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LONG-TERM BEHAVIOUR OF CEMENT PASTES USED FOR NUCLEAR WASTE DISPOSAL: REVIEW OF PHYSICO-CHEMICAL MECHANISMS OF WATER DEGRADATION

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ABSTRACT

A review of the main physico-chemical processes involved in water degradation of cement paste that are potentially important for a radioactive waste disposal is given in this paper. Their effects at the various relevant time scales are evaluated. © *1998 Elsevier Science Ltd*

Introduction

Hydraulic binders are materials used for the containment of low-level radioactive waste in France, and may be used in future deep disposal sites as confinement barriers. The very-long-term behaviour of these materials has been under study at the National Agency for Radioactive Waste Management (ANDRA) in collaboration with the French Atomic Energy Commission (CEA) for several years for these reasons. The results of these studies constitute one of the key points in the demonstration of necessary safety measures that need to be taken before future deep storage sites can be put into service.

Hardened cement paste is a porous material filled with a solution in thermodynamic equilibrium with solid hydrates. Attack on cement pastes by water with a low mineral content and approximately neutral pH is one of the worst possible scenarios which can be envisaged, because the hydrates, which are stable at approximately pH 13, are no longer in thermodynamic equilibrium and risk being dissolved. The fact that subterranean waters at proposed storage sites for radioactive waste have lower pH than the interstitial solution of the cement paste (1–2) is therefore of importance.

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The first leaching experiments were performed on ordinary Portland cement (OPC) pastes (3–5) and showed some important features of the degradation behaviour. However, a complete understanding of the physico-chemical processes was difficult because of the complexity of the material. For this reason, experiments on model pastes were undertaken to clarify for example the role of aluminium and iron. These two elements can enter the structures of calcium silicate hydrates and modify their properties (6).

In this paper we give a comprehensive report of the results of degradation experiments performed on several cement pastes placed in contact with totally demineralised water at 20°C. We attempt to provide a summary of all the physico-chemical processes which have been elucidated over the last few years, and evaluate their effects according to the various time scales relevant for the disposal of nuclear waste.

Transport by Diffusion in the Liquid Phase and Local Chemical Equilibrium

The interstitial solution contained in the porous structure of a cement paste is highly charged with alkaline Na^+ and K^+ in particular, and OH^- and Ca^{2+} ions. The contact of this material with an aqueous solution of low mineral content creates concentration gradients in the interstitial solution between the surface and the core of the cement paste. These gradients are responsible for transport of the species in the interstitial solution by diffusion. Moreover, they disturb the reigning equilibrium between the interstitial solution and solid phases and lead to the dissolution or precipitation of the solid phases. Cement paste degradation is therefore induced by a combination of diffusion-transport effects and chemical reactions. The degradation kinetics in the paste depend thus upon the kinetics of each of these two phenomena (7).

The Approximation of Local Chemical Equilibrium

Previous studies have shown the relevance of the concept of local chemical equilibrium for understanding the degradation of cement pastes (3–5). This approximation holds when the kinetics of diffusion are slower than the kinetics of reaction inside the paste. It is particularly well-adapted to the case of the degradation of a Portland cement paste. In this case, a layer of very low solubility forms at the surface of the paste and does not dissolve on observable time scales. The diffusion takes place between a fixed solid-liquid interface and a diffusion front, which moves toward the core of the paste. The diffusion kinetics slow down with time, and, after a transitory time, the conditions for local chemical equilibrium are achieved inside the sample. This case has been modeled and it was shown that the degree of leaching (degraded depth and quantity of the various species lixiviated) is proportional to the square root of time. In addition, abrupt edges of dissolution are predicted and observed (5–7).

The key point of the model is the presence at the surface of the sample of a fixed solid-liquid interface. In the presence of totally demineralised water the superficial layer will eventually dissolve, and it is thus important to know what are the conditions of stability of the superficial layer. Although for a well-designed cement barrier one will select conditions where the superficial layer is stable, we shall discuss the effect of surface dissolution on leaching behaviour.

