

Op-c-fly ash cementitious systems: study of gel binders produced during alkaline hydration

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Abstract In the present paper, experiments were performed on blended cements containing 30% Portland cement clinker and 70% fly ash. The powdery material was mixed with deionised water for “normal” hydration, and with two different alkaline solutions for “normal” alkaline activation. The mechanical strength developed by this highly blended cement differed significantly depending on the hydrating solution used. XRD, FTIR and ^{29}Si MAS-NMR characterisation studies were conducted to obtain information on the complex structural nature of the hardened matrices, which in all cases consisted of a mixture of amorphous gels (C-S-H + N-A-S-H gel). These highly blended cements are able to comply with the specifications defined in the European Standard EN-197-1:2000.

Introduction

Portland cement production—1.5 billion tonnes yearly worldwide—contributes substantially to global atmo-

spheric pollution (~5% of total CO₂ emissions) [1]. It is generally agreed that such emissions need to be reduced if the Kyoto commitments are to be met. The Spanish cement industry, in particular, increased CO₂ emissions by 28.5% from 1990 to 2002, whilst the objective was a total rise of only 15% between 1990 and 2012.

The replacement of clinker by pozzolanic materials and the use of new alternative binders are two of the various methods from which the Portland cement industry may benefit in its attempt to lower CO₂ emissions.

Countless papers were written in the last century on the replacement of clinker with materials such as fly ash, natural pozzolans, slag and so on. Standards everywhere define the types of materials apt for use as replacement as well as the maximum amount of clinker that can be replaced [most of standards limit the maximum content of fly ash in cement to 55% (cement type IV, EN 197-1:2000)]. In this study, attention focuses on fly ash as a replacement material (much more than the maximum established in the standards) and alkaline activation as an alternative cementing procedure.

In the alkali activation of fly ash, the powdery grey waste from coal combustion (FA) is mixed with certain alkaline activators (alkaline solutions) and the resulting paste is then cured at mild temperatures to produce hardened materials [1–6]. Previous research [7, 8] has shown that the main reaction product formed in such systems is an amorphous aluminosilicate gel exhibiting short-range order in its three-dimensional structure. Small amounts of certain crystalline zeolites, such as hydroxysodalite, herschelite or analcime to name a few, are often found in these systems, depending on the composition of the initial mix and curing conditions [9].

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This product is consequently regarded to be a “zeolite precursor”.

The hydration of ordinary Portland cement with highly alkaline solutions, however, has been shown to alter its normal hydration process [10, 11], with considerable delays in the formation of the main reaction products and the appearance of new products (sodium calcium carbonates and sodium sulphate). The C-S-H gel may even decompose in such media.

The possibility of obtaining a good cement in “class F fly ash—OPC clinker—alkaline component” systems was first proved in 1974 [12]. Further studies [13, 14] showed that compression strengths of up to 65 MPa could be reached within 28 days. In addition, these systems were found to be particularly resistant to acid attack.

Previous research conducted at the Eduardo Torroja Institute [15, 16] showed that C-S-H (main hydration product in Portland cement systems) and N-A-S-H (main reaction product of type F fly ash activation) gels are compatible. Moreover, when the activating compounds used were metakaolin and $\text{Ca}(\text{OH})_2$, the OH^- concentration was found to have a threshold value [15]: at higher concentrations the “zeolite precursor” prevailed in the resulting paste, whereas at lower levels of OH^- the C-S-H gel was the main reaction product. In a more recent study of the “blast furnace slag—metakaolin—alkaline component” system, Van Deventer et al. [17] obtained interesting results that concur, generally speaking, with the present findings.

The potential technological impact of manufacturing blended cements with a high fly ash content without forfeiting the excellent performance of normal Portland cement concrete prompted the present exploration of the mechanical and mineral properties of a cementitious system comprising 70% fly ash and 30% Portland clinker, when hydrated with different alkaline solutions.

Experimental

Materials

The experiments run in this study were conducted on class F fly ash and Portland cement clinker. The

chemical composition of these materials is shown in Table 1. Laboratory grade reagents were used to prepare the activators: both the pellet-form NaOH (98% purity) and the sodium silicate (water glass)—density 1.38 g/cc, composition: 8.2% Na_2O , 27% SiO_2 and 64.8% H_2O —were supplied by Panreac S.A.

