Electrokinetic Phenomena in Remediation of Construction Materials from Heavy Metals Contamination

Marta Castellote, Samuel Botija, and Carmen Andrade

Eduardo Torroja Institute for Construction Science, IETcc-CSIC, Serrano Galvache 4, 28033-Madrid-Spain, E-mail:<martaca@ietcc.csic.es>, <sambotija@hotmail.com>,<andrade@ietcc.csic.es>

ABSTRACT

The development of an electroosmotic flux, with the corresponding dragging due to water transport, is a crucial mechanism to succeed in the treatments of electrokinetic decontamination of construction materials. Therefore, it is of great interest trying to optimize the treatment by the addition of specific electrolytes enhancing the electrokinetic phenomena. Most of the data of zeta potential found in literature for construction materials are based in micro-electrophoresis measurements, which are quite far of the real conditions of application of the remediation treatments. In this paper, electrophoretic and electroosmotic experiments, with monolithic and powdered material respectively, have been carried out for mortar and brick clean and contaminated with Cs, Sr, Co, Cd, Cu and Pb. The electrolytes tested have been distilled water, Na$_2$-EDTA, oxalic acid, acetic acid and citric acid.

INTRODUCTION

In the last years, decontamination of constructions materials has become a subject of great interest, mainly related to radioactive elements, finding trials with different types of treatments [Morillon and Pilot, G., 1989; Cornelissen, and Van Hulst, 1990; Krause, T.R., and Helt, J.E., 1993; Hamilton et al, 1998] including a few studies on electrokinetic treatments to decontaminate concrete [Sugimoto et al, 1995; DePaoli, et al, 1997; Castellote et al, 2002; Popov et al, 2006, 2007 and 2008]. The decontamination of construction materials by application of electrical fields profits mainly of two different phenomena among that occurring when an electrical field is applied to a porous material: electromigration and electrokinetic effects. In addition, adsorption and desorption processes in the liquid/solid interphase has also to be taken into account.

When two phases are placed in contact there develops, in general, a difference in potential between them. As a consequence, the region between two adjoining phases is marked by a separation of electric charges, so that near to or on the surface of one phase there is an excess of charge of one sign and the balancing charge is distributed through the adjoining surface regions of the other phase. When one of these phases is caused to move tangentially past the second phase there are observed a number of phenomena which are grouped under the generic name of...
“electrokinetic effects”. When the solid remains stationary and the liquid moves in response to an applied electrical field this is called electro-osmosis [Hunter, 1981]. This is the case of a monolithic material when submitted to an external electrical field. If one phase consists of a liquid in which the second phase is suspended as particles of solid, then, the particles can be induced to move by applying an electric field across the system. This is called electrophoresis [Hunter, 1981].

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, which is considered to lie close to the solid surface, and within which the fluid is stationary during an electrokinetic process (surface of shear) [Hunter, 1981].

Several experiments have been carried out to determine zeta-potential in cementitious materials, mainly from cement or synthetic CSH suspensions, by the microelectrophoresis technique [Popov et al, 2007; Nägeler, 1985, 1986, 1987, 1989; Chatterji, and Kawamura, 1992, Banfill, 1994; Yang et al, 1997; Nachbaur et al, 1998; Viallis-Terrisse, et al, 2001, Labbez et al, 2007], but also using other techniques as acoustophoresis [Flatt, and Ferraris, 2002], which are very important to know the basic features of the electrokinetics for these materials but are quite far of the real conditions of application of the remediation treatments. By the first time, the authors were able to demonstrate and quantify the electroosmotic flux through monolithic hardened carbonated concrete [Andrade et al, 1999] in realkalisation tests with carbonated concrete, following in situ the experiment by neutron diffraction analysis [Castellote et al, 2006], studying the influence of the external solution [Castellote et al, 2003], and the composition of the binder [Castellote et al, 2006-b].

Additionally, it is of great interest trying to optimize the treatment by the addition of specific electrolytes enhancing the electrokinetic phenomena, that are of common use in soil remediation techniques and that are very scarce when dealing with construction materials [Popov et al, 2007 and 2008].

Covering both points, in this paper electrophoretic and electroosmotic experiments have been carried out for mortar and brick clean and contaminated with Cs, Sr, Co, Cd, Cu and Pb [Castellote et al, 2010]. The enhancing electrolytes tested have been distilled water, Na₂-EDTA, oxalic acid, acetic acid and citric acid. The zeta potential values have been determined through both different techniques.

