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Impedance spectra of hydrating cement pastes

C. A. SCUDERI, T. O. MASON, H. M. JENNINGS*
*Materials Science and Engineering, and *Civil Engineering, Northwestern University,*
The McCormick School of Engineering and Applied Science, Science and Technology Center
for Advanced Cement-Based Materials, Evanston, IL 60208, USA

Complex impedance spectra were obtained over the frequency range 5 Hz to 13 MHz on Portland cement pastes with water/cement ratios of 0.3, 0.35, and 0.4 at various hydration times from 6 h to 24 days. Features of the spectra which could be associated with the bulk material and which could be separated from the electrode arc, were studied. The overall bulk resistance of each paste was thereby determined as a function of hydration time. Bulk features evolved from a simple high-frequency intercept to an intercept with a single arc, then an intercept with two overlapping arcs, and back to an intercept with a single arc. A plausible equivalent circuit was developed involving an electrode *R/C* network and constant phase element in series with one or two bulk *R/C* networks and a bulk resistor. Possible physical interpretation is discussed but assignment of equivalent circuit elements to microstructural features and/or processes will require microstructural characterization and a knowledge of pore-phase chemistry and properties.

1. Introduction

Despite numerous studies of d.c. or low-frequency a.c. conductance of hydrating cement pastes (see Perez–Pena *et al.* [1] for a review), complex impedance spectra have been obtained for these important materials only recently [2]. This is particularly surprising because cement microstructure, particularly in the latter stages of hydration (a high conductivity pore/water phase embedded in a low-conductivity matrix), should be an ideal candidate for two-phase Maxwell–Wagner modelling of discrete arcs in impedance or admittance spectra (see Bonanos *et al.* [3] for a thorough discussion).

McCarter *et al.* [2] presented preliminary impedance results on Portland cement pastes with a water/cement ratio of 0.3 at 1, 14, and 25 days hydration. Although the clinker composition was given, the electrode and specimens' geometry were not specified. A single arc was obtained in the impedance plane, covering 20 Hz to 110 MHz, with a small detectable "tail" at the lowest frequencies. McCarter *et al.* interpreted the "tail" as indicative of electrode effects and the slightly depressed arc as evidence of Maxwell–Wagner effects in the bulk. In particular, they noted that the bulk resistance, given by the intersection of the arc with the electrode "tail", increased steadily with time, as did the depression of the arc below the real axis. This was attributed to "a spread of relaxation times" as hydration proceeds.

The present study was undertaken to examine more closely the impedance behaviour of cement pastes throughout the hydration process, giving special attention to bulk features of the spectra. Changes in the overall bulk resistance and in the individual bulk features were monitored carefully as a function of hydration time. Equivalent circuit models were developed for each kind of spectrum obtained. It should be possible to correlate these models, and the associated fit parameters, with changes taking place in the evolving microstructure. Impedance spectroscopy should, therefore, prove to be a useful tool in the study of the hydration of cement.

2. Experimental procedure

Portland cement pastes were made from clinker with a Bogue composition of 57% C_3S, 16.5% C_2S, 10.1% C_3A, and 8% C_4AF (where $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, and $F = Fe_2O_3$). Three water/cement ratios (0.3, 0.35, and 0.4) were used. Pastes were hand-mixed for 3 min and then poured into 1.27 cm i.d. × 1.27 cm unpolished stainless steel cylinders on Plexiglass bases. Unpolished stainless steel rods (0.64 cm o.d. by 1.91 cm) were inserted immediately along the centreline of each cylinder until contact was made with the Plexiglass base. The amount of paste was gauged carefully to bring it level with the top of the outer cylinder after the rod had been inserted. After initial setting, approximately 6 h, specimens were free-standing and could be separated from the base for the electrical measurements. Between measurements, specimens were returned to the base and were stored in moist air in a sealed plastic chamber containing excess water.

