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Treatment and Disposal of Irradiated Graphite and Other Carbonaceous Waste

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T6.3.2/D6.3.3 – Retention properties of cement for ^{36}Cl

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1 Context and objectives

CARBOWASTE Work Package 6 deals with disposal issues for i-carbonaceous waste and also provides performance assessments for the waste packages entering into environmental compatibility investigations. The graphite behaviour in the disposal is indeed characterized by the release of radionuclides, present in the inventories, in contact with groundwater. Then, highly radioactive graphite and other carbonaceous wastes[1] behaviour in the disposal can be improved by designing appropriate waste packages.

An important concern is the mobility of radionuclides in the waste package and its surrounding under repository conditions prior to and after water access. Graphite wastes usually contain the long-lived isotope ^{14}C and could also contain the very long-lived isotope ^{36}Cl arising from processes designed to remove heavy metal impurities during manufacture and/or sulphur residual in the virgin material. The long-lived activation product ^{36}Cl is the major contributor to a potential dose resulting from disposal of i-graphite.

One of the issues of Task 6.3 is to determine the mobility of radionuclides (*e.g.* ^{36}Cl) in engineered barrier materials such as cement pastes.

Concrete waste packages are going to be altered during the disposal due to leaching by natural water entering in the system. Retention properties of such a package depend on the mineralogical composition of the cement pastes, the alteration state of the material and the geochemical conditions of the water.

The present study aims at measuring distribution ratio ($R_d = [^{36}Cl^-]_{solid}/([^{36}Cl^-]_{solution})$ of ^{36}Cl in contact with a hydrated cement paste, under controlled atmosphere, considering:

- ✓ Dependency with the alteration state of the cement paste;
- ✓ Kinetics of retention;
- ✓ Reversibility of retention;
- ✓ Saturation effect arising from stable chloride already present in natural water.

[1] Concentrate residues from graphite treatment, pyrolytic coatings of the fuel particles or whole graphite matrices of fuel elements from GCR reactors.

2 Materials and methods

Studying the ^{36}Cl retention as a function of the alteration state of the cement pastes requires an accurate characterization of the material prior to sorption measurements.

2.1 Materials

The material studied is an Origny cement (CEM-V), which was mixed with water in 1997 (water to cement ratio, w/c, = 0.38). During four years, the resulting CEM-V paste was kept in a portlandite ($Ca(OH)_2$) saturated solution to prevent carbonation and continue the hydration processes. In 2001, the samples were dried, crushed and sieved under a flow of argon. Several sieved fractions were then stored in HDPE vials into desiccators flushed with argon before closure (Pointeau *et al.*, 2004).

A specific fraction of the powder has been used in the present study (100 µm < ∅ < 200 µm). Fresh, deteriorated and degraded cement pastes were obtained by leaching different amounts of cement powder in closed batches under various conditions (solid to water ratio and composition of solution):

1. fresh state: leaching of cement powder in artificial fresh cement pore water (cement to water ratio 111 $g.l^{-1}$). Such a solution is prepared by dissolving NaOH, KOH and CaO in degassed deionised MilliQ® water (18,2 MΩ; [C] < 5 10^{-7} $mol.l^{-1}$). The pH of this solution is about 13.3;
2. deteriorated or degraded state: leaching of cement powder in degassed deionised MilliQ® water (cement to water ratios ranging from 4 to 93 $g.l^{-1}$);
3. "natural" deteriorated state: leaching of cement powder in synthesised water representative of the porewater of a subsurface disposal site (see Table 1) (cement to water ratio 93 $g.l^{-1}$).

Table 1: Targeted composition of the porewater (modified from Poisson, 2005)

Species	Concentration ($mol.l^{-1}$)
Na^+	2.90 10^{-3}
K^+	1.00 10^{-4}
Ca^{2+}	3.41 10^{-4}
Cl^-	4.50 10^{-4}
SO_4^{2-}	1.15 10^{-4}
HCO_3^-	3.00 10^{-3}

2.1.1 Characterization of cement paste alteration states

The different states of alteration were defined by pH values and Ca concentration measured in the solution at equilibrium with the CEM-V cement paste according to the methodology of Pointeau *et al.* (2008).

The fresh state was characterized by a pH of 13.2 and [Ca] of 8.4 10^{-4} $mol.l^{-1}$, the deteriorated state by a pH of 12.5 and [Ca] of 9.2 10^{-3} $mol.l^{-1}$ and the degraded state by a pH of about 12 and [Ca] of 6.0 10^{-3} $mol.l^{-1}$ (see Figure 1).

