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Cement and Concrete Research 35 (2005) 1204–1209

Cement and Concrete Research

Microstructure development of alkali-activated fly ash cement: a descriptive model

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Received 29 January 2004; accepted 30 August 2004

Abstract

The microscopic study of a set of alkali-activated and thermally cured fly ash samples enabled the authors to establish a descriptive model for the microstructural development of fly ash-based cementitious geopolymers.

The morphology of most fly ash particles (perfect spheres) not only makes microscopic research highly productive but facilitates the formulation of hypothesis explaining the fly ash activation over time through a series of consecutive steps that can be successfully fitted to real situations.

Keywords: Fly ash; Alkali activation; Microstructure; Model

1. Introduction

The copolymerization of the individual alumina and silica components that takes place when aluminosilicate source materials are dissolved at a very high pH yields amorphous [1–5] “zeolitic precursor” (sometimes called “geopolymer”).

Whilst the product of the fly ash activation reaction is similar in cementitious properties to ordinary Portland cement (OPC), the process itself entails certain financial and environmental advantages over traditional OPC manufacture.

In such activation, the fly ash is mixed with alkaline activators (alkaline solutions) and the resulting paste is solidified by curing. In this process, the glassy constituent of the fly ash is transformed into well-compacted cement. The advent of advanced instrumental techniques, such as MASNMR, SEM, TEM, etc., has helped to clarify important aspects of the structure and morphology of these new materials. Hence, previous studies [3,6,7] have found that the main reaction product of such systems is a short-range ordered amorphous aluminosilicate gel: a three-dimensional structure where the Si occurs in a variety of environments, with a predominance of Q^4(3Al) and Q^4(2Al). This material could consequently be considered to be a “zeolite precursor”. Indeed, small amounts of certain zeolites such as hydroxysodalite, herschelite, etc. are often detected in these systems [3,6].

It is within this intertexture where the main objective of this work was defined: To establish a singular and conceptual model capable to describe the general process of alkaline activation of fly ashes, independent on the experimental conditions at which the activation is produced; that is to say, independent on the particular characteristics of fly ashes, on the type and concentration of the activating dissolution, etc.

The authors of the present paper, according to previous results [3,6–9], consider that experimental conditions at which alkali activation is conducted will specially affect the chemical composition of the reaction products and also to the kinetics of reactions but not to the mechanisms controlling the setting and hardening process of the material.

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doi:10.1016/j.cemconres.2004.08.021

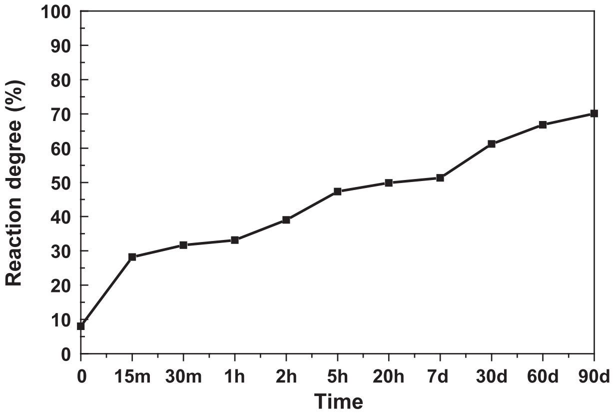

Fig. 1. Evolution of the reaction degree of a fly ash activated with a 8 M NaOH dissolution. Curing temperature: 85 °C.

The proposed model is mainly based on some data gathered through the different electron microscopy techniques since pictures strongly facilitate the comprehension of the steps through which the alkaline activation of fly ashes flows. Nevertheless, the bases supporting the model are in good agreement with other results provided by XRD, FTIR, MAS-NMR, etc. These results have not been included in the paper as they can be extracted from the bibliography [3,6,7].

2. Experimental

This survey was conducted on a class F fly ash with the following chemical composition: 53.09% SiO_2, 24.80% Al_2O_3, 8.01% Fe_2O_3 and 2.24% CaO. The ash was mixed with an 8 M solution of NaOH, ("solution/ash" ratio=0.35). The resulting paste was poured into small plastic moulds and oven-cured at 85 °C for 5 h, 24 h and 60 days. The hardened pastes were removed from the oven at the specified ages and immediately frozen in acetone for subsequent testing:

(1) The degree of reaction at each particular instant of the process is determined by attacking the sample, at room temperature, with ClH 1:20. This chemical attack dissolves the silicoaluminate gel formed as a consequence of the alkaline activation of the fly ashes and also those zeolites, which could have crystallized. However, the acidic attack hardly affects the unreacted ash particles [8,9].

