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Study of dielectric and electrical properties of mortar in the early hydration period at microwave frequencies

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The dielectric constant, ε, and electrical conductivity, σ, of mortars with various sand–cement ratios, s/c, were measured for the first 30 h hydration using microwave techniques in the frequency range 8.2–12.4 GHz. The ε and σ of the mortars were found to increase linearly with increasing water–solid ratio $w/(s+c)$, but decrease with increasing s/c. It was found that as long as the s/c values were the same, the rate of changes in ε and σ of the mortars were the same. It appears that the s/c is the key factor controlling the rates of changes in dielectric and electrical parameters of cement hydration in mortar. The relationship between compressive strength and dielectric and electrical properties of mortars was also discussed.

1. Introduction

Cement is one of the most widely used construction materials. Mechanisms of cement hydration have not been fully understood yet as the cement hydration involves very complicated chemical and physical processes. A better understanding of the mechanisms of hydration and microstructural development in the cement paste, mortar and concrete can be achieved if the chemical reactions and the phase transitions involved in the cement hydration can be monitored *in situ*.

There are various methods to study the cement hydration. The principal methods are X-ray diffraction [1, 2], electron microscopy [3–8], thermal analysis [9, 10], conduction calorimetry [11] and electrical properties measurement [12–29], among which conduction calorimetry and the electrical methods are suitable to study the cement hydration *in situ*. The electrical method can be used as an effective way to study the progress of cement hydration and to monitor structural changes occurring in the cement paste, mortar and concrete. During cement hydration, the water molecule in cement pastes or in mortars changes from free water to water bound in various states of hydration or crystallization. The electrical and dielectric properties of cement paste or mortar, such as ionic conduction, polarization ability, dielectric relaxation and dielectric loss, will change with hydration. Moreover, because a dipolar molecule changes from one bonding state to another, its ability to orient in an applied electric field changes. Thus, the changes in the dielectric constant and electrical conductivity during hydration will be related to the bonding state of cement paste or mortar, and therefore related to the changes of hydration products. The sensitivity of the dielectric constant and electrical conductivity to water content and the microstructure of cement paste and mortar suggests that these parameters should provide the information of cement hydration and be used to monitor the hydration process in cement paste and mortars.

Most measurements of the electrical and dielectric parameters of cement are performed in the lower frequency using a "capacitor" method, i.e. the cement paste as a dielectric medium is placed between two electrodes to form a capacitor. The changes in capacitance of this "cement capacitor" is monitored during hydration. The dielectric constant and electrical conductivity (or resistivity) of cement paste are then obtained from the capacitance measurement. It was reported [27] that an unknown "electrode polarization" effect will be introduced when the "capacitors" method is used. This effect often causes difficulty in interpreting the conductance measurements.

An alternative is to use the microwave technique because the electrodes are not needed in microwave measurements. As microwaves are absorbed by water molecules, dielectric measurement at microwave frequencies is sensitive to the water content and the ionic concentration of a cement paste. The measurements of dielectric constant and electrical conductivity of cement or mortar samples at microwave frequencies could be used to follow the hydration of cement, because the changes in dielectric constant and conductivity can be associated with the different stages of hydration. The microwave method has been used to

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study the cement hydration and slag cement hydration in the early period [30, 31]. Although some microwave measurements of cement paste have been reported [13, 26, 30–34], the study of dielectric and electrical properties of mortar is rare [22, 28, 29, 32].

In this paper, we report the results of *in situ* measurements of changes in the dielectric and electrical properties of mortars with various sand to cement ratio (*s*/*c*) in the first 30 h hydration in the microwave frequency range of 8.2–12.4 GHz. Some factors which affect the hydration are also discussed.

