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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

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

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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 ($T_{1/2} = 3.01 \times 10^5 \text{ y}$) 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

T_0

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 N_2 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 Ca^{2+} ,
1.5 mM SO_4^{2-} , 1mM Cl^-
and pH ~ 13,5

Sample cutting



1 sample of **HCP** with L ~ 3 mm
 $\phi = 50$ mm; $\omega(\text{H}_2\text{O}) = 33\text{-}35\%$



1 sample of **concrete** with L ~ 30 mm
 $\phi \sim 113$ mm; $\omega(\text{H}_2\text{O}) = 5\text{-}6\%$

Saturation/hydration in ACW solution

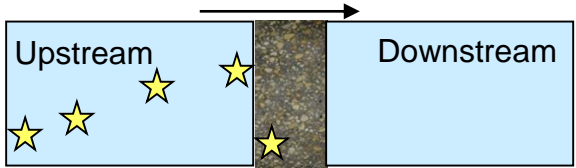
(~ 3-6 m)



$T_{0+1 \text{ year}}$

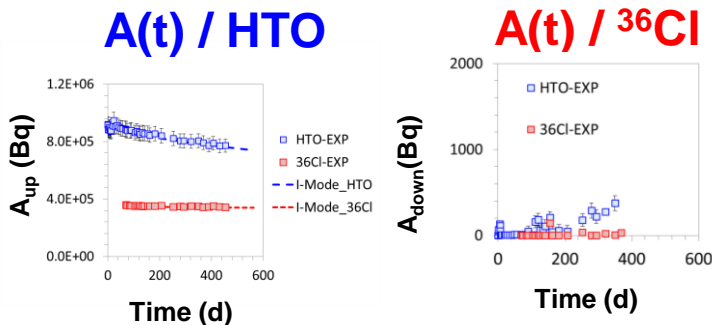
HTO AND ³⁶CHLORINE DIFFUSION CLASSICAL PROTOCOL

T_{diff=0}



1 - Adding RN cocktail in the upstream compartment

A(HTO) = 5.3 MBq/L + A(³⁶Cl) = 2.1 MBq/L (HCP cell)
A(HTO) = 3.2 MBq/L + A(³⁶Cl) = 1.3 MBq/L (concrete cell)



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

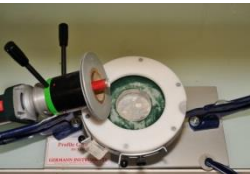
V_{up} = V_{down} = ACW
[LiCl]_{up} = 30mM
pH = 13.5

A_{up} = variable
A_{down} (³⁶Cl) = 0 or > 0
A_{down} (HTO) > 0

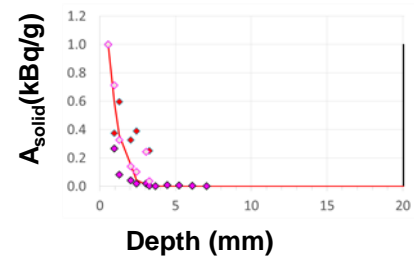
³H -³⁶Cl β liquid scintillation counting (LSC)

3 – Quantitative diffusion profile determination for ³⁶Cl

Sample grinding



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Cementitious powder lixiviation + ³⁶Cl β LSC

4-Diffusion modeling / interpretation

I-Mode simulation tool

I-Mode = Interpretation Model Of Diffusion Experiments
Radwan et al. (2005 & 2006)

