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Alkali-activated fly ash/slag cement
Strength behaviour and hydration products

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Abstract

The activation of fly ash/slag pastes with NaOH solutions have been studied. The parameters of the process studied are: activator concentration (NaOH 2 and 10 M), curing temperature (25°C and 65°C), and fly ash/slag ratios (100/0, 70/30, 50/50, 30/70, and 0/100). The equations of the models describing the mechanical behaviour of these pastes have been established as a function of the factors and levels considered. The ratio of fly ash/slag and the activator concentration always result to be significative factors. The influence of curing temperature in the development of the strength of the pastes is lower than the contribution due to other factors. At 28 days of reaction, the mixture 50% fly ash/50% slag activated with 10 M NaOH and cured at 25°C, develop compressive mechanical strengths of about 50 MPa. The nature of the reaction products in these pastes has been studied by insoluble residue in HCl acid, XRD, FTIR and MAS NMR. It has been verified that slag reacts almost completely. It has also been determined that the fly ash is partially dissolved and participates in the reactive process, even in pastes activated at ambient temperature. The main reaction product in these pastes is a hydrated calcium silicate, like CSH gel, with high amounts of tetracoordinated Al in its structure, as well as Na ions in the interlayer spaces. No hydrated alkaline aluminosilicates with three-dimensional structure characteristics of the alkaline activation of fly ashes were formed.

Keywords: Alkaline activation; Fly ash/slag blends; Mechanical properties; Hydration products

1. Introduction

Blast furnace slags and fly ashes are well-known materials in construction and they are used to produce blended cements and concretes. Blast furnace slag cements are characterised by their low hydration heat and high sulfate and water-sea resistance. On the other hand, traditionally, fly ashes have been used as pozzolanic material to enhance physical, chemical and mechanical properties of cements and concretes.

However, only amounts of 20–30% of slags and fly ashes producted are used in these terms and the excess is stored in large extensions. The utilisation of these excesses in the manufacturing of other building materials would contribute to the elimination of an environmental problem and to the development of new high-performance materials.

An attractive alternative to Portland cements are the binders obtained by alkaline activation of different materials. These new cements are characterised by their high mechanical strengths and also, they do not require high energy costs in their manufacturing process. Depending on the nature of the raw materials to be activated, different reaction products are developed which have different microstructures [1,2]. Due to these differences, two models or groups of alkaline activation processes exist.

In the first model, the raw material is placed in the lime-rich zone of the $CaO-SiO_2-Al_2O_3-MgO$ quaternary system, with SiO_2/Al_2O_3 and CaO/Al_2O_3 of about 3. In the second model, the original material has low CaO contents (lower than 1% wt.) and high SiO_2 and Al_2O_3 percentages (SiO_2/Al_2O_3 ratio of about 1.3).

The first model is mainly referred to the alkaline activation of glassy blast furnace slags. Related to the properties and characteristics of alkali-activated slag cements and concretes, some advantages with respect to traditional Portland cements and concretes like earlier and higher mechanical strengths, lower hydration heat and better resistance to

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aggressive chemicals, are worth mentioning. They also present some disadvantages as quick setting and high shrinkage with microcracking formation [3]. The alkaline activation of slags has been extensively studied [4–7]. The main reaction product is a hydrated calcium silicate, like CSH gel. This phase is different from that formed in the Portland cement hydration and has lower C/S ratio. The formation of other phases or hydrated compounds depends on the type and amount of the activator used, structure and composition of the slag and curing conditions of hardening.

A material of the second "model" susceptible of being activated are the aluminosilicate fly ashes. In this activation, the reaction temperature plays an important role. At ambient temperature, the reaction rate is very low. However, if the process occurs at temperatures between 40°C and 85°C, the reaction rate is notably increased making it possible to obtain mortars with 20 MPa at 2 h of curing. This activation has been less studied. The reaction product obtained is, in this case, an inorganic polymer of amorphous nature formed by hydrated aluminosilicates chains, where negative charges are balanced by alkaline ions. The polymer structure depends on the activator used [8].

