Determination of the Zeta Potential in Hardened Cementitious Materials by Electro-Osmotic Experiments

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The study of the properties of the interfaces between the solid phases and the pore water solution in hardened cementitious matrixes is a key point to understand a large number of properties and phenomena. At this respect, the zeta-potential is the key parameter in the establishment of the electrokinetic effects. Several experiments have been carried out to determine the zeta-potential in cementitious materials (mainly from cement, or synthetic CSH suspensions and by some microelectrophoresis techniques). To determine the zeta potential in hardened cementitious materials has not been made until recently. Electroosmotic experiments have been carried out on different mixes of hardened cementitious matrixes including concrete, mortar and pastes, different types of binders, carbonated and non-carbonated specimens and different test conditions. From these trials, the zeta potential values have been determined and the optimum experimental parameters and devices, as well as the influence of the composition of the matrixes, have been established.

1.   Introduction

At the surface of a solid in contact with an electrolyte there develops, in general, a difference in potential. When one of these phases (solid or liquid) is caused to move tangentially past the second phase, a number of phenomena, which are grouped under the generic name of "electrokinetic effects" can develop. The zeta-potential is the key parameter in the establishment of the electrokinetic effects. It can be defined as the average potential in an imaginary surface (surface of shear), which is considered to lie close to the solid surface, and within which the fluid is stationary during an electrokinetic process [1]. When the solid remains stationary and the liquid moves in response to an applied electrical field this is called electro-osmosis [1], which is the case of the experiments performed here using hardened cementitious materials through which the fluid moves. When the liquid does not move while the particles within it do, the phenomenon that takes place is named electrophoresis.

The knowledge of the electrokinetic phenomena is of great importance, as they control the chemistry and the interactions of the surface, that on the macroscopic level influences, among others, the chemical equilibria, the rate of reactions, and the transport processes.

Several experiments have been carried out to determine the zeta-potential in cementitious materials (mainly from cement, or synthetic CSH suspensions by microelectrophoresis techniques [2-9] or acoustophoresis [10]) mainly to know basic features of the nature of cement and admixtures during setting. The technological application of the electroosmosis in concrete arises when performing realkalisation experiments, noticing that the carbonate ions, in the positive compartment, penetrated towards the rebar [11-14] against the driving force of the electrical field, being able to create a carbonate/bicarbonate buffer that prevents further carbonation and helps to maintain the passivity of the rebars after the treatment. In [15] the demonstration of the electroosmotic flux through hardened carbonated concrete in realkalisation tests with carbonated concrete was reported. Since then, some more research have been carried out on determining zeta potentials on hardened cementitious materials [16-18], including the influence of the concentration of Na_2CO_3 in the anodic compartment [16], the in-situ monitoring of the experiments by analyzing, at the same time, the development of the electroosmotic flux and the microstructural changes in the surroundings of the rebar by neutron diffraction [17], and the influence of the composition of the binder and the carbonation of the sample, has been undertaken [18]. In this paper, a summary of different experiments carried out by the authors on different mixes, with different types of binders for carbonated and non-carbonated specimens, and different test conditions is presented. The optimum experimental parameters and devices are described, as well as the influence of the composition of the matrixes in the values of the zeta potential obtained.

2. Experimental

2.1 Materials and procedures

In order to study the accelerated transport of solution through concrete, it is possible to use different types of devices. For testing concrete specimens, the most useful is the ECD (electroosmotic cell device), which is an evolution of the classical two compartments migration cell [15]. In it, a disc of the material to be tested (around 2 cm depth) is used for separating the two chambers where cathode and anode are placed. Two meshes of activated titanium, or platinum, are used as electrodes.

Distilled water is introduced into the catholyte and 1M of Na_2CO_3 solution is used as anolyte. A voltage difference of 45 volts is applied between the electrodes. The volume of liquid in the catholyte and anolyte chambers has to be monitored as well as the potential drop at the surface of the disc by placing two reference electrodes in contact with the surfaces. These parameters can be monitored automatically by a data-logger connected to a computer (fig 1-a).

