

The electrical response characteristics of setting cement paste*

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Regarding the estimated values of ϵ_r for the material, a value of 10^6 would seem to be very high, even considering polarization or non-homogeneous Maxwell-Wagner effects, when it is considered that the relative permittivity of water is only 80.

Whilst an a.c. bridge measurement gives the results for a parallel configuration of C and R , this does not imply that the physical configuration is either a series or a parallel combination. For a given electrical admittance, the two configurations are interchangeable at any one frequency. Consider series and parallel configurations (Figure I). For equivalence, the electrical admittances must be equal at any particular frequency.

$$Y_p = \frac{1}{R_p} + j\omega C_p$$

and

$$Y_s = \frac{1}{R_s + \frac{1}{j\omega C_s}}$$

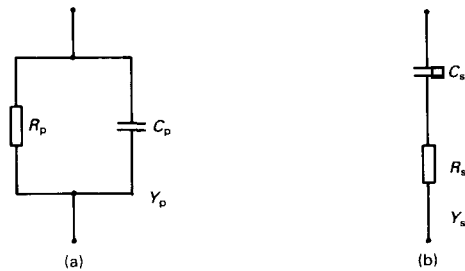
Equating these admittance values and separating real and imaginary parts gives:

$$R_p = \frac{1 + \omega^2 C_s^2 R_s^2}{\omega^2 C_s^2 R_s}$$

and

$$C_p = \frac{C_s}{1 + \omega^2 C_s^2 R_s^2}$$

where $\omega = 2\pi f$;
 $f = \text{frequency (Hz)}$.



(a) Parallel configuration

(b) Series configuration

Figure I: Electrical configuration.

Since C_s is generally very large, at higher frequencies

$$R_p = R_s$$

and

$$C_p = \frac{1}{\omega^2 C_s R_s^2}$$

Thus, if physically the circuit is a series circuit, C_p can be expected to decrease if f is increased.

Although the circuits are equivalent to any one frequency, over a range of frequencies, their performances are completely different and, in particular, if a square waveform is applied to the circuit of Figure II then, if the actual circuit is a series combination,

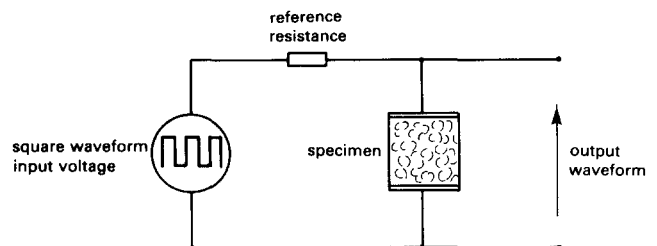


Figure II: Test circuit.

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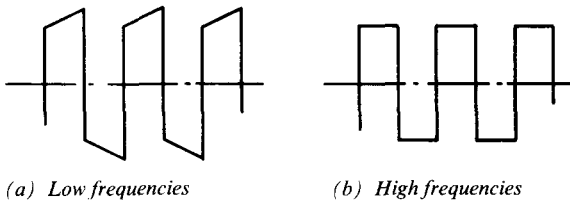


Figure III: Output waveforms: series circuit.

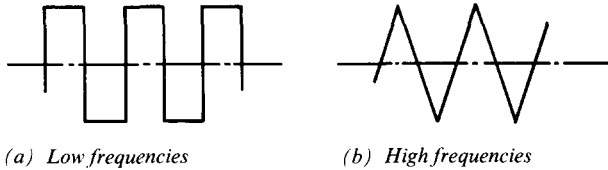


Figure IV: Output waveforms: parallel circuit.

the output waveform can be expected to follow the pattern of Figure III whereas, if the actual circuit is a parallel circuit, the output waveform will follow the pattern of Figure IV.

In experiments we have carried out⁽¹⁾ over the frequency range 2 Hz to 2 kHz, the waveform pattern for the series configuration is obtained.