Electrical contacts to the inner (rod) electrode and the outer (cylinder) electrode were made circumferentially via brass clamps. These were connected via short coaxial leads to an HP-4192A impedance analyser, which was connected to a personal computer that controlled all aspects of data acquisition. Measurements were made in the frequency range 13 MHz to 5 Hz with about 20 readings per decade of frequency.

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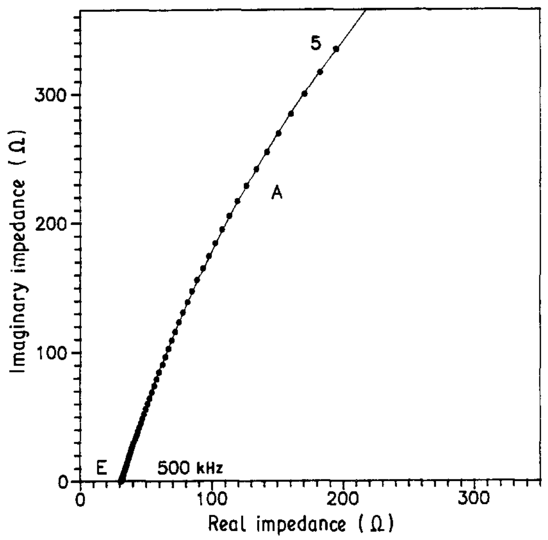

Figure 1 Impedance spectrum at 9 h on a 0.4 water/cement ratio paste over the frequency range 5 Hz to 500 kHz showing the electrode arc (feature "A") and a bulk resistance intercept (feature "E"). No bulk arc is visible. For a description of equivalent circuit elements, see Fig. 6 and the text.

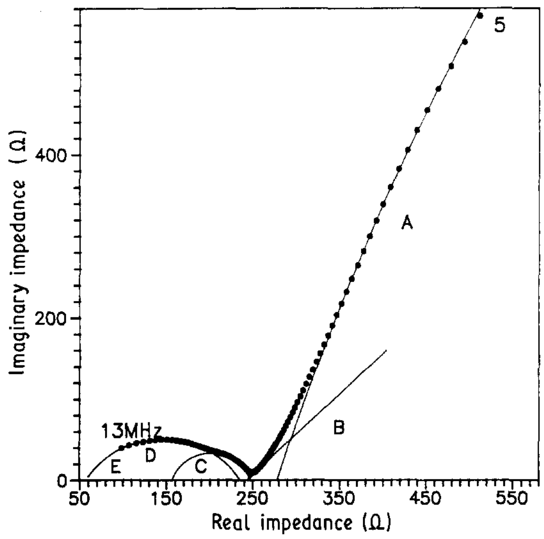

Figure 3 Impedance spectrum at 69 h on a 0.35 water/cement ratio paste over the frequency range 5 Hz to 13 MHz showing electrode features ("A" and "B") and bulk features ("C", "D", and "E"). Two bulk arcs can be discriminated. For a description of equivalent circuit elements see Fig. 6 and the text.

The procedure took less than 5 min. Data were saved to disk as ASCII files which were subsequently analysed via "Equivalent Circuit (EQUIVCRT.PAS)", a commercially available software package for the analysis of complex immitance spectra [4].

3. Results and analysis

The spectra obtained at a water/cement (w/c) ratio of 0.3 compared quite favourably with the results of McCarter *et al.* [2] on 0.3 w/c pastes at equivalent hydration times. It should be pointed out that nearly complete bulk arcs were obtained in the present study without recourse to the higher frequencies employed in their work. We speculate that this is due to differences in specimen geometry, although this requires confirmation. The agreement in bulk resistance between duplicate specimens at each water/cement ratio at any given time was better than 10%.

