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Formulating a low-alkalinity, high-resistance and low-heat concrete for radioactive waste repositories

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Abstract

Investigations were carried out in order to formulate and characterize low-alkalinity and low-heat cements which would be compatible with an underground waste repository environment. Several systems comprising Ordinary Portland Cement (OPC), a fast-reacting pozzolan (silica fume (SF) or metakaolin (MK)) and, in some cases, a slow-reacting product (fly ash (FA) or blastfurnace slag (BFS)) were compared. Promising results were obtained with some binary mixtures of OPC and SF, and with some ternary blends of OPC, SF and FA or BFS: pH of water in equilibrium with the fully hydrated cements dropped below 11. Dependence of the properties of standard mortars on the high contents of FA and SF in the low-pH blends was examined. Combining SF and FA seemed attractive since SF compensated for the low reactivity of FA, while FA allowed to reduce the water demand, and dimensional variations of the mortars. Finally, low-heat (ΔT<20 °C under semi-adiabatic conditions) and high strength (≈70–80 MPa) concretes were prepared from two low-pH cements: a binary blend made from 60% of OPC and 40% of SF, and a ternary blend including 37.5% OPC, 32.5% SF and 30% FA.

Keywords: pH; Mixture-proportioning; Pozzolan; Concrete; Radioactive waste

1. Introduction

1.1. Framework

The long-term management of substances produced by nuclear power plants has become a key challenge for society. One of the options is to dispose of medium or high-level and long-lived wastes in deep geological structures [1]. Current concepts are based on a multibarrier design approach. The engineered barrier, which could be a clay-based material (especially in the case of high-level and long-lived wastes), would protect the waste packages, postpone the arrival of water and fix radioelements after the decay of the packages containment properties. The geological barrier (host rock), selected for its stability over geological time scales, would prevent intrusion and, in the last resort, isolate any radionuclides that might potentially escape. Furthermore, a modular design could be adopted. This allows different types of packages to be placed in vaults accessed via handling galleries and thus to be separately managed. The packages would be taken down to depths of the order of 500 m through a system of vertical shafts. Association of concrete and swelling bentonite clay might be used to seal the vaults, as schematically shown in Fig. 1. In this context, it has been pointed out that the clay properties may be degraded by the high pH conditions set by the cement interstitial pore water [2]. 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 and characterize low-alkalinity and low-heat cements which would show an improved compatibility with the

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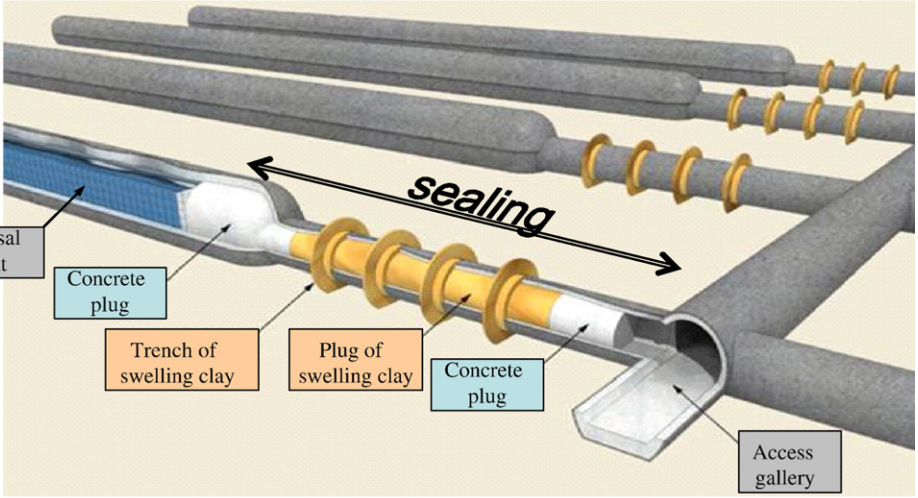


Fig. 1. Investigated concept of disposal for medium level wastes [1].

repository environment, and which could be used to elaborate high-strength concrete. Table 1 presents the set of criteria which were defined in a first approach.

1.2. How to formulate a low-pH cement?

1.2.1. Calcium silicate cements

A hardened paste of Ordinary Portland Cement (OPC) is a porous medium composed of solid phases and, for usual water/cement (W/C) ratios and curing conditions, of a liquid phase located in the porosity. The main solid components are portlandite, calcium silicate hydrates and hydrated aluminate phases, their respective proportions being roughly 20%, 70% and 10%. As for pore water, it is a very alkaline solution: typical concentrations after 180 d for pastes of W/C ratio 0.5 are 0.08 mol L^{-1} for Na^+ and 0.24 mol L^{-1} for K^+ for a low-alkali cement, and 0.16 mol L^{-1} for Na^+ and 0.55 mol L^{-1} for K^+ for a high-alkali cement [3–5]. The corresponding OH^- concentrations are 0.32 mol L^{-1} and 0.71 mol L^{-1} respectively, and the resulting pH values above 13. The pore water chemistry depends on the solubilities of the solid phases in presence. Its evolution during leaching of the cement paste by pure water can be schematically described as follows (Fig. 2) [6,7]. In a first stage, the pore solution is dominated by highly soluble alkali hydroxides and pH is above 13. In a second stage, the pore solution chemistry is controlled by dissolution of calcium hydroxide. The total dissolved calcium is about 20 mmol/L and pH is buffered at *c.a.* 12.5. In a third stage, C–S–H gel and in particular the C/S ratio of the gel determines the pore solution chemistry; pH drops continuously to *c.a.* 10.8. This process shows that a low pore water pH value can be achieved by a strong reduction in the alkali concentration, and an absence of portlandite when hydration is completed. Under these conditions, pH is controlled by the C–S–H dissolution: the lower the C/S ratio, the lower the pH.