Our approach is thus the following: inside the degraded zone we expect the local chemical equilibrium approximations to hold, and the experimental results will be analysed making use

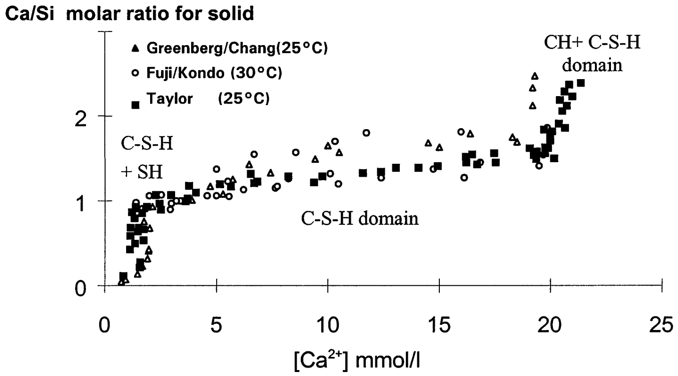

FIG. 1.
Changes in solid Ca/Si as a function of calcium concentration in solution in the CaO-SiO_2-H_2O system (4–6).

of this tool. In examining the superficial layer we will try to understand the various factors affecting the stability of the layer and how they are related to the transformations of the paste in deeper layers.

Concentration Gradients of Ca^{2+} and OH^- in Interstitial Solution

All of the main hydrates in cement contain calcium. The concentration of calcium in the interstitial solution participates in all chemical equilibrium and is therefore of particular interest. It is impossible to determine the profile for the concentration of Ca^{2+} in situ when the paste is in contact with an aqueous solution. However, the nature of this profile can be deduced from the solid Ca/Si profile in the degraded zone of a model paste containing only hydrated tricalcic silicate ($3CaO,SiO_2 = C_3S$).

Continuously Decreasing Profile for [Ca^{2+}] and [OH.

At equilibrium and at a given pressure and temperature, the CaO-SiO_2-H_2O system is univariant (Gibbs law) and completely determined by one parameter. Figure 1 gives the evolution of the solid Ca/Si as a function of calcium concentration in solution (9–11). By measuring the solid Ca/Si of a C_3S paste totally hydrated, the Ca^{2+} concentration in the interstitial solution can thus be deduced. Figure 2 shows the solid Ca/Si changes observed in the degraded zone of a hydrated C_3S paste leached with demineralized water (8). The Ca/Si ratio is observed to decrease continuously in the degraded zone of the C_3S paste (Fig. 1). This means according to Figure 1 and the approximation of the local chemical equilibrium that there is a continuous decrease of the calcium concentration in the interstitial solution between the core and the surface in contact with the aggressive solution as described in Figure 3.

Figure 3 shows this deduced profile of [Ca^{2+}] between intact C_3S paste and the external surface in contact with the aggressive solution. The concentration of associated silica species remains very low whatever the concentration of calcium in solution (9–11), and electroneu-

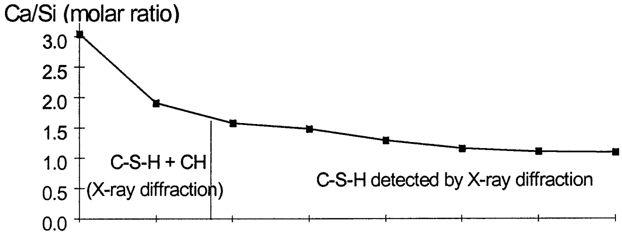

FIG. 2.

Changes in Ca/Si ratio in hydrated C_3S paste leached with demineralised water (8).

trality is maintained by the presence of hydroxyl ions ($[Ca^{2+}] \sim 2x[OH^-]$). The profile for $[OH^-]$ is similar to that for $[Ca^{2+}]$ in the degraded zone of C_3S paste.

Secondary Precipitations

Secondary precipitations are observed by X-ray diffraction in the degraded zone of cement paste subjected to water attack. Using a chemically inert reference introduced or already present in the paste, the intensity of diffraction peaks for all crystallised phases can be compared to the intensity of the peaks observed for the inert phase. The relative proportion of the crystalline phases can thus be obtained. This technique was used by Faucon et al. (7) on an OPC paste leached 6 months by demineralized water. Successive samples were taken every 50 to 100 microns from the surface in contact with the flowing water, to the core of the paste. Each sample was analysed by X-ray diffraction. Re-precipitations of AFm, ettringite, and calcite were observed (Fig. 4) and modeled (4–5). They are the consequence of local chemical equilibrium in the degraded zone.

