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Dielectric behaviour of hardened cementitious materials

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The dielectric behaviour of mature Portland cement pastes prepared at water/cement ratios 0·3 to 0·7, and pastes containing various percentages of silica fume at water/cement ratio 0·3 was investigated over a frequency range of 1 MHz to 1·5 GHz. The value of dielectric constant is water content dependent. A linear correspondence between dielectric constant and evaporable water was obtained for water-saturated pastes. Experimental results relating dielectric constants to porosity for Portland cement pastes hydrated for one year were in good agreement with Sen's approximation for rock, e.g. $\varepsilon'_e = 1{\cdot}5\varepsilon'_{cp} + P^{1{\cdot}5}(\varepsilon'_w - 1{\cdot}5\varepsilon'_{cp})$, where ε'_e = the real part of the effective dielectric constant, ε'_w = the real part of the dielectric constant of water, ε'_{cp} = the real part of the dielectric constant of cement paste and P is the porosity. Addition of silica fume appears to have a small and indirect effect on the dielectric constant value of the paste. This is due to the pore size effects and evaporable water content.

Introduction

The hydration of Portland cement involves the initial dissolution of CaO, $CaSO_4{\cdot}2H_2O$ or $CaSO_4{\cdot}\frac{1}{2}H_2O$, aluminate phases and alkali. This is followed by the reaction of C_3S and C_2S with free water and formation of C–S–H, calcium hydroxide ($Ca(OH)_2$), ettringite and other minor compounds, which bridge individual particles and fill up capillary pores. These reactions promote the formation of a rigid microstructure and strength development. The stability of C–S–H contributes to changes in morphology, interfacial regions, pore structure and intrinsic strength. These characteristics can be studied by means of impedance or conductance measurements.

Electrical conductivity measurement (ECM),[1–4] a.c. impedance spectroscopy (ACIS)[5–15] and dielectric constant measurement (DCM)[16–29] have been used in cement and concrete hydration investigations. Studies have indicated that specific parameters obtained from these methods are very sensitive to the hydration process, moisture content, temperature and microstructural characteristics of cement paste and concrete.

DCM is more sensitive than ECM and ACIS in the early detection of changes in hydrating cement systems. Large values (up to 10 000) of dielectric constant at early hydration times have been reported at low frequencies (less than 1 MHz). These values decreased rapidly with the maturity of the paste.[23–26,29] This is attributed to interfacial and double-layer polarization effects which become less important in hardened cement paste. The dielectric constant is much smaller (close to 80) at radio and microwave frequencies, depending on free water content in the paste.[17,19,21,22,26,27] Small values of dielectric constant, e.g. 7 to 20, were also observed in very low water/cement ratio pastes, compressed cement pastes and cement/polymer composite systems.[16] It was suggested that the dielectric properties of hydrating cement paste are closely related to its 'free-water' content.[18,19] There remains a paucity of published data on the dielectric properties of cement and concrete specially at radio frequencies. A summary of previous work is given in Table 1. In this study, the dielectric properties of hardened cement paste at various water/cement ratios were determined over the frequency range, 1 MHz to 1·5 GHz. The approximation, $\varepsilon'_e = 1{\cdot}5\varepsilon'_{cp} + P^{1{\cdot}5}(\varepsilon'_w - 1{\cdot}5\varepsilon'_{cp})$ relating the effective dielectric constant, ε'_e, to porosity (P) was tested for one-year hydrated Portland cement pastes. It will be discussed in detail in a following section. This preliminary work also revealed that the

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Table 1. Summary of relative dielectric constant data

