# Alkaline activation, procedure for transforming fly ash into new materials. Part I: Applications

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ABSTRACT

Alkaline activation is a chemical process in which a powdery aluminosilicate such as a fly ash is mixed with an alkaline activator to produce a paste capable of setting and hardening within a reasonably short period of time. The strength, shrinkage, acid and fire resistance of the resulting materials depend on the nature of the aluminosilicate used and the activation process variables.

The alkaline activation of fly ash is consequently of great interest in the context of new and environmentally friendly binders with properties similar to or that improve on the characteristics of conventional materials.

This paper briefly discusses a number of new applications for alkaline activated fly ash: i) in the precast industry for the manufacture of railway sleepers; (ii) for the production of lightweight materials; and (iii) as protective coatings on non-fire-resistant materials.

## 1.- **Introduction**

The literature on alkali-activated systems has been growing steadily since the nineteen fifties, but the considerable store of information now available is not easily assimilated. The results have often been interpreted rather empirically, sometimes with scant justification, while commercial interests have on occasion imposed restrictions on their dissemination. While fundamental studies have naturally been published, the comparison of findings is often hindered by differences in the experimental approach adopted by one or another research group. A more consistent picture of the chemistry underlying phase development and product performance has begun to develop only recently. In this context, the Spanish group authoring this paper (Eduardo Torroja Institute – CSIC -) has accumulated considerable experience with these alkali-activated systems over the last 20 years and has contributed to the growing body of literature on the systematic characterisation of the chemical fundamentals of these cements [**1-5**].

The reaction of a solid aluminosilicate with a highly concentrated aqueous alkali hydroxide or silicate solution produces a synthetic alkaline aluminosilicate material [4-**7**]. The processing of these materials, which may perform comparably to traditional cementitious binders in a range of applications, emits significantly less greenhouse gas than Portland cement manufacture [**8**]. Depending on the raw materials and processing conditions used, alkali-activated binders may feature high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity. These binders should not, obviously, be regarded to be a panacea for all material selection problems, but rather a solution that, with a suitable mix and processing design, may be tailored to optimise the properties and/or reduce the costs of a given application. This article addresses several aspects of the intrinsic structure and properties of these binders (inorganic polymers) and a number of possible applications. Images of the microstructure of alkali-activated fly ash (AAFA) produced in media with different alkalinities (a NaOH solution and a NaOH + sodium silicate solution mix) are reproduced in Figure 1.

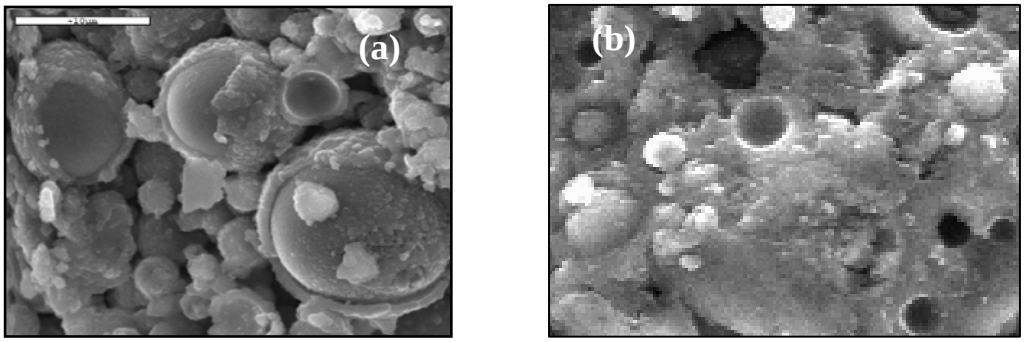


**Figure 1.** Fly ash activated with (a) 8-M NaOH solution; (b) NaOH + sodium silicate solution mix

### 1.1.- Background

In the nineteen fifties Glukhovsky [**9**] proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina. The Glukhovsky model divides the process into three stages: (a) destruction-coagulation; (b) coagulation-condensation; and (c) condensation-crystallization. More recently, several authors have elaborated on and extended Glukhovsky's theories and drawn from the body of knowledge on zeolite synthesis to explain the geopolymerisation process as a whole [**10-14**].

A highly simplified diagram of the reaction mechanism in alkaline activation processes [**14,15**] is shown in Figure 2 [**15**], which outlines the key processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate (N-A-S-H) gel.

For the sake of simplicity, the figure does not show the grinding or heating of raw materials required to vary the reactivity of aluminium in the system.