Representative impedance spectra for 9, 20, 69, and 479 h are given in Figs 1 to 4. As will be argued below, each spectrum consists of a small portion of a large arc which is identified as being due to the electrode (features "A" and "B") at low frequencies (high impedances) and an intercept defined at "E". At long times one or more arcs (features "C" and "D") which are identified as being due to bulk features of the specimen, appear at higher frequencies (lower impedances). The intercept of the electrode arc with the real axis or the minimum between the electrode and bulk arcs is taken as the overall bulk resistance. The values are plotted as a function of time for each of the

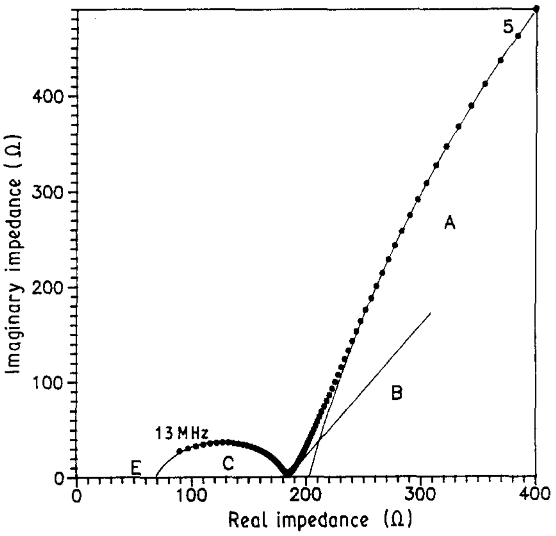

Figure 2 Impedance spectrum at 20 h on a 0.3 water/cement ratio paste over the frequency range 5 Hz to 13 MHz showing electrode features ("A" and "B") and bulk features ("C" and "E"). A single bulk arc is visible. For a description of equivalent circuit elements see Fig. 6 and the text.

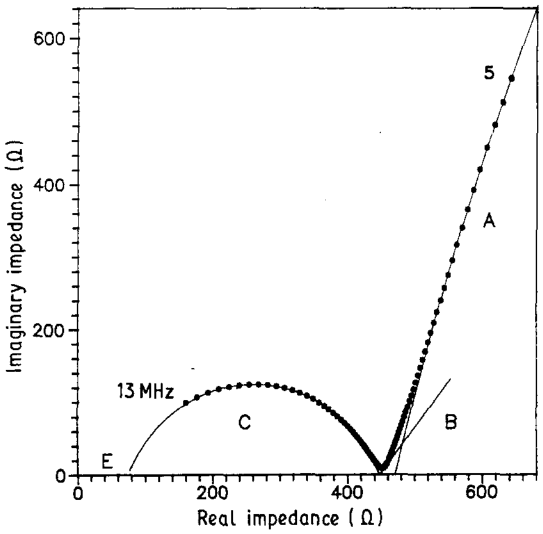

Figure 4 Impedance spectrum at 479 h on a 0.3 water/cement ratio paste over the frequency range 5 Hz to 13 MHz showing electrode features ("A" and "B") and bulk features ("C" and "E"). A single bulk arc is visible. For a description of equivalent circuit elements see Fig. 6 and the text.

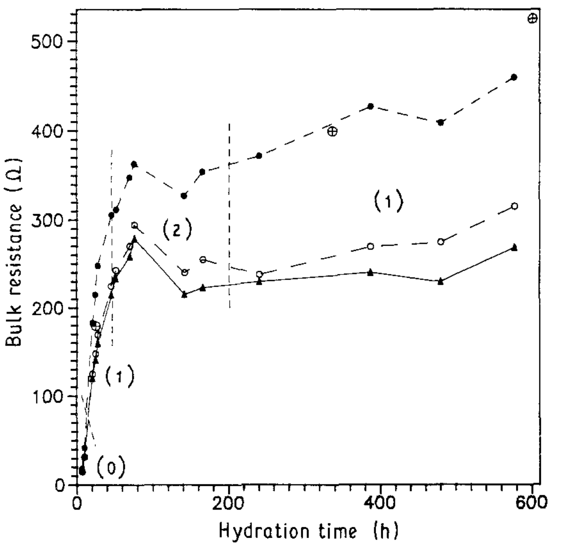

Figure 5 Bulk paste resistance (see text for definition) as a function of hydration time. Transitions in impedance spectra from no bulk arcs to one arc, two arcs, and again one bulk arc are indicated as dashed lines on the plot. The data of McCarter *et al.* [2] for a 0.3 water/cement ratio paste are superimposed on the diagram. w/c = (●) 0.3, (○) 0.35, (▲) 0.4, (⊕) 0.3 [2].

