

Low-pH Cementitious Materials Design and Characterisation

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1. Introduction

The most accepted engineering construction concept for high radioactive nuclear waste of underground repositories requires the use of cementitious materials for different purposes, as grouting for sealing cracks and fixing of rock bolts, or concrete lining for rock support of tunnels and plugs for closing at the mouth of the disposal drifts galleries. Concrete will also be used for construction of various auxiliary structures needed for the operation of the repository.

When conventional Ordinary Portland Cement (OPC) are used for the concretes in underground repositories, the contact with the ground waters creates a pore water leachate with a pH as high as 13.5. This alkaline plume of leaching waters might perturb the engineered barriers of the repositories, as for instance the bentonite buffer (backfill material or the near-field host rock), which is not stable in high alkaline media [1]. Some authors [1-6] have demonstrated that the interaction of OPC with underground waters producing the hyper-alkaline fluids is due to the leaching of sodium and potassium hydroxides. Once these alkaline hydroxides are released, the pH of the pore water solution in the concrete is controlled by the dissolution of one of the main phases of the OPC paste, the portlandite ($\text{Ca}(\text{OH})_2$), which is the responsible for the duration of the alkaline plume at the pH 12.6. Later on, between pH 12.6 and 10, the dissolution of the calcium from silicate hydrates of the CSH gel takes place [7-10].

The accepted solution to maintain the bentonite stability, which is function of the pH, is to develop cementitious materials that generate pore waters with $\text{pH} \leq 11$, because the corrosion velocity of the clay is significantly reduced below this value [1]. The feasibility of designing and utilizing low-pH cementitious materials in underground repositories for preventing these undesired processes are being investigated [2-5]. Therefore, it is evident that the decrease of the pore fluid pH from the initial state in the pore solution up to values close to 11 implies the use of OPC cements

with low content in alkalis and the reduction of the portlandite (the main source of OH⁻).

The research on low-pH cementitious materials is being addressed from different approaches depending on the type of cement used: 1) Calcium Silicate Cements (OPC based), 2) Calcium Aluminates Cements (CAC based), 3) Phosphate Cements (PC) and 4) Magnesia Cements (MC) [2-11].

A literature review on this topic shows that to reduce the content of portlandite, mineral additions with high silica content should be used [3, 11-13]. The amount of OPC is reduced and substituted by mineral additions to decrease the calcium hydroxide formation in the binder paste. Pozzolans, like silica fume (SF) and fly ashes (FA), are included in the mineral blends containing high silica content. The blends follow the pozzolanic reaction that consumes Ca(OH)₂ [11].

High pozzolan content in the binder should significantly modify most of the concrete “standard” properties. The challenge with these blends is, then, more complex if the employment of chemical admixtures, developed for OPC, is required. Both the compatibility and the bellow-the-admissible-level pore water pH have to be guaranteed. Therefore, a deep understanding of the performance of low-pH cementitious materials is needed.

This paper deals with the design of low-pH OPC-based components for technical use in the construction of sealing plug shotcrete with low mechanical requirements, in order to be used in underground radioactive waste repositories compatible with bentonite. High contents of silica fume (>20%) substituting partially the OPC have being employed and the physico-chemical properties of the new binders have been carefully analyzed. The research has been performed within the frame of the ESDRED EC project: "Engineering Studies and Demonstration of repository Designs", and the Spanish waste national management agency "ENRESA".

2. Experimental program

The binder formulations were prepared using Ordinary Portland Cement, OPC, with low alkaline and low aluminates content which has been partially substituted by high contents of non-condensed Silica Fume (SF) (20, 40 and 50%). These high contents of SF are not typically employed, so their physicochemical and technological properties are not known in the construction industry. The chemical composition of the OPC and SF are presented in Table 1. It is obvious that the SF introduces high SiO₂ and

low CaO percentages in the blend, although the alkaline content is similar for both raw materials.

Table 1. Chemical composition of OPC and SF.

