

Cementitious Systems with a High Mineral Admixture Content: Alkaline Hydration

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Abstract

The objective pursued in this study was to determine the mechanical properties and mineralogical and microstructural characteristics of a system containing a high percentage of mineral additions. System composition consisted essentially in: 15% Portland clinker, 15% blast furnace slag and 70% fly ash. The mix was hydrated with water and three different alkaline solutions. The resulting pastes were studied after curing for 28 days at ambient temperature and high relative humidity.

The results showed that the mechanical strength developed depends on the "hydrating" solution: with water, the material attained a 28-day compressive strength of 25 MPa. When hydration took place in an alkaline medium, however, strengths of up to 51 MPa were recorded. The findings also indicated that C-S-H gel was the main reaction product formed when the blended cement was hydrated with water, whereas a mix of different gels (C-A-S-H and (N+C)-A-S-H) was obtained when alkaline solutions were used.

1- Introduction

One of the principal challenges presently facing the construction materials scientific-technical community is the energy and environmental problems generated by the production of vast quantities of Portland cement (which accounts for ~5% of CO₂ emissions worldwide). The substitution of pozzolanic materials for clinker or the use of new alternative binders constitute promising lines of research in this regard.

The present study focused on the replacement of up to 85% of OPC with fly ash and blast furnace slag, with alkali activation as an alternative cementing process. The ability of "*type F fly ash – OPC clinker – alkaline component*" systems to yield good cement was first proved in 1974 [1]. Subsequent studies [2,3] showed that compression strengths of up to 65 MPa could be reached within 28 days. Moreover, these systems were found to be particularly resistant to acid attack.

It has long been established that the main reaction product forming in the hydration of Portland cement and the alkaline activation of blast furnace slag is a hydrated calcium silicate: C-S-H gel. The silicon tetrahedra in the gel bond to form linear chains in what is sometimes referred to as dreierketten structure [4-6]. In the alkali activation of type F fly ash, on the contrary, the main reaction product is an alkaline silicoaluminate: N-A-S-H gel, which has a three-dimensional structure [7-9].

Other essential differences affect the secondary reaction products: the formation of portlandite ($\text{Ca}(\text{OH})_2$) in OPC-based systems [6], and small amounts of certain crystalline zeolites, such as hydroxysodalite, herschelite, analcime and so on in alkali-activated fly ash (AAFA) systems [7-9].

Alonso and Palomo [10-11] and Van Deventer et al. [12] observed that the two gels (C-S-H and N-A-S-H) could be compatibly formed in blends of alkali-activated calcium hydroxide and metakaolin. The C-S-H gel predominated in weakly alkaline media (2M NaOH), while the inorganic polymer prevailed in very basic environments (10M NaOH).

On the basis of these findings, the present study aimed to determine the mechanical properties and mineralogical and microstructural characteristics of a cementitious system containing a high percentage of mineral additions (15% Portland clinker, 15% slag and 70% fly ash) when the reaction process took place in very alkaline media.

Be it said in this regard that the Portland cement hydration process is substantially retarded in very basic environments due to the common ion effect, with the increased concentration of OH^- ions in the system. Indeed, the CSH gel may even decompose in such media [13-14]. Nonetheless, a moderately (in the case of slag) or even very alkaline medium (fly ash) is needed to generate a material able to strengthen to acceptable levels within industrially viable periods of time [15-16].

2. Experimental

Materials All the experiments in this study were conducted on a system containing type F fly ash, blast furnace slag and Portland cement clinker. The chemical composition of the components is shown in Table 1. Laboratory grade reagents were used to prepare the activator solutions: both the pellet-form NaOH (98% purity) and the sodium silicate (wg) (density 1.38 g/cc; composition: 8.2% Na_2O , 27% SiO_2 and 64,8% H_2O) were supplied by Panreac S.A. Table 2 gives the composition of the hydrating liquids.