Though presented linearly, these processes essentially occur concurrently. The dissolution of the solid aluminosilicate source by alkaline hydrolysis (consuming water) yields aluminate and

silicate species. Aluminosilicate dissolution and weathering, on which an immense volume of data is available, constitute a field of scientific endeavour in themselves **[5, 16-18]** and are consequently not reviewed in detail here. The surface dissolution of solid particles and the concomitant release of (very likely monomeric) alumina and silica into the solution have always been assumed to be the mechanism responsible for the conversion of the solid particles during alkaline activation. The scientific consensus existing around this assumption, deduced from the literature describing alkaline dissolution, determined its inclusion in Figure 2. That notwithstanding, the actual processes taking place in particle-to-gel conversion in the highly alkaline and poorly solvated conditions prevailing during AAFA synthesis have never been confirmed.

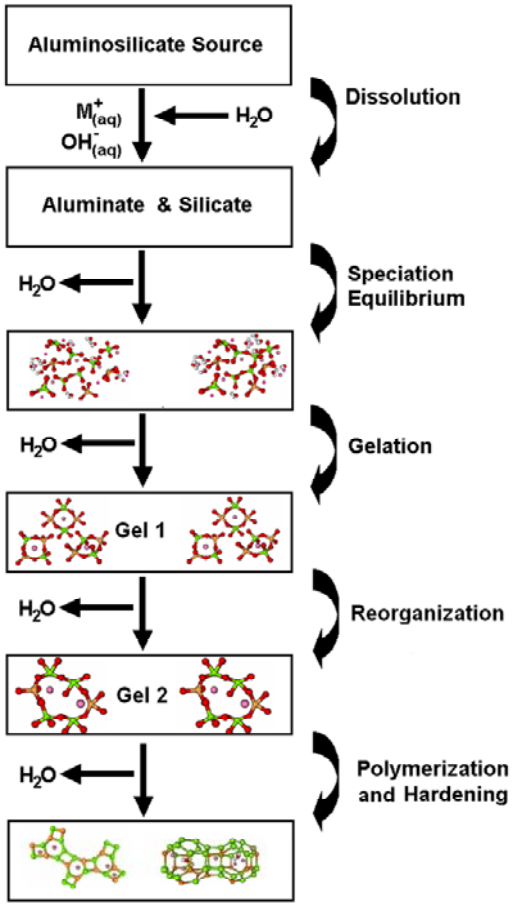


**Figure 2**. Conceptual model for Alkaline Activation Processes.

Once dissolved, the species released are taken up into the aqueous phase, which may contain silica, a compound present in the activating solution. A complex mix of silicate, aluminate and aluminosilicate species is thereby formed, whose equilibrium in these solutions has been studied extensively [**5, 16-18**]. Amorphous aluminosilicates dissolve rapidly at high pH, quickly generating a supersaturated aluminosilicate solution. In concentrated solutions this leads to the formation of a gel as the oligomers in the aqueous phase condense into large networks. This process releases the water that was nominally consumed during dissolution. Water, then, plays the role of a reaction medium while nonetheless residing inside the gel pores. This type of gel structure is commonly referred to as biphasic, the two phases being the aluminosilicate binder and water.

The time required for the supersaturated aluminosilicate solution to form a continuous gel varies considerably, depending on raw material processing conditions, solution composition and synthesis conditions [19-23]. Some, typically dilute, systems in fact never gel. Under such conditions, the concentration of dissolved silicon and aluminium is observed to oscillate due to the slow response in systems that are nowhere near equilibrium. After the gel forms, rearrangement and reorganisation continue in the system as intra-connectivity increases in the gel network. The end result is the three-dimensional aluminosilicate network commonly attributed to N-A-S-H gels. This is depicted in Figure 2 in the form of multiple ‘gel’ stages, consistent with recent experimental observations [5,14,15] and numerical modelling for fly ash-based materials. Figure 2 describes the activation reaction as the outcome of two successive, process-controlling stages.

The first, nucleation or dissolution of the fly ash and the formation of polymeric species, is highly dependent on thermodynamic and kinetic parameters and encompasses the first two steps proposed by Glukhovsky. Growth is the stage during which the nuclei reach a critical size and crystals begin to develop. These structural reorganisation processes determine the microstructure and pore distribution of the material, which are critical to determining many physical properties [5,23].

### 1.2. Applications for alkali-activated fly ash

An in-depth understanding of the mechanisms that govern the formation of cementitious products during the alkali activation of fly ash is an obvious pre-requisite to establishing the inter-relationships between starting composition, curing conditions, nanostructure and properties. The knowledge accumulated in this regard to date has made it possible to tailor the composition of the alkaline activator and the curing conditions to the features sought in the end product. The most recent research findings have confirmed the following.

- Concretes made with these materials can be designed to reach compressive strength values of over 40 MPa after short thermal curing times [**24**].
- Concrete made with alkali-activated fly ash (with no OPC) performs as well as traditional concrete and even better in some respects, exhibiting less shrinkage and a stronger bond between the matrix and the reinforcing steel [**24-26**].
- In addition to its excellent mechanical properties, the activated fly ash is particularly durable and highly resistant to aggressive acids, the aggregate-alkali reaction and fire [**27-31**].
- This family of materials fixes toxic and hazardous substances very effectively [**32-36**].