2. Experimental procedure

Investigations of the dielectric properties of materials at microwave frequencies are typically conducted by filling a rectangular waveguide section with a sample of the material, and the complex permittivity and permeability are then determined from the measurements of the reflection and/or transmission coefficients of the dominant waveguide mode [35, 36]. The transmission waveguide method is used for measuring the dielectric properties of materials in the frequency range 8.2–12.4 GHz (X band). The equipment used in this study consists of a microwave vector network analyser (Hewlett Packard HP8719C) with a coax-to-waveguide adapter (HP-X281C) and a sample holder consisting of a section of the standard WR-90 waveguide. An IBM-compatible personal computer (PC486) is used to receive data over an IEEE-488 bus and used for subsequent numerical analysis as well. A measurement software is used to perform all necessary network analyser control, calculation, and data presentation. The software controls the network analyser for measurement of the complex reflection coefficients S_{11} and S_{22}, and transmission coefficient S_{12} and S_{21} of the material sample. It then calculates the complex permittivity of the samples using these S parameters of the two-port line over the whole frequency range. The experimental set-up is shown schematically in Fig. 1. After mixing cement and sand with water, the sample was placed immediately into a waveguide which is connected with the two measurement planes, with one end of the sample hard against a PTFE plug. The insertion of the PTFE plug was to avoid leakage of water and mortar paste from the sample holder because the waveguide structure is set up vertically. The calibration of the measurement system at reference planes A and B was done before every measurement so that effect of the PTFE plug was removed.

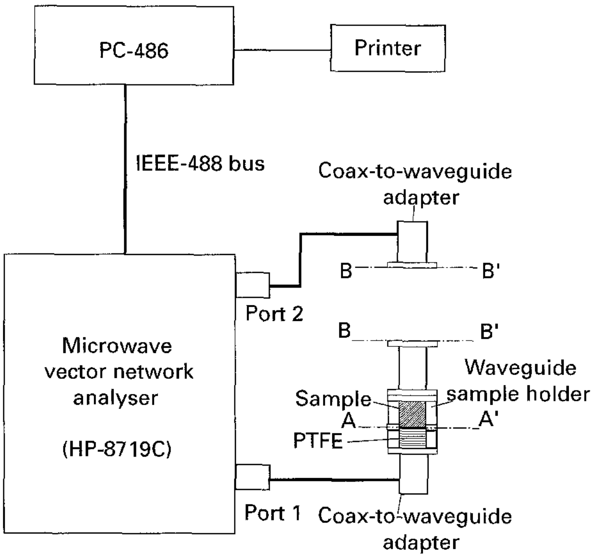

Figure 1 A schematic diagram of the experimental set-up.

TABLE I

	OPC
SiO_2	21.2
Al_2O_3	5.5
Fe_2O_3	3.2
CaO	63.4
MgO	1.7
SO_3	2.4
Na_2O	0.13
K_2O	0.68
Loss on ignition	1.0

Commercial ordinary Portland cement (OPC) and standard sand compiled to BS 4551 were used in this work. The composition of the cement is given in Table I. The OPC and sand were mixed using deionized water with the water to cement ratios (*w*/*c*) of 0.40 and 0.50 and the sand to cement ratios (*s*/*c*) of 0.35, 0.80, 1.25 and 1.70, respectively. The mortar samples were carefully compacted into a rectangular waveguide with size of $22.86 \times 10.16 \times 10.00\ \text{mm}^3$. The first measurement was made 5 min after mixing with water. Succeeding measurements were made at every 5–10 min during the first 5 h and then at every 0.5–2 h over the next 25 h. All microwave measurements were made at 23 ± 2 °C.

The compressive strength of the mortar samples were measured in order to understand the relationship between compressive strength and the sand to cement ratio. In the measurements, the water to cement ratio (*w*/*c*) was fixed at 0.4. Four 70 mm mortar cubes were prepared for each mixture and cured in a humidity cabinet with a RH of 95% at 25 ± 2 °C. The mortar cubes were crushed at the time of 12 and 24 h respectively. Compression test was carried out with an ELE compression machine (Digital Elect 2000) with a loading rate of $0.75\ \text{kN s}^{-1}$. The measurement error was within ± 0.2–0.6 MPa.

3. Results

The measurement technique used in this work can give the complex permittivity of the mortar samples directly. The real part of permittivity, ε', is the relative dielectric constant (in this paper we use the notation dielectric constant, ε, to represent the real part of the complex permittivity, ε'). Its imaginary part, ε'', is related to electrical conductivity, σ, via the formula $\sigma = \varepsilon_0 \varepsilon'' \omega$, where ε_0 is the dielectric constant in vacuum and ω is the angular frequency. Fig. 2a and b show the frequency dependence of the complex permittivity of the mortar with *w*/*c* ratio of 0.40 and *s*/*c* of 0.80, at time of 0.5, 12 and 24 h after mixing,