The hydrating liquids used in the investigation, in turn, were: L1 = deionised water; L2 = NaOH solution; and L3 = water glass + NaOH solution with $\text{SiO}_2/\text{Na}_2\text{O} = 1.5$. The two alkaline solutions were prepared to a density of 1.20 g/cm³.

Method

After fly ash and clinker (70:30) were thoroughly blended in a “*Turbula*” homogeniser, the various hydrating solutions (liquids L1, L2 and L3) 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 three resulting pastes (systems S1, S2 and S3) were poured into $1 \times 1 \times 6$ -cm³ prismatic moulds and stored in a moist cabinet (21 °C, 95% RH). The specimens were de-moulded after 24 h and returned to the moist cabinet for the duration of the curing process.

All pastes were tested for mechanical strength after 2 and 28 days. Fragments of the broken specimens were finely ground for XRD, FTIR, and ²⁹Si MAS NMR analysis. X-Ray diffractograms of powdered samples were obtained with a Philips diffractometer PW 1730, using $\text{CuK}\alpha$ radiation. Specimens were step-scanned at a rate of 2° min⁻¹, with 2θ in the range 2–60°, divergence slit = 1°, anti scatter slit = 1° and receiving slit = 0.1 mm. FTIR spectra were obtained on an ATIMATTSON FTIR-TM series spectrophotometer. Specimens were prepared by mixing 1 mg of sample in 300 mg of KBr. Spectral analysis was performed over the range 4,000–400 cm⁻¹ at a resolution of 1 cm⁻¹. ²⁹SiMAS NMR spectroscopic characterisation was conducted with a Bruker apparatus, model MSL-400. The resonance frequencies used in this study was 79.5 MHz and the spinning rates was

Table 1 Chemical composition of the raw materials

	L.O.I.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	CaO ^a free	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
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

^a CaO free determined by the ethilen glycol method (EN 196-4)

4 kHz. The measurements were made at laboratory temperature with TMS as external standard. The error in the chemical shift values was estimated to be lower than 1 ppm. Magnetic materials were removed from the samples prior to NMR spectra recording by exposing the sample to a strong magnetic field.

Small amounts of the ground powder were also subjected to Takashima's attack [18] to dissolve the calcium silicates (anhydrous and hydrated silicates) in the systems studied.

Results

Table 2 shows the compression 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. Interestingly, system 2 (solid hydrated with alkaline liquid L2) showed the poorest performance, whereas the highest strength values were attained with system 3 (made with soluble silica-containing liquid L3). The control system, hydrated with liquid L1 (pure water), had intermediate strength values. In terms of the liquid/solid ratios, the strength values did not, however, follow any logical pattern, inasmuch as in Portland cement systems, the highest strengths were observed at the lowest liquid/solid ratios. The inference, then, is that the presence of alkalis and soluble silica appear to play an important role in the hardening of these pastes.

The X-ray diffraction patterns of samples for the three systems studied at 2 and 28 days are given in Fig. 1. The most relevant information to be drawn from these diffractograms is as follows:

Mineralogically speaking, the paste hydrated with liquid L1 (pure water) behaves like a normal Portland cement. Portlandite is the main crystalline product of clinker hydration, although the amount of this mineral tends to decline with curing time as a result of both the pozzolanic reaction and carbonation (the intensity of the X-ray diffraction signals for calcite grows with time). After 28 days of hydration, most of the anhydrous silicates are converted into C-S-H gel.

The XRD findings for system S2 (paste hydrated with liquid L2) differ substantially from the results obtained for system S1. The first difference is that

portlandite does not appear as a hydration product in system S2. Moreover, the hydration rate of the anhydrous silicates in the clinker slackens: considerable amounts of alite can still be detected after 28 days of hydration. It should also be noted that some few Hydroxysodalite crystals (only observed under the electron microscope) are formed in this system after 28 days of hydration and that calcite peaks also grow after 28 days.

Lastly, system S3 is very similar to system S2, with no portlandite detected. Anhydrous calcium silicates are hydrated at a slower rate than in system S1 but faster than in S2. In this case, no crystallised zeolites are observed, although the calcite follows a very interesting pattern: calcium signals are moderate after 2 days of hydration, with a substantial rise in intensity after 28 days.

