Pergamon

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SCIENCE DIRECT

Cement and Concrete Research 34 (2004) 1837–1843

CEMENT AND CONCRETE RESEARCH

The complex impedance response of fly-ash cements revisited

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Received 22 July 2003; accepted 14 January 2004

Abstract

It has been reported in a previous study [Cem. Concr. Res. 29 (1999) 377; Cem. Concr. Res. 33 (2003) 197] that when a low-lime fly ash is introduced as a cementitious component, there are significant changes in the electrical response of the system, most notably, an enhancement in dielectric constant and the emergence of a plateau region in the complex plane. The changes in electrical behaviour were attributed to the spherical nature of the fly-ash particle, resulting in an enhancement in the double-layer polarization effects on the particle surface. In this paper, data are presented for three low-lime ashes, each displaying differences in their electrical behaviour. Through a systematic series of tests, a new interpretation for the origin of the characteristic electrical response is presented.

Keywords: Characterization; Electrical properties; Fly ash; Mortar; Loss on ignition

1. Introduction

The electrical impedance of ordinary Portland cement (OPC) pastes, mortars and concretes, in both the fresh (i.e., liquid) and hardened states, is now well documented. With reference to the schematic shown in Fig. 1(a), the complex impedance response comprises two distinct regions—the electrode response forming the right-hand side of the plot and the bulk (sample) response forming the left-hand side. The frequency increases from right to left across the plot, and the bulk resistance, *R*, of the system is obtained at the cusp between the electrode and bulk arcs. We have reported in a previous study [1,2] that when a low-lime fly ash is introduced as a cementitious component, there are changes in the complex response of the system. Fig. 1(b) presents a schematic of the complex impedance response of a system with fly-ash replacement. The following changes in the response have been noted:

(i) The two regions noted above, in relation to the plain OPC response in Fig. 1(a), become separated by the emergence of a plateau region, creating an impedance response, which is now characterized by three distinct zones: the electrode response, a *plateau* region due to the inclusion of fly ash and a high-frequency arc. As the level of replacement increases, the extent of the plateau region increases [1].

(ii) The addition of fly ash results in a displacement of the complex plot to right; that is, the system becomes more resistive due to the inclusion of fly ash.

We had previously postulated that the plateau region was due to the spherical nature of the fly-ash particle, resulting in an enhancement in double-layer polarization effects on the grain surface. In this paper, we present a new explanation for the origins of this feature based on a systematic series of experiments.

2. Experimental

2.1. Materials and sample preparation

A BSEN 196-1[3] mortar was used as a benchmark. This mortar had a composition of one part binder, three parts sand and a water/binder ratio = 0.5. A standard siliceous reference sand (BSEN 196-1: Section 5.1.2) was used, and the binder comprised of ordinary Portland cement and OPC partially replaced with fly ash (33% by mass). The OPC conformed to the BSEN 197-1 (CEM I

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doi:10.1016/j.cemconres.2004.01.013

