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Effect of sodium sulfate on the alkali activation of fly ash

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ABSTRACT

This paper discusses the effect of the presence of a small amount of SO_4^{2-} (a 16 group oxyanion) on the nature and chemical composition of the resulting N–A–S–H gel and zeolites (main reaction products from the alkaline activation of fly ashes). To this end, fly ash was activated with different alkaline solutions containing 2.5% by weight of sodium sulfate. The paste was cured in an oven at 85 °C for different periods of time. The presence of sulfate was observed to lengthen the time needed for certain percentages of N–A–S–H gel to precipitate, while shortening the time needed for a given percentage of zeolites to precipitate. This, in turn, had an adverse effect on the mechanical strength of the material.

1. Introduction

The reaction products obtained in the alkali activation of fly ash have been studied in depth by the authors of the present paper [1–5]. The research discussed here posed the possibility of including a series of products, considered *a priori* to be possible activation catalysts, in this system. The idea was based on the existing knowledge of the effect of the presence of small amounts of certain oxyanions belonging to periodic groups 15, 16 and 17 (such as nitrates, phosphates, arsenates, sulfates, bromates and iodates) on the nucleation and crystallization of certain zeolites [6–9].

Among the most prominent of the criteria that served as grounds for selecting the type of product to be added was the consolidation of an important line of international research: namely on the hydration, mechanical strength development and durability of Portland-fly ash blended cements with ash contents much higher than presently allowed in the standards, under highly alkaline conditions. The essential aim of the scientists pursuing this line of research is to contribute to energy savings and reduce CO_2 emissions. But of similar interest is the possible development of cements whose setting and hardening generate a new blend of cementitious gels for practical use: C–S–H + N–A–S–H [10–14]. The former, well known, is characteristic of Portland cement hydration, while the second is less well known and characteristic of the alkali activation of aluminosilicates such as fly ash.

In Portland cement manufacture, after leaving the kiln clinker is ground with a small amount of gypsum $CaSO_4 \cdot 2H_2O$ to control the initial hydration reactions and prevent flash setting. The amount of SO_3 added in this manner comes to around 2–3.5%.

The above precedents justify the choice of sulfate as the oxyanion to be studied as a possible alkali activation catalyst, for its presence may lead to conditions similar to those prevailing in these new binders with low Portland cement and high fly ash contents [14,15].

In another vein, Laha and Kumar [16] studied the effect of these promoters on the synthesis of mesoporous materials. These authors observed that nitrates, sulfates and phosphates were the compounds that shortened crystallization time most effectively. Using ^{29}Si NMR data for liquid samples, they were able to closely monitor the soluble Q^0–Q^4 units (mono-, di-, tri- or tetrasilicate species) in terms of crystallization time during the synthesis of certain zeolites. They concluded that the ratio between the Q^4 and the total silicate species (Q^0–Q^4) grew slightly at the beginning of the process and then declined at longer reaction times. The clear inference is that the Q^4 species are primarily responsible for the condensation involved in the formation of crystalline solids.

Therefore, bearing in mind that the systems studied here comprised Q^4 units [3], the hypothesis tested was that the addition of a small amount of sulfates might favour the condensation of these species and consequently accelerate the activation reactions.

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2. Experimental methods

2.1. Characterization of raw materials

Class F (ASTM C 618-03) fly ash from the Compostilla steam power plant in Spain was used in the present study. The chemical composition of the ash is given in Table 1, although a much more exhaustive characterization can be found in [17].

The ash was activated with three different alkaline solutions having practically the same sodium oxide content (~20%) but varying proportions of soluble silica. Solution N = NaOH 8 M; W15 = 85% NaOH 10 M + 15% sodium silicate solution (Waterglass); W84 = sodium silicate solution + NaOH pellets. The total silica content in the solutions was varied by adding different amounts of sodium silicate to the reaction media (in N $SiO_2/Na_2O = 0.00$, in W15 $SiO_2/Na_2O = 0.19$ and in W84 $SiO_2/Na_2O = 1.17$). The products used to prepare the solutions were laboratory grade reagents: ACS-ISO 98% NaOH pellets supplied by Panreac S.A. and sodium silicate (density = 1.38 g cm^{-3}) with the following composition: 8.2% Na_2O, 27% SiO_2 and 64.8% H_2O.