EXPERIMENTAL PROCEDURE

Materials

Two different materials have been used: Mortar and Brick. The mortar was cast with cement type IV-B-32.5 SR/BR, that includes fly ashes in their composition, with the mix proportion given in table 1, making cylindrical specimens of 75 mm diameter and 150 mm height. The brick was a solid type brick commonly used in facades, in which, cores of 75 mm diameter were taken. For the different tests to be performed, different samples were prepared. On one hand, monolithic specimens of 75 mm diameter and about 10 mm depth to perform the electroosmotic tests, and
powdered samples (diameter <100 μm) for the electroforetic measurements. On the other hand, for both procedures, clean and contaminated material was prepared.

**Procedures**

To contaminate the specimens, slices of 75 mm diameter and about 10 mm depth were contaminated saturating them with a nominally 0.05 M solution of Sr, Cs, Co, Cu, Cd and Pb that was prepared in distilled water with the corresponding chloride of each metal. The final concentration of each metal was dependent on their interferences with the other species and was analyzed by ICP. For the contaminated powdered samples, after contamination of the slices, they were grinded until a particle size less than 100 μm.

The micro-electrophoretic measurements were carried out with clean and contaminated powdered samples using a commercial zeta-meter. A high quality stereoscopic microscope is used to track colloidal particles inside a chamber in whose ends the electrodes are placed. Charged colloids move in the field and their velocity and direction are related to their zeta potential, that is calculated from the electroforetic mobility of the colloids, through the Smoluchowski equation. Powder suspensions in a solid/liquid ratio of 0.1gr:50 ml were prepared using different solutions: Distilled water, Na₂-EDTA, Oxalic acid, Acetic acid and Citric acid, at different concentrations: 0.001, 0.01, 0.05 and 0.1 M.

Electroosmotic tests have been carried out on monoliths of these hardened samples, by using the ECD (Electroosmotic Cell Device) and the calculations described in [Castellote et al, 2006-b], in order to obtain the zeta potential of the hardened material. The set-up of the 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 [Andrade, 1993] with the main modification that the ECD includes two capillary tubes in order to precisely measure the flow of transported liquid.

**RESULTS**

**Micro-electroforetic measurements**

In the figures 1 (a-b) and 2(a-b), the values of zeta potential obtained in micro-electroforetic measurements for mortar and brick respectively are presented.

In each of these figures, in the figure a), the values for the clean material in the different solutions at different concentrations are given. As a horizontal line parallel to the X-axis, the value in distilled water has also been depicted. In figure b), the values for the contaminated material for the same electrolytes are presented.

From figures 1 and 2, it can be deduced the influence of the type of electrolyte and of the concentration, being different depending on the type of material.

So, concerning clean mortar, as a general rule it can be said that the zeta potential values are in general negatives (-12.6 mV for distilled water) and that using the different solutions there is only a significant increase in the zeta potential values only in the cases of EDTA and Na₂CO₃ at
specific concentrations, being the most significant increase using EDTA. Specifically, two different trends can be distinguished: On one hand, Oxalic acid, EDTA and Sodium Carbonate, exhibits more positive values of zeta potential as more diluted the solution, reaching a kind of maximum at 0.1 M for EDTA and Na₂CO₃ and around 0.05 M for oxalic acid. Concerning acetic and citric acids, the tendency is the contrary; the values obtained are very close to that of distilled water, decreasing slightly the absolute value of the zeta potential towards a limit value, attributed again to the compression of the electrical double layer. Therefore, citric acid and acetic acid seem to be indifferent electrolytes for the system.

Fig. 1: Zeta potential obtained in micro-electroforetic measurements for mortar in different solutions. The horizontal line parallel to the X-axis is the value in distilled water.

Fig. 2: Zeta potential obtained in micro-electroforetic measurements for brick in different solutions. The horizontal line parallel to the X-axis is the value in distilled water.
In the case of contaminated mortar in general, the tendencies are similar to that of clean mortar with more attenuated differences with respect to water (~10.5 mV for distilled water), having more positive values. It is remarkable the case of Na$_2$CO$_3$ whose zeta potential increase its negative value being of the same order of the EDTA solution.

For brick, the differences between contaminated and clean material are very noticeable. The zeta potential values obtained for clean brick, increase towards more negative values mainly for Oxalic acid, EDTA and Na$_2$CO$_3$, being the increase higher as higher is the concentration of the solution. For these solutions, the increase with respect to the value for distilled water is quite high (~18.7 mV for distilled water). In the case of citric acid, this tendency is more attenuated and there is no increase in the case of acetic acid. For contaminated brick (~0.32 mV for distilled water) the values become much less negative being the tendencies quite similar to that of the mortar. It is remarkable the reversal of the sign of the zeta potential using citric acid.