Reference	Frequency range	Relative dielectric constant	Remarks
Perez-Pena *et al.* [16]	1 kHz to 2 MHz	6·9–17·8	Type I, III and MC500 cements, warm-pressed, w/c = 0·2, cured 1 day at 30°C
Gorur *et al.* [17]	Microwave	12–28 (ε')	OPC, w/c = 0·3 to 0·4, hydrated up to 48 hours
Wilson *et al.* [18, 19]	1 MHz–100 MHz	~100 and less	OPC, w/c = 0·5, cement:sand:aggregate = 1:1·5:3, cured 1 day
Yoon *et al.* [20]	10 kHz–1 MHz	20–30	OPC (Korea), w/c = 0·4, hydrated 2 hours, measured at 0 to −30°C
Olp *et al.* [21]	1 MHz–300 MHz	40–360, increase with hydration time	Type I Portland cement, w/c = 0·45 to 0·60, hydrated up to 24 hours
Al-Qadi *et al.* [22]	1 MHz–100 MHz	6–300	Type I Portland cement, w/c = 0·35 to 0·55, hydrated up to 28 days
McCarter *et al.* [23–26]	1 kHz	~10^6 and decreases with hydration time	OPC, w/c = 0·3 to 0·5, hydrated up to 24 hours
Taylor *et al.* [27]	10 MHz–50 MHz	65–115	OPC, w/c = 0·35, hydrated up to 52 hours
Wittmann *et al.* [28]	8·5 GHz–12·3 GHz	30–10	OPC, w/c = 0·4, hydrated up to 30 days
Coverdale *et al.* [29]	Low frequency ($? < f < 3$ MHz)	(a) 90 000 to 4000 (b) 4000 to 12 000	(a) OPC, w/c = 0·4, hydrated up to 120 hours (b) OPC, w/c = 0·2 to 1·0, hydrated 11 months

dielectric constant value of hydrated cement paste varies indirectly with original water/cement ratio and silica fume content.

Experimental procedures

Materials

Type 10 Portland cement was used. The chemical composition (mass %) is as follows: $SiO_2 = 19{\cdot}83$; $CaO = 61{\cdot}21$; $Fe_2O_3 = 3{\cdot}20$; $Al_2O_3 = 4{\cdot}18$; $MgO = 4{\cdot}09$; $SO_3 = 3{\cdot}93$; $Na_2O = 0{\cdot}45$ and $K_2O = 0{\cdot}82$. The silica fume was obtained from the SKW Co., Montreal, Quebec. Fresh cement was mixed at various water/cement ratios from 0·3 to 0·7. Paste samples containing silica fume were also studied, added to the cement in amounts ranging from 0 to 25% by mass. The water/solid ratio was 0·3. All the specimens were cast in cylindrical moulds, 3 cm diameter × 6 cm and cured in a 100% relative humidity environment for 24 hours and subsequently immersed in a saturated lime solution for 1 year. Cement paste samples were sliced to form 3 mm thick discs. They were tested under two conditions; first, under a water-saturated (surface free water was removed before each dielectric measurement) condition; second, after 24 hours vacuum drying.

Instrumentation

An HP 4291A RF Impedance/Material Analyser equipped with an HP 16453A Dielectric Material Test Fixture was used for dielectric measurements. Equipment and test fixture calibrations were carried out before each experiment. Data were collected using a frequency scan ranging from 1 MHz to 1·5 GHz at 22°C. Total porosity values of the hydrated cement pastes were determined by mercury intrusion porosimetry at pressures up to 408 Mpa, using an American Instrument Co. porosimeter. Porosity values based on mercury intrusion approximate capillary porosity values and do not include C–S–H gel pore space.

Evaporable and chemically combined water

The evaporable water content was determined by mass loss of cement paste vacuum heated at 105°C for 24 hours. The chemically combined water was determined by the mass loss between 105°C and 1000°C. The data was normalized on the basis of the cement content in the sample.

