

The Application of Impedance Spectroscopy to Cementitious Systems

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Abstract

A.C. impedance spectroscopy is now gaining favor as an investigative technique for monitoring the development of cement microstructure. The work presented extends the range of application of the method by showing the compositional dependence of the complex impedance of cement-aggregate-water systems (i.e. concrete and mortar), with attention being directed towards this material while still in the liquid state. It is shown that the bulk impedance response is linked to the aggregate-content of the system; furthermore, it is shown that such techniques could even be developed to identify the type of cementitious binder. Measurements were, in the main, taken over the frequency range 1Hz-15MHz. It is envisaged that a.c. impedance spectroscopy could find application in aspects of quality control of structural concrete.

Contents

1.1	INTRODUCTION	1-1
1.1.1	Background	1-1
1.2	A REVIEW OF PREVIOUS WORK ON ELECTRICAL PROPERTIES OF CEMENTITIOUS SYSTEMS	1-1
1.3	EXPERIMENTAL	1-3
1.3.1	Preliminaries	1-3
1.3.2	Mix Details	1-3
1.3.3	Impedance Measurements	1-4
1.4	DISCUSSION OF RESULTS	1-5
1.4.1	Impedance Spectra for Cement Paste	1-5
1.4.2	Impedance Spectra for Mortars	1-7
1.4.3	Impedance Spectra for Concretes	1-8
1.4.4	Influence of PFA Replacement on Impedance Response	1-10
1.5	CONCLUSIONS AND CONCLUDING COMMENTS	1-12
1.6	ACKNOWLEDGEMENTS	1-13
1.7	REFERENCES	1-13

1.1 INTRODUCTION

1.1.1 BACKGROUND

Cement is one of the main construction materials with world-wide consumption in excess of one billion tonnes. Quality control of concrete at all stages of construction is an absolute necessity to ensure the requirements of function and durability. Design and forecasting of concrete durability and performance becomes irrelevant if satisfactory quality control is not applied during construction. Current quality control methods for concrete are based on monitoring the quality and amount of the component materials before mixing, measuring the workability of the fresh mix using relatively crude methods, and then testing the strength of small prepared specimens after a period (commonly 28 days) of controlled storage. Traditional (empirical) workability tests, such as the slump test [1], compaction factor test [2] or VeBe test [3], do not analyze the concrete per se, and to satisfy the need of modern concrete practices (e.g. fast-track construction), a number of sophisticated techniques have been developed for the direct analysis of fresh concrete [4].

The work presented concerns itself with concrete while still in the liquid state and details novel developments in the application of a.c. impedance spectroscopy (ACIS) as a means of quality control. The compositional dependence of the electrical response of concrete is highlighted; it is also shown that the partial replacement of ordinary Portland cement (OPC) with pulverized fuel ash (PFA) produces a distinctive complex response. This latter point is also of interest as, given a fresh concrete, there are currently no simple methods for:

- a. detecting the presence of PFA in the mix, and
- b. evaluating the PFA content and that this complies with specification.

Both these aspects are of considerable importance to the Construction Industry in the design of concrete for durability where increasing use is being made PFA.

1.2 A REVIEW OF PREVIOUS WORK ON ELECTRICAL PROPERTIES OF CEMENTITIOUS SYSTEMS

Some of the first work on electrical measurements on hydrating cement paste can be traced back to the 1920's [5]. The prime motivation of this early work was to use electrical techniques to determine setting time. Since this time, numerous of papers have been published on the conductivity/resistivity of hydrating cement [see, for example, 6-17]. Such measurements are limited in a number of respects:

- a. measurements are invariably made at a single frequency or over a very limited frequency range, with data being interpreted in terms of ionic conduction through the continuous water-filled capillary cavities between the electrodes;
- b. frequency of the applied alternating electrical field is usually limited to low frequencies (i.e. 100Hz-10kHz), primarily to negate problems due to electrode polarization effects; and,
- c. further to (a) above, the macroscopic response of cement to an alternating electrical field is normally represented by a purely resistive model, little attention has been given to the existence of possible bulk polarization phenomena resulting in a quadrature component to the measured impedance.

Although wide-band ACIS is not a new technique, it is only relatively recently that this testing method has been applied to hardening Portland cement paste [18,19] with bulk impedance measurements being monitored over the frequency range 1Hz-15MHz. Since this initial application as an investigative technique for monitoring microstructural development in Portland cement, ACIS is now receiving considerable attention as a potentially powerful method in characterizing microstructural evolution and pore structure development in cements [see, for example, 20-36]. The advantages of ACIS over more traditional microstructural investigative methods (see below) include:

- a. measurements are carried out at normal temperatures and pressures hence the cement microstructure is not disrupted or damaged, which is particularly important during the early stages hydration when the cement paste is in a relatively weak, plastic state;
- b. relative to the techniques cited below, impedance measurements are made on much larger samples, hence bulk effects can be assessed (in practice concrete, hence cement, is cast in large volumes);
- c. samples do not require special preparation prior to testing; the method is non-invasive;
- d. measurements can be made as the cement hydrates i.e. in-situ; and,
- e. equivalent circuit models can be developed and features of the complex response can be directly linked to pore structure and degree of hydration.

