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Youssef El Bitouri, Laurie Buffo-Lacarriere, Alain Sellier, Xavier Bourbon. Modelling of chemical evolution of low pH cements at long term. NuwCem 2014, Avignon, France, Jun 2014, Avignon, France. hal-03759855

HAL Id: hal-03759855

<https://hal.science/hal-03759855>

Submitted on 24 Aug 2022

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NuwCem 2014, Avignon, France

Modelling of chemical evolution of low pH cements at long term

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Abstract: In the context of the underground radioactive waste repository, low-pH cements were developed to reduce interactions between concrete and clay barrier. These cements contain high proportions of mineral additions like silica fume, fly ash or blast furnace slag for example. The high ratio of cement replacement by pozzolanic additions allows to reduce the pH by a global reduction of Ca/Si ratio of the hydrates (according to the one observed on CEM I pastes). In order to predict the short term development of the hydration for each component of this cement, a multiphasic hydration model, previously developed, is used. The model predicts the evolution of hydration degree of each anhydrous phase and consequently the quantity of each hydrate in paste (CH, aluminates, CSH with different Ca/Si ratios). However, this model is not suitable to determine the long term mineralogical and chemical evolution of the material, due to the internal change induced by chemical imbalance between initial hydrates. In order to evaluate the chemical characteristics of low pH cement based materials, and thus assess its chemical stability in the context of radioactive waste storage, a complementary model of chemical evolution at long term is proposed. This original model is based on “solid-solution” principles. It assumes that the micro-diffusion of calcium plays a major role to explain how the different Ca/Si ratio of initial C-S-H tends together toward a medium stabilized value. The main mechanisms and full development of the model equations are presented first. Next, a comparison of the model with experimental data issue from EDS analysis on low pH cement allows to test the model.

Key Words: Low pH cement, chemical evolution, modeling

1. Introduction

One of the main concerns in the context of geological repository for radioactive waste is the chemical and physical degradation of the clay barrier (bentonite and host-rock) due to the high pH of the pore solution of a conventional cementitious material (Portland type), and the high increase in temperature caused by the hydration of cement within very massive elements. Research has therefore been carried out to develop “low-pH cements” compatible with this application. The principle of formulation of low pH cement is that a high amount of Portland cement is replaced by high amount of silica materials such as silica fume, blast furnace slag, fly ash. The main hydrates that form in hydrated Portland cement are “jennite-like” C–S–H (with a high C/S), portlandite, ettringite, AFm and AFt (Adenot, 1992). The addition of high amount of silica fume leads to the consumption of portlandite to form “tobermorite-like” C–S–H (with lower C/S). However, a large amount of residual silica remains unhydrated. At long term, the surplus of silica reacts with the high calcium C–S–H to form progressively more low calcium C–S–H (Lothenbach et al., 2011).

To assess the behavior of these materials at the long term, it is necessary to predict their chemical evolution. A multiphase hydration model (Buffo-Lacarrière et al., 2007) is used to predict the short-term development of the hydration for each component of the binder. The model predicts the evolution of hydration degree of each anhydrous phase and consequently the quantity of each hydrate in paste (CH, aluminates, CSH with different Ca/Si ratios). As it was developed for early age applications, the model is based on a fixed stoichiometry of each hydrate produced by the different anhydrous (CSH from clinker, CSH from pozzolanic additions, CH, aluminates). For binders with high content of silica, this model reveals not suitable to determine the long term mineralogical and chemical composition of the material, due to the internal change induced by chemical imbalance between hydrates. In order to evaluate the chemical characteristics of low pH cement based materials, and thus assess its chemical stability in the context of radioactive waste storage, a complementary model of chemical evolution based on a variable stoichiometry is proposed. The results given by hydration model constitute the initial conditions in terms of chemical data for modelling the chemical evolution at long-term.

The main mechanisms and full development of the model equations are presented first. Then, an application for a binary low-pH cement (clinker and silica fume) is presented. We will show, in particular, how the model can do evolve the initial C/S ratios of CSH toward a medium stabilized value.

2. Model of chemical evolution of low pH cement

Chemical attacks of cementitious materials correlate strongly with the cement hydration processes. In the latter case, anhydrous grains gradually hydrate by following phenomena under/over saturation causing their dissolution and precipitation of hydrates. Then, these reactions (dissolution/precipitation) are kinetically limited by diffusion phenomena through porosity of material. Furthermore, dissolution and/or precipitation of solid phases occur when the material is exposed to an aggressive environment. The kinetic of these changes is also governed by the diffusion of species through the porosity.