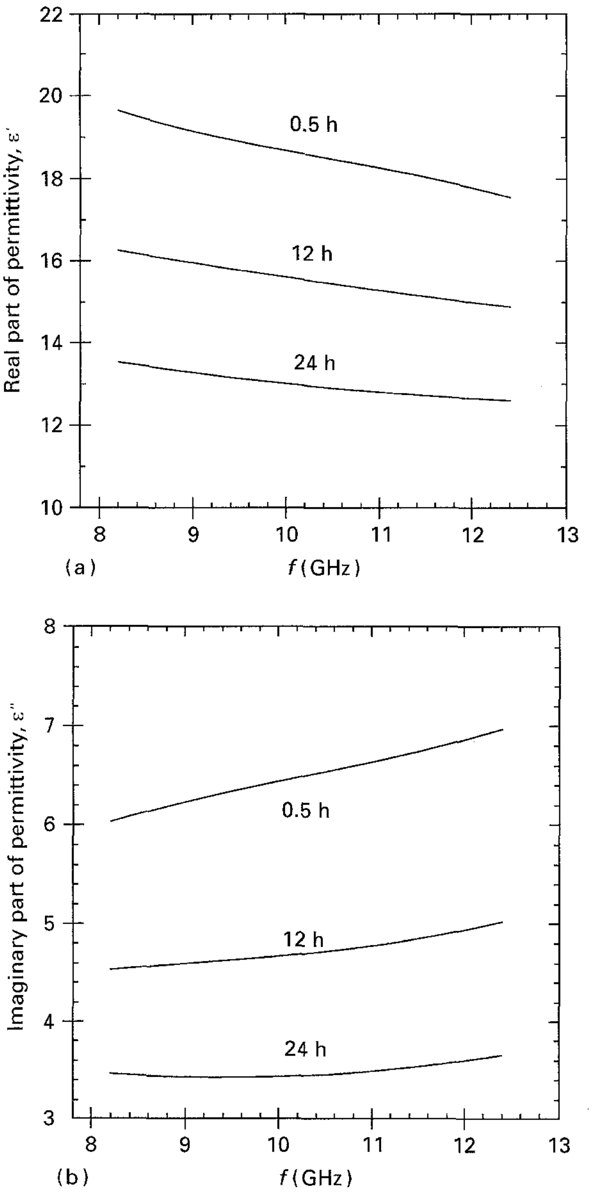

Figure 2 Frequency dependence of (a) the real part ε' and (b) the imaginary part ε'' of permittivity of mortar with $w/c = 0.4$ and $s/c = 0.8$, at times of 0.5, 12 and 24 h after mixing, respectively.

respectively. Both the real part, ε', and the imaginary part, ε'', of permittivity decrease with time. Because the frequency dependence of permittivity of the mortar is weak, it is therefore appropriate to focus our discussion on the dielectric properties of mortars at a chosen frequency of 9.5 GHz.

Fig. 3 shows the changes with time in the dielectric constant ε, and electrical conductivity, σ, of mortars with w/c of 0.40 corresponding to the different values of s/c at 9.5 GHz. Both values of ε and σ decrease with increasing s/c. The cement hydration process in the early period can be divided into four stages [35]. Stage I lasts about 15–20 min. In this stage, most ions are unbound charges in aqueous phase. These unbound charges polarize and move easily in the electrical field, resulting in a large dielectric constant and a large electrical conductivity. The ε values of all five samples decrease rapidly in this stage. Stage II (1–4 h) corresponds to the induction period. In this stage, the rapid leaching of ions from the cement grains causes a surface layer rich in hydrosilicate ions on the C_3S and C_3A phase. This surface layer, together with the cement grain and C–S–H form an electrical double layer, leading to the slow hydration rate in stage II. It was found that the ε values in this stage were almost constant. The rupturing of the electrical double layer