2.2. Alkali activation of fly ash

The pastes were made by mixing the fly ash with the activating solutions (with a "liquid/solid" ratio of 0.4). The pastes were subsequently cured in an oven at 85 °C for different reaction times (8 h, and 7, 28 and 180 days). The blend included a small amount (2.5% by weight) of sodium sulfate (99% pure Panreac S.A. PA-ACS-ISO). Sodium sulfate (S) was added to the different alkaline solutions that were subsequently mixed with the fly ash. The activated ash specimens (one mould of six prisms of $1 \times 1 \times 6$ cm/per paste) were subjected to standard cement strength tests (as per European code EN 196-1) at the various ages studied.

2.3. Determination of the percentage of reaction products

The hardened pastes were attacked with 1:20 HCl (by volume) in order to determine the percentage of reaction products generated at the respective reaction times. This procedure separates the reaction products (hydrate sodium aluminosilicate gel and zeolites) which are dissolved in the acid, from the unreacted ash, which remains in the insoluble residue [5,18,19].

2.4. Techniques

The crystalline phases present in the solids studied were quantified with Rietveld analysis.

2.4.1. X-ray powder diffraction data collection and sample preparation for quantitative phase analysis

Laboratory XRPD patterns were recorded in a Bragg–Brentano (reflection) X'Pert MPD PRO (PANalytical) diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 1.54059$ Å), [Ge(1 1 1) primary monochromator]. The optics used were a fixed divergence slit (1/2°), a fixed incident anti-scatter slit (1°), a fixed diffracted anti-scatter slit (1/2°) and an X́Celerator Real Time Multiple Strip (RTMS) detector, working in scanning mode with maximum active length. The samples were rotated during data collection at 16 rpm to enhance particle statistics. The X-ray tube operated at 45 kV and 35 mA. The data were collected from 10° to 70° (2θ) during ~15 min for the original and activated ashes to monitor the activation process.

In addition, all the patterns for artificial blends, i.e., ash with α-Al_2O_3, were recorded in the same angular range but for ~2 h to conduct Rietveld QPA, including the determination of the amorphous content [18].

3. Results and discussion

Table 2 shows the variation in compressive strength of alkali-activated fly ash with curing time for the three systems studied.

The findings show that mechanical strength rose in all the systems with curing time both in the presence and in the absence of sodium sulfate. The inclusion of sodium sulfate induced a decline in strength in all the systems with respect to their analogous sulfate-free systems, which was less intense at higher soluble silica contents. The W84 system (with a higher percentage of soluble silica) followed a similar pattern regardless of the presence or otherwise of sulfate, whose inclusion may have had a beneficial effect on the early age development of mechanical strength.

Table 2 shows the variation in degree of reaction with curing time for the three working systems. The degree of reaction rose with time in all the sulfate-free systems. This rise was less pronounced and the absolute values were lower in the systems containing the sulfate, some of which exhibited practically constant strength, an indication that the reaction failed to progress.

Table 1
Chemical analysis of the initial fly ash (%).

LI (%)	IR	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	Total
3.59	0.32	53.09	24.80	8.01	2.44	1.94	0.23	3.78	0.73	1.07	100

LI = loss on ignition; IR = insoluble residue.

Table 2
Evolution of mechanical strength and the degree of reaction of alkali-activated fly ashes in the presence and absence of sodium sulfate.

