



Use of quantitative digital autoradiography technique to investigate the Chlorine-36-labelled radiotracer transport in concrete experimental vs. modelling approaches

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FROM RESEARCH TO INDUSTRY



USE OF QUANTITATIVE DIGITAL
AUTORADIOGRAPHY TECHNIQUE TO
INVESTIGATE THE CHLORINE-36-LABELLED
RADIOTRACER TRANSPORT IN CONCRETE:
EXPERIMENTAL vs. MODELLING APPROACH

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S. Savoye, P. Fichet, C. Lim, S. Lefèvre and J. Page

Den-Service for the studies of the radionuclides behaviour
(SECR), CEA, Université Paris-Saclay

BARCELONA, 13TH SEPTEMBER 2017

Context and objectives:

- In the framework of nuclear radwaste disposal or for dismantling issue, necessity to have a robust approach to predict radionuclides (RN) reactive transport into porous media, such as concrete.
- ^{36}Cl ($T_{1/2} = 3.01 \times 10^5$ y) is soluble and mobile in cementitious media → major RN in terms of performance assessment
- Routine methods, through- or in-diffusion experiments are widely used:
 - ➔ To provide accurate transfer parameters of ^{36}Cl (and HTO, as reference) onto specific porous materials: hydrated cement paste (HCP) and concrete
- A second technique to determine RN profile in compact matrices
 - ➔ Localization and quantification of hot spots of radioactivity
 - ➔ Optimization of experimental conditions (time, radioprotection ...)
- **To evaluate benefits of autoradiography technique for diffusion experiments**

- Introduction
- Cementitious sample preparation
- Results obtained:
 - by classical HTO/³⁶Cl migration experiments
 - using lab-made in-diffusion set-up designed for digital autoradiography imaging
- Conclusions and perspectives

SAMPLE PREPARATION BEFORE DIFFUSION EXPERIMENT

T₀

Initial cure



CEM V/A (S-V) 42.5N CE PM-ES-CP1 NF "PMF3" – ROMBAS (Ciments Calcia)

- 1) **Hydrated Cement Paste, HCP:** w:c = 0.40;
 - 2) **Concrete:** w:c = 0.40 + filler + sand + gravel 2/10 + admixture;
- Minimum of **6 months** of cure @ 22°C +100 % RH

Sample characterization

- (1) **HCP + concrete:** crushed and sieved < 200 µm in N₂ glove-box
→ XRD solid characterization
- (2) **HCP:** porewater solution characterization
→ Using high-pressure squeezing technique + IC analyses

Classic cement phases assembly
Portlandite, AFm/AFt; CSH ...

Artificial Cement poreWater, ACW
211 mM K⁺, 77 mM Na⁺, 1.5 mM Ca²⁺,
1.5 mM SO₄²⁻, 1 mM Cl⁻
and pH ~ 13,5

Sample cutting



1 sample of **HCP** with L ~ 3 mm
 ϕ = 50 mm; $\omega(H_2O)$ = 33-35%



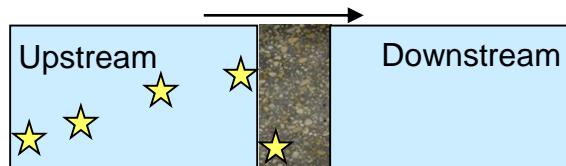
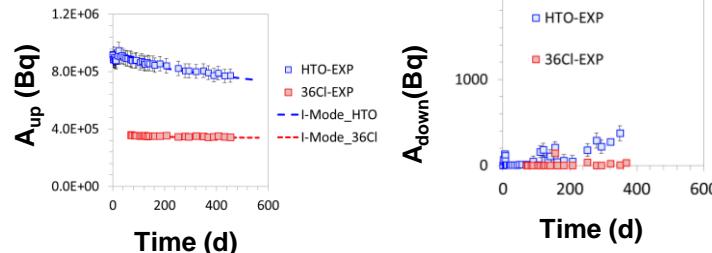
1 sample of **concrete** with L ~ 30 mm
 ϕ ~ 113 mm; $\omega(H_2O)$ = 5-6%

Saturation/hydration in ACW solution

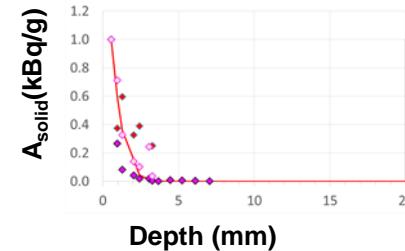
(~ 3-6 m)

**T_{0+1 year}**

HTO AND $^{36}\text{CHLORINE}$ DIFFUSION CLASSICAL PROTOCOL

 $T_{\text{diff}-0}$  $A(t) / \text{HTO}$ 3 – Quantitative diffusion profile determination for ^{36}Cl 

