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Mineralogical and microstructural characterisation of alkali-activated fly ash/slag pastes

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Abstract

A mechanical, mineralogical and microstructural characterisation of the cement pastes obtained by alkaline activation of fly ash/slag mixtures cured at different temperatures has been carried out. The pastes obtained were characterised by XRD, FTIR, MAS NMR, SEM/EDX, atomic absorption and ion chromatography, also the insoluble residue in HCl was determined.

The results obtained have proved the existence of two different reaction products in those activated pastes. The average atomic ratios in the main reaction product were Ca/Si $\sim$ 0.8, Al/Ca $\sim$ 0.6, Si/Al $\sim$ 2–3. Such analysis corresponds to calcium silicate hydrate rich in Al, which includes Na in its structure. Other reaction product which was detected in the pastes as result of fly ash activation, was an alkaline aluminosilicate hydrate with a three-dimensional structure.

1. Introduction

The development of new binders alternative to traditional cements obtained by the alkaline activation of different industrial by-products (blast furnace slag and fly ashes) is an ongoing study and research topic of the scientific community. These new cements are characterised by their high mechanical performance, their low energy cost and low pollutant gases emission (CO_2, SO_2, NO_x, etc.) and their less environmental deterioration (almost exclusively usage of secondary raw materials instead of surface-excavated natural resources).

The cements obtained from a mixture of ground blast furnace slag and aluminosilicate fly ash have not been studied consistently. Smith and Osborne [1] and Bijen and Waltje [2] investigated cements made from the combination of 60% finely ground blast furnace slag and 40% fly ash activated by 7% sodium hydroxide. Smith and Osborne found that early strength properties were good but there was little gain in strength beyond 28 days though improved strength might be obtained by varying the proportions of slag and fly ash or by increasing the fineness of the slag. Bijen and Waltje found that this type of cements carbonated much faster than the reference made of slag cement and ordinary portland cement. This carbonation process was accompanied with a substantial reduction in compressive strength.

Shi and Day [3] studied the effect of two types of fly ash and the addition of lime on the strength development and hydration of fly ash/slag mixtures activated by NaOH and sodium silicate. They concluded the type of fly ash is connected with the nature of activator. The addition of a small amount of hydrated lime significantly increased the early-age strength by slightly decreased the later-age strength of the cements.

Recently, Puertas et al. [4] studied the strength behaviour and hydration products of fly ash/slag pastes activated with NaOH. At 28 days of reaction, the mixture 50% fly ash/50% slag activated with 10 M NaOH solution and cured at 25 °C develops compressive strengths higher than 50 MPa. The fly ash/slag ratio is the most relevant factor on the strength development. The main reaction product is a hydrated calcium silicate, like CSH gel, with high amount of tetraco-ordinated Al in its structure.

In the present work a mechanical, mineralogical and microstructural study of the cement pastes obtained by alkaline activation of fly ash/slag mixtures cured at different temperatures has been carried out.

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2. Experimental work

2.1. Materials

The chemical composition of Spanish fly ash and blast furnace slag used in this work is shown in Table 1. Chemical reagent NaOH was used as activator.

X-ray diffraction analysis indicated that the slag consisted mainly of a glassy phase and no crystalline phases were detected. Through FTIR, it was classified as a melilite with a mineralogical composition close to A_5G_5 (A = Akermanite and G = Gehlenite). By means of XRD it is confirmed that the fly ash consisted in a glass phase, quartz and mullite.