Both activation processes have advantages and disadvantages. From the knowledge of both materials, it is known that the disadvantages of one activation process can be balanced with the other one. Bibliography existing about the joint activation of fly ashes and slags is scarce, with only the work of Smith and Osborne [9], Bijen and Waltje [10] and Shi and Day [11]. The results of these authors are contradictory in many occasions with gaps of knowledge about the hydration processes and the development of strengths.

The aim of the present work is to know the strength behaviour of fly ash and blast furnace slag mixtures when they are alkaline-activated, likewise, to study its hydration products.

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.

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

Table 2
Factors and levels considered

Factors	Levels
A=Activator concentration	−1: NaOH 2 M; +1=NaOH 10 M
B=Curing temperature	−1: 25°C; +1=65°C
C=Fly ash/slag ratio	−2: 100/0; −1: 70/30; 0=50/50; +1: 30/70; +2: 0/100

X-ray diffraction (XRD) 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. Variables of the process and tests

The variables considered in this activation process were:

- Fly ash/slag ratio (% mass): 100/0, 30/70, 50/50, 70/30 and 0/100;
- Activator solution concentration NaOH: 2 and 10 M;
- Curing temperature: 25°C 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 25°C.

Considering these parameters, the pastes were elaborated in prismatic moulds of 1 × 1 × 6 cm. At determined ages (1, 7, 28, and 90 days), compressive strengths of these specimens were tested. The liquid/solid ratio of all pastes was fixed constant at 0.35. The results obtained were statistically analysed through a complete experimental design ($2^2 \times 5$) [12,13]. The methodology employed has been described in previous works [14,15]. The nomenclature used in the variables and levels definition is shown in Table 2.

Some pastes were also studied by the following tests:

- Insoluble residue in HCl acid according to the Spanish standard UNE80-223-85;
- Mineralogical analysis by FTIR and XRD;
- MAS NMR. Previously to obtain the spectrum the Fe metallic was extracted from the samples.

3. Results and discussion

3.1. Mechanical strength behaviour

The evolution of the compressive mechanical strengths of the pastes studied is shown in Fig. 1. The analysis of