	Compressive strength (MPa)					Reaction degree (%)				
	8 h	20 h	7 days	28 days	180 days	8 h	20 h	7 days	28 days	180 days
NS	10.53	13.76	35.46	37.16	40.51	44.12	47.77	46.04	46.36	46.8
N	19.38	54.45	55.53	68.59	77.98	47.18	49.83	51.3	61.22	73.72
W15S	12.19	14.31	42.47	47.33	63.26	45.44	46.29	46.53	48.25	51.88
W15	16.43	48.15	56.11	65.3	73.72	47.82	51.62	54.44	58.58	71.04
W84S	45.38	54.96	57.66	67.57	69.27	32.27	38.57	38.46	38.75	41.13
W84	43.12	46.92	52.92	55.87	79.27	35.47	36.18	39.18	42.54	50.75

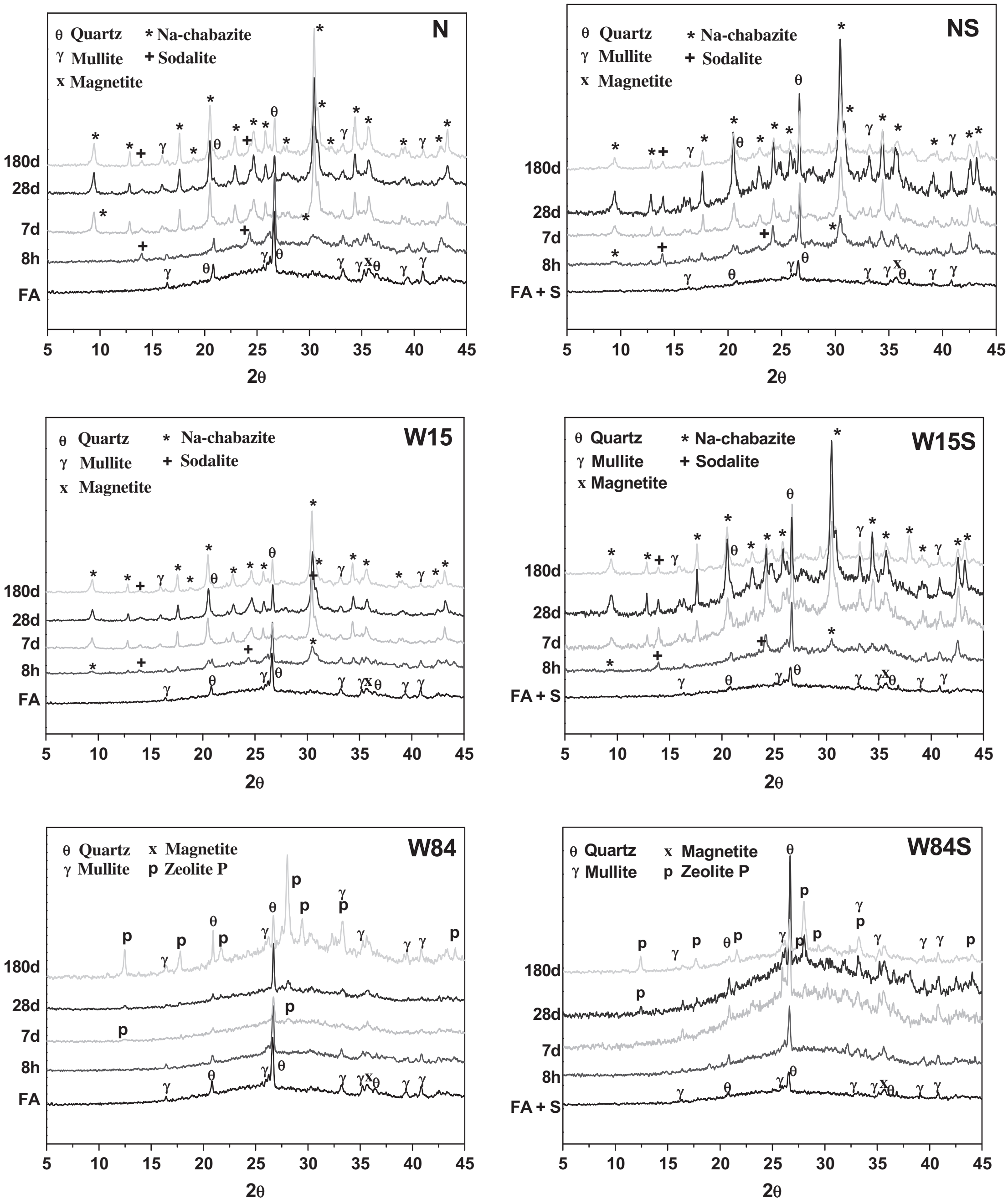

Fig. 1. Diffractograms of the three systems in the presence and absence of 2.5% sodium sulfate.

Fig. 1 contains the 8-h and 7-, 28- and 180-days X-ray diffractograms for fly ash activated with alkaline solutions in the presence and absence of sodium sulfate. The main reaction product in both systems was hydrated sodium aluminosilicate gel (N–A–S–H gel) (see halo at 25–40°). The minority crystalline phases existing in the initial material (quartz, mullite, magnetite) were also detected in these systems, along with a series of zeolite species: hydroxysodalite, chabazite–Na, zeolite P and phillipsite. Another relevant finding was that neither sodium sulfate nor any other crystalline sulfate compound was detected on the XRD traces in Fig. 1. A possible explanation may be that the solution was highly diluted, for as the figure shows, sulfates were not found even on the diffractogram for the sulfate-containing non-activated ash.

