# 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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# INTRODUCTION

## 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 x $10^5$ 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**

# CONTENT

- Introduction
- **Cementitious sample preparation**
- **Results obtained:**
  - **by classical HTO/$^{36}$Cl 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; $\omega(H_2O)$ = 33-35%

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

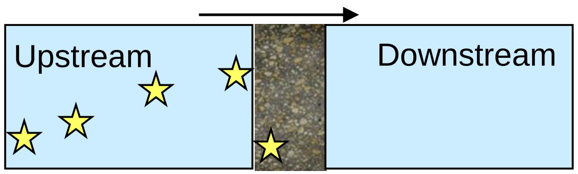
**Saturation/hydration in ACW solution**

(~ 3-6 m)


$T_{0+1\ year}$

# HTO AND $^{36}$CHLORINE DIFFUSION CLASSICAL PROTOCOL

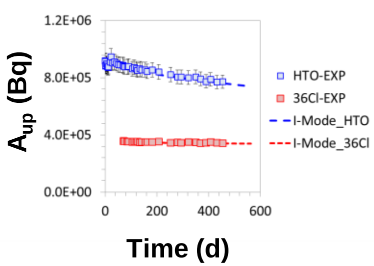
$T_{diff\_0}$



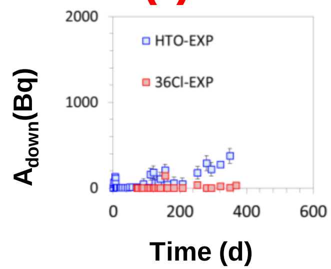

1 - Adding RN cocktail in the upstream compartment

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

**A(t) / HTO**




**A(t) / $^{36}$Cl**



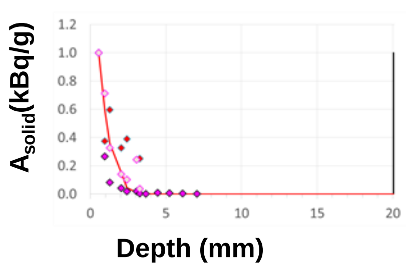

2- Evolution of $A_{up}$ (and $A_{down}$) as a function of time

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

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

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

3 – Quantitative diffusion profile determination for $^{36}$Cl


Sample grinding

Cementitious powder lixiviation + $^{36}$Cl β LSC

4-Diffusion modeling / interpretation

I-Mode simulation tool

*I-Mode = Interpretation Model Of Diffusion Experiments*

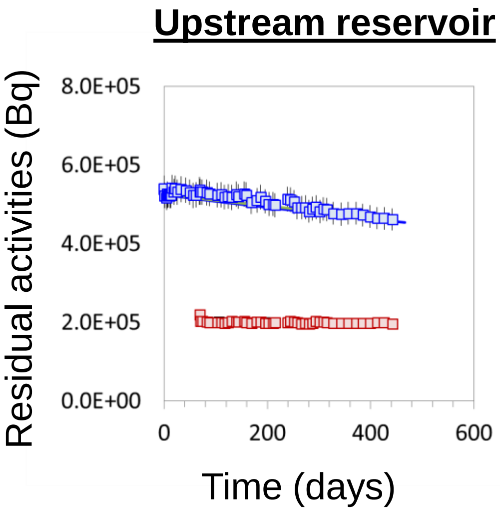
Radwan *et al.* (2005 & 2006)