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 $T_{\text{diff}-0 + \sim 1.5 \text{ year}}$

1 - Adding RN cocktail in the upstream compartment

$$A(\text{HTO}) = 5.3 \text{ MBq/L} + A(^{36}\text{Cl}) = 2.1 \text{ MBq/L} \text{ (HCP cell)}$$

$$A(\text{HTO}) = 3.2 \text{ MBq/L} + A(^{36}\text{Cl}) = 1.3 \text{ MBq/L} \text{ (concrete cell)}$$

2- Evolution of A_{up} (and A_{down}) as a function of time

$$V_{\text{up}} = V_{\text{down}} = \text{ACW}$$

$$[\text{LiCl}]_{\text{up}} = 30\text{mM}$$

$$\text{pH} = 13.5$$

$$A_{\text{up}} = \text{variable}$$

$$A_{\text{down}} (^{36}\text{Cl}) = 0 \text{ or } > 0$$

$$A_{\text{down}} (\text{HTO}) > 0$$

 ^3H - ^{36}Cl β liquid scintillation counting (LSC)

Sample grinding

Cementitious powder lixiviation + ^{36}Cl β LSC

4-Diffusion modeling / interpretation

I-Mode simulation tool

I-Mode = Interpretation Model Of Diffusion Experiments

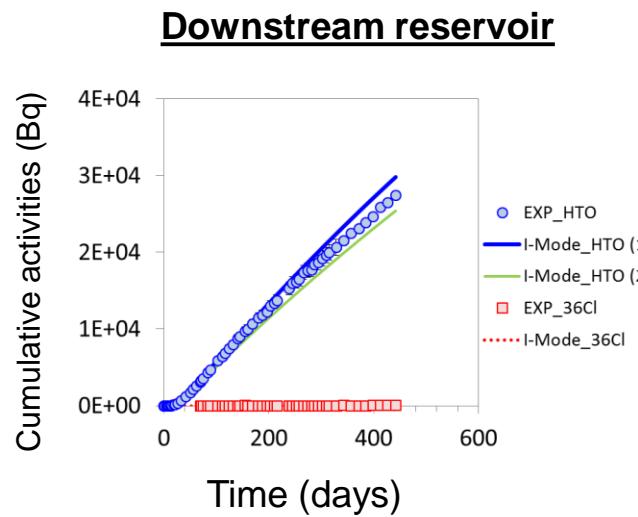
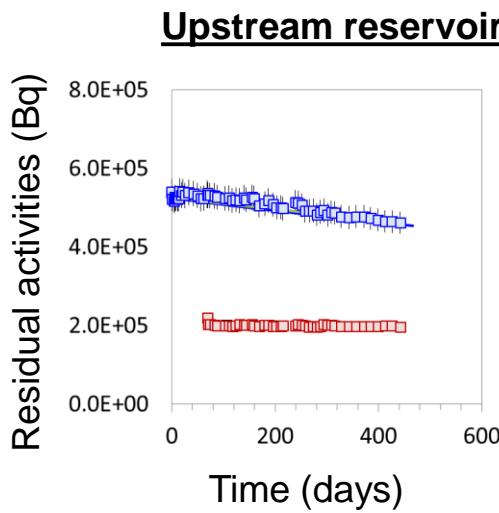
Radwan et al. (2005 & 2006)

Diffusion parameters (ωR and D_e) for HTO and for ^{36}Cl

RESULTS OBTAINED FOR HTO AND ^{36}Cl DIFFUSION THROUGH HCP SAMPLE



Step 2- Evolution of A_{up} (and A_{down}) as a function of time



First estimations of diffusion parameters

$$D_e(\text{HTO}) = 3.0 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(\text{HTO}) = 0.5$$

$$D_e(\text{HTO}) = 2.5 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(\text{HTO}) = 0.3$$