To formulate a low-pH cement, adding pozzolanic materials to OPC should be advantageous in at least three respects: *(i)* portlandite formed by the hydration of OPC is converted into C–S–H by pozzolanic reaction, *(ii)* OPC is diluted, and *(iii)* the C/S ratio of C–S–H is lowered, which enhances their sorption capacity of alkalis and reduces their equilibrium pH [8,9]. When mixed with OPC, low-CaO fly ash (FA) is effective to reduce the portlandite content [10] and heat output during cement hydration [11]. However, even with incorporation rates exceeding 50%, the interstitial solution of the hydrated material is buffered by residual portlandite and pH remains above 12 [12–14]. Owing to their fineness and chemical composition, silica fume (SF) and metakaolin (MK) are much more reactive,

Table 1
Specifications for low-pH materials

Cement	Concrete
•Chemical compatibility with clay	•High strength
↳ Pore solution with low alkalinity	↳ Compressive strength after 90 d of curing at 20 °C and 100% HR ≥ 70 MPa
↳ pH ideally below 11	•Low-heat output
•Low heat of hydration	↳ Temperature rise under semi-adiabatic conditions below 20 °C
•Easy supply	•Dimensional stability
•Resistance with regards to chemical processes from the geological medium (sulphate attack)	•pH buffer and sorption of radionuclides •Low diffusivity and permeability to limit fluid transfer

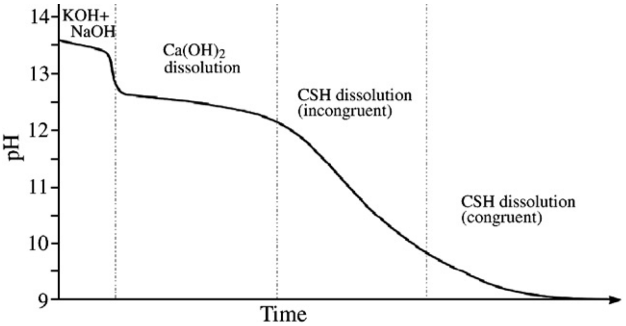


Fig. 2. Schematic evolution of pore solution pH during leaching by pure water of sulphate resistant Portland cement paste [6,7].

Table 2
Previously reported low-pH concretes

Reference	OSF concrete [51]	LHHPC concrete [49]	36F concrete [50]
Blend composition (%)	OPC: 40 SF: 20 FA: 40	OPC: 50 SF: 50	OPC: 83.3 SF: 16.7
OPC content (kg/m^3)	200	97	150
Pozzolanic additions (kg/m^3)	FA: 200 SF: 100	SF: 97	SF: 30
Cement content (OPC+additions) (kg/m^3)	500	194	180
W/OPC	0.75	1	0.98
W/C (OPC+additions)	0.3	0.5	0.82
Aggregates content (kg/m^3)	1656	1935	2005.5
Sand/aggregates (kg/m^3)	1.208	0.861	1.900
Quartzitic filler (kg/m^3)	–	194	200
Plasticizer content (cement weight %)	3	5.3	1.2
Slump after mixing (mm)	72.5	–	450
Temperature rise (adiabatic conditions)	50.2 °C	≈20 °C	–
Compressive strength (MPa)	105.7 (91 d)	≈80 (90 d)	54.6 (91 d) 77.8 (1 y)
Total shrinkage (μm/m)	−516 (90 d)	–	≈−500 (90 d)
pH of water equilibrated with crushed material	11 (28 d – Water/Solid=40/1)	10.6 (90 d – Water/Solid=1/1)	11.7 (28 d – Water/Solid=1.675/1)

their minimum replacement rate of cement to remove all portlandite ranging from 25% to 40% depending on the studies [15–19]. Furthermore, these two additions are known to improve some properties of the cementitious materials: bleeding is limited [20,21], porosity is refined [16,17,22–25], which in turn reduces permeability and diffusivity [26–29], and increases mechanical strength [30–34]. However, some difficulties might be expected with high contents of SF or MK: bad workability of the grout due to the important water demand of the two compounds [19,27], inhomogeneous dispersion of SF in the grout [35,36], dilatant behaviour of superplasticized pastes containing MK [37], strong autogenous shrinkage resulting from the decreased pore size [38], and significant temperature rise in massive concrete since SF or MK additions are not reported to reduce notably the heat of hydration [39–41]. Ternary blends consisting of OPC, of a fast-reacting pozzolan (SF or MK) and of a slow-reacting pozzolan (FA) might offer significant advantages over binary blends: SF or MK would improve the early age performance of concrete with FA continuously refining the properties of the hardened concrete as it matures [42–48].

Design of high strength concretes from blends of OPC and pozzolans with high replacement levels of cement has already been reported (Table 2). Gray and Shenton [49] used a blend comprising equi-amounts of OPC and SF. Density was increased by including a quartzitic filler. The W/C ratio was kept at a value as high as possible in order to promote hydration of cement without being detrimental to the properties of the hardened product. The cement content was maintained at a low value so as to limit heat output during hydration. Lagerblad [50] adopted similar principles to formulate a concrete, but the silica fume content was reduced. The concrete designed by Mihara et al. [51–53] differed by its blend composition, which additionally contained fly ash, its high cement and low water contents. It was thus characterized by a higher temperature rise during hydration,

Table 3
Characteristics of the blends components

		Silica fume	Fly ash	Metakaolin	Blastfurnace slag	OPC
Chemical composition (weight %)	SiO_2	95.00	50.80	54.4	36.20	22.84
	Al_2O_3	0.60	25.40	38.4	11.10	2.70
	CaO	0.40	5.50	0.1	42.30	67.41
	Fe_2O_3	<0.05	7.10	1.27	0.97	1.84
	MgO	0.30	1.80	<0.20	7.60	0.81
	MnO	n.d.	0.06	n.d.	0.15	n.d.
	P_2O_5	n.d.	1.07	n.d.	<0.05	n.d.
	TiO_2	n.d.	1.25	1.60	0.51	n.d.
	K_2O	0.29	1.40	0.62	0.34	0.23
	Na_2O	<0.20	0.50	<0.20	<0.20	0.14
	Na_2O+K_2O	$0.29 \ll 0.49$	1.45	$0.62 \ll 0.82$	$0.34 \ll 0.50$	0.37
	SO_3	<0.20	0.50	<0.20	–	2.23
	Sulfur	<0.10	–	–	0.90	<0.01
	Loss on ignition at 1000 °C	4.20	3.80	1.9	<0.10	1.72
Granulometry (μm)		–	$d_{10}=3.3$ $d_{50}=21.5$ $d_{90}=156.3$	$d_{10}=1.2$ $d_{50}=5.9$ $d_{90}=52.3$	$d_{10}=3.4$ $d_{50}=19.8$ $d_{90}=51.9$	$d_{10}=2.6$ $d_{50}=18.5$ $d_{90}=50.3$
Specific area (m^2/g)		25 (BET)	2.6 (BET)	19 (BET)	3.4 (BET)	0.34 (Blaine)
Pozzolanic index (g/g — 42 d)		0.76	0.17	0.96	–	–

Densified silica fume: Chryso Silica.
Blastfurnace slag: Calcia-Ranville.
n.d.: not detected.
Metakaolin: AGS-Pieri.
OPC: CEM I 52.5 PM ES CP2-Lafarge Le Teil.
class F fly ash: Calcia.

