Pergamon

Cement and Concrete Research 30 (2000) 1947–1954

CEMENT AND CONCRETE RESEARCH

Simulated microstructure and transport properties of ultra-high performance cement-based materials

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Received 24 January 2000; accepted 14 April 2000

Abstract

Ultra-high performance cement-based materials expected to be used in nuclear waste containers were submitted to a leaching test in order to evaluate their long-term durability. Reactive powder concretes (RPC) were attacked by de-ionized water. Previous studies revealed a superficial degradation after leaching with a sound zone underneath an altered porous zone in which anhydrous silicates C_3S and C_2S were dissolved. To predict the long-term durability of RPC, the hydration rate of cement minerals, pozzolanic reactivity of silica fume, pore structure, and mechanisms of chemical reactions were needed. So first, the microstructure of RPC matrix was simulated using the NIST microstructural model. Then the transfer of Ca ions through percolating water was estimated using DIFFU-Ca, a model based on the local chemical equilibrium. This double modeling validates the damage process related to an instantaneous dissolution of anhydrous cement silicates at the degradation front which results in a higher connected pore space, and is in good agreement with experimental results. The long-term behavior is expressed as the depth of the altered zone, the leaching kinetics and the evolution of Ca concentration in the material.

Keywords: Hydration; Microstructure; Durability; Transport properties; Radioactive waste

1. Introduction

High integrity containers are expected to be used in the storage of Type B nuclear waste without cementation and for a maximum life cycle of 300–500 years [1]. Ultra-high performance cement-based materials like reactive powder concretes (RPC), are potential candidates. RPCs are constituted of Portland cement, silica fume, ground quartz, steel fibers and superplasticizers (Table 1). Their rheology is improved by using a superplasticizer which also results in a water/cement ratio as low as 0.2. The basic principles underlying their development have already been published by Richard and Cheyrezy [2]. They include the elimination of coarse aggregates, optimization of the granular skeleton, and densification of the cementitious matrix through a post-set heat treatment.

In order to evaluate their long-term durability, RPCs were submitted to a leaching test. Microscopic observations showed that de-ionized water leaching altered the matrix microstructure. A superficial degraded zone in which clinker silicates were dissolved, proceeded along a front ahead of a sound zone [3]. The same study indicated that the ground quartz, fine sand and steel fibers, were not involved in the degradation process. So they were considered as inert constituents and only the behavior of the RPC cementitious matrix was studied.

In this study, the NIST microstructural model elaborated by Bentz and Garboczi [4] is used for determining the cement and silica fume rates by hydration. A second model called DIFFU-Ca by Adenot and Aspart [5] takes into account the calcium leaching. This article shows that both models are able to evaluate the RPC long-term behavior [6].

2. Experiment

The RPC paste (Table 2) microstructure is composed of anhydrous clinker grains and silica fume spheres, well

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PII: S0008-8846(00)00288-X

Table 1
RPC composition

	Proportions to cement	Proportions in kg/m^3
Cement	1	713
Silica fume	0.325	232
Crushed quartz D50=4 μm	0.3	214
Fine sand D50=310 μm	1.43	1019
Fibers	0.275	196
Superplasticizer	1.8% (dry)	43
Water	0.2	143

Table 2
Composition of the RPC matrix

	Proportions to cement	Proportions in kg/m^3
Cement	1	1501
Silica fume	0.325	488
Superplasticizer	0.9% (dry)	45
Water	0.20	300

embedded in a very dense matrix as shown in a secondary electron SEM image (Fig. 1).

A leaching test simulates the worst attack of a container confining radioactive waste during its service life of 300–500 years. In this severe test, the sample is immersed in a de-ionized water bath [7]. The water is often renewed and maintained at a pH level as low as 7. Carbonation is avoided by bubbling nitrogen in the de-ionized water.