Results and discussion

Dielectric behaviour of hardened cement pastes

Water-saturated pastes. Plots of relative dielectric constant (ε_r) and dissipation factor ($\tan\delta = \varepsilon''/\varepsilon'$) versus frequency for water-saturated hardened Portland cement pastes prepared at various water/cement ratios are given in Fig. 1(a) and 1(b), respectively. The values of ε_r decrease rapidly at frequencies ranging from 1 to 200 MHz, then at a much slower rate as the frequency increases beyond 200 MHz. The water/cement ratio appears to have an effect on ε_r. The curves for

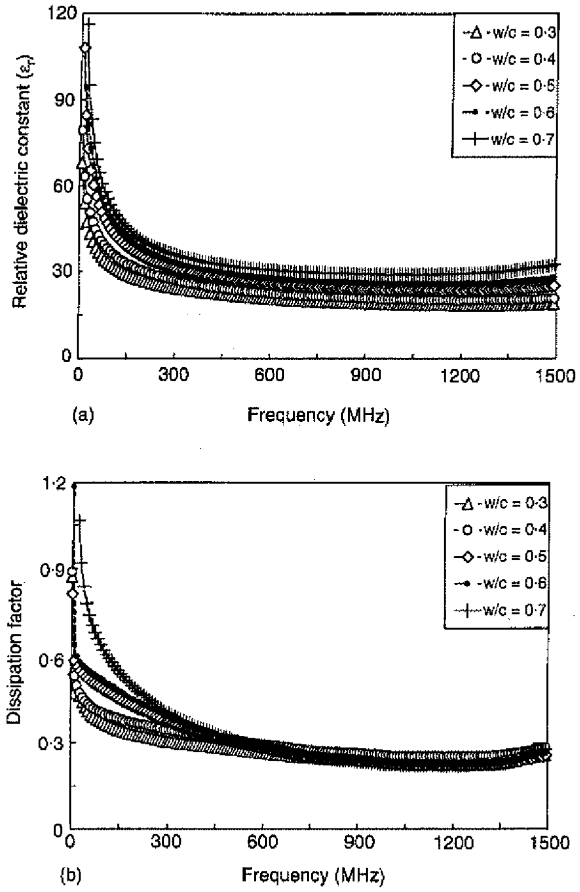

Fig. 1. Plots of dielectric parameters versus frequency for one-year-old water-saturated hardened cement pastes prepared at various water/cement ratios ranging from 0·3 to 0·7: (a) relative dielectric constant (ε_r); (b) dissipation factor ($\tan\delta = \varepsilon''/\varepsilon'$)

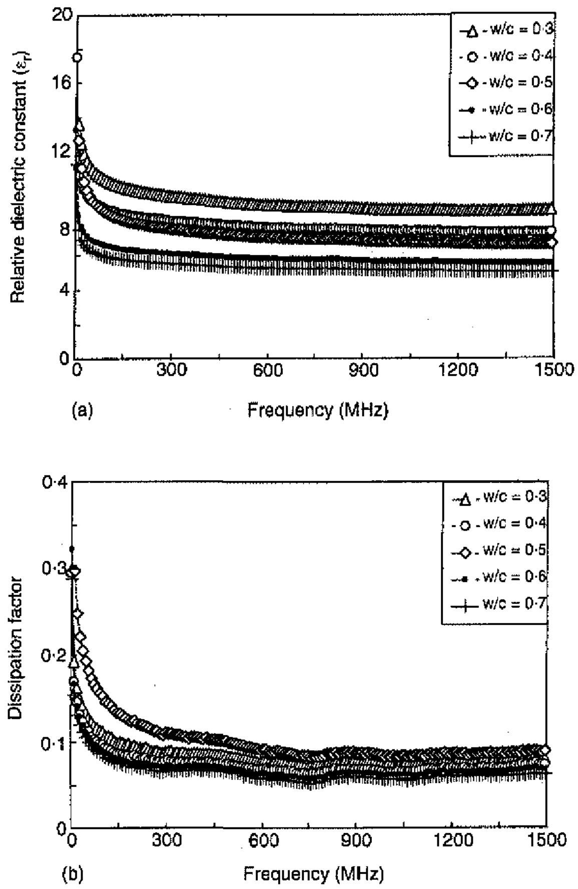

Fig. 2. Plots of dielectric parameters versus frequency for one-year-old vacuum-dried hardened cement pastes prepared at various water/cement ratios ranging from 0·3 to 0·7: (a) relative dielectric constant (ε_r); (b) dissipation factor ($\tan\delta = \varepsilon''/\varepsilon'$)

dissipation factor also decrease slightly with increase of frequency. The effect on dissipation factor of water/cement ratio is only detectable in the frequency range 1–400 MHz.

