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Alkali-activated fly ashes
A cement for the future

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Abstract

The alkali activation of waste materials (especially those coming from industrial and mining activities) has become an important area of research in many laboratories because it is possible to use these materials to synthesize inexpensive and ecologically sound cementlike construction materials. In the present paper, the mechanism of activation of a fly ash (no other solid material was used) with highly alkaline solutions is described. These solutions, made with NaOH, KOH, water glass, etc., have the common characteristic of having a very high OH^- concentration. The product of the reaction is an amorphous aluminosilicate gel having a structure similar to that of zeolitic precursors. Temperature and time of curing of specimens together with the solution/fly ash ratio are some of the variables that were studied. These variables have been shown to notably influence the development of the mechanical strength of the final product. Mechanical strengths with values in the 60 MPa range were obtained after curing the fly ash at 85°C for only 5 h.

Keywords: Alkali-activated cement; Fly ash; Composite; Fiber reinforcement; Waste management

1. Introduction

The alkali activation of waste materials is a chemical process that allows the user to transform glassy structures (partially or totally amorphous and/or metastable) into very compact well-cemented composites. Nowadays, the knowledge concerning the mechanisms controlling the alkali activation process is considerably advanced; however, there are still many things to investigate.

The first aspect to be emphasized in the general process of alkali activation is related to the variability of the kinetics and the governing mechanisms used to describe the mentioned process. Actually, two different models of alkali activation could be established, both corresponding to two very different conditions of the starting situation. A very well-known example of the first model is represented by the activation of blast furnace slags with a mild alkaline solution. With respect to this case, the reader is reminded that the mechanisms controlling the alkali hydration of a slag correspond to a complex process that is composed of several steps (including the initial destruction of the slag and a later polycondensation of the reaction products) and that the knowledge of the nature of these products has been the objective of many investigations, although some controversy still persists. In any case, most of authors agree in considering C-S-H gel the main reaction product [1–7].

The second model of alkali activation has been studied much less than the first, in spite of the fact that some investigations concerning this subject were already published during the 1960s [8]. Alkaline activation of metakaolin can be taken as an example.

Davidovits [9,10] described the alkali activation process of metakaolin in terms of a polymerical model. The products formed are characterized by elevated mechanical strengths. They have the following general formula [Eq. (1)]:

$$M_n[\text{-}(Si\text{-}O_2)_z\text{-}Al\text{-}O]_n \cdot wH_2O \qquad (1)$$

Where M is the alkaline element, - indicates the presence of a bond, z is 1, 2, or 3, and n is the degree of polymerization.

Similar schemes have been proposed for modelling the formation processes of zeolites and zeolite precursors. Among the elements establishing the similarities between the zeolite formation process and the alkali activation of metakaolin, the following can be mentioned: Concentration of chemical species, specifically $[OH]^-$ (critical factor in the synthesis of both types of material); temperature and time of curing; type of alkaline element; chemical composition of the reactant bulk; etc.

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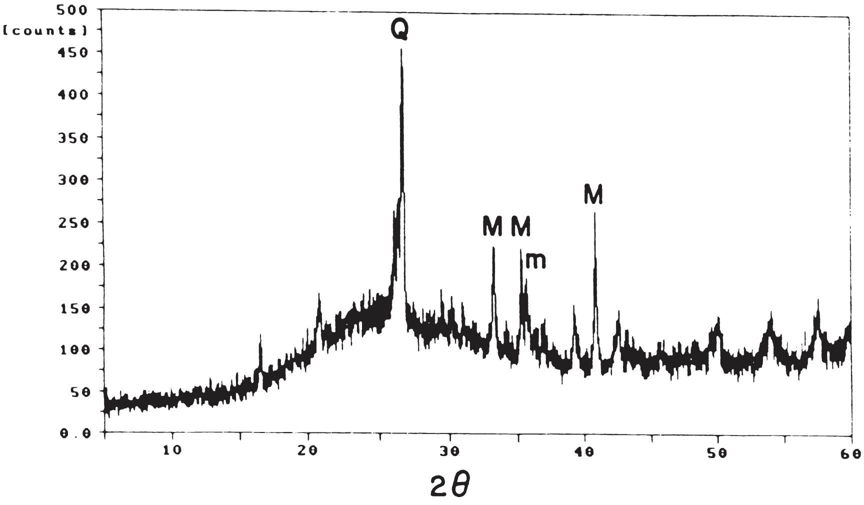

Fig. 1. X-ray diffraction pattern of the fly ash. Q = quartz; M = mullite; m = maghemite.

