"Alkaline Activation" as a procedure for the transformation of fly ashes into cementitious materials.

Part I. Fundamentals

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Abstract

The reaction of a solid aluminosilicates with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkali aluminosilicate material generically called a 'geopolymer', after Davidovits, but probably more appropriately referred to as an example of what is more adequate termed as gel N-A-S-H. These materials can provide comparable performance to traditional cementitious binders in a range of applications, but with the added advantage of significantly reduced Greenhouse emissions.

Depending on the raw material selection and processing conditions, alkali activated products can exhibit a wide variety of properties and characteristics, including high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. Despite this wide variety of commonly boasted attributes, these properties are not necessarily inherent to all alkaline silicoaluminous formulations.

Some general aspects to be remarked of this chemical process (alkaline activation), when applied to the case of fly ashes are: kinetics diversity, complexity of chemical reactions, different microstructure formations, etc... This paper summarizes the fundamental aspects about alkaline activation of fly ashes; it means authors describe the mechanisms governing the main chemical transformation of fly ashes into hardened and compact cementitious materials.

Keywords: fly ash, alkali activation, geopolymer, mechanisms of reaction, microstructure

1 Introduction

Portland cement concrete is today's construction material per excellence. It owes this pre-eminence to its mechanical strength, high value for money and generally good performance. Nonetheless, Portland cement manufacture raises certain energy and environmental issues, since it calls for temperatures of up to 1500 °C and raw materials whose quarrying mars the landscape, while emitting gases such as CO_2 and NO_x . Moreover, concrete poses certain durability problems, such as the aggregate-alkali reaction and attendant expansion, chloride-induced corrosion in reinforcing steel...[1, 2]).

A innovative option consists of developing alternative, less expensive and less environmentally damaging cements (involving lower CO_2 emissions or the re-use of industrial by-products), that exhibit characteristics or performance comparable to or even better than ordinary Portland cements (OPC). One such category of materials includes a series of binders generically known as alkaline cements [3-7]. Alkaline cements are cementitious materials formed as the result of the dissolution of natural or industrial waste materials (with amorphous or vitreous structures) in an alkaline medium. When mixed with alkaline activators, these materials set and harden, yielding a material with good binding properties.

The alkali activation of fly ashes (AAFA) has shown to be an effective alternative to the traditional OPC systems. The AAFA systems have exhibited an excellent behavior, even better than the analogous hydrated OPC systems. However the chemistry involved in the reaction mechanisms (alkali activation of aluminosilicates *vs* hydration of calcium silicates) is quite different, as will be explain in detail below.

2 Alkaline cements based on fly ashes (AAFA)

A wide variety of alkali-activated cements have been developed in the last few decades. One of the most representatives cements are which are based on the activation of materials comprising primarily aluminium and silicon $(Na,K)_2O-Al_2O_3-SiO_2-H_2O$ system) with low CaO contents such as metakaolin or type F fly ash (from coal-fired steam power plants). Fly ash and metakaolin are the most commonly used low calcium materials in alkaline cement and concrete manufacture, although for reasons of cost metakaolin is adopted more sparingly.

Fly ash is an industrial by-product generated in coal-fired steam power plants. Before its use as a fuel in these plants, coal is ground to a very fine powder. Coal combustion gives rise to heavy ash (known as bottom ash) and other much finer particles that are carried by smoke and trapped in precipitators to prevent their release into the air. Known as fly ash, this material is characterized by its peculiar morphology: hollow spheres that may or may not house other smaller spheres. It consists essentially of a vitreous phase and a few minority crystalline phases such as quartz (5-13 %), mullite (8-14 %) and magnetite (3-10 %) [5].

The alkali activation of fly ashes (AAFA) requires an intense working conditions to kick-start the reactions (highly alkaline media and curing temperatures of 60-200 °C). The main reaction product formed is a three-dimensional inorganic alkaline polymer, a *N-A-S-H* (or alkaline aluminosilicate), which is the main responsible of the mechanical-strength behavior and durable properties of these materials [4-7]. The secondary reaction products in this type of systems are zeolites such as hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite [8].

2.1 Reaction mechanisms

The hydration of the calcium silicates in Portland cement (C_3S and C_2S) yields portlandite ($Ca(OH)_2$) and a non-crystalline calcium silicate hydrate, generically known as C-S-H, the compound primarily responsible for the binding properties exhibited by the material [1].