For small specimens of cement paste or mortar, "tubular cells" are used (fig 1-b), which consists in the same concept than ECD but with both compartments made of glass tubes of 4 mm internal diameter in order to have a precise measurement of the flux of liquid. If an embedded rebar is acting as cathode and the direction of the flux is known to be towards the cathodic electrode, ponding cells can also be used (fig 1-c).
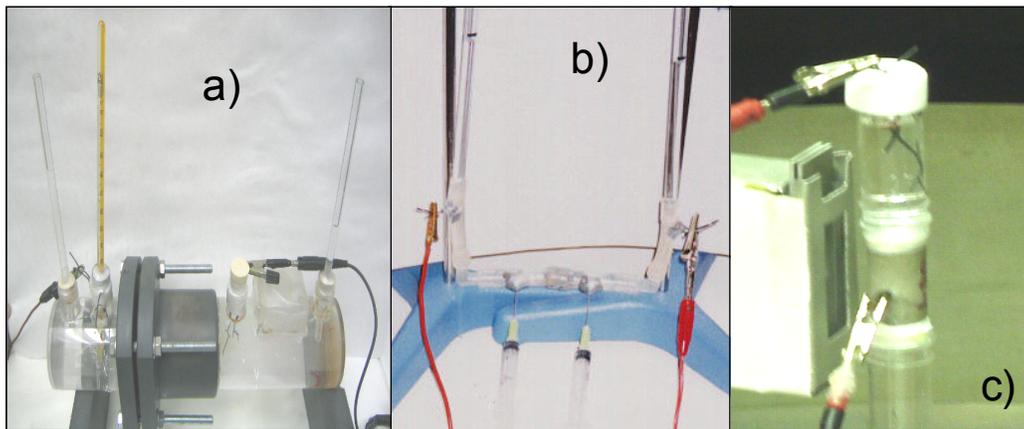

Figure 1: Experimental devices used for the experiments: a) ECD (electroosmotic cell device), b) tubular cell, c) ponding cell.

Several types of cementitious matrixes with different kind of binders have been tested: Four different mixes of concretes have been cast; one concrete made with cement with low C_3A content OPC (OPC-C), two concrete mixes made with OPC blended with silica fume (SF-C) and/or fly ashes (FA-C) and one mix fabricated with Calcium Aluminate Cement (CAC-C). In addition, pastes prepared with OPC (OPC-P) and with a 35% of replacement of by fly ash have been also tested (FA-P). Finally, there were tested two types of mortar, one of them with OPC cement with high C_3A content OPC (OPC-M) (tested with different concentrations of Na_2CO_3 in the anodic side), and another including fly ash in the composition (FA-M). Some of the mixes, prior to the electroosmosis tests, were carbonated at 65% RH, 20±2ºC, and 100% CO_2 concentration. A summary of the mixes tested is given in table 1.

Table 1: Summary of the mixes tested

Mix	OPC-C	FA-C	SF-C	CAC-C	OPC-P	FA-P	OPC-M	FA-M
Cement type	I-42.5 R/SR	I-42.5 R/SR	I-42.5 R/SR	CAC	I-42.5 R/SR	I-42.5 R/SR	I-42.5 R/SR	I-42.5 R/SR
Cement (Kg/m^3) / %	300	249	459	300	100%	65%	100%	64%
Fly ash (Kg/m^3) / %	-----	24	-----	-----	-----	35 %	-----	36%
Silica Fume(Kg/m^3)	-----	27	92					
w/c	0.55	0.45	0.45	0.45	0.5	0.5	0.5	0.4
Carbonated	Yes/No	No	No	No	Yes	Yes	Yes	No

2.2. Calculation of the zeta-potential

Calculation of the zeta potential has been made according to equation 1 [1]:

$$x = V\frac{4ph}{qDE}$$ (1)

where: x: zeta-potential, **V**: liquid volume electroosmotically transported in a second, **D**: dielectric constant, **E**: electrical field applied, **q:** transversal area for the flux of liquid and h: liquid viscosity coefficient.