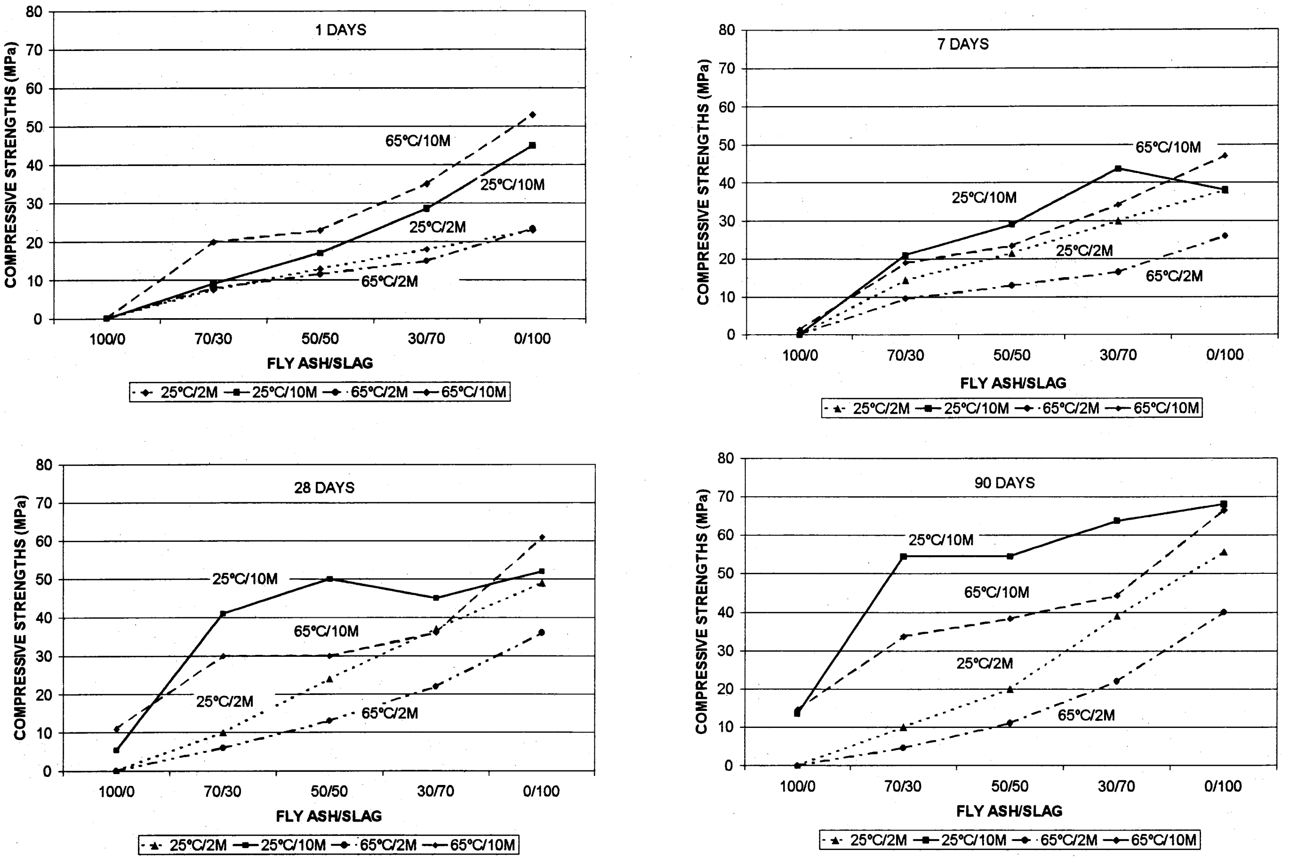

Fig. 1. Compressive strengths of mortars at different ages.

these graphs indicates that, in all mixes and at all ages studied, when slag content increases in the pastes, compressive strength also increases. The strength development is closely related to the NaOH solution concentration. As it can be observed in the figures, the highest strengths are reached at 10 M activator concentration. The temperature increase has no positive effect in strength development except for the results at 1 day of reaction with 10 M solution in which mechanical values are slightly higher than those at 65°C. In most pastes, the mechanical strengths were equal or higher when curing temperature was 25°C. It is interesting to mention the values obtained in mixtures 50% fly ash/ 50% slag activated with 10 M NaOH at 25°C; at 28 days, compressive strengths are of about 50 MPa. At 90 days, these values are slightly increased.

Over all the values obtained, a statistical analysis was carried out through a factorial experimental design. The design had $2^2 \times 5$ experiments for each test age. The significance assigned to each single factor studied, as well as their interactions, were determined. The F-tests in the ANOVA table decomposes the variability of responses into contributions due to different factors. The p-values obtained with the ANOVA table determine the statistical significance of each factor and their interactions. When the p-values are less than 0.05, the factors or their interactions have a statistically significant effect on the response at the 95.0% confidence level. In Table 3, the p-values obtained are shown.

From the three factors considered, always significative are: activator concentration and fly ash/slag ratio. Curing temperature is not a significative factor at 1 and 7 days. At the rest of ages, this factor has p-values notably higher than the other two factors. This means that its influence in the development of strengths is lower than

Table 3
p-Values for the factors considered

Compressive strength (days)	p-Values
1	$A=0.0015$
	$B=0.2934$
	$C=0.0000$
7	$A=0.012$
	$B=0.0955$
	$C=0.0002$
28	$A=0.0002$
	$B=0.0443$
	$C=0.0000$
90	$A=0.0000$
	$B=0.0094$
	$C=0.0000$

A=activator concentration; B=curing temperature; C=fly ash/slag ratio; AC=binary interaction (activator concentration and fly ash/slag ratio); AB=binary interaction (activator concentration and curing temperature).

the contribution due to the other two factors. The most significative factor because of its lowest *p*-value is the fly ash/slag ratio.

The mathematical equations explaining the mechanical behaviour of the fly ash/slag mixtures alkali-activated studied in the present work, are shown in Table 4.