The FTIR spectra for the various anhydrous and hydrated systems (made with liquids L1, L2 and L3) are shown in Fig. 2. These spectra, all of which correspond to pastes cured for 28 days, provide further information (in addition to the XRD data) on the events taking place in the alkali activation of the systems studied. Indeed, their interpretation clarifies certain aspects of the non-crystalline phases formed during hydration.

Attention is drawn, in Fig. 2a), to the shifting position of the main band on the spectra, namely the internal stretching band generated by the silicates (T–O asymmetrical stretching vibrations), which appears at $1,088\text{ cm}^{-1}$ in the ash, at 927 cm^{-1} in the Portland cement clinker and at $1,088\text{ cm}^{-1}$ with a small shoulder at 927 cm^{-1} in the blend. The difference in the position of this band on the ash and cement spectra is due, naturally, to the different nature of these two materials (majority of crystalline calcium silicates in the Portland cement and of vitreous silicoaluminates in the ash). Consequently, the FTIR spectrum of the blend is the result of adding the two individual spectra, although the spectrum of the majority component prevails.

Hydrating the material with water (L1) prompts a significant change in the initial spectrum, with the disappearance of the shoulder at 927 cm^{-1} corresponding to the cement and a slight shift in the main band from $1,088$ to $1,080\text{ cm}^{-1}$ (see spectrum S1). This may confirm the XRD results: the Portland cement

Table 2 Mechanical strength

Blended cement	Liquid	Liquid/solid ratio	2-day compression strength (MPa)	28-day compression strength (MPa)
70% FA + 30% Clinker	L1	0.325	11.23	28.91
	L2	0.407	4.83	24.72
	L3	0.487	12.91	36.94

Fig. 1 X-ray diffraction patterns of cementitious material hydrated with liquids L1, L2 and L3. **(a)** Diffractograms for pastes cured for 2 days. **(b)** Diffractograms for samples cured for 28 days. In all cases, the pattern at bottom (S) corresponds to the blended cement before hydration

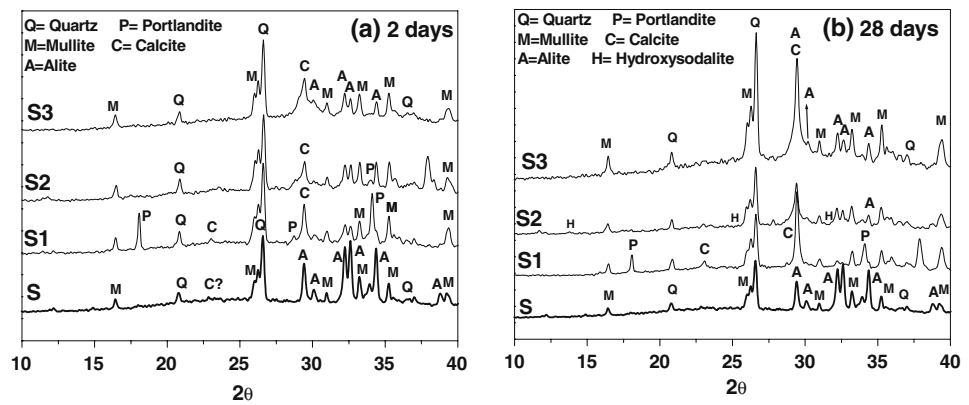
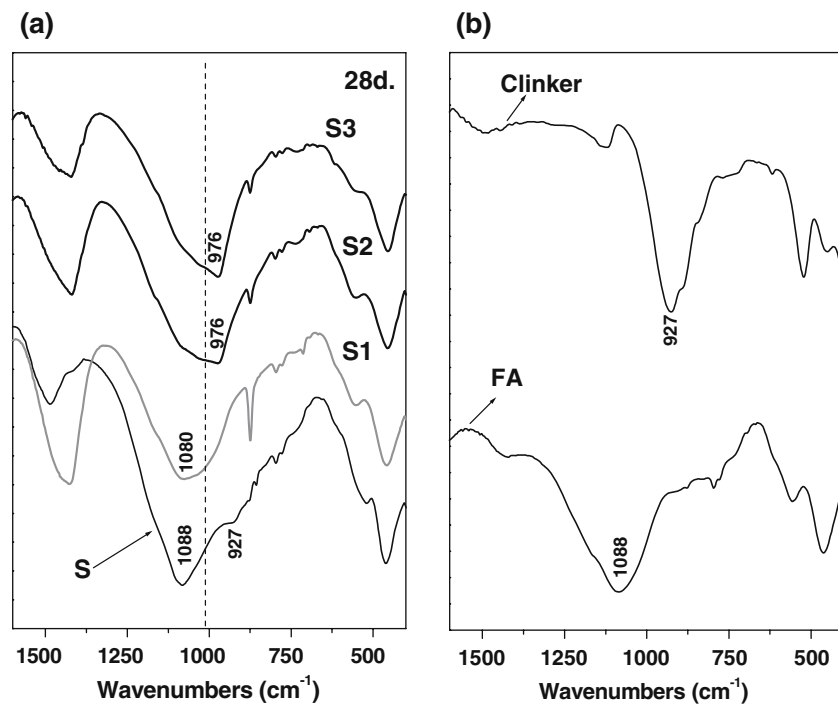