The chemical stability of the solid phases in cement paste can be evaluated from a thermodynamic and kinetic approach. The thermodynamic approach uses the analysis of the solubility of the solid phases and allows knowing the equilibrium states. This is based on the assumption of local chemical equilibrium which considers equilibrium between solid and the solution in contact. Any variation in the composition of this solution would lead to a transformation in the solid phase (Adenot, 1992). The kinetic aspect is mainly based on an approach of reactive transport.

2.2. Main mechanisms

The cement notation is adopted to write the formula of oxides. Table 1 presents the notation system adopted for the modelling.

Table 1.Nomenclature

i	Clinker		Silica Fume		...	
k j	anh	hyd	anh	hyd	anh	hyd
C	C	CH	-	-		
S	S	C _{1,7} SH	S	C _{1,15} SH		
A+F	-	C ₃ AH ₆ AFm, Aft...	-	-		

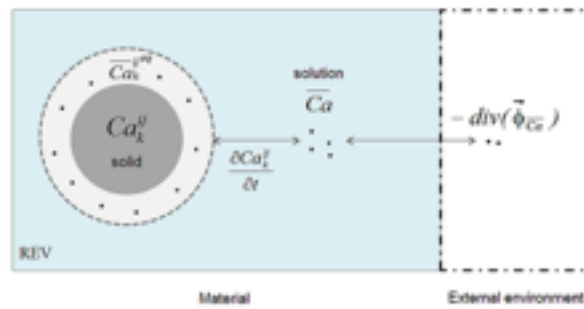


Fig. 1. Main mechanisms

The chemical evolution model assumes that the single evolution of calcium describes the chemical evolution of cement-based materials (Gérard et al., 1998) (only the calcium in solution is assumed to diffuse) (Fig.1). Therefore, the model is based on the resolution of the mass balance equation (eq.1) for calcium only:

$$\frac{\partial(w\overline{Ca})}{\partial t} = -div(\vec{\phi}_{\overline{Ca}}) + S_{\overline{Ca}} \quad (1)$$

And:

$$S_{\overline{Ca}} = -\sum_{ij,k} \frac{\partial Ca_k^{ij}}{\partial t} \quad (2)$$

Where: Where t is the time, \overline{Ca} is the calcium concentration in pore solution (mol/m³ in solution), Ca_k^{ij} is the solid calcium (mol/m³ of material), w is the water content. The source term $S_{\overline{Ca}}$ describes the intake of calcium in the liquid phase by dissolving solid phases, and calcium intake in the solid phase by precipitation of liquid calcium (eq.2).

Moreover, the dissolution and precipitation of calcium solid phases obey the chemical equilibrium (Adenot, 1992) (Fig.2). The dissolution of solid calcium occurs when the global concentration of calcium (\overline{Ca}) is lower than the concentration in equilibrium with the solid ($\overline{Ca}_k^{ij^{eq}}$) which depends only on Ca_k^{ij} . When the calcium concentration is greater than the local concentration, the solid calcium precipitates:

$$\frac{\partial Ca_k^{ij}}{\partial t} = \frac{I}{\tau_k^{ij}} \left(\overline{Ca}_k^{ij^{eq}} - \overline{Ca} \right) \quad (3)$$

The equilibrium concentrations $\overline{Ca}_k^{ij^{eq}}$ are determined thanks to the solid/liquid thermodynamic equilibrium which is summarized into a global equilibrium curve presented in Fig.2. This curve presents C/S molar ratio of solid phases as function of liquid calcium concentration (at equilibrium). When the concentration varies from 0 to 2 mmol/l, the ratio C/S roughly increases. This abrupt change in the solid without significant change in the liquid characterizes an invariant point where coexist silica gel and C-S-H with low C/S. Between 2 and 19 mmol/l, the C/S ratio increases slowly which describes a partial calcification of C-S-H. Between 19 and 22mmol/l, the C/S ratio roughly increases. This invariant point characterizes the existence of C-S-H with high C/S ratio (1,7-1,8) and portlandite. For calcium aluminates, the stability domain is located in the second zone, ie, between 2 and 19 mmol/l (Adenot, 1992). In this modeling, it is assumed that the dissolution/precipitation equilibrium of anhydrous calcium corresponds to the last zone (from 19 to 22mmol/l).