After 6 months of leaching, a sample extracted from the solution exhibits a superficial degradation clearly observed in a backscattered electron image i.e. a sound zone underneath an altered porous zone in which anhydrous silicates C_3S and C_2S are dissolved (Fig. 2).

3. Modeling

The prediction of RPC long-term durability requires the knowledge of several parameters including the hydration rate of each cement mineral, pozzolanic reactivity of silica fume, pore structure, and mechanisms of chemical reactions. The experimental study, first conducted by X-ray diffraction and microscopic image analysis, did not permit to determine correctly these parameters as the amount of remaining anhydrous phases like C_3A or hydrates like portlandite CH could be very low. Thus, a 3D computer simulation of Portland cement hydration and microstructure development was performed using the two steps of the NIST model (Fig. 3).

The first step characterizes the anhydrous cement by its grading curve and the amount and distribution of its different constituents (C_3S, C_2S, C_3A, C_4AF, gypsum) as determined by a SEM/EDS image analysis. The grading curve leads to the distribution of cement spheres dispersed within a given volume of 100 × 100 × 100 pixels (1 pixel=1 μm). Some spheres are mono-mineral corresponding to gypsum and others represent poly-phased clinker grains in which the volume fraction of each phase is reproduced. Thus, the first step reconstitutes the cement microstructure before hydration.

The second step corresponds to the cement hydration. At that stage, silica fume spheres are introduced as 1-pixel particles. The model uses random walkers to simulate the chemical reactions of all phases during hydration [8] as described in Fig. 4 [9]:

- Digitalization of cement grains (in water)
- Identification of soluble pixels
- Random dissolution of soluble pixels
- Diffusion, collision and reaction to form the hydrates

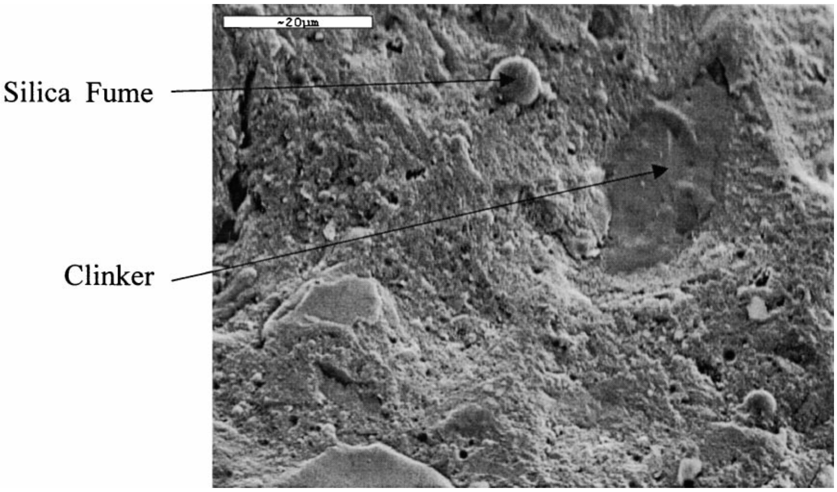


Fig. 1. Microstructure of a RPC. Secondary electron image SEI.

