



Long-Term Behaviour of Concrete: development of operational model to predict the evolution of its containment performance

Application to cemented waste packages

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abstract

In order to describe the main phenomena during different stages of cement waste packages life-time and to predict the long-term behaviour (containment performance) of concrete, coupled experiments and modelling studies are achieved. With respect to logical methodology, improvement of these studies is accomplished. Degradation of concrete in low mineralised, carbonated and sulphated water lead to an evolution of chemical characteristics (dissolution/precipitation of solid phases) and of transport properties which must be included or coupled in retention/transport modelling of radio nuclides to predict containment performance.

keywords: concrete, long-term behaviour, degradation, phenomenology, modelling

1 - INTRODUCTION

Within the framework of the radioactive waste package conditioning of intermediate level to long-lived waste, hydraulic binders are used not only as encapsulation or blocking up materials, but also for the conception of containers and super-containers.

In order to take into account the main processes implicated in concrete alteration and to have an overall view on the potential phenomena involved in the different stages of concrete life in nuclear waste containment, a first step is to build a methodology. Review of scientific knowledge on the physical and chemical behaviour of hydraulic binders allows to identify and to sketch potential events describing the concrete evolution in close or open system (in unsaturated and saturated conditions). In relationship with this approach, phenomenological studies have been performed in order to understand each elementary process by simplified experimental tests. This paper presents results obtained concerning concrete evolution in a saturated open system. The main phenomena, having a tendency to modify the confinement properties of cemented waste package in this system are:

- chemical degradation by a neutral or slightly basic ($\text{pH} < 11,5$) solution leading to dissolution / precipitation of mineralogical solid phases.
- carbonation linked to carbonate present in natural water. This type of degradation is mainly characterised by calcite precipitation in porous space.
- external sulfate attack leading to significant mechanical damage (cracking) related to the precipitation of secondary solid phases such as ettringite and/or gypsum.

When the phenomenological mechanisms are well understood, translating in mathematical formulation can be executed and the model is validated by comparison of the measured and calculated data.

Finally modelling of degradation (chemical and transport parameters evolution of concrete) coupled with transfer / retention model allow to predict the evolution of confinement properties for cemented waste package.

2- PRESENTATION OF THE METHODOLOGY

Alteration of the concrete waste package (loss of its containment properties) must be considered taking into account the different stages of its life: evolution in an unsaturated, open system (under a damp, gaseous atmosphere) then evolution in a saturated, open system (under water). Thus, this alteration can be due to either matter exchanges with outside (drying, re-saturation, atmospheric carbonation, leaching by water containing more or less corrosive species...), or to different interactions between its own components (waste/matrix/container: alkali-aggregate-reaction, neo-formation of ettringite, waste/matrix interaction,...) and/or thermal, mechanical and radiolytic stresses,...(see Figure 1).

