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Electromagnetic properties of mortars over a broad frequency range and different curing times

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A large dielectric measurement cell, with 54 ml sample volume, was designed and calibrated to operate over a 1 MHz–3 GHz frequency range. The cell was used to measure the dielectric constants and conductivities of concretes over a broad frequency range and different curing times. The water/cement/sand ratios of the concrete were changed to study the dependence of the electromagnetic properties on them. Chemical admixtures to retard and accelerate the curing process of concretes were also added. It was found that the electromagnetic properties of concretes vary significantly over the frequencies. Furthermore, during the curing process, the water/cement/sand ratios and chemical admixtures of concretes affected their electromagnetic properties. A relationship of the electromagnetic properties of concretes to their various physical states and constituent components could be used for the quality control of concretes in construction work.

1. Introduction

The dielectric constants and conductivities of materials have been used to infer the physical and chemical states of materials [1–3]. Recently, there has been renewed interest on the electrical properties of concrete [4–13]. The dielectric constant of a material is proportional to the displacement current while its conductivity is proportional to its conduction current. Because the displacement current in Maxwell's equations is proportional to $\varepsilon \partial E/\partial t$ and the conduction current is proportional to σE, the conduction current dominates in a conductive material [14, 15]. Hence, at low frequencies, the conductivity of concretes is easier to measure. A historical review of resistivity measurements of concrete is given by Perez-Pena *et al.* [13].

At higher frequencies, the displacement current dominates over the conduction current in a conductive material. Hence, the dielectric constants of concretes have been measured at the microwave frequencies ($>$ 1 GHz) [5, 7]. However, the electromagnetic properties (both the dielectric constant and conductivity) of concretes over frequencies ranging from radio waves to microwaves have not been reported.

If the variations in the dielectric constant and conductivity of curing cement are monitored in this laboratory setting, better insight can be gained on how actual concrete behaves in the hardening process. The different mixtures tested have different amounts of constituent components, such as water, sand, and cement. The dielectric constant of the mixture may be a good indicator of the water content because of the large difference in the dielectric constant of water ($\varepsilon_r = 80$) and that of dried concrete ($\varepsilon_r \simeq 10$) [16]. Therefore, a mixture with a higher dielectric constant should have a larger percentage of water than a mixture with a lower dielectric constant. The behaviour of the dielectric constant could also indicate the chemical reactions taking place in the curing process [17]. In addition, the conductivity could be an indication of the presence of salts (e.g. chlorides) in saturated concrete, because conductivity generally increases with ionic concentrations.

This paper describes the study of the electromagnetic properties of different cement mixtures over the frequency range 1 MHz–3 GHz. The goals are to develop a reference data base for suitable characterization of these properties and to identify the frequency range which would yield the most information on the properties of actual concretes. This knowledge will aid in the future task of developing an electromagnetic sensor to perform on-site monitoring of concrete.

The dielectric measurement cell used here is a coaxial-type cell [1–3, 16] which has a sample volume of 54 ml (see Fig. 1), and is designed specifically for the testing of mortars. The large cell volume will average the fluctuations in the electromagnetic properties of the concrete mortar caused by the heterogeneities inherent in the composite structure. Commercially available cells were too small for such an application [18, 19]. From the measured scattering parameters (*S*-parameters) of the cell, the electromagnetic properties of the sample can be calculated. The cell has been calibrated over a frequency range 1 MHz–3 GHz, and tested by measuring material with known electromagnetic properties over this frequency range, e.g. water, teflon, and air. A detailed description of the cell