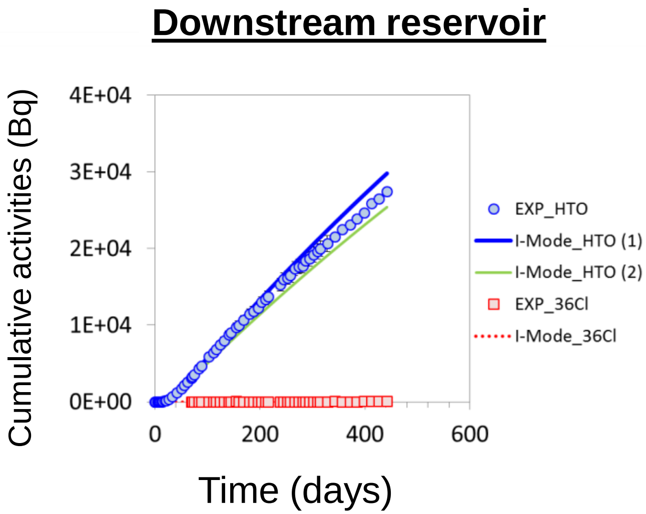
$T_{diff\_0\ +\ \sim 1.5\ year}$

**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



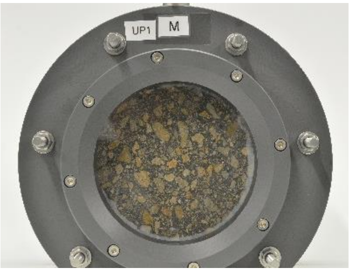

**First estimations of diffusion parameters**

$D_e$(HTO) = 3.0 $10^{-13}$ $m^2/s$ ; $\omega R$(HTO) = 0.5
$D_e$(HTO) = 2.5 $10^{-13}$ $m^2/s$; $\omega R$(HTO) = 0.3

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

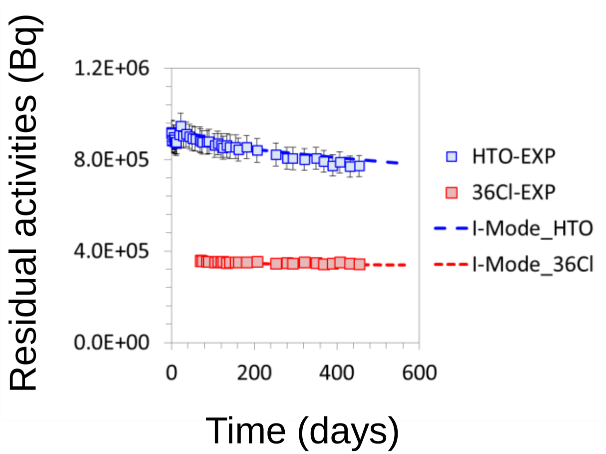
- **Confirmation that $^{36}$Cl species migrate slower than HTO**
  - **HTO can be considered as conservative for $^{36}$Cl transfer**
- **Confirmation of the batch $^{36}$Cl sorption experiments: high delay onto diffusion**
  - **Diffusion profile into the solid is needed to constrain parameters fits**

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

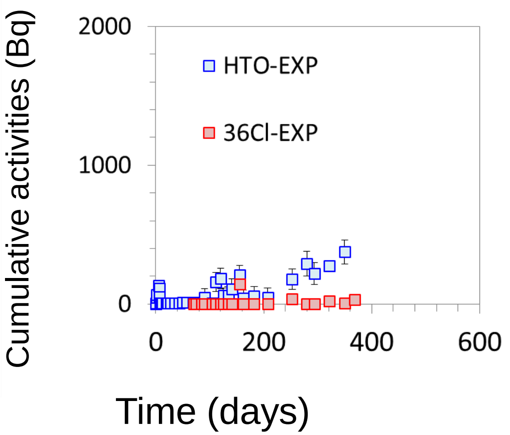



Step 2- Evolution of $A_{up}$ (and $A_{down}$) as a function of time

**Upstream reservoir**




**Downstream reservoir**




First estimations of diffusion parameters

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

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

# COULD IT BE POSSIBLE TO SAVE SOME TIME ?

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

## Optimized $^{36}Cl$ in-diffusion conditions

**quantitative**

In-lab diffusion set-up

**$^{36}Cl$-sensitive**

widely used technique

optimized resolution

**mapping**

Imaging trace quantities

## Digital autoradiography imaging technique

Haudebourg & Fichet (2016) J. radioanal Nucl Chem – vol.309 (2) pp.551-561

# 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

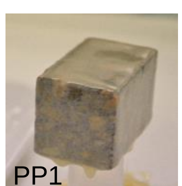
(3)

