

Long-term behaviour of concrete in water saturated media - Experimental and modelling approach

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Abstract – *In the context of the nuclear long-lived management, cement-based materials are currently used for waste encapsulation and containers development. Such materials are also likely to be used for engineered barriers in deep repositories. Various types of cement – CEM I, CEM V – have been currently studied, mainly to evaluate materials long-term durability. Studies have been performed on the leaching behavior of hardened cement pastes based on these cements. The effect of temperature is taking into account. Leaching experiments for 25°C, 50°C and 85°C were carried out with a standard test developed at CEA. Experimental results were analysed and calculations were made to estimate calcium fluxes and degraded thicknesses. Experimental and modelling results were compared.*

INTRODUCTION

This thematic investigates the processes causing irreversible chemical and structural alterations of cementitious materials resulting in macroscopic loss of its properties. The final objective is to predict the long term behavior and to assess the residual transport and mechanical properties during the life time of concrete structures used in the context of nuclear waste management. Experimental studies and improvement of modelling tools are therefore essential.

The degradation processes relevant for the repository or for the waste canisters have been reviewed, identified in a research program document [1]. The timescales and the final degradation products depend on many variables such as the nature of the aggressive water, the temperature, the type of cement used, the amount of mixing water (water/cement mass ratio), the type of aggregate, the type of admixture and additions. To fully describe the degradation processes, all these variables should be considered.

The study of deteriorations in geological environment imposes to taking into account the chemistry of the repository site water. The first step consists of examining finely the interactions of a material with an identified water type (de-ionized water, carbonated water, sulphated water) taken separately. Secondly the purpose is to study the behavior when these ions are present in water simultaneously and close to the natural site water chemistry.

Only the effect of the temperature (25°C, 50°C, 85°C) on the degradation processes is presented and for two types of cement based material: a portland cement (CEM I) and a blended blast furnace, slag cement and fly ashes (CEM V)

EXPERIMENTAL RESULTS ON THE HYDROLYSIS AND DECALCIFICATION OF THE CONCRETE

Under water environment, the mineralogical evolution of the concrete phases is expected to be dominated by the dissolution of portlandite ($\text{Ca}(\text{OH})_2$) and the decalcification of the calcium silicate hydrate (C-S-H) gel. Both phases represent about 70% of the cement paste volume. In order to evaluate the dynamic propagation of the degraded thickness, and to carry out phenomenological knowledge, leaching experiments have been achieved using experimental procedure developed at the CEA research laboratory on the concrete behavior [2]. The samples are leached in deionised and decarbonated water which is thermo-regulated at $25 \pm 1^\circ\text{C}$; $50 \pm 1^\circ\text{C}$ and $85 \pm 1^\circ\text{C}$.

Such an experimental protocol allow to carried out the amount of chemical compound leached out of the cement paste (OH^- , Ca^{2+} , SO_4^{2-} , Al^{3+} ...) and the thickness of the degraded zone. Optical microscopy characterization, XRD profiles, SEM analysis on solid samples are also performed in order to characterized chemical and mineralogical evolution.

For each sample and each temperature several leaching tests have been performed for various dates (3, 6, 12 months) allowing to carried out a kinetic of the degradation front propagation (limited by portlandite dissolution front).

Leaching solution analysis

For each temperature the main ions leached are OH^- and Ca^{2+} ions and their evolutions must be fit by square root of time laws. The amount of leached calcium become more intense when the temperature increase. For each type of cement paste (CEM I – fig. 1 and CEM V – fig. 2), relating to 25°C, total amount of calcium is multiply by about 1.7 for 50°C and about 3 for 85°C.