Vacuum-dried pastes. Similar plots of the dielectric data for vacuum-dried pastes are given in Fig. 2(a) and 2(b). The ε_r curves decline rapidly at frequencies 1–50 MHz. Relatively constant values of ε_r, about 5–10 depending on water/cement ratio, were observed as the frequency increased beyond 100 MHz. The dissipation factors are relatively low. They also decrease slightly with an increase in frequency from 1 MHz to 50 MHz.

Water-saturated pastes containing silica fume. The curves of relative dielectric constant and dissipation factor versus frequency for pastes containing silica fume ranging from 6% to 25% by mass of cementitious solids are very similar to those of pure cement paste systems (Fig. 3(a) and 3(b)). The values of dielectric constant for pastes containing silica fume are slightly smaller than those of pure cement paste at the same frequency. The higher the percentage of silica fume, the smaller is the relative dielectric constant except for pastes containing 20% and 25% silica fume.

Relative dielectric constant values, recorded at various frequencies, for vacuum-dried and water-saturated cement pastes, and pastes containing silica fume is given in Table 2. Examination of the data indicates the following:

(i) The values of dielectric constant, ε_r, and dissipation factor, $\tan\delta$, for water-saturated pastes are larger than those for vacuum-dried pastes.
(ii) Water/cement ratio has a larger effect on both the dielectric constant, ε_r, and dissipation factor, $\tan\delta$, in water-saturated pastes than in vacuum-dried pastes.
(iii) Higher water/cement ratio preparations have larger dielectric constant values for water-saturated specimens. Lower water/cement ratio preparations have larger dielectric constant values for vacuum-dried specimens.
(iv) The values of dielectric constant, ε_r, for pastes containing silica fume are slightly smaller than those for pure cement paste prepared at the same water/cement ratio. Paste with 15% silica

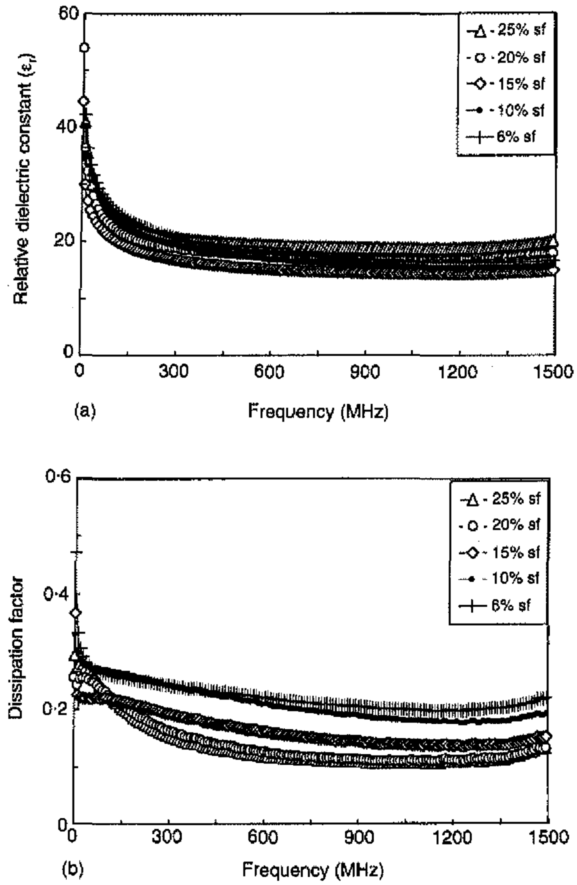

Fig. 3. Plots of dielectric parameters versus frequency for one-year-old water-saturated hardened cement pastes containing 6 to 25% silica fume at a water/cement ratio of 0·3: (a) relative dielectric constant (ε_r); (b) dissipation factor ($\tan\delta = \varepsilon''/\varepsilon'$)

fume addition has the smallest value of ε_r. A slight increase of ε_r was observed for paste containing 20% and 25% silica fume.

