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Cement and Concrete Composites 21 (1999) 1–9

Cement & Concrete Composites

Durability of Reactive Powder Composites: influence of silica fume on the leaching properties of very low water/binder pastes

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Received 31 March 1998; accepted 9 July 1998

Abstract

Reactive Powder Composites are new cement-based materials which could be used for the storage of nuclear wastes thanks to their excellent microstructural properties. This paper studies their durability when submitted in the laboratory to a water leaching attack. In order to understand the behaviour of the hydrates (C–S–H), the study was carried out on a pure cement paste and on a cement+silica fume paste. The beneficial effect of silica fume is demonstrated from considerations on the calcium leaching, from XRD analysis, from SEM observations and from the tritium diffusion and pore distribution analysis. It was found that the leaching greatly affects the microstructure, especially that of the anhydrous cement grains remaining in the paste. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Image analysis; Leaching; Nuclear waste storage; Porosity; Reactive Powder Composites; SEM; Silica fume; Tritium diffusion; XRD

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1. Introduction

Reactive Powder Composites (RPCs) are well-known for their high strength resistance. Their very low porosity gives them important durability and transport properties and makes them potentially a suitable material for the storage of nuclear waste. The efficacy of an RPC has to be evaluated under severe leaching conditions which simulate the worst attack on a container confining radioactive wastes. This paper describes a study which was carried out on a pure cement paste and on a cement+silica fume paste in order to better understand the behaviour of the RPC hydrates in this aggressive medium and the influence of the silica fume. Results on the kinetics of leaching, on the microstructural and mineralogical changes, on tritium diffusion and on porosity are presented.

2. Waste management strategy

The French nuclear industry, like other industries, generates wastes. The harmful effects of these wastes are due to their radioactivity which can differ greatly depending on the type, intensity and lifetime of the material. In France, the wastes are divided into three categories [1]:

- *Type A wastes*: short-live wastes, with low to medium activity. These are now stored in surface sites managed by ANDRA (French National Radioactive Waste Management Agency) and represent 90% of the produced wastes.
- *Type B wastes*: low and medium activity wastes containing long half-life radionuclides (generally α). These include cladding and rod ends from nuclear fuel reprocessing.
- *Type C wastes*: high-activity, long half-life wastes. These are for instance, fission product solutions from reprocessing which concentrate the essential initial activity of irradiated fuel. These wastes are vitrified and stored in shafts at the reprocessing site until after their decay heat has peaked.

This paper will be concerned only with the type B wastes for which the final storage solution is not yet chosen. The law governing these radioactive wastes was passed on 30 December 1991 [2] and has the following regulation: "the deep (and permanent) disposal of type B wastes will not be decided before 2006 and therefore the action will not be taken before 2015–20. It can be seen that an intermediate facility suitable for a long period of storage must be developed." This can be

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PII: S0958-9465(98)00025-0

envisaged only if long-term safety conditions can be guaranteed, which implies the placing of wastes in a container that by itself ensures provision of a containment barrier: the High Integrity Container (HIC). The specifications of such a container are now being defined by the French Atomic Energy Commission (CEA). The CEA is also carrying out studies regarding the permanent disposal of the wastes, especially the aggression by de-ionized water. The new cement-based material RPC seems to be suitable for the storage of nuclear wastes thanks to a very dense microstructure which leads to better transport properties than High Performance Concrete or Ordinary Concrete [3]. However, the RPC has to be evaluated regarding its behavior when submitted to a leaching test.

3. The Reactive Powder Composite

The RPC is a class of concrete which possesses a high silica fume content (25% of the total binder material) and a very low water to cement ratio (0.20). A heat treatment process is applied to the RPC after demolding, at temperatures between 20°C and 400°C. This process enhances hydration and pozzolanic reactions, leading to improved both mechanical and microstructural properties [3]. The compressive strength of RPC ranges between 200 and 800 MPa. Finally, steel fibres can be introduced into the mixture to improve the ductility.

It should be pointed out that RPC is not only a high-strength material, but also *exhibits excellent microstructural and durability properties*. By adjusting the RPC composition, heat treatment and steel fibre content, it has been possible to find an RPC mixture that best fits the characteristics required (Table 1).