Methods: After fly ash, slag and clinker (70:15:15) were thoroughly blended in a "Turbula" homogeniser, the various working solutions (see Table 2) were mixed with the blended cement. The liquid/solid ratio used was as required in each case to obtain pastes of a normal

consistency pursuant to Spanish standard UNE-80-116-86. The four resulting pastes (systems SH, SN, SWA and SWB) were poured into 1x1x6-cm prismatic moulds and stored in a moist cabinet (21°C, 95% RH). The specimens were de-moulded after 24 hours and returned to the moist cabinet for the duration of the curing process.

Table 1.-Chemical composition of the raw materials

	L.O.I.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	free CaO	SO ₃	Na ₂ O	K ₂ O	I.R.	BLAINE (m ² /Kg)
Fly ash	2.06	54.3	29.17	5.68	3.17	1.72	0	0.42	0.36	3.40	0.97	317
Slag	2.07	33.1	15.49	0.47	6.31	39.32	0.08	0.39	0.42	0.39	1.83	470
Clinker		21.03	5.03	3.71	2.46	64.59	1.35	1.33		1.22		350

L.O.I. = Loss on ignition; *I.R.* = Insoluble residue

Table 2. Hydrating liquids used

Solution	Formula	S/N ⁽¹⁾	Density g/l	Concentration %	pH	Composition %		
						Na ₂ O	SiO ₂	H ₂ O
H	H ₂ O	-	1000	100	7.1	0	0	100
N	NaOH	0	1200	18.3	13.3	14.2	0.0	85.8
WA	Na ₂ O.1.0SiO ₂	1.0	1300	24.5	13.3	12.4	12.1	75.5
WB	Na ₂ O.1.5SiO ₂	1.5	1200	16.5	13.3	6.7	9.8	83.5

⁽¹⁾SiO₂/Na₂O ratio

The pastes were tested for mechanical strength after 2 and 28 days. Fragments of the broken specimens were finely ground for XRD, FTIR, BSEM and ²⁹Si NMR analysis. The respective testing conditions for all these analytical techniques have been described in previous papers [7,16,17].

3. Results and discussion

1-Mechanical strength

Table 3 shows the compressive strength developed by the pastes at 2 and 28 days. As might be expected, compressive strength was found to increase with curing time in all the systems studied.

Table 3.- Compressive strength

System	Solution/binder ratio	Compressive strength (MPa)	
		2 days	28 days
SH	0.332	5.21	25.69
SN	0.390	7.30	21.09
SWA	0.422	13.63	51.87
SWB	0.495	13.04	31.97

The results differed, however, with the nature of the activators. Slightly higher compressive strength values were found for the SW systems, both at the early age (2 days) and at terminus (28 days). In fact, the highest strength value (\approx 52 MPa) was attained with system SWA (solid hydrated with the WA alkaline liquid), followed by SWB. In other words,

the inclusion of soluble silica in the activating solution enhanced mechanical strength. The inference, then, is that the presence of alkalis and soluble silica appear to play an important role in the hardening of these pastes.

2- Mineralogical and microstructural characterization

The X-ray diffraction patterns for anhydrous blend M (fly ash/slag/clinker, 70/15/15) and the materials obtained after hydration with water and the alkaline solutions (N, WA, WB) are given in Figure 1. The diffractograms of the three components overlap in the trace for the raw mix – hence the amorphous halo. Peaks for the crystalline phases are also visible: quartz, mullite, gellenite, merguinite, alite and so forth.

It is very difficult to characterize the gels with XRD techniques. Indeed, the diffractograms are very similar to one another. Nonetheless, certain differences can be distinguished. The tiny amount of portlandite detected in system SH indicates clinker silicate reactivity. The portlandite peak tends to decrease with curing time, however, as a result of both the pozzolanic reaction and carbonation (the intensity of the calcite signal increases). At 28 days, most of the anhydrous silicates are transformed into C-S-H gel.

The findings for alkaline systems SN, SWA and SWB differ substantially from the above. The hydration rate of the anhydrous silicates in the clinker slackens: some alite can still be detected after 28 days of hydration. No peaks associated with crystalline calcium hydroxide (portlandite) are observed in these XRD patterns.