2.2. Tests carried out

The cement pastes were prepared in prismatic moulds of 1 × 1 × 6 cm. The fly ash/slag ratio was 50/50 (wt.%). NaOH 10 M was used as activator solution. The liquid/solid ratio was 0.35. Two curing temperatures were used: 22 and 65 °C. The pastes were maintained at 65 °C during the first 5 h. For the rest of the curing time, the specimens were maintained at ambient temperature and 98% of RH; the same as the specimens cured at 22 °C. The prismatic pastes were mechanically tested at 7 and 28 days of curing. At these times the following tests were carried out:

- Flexural and compressive strengths. Firstly, the prisms were tested at flexural strengths and after the two pieces obtained were tested at compressive strengths. Different press were used for those determinations.
- Mineralogical characterisation: X-ray diffraction (XRD) and infrared spectroscopy (FTIR).
- Insoluble residue in HCl according to the Spanish standard UNE 80-223-85; and Na total content and Na fixed in the products by atomic absorption (AA) and ion chromatography (IC), respectively.
- Microstructural characterization by SEM/EDX and ^{29}Si and ^{27}Al MAS NMR.

Table 1
Chemical composition (wt.%)

	Fly ash	Slag
CaO	5.51	41.45
SiO_2	51.49	35.50
Al_2O_3	29.03	12.15
Fe_2O_3	7.67	1.01
MgO	2.35	8.34
SO_3	–	0.18
S^{2-}	–	0.92
Na_2O	0.66	0.58
K_2O	2.83	0.64
Blaine fineness (m^2/kg)	398	460

3. Results and discussion

Mechanical strengths results are presented in Table 2. From these results it is deduced that at seven days the mechanical strengths are very similar in both curing conditions, obtaining compressive strength values around 30 MPa. At longer-age (28 days) the mechanical values are higher in the pastes cured at 22 °C than those obtained at 65 °C. It is interesting to point out that, cement pastes with compressive strengths above 60 MPa can be obtained after 28 curing days cured in room temperature.

In Fig. 1 the evolution of insoluble residue in the HCl of the different activated samples is shown. That residue is assumed to correspond to the unreacted fly ash. In mixtures of 50% fly ash/50% slag without activation, the Insoluble Residue (IR) value is 38.9%, that corresponds to the part of the fly ash insoluble in this selective treatment. As it is seen in the graph, as reaction time increases, the IR of the pastes decreases. However, curing temperature does not affect the residue value. After seven days reaction, the insoluble residue diminishes to around 23%, while at 28 days the decrease of the insoluble residue is 30%. These variations within the insoluble residue in HCl indicate that fly ash used as cement raw material partially and progressively reacts during the reaction process. These results do not clarify the different mechanical strengths observed at 28 reaction days.

Table 2
Mechanical strengths results

Time (days)	22 °C (MPa)		65 °C (MPa)	
	Flexural	Compression	Flexural	Compression
7	6.3 ± 0.4	31.9 ± 1.6	5.3 ± 0.3	30.0 ± 1.9
28	13.5 ± 1.2	63.5 ± 1.2	4.4 ± 079	53.3 ± 0.3

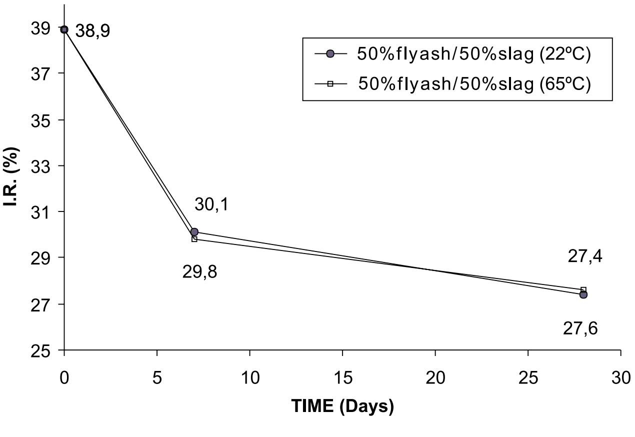

Fig. 1. Insoluble residue in HCl acid on activated pastes.