Evaporable and chemically combined water

The water content in the pastes is usually described by the term 'evaporable water', which is defined as the sum of the capillary water and adsorbed or intercalate water between C–S–H layers. The evaporable water can be easily determined from the mass loss of the paste vacuum dried at 105°C for 24 hours. The water content or evaporable water in the pastes appears to have an important contribution to the ε_r values. Figure 4(a) is a plot of the dielectric constant (ε_r) versus evaporable water (g/g of cement). The water saturated pastes prepared at higher water/cement ratios give rise to larger ε_r values. This is because pastes prepared at high original water/cement ratio have high porosity values. They contain more evaporable water including adsorbed water and intercalate water between C–S–H layers in the water-saturated condition than pastes prepared at low water/cement ratio (Fig. 4(b)). It is apparent that evaporable water is the main contributor to the dielectric constant reading since chemisorbed or chemically bonded water molecules may fail to follow the alternating field in the frequency range investigated (i.e. 1 MHz–1·5 GHz). The lower ε_r values for pastes prepared at low water/cement ratio and pastes containing silica fume additive can also be explained on this basis.

The ε_r data recorded for vacuum-dried pastes at various frequencies is plotted against the original water/cement ratio in Fig. 5(a): linear behaviour was observed. The regression coefficients are 0·97–0·99 for all curves. In contrast to water-saturated pastes, the values of ε_r decrease as the water/cement ratio increases. It appears that the chemically bound water (in C–S–H and $Ca(OH)_2$) is not the sole contributor to the paste dielectric property since the chemically bound water increases with increase of water/cement ratio as indicated in Fig. 5(b). It is suggested that the dielectric constant of C–S–H is lower than that of unhydrated cement. Further experiments will be carried out to clarify this point.

Effect of porosity

It has been reported that the measurement of dielectric constant can provide information on the water-filled porosity of sedimentary rocks without water conductivity data if high frequency (normally in the GHz range) is utilized.[30] An approximate relation between the real part of the effective dielectric constant, ε'_e, and porosity, P, suggested by Sen *et al.*,[31] can be applied to a water saturated cement paste system as expressed below:

$$\varepsilon'_e = 1{\cdot}5\varepsilon'_{cp} + P^{1{\cdot}5}(\varepsilon'_w - 1{\cdot}5\varepsilon'_{cp}) \qquad (1)$$

where ε'_w and ε'_{cp} are the real part of dielectric constants of water and cement paste solids. The d.c. limit given by Equation (1) holds at low frequencies for which the inequalities $\sigma_w \gg \omega\varepsilon_o(\varepsilon'_w - \varepsilon'_{cp})$ and $\sigma_e \gg \omega\varepsilon_o(\varepsilon'_e - \varepsilon'_{cp})$ are satisfied. The terms σ_w and σ_e are the conductivities of water and water saturated cement paste, and follow Archie's Law ($\sigma_e = \sigma_w P^{1{\cdot}5}$). A plot of ε'_e versus $P^{1{\cdot}5}$ produces a linear relationship with the intercept $1{\cdot}5\varepsilon'_{cp}$ and slope ($\varepsilon'_w - 1{\cdot}5\varepsilon'_{cp}$). The experimental ε'_e data obtained from water-saturated pastes versus the porosity term $P^{1{\cdot}5}$ are plotted in Fig. 6. Linear curves predicted from Equation (1) were obtained. The values of the intercepts and slopes are listed in Table 3.

The calculated dielectric constant value for cement paste is about 11 (the imaginary part of the dielectric constant is negligible). This is close to those values obtained from the vacuum dried samples (6–11). The slight difference may be due to the intercalate water between C–S–H layers. The values of ε'_w (63 and 79) are also quite close to 80, the value for pure water. The relatively good agreement suggests that Equation (1) is applicable to cement paste systems.

