

Setting behaviour of waste-based cements estimated by impedance spectroscopy and temperature measurements

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This work describes the study of phase development during the setting of various clinker formulations prepared with industrial wastes or by-products, namely sludges (generated in the Al-anodising and surface coating industrial processes, in potable water filtration/cleaning operations and in the cutting process of natural marble) and foundry sand. For comparison, similar formulations were also prepared with commercial high purity grade raw materials and processed in identical conditions. To circumvent the experimental restrictions imposed by the use of Vicat's needle (i.e. large amount of material), electrical resistivity measurements were conducted by alternate current (a.c.) impedance spectroscopy to follow the hydration process and setting behaviour. During setting, the temperature evolution of the water/cement pastes was also recorded. Impedance spectroscopy (IS) studies were found to be a reliable method and, in some systems, can be a more sensitive technique to detect on-going hydration reactions.

Keywords: wastes, cement, setting, impedance spectroscopy.

Fraguado de cementos basados en residuos estimado por espectroscopia de impedancia y medidas en temperatura.

Este trabajo describe el estudio del desarrollo de fases durante el fraguado de diferentes formulaciones de clinker preparados con residuos industriales o subproductos, denominados barros (generados en los procesos de recubrimientos industriales por anodizado de Al, en procesos de filtración/depuración de agua potable y en procesos de corte de mármol) y arenas de fundición. Con el objeto de comparar, se prepararon formulaciones similares a partir de materias primas comerciales de alta pureza y procesadas en idénticas condiciones. Para sortear las restricciones experimentales de inherentes a la aguja de Vicat (esto es, grandes cantidades de material), se realizaron medidas de resistividad eléctrica en corriente alterna (a.c.) de espectroscopia de impedancia para seguir el proceso de hidratación y fraguado. Durante el fraguado, la evolución de la temperatura de las pastas de agua/cemento se registró. Los estudios de espectroscopia de impedancia mostraron ser un método fiable y en algunos casos, pueden emplearse como técnica sensible para detectar el inicio de las reacciones de hidratación.

Palabras clave: residuos, cemento, fraguado, espectroscopia de impedancia.

1. INTRODUCTION

Increasing industrial activity and natural mineral resources rising costs, have forced the transforming industry to review the logistics of raw materials supply. Within this scenario, upgrading industrial wastes to secondary materials becomes interesting, both technically and economically, for a wide range of applications (1), including the fabrication of concretes and mortars (2). Traditionally, waste products are landfilled. However, there might be reuse or recycle alternatives that should be investigated and eventually implemented (3-6). Other than the usual limited incorporation in ceramic bodies with a given shape and size, particulate products such as expanded clays, cement and refractory mortars, offer increased capabilities for high incorporation levels of rejects (7,8). In particular, cement fabrication also involves a huge consumption of natural raw materials (e.g. limestone and clay) and recently new waste-based formulations have been tried. The so-called eco-cement (9,10) is the best example, amongst several known cases of minor incorporation of wastes, such as fly ash and slag (11).

The continuous processing of clinker in industrial rotary

kilns is difficult to simulate in the laboratory. Nevertheless, the lab-scale production of clinkers from industrial wastes and by-products was successfully carried out and is described in previous studies (12,13). In the latter, the general characteristics of the waste-based formulations were compared with those of the corresponding compositions prepared with commercial high purity grade raw materials, to clarify the effect of minor components present in the waste materials on the final products properties.

However, other important properties, like setting time, are more difficult to test in the laboratory if the standard characterisation methods are to be used (in this case, Vicat's needle), since they require reasonably high amounts of material. To overcome these limitations, new characterisation methods have been introduced in recent years, in the study of such properties.

Electrochemical methods appear to have distinct advantages in the study of cement hydration. In particular, a.c. impedance spectroscopy measurements (IS) might provide useful information related to both ion concentration of pore solution and microstructural changes in hydrating

cement pastes. Several papers (14-20) were published in the last decade, describing the attempts to discuss the response of the system in terms of a representative equivalent circuit, and define the physical meaning of each component in relation to the microstructure of the hydrating cement paste. Different systems were investigated (simple or reinforced cement of several types, concrete, etc.) and experimental limitations were identified (e.g. electrode contact effects). Due to the systems complexity, some discrepancies still remain. Nevertheless, a typical Nyquist plot of a cement-based paste usually includes 3-4 characteristic features (15): (i) a low frequency arc, whose maximum imaginary component occurs in the mHz range, related to the electrode or product layer response; (ii) one or two intermediate frequency arcs, ascribable to an interfacial/intergranular response caused by electrode imperfections or by transitions between different components (e.g. fibre reinforced pastes); and (iii) a high frequency (MHz) arc, corresponding to the bulk response.

