Use of quantitative digital autoradiography technique to investigate the chlorine-36-labelled radiotracer transport in concrete

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ARTICLE INFO

ABSTRACT

This work presents the capability of digital autoradiography, a non-destructive technique, to improve diffusion parameters determination by mean of high resolution radionuclide mapping. The results show a good agreement between Cl-36 diffusion profiles acquired by digital autoradiography compared to the classic protocol based onto multi-step-abrasive-surface-peeling procedure. The digital autoradiography technique has been successfully used to localize and quantify Cl-36-labelled radiotracer on the surface of a concrete sample and into the contaminated depth. This study shows how optimized in-diffusion investigations can be performed in only 100 days to assess the diffusion parameters of Cl-36 in a low diffusive concrete sample, prepared from a composite cement (CEM V/ A), while a through-diffusion experiment would take several years to reach diffusion steady state for tritiated water, considered as the reference tracer, and consequently, to allow the estimation of the diffusion parameters for Cl-36.

1. Introduction

In the framework of radioactive waste disposal or for dismantling issues, a robust approach is required to properly predict the transport of radioactive contaminant in porous materials, such as cement-based materials which are one of the most important constituents of engineered barriers of the facilities. Depending on the studied radionuclide, performing through- or in-diffusion experiments in porous media (such as clay, hardened cement paste (HCP) or in concrete sample) is considered as a routine method to determine transport properties (e.g. Van Loon et al. (2005), Savoye et al. (2012) and Larbi et al. (2016)). This method is robust but time-consuming. In particular, in-diffusion tests imply a multi-step procedure to acquire quantitative radionuclide activity measurements as a function of the depth in the cement matrix. Micro-grinding is usually performed (e.g. Van Loon et al. (2005), Savoye et al. (2012) and Savoye et al. (2018)). Alternatively, hot-spots localization for a β-emitter on the surface of a contaminated concrete sample can easily be done by digital autoradiography, especially in the framework of decommissioning issues (e.g. Haudebourg and Fichet (2016)). In cement-based materials, autoradiography technique has also been used to investigate radionuclide mapping such as Cs-137, Cl-36 or I-129 in a radial diffusion configuration (e.g. Felipe-Sotelo et al. (2014); Hinchliff (2015); Van Es et al.

(2015)).

The aim of the current study is to test the ability of digital autoradiography as a non-destructive and complementary technique to localize and quantify radionuclide activity on the surface and within a low diffusive material such as concrete, and finally to determine by modelling radionuclide diffusion properties.

As reference, a classic migration experiment in a fully saturated concrete sample was performed with i) batch sorption experiment to a priori evaluate diffusion delay of Cl-36 and ii) a long term tritiated water (HTO) and Cl-36 through-diffusion experiment to estimate radionuclide diffusion parameters (i.e. the effective diffusion coefficient, D_e and the material capacity factor, α). From these first measurements, one can consider that a period of 369 days of diffusion is not sufficient to reach accurate Cl-36 diffusion parameters without a Cl-36 profile determination. Only a good estimation of HTO diffusion parameters can be obtained. The idea was to save some experimental time by optimizing the in-diffusion set-up and to be able to compare a direct quantitative Cl-36 profile measured by digital autoradiography and an un-direct quantitative Cl-36 profile obtained by the routine multi-step abrasive peeling protocol. Quantitative digital autoradiography calibration was obtained by means of specially prepared Cl-36-HCP-standard characterizations.

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Table 1
Concrete formulation.

Component	Nature	Origin	Quantity
Cement	CEM V/A 42.5	Calcia, ROMBAS, France	470 kg/m^3
Filler	C6	Sibelco, France	78 kg/m^3
Sand	Calcareous [0–4]	–	912 kg/m^3
Gravel	Calcareous [4–10]	–	624 kg/m^3
Water	–	–	188 kg/m^3
Superplasticizer	Viscocrete® Tempo9	SIKA	4.7 kg/m^3

2. Materials and methods

2.1. Preparation of the samples

Cement based materials have been prepared using a CEM V/A composite cement (CEM V/A (S-V) 42.5N CE PM-ES-CP1 NF "PMF3"–ROMBAS, Calcia).

Concrete samples were prepared using the formulation reported in Table 1 with a water to cement (W/C) mass ratio of 0.40. The concrete sample was poured into closed cylindrical molds (113 mm in diameter and 230 mm in height) and initially cured at 100% relative humidity chamber for 3 months.

In the meantime, cement paste samples were also prepared with W/C mass ratio of 0.40. Then, the samples were poured into closed cylindrical polyethylene plastic molds (51.5 mm in diameter and 53.0 mm in height) and initially cured at 100% relative humidity chamber for 28 days. After the curing period, some hardened cement paste (HCP) samples were subjected to a high-pressure squeezing extraction to collect the cement pore solution. The extracted cement pore solution was then characterized by ion chromatography (DIONEX DX 120 column, using 20 mM methanesulfonic acid as eluent for cation measurements and DIONEX DX 600 column with 14 mM NaOH eluent for anion measurements). These characterizations enabled the determination of the chemical composition of artificial cement porewater (ACW). This alkaline solution was used to equilibrate all HCP and concrete samples during additional cure and diffusion experiments. The ACW is a portlandite (Ca(OH)$_2$) saturated solution in addition with (79 ± 2) mmol/L of Na$^+$, (291 ± 2) mmol/L of K$^+$ resulting to a pH value of (13.5 ± 0.1). Minor species such as Cl$^-$ and SO$_4{}^{2-}$ are also added to the ACW at (0.57 ± 0.03) mmol/L and (0.96 ± 0.04) mmol/L, respectively. The ACW is systematically filtered (Nylon, 0.45 μm, Nalgene) to remove the excess of portlandite before its use in experiments.

After this initial curing period, the HCP and concrete samples were maintained in ACW for at least 6 months to achieve a better hydration and saturation prior to be used for migration experiments.

2.2. Cl-36 and HTO activity measurements by liquid scintillation counting technique

Cl-36 solutions were prepared by diluting a commercial certified Cl-36 source (T$_{1/2}$ = (302 ± 4) 10^3 years, β-E$_{max}$ = 709.5 keV) (purchased from Eckert&Ziegler Isotope products, Germany). The Cl-36 specific activity of the standard solution is (0.767 ± 0.018) MBq/g, with 100 μg Cl/mL of solution as carrier.

Tritiated water solutions were prepared by diluting a commercial H-3 (T$_{1/2}$ = (12.312 ± 0.025) years, β-E$_{max}$ = 18.6 keV) certified standard solution purchased from (LEA-CERCA, France). The H-3 activity of the stock solution is (808 ± 24) kBq/g.