**Electroosmotic experiments**

The accumulated electroosmotic flux, for the two materials with the different solutions has been measured and it has resulted that for both materials, using distilled water as electrolyte, when they are not contaminated, even the fluxes measured are very small (in the case of mortar), they are detectable. In the case of brick they goes towards the catolyte, what means that the surface charge of the materials is negative. In the case of mortar, it tends to the anolyte. When the materials are contaminated, the values of the surface charge become more positive, leading in the cases of brick to positive values of the zeta potential. Apart from these cases with water, the only flux detected towards the positive chamber has been in the case of mortar using acetic acid as electrolyte.

As a general trend, it can be said that for the three materials, the maximum amount of liquid collected was in the case of citric acid. No EOF was detected with sodium carbonate, for mortar and very small one in the case of brick.

From the measured flux, and considering in each moment the effective potential measured between the two sides of the specimen, the differential zeta potential values have been calculated through the different experiments. The values obtained have been presented in figure 3.
From figure 3, it can be deduced that the shape of the curves giving the zeta potential are quite different depending on the material and on the dissolution used: Mortar exhibits much smaller values than the other materials, being the higher absolute value that corresponding to distilled water with contaminated mortar, being that positive. The enhancing solutions behaves differently, obtaining with acetic acid positive zeta potential in not higher magnitude than water and giving negative values of the zeta potential the rest of solutions, with the maximum absolute value for Na2-EDTA.

In the case of brick, as it was noticeable in the EOF graphs, the maximum zeta potential is obtained for citric acid, only in one region of the charge density diagram.

**DISCUSSION**

In order to understand the processes involved in the changes in the surface charge of the different materials in different media, it is important to know the composition and structure of the materials:

Cement paste is a random composite material, made up of anhydrous cement, capillary pores, and various other chemical phases that are a result of the hydration reactions between water and cement [Taylor, 1990]. The main reaction product phase is an amorphous or at best poorly crystalline calcium silicate hydrate gel, produced via a hydration reaction and denoted C-S-H. Other important phase is Portlandite, Ca(OH)$_2$, that conforms about a 20% of the solid phases of the cement paste. The aqueous solution of the porous network of cementitious materials is a highly alkaline liquid rich in Na+, K+, OH$^-$ and saturated in Ca$^{2+}$, in equilibrium with the precipitated portlandite.

Concerning brick, its main ingredient is clay, silicates hydrated of aluminium. In the firing process clay minerals break down, release chemically bound water and change into a mixture of
mainly quartz and mullite (3AlO3. 2SiO2), containing the impurities and substitutions of the original clay, mainly Fe and Mg.

Additionally, the theoretical affinity of each metal (contaminants and constitutive of the materials) to bound to the enhancing electrolytes, that is to say, the relevant constants of the quelation equilibriums (log β) and that of precipitation (pKs) for the different solutions and metals involved in these processes are also very important to know in order to deduce the behaviour of each specie in every system.

In the electrophoretic measurements with clean mortar in distilled water, negative values of zeta potential has been obtained, even though in literature positive values have been reported [Viallis-Terrisse, et al, 2001, Castellote et al, 2006-b, Popov et al, 2008]. This difference has been attributed to the dilution effect. When making a suspension of the mortar powders in water, precipitated Ca(OH)2 is dissolved and therefore, Ca ions are desorbed from the sites in the CSH, leading to negative values of the zeta potential, in accordance with [Viallis-Terrisse, et al, 2001]. Concerning the effect of different solutions as enhancing electrolytes, as said, in general two groups can be identified (On one hand EDTA, oxalic acid and Na2CO3 and on the other hand acetic and citric acid). The behaviour of the former group, increasing the negative charge of the matrix, as the concentration of the solution increases, is attributed to increasing the desorption of positively charged species, Ca2+, by quelation or complexation of them and so, removing them to the solution as soluble species, or by formation of insoluble Ca-species that remove it from the solution by precipitation and induces again the desoption of more Ca. In fact, Ca2+ is very easily complexed by EDTA (Ca2+ / Y4-; log β1 =11.0) and it is also very favourable to the formation of insoluble calcium oxalate and calcium carbonate (pKs of 8.7 and 8.4 respectively). The change of tendency at higher concentrations is attributed to the compression of the electrical double layer due to the increase in the ionic strength.

On the contrary, for acetic and citric acids, the tendency is different; they seem to be indifferent electrolytes for the system obtaining values very close to that of distilled water. In fact, citric acid can form complexes with Ca, but less strong than that of EDTA (Ca2+ / Hcit3- / Hcit2- / Hcit-; log β1 =4.8/3.3/1.1) and at the dilution of the system, the complexes, if formed, do not seem to affect the remaining Ca absorbed. Acetic acid forms soluble salts with Calcium.

