

# DIFFUSION OF TRITIATED WATER AND IONS THROUGH THE TOURNEMIRE ARGILLITE (FRANCE) IN PRESENCE OF ALKALINE FLUIDS

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## PROGRAM CONTEXT

- Radioactive waste disposal may contain high amounts of concrete
  - Claystones are potential host rocks
- Question: What are the effects of alkaline solutions resulting from concrete leaching on the properties of claystone?**

EXPERIMENTAL PROGRAM DEVELOPPED BY IRSN  
 Applied to the Tournemire argillite

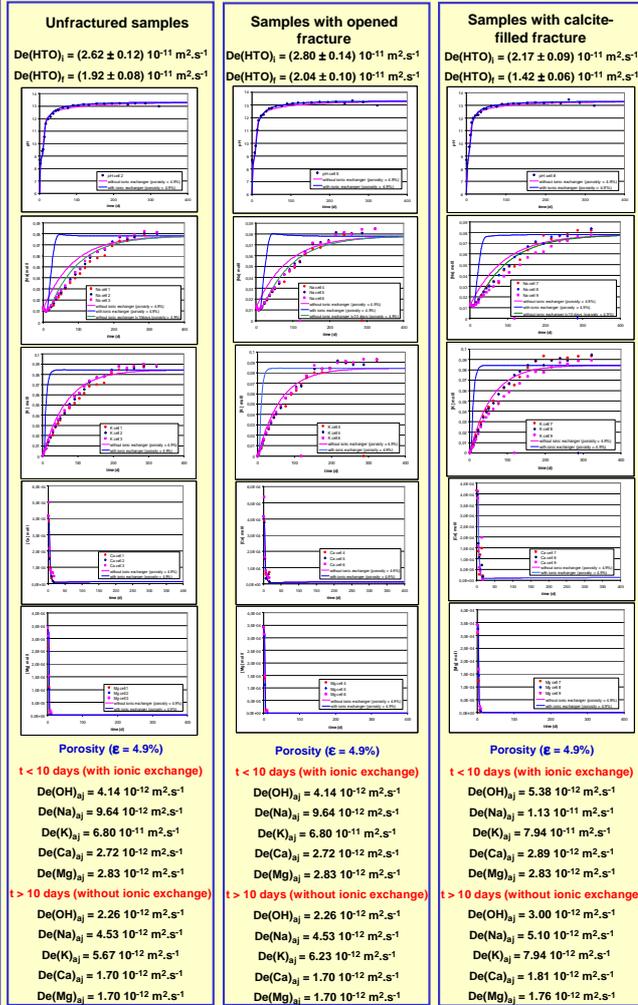
- Batch experiments
  - Advection experiments
  - Diffusion experiments
  - Natural analogues observations (Posters P/AP/18 & P/MTPM/25, this meeting)
- in presence of hyperalkaline fluids

Diffusion experiments aims

- Determine the diffusion coefficient of HTO, OH, Na, K, Ca, Mg in both fractured and not fractured argillites in contact with alkaline fluids
- Observe the argillite at the end of experiments (precipitations and alteration front)

## DIFFUSION AND MODELLING (CEA & IRSN)

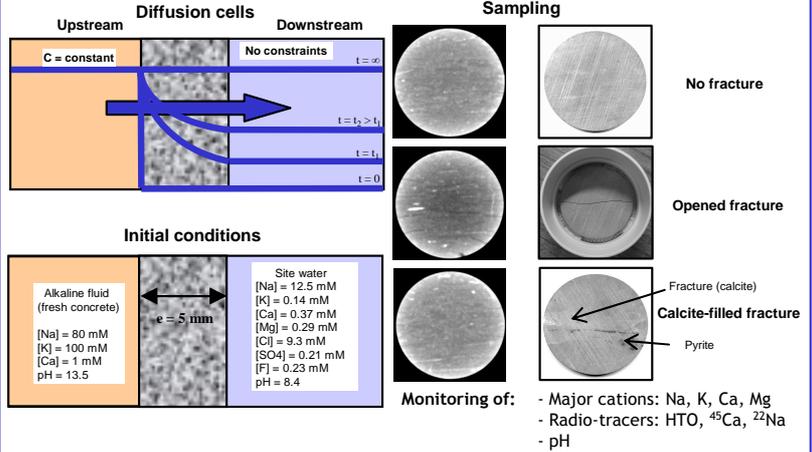
Evolution of the downstream reservoir



- Diffusion: Increase in pH and Na and K concentrations to reach values measured in the upstream reservoir - Fast decrease in Ca and Mg concentrations - Similar behaviour of the unfractured and the opened fracture samples - Larger heterogeneity of the results from the sample containing a calcite-filled fracture - Decrease of De(HTO) of 25-30% during the alkaline fluid diffusion process