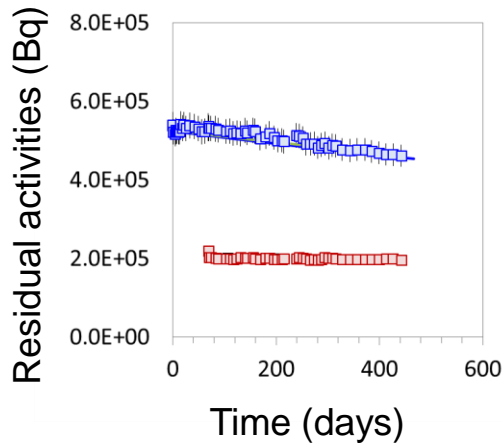
T_{diff=0} + ~1.5 year

Diffusion parameters (ωR and D_e) for HTO and for ³⁶Cl

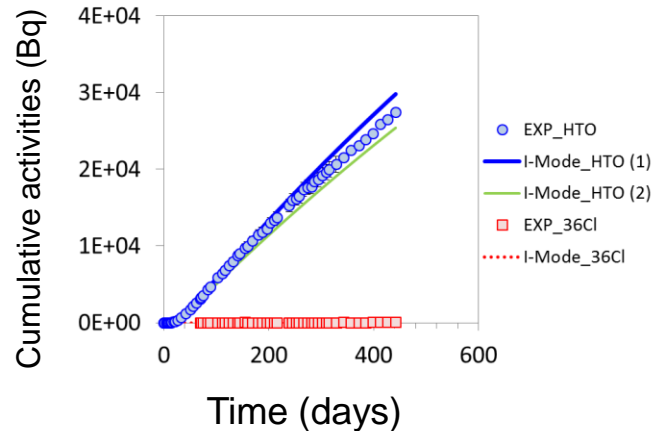


Step 2- Evolution of A_{up} (and A_{down}) as a function of time

Upstream reservoir



Downstream reservoir



First estimations of diffusion parameters

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

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

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

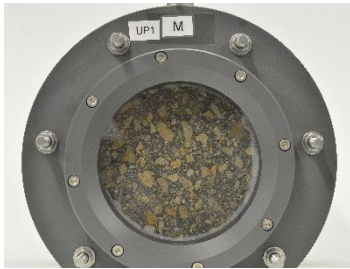
Confirmation that ^{36}Cl species migrate slower than HTO

- HTO can be considered as conservative for ^{36}Cl transfer

Confirmation of the batch ^{36}Cl sorption experiments: high delay onto diffusion

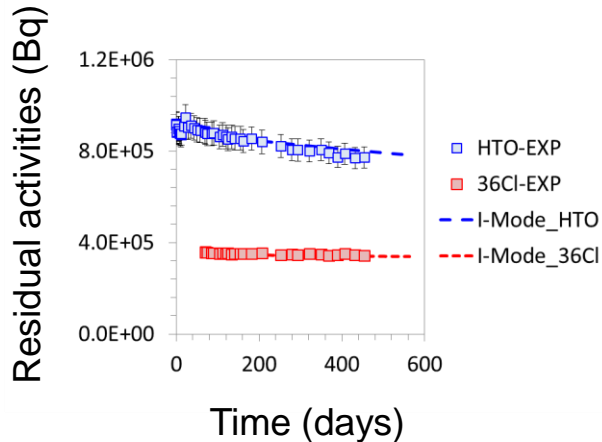
- Diffusion profile into the solid is needed to constrain parameters fits

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

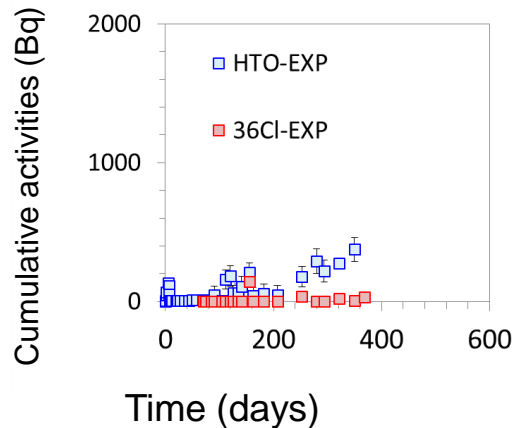


Step 2- Evolution of A_{up} (and A_{down}) as a function of time

Upstream reservoir



Downstream reservoir



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

In-lab diffusion set-up

widely used technique

^{36}Cl -sensitive

optimized resolution

mapping

Imaging trace quantities

Digital autoradiography imaging technique

SAMPLE PREPARATION BEFORE AUTORADIOGRAPHY DEDICATED MIGRATION EXPERIMENTS

T_0

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 N_2 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 Ca^{2+} ,
1.5 mM SO_4^{2-} , 1mM Cl^-
and pH ~ 13,5