The use of this equation implies no assumptions on the potential distribution in the electrical double layer, saving that it obeys Poisson´s equation. Also it is assumed that the layer between the shear plane and the wall of the pore is unaffected by the applied electrical field and that D and η retain their normal bulk values, even though it is known that this is not a real situation. The extreme limits of the values for the dielectric permittivity can be varied from 6 to 80; for water, the limiting value of 6 corresponds to zero orientation polarization. For the outer zone, a somewhat lower level of water organization would lead to 20< D < 40. For the bulk of the liquid, D≈ 80 [1].

In present paper, the values for the bulk, D≈80, and the extreme values of D≈6 have been used when making the calculations. It has to be pointed out that that is only a matter of a factor, and the conclusions obtained are the same using any of the values within the range of water permittivity.

The value of q, transversal area, has been normalized by means of the porosity to the cross section available to the liquid to pass through. This assumes cylindrical pores in the perpendicular direction of the flux of liquid.

3. Results and discussion

3.1. Establishment of the electroosmotic flux

As the realkalisation experiment goes on, there are one (or several) points in which there is a sudden increase in the current circulating. This increase has been detected in every experiment performed and a parallelism between the sudden increase in the current and the electroosmotic flux has been deduced. As an example, in figure 2, the derivative of the curve of current intensity in function of time has been depicted together with the values of zeta potential calculated according to equation (1) for the OPC-M sample using 0.1 M Na_2CO_3 in the anolyte. As a detail in the left upper part of the graph, the original curve of current intensity has been also depicted. From figure 2, it is deduced the correspondence between the abrupt change in the slope of the intensity curve and the electroosmotic flux.
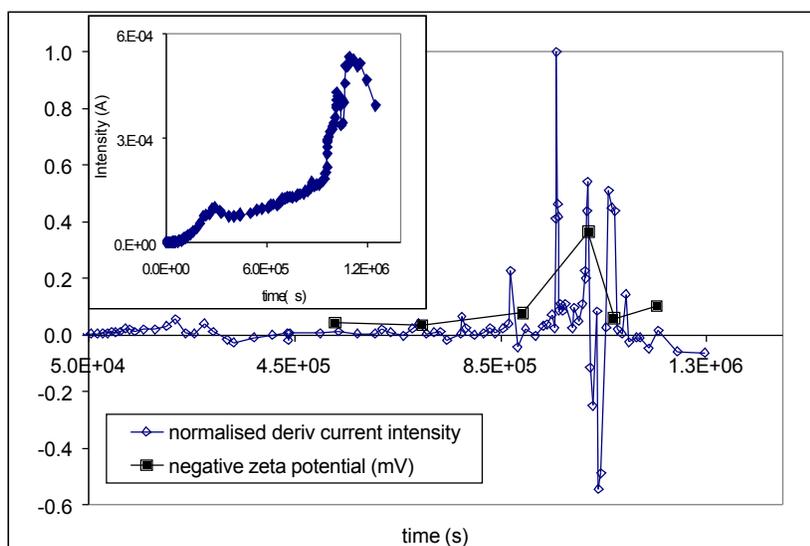

Figure 2: Derivative of the curve of current intensity in function of time and zeta-potential values for the sample OPC-M using 0.1 M Na_2CO_3 in the anolyte. The detail in the left upper part of the graph shows the original curve of intensity.

The other possibility for the flux detected in this type of experiments could be the water associated to the solvating sphere of Na^+ ions penetrating due to migration forces [19]. In order to verify this hypothesis, on site acquisition of neutron diffraction patterns, at the same time than the application of the electrical field, was carried out for the OPC-P and FA-P

[17] samples. The experiment was designed casting the specimens with deuterated water, while the Na_2CO_3 solution was prepared with ordinary distilled water. If electroosmotic flux took place there would be an abrupt increase in the background of the diffraction patterns due to incoherent scattering of the H of the water. The evolution of the integration of the backgrounds of the diffraction patterns (normalized intensity at the low 2θ region) in the cathodic area of the sample is presented in figure 3-a for the FA-P sample, where it can be detected 4 pulses of increase.