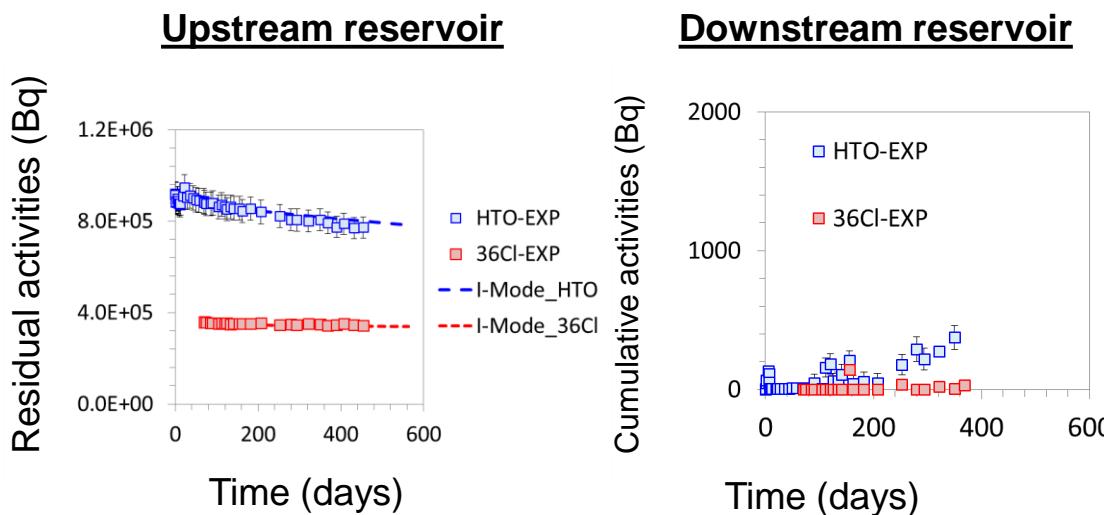
$$D_e(^{36}\text{Cl}) = ?? \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = ??$$

- Confirmation that ^{36}Cl species migrate slower than HTO
 - HTO can be considered as conservative for ^{36}Cl transfer
- Confirmation of the batch ^{36}Cl sorption experiments: high delay onto diffusion
 - Diffusion profile into the solid is needed to constrain parameters fits

RESULTS OBTAINED FOR HTO AND ^{36}Cl DIFFUSION THROUGH CONCRETE SAMPLE



Step 2- Evolution of A_{up} (and A_{down}) as a function of time



First estimations of diffusion parameters

$$D_e(\text{HTO}) = 3.0 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(\text{HTO}) = 0.1$$

$$D_e(^{36}\text{Cl}) = ?? \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = ??$$

- Similar HTO/ ^{36}Cl diffusion behaviour observed for HCP and concrete
- Confirmation that ^{36}Cl species migrate slower than HTO
 - HTO can be considered as conservative for ^{36}Cl transfer
- Confirmation of the batch ^{36}Cl sorption experiments: high delay onto diffusion
 - Diffusion profile into the solid is needed to constrain parameters fits

- « Classical » diffusion experiments need improvement in terms of experimental time

Optimized ^{36}Cl in-diffusion conditions

quantitative

widely used technique

In-lab diffusion set-up

^{36}Cl -sensitive

optimized resolution

mapping

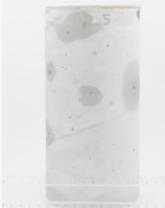
Imaging trace quantities

Digital autoradiography imaging technique

SAMPLE PREPARATION BEFORE AUTORADIOGRAPHY DEDICATED MIGRATION EXPERIMENTS

T₀

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211 mM K⁺, 77 mM Na⁺, 1.5 mM Ca²⁺,
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and pH ~ 13,5

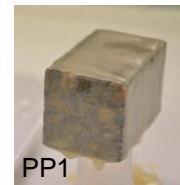
Sample cutting

(3)

2 samples of **HCP** with L₁ ~ 3 mm
L₂ ~ L₃ ~ 35 mm2 samples of **concrete** with L₁ ~ 30 mm
L₂ ~ 50 mm; L₃ ~ 30 mm

Saturation/hydration in ACW solution

(1) Forcing one direction path for diffusion

(2) Contact with V_{mini} ACW solution in N₂-filled closed container**T_{0+7 months}**

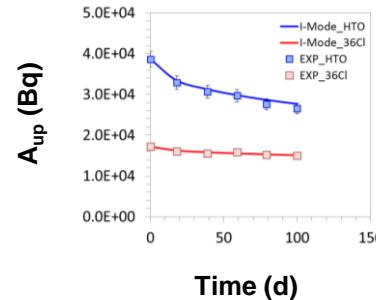
$T_{\text{diff_0}}$

Upstream

**1- Adding RN cocktail in the upstream compartment**

$$A(\text{HTO}) = 2.3 \text{ MBq/L} + A(\text{Cl}^{36}) = 1.2 \text{ MBq/L} \text{ (HCP in-diff cell)}$$

$$A(\text{HTO}) = 3.0 \text{ MBq/L} + A(\text{Cl}^{36}) = 1.4 \text{ MBq/L} \text{ (concrete in-diff cell)}$$