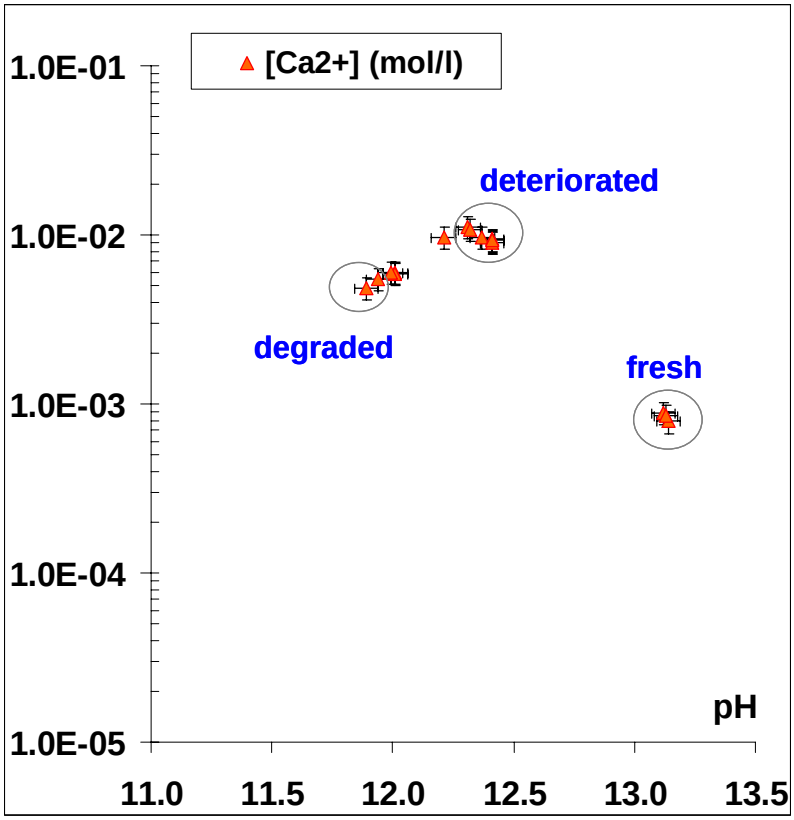

Figure 1: Concentration of calcium vs pH values measured in solutions at equilibrium with the CEM-V cement paste (uncertainties on pH values and Ca concentration measurements are 0.05 and 15% respectively)

Solid characterization based on qualitative X-Ray Diffraction (XRD) was also carried out in order to verify the disappearance of portlandite peaks between fresh paste and degraded paste.

Figure 2 compares the full XRD spectra of fresh and degraded pastes and Figure 3 shows a zoom on the portlandite peak at $2\theta = 21.85$. The decrease of this portlandite peak and increase of the ettringite peaks surrounding at degraded state confirm the degradation of the cement paste as expected.

One should also notice the identification of calcite peaks, especially at $2\theta = 44.2$ for the fresh paste. This observation highlights the possible carbonation of the raw material after 7 years of storage (from 2001 to 2008).