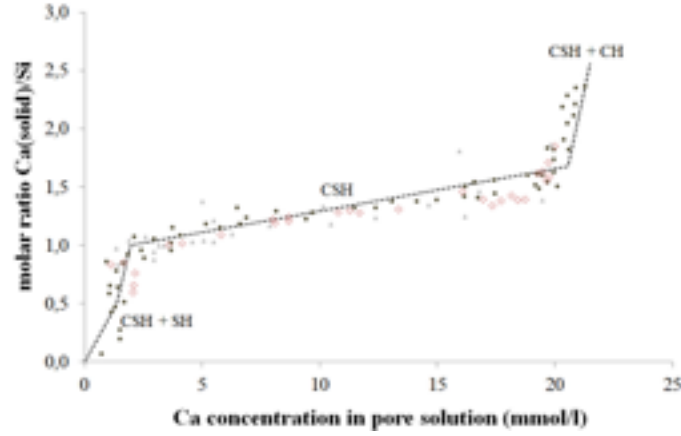


Fig. 2. Equilibrium solid calcium / liquid calcium

It should be noted that, reactions of dissolution/precipitation depend, not only of the equilibrium, but also of the micro-diffusion of calcium from the most concentrated site to the least concentrated site (Gawin et al., 2008). So, to take this into account, a characteristic time which describes the delay of reactions (dissolution/precipitation) due to the micro-diffusion of calcium is defined:

$$\tau_k^{ij} = \tau_{ref} \cdot f(Ca_k^{ij})^l \cdot g(w) \cdot h(T) \quad (4)$$

Where:

- τ_{ref} : reference characteristic time,
- $f(Ca_k^{ij})$: accessibility of solid calcium
- $g(w)$: influence of water content,
- $h(T)$: influence of temperature

The function f in equation (II-4) models the effect of the hydrates layer, surrounding the anhydrous compounds, on the diffusion of calcium. For hydrates, as their surface is directly accessible, the function is equal to 1 (no reduction of the accessibility). For anhydrous phases able to retain or release calcium, the function is lower than 1 because their accessibility is reduced by the layer of hydrates created at their surface during hydration. As the decalcification of this layer enhances micro-diffusion of calcium, the function f is increasing with the decrease of calcium content. As this accessibility is managed by diffusion an exponential function is chosen (Table.2).

Table 2. Values of f (Ca)

k	$f(Ca_k^{ij})$	
	anhydrous	hydrates
j		
C	$\exp\left(-\int \frac{\partial Ca_S^{ihyd}}{\partial t} dt\right)$	1
S	$\exp\left(-\int \frac{\partial Ca_S^{ihyd}}{\partial t} dt\right)$	1
A+F	untreated	1

The function g in equation (II-4) models the effect of water content:

$$g(w) = \frac{I}{w} \quad (5)$$

The function h in equation (II-4) models the thermal activation of the phenomenon of micro-diffusion. This data is described by a thermal activation law as it was proposed and experimentally validated by (Peycelon et al., 2006), with an activation energy E_a^D of 44 kJ/mol :

$$h(T) = \exp\left(\frac{E_a^D}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (6)$$

2.2. Chemical evolution binder B₄₀

2.2.1. Input data and model parameter

The low-pH cement modelled (named B₄₀) is that used in the experiments described by (Bach et al., 2012). This cement contains 60% of Portland cement and 40% of silica fume. It has a pore solution pH in the range 11-11,5. So as to predict the short term development of the hydration for each component of this cement, the multiphasic hydration model is used (for a complete explanation of the hydration model, see Buffo-Lacarrière and al., 2007). The model predicts the evolution of hydration degree of each anhydrous phase, and thus, the quantity of each solid phase in paste as presented in Table 3. This mineralogical composition is predicted at 28 days. The latter is chosen as moment of transition from the hydration model to the equilibrium model. The water content of paste is of about 0,41 m³/m³.

Table 3. Quantity of each solid phase in paste predicted by the hydration model at 28 days

Solid phase	Anhydrous clinker	CSH (C/S=1,7)	CH	Aluminates	Anhydrous silica fume	CSH (C/S=1,15)
Quantity (mol/m ³ of paste)	1101 (C) 338 (S)	2207	22	274	5176	2112

These concentrations are the input data of the equilibrium model. Table 4 presents these concentrations is the system of notations used for the model. We can note that the main part of the silica is content in the residual anhydrous of silica fume which will mainly “attract” calcium of other solid phases.

