

Neutron diffraction as a tool to monitor the establishment of the electro-osmotic flux during realkalisation of carbonated concrete

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Abstract

Realkalisation is an electrochemical technique for repairing concrete structures damaged by rebar corrosion due to carbonation. The treatment aims at restoring alkalinity of the concrete by application of a continuous current between the rebar, acting as a cathode, and an external auxiliary electrode placed in a carbonate solution and connected to a positive pole of a power supply. Here we report the application of neutron diffraction in the in situ monitoring of a realkalisation treatment, analysing at the same time the development of the electro-osmotic flux and the microstructural variations in the surroundings of the rebar.

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1. Introduction

A difference in potential exists at the surface of a solid in contact with an electrolytic fluid. When one of these phases is caused to move tangentially past the second phase a number of phenomena, grouped under the generic name of "electrokinetic effects", can develop. When the solid remains stationary and the liquid moves in response to an applied electrical field this is called electro-osmosis [1], which occurs when concrete is submitted to the electrochemical treatment of realkalisation.

In a concrete structure, the treatment of realkalisation consists of applying continuous current between the rebar (acting as negative electrode or cathode) and an auxiliary external electrode, placed in a carbonate solution and connected to the positive pole of the power supply, with the aim of restoring the alkalinity of the concrete loss by the carbonation process. This restoration seems to be primarily provided by the generation of OH^- at the rebar level, through the reaction of water electrolysis at the steel acting

as the cathode. However, it has been claimed [2–6] that carbonate ions also penetrate towards the rebar by electro-osmotic processes.

Recently, the theoretical equations of electro-osmosis were applied to the case of concrete [6]. The electro-osmotic flux through hardened, carbonated ordinary portland cement (OPC) concrete was observed and quantified [7], and laboratory trials applying this method to OPC mortars were reported [8]. Additionally, the influence of the external solution was analysed revealing that the pH of the anolyte was a determining parameter on the zeta potential and consequently on the establishment of the electro-osmotic flux [8]. Here, a summary of a realkalisation treatment of an OPC cement paste followed in situ using neutron diffraction is reported [9]. The experiment was performed using the D20 instrument of the Institute Max von Laue–Paul Langevin (ILL), in Grenoble, France.

2. Experimental

OPC cement paste was prepared with deuterated water (99.95% purity) using a water-to-cement ratio of 0.5.

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The specimens were cast in cylindrical moulds of 2.2 cm in internal diameter and 6 cm in length, with a rebar placed perpendicularly to the axis of the cylinder of the specimen. Prior to the realkalisation test, the specimen was carbonated in a controlled environment at 65% relative humidity, 20(2) °C, and 100% CO₂ concentration in a climatic chamber. A receptacle was glued onto the top of the cylinder of cement paste and filled with a 1 M Na₂CO₃ solution prepared using distilled water. It was postulated that the electro-osmosis could be monitored by following the increase in background of the neutron diffraction data due to the incoherent scattering from hydrogen in the water.

An activated titanium mesh was introduced in the carbonate solution compartment and was electrically connected to the positive side of the power supply. The rebar embedded in the sample was used as negative electrode. A voltage drop of 72 V DC was applied and the current passing through the specimen was monitored.

The electrical treatment was followed in situ using neutron diffraction data gathered on the D20 instrument at the ILL, in Grenoble, France. The neutron diffraction data were collected every 120 s, over the 2θ range 10–150°. The neutron beam size was $8 \times 12 \text{ mm}^2$, and was centred in the middle of the sample, monitoring $4 \times 12 \text{ mm}^2$ of the rebar and of the sample area closer to the negative electrode. The wavelength of the incident neutron beam was determined to be 1.28(2) Å using a Si standard from the National Bureau of Standards.

The powder diffraction patterns have been analysed by a standard procedure. The crystalline phases calcite, vaterite and portlandite, were identified in the diffraction data using a search-match procedure. Selected peaks from these phases were each fitted using a single Gaussian curve and the intensity for each was used to monitor the quantitative variation of these phases throughout the experiment.

3. Results and discussion

As the specimen was prepared using deuterated water and the Na₂CO₃ solution was prepared using ordinary distilled water, electro-osmosis would result in an increase in the background of the diffraction patterns due to incoherent scattering from the hydrogen in the water.

The integrated intensity of the background of the diffraction patterns was normalised to unity at low 2θ , regions where no diffraction peaks were observed, and its time dependence shown in Fig. 1. In Fig. 1, the peak in the background indicates the electro-osmotic process.

Analysis of the diffraction patterns revealed calcite as the main phase, and portlandite at the latest stages of the experiment. Valerite was also identified. The most intense and isolated peak from each phase was fitted with a Gaussian curve, and the variation of peak height with time was recorded for each phase. The peak heights were normalised as a function of the charge density (Fig. 2).