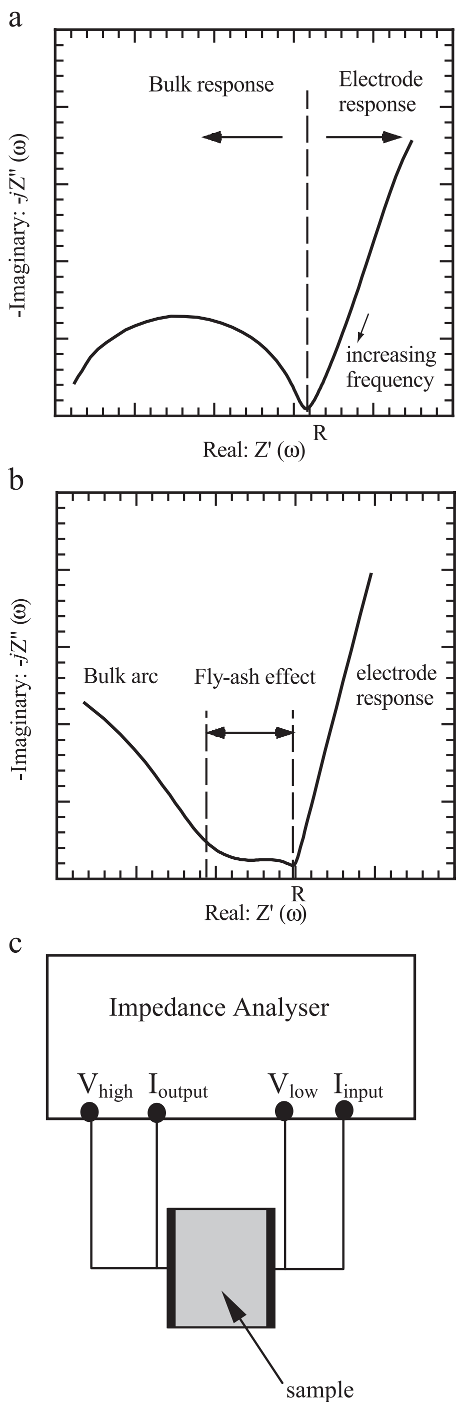

Fig. 1. Schematic diagram of (a) the impedance response of a plain Portland cement system, (b) a system with Portland cement partially replaced by fly ash and (c) experimental testing arrangement.

42.5N) [4]. The fly ashes used in the study are presented in Table 1.

The mortar mixtures tested are given in Table 2. The materials were initially dry-mixed in a Hobart planetary motion mixer for 2 min; distilled water was then added, and mixing continued for a further 5 min. The samples were compacted into rigid perspex cells for electrical measurements and are detailed below. Once compacted in the cell, the top surface of the sample was smoothed and covered with a small sheet of perspex.

Table 1
Oxide analysis and fineness of ashes used within the experimental programme

ASH	L	B	E
Fineness (% retained on 45 μm)	8.0	9.5	11.6
Oxide%			
SiO_2	51.0	50.5	54.3
Al_2O_3	27.4	24.7	24.7
Fe_2O_3	4.6	7.4	9.2
CaO	3.4	2.6	5.9
MgO	1.4	1.5	1.9
SO_3	0.7	0.8	0.69
TiO_2	1.6	1.0	1.4
K_2O	1.0	3.0	1.7
Na_2O	0.2	0.8	0.6
LOI	5.5	5.3	1.9

2.2. Electrical measurements and test cells

The test cells were of internal dimensions 50 × 50 × 50 mm. Stainless-steel electrodes with dimensions of 50 × 50 × 3 mm (thick) were attached to two opposite faces of the cell. Stainless-steel connections were passed through the cell walls and secured to the electrodes. All impedance measurements were acquired using the Solartron 1260 impedance analyser, operating in voltage-drive mode, with the signal voltage being 100 mV. A logarithmic sweep over the frequency range 1 Hz–1 MHz was used with the data, recorded at 20 frequency points per decade within this range. The connection to the impedance analyser was by means of short, individually screened coaxial cables to the voltage (V), high/low and current (I) output/input terminals

Table 2
Mix proportions (by mass) used in the experimental programme

	OPC	Fly ash	Sand	w/b[a]	Glass spheres	Carbon	Comments
Mix 1	1	–	3	0.5	–	–	
Mix 2	0.77	0.33	3	0.5	–	–	
Mix 3	–	1	3	0.5[+]	–	–	
Mix 4	–	–	3	0.5[+]	1	–	The w/b ratio is based on the mass of the glass spheres.
Mix 5	–	1	3	0.5[+]	–	–	Carbon removed from ash.
Mix 6	–	1	3	0.5[+]	–	0.06	Carbon removed from ash.
Mix 7	–	–	3	0.5[+]	1	0.06	The w/b ratio is based on the mass of the glass spheres.

[a] w/b=(mass of water)/(mass of OPC + fly ash).
[+] Gauging water had similar electrical conductivity with pore water in Mix 2.

(Fig. 1(c)). Cable impedance was nulled from the measurements, and all data were logged by a PC.