Mineralogical characterisation carried out by XRD has proved that the crystalline reaction products are $CaCO_3$ (calcite) and hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$). Some reflections at 4.90, 2.61 and 1.93 Å are present in all diffractograms, they would be due to the presence of low proportion to $Ca(OH)_2$ in the pastes. In all diffractograms "halos" are observed, indicating the presence of other low-crystalline compounds. The diffraction lines corresponding to quartz and mullite from the raw fly ash are observed.

In Fig. 2, IR spectra obtained are shown. The IR spectra obtained after seven days of reaction show some differences compared to those obtained at 28 days. Also, some variations are observed depending on the curing temperature. The IR spectrum of the sample cured at 22 °C after seven days (A spectrum) has a sharp and very intense absorption band at 952 cm^{-1} and another at 1035 cm^{-1}. The first one corresponds to the stretching vibration, v_3 (Si–O), of SiO_4 tetrahedron of the slag (956 cm^{-1}) although in this spectrum such band is a very broad one. In IR spectrum of the sample cured at 65 °C and seven reaction days (C spectrum), this band is not sharp any more and slightly shifts towards higher frequencies (959 cm^{-1}). In spectra from samples at 28 days, independently of curing temperature (B and D spectra), the band is a very broad one, and reaches its maximum around 975 cm^{-1}. Absorption at 1035 cm^{-1}, observed in spectrum A, diminishes its intensity as curing temperature and reaction time increases, becoming a shoulder in those spectra. This absorption is not present in IR spectra of original slag and fly ash. Other interesting variations are observed in region 500–400 cm^{-1}, where bands connected with vibration v_4 (O–Si–O) of tetrahedral groups appear. In all spectra of activated samples, a band is clearly visible towards 452 cm^{-1}, which is slightly shifted towards frequencies lower than those of the fly ash IR spectrum (457 cm^{-1}) and very far away from the one appearing in the slag spectrum (505 cm^{-1}). Also there is some new absorption of low intensity at 488 and 425 cm^{-1}. In all spectra, a low intensity absorption is observed at 1075 cm^{-1}, which indicates that some fly ash remains without reaction.

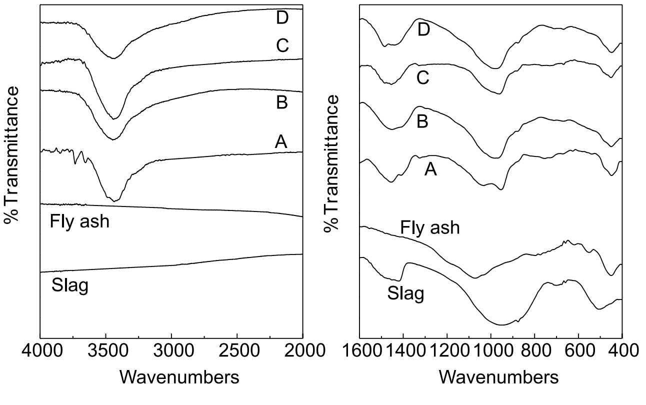

Fig. 2. Infrared spectra of 50% fly ash/50% slag. A: seven days of hydration, 22 °C; B: 28 days of hydration, 22 °C; C: seven days of hydration, 65 °C; D: 28 days of hydration, 65 °C.

In 3500 and 1600 cm^{-1} region, water stress (O–H) and deformation (H–OH) bands, respectively, become visible. These bands do not appear in anhydrous slag and fly ash spectra. In spectra of activated pastes these bands indicate the presence of water molecules from crystallisation or from absorption of the reaction products. Nevertheless, no remarkable variations are found in the different spectra. Yet, in all the spectra of the pastes an absorption of very low intensity appears around 3640 cm^{-1} that can be ascribed to the vibrations of groups OH, of the $Ca(OH)_2$, already identified through XRD.