This work aims to throw light into the setting behaviour and further clarify the interpretation of a.c. IS measurements of hydrating waste-based cement pastes.

2. EXPERIMENTAL PROCEDURE

Four waste materials were selected and characterised, namely, (i) Al-rich anodising sludge (A-sludge), (ii) sludge from the filtration/clarification of potable water (W-sludge), (iii) sludge generated in marble sawing processes (M-sludge), and (iv) foundry sand (F-sand). The foundry sand was milled and sieved through 75 μm ; the other materials were used in the as-received condition. Their full characterisation is detailed elsewhere (21-23). The average chemical composition was determined by X-ray fluorescence (XRF, Philips X'UNIQUE II), and Figure 1 shows their location in the SiO_2 - Al_2O_3 - CaO ternary composition diagram.

Two clinkers (C1 and C2) were prepared with those industrial wastes and also, for comparison purposes, with commercial high purity grade raw materials (standard compositions C1-P and C2-P): alumina (CT3000, Alcoa), calcite (M1, Calcitec), and sand (P500, Sibelco). Batches were ball-milled and homogenized for 60 minutes in porcelain jars and then fired at 1450°C (10°C/min heating rate, 1 h soaking at the maximum temperature, and 20°C/min cooling rate). Sintered powders were also milled (as described before, but just for 30 min) and characterized by X-ray diffraction (XRD, Rigaku Geigerflex D/max - Series, $\text{CuK}\alpha$ at 40 kV and 50 mA).

To prepare the corresponding cements, calcium carbonate (10 wt%) and sulphate hemi-hydrate (5 wt%) were added to the clinkers before milling. For comparison, ordinary Portland (PC, Secil - type I) and alumina-based (AC, Lafarge Aluminates - Ternal White) commercial cements were also evaluated.

The beginning of setting was inferred from temperature measurements on fresh pastes (with a water/cement weight ratio, w/c , of 0.4). Finally, impedance measurements were carried out using a Hewlett Packard 4284A impedance bridge in the frequency range of 20 to 10^6 Hz. Tests were performed under controlled ambient conditions (22-24 °C, ~55% relative humidity) on test bars (18x9x8 mm) cast from the cement pastes into plastic moulds. Polished copper coupons were employed as electrodes, cast in place at the far ends of each

specimen and clamped by a flexible spring. The embedded area was ~0.8 cm^2 .

Curve fitting and interpretation were done using a specific routine program (24). Impedance responses were automatically extracted from the impedance spectra at a fixed frequency of 10 kHz or manually fitted to separate bulk and intergranular contributions.

3. RESULTS AND DISCUSSION

3.1. Clinkers composition

Compositions C1 and C1-P belong to the compatibility triangle C_2S - C_3S - C_3A in the phase equilibrium diagram of the S-A-C system (Figure 1). As expected, XRD analysis of C1-P showed that C_3A , $\beta\text{C}_2\text{S}$, and C_3S are the major crystalline phases present. However, C1 presents gehlenite (C_2AS), mayenite (C_{12}A_7) and calcium aluminium oxide sulphate, in addition to $\gamma\text{C}_2\text{S}$. Mineralogical compatibility relationships predicted by the phase equilibrium diagram of the S-A-C system (Figure 1) are hardly respected in this case, as a consequence of a departure from equilibrium conditions or the effect of impurities. The presence of $\gamma\text{C}_2\text{S}$ in C1 might explain the observed dusting (as the result of the expansive crystallographic inversion of high temperature C_2S polymorphs). Besides, gehlenite does not have hydraulic characteristics and the sulphate might also induce expansive