4. Experiment

4.1. Materials

The RPC composition for nuclear industry is given in Table 1. The cement is an OPC type CEM I, the white silica fume has a BET specific area of 12 000 m^2/kg and the superplasticizer is a polyacrylate. The mixture was heat treated in humid air at 90°C for two days after demolding. Its microstructure appears as a dense material (Fig. 1).

Table 1
RPC composition

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

This RPC has a compressive strength of 216 ± 25 MPa and a porosity of 4 ± 1% [as measured by Mercury Intrusion Porosimetry (MIP)].

As almost 60% of the RPC is made of 'inert materials' such as sand, quartz and fibres, we planned to investigate first the hydrates behaviour in an aggressive medium. Matrices were studied for this work: a pure cement paste and a cement+silica fume paste. They have the same w/c (0.20) as the RPC and were submitted to the same heat treatment (90°C for two days) in order to focus on the effect of the silica fume.

4.2. Methods

The leaching test simulates the worst attack on a container confining radioactive wastes during its service life (300–500 yr) [3]. In this severe test, the sample is immersed in a de-ionized water bath maintained at a pH level as low as 7 (Fig. 2). The water is often renewed to maintain it in a de-ionized state and used to measure the concentration in the solution of the following ions: OH^-, Ca^{2+}, Na^+, K^+, Si^{4+}, SO_4^{2-}, Al^{3+}, Mg^{2+} ,Fe^{2+}, Fe^{3+}. In our case, 32 slices 4 mm thick and 70 mm in diameter were held together and rotated in the bath. Carbonation is avoided by bubbling nitrogen into the de-ionized water. After predetermined periods, eight samples were extracted from the solution, examined by SEM, analysed by XRD and their pore size distribution measured by MIP. A tritium diffusion test is then carried out, assuming that it reproduces the transfer of the radio-elements through the material. The tritium was chosen due to its low interaction with the cement composite.

5. Results

Adenot [5] showed that the result of the leaching process on a cement paste can be considered as an assemblage of multi-mineral domains of constant mineralogy (zones), separated by mobile boundaries (dissolution or precipitation fronts) (Fig. 3).

5.1. Kinetics of leaching

The amount of calcium leached (mole/m^2) versus square root of time (days$^{1/2}$) for the two mixes used are shown firstly in Fig. 4 and then in Fig. 5, relative to the amount of cement which they contained. It can be observed that the amount of ions released is proportional to the square root of time. This means that the leaching fluxes are imposed by diffusion, that being very slow compared to the dissolution–precipitation chemical reaction [4].

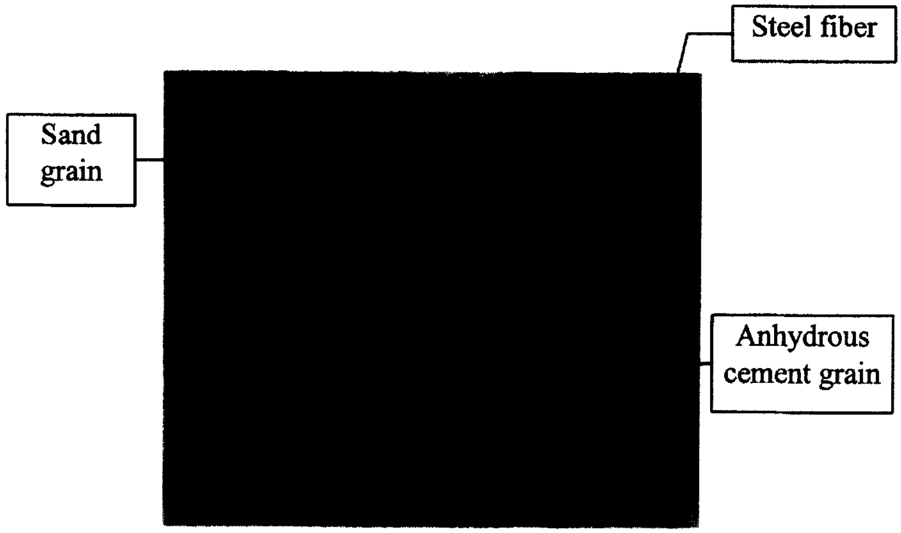

Fig. 1. Microstructure of an RPC. Backscattered electron image (BSEI).