Table 4. Mineralogical composition at 28 days (mol/m³ of paste)

i	Clinker		Silica Fume	
k j	anh	hyd	anh	hyd
C	1101	22	-	-
S	338 (3,4% of total silica)	2207 (22,4% of total silica)	5176 (52,6% of total silica)	2112 (21,5% of total silica)
A+F	-	274	-	-

The only model parameter is the reference characteristic time managing the micro-diffusion of calcium in the neighborhood on the silica phase (eqs 3 and 4). This parameter must be fitted on experimental results. In this study, it was calibrated on the measurements of liquid calcium concentrations performed by (bach et al., 2012).

2.2.2. Calcium equilibrium relation applied to the binary paste

As the calcium in solution is used to characterize the chemical equilibrium, the equilibrium calcium concentrations for each compound are calculated using the equilibrium curve by linear interpolation of the characteristic points (Fig.3, Fig.4). The average of these concentrations is the initial calcium concentration.

Table 5. Equilibrium calcium concentration of anhydrous calcium (clinker_anh_C), portlandite (clinker_hyd_C) and aluminates (clinker_anh_A+F) (mol/m³ of paste)

Ca _{eq} (mmol/l)	Solid calcium of clinker_hyd_C and clinker_anh_C	Solid calcium of clinker_hyd_A+F
0	0	0
2	0	10
19	10	995
22	1120	996
22,1	1123	997

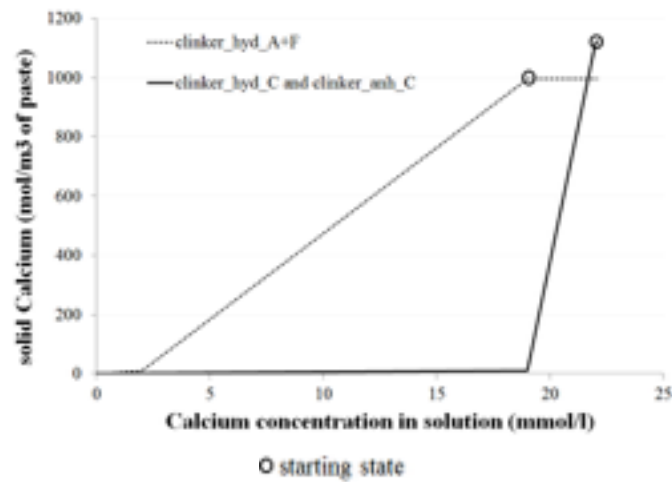


Fig. 3. Equilibrium curve of anhydrous calcium, portlandite (clinker_hyd_C and clinker_anh_C) and calcium aluminates (clinker_hyd_A+F)

Table 6. Equilibrium calcium concentration of each silica compound (mol/m³ of paste)

C_{aeq} (mmol/l)	C/S	Solid calcium of clinker_hyd_S	Solid calcium of clinker_anh_ S	Solid calcium of SF_hyd_S	Solid calcium of SF_hyd_S
0	0	0	0	0	0
1,5	0,5	1104	169	1056	2588
2,0	1,0	2207	337	2112	5176
21,0	1,7	3752	575	3590	8799
21,6	1,7	3752	575	3590	8799

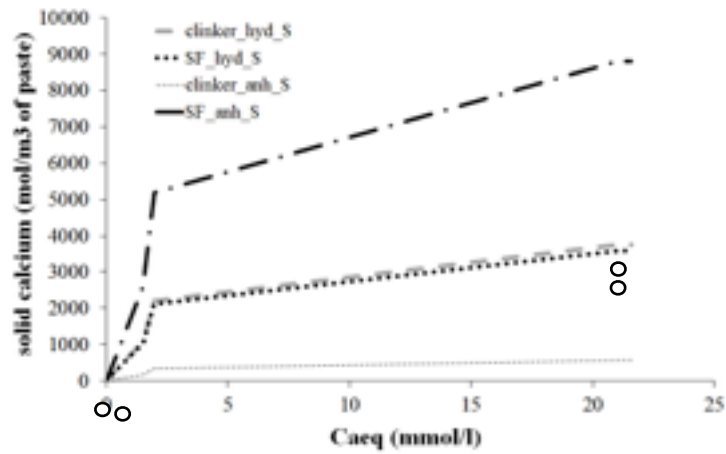


Fig. 4. Equilibrium of each silica compound

According to equilibrium diagram, there exist local concentration gradients due to the chemical imbalance between initial compounds (given by hydration model), which induces microdiffusion of calcium (Fig.5). An internal re-equilibrium of calcium occurs, and the system evolves toward a chemical equilibrium state.