Fig. 2 **(a)** FTIR spectra of the OPC + fly ash anhydrous system and the products generated by that solid hydrated with liquids L1, L2 and L3 and cured for 28 days. **(b)** FTIR spectra of the original fly ash and Portland cement clinker



hydrates, generating the characteristic C-S-H gel responsible for the development of its mechanical strength. This C-S-H gel gives rise to a wide band in the infrared, at around $960\text{--}970\text{ cm}^{-1}$, that overlaps with the main band of the ash and is difficult to distinguish in the respective spectrum in Fig. 2. As the ash, in turn, barely reacts under these conditions (outside the pozzolanic reaction), its FTIR spectrum remains intact.

But these changes are more clearly visible in Fig. 3, showing: FTIR spectra for the initial mix hydrated with water (L1) after 28 days; for the same material after the Takashima’s attack: attack with methanol + salicylic acid [18]; and the spectrum resulting from subtracting the latter from the former.

The methanol + salicylic acid attack dissolves the (anhydrous and hydrated) calcium silicates in the Portland cement but does not affect the fly ash [19]. For this reason, the spectrum C in Fig. 3 largely concurs with the C-S-H gel spectrum: wide band centred around 964 cm^{-1} attributed to Si-O stretching vibrations in the Q^2 tetrahedra, whose frequency varies systematically with the C/S ratio. The position of this band suggests that the C-S-H gel formed is similar to the band for 1.4-nm tobermorite [20], leading to the belief that the formation of this compound is responsible for the development of mechanical strength in this system (see Table 2).

The FTIR spectroscopy of the blended cement hydrated with the soda solution (system S2) reveals

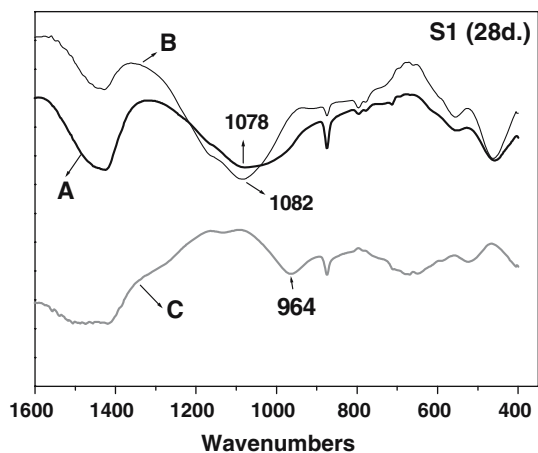


Fig. 3 A FTIR spectrum of the product generated by the cementitious system hydrated with water and cured for 28 days. B FTIR spectrum after the paste is attacked with methanol + salicylic acid. C FTIR spectrum resulting from subtracting B from A