This does not rule out the possible formation of amorphous calcium hydroxide, however, whose presence would be subsequently confirmed by the BSEM results. Systems SN and SWA are also observed to contain $C_4A\bar{C}H_{13}$ carboaluminates, a species detected by other authors in slag alkali activation processes [15]. Hydroxysodalite, a zeolite generally found in alkali-activated fly ash systems [16-17], appears in the SWB system.

The pastes in all the systems are likewise observed to undergo carbonation, although this may be partially induced by the prior carbonation of the initial blend (question under study).

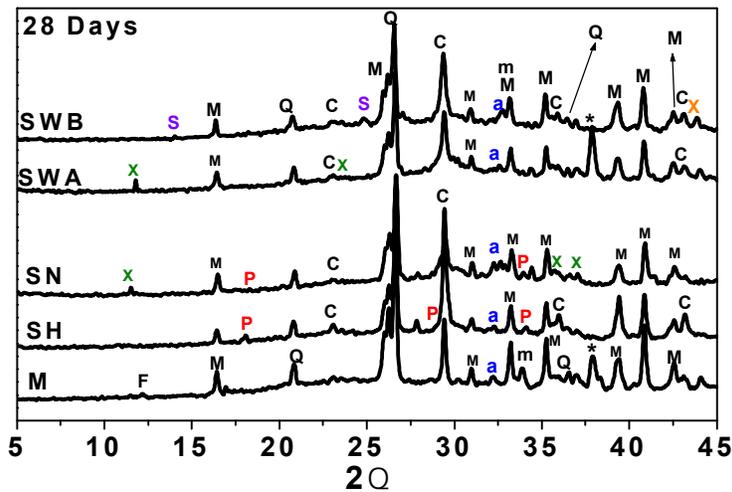


Fig. 1 28-day XRD patterns for raw mix M and activated pastes SH, SN, SWA and SWB
 (Q= quartz; M=mullite; A= akermanite; G=gelenite; m= merguinite; C=calcite; a= alite; P=portlandite; S=hidroxysodalite; X= C_4ACh_{13} ; * apparatus signal).

Figure 2 shows the FTIR spectra for the same 28-day samples: raw mix M and systems SH, SN, SWA and SWAB. Bands 1 and 3 in these spectra correspond to the presence of carbonates in the form of calcite. Double band 4 is due to quartzite and band 5 to mullite. Bands 2 and 6, associated with T-O and Si-O-Si bond vibrations, respectively, provide the most relevant information about the cementitious gels generated in each system.

Raw mix M has a very narrow band with a minimum at 930 cm^{-1} associated with T-O (T=Si or Al) bond asymmetric stretching vibrations. This band is the sum of the ash (1060 cm^{-1}), slag (948 cm^{-1}) and clinker (930 cm^{-1}) bands [6,15-17]. The difference in the position of this band on the ash, slag and cement clinker spectra is due, logically, to the different nature of the component materials: primarily calcium silicates (most of which are crystalline in Portland cement and vitreous in slag) and vitreous silicoaluminates (ash). Consequently, the FTIR spectrum of the blend of prime materials is the sum of the individual spectra, although the spectrum of the majority component, in this case the fly ash, prevails.

In system SH (hydration with water) the T-O bond stretching band is shifted to 1079 cm^{-1} , an indication that the main component of that band is due to the presence of unreacted fly ash. The “Portland cement” component of the working mix hydrates, generating the characteristic C-S-H gel responsible for the development of its mechanical strength. This gel emits a wide band in the infrared, at around $960\text{-}970\text{ cm}^{-1}$ [18], which overlaps with the main band of the ash [17] and is difficult to distinguish in the SH spectrum in Figure

2. This result confirms that ash reactivity (barring pozzolanic reaction) is low in the absence of a highly alkaline medium, and therefore its FTIR spectrum remains intact.