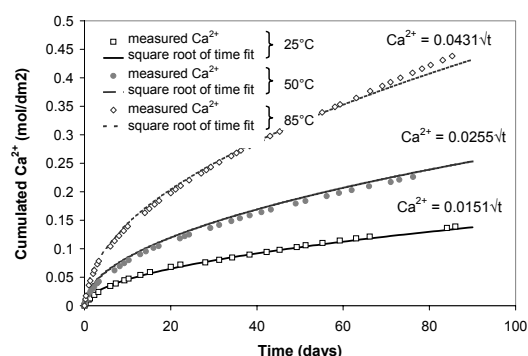


fig.1: amount of calcium leached out of CEM I cement paste

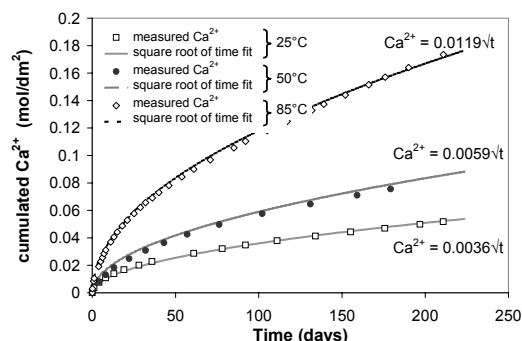


fig.2: amount of calcium leached out of CEM V cement paste

Degraded thickness evolution

The evolution of the thickness of degraded zone due to the leaching also increase with the temperature increasing (table 1). With reference to 25°C, the increasing of degraded front propagation by square root of time unit is about equal to the same factor carried out for calcium leached amount (1.7 for 50°C and 3 for 85°C)

TABLE 1: kinetics of degradation front propagations (mm/ $\sqrt{\text{days}}$)

	25° C	50° C	85° C
CEM I	0.19	0.29	0.55
CEM V	0.04	0.07	0.14

HYDROLYSIS / DECALCIFICATION MODELLING

Leaching modelling assumes to describe coupled chemical and transport processes. Chemical dissolution of C-S-H can be modeled with more or less complex approaches based on thermodynamic or solubility. The thermodynamic way allows to take into account not only C-S-H and portlandite but also the other phases included in the cement paste. The accuracy of calculation depends essentially on the used thermodynamic data. As noted by several authors, the feedback of dissolution or precipitation on transport parameters must be taken into account in order to have a rigorous approach. Coupled chemical transport tools have been developed including specific chemical/transport retroaction laws [3] [4] [5]. They are yet used to model concrete degradation [4] [6] [7]. Regarding an operational point of view, modeling must be easily performed with a little set of variables. Such a type of simplified model have been carried out.

Only majors equations and variables are kept. The influence of the simplifications on the final results have been evaluated with respect to the phenomenological model and with respect to the experimental data.

The simplified model, named Diffu-Ca, assumes that the single evolution of calcium describes the leaching of cement based materials.

Therefore, the model Diffu-Ca is based on the resolution of the mass balance equation for calcium (Equation 1):

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

with:

C_{Ca} = calcium in the pore solution

S_{Ca} = calcium in the solid phase

D_e = effective diffusion coefficient

Φ = porosity

t : time

In this equation calcium solid source term member $\left(\frac{\partial S_{Ca}}{\partial t}\right)$ is link to the equilibrium between the main solid calcium phases (portlandite and C-S-H) and the calcium concentration in pore solution

The relationship between the calcium in the solid phase (S_{Ca}) and the calcium in the pore solution (C_{Ca}) have been studies by several authors for a temperature range of 17 to 30°C [8], [9], [10], [11]. A smaller number of data [7], [12], [13] for elevated temperatures allow nevertheless to build equilibrium relationship for 50°C and 85°C.

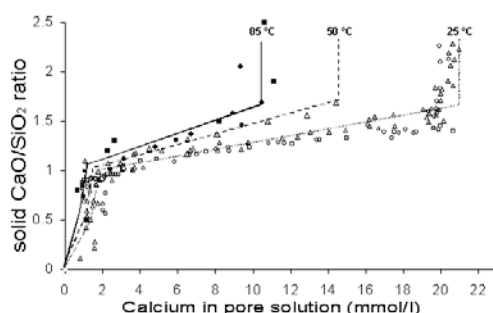


fig.3: relationship between CaO/SiO₂ ratio in solid and concentration of calcium in pore solution

The porosity (Φ) is directly linked to the mineralogy (type and content of the existing solid phases) and corresponds to a volume balance relationship (equation 2).

$$\Phi = 1 - V_{CH} - V_{C-S-H} - V_{Ett} \quad (2)$$

with:

Φ = porosity

V_{CH} = volume fraction of portlandite

V_{C-S-H} = volume fraction of C-S-H

V_{ett} = volume fraction of ettringite

As shown previously, the occurrence and the amount of portlandite, C-S-H and ettringite must be directly linked to the concentration of calcium in pore solution. Then the porosity should be calculated as a function of the calcium concentration in pore solution.