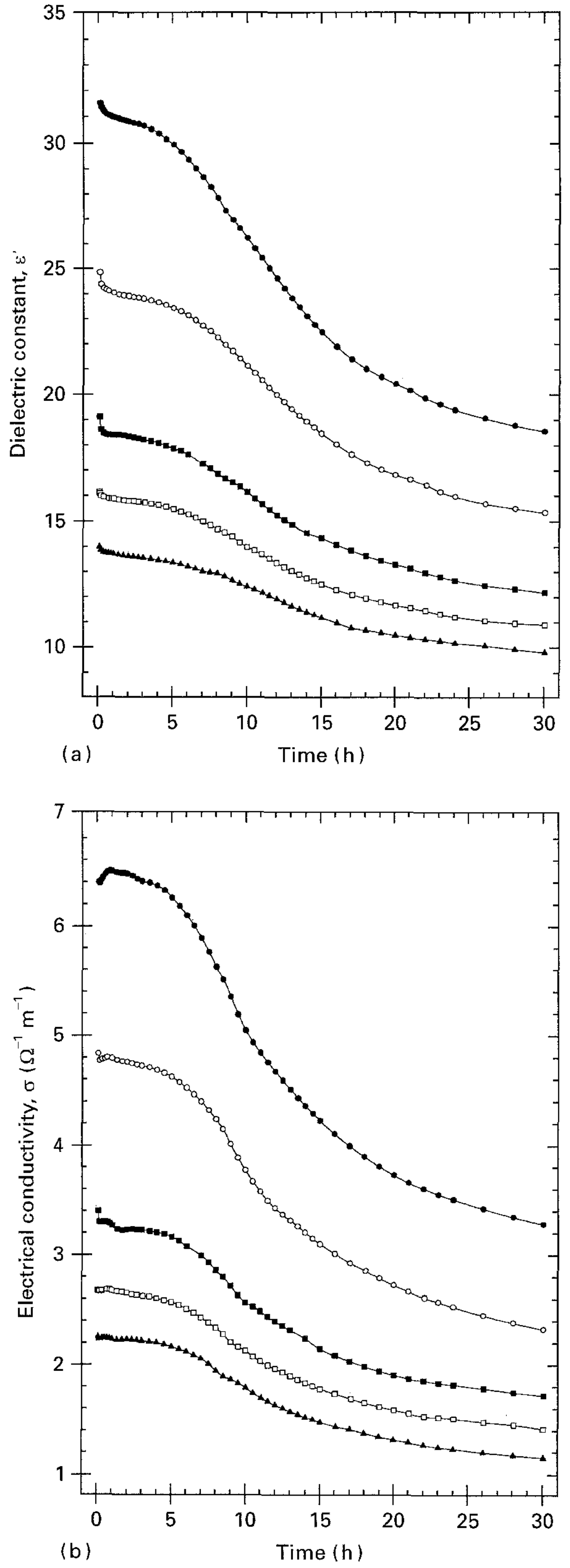

Figure 3 Variations of (a) dielectric constant, ε, and (b) electrical conductivity σ, with time at 9.5 GHz for mortars with different s/c values of (●) 0, (○) 0.35, (■) 0.80, (□) 1.25 and (▲) 1.70, respectively, and w/c of 0.40.

TABLE II

w/c	s/c	$w/(s+c)$	Time of onset of rapid drop (h)		Rate of decrease in the first 20 h (h^{-1})		Rate of relative change in the first 20 h (%)	
			t_ε	t_σ	$t_{\varepsilon 1}$	$r_{\sigma 1}$	$r_{\varepsilon 2}$	$r_{\sigma 2}$
0.4	0	0.4	2.5	2.5	– 0.55	– 0.15	34.00	42.48
0.4	0.35	0.296	3.0	4.0	– 0.38	– 0.11	29.86	42.96
0.4	0.80	0.222	3.5	4.5	– 0.27	– 0.07	27.55	41.48
0.4	1.25	0.178	4.5	5.5	– 0.22	– 0.06	26.16	40.38
0.4	1.70	0.148	5.0	6.0	– 0.17	– 0.05	23.13	40.93
0.5	1.25	0.222	4.5	5.5	– 0.22	– 0.06	24.47	36.32

allows water to reach the cement grains, leading to accelerated dissolution of the grain. The third stage starts at about 3–5 h after mixing with water. The value of ε starts to decrease rapidly at the beginning of this stage. The initial time, t_ε, at which ε starts to decrease rapidly varies with the s/c value; the smaller the s/c value, the earlier is the t_ε (see Table II). At 5–18 h (stage III), ε decreases at the fastest rate. The rate of decrease in ε ($r_{\varepsilon 1}$) depends on its s/c value. The larger the s/c value, the smaller the $r_{\varepsilon 1}$ (see Table II). The last stage (stage IV) starts at about 18–20 h and it can last for about 1 yr. During this stage, the slow diffusion-controlled formation of C–S–H and CH takes place. In 20–30 h, the ε decreases almost linearly but at a slower rate, and the rate of decrease in ε depends on its s/c value.