The Cl-36 and HTO activities in solution samples were diluted in MilliQ water (18.2 MΩ cm^{-1}, Millipore), added to a scintillator cocktail (Ultima-Gold, Perkin) and measured depending if the tracers were mixed or not in the same solution in dual or single mode, respectively, by a β−liquid scintillation counter (Packard TRICARB 2700, USA). Liquid scintillation background measurements were performed in a

similar way using MilliQ water without radiotracers. The counting efficiencies for Cl-36 (and for HTO) were determined by measuring a solution with a known Cl-36 (or HTO) activity in different quenched solutions (a mixture with variable water:acetone ratio as quencher).

2.3. Digital autoradiography technique

The Digital Autoradiography (DA) technique was used to visualize and quantify Cl-36 activity on HCP and concrete surface samples. For that purpose, a compact cement-based sample doped with Cl-36 was placed in close contact with specific screens for digital autoradiography (DA screen) during an optimized exposure time and in a dark room in order to avoid an erasing process on the sensitive surface of the screen occurring with strong light. Screens used in this experiment are TR type (Perkin Elmer). The DA technique is a non-destructive technique that produces an image from the decay emissions such as alpha, beta and gamma radiation even for low energy emitter like Cl-36. The DA characterization begins with exposure of the screen to the ionizing radiation. The flexible screens used contain photostimulable crystals, for example BaFBr:Eu^{2+}, which accumulate and store radiation information when placed in close contact with a radiation source. The accumulated signal can be scanned all over the screen surface by a He−Ne laser (with a spatial resolution of around 160 μm) installed in a Cyclone system (Perkin Elmer). Spatial resolution of 150 dpi (dots per inch) was chosen for this study to obtain a measurement each 0.169 mm. In the case of profile acquisition the resolution was increased to achieve data each 0.042 mm (using a 600 dpi resolution available with the Cyclone system). The specific DA scanner converts the scanned information into Digital Luminescence Unit (DLU) in each pixel. The whole image with the 150 dpi resolution represents a total of 1452*749 pixels. Using ImageJ (https://imagej.nih.gov/ij/download/) and Kartotrak softwares (Géovariances, France) the resulting contrasted image is expressed as a distribution map in color scaling from light blue to red in order to represent low and high activity, respectively.

2.4. Cl-36-doped-HCP used as standards for digital autoradiography

Nine CEM V/A HCP samples with W/C ratio of 0.40 have been prepared with a well-known amount of Cl-36 solution added in the water. These Cl-36-doped-cement samples were poured into closed PE plastic mould (48 mm in diameter and 10 mm in height) and cured in sealed bags during 28 days. After curing, the samples were unmolded and characterized. For each Cl-36-profile determination, the Cl-36-standards were systematically placed onto a DA screen to improve accuracy. The exposure time was in a similar range (from 3 to 5 days) and then, it was possible to convert in Bq/g the digital light unit per surface unit per exposure time (in DLU/mm^2/days) obtained after treatment of each pixel of the autoradiography image. The prepared Cl-36-HCP-standards were ranged between 0 and 4600 Bq/g with (47.4 ± 0.1) mm of diameter and (6.4 ± 0.3) mm of thickness. Two of the nine prepared standards were dedicated to check the homogeneity of Cl-36 distribution in order to choose from the bottom-surface to the top-surface which is the most representative for the calibration. The seven other standards were dedicated to DA calibration.

2.5. Cl-36 batch sorption experiments carried out with HCP and concrete

In order to evaluate a priori the diffusion delay of Cl-36 through HCP or concrete samples, batch sorption experiments were performed on dispersed materials. All batch sorption experiments were carried out in polypropylene copolymer (PPCO) centrifuge tubes (Nalgene) with polypropylene screw closure. Solid samples were crushed and sieved (< 200 μm) in an inert-atmosphere-filled glove-box (P$_{CO2}$ < 1 ppm). Batch sorption experiments were carried out in ACW with [Cl$^-$]$_{initial}$ in a range from 10^{-3} M to 1.4 10^{-1} M using Cl-36 radiotracer and stable LiCl concentrated solution (Aldrich). The solution-to-solid ratio is

(30 ± 2) L/kg for both HCP and concrete solids. After 7, 28 and 90 days of contact time, the suspensions were ultracentrifuged (at 50 000 g for 1 h, Beckmann) before sampling the supernatant. The residual amount of radiotracer in solution was determined by liquid scintillation counting. Experimental results are expressed as distribution ratio (R_d) in L/kg, as defined by Eq. (1).

$$R_d = \frac{[Cl]_{solid}}{[Cl]_{solution}} = \frac{(A_{ini} - A_{solution})}{A_{solution}} \times \frac{V}{m} \tag{1}$$

A_{ini} (cpm) and $A_{solution}$ (cpm) are the introduced activity and the supernatant activity measured after each contact time, respectively; V (L) is the volume of solution and m (kg) is the dry mass of solid. A_{ini} (cpm) is measured from a "blank sample" which was similarly prepared without cementitious materials. The batch sorption experiments were carried out in a glove box with $P_{CO2} < 1$ ppm so as to avoid sample alteration by atmospheric carbonation.

2.6. HTO and Cl-36 through-diffusion experiments carried out with concrete

A classical through-diffusion set-up was used to measure HTO and Cl-36 diffusion behaviour through a fully-saturated concrete sample. For that purpose, a concrete sample of 112.8 mm diameter and 30.3 mm of thickness was sealed using an epoxy resin (Araldite, Hunstman Advanced materials) into a sample holder and placed in a diffusion cell between two compartments. The thickness of the sample dedicated to the through-diffusion experiment corresponds to 3 times the maximum-observed-gravel-size in order to avoid any preferential path through the interfacial transition zone of the concrete sample. The upstream compartment was filled with *c.a.* 300 mL of ACW with 3.2 10^6 Bq/L of HTO (diluted from a LEA/CERCA radioactive stock solution) during the first 70 days. Then, a stable chlorine solution was added to achieve 30 mM of LiCl. Finally, an initial Cl-36 activity of 1.2 10^6 Bq/L was obtained by dilution from an Ecker&Ziegler radioactive stock solution. The downstream compartment was filled with *c.a.* 300 mL of ACW. Regular samplings were performed for 369 days and measured by LSC technique in dual mode. The 1-mL-samplings in the downstream compartment were replaced by the same volume of a freshly prepared ACW and the 0.1-mL-samplings of the upstream compartment were replaced by the same volume of the initial prepared upstream solution (i.e. containing LiCl, HTO and Cl-36). Note that in the through-diffusion experiment protocol proposed in this study, the volume of the downstream reservoir solution is not fully renewed after each sampling, in order (i) to have a more accurate radiotracer activity measurement from a sampling to the other and (ii) to limit as much as possible perturbations such as carbonation or chemical imbalance.