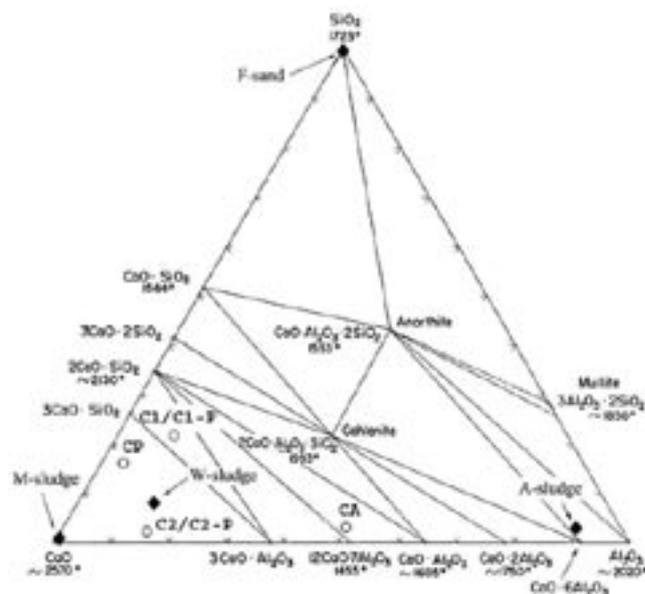


Fig. 1- Location, in the composition diagram of the SiO_2 - Al_2O_3 - CaO ternary system, of the wastes and the compositions investigated.

reactions in the cement. As a consequence, the mechanical performance of the corresponding cement is weak (12).

C2 clinker contains $\text{CaO} + \text{C}_3\text{A} + \text{C}_3\text{S}$ (as observed by XRD), which are the expected equilibrium phases but calcium aluminium oxide sulphate and $\beta\text{C}_2\text{S}$ are also present. In C2-P clinker the presence of the sulphate is not so evident.

3.2. Setting behaviour

Given that chemical reactions that occur during cement setting can cause significant changes in temperature, the

beginning of setting might be detected from temperature measurements. Figure 2 compares the temperature/time curves obtained for the six cements investigated. Commercial samples show the expected behaviour (14): (a) CA: (i) hydration of gypsum accompanied by a significant consumption of free water (in the first 1.5 h), (ii) an "induction" period, while hydration continues at a relatively slow rate, and (iii) rapid hydration and beginning of setting (after 6 hours), which is complete after ~12 hours; (b) CP: (i) hydration of gypsum (in the first 1.5 h), and (ii) continuous

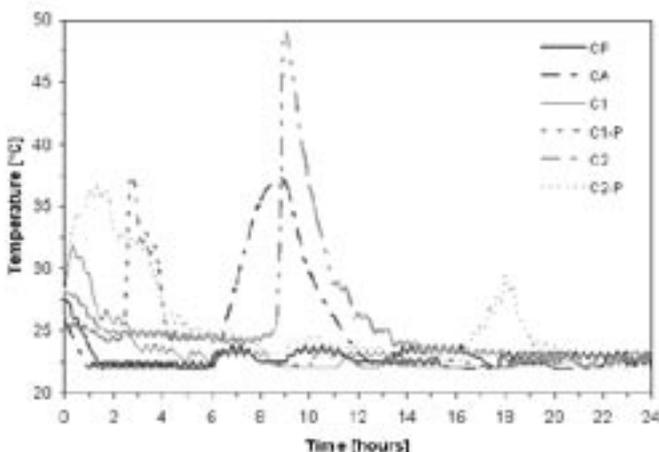


Fig. 2- Temperature variation of cement pastes during setting.

hydration at a relatively slow rate, involving the formation of calcium hydroxide and C-S-H gel.

The C1-based cements show a comparable behaviour to that of commercial ordinary Portland cement (CP). However, the first reaction seems to be delayed in the oxide-based C1-P formulation and starts only after 2 hours. The beginning of setting in both C1 and C1-P is hard to detect by temperature measurements but seems to occur at 660 and 310 minutes,

TABLE I. RELEVANT CHARACTERISTICS OF HYDRATED CEMENTS.

Property / Cements	CP	CA	C1	C1-P	C2	C2-P
Initial setting time (min)	~ 360	~ 366	~ 660	~ 310	~ 520	~ 540
Compressive strength [MPa] (after 7 days)	14.0	24.0	3.12	5.32	15.4	-
Compressive strength [MPa] (after 28 days)	22.0	44.0	3.22	10.5	23.3	-

respectively (Table 1). Thus, C1-P is more reactive, as expected from the presumed absence of gehlenite.

Differences between the estimated initial setting time in C2 and C2-P cements are small: C2-P shows a very weak exothermic reaction around 540 min, whereas a stronger peak starting around 520 min is observed for C2. However, there are sharp differences in mechanical properties development: dusting is observed in C2-P clinker, which can only be explained by the presence of a higher free lime content, whereas in C2, the presence of impurities brought in by the waste materials might increase the reactivity of the material, hence ensuring the complete combination of lime.