From all these parallelisms, from the data collected from the literature and from our own experience [11–15], we have concluded that the amorphous polymer produced in the alkaline activation of metakaolin is a zeolitic precursor.

Summarizing, the two main differences characterizing both models of alkali activation are:

- Composition of the material to be activated. Essentially, Si and Ca in the first case, while Si and Al dominate the second one.
- Concentration of the activator: low to mild for the first model and high for the second.

In the present paper, the alkali activation of a fly ash (with high concentration of activator) has been studied and the similarity of the process compared with the alkaline activation of metakaolin has been established.

2. Methods

2.1. Materials

A Class F fly ash from Pennsylvania Power and Light Co.'s Montour County power plant was tested. The chemical and mineral composition of the fly ash are presented in Fig. 1 and in Table 1, respectively.

Four activator solutions were prepared immediately before the mixing with the fly ash. The composition of the solutions and the composition of the starting chemicals are given in Table 2.

Table 1
Chemical composition of the fly ash (% wt)

SiO_2	Al_2O_3	Fe_2O_3	Na_2O	K_2O	TiO_2	MgO	CaO	MnO	L.O.I.*
53.2	26.0	7.95	0.29	2.59	1.38	0.97	3.57	0.04	2.22

*Loss on ignition.

2.2. Method

The evolution of the reaction between the fly ash and the activator solution was followed by means of some calorimetry tests (the fly ash was placed into the sample holder and the activator solution injected when the sample had reached thermal equilibrium).

The products of the activation reaction were mechanically and mineralogically characterized (mechanical strengths were statistically analyzed). The starting mixtures were prepared by mixing the fly ash with the activators for 2 min in a small IPENSA mixer (Spain). The mixes were cast into 1 × 1 × 6 cm molds, which were placed into a sealed container (keeping the relative humidity at ~100%) and then cured in an oven at the testing temperature. Two temperatures (65 and 85°C) and two liquid/solid ratios (0.25 and 0.3) were tested. At the ages of 2, 5, and 24 h, the prisms were taken out of the oven, demolded, mechanically tested, and mineralogically and microstructurally studied by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope/energy dispersive X-ray spectroscopy (SEM/EDS).

3. Results

Calorimetry data are reported in Figs. 2, 3, and 4. The figures show the evolution of the heat dissipated during the

Table 2
Activators used

	Na_2O (%)	K_2O (%)	SiO_2 (%)	H_2O (%)
Sodium silicate	8.9	–	28.7	62.4
Potassium silicate	–	12.65	26.5	60.85

Solution 1, NaOH 12 M; solution 2, KOH 18 M; solution 3, [NaOH (pellets) + sodium silicate]; solution 4, [KOH (pellets) + potassium silicate]. The SiO_2/Na_2O total ratio in solution 3 was 1.23. The SiO_2/K_2O total ratio in solution 4 was 0.63.

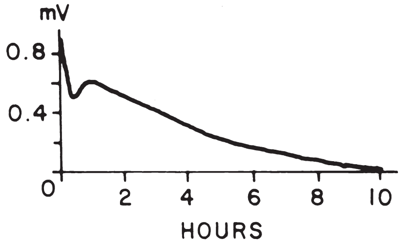

Fig. 2. Solution 1. Test duration: 10 h.

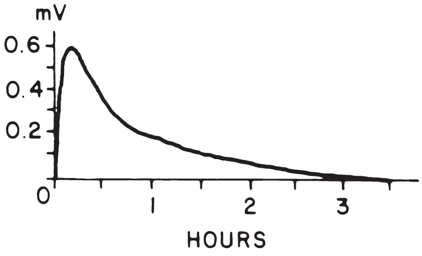

Fig. 4. Solution 3. Test duration: 4 h.

reaction (at 65°C) between the fly ash and the activator solution (liquid/solid = 0.25).