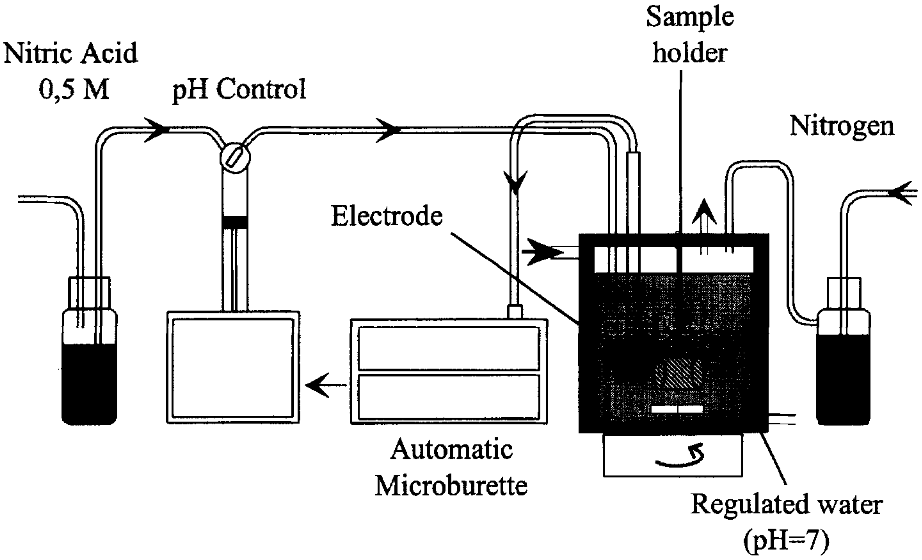

Fig. 2. Experimental apparatus for leaching test.

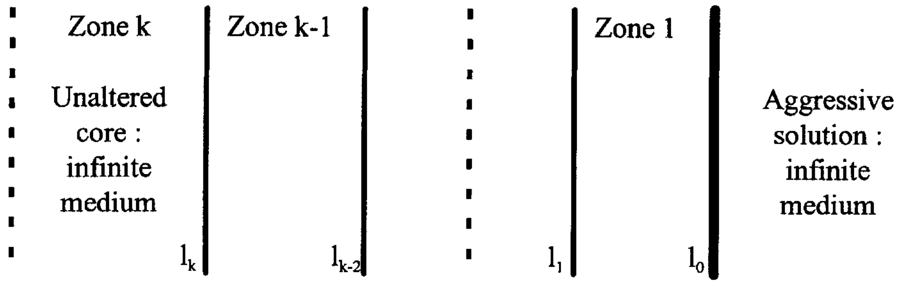

Fig. 3. Representation of the unidirectional zoning of the degrated cement paste in accordance with Adenot[3].

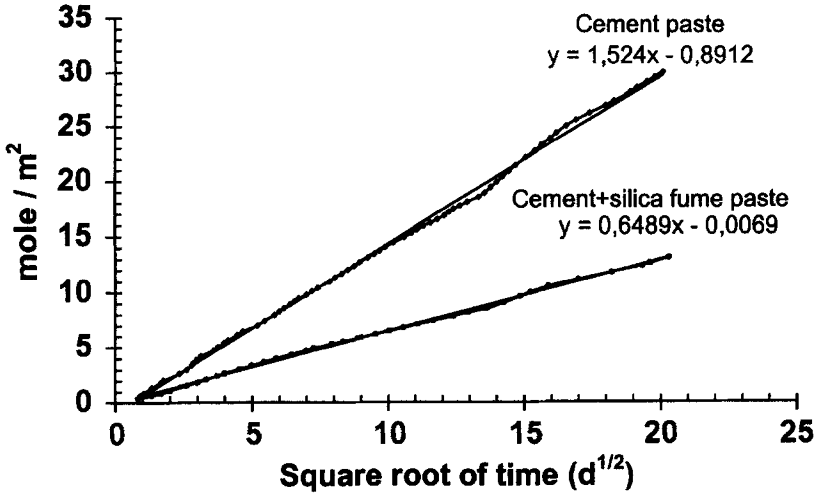

Fig. 4. Calcium leaching.

