Macro and micro aspects of the transport of chlorides through cementitious membranes

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Introduction

The presence of chlorides at the steel-concrete interface level is the main factor responsible for the corrosion of rebars in concrete. In new structures the penetration rate of chloride ions through the concrete cover is a key aspect in the service life prediction. In damaged structures, the rate of chloride transport is also of major importance for the application of chloride extraction techniques. In that context, the forced migration test is employed as an accelerated and useful method to determine the chloride transport coefficients [1]. However, microstructural changes are caused by the application of electrics fields [2], which makes those tests controversial.

Studies based on electrochemical impedance spectroscopy, EIS, [2,3] have evidenced the presence of several ionic conduction phenomena concurrent in cementitious materials which involve percolating conduction and ionic exchange between the pore's solution and pore's walls. As each phenomenon occurs at a specific frequency, it is possible to tune the frequency of the migration experiment signal to act on the conduction paths, increasing the current efficiency and diminishing the structural damage.

The chloride diffusion coefficients obtained for concrete either through diffusion or migration experiments are always controversial and strongly dependent on the testing conditions and concrete type. However, all procedures have in common that the amount of transported chloride is referred to the geometrical surface normal to the transport direction. In neither case the pore structure of the material is considered.

The present contribution is devoted to rationalise the macro approaches on the transport of chlorides in the light of microstructural information obtained from impedance spectroscopy measurements and scanning electrochemical microscopy, SECM. A new insight in the field is provided, highlighting the need of microstructural information for reliable results.

Experimental

Cement paste samples were prepared using Portland cement type CEM I 52.5R according to the composition, specifications and conformity criteria of EN 197-1:2000, with a water to cement ratio of 0.5. The water-cement mix were cast in cylindrical moulds of 9 cm in diameter and 20 cm in height, and cured in 100% RH chamber for 24 hours. Afterwards, the samples were demoulded and maintained in the same chamber for a minimum of 28 days before starting the measurements. The cement paste samples were cut into 2.5 cm thick slices to be used in the permeation experiments. Prior testing the samples were pre-conditioned following a standardized water saturation procedure [4].

The experimental set-up for **macro-migration experiments** consisted of a classical permeation cell with two-solution compartments at both sides of the cementitious sample under test. The upstream (or cathodic) compartment was filled with 1 M sodium chloride solution, containing also sodium hydroxide and potassium hydroxide to $[OH^-]$= 0.5 M. The downstream (or anodic) compartment was filled with just sodium hydroxide and potassium hydroxide solutions to $[OH^-]$= 0.5 M. The concentrations for NaOH and KOH were chosen in order to avoid decalcification and to approach the pore solutions of the tested concrete. Each electrolyte compartment was 200 cm^3 in volume. A schematic view of the experimental cell is given in Figure 1A.

For **micro-diffusion experiments** a special cell was designed (see Figure 1B) to allocate the SECM tip, the counter and the reference electrodes. The flux of chlorides through the cement paste membrane placed between the up and down stream compartments is detected using the SECM tip.

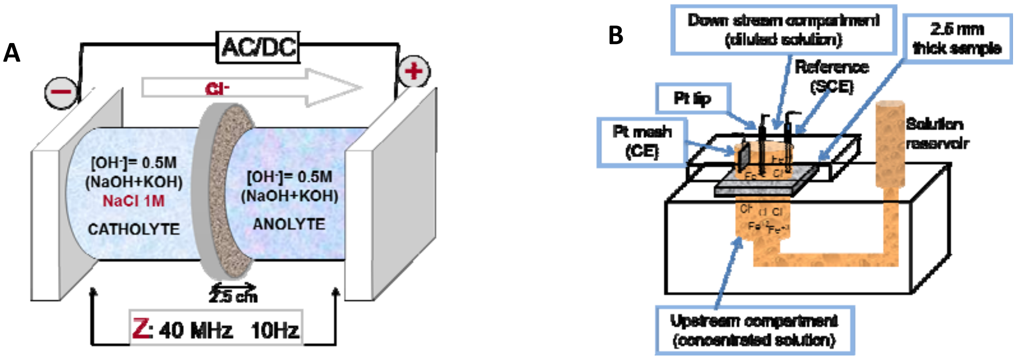


Figure 1: Experimental set-ups for A) the macro-migration experiments, and B) The diffusion SECM experiments

Results and Discussion

Some results of the macro-migration experiments performed under DC current (3 mA.cm^{-2}) and pulsed current (6 mA, 50% duty cycle) are presented in Figure 2. It can be seen in Figure 2A that the flux of chlorides at the steady state, obtained from the slope of the straight lines, is almost twice under AC than DC conditions. The diffusion coefficients obtained are 2.16x10^{-8} cm^2.s^{-1} and 0.87x10^{-8} cm^2.s^{-1}, respectively. Meanwhile, the impedance of the samples tends to increase during the first days of the test and then decreases, as shown in Figure 2B, which evidences the dynamics of the conduction paths in the bulk material due to the reaction of the chlorides with the solid phases of pores.