In alkaline systems SN, SWA and SWB the wide band due to Si-O bond asymmetric stretching vibrations appears at frequencies of from 1020/1040 cm^{-1} , i.e., much higher than the frequencies observed in C-S-H gel [18]. This may be indicative of the formation of more polymerized gels with a higher Si content (due to the possible presence of Q^3 and Q^4 units with nAl). Generally speaking, these spectra are fairly similar to the signals obtained in fly ash alkali activation processes [17].

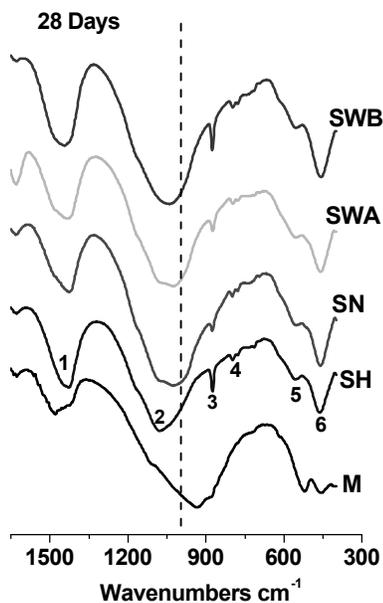


Tabla XXX. Band 2 shift

Sample	Band n_3 (T-O)
M	930 cm^{-1}
SH	1079 cm^{-1}
SN	1027 cm^{-1}
SWA	1030 cm^{-1}
SWB	1040 cm^{-1}

Fig.2 FTIR spectra for raw mix M and pastes activated with solutions H, N, WA and WB

Paste microstructure as revealed by BSEM is shown in **Figure 3**. The presence of unreacted clinker, blast furnace slag and fly ash particles is detected in all cases (see Figure 3, particles marked C, S and F, respectively). Of the four matrices studied, SWA is the most compact and dense, followed in descending order by SWB, SN and SH. This justifies, in part, the higher mechanical strength observed in system SWA.

In all the micrographs, the cement particles (particles C, analysis V) are encircled by a lighter colour, Ca-rich ring (points 1, 5 and 8, analyses I and VI), a clear sign that they are under attack. As this ring is associated with microcrystalline portlandite, it is difficult to detect with XRD. An Si- and Ca-rich gel can be seen to be forming at a short distance from the particles (see points 2, 3, 6 and 9, analyses II, III and VII). For system SH this gel has a mean Ca/Si ratio of 0.8/0.9 (point 2, analysis II), whereas in the alkaline systems (SN, SWA and SWB) the gel is found to contain a higher percentage of Al (points 3, 6 and 9 and analyses III and VII), and therefore a slightly lower Ca/Si ratio. The C-A-S-

H-type gels seen to be forming have a Ca/Si ratio of around 0.7/0.8 and an Si/Al ratio of ~3.