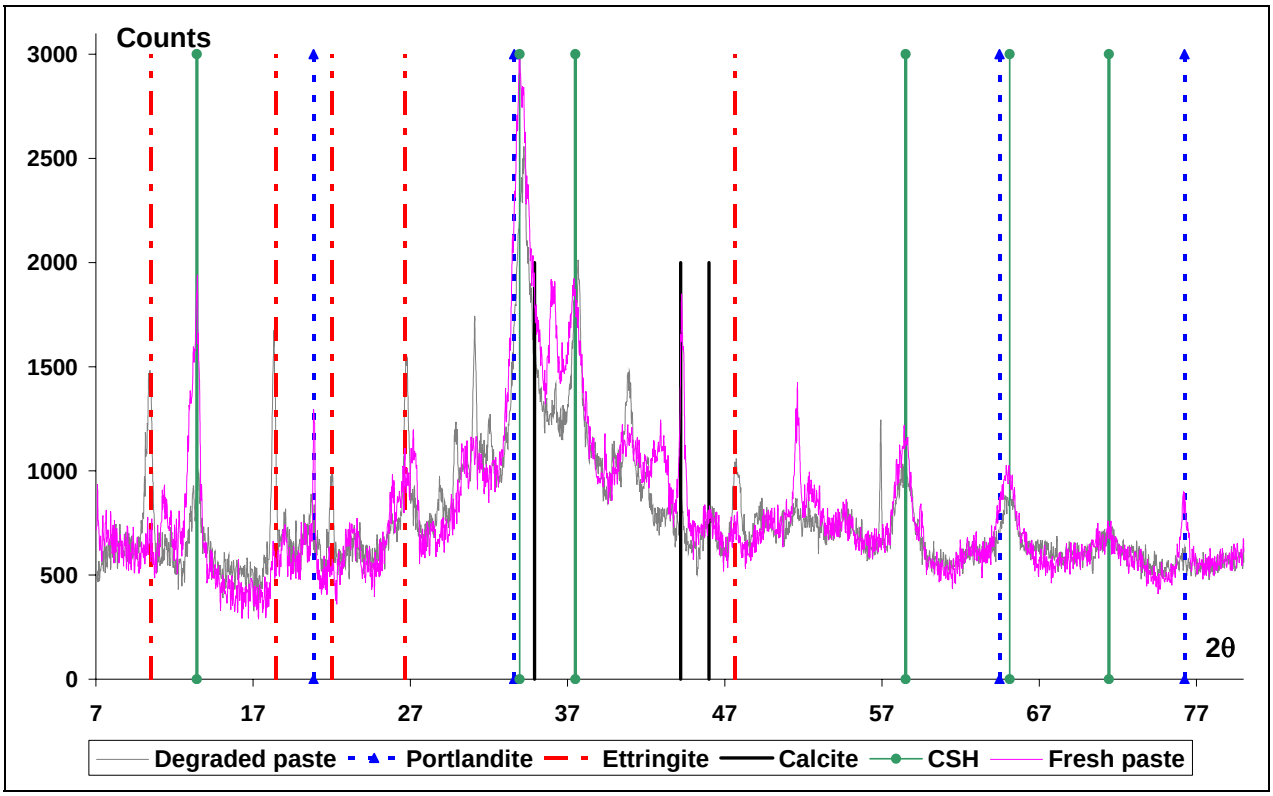

Figure 2: Full diffractograms of fresh and degraded pastes

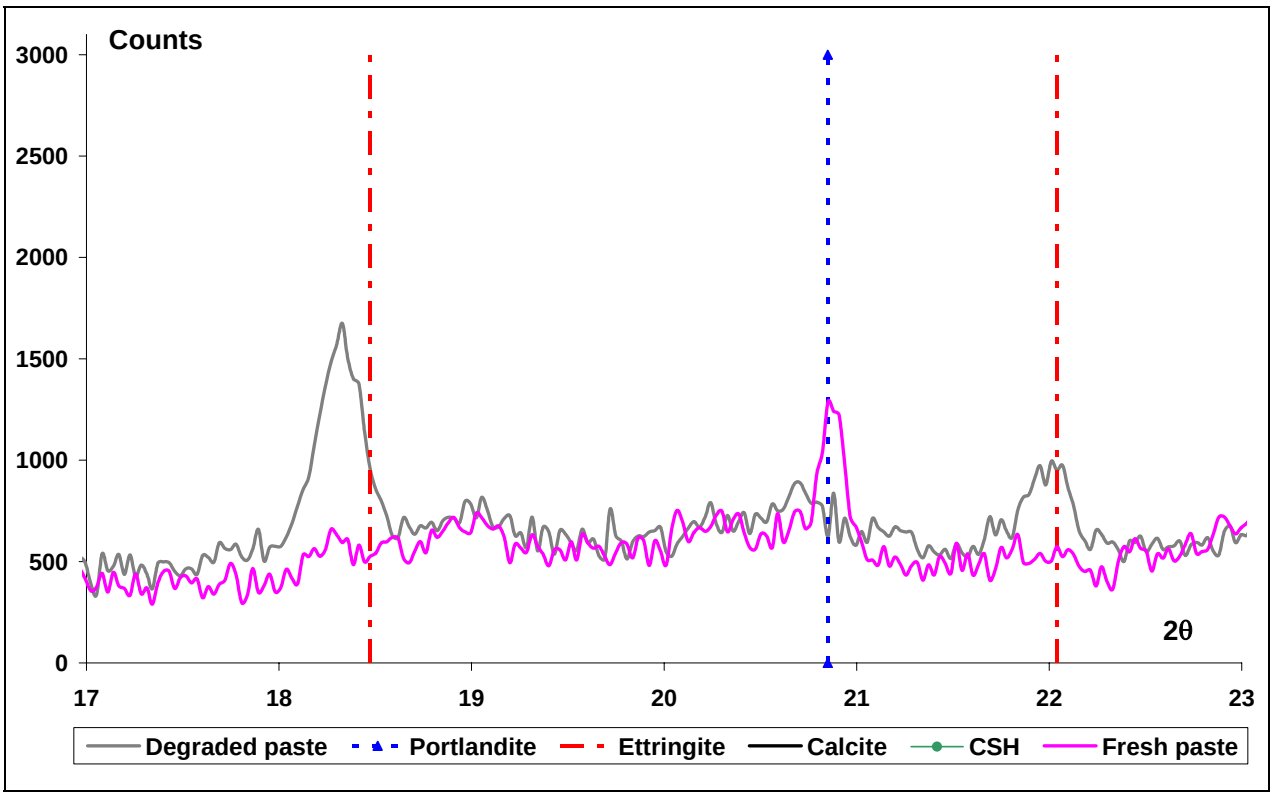

Figure 3: Zoom at 2θ=21.85 of diffractograms of fresh and degraded pastes

2.1.2 Characterization of supernatant solutions

^{36}Cl retention will strongly depend on the total chloride concentration in the storage (coming from the cement pore water and from the "natural" water). In order to assess initial stocks provided by the cement paste at each alteration state, the major ions' concentrations were measured in the liquid phases at equilibrium with cement pastes. Concentrations of major cations were measured by atomic absorption and concentrations of major anions by ionic chromatography (see Figure 4).