the following (see Fig. 2): the main band in the control spectrum centred at $1,088\text{ cm}^{-1}$ is converted into a band with a semi-flat peak (almost certainly enveloping several signals) whose lower end shifts very perceptibly towards a frequency of around 976 cm^{-1} . This shift indicates that a cementitious gel or even a mix of gels forms as a result of activation. Be it said that the exact position of this band depends on the amount of material reacting. And C-S-H gels usually have a band at around 960 cm^{-1} , whereas in N-A-S-H gels, peaks are generally found at higher frequencies (from 980 to $1,000\text{ cm}^{-1}$), the exact position depending on the Al/Si ratio in the gel formed [7]. The specific frequency at which the S2 system signal appears concurs with what in the literature is attributed to the aluminium-rich alkaline aluminosilicate gel generated in the early stages of the alkali activation of fly ash [7]. It may therefore be reasonably assumed that the N-A-S-H gel is the agent chiefly involved in the development of mechanical strength in this paste. Nonetheless, to verify whether in this case C-S-H had also formed as a result of Portland cement hydration, samples were again selectively attacked with methanol and salicylic acid.

Figure 4 shows the FTIR spectra of the paste generated after the initial blended cement was activated with soda (L2), the residue after the Takashima attack, and the component dissolved during the attack (the spectra found when the latter is subtracted from the former); this procedure again reveals the existence of a band at 966 cm^{-1} typical of the C-S-H gel.

In short, FTIR spectroscopy suggests that the cementitious product formed as a result of the (NaOH)

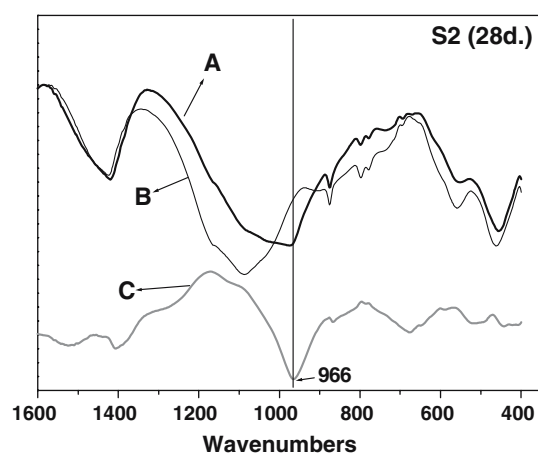


Fig. 4 A FTIR spectrum of the product generated by the cementitious system when hydrated with soda and cured for 28 days. B FTIR spectrum after the paste is attacked with methanol + salicylic acid. C FTIR spectrum resulting from subtracting B from A

alkali activation of the blended cement studied contains two different components: N-A-S-H gel from the ash (majority cementitious phase) and C-S-H gel from the Portland cement.

Finally, FTIR spectroscopy results for the cement mixed with solution L3, which contains soluble silica (waterglass), (see Fig. 2) are similar to the pattern observed for the paste produced with solution L2: i.e., the T-O bond vibration band clearly shifts from $1,088\text{ cm}^{-1}$ to lower frequencies. This shift is closely related to the conversion of the fly ash into cementitious material as a result of alkali activation.

In this case also the paste was attacked with methanol + salicylic acid to verify the possible existence of a C-S-H gel. Figure 5 shows the FTIR spectra for the material generated after the cementitious mix is activated with solution L3, the residue after the Takashima attack, and the component dissolved in the attack (the spectra found when the latter is subtracted from the former).

Here again, this procedure reveals the presence, in the spectrum C, of a band at 966 cm^{-1} typical of the C-S-H gel. FTIR spectroscopy indicates, then, that the cementitious product formed as a result of alkali activation of the blended cement studied with a water glass-containing caustic solution likewise comprises two different components: N-A-S-H gel from the ash (majority phase) and C-S-H gel from the Portland cement or even from the reaction between the calcium in the cement and the soluble silica in liquid L3. Coexistence of both gels was already observed in previous investigations carried out with different working materials [21–23].