Table 4
pH evolution of the suspensions prepared from binary blends

Blend composition	pH			
	17 d	29 d	40 d	57 d
OPC 40% SF 60%	10.4	10.7	10.4	10.3
OPC 50% SF 50%	10.5	10.4	10.5	10.3
OPC 60% SF 40%	11.4	11.1	11.0	10.9
OPC 70% SF 30%	12.2	12.2	12.1	12.1
OPC 40% MK 60%	11.9	12.0	12.1	12.1
OPC 50% MK 50%	12.1	12.1	12.2	12.1
OPC 60% MK 40%	12.2	12.2	12.3	12.2
OPC 70% MK 30%	12.5	12.5	12.5	12.5

but also by a higher mechanical strength. When immersed under water, the equilibrium pH of the three concretes was reduced by more than one unity as compared with a probe made from OPC.

1.2.2. *Other types of cements*

Other binders, involving different hydration reactions, do not produce portlandite, and have less alkaline pore solutions. Their potentialities to match the requirements of Table 1 were thus reviewed.

1.2.2.1. Calcium aluminate cements. The pore water pH of calcium aluminate cements, ranging from 11.4 to 12.5, is reduced as compared to OPC [54]. However, direct use of these binders comes up against three difficulties: *(i)* the pore solution pH still exceeds the target value (pH 11), *(ii)* a rapid heat evolution during hydration generates major temperature rise [55], and *(iii)* a conversion process, which involves the transformation of the metastable hydrates CAH_{10} and C_2AH_8 formed below 30 °C into the higher density hydrates C_3AH_6 and AH_3 with the liberation of water, results in an increase in porosity and a decrease in strength [56]. Adding a sufficient quantity of pozzolans might be an interesting solution since it has the beneficial effects of reducing heat output due to cement dilution, of decreasing the pore solution pH, and of counter-acting the strength loss with time [57–60]. One of the reasons for this latter phenomenon is believed to be the formation of strätlingite C_2ASH_8 in preference to C_3AH_6. Silica also reacts with calcium in solution, inhibiting the formation of C_2AH_8 initially, and C_3AH_6 after conversion. Investigations have thus been recently undertaken in order to check the feasibility to design a low-pH cement from a blend comprising 80% calcium aluminate cement and 20% silica fume [61].

1.2.2.2. Calcium sulfoaluminate cements. Raw mixes for calcium sulfoaluminate (CSA) clinkers differ from these for OPC in that they contain significant amounts of sulfates. Therefore, the reactions and products are different. The CSA clinker is mainly composed of yeelimite ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$), belite ($C_2S$) and an Al-rich ferrite [62]. After cooling, it is interground with gypsum to a fine powder. By increasing the proportion of gypsum (typically from 10 to 25%), a series of cements, ranging from rapid hardening to shrinkage-compensating, and eventually to self-stressing, can be produced [63]. CSA cement pastes harden through the formation of an initial ettringite skeleton, and its subsequent infilling by mixtures of ettringite, calcium monosulfoaluminate hydrate, C–S–H, alumina and ferrite gel [64,65]. The reported pore solution pH values of CSA mortars are highly variable, ranging from 8.5 to 13 [66–69]. In order to get more accurate data, additional experiments have thus been carried out on cement pastes (W/C 0.4) with increasing gypsum contents (from 0 to 30%). The pastes were cured for 90 d in air-tight bag at room temperature before being crushed to a size below 80 nm and put under water (batch experiments with a liquid/solid ratio of 9 mL/g). Whatever the gypsum content, pH of the suspensions rapidly reached the equilibrium value of 11.8, which could indicate a control of the solution chemistry by ettringite dissolution, and which exceeded the target value expected for low-pH cements. CSA cements were thus discarded in a first approach.

1.2.2.3. Phospho-calcic cements. Phospho-calcic cements could seem attractive at first sight. Hydroxyapatite, which is the thermodynamically stable resulting product, has a very low solubility in neutral or basic medium and leads to equilibrium pH within the range 7–9 [70–75]. However, up to now, very few materials have been designed to be workable using contemporary engineering practices, and they all show poor mechanical strength.

1.2.2.4. Magnesia phosphate cements. The last cements under consideration were the magnesia phosphate binders, the pore solution pH of which being typically within the range 7–8 [73]. These cements, which are based on an acid–base reaction between deadburnt magnesia and a phosphate salt [74–78.], have however a redhibitory drawback, their very rapid heat release, which precludes their use for massive concrete.

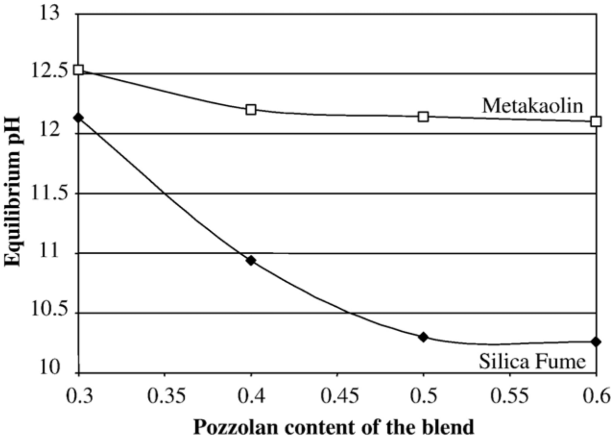
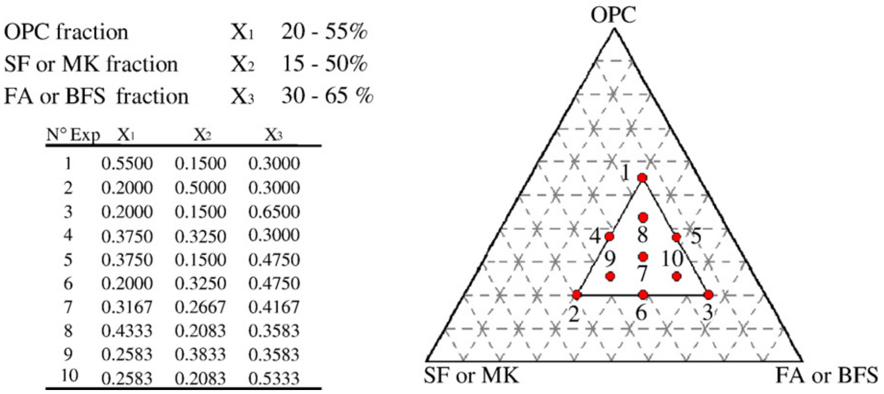


Fig. 3. Equilibrium pH of binary blends consisting of OPC and SF or MK.