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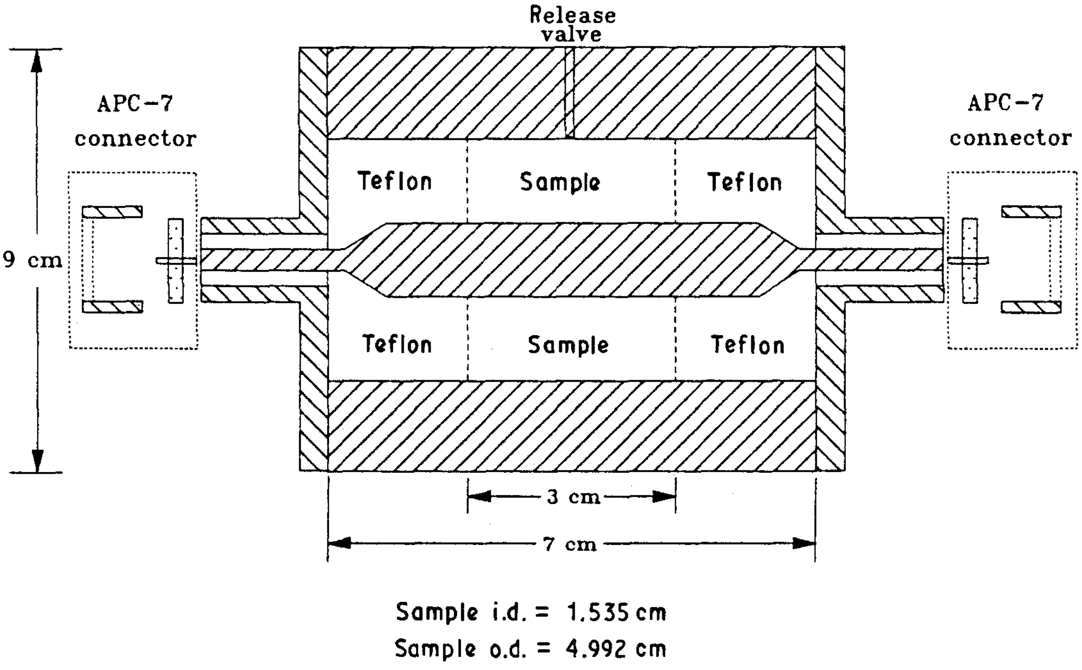

Figure 1 The coaxial measurement cell.

construction and calibration is given in [16]. This method of measurement is more accurate than the horn antenna measurement in [5], and more broadband than the waveguide measurement in [7]. At low frequencies ($\ll 1$ MHz), the dielectric constant measurement is often contaminated by electrode polarization effects, whereby four-electrode measurements have to be used [20, 21]. However, we are outside this low frequency range.

2. Experimental procedure

Several pastes and mortars were tested, using a commercial Type I Portland cement. The sample compositions are listed in Table I. Quantities were initially adjusted to give free flowing mixes that could be easily moulded, without appreciable bleeding. The sand used to prepare mortars was a quartz sand with a gradation conforming to ASTM C109. Also, calcium chloride and gluconic acid (30 wt % solution) were used to modify setting times. They were added to the mix water at rates of 2 g $CaCl_2 \cdot 2H_2O$ or 1 ml gluconic acid solution.

Pastes were mixed by hand in a beaker for several minutes and then placed in the brass cell. The exposed metal surfaces were coated with a very thin layer of grease to prevent the sample from adhering to the cell walls. A sample measured with and without the grease showed that the grease had no effect on the measurements. The temperature rise over time in a sample of the hydrating paste was measured in a closed system using a thermister embedded in the paste. The output is recorded by a computer which also calculates a temperature–time profile.

The cell was propped up vertically with the teflon piece and the endplate removed from the upper end, in order to pour the mixture into the mould. Then the teflon piece was pushed into the end of the cell to contain the cement in the centre section. Excess cement and trapped air were forced out of the centre section through a small screw hole. The screw was replaced before testing began. Once the teflon piece was in place, the additional endplate and connector were attached and the cell was ready for measurement.

3. Results and discussion

3.1. Cement paste measurements

Typical data for the hydrating cement paste are shown in Fig. 2. A marked change in dielectric constant with

TABLE I Compositions of samples used in this study

Cement (g)	Water (ml)	Sand (g)	Admixture	w/c	s/c	w/(s + c)
100	50	–	–	0.50	–	0.50
100	60	125	–	0.60	1.25	0.27
100	55	125	–	0.55	1.25	0.24
100	50	125	–	0.50	1.25	0.22
100	45	125	–	0.45	1.25	0.20
100	55	200	–	0.55	2.00	0.18
100	60	275	–	0.60	2.75	0.16
100	50	125	1 ml gluconic acid	0.50	1.25	0.22
100	50	125	2 g $CaCl_2 \cdot 2H_2O$	0.50	1.25	0.22

