



# Mobility of chloride through cement-based materials under partially saturated conditions

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## ABSTRACT

This work presents two complementary techniques to study <sup>36</sup>Cl and stable chloride diffusion through unsaturated cement-based materials for saturation degrees ( $S_w$ ) ranging from 0.18 to 1. The first technique is based on steady-state through-diffusion method where suction (up to 9 MPa) is controlled using osmosis process. In the second technique, in-diffusion experiments are performed by putting into contact a spiked-fresh-cement paste with a CEM-V/A-hardened-cement paste (HCP) sample (initial water to cement ratio of 0.4) having a given water saturation imposed by saline solution method. After a controlled diffusion time, the <sup>36</sup>Cl activity profiles within the samples are acquired by means of the abrasive peeling method and <sup>36</sup>Cl activity is determined by liquid scintillation counting (LSC) technique. The application of the first technique resulted in data showing a sharp decrease of the effective diffusion coefficient ( $D_e$ ) (by a factor of ten) between the experiments done on the fully-saturated HCP sample and the HCP sample at  $S_w = 0.85$ . Moreover, duplicate in-diffusion experiments carried out on HCP samples partially-saturated at  $S_w = 0.86$  provided <sup>36</sup>Cl  $D_e$  range well bracketing the one determined by the first approach at  $S_w = 0.85$ . Four other in-diffusion experiments were thus performed on HCP samples with saturation degrees down to 0.18. Interpretation of the experimental results showed a very small decrease of  $D_e$  values for  $S_w$  from 0.74 to 0.41 and a sharp decrease for  $S_w$  from 0.41 to 0.18. Lastly, comparison with the diffusive behavior of tritiated water (HTO) through unsaturated CEM V/A HCP samples clearly indicated that diffusion of chloride was more affected by desaturation than HTO. Its ionic form would restrict chloride to the liquid phase whom continuity is broken when dehydration is strong enough.

## 1. Introduction

Diffusion of ionic species into cement-based materials has been extensively investigating since this transport phenomenon is a key parameter for modelling processes related to contaminant transport in cement-based barriers, assessment of rebar corrosion in civil concrete structures and long-term behavior of nuclear waste disposal systems based on cement-based engineered barriers (Andra, 2005; Macé et al., 2012; Patel et al., 2016). Moreover, there are many situations where cement-based materials can be partially water-saturated, like in a deep geological facility for the disposal of long-lived intermediate and high level nuclear waste. In this case, the degree of saturation of cement-based materials should be controlled by the surrounding relative humidity that is imposed by ventilation of the underground drifts and shafts during the exploitation period, and by gas generation (anoxic corrosion, radiolysis ...) during the post-closure period. Under these various conditions, the saturation degree of cement-based material could go down to tens of percents (Andra, 2005) and, the radionuclide

diffusive rate can thus be strongly impacted.

An extensive review was recently provided by Zhang and Zhang (2014) on diffusion in unsaturated cement-based materials. However, they reported only few studies dealing with the determination of diffusion coefficients through unsaturated cement-based materials because performing such measurements still remains a challenging task. Two types of approaches were identified: the measurement of electrical resistivity and the in-diffusion method. The first is an indirect method where diffusivity can be obtained from the link between resistivity and diffusion, using Nernst-Einstein equation (Olsson et al., 2012; Mercado-Mendoza et al., 2014; Zhang and Ye, 2017). This method is very fast, limiting disturbance of materials. However, as mentioned by Patel et al. (2016), resistivity measurement tends to overestimate diffusivity compared to other techniques for cement-based materials with low capillary porosity, especially under fully-saturated conditions. The second technique consists in making the tracer of interest diffuse into unsaturated materials over a certain period and then acquiring tracer profile in the sample. Several techniques were developed for properly putting in