Figure 3 shows the impedance spectra ($-Z''$ vs. Z')

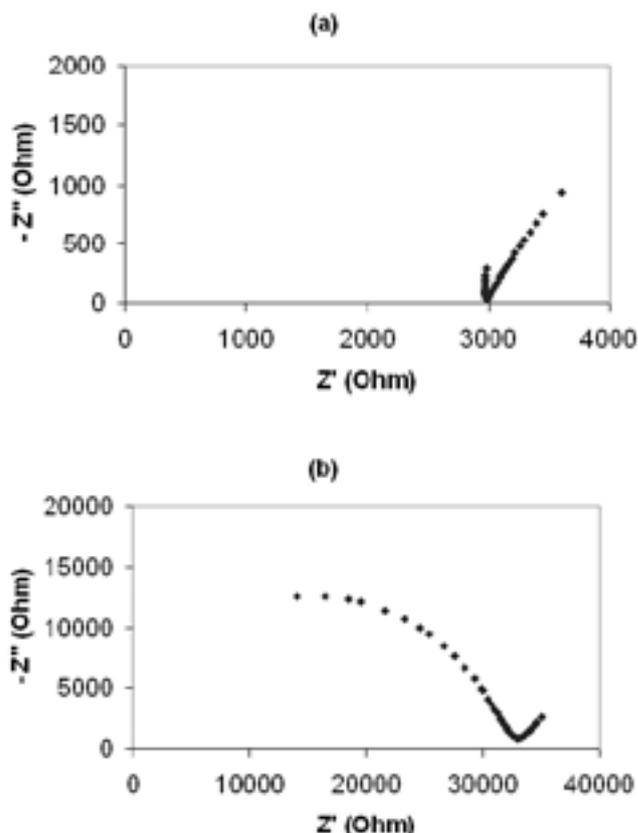


Fig. 3- Impedance spectra of commercial cements: (a) CP at 597 min; (b) CA at 293 min.

of CP and CA samples, acquired at the hydration times shown. At first, the response seems to involve two arcs (partially visible): the one in the right (low frequency range) is normally ascribed to the interfacial/intergranular response caused by electrode imperfections or by transitions

between different components; the other one, visible in the kHz frequency range, is attributed to the bulk response. Their intersection with the Z' axis gives the corresponding impedance, herein named R2 and R1, respectively. Since the available impedance bridge precludes the use of frequency values lower than 20 Hz, estimation of R2 can be very difficult or uncertain, especially for longer hydration times or highly resistive samples.

Generally speaking, the microstructure changes that occur in hydrating cements are the result of the consumption of free water and the precipitation of hydration products, giving rise to a denser matrix (suppression of pores). This results in an increase of bulk paste impedance and a decrease

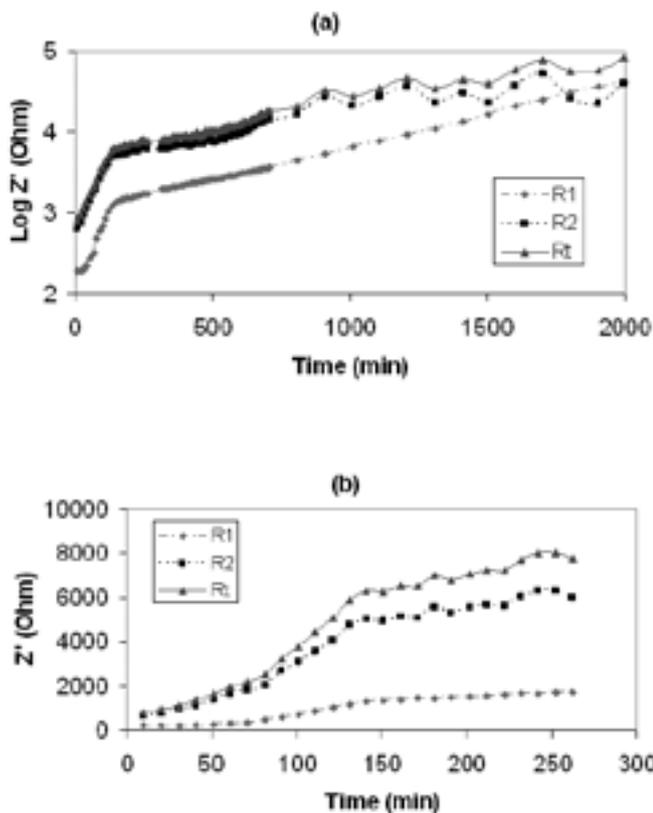


Fig. 4- Evolution of impedance components R1, R2 and Rt ($R_t = R_1 + R_2$) of CP paste with hydration time: (a) full time scale; (b) detailed view of the first 5 hours of hydration. Estimates were obtained from manual fitting.

