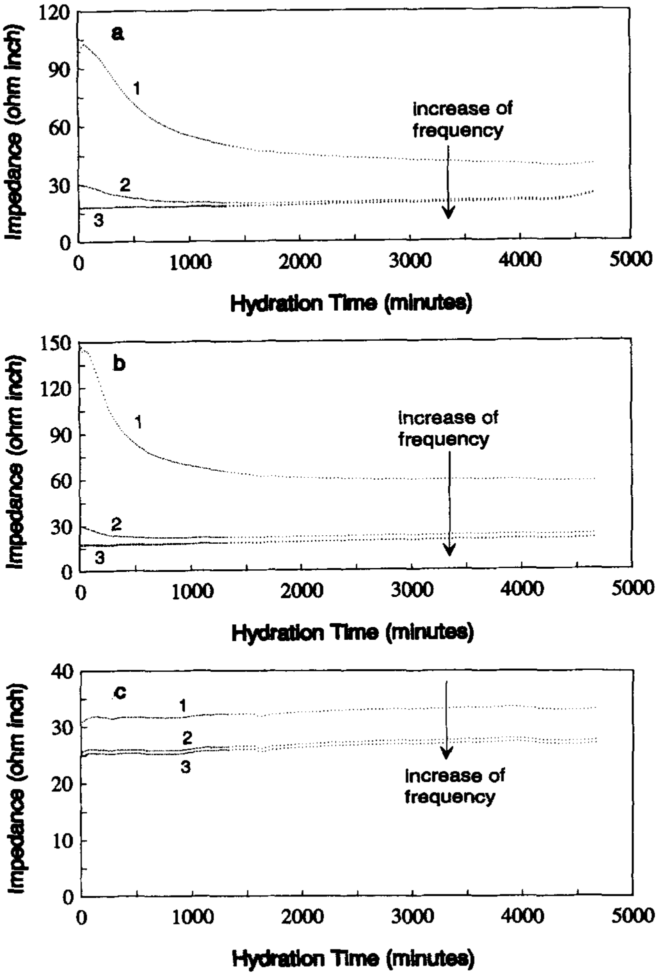

FIGURE 5. Impedance response versus hydration time for pastes containing 0.2% (by weight) phosphonates: (a) ATMP, (b) HEDP, and (c) DTPMP. The numbers 1–3 correspond to the recorded frequencies 1, 10, and 100 kHz and 1 MHz, respectively.

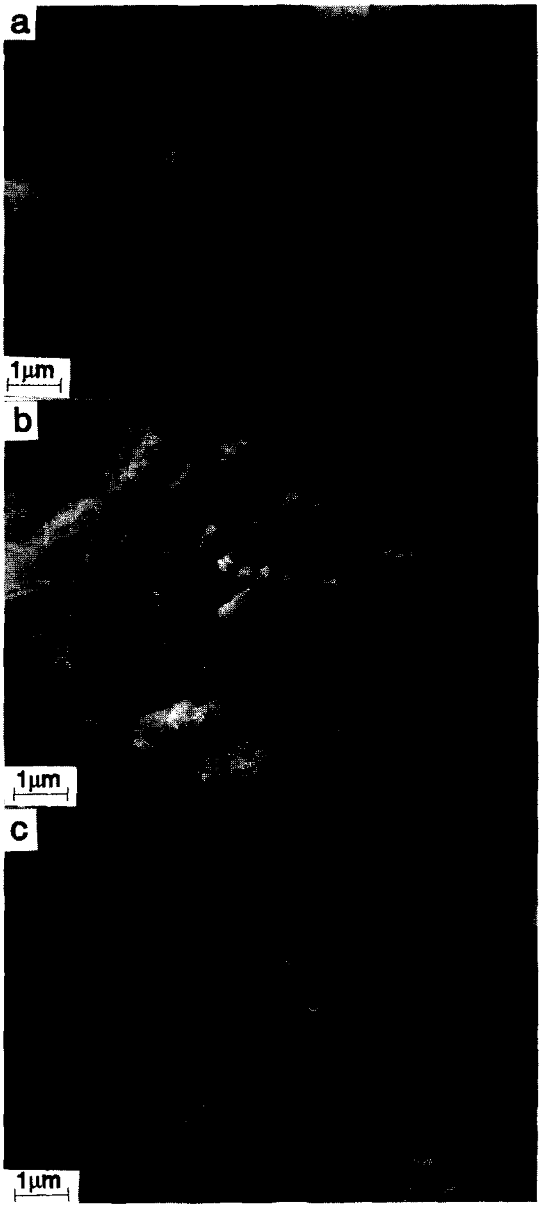

FIGURE 6. Scanning electron microscopy micrographs for paste and pastes containing 0.2% (by weight) phosphonates at a hydration time of (a) ATMP, 75 hours; (b) HEDP, 75 hours; (c) DTPMP, 75 hours; (d) OPC, 10 minutes; and (e) OPC, 2 hours.