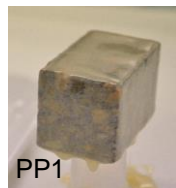
Sample cutting

- (3)  2 samples of **HCP** with $L_1 \sim 3 \text{ mm}$
 $L_2 \sim L_3 \sim 35 \text{ mm}$

-  2 samples of **concrete** with $L_1 \sim 30 \text{ mm}$
 $L_2 \sim 50 \text{ mm}$; $L_3 \sim 30 \text{ mm}$

Saturation/hydration in ACW solution

(1) Forcing one direction path for diffusion



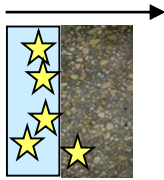
(2) Contact with V_{mini} ACW solution in N_2 -filled closed container



$T_{0+7 \text{ months}}$

T_{diff-0}

Upstream



1- Adding RN cocktail in the upstream compartment

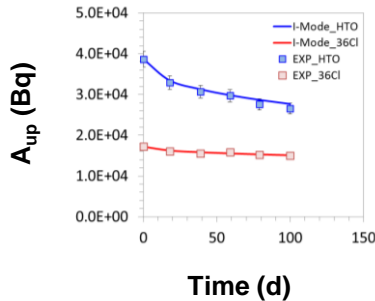
$A(\text{HTO}) = 2.3 \text{ MBq/L} + A(^{36}\text{Cl}) = 1.2 \text{ MBq/L}$ (HCP in-diff cell)

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

2- Evolution of A_{up} as a function of time

$A_{up}(t) / \text{HTO}$

$A_{up}(t) / ^{36}\text{Cl}$

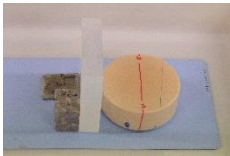


$V_{up} = \text{ACW}$
 $[\text{LiCl}]_{up} = 30 \text{ mM}$
 $\text{pH} > 13$

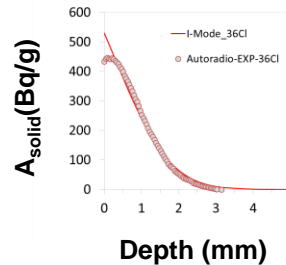
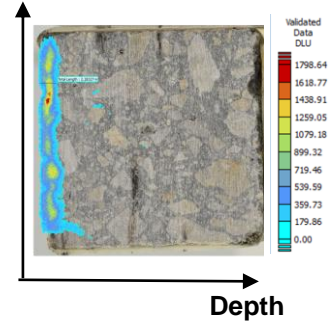
$A_{up} = \text{variable}$

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

3 - Quantitative diffusion profile determination for ^{36}Cl



Signal Intensity (DLU)



Digital autoradiography

Image J + Kartotrak software (geovariances)