A general expression for the equations presented is the following:

$$R_{\mathrm{d}}^{\mathrm{C}} = \mu + A_1 X_A + B_1 X_B + \delta_{Cd} + \epsilon$$

where μ is the general mean of the estimated values; A_1 and B_1 represent the coefficients associated with *A* and *B* factors (see Table 2). They are determined by least squares means. X_A and X_B are the variables having − and + values according to *A* and *B* factors with −1 or +1 levels, respectively. In the two-level factorial designs (factors *A* and *B*, see Table 2), there is a unique parameter by factor: the effect of each factor is defined as the expected increment in the response when this factor goes from − to +. δ_{Cd} represents the *C* factor (see Table 2) defined by five levels (−2, −1, 0, +1 and +2). It takes different values or coefficients for each level, and they are described in the same table. Finally, ϵ represents the random errors in the measurements.

These equations provide the analysis of the joint influence of the three factors considered in the development of mechanical strengths at the different ages studied. From the analysis of these equations it is deduced that:

As reaction time increase, from 1 to 90 days, the independent term of the equations increases. That is, the activation processes progress with time.

The sign before the coefficient of factor *A* (activator concentration) is positive in all equations. This means that when concentration of NaOH is 10 M (level +1), compressive strengths are always higher that when NaOH concentration is 2 M (level −1). The values of that coefficient, in general, increase with reaction time, as it can be seen in the equations. The influence of activator concentration increases with time, with higher differences in strengths as a function of activator concentration. This is probably related with the different nature of the reaction products formed.

The effect of factor *B* (curing temperature) is variable at the different ages studied. At 1 day, the sign of the coefficient of this factor is positive indicating that at this age, higher strengths are obtained when the curing is carried out at 65°C. At the rest of the ages, this sign is negative indicating that the pastes cured at 25°C develop higher strengths than those treated at 65°C. Similar results have been obtained by other authors studying the effect of curing temperature on alkaline activation of blast furnace slag [14,16,17]. An explanation to this phenomenon is that, increasing temperature favours the dissolution of reactive species, mainly that of the slag, but also that of the fly ash in some degree. As a consequence of that intense reactive process, a larger amount of product is formed with a more heterogeneous and dense distribution and microstructure different to that obtained if curing temperature would be lower. This paste densification makes difficult the diffusion process at longer reaction times with the subsequent delay of later reactions.

The influence of factor *C* (fly ash/slag ratio) is determinant in the development of compressive strengths. As it is indicated by δ_{Cd} coefficients (see Table 4) in going from level −2 to level +2 (as fly ash content in the mixture decreases), the contribution to the final strength increases. With high fly ash contents, the sign of these coefficients is negative and their absolute value is high. In mixtures 50%/50%, the coefficient value is close to zero. Finally, in mixtures with high slag contents, the coefficients have positive sign and high absolute values. These results indicate that the slag reacts more in these mixtures contributing massively to the final strengths. The contribution of fly ashes to the strengths is lower.

3.2. Hydration products

To study and characterise the reaction products formed, the mixture having 50% fly ash/50% slag was selected, because at 28 days, this mixture activated with 10 M NaOH and cured at 25°C develops strengths of about 50 MPa. These values are 95% of those obtained in the paste with only slag and that proportion is of 80% at 90 days. In any case, these results indicate that fly ash has some contribution

Table 4
Mathematical equations for compressive strengths

Time (days)	Mathematical equations
1	$R_1^{\mathrm{C}} = 17.68 + 5.68X_A + 1.55X_B + \delta_{\mathrm{C1}} + \epsilon$ ($\sigma \cong 2.39$)
7	$R_7^{\mathrm{C}} = 21.54 + 4.68X_A - 2.04X_B + \delta_{\mathrm{C7}} + \epsilon$ ($\sigma \cong 3.84$)
28	$R_{28}^{\mathrm{C}} = 27.42 + 7.70X_A - 4.10X_B + \delta_{\mathrm{C28}} + \epsilon$ ($\sigma \cong 6.27$)
90	$R_{90}^{\mathrm{C}} = 32.49 + 12.29X_A - 5.42X_B + \delta_{\mathrm{C90}} + \epsilon$ ($\sigma \cong 5.23$)