2 samples of **HCP** with $L_1$ ~ 3 mm
$L_2$ ~ $L_3$ ~ 35 mm

2 samples of **concrete** with $L_1$ ~ 30 mm
$L_2$ ~ 50 mm; $L_3$ ~ 30 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**

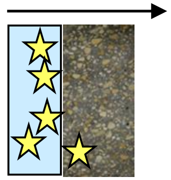


$T_{0+7\ months}$

# AUTORADIOGRAPHY DEDICATED PROTOCOL

$T_{diff\_0}$

Upstream



## 1- Adding RN cocktail in the upstream compartment

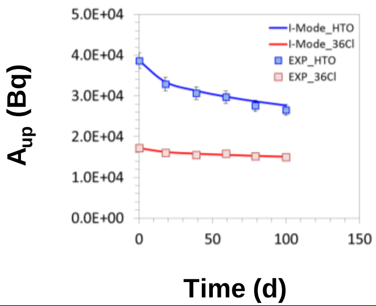
A(HTO) = 2.3 MBq/L + A($^{36}$Cl) = 1.2 MBq/L (HCP in-diff cell)

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

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

**$A_{up}(t)$ / HTO**

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

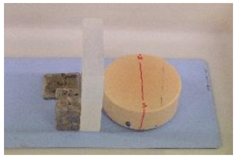


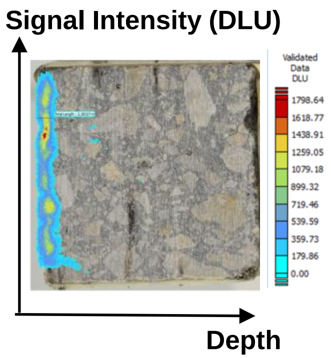

$V_{up}$ = ACW
$[LiCl]_{up}$ = 30 mM
pH > 13

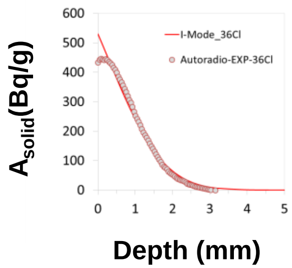
**$A_{up}$ = variable**

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

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






## 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)

$T_{diff\_0 + 150\ days}$

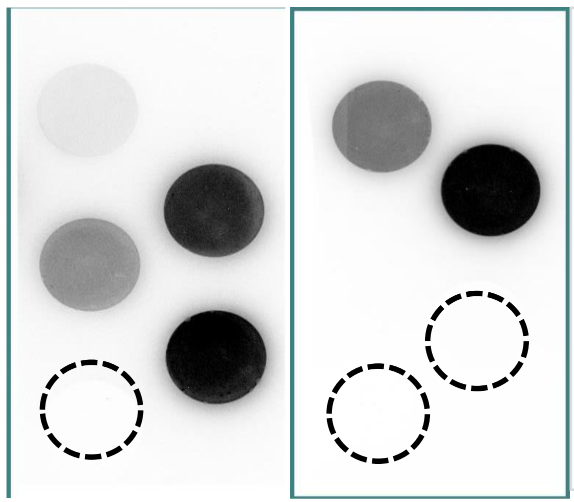
**Diffusion parameters (ωR and De ) for $^{36}$Cl**