	LI*	IR*	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO (total)	MgO	SO ₃	Na ₂ O	K ₂ O	CaO (free)	Part. Size (µm)
OPC	4.34	1.13	18.0	4.85	5.26	62.4	1.84	3.28	0.18	0.35	1.92	<28.3
SF	0.09	0.06	91.8	0.59	3.74	1.3	0.92	-	0.15	0.37	0.01	<2.3

*LI: lost of ignition; *IR: insoluble residue.

Cement pastes and mortar samples were fabricated for testing. Deionized water was used for the elaboration of the cementitious materials. A water/binder (w/b) = 0.5 was used for the pastes, while for the mortars the w/b and binder/sand (b/s) proportions varied. Standard mortar prism 4x4x16 cm were employed for mechanical properties determination. All the samples were cured in a chamber at 98% RH and 21±2°C temperature. Samples fabricated with OPC but without mineral addition were used as reference.

The compatibility with some admixtures was also studied. Two accelerators (Ac-1: with alkaline content and pH=13; Ac-2: alkali free and pH=3) and one superplasticizer (SP) were used.

The changes in the composition of the pore fluid and the solid phases at different days of hydration (2, 7, 30 and 90 days) were evaluated in the cement pastes. The pore fluid was extracted using the Pore Pressing Technique [14-15]. The ionic composition of the pore fluid was determined: pH, OH⁻ (by automatic titration with HCl 0.05N), Ca²⁺, Na⁺, K⁺ and SO₄²⁻ by ionic chromatography, and SiO₄²⁻ by photometry. Besides, the evolution of the pore fluid pH was followed using a leaching method where a solid powder paste/deionized water=1/1 was employed. This method has previously been calibrated with the Pore Pressing Technique [2].

The evolution of hydration of the binder pastes was determined by stopping the curing at different ages, after powdering the samples and removing the free water by adding a mix of ethanol and acetone. DTA/TG tests have been employed to study the evolution of the microstructure composition of the solid phases in the fabricated pastes. These analyses were performed from room temperature to 1200°C at a heating rate of 10°C/min. XRD analyses of the solid phases were also made from a 2θ value of 5° to 60° at steps of 0.02° and CuKα₁ radiation. Backscattering microscopy was employed for the observation of the hydrated binder

formulations and EDAX analyses of the pastes were performed for Ca/Si determination. The changes in pore microstructure using mercury porosimetry were also assessed.

The mechanical properties of the binders were analyzed in standard mortars ($w/b=0.5$; $b/s=1:3$). The compatibility with accelerators and superplasticizers was studied in both paste and mortar samples. In the binder pastes mixed with the accelerators, the setting time was measured (using the Vicat method) and also the pore fluid pH. The mechanical properties were determined in mortar samples, varying the w/b and b/s ratios. The water demand of the mortars for a given consistency (flow-table test) was determined on a comparative basis.

3. Results.

3.1. Changes in pore fluid composition.

The evolution of the pore fluid pH, measured with the leaching test 1/1, is showed in figure 1. The higher the increase in SF content of the binder, the higher the decrease of the pore water pH of the paste. This effect is more relevant at longer curing times (90 days). The percentage of SF in the cement formulation has to be above 40% to obtain a pH near 12 at 90 days and with a 50% of SF pH is under this value.

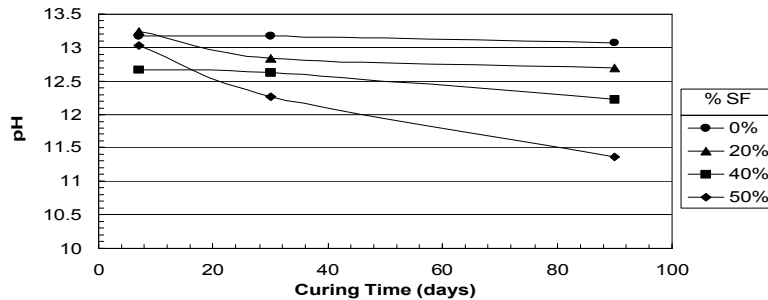


Figure 1. Evolution of the pH of pore fluid paste (leaching method 1/1).

