Design and Characterization of Low-heat and Low-alkalinity Cements

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Investigations were carried out to formulate and characterize low-alkalinity and low-heat cements which would be compatible with an underground waste repository environment. Several systems comprising Portland cement, a pozzolan (silica fume or fly ash) and blastfurnace slag were compared. All blends were characterized by high amounts of additions, the OPC fraction ranging only from 20 to 60%.

Cement hydration was studied using several techniques: XRD, TGA-TDA, calorimetry, pore solution extraction, SEM. The most outstanding result obtained with some ternary blends was the drop in the pore solution pH by more than one unity as compared with control samples elaborated with commercial cements. The alkali content of the interstitial solution ($\approx$ 1 to 4 mmol/L) was also strongly reduced. The blends exhibited a low heat output as required. Leaching tests carried out in pure water indicated a very slow decalcification of the samples.

I. Introduction

I.1. Framework

The French Parliament Act of 30 December 1991 defined three complementary lines of research with the objective to find a solution to manage high-level and intermediate-level long-lived radioactive wastes over the very long term. One of the options examined by Andra (The French National Agency for Nuclear Waste Management) is to dispose radioactive wastes in deep geological structures. The disposal concepts are based on a multibarrier design approach. The barriers would be: the waste package (the waste and the material used to stabilise it in a suitable overpack), the engineered barrier inserted between the waste package and the rock, and the geological barrier, i.e. the actual rock.

Clay has been chosen to constitute the geological barrier for its low permeability which leads to few water flows and for its stability over geological time scales. Clay may also be used as a main component in the storage framework. For instance swelling bentonite could be used to seal some tunnels in association with concrete. In this context, it has been pointed out that the clay properties may be altered by the high pH conditions set by the cement pore water. Moreover a high temperature

rise caused by cement hydration in massive concrete could induce microcracking of the material with negative consequences on its long term evolution. Investigations have thus been carried out to formulate low-alkalinity and low-heat cements referred as "low-pH" cements, which would show an improved compatibility with the repository environment and which could be used to elaborate high-strength concrete.

A list of specifications to be checked by the concrete materials has been defined including easy supply of the raw materials, pore solution pH below 11 and temperature rise during hydration less than 20°C.

This article is devoted to the chemistry of the "low-pH" cements. Several blends were designed and used to prepare cement pastes which were then characterized over a one-year period. 7 months-old samples were then submitted to leaching by pure water.

I.2 How to formulate a low-pH cement?

The pore solution pH of a cement paste is controlled by the most soluble component until its entire dissolution (Fig.1).
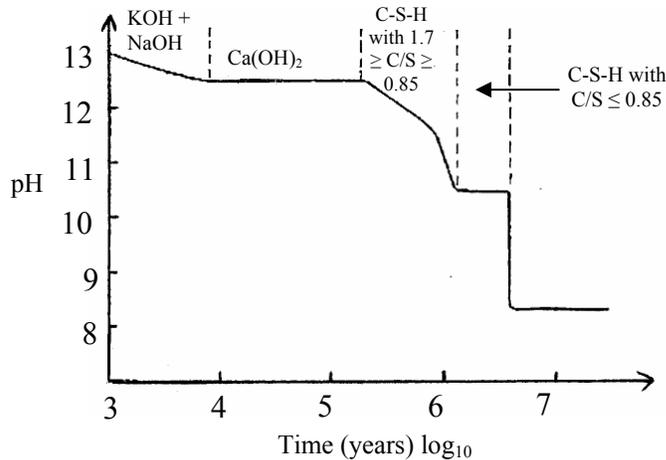
Figure 1: Schematic illustration of pH evolution in cement equilibrated porewater [1]

To reach a pH below 11, three conditions should be checked: 1) strong reduction in the alkali concentration, 2) absence of portlandite in the hydrated cement, 3) pH controlled by C-S-H with a low CaO/SiO_2 ratio. Adding pozzolans to Ordinary Portland Cement (OPC) seems to be attractive: portlandite formed by the hydration of OPC should be converted into C-S-H by the pozzolanic reaction, the CaO/SiO_2 ratio of C-S-H hydrates should be lowered, which should in turn enhance their sorption capacity of alkalis and reduce their equilibrium pH. Furthermore OPC would be diluted, which should lead to a decrease in the heat output during hydration.