FTIR results indicate the formation of reaction products as a consequence of the alkaline activation of slag and fly ash. The nature of such products evolves with time. Between 7 and 28 reaction days there are substantial changes in spectra of region 1100–900 cm^{-1}. It is assumed that the band observed around 950–980 cm^{-1} is the result of the formation of a calcium silicate hydrated, type CSH gel, in pastes that had been activated. The shift towards higher frequencies observed in that band, as the reaction time increases, indicates a higher polymerisation degree. Previous studies [4] have already proved that calcium silicate hydrated developed in this type of paste included $AlO_4 + Na$ as a substitution of SiO_4. However, it has to be taken into account that in this region of the spectrum vibrations from other phases could show up, having a higher aluminium content, probably developed during the alkaline activation of fly ash. In agreement with Palomo et al. [5] research the main band, due to Si–O and Al–O vibrations, which is located at 1075 cm^{-1} in fly ash, moves towards lower frequencies when those are activated. The alkaline activation of fly ash leads to the formation of an alkaline aluminosilicate of amorphous nature and three-dimensional (3D) network. Its IR spectrum shows a band at 997 cm^{-1} associated with v_3 (Si–O), and other absorption located in 691 and in 426 cm^{-1}. The band around 997 cm^{-1} cannot be discerned very clearly in spectra, instead, another is seen around 1035 cm^{-1} that stays in spectra of activated pastes together with the band in 426 cm^{-1}. Al–O vibrations from the other existing compounds cause interference in absorption at 691 cm^{-1}.

The results obtained by NMR and SEM/EDX have confirmed that the presence of calcium silicate hydrate and an alkaline aluminosilicate hydrate as the reaction products in these activated pastes. In Fig. 3(a) ^{29}Si MAS NMR spectra obtained are shown. The anhydrous slag spectrum displays a wide asymmetric signal whose maximum is near −74 ppm, this signal corresponds to dimeric Q^1 units. The anhydrous fly ash spectrum displays a wide asymmetric signal formed by different

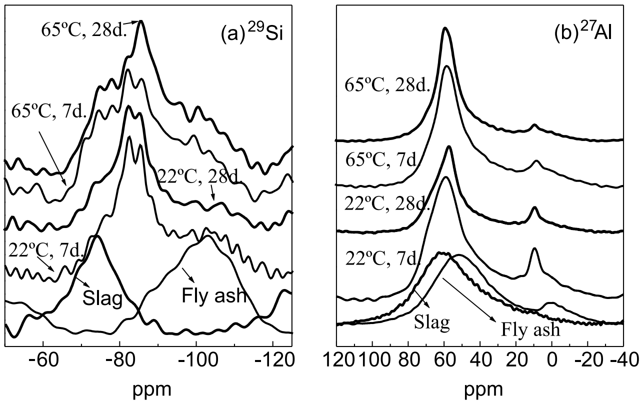

Fig. 3. MAS NMR (a) ^{29}Si and (b) ^{27}Al spectra of 50% fly ash/50% slag.

components, the main signal at −103 ppm corresponds to Q^4 units [6]. ^{29}Si MAS NMR spectra of activated pastes display a wide and asymmetrical signal formed by several maxima. Comparing those spectra with that of no reacted materials (slag and fly ash) an important shift of the spectrum is detected. Chemical shift (in ppm) of different peak used in deconvolution of spectra are given in Table 3.

The assignment of NMR components was based on reported values obtained in aluminosilicates [7–10]. According to published data the peaks appearing between −66 and −73 ppm are assigned to Q^0 units; between −74 and −78 ppm are assigned to Q^1 units; between −83 and −88 ppm to Q^2 units, between −95 and −100 ppm to Q^3 units and between −103 and −115 ppm to Q^4 units. The substitution of Si by Al shift signal 3 or 5 ppm towards more positive values; from this fact the peak appearing at −82 to −84 ppm can be ascribed to Q^2(1Al).