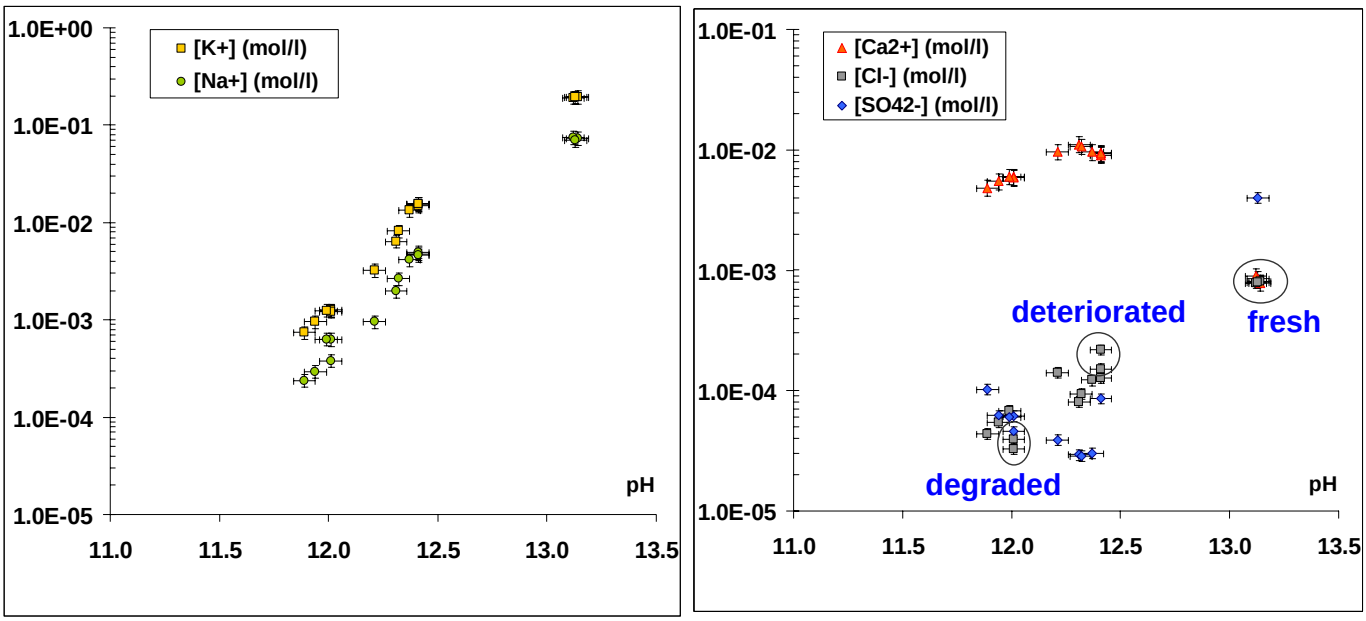

Figure 4: Concentrations of Na^+, K^+ (left) and Ca^{2+}, SO_4^{2-} and Cl^- (right) in cement paste solutions at every alteration states (uncertainties on pH values, cations and anions measurements are 0.05, 15% and 10% respectively)

It was therefore possible to determine the initial stock of stable chloride released by the cement pastes. It was derived from measured chloride concentrations in supernatant solutions:

- ✓ At fresh state: 7.9×10^{-9} mol.g^{-1} of dry paste;
- ✓ At deteriorated state: 2.0×10^{-6} mol.g^{-1} of dry paste;
- ✓ At degraded state: 6.8×10^{-6} mol.g^{-1} of dry paste.

The characteristics of supernatants solutions are similar to those obtained in previous studies using a CEM-I paste (Pointeau *et al.*, 2008) and F44 cement paste (Blin *et al.*, 2008).

2.2 Methods

The distribution ratio of ^{36}Cl between solid phases and equilibrium solutions (R_d) was measured by performing classical batch experiments. These experiments were carried out under controlled atmosphere, in a N_2-filled glove box, in order to prevent carbonation of the cement pastes.

Each set of batches contained a specific mass of crushed cement paste leached by solutions of varying compositions:

1. at fresh state: cement to water ratio 111 $g.l^{-1}$ using artificial fresh cement pore water solution;
2. at deteriorated state: cement to water ratio 92.5 $g.l^{-1}$ using degassed deionised MilliQ® water;
3. at "natural" deteriorated state: cement to water ratio 92.5 $g.l^{-1}$ using synthesised "natural" water.
4. at degraded state: cement to water ratio 7.5 $g.l^{-1}$ using degassed deionised MilliQ® water;

R_d values were determined according to:

$$R_d = \left(\frac{A_{ini} - A_{eq}}{A_{eq}} \right) \times \frac{V}{m}$$

with A_{ini}, the total initial activity of ^{36}Cl introduced in a batch (Bq), A_{eq}, the residual activity of ^{36}Cl in solution after a specific time of contact (Bq), V the volume of solution (mL) and m the mass of dry solid paste (g).