The retarding effect of phosphonates in the hydration of cement paste may be partially attributed to the formation of a complex layer incorporating calcium ions on the surface of unhydrated cement particles. It appears to stabilize the very early hydration product, C-S-H(m), inhibiting further hydration reactions. Poisoning of nucleation processes associated with CH and C-S-H phases may occur. The retarding effect is prob-

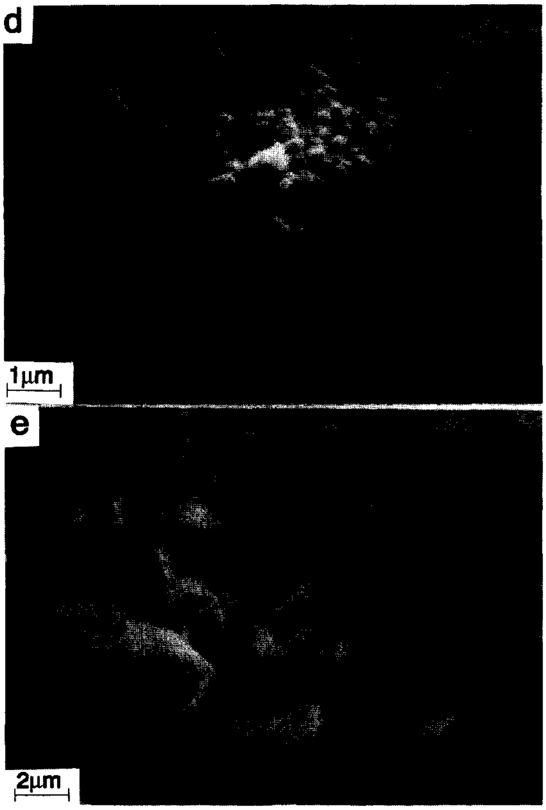

FIGURE 6. Continued

ably related to the chelating capability of the phosphonates. Strength of the chelating effect appears to be related to the efficiency of retardation.

Conclusions

Impedance and capacitive response of cement paste are dependent on ionic concentration changes in the liquid phase and the microstructural development of the hydrating systems. The impedance method appears to be a quick method of characterizing hydration effects attributed to chemical additives in cement and concrete systems.

The impedance behavior of pastes containing phosphonates, specifically ATMP, HEDP, and DTPMP, reflects the presence of a long induction period of up to 20 and more than 75 hours for dosages of 0.05% and 0.2%, respectively. These compounds appear to have strong chelating or complexing capability.

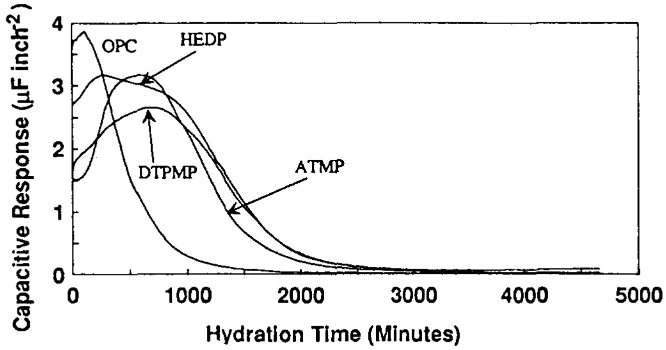

FIGURE 7. Capacitive response versus hydration time recorded at a frequency 1 kHz for pure OPC paste and pastes containing 0.05% phosphonates.

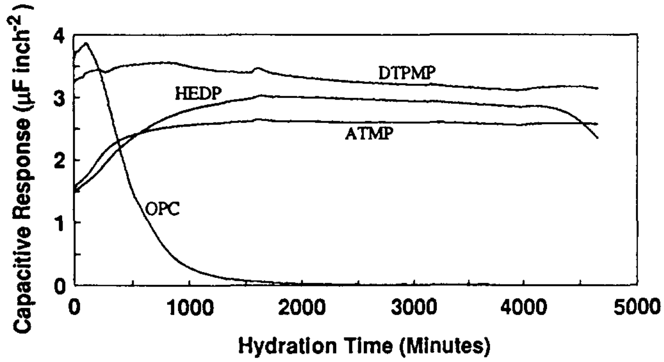

FIGURE 8. Capacitive response versus hydration time recorded at a frequency 1 kHz for pure OPC paste and pastes containing 0.2% phosphonates.

Acknowledgments

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