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 ^{36}Cl

$T_{diff-0} + 150 \text{ days}$

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

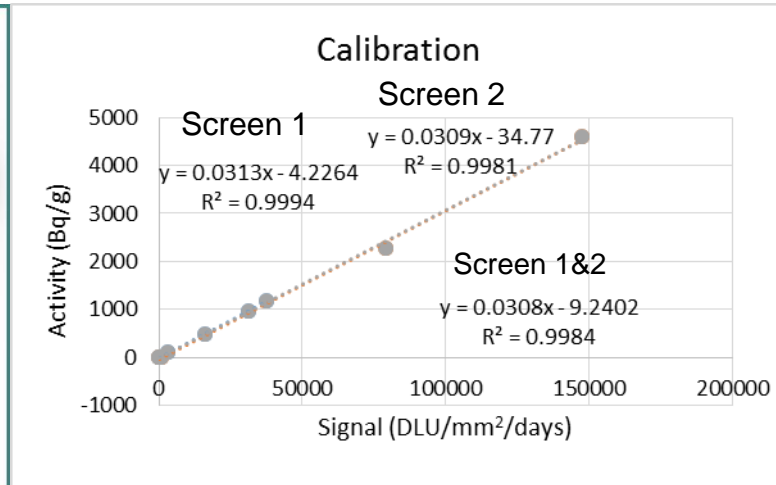
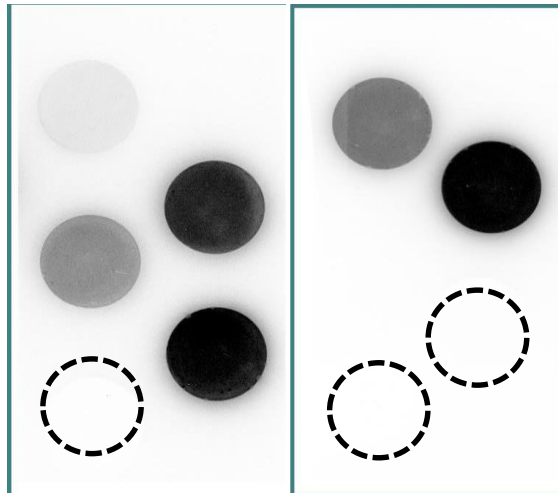
Screen 1