Rietveld QPA was used for the quantitative analysis of the cement paste phases at different ages, with and without sodium sulfate. The findings are given in Table 3. The non-crystalline fraction of the material consisted in the vitreous component of the unreacted ash plus the amorphous hydrated sodium aluminosilicate gel (N–A–S–H gel), the main product formed during alkali activation of the ash. The crystalline structures used for the Rietveld refinement are given in Refs. [18,19].

The materials were attacked with 1:20 HCl (by volume) to determine the percentage of reaction products (N–A–S–H gel and zeolites) generated at the different thermal curing times, for these reaction products dissolve in the acid solution [18,19]. Consequently, the data obtained from the acid attack (see Table 2), together with the X-ray diffraction findings (see Table 3), can be correlated as per Eqs. (1)–(3) to determine the percentage of vitreous phase in each sample, as well as the amount of hydrated sodium aluminosilicate gel present in the working materials (see Table 4).

Table 3
Application of the Rietveld method to phase quantification in alkali-activated ash in the presence and absence of sulfates.

	N				NS			
	8 h	7 days	28 days	180 days	8 h	7 days	28 days	180 days
Non-crystalline phases[a]	86.8	71.4	68.5	57.1	87.0	69.4	70.4	70.5
Zeolites (Z)	4.9	24.8	28.1	36.5	6.0	21.4	22.8	22.2
Other (Mu + Q + Fe)	8.3	3.8	3.4	6.4	7.0	9.2	6.7	7.4
	W15				W15S			
Non-crystalline phases[a]	78.1	66.0	63.0	55.4	80.0	76.7	70.2	58.9
Zeolites (Z)	11	30.0	33.0	38.5	12.8	16.5	22.4	35.2
Other (Mu + Q + Fe)	10.9	4.0	4.0	6.1	7.1	6.7	7.4	5.9
	W84				W84S			
Non-crystalline phases[a]	91.9	96.5	95.3	83.1	93.1	93.3	91.8	85.3
Zeolites (Z)	–	–	1.8	11.1	–	–	1.9	8.6
Other (Mu + Q + Fe)	8.0	3.6	2.8	5.8	7.0	6.7	6.8	6.0

[a] Non-crystalline phases = vitreous phase in the ash + N–A–S–H gel.