Similar to that of ε, the change in electrical conductivity, σ, with time also shows a decreasing (Fig. 3b). It was found that only OPC paste has an increase in σ within the first hour of hydration and then σ starts to decrease from its maximum. No such increase in σ was observed in the mortar samples. In the first period of hydration (within 30 min), the value of σ for the mortars decreased a little or remains unvaried. In stage II (up to about 4–6 h), σ values of the mortar samples change little until the initial time, t_σ the beginning time of stage III. In stage III all samples have the most rapid rate of decrease in σ. The rate of decrease in $\sigma(r_{\sigma 1})$ depends on its s/c value. The larger the s/c value, the smaller the $r_{\sigma 1}$ (see Table II). The t_σ of mortar is also related to the s/c value; the larger the s/c value, the longer is the t_σ. The initial times of t_ε and t_σ as well as the corresponding rates of change in ε and σ in stage III, $r_{\varepsilon 1}$ and $r_{\sigma 1}$, are given in Table II. It was also found that the initial time, t_σ has about a 1 h delay compared with its t_ε for all mortar samples under study. But the OPC has the same initial time (about 2.5 h) of rapid decrease in both ε and σ (see Table II). This delay might be related to some mechanisms in the mortar. This phenomenon will be discussed later.

Fig. 4 shows the relative change in dielectric constant $\varepsilon(t)/\varepsilon(t_0)$ and the relative change in electrical conductivity $\sigma(t)/\sigma(t_0)$ of mortars with different s/c value at 9.5 GHz. The $\varepsilon(t_0)$ and $\sigma(t_0)$ are the initial values of ε and σ, respectively, at time $t_0 = 5$ min after mixing with water. The relative changes in ε and σ represent the rate of changes in ε and σ which may be related to the hydration rate of mortars. It was found that the relative changes in σ are the same for the mortars with different s/c values, i.e. the mortars have the same rate of change in σ although their values of σ decrease with increasing the s/c value. However, the relative changes in ε for mortars with various s/c have almost the same rate within the first 5 h but different rates after 5 h. The mortar with higher s/c value has a lower rate of change in ε. It was also observed that the change in conductivity was faster than that of the dielectric constant, especially in the case of high s/c value. The relative change rates in ε and σ, which are defined as $r_{\varepsilon 2} = \{[\varepsilon(t_0) - \varepsilon(t)]/\varepsilon(t_0)\} \times 100\%$ and $r_{\sigma 2} = \{[\sigma(t_0) - \sigma(t)]/\sigma(t_0)\} \times 100\%$, respectively, at 20 h are given in Table II. We find that the values of $r_{\sigma 2}$ for all samples are larger than the corresponding $r_{\varepsilon 2}$, and the difference in $r_{\sigma 2}$ for different mortars is smaller than that of $r_{\varepsilon 2}$.

In the microwave range, ε and σ of mortars increase linearly with increasing $w/(s + c)$ value, as shown in Fig. 5. The slope of the straight line becomes smaller with the time of hydration. Fig. 6 shows the dependence of ε and σ of mortars on the s/c. Both ε and σ decrease with increasing s/c value, but the decreases are not linear. The rate of decrease becomes slow with time.

The compressive strength of mortars with various s/c values and a fixed w/c of 0.4 are given in Table III. The measurements were made at the time of 12 and 24 h, respectively. Surprisingly, it was found that the difference in the compressive strength of the mortars with various s/c values was within the error range ($\pm$ 0.2–0.6 MPa), indicating that the compressive strength of mortar samples studied was almost independent of the s/c values. Comparing the results that ε and σ of the mortars are sensitive to the s/c values, it was found that ε and σ of mortars have no direct relationship with the compressive strength in our samples.