OPC fraction X_1 20 - 55%
SF or MK fraction X_2 15 - 50%
FA or BFS fraction X_3 30 - 65 %

N° Exp	X_1	X_2	X_3
1	0.5500	0.1500	0.3000
2	0.2000	0.5000	0.3000
3	0.2000	0.1500	0.6500
4	0.3750	0.3250	0.3000
5	0.3750	0.1500	0.4750
6	0.2000	0.3250	0.4750
7	0.3167	0.2667	0.4167
8	0.4333	0.2083	0.3583
9	0.2583	0.3833	0.3583
10	0.2583	0.2083	0.5333

Fig. 4. Experimental domain and selected design.

1.3. Objectives of the work

It was concluded from the literature review that low-pH and low-heat cement may be obtained by blending OPC, or possibly calcium aluminate cements, with high amounts of artificial pozzolans such as silica fume, metakaolin or low CaO-fly ash. An experimental program was then undertaken at the laboratory scale to supplement the literature data. Emphasis was placed on the design of blends of calcium silicate cements and pozzolans. The objective was to test and compare blends described in the literature, to perform a more systematic investigation of the binary or ternary systems composed of OPC or slag and pozzolans (silica fume, metakaolin, and fly ash) in order to identify alternative formulas, and to check the feasibility to design a low-heat and high strength concrete from the most promising blends.

2. Experimental

2.1. Components of the blends

Table 3 shows the composition and properties of the components used to design low-pH blends. Three pozzolans were investigated: silica fume, which was used in a densified form for easier handling, commercial metakaolin, and low-CaO fly ash. They were characterized by their pozzolanic index, which represents the amount of portlandite reacting with one gram of pozzolan. SF and MK were much more reactive than FA in the short term, which was due for a part to their high specific area. The two hydraulic compounds (OPC and BFS) were selected for their low alkali content.

2.2. Blend selection

In a first step, blends were selected according to the following criterion: pH of water in equilibrium with hydrated cement should be below 11. Given the very long time required to get complete hydration of cement under standard curing conditions, a special procedure was developed. Experiments were carried out under nitrogen atmosphere on cement suspensions (W/C ratio of 9 mL/g) under mild milling conditions. Hydrates formed at the surface of the cement grains were eroded, and anhydrous cement was thus maintained in direct contact with water. The suspension pH was monitored until stabilization. The solid phases were then analyzed using XRD (Siemens D8 — Copper anode $\lambda_{K\alpha 1}=1.54056$ Å) and TGA (TA-SDT 2960).

2.3. Design of mortars

Standard mortars were prepared from cement, water and siliceous sand (0/2 mm). The water/cement and sand/cement ratios were fixed respectively to 0.5 and 3. Mixing was performed with a standard mortar mixer (European standard EN 196-1) according to the following sequence: *(1)* introduction of water, *(2)* addition of the pre-mixed pulverulents while maintaining slow stirring, *(3)* adjustment of the grout workability with a superplasticizer made of polycarboxylic ether (Chryso Fluid Optima 175), and *(4)* mixing at high speed for 3 min.

The elaborated materials were characterized by measuring various parameters according to standard procedures: bleeding (French standard NF P 18-359), Vicat setting (EN 196-3), heat of hydration (NF P 15-436), compressive strength (EN 196-1), and swelling or shrinkage (NF P 15-433) of prismatic samples ($4 \times 4 \times 16$ cm^3) cured for 1 year at 20 °C under water, in air or in an air-tight bag. Porosity was characterized using mercury intrusion porosimetry (Micromeritics Autopore III —

Table 5
Measured responses

		OPC/SF/FA blends			OPC/MK/FA blends			OPC/SF/BFS blends		
pH at		17 d	29 d	73 d	29 d	40 d	59 d	17 d	40 d	112 d
Run	1	12.34	12.18	12.14	12.36	12.40	12.44	12.70	12.25	12.26
n°	2	11.27	11.14	10.99	11.70	11.63	11.59	10.88	10.24	10.14
	3	11.99	11.67	11.51	11.83	11.84	11.78	12.24	11.95	11.70
	4	11.33	11.10	10.98	11.85	11.96	11.96	11.88	11.18	10.72
	5	12.04	11.57	11.35	12.07	11.97	11.95	12.41	12.18	11.96
	6	11.29	11.13	11.00	11.76	11.73	11.69	11.66	10.81	10.47
	7	11.53	11.25	11.04	11.92	11.96	11.92	12.01	11.45	11.15
		11.45	11.18	10.98	11.93	11.94	11.90	12.03	11.50	11.12
		11.43	11.16	10.99	12.05	12.08	11.95	12.03	11.51	11.17
	8	11.94	11.58	11.31	12.20	12.14	12.05	12.35	12.03	11.87
	9	11.15	10.99	10.87	11.74	11.80	11.76	11.41	10.66	10.37
	10	11.79	11.47	11.25	11.94	11.94	11.94	12.16	11.84	11.48

Table 6
Estimated model coefficients

		OPC/SF/FA blends			OPC/MK/FA blends			OPC/SF/BFS blends		
pH at		17 d	29 d	73 d	29 d	40 d	59 d	17 d	40 d	112 d
Model coefficients	b_1	15.882	19.017	19.685	16.132	17.505	16.634	14.690	15.351	19.547
	b_2	16.047	16.854	15.504	15.336	15.209	13.424	8.012	14.521	20.415
	b_3	13.645	14.446	14.346	12.795	13.967	13.187	12.905	14.694	15.861
	b_{12}	−20.295	−30.775	−26.836	−24.199	−26.448	−16.693	−1.861	−25.536	−53.538
	b_{13}	−5.731	−17.235	−19.146	−9.591	−17.005	−12.668	−4.257	−8.766	−19.392
	b_{23}	−14.370	−17.117	−12.774	−12.604	−16.368	−9.769	0.207	−25.023	−40.000
	b_{123}	16.064	41.301	24.849	61.182	−81.662	49.640	15.785	76.964	125.579

investigated pressures ranging from 0.8 to 530,000 psia). Crystallized phases of the hardened mortars were identified using XRD, and the portlandite content was estimated using TGA.

2.4. Design of concrete

The concrete samples included crushed limestone aggregates, the properties of which were determined: density 2.7, grain size 0/4 mm and 4/15 mm, water absorption 1%, Los Angeles coefficient 24, Micro-Deval coefficient 15. They were prepared with a 50 L mixer according to the following procedure: *(1)* mixing of the aggregates for 30 s, *(2)* addition of cement and mixing for 1 min, *(3)* addition of water and superplasticizer (Chrysofluid Optima 175) and mixing for 2 min, *(4)* measurement of the concrete workability with the Abrams cone (European standard EN 12350-2), *(5)* possible adjustment of the water and superplasticizer contents in case of insufficient slump.