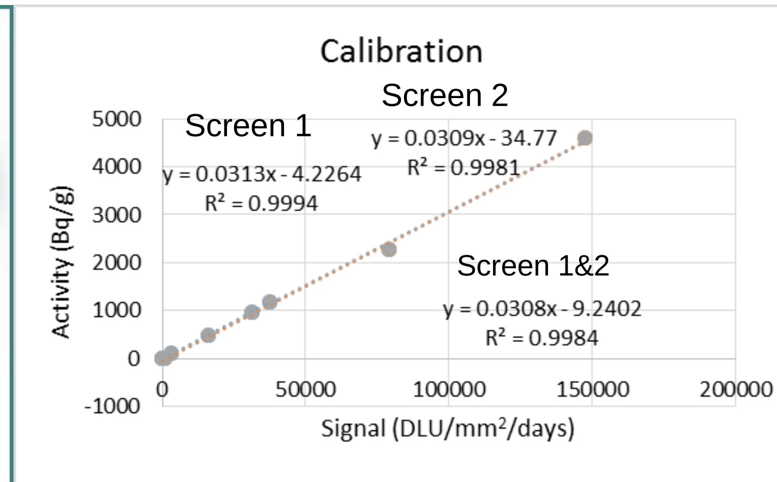
# $^{36}$Cl CALIBRATION USING AUTORADIOGRAPHY

- **HCP-ROMBAS standards (w/c: 0.40, Ø = 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

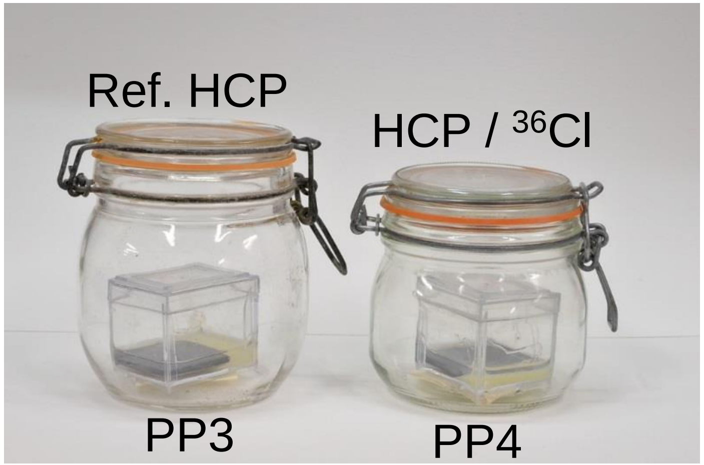





**<u>Results obtained after 5 days of exposure</u>**

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

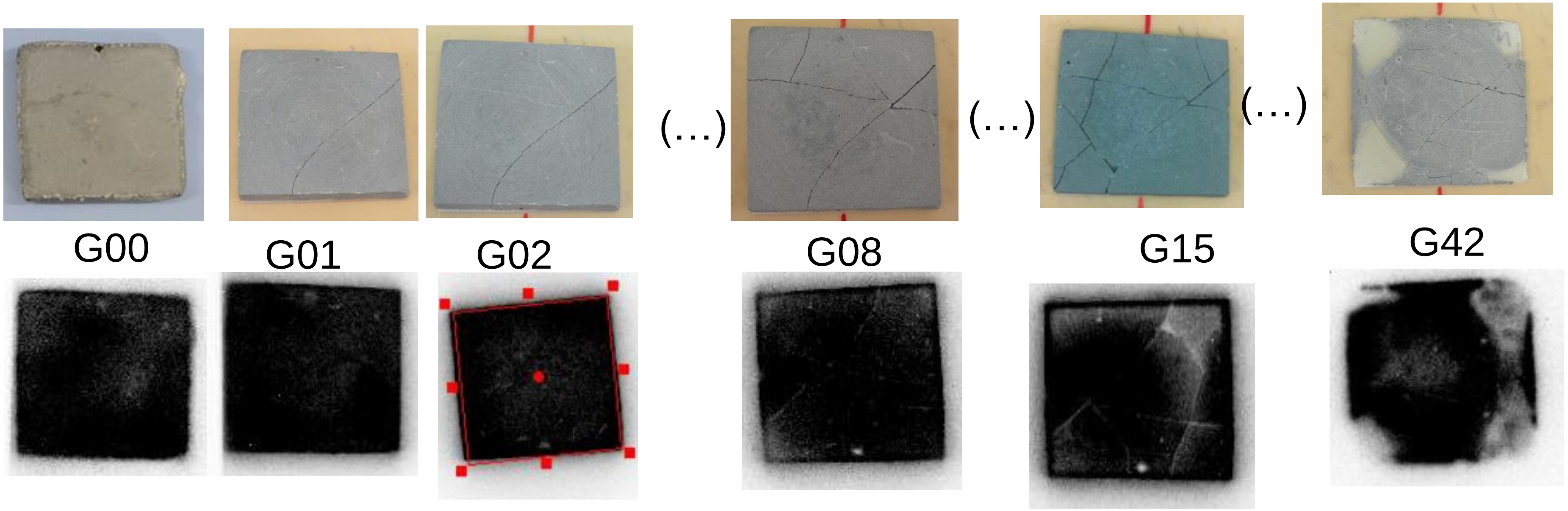
# $^{36}$Cl DIFFUSION PROFILE DETERMINATION