4. Discussion

When cement and sand are mixed with water, a series of chemical reactions take place. The reactions of cement in mortar with water progress at different rates for the various mineral phases and involve both hydrolysis and hydration processes. There are many factors which affect ε and σ of the mortars in the hydration processes. The main factors are the changes in physical state of the water and in ionic concentra-

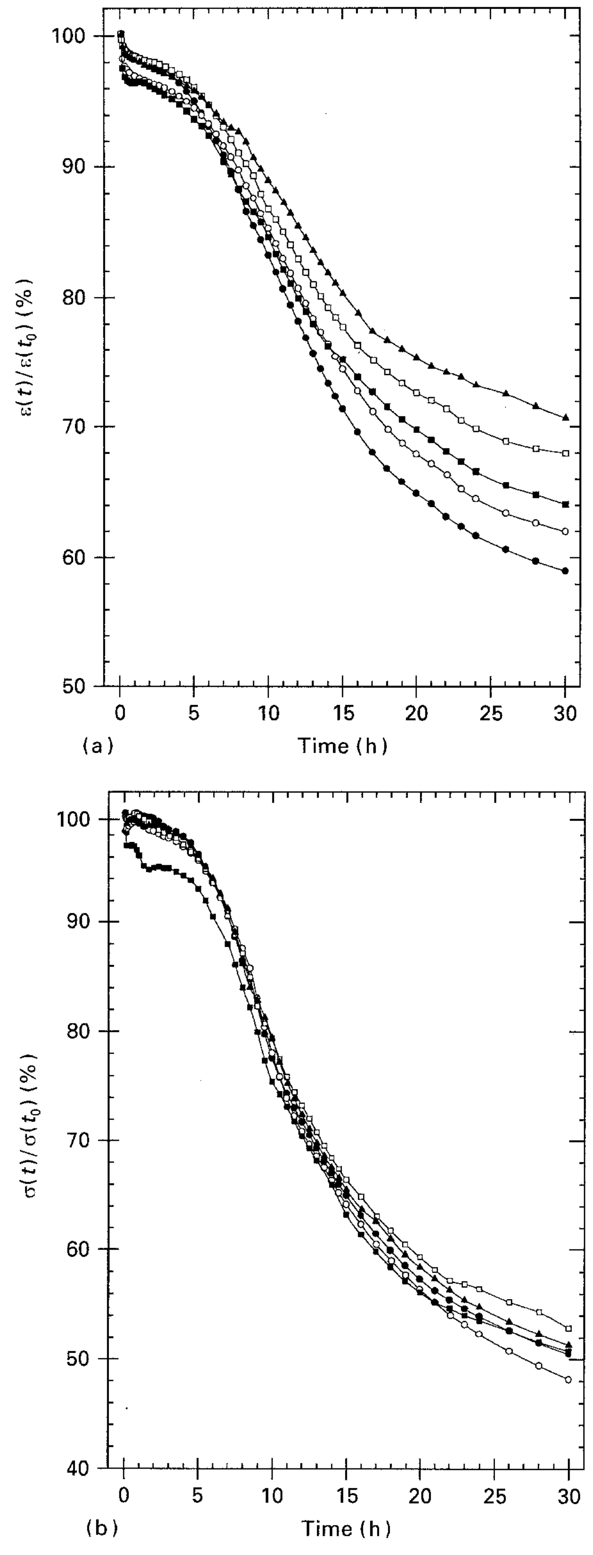

Figure 4 Variations of relative changes in (a) dielectric constant $\varepsilon(t)/\varepsilon(t_0)$ and (b) electrical conductivity $\sigma(t)/\sigma(t_0)$ with time at 9.5 GHz for mortars with w/c of 0.4 and with s/c values: (●) 0, (○) 0.35, (■) 0.80, (□) 1.25, and (▲) 1.70.

tion within the water; the changes in the ability with which dipoles and polar molecules can move within the cement paste or mortars; the changes in the surface charges of cement grain as well as the temperature of the cement system. All these factors will change with the hydration processes and be reflected by the dielectric constant and electrical conductivity of mortars. The changes in ε and σ of mortars are related to the variations of the dipoles and the charges during the hydration process.