AFm provides a good example of how these re-precipitations come about. A general solubility constant is:

$$K_s = [Ca^{2+}]^w[Al(OH)_4^-]^x[OH^-]^y[X]^z$$

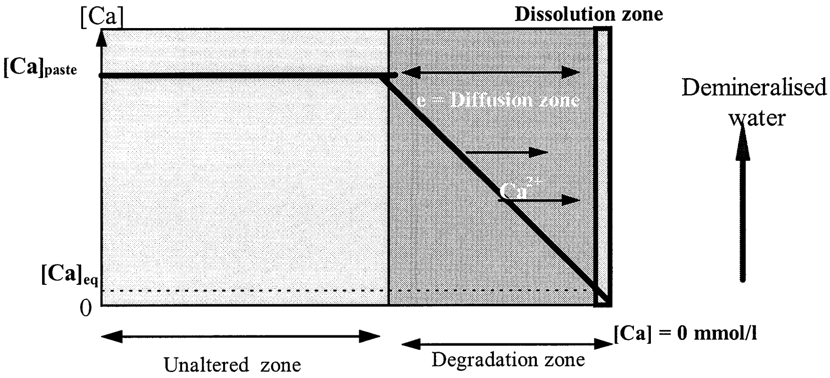

FIG. 3.

Model of the progressive (but not necessarily linear) decrease in $[Ca^{2+}]$ in interstitial solution of C_3S cement paste under leaching by demineralised water.

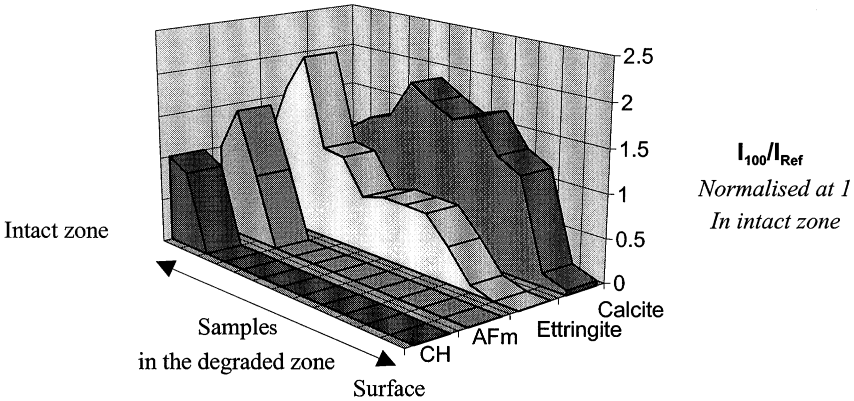

FIG. 4.
Changes in crystallised hydrates initially present in Portland cement paste following 6 months of leaching with a demineralised solution (7).

with $[X] = [SO_4^{2-}]$ for the sulpho-aluminates, or $[X] = [CO_3^{2-}]$ for the carbo-aluminates.

As already indicated, leaching of water induces a decrease of $[Ca^{2+}]$ and $[OH^-]$ in the interstitial solution from the core towards the surface of the paste (Fig. 5). Due to local chemical equilibrium, the concentrations of the other ions in the solubility product of AFm must increase, to compensate for these decreases. Hence, there is a local increase in the concentrations of $Al(OH)_4^-$, SO_4^{2-} and CO_3^{2-}. As diffusion occurs from the higher to lower concentrations, a maximum concentration in a degraded zone allows diffusion of the ionic species considered both inwards and outwards (Fig. 5). The backward diffusion gives rise to re-precipitation of Afm (Fig. 5). The dissolution of Portlandite releases the calcium required for the precipitation of secondary AFm. A similar process is responsible for secondary precipitation of ettringite and calcite.

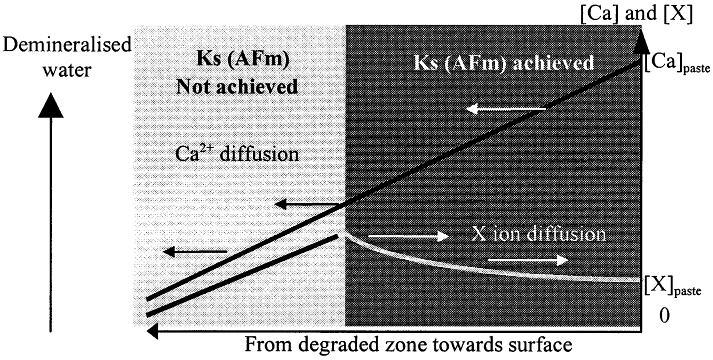

FIG. 5.
Proposed model of the concentration profiles in the interstitial solution responsible for the AFm secondary precipitation in the degraded zone ($X = SO_4^{2-}$ or CO_3^{2-}).