We believe that the high value of series capacitance is due to the formation of a layer of gas at the electrodes because of electrolytic action. This gas layer will be of molecular thickness and, despite a relative

permittivity of approximately 1, will result in a high value of capacitance because of its very small thickness. The value of capacitance also depends on area, and in this case the area will be the effective value for conduction A . Thus:

$$C_s \propto A$$

$$R_s = R_p \propto \frac{1}{A}$$

and

$$C_p \propto \frac{1}{C_s R_s^2} \propto A$$

Thus, for either the effective series or the parallel values of capacitance, the capacitance can be expected to fall as hydration progresses and the effective area for conduction, which is determined by free water paths, is reduced. This must also result in an increase in measured resistivity.

Although the relatively high value of capacitance can be explained in terms of a gas layer, the bulk material will still have a relative permittivity value associated with it. This value will, however, only become apparent at higher frequencies. Measurements carried out by ourselves and other workers^(2,3) suggest values in the range 50–100 at high frequencies for concrete and cement paste.

Reply by the authors

Mr Wilson and Dr Whittington's contribution on our paper is appreciated and we would comment on the main points raised as follows.

(1) With regard to the series or parallel electrical models, both models are interchangeable; in other words, the equivalent parallel model can be calculated from the series values of C_s and R_s and vice versa. We have checked this to be the case in practice, as the component bridge we are using (Wayne Kerr B905) can give capacitive and resistive values for both models. The reason we have chosen the parallel model is that we are regarding the cement paste as a 'lossy dielectric', where there is not only a polarization current (quadrature component) but also a leakage of current through the resistive element (in-phase component).

(2) In measurements on electrolytic solutions the phenomenon of electrode polarization can be regarded as a piling-up of ions at the electrodes when a direct current is passed through the system. The same effect occurs with alternating current if the frequency is low enough to allow ions to concentrate at

the electrodes during each half-cycle. It can be shown theoretically that, if electrode polarization is the only factor contributing to polarization capacity, the capacitance should decrease as the inverse square root of the frequency, i.e. $\propto (\text{frequency})^{-0.5}$. The build-up of ions at the electrodes, without discharge, or the formation of a thin layer of gas would result not only in high dielectric constants for the layer, but also in extremely high resistances for the sample—this resistance being frequency-dependent. The resistance would drop from virtually an infinite value at d.c. (direct current)—as no conduction can take place across the layer of 'gas'—to negligible proportions as the frequency of the applied electrical field increases. In fact, Mr Wilson and Dr Whittington must have noticed such an effect in their low-frequency work⁽¹⁾. If, as they explain, high dielectric constants are due to the formation of a gas layer at the electrodes, then the impedance of their series model would be infinite. For the frequency employed in our work (1000 Hz), we have not found this to be the case for either model—signifying negligible electrode polarization.

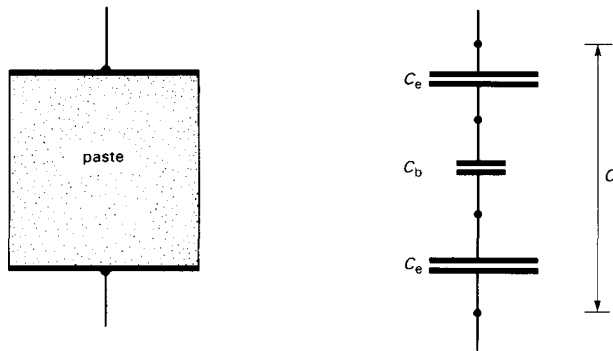


Figure V: Series combination of electrode and bulk capacitances.

(3) The drop in resistance (due to electrode polarization) with increasing frequency would predominate over very low frequencies. A significant drop in resistance with increasing frequency would indicate the existence of electrode polarization effects and a frequency must be reached at which electrode polarization effects become negligible. Work has advanced quite considerably since publication of our paper and we have investigated the effect of varying the frequency of applied electrical field over the range 100 Hz–10 kHz. Over this range we have found negligible change in resistance. If electrode polarization effects did predominate, one would expect noticeable changes in resistance.