From the calorimetrical point of view, the effects of solution 4 on the fly ash are almost identical to the effects produced by solution 3. The effect of the activator-fly ash ratio is not significant (the differences in the calorimetry curves are hardly perceptible when that ratio is 0.25 or 0.3); however, calorimetry is very sensitive to the effect of temperature. Due to the increase of temperature, the fly ash activation is accelerated; then the calorimetry curves appear to have only one sharp peak (the maximum corresponding to 8–10 min of reaction), which ends after 1 to 2 h of reaction.

The compressive strength of the samples can be seen in Table 3. These mechanical strengths have been evaluated through a multifactorial analysis of the variance. In Table 4, variables (factors) considered for carrying out the mentioned analysis as well as their level of variation are shown.

The mathematical models describing the mechanical behaviour of the material for each of the testing ages are as follow [Eq. (2), (3), and (4)]:

$$\text{Compressive strength}_{(2\text{ h})} = 7.618 + 7.081\ X_A + \delta_{D2h} + \delta_{AD} + \varepsilon \qquad \varepsilon = (0\text{–}2.54) \quad (2)$$

$$\text{Compressive strength}_{(5\text{ h})} = 19.506 + 9.106\ X_A + \delta_{D5h} + \varepsilon \qquad \varepsilon = (0\text{–}5.63) \quad (3)$$

$$\text{Compressive strength}_{(24\text{ h})} = 35.925 + 5.412\ X_A + \delta_{D24h} + \varepsilon \qquad \varepsilon = (0\text{–}8.079) \quad (4)$$

Combining these data with the results obtained through the characterization of the reaction products by XRD, FTIR, and SEM/EDX, we can extract the following information.

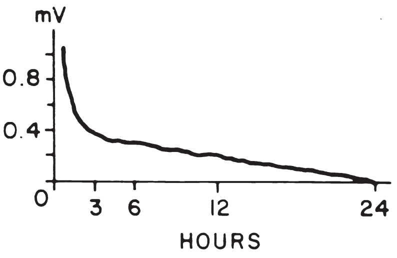

Fig. 3. Solution 2. Test duration: 24 h.

According to the X-ray data, the material obtained when the fly ash is activated with solutions of alkali hydroxide mixed with sodium silicate or potassium silicate (solutions 3 and 4) does not contain any crystalline phase except the ones existing in the fly ash (quartz, mullite, and maghemite). This fact is independent of the temperature and time of curing and of the solution/fly ash ratio. Those samples proceeding from the activation of the fly ash with solution 1 (NaOH solution) have some hydroxysodalite together with the minerals of the fly ash; meanwhile, the reaction between the fly ash and solution 2 generates a product containing potassium carbonate and potassium bicarbonate. The whole samples studied by means of XRD contained (besides the already mentioned phases) an amorphous component. The typical halo appearing in the diffractograms provide evidence of this.

The FTIR spectra of samples activated for 24 h at 65 and 85°C show interesting differences when compared with the spectrum of the starting fly ash (see Fig. 5). During the reaction the band at 800 cm^{-1}, due to AlO_4 vibrations, disappears and a new band at around 700 cm^{-1} appears, as well as the bending vibration bands due to H_2O in the regions of 1600 and 3400 cm^{-1}. The main band due to Si-O and Al-O vibrations, which is at 1060 cm^{-1} in the fly ash, moves towards lower frequencies ($\approx$1000 cm^{-1}). This movement of the band is higher when solutions 1 and 2 are used as activators than when activators consist of solutions 3 and 4.