The mass of dry solid paste is calculated considering a mass loss estimation of ~7%. This estimation is based from the mass measurement of a cement paste sample dried at 105°C during 16 days. Then, for deteriorated and degraded states, an additional mass loss of 0.8% is considered taking into account portlandite dissolution during alteration (calculated from Ca concentrations measured in supernatants).

For every alteration states, R_d values were measured as a function of time and stable chloride concentrations in the equilibrium solutions (chloride from the solid paste, from a specific amount of a NaCl solution addition and, in one case, from synthesized "natural" water).

3 Results

3.1 Kinetic study

As mentioned, R_d values were measured in each case after a contact time between solid and solution ranging from one week to 7.5 months. In every batches, the evolution of R_d values *vs.* time is similar. Figure 5 only shows the results obtained at the lowest chloride concentration, *i.e.* when no stable chloride is added to the liquid phase (stable chloride present in solution is only coming from the cement paste itself and, in one case, from the synthesized "natural" water).

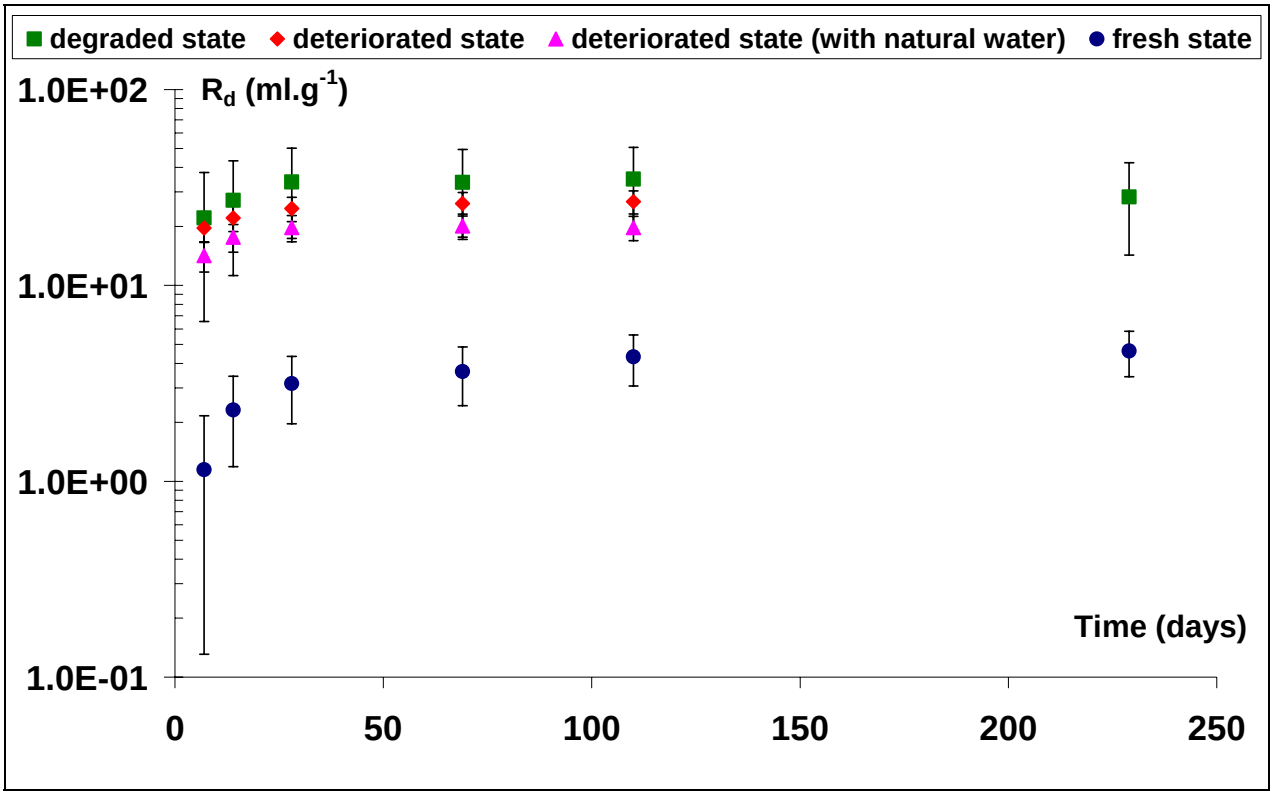

Figure 5: Measured R_d values vs. the time of contact between solid and solution for the different states of alteration

The gradual increase of ^{36}Cl distribution ratio *vs.* time suggests "fast" sorption processes (likely surface sorption phenomena) that could be slowed by a phenomenon of hydration inside the grains. Whatever the case, the R_d values slightly increase during the first month, and no evolution is observed afterwards. Beyond one month R_d reaches a steady mean value.

