ALTERATION OF THE TOURNEMIRE ARGILLITE (FRANCE) SUBMITTED TO AN ALKALINE PLUME: THROUGH-DIFFUSION EXPERIMENTS

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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
- Engineered analogues observations

→ in presence of hyperalkaline fluids

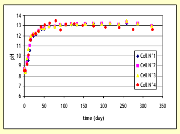
Diffusion experiments aims

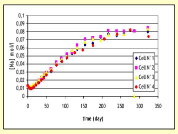
- *Determination of the diffusion coefficient of HTO (and Na, K, Ca, Mg) in both fractured and not fractured argillites in contact with alkaline fluids*
- *Observation of the argillite at the end of experiments (precipitations and alteration front)*

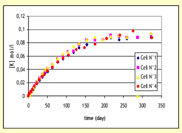
DIFFUSION (CEA)

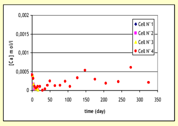
Evolution of the downstream reservoir

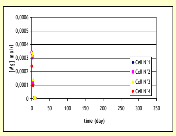
N1 / site









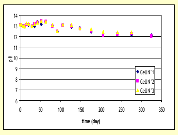


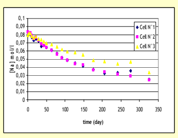
Unfractured sample (1)
$De(HTO)_i = (2.62 \pm 0.12)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (1.92 \pm 0.08)\ 10^{-11}\ m^2.s^{-1}$

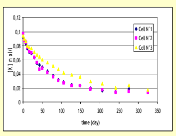
Sample with opened fracture (2)
$De(HTO)_i = (2.80 \pm 0.14)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (2.04 \pm 0.10)\ 10^{-11}\ m^2.s^{-1}$

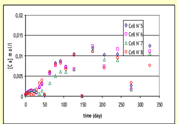
Sample with large tectonic fracture filled with calcite (3)
$De(HTO)_i = (2.17 \pm 0.09)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (1.42 \pm 0.06)\ 10^{-11}\ m^2.s^{-1}$

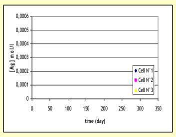
N2 / N1









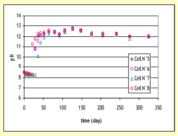


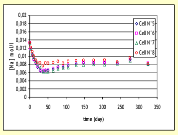
Unfractured sample (1)
$De(HTO)_i = (1.92 \pm 0.08)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (7.89 \pm 0.34)\ 10^{-12}\ m^2.s^{-1}$

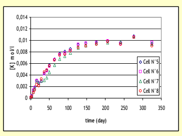
Sample with opened fracture (2)
$De(HTO)_i = (2.04 \pm 0.10)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (8.24 \pm 0.34)\ 10^{-12}\ m^2.s^{-1}$

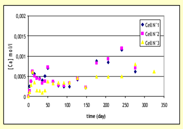
Sample with large tectonic fracture filled with calcite (3)
$De(HTO)_i = (1.42 \pm 0.06)\ 10^{-11}\ m^2.s^{-1}$
$De(HTO)_f = (4.78 \pm 0.18)\ 10^{-12}\ m^2.s^{-1}$

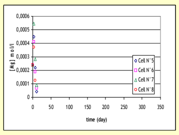
N2 / site









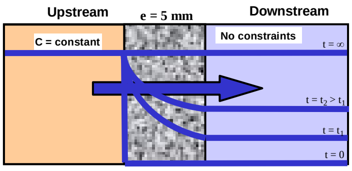


MODELLING (IRSN)

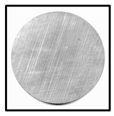
Preliminary modelling in the case of the N1 diffusion process:
- Effect of the multi-site cation exchanger (Jacquier P., Ly J., Beaucaire C. (2004). Applied Clay Science, 26, 163-170) **:**
Experimental data fitted (1) taking into account the ionic exchange phenomenon during the 10 first days of the experiments and (2) considering this phenomenon negligible for longer time scales
- Low effect of the porosity value (De(ε = 4.9 %) ≤ De(ε = 12 %))

DIFFUSION EXPERIMENTS (CEA - IRSN)

Diffusion cells

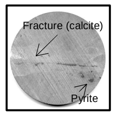


Sampling



No fracture

Opened fracture



Calcite-filled fracture

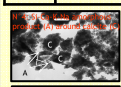
N° Cell	Sliced rock material (structure / strat. orientation)	1rst phase	2nd phase
1	No fracture (0°)	N1 / site	N2 / N1
2	Opened fracture (0°)	N1 / site	N2 / N1
3	Large tectonic fracture filled with calcite (60°)	N1 / site	N2 / N1
4	Thin tectonic fracture filled with calcite (0°)	N1 / site	
5	No fracture (0°)	N2 / site	
6	Opened fracture (0°)	N2 / site	
7	Large tectonic fracture filled with calcite (0°)	N2 / site	
8	Large tectonic fracture filled with calcite (60°)	N2 / site	