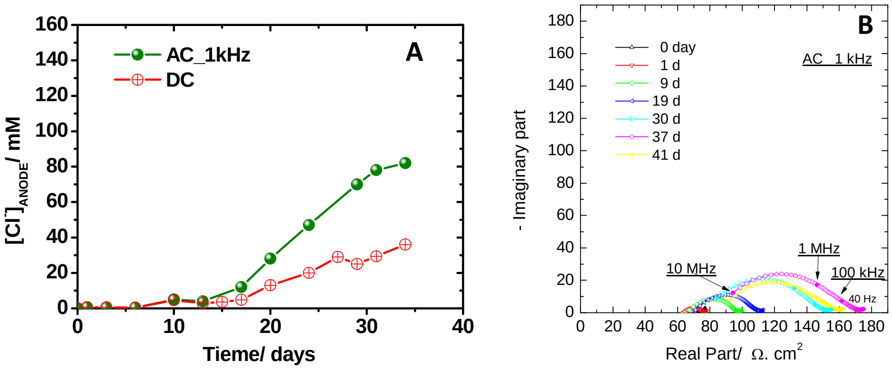
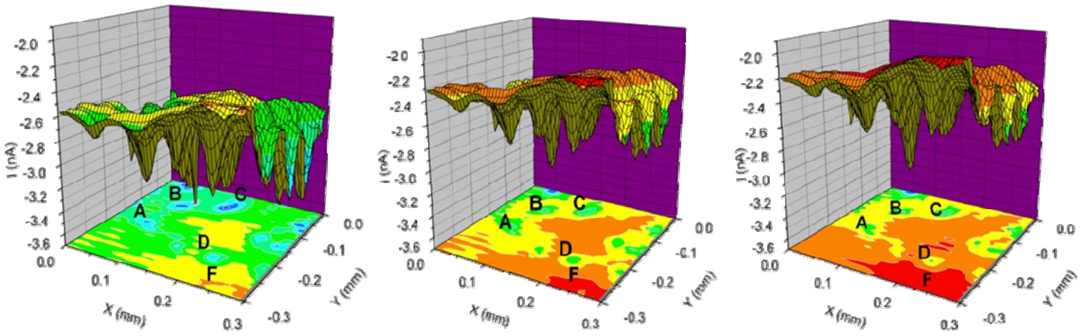


Figure 2: A) Flux of chlorides under AC and DC fields. B) Evolution of the impedance of the cement paste samples during the AC migration experiment.

The ionic exchange between the pore walls and the electrolyte is visible through the impedance spectrum of the cement paste [5] and can be pointed as responsible of the better efficiency of the current in terms of chloride transport under AC conditions when the frequency approaches the characteristic time constant of the exchange process.

The existence of a percolating pore network and its dynamic behavior can be visualized using SECM in a cell arrangement as that presented in Figure 1B. Some topographic results using in the upstream compartment potassium ferricyanide as mediator are depicted in Figure 3. The ionic flux is limited to small fractions of the surface (active areas) corresponding to the outer side of the bulk percolating pore network. Moreover, the size of those active areas changes over time, in accordance to what is observed in macroscopic impedance measurements.



t=0 (2.6%) t=80 min. (5.6%) t=410 min. (2.9%)

Figure 3: SECM topographic maps of a fixed area showing the dynamics of the pore network during the diffusion experiment (up to 410 min.). The apparent fraction of "active surface" (%) has been estimated from the corresponding area fraction projected in the XY plane.

Measurements performed on the flux of chlorides (obtained by oxidation of chloride ions at the SECM tip) show that the transport time through the membrane is not compatible with the diffusion coefficient determined in the macroscopic experiments. However, a good correlation has been found when the mobility of chlorides in free solution is normalized by the active surface corresponding to the percolating pore network. This result points to the existence of a geometrical factor in the transport of chlorides through cementitious membranes.

Conclusions

Results were presented on the transport of chlorides through cement paste membranes at the macro and micro scales. The process is of dynamic character due to the reaction of chloride ions with the cement matrix. That reaction seems to occur only in a small fraction of the bulk material that corresponds to a pore network. The reaction occurs at pore walls, which makes the transport sensitive to AC signal if the proper frequency is chosen. SECM examination of the flux of chlorides has allowed establishing a relationship between diffusion coefficient and geometry of the pore network.

Acknowledgements

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References

[1] K.D. Stanish, R. D. Hooton, M.D.A. Thomas, Testing the chloride penetration resistance of concrete: A literature review, Federal Highway Administration (USA), Publication No. FHWA-RD-00-142 (2000).

[2] B. Díaz, X.R. Nóvoa, M.C. Pérez, Cem. Concr. Composites 28 (2006) 237.

[3] M. Cabeza, P. Merino, X. R. Nóvoa, I. Sánchez, Cem. Concr. Composites 25 (2003) 351.

[4] ASTM Standard C 1202-97, Standard test method for electrical indication of concrete's ability to resist chloride ion penetration, Annual Book of ASTM Standard Section 4, vol. 04.02, 2000.

[5] M. Cabeza, M. Keddam, X.R. Nóvoa, I. Sánchez, H. Takenouti, Electrochim. Acta 51 (2006) 1831.