

Short Communication

Permeability of Paint Films Towards Chloride Ion

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An apparatus for determining the permeability of paint films towards chloride ion is described. This set-up implements the time-lag method and consists of a permeation cell made up of two chambers divided by a supported paint film. The upper chamber contains an aqueous sodium chloride solution and the lower one, water. The permeability is obtained from the conductivity history read at the lower chamber. Osmotic pressure issue is addressed and the reproducibility of the results reported.

The time-lag method is not described in any standard. The requirement concerning "surface protection systems for concrete" for chloride ion permeability is not quantified in prEN 1504-2. The standard establishes that this requirement is "subject to national standards and national regulations" but when the capillary adsorption of water is lower than 0.01 kg/(m²h^{0.5}) the diffusion of chloride ion is not to be expected. Some experimental results prove this is not correct and, in Portugal, the National Laboratory of Civil Engineering (LNEC) has proposed a threshold permeability value of 10⁻¹⁴ m²/sec for coatings claiming to be corrosion protective.

Keywords: Chloride ion permeability, time-lag method, prEN 1504-2, permeation cell, concrete corrosion

Coating systems are widely used for decorative and protective purposes. Responding to current needs, the European Union is preparing standards to define the threshold values of the coating characteristics that are mainly responsible for conferring protection to reinforced concrete.¹

The penetration process of chloride ions is very slow, so all the methods used to measure chloride ion permeability have to be accelerated ones. There are several methods to determine concrete permeability towards chloride ion, e.g., salt ponding test, rapid chloride permeability test, and electrical migration techniques,

among others.² However, few references were found on the determination of coatings permeability towards chloride ion.

Chloride ions can be transported through a coating film dissolved in water or by an ion exchange mechanism.^{3,4} This means that it is not possible to regulate the chloride ion transport by simply regulating the liquid water permeability, as stated in prEN 1504-2;¹ direct determinations must be performed. In Portugal, the National Laboratory of Civil Engineering (LNEC) has proposed a threshold permeability value of 10⁻¹⁴ m²/sec towards the chloride ion for coatings claiming to be corrosion protective.

TIME-LAG METHOD

The so-called time-lag method is commonly used to obtain the permeability of membranes.^{5,6} A concentration step perturbation is performed in one chamber of a two-chamber permeation cell, which is divided by the membrane, and the response followed by analyzing the concentration at the other chamber. It is known as the time-lag method because there is a time-lag between the perturbation and the onset of the concentration rise on the other side of the membrane. A typical time-lag response can be seen in *Figure 1*.

The slope of this curve is related to the membrane permeability while the time-lag (the time at the interception of the tangential line with the abscissa) is related to the diffusion of the species across the membrane. During a time-lag experiment, the concentration in the upper chamber remains mostly constant and in the lower chamber increases very slightly, so it can be assumed that the driving force is approximately constant. To understand the shape of the time-lag response curve, we have to realize that a solute particle has to cross the membrane until it is released on the other side of it. A steady state mass transfer between the two chambers stabilizes only after a while, precisely when the upper blending curve becomes straight (*Figure 1*). From this point on it is possible to obtain the membrane permeability. The slope of this curve is directly related to the species flux; it translates the increase of the solute concentration at the steady-state on the lower chamber.

The flux across the membrane is proportional to the concentration gradient across the membrane divided by its thickness:

$$N = L \frac{C_U - C_L}{\delta} \quad (1)$$

where N is the flux, C_U and C_L are the concentration in the upper and lower chambers, respectively, δ is the membrane thickness, and L is the permeability of the membrane.

If the experiment is run for a long time, the curve represented in *Figure 1* eventually starts bending down, due

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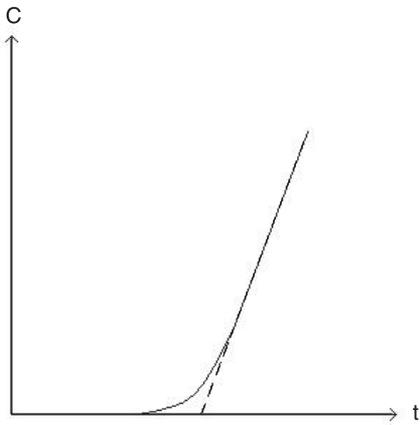


Figure 1—Typical time-lag response.

to the concentration driving force decrease (the concentration decreases in the upper concentration chamber and increases in the lower chamber).