(4) Mr Wilson and Dr Whittington claim that electrode polarization effects predominate over bulk effects. If this were the case, the dielectric constant would remain reasonably constant with time, as the capacitance of the 'air-gap' would remain constant. In fact, the variation of dielectric constant with time displays a marked fluctuation, which would suggest that it is the bulk effects (i.e. polarization mechanisms within the cement paste) that are having a considerable influence upon the over-all dielectric constant.

Furthermore if, as Mr Wilson and Dr Whittington suggest, a thin layer of gas is formed at the electrodes then, as they explain, this would result in a very high capacitance value for the layer. This capacitance, C_e , can be visualized as being in series with the bulk capacitance, C_b , of the cement paste (Figure V), the capacitance, C , of the combination being,

$$1/C = 1/C_e + 1/C_b + 1/C_e$$

If C_e (as is suggested) is very much greater than C_b , then $1/C_e$ will be negligible in comparison to $1/C_b$ and thus

$$C \simeq C_b$$

and bulk effects will control the measured capacitance C !

(5) As explained in (3), we have conducted extensive tests over the frequency range 100 Hz–10 KHz. The shapes of the curves (Figure VI) remain more or less the same over this frequency range, with only the

magnitude of the dielectric constants decreasing with increasing frequency (dielectric dispersion). The fall in dielectric constant with increasing frequency is too great to be explained solely by an inverse square root relationship—see (2) above, assuming electrode polarization effects did predominate. This would suggest that other polarization mechanisms are becoming non-operative as the frequency increases—these being associated with the bulk material.

(6) Regarding the high dielectric constants for cement paste in its early hydration stages, it is not unusual for colloidal solutions to have high dielectric constants. Polarization of the double layer⁽⁴⁻⁶⁾ around the cement grain can induce large effective dipole moments and result in high dielectric constants. The values of 50–100 quoted by Mr Wilson and Dr Whittington are for relatively mature concrete specimens at high frequencies; we are concerned with cement paste and mortars in the liquid state and very early stages of hardening at medium frequencies.

(7) Electrode polarization effects are visible when d.c. is applied to an electrolytic solution by the formation of gas bubbles at the electrodes. The formation of gas at the electrodes would not only be visible but also lead to honeycombing of the cement paste in the vicinity of the electrode and virtually zero bond between the electrode and the cement paste prism. No such physical evidence of these features has been found.

In conclusion, whilst we accept that electrode polarization effects do occur with d.c. and periodically reversed d.c., they are considerably reduced as frequency increases and have virtually been reduced to zero for frequencies in excess of about 50 Hz. The fluctuations in dielectric constant are attributable to polarization mechanisms within the bulk material. Both parallel and series models are interchangeable over the frequency range 100 Hz–10 kHz for the cement paste during the early stages of hydration and agree well with the simplified form of the equations:

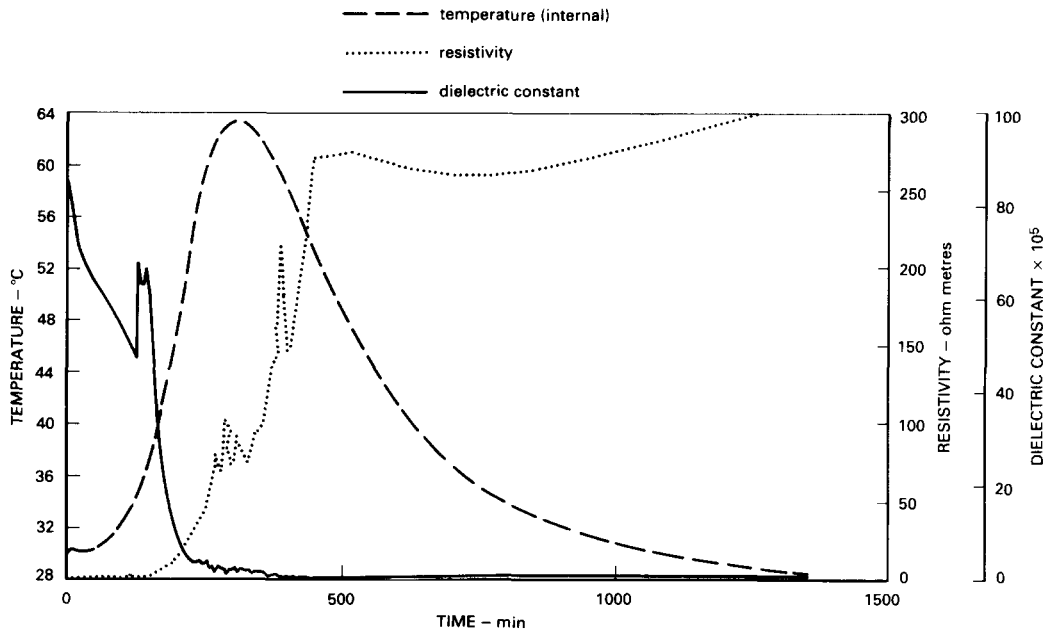
$$R_s \simeq R_p$$

and

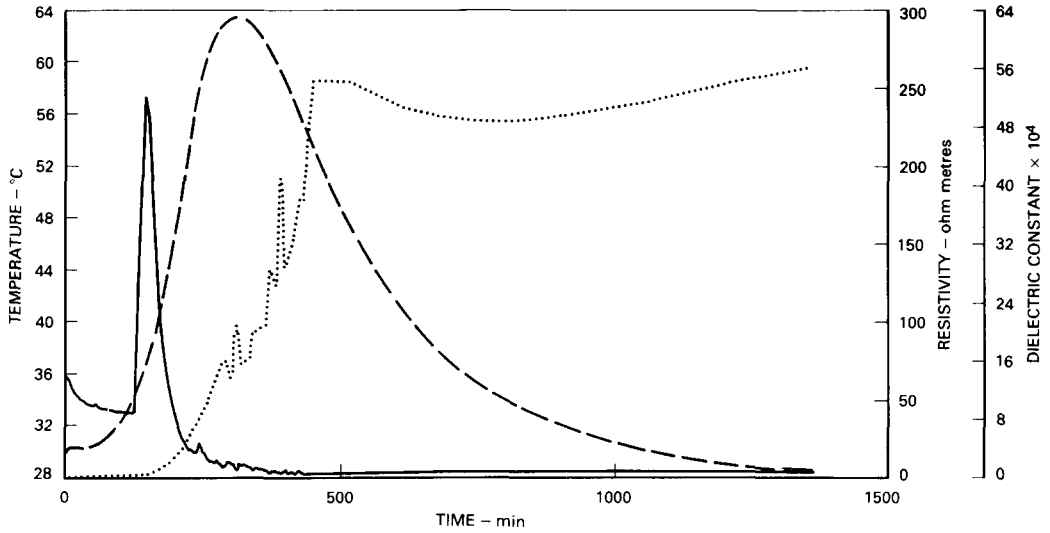
$$C_s \simeq \frac{1}{\omega^2 C_p R_p^2}$$

Experimental and calculated values using these equations are given in Table 1, the values being taken 10 minutes after mixing.

