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Cement and Concrete Research 36 (2006) 1915 – 1921

Influence of the composition of the binder and the carbonation on the zeta potential values of hardened cementitious materials

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Received 25 November 2005; accepted 29 May 2006

Abstract

Electroosmotic experiments have been carried out on eight 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 have been established. In addition, the influence of the composition of the binder on the zeta potential has been quantified indicating that higher amounts of Al_2O_3 in the binder lead to higher positive values of zeta potential, while the SiO_2 acts just on the opposite side. This has been explained in terms of the different i.e.p. (isoelectric point) for both oxides. Concerning the influence of carbonation, it increases the absolute value of the zeta potential toward more negative values; this behaviour has been attributed to the influence of the specifically adsorbed Ca^{2+} in the negative sites of the surface in the non-carbonated samples.

Keywords: Electroosmotic flux; Composition of the binder; Carbonation; Zeta potential; External solution; Hardened cementitious matrix

1. Introduction

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 whose explanation only can be found at the nano-scale. As an example, it can be pointed out that the adsorption and transport of different species into concrete, or electroosmotic phenomena in realkalisation treatments are main concerns regarding durability of structures.

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 electroosmosis [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 the electrophoresis.

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) [2–10], but also using other techniques as acoustophoresis [11] (having the advantage of being able to be performed in concentrated solutions), which are very important to know basic features of electrokinetic nature of cement and admixtures during setting. However, in addition to these tests in solutions, usually very diluted, it is necessary to perform experiments in hardened cementitious materials, as are the real conditions, with the real pore and the restrictions imposed by the pore sizes.

In a previous paper, the authors were able to demonstrate and quantify the occurrence of an electroosmotic flux through hardened carbonated concrete [12] during the realkalisation processes. Then, the influence of the external solution (concentration of Na_2CO_3 in the anodic compartment) was analysed resulting that the pH in the anolyte was one determining parameter of the zeta potential and consequently a key aspect in the establishment of the electroosmotic flux [13]. The following

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doi:10.1016/j.cemconres.2006.05.033

Table 1
Mixes used in the study

	Mix							
	A	B	C	D	E	F	G	H
Type of matrix [a]	C	C	C	C	P	P	M	M
Cement label	1	1	1	3	1	1	2	1
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-52.5 R	I-42.5 R/SR
Cement	300 kg/m^3	249 kg/m^3	459 kg/m^3	300 kg/m^3	100%	65%	100%	64%
Fly ash	–	24 kg/m^3	–	–	–	35%	–	36%
Silica fume	–	27 kg/m^3	92 kg/m^3					
w/c	0.55	0.45	0.45	0.45	0.5	0.5	0.5	0.4
Carbonated	Yes and no	No	No	No	Yes	Yes	Yes	No

[a] C: Concrete; M: Mortar; P: Paste.

step followed by the authors was the in-situ monitoring of a realkalisation experiment analysing, at the same time, the development of the electroosmotic flux and the microstructural variations in the surroundings of the rebar [14]. In this paper, the influence of the composition of the binder and the carbonation of the sample has been studied.

2. Experimental

2.1. Materials

In the present research, several types of cementitious matrixes with different kinds of binders have been used. The different mixes are presented in Table 1, in which they have been labelled using different letters. Four concretes with different dosages have been cast; one concrete was made with a low C_3A OPC (A), two concrete mixes made with OPC blended with different amounts of silica fume and/or fly ashes (B and C) and one mix fabricated with Calcium Aluminate Cement (CAC) (D). In addition, pastes prepared with OPC (E) and with 35% of fly ash replacement (F) have been also tested. Finally, two mortars were tested, one with the low C_3A OPC (G), and another including fly ash in the composition (H).

The chemical composition of the different binders used is given in Table 2.

Some of the mixes, prior to the electroosmosis tests, were carbonated at 65% RH, 20±2 °C, and 100% CO_2 concentration (see Table 1). The specimens were held in the chamber until negligible increase in weight was recorded. The fully carbonated state was confirmed by breaking duplicate specimens and spraying phenolphthalein indicator on the fresh fractures.