After a literature review [2] and several preliminary studies [3], different blends were selected (Table 1).

Table 1: Composition of the investigated blends

	OPC	CEM V*	Silica fume (SF)	Fly ash (FA)	Slag
B	60%	-	40%	-	-
T1	37.5%	-	32.5%	30%	-
T2	37.5%	-	32.5%	-	30%
T3	20%	-	32.5%	-	47.5%
Q	-	60%	40%	-	-

CEM V*: comprising 22% of slag, 22% of fly ash and 55% of clinker

II. Experimental

II.1. Materials

Table 2 shows the composition of the products used to design the low-pH blends.

Table 2: Chemical composition (weight %) of the blends components ([a]Ordinary Portland Cement CEM I (Lafarge, Le Teil), [b]CEM V/A (Calcia, Airvault), [c]densified silica fume ChrysoSilica, [d]fly ash, [e]blast furnace slag (Calcia, Ranville)). n.m. = not measured

	OPC[a]	CEM V[b]	SF[c]	FA[d]	Slag[e]
CaO	67.41	46.42	0.40	5.52	42.3
SiO_2	22.84	29.44	95.00	49.48	36.2
Al_2O_3	2.7	11.36	0.60	29.17	11.1
Fe_2O_3	1.84	3.20	< 0.05	6.23	0.97
MgO	0.81	3.02	0.30	2.08	7.6
MnO	n.m.	0.11	n.m.	0.08	0.15
Na_2O	0.14	0.21	<0.20	0.58	< 0.20
K_2O	0.23	1.06	0.29	1.22	0.34
SO_3	2.23	2.81	< 0.20	0.64	n.m.
S^{2-}	< 0.01	0.16	< 0.10	n.m.	0.9
P_2O_5	n.m.	0.58	n.m.	0.70	<0.70
TiO_2	n.m.	0.64	n.m.	1.61	0.51
Fire loss at 1000°C	1.72	1.48	3.10	2.20	< 0.10

Three hydraulic compounds were tested (OPC, a commercial blend (FA – slag – OPC, referred as CEM V according to European standard EN 197-1) and blast furnace slag), as well as two pozzolans (FA and a more reactive one, SF). OPC and slag were chosen for their low alkali content. SF was selected in a densified form for easier handling.

II.2. Methods

Cement pastes (W/C = 0.5) were characterized using mercury intrusion porosimetry (Micromeritics Autopore III – investigated pressures ranging 0.8 to 53000 psia). Crystallized phases were identified using XRD (Siemens D8 – Copper anode $\lambda_{K\alpha1}$ = 1.54056 Å), and the portlandite content was estimated using TGA (TA-SDT 2960). Si/Ca and Al/Ca ratios of ordinary Portland cement and low-pH blends were investigated by

performing X-ray microanalyses using energy dispersion spectroscopy (Philips XL PW6631/01 LaB$_6$ filament).

The heat output during hydration was investigated on cement pastes (W/C = 0.4 except for Q, 0.45) using Langavant semi-adiabatic calorimetry (according to European standard EN 196-9).

The pore solution of cement pastes cured for 2, 6 and 12 months in sealed bag at 20°C (W/C = 0.5, cylindrical samples h = 10 cm and Ø = 6.7 cm) were extracted using pressure (WALTER BAI 102/3000 – HK4, applied strength within the range 0 – 1700 KN). Their pH values were measured with a high alkalinity pH electrode, and the Na$^+$, K$^+$, Ca^{2+} and SO$_4^{2-}$ concentrations were determined using ionic chromatography.