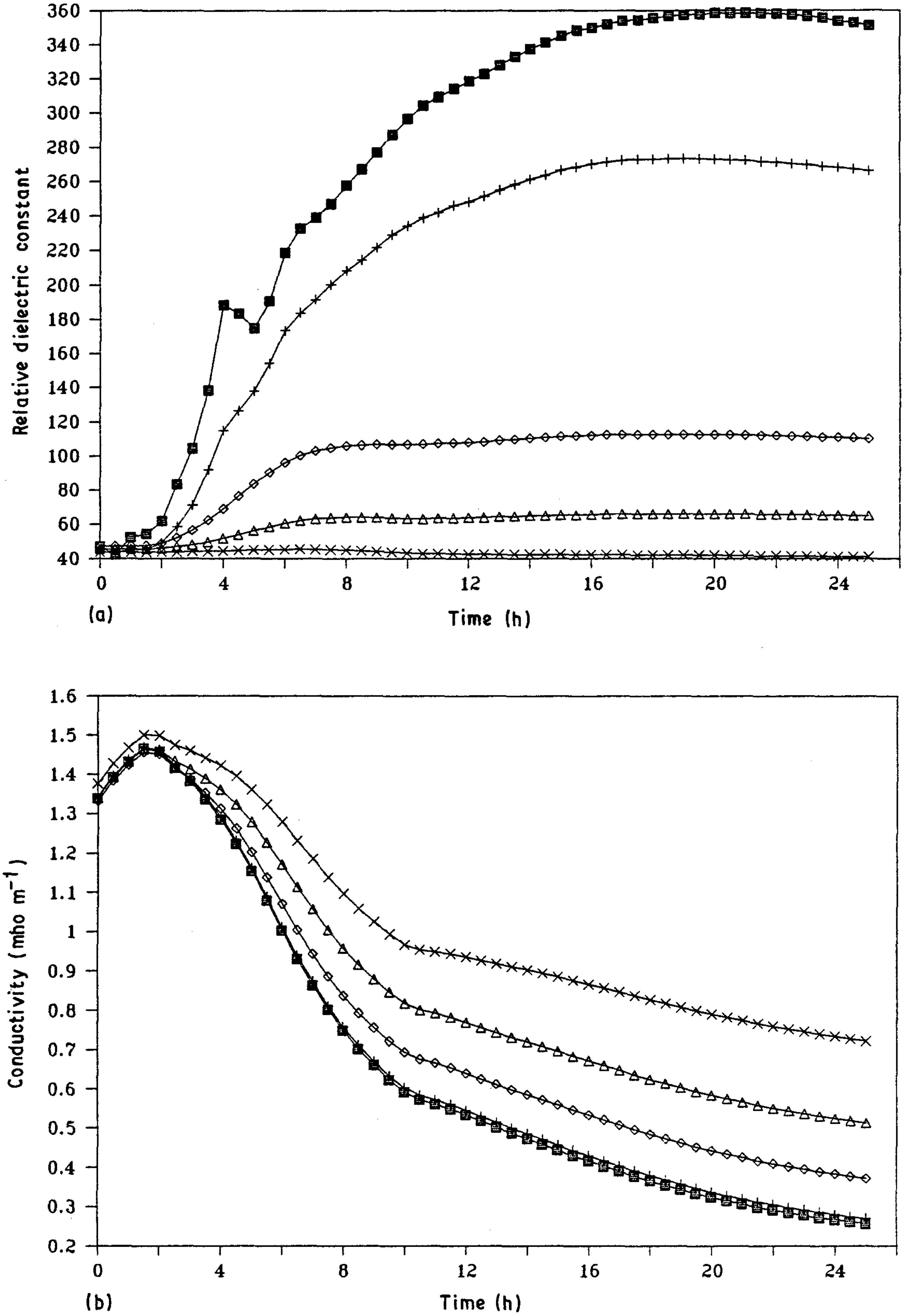

Figure 2 Time dependence of the electrical properties for a hydrating cement paste with w/c ratio of 0.50: (a) dielectric constant (b) conductivity. (■) 1 MHz, (+) 3 MHz, (◇) 30 MHz, (△) 100 MHz, (×) 300 MHz.