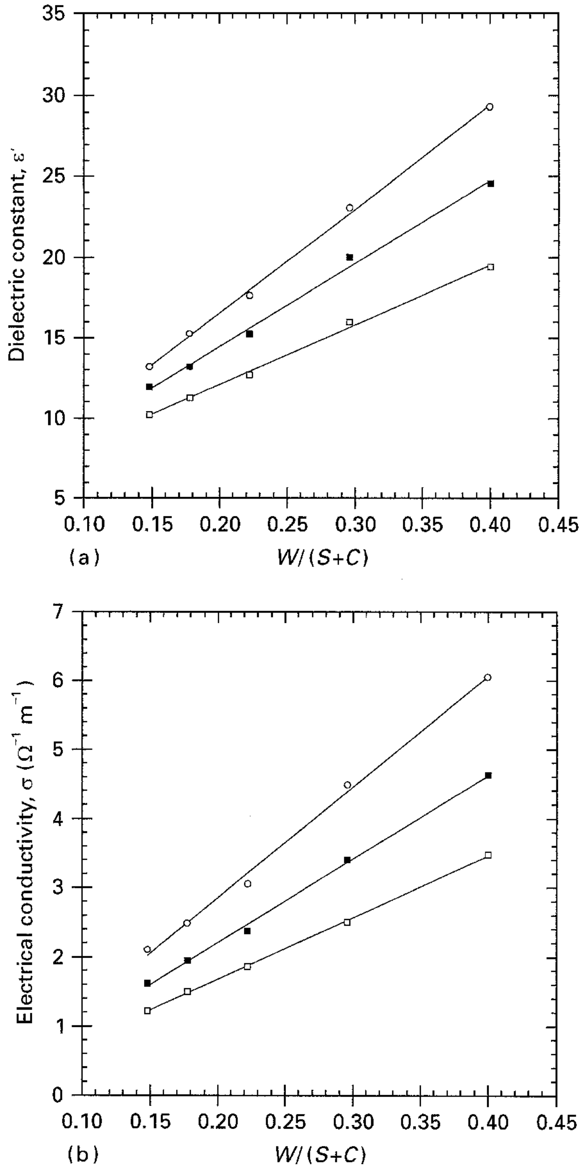

Figure 5 Variations of (a) dielectric constant, ε, and (b) electrical conductivity, σ, of mortars with $w/(s + c)$ at 9.5 GHz. Time after mixing: (○) 6 h, (■) 12 h, (□) 24 h.

It was noticed that the initial time, t_σ, had a 1 h delay compared with the t_ε for all mortar samples, but this delay does not occur in the pure OPC cement sample (see Table II). This phenomenon inspires us to assume that the interfacial layers between sand and cement may lead to the delay. A large number of interfacial layers appears due to the addition of sand into cement paste. When cement is mixed with water an exchange of ionic species is initiated between the solids and the liquid phase [20]. We suppose that the electrical environment for ionic species on the sand surfaces is different from the electrical environment for ionic species in the cement paste. The conducting property of ionic species in the interfacial layers will therefore differ from that of those in the cement paste. Because the sand does not react with the water and does not contribute to the hydration, the rate of consumption of water on sand interfaces is lower than that of cement grains. Hence, ions in the interfacial