The reaction mechanisms in alkaline cements differ from the mechanisms observed in OPC. Glukhovsky [3] was one of the first authors in explore the reaction mechanisms involved in the alkaline activation of aluminosilicates. So that he considered the works of Carman and Iler [9] about the theory of silicic acid

polymerization (See Fig. 1), according to which the process takes place in three well-known steps: (a) monomer polymerization and particle formation (b) particle growth (c) inter-particle bonding to form branched chains, networks and ultimately the gel. Depending on the alkalinity of the medium, the particle evolves in one way or other. For pH values of under 7, or between 7 and 10 in the presence of salts (which act as flocculating agents), the particle aggregate evolves to form a three-dimensional structure; by contrast, at pHs values between 7 and 10 but in absence of salts, particle grow in size and decline in number to for a sol (a colloidal suspension of very small solid particles in a continuous liquid medium).

Based on this theory, *Glukhovsky* [3] proposed a general mechanism for the activation reactions in these materials, consisting of three different stages: (a) Destruction-Coagulation; (b) Coagulation-Condensation; and (c) Condensation-Crystallization.

In the first stage, destruction-coagulation, the OH⁻ ions initiate the reaction with the rupture of the Si-O-Si bonds (eq. 1). This takes places by the action of the OH⁻ redistributing the electron density around the silicon atom and rendering the Si-O-Si bond more susceptible to rupture. As consequence, silanol (-Si-OH) and sialates (-Si-O⁻) species are formed. The presence of alkaline metal cation neutralizes the resultanting negative charge. The appearance of (Si-O⁻-Na⁺) bonds hinders the reverse reaction from forming siloxane bonds



Inasmuch as the hydroxyl groups affect the AI-O-Si bond in the same way, the aluminates in the alkaline solution form complexes, predominantly $AI(OH)_4^-$ (Eq. 2).



In the second stage, Coagulation-Condensation, accumulation enhances contact among the disaggregated products, forming coagulated structure where the polycondensation takes place (Eq. 3) This reaction is catalyzed by the OH- ions. The clusters formed by the polymerization of silicic acid grow in all directions, generating colloidal particles. Aluminates also participate in the polymerization reaction, substituting isomorphously for silicate tetrahedra. While the alkaline metal catalyses destruction in the first stage, in the following two it is a structural component.



In the last stage, Condensation-Crystallization, the presence of particles in the initial solid phase prompts the precipitation of product whose compositions is determined by the mineralogical and chemical composition of the initial phase, the alkaline component and the hardening conditions.

Davidovits [10] in the 80's developed a kind of material which result from the hydroxylation and polycondesation reactions of natural minerals (such as clays, and natural puzzolans) and industrial wastes (such as slags, fly ash...) alkali activated at 160 °C. As consequence of these reactions, a mineral polymer material (with 3D cross-linked polysialate chains) precipitated. This product was called *Geopolymer*.

More recently (90's), others authors have developed and expanded Gluchovsky's theories applying the Zeolite Synthesis knowledge. In this sense Palomo and co-workers [11] propose the scheme plotted in the Fig. 2(a) to describe the alkaline activation of aluminosilicates. The process involves basically, two main steps (a) the first one Nucleation, in which the aluminosilicates dissolve in the alkaline medium favoring the formation of zeolite precursor (a stage that encompasses Glukhovsky's first two stages and is heavily dependent upon kinetic and thermodynamic parameters), and the second one (b) growing, in which several nuclei reach a critical size and crystal begin to develop. Whit the time, the final product would be a zeolite.

In short, N-A-S-H gel formation entails a series of stages that can be summarized as follows (see Fig. 2(b) [12]): when the source of aluminosilicate comes into contact with the alkaline solution it dissolves into several species, primarily silica and alumina monomers. These monomers interact to form dimers, which in turn react with other monomers to form trimers, tetramers and so on. When the solution reaches saturation an aluminosilicate gel, N-A-S-H gel, precipitates. This gel, known as *Gel 1*, is initially Al-rich (Si/Al≈1) and constitutes a meta-stable, intermediate reaction product [12]. Its formation can be explained by the high Al³⁺ ion content in the alkaline medium in the early stages of the reaction (from the first few minutes through the first few hours), since the reactive aluminium dissolves more quickly than silicon because Al-O bonds are weaker than Si-O bonds. As the reaction progresses, more Si-O groups in the original source of aluminosilicate dissolve, raising the silicon concentration in the reaction medium and its uptake in the gel. The N-A-S-H gel so formed, *Gel 2*, is richer in silica (Si/Al ≈ 2) and is primarily responsible for the high mechanical strength observed in (OPC-free) alkali-activated fly ash cement These structural reorganization processes determine the final composition of

the polymer as well as pore microstructure and distribution in the material, which are critical factors in the development of many physical properties of the resulting cement.