3. Results and discussion

3.1. Influence of fly-ash source

3.1.1. Complex impedance

Fig. 2(A) displays the complex impedance plot for the plain OPC specimen (Mix 1) and the data for the three ashes in Table 1 (Mix 2), with measurements presented 20 min after gauging; Fig. 2(B) displays the same samples 72 h after initial mixing. These figures corroborate previous work. For the plain OPC system, a typical two-arc response is clearly discernible in Fig. 2(B), with the electrode polarization arc forming the right-hand side of a V-shaped plot and with the bulk arc (sample response) forming the left-hand side. The bulk arc is not as prominent in Fig. 2(A), as the mixes are in the fresh state, and the measured impedances are low. Furthermore, the bulk semicircular arc is not fully developed in either figure [as depicted in Fig 1(a)] due to the upper frequency limit of 1 MHz in the current work. As with previous work, the samples with fly-ash replacement display both increased resistance in comparison with Mix 1 (plots are displaced to the right) and the existence of the plateau region between the electrode and the bulk arcs. Again, the electrode arc, plateau region and bulk arc are prominent in Fig. 2(B); in the fresh mixes [Fig. 2(A)], only the electrode arc and plateau region are discernible, for the reasons given above, in relation to OPC.

Unlike previous work, which presented data for one ash, there are detectable differences between the three fly ashes presented. Ash L displays the most distinct plateau region, which takes the form of a circular arc, whose centre is depressed below the real (resistance) axis. Ash B also displays a circular arc, but the extent of the plateau region is less than that of Ash L. Ash E, although having similar resistances to Ash B, displays a plateau region that is not as prominent or arc-shaped as the ashes L or B are. The differences are further highlighted in Fig. 2(C), whereby both the resistance and reactance measurements in Fig. 2(A) are *normalised* (i.e., divided) by the respective *resistance* at the point between the electrode arc and the sample response [i.e., R on Fig. 1(a) and (b)]. This process assists in comparing ashes, as there are minor differences in the ionic conductivity of the pore fluid due to the oxide composition of the fly ash, particularly the alkali oxides.

3.1.2. Dispersion in dielectric constant and conductivity

The conductivity and dielectric constant were obtained by converting the resistance and capacitance from the impedance data in Fig. 2(A) and are plotted in the frequency domain as displayed in Fig. 3(A) and (B), respectively. This presentation format gives a clearer view of the dispersive behaviour of the system. (Note: The geometry of the test cell also had to be used in converting capacitance and resistance to, respectively, dielectric constant and conductivity).

In Fig. 3(A), at frequencies below 100 Hz, the conductivity is seen to decrease to low values and is due to the dominance of the electrode polarization processes and is unrelated to bulk effects. At frequencies above approximately 1 kHz, the increasing slope on the conductivity plots for the fly-ash mortars is evidence of the presence of dispersion due to dielectric relaxation phenomena. By contrast, the conductivity of plain OPC mortar remains virtually constant at frequencies in excess of the cusp-point frequency of 70 kHz. The dispersive effect is most pronounced in the case of Ash L, which, although having the lowest conductivity, also has the most distinctive plateau region in the complex impedance plane. Ash B mortar displays a similar dispersion characteristic with Ash L. Ash E mortar shows the least pronounced dispersion characteristic, which accords with its less pronounced plateau region. In Fig. 3(B), the enhancement in the dielectric constant, ε_r, of the fly-ash mortars over that of the plain OPC specimen is most evident between 1 kHz and 1 MHz. Again, the relative differences between the fly-ash mortars are visible, with Ash L showing the most pronounced dielectric enhancement, and Ash E the least dispersed.

3.2. Origins of the fly-ash effect

We have postulated [1] that the plateau region is a geometrical effect and is related to the spherical nature of the fly-ash particles, which results in an enhancement in the double-layer polarization processes (hence dielectric constant) on the particle surface. We now reject this hypothesis and propose a new explanation for the origins of this feature based on a more systematic series of tests. For this suite of tests, Ash L was used throughout, with measurements taken 20 min after mixing.