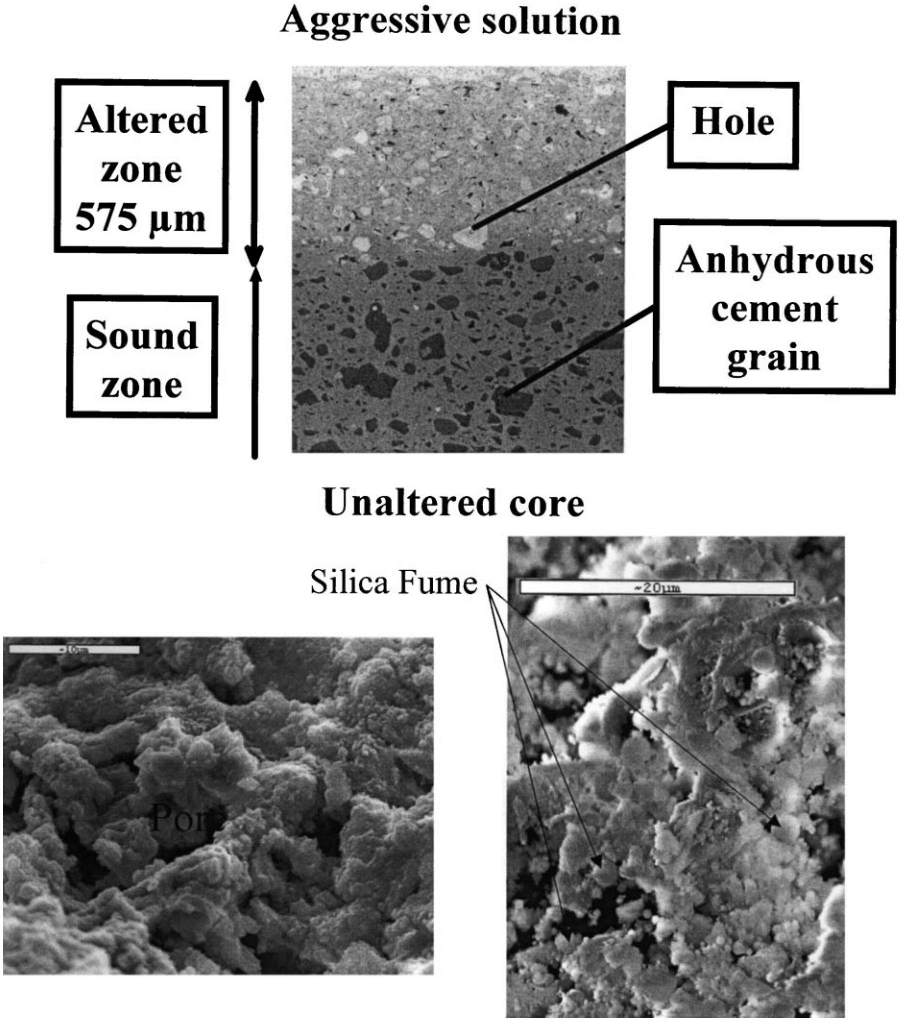


Fig. 2. RPC matrix after a 6-month leaching (a) SEI (b) BSEI.

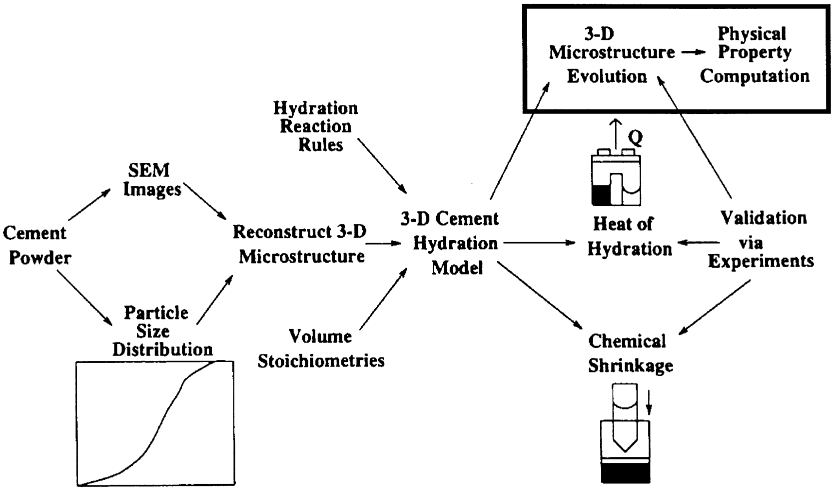


Fig. 3. The NIST microstructural model [4].