EXPERIMENTAL CONFIGURATION

The design of the permeation cell for obtaining the permeability of paint films towards chloride ion is shown in *Figure 2*.

The upper chamber is designed to contain the aqueous sodium chloride solution (2.5 M). It has a larger volume than the lower chamber, which is designed for receiving deionized water. The two chambers are separated by the paint film, which is supported on Kraft paper (400 μm thick), with the paint surface down (*Figure 2*). When two solutions such as those described above make contact through a

semi-permeable membrane, osmotic pressure develops and may rise up to very high levels. To prevent this, both the upper and lower solutions are brought into contact with the atmosphere through holes (see *Figure 2*). Water crosses the paint film from the lower to the upper chamber while chloride and sodium ions cross the paint film from the upper to the lower chamber. To assure that the amount of water at the lower chamber stays constant, a small container with water is used. On the other hand, the upper chamber is not completely filled with the aqueous sodium chloride solution in order to allow room for the permeated water. The upper chamber has a volume approximately three times larger than the lower one, precisely to assure that the sodium chloride concentration is maintained approximately constant during the experiment. The sodium chloride concentration history at the lower chamber is followed using a conductivity electrode. The conductivity is directly proportional to the sodium chloride concentration for low concentrations. A magnetic bar should be placed at the lower chamber for homogenizing the lower solution and to allow for the correct reading of conductivity.

It should be emphasized that the amount of chloride ions remains constant in the lower chamber despite the water flow from the water container, because this water flow balances only the water that crosses the paint film to the upper chamber. On the other

hand, the water entering the lower chamber ensures that no air bubbles are formed beneath the paint surface, reducing the permeation area.

Figure 3 shows a photo of the permeation cell used in the present work. The lower chamber volume is 75 cm^3 while the upper one is 200 cm^3 and the body of the permeation cell was made of acrylic (plexiglass).

The paint film to be analyzed was produced by applying the paint on a sheet of Kraft paper (400 μm thick) following the paint manufacturers recommendations. The paint was allowed to dry for seven days at 296.15 $\text{K} \pm 1 \text{ K}$ temperature and 50% $\pm 5\%$ of relative humidity (EN 23 270). Circular test panels with 9-cm diameters were then cut using a special tool and the paint film thickness was obtained using a digital micrometer—Mitutoyo®, 0-25 $\text{mm} \pm 1 \mu\text{m}$. The conductivity was measured using a WTW conductometer, model InoLab® Cond level 2, with a TetraCon 325 electrode. The supported paint film was placed in the permeation cell, which was tightly closed, and the conductivity electrode was inserted. The deionized water was fed to the lower chamber using a 100 cm^3 syringe. The water amount used for filling this chamber was obtained by weighing the syringe before and after the injection of water. The permeation cell was then placed horizontally for filling the water container and the upper chamber, which was almost full with a known amount of a 2.5 M aqueous sodium chloride solu-

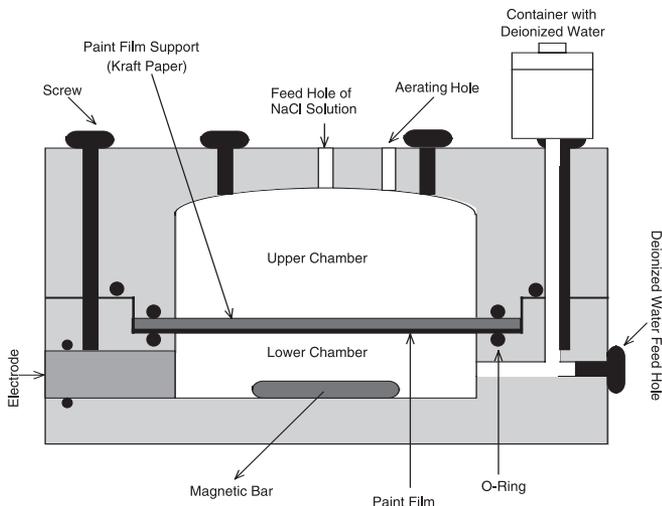


Figure 2—Scheme of chloride ion permeation cell.