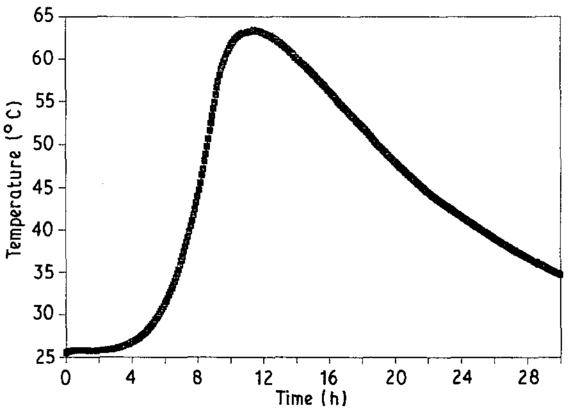

Figure 3 Temperature versus time for a hydrating cement paste with w/c ratio of 0.50.

time is observed only for frequencies below 30 MHz, whereas conductivity changes were similar at all frequencies, although larger at low frequencies. The peak in conductivity correlates with the upturn in dielectric constant. The rapid increase in this latter property corresponds closely to the attainment of maximum temperature, shown in Fig. 3. The increase in dielectric constants with time may be attributable to the counterion polarization and the formation of double layers on the hydrated cement particles [22]. Note that above 300 MHz, the dielectric constant actually decreases with curing time indicating that the water molecules are becoming tightly bound in the cement paste. The same phenomenon is observed, for example, in the drop of dielectric constant from 80 in water to about 3.2 in ice due to the hindered rotation of H_2O molecules, mitigating its polarizability. The eventual decline in the dielectric constant at low frequencies was expected as it has been shown that dielectric enhancement due to electrochemical effects is a consequence of the interaction of the counterions in the double layer with an ionic charge cloud in the ionic solution [22].

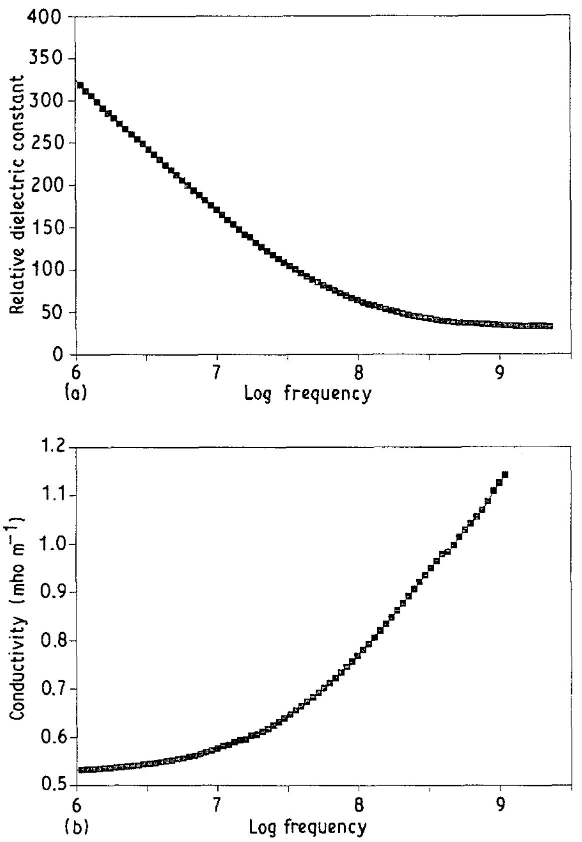

Figure 4 Variation of the electrical properties with frequency, after 12 h hydration (same sample as in Fig. 2): (a) dielectric constant (b) conductivity.

The variation of paste properties with frequency over the range of 1 MHz–3 GHz (6–9.5 on the log frequency scale) are shown in Fig. 4. The data were taken 12 h after mixing. The dielectric constant is high at low frequencies and decreases with increasing frequency. This pattern of decreasing dielectric constant with increasing frequency was seen to be the case for all samples tested. The high dielectric constants at low frequencies might be attributable to electrochemical effects [20–22], or geometrical effects [23]. These effects are known to affect the dielectric constants of rocks and biological suspensions at low frequencies [20]. Also, the conductivity increases slowly at low frequencies but more rapidly near 1 GHz. This is attributed to the microwave absorption of water [24], causing an increase in the effective conductivity of the mixture. The dielectric constant and the conductivity are related by the Kramers–Kronig relationship or the causality condition [25], which states that if the conductivity increases with frequency then the dielectric constant decreases with frequency. Mathematically, this relationship is known as the Hilbert transform.