Table 4
Percentages of N–A–S–H gel and the vitreous component of the unreacted fly ash in the working systems.

		N				NS			
		8 h	7 days	28 days	180 days	8 h	7 days	28 days	180d
Non-crystalline phases	N–A–S–H gel[a] (G)	42.48	26.50	33.12	37.22	38.12	24.64	23.56	24.60
	Unreacted vitreous content in the ash	44.32	44.90	35.38	19.88	48.88	44.76	46.84	45.90
		W15				W15S			
Non-crystalline phases	N–A–S–H gel[a] (G)	36.82	24.44	25.58	32.54	32.64	30.03	25.85	16.68
	Unreacted vitreous content in the ash	41.28	41.56	37.42	22.86	47.36	46.67	44.35	42.22
		W84				W84S			
Non-crystalline phases	N–A–S–H gel[a] (G)	35.47	39.18	40.74	39.65	32.27	38.46	36.85	32.53
	Unreacted vitreous content in the ash	56.43	57.32	54.56	43.45	60.83	54.84	54.95	52.77

[a] Percentage of N–A–S–H gel found with Eqs. (1) and (2).

$$\alpha(\%) = G(\%) + Z(\%) \quad (1)$$

where α is the degree of reaction (% phase dissolved in 1:20 HCl, see Table 2); G is the percentage of hydrated sodium aluminosilicate gel formed and Z is the percentage of zeolites (obtained with the Rietveld procedure, see Table 3). Therefore the amount of gel is $\alpha - Z$.

$$\mathrm{IR}(\%) = \mathrm{VP}(\%) + \mathrm{Mu}(\%) + \mathrm{Q}(\%) + \mathrm{Fe}(\%) \quad (2)$$

where IR is the insoluble residue in 1:20 HCl (% insoluble phase, see Table 2); VP is the percentage of unreacted vitreous phase; Mu is the percentage of mullite; Q is the percentage of quartz and Fe is the percentage of magnetite (all found with the Rietveld method, see Table 3).

$$\alpha(\%) + \mathrm{IR}(\%) = 100 \quad (3)$$

Fig. 2 shows the variation in the percentage of N–A–S–H gel formed, the percentage of crystallized zeolites and the mechanical strength developed by the ash activated in the presence and absence of sodium sulfate.

The findings show that while the presence of sulfates was responsible for the overall decline in the amount of product formed, they also raised the percentage of zeolites at early ages (8 h) (see Table 3, Fig. 2). The zeolites synthesized in the three pastes were identical to the ones forming in the absence of Na_2SO_4.

Regardless of the presence of absence or sulfates, in all the systems in general the amount of N–A–S–H gel rose with the degree of reaction. At older ages, however, the percentage of gel forming appeared to decline to the benefit of zeolite formation. This was attributed to the fact that the gel is a zeolite precursor which ultimately evolves in that direction. This effect was more intense in the absence of soluble silica, which retards zeolite formation [4]. Since less N–A–S–H gel, which is primarily responsible for the mechanical properties of the material, formed in the systems containing sulfate, strength was lower in these systems (Fig. 2).

Interpretation of the results in terms of the possible capacity of sulfates to shorten the time needed to synthesize the reaction products (oxyanion as zeolite crystallization promoter [16]) was facilitated by the introduction of the following two concepts: T_g was defined to be the time lapsing from the initiation of dissolution of the chemical species in the reactive medium until gelling begins; and T_z to be the time lapsing from the initiation of the dissolution of the chemical species in the reactive medium until the first zeolites begin to crystallize. In light of the difficulties inherent in accurately identifying the timing of these events, however, in the present paper arbitrary times were defined on the basis of the precipitation of a certain amount of N–A–S–H gel and the crystallization of a certain amount of zeolite. Hence, T_z^n ($n = 1$, 5 or 10) is the amount of time needed for 1%, 5% and 10% of the zeolites to crystallize while T_g^m ($m = 20$, 30 or 40) is the time required for 20%, 30% or 40% of the N–A–S–H gel to form.