Table 2. Composition of the pore fluid of low-pH pastes. 90 days.

Sample	pH	OH ⁻ (ppm)	Na ⁺ (ppm)	K ⁺ (ppm)	Ca ⁺² (ppm)	SiO ₃ ²⁻ (ppm)	SO ₄ ²⁻ (ppm)
Ref.	13.17	2550	382	3628	461	0.56	27
40%SF	12.22	539	119.7	321.8	612.1	9.82	84.4
50%SF	11.20	51	165.1	368.6	650.9	60.27	2180.8

Table 2 shows the pore fluid composition, from pore pressing tests after 90 days of hydration. A decrease in the alkaline content is evident in binder formulations with high contents of SF, while Ca²⁺ increases in the pore fluid respect to OPC without blending addition. The increase of the

SO_4^{2-} content in the paste with the lowest pore fluid pH is also very significant. Figure 2 shows the evolution with curing time of the Na^+ , K^+ and Ca^{2+} contents in the pore solution of the 40%SF sample.

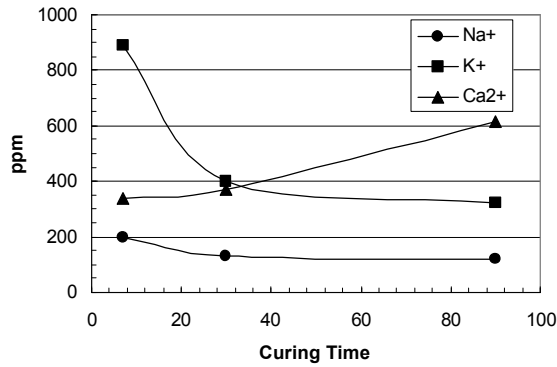


Figure 2. Evolution of Na^+ , K^+ and Ca^{2+} contents in the 40%SF pore fluid.