The beneficial effect of the silica fume is clearly visible. The cement paste contains $Ca(OH)_2$ resulting from the primary hydration of cement. This phase is very soluble and is first attacked by de-ionized water. The other paste contains 30% of silica fume per unit of cement, so that almost all $Ca(OH)_2$ is consumed in the pozzolanic reaction. The leaching occurs on C–S–H only in this case, causing its decalcification. This phenomenon is much slower than the $Ca(OH)_2$ dissolution. It also takes place in the pure cement paste in addition to the attack on the portlandite ($Ca(OH)_2$).

5.2. *X-ray diffraction*

The XRD patterns shown in Fig. 6 and Fig. 7 correspond to the sound part and to the external layer of the degraded samples after a 6-month leaching. As expected, these degraded samples appear as Adenot described them (Fig. 3): an unaltered core (the sound part) and several altered zones.

The sound part of the cement paste contains $Ca(OH)_2$, which has been leached in the altered part. The cement+silica fume paste does not contain $Ca(OH)_2$ due to its high silica fume content.

With a w/c of 0.20, the cement is not fully hydrated, that is why anhydrous compounds remain in the standard samples (not leached). The sound part has the same properties than the standard sample and is not presented in order not to overload the graph. An image analysis was made to determine the degree of hydration as presented by Mouret *et al.* [6]. The method consists of obtaining a Back Scattered Electron Image (BSEI) by inverse polarity so that the greater the mean atomic number of a solid phase, the darker this solid phase appears on the screen. In that condition, unhydrated clinker compounds appear black. The

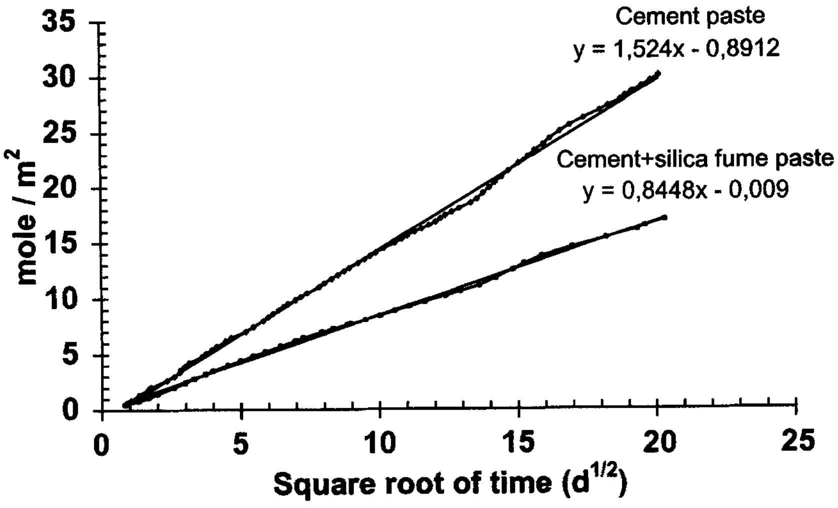

Fig. 5. Calcium leaching with respect to the quantity of cement.

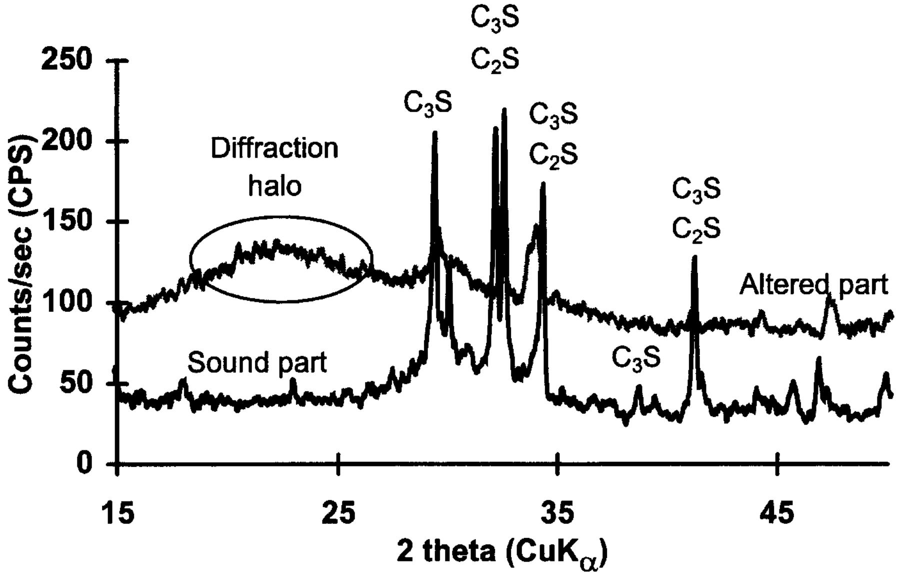

Fig. 6. XRD diffractogram of the cement paste after a 6-month leaching.