If this increase had been associated to the solvating sphere of Na^+ ions that would have implied an increase in the background following a smooth process with a linear dependency with the charge density, as shown in figure 4-b for data taken from the OPC-C experiment [15], which obviously, is not the case. That is, the flux detected cannot be mainly associated to the attraction of sodium ions towards the cathode, in spite they move solvated by a first solvation shell of around 4±1 water molecules [20].
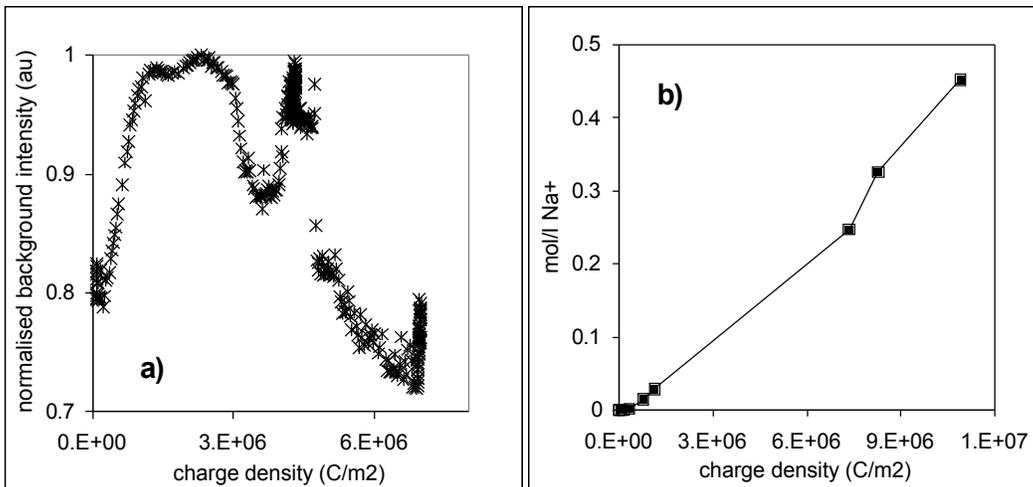

Figure 3(a-b): Evolution, during realkalisation treatments of: a) normalised background (in arbitrary units) of the neutron diffraction patterns in the cathodic zone of the sample FA-P. b) concentration of Na+ in the cathodic compartment for the experiment with the carbonated sample OPC-C.

3.2. Zeta-potential values

The zeta-potential values calculated by equation 1, for different mixes, are given in figure 4. The values given as zero of zeta potential means non-detectable flux at the conditions of the experiment. In the left Y axis of figure 4, the values are calculated using $D \approx 80$ in equation 1, while in the right Y axis, the dielectric permittivity, $D \approx 6$, has been used in the

calculations. For each case, the percentage of SiO_2 and Al_2O_3 in the binder is given.

From results in figure 4, it can be deduced that the composition of the cements seems to be one of the key parameters as long as the resulting zeta potential is concerned (indicated by the percentage of SiO_2 and Al_2O_3 in the mixes). In addition, for the same composition, carbonated specimens have more negative and higher absolute values, than non carbonated specimens. In addition, it can also be deduced that the zeta potential values are very dependent on the external solution, being higher using a Na_2CO_3 solution than using water as anolyte.