Measurements of pH and Ca^{2+}, Na$^+$, K$^+$ and SO$_4^{2-}$ concentrations were also carried out on cement suspensions prepared by mixing crushed cement paste samples (cured for 6 months and one year in sealed bag at 25°C) with ultrapure water (liquid to solid ratio of 9 mL/g) and stirring for 24h. Experiments and measurements were carried out under nitrogen atmosphere.

4*4*16 cm samples of cement paste (blends B, T1 and T2) with a W/C = 0.4 were prepared and cured for seven months at 100% relative humidity and constant temperature (20°C). Then they were cut in 3 cm-thick slices and put in cylindrical tanks for calcium leaching tests [4]. In all the tests, the pH and temperature were kept constant, respectively, at 7 and 20°C. Nitric acid at a concentration of 0.25 mol/L was added automatically to the solutions to regulate the pH. To avoid carbonation of the samples during the tests, nitrogen gas was continuously injected in the tanks. Sampled slices of cement pastes were immersed in a 1.8 L tank filled with deionized water. The samples were protected from lateral degradation by a polymer coating, and the external attack occurred in one direction only. To maintain experimental conditions constant during the tests, the solution was renewed at regular intervals, in connection with the quantity of added nitric acid. This quantity was directly related to the amount of calcium leached from the cement paste. The solutions were constantly stirred to avoid any local increase in concentration. The mineralogy of the leached zone was assessed by scrapping progressively the samples from the external surface to the center of the slices. With the help of XRD (Pan Analytical Xpert Pro - Copper anode λ$_{Kα1}$ = 1.54056 Å) analyses, it was possible by this way to determine the crystallized phases within slices of 100 µm thick, parallel to the leached surface.

III. Results and discussion

III.1. Hydration of cement paste

III.1.1. Characterization of the solid
a) Portlandite content

Evolution with time of the portlandite content in the cement pastes is shown in Fig.2.
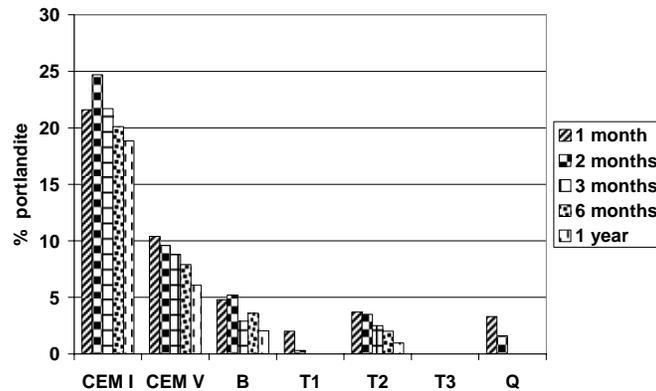
Figure 2: Portlandite evolution in the several blends tested

Portlandite was totally depleted in blends T1 and Q after 3 months of curing, while it could still be detected after 1 year in blend T2. T1 and T2 differed only by the fact that FA (in T1) was replaced by slag in T2. Thus, FA revealed more effective to consume portlandite, which may be explained by its higher silica content. Quite unexpected results were obtained for blend B: despite its high SF content, the most reactive product of the investigated pozzolans, portlandite was still present after 12 months. This resulted from an inhomogeneous dispersion of SF in the paste. According to Hong and Glasser [5], SF up to 15-20% cement replacement should be enough to react with all portlandite if properly dispersed. Whatever the age of the sample, T3 never contained portlandite, which may result from its very low content of clinker (20%). In the commercial CEM V cement, the amount of portlandite decreased, but slower than in the low-pH cements which all contained silica fume. Thus, properly dispersed SF was the most effective pozzolan for a rapid depletion of portlandite. These results were confirmed by XRD analyses.

