Electrochimica Acta 124 (2014) 61–68

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

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

B. Díaz[a], X.R. Nóvoa[a,*], B. Puga[a], V. Vivier[b]

[a] ENCOMAT Group, Universidade de Vigo, EEI, Campus Universitario, 36310 Vigo, Spain
[b] LISE – UPR 15 du CNRS, 4 Place Jussieu, 75252 Paris Cedex 05, France

ARTICLE INFO

Article history:
Received 12 February 2013
Received in revised form 23 August 2013
Accepted 24 August 2013
Available online 31 August 2013

Keywords:
Cement paste
Chloride transport
EIS
SECM
Diffusion

ABSTRACT

A study of the transport of chlorides through hardened Portland cement paste membranes is reported. The flux of chlorides was induced by migration (AC and DC fields) and diffusion.

Two parallel studies were developed. A macroscopic one where the migration of chlorides was followed by Electrochemical Impedance Spectroscopy (EIS) and a microscopic one in which the natural diffusion was investigated using the scanning electrochemical microscopy (SECM). Both studies have revealed to be complementary. The local investigations performed with the SECM were successfully employed for the interpretation of the EIS data.

The results have shown that the transport of chlorides occurs mainly through pores of sub-micrometre equivalent diameter. The study of the transition time has allowed to conclude that the diffusion coefficient approaches the usual value obtained in bulk solution. The macroscopic study has allowed presenting an explanation for the beneficial effect of the AC current in the transport of chlorides. A possible method for estimating the flux of chlorides from the percolation resistance is also discussed.

© 2013 Elsevier Ltd. All rights reserved.

1. 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] and several standard methods have been established and used [2,3]. However, significant microstructural changes are caused by the application of electrics fields [4] that, among other already known aspects dealing with surface treatments [5–7], makes those tests controversial.

Investigations based on Electrochemical Impedance Spectroscopy, EIS, [8,9] have already evidenced the presence of several concurrent ionic-conduction phenomena 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 electrical signal to act on the conduction paths, thus increasing the current efficiency on the ionic transport and diminishing the structural damage [10]. The use of pulsed current has been reported to be beneficial for preserving the integrity of the concrete microstructure [11].

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 [12,13]. However, all procedures have in common that the amount of transported chlorides is referred to the geometrical surface normal to the transport direction. In neither case the pore structure of the material is taken into account although in some studies a "formation factor" was introduced [14,15].

The present contribution is aimed at rationalising the macroscopic 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.

2. 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

---

[*] Corresponding author. Tel.: +34 986812213; fax: +34 986812201.
E-mail address: rnovoa@uvigo.es (X.R. Nóvoa).

0013-4686/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2013.08.105

chamber for 24 h. 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. Unless otherwise stated, the samples were pre-conditioned prior testing following a standardized water saturation procedure [3]. It should be mentioned that the probability for large pores to percolate the sample is almost null. Indeed, the thickness of the samples was chosen to cancel the presence of large percolating pores (inherent in small thicknesses) or cracks (formed during cutting and polishing, due to mechanical stress in thin samples). In this way the samples are representative of the real rebar's cover thickness (larger than 2–3 cm), but are thin enough to develop the microscale experiments within a reasonable and reproducible time scale. The samples microstructure was evaluated using mercury intrusion porosimetry (MIP) performed with an Autopore IV 9500 from Micromeritics. The covered pores diameter range is from 18 μm down to 5 nm.

2.1. Setup for macroscopic permeation experiments

The experimental setup 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 only sodium hydroxide and potassium hydroxide solutions to $[OH^-] = 0.5$ M. The concentrations for NaOH and KOH were chosen to be similar to the pH of the pore solutions of the cement. Each electrolyte compartment was 200 cm^3 in volume. A schematic view of the experimental cell is given in Fig. 1.

As depicted in Fig. 1, the AC or DC electric fields were applied to the cementitious membrane using two graphite sheets located at both ends of the cell. The specimens were subjected to two regimes, direct current and pulsed current. In both regimes the nominal current density applied was 0.3 mA cm^{-2}. As the pulsed current was applied as a square wave of 50% duty cycle, the imposed current during the "on" time was 0.60 mA cm^{-2} to reach the average effective value of 0.3 mA cm^{-2}. The investigated frequency was 1 kHz. In all cases the potential drop across the cell was about 12 V.