Table 2. Values of dielectric constant, ε_r, of vacuum-dried and water-saturated hardened Portland cement pastes and pastes containing silica fume

Values of relative dielectric constant, ε_r, for water-saturated hardened OPC pastes						
w/c ratio	54 MHz	100 MHz	200 MHz	300 MHz	500 MHz	1 GHz
0·3	38·37	32·41	27·08	24·52	21·59	18·78
0·4	44·43	37·04	30·25	27·04	23·44	20·25
0·5	56·35	44·97	35·11	30·90	26·80	23·72
0·6	62·43	49·29	37·99	33·24	28·89	25·84
0·7	69·14	53·33	40·91	36·05	31·72	28·97
Values of relative dielectric constant, ε_r, for vacuum-dried hardened OPC pastes						
0·3	10·97	10·35	9·77	9·46	9·09	8·68
0·4	9·14	8·69	8·27	8·04	7·73	7·40
0·5	9·18	8·46	7·38	7·54	7·17	6·78
0·6	6·88	6·56	6·25	6·10	5·87	5·63
0·7	6·20	5·92	5·67	5·52	5·33	5·12

Values of relative dielectric constant, ε_r, for water-saturated hardened Portland cement pastes containing various amounts of silica fume. w/c ratio = 0·3

Silica fume (%)	54 MHz	100 MHz	200 MHz	300 MHz	500 MHz	1 GHz
6	29·32	25·94	22·55	20·74	18·61	16·49
10	28·03	24·54	21·09	18·26	17·29	15·54
15	22·81	20·44	18·01	16·76	15·43	14·33
20	25·70	22·56	19·89	18·75	17·69	16·86
25	27·95	24·52	21·80	20·70	19·64	18·80

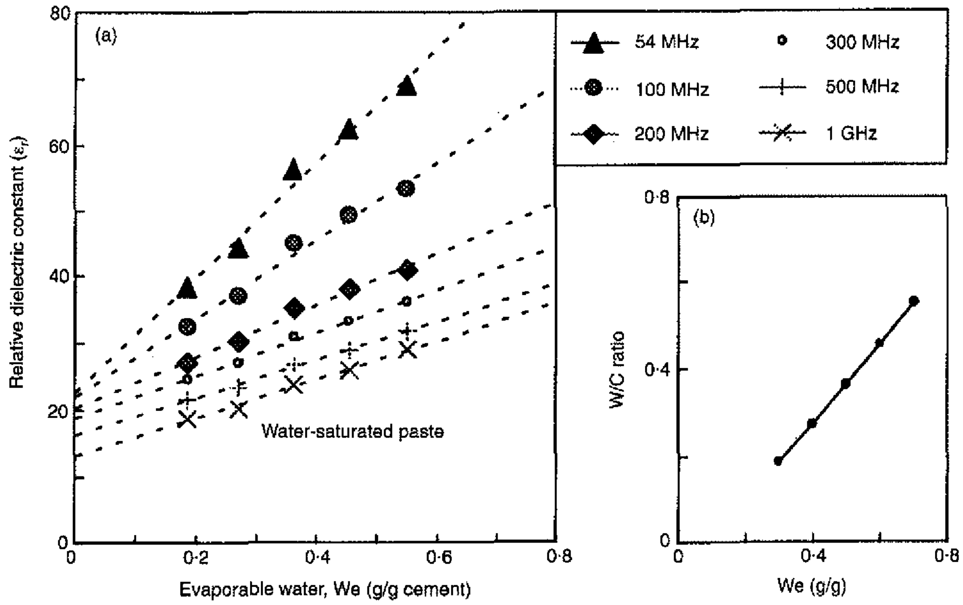

Fig. 4. Plot of (a) dielectric constant (ε_r) versus evaporable water content (g/g of cement); and (b) water/cement ratio versus evaporable water content (g/g of cement) in the water-saturated condition