2.2. Methods

Different types of devices have been used in order to study the accelerated transport of solution through concrete depending on the sample. For some of the concrete specimens, “classical migration cells” have been used [12], for the carbonated mortar specimens “tubular cells”, using the same concept but with much smaller sizes in order to measure much more accurately the electroosmotic flux, were developed [13]. The pastes were tested using ponding cells [14]. Different voltages have also been applied (ranging from 12 to 72 V DC) and different electrolyte solutions have been used (water and 1 M Na_2CO_3). From the experience using these different conditions and devices, the optimum experimental parameters and arrangements have been established and an ECD (electroosmotic cell device) has been designed.

The summary of the experimental conditions used for the different tests and mixes is given in Table 3.

The set-up of the recommended ECD is very similar to the migration cell used by the authors to determine the diffusion coefficient of different ions through concrete by migration tests [15]. However, the ECD includes two capillary tubes, in order to measure precisely the flow of liquid. The arrangement used for the ECD test is shown in Fig. 1. In summary, a disc of the material to be tested (between 1 and 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 1 M of Na_2CO_3 solution is used as anolyte. A voltage difference of 45 V 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

Table 2
Chemical composition of the binders used (%)

	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)
Cement 1: I-42.5 R/SR	20.20	2.37	4.10	65.84	1.85	3.8	0.11	0.65
Cement 2: I-52.5 R	19.37	6.12	3.13	62.86	1.78	3.23	0.18	1.00
Cement 3: CAC	1.59	44.45	14.75	36.64	0.72	0.11	0.09	0.07
Fly ash	48.71	25.18	5.18	12.09	1.61	0.43	0.61	3.28
Silica fume	96.32	0.00	0.00	0.67	0.49	0.00	0.15	0.39

Table 3
Experimental conditions used for the different tests and mixes

	Mix									
	A		B		C	D	E	F	G	H
Type of matrix[a]	C		C		C	C	P	P	M	M
Carbonated	Yes and No		No		No	No	Yes	Yes	Yes	No
Type of device (cell)	Classical		ECD		ECD	ECD	Ponding	Ponding	Tubular	ECD
ΔV (V)	30		28		28	12	72	72	12	40
Electrodes										
Anode	Steel		Titanium				Titanium		Titanium	
Cathode	Steel		Titanium				Steel		Titanium	
Anolyte[b]	NaCO	DW[c]	NaCO	GW	NaCO	NaCO	NaCO	NaCO	NaCO	DW
Catholyte[b]	DW	DW[c]	GW	GW	GW	GW	DW	DW	DW	DW

[a] C: Concrete; M: Mortar; P: Paste.

[b] NaCO: 1 M Na_2CO_3; DW: distilled water; GW: granitic water.

[c] Only with the carbonated specimen.

parameters can be monitored automatically by a data-logger connected to a computer.

2.3. Calculation of the zeta potential

Calculation of the zeta potential has been made according to Eq. (1) [1]:

$$\xi = V\frac{4\pi\eta}{qDE} \tag{1}$$

where: ξ: 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 η: 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 assumption. 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, $D\approx 80$ [1].

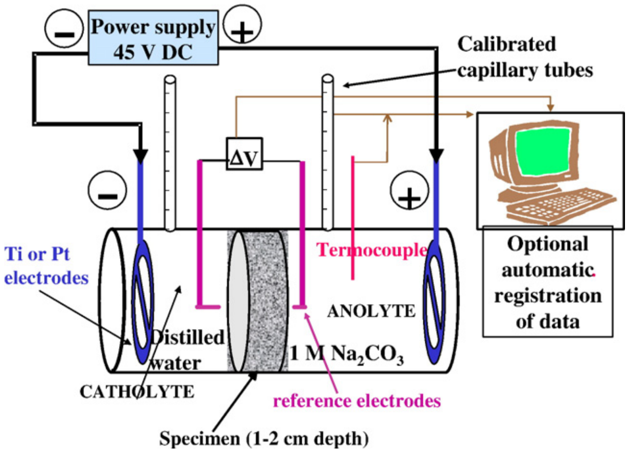

Fig. 1. Set-up of the ECD (electroosmotic cell device).

