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UTILIZATION OF IMPEDANCE SPECTROSCOPY FOR STUDYING THE RETARDING EFFECT OF A SUPERPLASTICIZER ON THE SETTING OF CEMENT

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ABSTRACT

The electrical resistivity and conductivity of cement pastes with different dosages of a superplasticizer have been determined using impedance spectroscopy. The evolution of these parameters during the first 24 h after mixing indicates that the incorporation of the superplasticizer leads to a retardation of the setting process, the significance of which increases with the dosage. It appears that the incorporation of the superplasticizer extends the dormant stage of hydration and delays the onset of the accelerating stage, without affecting its rate. Comparisons are made with penetration measurements with the Vicat apparatus. © *1998 Elsevier Science Ltd*

Introduction

Electrical impedance (*Z*) is the resistance offered by a material to the flow of current through it. Under a sinusoidally alternating electric field, which is not in phase with the current flow, impedance is defined as a complex quantity (described by real and imaginary components, resistance *R* and reactance *X*, respectively) and is a function of the frequency of the applied field. The resistance can be related to the inherent electrical resistivity (ρ) of the material as: $R = \rho\, C_c$, where C_c is the cell constant, which depends on the geometry of the conducting body; ρ is measured in Ωm. Similarly, the real component of the admittance, which is the inverse of the impedance, can be related to the material conductivity (σ), the inverse of resistivity.

Impedance spectroscopy (IS) has recently led to promising applications in the study of cement pastes (see reviews in references 1–3). In IS, measurements are made over a range of frequencies and usually presented in a Nyquist plot, showing the imaginary versus real components of the impedance, which generally takes the form of two complete or partial semi-circular arcs. The low-frequency arc is dominated by the polarization resistance of the electrodes, and the high-frequency arc by the behavior of the bulk material, though mea-

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surements at very high frequencies (MHz range) can be affected by stray capacitive/inductive effects (2,4). It has been shown that the most reliable parameter that can be obtained from IS is the bulk resistivity of the material (ρ_β), which is found at the intersection of the two arcs where the imaginary component is practically zero (2,4,5). The cutoff frequency, at which the intersection occurs, depends on the composition of the cement paste and decreases with hydration time (2,4,6). For fresh cement paste, McCarter (7) found ρ_β to be about 0.1 Ωm (for water-cement ratios of 0.3–0.6), and Christensen et al. (2,6) observed that it increases with time.

In wet pastes, the high-frequency (bulk) arc is very small (2). Therefore, the imaginary component of the impedance is negligible for frequencies higher than the cutoff frequency (7), implying that single frequency impedance measurements at those frequencies can yield good approximations of the bulk resistivity of young cement pastes. Early studies of paste resistivity were, however, performed at low frequencies (see review in references 3). One such work was that of Calleja (8), who used the evolution of the resistance at 1 kHz as a less empirical alternative to the Vicat test for studying the setting of cement pastes. He found a close relationship between the evolutions of the resistance and temperature of the paste with time.

Since the 1980s, further work on electrical resistivity has studied its relationship with various aspects of cement paste behavior, and the influence of cement composition and admixtures (3). Whittington et al. (9) observed that the resistivity of cement paste was initially independent of the water-cement ratio (in the range of 0.4–0.6) but became inversely proportional to it after hardening, as confirmed by Christensen et al. (6). Tamás (10) obtained conductograms, giving the evolution of the electrical conductivity with time, for cement pastes during hydration, and showed that the conductivity initially increases, reaches a maximum after 1–3 h, and later decreases. It was concluded that the decrease in conductivity with time is a result of the decrease in the number and/or the mobility of ions in the paste. It was also seen that the addition of a retarder (citric acid) led to a lower maximum conductivity and a flatter evolution with time. Tamàs et al. (11) studied the variability of the conductograms and observed that their shapes, including the occurrence of the maximum, were fully reproducible and concluded that the scatter in the conductivity data was within ± 20% of the observed value.