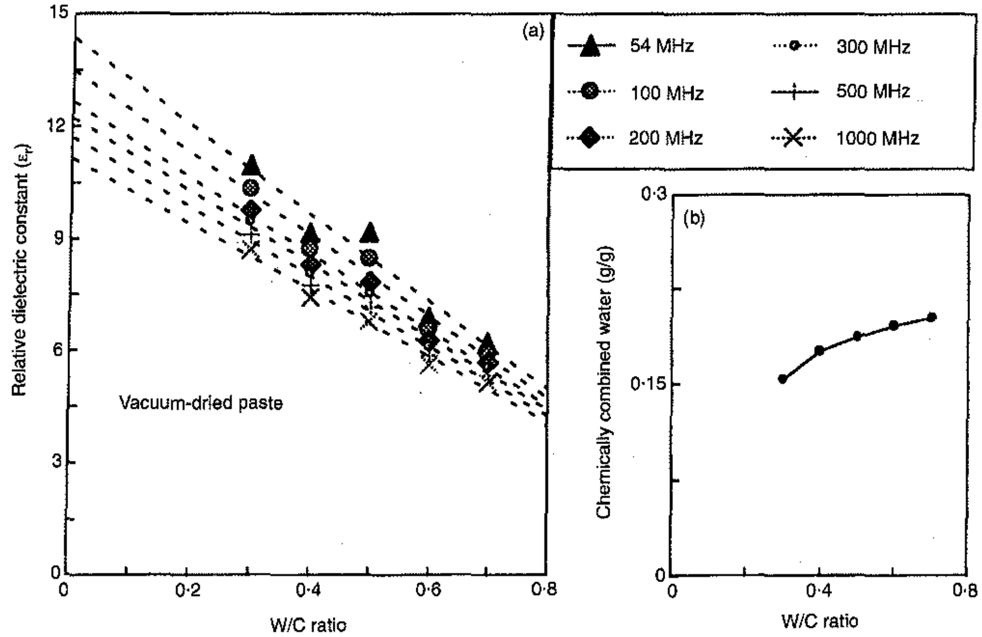

Fig. 5. Plot of (a) dielectric constant (ε_r) versus the original water/cement ratio; and (b) water/cement ratio versus the chemically combined water content (g/g of cement)

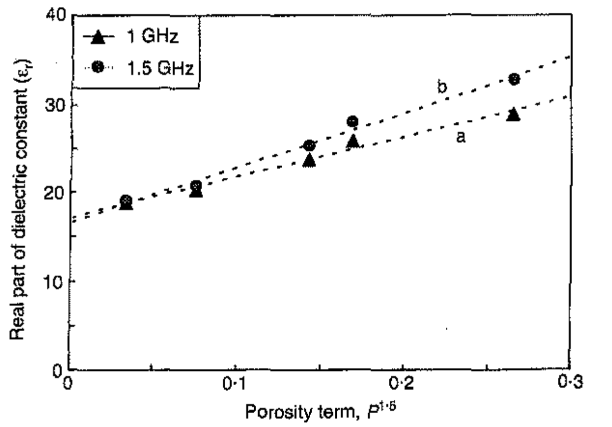

Fig. 6. Plot of the effective dielectric constant, ε'_e, obtained for water saturated pastes versus the porosity term, $P^{1.5}$

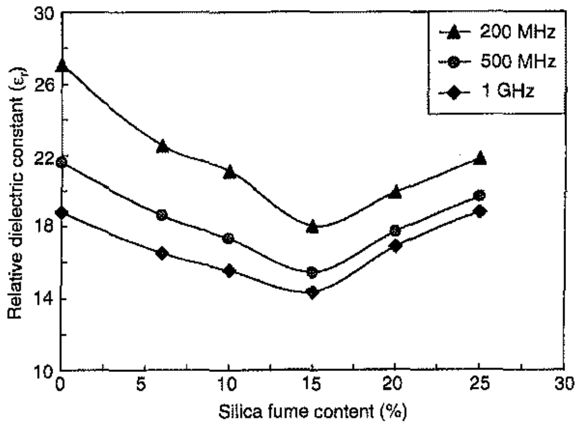

Fig. 7. Plots of relative dielectric constant (ε_r) versus silica fume content of cement paste at frequencies of 200 MHz, 500 MHz and 1 Ghz. The water/solid ratio was 0·3