2.2 Microestructure of the AAFA paste

The microstructure and the chemical composition of the N-A-S-H gel depend of several factors such as the mineral composition of the raw material, the particle size, activator type, the concentration...but in general terms the mechanism controlling the general activation process are independent of the above variables.

Fernández-Jiménez *et al* [13], based on the collected data from the a FAA SEM/EDX study, proposed a model to explain the reaction taking place during fly ash alkali activation (See Fig. 3). As Fig. 3(a) shows, the process begins with chemical attack on the surface of FA particle and then expands to form a hole, exposing smaller particles to a bi-directional attack (from the out-side in and from the inside out (fig. 3 (b)). Consequently, reaction product is generated both inside and outside the shell of the sphere, until the ash particle is completely or almost consumed (Fig. 3(c)). The mechanism involved at this stage of the reaction is dissolution. At the same time, as the alkaline solution penetrates and contacts 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 (Fig. 3 (e)). As alkaline activation continues, the unreacted fly ash reaction product may be no affected by the very high pH associated with the activator, thereby reducing the reaction state. In this case activation is governed by a diffusion mechanism.

Moreover, the process described is 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 (pH). Several morphologies can co-exist in a single paste: un-reacted particles, particles attached by the alkaline solution but which maintain their spherical shape, reaction product and so on.

2.3 Nanostructure of the N-A-S-H gel obtained from the AAFA

N-A-S-H gel formation involves a succession of hydrolysis and condensation reactions (of silicates and aluminates species) to finally conclude with the precipitation of the final product: a three dimensional aluminosilicate network commonly attributed to N-A-S-H gel. But the aluminosilicate network tends to be unbalance; the deficit of charge, which is associated to the substitution of silicon per aluminium (Si⁴⁺ per Al³⁺), is compensated by the hydrated sodium.

Nuclear Magnetic Resonance (NMR) has shown to be a very good technique which has contributed to understand the N-A-S-H gel structure. ²⁹Si MAS-NMR allow to identify the different kind of Q⁴(nAl) (n= 0, 1, 2, 3, 4) environments of he silicon species, commonly associated with 3D structures (See Fig.5). Nevertheless the assignment for the different components is quite complicated due to the overlapping. In the same way, ²⁷Al NMR has allowed to identify the presence of tetrahedral aluminum (q4 units, associated with one aluminium tetrahedra surrounding by four silicon tetrahedra) [11,14].

Fernández-Jiménez *et al* [12] showed that N-A-S-H gel coming from the alkali activation of fly ashes had a 3D structure composed basically by Q^4 (nAl) units, most of them Q^4 (3Al) and Q^4 (2Al) units, which proportions were conditioned by different factors such as the initial amount of silicon, aluminuna

and alkalis in the medium. A detailed description of the role of these three components is given below (bases primarily in MAS-NMR results).

2.3.1 The role of silicon in N-A-S-H gel structure

One of the factors to take into account in the design of the chemical composition and microstructure of N-A-S-H gels is the kind of alkaline activator. The Si which forms part of the N-A-S-H gel need not to come only from the raw material use as primary source of binder, it may also be present in the alkaline activator. In fact the presence of silicon in sodium silicate (one of the activators most used in these systems) is highly soluble and consequently incorporated to N-A-S-H gel. Nonetheless, the degree of silica polymerization in the sodium silicate (waterglass) solution, which depends of the SiO₂/Na₂O ratio, decisively conditions the structural stages involved in N-A-S-H gel formation[15].

Fig. 6(a) shows the ²⁹Si NMR spectra of three sodium silicate solutions with different SiO₂/Na₂O content (0.17, 0.60 and 1.90 respectively for solutions A, B and C). There is an increase of the degree of silica polymerization with the increase of the SiO₂/Na₂O ratio; i.e. solution A (with the lowest SiO₂/Na₂O ratio) is basically composed by Q^0 units (silica monomers), while solution C (with highest SiO₂/Na₂O ratio) shows more polymerized silica units (Q^1 , Q^2 even Q^3 units). Fig. 6(b) gives the ²⁹Si MAS-NMR spectra for the products formed over the time during the fly ash activation with the tree alkaline solutions (A, B and C). The main conclusion which ca be extracted fro this Fig. 6(b) is that the nature of the alkali activator plays and instrumental role in kinetics, structure and composition of the initial gel formed. During the early reaction stages (i.e. 8 hours) the ²⁹Si NMR spectra show quite important differences depending of the type of activator used, however at long term (i.e. 180 days) the spectra are practically the same regardless the activator employed. The addition of soluble silica affects the intermediate stages of activation reaction but not the end results.