In the case of contaminated mortar, the behaviour is quite similar to that of the clean material, tending to more positive values, due to the fact that the behaviour of most metals can be considered as equivalent to that of Ca in their binding with the anions of the enhancing solutions.

In the behaviour of brick in the electrophoretic cell, it is remarkable the big difference between the clean and contaminated material. There is a very big increase in the negative value of the zeta potential due to the effect of EDTA, oxalic acid and Na2CO3, that in this case has been attributed to the quelation/removal of constitutive species of the material, as could be Al, Fe or Mg. In the case of contaminated specimens, the electrolytes are reacting with the contaminant metals, more labile bound to the matrix, and therefore, the availability to act on the fixed elements is smaller and the behaviour found is very similar to that of mortar with the exception
of the reversal of the sign of the zeta potential with acetic acid, that might be due to secondary adsorption of positive complex, for example of PbCOOH$^+$. 

When performing the electroosmotic experiments, noticeable differences in behaviour with respect to the electrophoretic measurements are observed:

Concerning mortar, data in literature obtained by zeta potential measurements with powdered CSH in dilute solutions, established the Ca$^{2+}$ ions as potential determining ions for the CSH surface [Banfill, 1994; Yang et al, 1997; Nachbaur et al, 1998; Viallis-Terrisse, et al, 2001]. 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 [Viallis-Terrisse, et al, 2001]. This is in agreement with the results obtained here, as in the electroosmotic test with mortar, with hardened samples having their own calcium saturated pore solution, the zeta potential values in distilled water, are positive due to the adsorption of Ca ions on the negative sites of CSH. As expected the values are higher with the contaminated sample, as most of the metals are precipitated/adsorbed at the alkaline pH of the aqueous phase.

Concerning the different electrolytes, all the tested solutions (with the exception of sodium carbonate for which no flux was detected, and acetic acid that gives also positive sign due to the lack of binding with the metals either constituents or contaminants) reverse the sign of the $\zeta$, obtaining fluxes towards the catholyte and therefore negative surface charge of the walls of the pores in the matrix.

In this system, the quelant agents seem to be most effective than the precipitating ones, as here, precipitation takes place in the pores of the matrix while in the electrophoretic system, precipitation took place in the cell, removing Ca even more efficiently than quelants. Therefore, citric acid, that was not so effective in electrophoresis, takes here an important role, together with Na$_2$-EDTA, and also oxalic acid, that is also able to bind to calcium forming a soluble complex EDTA (Ca$^{2+}$/C$_2$O$_4^{2-}$,$\log \beta_1 =3.0$). So, in the case of oxalic acid there is a competition between precipitation and quelation reactions, dependent on the pH. For brick the general trends are quite similar, pointing out the considerable increase in the zeta potential in the case of citric acid that can be attributed to the complexation of Fe.

**CONCLUSIONS**

Comparison of the zeta-potential values obtained by micro-electrophoretic and electroosmotic experiments, with monolithic and powdered material respectively, for mortar and brick clean and contaminated with Cs, Sr, Co, Cd, Cu and Pb, using the several enhancing electrolytes (distilled water, Na$_2$-EDTA, oxalic acid, acetic acid and citric acid), has allowed to obtain the following conclusions:

- The contamination of a construction material by heavy metals can change their zeta potential causing even a reversal of the sign towards positive values. This difference depends on the type of contaminants and on the construction material.
• The remediation treatment of contaminated construction materials can be improved by the addition of specific electrolytes enhancing the electrokinetic phenomena.

• Even though the electrophoresis technique is very useful in order to establish the basic features of the processes, there can be important differences in the values obtained in suspensions by electrophoresis and those obtained by electroosmosis in monolithic samples which are mainly related to the porous network in the case of monoliths, the dilution and the timing of the experiment (instantaneous in the case of electrophoretic measurements and lasting days in the case of electroosmotic tests).

• This effects could be so important that both the sign and the absolute value of the zeta potential can be different depending on the technique used.

• The increases in the absolute values of the zeta potential are much more attenuated in the case of monolithic samples in electroosmotic experiments.

• The optimum enhancing solution found for each material might not be the same for both techniques: Precipitation agents, as CO$_3^{2-}$, seem to be very effective in the case of electrophoresis. However, if precipitation takes place in the pores, the $\zeta$ can be very close to zero. In electroosmotic experiments, chelating agents seem to be more effective.

• In general, citric acid has resulted to be the most effective increasing the $\zeta$ towards negative values for both materials.

• When using the electrophoresis technique, the conditions that operate in the monolithic samples has to be reproduced as possible in order to get reliable results, as these are the real matrices, with their concentrated and specific pore solution, where the phenomena that need to be understood take place.

REFERENCES