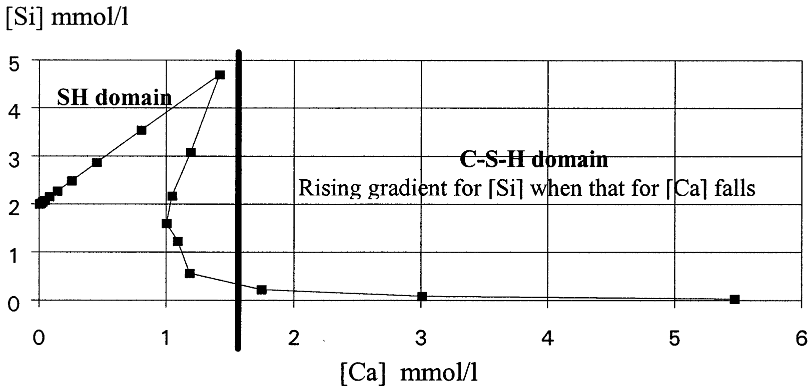

FIG. 6.
[Si] as a function of [Ca] in the $CaO\text{-}SiO_2\text{-}H_2O$ system at equilibrium (9).

Dissolution at Surface in Contact with Aggressive Solution

Local chemical equilibrium cannot be established at the surface in contact with an agressive weakly mineralised solution. The superficial layer will eventually dissolve for this reason. However, under certain conditions, dissolution is slight and remains so for relatively long periods of time.

Mechanism of Superficial Layer Dissolution

Leaching of C_3S paste is a good example of how superficial layer dissolution occurs. The re-precipitation of C-S-H with the lowest Ca/Si ratio in the degraded zone (Fig. 2) can only take place after establishment of local chemical equilibrium, and this implies that the solubility product for each C-S-H must be attained:

$$K_s\,(\text{C-S-H}) = [Ca^{2+}]^X[H_2SiO_4^-]^Y[OH^-]^Z$$

where x, y, and z are coefficients for functions of the Ca/Si ratio of the C-S-H.

As shown before, leaching induces a decrease in the concentration of $[Ca^{2+}]$ as well as $[OH^-]$ between the core and surface of the sample ($[Ca^{2+}] \simeq 2[OH^-]$ at neutrality, silica concentration being negligible). Compatibility with (1) needs thus an increase of $[H_2SiO_2]^{2-}$ in the interstitial solution.

However, the rising gradient for [Si] cannot be maintained in superficial layer when this layer is in contact with an aggressive demineralised solution. In fact, continuous leaching with demineralised water induces a decrease in [Si] and disrupts thermodynamic equilibrium in this layer (Fig. 7). The critical concentration of silica below which thermodynamic equilibrium cannot be maintained in the superficial layer of C_3S paste subjected to water degradation for 3 months is 0.2 mmol/L (12). The corresponding concentration for calcium is 1.8 mmol/L. The surface of the degraded zone will therefore start to dissolve when the concentration of calcium is less than 1.8 mmol/L (Fig. 7).

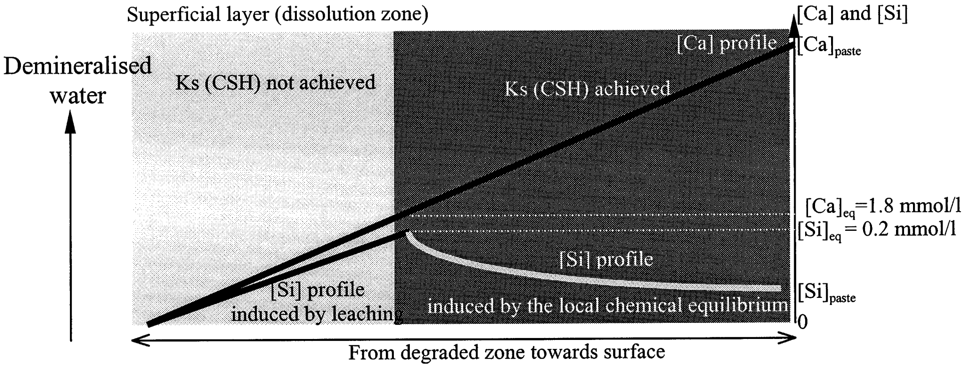

FIG. 7.
Concentration profiles in interstitial solution in the degraded zone.

Effect of Chemical Composition of the Paste

The kinetics for dissolution of the paste at the surface vary with the chemical composition of the paste, as shown in Figure 8 where the surface dissolution of a pure C_3S paste is compared with that of a C_3S paste containing 15% (by mass) of iron nitrate (8,13).