2.7. Cl-36 in-diffusion experiment carried out with HCP

An in-diffusion experiment was performed with a compact-fully-saturated-HCP sample (39.2 mm × 28.9 mm x 3.1 mm) sliced from the cylindrical HCP sample described in § 2.1. Five sides of the HCP sample were glued using an epoxy resin so as to allow diffusion to occur from one surface only. Then, the HCP sample was placed into a specific one-compartment-in-diffusion cell filled with 13 mL of ACW containing 30 mM of LiCl, 2.5 10^6 Bg/L of HTO and 1.5 10^6 Bq/L of Cl-36. The volume of solution for the in-diffusion experiment has been chosen as the best compromise between the minimum quantity to ensure the contact between the radioactive solution and the surface of sample and the minimum necessary H-3 and Cl-36 activities dedicated for one experiment. For 50 days, regular 0.1-mL-samplings were performed in solution. Each 0.1-mL-sampling was replaced by the same volume of the initial prepared solution (i.e. containing LiCl, HTO and Cl-36). HTO and Cl-36 activities were measured in the upstream compartment by LSC technique in order to monitor their diffusion extent into the HCP sample. After this diffusion time, the HCP sample was removed from the

in-diffusion cell and air-dried, particularly to avoid moisture on the DA screen. This HCP sample was dedicated to validate the autoradiography as a complementary technique for Cl-36-solid-profile acquisition. The top surface was first exposed during 3 days onto a TR screen (PerkinElmer). The resulting image in DLU/mm^2/days was then convert in Bq/g using a calibration curve performed with Cl-36-HCP-standards specifically prepared for that purpose (*Cf.* § 2.4). After exposure, the HCP surface was grinded. The powder was collected and 3-times leached in milliQ water in order to collect Cl-36 in solution. The 3 leached solutions were measured by LSC technique. The freshly abraded surface was then exposed to the DA screen. This step-by-step procedure was repeated up to ten times.

2.8. Cl-36 in-diffusion experiments carried out with concrete

An in-diffusion experiment of chlorine-36 has been especially designed for this purpose to provide diffusion properties of a compact-fully-saturated-concrete sample (5 cm × 3 cm x 3 cm). Prior to put in contact with the radioactive solution and similarly to the HCP sample, five sides of the concrete sample were glued to force the diffusion path. The concrete sample was placed in a specific one-compartment-in-diffusion cell filled with 12 mL of ACW with 30 mM of LiCl, 3.0 10^6 Bg/L of HTO and 1.4 10^6 Bq/L of Cl-36. The volume of the radioactive solution was also optimized for the same reasons as mentioned in § 2.7. During 100 days, similarly to the HCP in-diffusion experiment, regular 0.1-mL-samplings were performed in solution and measured by LSC technique to calculate the loss of radionuclides from solution to the porous material by diffusion. Each 0.1-mL-sampling was replaced by the same volume of the initial prepared solution (i.e. containing LiCl, HTO and Cl-36). After this diffusion time, the concrete sample was removed from solution and also air-dried to avoid moisture on the DA screen. A non-active concrete sample was also prepared in similar conditions in order to be considered as a "blank" sample for DA characterizations. The active concrete sample was cut in two pieces (with size 2.5 cm × 3 cm x 3 cm) using a manual saw, in order to minimize as much as possible radioactive dust production. The first half sample was dedicated to 40-steps-abrasive peelings and Cl-36 activity determination by LSC technique. The procedure for abrasive peeling and Cl-36 activity determination is described in § 2.7. The resulting sample thickness after each grinding-step was measured using a micrometer (Mitutoyo, Japan). The second half of the concrete sample was dedicated to DA characterizations and direct Cl-36 diffusion profile determination.

2.9. Experimental results treatment

The analysis of diffusion experiments is based on the Fick's second law, given in Eq. (2):

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\propto} \frac{\partial^2 C}{\partial x^2} = \frac{D_e}{\omega R} \frac{\partial^2 C}{\partial x^2} \tag{2}$$

Where C is the concentration or activity per volume unit in the solute phase (Bq.m^{-3} of pure water); t, the time (s); D_a, the apparent diffusion coefficient (m^2.s^{-1}); x, the distance in the porous material (m), D_e, the effective diffusion coefficient (m^2.s^{-1}); ω, the diffusion-accessible porosity ($-$); α is the material capacity factor ($-$) and R the diffusion retardation factor ($-$).

The material capacity factor is linked to the diffusion retardation factor and the diffusion-accessible porosity, as described in Eq. (3):

$$\propto = \omega R = \omega \left(1 + \frac{\rho_{dry}}{\omega} K_d \right) = \omega + \rho_{dry} K_d \tag{3}$$

Where ρ_{dry}, the dry density of the solid (kg/m^3); and K_d, the distribution coefficient (m^3/kg).

Thus, depending on the type of diffusion experiments, different boundary and initial conditions need to be considered.

Usually in literature, the majority of through-diffusion experiment interpretation applied the time-lag method, based onto analytical solution of Eq. (2) proposed by Crank (1975) (see *e.g.* Shackelford (1991)). The numerical tool *I-Mode* (Interpretation Model Of Diffusion Experiments), developed at CEA/SECR/L3MR laboratory, is dedicated for the data interpretation of one-dimensional diffusion experiments by modelling i) simultaneously the cumulative activity in the downstream reservoir and the remaining activity in the upstream reservoir, for through-diffusion experiments and ii) the remaining activity in the upstream reservoir and the diffusion profile in the solid, for in-diffusion experiments. This tool is implemented in Excel software using Visual Basic for Applications. For given fixed initial conditions, the Laplace transform technique is applied and semi-analytical solutions are proposed by Didierjean et al. (2004) and Moridis (1999).

For a through-diffusion system, boundary and initial conditions are as follows:

$$C(x = 0, t = 0) = C_0, \text{ (initial conditions in the upstream reservoir)}$$
$$(4)$$

$$C(x = L, t = 0) = 0, \text{ (initial conditions in the downstream reservoir)}$$
$$(5)$$

$$C(x = 0, t > 0) = C_u(t), \text{ (upstream boundary conditions for } t > 0)$$
$$(6)$$

$$C(x = L, t > 0) = C_d(t), \text{ (downstream boundary conditions for } t > 0)$$
$$(7)$$

Here, through-diffusion results were analyzed by a least-square fitting of the model to the experimental data of the cumulative activity in the downstream reservoir and the residual activity in the upstream reservoir.

For the in-diffusion system, boundary and initial conditions are as follows:

$$C(x = 0, t = 0) = C0, \text{ (initial conditions in the upstream reservoir)}$$
$$(8)$$

$$C(x = L, t = 0) = 0, \text{ (initial conditions in the solid)} \quad (9)$$

$$C(x = 0, t > 0) = Cu(t), \text{ (upstream boundary conditions for } t > 0)$$
$$(10)$$

Here, in-diffusion results were analyzed by a least-square fitting of the model to the experimental data of the residual activity in the upstream reservoir and the diffusion profile in the solid.

Lastly, the uncertainties on experimental data were estimated by propagation of analytical error variances (σ_{V1}^2, σ_{V2}^2, etc …) following the Gaussian error propagation law. The adopted approaches used for determining the uncertainties on experimental data are described in Savoye et al. (2012) for through-diffusion experiments and in Van Loon and Müller (2014) for in-diffusion experiments.