Screen 2



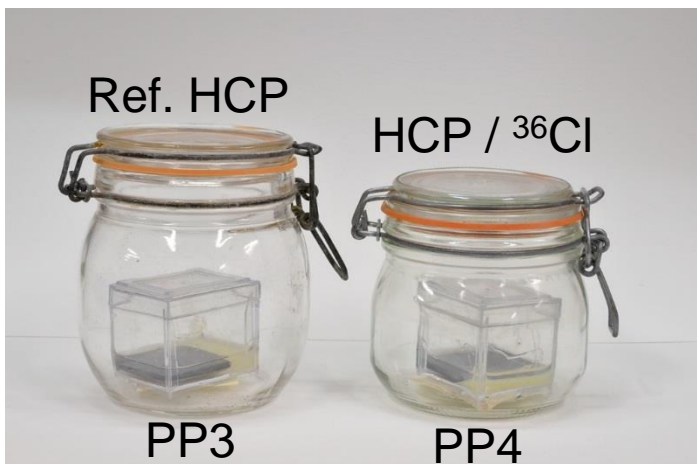
Screen 1

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

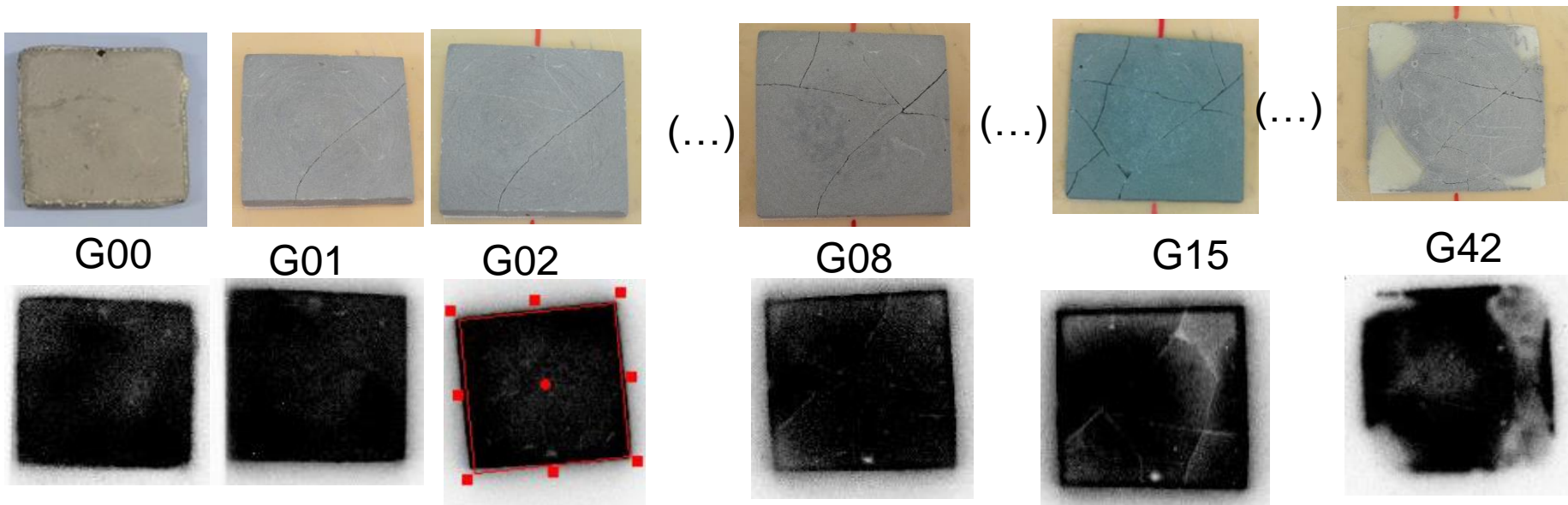
10 mL ACW + 30 mM LiCl

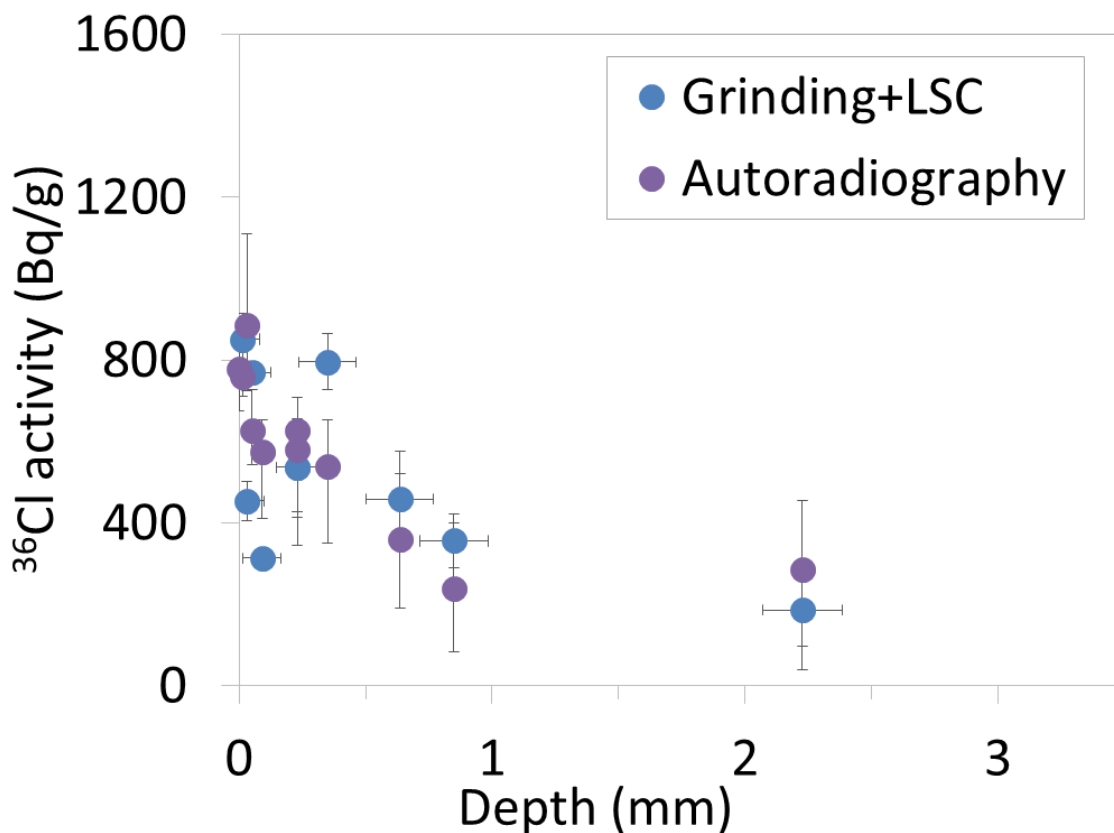
A(HTO) = 2.3 MBq/L

A(³⁶Cl) = 1.2 MBq/L

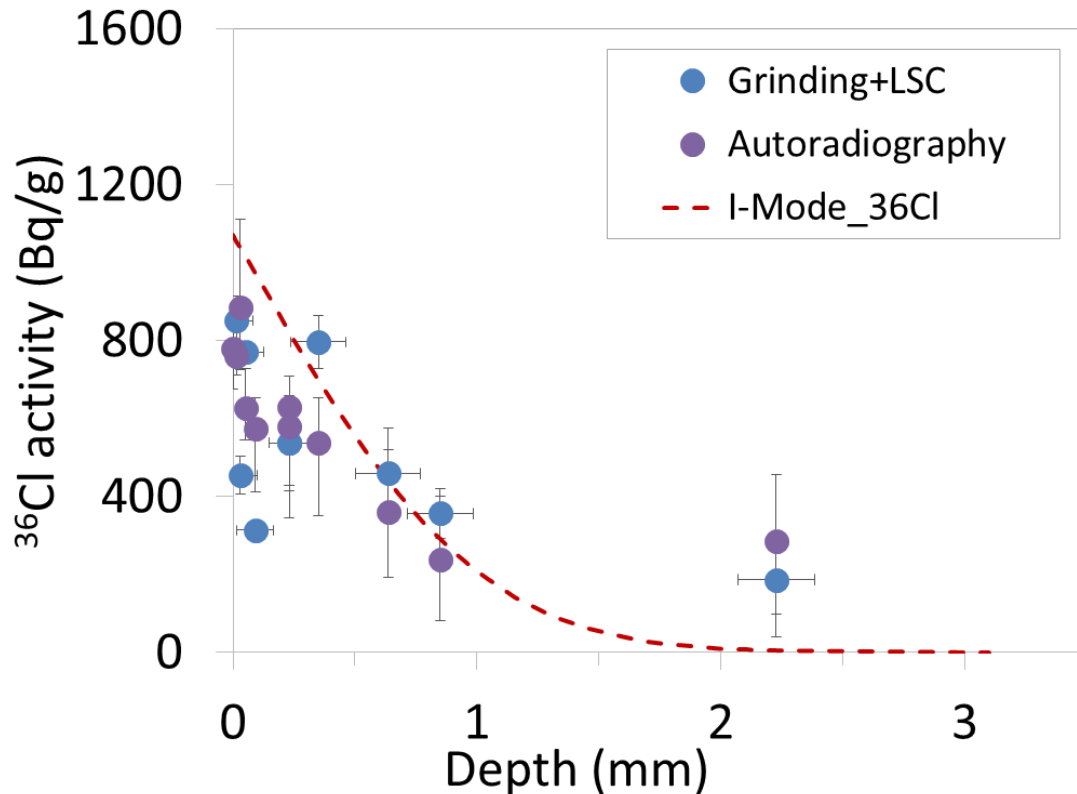