Some studies have focused on establishing the fundamental relations between the evolution of the resistivity of cement paste and the hydration processes. Perez-Pena et al. (12), in a comparative study of the evolution of the heat of hydration and conductivity, determined that the maximum conductivity reached at about 1 h coincided with the dormant (athermic) stage of hydration seen after a rapid decrease in the heat of hydration and where there is no further dissolution of ions due to the supersaturation of the solution. They concluded that the subsequent decrease in conductivity coincided with the accelerating stage, reflected as a rapid increase in the heat of hydration with time, where there is a decrease in the mobility of the Ca^{2+}, OH^- and SO_4^{2-} ions due to their incorporation in the hydration products (precipitation reactions). The last part of the curve was associated with the end of the high rate of heat development.

In this work, preliminary results of an IS-based study of the setting of cement pastes are presented. Impedance measurements of pastes with different superplasticizer contents are used to determine the evolutions of the bulk resistivity and conductivity for studying the retardation of the setting due to the incorporation of the admixture. This phenomenon is of practical importance because most concretes, especially high-performance concretes, are

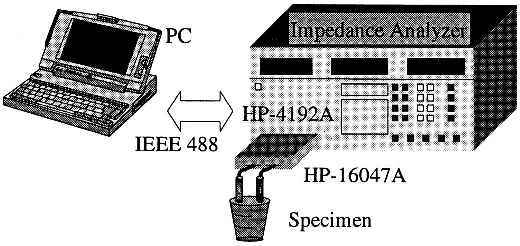

FIG. 1.
Configuration of test setup.

produced with superplasticizers to obtain high workability at low water-cement ratios. Excessive retardation of the setting can lead to delays in the removal of formwork and load application, resulting in higher project costs. The advantage of the methodology used here is that it is non-destructive, relatively simple and easy to interpret. The results are contrasted with data from the conventional Vicat penetration test.

Impedance Measurement Technique

In the design of the test setup for the impedance measurements, there are several aspects that should be considered carefully, such as the choice of the specimen geometry and the electrodes. In the present study, these choices are made with the objective of keeping the methodology simple, and an experimental calibration is used to account for their effects. The electrodes were two stainless steel threaded rods of 2.8 mm diameter, embedded 9 mm apart (center-to-center) in the cement paste. This configuration avoids the loss of contact that can occur between the hardening paste and external electrodes (11). The paste was placed in a thin-walled plastic container, with the shape of a truncated cone (bottom diameter = 45 mm, top diameter = 56 mm, height = 60 mm), and the electrodes were mounted at the center of its lid and embedded 35 mm deep in the paste. Note that the technique is valid for containers of any shape, as long as a representative volume of the paste surrounds the electrodes. Similarly, the form of the electrodes does not have to be the same as that used here.

The equipment used for the measurements was an HP 4192A impedance analyzer interfaced to a computer through an IEEE 488 bus (Fig. 1). Two 1-μF plastic capacitors were placed between the electrodes and the analyzer to eliminate any dc bias voltage, and short cables were used to minimize inductive effects. The effects of the capacitors and cables can be corrected through established procedures (13). Moreover, their effects on the real component of the impedance, which is used for determining ρ_β, are negligible. The measurements were made with a 0.3 V excitation voltage and registered at about every 6 min., beginning 10 min. after mixing, using software based on LabWindows CVI. The range of frequencies used in the IS was 1 kHz to 1 MHz, with 3 samples in each decade.

Since the specimen and electrode configuration are such that analytical solutions for the cell constant (C_c), which relates the resistivity to the resistance, cannot be easily formulated, it is determined experimentally. A container identical to that used for the pastes is filled with a saline solution (154 mmol/liter of NaCl) of known resistivity (0.58 Ωm at 20°C), which is