3. Results and discussion

3.1. Chloride batch sorption experiment

Fig. 1 represents the evolution of the R_d value (expressed in L/kg) as a function of chloride concentration in solution for HCP and concrete suspensions and for different contact times ranging from 7 to 90 days. The R_d value corresponds to the distribution ratio of chloride between the solid and the solution. A high R_d value means a high retention of the species in the solid. In this study, as no attempts were performed to check the sorption reversibility and kinetics did not clearly demonstrate that thermodynamic equilibrium was reached, the term "R_d" is used for the batch sorption experiments, instead of K_d. Fig. 1 clearly reveals the effect of chloride concentration for chloride retention in cement-based materials. For the HCP sample, the higher the chloride concentration,
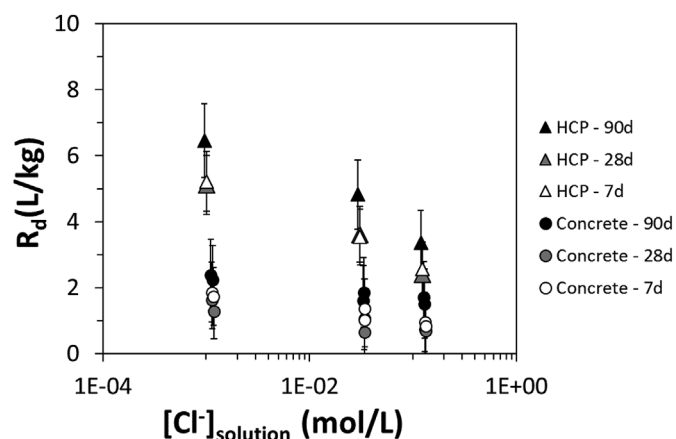

Fig. 1. Cl-36 distribution ratio, R_d evolution onto HCP and concrete as a function of sorption contact time and chloride concentration in solution.

the lower the R_d value, suggesting a lower retardation onto diffusion for high chloride initial concentration. This result is consistent with literature results (e.g. Ochs et al. (2016)). Due to the associated uncertainties, it could be difficult to conclude regarding the effect of contact time on the R_d values. One can assume that the R_d value tends to increase with time, suggesting a slow sorption process, such as solid-solution formation. For the concrete sample, the R_d values can be considered constant in the range of investigated concentrations and contact time. A classic dilution effect is observed onto R_d value from HCP to concrete, since chloride does not have affinities for calcareous aggregates and HCP represents roughly less than 40% of the concrete material. Based onto these sorption results, an initial LiCl concentration of 30 mM has been chosen to perform diffusion experiments. For higher chloride concentration, one can expect the formation of Friedel salt ($3CaO.Al_2O_3.CaCl_2.10H_2O$) or Kuzel salt ($3CaOAl_2O_3(CaSO_4)_{0.5}(CaCl_2)_{0.5}:11H_2O$), which participates to the chloride binding in cementitious media (Ochs et al., 2016). According to the batch sorption experiments, the value of 30 mM of LiCl added to Cl-36 diffusion experiment for HCP and concrete samples seems to be a good compromise between having a low sorption capability and thus, a low retardation onto chlorine diffusion and avoiding any chloride-binding-phase precipitation.

3.2. HTO and Cl-36 through-diffusion experiment

HTO and Cl-36 activities measured and modelled into the upstream and the downstream compartments were presented in Fig. 2. Note that, the x-axis origin corresponds to the moment when HTO was injected in the upstream compartment. Regarding HTO, its decrease of activity in the upstream compartment is similar to the calculated activity if taking into account only the radioactive decay of H-3, which can be interpreted with a low diffusivity for HTO in this material. Data show a significant cumulative activity in the downstream compartment after more than 200 days for HTO. The diffusive steady state for HTO is yet not reached after 369 days of diffusion, that is why *I-Mode* curves in Fig. 2 are represented in dash line. However, based onto the first 369 days of diffusion, a first estimation of HTO diffusion parameters based onto upstream and downstream compartment data can be performed and it gives for HTO diffusion {$D_e = 3.10^{-13} \text{ m}^2/\text{s}$ and $\alpha = 0.11$}. Effective diffusion parameter value obtained for the present study is consistent with already published data for CEM-V-cement based material (see e.g. Richet et al. (2004) and Bejaoui and Bary (2007)). Based onto these diffusion parameters values, some 5.5 years would be necessary to achieve the steady state for HTO. Tits et al. (2003) obtained a K_d value of (0.8 ± 0.1) L/kg for HTO in a CEM I HCP sample with W/C = 1.2. Ochs et al. (2016) selected a K_d value of 0 L/kg as the best
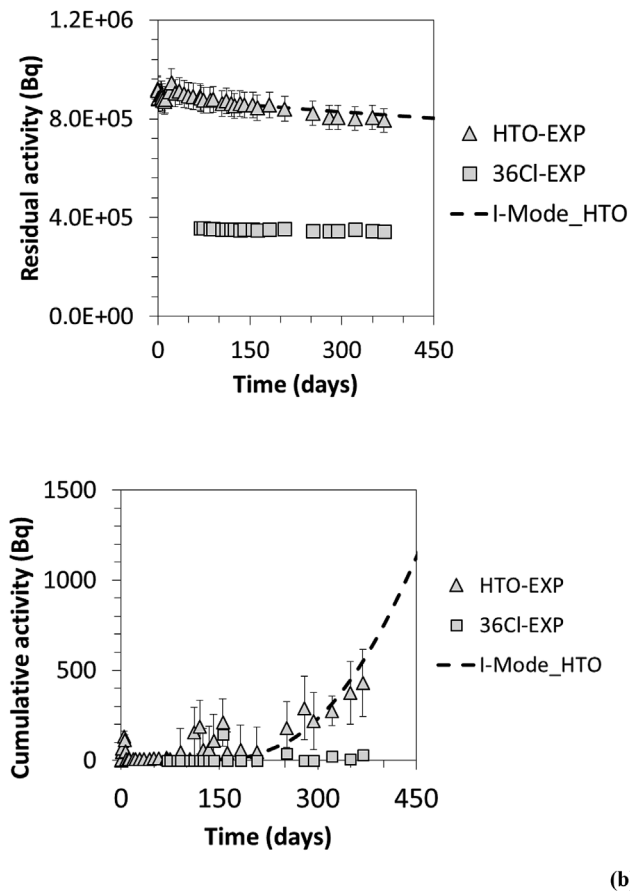
(a)

(b)

Fig. 2. HTO and Cl-36 activities in the upstream compartment (a) and in the downstream compartment (b) measured in a classical through-diffusion set-up.

estimate over all degradation range of the cement paste. In this work, some attempts were performed to measure the HTO retention in the CEM V/A concrete. No significant R_d value was obtained. Based onto Eq. (3) and considering 0 L/kg for HTO sorption, the diffusion-accessible porosity, ω, of the investigate CEM V/A concrete sample can be directly calculated from experimental HTO diffusion parameters and is equal to 0.11.