A series of samples was fabricated in which the OPC component was completely removed and, instead of using distilled water, a simulated pore solution was used to compensate for the loss of ionic conduction in the pore fluid caused by the removal of the OPC. These specimens thus contained sand, fly ash and ionic solution (Mix 3 in Table 2). In another set of samples, the fly ash was completely removed and substituted by glass spheres of diameter $\approx 20-30$ μm, together with sand and ionic solution (Mix 4 in Table 2). The purpose of the glass spheres was to produce a material that was physically identical to the fly-ash particles in terms of diameter and shape. The impedance plots for these mixes over the frequency range 40 Hz–1 MHz are presented in Fig. 4(A). The plot for the sample containing the sand and glass spheres (Mix 4) can be seen to have similar characteristics with that of the plain OPC, with a sharply defined cusp point, occurring at a frequency of ≈ 45k Hz; no plateau region is evident, however. The sand and fly-ash plot (Mix

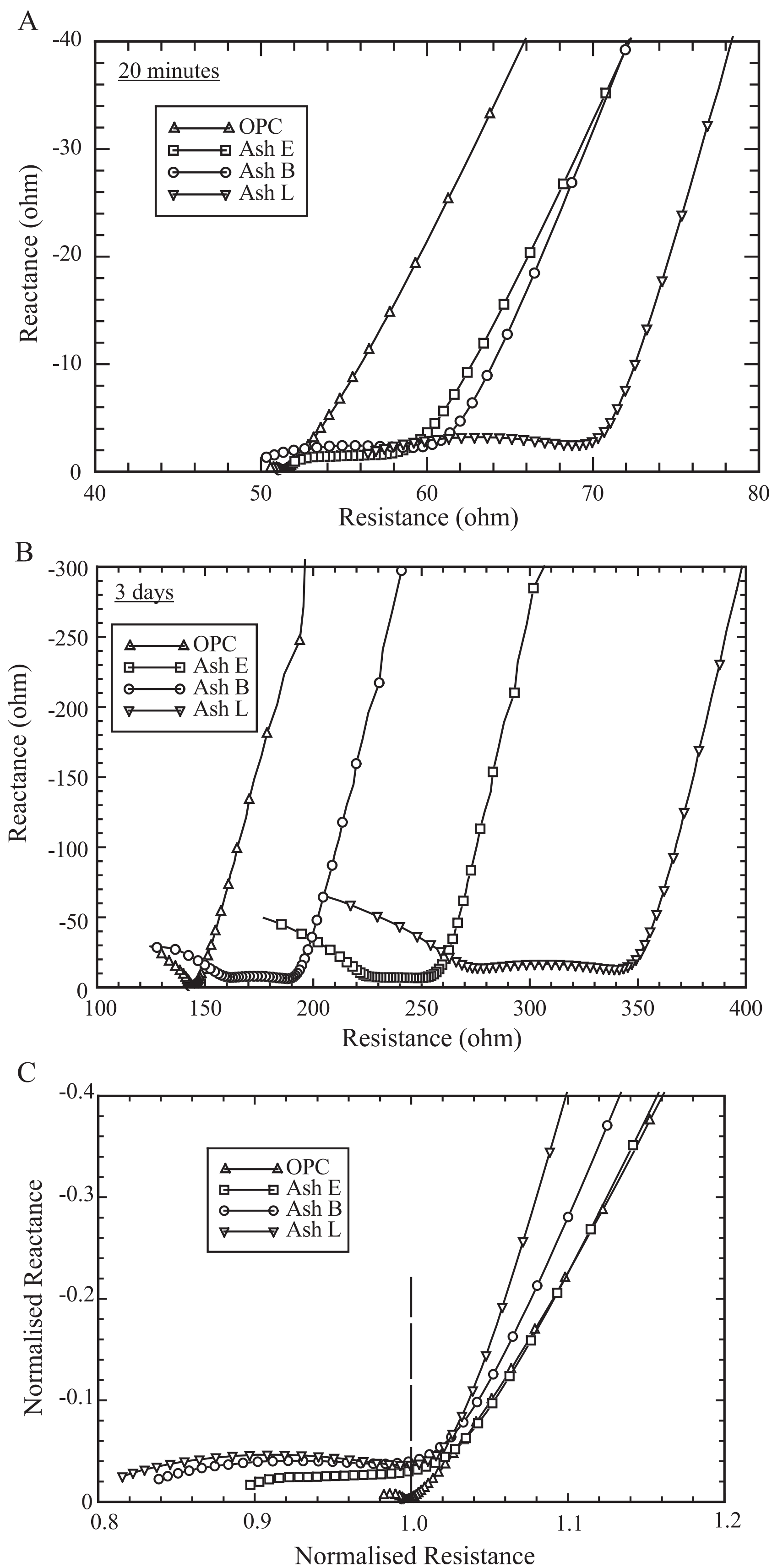

Fig. 2. (A) Impedance response of plain Portland cement mortar and mortars partially replaced with ashes in Table 1, data presented 20 min after gauging; (B) impedance of mortars in Panel (a), 3 days after gauging; and, (C) normalised impedance response for plots in Panel (a).