3.2. Changes in microstructure of solid phases.

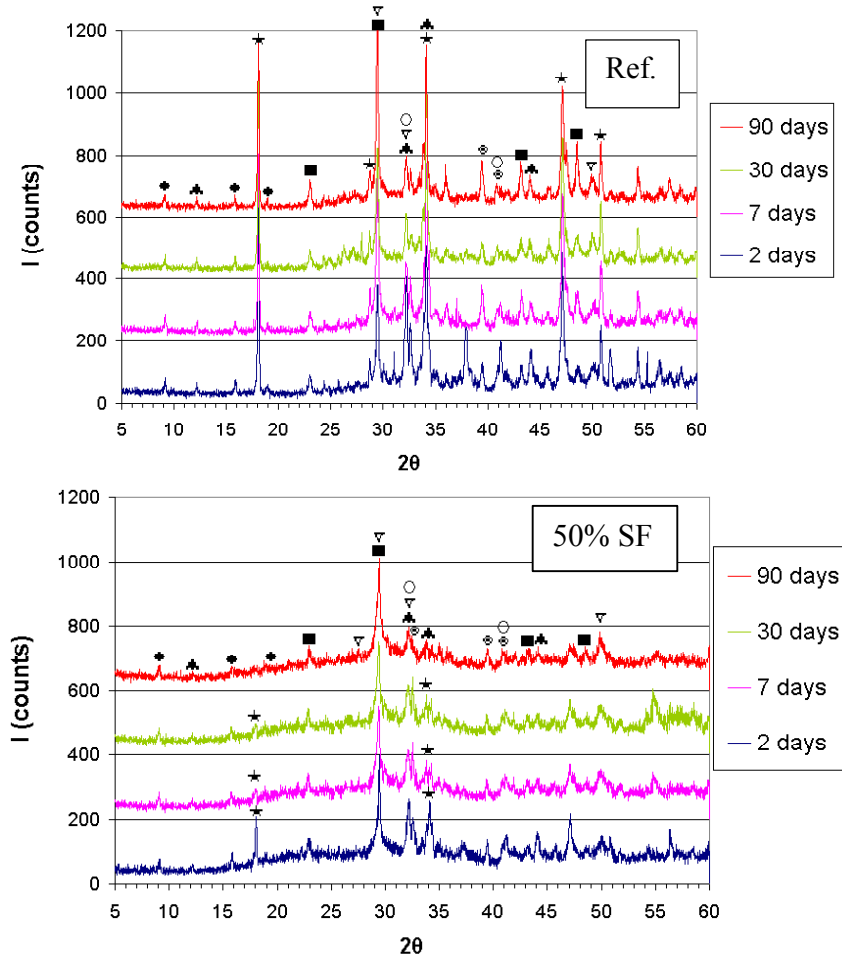


Figure 3. XRD evolution of Ref (up) and 50%SF (down) pastes.
 ∇ : CSH gel; \blacksquare : CaCO_3 ; $+$: portlandite; \odot : C_2S ; \circ : C_3S ; \oplus : C_4AF ;
 $\square\cdot$: quartz; \star : ettringite.

The results of XRD analyses of cements pastes containing 50% SF are considered in figure 3, at several days of standard curing. The reference sample without blend addition is used for comparison. The portlandite peaks in 50%SF sample decrease with curing time and has fully disappeared at 90 days, while in the reference sample the portlandite peaks increase in size with hydration evolution. The peaks attributed to anhydrous grains of OPC, belite (C_2S) and alite (C_3S), are more clearly observed in the reference sample; in fact, with 50% SF addition these peaks decrease with the evolution of hydration. Peaks attributed to the crystalline CSH and ettringite could also be identified in the paste with high SF content, although the pH has significantly decreased at 90 days (pH <11), which indicates that ettringite remains stable even at these low pH.