**Solution in contact with PP4**
10 mL ACW + 30 mM LiCl
A(HTO) = 2.3 MBq/L
A($^{36}$Cl) = 1.2 MBq/L

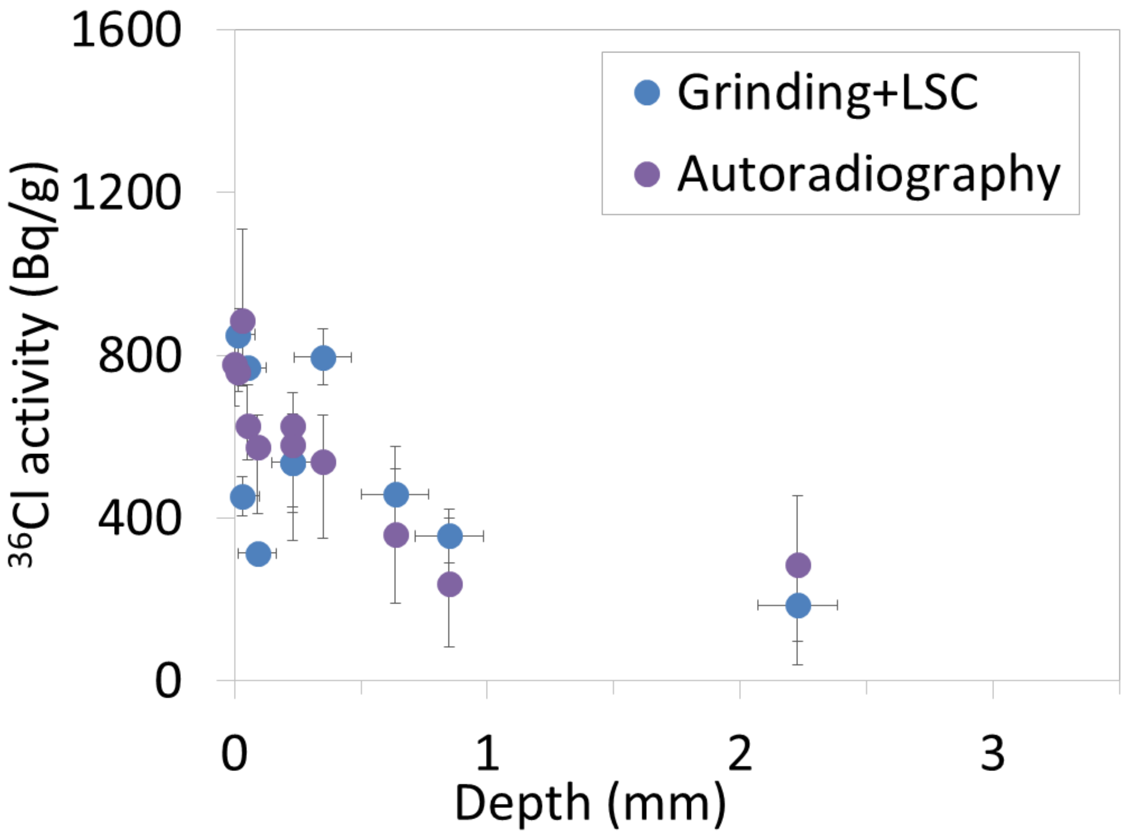
Diffusion during 50 days