Diffusion during 50 days

Step by step μ -grinding + autoradiography imaging of selected resulting surface



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

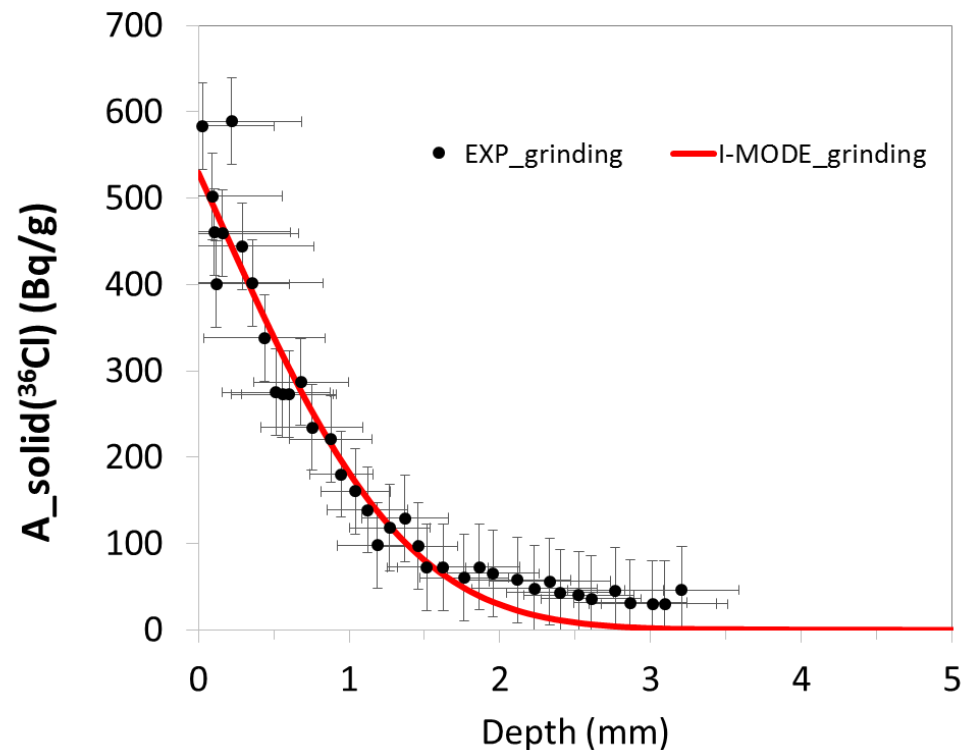
^{36}Cl diffusion profile obtained after 100 days of diffusion in the concrete samplePP2-1/2 sample dedicated to surface μ -grinding + LSCSurface picture of PP2 -1/2 (before μ -grinding)

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]

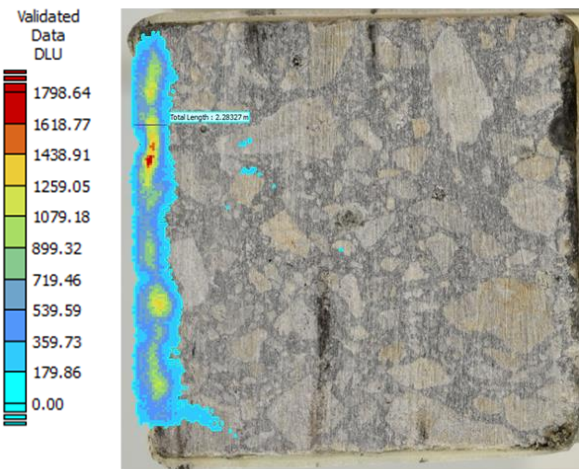
$$D_e(^{36}\text{Cl}) = 5.15 \cdot 10^{-14} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 0.9$$