But in any case, retention of ^{36}Cl by cement paste is weak: a maximum R_d value of 35 $ml.g^{-1}$ is obtained for the degraded state.

3.2 Influence of cement paste alteration on ^{36}Cl retention

Figure 6 compares R_d values measured after 3.5 months *versus* pH values of the corresponding supernatant solutions, *i.e.* as a function of the alteration state of the CEM-V cement paste.

These results are compared to previous results obtained onto F44 cement paste. F44 cement paste is prepared from a CEM-I cement (w/c = 0.33) and admixture of silica fume (Blin *et al.*, 2008). Taking into account accurate definitions, it is neither a CEM-I nor a CEM-V cement paste but it is currently considered as a CEM-V cement paste.

At similar pH values, the retention of ^{36}Cl onto F44 cement pastes is higher. This discrepancy is probably due to the varying initial compositions of both cements and maybe due to the aging of the CEM-V cement paste used in present study (possible calcite formation during storage). Up to now, retention processes for chloride are not well-defined, therefore, it is still difficult to conclude about these observations.

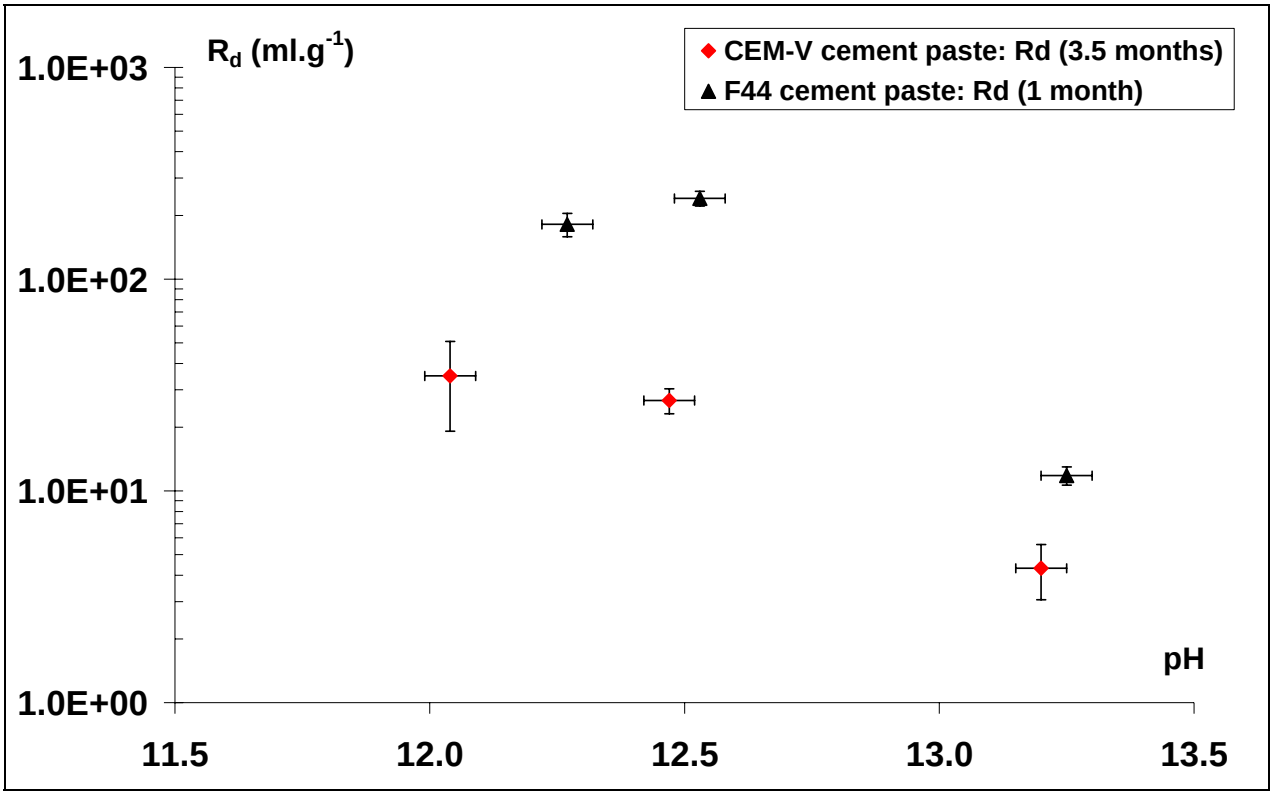

Figure 6: R_d values of ^{36}Cl onto CEM-V cement paste as a function of alteration state compared to R_d values previously measured on F44 cement paste

3.3 ^{36}Cl retention isotherms

The evolution of R_d values of ^{36}Cl measured as a function of total chloride concentrations in equilibrium solutions is shown in Figure 7. Sorption values after 3.5 months of contact between solid and solution were selected in order to make the comparison easier with desorption experiments afterwards.

As observed in the kinetics experiment, distribution ratios values are the lowest on the CEM-V cement paste at fresh state.