The presence of iron nitrate reduces the kinetics of dissolution of C_3S paste. Moreover, it has been observed that the solubility of calcium in the superficial layer of C_3S paste containing iron nitrate is less than that for pure C_3S paste (Table 1). In the case of an OPC paste which owns a lower calcium solubility than the two previous pastes, no superficial dissolution was detected after 3 months of leaching (8,12,13).

^{57}Fe Mossbauer spectroscopy provides information about the sites occupied by iron in minerals. This technique was used to study the influence of iron during degradation of cement pastes (6,8,14). The results indicate that trivalent iron, introduced in the form of iron nitrate in the C_3S paste or under the form of C_4AF in a OPC paste, is not leached or slightly leached. We have observed in the case of the OPC degraded layer that trivalent iron ions released by dissolution of crystalline hydrates (e.g., in the AFm phase) are exchanged with calcium ions in the C-S-H of low Ca/Si owing to a tobermorite-like structure (Fig. 9). This reaction seems

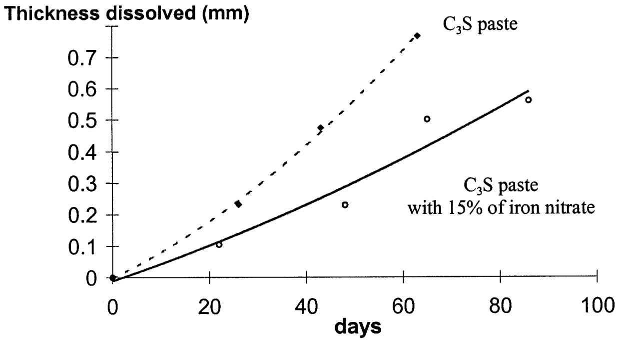

FIG. 8.
Thickness of surface layer dissolved over time for two cement pastes (8,13).

TABLE 1
Solubility of calcium from the superficial layer of different cement pastes (8, 12, 13).

	C_3S paste	(C_3S + iron nitrate) paste	OPC paste
[Ca] mmol/L	1,8	0,6	0,3

to be accompanied by a decrease of the solubility of calcium in the C-S-H (Fig. 9). Dissolution of aluminium-containing phases also release Al^{3+} ions, which are incorporated in C-S-H (15)of low Ca/Si, increasing their capacity for Fe^{3+} exchange (Fig. 9). The exchange reactions that take place in the degraded zone can be expressed as follows.

- Ion exchange in (C_3S + iron nitrate) paste:

$$(Ca^{2+} + H^{+})_{\text{C-S-H}} \rightarrow Fe^{3+}{}_{\text{C-S-H}}$$

- Ion exchange in the OPC paste:

$$(Ca^{2+} + H^{+})_{\text{C-S-H}} \text{ and } (Ca^{2+} + Si^{4+})_{\text{C-S-H}} \rightarrow (Fe^{3+} + Al^{3+})_{\text{C-S-H}}$$

The phase which has the lowest calcium solubility thus appears to have a (C,F)-(S,A)-H type formula.

Degradation Kinetics

Competition Between Diffusion and Surface Dissolution

If surface dissolution can be neglected, degradation is controlled by diffusion and the thickness of the degraded zone obeys a law of the form (4–5):

$$e = \sqrt{D_{\text{app}} t}$$

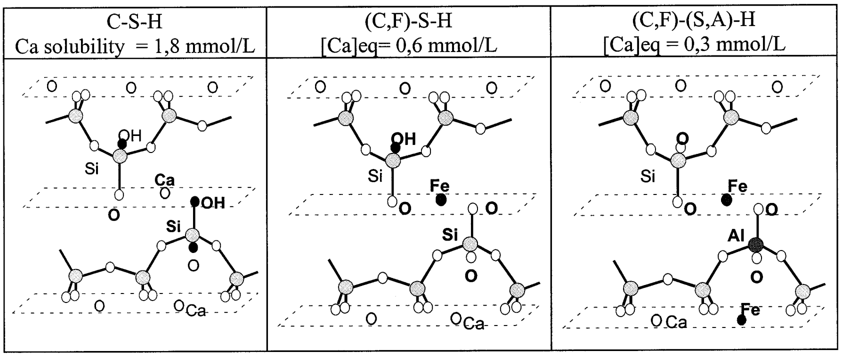

FIG. 9.
Structure of different types of C-S-H present in the superficial layer of cement paste (results of ^{57}Fe Mossbauer spectroscopy and ^{29}Si and ^{27}Al solid NMR (8,12,13,15,16).