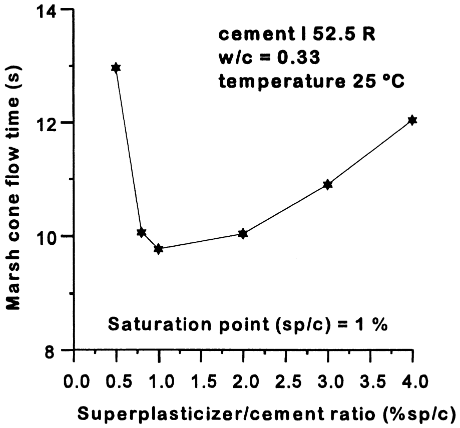

FIG. 2.
Flow time curve used in the selection of the superplasticizer dosages.

in the same order of magnitude as that of the wet cement paste. As the imaginary component of the impedance for this solution is negligible over a wide range of frequencies (14), the cell constant can be calculated directly from its impedance. Prior to the calibration of the cell constant, the correction due to the capacitors and cables was determined by short circuiting the cables. Further details of the technique can be found in reference 15.

Materials Studied

Cement of type CEM I 52.5 R, sulphonated naphthalene formaldehyde condensate superplasticizer (solid content = 35%, pH = 6.5–8.5), and tap water were used in the study. A water-cement ratio (w/c) of 0.33, and superplasticizer/cement (sp/c) dosages of 0, 0.5, 1, and 4% (by weight, with respect to the solid content) were considered. The tests were conducted at a temperature of about 20°C.

The pastes were prepared in a 5-liter planetary blender with two velocities, 60 rpm (low) and 120 rpm (high), with the following sequence: cement and water in the ratio of w/c = 0.245 were first mixed at low speed for 2 min., then the superplasticizer and the rest of water necessary to obtain the w/c = 0.33 were added, and the paste mixed 30 s at low speed and 2.5 min. at high speed.

The superplasticizer dosages used in the study were chosen based on results of Marsh Cone tests described in reference 16. The flow times obtained for different dosages are plotted in Figure 2. It can be seen that beyond the saturation dosage of about 1%, the fluidity of the paste does not increase appreciably. This led to the choice of 0.5, 1, and 4% as the dosages to be studied, with two normal values and another excessively high, in addition to the plain paste.

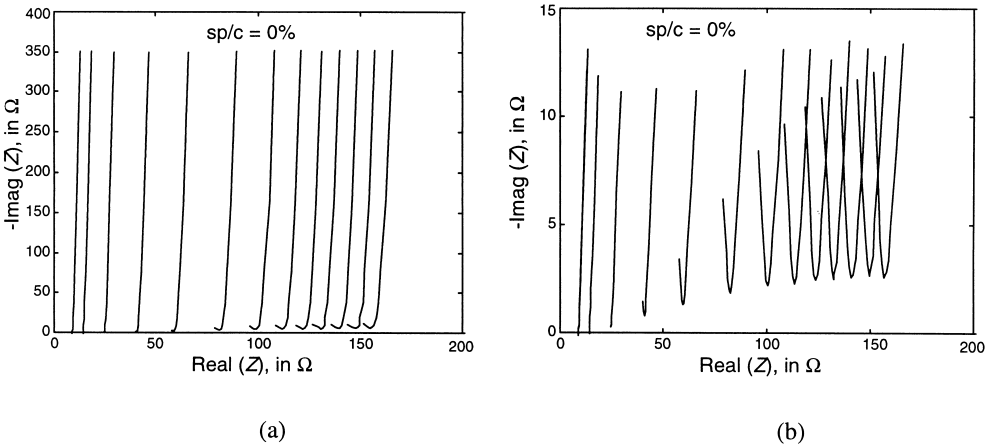

FIG. 3.
Data from impedance spectroscopy of the plain cement paste (sp/c = 0%), (*a*) before correcting for the effects of the capacitors and the cables, and (*b*) after correction (Nyquist plots).