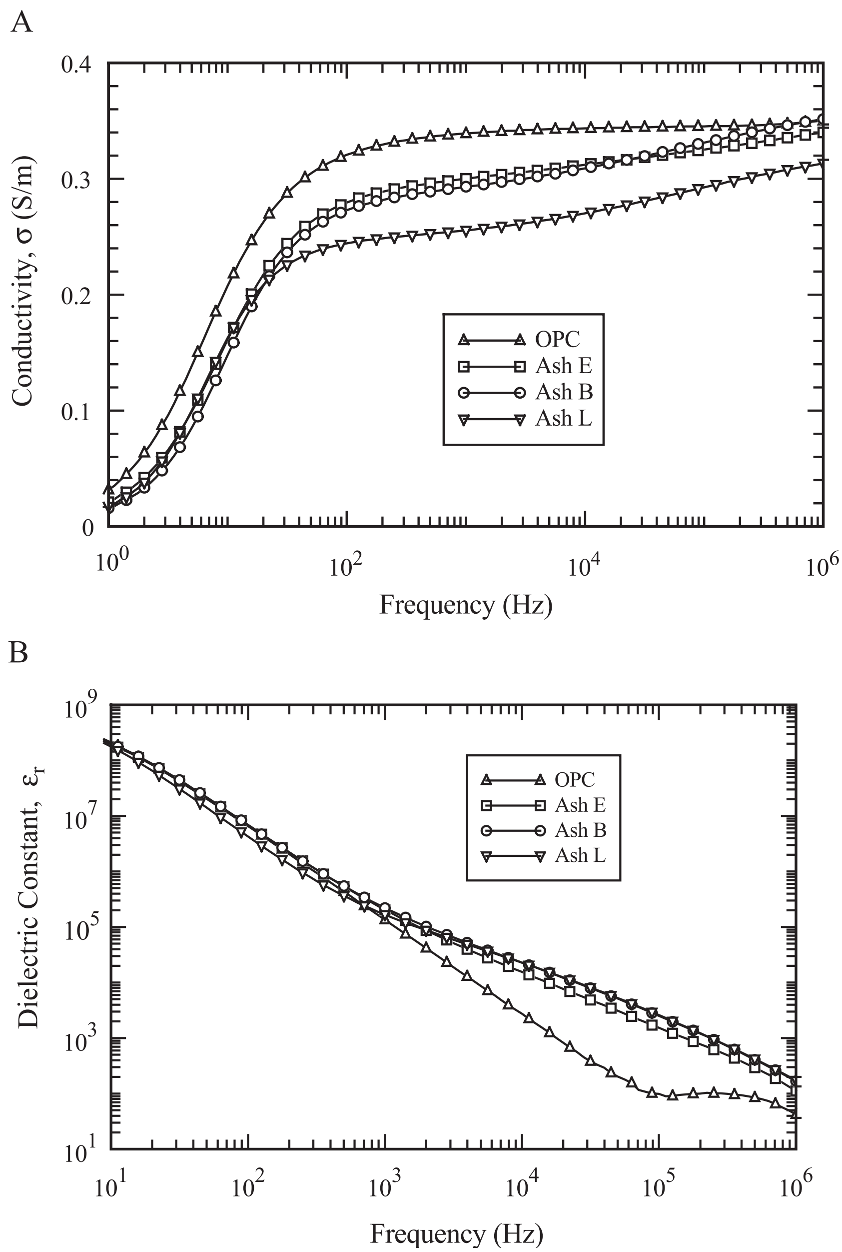

Fig. 3. Showing dispersion in (A) conductivity and (B) dielectric constant for the mortars mixes presented in Fig. 2(A). Dispersion is characterised by an increase in conductivity and a decrease in dielectric constant with increasing frequency.