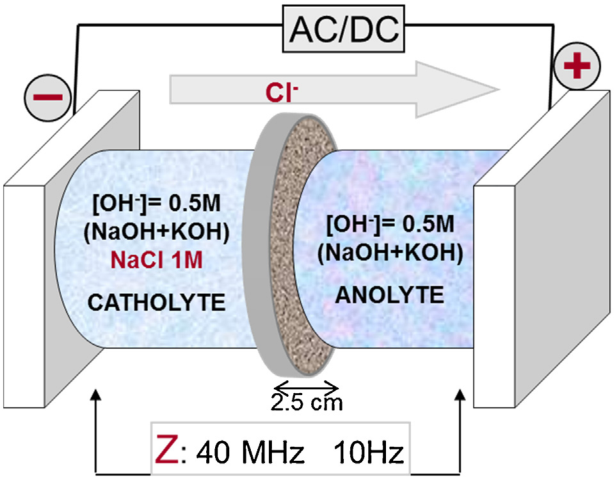

Fig. 1. Schematic view of the experimental permeation cell employed for the macroscopic experiments. Each compartment is 10 cm in length and 5 cm in diameter, thus containing 200 cm^3 solution in each compartment with a cross section area of 20 cm^2.

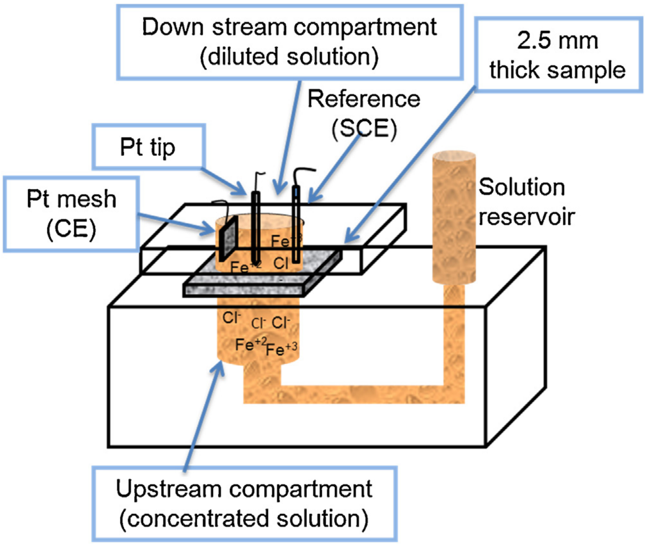

Fig. 2. Schematic view of the experimental permeation cell employed for the microscopic experiments of natural diffusion.

The impedance of the cell was measured periodically between 40 MHz and 10 Hz to assess the evolution of the resistivity of the membrane, through which the diffusion coefficient can be derived [8]. The impedance measurements were performed using an Agilent 4294A impedance/gain-phase analyser, which allows impedance frequency range investigation from 100 MHz down to 10 Hz in pure AC mode. This instrument allows capacitance measurements down to 10^{-14} F with a maximum resolution of 10^{-16} F.

The cross-section of the sample in contact with the electrolyte was 20 cm^2 and the measurements were corrected for the ratio sample's geometrical cross section to cross section in contact with the electrolyte as described in [16].

2.2. Setup for microscopic permeation experiments

For micro-diffusion experiments, a specific experimental setup was designed (Fig. 2) in which a 2.5 mm thick cement paste slice acts as membrane between a concentrated (0.5 M) KCl solution (upstream compartment) and a diluted (0.01 M) KCl solution (downstream compartment). Small amounts (5 mM and 50 mM) of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ salts were added to the chlorinated solutions when a redox mediator was required for surface imaging purposes.

The downstream compartment allows the scanning electrochemical microscopy (SECM) experiments to be performed and contains the tip, the counter electrode (a Pt mesh), and the reference electrode (a saturated calomel – SCE).

The flux of chlorides through the cement paste membrane stream compartments was detected using the SECM tip polarised at the appropriate potential. The whole SECM setup used in this work has already been described elsewhere [17,18].

3. Results

Microstructural characterisations of the samples were performed by mercury intrusion porosimetry. The results depicted in Fig. 3 are in good agreement with those reported for a similar system [19], with two main pore families centred at about 20 and 90 nm in diameter, the overall porosity being about 14%.

Download English Version:

https://daneshyari.com/en/article/186339

Download Persian Version:

https://daneshyari.com/article/186339

Daneshyari.com