Fly ash/slag ratio (level)	100/0 (−2)	70/30 (−1)	50/50 (0)	30/70 (1)	0/100 (2)
δ_{C1}	−17.68	−6.63	−1.33	+7.27	+18.40
δ_{C7}	−19.89	−5.56	+0.28	+9.48	+15.68
δ_{C28}	−26.07	−5.47	+2.10	+7.30	+22.15
δ_{C90}	−25.51	−5.59	−1.54	+7.63	+25.01

to final strengths, even at low curing temperatures. As it is known, the dissolution and reaction of fly ashes in strong alkaline media is very favoured at temperatures higher than 65°C [8]. At ambient temperature, the reaction of the fly ash is extremely slow. In order to know the contribution of the fly ashes in these mixtures, the insoluble residue in HCl was determined. That residue is assumed to correspond to the unreacted fly ash. The results obtained in the paste 50% fly ash/50% slag are presented in Fig. 2.

In mixtures of 50% fly ash/50% slag without activation, the value of I.R. was 37.05%, that corresponds to the part of the fly ash insoluble in the selective treatment. As it is seen in the graph, as reaction time increases, the I.R. of the pastes decreases. In the pastes activated with 10 M NaOH and cured at 25°C, at 90 days of reaction I.R. is 38% lower than the reference value. This means that fly ash has been partially dissolved and has participated in the activation reaction process.

In order to know the nature of the reaction products formed in these pastes with 50% fly ash/50% slag, they were studied at 28 days by XRD, FTIR and MAS NMR.

The results obtained by XRD have demonstrated that in the pastes obtained after treatment with 2 M NaOH (both 25°C and 65°C), the unique crystalline reaction product is $CaCO_3$ (calcite). In pastes obtained with 10 M, hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) and pirssonite ($Na_2Ca(CO_3)_2\cdot 2H_2O$) are identified besides calcite. In all diffractograms "halos" are observed, indicating the presence of other low-crystallinity compounds. Also, diffraction lines corresponding to quartz and mullite from the raw fly ash are observed.

In Fig. 3, IR spectra obtained are shown. Those corresponding to the pastes activated with 2 M NaOH solution at 25°C and 65°C are practically equal. Both show the development of a broad and diffuse band at about 1024 cm^{-1}. This absorption is differentiated from stretching vibrations, ν_3 (SiO), of SiO_4 tetrahedra for the slag (956 cm^{-1}) and from the fly ash (1075 cm^{-1}). In these spectra, another band with lower intensity placed at about 964 cm^{-1} is also observed. The band associated to deformation vibrations ν_4 (OSiO) of the same tetrahedral groups is shifted in the spectra of hydrated pastes to lower frequencies ($\sim$448 cm^{-1}). The IR spectra of pastes activated with 10 M NaOH present differences with respect to those described. In this case, a well-defined and less broad band at 966 cm^{-1} is observed. The same as for the IR spectra of pastes activated with 2 M NaOH, curing temperature does not seem to affect the nature of the products formed because their IR spectra are identical. The band at 448 cm^{-1} is maintained, but another band is observed at 489 cm^{-1}. The region at 750–600 cm^{-1} associated to AlO bonds vibrations is modified with respect to the spectra of slag and fly ash. In all spectra, a vibration at 1075 cm^{-1} that indicates the presence of unreacted fly ash remains.