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contact tracer with targeted unsaturated cement-based material. Climent et al. (2002) and Vera et al. (2002) generated close to unsaturated materials PVC combustion gases, which contain HCl, acting as a source of chlorine. Nielsen and Geiker (2003) contaminated their samples by immersing them in NaCl-enriched solution for 2 h followed by drying the sample surface. Dridi and Lacour (2014) used the half-cell method for studying lithium diffusion. They placed two unsaturated samples prepared with the same material (Li-source and Li-target) into contact with each other in a sealed cell. The source sample was uniformly doped with lithium, while the target sample was tracer free. For all these studies, at the end of the diffusion time, the curve-fitting of the tracer profile to the analytical solution to Fick's second law enables the determination of the tracer diffusion coefficient. However, as in-diffusion method is a non-steady-state method, only the apparent diffusion coefficient can be estimated from the tracer profile. Therefore, all the chemical effects, e.g., chloride binding and porosity, have to be separately determined so as to evaluate the effective diffusion coefficient, or the diffusivity.

Lastly, all these diffusion testing used saturated saline solution method for imposing suction to cement-based materials. However this method is known to be mainly adapted to suctions higher than 8.5 MPa, since below this value the relative uncertainty on the imposed suction is significant, higher than 15% (Cuisinier and Masroui, 2005). We recently presented a new setup allowing through-diffusion method to be performed through compacted clay materials or clay-rocks under partially-saturated conditions using osmotic approach (Savoye et al., 2010, 2012a, 2014, 2017). As already mentioned by Cuisinier and Masroui (2005), osmotic approach enables one to impose suction up to 9 MPa associated to very low uncertainties on its estimation. It means that this method is complementary with respect to the saline solution method for investigating degrees of saturation close to full-saturation. Another advantage of osmotic method lies in the fact that all the type of diffusion testing used under fully-saturated conditions can be used, such as the steady-state through-diffusion method. In this case, effective diffusion coefficient of reactive solutes, e.g. chloride, is directly measured from the steady-state part of the cumulative activity curve (Shackelford, 1991), while the extent of the adsorption/binding of ions can also be estimated from the analysis of the transient part of the tracer cumulative activity curve (Savoye et al., 2015).

The aim of the present work is to investigate the diffusion of chloride ( $^{36}\text{Cl}$  and stable Cl) through cement-based materials under a large suction range (0–170 MPa), using two complementary techniques. Both enable the study of a large range of water saturation degree. The first technique allowed  $^{36}\text{Cl}$  through-diffusion experiments to be conducted under suction values imposed by osmosis up to 9 MPa. The second technique was based on the recommendations given by Dridi and Lacour (2014) for improving the half-cell method they developed. To this end, a small amount of fresh cement paste doped with  $^{36}\text{Cl}$  and stable Cl was placed onto a target unsaturated cement-based material sample so as to play the role of source. In this case, the assembly can be placed in a desiccator at controlled relative humidity without the use of diffusion cell. The use of  $^{36}\text{Cl}$  radiotracer enables the acquisition of a  $^{36}\text{Cl}$  sample profile with a high accuracy by means of the high-resolution abrasive technique developed by Van Loon and Eikenberg (2005) for clay materials, coupled to  $^{36}\text{Cl}$  liquid scintillation counting (LSC) measurements specially optimized for cementitious leachate solution.

## 2. Materials and methods

### 2.1. Preparation of the samples

Cement pastes based on a CEM V/A cement (trade name CEM V/A (S-V) 42.5N PM-ES-CP1 NF “PMF3”, Rombas, Ciments Calcia) were used for this study. Cement paste samples were prepared with an initial water to cement ratio of 0.4 (W:C). They were poured into closed cylindrical polyethylene plastic molds (51.5 mm in diameter and 53.0 mm

**Table 1**

Overview of the experimental conditions used for the first technique based onto osmosis.