2- Evolution of A_{up} as a function of time $A_{\text{up}}(t) / \text{HTO}$ $A_{\text{up}}(t) / \text{Cl}^{36}$ 

$$\begin{aligned} V_{\text{up}} &= \text{ACW} \\ [\text{LiCl}]_{\text{up}} &= 30 \text{ mM} \\ \text{pH} &> 13 \end{aligned}$$

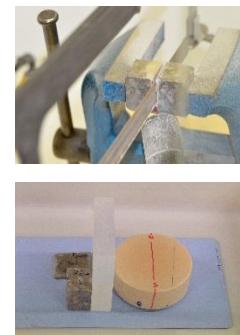
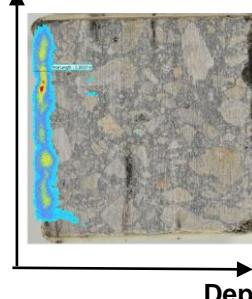
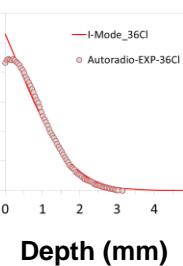
 $A_{\text{up}} = \text{variable}$ ${}^3\text{H} - {}^{36}\text{Cl} \beta$ liquid scintillation counting (LSC)**3 - Quantitative diffusion profile determination for Cl^{36}** **Digital autoradiography**

Image J + Kartotruk software (geovariances)

Signal Intensity (DLU)

 $A_{\text{solid}}(\text{Bq/g})$ **4 - Diffusion modeling / interpretation**

I-Mode simulation tool

I-Mode = Interpretation Model Of Diffusion Experiments

Radwan et al. (2005 & 2006)

Diffusion parameters (ωR and D_e) for Cl^{36} $T_{\text{diff_0} + 150 \text{ days}}$

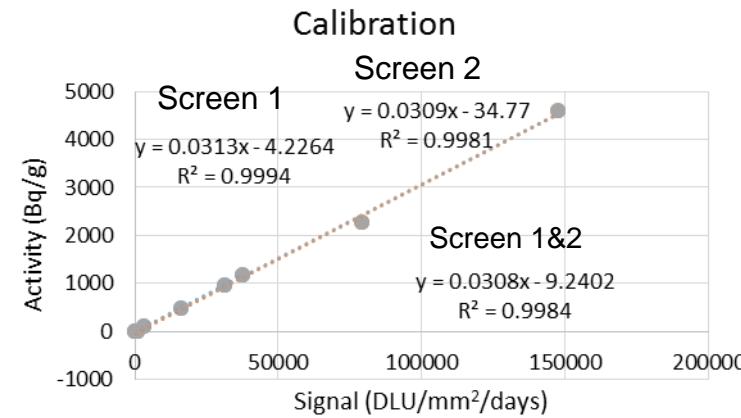
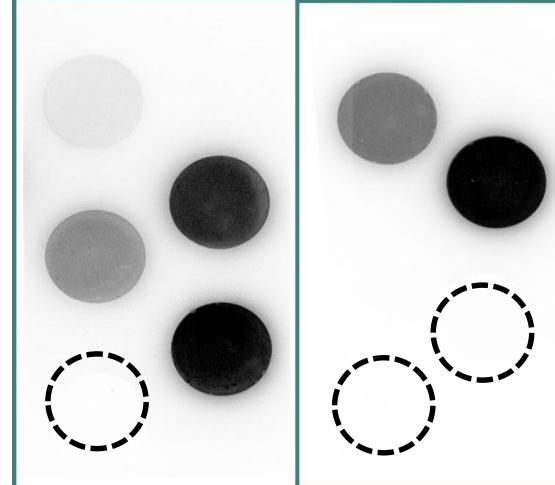
^{36}Cl CALIBRATION USING AUTORADIOGRAPHY

- HCP-ROMBAS standards (w/c: 0.40, $\varnothing = 47$ mm) cured in sealed bags have been prepared with well-known activities of ^{36}Cl
 - From 0 to 4 600 Bq/g

Screen 1 Screen 2

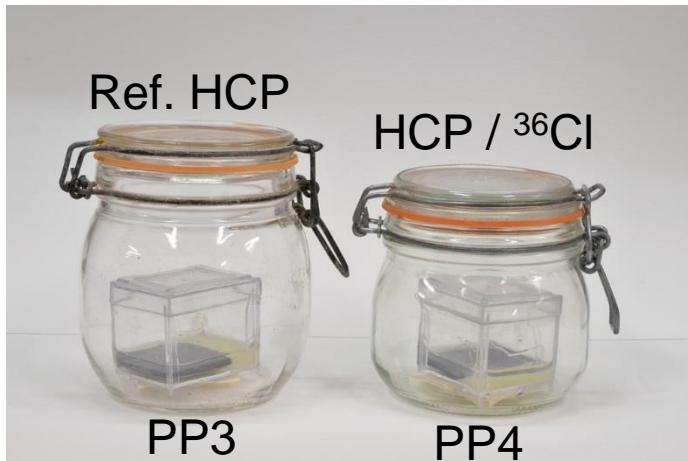


Screen 1 Screen 2



Results obtained after 5 days of exposure

- Linearity of the calibration → autoradiography signal can be converted in Bq/g using HCP standards measurements