(2) The samples were studied by SEM/EDS under a JEOL JSM 5400 scanning electron microscope equipped with a LINK-ISIS energy dispersive (EDS) analyser. Transmission electron microscopy (TEM) studies were made with a double tilting goniometer stage of ±45°. The equipment was a JEOL 2000 FX II. Specimens for study were crushed and dispersed in acetone and then transferred to holey carbon-coated copper grids.

3. Results

In Fig. 1, the values of the degree of reaction of a fly ash activated with the 8 M NaOH dissolution have been plotted versus the time of thermal curing at 85 °C. Results show, as expected, the degree of reaction continuously increasing with time. However, it should be remarked from this figure the especially high degree of reaction reached during the first hours of the thermal curing.

The micrographs presented in this paper depict the typical microstructure developed by the material at specific reaction times (see Figs. 2–5).

Fig. 2a is a SEM image showing the characteristic morphology of the original fly ash. This ash consists of a series of spherical vitreous particles of different sizes (diameters ranging from 200 to 10 μm). Whilst usually hollow, some of these spheres may contain other particles of a smaller size in their interiors.

Fig. 2b shows the first changes detected in the microstructure of the fly ash system as a consequence of the caustic dissolution attack and posterior thermal curing (5 h at 85 °C). The degree of reaction at this stage is low–moderate (45.35%, see Fig. 1). Here, the spheres seem to be almost intact or appear within other spheres, depending on the degree of local reactivity. Actually, in the early stages of the process, the alkaline dissolution dissolves part of the shells of the spheres, exposing the smaller particles (trapped inside the larger ones) to the alkaline attack as well. At this particular reaction time, the reaction product is a sodium silicoaluminate with a Si/Al ratio of 1.6.

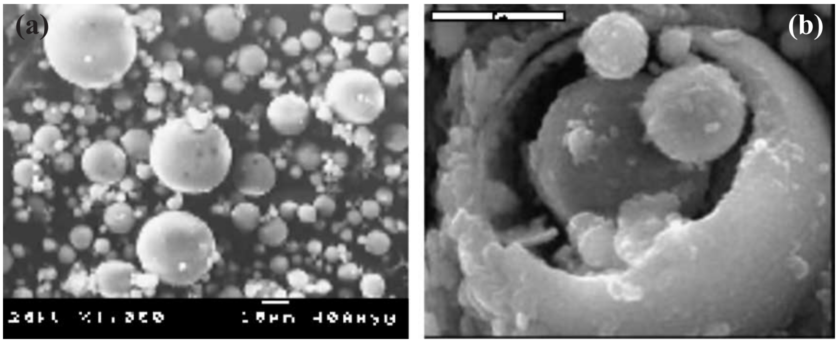

Fig. 2. SEM pictures: (a) original fly ash, (b) fly ash activated with 8 M NaOH for 5 h at 85 °C.

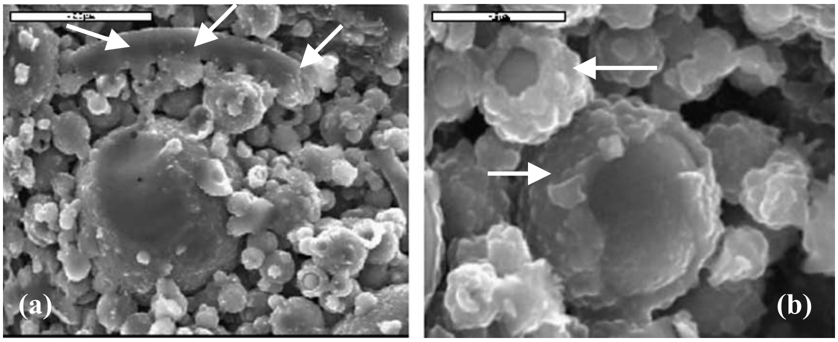

Fig. 3. SEM pictures. Fly ash activated with 8 M NaOH for 20 h at 85 °C; (a) reaction process of a large sphere, (b) singular details of the reaction of some small spheres.

Fig. 3a and b shows the fly ash particles in a more advanced stage of the reaction (degree of reaction=50.00%). The pictures correspond to a system cured for 20 h at 85 °C. In Fig. 3a, the reactive process of a large fly ash sphere has been frozen at that particular time (some rests of the particle outer wall have been arrowed in the picture). The main reaction product from the alkaline attack is that sodium aluminosilicate gel that in the precipitation step is getting compacted with more gel proceeding from other particles giving place to a cementitious matrix. Additionally, in Fig. 3a, some small fly ash particles which have reacted with the alkali dissolution are observed to co-exist with some remaining unreacted spheres and even with some other particles partially covered with reaction products. These spheres (better seen at Fig. 3b) will obviously react very slowly In this stage, the Si/Al ratio of the main reaction product is on the order of 1.8–2.0; in other words, the Si content is substantially higher than in the gel shown in Fig. 2b. Additionally, the variation in fly ash particles reactivity ranges from no appreciable reaction to surface dimpling and finally fly ash particles inside shells, denoting reaction or simply empty shells, indicative of a full reaction (Fig. 3b). This variability, reported in a previous paper [10], suggests either: (i) differences in the granular properties of the fly ash or (ii) limited availability of some fly ash grains for alkaline attack.