Sample	PEG concentration, (g PEG/g of ACW excluding PEG)	Saturation degree of HCP samples, (–)	Initial $^{36}\text{Cl}$ mass activity, (MBq/kg of ACW excluding PEG)	Diffusion time, (day)
Osm 1	0	1	0.897	90
Osm 2	0.95	0.85	0.933	520
Osm 3	0.95	0.85	dedicated to saturation measurement	

in height) and initially cured at 100% relative humidity chamber for 28 days. After the curing period, some samples were submitted to a high-pressure extraction so as to collect the cement pore-water solution. This extracted cement pore solution was then characterized to determine its chemical composition by ion chromatography (DIONEX DX 120 column, using 20 mM methane sulfonic acid as eluent for cation measurements and DIONEX DX 600 column with 14 mM NaOH eluent for anion measurements). The chemical composition of artificial cement water (ACW) corresponds to a  $\text{Ca}(\text{OH})_2$  oversaturated solution in addition with  $(79 \pm 2) \text{ mmol L}^{-1}$  of  $\text{Na}^+$ ,  $(291 \pm 2) \text{ mmol L}^{-1}$  of  $\text{K}^+$ ,  $(0.57 \pm 0.03) \text{ mmol L}^{-1}$  of  $\text{Cl}^-$  and  $(0.96 \pm 0.04) \text{ mmol L}^{-1}$  of  $\text{SO}_4^{2-}$  resulting in a pH value of  $(13.5 \pm 0.1)$ . The other hardened cement pastes (HCP) samples were then removed from the mold and kept for at least 6 months prior to be used in the ACW solution.

For the through-diffusion experiments using osmosis technique, a HCP specimen was machined using a lathe to obtain a 36-mm-diameter cylinder. Three sub-samples were then sliced using a diamond wire saw under water into 1.3-mm thick disks (Table 1). These disks were then stored in desiccator containing a KI-oversaturated saline solution at  $(22 \pm 2)^\circ\text{C}$  with a relative humidity, RH, of 69% under hydric equilibrium, which was achieved after ca. 2 months taking into consideration the mass stabilization. This initial dehydration of the HCP samples at a level lower than those imposed by the osmotic method prevents any shrinkage phenomena (only hydration pathway). Therefore, these samples were partly re-saturated using osmotic technique (Table 1). One sample was dedicated to the determination of its saturation degree and the other ones for the through-diffusion experiments.

For the in-diffusion experiment, a HCP specimen was placed on a lathe to obtain a 49-mm diameter cylinder. Eleven sub-samples were then sliced using a diamond wire saw under water into 2.5-mm thick piece (Table 2) and put thus in ACW. After two months, these samples were emplaced in desiccator containing a  $\text{K}_2\text{H}_3\text{O}_2$ -saturated saline solution at  $(22 \pm 2)^\circ\text{C}$  with a RH of 23%, under hydric equilibrium, which was achieved after ca. 5 months (indicated by mass stabilization). Then, two of the samples were transferred in a desiccator containing a KI-saturated saline solution (RH = 69%), two ones in a desiccator containing a KBr-saturated saline solution (RH = 84%), two ones in a desiccator containing a  $\text{KNO}_3$ -saturated saline solution (RH = 90%), and the three last ones in a desiccator containing a  $\text{K}_2\text{SO}_4$ -saturated saline solution (RH = 98%). A maximum of 5 months was

**Table 2**

Overview of the experimental conditions used for the second technique based onto saline solution.

Sample	Saturated saline solution	Saturation degree of HCP samples, (–)	$^{36}\text{Cl}$ mass activity, (MBq/kg of solution)	Diffusion time, (day)
HCP 1	$\text{K}_2\text{SO}_4$	0.86	13.4	11
HCP 2	$\text{K}_2\text{SO}_4$	0.86	15.6	15
HCP 3	$\text{KNO}_3$	0.74	15.6	21
HCP 4	KBr	0.52	15.6	60
HCP 5	KI	0.39	16.7	77
HCP 6	KAc	0.18	16.7	99

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