Comparison between data for mixes with the same cement indicates that there is not a noticeable influence of the presence of aggregates in the zeta potential. In fact, this indicates that the normalization in the parameter q in equation 1 through the porosity is a correct assumption, as the zeta potential is generated in the pore walls which are within the cement paste and the value of porosity used in the normalization takes into account the amount of aggregates. In summary, the volumetric effect of the amount of paste is considered when making the calculations.
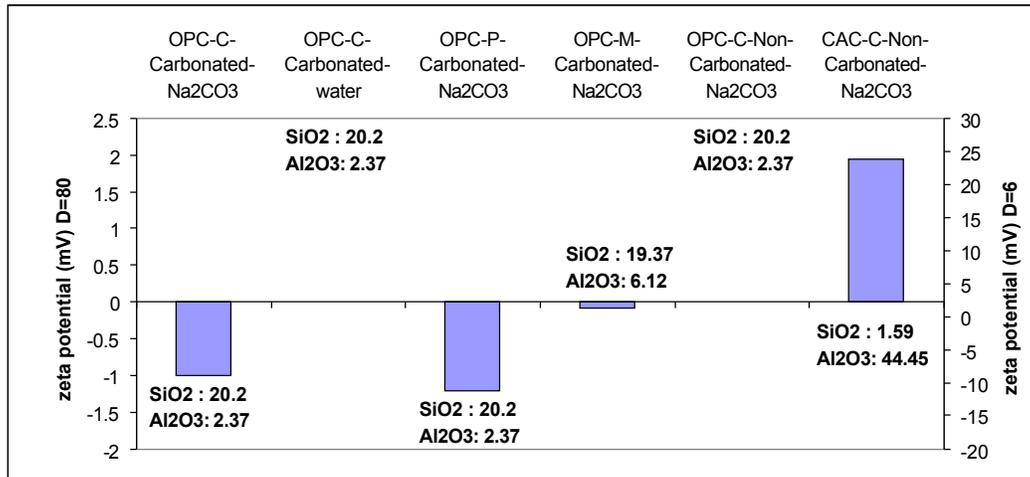

Figure 4. Zeta-potential values obtained calculated for different mixes in different conditions. (In the left Y axis, values for the dielectric permittivity D≈80; in the right Y axis, values for the dielectric permittivity D≈6). For each case, the percentage of SiO_2 and Al_2O_3 in the binder is given.

In order to study the influence of the chemical composition of the binder, carbonated and non-carbonated specimens have been correlated separately in function of the resulting percentages of the mayor different chemical compounds, for the experimental conditions of using 1 M Na_2CO_3 in the anodic compartment.

The best empirical relationships for both types of specimens, with the data of this research, using D≈80 in equation 1, are those including both the compositions of Al_2O_3 and SiO_2 and are given as equations 2 and 3. The rest of chemical species in the cement do not seem to have a significant influence on the value of zeta potential. In particular, the amount of CaO does not seem to play any significant role [18].

$$\zeta_{non\text{-}carbonated}=0.292+ 0.012*e^{0.11*(\%Al2O3)}- 0.0045*e^{0.0209*(\%SiO2)} \qquad (2)$$

$$\zeta_{carbonated}=-38.9 + e^{3.857+0.0052*(\%Al2O3)-0.0119*(\%SiO2)} \qquad (3)$$

From figure 4 and equations 2 and 3 it can be deduced that higher amounts of Al_2O_3 in the binder lead to higher positive values of zeta potential for carbonated and non-carbonated samples. On the opposite, an increase of the amount of SiO_2 leads to more negative values of zeta potential. This has been explained in terms of the different isoelectric point (i.e.p.) for both oxides, which means different global surface charge depending on the proportions of silicates and/or aluminates in the surface.

The (i.e.p.) for Al_2O_3 and SiO_2 takes place at a pH of 9.1 ± 0.2 and 2.0 ± 0.3 respectively [1]. That means that at pH higher than 9.1, both oxides exhibit negative surface charge; however, below 9.1 the surface charge of Al_2O_3 is positive while that of SiO_2 continues to be negative until a pH of 2.0. Therefore, and only considering the pH of the pore solution (H^+ and OH^- ions), assuming that the cement phases remain unchanged during carbonation (which is not really true, as $CaCO_3$ is formed and precipitated), the lower pH in the pore solution would imply a shift towards more positive values of zeta potential, which is in opposition to what was experimentally found. In fact, for the same amount of aluminates, in carbonated samples, the zero zeta-potential value is reached with a smaller amount of silicates in the matrix. This contradiction leads to deduce that apart from the pH, other factors are involved in the phenomena experimentally found, what has been attributed to the specifically adsorbed Ca^{++} in the negative sites of the surface in the non-carbonated samples [9], as their concentration of Ca^{++} is, for every sample, those of lime saturation [18].