The evolution of the effective diffusion (D_e) coefficient is determined from experimental results. These experimental data also lead to a relationship between effective diffusion

coefficient and porosity [14] [15]. This relationship have been carried out for 25°C.

Studies on the effect of temperature on effective diffusion coefficient in concrete show that D_e increase with temperature [16]. This evolution is mainly due to the decreasing of water viscosity (Stokes-Einstein law) in pore structure.

These data allow to establish an Arrhenius law linking effective diffusion coefficient and temperature (equation 3).

$$D_e = D_{e(0)} \exp\left[-\frac{E^*}{RT}\right] \quad (3)$$

with

T = temperature in Kelvin degree

R = gas constant (8,314 J/(mol.°K))

In this equation, the activation factor E^* is the same in CEM I and CEM V cement base material. Only the diffusion coefficient $D_{e(0)}$ is different.

It is possible to establish a ratio between diffusion coefficient for two temperature T_1 and T_2 and could be defined as follows:

$$\frac{D_e(T_2)}{D_e(T_1)} = \exp\left(5.29 \cdot 10^3 \left[\frac{1}{T_1} - \frac{1}{T_2}\right]\right) \quad (4)$$

with

T1 and T2 = temperature in Kelvin degree

Relating to 25°C, effective diffusion coefficient will be multiplied by 4 for 50°C and by 20 for 85°C.

For each temperature, relationship between porosity and diffusion coefficient is determined allowing to perform calculations taking into account the effect of temperature on the degradation of concrete.

COMPARISON BETWEEN EXPERIMENTAL RESULTS AND MODELLING

The model assesses, as a function of time, the profiles of calcium and hydroxyls (main components of the cement) in the interstitial solution, the porosity and the diffusion coefficient in the solid, and as well the quantities of leached out calcium and hydroxyls.

Output of model must be directly compare with experimental results. Such a comparison is presented in table 2 for CEM I cement paste and in table 3 for CEM V cement paste.

TABLE 2: comparison between experimental results (exp.) and modelling (mod.) for CEM I cement paste leaching.

		Amount of leached calcium (mol/dm ² /√days)	Evolution of degraded thickness (mm/√days)
25°C	exp.	0.015	0.19
	mod.	0.015	0.17
50°C	exp.	0.025	0.29
	mod.	0.026	0.31
85°C	exp.	0.043	0.55
	mod.	0.045	0.54

TABLE 3: comparison between experimental results (exp.) and modelling (mod.) for CEM V cement paste leaching.

		Amount of leached calcium (mol/dm ² /√days)	Evolution of degraded thickness (mm/√days)
25°C	exp.	0.0036	0.04
	mod.	0.0031	0.038
50°C	exp.	0.0059	0.07
	mod.	0.0057	0.071
85°C	exp.	0.0119	0.14
	mod.	0.0126	0.15

DISCUSSION AND CONCLUSION

This study compare the leaching behavior of various hardened cement pastes prepared with CEM I and CEM V cements. The effect of temperature have been investigated. For all temperature the experimental results obtained on leaching solution and on degraded sample after a degradation test based on a leaching procedure in pure water, confirmed that the decalcification process was controlled by diffusion.

For each type of cement base material (CEM I and CEM V) the temperature increase the degradation processes. The acceleration of degradation is mainly due to the increasing of diffusivity with temperature though chemical

solubility of main phases (portlandite and C-S-H) decrease.

Concerning the modelling aspect, Diffu-Ca code is able to generate calcium leached amount and degraded thicknesses which comply with the experimental data for various temperature (<85°C).

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