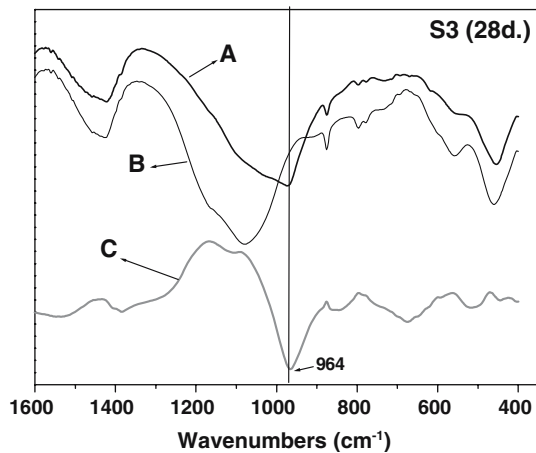


Fig. 5 A FTIR spectrum of the product generated by the cementitious system when hydrated with soda + waterglass and cured for 28 days. B FTIR spectrum after the paste is attacked with methanol + salicylic acid. C FTIR spectrum resulting from subtracting B from A

Figure 6, in turn, summarises the results of the ^{29}Si NMR analyses of the pastes. A careful look at that figure (the whole spectra) confirms the X-ray analysis and FTIR findings, namely that the chemical reactions prevailing in each system differ depending on the hydrating solution used.

Two clearly differentiated areas can be distinguished on the ^{29}Si spectrum for the unhydrated powder (Fig. 6A). On the one hand, the fly ash component has a wide asymmetric signal consisting in a series of peaks at around -89 , -98 , -104 , -108 and -119 ppm. The peak at -89 ppm is assigned to crystalline mullite $\text{Q}^3(3\text{Al})$ [24]; 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 [5, 25]. The clinker component, on the other hand, displays a more sharply defined signal at -72 ppm corresponding to the Q^0 units in the anhydrous calcium silicates [26].

When pure water (L1) is added to the cement blend the clinker component is the primary object of attack (see the spectrum B in Fig. 6). As a result, in spectrum 6B, the peak at -72 ppm (corresponding to the anhydrous silicates in the clinker) nearly disappears, while a new peak begins to emerge at -86 ppm. This new peak can be assigned to the Q^2 units in the C-S-H gel [26]. Spectrum 6B also shows that the fly ash component of the solid barely reacts even after 28 days of hydration: the pozzolanic reaction between the fly ash and the portlandite released during clinker hydration takes place slowly if at all.

The situation depicted in spectrum 6C (S2 at 28 days) is quite different, however. The amount of

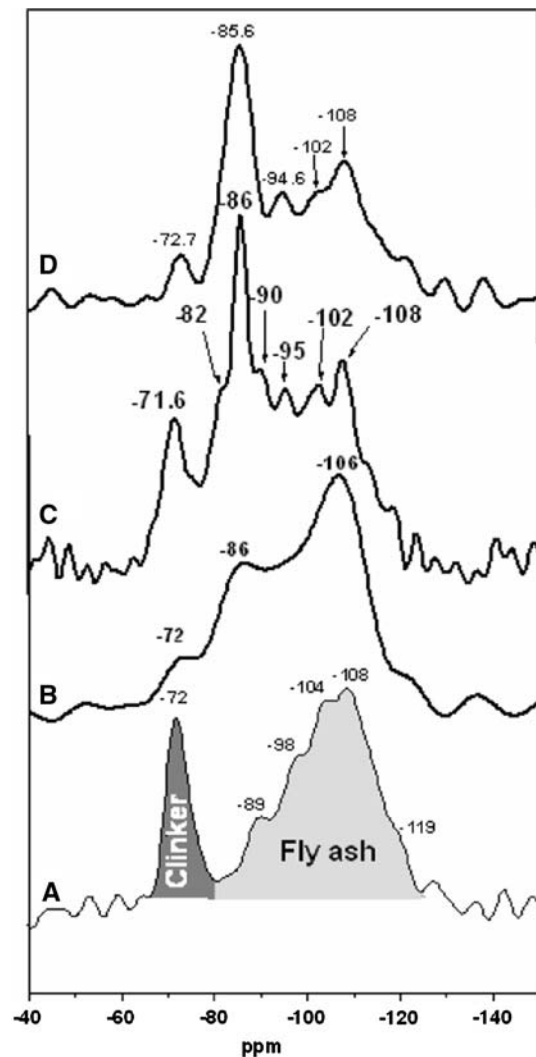


Fig. 6 ^{29}Si MAS NMR spectra: A initial raw mix (solid “S”); B 28 days after hydration with L1; C 28 days after hydration with L2; D 28 days after hydration with L3