The compressive strength was measured on cylindrical 11 × 22 cm samples after 28 d of curing under water at 20 °C, as well as on 7 × 7 × 28 cm^3 prismatic samples after 90 d of curing at 20 °C under water, in air-tight bag, or in air (50% relative humidity). The dimensional variations of the 7 × 7 × 28 cm^3 samples were also recorded during their whole period of curing (French standard NF P 18-427).

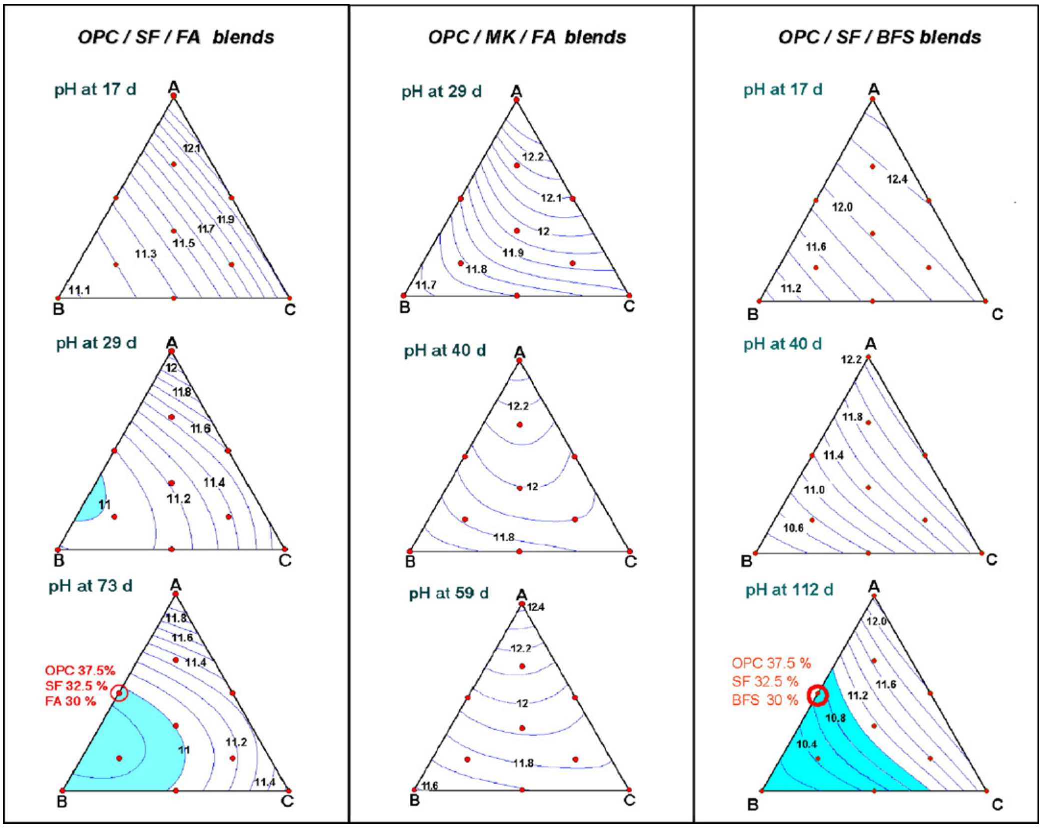


Fig. 5. Evolution of pH contour plots for OPC/SF/FA, OPC/MK/FA and OPC/SF/BFS blends. A: OPC 55% − SF or MK 15% − FA or BFS 30%. B: OPC 20% − SF or MK 50% − FA or BFS 30%. C: OPC 20% − SF or MK 15% − FA or BFS 65%.

3. Results and discussion

3.1. Blends selection

3.1.1. Binary blends

Binary blends consisting of OPC (40 to 70%) and SF or MK (30 to 60%) were first investigated (Table 4, Fig. 3). The pH of the suspensions was almost stabilized after 17 d. It decreased when the amount of SF increased. A levelling-off was however observed for SF contents above 50%. pH values below 11 could be obtained with blends containing at least 40% SF. As for MK, the equilibrium pH remained above 12 whatever the replacement level of OPC.

3.1.2. Ternary blends

The combination of a fast-reacting pozzolan such as SF or MK and of a slow-reacting compound such as fly ash or slag could result in a number of synergistic effects [43,46,47]. Potentialities of ternary blends were thus studied using experimental designs.

The factors were the fractions of OPC (X_1), SF or MK (X_2), and FA or BFS (X_3) in the blend. They checked Eq. (1), which was characteristic of a three-component mixture problem.

$$x_1 + x_2 + x_3 = 1 \tag{1}$$

The factors were constrained between a lower limit a_i and an upper limit b_i ($0<a_i<x_i<b_i<1$), which were selected by taking into account data from the literature and results of exploratory trials performed with extreme compositions. The resulting region of interest was a simplex, as shown in Fig. 4. Response surface methodology is based on the hypothesis that the responses (i.e. pH of the suspensions) can be approximated, within the range of the data, by a low order polynomial model. The postulated model was thus a special cubic polynomial in the canonical form.

$$\begin{aligned} y = {} & \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 \\ & + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 \end{aligned} \tag{2}$$

where y=response, β_i=model parameter to be estimated.

The positioning of experimental points within the experimental domain is of great importance to obtain a good precision on the estimates of the model parameters and, in a second step, on model-predicted response values. The well-known simplex-lattice design introduced by Scheffé [79] was used in order to estimate the 7 parameters of the model defined by Eq. (2). It included the 3 vertices of the simplex, the 4 edge centroids, and the overall centroid. Three validation points corresponding to mixtures regularly distributed in the investigated domain and as remote as possible from the other selected points were added, for a total of 10 runs (Fig. 4). Experimental data are summarized in Table 5. Two replicates of the overall centroid provided a measure of the experimental error. For each response, the model coefficients were estimated by standard least squares regression techniques (Table 6). Possible model deficiencies were looked for by using analysis of variance (ANOVA). The models provided a good correlation of the experimental data for all the investigated responses and were thus regarded as acceptable prediction tools.

From the response contour plots (Fig. 5), it can be seen that, after 17 d of hydration, pH of the suspensions made from OPC/SF/FA or OPC/SF/BFS blends mainly depended on the SF content: the higher the SF fraction, the lower the pH. Then, a curvature of the plots was noticeable, which indicated that FA or BFS had also begun to react. When equilibrium was reached (at 73 d or 112 d), all blends checking Eqs. (3) or (4) led to pH below 11.