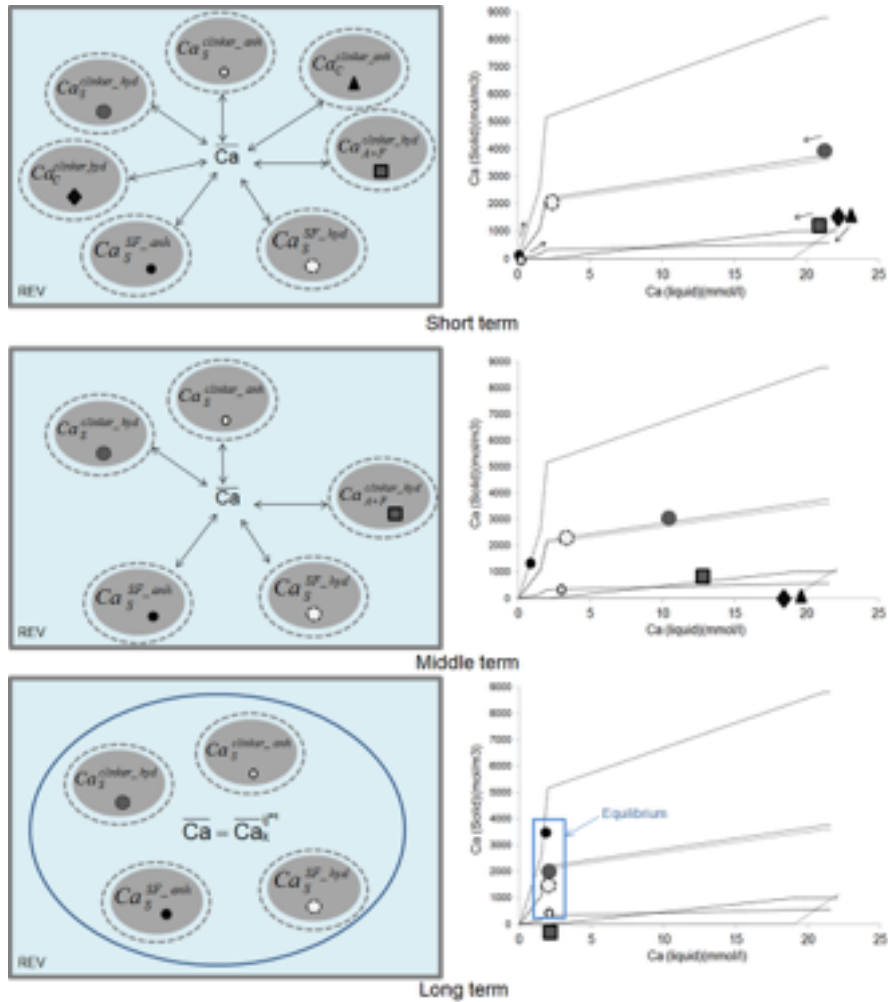


Fig.5. Chemical evolution of binary binder B40

2.2.3. Calibration of model parameter

As previously seen, the model parameter used in Eqs 3 and 4 must be calibrated on experimental results. The measurements of liquid calcium concentration were performed by (Bach et al. 2012). The evolution of these concentrations allows estimating the reference characteristic time. Fig.6 compares measured and predicted liquid calcium concentrations for a characteristic time equal to $1,6 \cdot 10^4 \text{s}$. For comparison, the characteristic times of micro-diffusion given by (Gawin et al.,

2008) have values ranging from about $5,8 \cdot 10^2$ s for the ettringite to $1,17 \cdot 10^4$ s for the portlandite. As can be seen in Fig.6, the numerical results reproduce the progressive decrease in calcium concentration. Furthermore, measured values are not significantly different than the calculated values. The liquid calcium concentration at equilibrium is of about 2 mmol/l.