**Solution in contact with PP4**

10 mL ACW + 30 mM LiCl

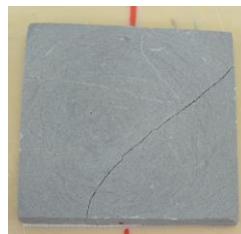
A(HTO) = 2.3 MBq/L

A(³⁶Cl) = 1.2 MBq/L**Diffusion during 50 days**Step by step μ -grinding + autoradiography imaging of selected resulting surface

G00



G01

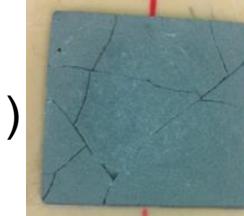


G02

(...)

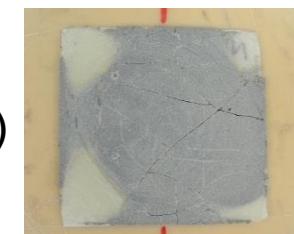


G08

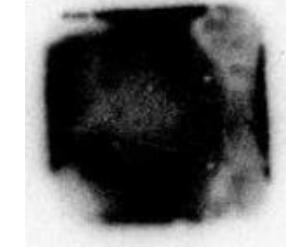
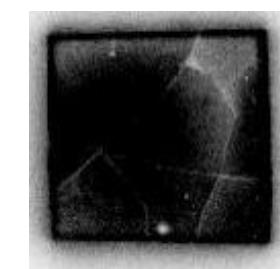
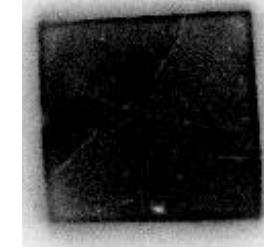
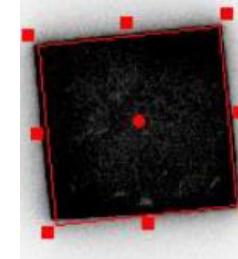


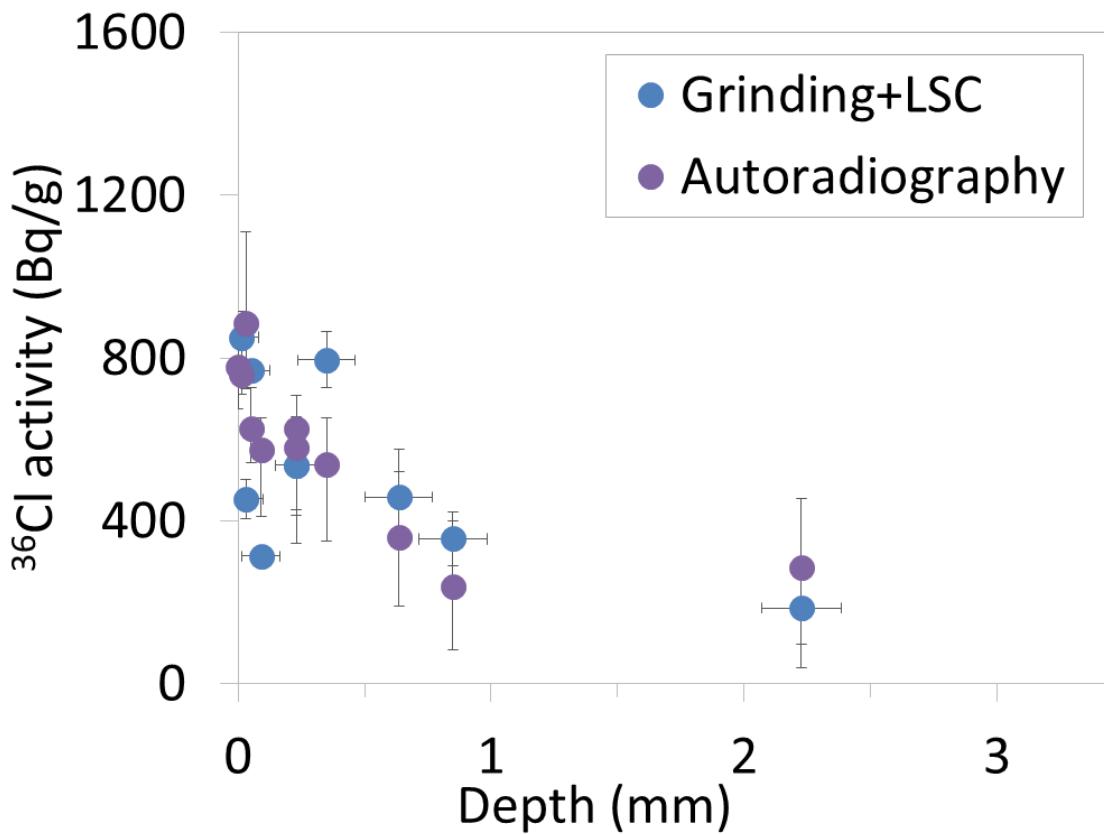
(...)