OPC/SF/FA blends:

$$\begin{aligned} & 19.685\ x_1 + 15.504\ x_2 + 14.346\ x_3 \\ & \quad -26.836\ x_1x_2 - 19.146\ x_1x_3 - 12.774\ x_2x_3 \\ & \quad + 24.849\ x_1x_2x_3 \leq 11 \end{aligned} \tag{3}$$

OPC/SF/BFS blends:

$$\begin{aligned} & 19.547\ x_1 + 20.415\ x_2 + 15.861\ x_3 \\ & \quad -53.538\ x_1x_2 - 19.392\ x_1x_3 - 40.000\ x_2x_3 \\ & \quad + 125.579\ x_1x_2x_3 \leq 11 \end{aligned} \tag{4}$$

OPC/MK/FA blends did not allow to meet the requirement of an equilibrium pH below 11: this latter always remained above 11.5. On the contrary, the binders comprising 37.5% OPC, 32.5% SF and 30% FA or BFS were selected for further experiment. Indeed, among all blends leading to pH below 11, they had *(i)* limited SF content, which should reduce water demand, plastic shrinkage and material cost, as well as *(ii)* a significant OPC content, which should provide high mechanical strength.

3.1.3. Discussion

The equilibrium pH was shown to depend mostly on the silica content of the binders whatever its origin (Fig. 6). pH values below 11 were obtained for silica contents higher than ≈50%, which was only checked by some of the OPC/SF, OPC/SF/FA, and OPC/SF/BFS blends.

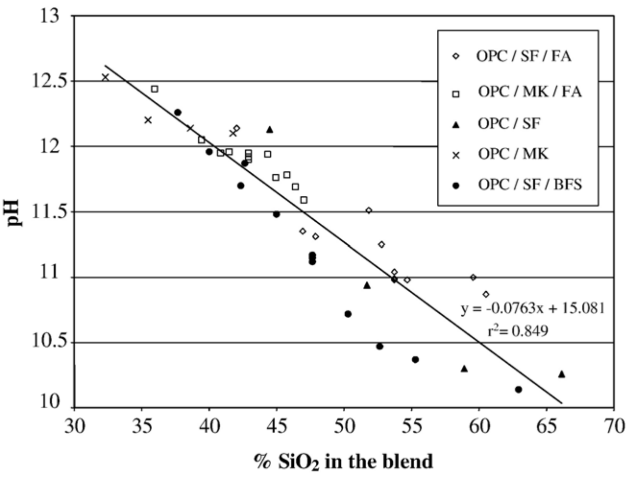


Fig. 6. Correlation between silica content in the binder and equilibrium pH.

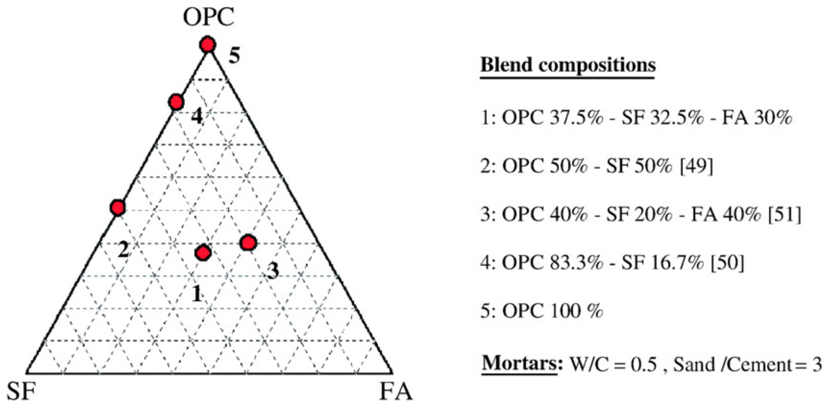


Fig. 7. Investigated mortar compositions.

XRD analysis performed on the solid fractions at the end of the experiments confirmed that the blends were almost fully hydrated since the anhydrous cement phases were not detected anymore, and that portlandite had been totally depleted by pozzolanic reaction. The absence of afwillite ($C_3S_2H_3$) was also checked. This phase, which can be prepared from C_3S by ball-milling with water, and which appears to be thermodynamically stable at ordinary temperature and pressure in the presence of lime and water [80], shows no similarities to C–S–H gel, and nothing resembling it can be obtained in cement pastes cured under usual conditions. The crystallinity of the samples was very low, the most intense peaks in the XRD patterns corresponding to non reactive phases brought by the pozzolanic compounds (quartz, mullite, hematite, and anatase), or to calcite that might have resulted from the carbonation of the samples during filtration and drying. Some hydrated phases were also detected: ettringite (traces), strätlingite in samples containing metakaolin, and hydrotalcite in samples containing BFS. The chemistry of the low-pH cements will be the subject of a subsequent article.

3.2. Elaboration and characterization of mortars

Mortar samples were elaborated using the selected ternary blend containing silica fume and fly ash. Their properties were compared to a probe made from OPC only, and to low-pH materials described in the literature [49–51] (Fig. 7, Table 7).

3.2.1. Properties of fresh grouts

The viscosity of the mortars after mixing increased strongly with their silica fume content, which was counteracted by adding increasing amounts of superplasticizer. The relationship between the superplasticizer content and the silica fume content

Table 7
Properties of mortars

	Blend #1	Blend #2	Blend #3	Blend #4	Blend #5 (probe)
Blend composition	CEM I 37.5% SF 32.5% FA 30%	CEM I 50% SF 50%	CEM I 40% SF 20% FA 40%	CEM I 83.3% SF 16.7%	CEM I 100%
Plasticizer content to get a workability comparable to that of the probe (/ weight of cement)	1.1%	2.6%	0.5%	0.3%	0%
Bleeding at 24 h	nul	nul	nul	nul	nul
Vicat setting	Beginning: 6 h End: 7 h	Beginning: 4 h End: 5 h	Beginning: 7 h End: 8 h	Beginning: 3 h End: 5 h	Beginning: 3 h End: 5 h
Temperature rise (°C) (Langavant calorimetry)	13.1	20.0	14.7	23.0	23.4
Total porosity (curing under water)	23.1% (3 m) 22.5% (6 m) 20.0% (1 y)	18.0% (3 m) 15.5% (6 m) 14.3% (1 y)	24.1% (3 m) 23.9% (6 m) 22.0% (6 m)	– – –	13.9% (3 m) 13.8% (6 m) 14.1% (1 y)
Porosity below 20 nm (% of total porosity) (1 year of curing under water)	67.6%	75.5%	57.9%	–	38.9%
Dimensional variations after one year of curing (μm/m)	Air: −1042 Bag: −474 Water: +324	Air: −1171 Bag: −591 Water: +349	Air: −923 Bag: −437 Water:+293	Air: −824 Bag: −337 Water: +225	Air: −660 Bag: −323 Water: +199
Compressive strength after one year of curing (MPa)	Air: 28.3 Bag: 46.7 Water: 60.3	Air: 61.3 Bag: 91.8 Water: 89.0	Air: 21.1 Bag: 44.3 Water: 51.7	Air: 32.2 Bag: 51.5 Water: 55.2	Air: 39.8 Bag: 62.6 Water: 65.4
Portlandite content after one year of curing in air-tight bag	Non detectable by TDA	Non detectable by TDA	traces	1.78%	5.50%
pH of suspension prepared from crushed mortar after one year of curing in air-tight bag (Liquid/Solid = 9 mL/g)	11.3	11.3	11.5	12.5	12.6