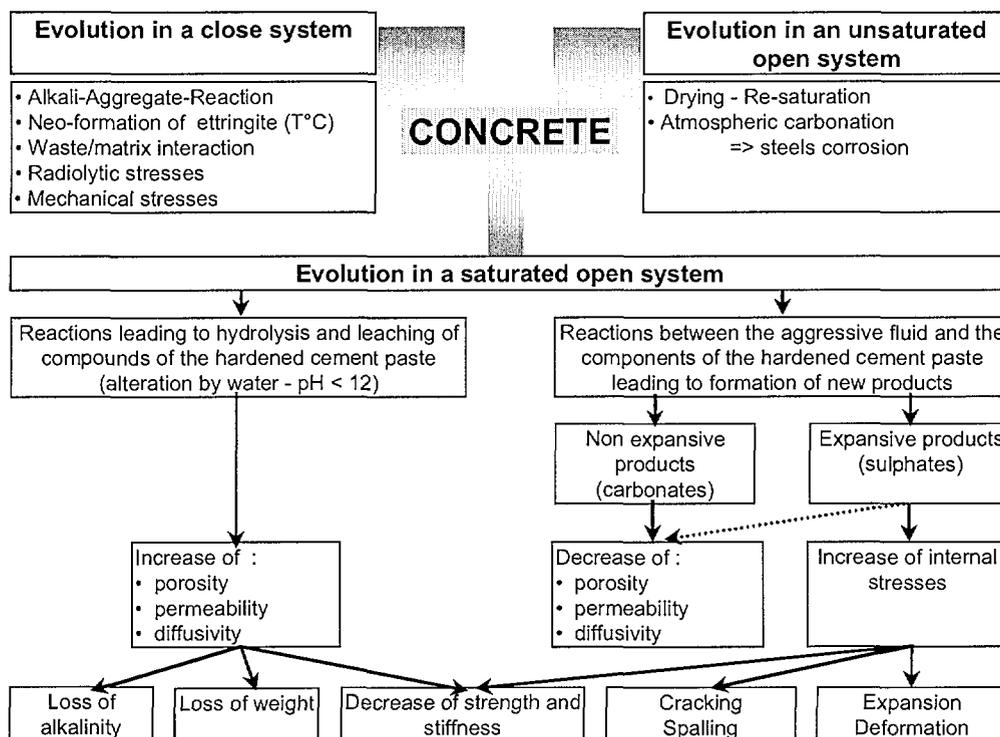


figure 1 : Schematic diagram of the different types of alterations that can be considered in a « concrete waste package »

Prediction of the very long-term evolution of waste packages performances requires the development of operational tools build on validated phenomenology.

The phenomenological comprehension relies on the experimental study of simplified systems allowing to assess the main parameters controlling involved mechanisms. Comparison of these experiments and phenomenological models enables to validate comprehension of the alteration mechanisms and also to quantify and to hierarchize them. From this hierarchy, simplifications are carried out, which will allow development of a predictive operational model. Validity and accuracy of this model are assessed in comparison with experimental results, phenomenological models, integrated experiments (coupling several alteration mechanisms) and similar old materials.

A degradation process consists of various partial processes: transport processes, chemical reactions and effects caused by changes of the phase assemblage and their feedback on transport parameters. The purposed of the research works is to understand each partial processes by simplified experimental investigations (part 3). The next step of these studies is to reach the description (knowledge of the main phenomenological mechanisms) of leaching condition and to be able to simulate (part 4) the impact of this leaching (main processes taken into account and correctly described).

3 - PRESENTATION OF THE PHENOMENOLOGY

3-1 LEACHING BY NEUTRAL OR SLIGHTLY BASIC SOLUTION

Concrete degradation by a neutral or slightly basic ($\text{pH} < 11.5$) solution leads to decalcification governed by diffusion. Local chemical equilibrium between solids and interstitial solution is also observed. The main phenomena observed correspond to the dissolution of portlandite ($\text{Ca}(\text{OH})_2$) and progressive calcium depletion of Calcium Silica Hydrates (C-S-H). This phenomena occurs between the dissolution front of portlandite to surface exposed to the external aggressive water [1],[2].

During degradation experiments, leached amounts of calcium, aluminium, sulphate, silica and hydroxyls have been measured. Except for aluminium which is practically not leached, amounts of the other ions leached are proportional to square root of time. Both ions, calcium and hydroxyls, represent the greatest part of leached ions with a proportion of one Ca^{2+} for two OH^- [3].

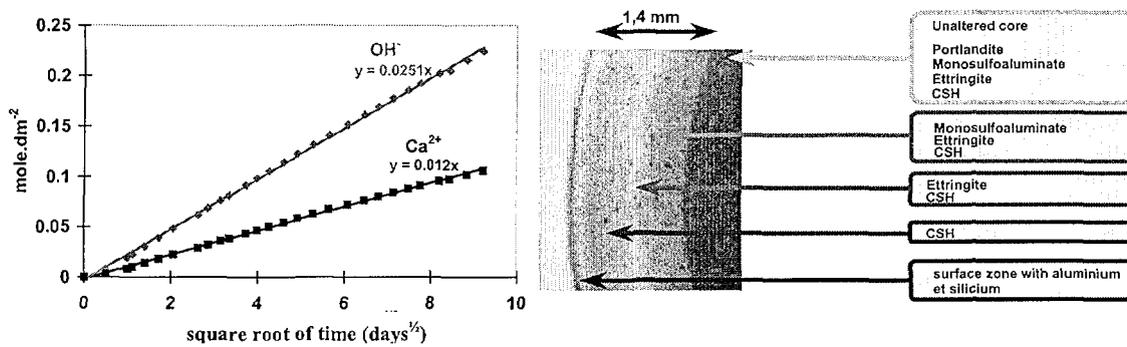


figure 2: cumulative amount of calcium and hydroxyls leached from OPC (CEM I) cement paste and solid zonation after three months of leaching in pure water (each zone in the degraded part is composed by a constant mineralogical assemblage with clearly defined dissolution fronts). Modelling evolution of transport parameters is also indicated [3].