G15

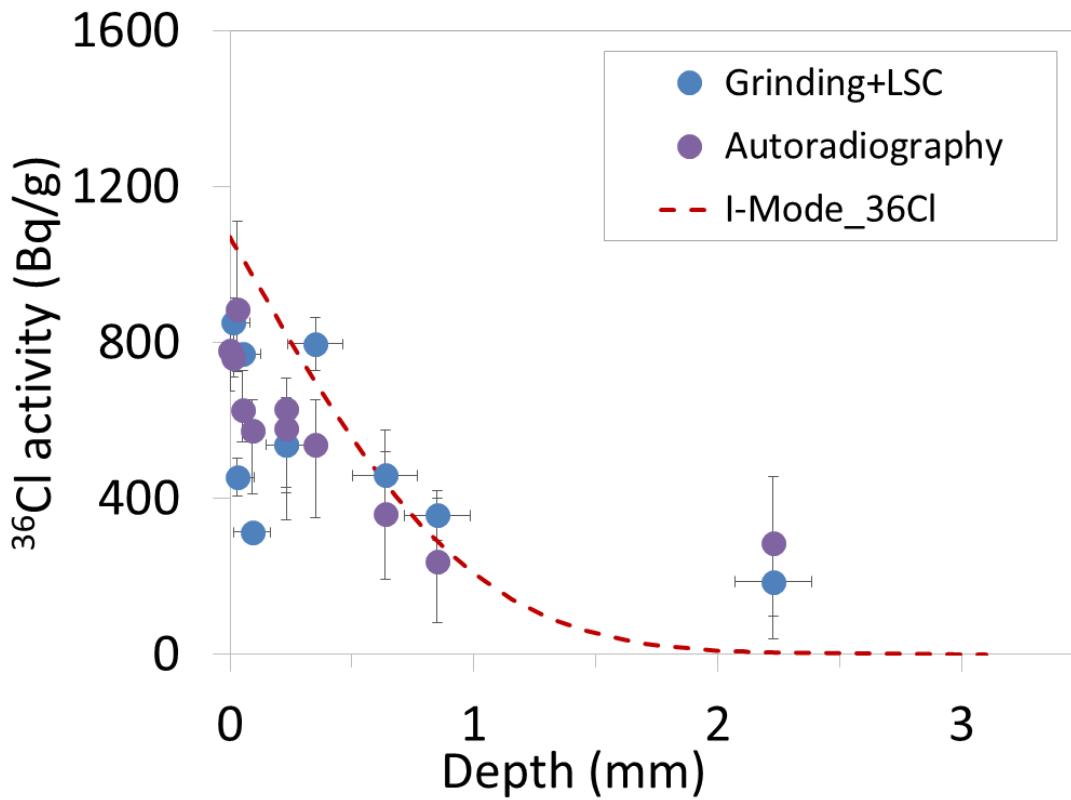


G42



Comparison between μ -grinding and autoradiography

Good agreement between the two experimental ^{36}Cl diffusion profiles

Comparison between μ -grinding and autoradiography

Bonus: estimation of diffusion parameters

$$D_e(^{36}\text{Cl}) = 1.10^{-13} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 1.5$$

Good agreement between the two experimental ^{36}Cl diffusion profiles

WHAT ABOUT THE CONCRETE SAMPLE ? (1/3)

^{36}Cl diffusion profile obtained after 100 days of diffusion in the concrete sample