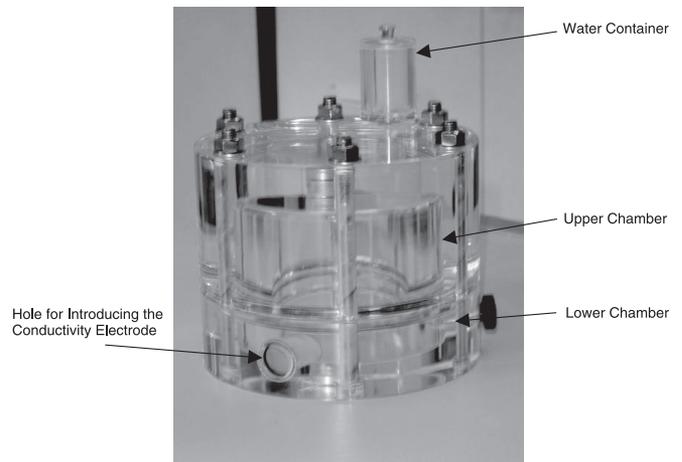


Figure 3—Chloride ion permeation cell.

Table 1—Experimental Results for Paints S and W (Relative Errors for Two Reads)

Paint	δ_f (μm)	L_f (m^2/sec)
S	180	$5.3 \times 10^{-16} \pm 1.5 \times 10^{-16}$
W	89	$6.0 \times 10^{-14} \pm 1.0 \times 10^{-14}$

tion. The free volume of the upper chamber should be enough to accommodate the permeated water during the experiment.

The permeation cell was then placed over the magnetic stirrer on a thermostatic cabinet (296.15 K temperature).

The entire unit was controlled by a computer which was connected to the conductometer via an RS 232 interface. The control/acquisition interface was developed in LabView® (National Instruments). The conductivity data acquired was then treated for the permeability determination using an Excel spreadsheet.

The thermostatic cabinet used in the present work was made from a high quality domestic refrigerator without freezer (Whirlpool®, Class A) and a fan heater (Fagor®, TRV-200). The fan from the fan heater was connected directly to the mains and made to work continuously while the heating system was connected to a temperature controller (Eurotherm®, 2216L) through a solid state relay (Eurotherm, SSR 50A) and worked whenever necessary to keep the temperature constant. The temperature controller used a K type thermocouple to read the temperature inside the cabinet, which was stable within 0.1 K.

EXPERIMENTAL

The developed permeation cell was used to characterize two commercial paints made by CIN, a high-quality waterborne paint (paint W) and a solvent-based paint (paint S). The waterborne paint contained a polymer in emulsion while the solvent-based one contained a soluble polymer. These paints' penetration in the Kraft paper support was verified to be negligible. The temperature of the thermostatic cabinet was set to 296.15 K. Determinations were performed two times with different test panels from the same Kraft paper sheet, for precision evaluation.

The conductivity history was recorded for the paint films. A calibration curve was used to convert the original conductivity history data into concentration data. The flux across the supported paint film (N) can be obtained from a mass balance to both chambers:

$$N = -\frac{V_U}{A} \frac{dC_U}{dt} = \frac{V_L}{A} \frac{dC_L}{dt} \quad (2)$$

By simplifying this equation one obtains:

$$\frac{d(C_U - C_L)}{dt} = -N \cdot A \left(\frac{1}{V_U} + \frac{1}{V_L} \right) \quad (3)$$

where V_L is the volume of the lower chamber, V_U is the volume of the upper chamber, A is the effective permeation area, C_L and C_U are the concentrations at the lower and upper chambers, respectively, and t is time. Introducing this equation into equation (1), it becomes:

$$\ln(C_U - C_L) = -\frac{L_C A}{\delta_c} \left(\frac{1}{V_U} + \frac{1}{V_L} \right) t + \ln(C_{U0} - C_{L0}) \quad (4)$$

where L_C is the permeability of the supported paint film, δ_c is the thickness of the supported paint film, C_{L0} is the initial concentration at the lower chamber, which should be $C_{L0} = 0$, and C_{U0} is the initial concentration at the upper chamber (this concentration is constant and equal to 2.5 M).

To obtain the paint film permeability, L_p it is necessary to know both the support permeability alone, L_s , and the permeability of the supported

paint film, L_c . Permeability could be compared to an electrical resistance so, using Ohm's law,⁶ the supported paint film permeability is the sum of two resistances in series (the support resistance and the paint permeability):

(5)

where δ_f is the paint film thickness and δ_s is the support thickness. Equation (5) translates the association in a series of two resistances, δ_f/L_f and δ_s/L_s . The permeability should be obtained from the time-lag curve portion that forms a straight line, because this corresponds to the steady state.