3.2. Mortar measurements

Fig. 5 shows typical data for mortars. The curves are similar to those for neat cement paste except for an overall reduction in the values for the electrical properties indicating that the response is dominated by the paste binder with dilution by the sand filler. A comparison of the electrical properties of the mortars is shown in Table II. The decrease in the peak dielectric constant and conductivity at low frequencies is proportional to the decrease in percentage of water in the mixture as shown in Fig. 6a. The dielectric constant also depends on the s/c ratio (Fig. 6b) because the dielectric constant of the sand will contribute to the value for the composite.

TABLE II Effect of mortar composition on electrical properties at 1 MHz

w/c	s/c	w/(s + c)	Peak dielectric constant	Peak conductivity (mho m^{-1})
0.50	–	0.50	359	1.47
0.60	1.25	0.27	241	0.75
0.55	1.25	0.24	216	0.75
0.50	1.25	0.22	217	0.76
0.45	1.25	0.20	212	0.71
0.55	2.00	0.18	160	0.55
0.60	2.75	0.16	131	0.43

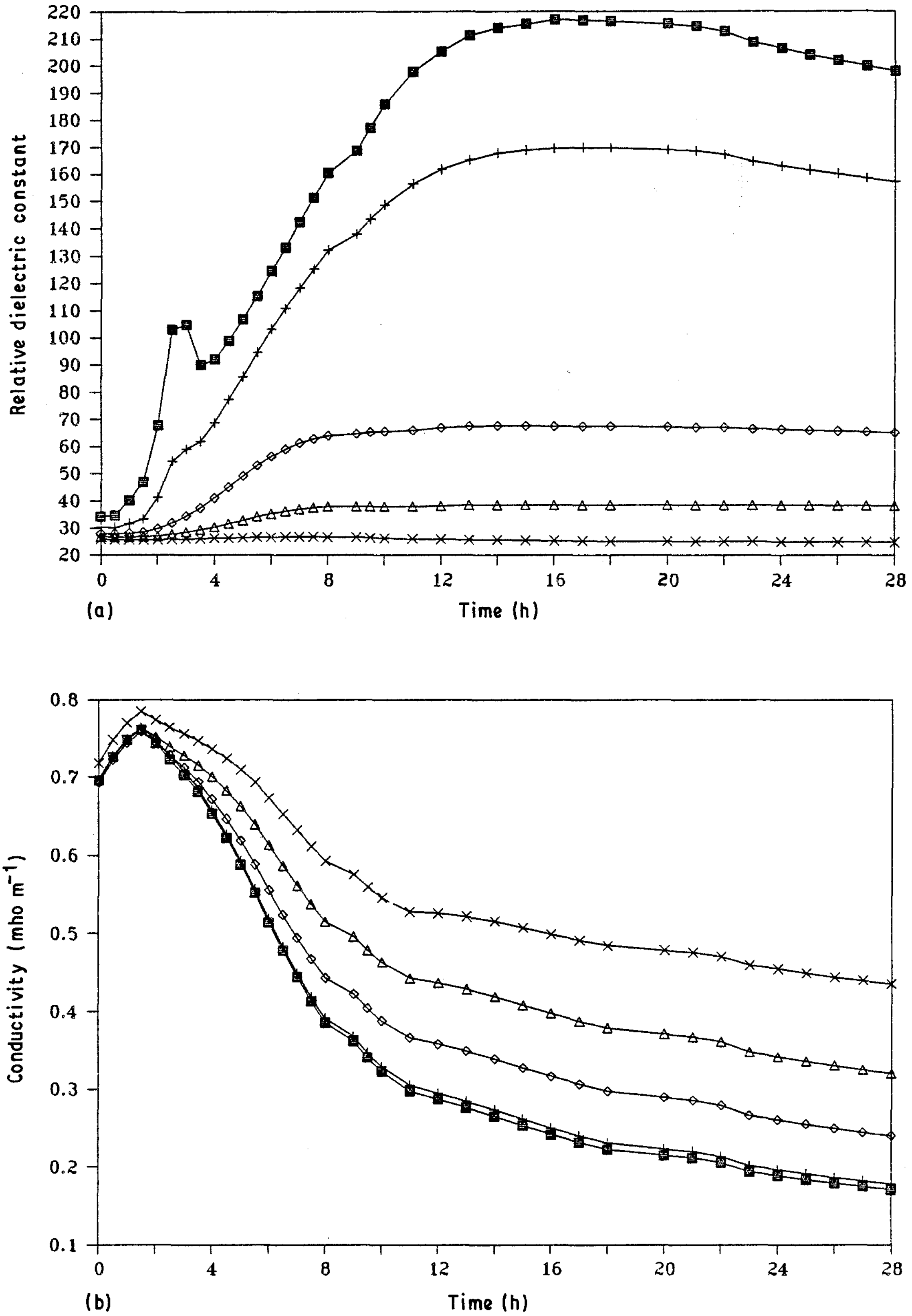

Figure 5 Time dependence of the electrical properties for a hydrating mortar with w/c and s/c ratios of 0.50 and 1.25, respectively: (a) dielectric constant (b) conductivity. For key, see Fig. 2.