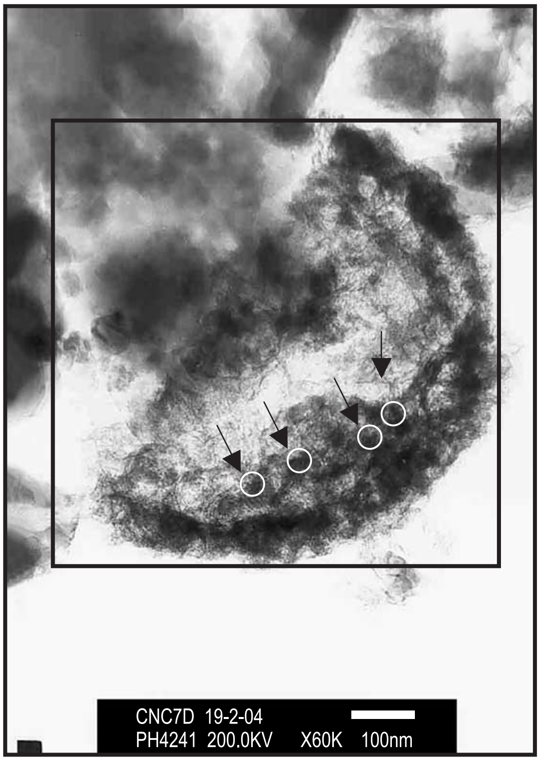

Fig. 4. TEM picture of a activated fly ash sample. Activator: 8 M NaOH dissolution. Curing conditions: 7 days at 85 °C.

A transmission electron microscope picture of the fly ash activated with NaOH 8 M 7 days at 85 °C is shown in Fig. 4. The spherical morphology of some fly ash particles becomes evident through this powerful technique of observation. The most interesting features to be remarked from Fig. 4 are those extracted from the observation of the rests of a large spherical fly ash particle which underwent a long reaction process (7 days at 85 °C). The mentioned rests include a semicircular crust of about 50–60 μm thick, probably partially pemeable. In the inner part of that big particle some small particles (25–35 μm diameter) have been arrowed. They are embedded into the sodium aluminosilicate gel ("zeolitic precursor") produced during the reaction process.

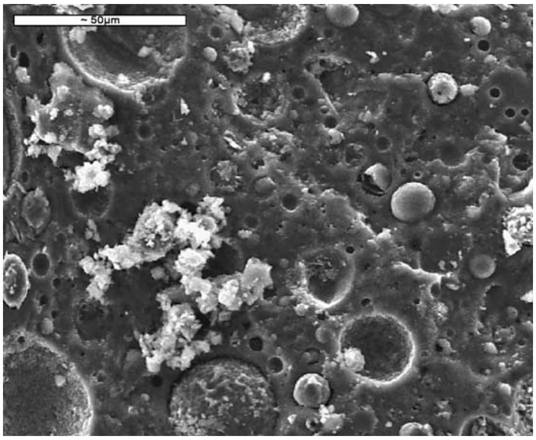

Fig. 5. Fly ash activated with NaOH 8 M and cured 60 days at 85 °C.

Finally, Fig. 5 shows the system evolution after 60 days at 85 °C (degree of reaction=66.83%). Here, the matrix has developed into a highly compacted paste, with a Si/Al ratio of 1.9–2.1. The non-reacted fly ash particles are embedded into the matrix, which bears the semispherical imprints of some of the grains that did.

4. Discussion

It is important to remark at the beginning of the discussion section that authors of this paper have enough background from their investigation (some already published) as to strongly believe that most of type F fly ashes are suitable to be alkali-activated [3,7,11,12]. In good agreement with other authors findings, we have demonstrated that there are some key factors influencing the potential reactivity of the fly ashes (reactive silica content, the vitreous phase content and the particle size distribution) [11,20]. However, we believe that none of these parameters substantially affect the mechanisms of activation.