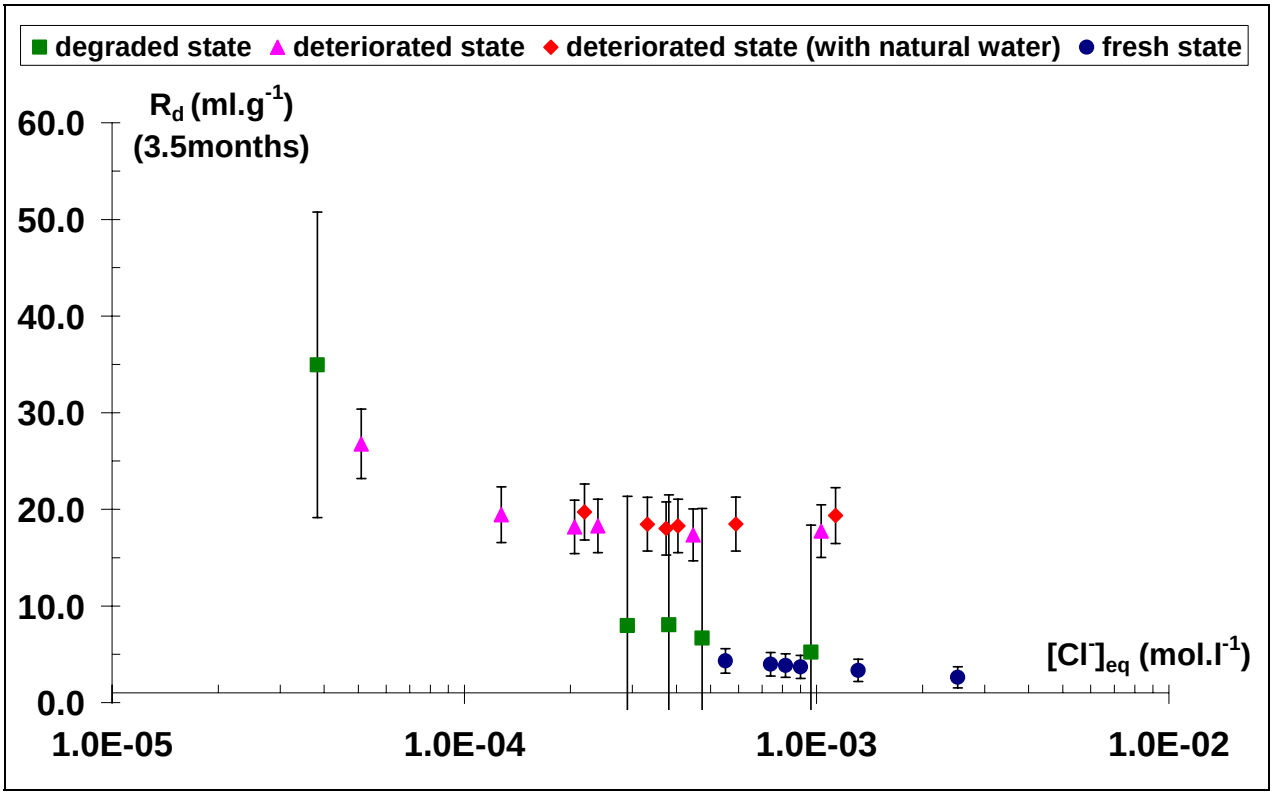

Figure 7: R_d measured after 3.5 months versus chloride concentration at equilibrium in solution at varying alteration states

The retention of ^{36}Cl is strongly reduced when chloride concentration increases, especially at degraded and deteriorated states. Based on these results, it appears important to be able to identify and quantify all chloride sources in a repository.

Concerning the deteriorated states, the retention isotherms give quite similar results regardless of the solution used for leaching the initial cement paste (degassed MilliQ® water or synthesized "natural" water). Theoretically, MilliQ® water is more aggressive than the synthesized "natural" water. Concentrations of major species in the synthesized "natural" water do not seem to be high enough to disturb the solid in a different way and the pH values of supernatant solutions are similar whatever the solution used for the leaching. Thus, without any measurement of the calcium concentration in supernatant solutions, we made the hypothesis that we reached a similar deterioration state whatever the solution used for the leaching. Only the saturation effect of chloride ions provided by the "natural" water is shown here.

3.4 Reversibility study

The sorption reversibility study was limited to both deteriorated states of the cement paste (in degassed MilliQ® water or synthesized "natural" water), for which the R_d measured are the highest when adding stable chloride ions.

At the end of the sorption experiments, batches were centrifuged and the solutions were removed. The remaining solid was then placed in contact with the appropriate equilibrium solution, free of ^{36}Cl (degassed MilliQ® water or synthesized "natural" water pre-equilibrated with a deteriorated cement paste). R_d values were then measured after 4 months of contact between solid and solution.

Resulting ^{36}Cl distribution ratios are shown in Figure 8 as a function of chloride concentration in solution.