unreacted clinker is relatively high even after 28 days of curing time (compare the peak at -72 ppm to its counterpart in spectrum 6A). These findings concur with previous research [10, 11], as well as with the XRD patterns described above. Initially, the sharp signal at -86 , together with the less intense peak at -82 ppm, might be associated with the formation of a C-S-H gel with aluminium in its structure: More specifically the peak at -82 ppm is associated with $\text{Q}^2(1\text{Al})$ units and the one at -86 ppm with $\text{Q}^2(0\text{Al})$ units, although the latter is shifted slightly with respect to other reports [26, 27]. The intensity of the -86 ppm peak, however, is not consistent with the existence of large amounts of unreacted clinker (solution L2 has no soluble silica content as a possible extra source of silicon for C-S-H gel formation). The signal at -86 ppm

may also be associated with $Q^4(4Al)$ units instead of the Q^2 units characteristic of a C-S-H gel, which, considered in the context of the existence of the series of less intense peaks at -90 , -95 , -102 and -108 ppm (associated with the presence of silica tetrahedra surrounded by 3, 2, 1 and 0 alumina [5]) would indicate the formation of a N-A-S-H-type inorganic polymer (as a result of the reaction between the fly ash and the caustic solution). This Al-rich gel has been detected in alkali-activated fly ash systems in the early stages of activation when the reaction is thermally accelerated [5, 8].

Finally, spectrum 6D (hydration with solution L3 after 28 days) reflects a situation that is completely different from the other studied cases: a weak signal at -72.7 ppm (indicating a high rate of hydration of the clinker component) and a high intensity signal at -85.6 ppm, attributed to a cementitious phase gel (probably the C-S-H gel formed in the system). Moreover, the width of this band, together with the presence of peaks at -94.6 and -102 ppm, are indicative of the existence of the above-mentioned N-A-S-H gel (probably richer in Si than the gel formed with L2 [5, 8, 25]).

Discussion

The hydration mechanisms in Portland cement were extensively studied in the twentieth century, and continue to be the object of research today [28]. This cumulative knowledge has led to a deep and fairly precise understanding of these mechanisms. And yet the literature on Portland cement hydration in a highly alkaline medium (caustic medium) is limited to a handful of papers, perhaps because the possibility of the industrial development of a new and highly alkaline cementitious system in which Portland cement is just one of several binders has only recently been envisioned.

The first results of the present research that should be addressed refer to the mechanical strength in the different systems studied. Table 2 shows that strength development in the system hydrated with water (S1) is relatively poor and similar to the behaviour observed in materials activated with solution L2 (European Standard EN 197-1:2000 establishes 32.5 MPa (28 days compressive strength) as the minimum mechanical requirement for any type of Portland cement). The S3 blends activated with solution L3, however, are compliant with the strength requirements laid down in EN 197-1:2000 and are comparable to the values for 32.5 cement. The first two conclusions to be drawn from this

finding are: that Portland cement hydration follows different pathways depending on the OH^- concentration and the presence of soluble silica in the medium; and that fly ash activation at laboratory temperatures is accelerated by the presence of Portland cement (at laboratory temperatures the OPC-free fly ash systems, under the same alkalinity as the systems studied here, exhibit slower development of mechanical strength than shown in Table 2).

The “anomalous” hydration of Portland cement in caustic media, reported in previous studies [10, 11], is interpreted to be due to the steep decline in the solubility of calcium at these levels of OH^- concentration. Indeed, in systems 2 and 3, portlandite (majority crystalline product of Portland cement hydration) either failed to precipitate or did so in undetectable quantities. It may also have been converted immediately into $CaCO_3$.

The positive effect of the presence of Portland cement on ash activation at laboratory temperature may be explained by the heat released during the hydration reaction; the energy from this heat would in turn activate the chemical reactions that originate fly ash setting and hardening in highly alkaline media.

In any event, the evolution of the systems studied can only be correctly interpreted if the above strength data are related to the mineralogical and microstructural information about these systems provided by FTIR spectroscopy, ^{29}Si MASNMR and XRD.