2.3.2 The role of aluminum in N-A-S-H gel

When silicate and aluminate solutions come in contact, the resulting aluminosilicate solution gels or precipitates to form zeolites or pre-zeolites. In alkaline aluminosilicates, the condensation reaction are chemically initiated by the aluminum, Although no definitive studies on how to enhance or reduce aluminium availability during the synthesis of alkaline mineral polymers have been forthcoming, both the activator and raw materials have shown to be able to control the release of this element. Determining the amount of aluminum available in the reactive system is crucial to properly formulating alkaline minerals polymers (N-A-S-H gels). In this sense Fernández-Jiménez et al. [12], interpreting FTIR and NMR results for fly ashes with similar reactive silica contents but different percentages of reactive alumina, demonstrated the importance of the role of aluminum in the gel formation kinetics. If and ash has high initial reactive alumina content, large amounts of aluminum are release into the solution, and as results, the fly ash is highly reactive. On the contrary, ash with low percentage of reactive alumina, which is consumed in the early phases of reaction, exhibits low reactivity. Their findings indicate that the reactive alumina in fly ash must exceed a certain threshold (~20 %) for the resulting material to exhibit good mechanical properties. Furthermore, excess aluminium concentration in the reactive medium shortens setting times and leads to more crystalline reactions products, such zeolites.

These authors [12] conclude from the findings in NMR results for different AAFA that the formation of an aluminium-rich aluminosilicate gel (Gel 1) in the first stage is favor (Gel 1), which evolves to a Sirich gel (Gel 2) (See Fig. 7)

2.3.3 The role of sodium in N-A-S-H gel

So far, we have seen that the role of alkali cations in the structure of hydrated aluminosilicate gels appears to be related to balancing the negative charge generated during the uptake of aluminuim tetrahedral units. Criado *et al* [17] studied the position of Na in the structure of the N-A-S-H gel (using ²³Na MAS-NMR studies) and observed a signal located around -10 ppm, which was attributed to the presence of partially hydrated sodium coordinated with the aluminium, replacing the silicon in a charge balancing arrangement.

However, Duxon *et al* [18] showed that sodium can neutralize the negative charge in two ways. This author observed two peaks on ²³Na MAS NMR for sodium aluminosilicates prepared with different Si/Al ratios. One at -4 ppm, which is attributed due to the sodium associated with aluminum inside the gel structure (compensation the deficit of charge) and the other one, at 0 ppm, appearing only in gels with Si/Al ratio lower than 1.40, which is associated with sodium present in solution that fills the pores, where it neutralizes the charge on Al(OH)₄⁻ groups. Garcia-Lodeiro *et. al* [19] in a ²³Na MAS-NMR study over a huge range of N-A-S-H gels with different Si/Al ratios, only observed a single peal around -5 ppm, which was attributed to partially hydrated sodium compensating the deficit of charge generated by the substitution of Si⁴⁺ per Al³⁺ in the aluminosilicates network.

3 Conclusions

The alkali activation of fly ash provides an alternative way to the use of traditional OPC mortars and concretes. The reaction mechanism, as well as the type of the final product involve different processes than the formation of a C-S-H gel, even although the excellent results exhibit by these new systems suggest that this new generation of cements can be consider the cements of the future.

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Fig. 1 Scheme for the polymerization of silicic acid, base on the model proponed by ller [9]



Fig.2 (a) Scheme propose for the precipitation of N-A-S-H gel [11] (b) Structural model for the formation of N-A-S-H gel [12]





Fig. 3 Conceptual model for the mechanism involved in the AAFA (based on SEM results)

Fig. 4 N-A-S-H gel structure



N-A-S-H gel structure (3D)

Fig. 5 (a) 29 Si-NMR (b) 27 Al-NMR spectra for synthetic N-A-S-H gels . Chemical shifts for the different Qⁿ environments



Fig. 6 ²⁹Si MAS-NMR spectra (a) Alkaline activators (A, B, C with SiO₂/Na₂O ratios of 0.17, 0.60 and 1.90 respectively) (b) products formed over time for AAFA



Fig. 7 Conceptual model of N-A-S-H gels precipitated at different stages of reaction