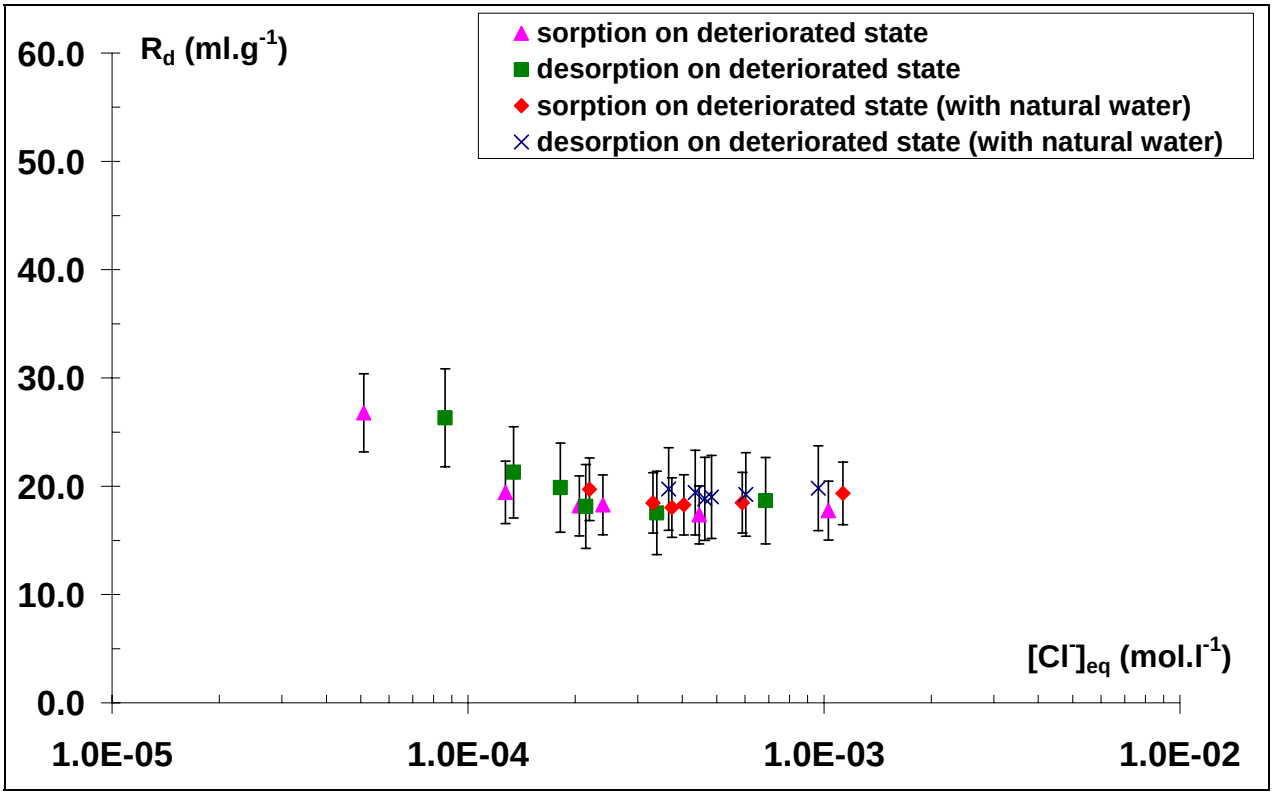

Figure 8: R_d measured after 3.5 months during sorption experiments and after 4.0 months during desorption experiments versus chloride concentration at equilibrium in solution

As in sorption condition, results of desorption isotherms at deteriorated state are very similar regardless of the supernatant solution used. Taking into account measurement uncertainties, one can conclude that, at equivalent chloride concentrations, the measured distribution ratios for sorption and desorption experiment are in the same range of values. In these conditions, ^{36}Cl sorption in deteriorated cement paste appears to be a reversible process.

4 Conclusions

The aim of this study was to quantify the retention of ^{36}Cl onto cement pastes constitutive of concrete that could be used for i-carbonaceous waste packages. ^{36}Cl retention properties depend on the alteration state of the cement paste and also on saturation effect generated by stable chloride ions provided by several sources in a repository (the "natural" water, the concrete itself…).

Wet chemistry measurements show that distribution ratios (R_d) values slowly increase during the first 20 days of contact time, and then, whatever the case, R_d reaches a steady mean value.

R_d values are relatively low. The maximum R_d value (35 $ml.g^{-1}$) was measured for the degraded state and at a low chloride concentration (4.8×10^{-5} $mol.l^{-1}$).

R_d values measured depend on the alteration state of the cement paste. Measurements at deteriorated states lead to conclude that the retention's process is reversible. Isotherms show that R_d values for ^{36}Cl strongly depend on the stable chloride concentration in solution. At high chloride concentration, the saturation effect is observed (non-linear sorption isotherm). Such results highlight the importance to know and quantify all main sources of stable chloride in order to be able to carry out performance assessment.

5 References

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