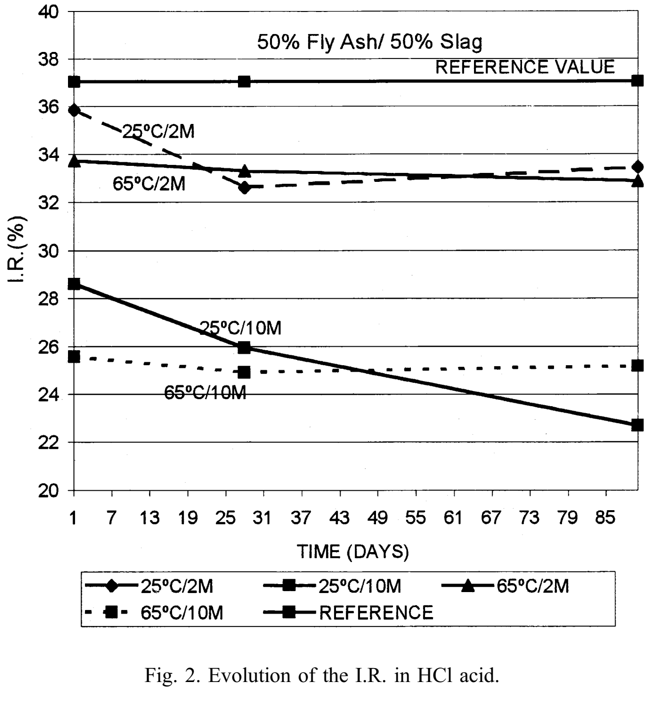

Fig. 2. Evolution of the I.R. in HCl acid.

Comparing IR spectra of pastes activated with 2 and 10 M NaOH solution, it is deduced that reaction products of different nature are formed.

As a consequence of the alkaline activation of slags, a hydrated calcium silicate of the CSH gel type is formed as the main reaction product. This gel phase is differentiated from that formed in the hydration of Portland cement because of its lower C/S ratio. According to Schilling et al. [18], this hydrated calcium silicate is mainly constituted of imperfect structures of tobermorite layers joint to isolated layers of $(C,M)_4AH_{13}$ intimately mixed in their structures. In previous research, it has been verified that in the IR spectra of CSH gels of these pastes, ν_3 (SiO) vibration is at about 973–994 cm^{-1}. The frequency of this band is directly related to the alkaline activator nature. The lowest frequencies are obtained when NaOH is used as activator and the highest ones when the activator is waterglass or Na_2CO_3 [19]. The results obtained in IR spectra of the pastes activated with 10 M NaOH solution indicate the formation of a hydrated calcium silicate (like gel CSH) similar to that generated in a Portland cement paste. Additionally, in these spectra, other absorption bands are observed at 1207 and 1172 cm^{-1}, which according to Mitsuda [20] are associated to the partial substitution of Si by Al in the gel structure; that substitution can become up to 15%. According to the same author, 960–965 cm^{-1} bands and those of bending at 445–450 cm^{-1} are not affected by that substitution. It must be considered that the isomorphic substitution Al→Si involves a no charge balance that would be corrected by the incorporation of sodium in the structure. The higher Na proportion in solution would favour the formation of CSH gel with the particularities described previously above (high incorporation of AlO_4+ Na substituting SiO_4). Sodium will enter the structure in interlayer spaces.