The joint effect of the curing temperature and the activator/fly ash ratio can be observed in Fig. 5. At the maximum

Table 3
Compressive strength (MPa) of prisms made with a activator/fly ash ratio of 0.25

Activator	Curing temperature (°C)	Activator/fly ash ratio 0.25 (time of curing)			Activator/fly ash ratio of 0.30 (time of curing)		
		2 h	5 h	24 h	2 h	5 h	24 h
Solution 1	65	0.0	0.0	21.2	0.0	1.8	17.3
	85	9.3	22.0	34.6	9.2	9.6	23.4
Solution 2	65	0.0	0.0	8.7	0.0	0.0	3.9
	85	1.4	9.4	23.3	2.6	16.4	27.3
Solution 3	65	4.3	31.7	52.7	0.0	30.0	62.6
	85	39.8	48.2	54.5	31.6	57.4	68.7
Solution 4	65	0.0	9.5	38.7	0.0	10.2	39.0
	85	7.7	34.3	63.0	16.0	31.6	35.9

Table 4
Factorial design: variables of work and levels of variation

Factor definition	Level values			
Temperature (°C)	65 $X_A = (-1)$			85 $X_A = (+1)$
Time (hours)	2 $t_B = (-1)$		5 $t_B = (0)$	24 $t_B = (+1)$
Activator/fly ash (% wt)	0.25 $X_C = (-1)$			0.3 $X_C = (-1)$
Type activator	Na(OH) $Ac_D = (1)$	K(OH) $Ac_D = (2)$	SS + Na(OH) $Ac_D = (3)$	KS + K(OH) $Ac_D = (4)$

reaction temperature (85°C) and the maximum amount of solution (liquid/solid = 0.3) the bands in the region of O-H vibration (≈3800–3450 cm^{-1}) and water molecules H-O-H (1650–1600 cm^{-1}) are drastically modified.

Figs. 6, 7, 8, and 9 show some microstructural characteristics of the alkaline cements obtained by mean of the activation of the fly ash.

As can be observed in these figures, the samples studied through SEM/EDX have quite different microstrutures. When the fly ash is activated with solution 1, the resulting material is a very porous one and the microspheres appear to be surrounded by a crust of reaction products. The adherence of the crust to the spheres does not seem to be very good and the bonding among grains is produced through necks of reaction products (see Fig. 6). In the bulk material, partially dissolved spheres with some mullite crystals on the surface can be found (see Fig. 7). The average molar ratios for the product of reaction is Si/Al = 1.5 and Na/Al = 0.48.

Materials obtained from the activation with solution 2 contain an excess of potassium that has not reacted with the