degree of hydration is calculated by counting on each image all the pixels identified as the anhydrous phase. According to the stereology rules, the area fraction derived is equal to a volume fraction, assuming a homogeneous and isotropic distribution of the cement grains through the paste. The degree of hydration (α) is calculated as:

$$\alpha = 1 - \frac{A}{\Gamma o} \qquad (1)$$

where A is the area fraction of anhydrous remnant cement grains present in the sample studied and Γo is the initial volume fraction of cement grains present in the fresh paste.

This calculation was made only on the cement+silica fume paste because it corresponds to the RPC's binder part. Ten fields at 480× magnification were investigated. This gives a degree of hydration in the sound part of 45% ($A = 26\%$ and $\Gamma o = 47\%$).

In the altered part, the anhydrous compounds have almost completely disappeared (Fig. 7). An $A = 6\%$ is found, compared to 26% in the sound part. First, it is possible that the water used for leaching has hydrated the cement. eqn (1) gives then a degree of hydration of 94%. But in this case, if some silica fume remains in the paste, it would have reacted with the portlandite

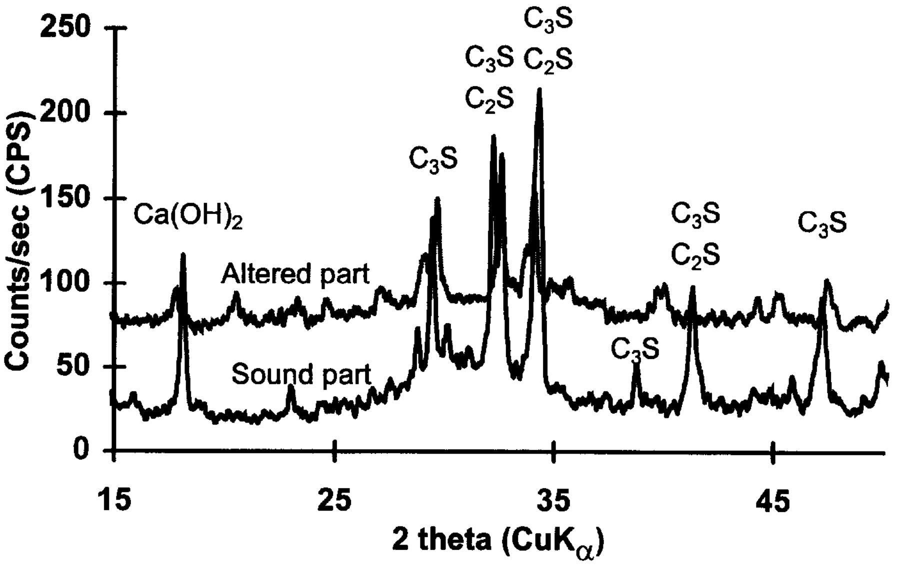

Fig. 7. XRD diffractogram of the cement+silica fume paste after a 6-month leaching.

produced by the hydration of cement. The diffraction pattern obtained from the altered part shows a halo characteristic of that obtained from an amorphous material. This halo corresponds to the silica fume (it has been verified by an analysis of the silica fume alone). There is no diffraction halo in the sound zone diffractogram because the unreacted silica fume represents less than 15% of the total sample mass and is below the limit of detection for the X-ray technique. Thus it seems that this unreacted silica fume represents a more important part in the altered layer and, therefore, one cannot consider that it reacted with $Ca(OH)_2$.

From these observations, it can be concluded that the disappearance of the anhydrous compounds in the altered layer cannot be attributed to a delayed hydration reaction.

5.3. Scanning electron microscope

The XRD analysis has opened an interrogation about what happens to the anhydrous compounds in the altered part of the sample. Figure 8 shows a BSEI of the cement+silica fume paste after a 6-month leaching which could help to answer the question.