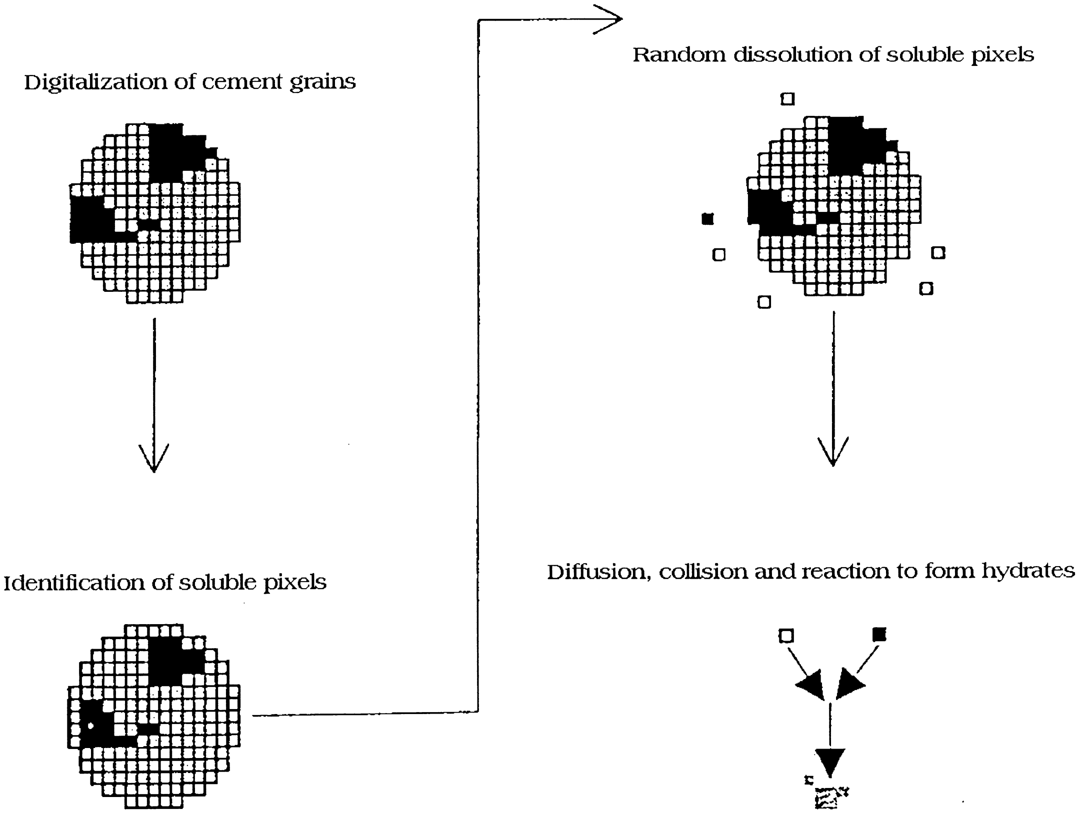


Fig. 4. Hydration of a cement grain after the NIST model [8,9].

During hydration, it is possible to follow the microstructural evolution and to determine when the pore structure becomes disconnected.

4. Microstructure before and after hydration

Three cement pastes were studied using the NIST microstructural model. They are (Tables 2–4) the RPC matrix, a very high performance (VHP) cement phase with silica fume [10] and a high performance (HP) pure cement paste. All the pastes contained the same Portland cement (71% C_3S, 13% C_2S, 4% C_3A, 6% C_4AF, 6% gypsum). The RPC samples were heat-treated after demolding. We shall consider that the heat treatment only accelerates the chemical reactions during hydration.