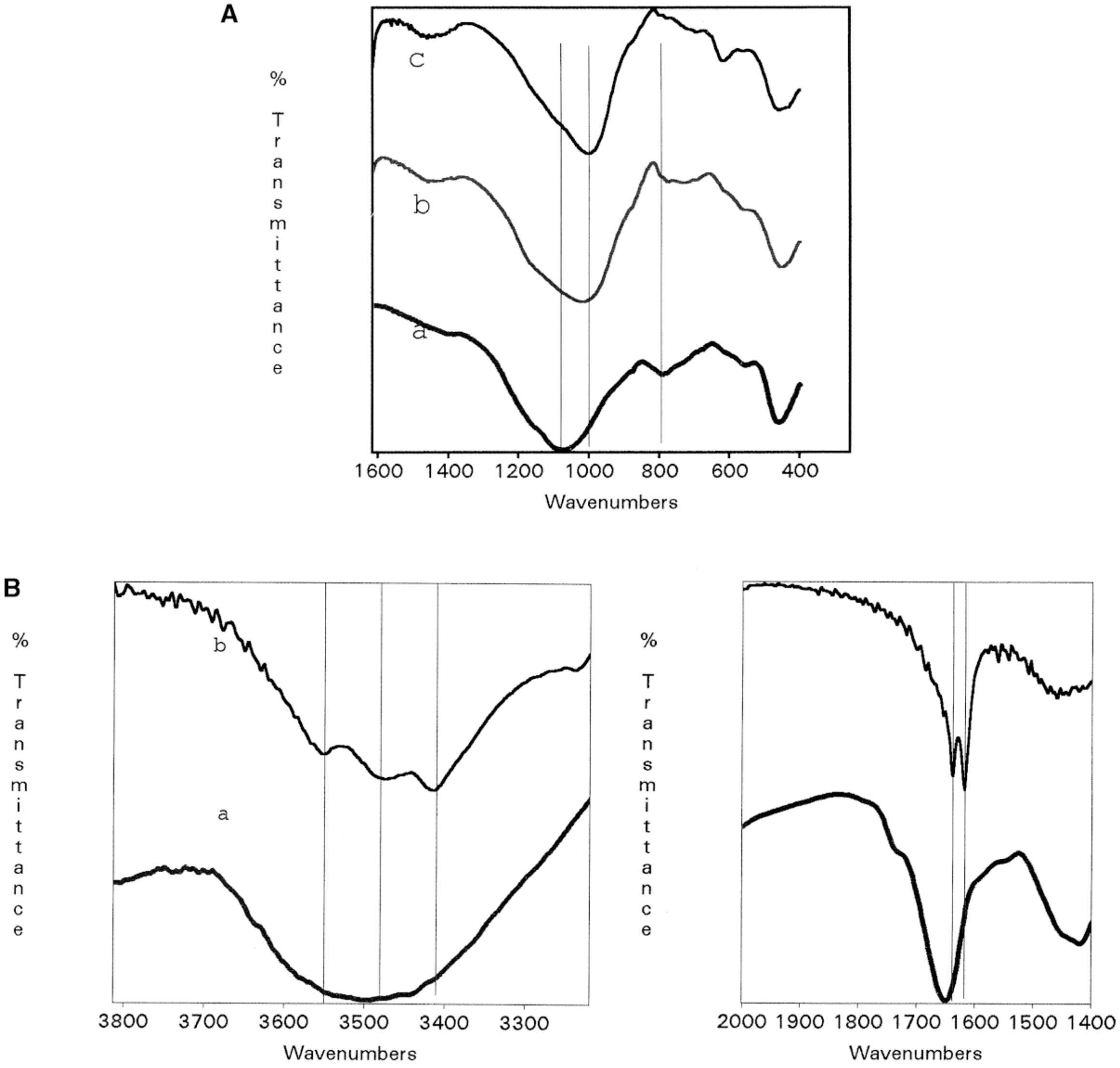

Fig. 5. (A) IR spectra of: (a) original fly ash, (b) fly ash activated with solution 3 for 24 h at 85°C (solution/fly ash = 0.3), and (c) fly ash activated with solution 1 at 85°C for 24 h (solution/fly ash = 0.3). (B) IR spectra of the fly ash activated with solution 3 for 24 h (solution/ash = 0.3): (a) curing at 65°C and (b) curing at 85°C.

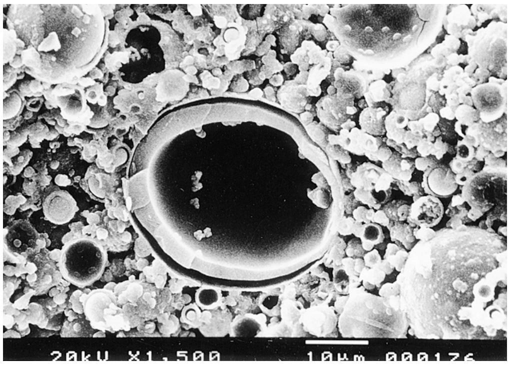

Fig. 6. Activation with solution 1 for 24 h at 85°C. General morphology: reaction products layer around the sphere. The composition of the layer is (molar ratio): Si/Al = 1.5 and Na/Al = 0.48.

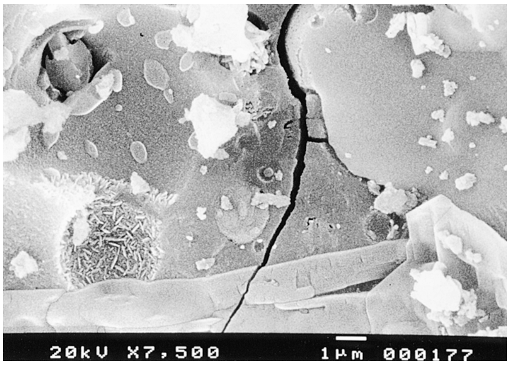

Fig. 8. Activation with solution 3 for 24 h at 85°C. The reaction product, with mullite crystals from a sphere, have the molar ratios: Si/Al = 2.8 and Na/Al = 0.46.

fly ash. Carbonates and bicarbonates are the main constituents of the sample. At this time it has not been possible to get reliable data on the chemical composition of the reaction products.