Traditional methods of examining the microstructure of cement include scanning and transmission electron microscopy (SEM, TEM), nuclear magnetic resonance relaxation methods (NMR), small angle X-Ray scattering, gas absorption-desorption and mercury intrusion porosimetry (MIP). Not all these techniques lend themselves directly for investigating the capillary pore network within cement (e.g. pore continuity, constrictivity, tortuosity), and for those that do, criticism could be levelled at sample preparation techniques, testing conditions, and sample size (for example). Regarding the point of sample size, if only a small volume of the sample is investigated, care must be taken in evaluating macroscale performance with microscale examination.

It should be pointed out that ACIS (with potentiostatic control) has been extensively developed for monitoring corrosion of steel in reinforced concrete, in such instances the upper frequency is limited to 50kHz or so; this is not the concern of the work presented. In the application for investigating microstructural development in cementitious systems, it is the bulk impedance response that is of interest and measurements are taken over the range 1Hz-15MHz (typically).

It is within this range that an arc develops in the complex plane. Such a development has only been possible through the development in instrumentation with the required frequency range, and it is for this reason that the Solartron 1260, with an upper frequency limit of 32MHz, is ideally suited for use in this field and, indeed, is extensively used by workers.

Virtually all of the published work on the application of ACIS to cementitious systems has, however, been undertaken on neat cement-pastes and mortars, with attention being directed to the later stages of hydration i.e. after setting and during the hardening process. At present, only limited data are available on the impedance response of cementitious systems during the very early stages of hydration (i.e. before setting), and even these data are obtained from neat cement pastes [20,27]. The influence of the addition of aggregate particles to the fresh paste on the complex response is relatively unresearched, although some data (during early hydration) are available on the high frequency dielectric properties of mortars (1MHz-3GHz) [37] and fixed frequency resistivity measurements on mortars and concretes [14-16].

The aim of this current work is to show the compositional dependence of the impedance response of cement-aggregate systems with the work presented concentrating on the early stages of hydration i.e. the initial hour after gauging. Complex impedance measurements were obtained over the frequency range 1Hz-15MHz.

1.3 EXPERIMENTAL

1.3.1 PRELIMINARIES

Concrete is a heterogeneous material comprising aggregate, cement and water mixed in varying proportions. The aggregate is further sub-divided into a coarse fraction and a fine fraction. The coarse aggregate fraction comprises a gradation of particles ranging from, approximately, 5-20mm, whereas the fine fraction has particle sizes within the range 150 μ m-5mm. A cement mortar, on the other hand, comprises a mixture of cement, water and fine aggregate. Cement particles themselves are of the order of 50 μ m. When water is added to cement particles, a series of complex chemical reactions occurs which result in eventual setting and hardening of the cement paste. Initial hydrolysis results in the interstitial aqueous phase becoming saturated with respect to Ca⁺⁺ and OH⁻, other ions such as Na⁺, K⁺ and SO₄²⁻ are also present. As the bulk resistivity of aggregates used in concretes are, typically, in the range 10⁴-10⁸ ohm-cm [10,38] and that of cement-paste (in the liquid state) approximately 100 ohm-cm [39] it could be concluded that, from an electrical point of view, concrete can be considered as non-conductive aggregate particles embedded in an ionically conducting cement-paste matrix. Indeed, this argument could be taken one stage further by proposing that the cement-paste itself could be considered as non-conductive cement grains surrounded by an ionically conducting, interstitial fluid phase.

The bulk resistivity, however, represents only one parameter at a particular frequency and the response can be written more completely as,

$$Z^*(\omega) = Z^I(\omega) - i Z^II(\omega) \quad (1)$$

where $Z^*(\omega)$ represents the complex impedance, $Z^I(\omega)$ and $Z^II(\omega)$ are, respectively, the real (resistive) and imaginary (reactive) components at a particular angular frequency, ω . Only by investigating the complex impedance over a range of frequencies can the complete picture be developed. The complex resistivity, $\rho^*(\omega)$, can be calculated from the complex impedance, $Z^*(\omega)$, by the relationship,

$$\rho^*(\omega) = Z^*(\omega) \frac{A}{d} \quad (2)$$

where, for a prismatic sample, A is the cross-sectional area and d the distance between the electrodes.

1.3.2 MIX DETAILS

Within the framework of a parametric study, a series of tests was undertaken on a wide range of concretes, mortars and cement pastes; however, for the purpose of this current work, only a selection of the mixes are presented primarily to highlight the testing methodology. The coarse aggregate had a nominal maximum size of 20mm and the fine aggregate conformed to Zone M [40]; a natural gravel aggregate was used throughout and was in an air-dry condition.

Ordinary Portland cement (OPC) was used for the testing programme; a series of tests was also conducted on concretes made with a blend of OPC and PFA. An oxide analysis of the cementitious materials is given in Table 1. The mixes tested are detailed in Table 2 with neat cement-pastes, mortar mixes and concrete mixes prefixed P, Mo, and C respectively. The specific gravity of the OPC was 3.15, the PFA was 2.20 and the aggregate was 2.70.

Mixing time was kept constant at two minutes as measured from the initial addition of water. Prior to gauging, the constituents were dry mixed for approximately 30 seconds.