3) still has the definite characteristic plateau. Interestingly, the frequency at which the arc of the plateau region for Mix 3 reaches its peak reactance is 45 kHz and corresponds to the cusp-point frequency of the plot for the glass spheres (Mix 4). Given that the materials are of comparable impedance and are, morphologically, very similar, it seems reasonable to conclude that the spherical nature of the fly ash is not responsible for the plateau region or for the enhancement in ε_r over the plain OPC mortar mix [Fig. 3(B)].

In the study of crack propagation and fibre orientation [5–7] in cement composites, complex impedance data for carbon-fibre-reinforced Portland cement pastes have been presented over the frequency range 0.5 Hz–10 MHz. It is of interest to note here that the plots for carbon-fibre-reinforced pastes displayed two very distinct semicircular bulk arcs, which is not dissimilar to the fly-ash response, although the arcs are not as pronounced in the case of fly ash. Attention thus focused on the carbon content of the ash, as quantified by the loss on ignition (LOI). Fig. 4(B) presents the impedance response for Ash L, which had its carbon removed by burning it off in a muffle furnace before being used (Mix 5 in Table 2); for comparative purposes, Mix 2 (Ash L) is also presented in this figure. From Fig. 4(B), this process has resulted in removing the plateau region, indicating a strong link between the characteristic plateau response and the LOI of the fly ash. In an attempt to