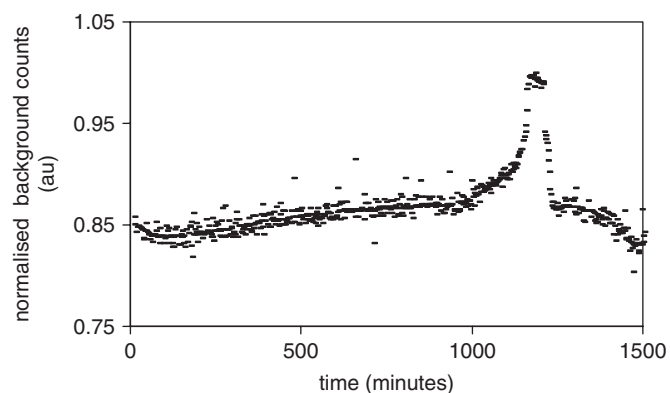


Fig. 1. Evolution of the normalised background (in arbitrary units) during the realkalisation treatment.

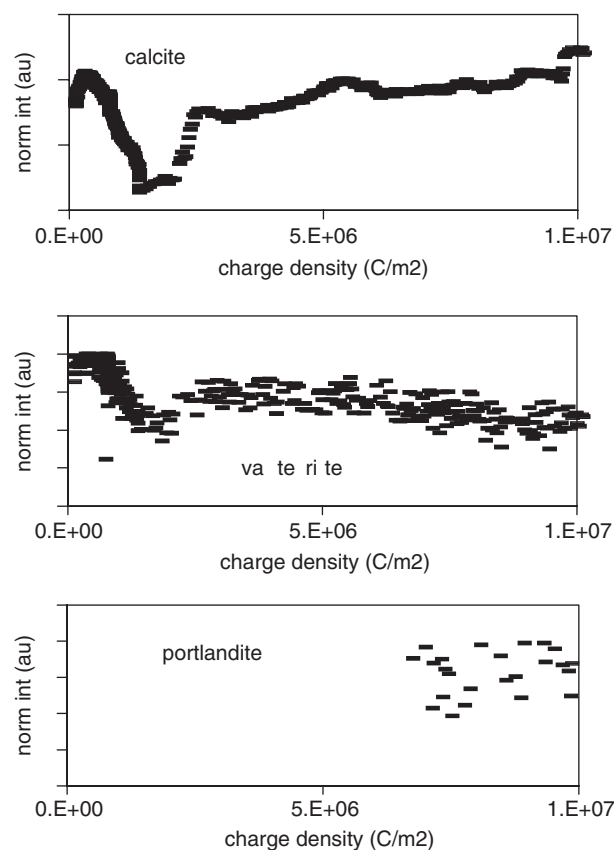


Fig. 2. Evolution of the normalised height of the identified phases as a function of the charge density.

The derivative of the background curve as a function of time was calculated in an effort to identify the time and conditions at which electro-osmosis occurs. A rapid increase in slope of the curve fitted to the background results in a maximum in its derivative, and the position of this maximum identify the onset of electro-osmosis.

Previously [8], the zeta potential of OPC mortars exposed to varying concentration of Na₂CO₃ were studied, as a function of the pH of the anolyte. The pH was calculated using the current dependence of the acid–base system, and equations for dissociation and hydrolysis of

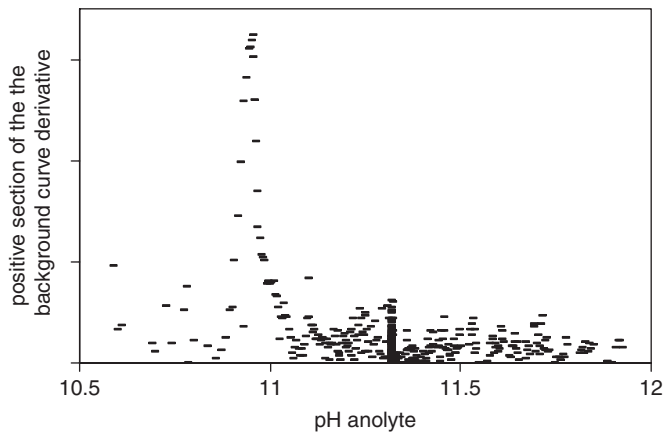


Fig. 3. Positive part of the derivative curves of the normalised background, as a function of the pH of the analyte.

Na_2CO_3 , the reactions at the electrodes, and reactions for the migration of the different ionic species. The pH of the analyte here was calculated in this way, and the positive part of the derivative of the background as a function of this pH is shown in Fig. 3. From Fig. 3 it can be deduced that the electro-osmotic flux is maximal at a pH of 10.9, within the range identified previously for OPC mortars [8].

This work shows the suitability of neutron diffraction and the different scattering from deuterium and hydrogen for the investigation of electro-osmosis in cementitious matrixes.

4. Conclusions

The application of neutron diffraction for the in situ monitoring of electro-osmotic flux during realkalisation of OPC has been demonstrated. This was achieved by designing the experimental set-up in a way to take profit of the incoherent scattering of the H of the water.

In addition, this technique allows the simultaneous monitoring of the evolution of the main phases involved in the process.

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