Table 3
Composition of the VHP cement paste with silica fume

	Proportions to cement	Proportions in kg/m^3
Cement	1	1757
Silica fume	0.10	176
Superplasticizer	1.8% (dry)	32
Water	0.20	344

Table 4
Composition of the HP cement paste

	Proportions to cement	Proportions in kg/m^3
Cement	1	1954
Superplasticizer	0.2% (dry)	13
Water	0.20	391

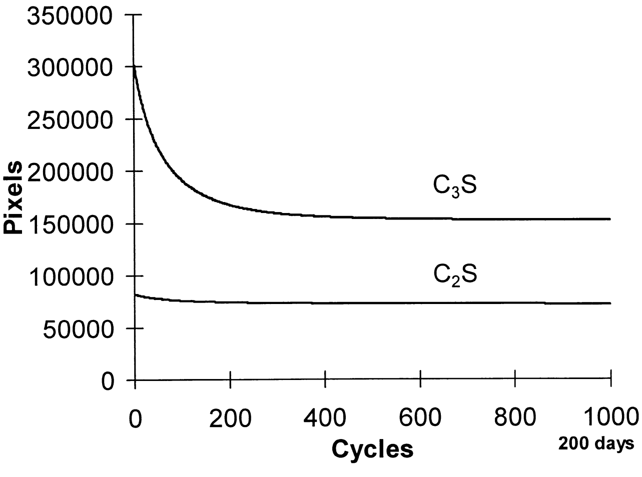


Fig. 5. Simulated hydration of C_3S and C_2S.

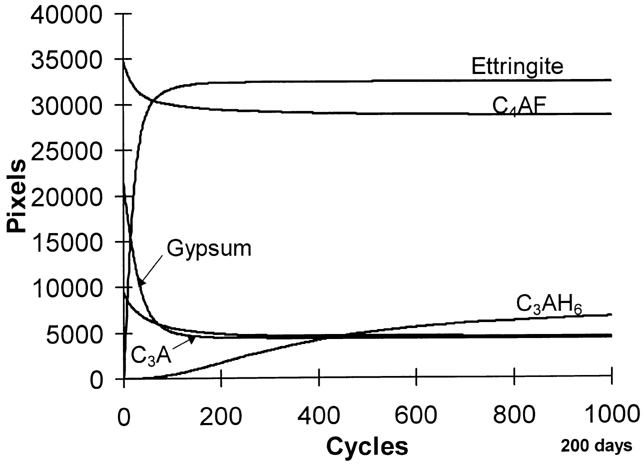


Fig. 6. Simulated hydration of C_3A and C_4AF.

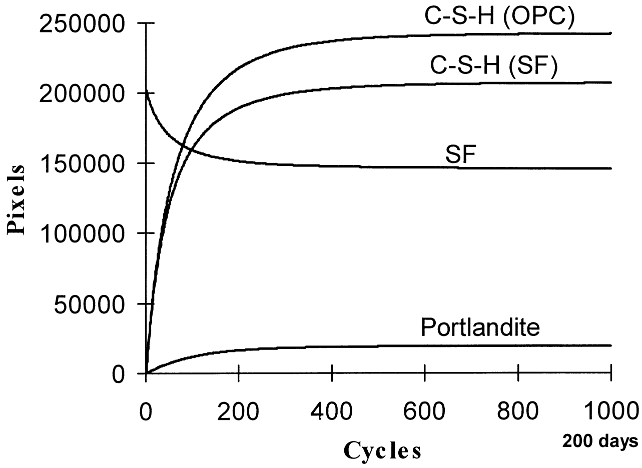


Fig. 8. Simulated appearance of CH and C-S-H.

4.1. RPC matrix

The model confirms that C_3S hydrates more rapidly than C_2S (Fig. 5) and C_3A more than C_4AF (Fig. 6). The model also shows that after 200 cycles of simulated hydration, corresponding to 40 days, 99% of the water is consumed and all hydration processes are stabilized. Almost all the gypsum is consumed, i.e. 80% at 100 cycles or 20 days. The monosulfoaluminate is not formed as the model considers the AFt→AFm transformation only when 95% gypsum have reacted. Instead, C_3AH_6 is taken into account. The ettringite formation results in a 6% desiccation porosity (Fig. 7). The silica fume is combined in C-S-H, up to 30% of its initial value (Fig. 8). It remains 2% CH. The balance of chemical reactions gives the distribution of all the phases after 1000 cycles of hydration or 200 days (Table 5). The rate of hydration is limited due to the low amount of water available and a large part of anhydrous phases still remains. Table 6 gives the hydration rate of the main phases in RPC. The global degree of hydration is 41% in volume. By SEM image analysis of 10 images, the global rate was 45%.