water/cement ratios studied in Fig. 5. The frequencies corresponding to these values are 500 kHz for 9 h, 35.5 kHz for 20 h, and 15.8 kHz for both 69 and 479 h. All these values are typical for spectra within each time period of Fig. 5 and are much larger than the 2 to 4 kHz "cut-off" frequencies which McCarter *et al.* [2] cited for eliminating electrode effects. This shows that the frequency domain for a given process, such as that occurring at an electrode, is a function of the choice of electrode and its geometry. D.c. or single-frequency a.c. measurements must, therefore, be interpreted with caution.

As expected, because the high-conductivity pore/water phase is consumed in the hydration process, the bulk resistance increases with time (Fig. 5). There are, however, some unexpected features. Most of the resistance change (increase) takes place before 75 h. This is followed by a sharp drop between 75 and 140 h, and then an increase gradually to 24 d, the maximum time studied. The rate of increase after 140 h decreases from w/c = 0.3 to 0.35 to 0.4, and is virtually negligible for the 0.4 water/cement ratio. At any given time the difference in resistance between the 0.3 and 0.35 w/c pastes is far greater than the difference in resistance between the 0.35 and 0.4 w/c pastes. The three data points of McCarter *et al.* [2] have been superimposed on Fig. 5. Although the agreement appears to be good, a true comparison cannot be made without a knowledge of their specimen geometry.

Perhaps the most significant finding of this study is a similarity in spectra of all three pastes at various times. At the shortest times (6 and 9 h), only the electrode arc is visible (see Fig. 1); hence this region is marked (0) for "no bulk arcs" in Fig. 5. Between 20 and 50 h, a single bulk arc is obtained in addition to the electrode arc (see Fig. 2); hence the designation (1) on the figure. Between 50 and 165 h, two arcs are detected in the bulk features (see Fig. 3) and this region is indicated as (2) in the figure. Finally, between 240 and 576 h, only a single bulk arc is discernable (see Fig. 4); hence the (1) designation.

EQUIVCRT [4] was employed to develop equivalent circuits and to simulate immittance spectra (impedance, admittance, modulus, etc.) to compare with the spectra in each region of Fig. 5. The best agreement was obtained with the equivalent circuit diagram shown in Fig. 6. From right to left the arcs correspond to the features observed from right to left in the experimental spectra of Figs 1 to 4. (The individual element curves in Figs 1 to 4 are merely a guide to the eye and do not represent the subspectra involved in a best fit.)

Element "A" represents a resistor/capacitor network which is associated with electrode effects. The resistor has a value in the 10^3 to 10^4 Ω range and does not change significantly with time. The capacitor has a value in the 10 to 100 μF range which also does not change significantly with time. This magnitude of capacitance is indicative of an interfacial process [5]. The electrode arc is slightly depressed below the real axis; when fit as a resistor-constant phase element (CPE), the frequency exponent is typically 0.8 to 0.9. (A pure capacitor would have a value of 1.0 – see below.)

The simplest spectrum, obtained at short times, is therefore a combination of a bulk resistor, "E", in series with a resistor/capacitor network representing the electrodes ("A"). Hansson and Hansson [6] interpreted the a.c. response of hydrating cement paste in terms of just such an equivalent circuit.