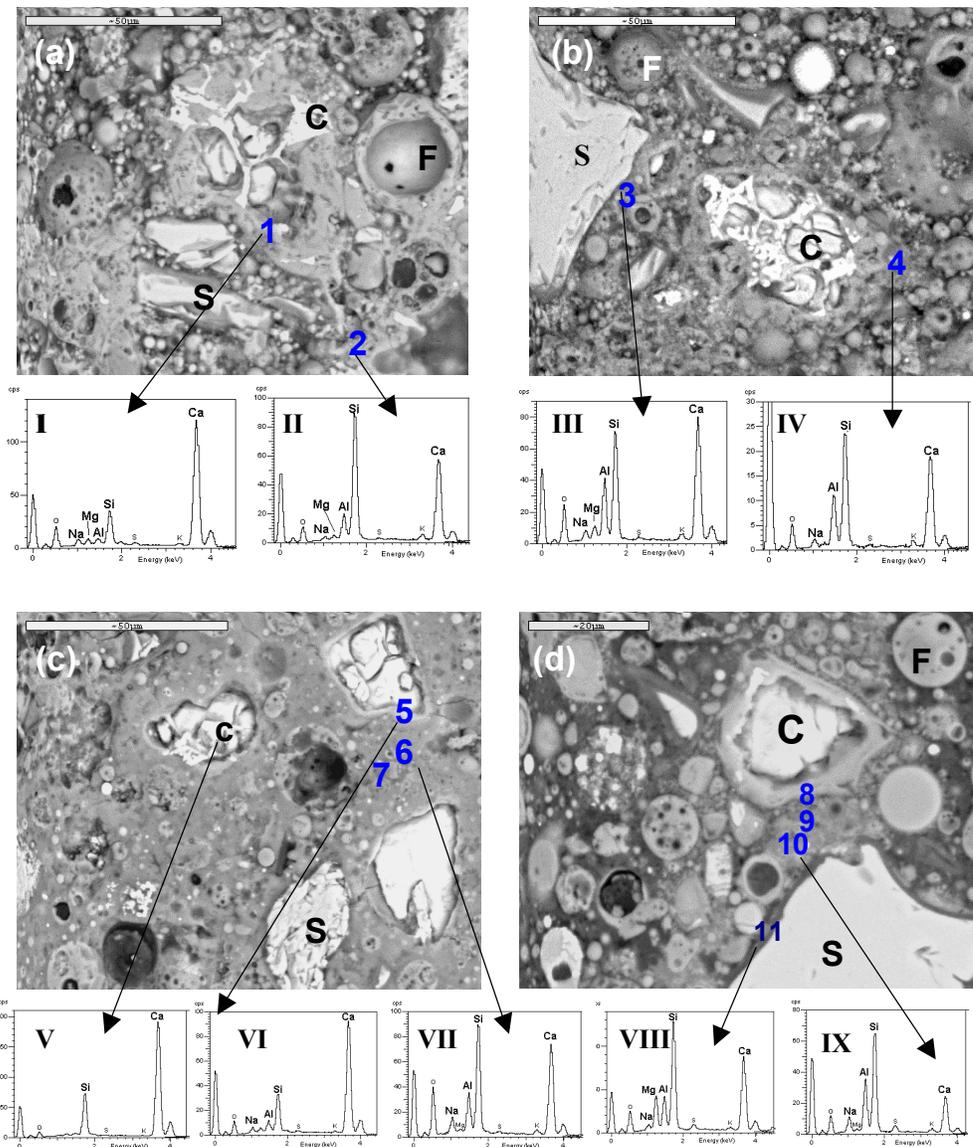


Figure 3. BSEM/EDX micrographs and traces for systems SH (a); SN (b); SWA (C) and SWB (D). (C=OPC clinker; S=blast furnace slag; F=fly ash)

In the latter three systems (SN, SWA and SWB), where an alkaline activator was used and fly ash reactivity was higher, the presence of another Si-rich gel (points 4, 7, 10 and 11 and analyses IV, VIII and IX) is detected. Here the Ca/Si ratio is less than 0.4, Na/Al is around 0.5-0.6; the Si/Al ratio is about 2.0/2.5 for systems SH and SWB and somewhat higher, on the order of 2.5/3.0, for system SWA. The main difference observed between these Si-rich gels and the gels observed in the alkali activation of fly ash or metakaolin [7-9] lies in the higher uptake of Ca in their structure. In all likelihood, a calcium-sodium silicoaluminate

gel is forming in the present case. Finally, the presence of Mg is detected in the areas adjacent to the slag particles (point 11, analysis VIII). In short, from the morphological standpoint it is difficult to establish where the C-A-S-H gel appears and where the (N+C)-A-S-H polymer forms without resorting to microanalysis.

Figure 4 shows the ^{29}Si and ^{27}Al NMR-MAS spectra for the 28-day samples. These spectra cannot be readily interpreted due to the overlapping signals emitted by the different gels formed and the unreacted prime materials.