Table 1 - Oxide Analysis of Cementitious Material

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O
OPC	20.68	4.83	3.17	63.95	2.53	2.80	0.54	0.08
PFA	53.08	30.14	7.20	1.68	2.50	0.20	0.41	0.30

Table 2 - Summary of mixes studied

MIX Ref. No.	Water-content (kg/m ³)	Cement-content (kg/m ³)	Fine Aggregate (kg/m ³)	Coarse Aggregate (kg/m ³)	Mean bulk resistivity at 20°C ohm-cm
Mo1	367	918	918	-	187
Mo4	274	685	1370	-	381
C1	150	300	816	1224	1469
C4	157	350	788	1183	1152
C5	175	350	770	1155	1122
C7	160	420	630	1260	919
C13	220	547	547	1094	603
P1	486	1620	-	-	85.6
P2	558	1394	-	-	82.1
P4	654	1090	-	-	81.5

1.3.3 IMPEDANCE MEASUREMENTS

After mixing, the material was vibration compacted in rigid, plastic cells. The internal dimensions of the test cells were 15x15x15cm (for concrete samples) and 5x5x5 cm (for mortar and paste samples) and considered large enough to obtain a representative, bulk impedance response. These dimensions also conformed to the British Standard cube size for strength tests on concrete and mortars [41]. Two opposite sides of the cell were fitted with 15x15cm (or 5x5cm) stainless steel electrodes (Type 304) with each electrode secured to the side of the cell by means of four stainless steel bolts; one bolt passed through the side of the cell which served as the point of electrical connection. Impedance measurements were taken using a Solartron 1260 Impedance Gain/Phase Analyzer operating within the frequency range 1Hz-15MHz.

Data were obtained at 150 spot frequencies within this range using a logarithmic frequency sweep. The Solartron 1260 operated in voltage drive mode with a signal amplitude of 1 volt held across the sample. Three samples were tested for each concrete mix and five samples tested for each neat cement-paste and mortar mix in Table 2. All tests were carried out at $20^{\circ}\text{C}\pm 2^{\circ}\text{C}$, 55-60%RH, Connections to the cells were made using a patent in-circuit testing module (Solartron Part No. 12603A); lead and cell open- and short-circuit residual impedances were nulled from the incoming data at all test frequencies. All data were logged by computer (see Diagram 1).

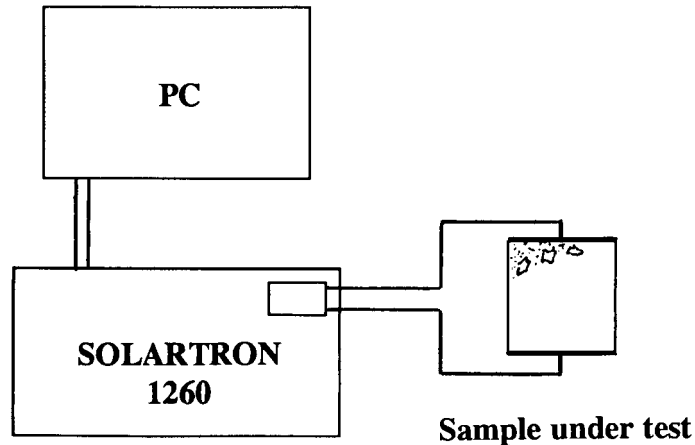


Diagram 1 - Schematic diagram of testing arrangement

1.4 DISCUSSION OF RESULTS

Due to the considerable number of tests undertaken, where possible, results have been presented and summarized in both Tabular and graphical formats together with typical impedance spectra. These data represent the electrical response taken 1 hour after initial gauging with water.

1.4.1 IMPEDANCE SPECTRA FOR CEMENT PASTE

Figure 1 displays typical complex resistivity responses for neat cement-pastes with water-cement ratios 0.3, 0.4 and 0.6.

Note: The water-cement ratio (w/c) is defined as the ratio of the mass of water to the mass of cement in a mix