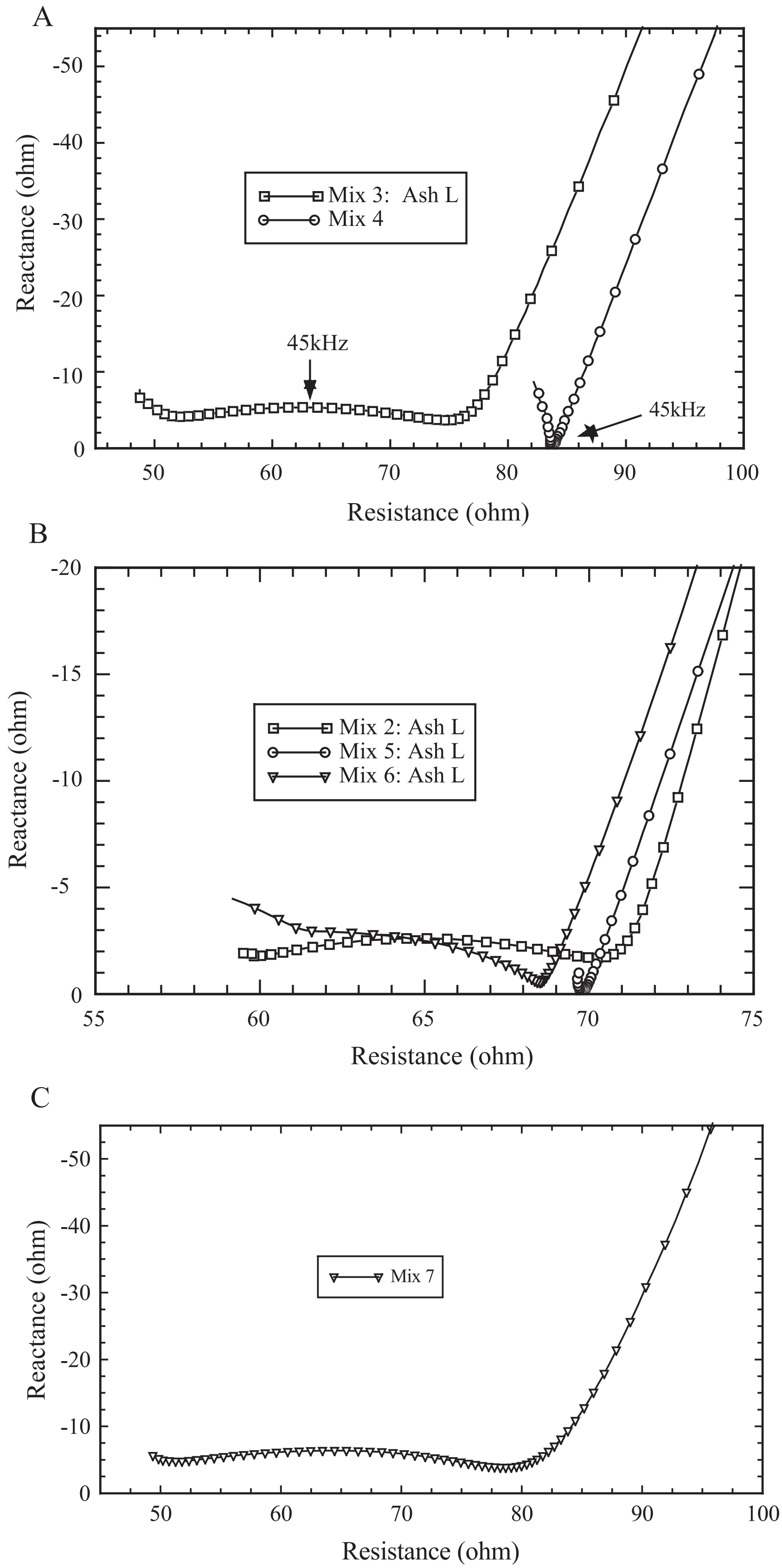

Fig. 4. Impedance response for (A) Mix 3 (Ash L) and Mix 4 (glass spheres); (B) Mix 2 (Ash L), Mix 5 (Ash L with carbon removed) and Mix 6 (i.e., Mix 5 with carbon added); and (C) Mix 7.

reinstate the plateau region, a small amount of carbon (in the form of graphite powder, ≈ 10 μm in size) was added to Ash L, which had had its carbon removed as before (Mix 6). The resulting complex impedance plot is presented in Fig. 4(B), and the plateau region has been restored. There are some minor discrepancies between the two curves, but the essential feature, viz., the plateau region, is present.

Further proof linking the plateau region to the unburnt carbon content of the ash was obtained from a synthetic mortar formulation, which contained no fly ash. Small quantities of carbon were blended with sand, glass spheres and ionic solution (Mix 7 on Table 2). The response form of this mixture is displayed in Fig. 4(C), and the plateau feature is present in this mixture.

3.3. Mechanism responsible for electrical behaviour

As noted above, the addition of fly ash to OPC causes an enhancement in the dielectric constant of the system over the range 1 kHz–1 MHz, which is also reflected in the emergence of the plateau region in the complex impedance plane. The series of tests indicate that it is neither the spherical nor the glassy nature of the fly-ash particle that is responsible for this enhancement, as previously postulated, but the unburnt carbon within the ash. The region of dispersion (i.e., the decrease in dielectric constant with increasing frequency) occurring in the kilohertz region is strongly indicative of a double-layer polarization process, which results in high dielectric constants for colloidal suspensions [8,9]. On gauging, the high ionic concentration within the interstitial aqueous phase provides a suitable environment for establishing an electrochemical double layer on particle surfaces, hence, such a polarization mechanism would predominate within the system. Furthermore, the inherent porosity of the unburnt carbon particles in fly ash provides it with a large surface area (≈ 30–40 m^2/g [10,11]) in comparison with OPC or fly-ash particles. Because double-layer polarization is a surface effect, this could account for the enhancement of this particular polarization process in fly-ash systems and in the dependence of the characteristic electrical behaviour on the LOI of the ash.

4. Concluding comment

The unburnt carbon content of the fly ash, quantified by the LOI, is responsible for the emergence of the distinctive plateau region in low-lime fly-ash systems when plotted in the complex impedance plane. The extent of the plateau region was found to be directly related to the LOI. A double-layer polarization process on the surface of the carbon was postulated to account for this feature. This work has potential practical significance, as well as fineness, an important factor in determining the suitability of a fly ash is its carbon content as this influences the effectiveness of certain admixtures. Impedance techniques could be exploited as a simple means of quality control in this respect.

Acknowledgements

The financial support of the Engineering and Physical Sciences Research Council (United Kingdom) is gratefully acknowledged (Grant GR/N16465). We also wish to express thanks to Dr. L. Sear of the United Kingdom Quality Ash Association and Mr. W. Armstrong of ScotAsh for technical support and arranging supplies of ash samples.

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