b) Hydration heat

The total heat of hydration of most low-pH cements (excepting B) was reduced as compared to OPC (T2: 215 J/g, T1: 195 J/g, T3: 150 J/g, OPC: 250 J/g) (Fig.3). It decreased with the clinker content as well as the hydration rate in the acceleratory period. Moreover, for similar cement replacement levels, the heat release of blend Q was smaller than that of blend B, which was due to the fact that CEM V hydration was less exothermic than OPC hydration. In the same way, the heat output of fly ash-containing blend T1 was smaller than that of slag-containing blend T2.
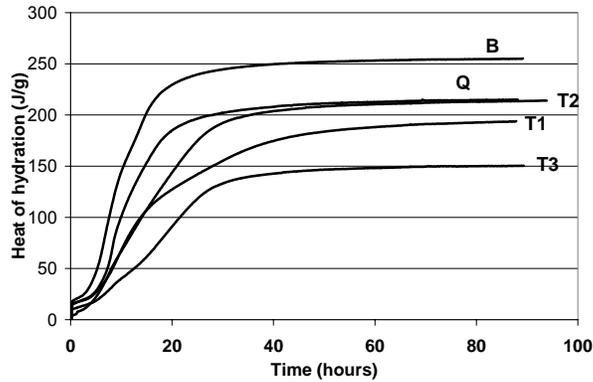
Figure 3: Heat of hydration of low-pH blended cements

c) Porosity

Porosity of cement pastes was characterized after 1 and 3 months of curing. Whatever the age of the sample, adding fly ash and slag resulted in an increase in the total porosity, which was maximum for T1 and T3 (Table 3). While the porosity of the commercial cements (OPC and CEM V) decreased with time, that of the low-pH cements remained almost constant. However their pore size distribution showed a progressive refinement (Fig.4).The fraction of pores with a diameter below 20 nm (related to C-S-H) increased with time and was much more important than that of OPC.

Table 3: Total porosity of cement pastes (%)

	OPC	CEMV	B	T1	T2	T3	Q
1 month	30.9	33.9	30.2	37.1	34.9	37.3	33.9
3 months	25.3	28.9	31.9	36.0	32.6	37.5	36.0
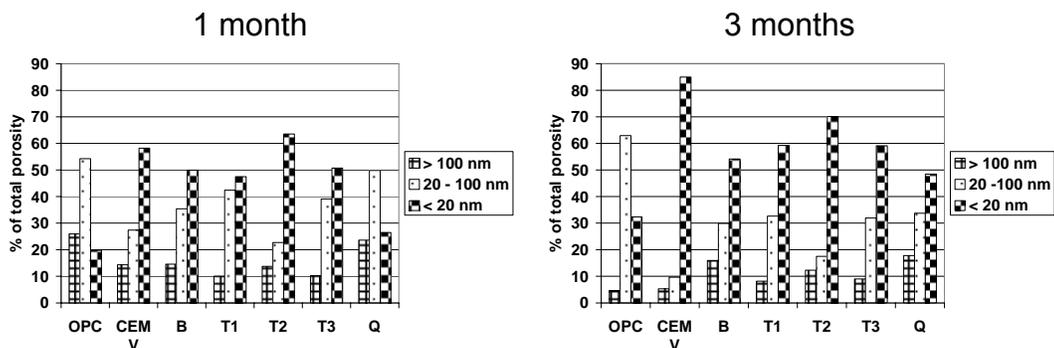
Figure 4: Pore size distribution of one month-old and three months-old cement pastes

d) Mineralogy of OPC and low-pH cement pastes

The mineralogy of the several cement pastes was investigated by XRD (Table 4).

Table 4: Mineralogy of the low-pH blends shown by XRD

	Components of the blends (age: 6 months)
B	C-S-H – Ca(OH)$_2$ – ettringite – C$_2$S – C$_3$S – Fe$_2$O$_3$ – CaCO$_3$ – SiO$_2$
T1	C-S-H – Ettringite – C$_2$S – C$_3$S – Fe$_2$O$_3$ – CaCO$_3$ – SiO$_2$ – mullite – Fe$_3$O$_4$
T2	C-S-H – Ca(OH)$_2$ – ettringite – C$_2$S – C$_3$S – CaCO$_3$ – hydrotalcite
T3	C-S-H – Ettringite – C$_2$S – C$_3$S – CaCO$_3$ – hydrotalcite
Q	C-S-H – Ettringite – C$_2$S – C$_3$S – CaCO$_3$ – SiO$_2$ - hydrotalcite