However, considering the uncertainties derived from the surface heterogeneity and that the real value to be used is dependent on the material and the solution in contact with the solid, which is different for different samples and changes continuously during the experiments, it is not clear which is the correct value to be used. So, for the sake of comparison, the values for the bulk ($D\approx 80$) have been used when making the calculations. Therefore, the absolute values calculated here has to be taken as comparative values, as if the smaller value for the permittivity ($D=6$) is used, the zeta potential values would increase its absolute value in more than one order of magnitude. It has to be pointed out that that is only a matter of a factor, but 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

The zeta potential values calculated by Eq. (1), for the different mixes are given in Table 4. Notice that the value given as 0.00 of zeta potential means non-detectable flux at the conditions of the experiment.

From results in Table 4, for mix A (cement type I, low aluminates) it can be directly deduced that 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 an Na_2CO_3 solution than using water as anolyte. On the other hand, the use of granitic water or distilled water does not seem to have any influence.

The porosity of the samples tested is also given in Table 4, where it can be observed that it includes a quite broad range of porosities. Comparison between data for the different mixes with different binders and those for concrete (A) and paste (E)

Table 4
Experimental conditions used for the different tests and mixes

	Mix							
	A	B	C	D	E	F	G	H
Type of matrix [a]	C	C	C	C	P	P	M	M
Carbonated?	Yes/No	No	No	No	Yes	Yes	Yes	No
Zeta potential (mV), anolyte: 1 M of Na_2CO_3	−1.01/0.00	−1.78	−4.09	+1.95	−1.2	−4.00	−0.075	–
Zeta potential (mV), anolyte: water	0.00/– (DW [b])	0.00 (GW [b])	–	–	–	–	–	−0.39 (DW [b])
Porosity (vol.%)	7.15/9.62	8.64	5.69	8.23	17.9	28.26	8.76	12.58

[a] C: Concrete; M: Mortar; P: Paste.

[b] DW: distilled water; GW: granitic water.

with the same cement indicates that there is no influence of the presence of aggregates in the zeta potential. In fact, this indicates that the normalization in the parameter q 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 taking into account the amount of aggregates. In summary, the volumetric effect of the amount of paste is considered when making the calculations.

On the other hand, it has to be remarked that the concrete with the calcium aluminate cement (mix D) is the only one that exhibits positive values of zeta potential.

4. Discussion

In previous refereed papers [13,14], using Na_2CO_3 as anolyte, it was found that the electroosmotic flux was dependent on the pH of the anolyte and independent on the concentration of Na_2CO_3. In the present research, some steps forward were tried in order to understand better the phenomena involved.

4.1. Influence of the chemical composition of the binder

From results in Table 4, the composition of the cements seems to be one of the key parameters as long as the resulting zeta potential is concerned. Therefore, carbonated and non-carbonated specimens have been correlated separately as a function of the resulting percentages of the major different chemical compounds, for the experimental conditions 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, are those including both the compositions of Al_2O_3 and SiO_2, and are given in Table 5 (Eqs. (2) and (3)), with their corresponding fitting parameters. 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. The comparison between experimental and fitted values (using Eqs. (2) and (3)) is given in Fig. 2 where it can be observed that the fitting of the data is very good.

In Fig. 3a and b an example of parametric analysis of both relationships for the amounts of Al_2O_3 and SiO_2 has been depicted. In Fig. 3a, as an example, the zeta potential calculated for a fixed amount of SiO_2 in the binder (23%, as it is a common value for the mixes with Portland cement) when varying the amount of Al_2O_3, is given. In Fig. 3b, with a fixed amount of 6% of Al_2O_3 in the binder, the percentage of SiO_2 has been varied.

From Fig. 3, built with the equations of Table 5, 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.

In order to find an explanation to this behaviour, let us consider the electrokinetic behaviour of the simple inorganic oxides Al_2O_3 and SiO_2. The surface hydroxyl groups on these oxides can be considered to be amphoteric, able to gain or lose a proton. So, it is possible to imagine the surface of the sample to be made up of neutral sites that adsorbs H^+ and OH^- ions [1].

Therefore, the sign of the charge of the surface will depend on the pH (H^+ and OH^- are potential determining ions), and a particular pH for which the zeta potential is zero exists. This is called the isoelectric point (i.e.p.).