In the present study, element "B" was added to improve the model results of the electrode arc at its intersection with the bulk arc. This is a constant phase element (CPE), whose impedance can be written [7]

$$Z(\mathrm{CPE}) = A_0^{-1}(j\omega)^{-n} \tag{1}$$

with the frequency exponent n such that $0 \leqslant n \leqslant 1$, and the real and imaginary components of the impedance, $Z = Z' - jZ''$ are

$$Z' = A_0^{-1}\omega^{-n}\cos[(\pi/2)n] \tag{2}$$

and

$$Z'' = A_0^{-1}\omega^{-n}\sin[(\pi/2)n] \tag{3}$$

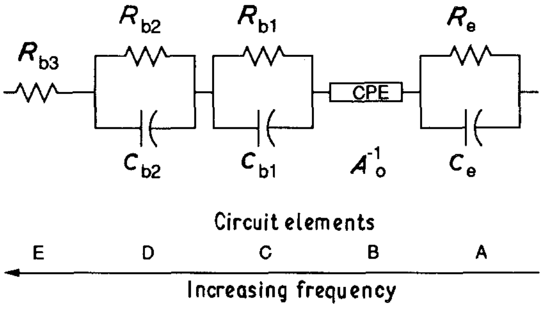

Figure 6 Equivalent circuit model used to fit the various experimental spectra. R_e and C_e are the electrode resistance and capacitance, respectively. A_0^{-1} stands for a diffusional (Warburg) impedance associated with the electrode interface. R_{b1}, R_{b3} and C_{b1}, C_{b3} represent the various bulk resistances and capacitances, respectively. See text for a description of individual elements.

where ω is the angular frequency. (For other definitions, see Fig. 6.) The CPE is a resistor if $n = 0$ ($A_0 = R^{-1}$), a capacitor if $n = 1$ ($A_0 = C$), and a Warburg impedance if $n = 0.5$. In contrast to n values in the range of 0.8 to 0.9 for element "A", indicative of capacitive character, the n values for the CPE (element "B") are close to 0.5. The corresponding A_0^{-1} values are of the order of 10^3 to $10^4\,\Omega$, consistent with Warburg character and most likely associated with some diffusional process at the electrode/paste interface. An excellent description of diffusion-related and constant phase elements is given elsewhere [5].

The remaining two elements, "C" and "D", are clearly associated with bulk phenomena. When a single bulk arc is obtained, as in Figs 2 and 4, the capacitor in the R/C element typically has a value on the order of 10 to 100 nF. When two arcs are discernable, as in Fig. 3, one R/C network has a capacitance in the 10 to 100 nF range whereas the other has a value of the order of 100 pF. These magnitudes are clearly indicative of bulk effects. Bulk arcs appear to be significantly depressed below the real axis (see Figs 2 and 4 – n values of 0.77 and 0.75 were obtained, respectively). When two arcs could be clearly deconvoluted, substantially higher individual n values were obtained. McCarter *et al.* [2] observed that the depression angle of their single bulk arc increased with hydration time. The present results suggest that the interpretation is somewhat more complicated by the presence of additional sub-arcs within the bulk features of the spectra.

Element "E" in the equivalent circuit represents a bulk resistance in series with the other elements. This can be seen as an offset value or the high-frequency intercept with the real axis in each of the spectra in Figs 1 to 4. Except at short reaction times, for which this resistance increases rapidly with time, the value of this resistance remains relatively constant, 60 to 80 Ω, throughout the hydration process.

4. Discussion

Impedance spectroscopy is a powerful tool for the separation of conduction processes in inhomogeneous or multiphase materials. The present study indicates that this technique should provide useful information about hydrating cement pastes, particularly in the later stages (beyond 1 d) of hydration. The corollary to this finding is that d.c. and single-frequency a.c. measurements may not be reliable techniques for studying changes in bulk conductance with time, and that impedance spectroscopy may be necessary to separate out bulk and electrode effects.

It is possible to model the impedance/admittance behaviour of hydrating cement pastes in terms of equivalent circuits such as that shown in Fig. 6. Such a model provides an important means for quantifying the changes in impedance behaviour with time throughout the hydration process. It should also be possible to correlate the equivalent circuit elements with processes and/or elements of the microstructure of hydrating cement pastes, and with changes in structure and properties with time.