Regarding Cl-36 diffusion and taking into account experimental uncertainties, no significant reduction of the initial tracer activity was measured in the upstream compartment during the diffusion experiment. That means that the decrease Cl-36 activity during this period is

less than 5% of the introduced Cl-36 activity. Such a behaviour can be explained by i) the high half-life period of Cl-36 inducing a low radioactive decay, ii) the low R_d value obtained for chloride and iii) a lower diffusivity compared to the one calculated for HTO. Accordingly, no activity was quantitatively detected in the downstream compartment. That reveals a very low diffusion process of chloride as already observed in comparable cement-based materials (*Cf.* Richet et al. (2004)). After 369 days testing, data do not allow an estimation of the diffusion parameters (D_e and α) for Cl-36 in a concrete sample, so that no *I-Mode* curve is presented for Cl-36 in Fig. 2.

3.3. Digital autoradiography calibration for Cl-36-activity measurement

Two of the nine prepared standards have been dedicated to check the homogeneity of Cl-36 activity distribution in the solid in order to be able to choose which surface is the most representative for the calibration. Results are presented in Fig. 3 and Fig. 4. Fig. 3a corresponds to the picture of top-surface of the Standard A and the resulting Cl-36 profile distribution of the Standard A after grinding from the top-surface to the core sample is presenting in Fig. 3b. Fig. 4a and b represent similar characterisations for the bottom-surface of the Standard-B. As shown in Fig. 3b, grindings from the top surface (with high roughness) of the Standard-A reveals that the Cl-36 activities measured in the first millimeter of this sample are not homogenous, whereas Fig. 4b reveals that grindings from the bottom smooth surface of the Standard-B provides a homogeneous Cl-36 profile. Moreover, including the uncertainties on the experimental data, measured-Cl-36 activity after grinding from the bottom surface was consistent with the calculated one. These results were confirmed by investigating by DA technique the top and bottom surfaces of the Standard-C prepared with 1190 Bq/g of Cl-36 (Fig. 5). Fig. 5a shows that the bottom surface of the Standard-C has a homogenous distribution of Cl-36-emmitter, characterized by a full filled surface in black colour in the raw DA image, while Fig. 5b clearly highlights heterogeneities on its top surface, characterized by different shade of grey on the raw DA image.

After mixing the cement powder with water, the cement paste was directly casted into closed plastic mould. As usually observed during the first hours of cure, some water laid at the top surface of the disc indicating some settlement process. After settling, the standard is not homogeneous in terms of porosity, cement phase content and saturation/hydration. On can expect that chloride will follow the water by diffusion though the porosity to reach some calcium silicate phases as potential sorbent phase. That is a possible explanation of the observed repartition of Cl-36.

For DA calibration, we did choose to expose only the bottom-surface of the standards. A good linearity (correlation coefficient, $R^2 > 0.99$)
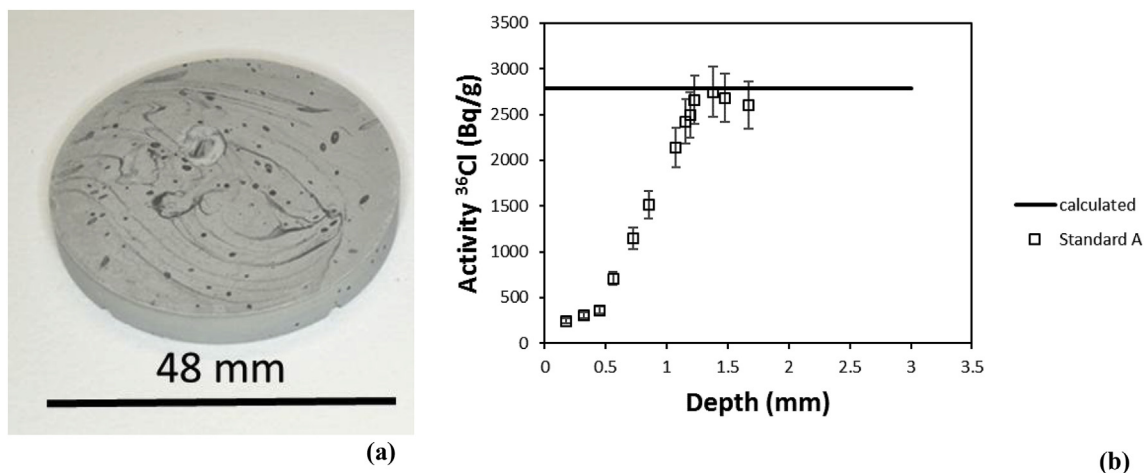

(a)

(b)

Fig. 3. Standard-A top-surface image before grinding (a) and corresponding Cl-36 activity profile of the 2800 Bq/g – Standard-A (b).
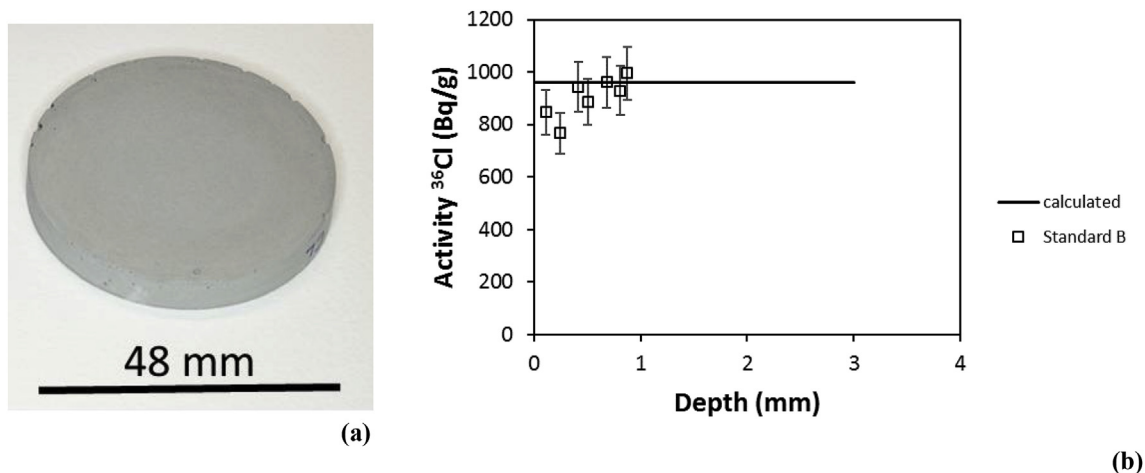
Fig. 4. Standard-B bottom-surface image before grinding (a) and corresponding Cl-36 activity profile of the 960 Bq/g –Standard-B (b).
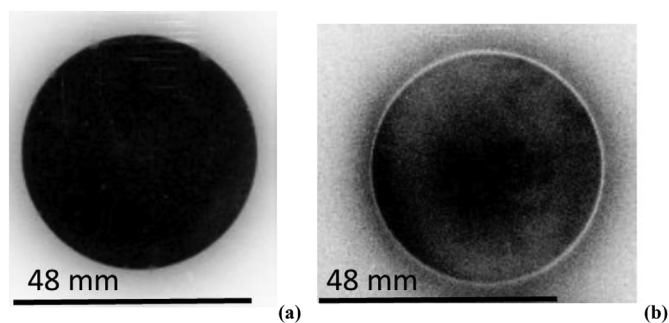