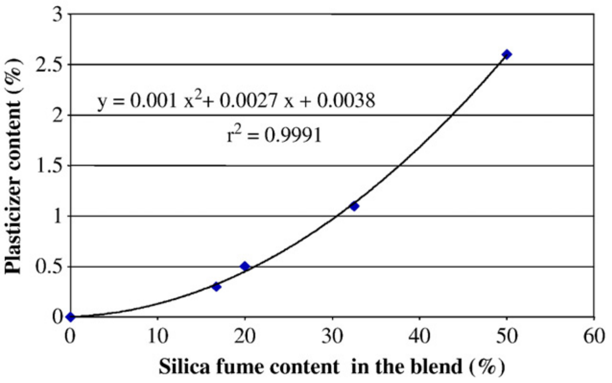


Fig. 8. Dependence of the plasticizer content (expressed as cement weight %) on the silica fume content of the blend.

could be well described by a second-order polynomial (Fig. 8). Setting occurred in less than 8 h for all samples. It was however slightly retarded for blends containing fly ash, the delay increasing with the FA content. This resulted from the cement dilution and from the low reactivity of fly ash at early age. The heat release during hydration was monitored using semi-adiabatic calorimetry. It decreased with the OPC content. The temperature rise was reduced by a factor 1.33 for the blend with the highest cement replacement level.

3.2.2. Properties of hardened mortars

The porosity was characterized after 3, 6 and 12 months of curing under water at ambient temperature. Whatever the age of the samples, adding pozzolanic compounds resulted in an increase in the total porosity, which was maximum for mortar #3 with the highest FA content. The porosity of 1-year old blended mortars was however refined as compared to the probe. The fraction (y) of pores with a diameter below 20 nm (related to the C–S–H gel) increased almost linearly with the SF content (x) (fitting function: $y=0.8123x+40.161-r^2=0.993$). It was also checked that the porosity of the blended mortars decreased with time all the more rapidly since the SF content was high, which once again resulted from the fact that SF was more reactive than FA.

Whatever the type of curing, the dimensional instability of $4\times4\times16$ cm^3 specimens increased with their SF content (Fig. 9). The shrinkage increase might have been a consequence of the porosity refinement. Indeed, empty porosity was created within the capillary pore system of the mortars' microstructure due to water depletion by cement hydration and desiccation. The largest pores emptied first, followed by pores of decreasing diameter. The water/air menisci created in the partly empty pores induced shrinkage, the magnitude of which depended on the diameter of the pores being emptied: the lower the pore diameter, the higher the stress.

The compressive strength of the specimens depended on the type of curing: the best values were logically achieved for samples cured under water, which thus had the highest degrees of hydration (Fig. 10). On the contrary, desiccation induced a strength reduction by a factor as high as 1.5. SF had three beneficial effects: it accelerated the hydration of OPC, it converted portlandite into C–S–H by pozzolanic reaction, and it densified the interfacial zone between cement pastes and aggregates. Thus, increasing the SF content of the blends resulted in a rapid hardening and in high compressive strength. On the contrary, the strength gain of FA-containing mortars #1 and #3 was slower and one-year old samples remained less resistant than the probe.

With no measurable portlandite present after respectively 6 and 3 months, the pH values of mortars #1 and #2 were significantly lower than that of the reference. However, they remained higher than that obtained in the first section with an accelerated hydration procedure. This discrepancy might be attributed to the fact that hydration of the mortars was not complete after one year: C_3S and C_2S peaks were still observed in the XRD patterns, together with ettringite, quartz and mullite (for mortar #1 only).

Blend #1 comprising 37.5% OPC, 32.5% SF and 30% FA seemed to constitute a good compromise between SF-rich (blend #2) and FA-rich (blend #3) formulas. SF compensated for low early strength of FA materials and allowed a total depletion of portlandite after 6 months of curing. As for FA, it limited the increased water demand of SF as well as the dimensional instability of the specimens.

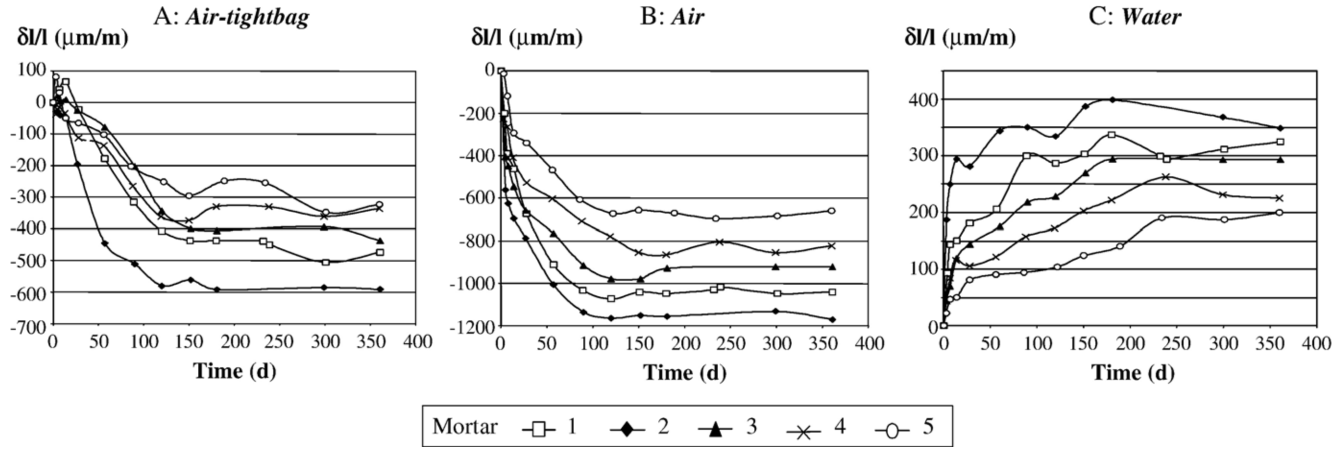


Fig. 9. Shrinkage or swelling of $4\times4\times16$ cm^3 specimens cured at room temperature in air-tight bag, in air or under water.

