Non-Destructive Testing for the In Situ Assessment of the Ionic Flux in Cementitious Materials

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Abstract: The study deals with the design, calibration and testing of a diffusive sampling probe for in situ assessment of ion mobility in binder-based matrix. In parallel, leaching tests were conducted to compare the ions release obtained under equilibrium condition with the dynamic flux induced by the diffusive sampling probe. The probe contains an ionic exchange resin that acts as sink, causing a re-supply of ions from the solid to the solution phase, and inducing diffusion fluxes from the mortar through a thin diffusion chamber. The flux depends on the quantity of mobile ions in the solid phase and on the exchanging rate from solid phase to solution. By means of the in situ sampling with this diffusive probe, information about the interaction of materials with the environment can be obtained. This information is very useful for the environmental impact assessment of the material and its durability.

Keywords: Diffusion, Durability, In situ probe, Mortar, Non-Destructive Testing (NDT).

1. INTRODUCTION

Mortars are used in new structures and in historic monuments as materials for restoration with structural, rendering, repointing and consolidation purposes. Wet and dry deposition of atmospheric pollutants is the main agent responsible for the damage of cementitious materials: in particular ions such as sulphates and chloride ions in polluted area and coastal zone [1]-[2]-[3] promotes cement-based deterioration and corrosion of embedded reinforcements. In particularly aggressive environments, stainless or galvanized steel reinforcements and hydrophobic treatments, able to make the binder paste less susceptible to water saturation [4]-[5], can be used to extend the service life of structures [6].

The measure of salts release from porous matrix is an important means for the evaluation of both environment impact of the material and its durability. Standard methods of analysis for water soluble salt [7] suggest solid liquid extraction of grinded material in equilibrium condition. This analysis gives information only on the soluble fraction of salt with respect the total amount. Furthermore, the results are obtained in release condition, that are not reliable from real ones. Other types of standard methods for the assessment of leachable salts are performed under conditions closer to in situ conditions. These leaching tests [8] are defined “dynamic” because of leaching solution is renewed at fixed time, in order to measure the diffusive flux of salts from the surface of the material. However, their execution condition is not
exactly dynamic, they have high detection limit, long deployment time (up to 16 days) and need a lot of samples to analyse.

The aim of this work is to explore the possibility of adopting a new sampling technique, already described in the literature for heavy metals dynamic speciation in soil [9]. This technique is very promising because it potentially allows in situ deployment, labile ions flux assessment and wide range of applicability (from bulk to trace element) [10].

2. MATERIALS AND METHOD

A. Probe description

The diffusive sampling probe consists of a water chamber filled with deionized water as diffusive cell, a membrane filter and an anionic exchange resin as adsorbent material (Fig. 1). In particular, the assembled device is composed of a modular polycarbonate ring (d = 3.7 cm, h = 0.8 cm) filled with deionized water, in direct contact with the cement matrix, as diffusive chamber; a membrane filter (cellulose nitrate "Purabind 08", 37 mm, 0.8 μm); a second polycarbonate ring filled with the anionic resin (1.2 g, DOWEX Monosphere 550A hydrated with deionized water) and the upper surface sealed.

In the probe, the resin catches the anions that spread from the cement matrix, so the concentration of the anions in the water chamber is kept low. Actually, the resin acts as a sink for anions, promoting the re-supply of the labile anions from the solid to the solution phases. The re-supply depends on the quantity of labile ions adsorbed on the solid phase and on the exchanging rate of the solid and solution phases. In this model, the probe deployment is based on the first Fick's law (Fig. 1).