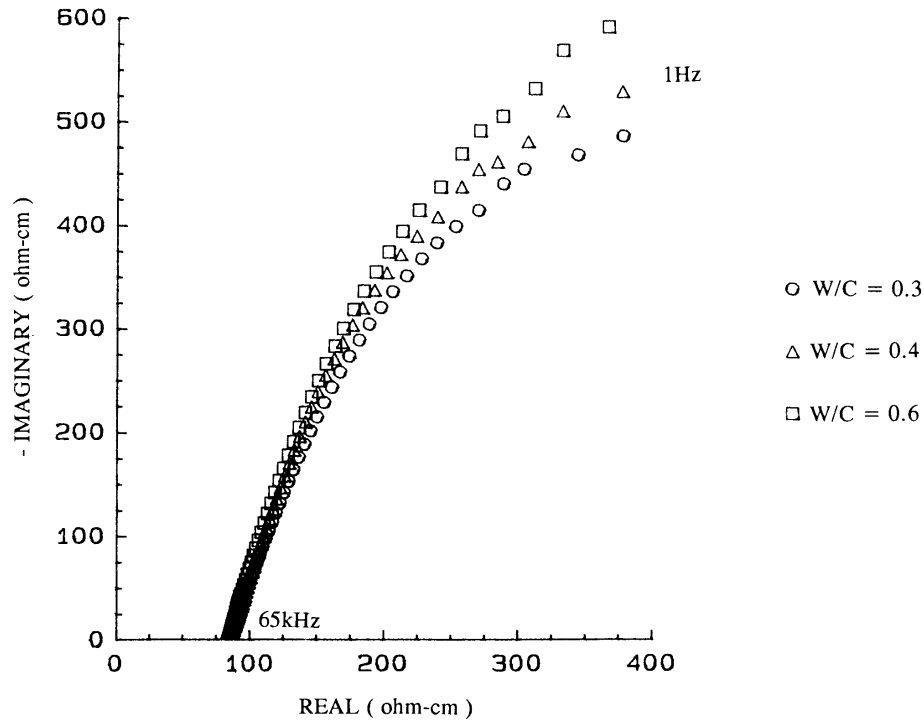


Fig 1 - Impedance response for neat cement-pastes over the frequency range 1Hz-65kHz. The response is dominated by the arc due to electrode/cement-paste interfacial effects. Note that all arcs converge to the same intercept on the real axis even though the w/c ratios are varied over the range 0.3-0.6.

In this instance, the complex response is presented over the frequency range 1Hz to 65kHz as the imaginary component was reduced to negligible proportions at the frequencies in excess of 65kHz. The response for each paste is dominated by a portion of a much larger arc, which can be identified as being due to processes at the electrode/cement-paste interface [19]. The intercept of this arc with the real axis represents the bulk resistivity of the sample. No high frequency arc was detected, thus the complex impedance response $Z^*(\omega)$ can be represented by the equation:

$$Z^*(\omega) = R_b + \left[\frac{1}{1/R_{ct} + i\omega C_{dl}} \right] \quad (3)$$

where R_b , R_{ct} and C_{dl} represent, respectively, the bulk (ionic) resistance, charge transfer resistance and double layer capacitance, the latter two terms relating to electrode polarization processes. Electrode effects are thus eliminated at frequencies in excess of 65kHz, i.e. the term in brackets in equation (3) becomes, effectively, zero. The bulk arc, resulting from polarization processes from within the cement paste, is not observed.

Another feature which is apparent from this figure is the convergence of the spectra to the same intercept with the real axis. This implies that the bulk resistivity of the pastes is virtually independent of water-cement ratio and corroborates the earlier finding that, at normal water-cement ratios, the resistivity of cement pastes is independent of w/c ratio [39]. The mean values of bulk resistivity obtained for the neat cement paste samples tested are presented in Table 2 (w/c ratios 0.3-0.6). The general shape of the spectra at this early stage of hydration (1 hour) are similar to those obtained for cement-pastes at approximately 9 hours hydration [20,27].

1.4.2 IMPEDANCE SPECTRA FOR MORTARS

The influence of the addition of fine aggregate to the cement paste is displayed in Figure 2a. In order that a comparison can be made, the spectrum for a neat cement paste of w/c ratio 0.4 is presented with mortars Mo1 (fractional volume of cement-paste, ($\phi_p = 0.660$) and Mo4 ($\phi_p = 0.492$) which also have a w/c ratio of 0.4.

Note: The fractional volume of cement-paste represents the combined volume of cement and water in 1 cubic meter of concrete

As previously explained, mortar could be considered as comprising a low conductivity aggregate phase dispersed in a high conductivity cement-paste matrix; hence, as the fractional volume of aggregate in the mix is increased it would be anticipated that the impedance of the system will increase. This is indeed the case as borne out by the experimental data, with the complex impedance values proportionally increased at all frequencies. The aggregate thus has a diluting effect.

As with the pastes, the spectra are dominated by electrode processes, with the intercept of the arc with the real axis obtaining the bulk resistivity. For Mo1 samples, the results are presented over the range 1Hz-65kHz, whereas for Mo4 samples the complex impedance could be measured over the range 1Hz-7MHz. What is also evident from the response for mortar Mo4 is the development of a high frequency bulk arc. This mortar has a higher aggregate content than Mo1. An enlargement of this arc is given in Figure 2b. If the bulk sample can be modelled by a parallel combination of resistor (R_b) and equivalent capacitor (C_b) (the latter being related to the constant phase element) then increasing the proportion of non-conductive aggregate phase in the cementitious system has the effect of increasing the resistance (R_b) of the sample. This results in shifting the time constant ($=R_b C_b$) of the bulk arc into an observable range. The frequency at which the low frequency arc turns over into the high frequency bulk arc varied between 22-25kHz for all the Mo4 samples tested.