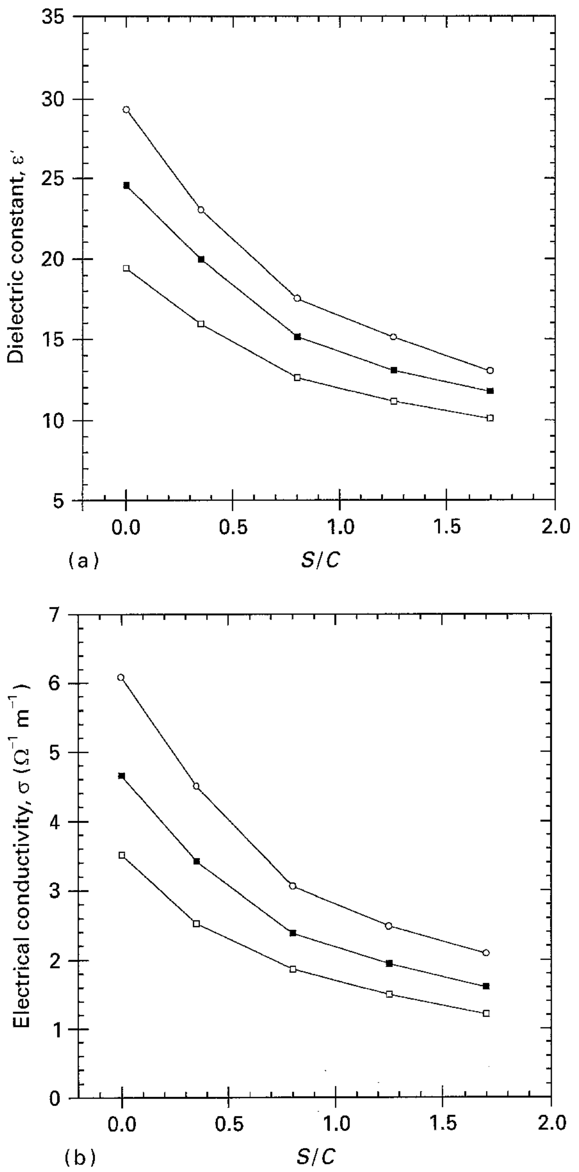

Figure 6 Variations of (a) dielectric constant, ε, and (b) electrical conductivity, σ, of mortars with s/c at 9.5 GHz. Time after mixing: (○) 6 h, (■) 12 h, (□) 24 h.

TABLE III

		Sample				
		1	2	3	4	5
s/c		0	0.35	0.80	1.25	1.70
Compressive strength (MPa):	12 h	8.4	7.8	7.8	8.0	7.8
	24 h	20.4	18.5	18.3	18.3	18.2

layers could still contribute the conduction when the mobility of ions in bulk cement paste decreases with hydration, leading to t_σ larger than t_ε.

The electrical conductivity, σ, represents the migration of ions in the materials. The value of σ is related to the number of ions involved in the conduction at the measured frequency range. The relative change of σ in the mortars with time is related to the w/c value and further to its ionic concentration. In contrast to σ, dielectric constant, ε, represents the dielectric properties in the whole material. The ε of the mortars is related not only to the w/c value but also to the s/c value, and its value is mainly controlled by the binding state of water and decreases with increasing the s/c value. Table II shows that there is a difference between $r_{\varepsilon 2}$ and $r_{\sigma 2}$. For fixed w/c of 0.4, the higher the s/c value, the smaller is the $r_{\varepsilon 2}$ and $r_{\sigma 2}$; however, the mortar with different s/c has a close value of $r_{\sigma 2}$ but different value of $r_{\varepsilon 2}$. We suppose that the dielectric constant ε is a "structural parameter" and related to not only the content of water but also cement and sand contents in the mortars; and the conductivity σ is mainly related by the concentration of ionic species in the mortars.

From Figs 5 and 6, we can see that both ε and σ at the microwave frequency range are proportional to $w/(s+c)$. In order to understand which factor is important to the electrical properties of the mortar, ε and σ of a mortar with $w/c = 0.5$ and $s/c = 1.25$, were measured and listed in Table II. Comparing this mortar with the mortar with w/c of 0.4 and s/c of 1.25, we found that the two mortars had the same values for t_ε, t_σ, $r_{\varepsilon 1}$ and $r_{\sigma 1}$ although they had different w/c and $w/(s+c)$. It appears that, whatever the values of w/c and $w/(s+c)$ have, the mortars will have the same (or similar) values for t_ε, t_σ, $r_{\varepsilon 1}$ and $r_{\sigma 1}$, as long as the s/c values are the same. This result indicates that the ratio of s/c is the key factor to control the rates of changes in dielectric and electrical parameters of cement hydration in mortar, and the values of ε and σ of mortar depending on the proportion of water, cement and sand.

5. Conclusion

The dielectric constant, ε, and electrical conductivity, σ, of mortars with various s/c values were measured for the first 30 h hydration using microwave techniques. It was found that ε and σ decrease with increasing the s/c. The mortars with different s/c values were found to have the same rate of change in σ; however, their rate of change in ε is almost the same in the first 5 h but different after 5 h. The ε and σ of the mortars were found to increase linearly with increasing $w/(s+c)$. We found that the initial time t_σ of rapid decrease in σ has a 1 h delay compared with the initial time t_ε of rapid decrease in ε for all mortars, but the delay does not occur in the pure OPC sample. This phenomenon may be attributed to the interfacial layer in mortars having a different conducting property compared with that of bulk cement paste. It was also found that as long as the s/c values of the mortars are the same, the rate of changes in ε and σ are the same or similar. It appears that the ratio of s/c is the key factor to control the rates of changes in dielectric and electrical parameters of cement hydration in mortar. The compressive strength of mortars with various s/c values were measured, and no direct relationship was found between compressive strength and the dielectric and electrical properties in our samples.

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