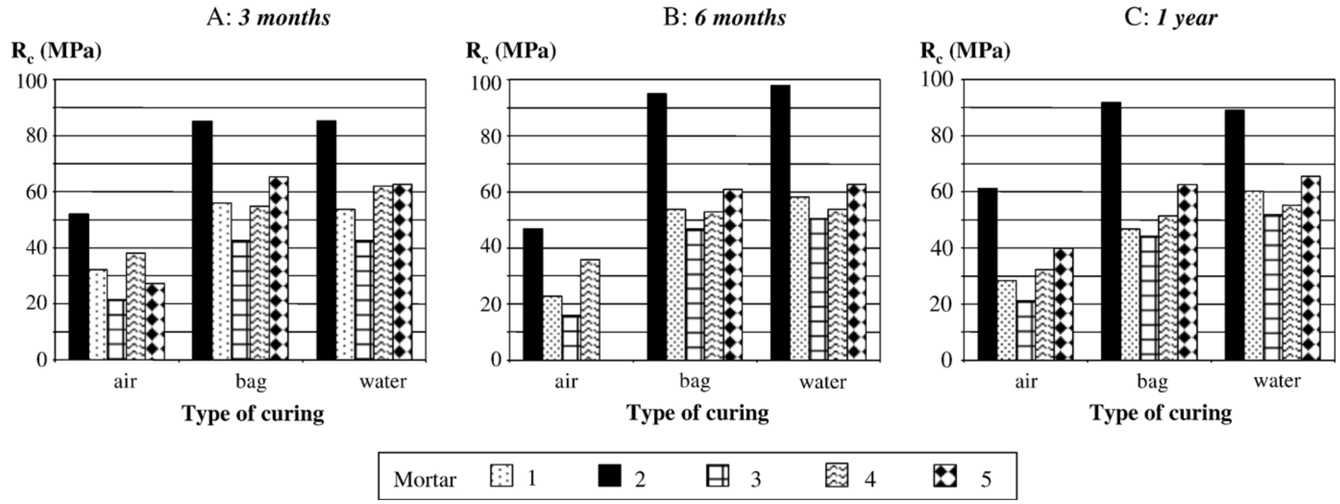


Fig. 10. Compressive strength of 4 × 4 × 16 cm^3 specimens cured at room temperature in air-tight bag, in air or under water.

3.3. Concrete mixture-proportioning

The next step was to design concrete from two low-pH binders: binary blend #2′ made from 60% OPC and 40% SF (the minimum SF content to get a pH below 11 under the experimental conditions of Section 3.1), and ternary blend #1 comprising 37.5% OPC, 32.5% SF and 30% FA. The desired properties were as follows: *(i)* the concrete should be workable, with a slump within the range 100–150 mm, *(ii)* the temperature rise under semi-adiabatic conditions should be below 20 °C, and *(iii)* the compressive strength after 90 d of curing under water should exceed 70 MPa.

Mixture-proportioning was performed using the conventional Dreux's method [81]. After the production of trials batch, minor adjustments on the plasticizer and water contents were carried out to obtain the required rheological properties, producing the actual recipes given in Table 8. The mix compositions proved to be satisfactory: it was possible, by simple means, to prepare workable concrete despite the very high amounts of pozzolans in the blends. Concrete made with blend #2′ matched all the requirements. As for concrete made with blend #1, its low-heat output should allow to increase the cement content of the recipe, which in turn should improve the mechanical strength of the samples.

Table 8
Concrete recipes and properties of resulting materials

Blend composition	Reference	1	2’	5
	% CEM I	37.5	60	100
	% SF	32.5	40	0
	% FA	30	0	0
Concrete recipe	Cement	400 kg/m^3	400 kg/m^3	400 kg/m^3
	Sand 0–4	710 kg/m^3	710 kg/m^3	710 kg/m^3
	Aggregates 4–15	1158 kg/m^3	1158 kg/m^3	1158 kg/m^3
	Water	160 kg/m^3	160 kg/m^3	132 kg/m^3
Concrete properties	Superplasticizer	4 kg/m^3	6 kg/m^3	3 kg/m^3
	Slump (mm)	100	140	145
	Temperature rise (°C)	14.2	20.6	23.3
	Heat of hydration (J/g of binder — 60 h)	184	248	273
	Compressive strength (MPa)	28 d — water: 55.0 90 d — water: 69.0 ± 3.7 90 d — bag: 66.6 ± 0.7 90 d — air: 48.1 ± 0.9	28 d — water: 77.0 90 d — water: 82.0 ± 2.0 90 d — bag: 78.4 ± 3.0 90 d — air: 67.5 ± 0.9	28 d — water: 84.0
	Dimensional variations (µm/m)	28 d — water: +110 90 d— water: +130 28 d — bag: −158 90 d — bag: −265 28 d — air: −265 90 d — air: −350	28 d — water: +75 90 d — water: +97 28 d — bag: −130 90 d — bag: −243 28 d — air: −260 90 d — air: −352	—

Temperature rise was measured on equivalent mortars in Langavant calorimeters.
Compressive strength at 90 d was measured on 7 × 7 × 28 cm^3 samples. The results were corrected so as to obtain estimates of the strength of 11 × 22 cm samples.

4. Conclusion

The work presented in this article aimed at designing a low-heat, low-alkalinity and high strength concrete which would be chemically compatible with clay materials in a deep geological repository for nuclear wastes. The main conclusions can be summarized as follows.

1. Low-pH cements can be designed from binary blends of OPC and SF containing at least 40% SF, or from ternary blends of OPC, SF and FA or BFS. A range of compositions was shown to lead to pH values below 11 for water in equilibrium with the fully hydrated blends.
2. Rising the silica fume content in the blends allowed to improve some properties of standard mortars elaborated with the low-pH cements: *(i)* it induced rapid hardening and high compressive strength, *(ii)* the porosity was refined, although the total porosity remained higher than that of a probe made from OPC, *(iii)* portlandite formed by OPC hydration was rapidly depleted. However, it also resulted in a bad workability of the grout, which had to be counteracted by adding increasing amounts of superplasticizer, and in a decrease in the dimensional stability of specimens cured under water, in air, or in an air-tight bag. Introducing FA to the blends allowed to decrease the viscosity of the grout and to improve the dimensional stability. However, hardening was slowed down, as well as portlandite consumption. A good compromise was obtained by combining SF and FA in a blend comprising 37.5% OPC, 32.5% SF and 30% FA.
3. Workable, low-heat and high strength concretes could be prepared from two low-pH cements (blend #1: 37.5% OPC, 32.5% SF and 30% FA, blend #2′: 60% OPC, 40% SF) using conventional engineering practices despite the very high amounts of pozzolans in the blends.

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