PP2-1/2 sample dedicated to surface μ -grinding + LSC

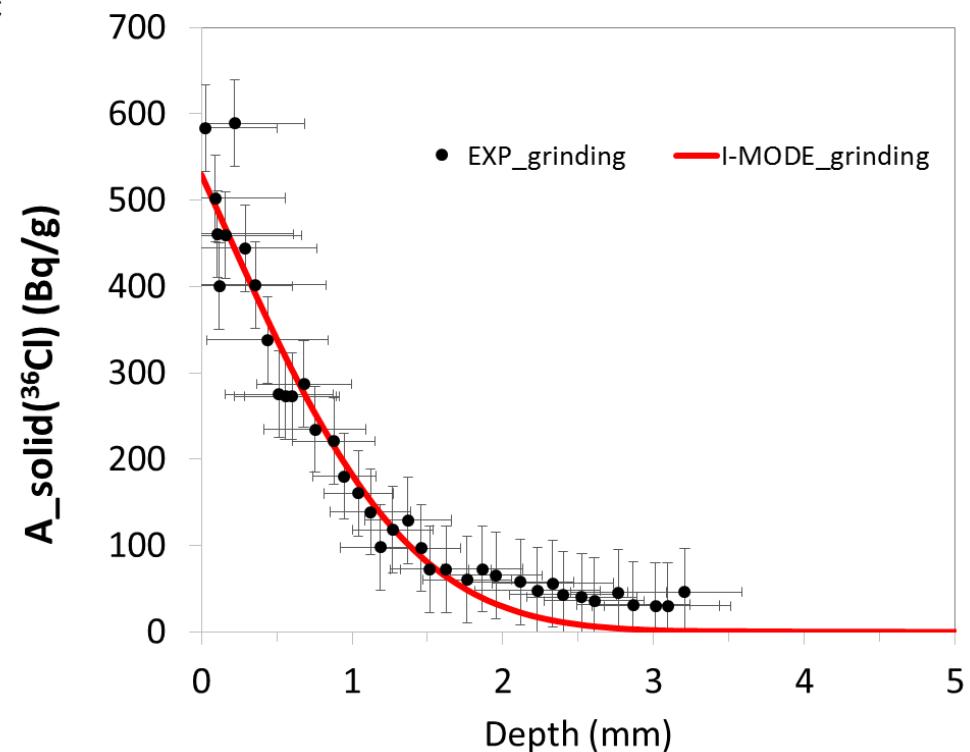


Surface picture of PP2 -1/2 (before μ -grinding)

First estimations of diffusion parameters

$$D_e(^{36}\text{Cl}) = 0.7 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 1.2$$

Diffusion parameter for F44-concrete [1]
 $D_e(^{36}\text{Cl}) = 5.15 \cdot 10^{-14} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 0.9$

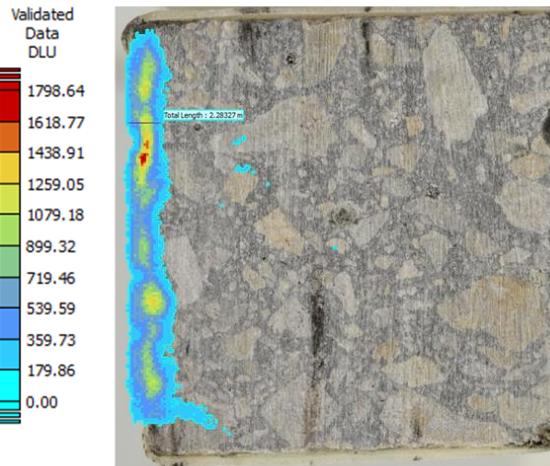


■ Good agreement with ^{36}Cl diffusion parameters obtained in a previous study [1]

WHAT ABOUT THE CONCRETE SAMPLE ? (2/3)

^{36}Cl diffusion profile obtained after 100 days of diffusion in the concrete sample

PP2-2/2 sample dedicated to autoradiography imaging



Profile image after 4 days of exposure

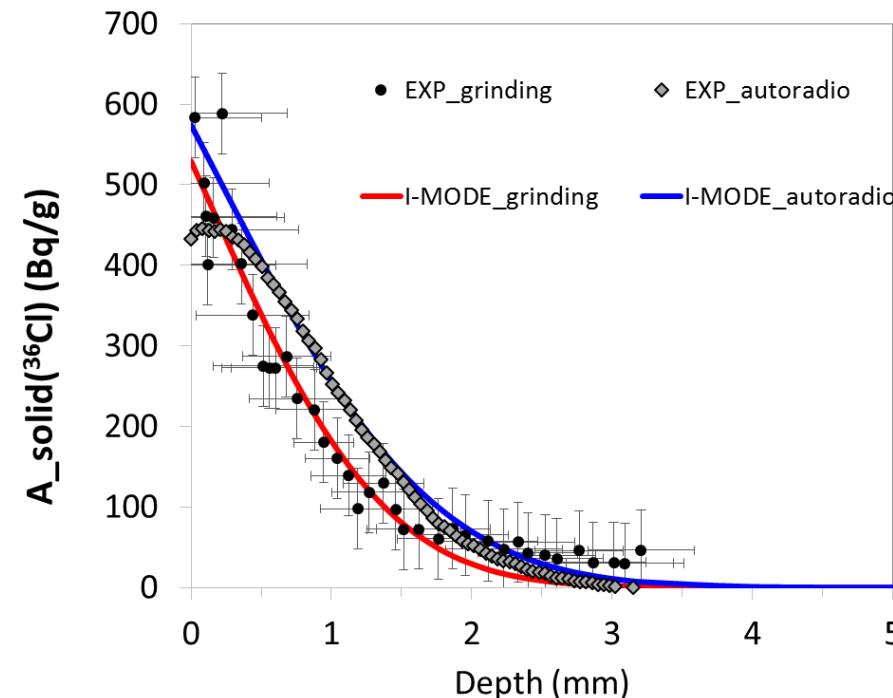
First estimations of diffusion parameters