In activated pastes new peaks were detected in ^{29}Si MAS NMR spectra in comparison to the anhydrous slag and fly ash (see Fig. 3(a) and Table 3). These results show that an important structural rearrangements has been produced. Two different type of reaction products can be detected. As consequently of slag reaction an amorphous calcium silicate hydrate with a dreierketten type structure is formed. In this structure linear chains of silica tetrahedra (Q^1 end chain and Q^2 units) are linked to central Ca–O layers, in which an important part of the bridging tetrahedral of the linear chain are occupied by Al (Q^2(1Al) units) [9,11].

In all activated paste spectra a signal between −88 and −90 ppm appears. This peak is assigned to Q^4(3Al) units and the interpretation of its presence is the formation of an amorphous alkaline aluminosilicate like a zeolitic gel compound due to the alkaline activation of fly ash. The intensity of that signal increases with the reaction time.

In Fig. 3(b) ^{27}Al MAS NMR spectra of the raw material (slag and fly ash) and the pastes are given. These spectra show the presence of a strong and broad asymmetric signal centred at +60 +58 ppm, that is formed by two signs one centred in ≈ +60 ppm due to tetrahedral aluminium (Al_T) and other centred in +30 ppm due to pentahedral aluminium (Al_P). In spectra of activated pastes the presence of a third peak at +8 ppm reveals the presence of octahedrally co-ordinated aluminium (Al_O). ^{27}Al MAS NMR of anhydrous fly ash shows a signal at +1.70 ppm assigned to Al_O of mullite. From this figure it can be seen that the most of Al in the activated pastes is tetrahedrally co-ordinated. That explains the presence of the Al in the alkaline aluminosilicate hydrated with 3D structure and also in the calcium silicate hydrate [11].

Different microstructures develop as a consequence of the reactive processes that happen between slag/ash mixtures and alkaline solution. The main reaction product corresponds to a calcium silicate hydrated with a whose average atomic ratios close to were Ca/Si ∼ 0.8, Al/Ca ∼ 0.6, Si/Al ∼ 2–3. This analysis corresponds to a calcium silicate hydrated, rich in Al, includes Na in its structure. Results obtained from AA and IC analysis of pastes has proved that they fix 30–40% of the initial Na added in the alkaline solution (see Table 4).

Particles of fly ash covered with a crust (Fig. 4) have been observed whose analysis can be in agreement with this of an alkaline aluminosilicate. Reactive process of fly ash can be seen in Fig. 5, which corresponds with a

Table 3
Results obtained from deconvolution of ^{29}Si and ^{27}Al MAS NMR spectra of pastes

	22 °C, 7 days (ppm)	22 °C, 28 days (ppm)	65 °C, 7 days (ppm)	65 °C, 28 days (ppm)	Assignment
^{29}Si	−72.09	−73.74	−72.54	−72.02	Q^1 (slag)
	−77.61	−79.63	−78.28	−76.69	Q^1 (chain end)
	−82.04	−82.23	−82.35	−82.07	Q^2(1Al)
	−85.59	−85.42	−85.77	−85.89	Q^2(0Al)
	−88.81	−88.94	−89.21	−90.15	Q^4(3Al)
	−101.88	−100.74	−100.00	−99.82	Q^4 (Fly ash)
^{27}Al	+59.80	+58.00	+58.50	+58.50	Al_T
	+30.00	+33.00	+34.00	+34.00	Al_P
	+9.89	+9.34	+9.70	+9.70	Al_O
	+1.70	+1.70	+1.70	+1.70	Al_O

Table 4
Na content in the activated pastes

	22 °C		65 °C	
	7 days	28 days	7 days	28 days
Na total (wt.%)	6.1	6.4	5.8	6.0
Na lixiviated (wt.%)	4.4	4.3	3.7	3.7
% Na Fixed	28	32	36	38

Na total of reference material (50% fly ash/50% slag) = 0.5%.
Na lixiviated in reference material = 0.06%.