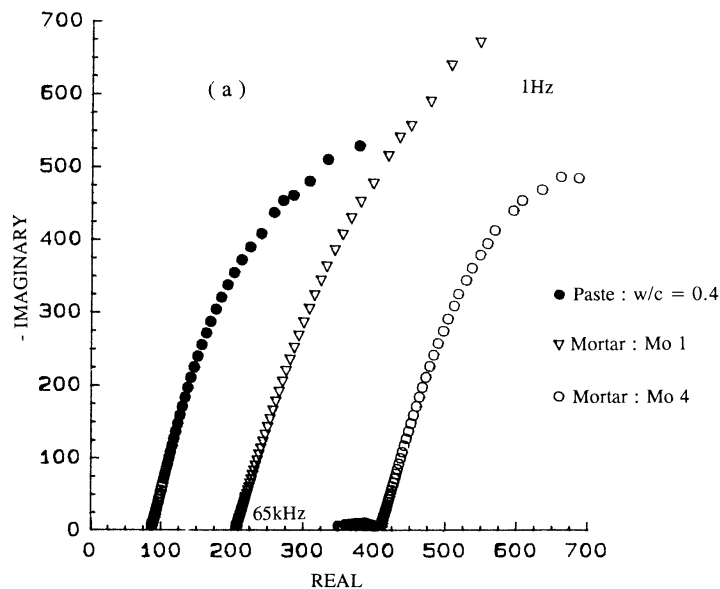


Fig 2a - Complex response for mortar samples Mo1 and Mo4. The response for a paste of w/c ratio = 0.4 is included for comparative purposes. Mo1 is presented over the frequency range 1Hz-65kHz whereas Mo4 represents the range 1Hz-7MHz.

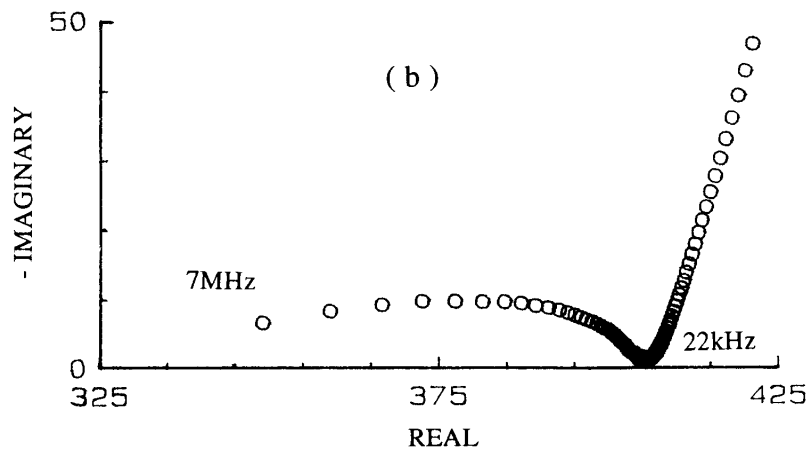


Fig 2b - Enlargement of the high-frequency arc for Mo4

1.4.3 IMPEDANCE SPECTRA FOR CONCRETES

Figure 3 presents the impedance response for the concrete mixes in Table 2. At one end of the range, Mix C13 represents a rich mix i.e. high cement-content with a high fractional cement-paste volume ($\phi_p = 0.392$) and, at the other end, mix C1 represents a lean mix i.e. low cement-content with a low paste content ($\phi_p = 0.245$). Normal structural concretes are represented by mixes C5 and C7 ($\phi_p = 0.286$ and 0.293 respectively) with regard to cement- and water- contents [42]. Data are presented within the frequency range 1Hz-10MHz.

It is immediately apparent that, as with the mortar samples, increasing the volume fraction of aggregate (mix becomes leaner), results in better definition to the high frequency arc associated with the bulk material. For mix C13, however, no high frequency arc was detected (although there is some slight deviation from the linear projection indicated) and the spectrum presented represents the frequency range 1Hz-65kHz, as before, the imaginary component was reduced to negligible proportions above 65kHz. Increasing the aggregate content has the effect of decreasing the fractional volume of conductive paste resulting in an increase in impedance. As with the mortar samples, the time constant of the bulk sample is moved into the frequency range under consideration.

It is interesting to compare concrete C13 with mortar Mo4, both with a water-cement ratio of 0.4. The mortar displays a high frequency bulk arc whereas, for the concrete, no such arc can be apparent. The bulk resistivity of C13 is greater than Mo4, which is as anticipated since the total aggregate content is greater in the case of the concrete.

Considering the mix proportions of the samples as shown in Table 2, although the total aggregate content of C13 is greater than Mo4, this mortar has a larger fine-aggregate content. The fine-aggregate will have a larger surface area than the same mass of coarse aggregate. Since, on mixing, the cement-paste coats the aggregate particles it could be postulated that the increased surface area (due to the fine aggregate) has a direct influence on the development of the high frequency arc, whereas total aggregate content would appear to influence the overall bulk resistivity of the sample.

As before, the frequency at which the low frequency arc turns over into the high frequency arc decreases with increasing leanness of mix - for mix C7 samples, this frequency was in the range 9-10kHz; for mix C5 samples this has decreased to 3kHz, and was in the range

1.6-2.2kHz for mix C1 samples. This feature is as a result of the increasing bulk resistance of the sample.