Results and Discussion

Data from the IS are shown in Figure 3a for the plain cement paste (sp/c = 0%), sampled every 2 h, during approximately 24 h. Each curve gives the low frequency part of the bulk arc and the high frequency part of the electrode arc, and more importantly, the intersection between them, implying that the cutoff frequency is always within the frequency range. As time progresses, the plots shift to the right with an increase in resistivity due to hydration. These curves were corrected for the effects of the capacitors and cables, resulting in the Nyquist plots of Figure 3b, from which ρ_β can be determined as a function of time. Note that the plots are not drawn in the conventional manner, with the same scale on both axes, because the response of interest is at the cutoff frequency. The corrected curves for the paste with sp/c = 4% are shown in Figure 4, where the plots are initially much closer to each other than in the neat paste, indicating that the electrical properties do not change appreciably with time. However, later plots are spaced further apart, implying that the rate of change in the impedance is higher over this period than for the neat paste. The trends for the pastes with sp/c = 0.5 and 1% lie between the two extremes. It was observed that the impedance cutoff frequency decreased with time, beginning with values in the MHz range and decreasing to about 20–50 kHz at 24 h, confirming the conclusions of Christensen et al. (2)

The trends obtained for ρ_β as functions of time are shown in Figure 5 for all the pastes studied here. It can be seen that all the curves increase monotonically, from about 0.2 Ωm at about 1 h (which is comparable to the values obtained by McCarter, 1994) to a range of 3.4–4.2 Ωm at about 1 day. The evolutions of the inverse of ρ_β, the bulk conductivity σ_β, are shown in Figure 6 in the form of conductograms, which are more indicative of the retardation of the setting of the cement paste. It can be seen that the drop in σ_β after the peak is delayed with the addition of the superplasticizer and that this delay increases with the sp/c dosage. Such trends were also observed by Tamás (10) in pastes with a set retarder (citric

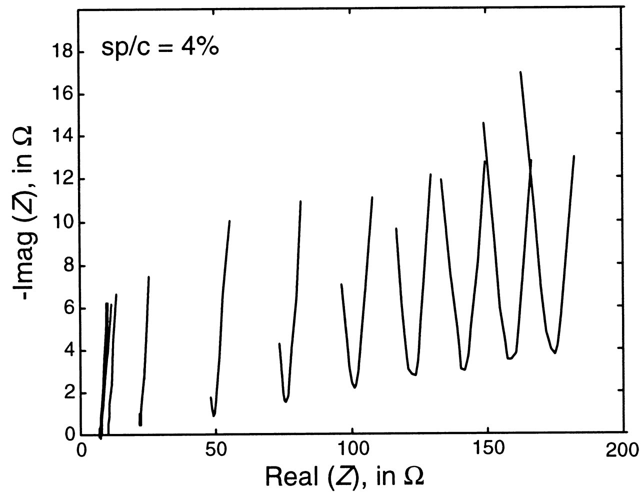

FIG. 4.
Nyquist plots for the cement paste with sp/c = 4%.

acid), along with a decrease in the peak conductivity that is not seen here. It appears that, for the dosages used, the incorporation of the superplasticizer does not influence the maximum value of σ_β. According to the explanations given by Perez-Pena et al. (12), these trends indicate that the addition of the superplasticizer extends the dormant stage of the hydration process, retarding the onset of the accelerating stage.

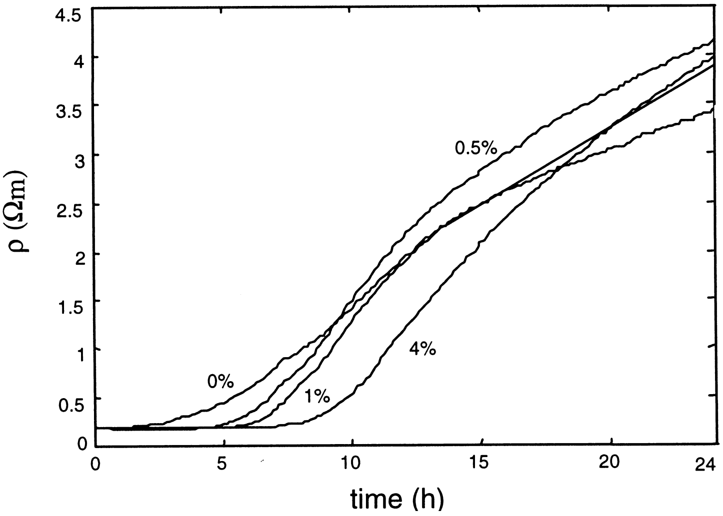

FIG. 5.
Evolution of the resistivity for different sp/c.