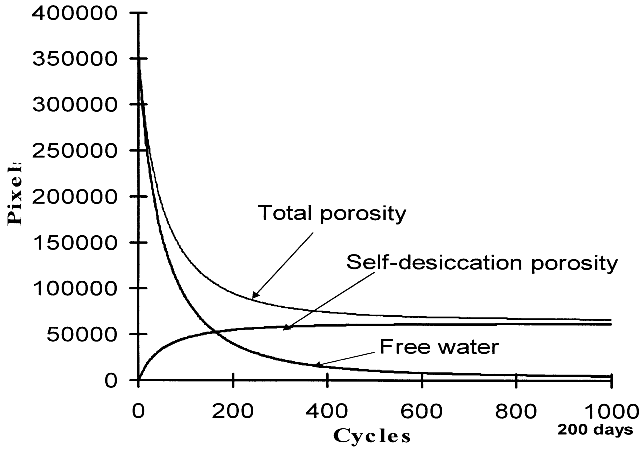


Fig. 7. Simulated porosity and water consumption.

4.2. VHP paste

The model applied to the VHP paste containing 8% silica fume gives a degree of hydration of 44% in volume or 43% in mass. The silica fume is more combined than in the RPC matrix (42% instead of 28%) and there remains more CH (8% instead of 2%). Less C-S-H is formed (Table 5).

Table 5
Composition after 200 days hydration (% in volume)

	RPC matrix	VHP paste	HP paste
Free water	0.27	0.08	0.02
C_3S	15.28	17.08	16.44
C_2S	7.20	8.58	9.41
C_3A	0.46	0.50	0.51
C_4AF	2.86	3.44	3.64
Gypsum	0.44	0.29	0.45
Silica fume	14.62	4.64	–
Portlandite	1.93	7.62	15.16
C-S-H (OPC)	24.45	31.78	39.64
C-S-H (SF)	20.91	12.69	–
Aluminates	4.39	5.98	7.65
Self-desiccation porosity	6.24	6.52	6.28

Table 6
Hydration rates for RPC matrix after 200 days hydration (% in volume)

C_3S	42
C_2S	12
C_3A	52
C_4AF	18
Gypsum	80
Silica fume	28

4.3. HP paste

In the absence of silica fume (Table 5) and at 200 days of hydration, there remains 15% CH by volume. The global degree of hydration is 50%. All the cement phases are more hydrated than in the RPC matrix and that at 20 days (Table 5). There is no more microstructural evolution after 80 days.

4.4. Conclusion

The NIST microstructural model offers a quantitative analysis of cement hydration, i.e. nature of hydrates as C-S-H, AFt, CH, remaining clinker phases, gypsum, silica fume, and pore structure. The model represents a close simulation of chemical reactions during cement hydration. In RPC, the end of hydration is achieved at 20 days. The incomplete hydration reveals a competition between cement minerals and pozzolanic silica fume, for water.

However, the model is not yet able to estimate separately the ionic diffusion through the two zones, degraded and sound, and needs to be supplemented for a prediction of RPC long-term durability.