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



# $^{36}Cl$ DIFFUSION PROFILE INTO THE HCP SAMPLE

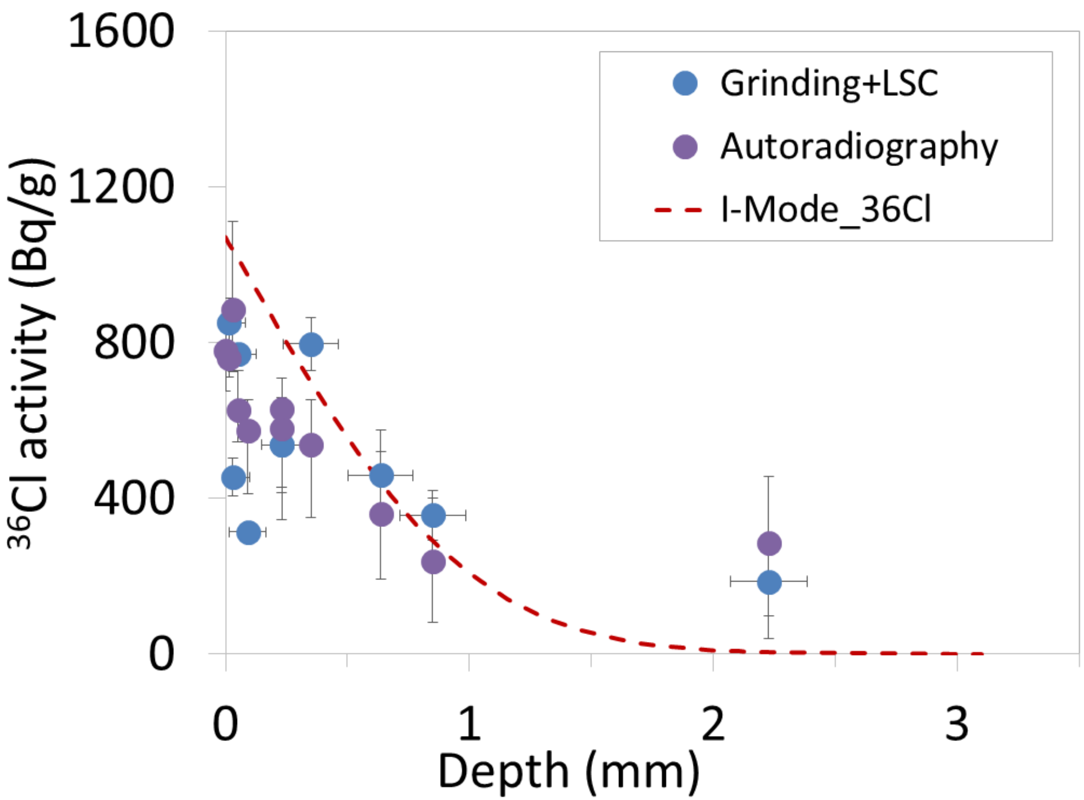
**Comparison between µ-grinding and autoradiography**