The main consequences of this chemical degradation context, for a conventional material are an increase of the porosity (10 to 20 %) and an increase of the diffusion coefficient (a factor of 5 to 10), which leads to a reduction in the containment capacity.

3-2 DEGRADATION IN CARBONATED WATER

Leaching experiment with water containing HCO_3^- have been performed. The aim of this experiment was to understand phenomenological mechanism for degradation in such conditions and to evaluate impact of carbonation on degradation kinetics.

After 200 days of alteration in carbonated water a superficial layer composed by calcite and 4 zones inside sample have been observed [4], [5]. These zones correspond to :

- zone 1 in which calcite (CaCO_3) and C-S-H are the dominant solid phases. This zone is characterised by a reduced porosity relating to the uncorroded zone
- zone 2 with Ettringite and C-S-H. In opposition with previous zone and with uncorroded zone this layer shows an increase of porosity
- zone 3 corresponding to an intermediate zone between undegraded and both leaching previous zones containing portlandite and ettringite as mineralogical assemblage.
- zone 4 uncorroded zone

The presence of carbonates in the solution leads, in the case of a Portland cement material, to the precipitation of calcite in porosity and to a slowing down in decalcification process of the cement paste. The main consequences are significant decrease of degraded thickness, leached quantities and diffusivity in the degraded part (a factor of ~20 for the thickness and the leached quantities, and by a factor of 200 to 400 for the diffusion coefficient of the altered zone).

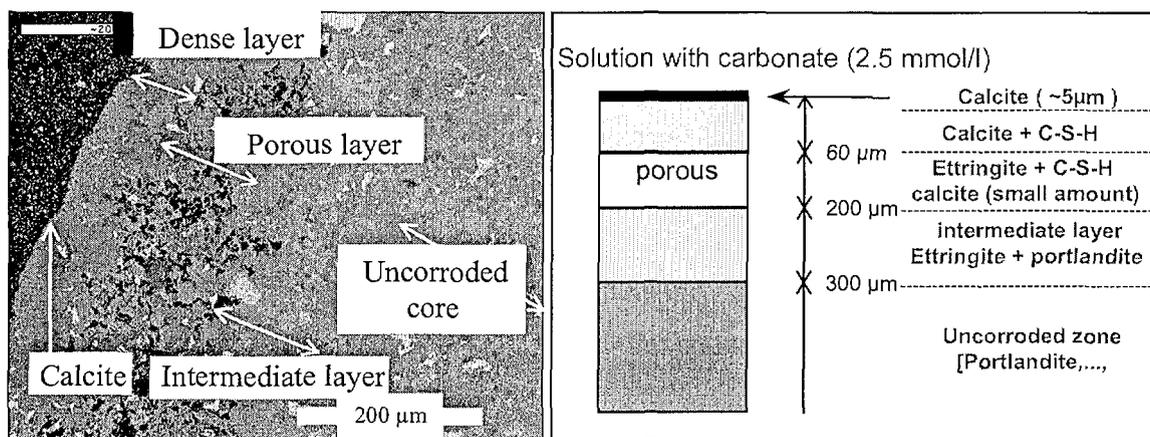


figure 3: microscopic aspect of CPA cement paste sample leached during 7 months in NaHCO_3 solution and description of mineralogical assemblage in each zone observed [5]

3-3 LEACHING OF CEMENT PASTE IN SULPHATED ENVIRONMENT

In order to study external sulphate attack and to carry out chemical and mechanical processes associated, leaching of cement paste in sulphated aggressive solution (15 mmol.L^{-1}) have been performed [6]. Experimental results show:

- 1- Simultaneous calcium leaching of the cement paste controlled by calcium concentration gradient between cement paste and leaching solution and penetration of SO_4^{2-} anions by diffusion from external water solution to interstitial cement paste solution.
- 2- Opposite flux of calcium and sulphate ions leads to reaction of sulfates with calcium, forming gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and to reaction between sulphates and anhydrous aluminates to generate ettringite mineral. The mineralogical profiles obtained by XRD analysis on degraded samples (tested during 5, 10 and 12 weeks in sulphate solution) show the existence of three zones :
 - a – the deepest zone with respect to the surface exposed, corresponding to a cement paste where portlandite content is significant and where no important reduction of calcium amount has taken place. In first approach and with respect to pure water degradation this zone corresponds to the unaltered part of the cement paste.
 - b – in which the mineralogical assemblage is constituted by portlandite – gypsum – ettringite.
 - c – where ettringite appears to be quantitatively the main phase
- 3- Cracking due to internal constraint.