The altered zone is clearly observed, the depth of which is 575 μm. In this zone, the anhydrous cement compounds are levelled off, leaving white holes which retain the shape of the silicates as seen on SEM examination on fractured surface (Fig. 9) [7]. However, silica fume spheres are still surrounded by some sort of amorphous C–S–H.

5.4. Tritium diffusion

After 0, 3 and 6-month leachings, three slices 4 mm thick were tested in a diffusion cell equipped with two watertight compartments. The upstream compartment was filled with a tritium solution (38.9 MBq/l) and the downstream with de-ionized water. At the steady state, the diffusion coefficient is determined following eqn (2) [8]:

$$\frac{QL}{C0} = Dt \qquad (2)$$

where Q is the diffused tritium amount at time t per unit area (MBq/m^2), L the slice thickness (m), $C0$ the tritium concentration in the upstream solution (MBq/m^3), D the tritium diffusion coefficient value of the material (m^2/s) and t the total diffusion time (s).

Results are shown in Table 2 and Table 3. For the standard samples (not leached), the presence of silica fume leads to a diffusion coefficient 200 times lower than that of the cement paste. This value is even ten times lower than the one found by Delagrave for a paste with a w/c of 0.265 and 6% of silica fume per cement unit [9]. This low tritium diffusion result is due to the decrease of w/c and to the heat treatment which enhances the pozzolanic action of the silica fume (30% of the cement mass).

However, after a 3-month leaching, the diffusion coefficient of the cement+silica fume paste is only four times lower than that of the cement paste. The multi-

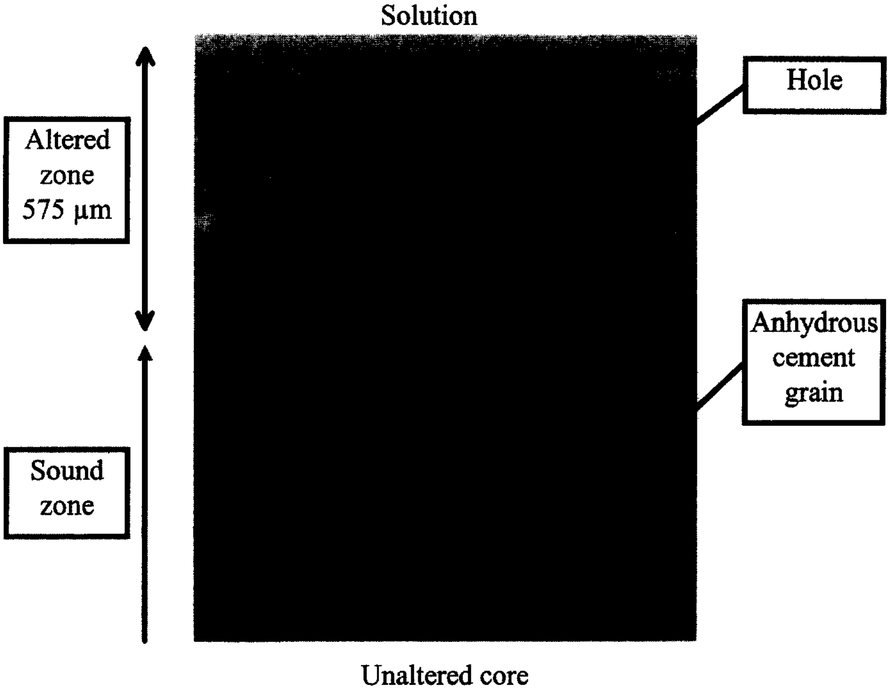

Fig. 8. BSEI of the cement+silica fume paste after a 6-month leaching.