From the standpoint of the reaction mechanisms, the alkali activation of fly ash, like the alkali leaching of silicates in zeolite formation [13], can be divided into a number of stages. If we accept the postulates on zeolites synthesis [16] as the main framework in which to incorporate alkali activation of fly ashes, then we can say that in the first step of the reaction (*nucleation*), the vitreous aluminosilicate component of the fly ash dissolves in the alkaline solution, favouring the formation of a certain amount of aluminosilicate gel. During nucleation, gel composition is significantly affected by thermodynamic and kinetic parameters. This period can be further divided into two substages that concur with the first two stages proposed by Glukhovsky for the alkali activation of materials with a high SiO_2 and Al_2O_3 content [14].

4.1. Dissolution

The aluminosilicates originally found in the ash dissolve, forming a series of ionic species.

4.2. Polymerization

The smaller molecules agglutinate to form larger molecules that precipitate in the form of a gel, in which some degree of short range structural order can be identified [3].

Both substages, dissolution and polymerisation, were in the past and are still being at present the main objective of study of some different authors [1,3,5–7,9,15]. On this basis, we are presenting our particular contribution for a better understanding of the alkaline activation of fly ashes.

With respect to the dissolution substage, it is important to remark that, at the same instant of putting in contact the fly ash particles with the alkaline dissolution of high pH, an immediate dissolution of the Al and Si constituting the vitreous component of the fly ash takes place. Data from conduction calorimetry tests (showing a rapid and intense release of heat when fly ashes and alkalis get in contact) [6], as well as the analytical data published by Van Deventer et al. (who found the existence of a type of synchronism correlating the Al and Si dissolution rate in a number of silicoaluminate minerals) [15], confirm for the of alkali activation of fly ashes a similar process to that of hydration of Portland cement during the first moments of the hydration. In the case of the fly ashes activation, the dissolution rate strongly depends on the pH of the activator system and some other experimental conditions.

With respect to the second part of nucleation (substage denominated polymerization) we consider, it is important to emphasize the following: According to previous works, it seems accepted that the “zeolitic precursor” (the already mentioned as the main reaction product of the alkali activation of the fly ashes) contains tetrahedra of Si and Al randomly distributed along the polymeric chains that are cross-linked so as to provide big enough cavities as to accommodate the charge balancing sodium ions [1–3,9,19]. Data obtained through NMR and FTIR confirm that: when the time of reaction increases a first formed *meta-stable/intermediate* Al-rich phase evolves to a more stable Si-rich phase [3,7]. This latter phase presents a three-dimensional structure in which Si is present in a variety of environments. This arrangement leads to Si environments such as Q^4(1Al), Q^4(2Al) and Q^4(3Al). The predominance of the Q^4(nAl) depends on the polymerisation degree, which depends on the curing conditions and the alkali activators used.

Finally, the second stage, known as growth, begins when the nuclei reach a critical size and the crystals begin to grow. Due to the very low “alkaline solution/fly ash” ratios prevailing under experimental conditions, this stage is extraordinarily slow (this particular fact establishes the main differences existing between the traditional way of synthesizing zeolites and preparing alkali-activated fly ash cement). The amount of liquid in the system affects to the saturation rate of ionic species but not to the rate of dissolution of those ionic species. On the other hand, the quick precipitation of the material affects its crystallinity. It is well known that zeolites usually need some time for crystallization and a minimum amount of liquid (suspension systems [18]). When the fly ash powder is mixed with a small volume of alkaline solution, a paste is formed which quickly transforms into a harden solid. In such a situation, there is not sufficient time and space for the gel (product of reactions) to grow into a well-crystallised structure such as in the case of zeolites formation.

The hypothetical evolution of this gel (zeolitic precursor) to form an orderly zeolitic crystal would entail depolymerization of the gel structure.

Fig. 6 contains a descriptive diagram modelling of the alkali activation of fly ash. Fig. 6a shows the initial chemical attack at one point on the surface of a particle, which then expands into a larger hole (see Fig. 2b), exposing smaller particles, whether hollow or partially filled with other yet smaller ashes, to bi-directional alkaline attack: i.e., from the outside in and from the inside out (see Figs. 6b and 3a). Consequently, reaction product is generated both inside and outside the shell of the sphere, until the ash particle is completely or almost completely consumed (Figs. 6c and 4). The mechanism involved at this stage of the reaction is dissolution. At the same time, as the alkaline solution penetrates and contact the smaller particles housed inside the larger spheres, the interior space of the latter starts to fill up with reaction product, forming a dense matrix.