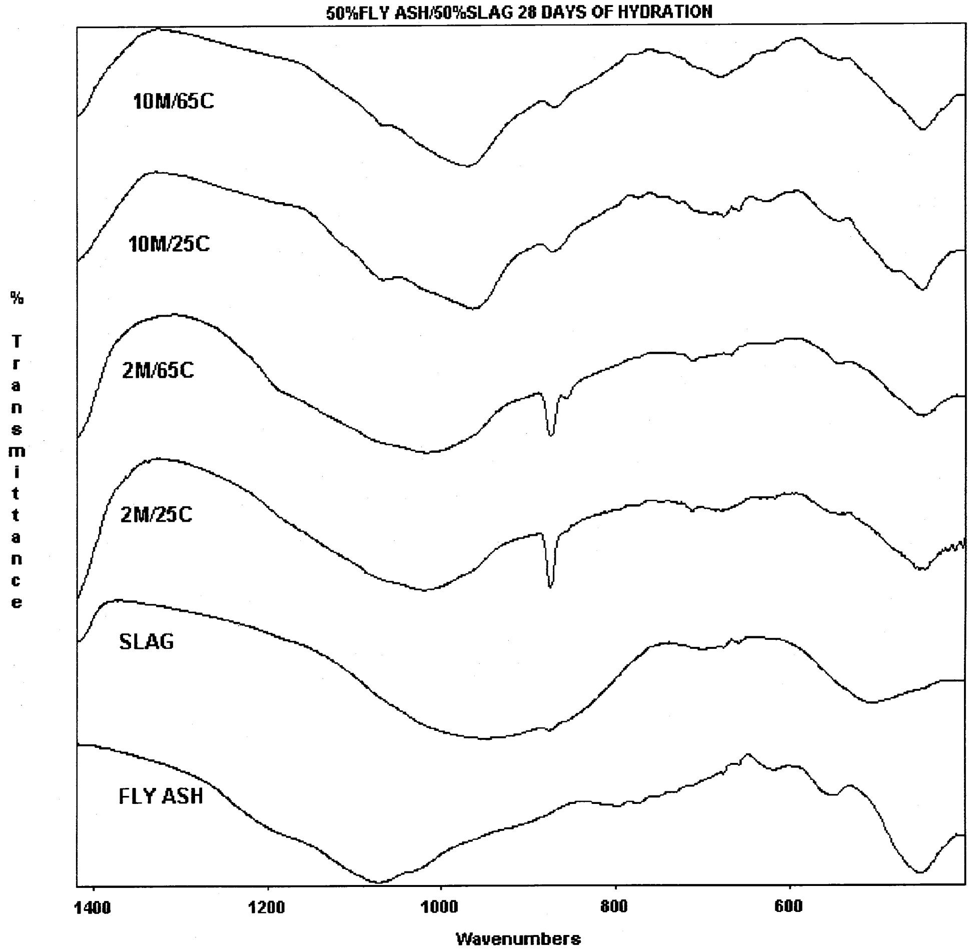

Fig. 3. IR spectra of slag and fly ash untreated and the pastes 50% fly ash/50% slag at 28 days of hydration.

The alkaline activation of fly ashes leads to the formation of an alkaline aluminosilicate of amorphous nature and 3D network, of a zeolitic type. The IR spectrum of the alkaline aluminosilicate has a band associated to ν_3 (SiO) at 997 cm^{-1}; other band characteristics of the presence of this inorganic polymer are placed at 691 and 426 cm^{-1} [21]. These absorptions are not observed in the IR spectra of the pastes studied.

In Fig. 4, the ^{29}Si and ^{27}Al MAS NMR spectra corresponding to the 50% fly ash/50% slag activated with 10 M NaOH solution and cured at 25°C at 28 days of reaction are shown. ^{29}Si spectrum shows three signals at -70.20 ppm (Q_0) it is a small signal, a second one at -76.00 ppm assigned to Q_1 unites, another very intense signal at -82.92 ppm due to dimmer unites Q_2 (1Al). The latter signal, besides the most intense one (corresponds around 50% of the total spectrum signals) has a certain width that indicates the existence of two signals overlapping in close regions and could correspond to similar dimmers with intercalated Al, but with little differences in bond lengths. The large intensity of this signal at -82.92 ppm confirms the Al substitution by Si in the CSH gel above mentioned. The CSH gel structure with $C/S>1.1$ ratios consist of Q_1 unites and in less proportion unites Q_2, whereas in those with $C/S<1.0$ ratios, the trend is to be rich in Q_2 unites [22,23]. According to the results obtained in the present study, the CSH gel produced, besides incorporating Al in its structure, corresponds to a gel with low C/S ratio. Finally, it is worth mentioning that the absence of Q_4 unites characteristics of the hydrated alkaline aluminosilicate with three-dimensional structure developed as the main product in the activation of fly ashes, permits to affirm the absence of this compound in the pastes generated by the joint activation of fly ash and slag.

The ^{27}Al MAS NMR spectrum has a signal at about 59.42 ppm corresponding to tetrahedral aluminium and, other broader and less intense signal at 9.54 ppm due to an octahedrically coordinated aluminium. Al_T/Al_O ratio is 4/1. Al_T corresponds to that in the CSH gel and that present in the raw products, fly ash or slag. The Al_O is from the reaction products already formed, because hydrotalcite is a phase present in these pastes. The Al_O from mullite is placed in values of about 2 ppm, far