in solid-liquid capacitance. An increase in the liquid phase ion concentration leads to a decrease in matrix impedance and an increase in charge density per unit interface (25). Figure 4a shows the general changes, with hydration time, of R1, R2 and Rt ($R_t = R_1 + R_2$), observed for CP sample, which might depend on the microstructure of the paste matrix and ion concentration in the liquid phase. Figure 4b details the behaviour during the first 5 hours and clearly shows that both R1 and R2 components tend to increase at a faster rate between 80 and 130 min. As previously mentioned, during this period the hydration of gypsum occurs, accompanied by significant consumption of free water. For longer times, the impedance tends to increase at a fairly constant rate, as observed by other authors (14,15). It is well known that the hydration of C_3S and C_2S gives rise to a microstructure consisting essentially of a rigid calcium hydroxide network and C-S-H gel. Dissolution of calcium hydroxide contributes to a higher ion concentration in the liquid phase, resulting in low matrix impedance. There is a combination of the above two opposing effects and this is the rationale for the observed small but steady increase of impedance.

Figure 5a shows the general changes, with hydration time, of the impedance values of CA sample and evidences the difficulty in using very low frequency values. For hydration times in excess of 300 minutes (see also Figure 5b), the determination of R2 becomes impracticable. In these samples, the intersection of the bulk arc with the Z' axis generally occurs at ~ 10 kHz, enabling the automatic

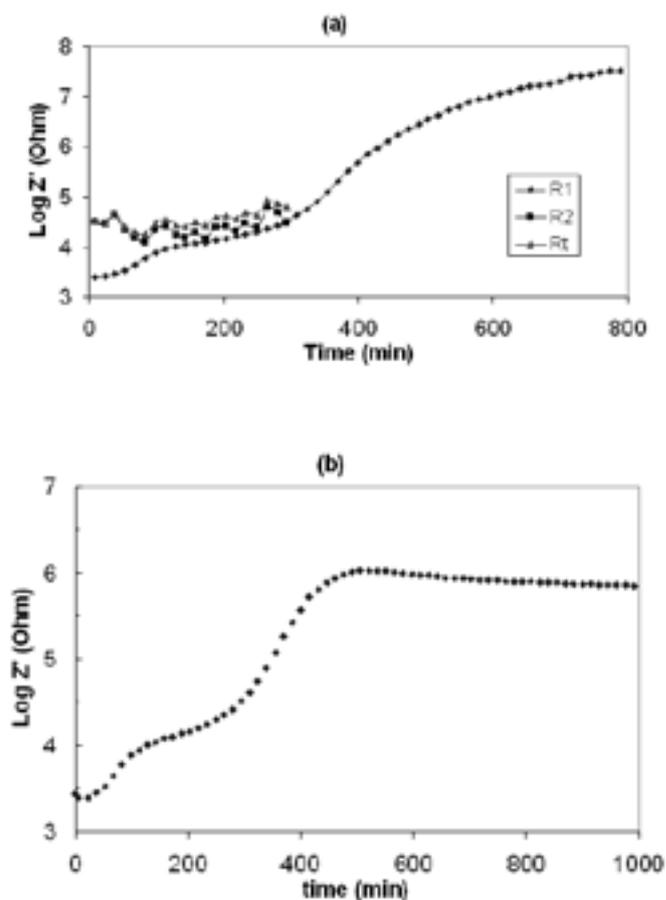


Fig. 5- Evolution of impedance of CA paste with hydration time: (a) components R1, R2 and Rt ($R_t = R_1 + R_2$) estimated from manual fitting; (b) R1 bulk or matrix component automatically extracted at 10 kHz.

extraction of R1 values, as suggested by Gu et al. (14) for the so-called matrix or bulk impedance. Figures 5a and 5b compare the R1 values and show a similar evolution, which validates this assumption. Differences become larger for longer periods, due to the mentioned fitting difficulties. Initial impedance values for CA pastes are higher than those for CP pastes, due to the lower ion concentration (free or hydrated ions) in the liquid phase of CA pastes. In CP pastes, CH is a source of Ca^{2+} and OH^- ions for the pore solution.