Activating with solution 3 involves the generation of a microporous material (see Fig. 8). In this case, the studied samples contain spheres (from the fly ash) joined to each other with a continuous mass of reaction product acting like a cement. Also, some crystals of mullite and unreacted spheres (having high proportions of Al and/or Fe) have been detected. The average molar ratios found in this product of reaction was: Si/Al = 2.8 and Na/Al = 0.46.

When the activator is a solution of potassium, the K/Al molar ratio is 1.55 and the Si/Al ratio 2.6 (see Fig. 9). This different Me/Al ratio, depending on the alkali cation, means that some OH^- or Al^{3+} ions should compensate for the charges.

It is interesting to remark that independent of the activator used (NaOH or NaOH + sodium silicate), the Na/Al ratio of the alkaline cement is constant. However, the Si/Al ratio of the material increases (almost doubles) when the activator is NaOH + sodium silicate.

4. Discussion and conclusions

The alkali activation reaction of fly ashes takes place through an exothermic process of dissolution during which the breakdown of the covalent bonds Si-O-Si and Al-O-Al in the glass occurs and ions (silicon and aluminium) pass into the solution. The products generated due to the destruction of the fly ash structure start to accumulate for a period of time (induction period), during which heat release hardly exists. Finally, a condensation of the structure is produced (strongly exothermal step), which involves the appearance of a cementitious material with a poorly ordered structure but having a high mechanical strength.

The activation reaction is notably influenced by the parameters studied in the present investigation. For example, temperature for example is a reaction accelerator. Its effect is so intense that the reaction steps overlap each other and calorimetry cannot detect these steps separately. In general terms, if all the factors remain constant, the temperature increase tends to result in a gain of mechanical strength.

The type of solution used for the activation of the fly ash is essential in the development of reactions. When the alkali

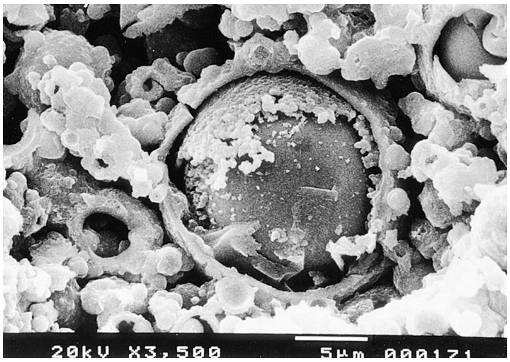

Fig. 7. Activation with solution 1 for 24 h at 85°C. The sphere in the middle of the picture is being attacked. It is surrounded by the products of reaction. On the upper part of the sphere some deposits can be seen.

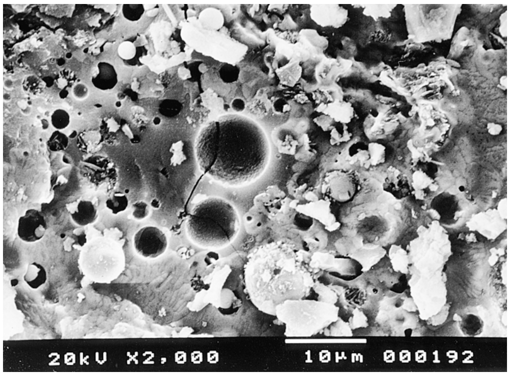

Fig. 9. Activation with solution 4 for 2 h at 85°C. The product of reaction is a microporous material with molar ratios 0.46 Si/Al = 2.6 and K/Al = 1.55.

solution contains soluble silicates (sodium or potassium silicate), the reactions occur at a higher rates than when hydroxides are used as the activators. Again, the reaction steps overlap each other and the solid evolves in such a way that the dissolution of chemical species, accumulation of reaction products, and polycondensation of the structures occur almost simultaneously. The immediate consequence is that mechanical strength development is quicker in the first case (samples activated with soluble silicates) than in the second case (samples activated with hydroxides).

The last aspect to be emphasized concerning the alkali activation process is due to the alkaline element and its concentration in the solution. Solution 1 gives better results (faster activation and higher strength) than solution 2. The explanation for this observation is not still clear. Some additional experiments showed than an excess of OH^- concentration in the system involved a strength decrease of the alkali cement (remember that solution 1 is 12 M and solution 2 is 18 M), but further investigations on this topic are needed.