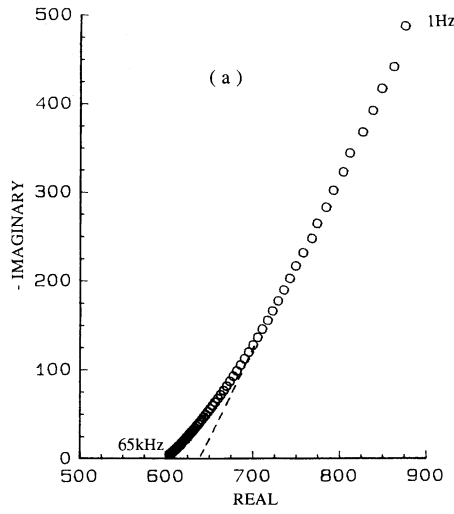


Fig 3a - Concrete mix C13 (1Hz-65kHz)

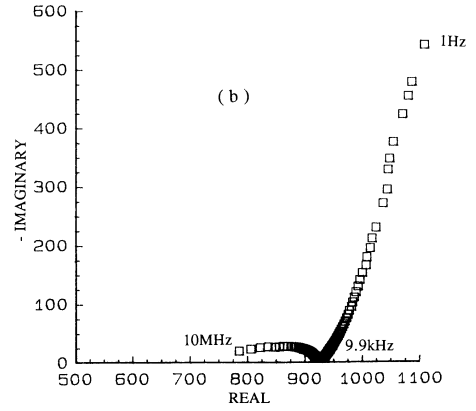


Fig 3b - Concrete mix C7 (1Hz-10MHz)

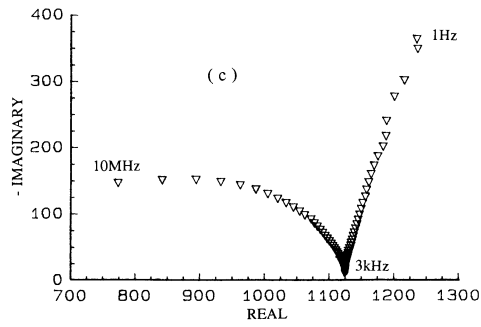


Fig 3c - Concrete mix C5 (1Hz-10MHz)

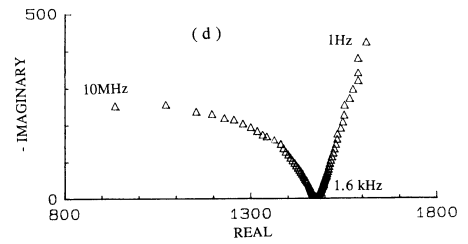


Fig 3d - Concrete mix C1 (1Hz-10MHz)

Figure 3 - Impedance Plots for Concrete Mixes

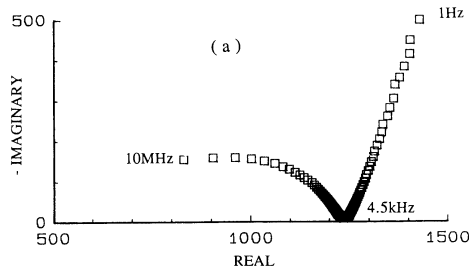


Fig 4a - Impedance response of concrete mix C4

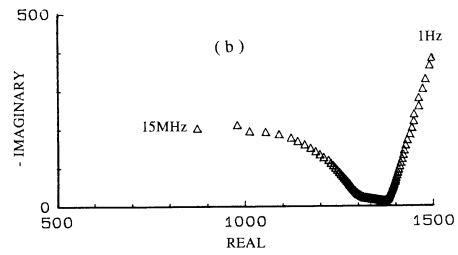


Fig 4b - Response from Mix C4 with 10% PFA replacement

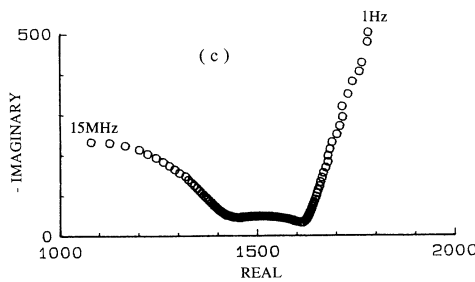


Fig 4c - Response from Mix C4 with 30% PFA replacement

Fig 4 - Impedance Response from Concrete Mixes

1.4.4 INFLUENCE OF PFA REPLACEMENT ON IMPEDANCE RESPONSE

In this set of tests, the ordinary Portland cement in mix C4 was replaced at two levels - 10% and 30% by original mass of OPC as detailed in Table 3. The mix-ratio was kept constant throughout as was the water-cementitious material ratio (= 0.45). The resulting spectra are presented in Figure 4 with the level of replacement indicated.

Table 3 - Summary of results from OPC/PFA mixes

Blend/Ratio OPC/PFA (% by mass)	f_a	f_b	f_c
100/0	4.5 kHz	not applicable	not applicable
90/10	450-550 Hz	no maximum	60-70kHz
70/30	150 Hz	9-10 kHz	100-115 kHz

Note: Where a frequency range has been given, this represents the maximum and minimum values obtained from the samples of the same mix. Where only one value has been given, all samples returned this frequency.

Two noticeable features are displayed by these spectra (taken over the range 1Hz-15MHz):

- a. as the level of replacement increases, the impedance spectrum for the sample becomes progressively more displaced to the right and the radius of the high frequency arc increases. This indicates an overall increase in sample impedance; and
- b. increasing the replacement level results in the development of a distinctive plateau region between the low frequency spur (electrode effect) and the high frequency bulk arc. The extent of this plateau region is almost directly proportional to the level of replacement. To the best of the Author's knowledge, this is the first reported identification of such a region.