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

³⁶Cl 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

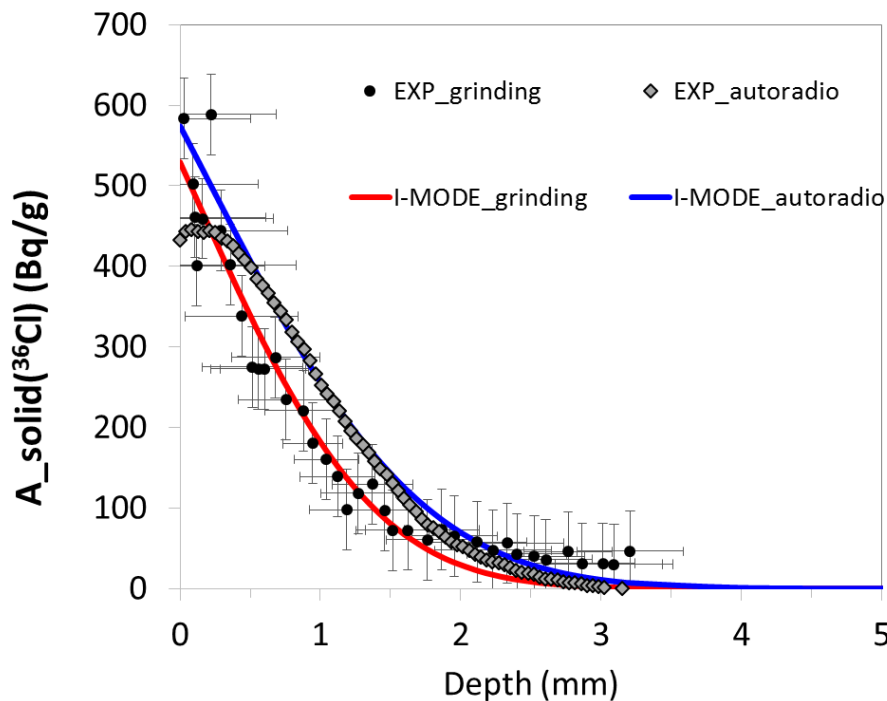
First estimations of diffusion parameters

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

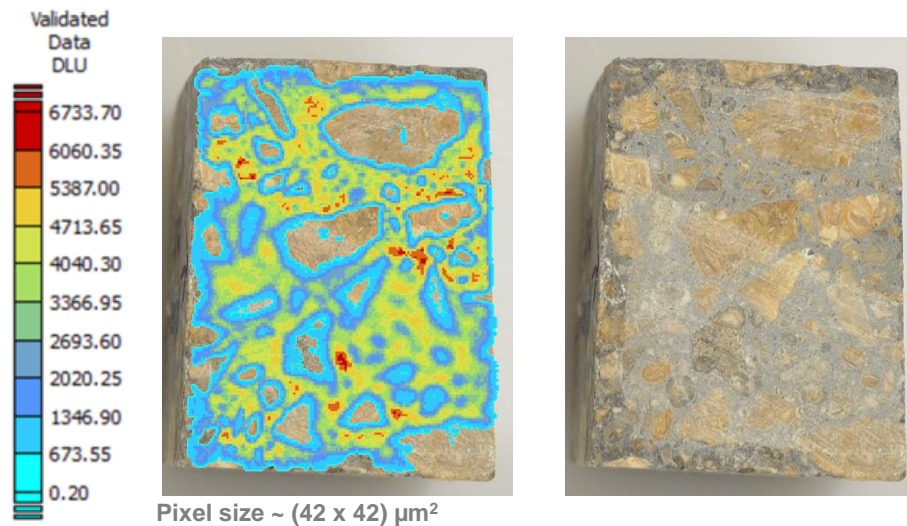
$$D_e(^{36}\text{Cl}) = 1.2 \cdot 10^{-13} \text{ m}^2/\text{s}; \omega R(^{36}\text{Cl}) = 1.3$$

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 ³⁶Cl diffusion profiles are coherent

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

Surface mapping after 4 days of exposure

- ^{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

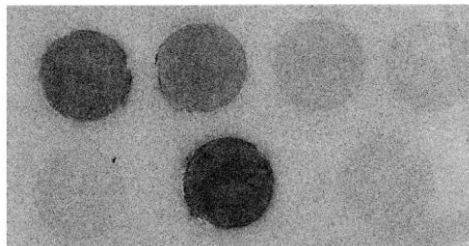
For ^{36}Cl : fast in-diffusion experiments coupled with digital autoradiography imaging and a diffusion modelling tool lead to give a good estimation of diffusion parameters

- 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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