Fig. 5. Raw DA image in black and white shade obtained after 3 days of exposure for the Standard-C containing 1190 Bq/g of Cl-36: bottom-surface (a) and top-surface (b).
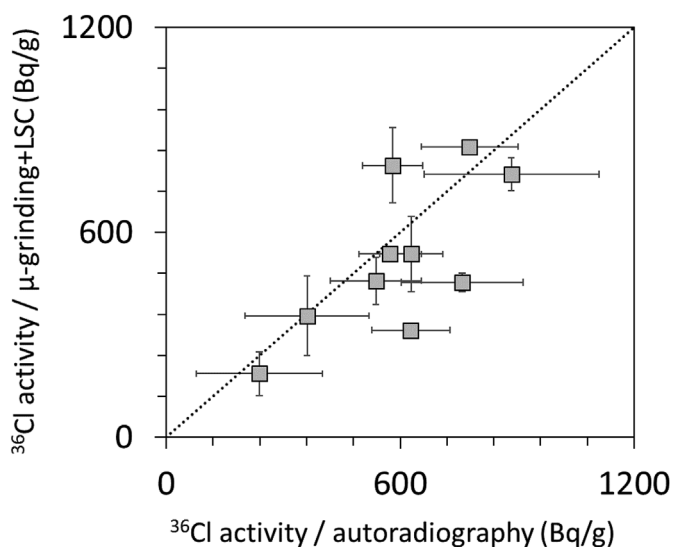

Fig. 6. DA calibration curves using seven Cl-36-HCP standard and two DA screens.

Fig. 7. Comparison of Cl-36 activity measured by digital autoradiography and by liquid scintillation counting onto the same step-by-step grinded HCP sample and after 50 days of Cl-36–in-diffusion experiment.

Fig. 8. HTO and Cl-36 activities measured in the upstream compartment of the in-diffusion set-up of the concrete sample.

is then obtained between results obtained by DA measurements in DLU/mm^2/days and calculated activity in the Cl-36 standard HCP in Bq/g. Several calibrations using the seven Cl-36-HCP-standards have been performed using different DA screens and a reproducible slope from one exposure to the other has been found, independently on the calibration range and on the DA screen used (Fig. 6). Based onto this result, the DA technique can be used for cement-based samples as a quantitative characterization.

Finally, Fig. 7 represents the relationship between Cl-36 activity measurements performed i) by quantitative DA characterization and ii) by LSC after grinding the HCP sample as aforementioned in contact
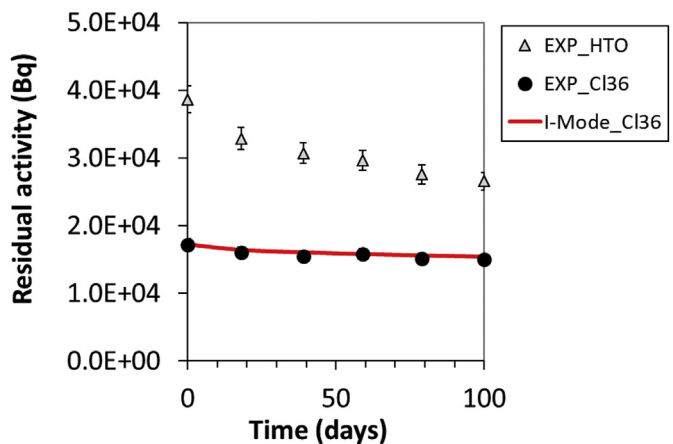
with a Cl-36 solution during 50 days (*Cf.* § **2.7** for HCP in-diffusion preparation details). The quantitative DA characterization gives high uncertainty (up to 30%) compared to the one calculated for the
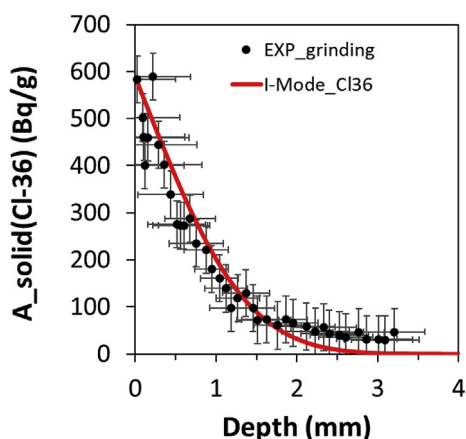
Fig. 9. Comparison between experimental and modelled Cl-36 profiles obtained by using the classical procedure (μ-grinding + liquid scintillation counting).

grinding procedure. This is attributed to the quality of the HCP surface after each grinding leading to an imperfect contact with the DA screen. By way of comparison, a line with unit slope is drawn in the graph of Fig. 7 to illustrate that both Cl-36 activities measurements are each other consistent.

The correlation is considered sufficient between both techniques leads to consider the DA method as a complementary non-destructive tool to localize and quantify Cl-36 activity at the surface of a cement-based sample.

3.4. Cl-36 short time in-diffusion experiment for a concrete sample

During 100 days, the solution in contact with the concrete sample was sampled for determination of the HTO/Cl-36 activities by LSC in order to quantify the radionuclide activity loss and therefore the activity diffused into the solid (Fig. 8). As observed for the through-diffusion experiment, presented in Fig. 2, HTO activity decrease in the upstream compartment is more pronounced that the one for Cl-36. As expected, the evolution of HTO and Cl-36 activities for in-diffusion experiment confirms what observed in the through-diffusion experiment: chloride diffusivity is lower than HTO diffusivity in this concrete. No estimation of HTO diffusion parameters can be done only based onto

upstream compartment data. However, the Cl-36 activity evolution is taken into account for Cl-36 activity profile interpretation.

After 100 days of diffusion, the concrete sample was air-dried and cut in two pieces for the two different Cl-36 profile determinations.

For the first half of the sample, the experimental profile is obtained by using the routine procedure for Cl-36 profile determination i.e. step-by-step micro-grindings, concrete-powder leaching and Cl-36 activity determination by LSC is given in Fig. 9. Using the I-Mode tool and based onto the evolution of Cl-36 activity in solution and the Cl-36 profile, the following diffusion parameters have been modelled from data best fit (series "I-Mode_Cl36" in Fig. 8 and in Fig. 9):

- *Method 1*: μ-grinding + Cl-36 LSC: $\{D_e = 7.1\ 10^{-14}\ \text{m}^2/\text{s};\ \alpha = 1.2\}$.