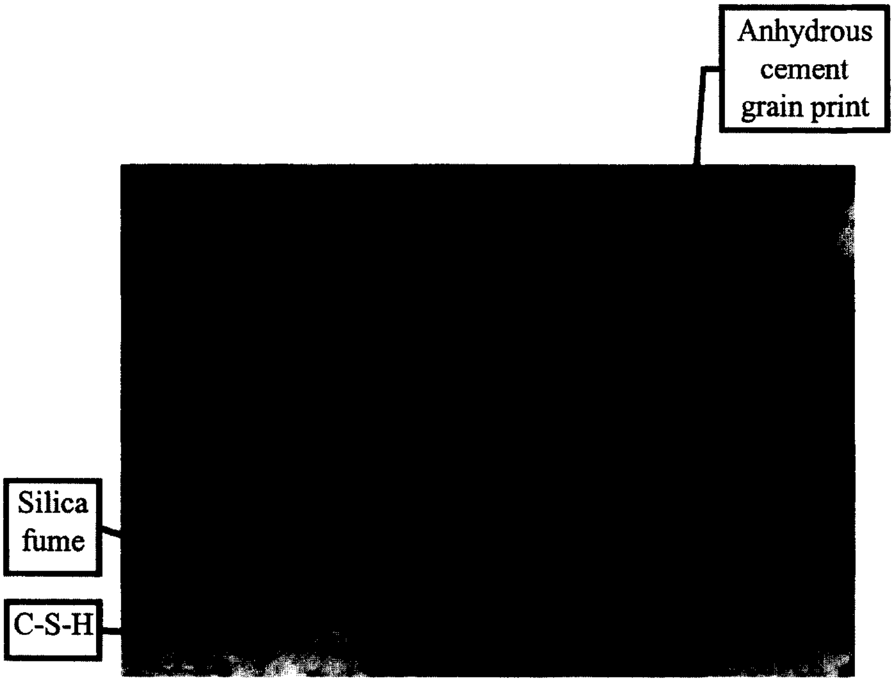

Fig. 9. SEI-SEM of RPPPC paste after a 3-month leaching, altered layer.

plication factor between the two pastes dropped to 2 after a 6-month leaching. It seems that the leaching process affects more the paste with silica fume although its degradation depth is far inferior (Tables 2 and 3). These results may be attributed to a percolation phenomenon. Actually, the cement+silica fume pore connectivity before leaching could be below a percolation threshold, that could explain why its tritium diffusion coefficient is very low and the steady state so long to obtain (over than 500 days!). The leaching process could lead to the creation of a percolation path, which could illustrate the fact that it takes only 14 days to reach the steady state after a 3-month leaching and the coefficient is then 100 times higher.

Table 2
Tritium diffusion coefficient of the cement paste

	Standard	3 months	6 months
D (m^2/s)	2.0×10^{-12}	3.5×10^{-12}	5.6×10^{-12}
Degradation depth (mm)	0	1	1.33
Time to the steady state (days)	24	14	14

Table 3
Tritium diffusion coefficient of the cement+silica fume paste

	Standard	3 months	6 months
D (m^2/s)	1.0×10^{-14}	9.2×10^{-13}	25×10^{-13}
Degradation depth (mm)	0	0.40	0.58
Time to the steady state (days)	550	14	14

5.5. *Porosity*

Figure 10 shows the MIP study for the standard samples. The main detectable porosity of the cement paste is between 0.01 and 0.02 μm. In accordance with Baroghel-Bouny [10], this peak would represent an intrinsic characteristic of the cement paste whatever the w/c. For the cement paste containing silica fume, this peak does not appear and most of the porosity is below the detection limit (0.003 μm). MIP does not give access to the hydrates porosity.

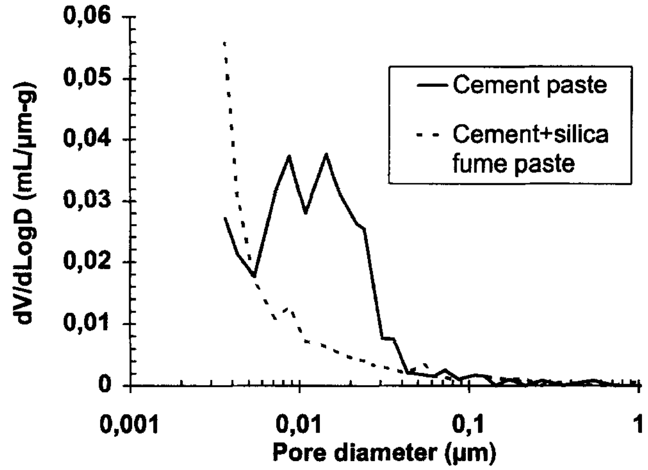

Fig. 10. MIP results for the standard samples (not leached).