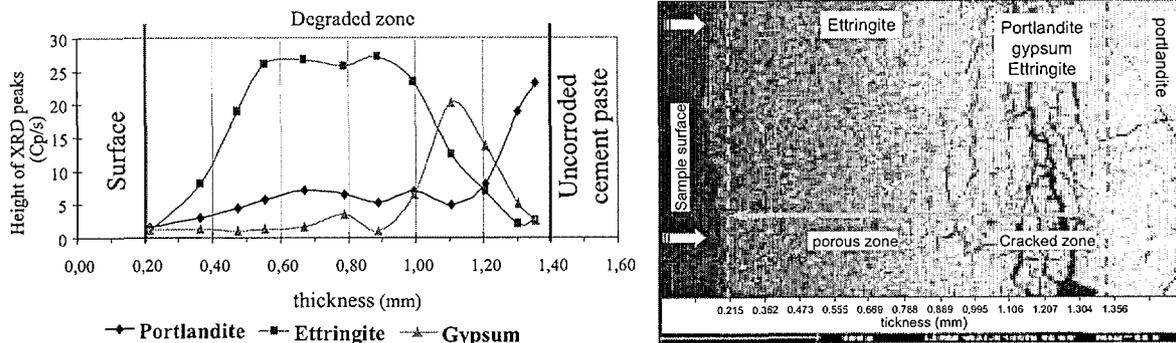


figure 4: XRD analysis in degraded zone of the cement paste sample leached in sulphate solution during 12 weeks and view of degraded sample with illustration of ions flux [6].

As long as cracking is not intense, precipitated sulphated solids have neither incidence on evolution of degraded thickness nor on leaching of calcium and hydroxyls [7]. Degraded thickness and amount of calcium leached for a same time of leaching are equivalent in sulphated water environment and in pure water. Therefore, the containment capacity evolves similarly to degradation in pure water.

4 - OPERATIONAL MODELLING

The modelling approach consists of the coupling of a degradation/decalcification model to a transport/retention model, progressively integrating the knowledge and data acquired in the course of the studies.

The operational model (Diffu-Ca) [8] has been validated (table 1) on the basis of OPC (ordinary portland cement) pure paste, mortar and concrete altered by low mineralised water [9]. It assesses, as a function of time, the profiles of calcium and hydroxyls (main components of the cement) in the interstitial solution, porosity and diffusion coefficient in the solid, as well as the quantities of leached calcium and hydroxyls.

The operational model Diffu-Ca assumes that the single evolution of calcium describes the leaching of cement based materials since all hydrates contain calcium. Therefore, the model Diffu-Ca is based on the resolution of the mass balance equation for calcium (Eq. 1).

$$\frac{\partial (\phi \cdot C_{Ca})}{\partial t} = \text{Div}(D_e \cdot \text{Grad}(C_{Ca})) - \frac{\partial S_{Ca}}{\partial t} \quad (\text{Eq. 1})$$

Where:
t : time

C_{Ca} : calcium concentration in pore solution
 S_{Ca} : calcium concentration in the solid phase
 ϕ : porosity
 D_e : effective diffusion coefficient of calcium in the porous media.

In Eq. 1, the first term on the right-hand side stands for the diffusion process of the calcium in the liquid phase, which is assumed to be governed by Fick's law. The second term of the right-hand side of Eq. 1 accounts for the dissolution process, which leads to an arrival of calcium in the liquid phase.

The equilibrium between the solid calcium phases (portlandite and C-S-H) and the calcium concentration in pore solution is well identified and leads to a relation between the calcium in the solid phase S_{Ca} and in the pore solution C_{Ca} . The porosity is directly linked to the mineralogy (type and proportions of the existing solid phases). The porosity is thus calculated as a function of the calcium concentration by assuming a rapid dissolution of portlandite followed by a progressive dissolution of ettringite and monosulphoaluminate.

