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SCIENCE DIRECT
Fuel 84 (2005) 2048–2054
FUEL
www.fuelfirst.com

Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products

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Received 10 November 2004; received in revised form 30 March 2005; accepted 30 March 2005
Available online 10 May 2005

Abstract

This paper deals with the alkaline activation of fly ashes for the production of a novel cementitious material and with the effect of curing conditions on the nature of the reaction products. Curing procedures favouring carbonation process negatively affects the development of mechanical strength of this new alkaline cement. Carbonation of the system involves its pH modification and consequently the modification of the nature of the reaction products and the kinetics of reactions.

Keywords: Fly ash; Alkaline cement; Curing; Carbonation

1. Introduction

The use of reinforced concrete in construction dates from the late 19th century. In the last 100 plus years, as the construction industry has evolved in keeping with both overall technological development and market demands, Portland cement has become the most profusely used commodity on our planet.

Mass production of concrete and the concomitant mass manufacture of cement have, however, been observed to have a very negative environmental impact (almost 1 tonne of CO_2 is released into the atmosphere for every tonne of cement manufactured). Cement production is, moreover, a very energy-intensive process.

The foregoing problems have been addressed for a number of years from different perspectives, which very schematically, can be grouped in two major lines of action:

- Improvements in the efficiency of Portland cement manufacturing processes.
- Enhancement of certain features of Portland cement by including chemical additives, mineral admixtures, etc. to fresh concrete.

In short, it is clear that enormous efforts were made throughout the 20th century to improve Portland cement concrete technology. At the same time, however, very limited research was conducted on new binders able to provide technical alternatives to conventional cement that could be produced at a fraction of the energy cost and environmental impact.

In this context, the idea of applying alkali activation to fly ash from steam plants, along the lines of previously successful applications of this process with other materials [1–8], was put forward in the Eduardo Torroja Institute [9].

Synoptically, the material proposed to replace Portland cement in concrete for use in construction is a binder prepared by mixing type F fly ash from coal-fired steam power plants with a highly alkaline solution. As this paste sets and hardens under moderate thermal conditions, the resulting precipitate is a gel with cementitious properties.

From the chemical standpoint alkali activation of fly ash is a process that differs widely from Portland cement hydration, but is very similar to the chemistry involved in the synthesis of a large groups of zeolites [10–11]. The main reaction product in the alkali activation of fly ash is an alkaline aluminosilicate gel; that is to say a precursor of certain crystalline zeolite species [10]. This product is structured around tetrahedrally co-ordinated silicon and aluminium, forming a polymer chain in which the Al^{3+} ions

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doi:10.1016/j.fuel.2005.03.030

Table 1
Chemical analysis of 'CP' fly ash

	L.O.I	I.R.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	TiO_2	Total
%Wt	3.59	0.32	53.09	24.80	8.01	2.44	1.94	0.23	3.78	0.73	1.07	100

According to UNE 80-215-88 and UNE 80-225-93. L.O.I., loss on ignition; I.R, insoluble residue in HCl (UNE).

replace the Si^{4+} ions. The resulting net anionic charge is compensated by the capture of monovalent alkaline cations.

In technological terms, the long experience acquired with Portland cement concrete has revealed the importance of the conditions in which the product is manufactured and laid. The concrete curing process has a substantial impact on the quality and durability of the material: it is during that process that the necessary environmental conditions must be created to keep the concrete moisture content at saturation or near saturation levels and thereby ensure full hydration of the cement (the ongoing hydration reactions in Portland cement are essential to increasing concrete mechanical strength and durability [12–15]).

In the alkali activation of fly ash, the objective pursued in the curing process is to attain conditions that optimise the polymerisation reactions (technologically speaking). The time required for appropriate alkali activation depends, in this case, on ash type and fineness, on the activating solution/fly ash ratio, on temperature, time, and on nature and concentration of the alkali activator [16,17].

2. Experimental

2.1. Materials

The fly ash used in the present study was a Spanish ('CP') fly ash whose chemical composition is shown in Table 1. A very exhaustive characterisation of the fly ash was previously published by the authors [18]. The initial chemical compositions of the activating solutions, in turn, are given in Table 2.

The reagents used to prepare the activators were laboratory grade: both the pellet-form NaOH (98% purity) and the sodium silicate, which had a density of 1.38 g/cc and a composition comprising 8.2% Na_2O, 27% SiO_2 and 64.8% H_2O, were supplied by Panreac S.A.

2.2. Method

The fly ash was mixed with the different activating solutions (solutions A and B, see Table 2) at a constant 'solution/ash' ratio of 0.4. After mixing, the pastes were immediately poured into prismatic moulds measuring $1 \times 1 \times 6$ cm. These were then heated to 85 °C for different lengths of time: 5, 12, and 20 h and 7 days.

The heating conditions were also varied to ascertain whether the curing atmosphere affected the mechanical and mineralogical evolution of the materials. Two alternative curing systems were studied:

method 1: the moulds were placed in air-tight receptacles containing a certain amount of water, which was not, however, in contact with the moulds.
method 2: the moulds were introduced directly into the oven alongside a porcelain capsule containing water.

After the materials were removed from the oven at the specified times, their mineralogical content was characterised by FTIR and XRD. The degree of reaction attained was also determined, using a method described in a preceding paper [19]; ion chromatography was used to determine the soluble sodium content. The sodium was extracted from 3-g samples (previously vacuum-dried to a constant weight) that were placed in a flask with 250 cc of deionised water. The mixture was magnetically stirred for 3 h. Thereafter, the system was filtered and water was added to the filtered solution to a total volume of 500 cc. This was the solution analysed for sodium content.

Finally, the mechanical properties of the different alkali-activated fly ash samples were determined by breaking the prismatic specimens with an Ibertest (Autotest—200/10—SW) compression tester.

3. Results

Figs. 1 and 2 shows the diffractograms for all the materials prepared in the study (including the initial 'CP' fly ash). All have a small halo in the $2\theta = 20$–$35°$ region, characteristic of amorphous and/or vitreous compounds. In all cases (except in the original ash), the presence of this halo is due, at least in part, to the alkali aluminosilicate gel formed as the primary reaction product in ash activation.

Table 2
Chemical composition and pH of activating solutions

	Na_2O (%)	SiO_2 (%)	H_2O (%)	pH
Solution A: NaOH	7.81	–	92.19	13.93
Solution B: NaOH + waterglass	8.29	1.22	90.49	13.83