Table 3. Intercept and slope values for the curves of Fig. 6

Curve	Intercept	Slope	ε'_{cp}	ε'_w
a	17·2	45·9	11·5	63·2
b	16·6	62·3	11·1	79·0

Effect of water/cement ratio and silica fume content

A plot of ε_r versus silica fume content at frequencies of 200 MHz, 500 MHz and 1 GHz is shown in Fig. 7. The value of ε_r decreases as silica fume content increases to about 15% then recovers slightly. This phenomenon can be attributed to the densification effect of silica fume. Ultra-fine silica fume particles fill the space between cement grains and react with $Ca(OH)_2$ to form C–S–H gel with a lower Ca/Si ratio. Thus porosity and pore size are reduced by hydration and pozzolanic reaction. The pore population contains a greater population of fine pores at the same total porosity. This results in a lower value of dielectric constant. This effect was also observed in impedance studies of cement–silica fume compressed systems. The impedance increased with silica fume content up to 15% and decreased at 20% and 25% (Fig. 8). This may reflect changes to the

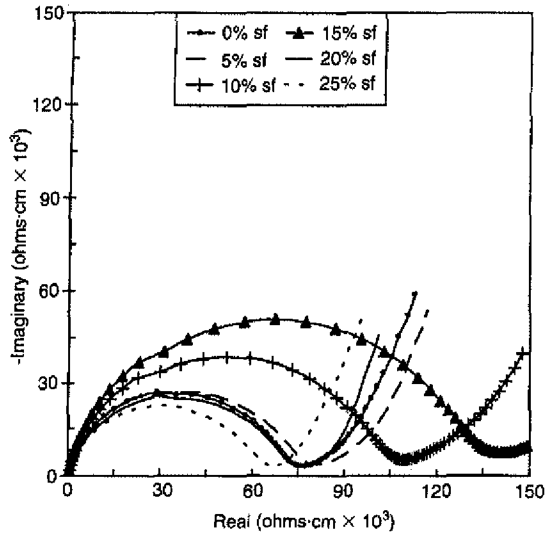

Fig. 8. The high frequency impedance semicircles of low porosity cement–silica fume system compressed at 300 MPa (w/s = 0·09)

paste microstructure at high dosages of silica fume. The excess silica fume is considered to be inert material due to the absence of sufficient $Ca(OH)_2$ reactant in the cement paste. In this case, the microstructure of the system is more porous than that at the optimum addition. This evidence is compatible with mechanical property and durability data reported elsewhere.[32]

Conclusions

Dielectric constant values for hardened Portland cement pastes in the RF range show a rapid decrease in the interval 1 MHz to 100 MHz. They reach relatively constant values at higher frequencies. The values of dielectric constant and dissipation factor for water-saturated pastes are larger than those for vacuum-dried pastes. The value of dielectric constant is water content dependent.

The approximate relation $\varepsilon'_e = 1{\cdot}5\varepsilon'_{cp} + P^{1{\cdot}5}(\varepsilon'_w - 1{\cdot}5\varepsilon'_{cp})$ was tested for hydrated Portland cement pastes. The good agreement suggests that the equation is applicable to cement paste systems.

Larger dielectric constant values are associated with larger amounts of evaporable water in the water-saturated cement pastes. A linear relationship between dielectric constant and evaporable water was obtained for water-saturated cement pastes. The addition of silica fume particles fills the space between cement grains and reduces the porosity and pore size of the paste. This can result in a lower volume of capillary water (free water) and smaller dielectric constant values.

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Discussion contributions on this paper should reach the editor by 28 July 1997.