If now we focus the discussion on the product or products obtained through the activation of the fly ash, we can deduce the following interesting conclusions.

The first point to be emphasized is that the new cementitious material is an amorphous alkali silicoaluminate (containing small proportions of quartz, mullite, and maghemite from the original fly ash), similar to that obtained in the alkali activation of metakaolin. The authors [15] have considered that these products are a zeolite precursor of some sort.

During the first step of the reaction the amorphous portion of the fly ash begins to dissolve; in accordance with the FTIR results, the Al in tetrahedral coordination reacts (the band in 800 cm^{-1} disappears) but the Al in octahedral coordination does not (the band in 560 cm^{-1} due to mullite persists).

The FTIR spectra indicate that after the third step of the general process of activation (condensation-crystallization), a reorganization of the structure is produced: the stretching band Si-O, Al-O in 1060 cm^{-1}, moves towards lower frequencies ($\approx$1000 cm^{-1}), and a new band in 700 cm^{-1} appears. This is due to the formation of a structure at which the SiO_4^{4-} groups are replaced by AlO_4^{3-} groups as network formers. The charge difference is compensated with an alkaline ion.

The movement of the mentioned stretching band is not the same for all the samples; in fact, the lower the Al/Si ratio is, the wider the movement is. Simultaneously, the microanalysis of the reaction products indicate that the activation of the fly ash with solutions 3 and 4 produces a material with high Si/Al ratio (higher than those products generated in the activation with solutions 1 and 2). In other words, the higher the portion of Si replaced by Al in the structure, the lower the frequency is at which appears the stretching band of bonds Si-O and Al-O appears.

The last remarkable observation concerning the IR data is that the spectra of the samples obtained at 85°C and with a liquid/solid ratio of 0.3 (only these samples) show some intense and sharp bands in the 3000–4000 and 1600 cm^{-1} range (Fig. 5). The rest of the bands of these spectra remain the same, as was explained before for the whole samples. These new bands are interpreted as belonging to a crystalline phase that has not yet been identified. Identical samples activated at lower temperatures (65°C) and/or lower liquid/solid ratio (0.25) do not generate such crystals. By mean of XRD no additional crystalline phase is detected. We deduce that the crystal size is too small. Some investigations are being carried out in order to clarify this topic.

Finally, some conclusions directly related to the mechanical strength can be deduced from the interpretation of the statistical analysis. Eqs. (2), (3), and (4) indicate that:

- The significant factors affecting the mechanical strengths are always the temperature and the type of activator. The binary interaction “temperature-type of activator” is also significant when the time of curing is 2 h.
- The activator/fly ash ratio factor is never a relevant one.
- Temperature is especially important for 2 and 5 h of curing. Mechanical strengths of prisms cured at 85°C are much higher than those cured at 65°C. This rise of strength is much smaller when curing time is 24 h.
- The longer the time of curing, the higher the average strength is.
- From δ_D values (see Table 5) it is easily deduced that activator 3 is the one generating the highest compressive strengths (more than 35 MPa at 85°C of curing temperature and 2 h of curing time).

As a final summary it is considered important to emphasize the technological properties of the activated fly ashes through a strong alkaline process:

- A strong material with a network structure is obtained.

Table 5
V. δ_D and δ_{AD} values

δ_D	NaOH (sol. 1)		KOH (sol. 2)		SS + NaOH (sol. 3)		KS + KOH (sol. 4)	
δ_{D2h}	−2.993		−7.518		+11.30		+1.69	
δ_{D5h}	−11.15		−13.05		+22.318		+1.89	
δ_{D24h}	−11.80		−20.12		+23.7		+8.22	
	2h							
AD	(−1,1) 2.456	(+1,1) −2.456	(−1,2) 6.081	(+1,2) −6.081	(−1,3) −9.693	(+1,3) +9.693	(−1,4) +1.156	(+1,4) −1.156

- It looks like a ceramic: smooth, glassy, and shiny.
- Waste materials are used for its fabrication.
- The workability of the fresh mixture is very good at very low liquid/solid ratios.
- 2 to 5 h curing time is needed.

Acknowledgments

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