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

# $^{36}$Cl DIFFUSION PROFILE INTO THE HCP SAMPLE

## Comparison between µ-grinding and autoradiography




**Bonus: estimation of diffusion parameters**

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

- **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**

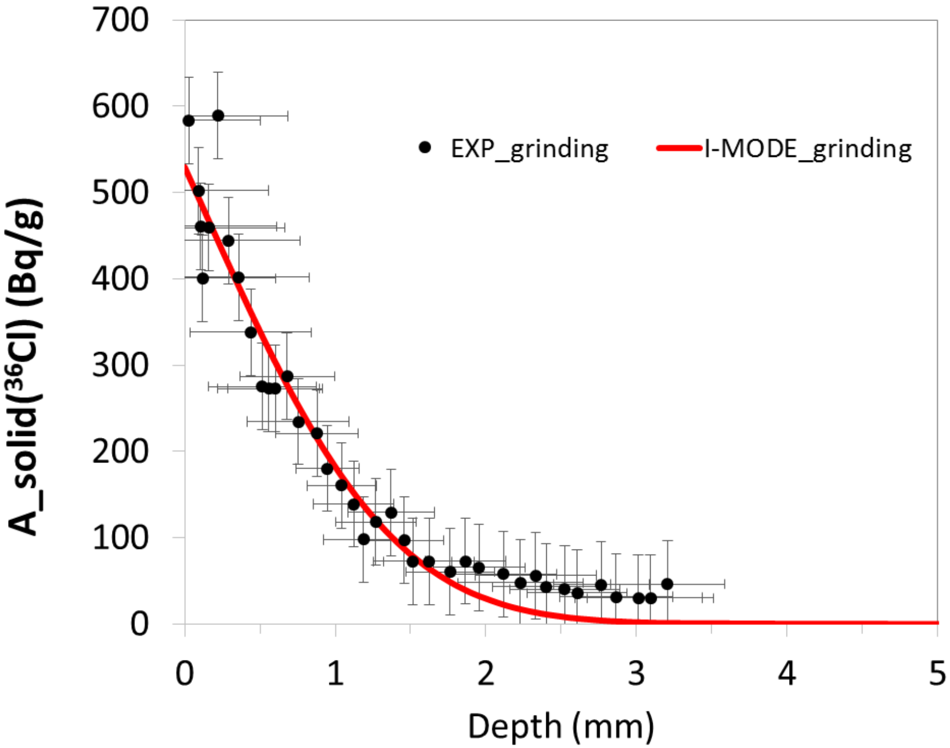
**Surface picture of PP2 -1/2 (before µ-grinding)**

First estimations of diffusion parameters

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

**Diffusion parameter for F44-concrete [1]**

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




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

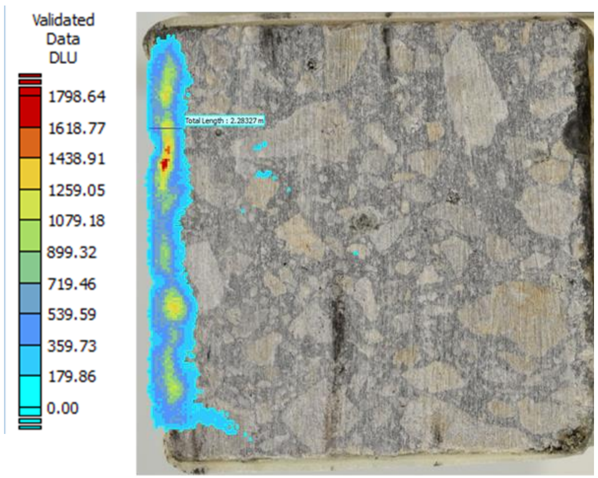


[1] Macé *et al.* (2013) 3rd International Workshop Mechanisms and modelling of waste/cement interactions, Murten, Switzerland