In CA sample the first rapid increase of matrix impedance is again due to the presence of gypsum and possibly to the formation of ettringite (26). However, there is a clear second sharp increase, starting at about 5 hours, which might be attributed to hydration of aluminates (26). This phenomenon consumes a significant quantity of free ions and water from the liquid phase, resulting in the sudden increase of impedance and heat release. Figure 2 shows that this sudden increase of impedance corresponds to the second temperature peak and marks the beginning of setting. The impedance decrease (or stabilisation) that follows the maximum is explained by the dissolution of hydrates and formation of ionic species. Accordingly, and as suggested by other authors (14), the setting times of pastes were estimated from the corresponding impedance curves at the second sudden rise of matrix impedance.

C1 and C1-P formulations are ordinary Portland type

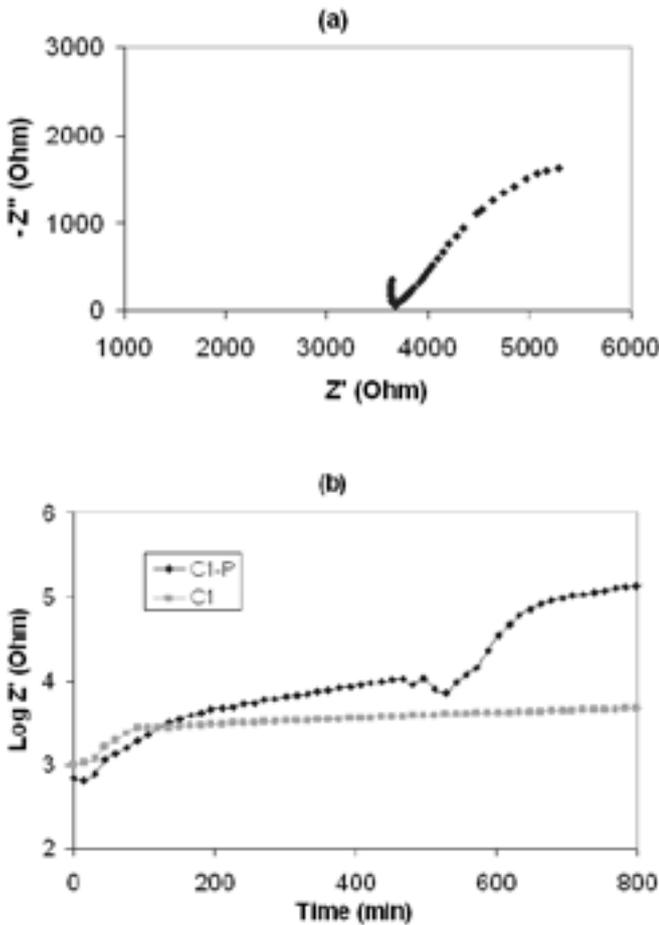


Fig. 6- Impedance evolution of C1 and C1-P with hydration time: (a) spectra of C1 paste at 452 min; (b) R1 bulk or matrix component automatically extracted at 10 kHz.

cements. As expected, their impedance spectra and the evolution of resistance values upon hydration (see Figure 6) are very similar to those of the CP paste. The spectrum of C1 paste obtained at 452 min, shown in Figure 6a, is remarkably similar to that of CP paste at 597 min, shown in Figure 3a. The corresponding impedance values are also very similar and their evolution with hydration does not present any abrupt increase after gypsum reaction is completed (> 1.5 hr). In that sense, the estimation of the initial setting time from these results is rather difficult, as happened by measuring the temperature changes. As mentioned before, C1-P is more reactive than C1 and a second rise in bulk impedance is easily observable in Figure 6b at ~10 hours hydration, in agreement with the estimates derived from the temperature/time curve of C1-P. In this case, the IS technique shows a better sensitivity than the temperature measurements, to detect the beginning of the setting process. The comparatively higher impedance values presented by the C1-P paste are justified by its higher purity level, hence lower amount of soluble species in the pore solution.