In the case of Al_2O_3 and SiO_2 it is possible to write [16]:

$$> AlOH_2^{1/2+} \leftrightarrow > AlOH^{1/2-} + H^+, K1 \tag{4}$$

$$> SiOH^{1/2+} \leftrightarrow > SiO^{1/2-} + H^+, K2 \tag{5}$$

At 25 °C, the values of both constant of equilibrium are very different: K1 is around 10^{-10} [17], and K2 is around 5×10^{-6} [16]. This leads to isoelectric points also very different for these two oxide systems. So, the (i.e.p.) for Al_2O_3 and SiO_2 takes place

Table 5
Best empirical correlations for both types of specimens

$$\zeta_{\text{non-carbonated}} = a + (b^*\exp(c^*(\%Al_2O_3) + d^*\exp(e^*(\%SiO_2)) \tag{2}$$

R=0.999

a	b	c	d	e
0.292	0.012	0.110	−0.0045	0.0209

$$\zeta_{\text{carbonated}} = a + \exp(b + c^*(\%Al_2O_3) + d^*(\%SiO_2)) \tag{3}$$

R=0.995

a	b	c	d
−38.90	3.857	0.0052	−0.0119

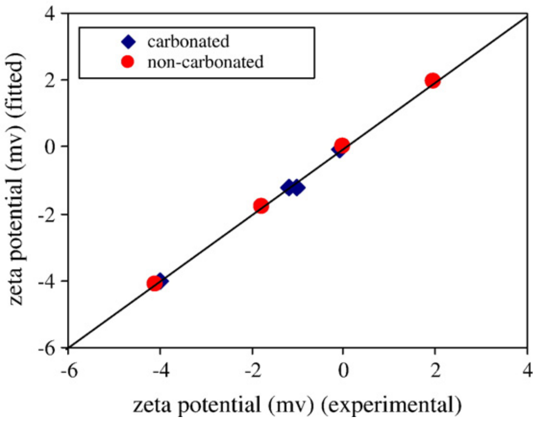

Fig. 2. Experimental and fitted data for the zeta potential of the different mixes (see correlations in Table 5).

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, under 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.

Certainly, the electrokinetic behaviour of the cement paste is not supposed to behave as a simple combination of the pure oxides from which it is formed. However, the hydrated surfaces become charged in contact with an electrolyte solution, which is due to dissolution of surface species or adsorption of ions from the solution. Thus, the different i.e.p. for both oxides, of course not trying to apply directly the corresponding values, which leads to different global surface charge depending on the proportions of silicates and/or aluminates in the surface, can qualitatively explain the experimental behaviour.

4.2. Influence of pH of the aqueous phase

Following the previous discussion, for every mix, at every pH in the aqueous phase, there will be a combination of Al_2O_3 and SiO_2 that will lead to a zero value of the zeta potential. In Fig. 4a and b, the contour lines corresponding to the zero value of zeta potential for carbonated ($pH<9$) and non-carbonated ($pH>9$) samples, whose pH is different, are depicted. In these figures, data are displayed as the projection of the three-dimensional pictures obtained after representing the equations given in Table 5 for different proportions of Al_2O_3 and SiO_2 and selecting the corresponding to $\zeta=0$.

The area above the iso zero-potential lines in Fig. 4 corresponds to negative zeta potential values and the one below corresponds to positive zeta potential values.

On the other hand, the results of Table 4 indicated that for non-carbonated concrete, the values of zeta potential are very small in absolute value; even, in some cases it was not possible to detect any flux passing through the specimens when making the experiments, at the conditions of the tests. However, from a specific value of SiO_2 in the binder (which depends on the amount of Al_2O_3), the electroosmotic flux starts to increase noticeably and it is possible to detect some event in non-carbonated specimens.

According to the reasons given in the previous paragraph, 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 (see Fig. 4). This contradiction leads to deduce that apart from the pH, other factors are involved in the phenomena experimentally found.

4.3. Other possible influencing factors: adsorption of Ca^{2+} ions

In order to understand this behaviour, first of all, it has to be reminded that, as said, the percentage of CaO in the cement has not been revealed as a significant parameter. This is not in disagreement with the data in the literature obtained by zeta potential measurements with powdered CSH in dilute solutions [7,9,10] which established the Ca^{2+} ions as potential determining ions for the CSH surface. In fact, they established that at low concentrations of Ca in solution, the zeta potential is negative, and at higher Ca^{2+} content, the zeta potential values become positive, with a point of zero charge of 2 mmol/l [10]. This is in agreement with the results obtained here, as present experiments have been carried out with hardened samples having their own pore solution.