All sample contained anhydrous phases (C$_2$S, C$_3$S), ettringite and traces of calcite. Portlandite was detected in blends B and T2 and hydrotalcite in slag-containing blends (T2, T3, Q). Three of them were analysed using EDS.
Fig.5 shows a plot of Al/Ca against Si/Ca ratios for individual X-ray microanalyses from varying parts of the microstructures of 6 months-old cement pastes.
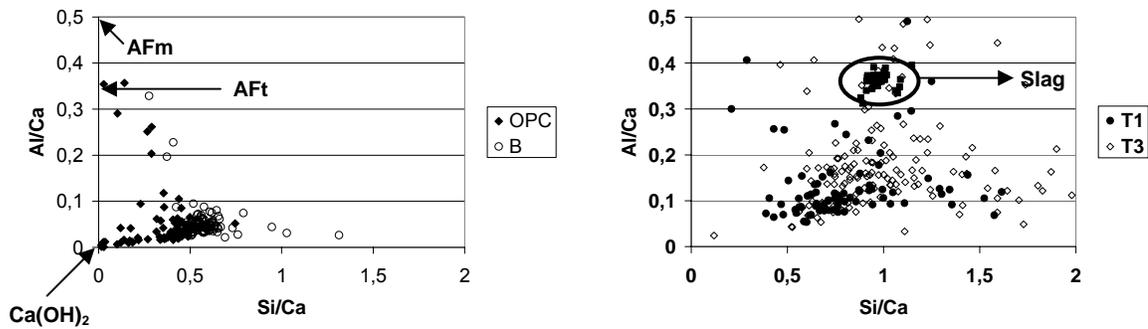
Figure 5: Al/Ca vs Si/Ca atom ratios for individual X-ray microanalyses of Portland cement paste and low-pH cement pastes (age: 6 months)

Most analyses on the OPC paste clustered for Si/Ca ratio between 0.4 and 0.5 and corresponded to C-S-H. The spots analysed were not chosen at random, thus portlandite (Si/Ca = 0) was underestimated. The analyses intermediate between those of C-S-H and CH, AFt or AFm probably corresponded to mixtures below the micrometer scale of C-S-H and the relevant phase.
Blend B was characterized by C-S-H with a higher Si/Ca ratio (within the range 0.5 – 0.6). Mixtures with portlandite were scarce. Analyses performed on blends T3 and T1 were much more dispersed. For most spots in the C-S-H zone, both the Si/Ca and Al/Ca ratios were increased, which could be related to the higher silica and alumina contents of these systems (T1: CaO 27.0%, SiO$_2$ 54.3%, Al$_2$O$_3$ 10.0%, T3: CaO 33.7%, SiO$_2$

52.6%, Al_2O_3 6.0%) as compared to OPC (CaO 67.4%, SiO_2 22.8%, Al_2O_3 2.7%).

III.1.2. Characterization of the interstitial solution

The pore solution pH values of the blends decreased with time and were within the range [11.7 – 12.4] after one year of hydration. They still exceeded the target pH of 11, but were however reduced by more than one unity as compared to OPC and CEM V cements (Table 5).

Table 5: Evaluation of the pore solution pH. Measurements carried out on extracted interstitial solution (IS) and cement suspensions (CS).

pH	IS 2 months	IS 6 months	CS 6 months	IS 1 year	CS 1 year
OPC		13.2	12.6	13.1	12.6
CEM V		13.4	12.6	13.3	12.4
B	12.4	12.6	12.5	12.2	12.4
T1	12.4	12.2	12.2	11.7	11.7
T2	12.3	12.4	12.4	12.2	12.2
T3	12.1	12.0	12.0	11.7	11.8
Q	12.5	12.5	12.4	12.1	12.0

Differences could be noticed between the blends: the smallest pH values were recorded for T1 and T3 and the highest for blends B and T2. Comparing data relative to blends T1 and T2 showed that associating SF to FA instead of slag led to a stronger pH reduction.
Given the difficulty to extract pore solution under pressure, two protocols were compared: (i) pore solution extraction, and (ii) preparation of a suspension by mixing ground cement paste with ultrapure water for 24h. The pH values measured in both cases were very similar except for OPC and CEM V.
The compositions of the pore solution extracted from two, six and twelve months-old samples are presented in Table 6.