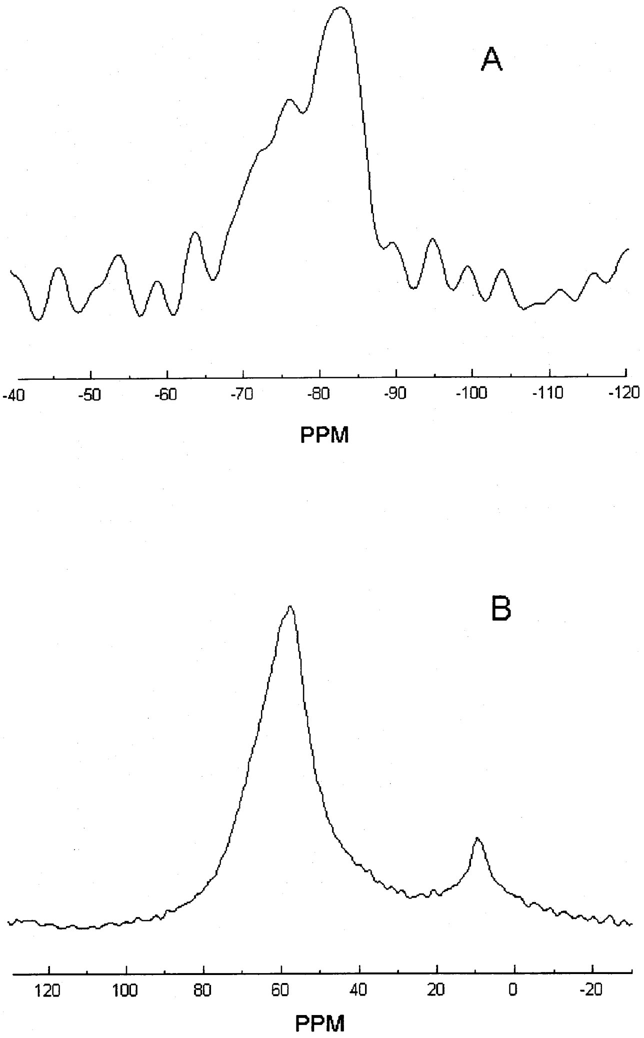

Fig. 4. MAS-NMR spectra for NaOH activated 50% fly ash/50% slag pastes at 28 days. (A) ^{29}Si MAS-NMR and (B) ^{27}Al MAS-NMR.

from the shift of 9.54 ppm found in these spectra. Although these pastes also contain mullite and it was identified by XRD.

According to the results described, under these test conditions and in 50% fly ash/50% slag pastes activated with 10 M NaOH, blast furnace slag is almost completely dissolved. The fly ash is also dissolved, but with slower rate and lower proportion. As a consequence of those dissolutions, condense and precipitate an amorphous hydrated calcium silicate (like CSH gel) that incorporates Al and alkaline ions in its structure. No hydrated alkaline aluminosilicate with three-dimensional structure characteristic of the alkaline activation of fly ashes is formed.

4. Conclusions

The main conclusions extracted from this work are:

(1) From the statistical analysis of the results obtained in the present work, with the factors considered at the selected levels and applying the analysis of variance within a confidence limit of 95%, it is deduced that:

(i) The equations of the models describe the mechanical behaviour of the alkali-activated fly ash/slag pastes.

(ii) Of the three factors considered, those always significative are the fly ash/slag ratio and the activator concentration. The influence of curing temperature in the mechanical development of the pastes is lower than that contribution due to the other two factors.

As slag content in the pastes increases, compressive strengths increase. The strength development is directly related to NaOH concentration, and higher strengths are obtained when activator concentration is 10 M. This is associated with the different nature of the reaction products formed. Curing temperature has a positive effect in the strength increase at the first days of reaction. At longer ages, the effect is inverse and strengths are higher when curing temperature is 25°C.

(2) 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 of 50 MPa. These values are 95% of those obtained with only slag presence in the pastes. In these samples, the slag is practically dissolved. It has been verified that, in spite of the ambient temperature at which activation is produced, fly ash is partially dissolved and is involved in the reactive process.

(3) The main reaction product in the pastes 50% fly ash/50% slag activated with 10 M NaOH solution is a hydrated calcium silicate of the CSH gel type with high tetrahedrically coordinated Al amounts and interlayer Na ions in its structure.

(4) No hydrated alkaline aluminosilicate polymer characteristic of alkaline activation of fly ash cements is formed in these pastes.

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