One of the consequences of the massive precipitation of reaction products is that a layer of these products covers certain portions of the smaller spheres. This crust prevents their contact with the alkaline medium (Figs. 6e and 3b). Ongoing reactions within the bulk of the matrix consolidate such crusts, with the concomitant effect on the pH gradient across the fly ash reaction product. As alkaline activation continues, the unreacted fly ash buried under reaction product may not be affected by the very high pH associated with the activator, thereby reducing the reaction rate. In this case, activation is governed by a diffusion mechanism. The variation in the degree of reaction at different times (45.35% at 5 h, 50.00% at 20 h and 66.83% at 60 h, see Fig 1) may suggest variable permeability of the layers of hydration product.

Moreover, the processes described are not uniform throughout the gel but vary locally from one point in the matrix to another, depending on the distribution of particle size and the local chemistry (e.g. pH). Several morphologies may co-exist in a single paste: unreacted particles, particles attacked by the alkaline solution but which maintain their spherical shape, reaction product and so on (Figs. 6d and 5).

At this point, it is important to emphasize that the presence of soluble silica in the activating dissolution plays an important role in the microstructure development of these types of cementitious systems [17]. However, we think that this presence would mainly affect the chemistry of the phases involved in the reactions and even the kinetics, but no the mechanisms governing the reactions. In Fig. 7, the microstructure of an extra sample is shown. It belongs to a fly ash paste, which was activated by using sodium silicate as activating dissolution and then thermally cured at 85 °C for 20 h (19). The developed microstructure in this case looks like many types of glasses (almost absence of pores and very uniform and unshaped microstructure). This type of microstructure is only interrupted by the presence of some fly ash particles that have not yet reacted or by the presence of tracks of ash spheres. The content of Si and Na of this matrix is higher than in the rest of materials studied (Si/Al ratio=2.5–2.8 and Na/Al ratio=1.5–1.6). Nevertheless, this microstructure generated in the presence of soluble silicate ions is basically the same to that obtained with a NaOH dissolution and a long thermal curing time (see Fig. 4). It would confirm that the conceptual model presented in this paper could also describe the reactive process of fly ashes if soluble silica would exit in the system.

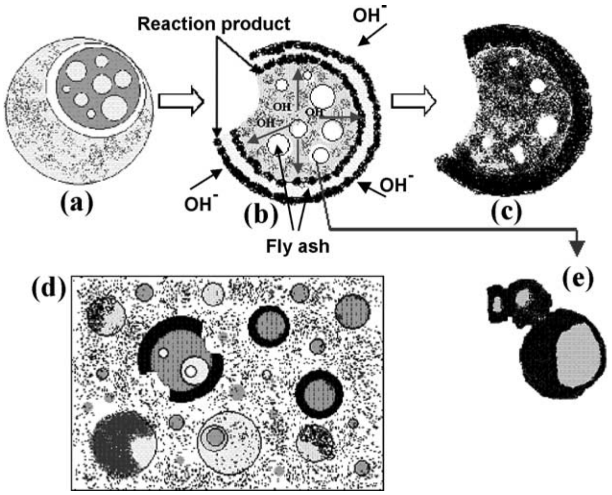

Fig. 6. Descriptive model of the alkali activation of fly ash.

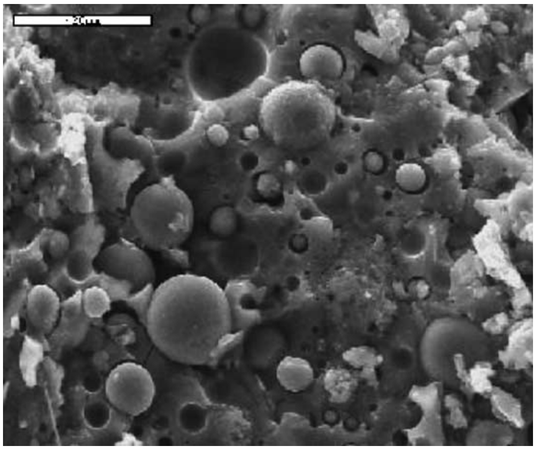

Fig. 7. Fly ash activated with sodium silicate (Ref. [19]).

5. Conclusions

Electron microscopy is a very useful tool for monitoring the microstructural development, over time, of the cementitious matrix generated as a result of the alkali activation of fly ash. Additionally, the spherical shape of fly ashes facilitates the formulation of a simple conceptual model capable of describing the general process of alkali activation of the ashes in the form of series of consecutive steps. This process is non-uniform and is governed by dissolution in the early stages of the reaction and by a diffusion mechanism thereafter.

The activation reaction rate as well as the chemical composition of the reaction products depend on several factors like for example the particle size distribution and the mineral composition of the starting fly ash, the type and concentration of the activator, etc. However, the mechanisms controlling the general process of activation are independent of those variables.

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