In Fig. 10, the DA image is compared to the visible image of the surface of the second half of the concrete sample previously in contact for 100 days with HTO and Cl-36. One can notice that it was not possible to investigate H-3 localization and quantification with the technique due to i) its lower maximum energy of the beta emission, E_{max} compared to the one of Cl-36 and ii) the fact that the concrete sample was air-dried before DA exposure. Consequently, in Fig. 10, only Cl-36 was localized on the surface of the concrete sample with a resolution of 150 dpi in the DA image. One can observe that the majority of the surface is in the range of green-yellow color, corresponding to an intermediate level of activity (around 500 Bq/g). This result could be interpreted by the lack of a preferential Cl-36 accumulation into a specific cement hydrate phase. However, some red colored areas (hot spots) seem to be randomly distributed on the surface of the sample, which could be linked to surface precipitation of Cl-36-containing salt after the drying process. Additionally, the DA image of Fig. 10 confirms by direct observation the lack of affinity of Cl-36 for the calcareous aggregates. The DA image in Fig. 11a is compared to the visible image of the profile of the concrete sample after 100 days of diffusion. Some hot spots can be observed and apparently, there are not clearly linked to a specific zone of the sample. It could be induced by an accumulation of Cl-36 solution in a small bubble. This hypothesis is quite difficult to assess since only visual-eye-check has been possible with this radioactive sample. The surface exposed to the DA screen corresponds to a square close to $(3 \times 3)\ \text{cm}^2$. One of the DA image post-treatment consists in converting the scanned image into a numerical matrix with a total of 1452*749 pixels. The sum of intensity coming from a vertical
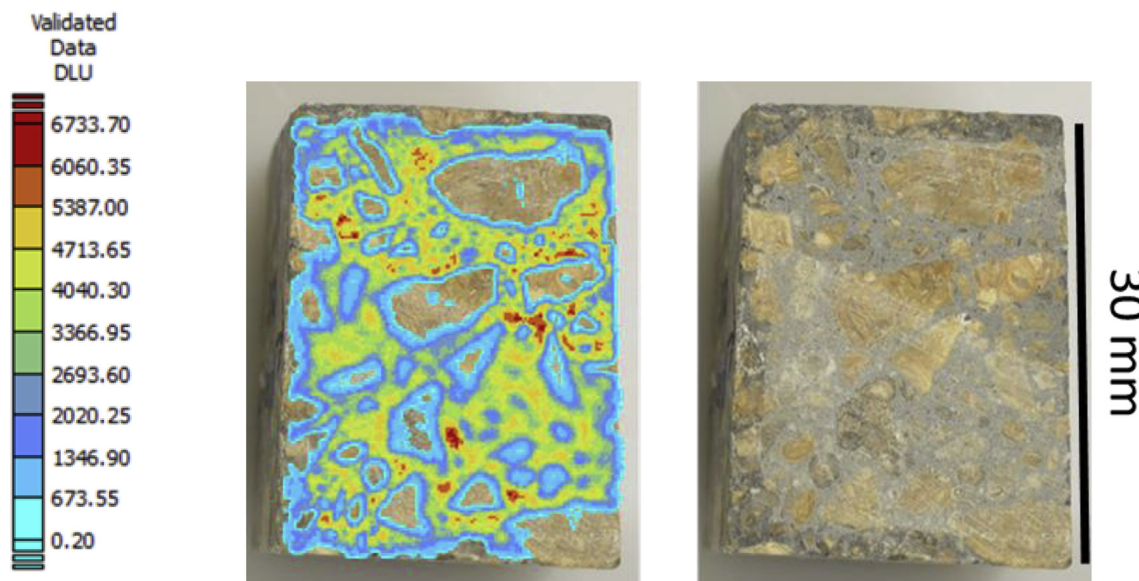

Fig. 10. Comparison between digital autoradiography image and concrete sample picture: results obtained after 3 days of exposure of the concrete surface previously in contact with the Cl-36 solution during 100 days.
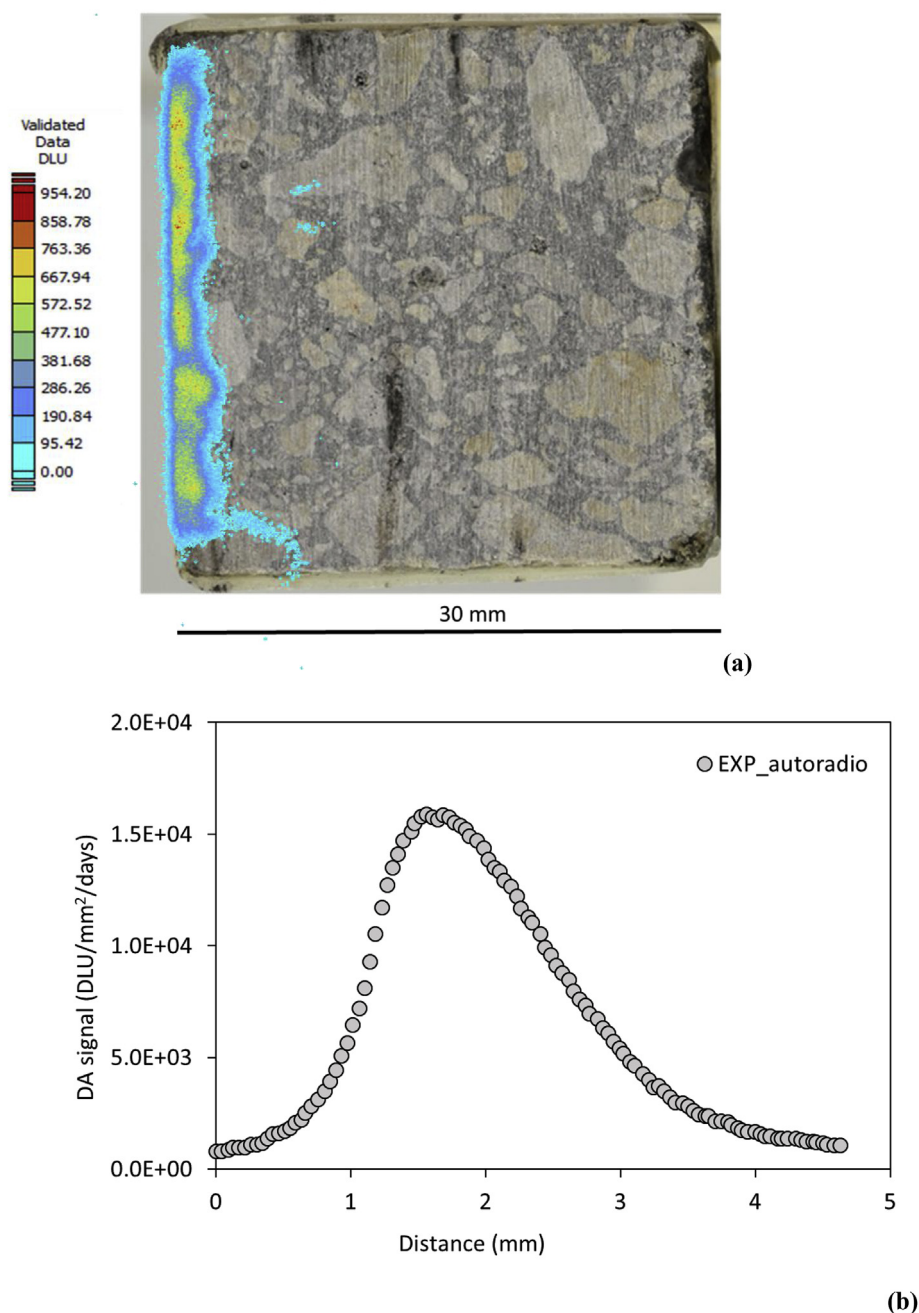
Fig. 11. Comparison between digital autoradiography image and concrete sample picture of the profile (a). Raw 600 dpi resolution Cl-36 profile obtained with digital autography after 3 days of exposure of the concrete sample previously in contact with the Cl-36 solution during 100 days (b).