- Modelling: Important effect of the multi-site cation exchanger: experimental data fitted (1) taking into account the ionic exchange phenomenon during the 10 first days of the experiments (in particular for Na) and (2) considering this phenomenon negligible for longer time scales (decrease of all De and calcite precipitation) - Low effect of the porosity value (De(ε = 4.9%) ≤ De(ε = 12%))

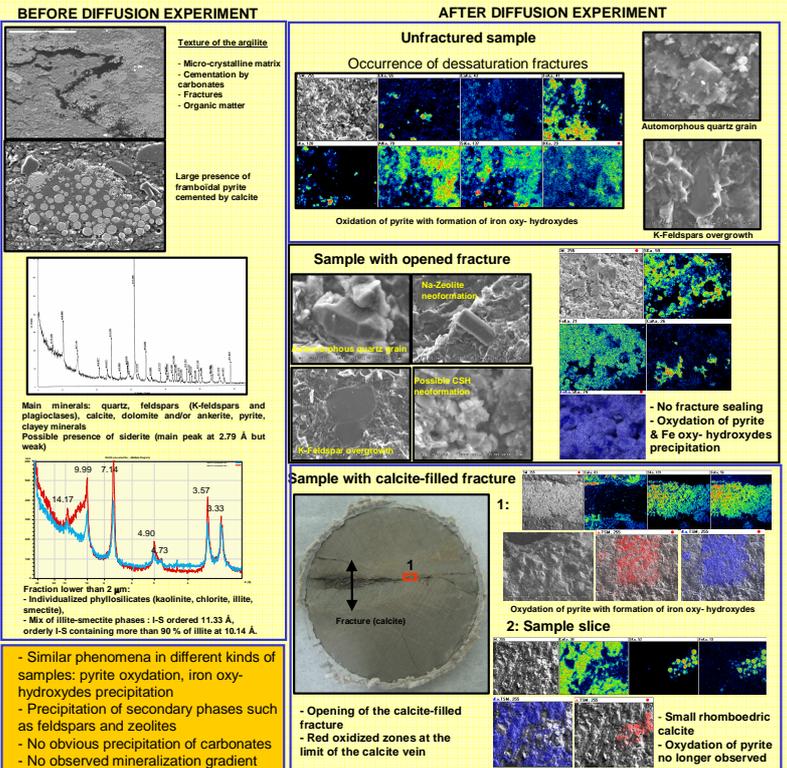
## DIFFUSION EXPERIMENTS (CEA)



## AFTER DIFFUSION EXPERIMENTS (IRSN & MNHN)

- Mineralogical characterization by SEM and XRD of clayey samples
  - Modelling assumptions (PhreeQC):
    - Transport by Fick's laws
    - Sample composition: calcite and dolomite
    - Sample porosity: geochemical (4.9% w/w) or total (12% w/w)
    - Retention by multi-site cation exchanger (Jacquier P., Ly J., Beaucaire C. (2004). Applied Clay Science, 26, 163-170)
- |   | Site 1          | Site 2          | Site 3          |
|---|-----------------|-----------------|-----------------|
| Exchange Capacity (mmol.g <sup>-1</sup> ) | 0.0650 ± 0.0015 | 0.0400 ± 0.0015 | 0.0300 ± 0.0015 |
| log K <sub>Na/H</sub>                     | 2.8 ± 0.3       | 4.9 ± 0.3       | 6.6 ± 0.1       |
| log K <sub>K/H</sub>                      | 1.1 ± 0.3       | 3.4 ± 0.4       | 5.4 ± 0.8       |
| log K <sub>Ca/2H</sub>                    | 4.0 ± 0.2       | 7.8 ± 0.4       | -               |
| log K <sub>Mg/2H</sub>                    | 4.0 ± 0.2       | 7.8 ± 0.4       | -               |

## MINERALOGICAL CHARACTERIZATION (IRSN & MNHN)



## CONCLUSIONS

- Diffusion coefficients for HTO, OH, Na, K, Ca, Mg decrease during the alkaline diffusion process - Cationic exchange phenomenon is dominant during the first 10 days of the experiments and negligible later: this is a consequence of a mineralogical evolution of argillite samples due to the alkaline fluid diffusion process
- No significant differences between the phenomena observed in unfractured and fractured clayey samples show that the discontinuities induced by the excavation works are readily sealed by the swelling property of the clayey rock when fully hydrated
- The tectonic fractured- zone slice shows larger heterogeneity than the two previous samples: the occurrence of calcite and pyrite veins in this zone plays a role in the diffusion process inasmuch as these minerals reduce both porosity and cationic exchange capacity of the rock