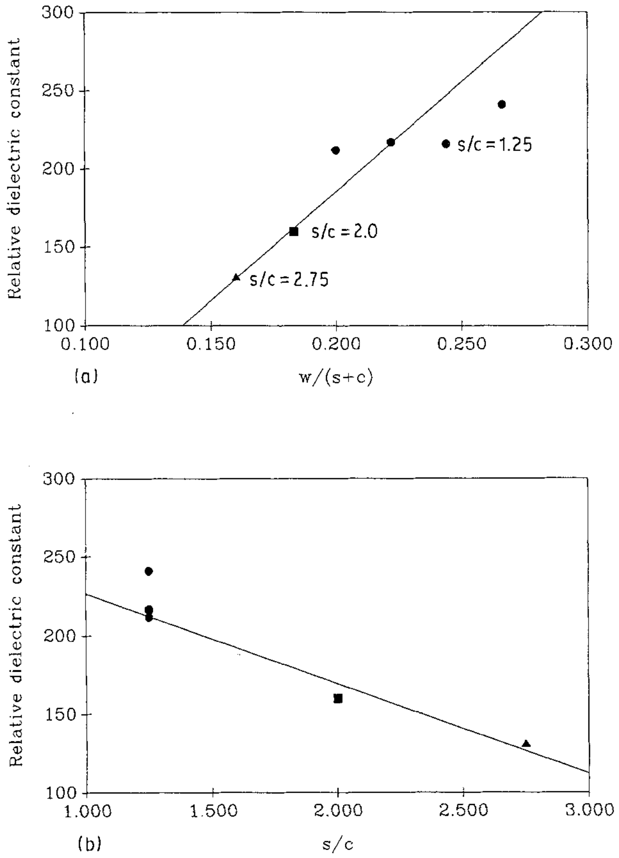

Figure 6 Comparison of the peak dielectric constant at 1 MHz for different mortars: (a) with varying water contents and (b) varying sand contents.

4. Chemical admixtures

Water-soluble chemical admixtures which modify the setting time were added to the mortar, in order to verify that the increase in dielectric constant at low frequencies and the peak conductivity were, in fact, the points at which the cement began to set and gain strength. The two chemical admixtures used were a retarding solution of gluconic acid, which increased the setting time, and calcium chloride, which decreased the setting time. The results at 1 MHz are shown in Fig. 7.

The initial low-frequency dielectric constant was much higher in the retarded mortar. This is attributed to reactions that occur immediately upon mixing involving the calcium aluminate phases [17], which are usually missed because of the cell preparation time. The increase in low-frequency dielectric constant, usually after 2 h, did not occur here until about 10 h. The conductivity curve in Fig. 7b is consistent with these changes. The initial period of conductivity increase, which previously took about 1 h, now lasted for almost 7 h before the long-term decrease was observed.

The mortar containing calcium chloride attained a more rapid peak dielectric constant, as expected. However, the time at which the dielectric constant started to increase and the conductivity to decrease was not much different from the control. Also, the conductivity values were much higher than in the control mortar. This observation is due to the increased ionic concentration in the aqueous phase from $CaCl_2$.

5. Conclusions

The *in situ* measurements of changes in the electromagnetic properties of mortars during setting and hardening have been measured over a broad frequency range of 1 MHz–3 GHz. The greatest changes in dielectric constant are observed at low frequencies from 1–30 MHz; above 100 MHz it is nearly constant with time. However, there is a gradual decrease in electrical conductivity with time at all frequencies.

The change in dielectric constant with time correlates with the early setting and hardening processes. The increase in dielectric constant over the first 15–20 h is attributed to a decrease in water mobility, as reflected by the decrease in conductivity, and an increased percentage of water associated with the hydration products.