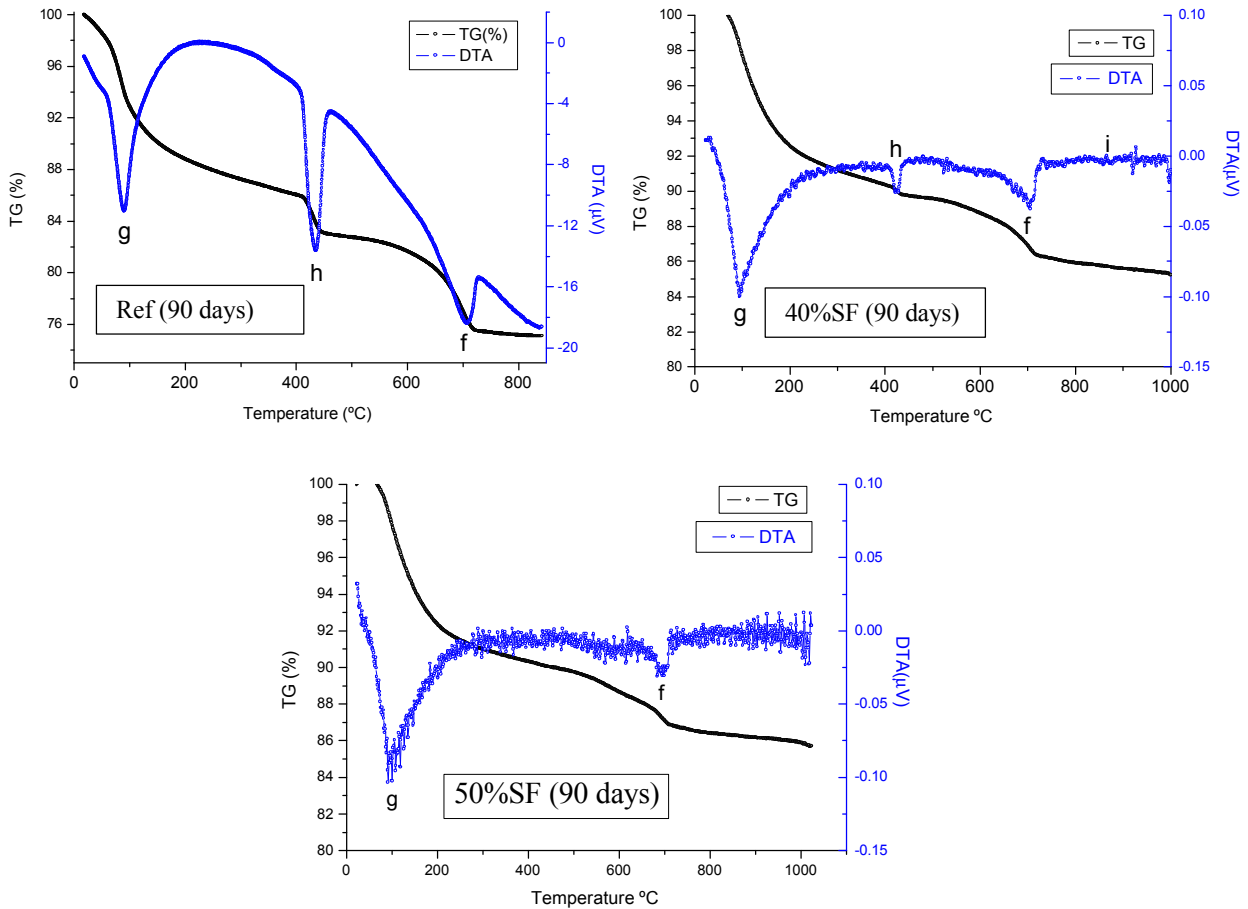


Figure 4. DTA-TG of Ref. (up-left), 40%SF (up-right) and 50%SF (down) at 2 and 90 days. g: CSH gel; h: portlandite; f: calcite; i: amorphous calcium silicate hydrates.

The DTA-TG analyses of the reference, 40%SF and 50%SF samples after 90 days of hydration are given in figure 4. The endothermic peak of the

portlandite (between 400-500°C) diminishes with the increase in the content of SF, even it disappears with 50%SF. The amount of CHS gel (endothermic peak between 100-300°C) increases notoriously with hydration in the cement pastes; however, at early ages of hydration (2 days) it is higher in the pastes with SF, as noticed in figure 5. The CSH composition of cement pastes containing SF, at 90 days, was studied using EDAX-SEM tests. The amount of anhydrous grains of cement are low and only composed by C₂S. The CaO/SiO₂ ratio of CSH ranges between 1.2 and 0.8.

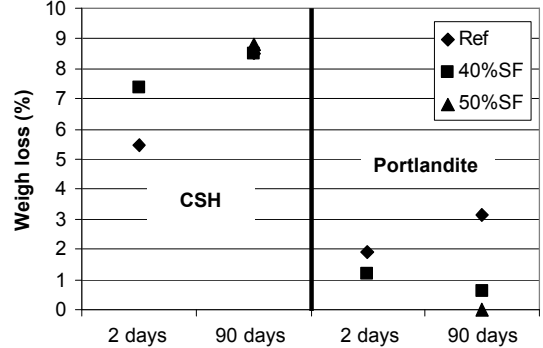


Figure 5. Weight loss of CSH and CH from TGs, at 90 days of curing.

3.3 Physical-mechanical properties of low-pH cements.

The porosity and the pore size distribution of the reference and 40%SF cement pastes are given in table 3. The total porosity is even higher in the low-pH paste. The difference is in the size of pores < 0.01µm, related with the region of gel porosity.

Table 3. Total porosity and pore size distribution of Ref and 40%SF pastes.