![Fig. 1. Schematic representation of the ion concentration through the diffusive chamber and the cement matrix and schematic view of the assembled probe.](image)

B. Probe calibration

The probe calibration was obtained by calculating the diffusion coefficients of anionic species (Cl\(^{-}\), SO\(_4^{2-}\), NO\(_3^{-}\)) as perceived by the probe itself. The devise was assembled and the diffusive chamber, filled with deionized water, was covered with a membrane filter (instead of direct contact with the cement matrix). Then the probe was inserted in a support and pushed into a tank containing 1 L of salts solution (NaCl, Na\(_2\)SO\(_4\), NaNO\(_3\), each anion 50 mg·L\(^{-1}\)) (Fig. 2).
After fixed time (24, 48 and 72 h; four replicas each time) the probe was recovered from the solution, the devise was disassembled and the resin was eluted with 50 ml of NaOH 1M over-night in a plastic vial, end over end shaken. The resin leachate (separated from resin by centrifugation) was overly basic for direct HPLC analysis and required neutralization, obtained by adding a cationic resin, H⁺ form (DOWEX G-26 H).

The amount of ion accumulated on the resin (M, g) was calculated as:

\[ M = \frac{C_{\text{eluant}}(V_{\text{NaOH}})}{f_e} \]  

\[ C_{\text{eluant}} \] is the eluant concentration measured by HPLC (g·cm⁻³), \( V_{\text{NaOH}} \) is the volume of NaOH 1M (50 cm³) and \( f_e \) is the elution factor adopted with a yield value of 0.8.

Diffusion coefficients, D (cm²·s⁻¹), were calculated using Eq. (2)

\[ D = \frac{\text{slope} \cdot g/A \cdot C \cdot 60}{\text{A} \cdot \text{g} \cdot \text{C} \cdot \text{60}} \]  

where \( A \) (10.8 cm²) is the exposed area of diffusion chamber with thickness \( g \) (0.8 cm), the ‘60’ converts the time from minutes to seconds, the unit of the salts solution concentration \( C \) is ng·cm⁻³. The slope, measured in ng min⁻¹, was obtained from the amount of ion accumulated on the resin at fixed time. This equation gives the diffusion coefficient value for the temperature at which the experiment was performed (\( T = 25\pm2 \) °C).

C. Deployment

Mortar specimens (20×20×20 cm) were manufactured with a water/cement = 0.35, sand/cement = 3 by weight and with different content of potassium nitrate (0, 0.5%, 1% and 5% w/w cement). CEM IIA/L 42.5 R and natural sand with \( d_{\text{max}} = 4\text{mm} \) were used as cement and aggregate respectively.

After 28 days of curing, the first ring of the device was sealed at the upper surface of the
specimens (four devices for each specimen) using silicon paste. The specimen was closed in a tank filled with deionized water (4 L), in order to obtain water saturation of the mortar, the upper face of the specimen was kept out of the water level. Saturation period was completed when also the upper face was hydrated (about 2 days). Then the polycarbonate rings were filled with deionized water, and the devices were assembled, layer above layer, with the membrane filter, the second ring, the pre-hydrated resin and finally the cover (Fig. 3).

In the tank, the water was renewed at t = 0 h and at t = 24, 48, 120, 168 h. Every time 10 ml of the water was kept and stored for final analytical step. At the same time, the resin from the probes was collected with a plastic Pasteur pipette and eluted with NaOH 1M.

The time-averaged concentration at the interface of the mortar and the diffusive chamber ($C_{\text{diff}} \approx \frac{M}{\text{g}} \cdot \frac{1}{\text{cm}^3}$) can be calculated from:

$$C_{\text{diff}} = \frac{M}{\text{g}} \cdot \frac{1}{(\text{DAt})}$$

$g$ is the diffusion chamber thickness (0.8 cm), $D$ is the ion diffusion coefficient in the diffusion chamber ($\text{cm}^2 \cdot \text{s}^{-1}$), $A$ is the exposed area (10.8 cm$^2$) and $t$ is the deployment time (s).

The probe operates on the local pore water concentration (at the interface mortar/probe) inducing its depletion below the equilibrium value. In response to this variation, ions desorb from the mortar solid phase to restore the pore water concentration to its equilibrium value. When ions are fixed on the soil, these fractions do not contribute to the equilibrium between solid and solution phases.