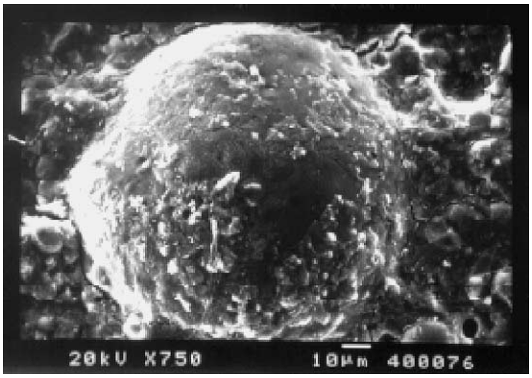

Fig. 4. Fly ash particle covered with a crust of reaction products.

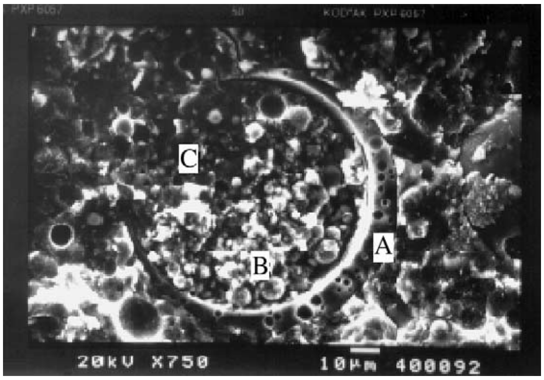

Fig. 5. Reactive evolution of fly ash particle.

fly ash particle partially reacted. In the same figure chemical analysis of marked points are shown. Point A corresponds to some fly ash that stayed no reacted. Point B particles are reaction products from fly ash (Si, Al and Na, practically exempt Ca). Finally point C agrees with the major matrix of the paste, where the Ca content is much higher. The described microstructure was observed in pastes activated at 7 and 28 days and cured within the two temperatures of the test.

From these results, it is deduced the mechanical strengths obtained in cement pastes obtained by alkaline activation of fly ash/slag mixtures are due to the formation of two different products, independently of curing conditions. The main reaction product is a low-crystalline calcium silicate hydrate with a dreierketten type structure. In this structure the linear chain of silica tetrahedra linked to central Ca–O layers, in which an important part of the bridging tetrahedra are occupied by Al. Na ions are also included in the structure compensating the charge balance. The polymerisation degree of this silicate increases with the reaction time. This product is formed mainly by the alkali activation of ground blast furnace slag.

The second reaction product is an amorphous alkaline aluminosilicate with a 3D structure as a zeolitic gel type. This product is a consequence of the alkaline activation of fly ash. The results obtained have proved that the reaction of fly ash with the alkaline activator increases with the reaction time.

From the results obtained it is deduced that curing temperature of the mixtures does not substantially affect the mineralogical composition of pastes. The different mechanical values obtained in the pastes cured at 22 and 65 °C, specially at 28 days, can be justified for the different microstructural arrangement formed as consequence of different rate reactions [12,13] and the heating regime adopted in the experimental program which could cause a thermal cracking. At 65 °C the activation process occurs at higher rate and that has influence in the spatial phase disposition.

4. Conclusions

From alkaline activation of fly ash/ground blast furnace slag two kinds of reaction products are obtained. The main reaction product is from slag activation process and has as average atomic ratios: $Ca/Si \sim 0.8$, $Al/Ca \sim 0.6$, $Si/Al \sim 2–3$. This analysis belongs to a low-crystalline calcium silicate hydrate rich in Al, which includes Na into its structure. In this structure linear chains of silica tetrahedra (Q^1 end chain and Q^2 units) are linked to central Ca–O layers, in which an important part of the bridging tetrahedra of the linear chain are occupied by Al (Q^2(1Al) units). The polymerisation degree of this silicate increases with the reaction time.

The reactive evolution of fly ash in the mixture and the morphology of its reaction products have been observed. This reaction occurs around fly ash particle and the reaction product corresponds to an amorphous alkaline aluminosilicate hydrate with 3D structure (Q^4(3Al) units).

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