line of pixels is calculated with a resolution of 600 dpi corresponding to collect data each 0.042 mm in horizontal direction. The distribution of Cl-36 activity expressed in DLU/mm²/days as a function of scanned distance is given in Fig. 11b. The maximum intensity value can be observed at a distance between the 38th and 39th pixel i.e. between 1.596 mm and 1.638 mm after conversion. The maximum intensity corresponds, after applying the calibration curve, to an activity of 450 Bq/g, which is consistent with the activity of 500 Bq/g observed at the surface of the sample (Fig. 10). The first part of the distribution of Cl-36 could be interpreted as an edge artefact because of a non-ideal contact between the sample and the DA screen. An off-set until the 39th pixel (i.e. 1.596 mm) was applied to correct the raw data and to be able to link the distance to the concrete sample diffusion depth. Finally, based onto the calibration curve acquired in parallel by exposing in similar

conditions the dedicated prepared Cl-36 HCP standards, the DA signal (in DLU/mm²/days) is converted in Bq/g as a function of depth, which represents de Cl-36 diffusion profile. The uncertainties were estimated regarding standard deviation calculated of each column of DA values. Based onto this experimental profile and using the I-Mode tool, the following diffusion parameters have been modelled from DA experimental data best fit (series "I-Mode_autoradio" in Fig. 12):

- *Method 2*: Cl-36 direct determination by DA non-destructive technique: $\{D_e = 1.0\ 10^{-13}\ \text{m}^2/\text{s}; \alpha = 1.0\}$.

The total Cl-36 activity in the solid can be determined from the diffusion experiment and from the model. Taking into account uncertainties, the experimental loss of Cl-36 based onto solution
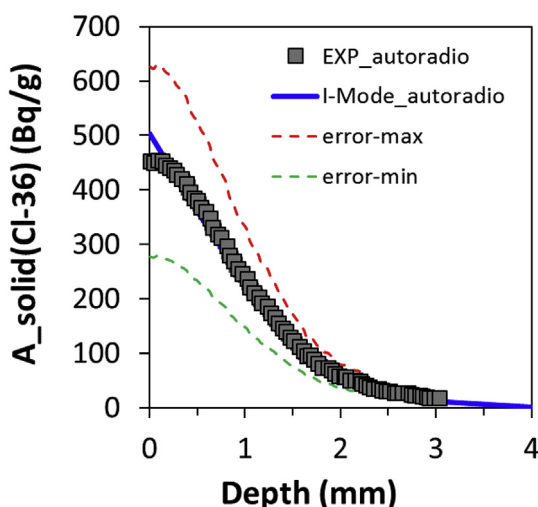
Fig. 12. Comparison between experimental and modelled Cl-36 profiles obtained with digital autoradiography characterizations with 600 dpi resolution.

measurement corresponds to $(2.2 \pm 2.3) \, 10^3$ Bq, which correspond to the activity expected in the solid. Using the grinding measurements, the sum of activities of Cl-36 measured in the solid gives $(1.4 \pm 0.1) \, 10^3$ Bq. Finally, based onto diffusion parameters obtained by method 1 and method 2, the expected activity of Cl-36 in the solid is $1.8 \, 10^3$ Bq and $2.1 \, 10^3$, respectively.

Considering the whole set of data and with respect to uncertainties, both experimental and modelled results are consistent in terms of Cl-36 surface activity, total Cl-36 activity in the solid, profile shape and maximal penetration depth (i.e. less than 3.5 mm after 100 days of diffusion). Diffusion parameters obtained by both methods are very similar and confirm a slower diffusion behaviour of Cl-36 compared to the preliminary one obtained for HTO from the classical through-diffusion experiment (with D_e(HTO) ≈ 3.5 D_e(Cl-36) and α(HTO) ≪ α(Cl-36)).

K_d values can be estimated from α value using Eq. (3) and considering $\rho_{dry} = 2.33 \, \text{g/cm}^3$ and $\omega = 0.11$. For chloride, we obtained a K_d value of 0.5 L/kg and 0.4 L/kg, from the profiles determined by the method 1 and the method 2, respectively. In similar conditions, these K_d values are lower than the distribution ratio, R_d, values obtained on dispersed system in batch sorption experiments, ranging from 0.7 to 1.9 L/kg for $[Cl^-]_{initial} = 30$ mM. Such discrepancy between the dispersed and compact systems is observed for highly-adsorbed-cation in clay-rock system (Altmann et al. (2015)) and can be interpreted by an increase of the reactive surface of the matrices induced by the sample crushing.

4. Conclusion

The digital autoradiography (DA) as a non-destructive technique has been successfully used to localize and quantify Cl-36-labelled radiotracer on the surface of a concrete sample and in the contaminated depth. Results obtained from this method show a good agreement with the classic protocol based onto multi-step-abrasive-surface-peeling procedure. Optimized in-diffusion investigations provided in only 100 days the diffusion parameters of Cl-36 in a low diffusive concrete sample, while a through-diffusion experiment would take at least 5 years. For the first time, a dedicated study has been performed to demonstrate the capability of a well-known technique, such as DA technique to improve in-diffusion experiments protocols. When the classical in-diffusion procedure is lab-time consuming and requires micro-grindings, DA technique appears as a powerful tool associated to a very

reasonable time to determine diffusion parameters of Cl-36 and a useful non-destructive method. However, this optimized in-diffusion approach is not suitable for HTO diffusion parameters determination mainly due to its volatile behaviour. For HTO diffusion, the through-diffusion protocol is still the reference way to determine its diffusion parameters. The optimized in-diffusion approach could present a real advance at least for β-emitter radionuclides interacting with concrete such as C-14 (in the framework of the characterization of organic additive behaviour in concrete, for example) or Ni-63 (as a highly chemical toxic relevant in waste disposal safety management).

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