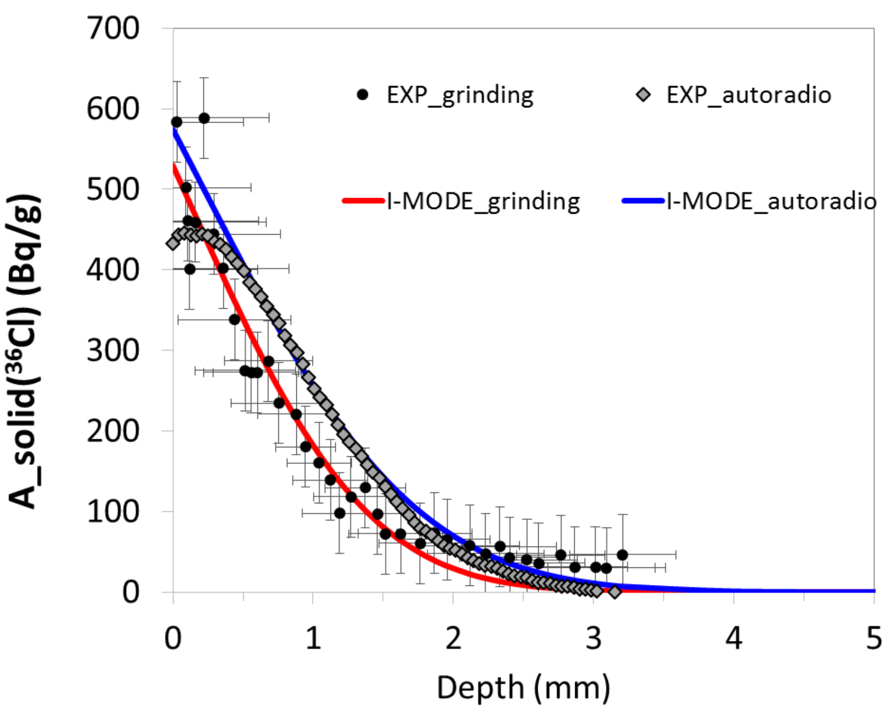
# WHAT ABOUT THE CONCRETE SAMPLE ? (2/3)

## $^{36}$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

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

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

**Diffusion parameter for F44-concrete [1]**

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

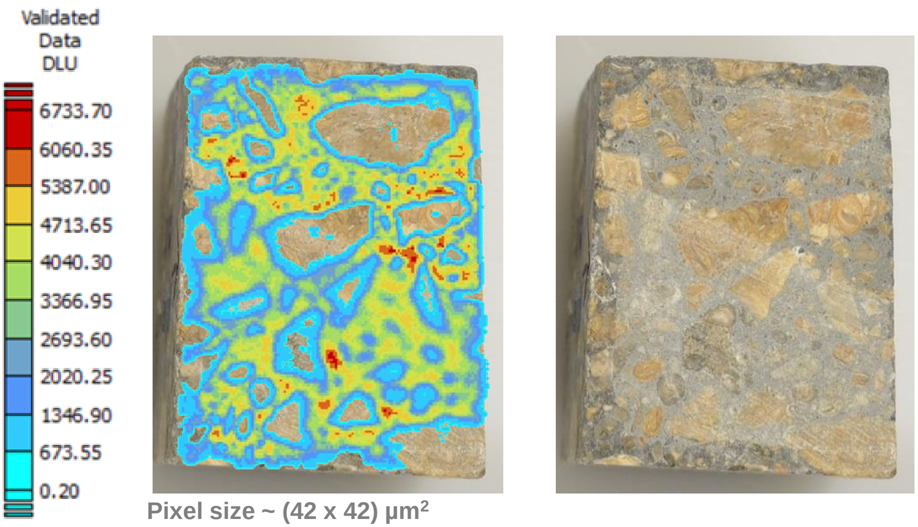
- **Both experimental $^{36}$Cl diffusion profiles are coherent**



[1] Macé *et al.* (2013) 3rd International Workshop Mechanisms and modelling of waste/cement interactions, Murten, Switzerland

# WHAT ABOUT THE CONCRETE SAMPLE ? (3/3)

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




Pixel size ~ (42 x 42) µm$^2$

**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**

# CONCLUSIONS AND PERSPECTIVES

**➔ 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

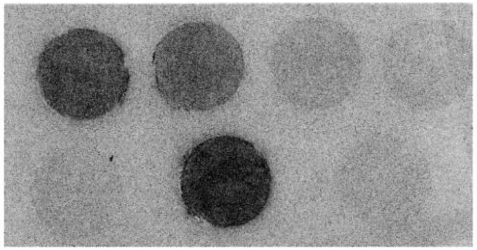
➔ uncertainties evaluation of diffusion parameters using both protocols is on going

➔ 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

ANDRA
La maîtrise des déchets radioactifs

RADIONUCLIDE MIGRATION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