TABLE 2
Calculated critical time "t_o" for degradation by immersion in a demineralised solution (8, 12, 17) (The order of the dissolution kinetics is taken equal to 2).

C_{eq} (mmol/L)	1.8	0.6	0.3
approximate ≪to≫	≈15 days	1 year	>10 years

The speed of progression of the diffusion front is then

$$V_1 = de/dt = \frac{\sqrt{D_{\mathrm{app}}}}{2\sqrt{t}}$$

$V_{1,}$ which is initially large, decreases with time. After a time t_0, the speed V_2 of superficial dissolution will not be negligible compared to V_1. The dissolution front will tend to catch up the diffusion front and this will stop the decrease of the fluxes of diffused species. The thickness of the diffusion zone will adjust itself in such a way that diffusion and dissolution fluxes are equal. The rate of degradation will become constant since diffusion and dissolution fluxes are no longer time-dependent.

Change of Regime: Critical Time t_0

Dissolution in the degraded zone occurs when the concentration of calcium in the interstitial solution is less than the Calcium solubility [Ca] equation of the C-S-H in this zone. Taking into account dissolution, Fick's second equation becomes:

$$\frac{\partial[\mathrm{Ca}]}{\partial t} = \mathrm{D}\,\frac{\partial^2[\mathrm{Ca}]}{\partial x^2} - \frac{a}{\phi}\,([\mathrm{Ca}]_{\mathrm{eq}} - [\mathrm{Ca}])^{\mathrm{n}}$$

where $[Ca]$ is the concentration of calcium (mmol/L) in the interstitial fluid; ϕ is the porosity of dissolution zone; t is the time (s); D is the diffusion coefficient for calcium in solution in the dissolution zone; n is the order of dissolution reaction; and a is the reaction constant.

The concentration of calcium decreases from $[Ca]_{eq}$ (in the innermost part of the dissolution zone) to zero (at the surface) when cement paste is attacked by a completely demineralised solution. The value for the dissolution term will be smaller, the smaller the value of $([Ca]_{eq} - [Ca])$ and hence of $[Ca]_{eq}$. On the other hand, dissolution will be faster for higher values of the order n. It has been found that superficial layers of C_3S paste (12) and Portland cement paste (8,17) follow second-order kinetics.

Due to the high solubility of its superficial layer ($[Ca]_{eq} = 1.8$ mmol/L), a C_3S paste leached by demineralised water will have a high surface dissolution rate, and after a relatively short t_0 time the kinetics of degradation will depart from a $t^{1/2}$ law. In the case of an OPC paste the superficial layer solubility is much smaller ($[Ca]_{eq} = 0.3$ mmol/L), and the t_0 time will be much longer. Table 2 gives the value of t_0 calculated by numerical integration of the Fick's second equation for three different $[Ca]_{eq}$ cases (12,17). It can be seen that the value of $[Ca]_{eq}$ corresponding to the OPC case gives a value that cannot be measured by laboratory experiments, whereas in the case of a C_3S paste the value of t_0 is very short.

Conclusions

Leaching of a cement paste by demineralised water produces a calcium concentration gradient which continuously decreases from the unaltered zone to the surface of the material. This gradient causes the development of a degraded zone in the cement paste and diffusion of calcium in the interstitial solution toward the attacking solution. The decrease in the concentration of calcium in this zone induces dissolution of Portlandite and secondary precipitations (AFm, ettringite, calcite) in the innermost part of the degraded zone. These precipitations dissolve in the outermost part of the degraded zone. The ratio for Ca/Si in the C-S-H decreases in a continuous manner between intact and degraded zones. Trivalent iron and aluminum, released from crystallised hydrates during dissolution, are partially incorporated into the C-S-H.

C-S-H of low Ca/Si, precipitated during degradation, dissolves on contact with the aggressive solution. Iron and aluminum incorporation enhance the stability of these C-S-H, which slows down the dissolution of the superficial zone to a significant degree. Two different regimes (diffusion versus surface dissolution) occur during demineralised-solution-induced degradation of cement pastes. The rate of superficial layer dissolution is negligible in the first case, and the kinetics of degradation is proportional to the square root of time. This situation will persist only if the solubility of the C-S-H in the superficial layer is low. The speed of dissolution of the superficial layer in the second case is equal to the speed of advancement of the diffusion boundary. However, when cement paste is degraded by natural water (in equilibrium with granite or clay for example), or infrequently renewed demineralised water, ions naturally present or leached into the solution will increase the stability of the superficial layer or maintain the rate of dissolution of this layer at a negligible level over a long period of time.

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