Sample	% total Porost.	Capillary pores > 1µm	Capillary pores 1-0.05µm	Capillary pores 0.05-0.01µm	< 0.01µm
Ref.	16	0.5	2.6	6.9	6
40%SF	19.2	0.7	2.2	6.3	10

The evolution of the compressive strengths of the mortars elaborated with low-pH binder formulations are given in figure 6. The high addition of silica fume does not seem to affect this property. In fact, it seems that the addition of 40% of silica fume improves the strength, even at early ages of hydration. With 50% SF, the compressive strength is similar to the reference one.

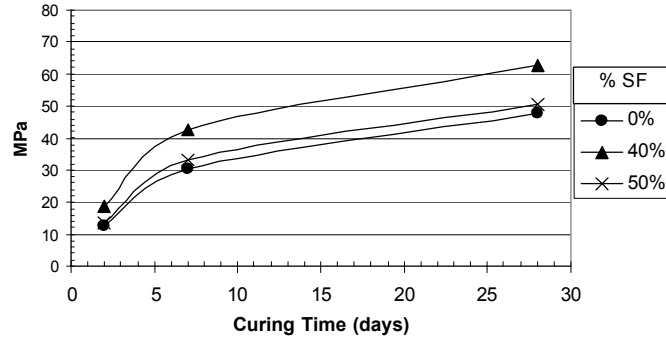


Figure 6. Evolution of compressive strength with time in low-pH mortars.

The compatibility of low pH binders with accelerated admixtures was evaluated through the determination of the setting time (initial and final). In the case of 40%SF, it is compatible with the alkali free accelerator (Ac-2), due to the initial setting time was <math><30''</math>. On the contrary, this sample is not compatible with Ac-1, the initial setting time being longer than 2 minutes. The recommended accelerator dosage was 6%. The addition of 50% of silica fume showed no compatibility with both accelerators. The SP efficiency was tested in mortars at a dosage of 2% by weight of cement. The water demand was the parameter assessed with regard to binder content. The low-pH pastes with high content of silica fume needs higher water to binder (w/b) ratios for an appropriate consistency than a standard OPC mortar. The evolution of the compressive strength of these mortars was also analyzed, which follows the expected trend of decrease when the w/b increases. As seen in table 4, the compressive strength of mortar+SP+Ac tends to decrease as compared when only SP was added. The strength decay detected was nearly 50%.

Table 4. Effect of accelerator on Compressive Strength and pH (40%SF mortar); b:s=1:3.

Sample	w/c	Compressive Strength (MPa)			pH (1/1)			
		2 d	7 d	28 d	2d	7d	28d	90d
40% SF	0.5	18.5	42	62	-	12.3	11.7	10.9
40%SF + SP	0.68	7.3	12.8	20.1	12.5	12.2	11.9	11.3
40%SF + SP + Ac-2	0.72	2.7	8.3	14.1	11.8	12.3	11.8	11.1

4. Discussion

4.1. CSH of low-pH cement formulations

The microstructure of the low-pH cement pastes elaborated is clearly different from the one typically found using standard OPC. For example, there is a great difference in the calcium silicate hydrates (CSH)

generated, which are the main binding phases in all Portland cement-based systems. The Ca/Si ratio of CSH in conventional portland cement pastes varies from 1.2 to 2.3 with a mean of 1.75 [16]. On the contrary, in the low-pH cements this ratio varies from 1.2 to 0.8. CSH gels with these CaO/SiO₂ ratios are typically considered to be formed by longer length chains of tetrahedral silica [17]. The Ca/Si ratios found in present work is in agreement with the work of Stronach and Glasser [18]. These authors said that to obtain a low pH in the cement materials the Ca/Si ratio must be lower than 1.1.

4.2. Design of a low-pH OPC formulation based on pore solution changes.

It is well known that, in cement materials based on OPC, the decrease of the pore fluid pH involves the utilization of mineral additions with high silica content in order to reduce the portlandite formation. In fact, in this work it has been demonstrated that increasing up to 50% the SF content, the pore fluid pH can be reduced more than one unit (see in table 2 the samples 40%SF and 50%SF). This is due to with 50% of SF the portlandite has totally disappeared. Taking into account the obtained results, this paper intends to introduce the role played by alkalis an calcium in the pore fluid pH of the low-pH cementitious materials.