The magnitude of the dielectric constant is a function of the amount of water in the system and the amount of sand (i.e. related to the w/(s + c) ratio). The magnitude of the electrical conductivity does not change markedly with w/c ratio or sand content, but is affected by ions introduced by chemical admixtures.

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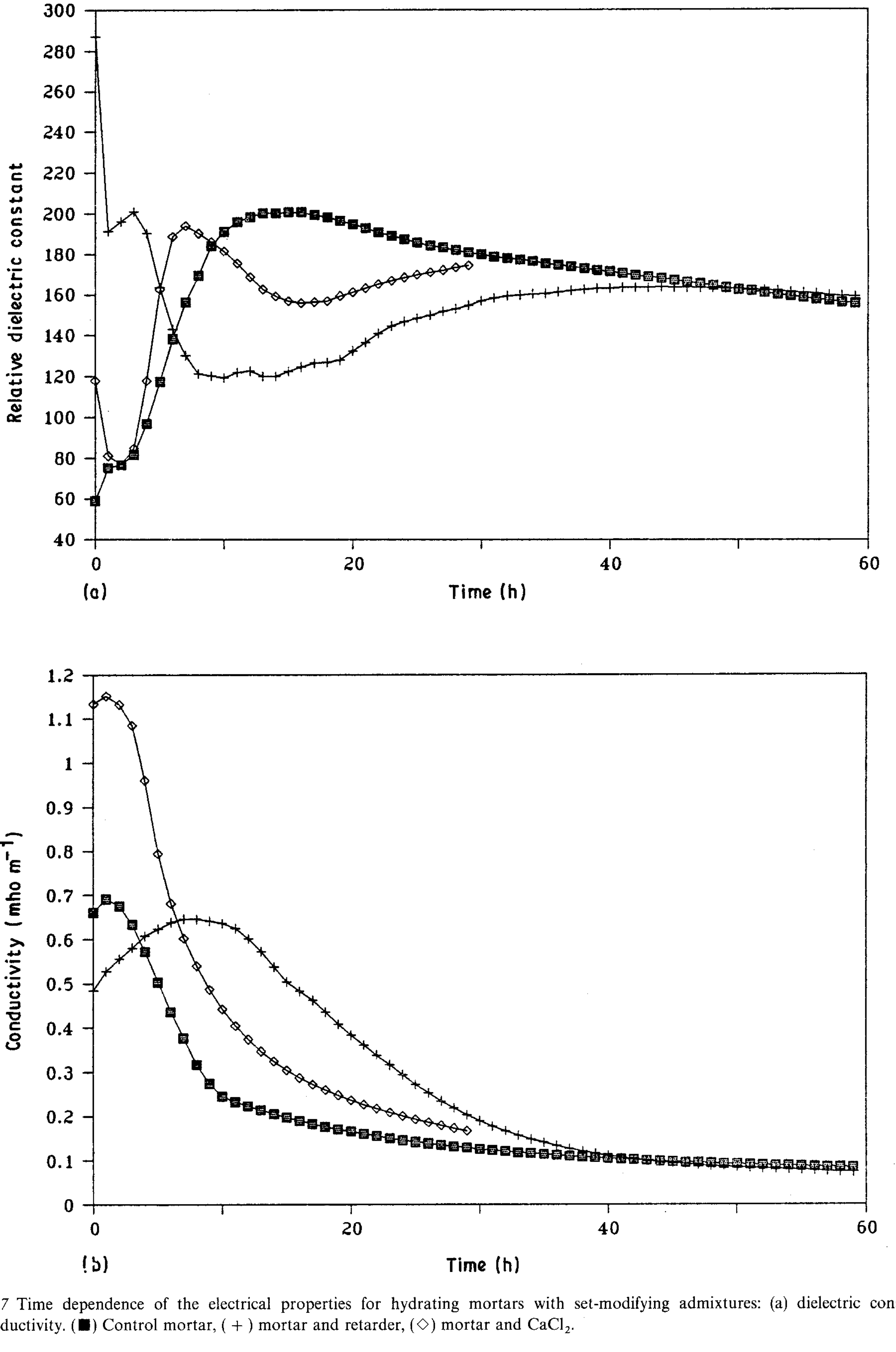

Figure 7 Time dependence of the electrical properties for hydrating mortars with set-modifying admixtures: (a) dielectric constant (b) conductivity. (■) Control mortar, (+) mortar and retarder, (◇) mortar and CaCl$_2$.

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