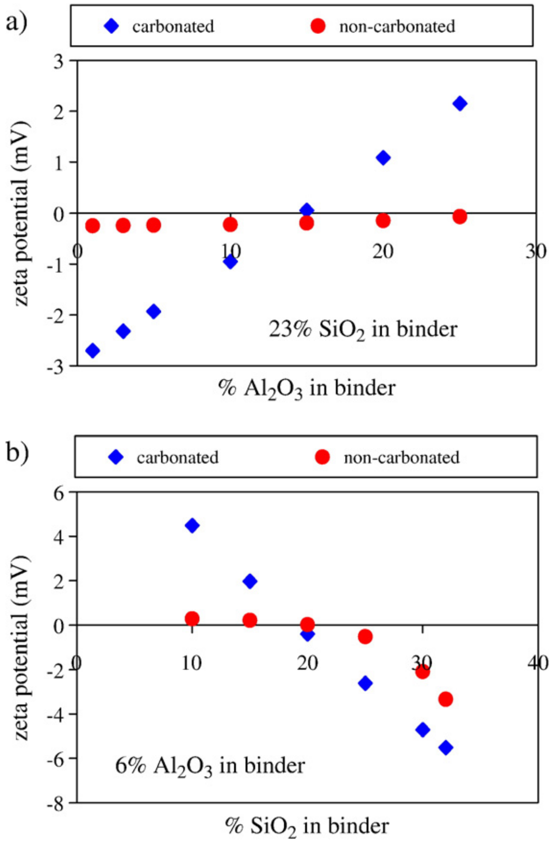

Fig. 3. Parametric analysis of both relationships (Eqs. (2) and (3)) for the amounts of Al_2O_3 and SiO_2 in the binders.

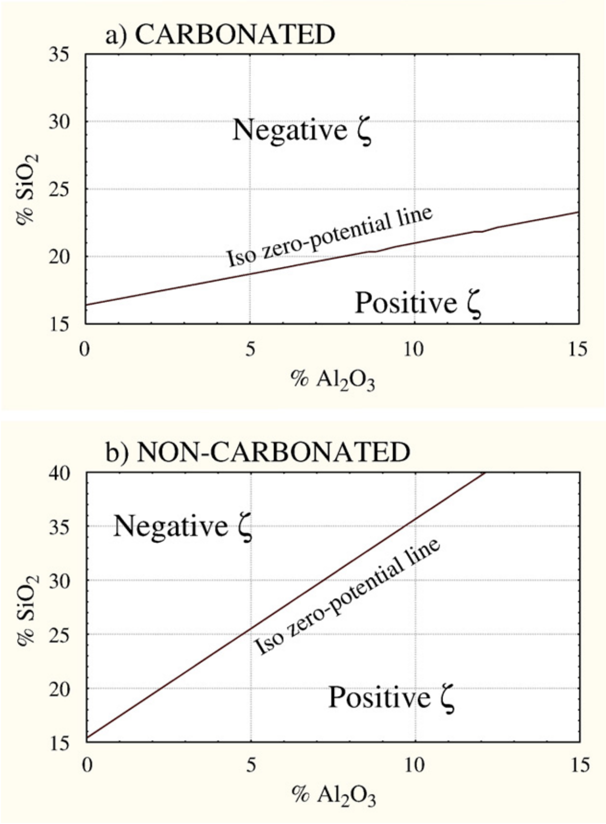

Fig. 4. (a, b) Contour lines corresponding to the zero value of zeta potential for (a) carbonated and (b) non-carbonated samples (according to Eqs. (2) and (3) in Table 5).

In the non-carbonated samples, there are $Ca(OH)_2$ precipitated, which means that the pore solution in equilibrium has the concentration of Ca^{2+} very close to that corresponding to the lime saturation (22 mmol/l) for every OPC mix, provided the pH is maintained at 12.6 with no alkali added to the solution. So, the $[Ca^{2+}]$ is not a variable for these samples.