Table 6: $[Na^+]$, $[K^+]$, $[Ca^{2+}]$ and $[SO_4^{2-}]$ (mmol/L) in the extracted interstitial solutions

	2 months				6 months				12 months			
	Na^+	K^+	Ca^{2+}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	SO_4^{2-}	Na^+	K^+	Ca^{2+}	SO_4^{2-}
OPC					77.9	71.8	0.2	0.8	92.9	77.1	0.02	1.1
CEM V					47.1	172.0	0.5	2.4	72.5	241.5	0.03	3.9
B	4.7	3.3	8.9	0.4	3.1	3.2	9.5	0.2	3.1	2.7	5.4	0.3
T1	2.0	1.1	11.0	ND	3.8	1.4	3.8	0.2	4.5	1.9	1.6	1.4
T2	3.6	1.4	7.3	ND	3.0	1.7	8.4	0.1	3.0	1.0	5.8	0.2
T3	3.5	1.3	4.5	0.2	2.9	1.5	4.7	0.6	2.9	1.1	4.2	0.9
Q	8.7	15.9	1.5	ND	7.5	11.5	3.9	0.1	7.3	9.3	0.1	0.3

ND: below the detection limit

The extracted interstitial solutions of the low-pH blends exhibited strongly reduced (up to a factor 20 to 200) contents of Na^+ and K^+ as compared with OPC. The calcium concentrations were in fairly good agreement with

C-S-H equilibrium data (Fig.6) for low-pH blends T1 and T3, but not for cement paste Q, which may be linked to its higher content of alkalies.
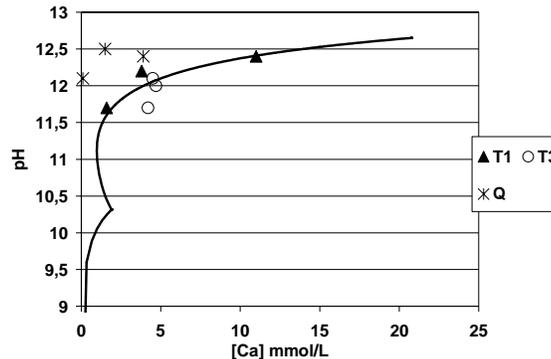
Figure 6: Equilibrium model of pure C-S-H at 20°C according to Nonat [7, 8] with data relative to two, six and twelve months-old low-pH cement pastes

This result shows that, in those materials, the pore solution chemistry was controlled by the C-S-H dissolution. The good agreement between the two protocols of pH measurement could then be explained as follows. The dilution factor in the suspension (W/C = 9 instead of 0.5 in cement pastes) was low enough to prevent total dissolution of C-S-H and the equilibrium concentrations remained unchanged. On the contrary, the pore solution pH of OPC and CEM V was dominated by highly soluble alkali hydroxides and pH was above 13. Preparing a suspension caused a dilution of the alkalies, and thus a pH reduction.
This might be explained by an inhomogeneity of the material, which would locally contain portlandite, this latter being isolated from the interstitial solution by the growing hydrates.

