

Mid-infrared spectroscopic studies of alkali-activated fly ash structure

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Abstract

Infrared spectroscopic techniques were used in the present study to acquire a deeper understanding of mid-range order in the alkaline aluminosilicate (zeolite precursor) formed in the alkali activation of fly ash. Experiments were conducted with three type F fly ashes containing different proportions of vitreous and crystalline (primarily mullite and quartz) phases, activated with an 8 M solution of NaOH. All the mixes were alkali activated at 85 °C for the following reaction times: 2 h, 5 h, 8 h, 20 h and 7 days. The results indicate that the amount of alkaline silicoaluminate formed as the main reaction product, and its Si/Al ratio, induce a shift in the T–O stretching band appearing at 950–1100 cm⁻¹. Moreover, the presence of zeolite-type crystalline phases generates substantial changes in the 800–500 cm⁻¹ area of the spectra. Selective chemical attacks were used to facilitate identification of the spectra bands.

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1. Introduction

The alkali activation of fly ash is a chemical process in which certain partially or wholly amorphous and/or metastable structures are transformed into compact cementitious skeletons. The main reaction product in mildly thermal (60–90 °C) alkali activation of fly ash is an alkaline aluminosilicate, described by several authors to be a “zeolite precursor” [1–6] and called “geopolymer” by other authors [7–10]. This aluminosilicate compound is characterised by a three-dimensional structure and long- and mid-range disorder that makes it X-ray amorphous. NMR [3] studies have shown that at short

range this gel has a three-dimensional structure in which the Si is found in a variety of environments, with a predominance of Q⁴(3Al) and Q⁴(2Al) units.

The alkali activation of fly ash is a relatively speedy process, in which reaction times are usually much shorter than required for zeolite synthesis. This explains the formation of amorphous or semi-crystalline structures as opposed to the crystalline structure of zeolites. The product obtained after fly ash activation is a material with good cementitious properties in which the unreacted particles remain embedded [4,5].

Nonetheless, the process calls for a very alkaline medium. On the one hand, the alkali catalyses the dissolution of the initial vitreous component (silica and alumina) and on the other actually forms a part of the final structure of the material, neutralising the charge generated by the substitution of an aluminium for a silicon tetrahedron [1–3].

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The paucity of information in the literature on the alkali activation of fly ash and the difficulties encountered in characterising the zeolite precursor-type gel formed in the activation reaction prompted the decision to conduct a study making more intensive use of infrared spectroscopy, a technique able to furnish information on chemical bond vibrations in the molecular units that comprise this new family of cementitious materials.

The primary aim of the present research is, therefore, to determine the correlation between the vibrational spectra obtained and the reaction product formed in the alkali activation of fly ash after different curing periods. Attention is nonetheless drawn to the fact that the joint presence of T–O vibrations (T = Al, Si) of diverse origin, namely the initial ash, the “zeolite precursor” and the crystalline zeolites formed during alkali activation, yields overlapping spectrum bands whose correct interpretation is fraught with difficulties.

In order to obviate this problem and maximise the volume of information obtained, in the present study both the original and the activated ash were subjected to selective chemical attacks. This procedure made it possible to differentiate, in the initial ash, between crystalline and amorphous phases; and in the activated ash, between the (amorphous) “zeolite precursor” and the vitreous component of the original ash. The procedure and the effect of these chemical attacks, with HF in the former case and HCl in the latter, are described in the literature [11,12].

2. Experimental

2.1. Characterisation of initial materials

Fly ashes from three different coal-fired steam power plants were analysed in the present study. All three type F (ASTM classification) ashes contained primarily SiO₂ and Al₂O₃. Their chemical composition and reactive silica content are given in Table 1.

Fig. 1, in turn, shows the particle size distribution of the three ashes. According to these results, all three have two particle size modes: one with values ranging from 10 to 45 μm, which accounts for 70–80% of the material, and the other with a value of 120 μm, associated with

larger particles and corresponding to 20–30% of the material.

After XRD and FTIR characterisation, the original fly ash was attacked with a 1% HF solution [11], which dissolves most of the vitreous phase. The insoluble residue, comprising the crystalline phases, was likewise characterised using the same XRD and FTIR techniques.

2.2. Alkali activation of the fly ash

The three ashes were activated with an 8 M solution of NaOH. The “alkali solution/fly ash” ratio used was the ratio required in each case to obtain a paste of normal consistency, namely 0.33, 0.4 and 0.56 for ashes A, B and C, respectively (UNE-EN 196-3). The pastes obtained were cured at 85 °C and 98% relative humidity for different lengths of time (2, 5, 8 and 20 h and 7 days). Samples were characterised by XRD and FTIR at each age.

After characterisation, the materials were attacked with a 1:20 solution of HCl to determine the degree of reaction [12]. This attack dissolves the reaction products formed in alkali activation (“zeolite precursor” and crystalline zeolites), but not the unreacted ash. The insoluble residue was likewise characterised by FTIR and XRD.

X-ray diffractograms of powdered samples were obtained with a Philips diffractometer PW 1730, using CuKα radiation. Specimens were step-scanned at a rate of 2°/min, with 2θ in the range 2–60°, divergence slit = 1°, antiscatter slit = 1° and receiving slit = 0.1 mm. FTIR spectra were obtained on an ATIMATTSON FTIR-TM series spectrophotometer. Specimens were prepared by mixing 1 mg of sample in 300 mg of KBr. Spectral analysis was performed over the range 4000–400 cm⁻¹ at a resolution of 1 cm⁻¹.

3. Results and discussion

The results obtained with infrared spectroscopic characterisation of both the initial fly ashes and the reaction products are set out below. As XRD was used only to confirm the identification of the crystalline phases present in the materials, reproduction of the diffracto-

Table 1
Chemical analysis of three types of fly ash

	Oxides (%)								
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Reactive SiO ₂
A	54.42	26.42	7.01	3.21	1.79	0.59	3.02	0.01	45.05
B	51.51	27.47	7.23	4.39	1.86	0.70	3.46	0.15	42.17
C	59.89	27.67	3.02	3.45	1.22	0.94	1.01	0.51	45.07

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