The results obtained for both paints are given in Table 1. Figure 4 shows the plot corresponding to the chloride ion concentration history for paint W. The permeability obtained from the support used, 400 μm Kraft paper sheet, was $1.5 \times 10^{-11} \text{ m}^2/\text{sec}$. It is noteworthy that the permeability of this paint obtained using the Kraft paper support, a sintered glass plate and an uncoated tile, were all very similar, pointing out that the Kraft paper was a good paint support. Also, the Kraft paper was the cheapest and easiest material with which to work.

The apparatus developed allows for the quick determination of paint film permeabilities, not only because the conductivity values are acquired each second using a computer, but also due to the permeation cell design, which uses a minimal lower chamber volume and thus a maxi-

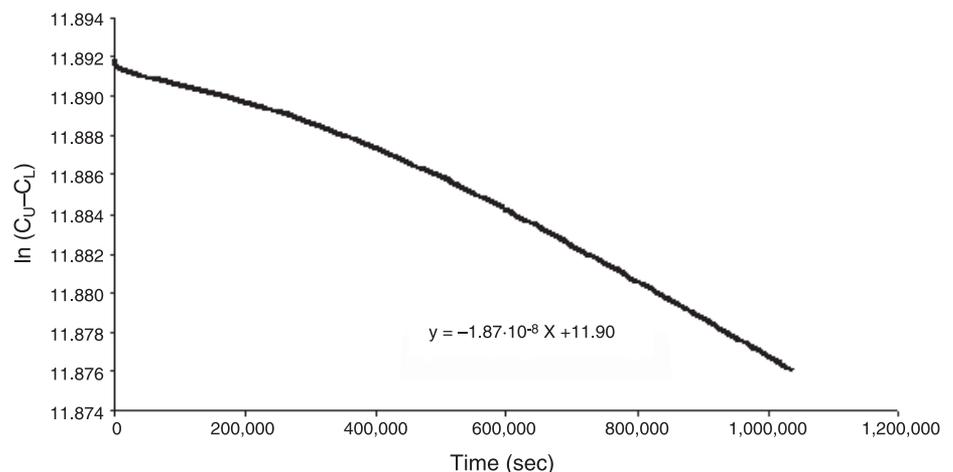


Figure 4—Chloride ion concentration history at the lower chamber for paint W.

mum sensitivity. It can be seen from *Table 1* that the results show an acceptable reproducibility.

CONCLUSIONS

The permeability towards chloride ion is a critical requirement for many surface coatings and/or treatments applied to reinforced concrete. It is then necessary to develop a suitable determination method for obtaining this permeability value. This article describes an implementation of the so-called time-lag method. An apparatus was successfully designed, built,

and optimized which allows for precise and fast determinations of paint films' permeability towards chloride ion. This set-up is recognized and adopted by LNEC, the Portuguese legal institution responsible for paint coatings quality compliance.

References

- (1) prEN 1504-2, "Products and Systems for the Protection and Repair of Concrete Structures—Definitions, Requirements, Quality Control and Evaluation of Conformity—Part 2: Surface Protection Systems for Concrete," April 2004.
- (2) Stanish, K., Hooton, R., and Thomas, M., "Testing the Chloride Penetration

- Resistance of Concrete: A Literature Review," Department of Civil Engineering, University of Toronto, Canada, 1997.
- (3) Costamagna, P., "Transport Phenomena in Polymeric Membrane Fuel Cells," *Chem. Eng. Sci.*, 56, 323-332 (2001).
 - (4) Gnusin, N., Berezina, N., Kononenko, N., and Dyomina, O., "Transport Structural Parameters to Characterize Ion Exchange Membranes," *J. Membr. Sci.*, 243, 301-310 (2004).
 - (5) Taveira, P., Costa, C., and Mendes, A., "On the Determination of Diffusivity and Sorption Coefficients Using Different Time-Lag Models," *J. Membr. Sci.*, 221, 123-133 (2003).
 - (6) Mulder, M., *Basic Principles of Membrane Technology*, 2nd Ed., Kluwer Academic Publishers, Dordrecht, 1996.