The ^{29}Si spectrum for the initial mix (Figure 4 (a)-M) is clearly divisible into two parts, one with a wide signal between -85 and -120 ppm attributed to the fly ash component [7,19] and the other with a sharper and narrower peak between 70 and 80 ppm associated with calcium silicates from the clinker and slag [4,5,20]. The wide fly ash signal can, in turn, be regarded to be formed by the sum of other signals centred at -89, -98, -104, -108 and -119 ppm. The peak at -88 ppm is attributed to crystalline mullite $\text{Q}^3(3\text{Al})$ [21]; the peaks appearing at values higher than -108 ppm are assigned to different types of crystalline quartz and the remaining peaks are attributed to the glassy component of the fly ash [7,8,19,22,23]. The sharp signal centred at -72 ppm corresponds to the Q^0 units in the anhydrous calcium silicates [4,20]; the small peak at -74 ppm is associated with the Q^1 units in the slag [5].

The signal at -72 ppm (corresponding to the anhydrous silicates in the clinker) nearly disappears in the system SH (water-hydrated) spectrum. At the same time the peak at -74 ppm due to unreacted slag becomes much more visible and a new peak appears at -86 ppm, which can be assigned to the Q^2 units in the C-S-H gel. Finally, the rest of the signals, at -96, -104 and -108 ppm are associated with practically unreacted fly ash particles (the pozzolanic reaction between the fly ash and the portlandite released during clinker hydration takes place slowly, if at all).

The alkali-activated system spectra (SN, SWA and SWB) are fairly similar, with the exception of apparently lower fly ash reactivity in system SWB. A peak appears at -72 ppm in all three systems, confirming lower clinker reactivity in highly alkaline systems. It is difficult to venture a conclusion about slag reactivity due to possible signal overlapping. What is clearly visible is an intense signal at -85 ppm, and other less intense peaks at -90, -96, -102 and -108 ppm (see the SWA spectrum, where resolution is highest). These signals cannot be readily assigned, since, as seen in the BSEM results, the gels formed contain aluminium in their structure. As a result, certain signals – for units $\text{Q}^2(0\text{Al})$, $\text{Q}^3(n\text{Al})$ and $\text{Q}^4(4\text{Al})$ for instance –, may overlap at around $-85\pm 1\text{ppm}$ [23].

Given the intensity of the -85 ± 1 ppm signal here compared to system SH and the presence of unreacted clinker, it is hard to attribute this peak exclusively to the formation of the Q^2 units characteristic of C-S-H-type gels. The signal is more likely to also be due – and to a greater extent – to the presence of $\text{Q}^4(4\text{Al})$ units. This hypothesis is supported by the existence of the series of less intense peaks at -90, -95, -102 and -108 ppm which, together with the signal at -85 ppm may, according to the literature on aluminosilicates, be associated with

the presence of silica tetrahedra surrounded by 4, 3, 2, 1 and 0 alumina [7,8,19,22,23]. Taken in conjunction with the FTIR and BSEM findings, this confirms that when such mixes react in very alkaline media the product is an N-A-S-H-type gel or a (C+N)-A-S-H inorganic polymer (as a result of the reaction between the fly ash and the caustic solution).