3. RESULTS

Fig. 4 shows the trend in time of the mass accumulated into the resin by sampling in salts solution during probe calibration test. The calculated anion diffusion coefficients, as perceived by the probe, have values quite similar to those reported for diffusion in water [11] (Tab. 1).

| anion | $\text{slope} \ [\text{ng} \cdot \text{min}^{-1}]$ | $D \ [\text{cm}^2 \cdot \text{sec}^{-1}]$ |
|-------|---------------------------------|---------------------------------|
| Cl$^-$ | 0.55                            | 1.4E-05                         |
| NO$_3^-$ | 0.22                            | 5.5E-06                         |
| SO$_4^{2-}$ | 1.50                          | 3.7E-05                         |

From the anion concentrations measured in water, periodically renewed in the tank, the trend in time of the fluxes of ions released under equilibrium condition are obtained. If the flux of
ions expressed as meq·s⁻¹·m⁻² (J) is plotted against the time (s) in log/log-scale [12], the results of a thank leach test allows to deduce the prevailing leaching mechanism (Fig. 5). The gradient values are in the range 0.72 – 0.94, typical of a material with very low porosity (as a mortar with w/c = 0.35). In Fig. 6, the ions concentration at the specimen-water interface, obtained with the new passive probe, are reported. Four probes were applied at each specimen, but the result are relative to only one replica, because of the difficulties in keeping polycarbonate ring sealed to the mortar surface under water saturation condition.

![Fig. 5. Leaching rate: flux of ions (J) vs. time in water under equilibrium condition.](image)

![Fig. 6. Averaged concentration (C_{diff}) at the specimen-water interface after 24 and 120 h.](image)

The probe shows good analytical ability to distinguish the different mortar compositions. Different specimens showed similar value of C_{diff} with respect to SO₄²⁻ and Cl⁻, but increasing value with increasing NO₃⁻ content. Moreover, while the leaching rates from thank leaching test (equilibrium condition, Fig. 5) are similar for the different ions, the dynamically sampled fluxes are different (Fig. 6). In particular, the concentration at the specimen-water interface (C_{diff}) remained quite constant after 24h and 120h for NO₃⁻ but not for Cl⁻ and SO₄²⁻. In Table 2, the relative values of C_{diff} normalised on the chlorides concentration are reported. The greater the NO₃⁻ content in the mortar, the greater its capability to resupply the liquid phase if compared with chlorides, that have the main fraction fixed on the mortar solid phase. If an ion is present in fixed form it can resupply the lowering in concentration only by diffusion from internal pore water. On the other hand, if an ion present in solid phase is labile (not fixed) and its velocity of exchange between solid and liquid phases is high, the concentration at the interface remains quite constant in time.
Table 2. Concentration at the water-specimen interface normalised on $C_{\text{diff}}$ of Chloride

| specimen | Cl$^-$ | NO$_3^-$ | SO$_4^{2-}$ |
|----------|--------|----------|-------------|
| 24 h     |        |          |             |
| 0%       | 1      | 4        | 6           |
| 0.5%     | 1      | 4        | 4           |
| 1%       | 1      | 10       | 8           |
| 5%       | 1      | 34       | 5           |
| 120 h    |        |          |             |
| 0%       | 1      | 6        | 7           |
| 0.5%     | 1      | 13       | 23          |
| 1%       | 1      | 28       | 14          |
| 5%       | 1      | 255      | 14          |

4. Conclusions

The results are referred to the first application of dynamic speciation technique to cement-based matrix. The passive probe, developed to the purpose, shows good analytical control in water. The diffusion coefficients calculated for the anions as perceived by the probe, are similar to those reported for diffusion in free water. The technique is able to distinguish between the labile and the fixed fraction of the ions in the matrix. It is able to measure the concentration of the ions directly at the surface of the mortar. However, the measurement reproducibility on mortar needs improvement efforts focused on maintaining saturation condition of the mortar and good contact with the probe. The probe can be assembled with different adsorbent materials and potentially it is able to dynamic speciation of both anions, cations and organic molecules. The first results are promising enough for inducing further investigations.

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The published references are not correct.

Please replace with:

[1] V. Corinaldesi, G. Moriconi, F. Tittarelli, “Thaumasite: evidence for incorrect intervention in masonry restoration, Cement & Concrete Composites”, vol. 25 (8), pp. 1157-1160, 2003.
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