The evolution of the effective diffusion coefficient (i.e. coefficient of global diffusion through porous material) is determined from experimental results obtained with a two-compartment diffusion cell on OPC cement pastes with different Water/Cement ratio and then different porosity. These experimental results lead to a relationship between effective diffusion coefficient and porosity.

		Experimental results	Diffu-Ca
OPC paste in low mineralised water (pH = 7)	calcium leached	0,012	0,0135
	degraded thickness	0,15	0,16
OPC paste in slightly basic (pH<11.5) solution	calcium leached	0,009	0,0125
	degraded thickness	0,12	0,16
OPC mortar in low mineralised water (pH = 7)	calcium leached	0,0061	0,0067
	degraded thickness	0,14	0,16
OPC concrete in low mineralised water (pH = 7)	calcium leached	0,0046	0,0045
	degraded thickness	0,15	0,16

Units : calcium leached : mol/dm²j^{1/2} --- degraded thickness : mm/j^{1/2}

table 1 : comparison between experimental results (see figure 2 for OPC paste in low mineralised water leaching experiment) and calculated kinetics for calcium leached and degraded thickness.

The modelling of alteration by a solution containing carbonates or/and sulphates is in progress. Experimental results have shown that leaching in carbonated water necessarily induces strong porosity variations and hence influences transport phenomena. In order to simulate carbonates action and calcite precipitation transport parameters will be adjusted in degraded zone relating to carbonate concentration. In this case, modelling should be only used to simulate leaching in term of calcium-leached amount and degraded thickness.

Improvement of this model is still in progress in order to include effect of carbonates, calcite precipitation and feedback on transport parameters. In this case, not only calcium-leached amount and degraded thickness will be assessed but also porosity and diffusion coefficient in the solid. A first simplified model have been developed and analytical equations have been resolved.

As long as cracking is not intense, precipitated sulphated solids have neither incidence on evolution of degraded thickness nor on leaching of calcium and hydroxyls. In agreement with previous results and with respect to effective diffusion coefficient determined from experimental measurement the degraded zones due to sulphated water and low mineralised water leaching have the same transport characteristics. In order to describe chemical processes induce by sulphate degradation, phenomenological model and translating in operational model are in progress.

Diffu-Ca model coupled with a transport/retention model will allow to predict migration of radionuclides to take into account:

- in first time only the effect of the transport parameter evolutions (diffusion coefficient) due to chemical reactions.
- in second time the effect of diffusivity evolution and the influence due to chemistry evolution in the degraded layer (pH, Ca/Si ratio of C-S-H) on the radio nuclides solubility.

The Diffu-Ca model, integrated into the numerical tool developed by CEA (CASTEM 2000), will predict the evolution of the containment of a radioactive element which would not "chemically interact" with concrete, in the case of its external alteration by water.

5 – CONCLUSIONS

In agreement with a logical approach defines with respect to scientific knowledge on concrete degradation in unsaturated and saturated environment and in order to take into account the main phenomena involved in nuclear waste containment during different stages of waste package life, both experimental and modelling studies have been achieved. The studies carried out for the comprehension of concrete alteration mechanisms in saturated environment have been focused on low mineralised, carbonated and sulphated water degradation.

The main consequences of leaching in low mineralised water, for a conventional material are an increase of the porosity and an increase of the diffusion coefficient due to dissolution of portlandite, which leads to a reduction in the containment capacity.

The presence of carbonates in the solution leads, in the case of a portland cement material, to precipitation of calcite in porosity and to a slowing down in decalcification process of the cement paste. The main consequences are significant decrease of degraded thickness, leached quantities and diffusivity in the degraded part

As long as cracking is not intense, precipitated sulphated solids have neither incidence on evolution of degraded thickness nor on leaching quantities of calcium and hydroxyls. Degraded thickness and amount of calcium leached for a same time of leaching are equivalent in sulphated water environment and in pure water. Therefore, the containment capacity evolves similarly to degradation in pure water.

Improvement of operational modelling consists of the coupling of a degradation/decalcification model to a transport/retention model, progressively integrating the knowledge and data acquired in the course of the studies.

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