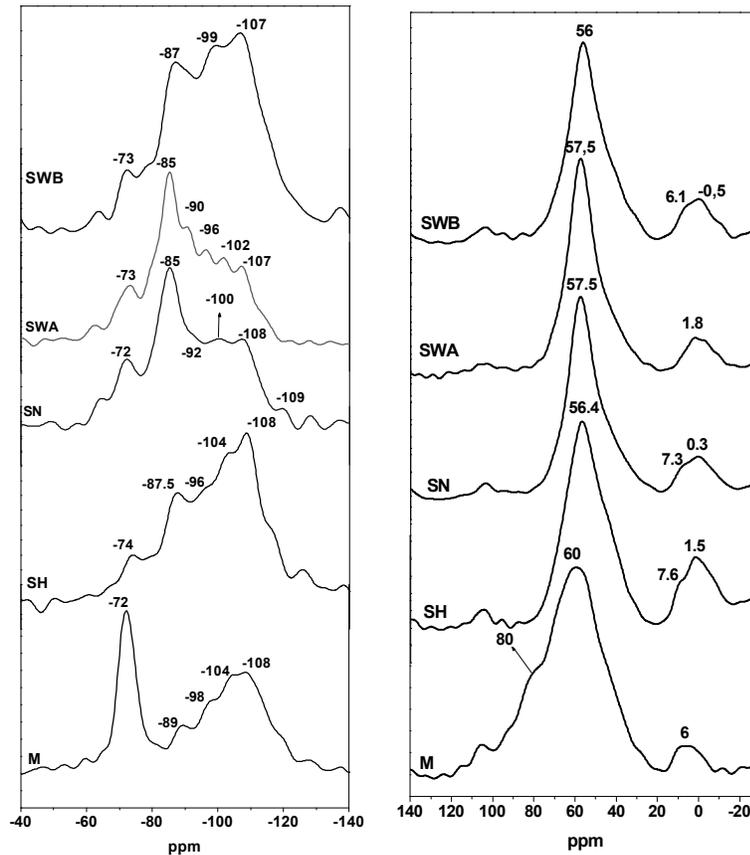


Figure 4. (a) ^{29}Si and (b) ^{27}Al NMR-MAS spectra

The above hypothesis is likewise consistent with the ^{27}Al NMR-MAS spectra (see Figure 4(b)). As this figure shows, the raw mix (spectrum M) presents a wide, asymmetric band at +60 ppm with a shoulder at +80 ppm associated with tetrahedral aluminium (Al_T). This band is the result of the overlapping of the bands attributed to the aluminium in the clinker (+80 ppm [2]), slag (60 ppm [5]) and fly ash [+54 ppm [7,19]]. The low intensity signal observed at around 6 ppm is associated with the presence of a small amount of octahedral aluminium (Al_O), primarily in the ash [7,19].

As a result of the reactions in general, the shoulder at +80 ppm is observed to disappear, while the signal at +60 ppm narrows and shifts to +56 ppm. In the SH reference (water-hydrated) system, the Al_T signal remains wide, probably due to a substantial contribution from the unreacted ash. In systems SN, SWA and SWB,

however, this signal narrows and appears at positions characteristic of Al in zeolite precursor ($Alq^4(4Si)$) environments [22,23]. In other words, the aluminium tetrahedra are primarily surrounded by four silicon tetrahedra, which would confirm the formation of three-dimensional structures.

The Al_O is observed to vary very little: the presence of a shoulder at around +7/+8 ppm may be due to the formation of calcium aluminates whose crystallinity must be very low [20], for they are not detected by XRD.

In short, all the findings of this study show that a strong cementitious material can be obtained from a blend with a low Portland cement content as a result of the simultaneous formation of two types of gel (C-A-S-H and (N+C)-A-S-H).

In alkaline media the dissolved calcium species appear to react with the silicates and aluminates to form calcium silicates and calcium silicoaluminates. The addition of calcium enhances the mechanical properties of the matrices, a finding that concurs with previous observations [24] that showed calcium to have a beneficial effect on inorganic polymer strength. In any event, however, acceptable mechanical strength cannot be reached without soluble silica. The addition of this compound leads to the formation of denser matrices with Si-richer gels (see Table 3, system SWA) which in turn contribute to the production of a strong material able to set and harden at ambient temperature.

Nonetheless, given that calcium solubility declines with rising pH [3,14], it is not clear how calcium forms structural bonds with the polymer nor why its presence plays an instrumental role in the development of the mechanical properties of the polymer. A need is felt for further research to explore these questions in the near future.

4-Conclusions

The findings of this study show that a strong cementitious material can be obtained from a blend with a low Portland cement content ($\leq 15\%$) when hydrated at ambient temperature in a highly alkaline medium.

Two types of gel (C-A-S-H and (N+C)-A-S-H) may precipitate in the alkaline medium, where the alkaline polymer is the majority product and primarily responsible for the mechanical strength developed. The presence of soluble silica in the activator plays a determining role in the development of mechanical strength.

Acknowledgements

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