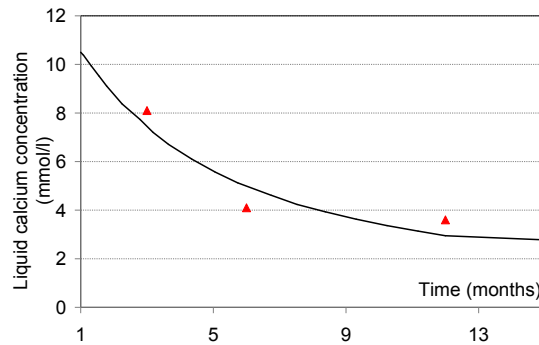


Fig. 6. Evolution of liquid calcium concentration (Bach et al., 2012)

2.2.4. Illustration of calcium re-equilibrium on the binary binder

Fig.7 shows the evolution of solid calcium of each compound over time. Dissolution of portlandite and anhydrous calcium (hyd and anh_C) occurs rapidly, when calcium concentration is lower than 22 mmol/l, followed by a progressive dissolution of calcium aluminates (hyd_A+F). Calcium released participates in the calcium rebalancing of silica compounds. The calcification/decalcification of silica compound (anh_S) (hyd_S) occurs progressively, and leads to system at chemical equilibrium.

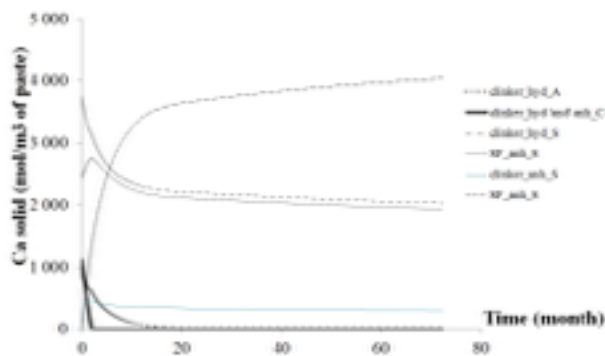


Fig. 7. Evolution of solid calcium

The evolution of the C/S molar ratio allows visualizing the calcification/ decalcification of silica compounds (Fig.8). For the clinker anhydrous silica (clinker_anh_S), the C/S molar ratio increases very rapidly to a maximum value and then gradually decreases. The rapid increase is due to the amount of clinker anhydrous silica which represents only 3,4% of the total silica. The molar ratio of hydrated silica (SF_hyd_S), initially at 1,15, increases slightly and then gradually decreases, while the anhydrous silica of SF (SF_anh_S) and clinker hydrated silica (clinker_hyd_S) follow the same trend, on the rise for the first or down for the second. The slope changes (at 2 and 20 month) are due to the presence of calcium sources (anhydrous calcium and aluminates), and the different characteristic times used.

The C/S molar ratio in the B40 paste hydrates (cured at 20°C) was estimated by EDS analysis on polished cross sections prepared from 6-month old samples (Bach et al, 2012). The distribution mode is $0,85 \pm 0.05$. Bach indicates that the system tends towards this value at long term, which is in good agreement with the calculated value (Fig.8.).

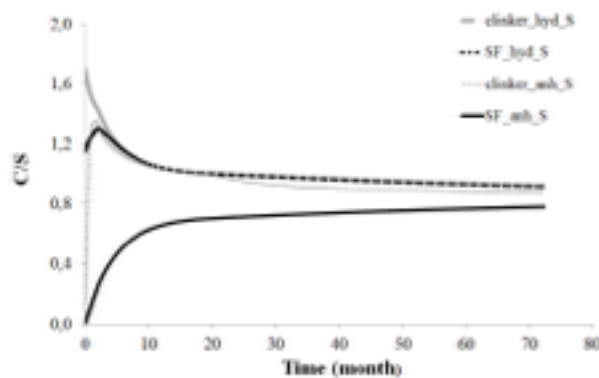


Fig. 8. Evolution of C/S molar ratio of each silica compound

2. Conclusion

To predict the long-term evolution of concrete used for the radioactive waste repository, a modelling of the chemical evolution has been presented. This modelling is based on “solid-solution” principles. Its resolution with a numerical method requires the knowledge of the equilibrium relation between the solid and the liquid phase, the quantity of each compound in paste, the variation of the water content and the calibration of kinetic parameter.

The model allows treating calcification/decalcification of C-S-H and thus knowing the equilibrium state towards which evolves a binder highly substituted. An experimental campaign based on EDS analysis is underway. It consists to determine the evolution of the distribution of C/S molar ratio over the time, in order to test the model.

Additional databases will be added to this model, considering the effects of other factors, such as temperature and water content. The coupling of the model with a mechanical model in order to predict the long-term behavior of concrete will be performed.

Acknowledgments. The present investigation was carried out with financial support from the ANDRA (Agence Nationale pour la Gestion des Déchets Radiatifs)

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