$$D_e(^{36}\text{Cl}) = 0.7 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 1.2$$

$$D_e(^{36}\text{Cl}) = 1.2 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 1.3$$

Diffusion parameter for F44-concrete [1]

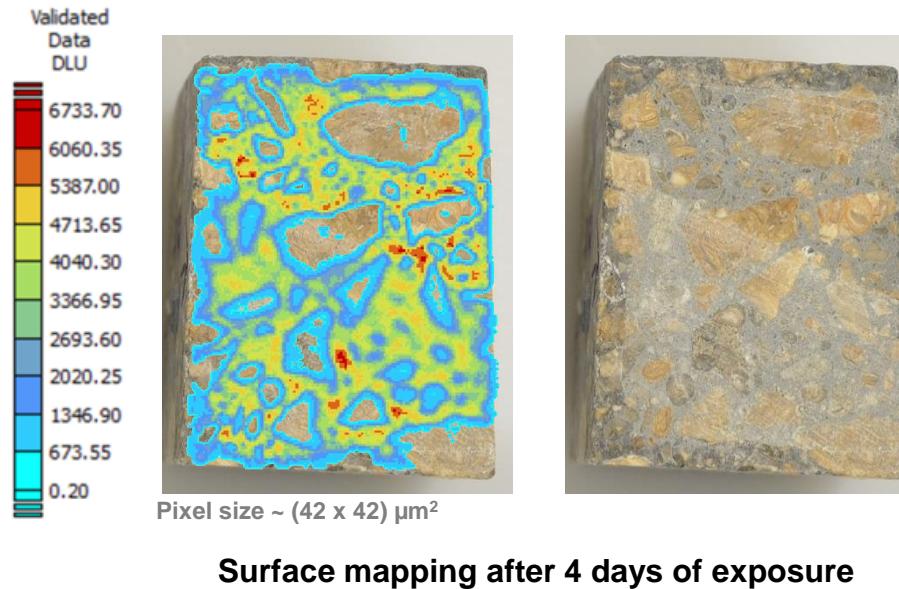
$$D_e(^{36}\text{Cl}) = 5.15 \cdot 10^{-14} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 0.9$$



■ Both experimental ^{36}Cl diffusion profiles are coherent

WHAT ABOUT THE CONCRETE SAMPLE ? (3/3)

^{36}Cl surface mapping obtained after 100 days of diffusion in the concrete sample



- ^{36}Cl repartition is quite homogeneous onto the surface
- No activity is measured at the surface of gravels: confirmation that gravels are non reactive with chlorine

→ Providing accurate transfer parameters of ^{36}Cl (and HTO, as reference) onto specific porous materials: HCP and concrete

For HTO : long-term through-diffusion experiments are necessary to achieve its diffusion parameters

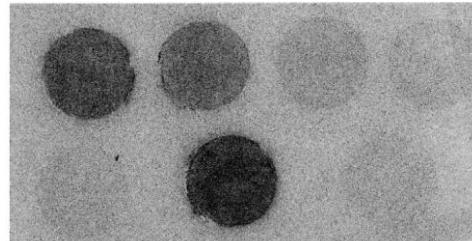
For ^{36}Cl : fast in-diffusion experiments coupled with digital autoradiography imaging and a diffusion modelling tool lead to give a good estimation of diffusion parameters

- consistencies between μ -grinding and autoradiography results
- uncertainties evaluation of diffusion parameters using both protocols is on going
- could be used for rapidly obtaining diffusion profiles → save time → save money!

→ To evaluate benefits of autoradiography technique for diffusion experiments

A fast localization and quantification technique of a β -emitter is a great benefit for migration experiment

Next step : ...



more RNs to be tested
 ^{63}Ni -doped HCP standards
17 days of exposure



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