5. Prediction of long-term durability under leaching

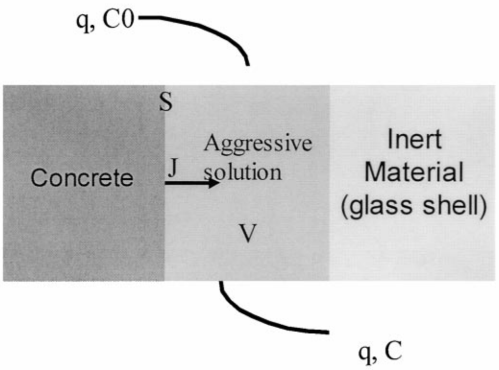
The DIFFU-Ca model [5] is based on the local chemical equilibrium. The leaching rate is controlled by ionic diffusions from the material toward the aggressive solution (Fig. 9). Previously, the model only integrated the complete cement hydration. For RPC, the model needs to take into account both remaining anhydrous phases and hydrates. The RPC degradation under leaching is related to a straight front between the sound zone high in remaining anhydrous phases and low in porosity, on one hand, and the altered zone with no anhydrous minerals (C_4AF excepted) and high in porosity, on the other (see Fig. 2). The leaching process will be simulated considering that in the sound zone, the C_3S and C_2S dissolution is extremely slow, thus negligible but that in the degraded zone the silicate disappearance is instantaneous at the leaching front. The front progression is restricted by the diffusion of dissolved species in the degraded zone. DIFFU-Ca calculates calcium profiles in the pore solution and in the solid, porosity, diffusion coefficients and leached Ca flow.

5.1. DIFFU-Ca applied to the RPC matrix

In the RPC matrix, the hydration is incomplete and due to the high dosage in silica fume, the C-S-H has a lower C/S than in Portland cement. Silicates C_3S and C_2S are leached, probably also C_3A and gypsum. Only C_4AF and silica fume are inert facing percolating water.

$$\frac{\partial(\phi_v.C)}{\partial t} = \frac{\partial(D.\phi_s.\partial C)}{\partial(\partial x)} - \frac{\partial S}{\partial t} \qquad (1)$$

$$\frac{VdC}{dt} = S.\phi.D\frac{\partial C}{\partial x}\Big|_{x=0} + q.(C_0 - C) \qquad (2)$$



C : Ca concentration in solution (mol/dm^3)
C_0 : initial Ca concentration in the aggressive solution (mol/dm^3)
S : Ca concentration in the solid
Φ : porosity
x : depth (dm)
V : volume of the aggressive solution (dm^3)
q : flow of the aggressive solution (dm^3/j)
S : material area in contact with the aggressive solution (dm^2)
$J = S.\phi.D\frac{\partial C}{\partial x}$: flux of leached Ca

Fig. 9. DIFFU-Ca model.

The following assumptions are adopted to simulate the RPC leaching with DIFFU-Ca.

(1) The hydration rate of each phase is determined using the NIST microstructural model (Table 6).

(2) SO_4^{2-} ions are combined in ettringite.

(3) Hydrates are in equilibrium with the pore solution: all C-S-H in the sound zone have a C/S = 1.46 [6] and there is no more CH. On the contrary, anhydrous phases are not in equilibrium, i.e. the dissolution is slow when the Ca concentration is 16 mmol/l but total when the Ca concentration is less than 16 mmol/l. The 16-mmol/l corresponds to the equilibrium with C-S-H of C/S = 1.46, when there are only calcium and silicium in solution.

5.2. Modeling results

The obtained results characterize the calcium profiles in the solid, the degraded depth and the calcium leaching flow after 10 simulated days. Actually, the process is the same whatever the degradation time. Only the depth of zones increases vs. $\sqrt{t}$ (t = time).