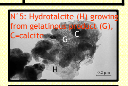
Site: synthetic site solution ([Na] = 12.5 mM, [K] = 0.14 mM, [Ca] = 0.37 mM, [Mg] = 0.29 mM, [Cl] = 9.3 mM, $[SO_4]$ = 0.21 mM, [F] = 0.23 mM, pH = 8.4)
N1: synthetic fresh concrete fluid ([Na] = 80 mM, [K] = 100 mM, [Ca] = 1 mM, pH = 13.12)
N2: synthetic moderately degraded concrete fluid ([Na] = 8 mM, [K] = 10 mM, [Ca] = 30 mM, pH = 12.73)

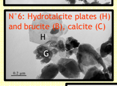
Monitoring of: Major cations (Na, K, Ca, Mg), radio-tracers (HTO, ^{45}Ca, ^{22}Na), pH
At the end of experiments: upstream and downstream fluids filtration, filters and samples analyses

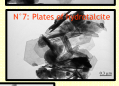
FILTERS CHARACTERIZATION (MNHN)

N° Cell	Upstream	Downstream
4	Important white deposit (calcite, Si-Ca-K-Na amorphous product)	Thin deposit corresponding to « argillite contamination » (clays, quartz, iron sulphur / hydroxydes)
5	Important white deposit (calcite, brucite, hydrotalcite, Mg-Al-Si amorphous gel)	Thin white deposit (calcite)
6	Important white deposit (calcite, brucite, hydrotalcite, Mg-Al-Si amorphous gel)	Thin white deposit (calcite)
7	Important white deposit (calcite, brucite, hydrotalcite, Mg-Al-Si amorphous gel)	Thin white deposit (calcite)
8	Important white deposit (calcite, brucite, hydrotalcite, Mg-Al-Si amorphous gel)	Thin white deposit (calcite)







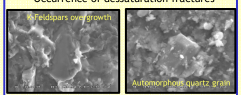


SAMPLES CHARACTERIZATION (IRSN - Nîmes)

N1 / site

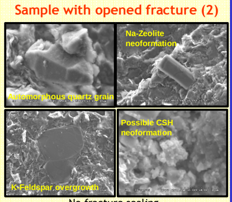
Unfractured sample (1)

Occurrence of dessaturation fractures



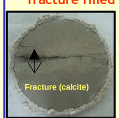
Pyrite oxydation - Fe oxy-hydro. precipitation

Sample with opened fracture (2)



No fracture sealing
Pyrite oxydation - Fe oxy-hydro. precipitation

Sample with large tectonic fracture filled with calcite (3)

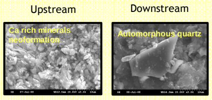


- Opening of the calcite-filled fracture
- Red oxidized zones at the limit of the calcite vein

- Pyrite oxydation - Fe oxy-hydro. formation in the calcite vein
- Small rhomboedric calcite in the sample slice

Sample with thin tectonic fracture filled with calcite (4)

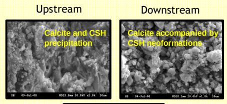
Upstream / Downstream



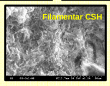
N2 / site

Unfractured sample (5)

Upstream / Downstream

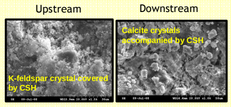


Profile

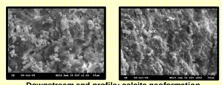


Sample with opened fracture (6)

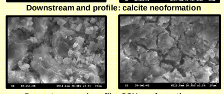
Upstream / Downstream



Sample with large tectonic fracture filled with calcite (7)



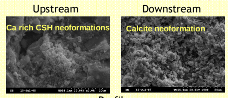
Downstream and profile: calcite neoformation



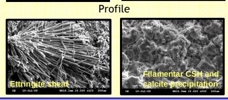
Downstream and profile: CSH neoformation

Sample with large tectonic fracture filled with calcite (8)

Upstream / Downstream



Profile



CONCLUSIONS

- HTO diffusion coefficients during the alkaline diffusion processes: decrease of 25-30 % during the N1 diffusion process and then of 60-70 % during N2
- Precipitation phenomena is less intense during the N1 diffusion process than N2: the alkaline plume induces calcite precipitation (in particular in upstream faces) and CSH neoformation (in particular in downstream faces)
- No significant differences between the phenomena observed in unfractured and fractured clayey samples show that discontinuities are readily sealed by the swelling property of the clayey rock when fully hydrated
- The tectonic fractured-zone slices show larger heterogeneity than the samples without discontinuities: 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

Mechanisms and modelling of waste/cement interactions, 2nd International Workshop, Le Croisic 2008