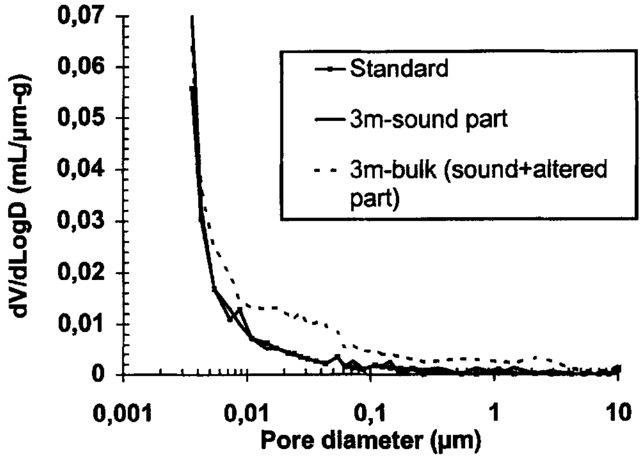

Fig. 11. Cement+silica fume MIP results before and after a 3-month leaching.

In Fig. 11, the cement+silica fume paste pore distribution before and after a 3-month leaching is represented. The sound part curve is superimposed to the standard curve, meaning that they have the same porosity. Nevertheless, in the bulk (sound+altered part), the porosity is systematically higher at any pore diameter smaller than 4 μm. The increase in the porosity in the bulk can be attributed to the altered layer and may correspond to the holes observed under microscope (Fig. 8).

In order to complete the MIP study, the BET technique was used on an RPC slice ground (120 mg) before and after a 3-month leaching, as already used for high performance cement pastes [10] (Fig. 12). A peak was found at 1.6 nm for each sample: this corresponds to the C–S–H porosity. A previous NMR study of RPC [11] has already detected a similar peak at 1.4 nm. Apparently, the porosity of the C–S–H remains unchanged after three months of leaching. The increase of the diffusion coefficient after leaching, therefore, should not be attributed to an increase of the intrinsic porosity of the hydrates. It appears that the leaching affects the mesoporosity (between the micro and the macro).

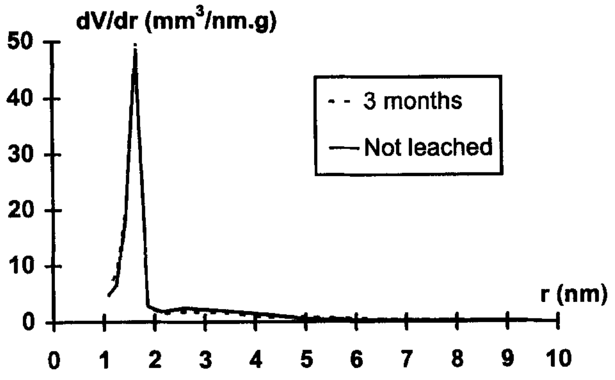

Fig. 12. BET pore size distribution of RPC.

6. Conclusion

This study can be summarized into two major results:

On one hand, the beneficial effect of the silica fume on the durability has been demonstrated from considerations on calcium leaching, degradation depth, tritium diffusion or porosity.

On the other hand, the leaching process leads to the disappearance of the anhydrous compounds in the altered zone. This was first shown by XRD analysis and confirmed by SEM observations.

The leaching test as it was performed is very severe and tends towards the loss of the advantageous effects brought by the silica fume. If the anhydrous clinker is leached, it cannot be hydrated, so no portlandite is produced and there is no more pozzolanic reaction possible.

An in-depth study of the RPC microstructure of the altered layer is needed to compared it to the sound layer. The interfaces between cement grains and hydrates have to be considered as important parameters for the RPC durability. It is hoped that the investigation of the material by means of Small Angle Neutrons Scattering (SANS) experiments will give some information on the shape of the grains and of the holes and on the structure of the interfaces. Modelling the diffusion as a function of the porosity and of the percolation network is also in progress to determine if the RPC exhibits a percolation threshold due to the leaching process.

Acknowledgements

The authors gratefully thank Mrs Ruscassier, Mr Mouret and Mr Ringot from INSA Toulouse (France) for their contribution to the image analysis.

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