Regarding (a) above, PFA is relatively inert during early hydration having little hydraulic properties of its own, it is only after setting and during hardening of the OPC that pozzolanic activity occurs. Being inert, it is equivalent to the addition of low-conductivity fine aggregate to the mix. This will, as a consequence, increase the impedance of the system. Regarding (b), examination of the hard-copy of data reveals that the plateau region is a very flat arc, and is shown schematically in Figure 5.

The respective frequencies f_a , f_b , and f_c for each replacement level are given in Table 3. The spur at the right hand side of the spectrum (see Figure 4) will represent electrode/concrete interfacial effects as with the OPC concretes, hence the plateau must be a bulk feature and a characteristic of the PFA. One plausible explanation of this region could be as a result of the distinctive spherical shape (cenospheres) of the PFA particles, as opposed to the angular shape of cement grains or aggregate, coupled with their lower specific gravity. Work is continuing in this respect.

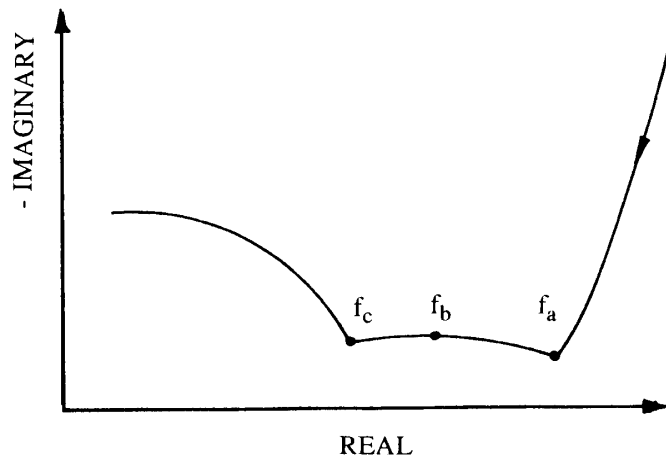


Fig 5 - Schematic diagram of the complex impedance response from an OPC/PFA concrete

1.5 CONCLUSIONS AND CONCLUDING COMMENTS

This paper presents the results from an extensive series of tests on the complex impedance response of cement-pastes, mortars and concretes 1 hour after gauging. The compositional dependence of the complex impedance of cement-aggregate systems has been shown with tests being carried out on samples of realistic size and mix proportions. The study has confined itself to the frequency range 1Hz-10MHz for OPC mortars and concretes and 1Hz-15MHz for OPC/PFA concretes. Some of the work corroborates previous findings but extends these electrical measurements by obtaining the complete electrical response. The following conclusions can be drawn:

1. It has been shown that the impedance response of neat cement-pastes is dominated by a low frequency arc attributed to electrode/cement-paste interface effects in the frequency range 1Hz-65kHz. The intercept of this arc with the real axis defines the bulk resistance of the paste which can only be accurately identified using a.c. impedance techniques. It was shown that the bulk resistivity of neat cement pastes is virtually independent of the water-cement ratio (over the range 0.3-0.6). No bulk arc could be detected at this early stage of hydration for the neat cement pastes.
2. The addition of aggregate particles to the paste has the effect of increasing both the resistive and, to a lesser extent, the reactive components of the complex response. Typical impedance spectra have been presented and it was shown that, as the proportion of the aggregate increases, a high frequency (bulk) arc can be detected. Furthermore, the development of a high frequency arc depends not only on total aggregate content but also aggregate size; the fine aggregate fraction has an influence in the development of the bulk arc. It is proposed that this is due to an increased in surface area of the aggregate. No such arc was detected for rich mortar and concrete mixes.
3. It has been shown that the bulk resistivity of both mortars and concretes is almost entirely dependent upon the fractional volume of cement-paste within the mix. Increasing the aggregate content has the effect of reducing the cross-sectional area of the conducting phase.
4. The addition of PFA to the mix, as a replacement material, produces a distinctive response with three regions being identified: one due to electrode processes at the low frequency region (<400Hz, approximately); a flat arc due to the PFA at medium frequencies (400Hz-150kHz, approximately) and a high frequency arc due to the aggregate (>150kHz). The development of the plateau region is directly proportional to the replacement level.

The prime aim of the work presented has been to highlight a use for impedance spectroscopy techniques other than for corrosion monitoring. The particular application focuses on impedance spectroscopy as a potentially useful technique in the quality control of structural concrete.

There are considerable, and obvious, advantages in being able to evaluate the proportion of the constituent parts of concrete while still in the fresh state and that these comply with specification - if they do not, then remedial measures can be taken immediately, i.e. before the concrete has set. The developments outlined above have only been possible with the advances made in instrumentation and it is fortuitous that the bulk impedance response for concrete (both in the hardened and liquid state) develops in the frequency range 10kHz-15MHz. This range is within the capabilities of the Solartron 1260 and thus make it ideally suited for these measurements.