In OPC pastes the increase in the content of alkalis, Na⁺ and K⁺, contributes to increase the pH in the pore water, i.e. the generation of higher alkaline plumes. However this general rule can not be used if high contents of mineral additions are used, as it can be seen in figure 7, which shows the influence of alkalis in the pH of the pore fluid.

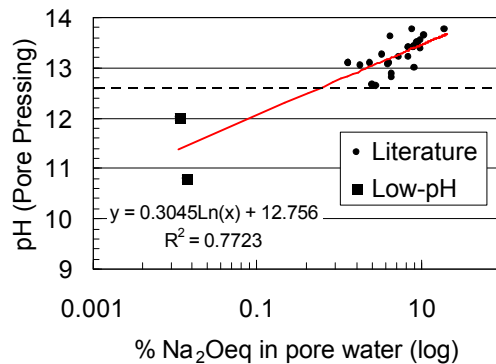


Figure 7. Influence of Na₂O_{eq} on pH.

But there is another important thing regarding the alkaline content in the pore fluid of low-pH OPC pastes. Taking into account that the alkaline contents of both raw materials (OPC and SF) are similar (see table 1), it has to be emphasized that after 90 days of hydration, there are less alkalis in the pore fluid of the low-pH cement pastes than in the pore fluid of the

paste without SF (ref OPC) (see table 2). This could be explained considering a binding process during hydration that removes the alkalis from the pore solution of low pH pastes. This binding would be taking place inside the new CSH gel. The results shown in figure 2 are in agreement with those published by Glasser and Marr in 1985 [19]. They said that silica fume is very effective in removing K^+ from the pore fluid, due to the formation of smaller Ca/Si ratios in the cement pastes. C-S-H gels with high Ca/Si ratios, have a positively charged surface, but as the Ca/Si ratio decreases the charge becomes neutral, leaving van der Waals forces to operate, and at the lowest Ca/Si ratios the surface charges become negative. In fact, Hong and Glasser [20] demonstrated that the binding process is more effective when the Ca/Si ratios of gels C-S-H are between 1.2 and 0.85, as they are in the low pH cements of the present work.

Taylor [21] concluded from pore analysis that sodium is better bonded into hydrated cement paste than potassium, so it is obvious that this binding process has to be study more extensively in order to understand not only how this process takes place but the highest affinity of the C-S-H gels for K^+ or Na^+ .

In the present work with low pH cements the alkaline content (both Na^+ and K^+) in the aqueous phase of pastes is lower at longer times of curing, so it is possible that in the CSH gels of the low-pH cements, the ions Na^+ and K^+ are gradually bonded and probably substituted by Ca^{2+} , due to a need for electro-neutralisation of the system, which agrees with the increase of Ca^{2+} in the pore fluid indicated in figure 8.

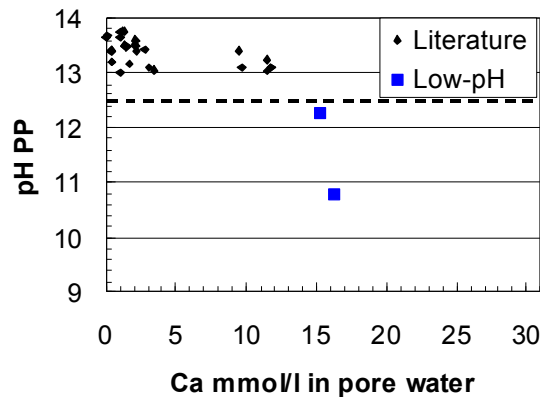


Figure 8. Calcium content in pore solution Vs pore water pH of OPC based formulations.