Given that the material hydrated with liquid L1 (water) is merely a highly blended cement (here it has been basically used as a reference material) and that blended cement hydration has been extensively studied, there is little point in devoting time and space to a discussion of the hydration products observed in this system or its evolution over time, both of which concurred wholly with expected behaviour.

Attention should be drawn, however, to the presence of a hydroxysodalite-type zeolite in the crystalline phases of the cementitious matrix formed by the material activated with alkaline solution L2. This may be an indication of the reaction of the fly ash in the original solid with the alkalis and hydroxyl ions in the medium to form the alkaline silicoaluminate gel characteristic of the activation of this sort of materials. One development would confirm the idea that the cementitious matrix under formation consists essentially in the “zeolite precursor” (alkaline aluminosilicate gel) generated by the fly ash during activation, rather than the C-S-H gel generated by Portland clinker during hydration: the presence of substantial quantities of anhydrous silicates (alite and belite from the clinker). The absence of portlandite among the

crystalline phases of this material (regardless of curing time) and the appearance of moderate amounts of calcite are also significant in this regard, providing further evidence that the clinker component in the original solid does not hydrate “normally”. This naturally has an adverse effect on the amount of C-S-H precipitating in the system. It may consequently be inferred that the clinker component contributes only scantily to the development of mechanical strength in the curing times considered.

The crystalline phases found in the original ash (essentially quartz and mullite) naturally appear in the hydrated system as well, since such phases are virtually inert under the conditions studied [25].

Scarcely any differences are observed between the crystalline phases identified in the above system (activated with liquid L2) and the phases found in the material hydrated with liquid L3. These small differences may be indicative of significant information, however. No zeolite crystal is found in paste S3, for instance; which does not necessarily mean that N-A-S-H is not formed, because a high silica content in aluminosilica systems is known to retard zeolite crystallisation [29]. Moreover, part of the clinker in system S3 remains unhydrated after 28 days, and no portlandite is detected, although calcite is found to be present. The alite and belite content in this paste is significantly lower than in the S2 paste, but higher than in S1. In other words, the C-S-H gel formed in system 3 as a result of the “normal” hydration of the clinker component does not by itself explain the development of greater mechanical strength than in system S1.

The interpretation of the ^{29}Si NMR signals helps to understand the microstructural evolution of the cementitious matrices studied and therefore to interpret the nature of the gels that make up the skeleton responsible for the strength of these materials. In this respect, the component to which the peak at -86 ppm in spectra 6C and 6D is attributed is of key importance, since such peak may be associated with either the C-S-H gel (Q^2 units) or the N-A-S-H gel [$Q^4(4Al)$ units]. Naturally, the presence of anhydrous silicates in both spectra (signal at -72 ppm) supports the thesis that C-S-H is not the only binder formed in systems S2 and S3. The gel does, however, form a part of both binders, since part of the clinker disappears (is hydrated) in these systems: note the modification of the signal at -72 ppm in spectra 6B and 6C compared to spectrum 6A. Moreover, the selective methanol + salicylic acid attacks on the two materials provide further proof of the existence of the C-S-H gel (see Figs. 4, 5).

Finally, the presence of low intensity signals at -90 , -95 and -102 ppm in spectra 6C and 6D is significant,

since in earlier papers [7, 29], these signals were identified as pertaining to the N-A-S-H gel and attributed to Q^4 units with 3, 2 or 1 aluminium.

In short, the working techniques used show that the precipitation of a mix of gels (C-S-H and N-A-S-H) is responsible for the setting and hardening of this type of (fly ash-rich) super-blended cement when highly alkaline hydration solutions are used. These results are wholly consistent with the data published in earlier papers by Krivenko et al. [30] working with blast furnace slag and van Deventer et al. [17], who conducted in-depth studies of the reactivity of systems containing metakaolin and blast furnace slag.

Conclusions

Highly blended cements containing 30% Portland cement clinker and 70% fly ash, may develop similar mechanical strengths than standard cements (70% OPC + 30% fly ash) just by incorporating alkaline activators in the system. However, it is important to remark that the type of activator added to the system highly affects its mechanical development. The precipitation of a mix of gels (C-S-H and N-A-S-H) is responsible for the setting and hardening of this type of alkaline-hydrated (fly ash-rich) super-blended cement.

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