Figure 7a illustrates the impedance spectra for C2 paste at 542 min while Figure 7b shows the evolution of impedance values for C2 and C2-P pastes with hydration time. C2-P impedance values are very high even for short hydration periods, and always above those for C2 (although not shown, measurements were extended up to 5000 minutes

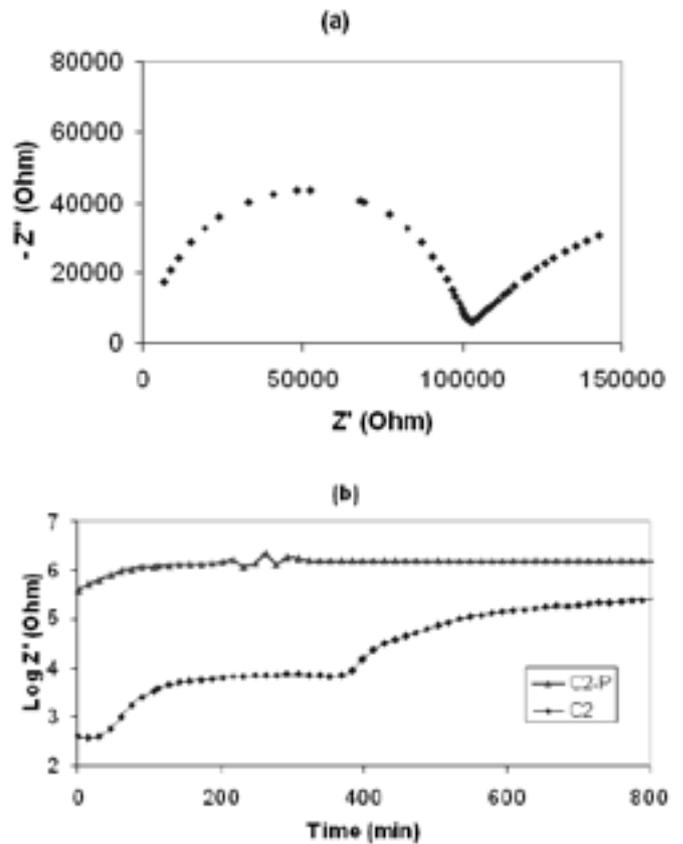


Fig. 7- Impedance evolution of C2 and C2-P with hydration time: (a) spectra of C2 paste at 542 min; (b) R1 bulk or matrix component automatically extracted at 10 kHz.

hydration). As a consequence, estimations of the bulk impedance are less accurate. The poor reactivity of this material, suggested by the small temperature rise observed in Figure 2, is thus confirmed. The mentioned dusting tendency of the corresponding clinker might induce the formation of higher amounts of pores and lack of contiguity for electrical conduction through the paste. By contrast, the waste-based C2 paste shows a well-defined setting reaction, starting at ~400 min (Figure 7b), also clearly detected on the temperature/time curve but only at ~520 min (Figure 2). Since these measurements were not conducted in simultaneous, changes in the ambient conditions (temperature, moisture content) might explain this slight discrepancy. Future and experimentally refined measurements will be conducted to clarify these aspects.

4. CONCLUSIONS

The matrix impedance of hydrating pastes is the result of the combined effects of changes in the ionic concentration of the liquid/intergranular phase and in the microstructure. In that sense, IS follows in detail the setting process, showing a good agreement with predictions obtained from temperature change measurements. When the standard Vicat's needle method to determine the initial setting time is precluded by materials availability, IS studies are a reliable alternative and, in some systems, IS can be a more sensitive technique to detect on-going hydration reactions.

The IS technique was tested in the characterisation of CP and CA commercial pastes, which showed the expected behaviour: the impedance tends to increase at a reasonably constant rate with hydration time in the CP paste whereas a clear second sharp increase is detected in CA paste due to hydration of aluminates.

Two waste-based formulations, C1 and C2, and their oxide-base counter-parts, C1-P and C2-P, were characterised afterwards. C1 and C1-P are ordinary Portland type compositions and both their impedance spectra and the evolution of resistance values upon hydration are very similar to those for CP paste. C1-P is more reactive than C1 paste and a second rise of bulk impedance is easily observable at ~10 h hydration.

The oxide-based C2-P paste was found to be less reactive than its waste-based counter-part C2. Impedance values for C2-P are always very high, even in the early stages of hydration, and its poor reactivity was confirmed by the absence of the second rise of impedance, which is clearly visible in C2 paste impedance spectrum.

ACKNOWLEDGEMENT

Financial support by CAPES-MEC, Brazil, is greatly appreciated (F. Raupp-Pereira, Ph.D. grant).

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Recibido: 29.11.05

Aceptado: 24.08.06