In fact, other important feature to stress out from pore pressing analyses of low pH pastes is the increase of the amount of calcium dissolved in the pore solution of OPC mixes at pHs under 12.5. In the 40%SF sample the

increase in calcium content can be partly attributed to the maintenance of the portlandite equilibrium [22]. But, in 50%SF, due to the total consumption of the portlandite in the pozzolanic reaction, this calcium could come from a decalcification of CSH. This decalcification and the lower content of CaO in the formulations of low-pH cement pastes will explain the lower Ca/Si ratio of the CSH formed. In fact, these Ca/Si ratios are lower than those expected from the data published in the literature [23, 24] for synthetic C-S-H, as it can be seen in Figure 9. Obviously, several factors should be considered comparing data from Ca/Si ratios of synthetic C-S-H (available in literature) and Ca/Si ratios of C-S-H in low pH cement pastes (as in present study), such as the presence of alkalis in the pore fluid and other cement phases apart from C-S-H, which should affect the pore solution equilibrium with solid phases.

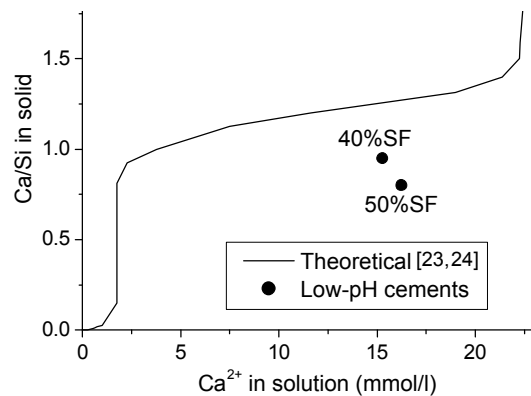


Figure 9. Ca²⁺ in solution expected for different Ca/Si ratios of the C-S-H. The theoretical values has been selected as typical from the results of many investigations [23, 24]

4.3 Technological properties of low-pH cements.

The relevant increase of the compressive strength with the addition of 40% of SF can be explained by three reasons: 1) the higher CSH gel content in the low-pH cement pastes at early ages, 2) the presence of pores with a lower size (see table 3), and 3) the packing density achieved by partial substitution of OPC by SF of lower particle size (see table 1).

With respect to the higher CSH content, taking into account the results presented in Figure 4, it can be said that in the low-pH pastes the hydration process of the binder at early ages (2 days) is accelerated. The acceleration might be attributed to a filler effect of the SF.

Concerning the compatibility of chemical admixtures with low-pH binders, the decrease of pH produced by the accelerator free of alkalis (Ac-2), coincides with previous work [25], where it is considered that the inclusion of accelerators in a cementitious system initially causes the formation of

less amount of portlandite and of CSH, but an increase in the amount of ettringite. This increase of ettringite is due to the increase in $\text{Al}(\text{OH})_4^-$ and SO_4^{2-} in the mix, generated by the accelerators free of alkalis. The obvious effect is the fast setting but further hydration evolution induces an strength decay not yet understood.

As final comment, in present study, the developed low-pH binders fulfill the requirement to be used in the construction of a shotcrete plug of high radioactive waste repositories. In particular, the binder formulation containing 60% OPC and 40% SF has shown physical-chemical properties with a great technological interest.

5. Conclusions

- The use of cement binders with high content of SF produces low pH pore waters. $\text{pH} < 12$ are measured in present work.
- The microstructure of the low-pH cement pastes elaborated is different from the conventional OPC pastes. The CSH generated with low pH cement contains Ca/Si ratio 1.2 to 0.8.
- In the low-pH pastes an acceleration in the hydration process of the cement at early ages takes place.
- The alkali content in the pore water pH of low pH cements is not a controlling factor and it is possible that, in the CSH gels of the low-pH cements, the ions Na^+ and K^+ are gradually bonded and probably substituted by Ca^{2+} .
- The behaviour of chemical admixtures in low-pH cementitious formulations is not easily predicted and the type of cement formulation used is determinant of the compatibility with the admixtures used.

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