Calcium profiles in the solid (Fig. 10A) show a sharp decrease when anhydrous phases are leached. Then a

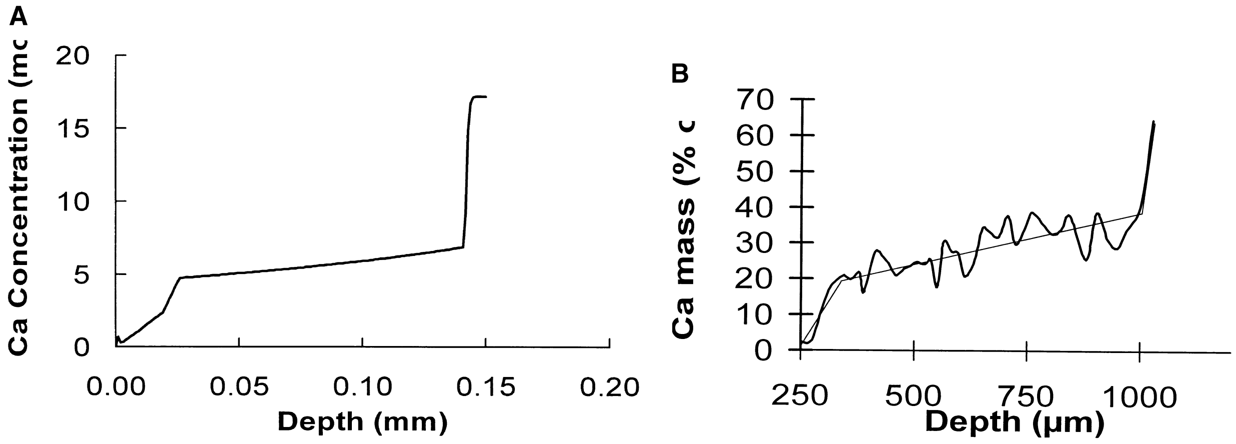


Fig. 10. Ca profiles in the solid. (A) Model after 10-day leaching, (B) EPMA after 6-month leaching.

progressive decrease is related to the C-S-H leaching. The simulated profile is comparable to that measured by EPMA (Fig. 10B). The calculated Ca leaching flow is 0.55 mol $J^{-1/2}$ m^{-2}. The chemical analysis of the leachate was 0.65 mol $J^{-1/2}$ m^{-2}. Considering the simplified chemistry of DIFFU-Ca, the difference between the two values appears as acceptable.

5.3. Prediction of the degraded depth

The measurement of the degraded zone with a caliper results in the formula:

$$d_{\mathrm{mm}} = 4.08 \times 10^{-2}\sqrt{t}$$

The DIFFU-Ca model gives:

$$d_{\mathrm{mm}} = 4.52 \times 10^{-2}\sqrt{t}$$

The degraded depth (Table 7) is slightly overestimated by the model. However, the high friability of the superficial degraded zone may lead to a measured value lower than the real one. The extrapolated depth is 15 mm at 300 years in our experimental conditions.

5.4. Conclusion

The hydration rate of each phase given by the NIST model is used in the DIFFU-Ca model for predicting the RPC long-term behavior. There is a good agreement between experimental and estimated data regarding Ca concentration in the solid, degraded depth evolution, and leached Ca amounts.

Table 7
Degradation depth (mm)

	3 m	6 m	12 m	18 m	300 years (extrapolated)
Experiment	0.40	0.58	0.75	0.93	13.50
Model	0.43	0.61	0.86	1.05	14.95

6. General conclusion

(1) Both NIST and DIFFU-Ca models, microstructural evolution and calcium transfer through percolating water, are in good agreement with the experiment.

(2) These data validate the prediction of the hydration rate and the phenomenology related to the instantaneous dissolution of remaining anhydrous phases at the degradation front level. Thus, the degradation is proportional to $\sqrt{t}$ and is the consequence of the diffusion of dissolved species from the material toward the solution.

(3) The RPC matrix is durable as long as a sound zone persists.

(4) Considering only the calcium concentration, the degraded depth is 14–15 mm at 300 years for the RPC matrix, in our experimental conditions of leaching. This value could be taken into account to determine the thickness of high integrity containers to be used in the storage of Type B nuclear waste without cementation.

Acknowledgments

The authors are most grateful to Dale Bentz from NIST for his help in using the microstructural model and to Philippe de Parseval from Université Sabatier in Toulouse for the EPM analyses.

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