Concerning the carbonated samples, none of them has portlandite precipitated; this corresponds to well carbonated samples. Therefore, the amount of Ca^{2+} in solution is much smaller, as the molar solubility of $CaCO_3$ at pH of 8–9 is around 1 mmol/l. According to [10] this Ca^{2+} concentration (without taking into account the possible modification in the CSH) would lead to negative zeta potential.

These trends for Ca^{2+} are in principle confirmed in the present experiments, in which, it can be seen that for non-carbonated specimens, the values of zeta potential are very low in absolute value, which has been attributed to the specifically adsorbed Ca^{2+} in the negative sites due to the surface ionized groups. Therefore, the presence of Ca^{2+} has a balancing effect in non-carbonated samples that imply much smaller influence of the composition (SiO_2/Al_2O_3 ratio) of the samples (Fig. 3) than when the samples are carbonated.

So, the effect of carbonation, and the fact of having found different form of the best fitting equations for non-carbonated and for carbonated specimens, might be attributed to the different Ca^{2+} concentrations in the aqueous phase. However, it is premature to draw up definite conclusions as it remains the study of the effect of the calcium carbonate precipitated onto the surface of the pores, or the compression of the double layer when increasing the concentration of the pore solution, which has not been undertaken in this study. More research is being carried out by the authors to clarify this point.

4.4. Influence of the external solution in the anolyte

The relationships, Eqs. (2) and (3), given in Table 5 are only valid for 1 M $NaCO_3$ in the anolyte when making the experiments. From values in Table 3 it can be deduced that in some cases (A and B), when using water in the anolyte, no flux passing through the specimen could be detected, at the conditions of the experiment, while using 1 M Na_2CO_3 it was detectable and measurable.

These differences have been interpreted in terms of pH of the anolyte. In [13], using different concentrations of Na_2CO_3 (between 0.1 M and 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, the flux cannot 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 are fulfilled. At this point, the value of the zeta potential is maximum and an increase of the electroosmotic flux takes place. Because these conditions do not remain constant, due to the continuous generation of H^+ and OH^- at the electrodes, the zeta potential starts to decrease until no more flux is detected. These optimal conditions were related to the pH in the anolyte independently of the initial concentration of Na_2CO_3.

That optimum pH, that was established to be around 10 [13,14], cannot be reached when starting from water 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. The data in this research are not sufficient to establish a relationship between the composition of the cement in the matrix and the optimum pH in the anolyte to get the optimum zeta potential. More research is being carried out in order to solve this gap.

5. Conclusions

In the present research, electroosmotic experiments have been carried out on eight different mixes of hardened cementitious matrixes including different types of binders, carbonated and non-carbonated specimens and different tests conditions. The conclusions that have been drawn, that are applicable to the ranges of compositions and conditions tested here, can be summarised as follows:

1. The optimum experimental parameters and devices have been established and the ECD (electroosmotic cell device) has been designed, which includes capillary tubes, to measure more accurately the flow of liquid. The thickness of the specimen to be used is between 1 and 2 cm. The electrodes are two meshes of activated titanium, or platinum, between which 45 V DC

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

2. In the experiments performed with OPC cement, even substituted with mineral additions, when a flux of liquid passing through the specimen was detected, it took place always towards the cathodic compartment, which implies negative values of the zeta potential. The CAC is the only one that exhibited positive values of zeta potential, with the flux detected towards the anolyte.
3. The absolute values of zeta potential calculated here should be taken for comparative purposes provided that a value of the dielectric permittivity of 80 was used for the calculations. Using the smaller value ($D=6$), typical of electrochemical double layers on metals, the zeta potential values increase its absolute value in more than one order of magnitude. It has to be pointed out that that is only a matter of a factor, but the conclusions obtained are the same using any of the values within the range of water permittivity.
4. There is no noticeable influence of the presence of aggregates in the zeta potential, which is attributed to the fact that the volumetric effect of the amount of paste has been considered when making the calculations.
5. The composition of the cements 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.
6. 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.
7. The rest of chemical species in the cement do not seem to have significant influence in the value of zeta potentials obtained.
8. 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^{2+} in the negative sites of the surface in the non-carbonated samples, as their concentration of Ca^{2+} is, for every sample, those of lime saturation.
9. For the same sample, making the experiment with Na_2CO_3 or water as 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.

Acknowledgements

The authors acknowledge the funding provided by the Spanish MMA through Project No. 055/2004/3.

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