1.6 ACKNOWLEDGEMENTS

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1.7 REFERENCES

1. British Standards Institution, BS 1881, Part 102: 1983 'Method for determination of slump'.
2. British Standards Institution, BS 1881, Part 103: 1983 'Method for determination of compaction factor'.
3. British Standards Institution, BS 1881, Part 104: 1983 'Method for determination of VeBe time'.
4. Dhir R K, Munday J G L and Ho N Y, *Mag. Conc. Res.*, Vol. 34, No. 119, June, 1982, pp59 - 73.
5. Schimizu Y, *The science reports of the Tohoku Imperial University, First Series, Shendai, Japan*, Vol. 17, No. 1, Jan., 1928, 28pp.
6. Baire M G, *Revue des Materiaux de Construction et de Travaux Publics (Paris)*, No. 272, 1932, p182.
7. Kind V A and Zhuraler V F, *Tsement*, Vol. 5, No. 9, 1937, pp21 - 26.
8. Calleja J, *Jrnl. of Amer. Conc. Inst.*, Vol.23, No.7, 1952, pp329 - 332.
9. Hammond E and Robson T D, *The Engineer*, Vol. 199, 1955, 21st Jan., pp78 - 80, and 28th Jan., pp 114 - 115.
10. G E Monfore, *Jrnl. of the PCA Res. and Development Labs.*, 10, 2, May, 1968, pp35-38.
11. Sriravindrarajah R , and Swamy R N, *ASTM (Cement, Concrete and Aggregates)*, Vol. 4, No. 2, Winter, 1982, pp73 - 80 .
12. Bars J B, Camps J F and Debuigne J, *Materiaux et Constructions*, Vol. 15, No. 85, 1982, pp33 - 37.
13. Tamas F D, *Cem. and Conc. Res.*, Vol. 12, No. 1, 1982, pp115 - 120.
14. Whittington H W, McCarter W J and Forde M C, *Mag. Conc. Res.*, Vol. 33, No. 114, 1981, pp48 - 60.
15. Hughes B P, Soleit A K D and Brierly R W, *Ibid*, Vol. 37, No. 133, 1985, pp243 - 248.
16. Morelli R, 'Resistivity testing of concrete', PhD Thesis, University of Edinburgh, 1985, 179pp.
17. Tamas F D, Farkas M, Voros M and Roy D, *Proc. 8th Int. Congress on Chem. of Cement, Rio-de-Janeiro, Sept.*, Vol. VI, 1986, pp374 - 380.
18. W J McCarter, S Garvin and N Bouzid, *Jrnl. of Matl. Sci. Lett.*,7 ,1988 ,pp 1056-1057.

19. W J McCarter and R Brousseau, *Cem. and Conc. Res.*, Vol. 20, No. 6, 1990, pp891-900.
20. C A Scuderi , T O Mason and H M Jennings , *Jrnl . of Matl . Sci .* , 26, 1991, pp349-353.
21. K Brantervik and G A Niklasson , *Cem and Conc. Res.*, 21, 4, 1991, pp496 - 508.
22. A Berg, G A Niklasson, K Brantervik, B Hedberg, L O Nilsson, *Sol. State Comm.*, Vol. 79, No. 1, 93-96, 1991.
23. G Ping , X Ping , J J Beaudoin and R Brousseau , *Cem. Conc. Res.*, 22, 5,1992, pp833-840.
24. J J Beaudoin and P W Brown, *Proc. 9th Int. Congress on the Chemistry of Cement*, New Delhi, India, Nov., 1992, Vol. 1, pp495-525.
25. R T Coverdale and H M Jennings, *Ibid*, Vol. IV, pp16-21.
26. E J Garboczi and D P Bentz , *Ibid* , Vol . VI , pp3-15 .
27. B J Christensen, T O Mason and H M Jennings, *J. Am. Ceram. Soc.*, 75, 4, 1992, pp939-945.
28. A Berg, G A Niklasson, K Brantervik, B Hedberg, L O Nilsson, *J. Appl. Phys.*, Vol. 71, No. 12, June, 1992, pp5897-5903.
29. P Gu, P Xie, J J Beaudoin and R Brousseau, *Cem. and Conc. Res.*, 22, 5, 1992, pp833-840.
30. *Idem*, *Ibid*, 23, 1, 1993, pp157-168.
31. P Xie, P Gu, Z Xu and J J Beaudoin, *Ibid*, 23, 2, 1993, pp359-367.
32. P Gu, P Xie and J J Beaudoin, *Ibid*, 23, 3, 1993, pp581-591.
33. Z Xu, P Gu, P Xie and J J Beaudoin, *Ibid*, 23, 4, 1993, pp853-862.
34. *Idem*, *Ibid*, 23, 5, 1993, pp1007-1015.
35. R T Coverdale, B J Christensen, H M Jennings, T O Mason, D P Bentz and E J Garboczi, *Jrnl. Matl. Sci.*, 29, 1994, pp4984-4992.
36. *Idem*, *Ibid*, 30, 1995, pp712-719.
37. K Olp, G Otto, W C Chew, J F Young, *ibid*, 26, 1991, pp2978-2984.
38. C A Heiland, *Geophysical Exploration*, Hafner Publishing Co., 1968.
39. W J McCarter, *Cem. and Conc. Res.*, 17, 1, 1987, pp55-64.
40. British Standards Institution, BS 812: Testing aggregates: Part 103: 1985.
41. British Standards Institution, BS 1881: Part 108: 1983, 'Method for making test cubes from fresh concrete'.
42. British Standards Institution, BS 8110: Structural Use of Concrete: Part 1: 1985 'Code of practice for design and construction'.