III.2. Leaching of cement pastes

III.2.1. Characterization of the degraded solid

From the first samples taken out of the leaching solution, we tried to estimate a position of the degradation front for each cement paste. The degraded thickness was visually estimated through microscope observations as shown in Fig.7. On these images, the degraded zones corresponded to the grey zones and the sound cores, which colored phenolphtaleine, appeared in purple. Whatever the sample, the degraded thickness (at least in term of pH) was comprised between 0.6 and 0.7 mm after 4 months of leaching.
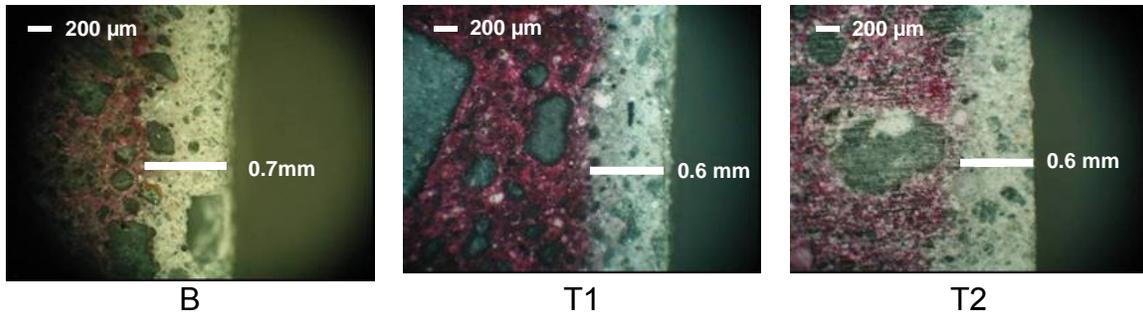
Figure 7: Pictures of the samples (B, T1 and T2) after 4 months of leaching. In each sample, dark areas corresponded to badly dispersed SF.

XRD analyses were carried out to confirm the magnitude of the degraded thickness estimated by microscopy. The samples surface was scrapped off step by step (thickness ≈ 100 µm for each step), to obtain XRD profiles (Fig.8).
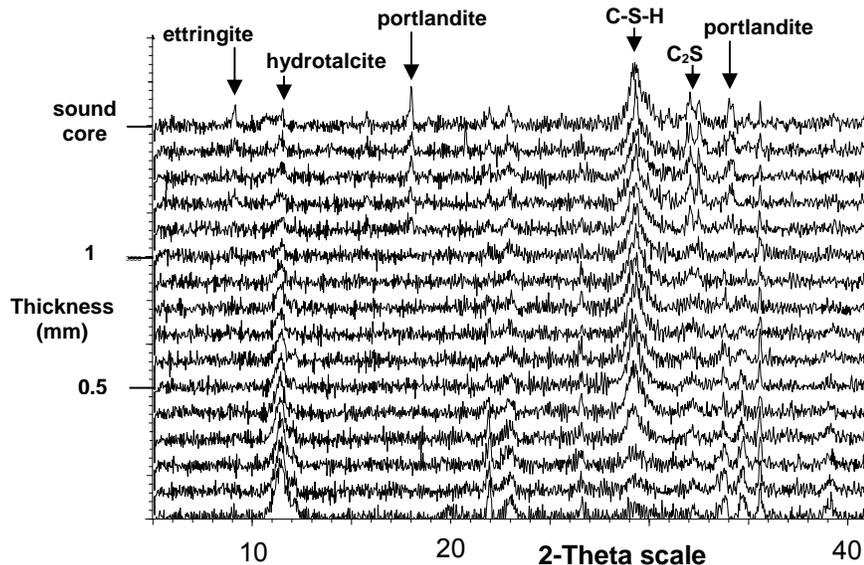
Figure 8: XRD pattern of T2 degraded zone (from the surface (bottom) to the sound core (top))

The sound core mineralogy of low-pH cement pastes was described in section III.1.1.d. When the samples were immersed in pure water (pH 7), several phenomena were noticed near the exposed surface:
- ✓ decrease in the magnitude of the C-S-H peak, which corresponded to a progressive decalcification of the material,
- ✓ disappearance of portlandite for blends B and T2,
- ✓ disappearance of ettringite whatever the sample,
- ✓ enrichment (precipitation?) in an hydrotalcite-like phase for blend T2 (containing slag),
- ✓ partial (blend B) or total (blends T1 and T2) depletion of C_3S and C_2S, due to dissolution and possibly hydration.