At this point, a brief discussion of equivalent circuit redundancy is in order. As pointed out by Boukamp [4], the same impedance spectrum can be explained by a variety of different equivalent circuits. For example, with the proper choice of circuit elements, it can be shown that the two circuits in Fig. 7a and b will yield an identical impedance spectrum. Using subcircuit b instead of subcircuit a (elements "E", "D", and "C" in Fig. 6) in series with the electrode elements "A" and "B", virtually equivalent fits were obtained for experimental spectra involving one or two bulk arcs. To determine which equivalent circuit best represents the actual situation requires additional information, such as can be obtained via *in situ* microstructural characterization.

Although it is not possible at this time to assign significance to individual circuit elements, it may be instructive to review the work of Bonanos and Lilley [8]. They measured complex immittance spectra of NaCl single crystals (low-conductivity matrix) at high temperatures with high-conductivity Suzuki phase precipitates, and obtained results, ignoring electrode effects, not unlike those in the present study. Bonanos and Lilley [8] were able to derive the formal relationships between a Maxwell–Wagner approach involving

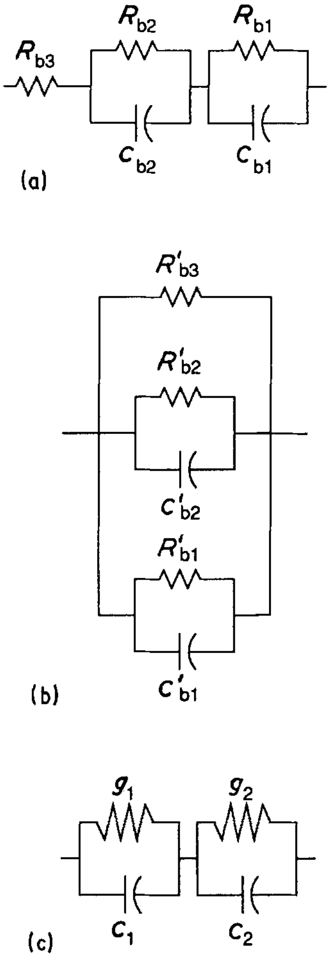

Figure 7 Circuits (a) and (b) yield identical impedance spectra with a proper choice of components. Circuit (c), proposed by Bonanos and Lilley [8], as equivalent to a Maxwell–Wagner model involving a high-conductivity dispersed phase in a less conductive matrix.

a high-conductivity second phase embedded in a low-conductivity matrix (model parameters σ_1, ε_1, σ_2, ε_2, x_1, and x_2, where σ is the conductivity, ε the dielectric constant, and x the volume fraction) and the equivalent circuit in Fig. 7c (model parameters g_1, c_1, g_2, and c_2, where g is the conductance and c the capacitance). The work of Bonanos and Lilley [8] suggests, therefore, that the equivalent circuit of Fig. 6 may be appropriate for hydrating cement pastes.

A second important result of the work by Bonanos and Lilley [8] and emphasized by Bonanos *et al.* [3] is that, depending upon the relative conductances and capacitances for the two elements in circuit shown in Fig. 7c, better resolution of individual arcs could be obtained in either the impedance or the modulus plane. In the present study, not much detail was seen in the modulus spectra; however, nearly equivalent resolution of the two bulk arcs, when observed, was obtained in impedance and admittance plots. We found EQUIVCRT [4] especially versatile in transforming data between the various representations, e.g. impedance, admittance, modulus, etc.

Ongoing work is aimed at correlating the changes observed in the impedance with changes in cement paste microstructure, as observed *in situ* by scanning electron microscopy, and also with changes in pore-phase chemistry and conductivity. Once the basic relationships are understood, it should be possible to conduct a number of studies of cement hydration as functions of composition, water/cement ratio, additives, mixing, second phases, etc.

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