3.3. Influence of the external solution in the anolyte

The equations 2 and 3 are only valid for a dissolution of $NaCO_3$ in the anolyte when making the experiments. From values in figure 4 it can be deduced that when using water in the anolyte, no flux passing through the

specimen could be detected, at the conditions of the experiment, while using 1M Na_2CO_3 it was detectable and measurable.

These differences have been interpreted in terms of pH of the anolyte. In [16], using different concentrations of Na_2CO_3 (between 0.1M to 2 M), the authors established that the electroosmotic flux was independent on the concentration of Na_2CO_3 initially used as anolyte. As a common trend, with any kind of solution, at the initiation of the experiment, no flux can be noticed. However, as the composition of both compartments are continuously changing during the test, due to the electrode reactions of water hydrolysis, it arrives a moment when the optimum conditions of pH in the anolyte are fulfilled. At this point, the value of the zeta potential is maximum and an increase of the electroosmotic flux takes place and can be detected as a sudden increase in the current passing through the cell (see figure 1). Due to the continuous generation of H^+ and OH^- at the electrodes, these conditions do not remain constant, the zeta potential starts to decrease and the flux stops. These optimal conditions were related to the pH in the anolyte independently of the initial concentration of Na_2CO_3.

That optimum value of pH, that was established to be around 10 [16, 17] for the mixes tested, cannot be reached when water is in the anolyte in the conditions of present tests. This might be the reason for having much smaller values of zeta potential when using water in the anolyte. Until now, there is not enough data to establish a relationship between the composition of the cement in the matrix and the optimum pH in the anolyte to get the optimum, or the higher in absolute value, zeta potential. More research is been carried out in order to solve this gap.

4. Conclusion

Electroosmotic experiments have been carried out on different mixes of hardened cementitious matrixes including concrete, mortar and pastes, different types of binders, carbonated and non-carbonated specimens and different test conditions. From these trials, the following conclusions have been obtained.

- Different experimental devices can be used to obtain the zeta potential through hardened cementitious materials. For testing concrete specimens, the optimum one is the ECD (electroosmotic cell device) that includes capillary tubes, to measure more accurately the flow of liquid. The thickness of the specimen to be used is about 2 cm. The electrodes are two meshes of activated titanium, or platinum, between which 45 Volts DC have to be

applied; the catholyte is distilled water and 1M of Na_2CO_3 solution is used as anolyte.

- The chemical composition of the binder seems to be one of the key parameters as long as the resulting zeta potential is concerned. Empirical relationships have been obtained, for both carbonated and non-carbonated specimens, which are dependent on the compositions of both Al_2O_3 and SiO_2.

- Higher amounts of Al_2O_3 in the binder lead to higher positive values of zeta potential; on the opposite, increasing the amount of SiO_2 leads to more negative values for carbonated and non-carbonated samples. This has been explained in terms of the different i.e.p. for both oxides, which means different global surface charge depending on the proportions of silicates and/or aluminates in the surface.

- For non carbonated concrete, the values of zeta potential are comparatively small in absolute value, which implies that in some cases it was not possible to detect any flux. This has been attributed to the specifically adsorbed Ca^{++} in the negative sites of the surface in the non-carbonated samples, as their concentration of Ca^{++} is, for every sample, those of lime saturation.

- For the same sample, making the experiment with Na_2CO_3 or water the anolyte leads to different values of zeta-potential. Further experiments are needed to establish the relationship between the composition of the cement in the matrix and the optimum pH in the anolyte to get the optimum zeta potential for the maximum flux.

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