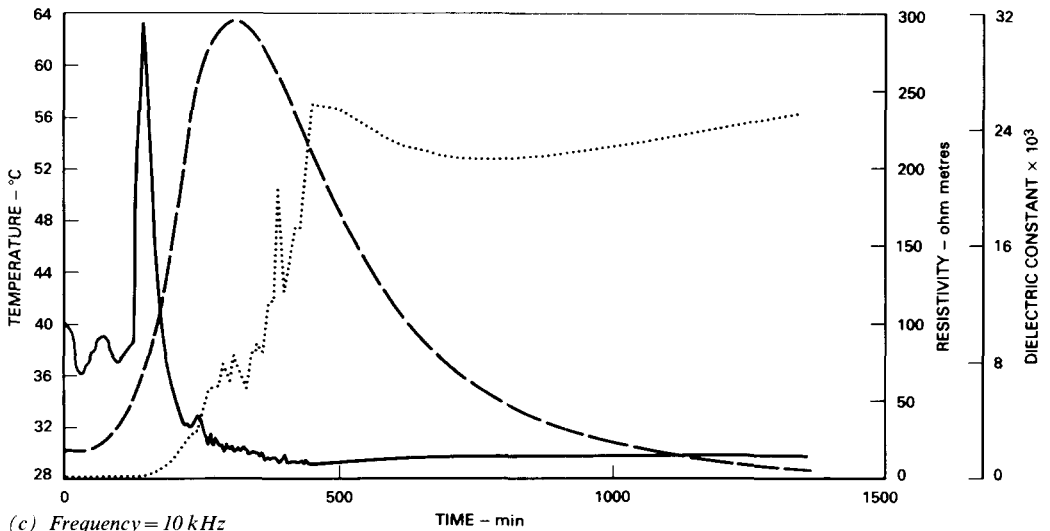
Whilst we also accept that the effective area available for conduction is decreased as the cement grains segment and the capillary pores become blocked, it must be remembered that the resistivity will increase due to a reduction in ionic concentrations within the capillary water due to the hydration process. It would be difficult to quantify the division between these mechanisms.



(a) Frequency = 100 Hz



(b) Frequency = 1 kHz



(c) Frequency = 10 kHz

Figure VI: Variation of temperature, resistivity and dielectric constant during initial 24 h after gauging with water. Ordinary Portland cement paste, w/c = 0.25.

TABLE 1: Calculated and experimental values for series model.

Frequency (Hz)	Parallel model (measured)		Series model (calculated)		Series model (measured)	
	R_p (ohms)	C_p (Farads)	R_s (ohms)	C_s (Farads)	R_s (ohms)	C_s (Farads)
100	9.134	8.25×10^{-6}	9.134	3.67×10^{-3}	9.092	3.707×10^{-3}
400	8.866	696×10^{-9}	8.866	2.90×10^{-3}	8.857	2.914×10^{-3}
1000	8.915	142×10^{-9}	8.915	2.247×10^{-3}	8.905	2.256×10^{-3}
10000	8.861	6.9×10^{-9}	8.861	468×10^{-6}	8.854	460×10^{-6}

REFERENCES

1. WILSON, J. G., WHITTINGTON, H. W. and FORDE, M. C. Microprocessor based system for automatic measurement of concrete resistivity. *Journal of Physics E*. Vol. 16, 1983. pp. 700–705.
2. WILSON, J. G., WHITTINGTON, H. W. and FORDE, M. C. Dielectric properties of concrete at different frequencies. *Proceedings of the Fourth International Conference on Dielectric Materials, Measurements and Applications, Lancaster*. London, Institution of Electrical Engineers, 1984. pp. 157–160.
3. TAYLOR, M. A. and ARULANANDAN, K. Relationships between electrical and physical properties of cement pastes. *Cement and Concrete Research*. Vol. 4, No. 6. November 1974. pp. 881–897.
4. SCHWAN, H. P., SCHWARZ, G., MACZUK, J. and PAULY, H. On the low-frequency dielectric dispersion of colloidal particles in electrolytic solutions. *Journal of Physics and Chemistry*. Vol. 66. 1962. p. 2626.
5. SCHWARZ, G. A theory of the low-frequency dielectric dispersion of colloidal particles in electrolyte solution. *Journal of Physics and Chemistry*. Vol. 66. 1962. p. 2636.
6. HASTED, J. B. *Aqueous dielectrics*. London, Chapman and Hall, 1973. pp. 172–173.