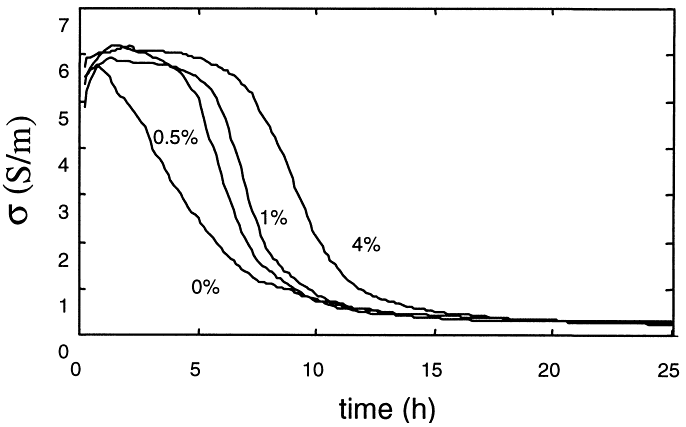

FIG. 6.
Evolution of conductivity for different sp/c.

As proposed by Calleja (8), conductivity measurements can be used to quantify the retardation of the setting of cement paste. Supposing that the beginning and the end of the setting can be taken, respectively, as the time at which σ_β has decreased by 20% and 80%, relative to the peak value, the data in Table 1 are obtained. It can be seen that the retardation effect is well reflected by the results.

In order to compare the data with conventional penetration measurements made with the Vicat apparatus, tests were performed on identical pastes using a needle with a diameter of 1.13 mm and a probe weight of 300 g (17). Initially, as the paste has a very high fluidity, the needle penetrates completely and reaches the base of the mold. As setting occurs, the resistance against penetration increases, leading to incomplete penetration and ultimately no penetration at all. The time of the first reading when there is no complete penetration (i.e., the needle does not reach the base) was taken as the beginning of setting. The time of the first reading when there is zero penetration (i.e., the needle does not penetrate the surface) was

TABLE 1
Beginning and end of setting defined in terms of conductivity and vicat penetration tests.

sp/c content (%)	From conductivity measurements (h)		From Vicat penetration measurements (h)	
	Beginning	End	Beginning	End
0.0	2.5	7.9	1.9	3.5
0.5	5.1	8.5	5.0	6.8
1.0	6.1	9.3	6.5	8.3
4.0	7.7	11.4	7.2	9.3

taken as the end of setting. Note that these times are not the standard initial and final setting times of pastes with normal consistency. The results obtained are given in Table 1. It can be observed that beginning of setting compares well with that obtained from the conductograms. However, the end of setting is much earlier, indicating that the conductivity measurements reflect the end of the accelerating stage better, as suggested by the studies of Perez-Pena et al. (12), and Jiang and Roy (18).

In terms of the mechanisms of the superplasticizer action, the results imply that the concentration of ions in the aqueous solution of the cement paste is not significantly modified during the dormant stage. Also, the trends appear to support the theories of the formation of an adsorption layer on the cement particle (hindering the diffusion of water and calcium ions) and complexes with Ca^{2+} (retarding the supersaturation of the solution and precipitation reactions) due to the superplasticizer that delay the hydration of the cement paste (5,19–21).

Conclusions

A simple method has been designed and implemented for quantifying the electrical resistivity and conductivity of fresh cement pastes through impedance spectroscopy. The retardation of the setting of cement paste due to the incorporation of a superplasticizer has been studied during the first 24 h using this technique. It appears that the retardation is due to a prolongation of the dormant stage of the hydration process, which delays the onset of the accelerating stage. Comparisons with results from the Vicat penetration test indicate that the conductivity measurements characterize the end of setting better.

Acknowledgments

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