These values were obtained by plotting the percentage of zeolites versus time, in specimens with and without sulfates. The same approach was used to graph the percentage of gel. An extrapolation based on these graphs yielded the formation times for certain percentages of zeolites and N–A–S–H gel which are shown in Table 5.

Further to the data in this table, in the early ages the presence of sodium sulfate in the systems significantly shortened the zeolite crystallization time. This effect was limited, however. The 1% threshold for crystallized zeolite $\left(T_z^1\right)$ was reached sooner in all the systems with sulfates (the time was shortened by 24 min, 6 min and 15 h in systems NS, W15S and W84S, respectively). In systems NS and W15S crystallization time T_z^5 also dropped, by

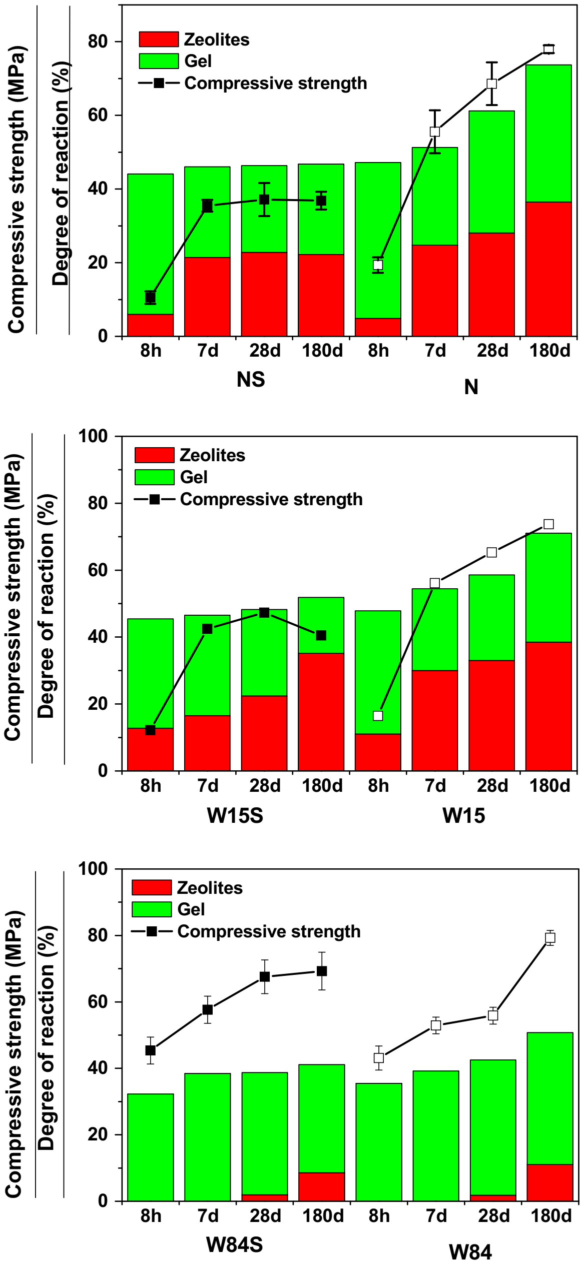

Fig. 2. Variation in the percentage of degree of reaction (percentage of crystallized zeolites and percentage of N–A–S–H gel formed) and mechanical strength in the working pastes in the presence and absence of sodium sulfate.

Table 5
Formation time, in hours, of certain percentages of zeolites and N–A–S–H gel, in the presence and absence of sodium sulfate.