The degradation depth estimated by the disappearance of portlandite and/or ettringite (Table 7) was not in good agreement with that inferred from microscopic observation. In that latter case, the change in colour of phenolphtaleine occurred for a pH value (≈ 10) much lower than the equilibrium pH of portlandite or ettringite. These preliminary experiments thus show that more investigations are needed to identify the best indicator to detect the limit between the uncorroded core and the degraded zone. One possibility may be to use other techniques such as LIBS or X-ray microanalyses in order to obtain the Ca/Si ratio evolution in relation with the degradation depth.

Table 7: Zone of appearance of portlandite and ettringite in the leaching cement pastes

	Portlandite	Ettringite
B	[1 -1.1] mm	[0.95 – 1.05] mm
T1		[0.8 – 1] mm
T2	[1 – 1.2] mm	[1.2 – 1.35] mm

III.2.2. Characterization of the leaching solution

Fig.9 shows the cumulative quantities of OH^- and Ca^{2+} released in the leaching solution as a function of the square root of time for samples B, T1 and T2.
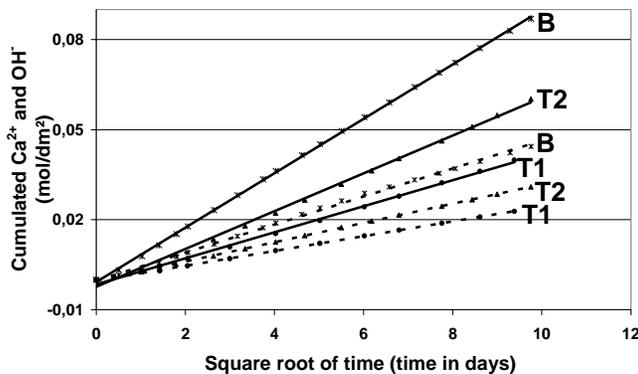
mmol/dm²/day$^{0.5}$	OH^- flux	Ca^{2+} flux
B	9.1	4.7
T2	6.3	3.2
T1	4.3	2.5

Positive fluxes refer to outward fluxes.

Figure 9: Ca^{2+} (dotted line) and OH^- (full line) fluxes during leaching of cement pastes in pure deionized water

Blend B showed the highest decalcification rate and T1 the smallest. The rate values could be compared with reference data: decalcification of the investigated blend was much slower than that of OPC (13 ± 2 mmol/dm²/day$^{0.5}$) and rather similar to that of CEM V (3 ± 0.4 mmol/dm²/day$^{0.5}$) [9].
For blends B and T2, the ratio between the hydroxyl and calcium fluxes was close to 2 (1.94 for B and 1.97 for T2) showing that the main process was dissolution of portlandite. This phase was effectively observed in the samples before leaching (see section III.1.1.a). For samples T1, which

didn't contain portlandite anymore, the flux ratio was significantly below 2 (1.72) and it is assumed that the Ca^{2+} flux was balanced by the release of OH^- and sulphate anions.

IV. Conclusions

Cement pastes prepared with four blends containing high amount of silica fume, fly ash and/or slag were investigated. Their main properties were as follows:
- ✓ reduced heat of hydration as compared to OPC,
- ✓ refinement of the porosity, although the total porosity remained higher than that of the probe,
- ✓ pore solution with a pH comprised between 11.7 and 12.4 after one year of curing, and with very strongly reduced Na^+ and K^+ concentrations as compared to an OPC reference,
- ✓ slow decalcification rate under leaching by pure water.

For cement pastes T1 and T3, the pore solution chemistry seemed to be dominated by the C-S-H dissolution. In that case, an alternative method to pore solution expression was proposed to estimate the pH of the interstitial solution. pH could be simply measured on a cement suspension (liquid to solid ratio of 9 mL/g) stirred for 24 h under nitrogen atmosphere.

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