	Zeolite (%)			N–A–S–H gel (%)		
	T_z^1 (h)	T_z^5 (h)	T_z^{10} (h)	T_g^{20} (h)	T_g^{30} (h)	T_g^{40} (h)
NS	1.1	6.7	50.0	4.1	6.3	–
N	1.5	8.8	49.3	3.7	5.7	7.6
W15S	0.5	3.1	6.2	4.9	7.4	–
W15	0.6	3.6	7.3	4.3	6.5	–
W84S	418.6	2332.6	–	4.9	7.4	–
W84	433.7	1924.8	3912.2	4.5	6.7	443.7

2 h and 30 min, respectively. Finally, in system W84S it took longer to reach 5% zeolite crystallization and 10% was not reached at any time during the trial.

The presence of Na_2SO_4 also appeared to have an adverse effect on fly ash activation, for after a certain point N–A–S–H gel appeared to precipitate much more slowly or not at all. In fact, the amount of time, T_g^m, it took to form 20%, 30% or 40% N–A–S–H gel was consistently longer than in the reference systems (see Table 5). In the sulfate-containing systems, the N–A–S–H gel failed to reach the 40% level in the experimental period, which would explain the lesser strength development in this material compared to the material prepared without Na_2SO_4 [4].

This decline in zeolitization time was probably due to the presence of oxyanions such as SO_4^{2-}, which prompts the dehydration of the silicate anions and the sodium cation [20] (because as a strong electrolyte with high hydration energy (−258.1 kcal/mol) [21], this oxyanion tends to self-hydrate, drawing water from the silicate anion coordination spheres and alkaline cations). Water uptake by the sulfates provides for greater proximity and hence interaction between the silicate and alkali anions, which in turn favours zeolite precipitation during the early hours of the reaction [20]. In other words, while sodium sulfate promotes crystallization, these effects are only perceived at very early reaction times.

Provis et al. conducted studies on the kinetics of geopolymer formation in the alkali activation of metakaolin and the changes in its structure when inorganic salts were added [22]. According to alternating current impedance spectroscopy (ACIS) readings, the presence of Cs_2SO_4 raised material conductivity substantially, which translated into a slight retardation of gelling followed by major destruction of the gel structure. The authors of the present paper believe that this retardation in gel formation in all the systems might have been due to the negative charge on the sulfate ions present in the solution pores (which are repelled by the negative charge on the aluminosilicate structure), which would have obstructed the condensation reactions.

The foregoing results therefore confirmed the role of sodium sulfate in promoting crystallization, supporting the findings reported by Kumar and Ocanto [6–9]. Sodium sulfate catalyzes the crystallization stage (changing reaction kinetics, accelerating zeolite formation in the early ages and retarding or interrupting gel formation, with the concomitant lesser development of mechanical strength) but does not intervene in the reaction, for no new products are formed nor is the compound taken up in the structure of the end products, as the XRD findings show.

4. Conclusions

The chief conclusions to be drawn from this study are:

- The findings indicate that the presence of sulfate (in the form of Na_2SO_4) in the alkaline activation of fly ash accelerates the conversion of N–A–S–H gel into zeolites: in other words, the sulfate drives zeolite crystallization. Nonetheless the results do not appear to support the starting hypothesis to the effect that sulfate might accelerate ash dissolution and subsequent condensation of the SiO_2 and Al_2O_3 species, i.e., fly ash activation. In fact, in the presence of sodium sulfate, the rate of the fly ash alkali activation reaction declined (lower degrees of reaction and consequently lower mechanical strength were recorded).
- The effect of sulfates as an activation retarding agent was more relevant when NaOH was the activator. Nonetheless, their effect on the degree of reaction and mechanical strength development waned when the soluble silica content in the medium was raised. The reasons for this behaviour are unclear at this writing.
- The presence of sulfates in these systems was not observed to occasion the formation of new compounds, nor could their

uptake in the reaction products (N–A–S–H gel and zeolites) be verified.
- Sulfates are believed to retard N–A–S–H gel formation because the presence of sulfate ions in the solution in pores may repel the negative charge on the aluminosilicates. This would obstruct the condensation reactions and lower the degree of ash solubilization due to the slight decline in the pH in the medium.

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