The present paper focuses on three possible applications for alkali-activated fly ash in the production of materials with special properties, namely:

1- monoblock railway sleepers
2- lightweight matrices in place of traditional cores in sandwich panels
3- fire-resistant coating.

In all these applications, the materials generated by the alkaline activation of fly ash constitute a single family of composite materials with characteristics attributable to cement, fired clay and zeolites (such as rapid mechanical strength development, fire resistance, dimensional stability, acid resistance and excellent bonding to reinforcing steel).

## 2. Prestressed sleepers made with the long line method

The proposed use of alkali-activated fly ash concrete as the binder in the manufacture of railway sleepers is based on the considerations set out below.

i) Concrete railway sleepers are elements of a “manageable” size but extraordinarily complex, technologically speaking. Their design and production require materials that ensure strength, durability, good bonding to the reinforcement and volume stability. Activated fly ash concrete meets all these requirements.

ii) Conventional precasting processes usually call for accelerated thermal curing of the concrete. Optimal alkaline activation of fly ash is attained under similar thermal curing conditions. Consequently, production processes need not be substantially altered to accommodate the change from one prime material (Portland cement) to others (fly ash and alkaline activators).

iii) In prestressed elements, the steel reinforcement is prestressed before the concrete is cast in the mould. Given that alkali-activated fly ash concretes can develop very high early age strength (in the first 12-20 hours) and bond well to the reinforcement, the time the concrete must remain in the mould can be shortened. That, in turn, would lead to a significant rise in plant productivity.

iv) The difficulties encountered in attaining acceptable quality and durability in conventional concrete products subjected to accelerated curing cannot be readily surmounted today. The difficulty lies in the fact that the measures recommended in codes of good practice (such as the limitation of curing temperatures to 60 ºC or the use of aggregate that remains inert at high temperatures) are normally insufficient and nearly always incompatible or scantly reconcilable with mass production. The use of activated ash could change the present scenario radically. Alkaline concrete made from activated ash can be expected to be highly durable, given its chemical-mineralogical similarity to certain natural and extraordinarily stable zeolites.

Finally, the economic and ecological issues involved also merit attention. Fly ash (which is being proposed as a total substitute for Portland cement in concrete manufacture) is an industrial by-product widely available on all six inhabited continents. It is generally found in stockpiles that occupy broad expanses of land because this waste is non-consumable.

### *2.1. Industrial trials for producing OPC-free railway sleepers*

Three preliminary trials were initially conducted at the plant. In each, two prestressed monoblock sleepers were made with activated fly ash concrete. A homogeneous mix was prepared in a small (125-litre) concrete mixer with materials dosed per cubic metre as shown in Table 1.

Table 1. **Concrete dosage** used to manufacture the sleepers

| **Material ($m^3$)** | **FIRST TEST SPECIMENS** | **SECOND TEST SPECIMENS** | **THIRD TEST SPECIMENS** |
|---|---|---|---|
| **FLY ASH** | 465 Kg | 465 Kg. | 465 Kg. |
| **SILICA SAND** | 825 Kg | 825 Kg | 825 Kg |
| **AGGREGATE** | 1050 Kg | 1050 Kg | 1050 Kg |
| **ACTIVATOR** | NaOH [$Na_2O$]=8,7% | NaOH +W<br>[$Na_2O$]=16.0%<br>[$SiO_2$] =2.5% | NaOH +W<br>[$Na_2O$]=18.0%<br>[$SiO_2$] =2.0% |
| **LIQ/SOLID RATIO** | 0.37 | 0.50 | 0.52 |
| **CURING COND.** | 20 h, 85 ºC | 20 h, 85 ºC | 10 h, 110 ºC |

The specimens made for the first trial were kept in a mould at a temperature of 85 to 90 ºC for 20 hours. In the second trial, the activating solution was modified to improve the mechanical

properties of the material. The third and last trial aimed to optimise concrete batching (further to the findings for the two previous trials) and curing conditions. To this end, the alkali activator concentrations were again modified and the flow of steam was changed slightly to raise the curing temperature to 110-115 ºC. The curing time was shortened to 10 hours.

Fifteen-centimetre cubic moulds were filled with the same concrete used to prepare the sleepers and cured under the same conditions to determine the mechanical strength of the material (see Figure 3).

The findings for these concretes, studied with a view to the manufacture of railway sleepers, showed that the material obtained developed high mechanical strength in a relatively short period of time (30 MPa after 6 hours at 95 ºC and 40 MPa after 10 hours at 115 ºC). Hence, as in Portland cement, curing temperature played a significant role in the results, although its effects differed, for the durability of this new cementitious material was unaffected by alterations in temperature. This constitutes an additional advantage to alkali-activated fly ash concretes from the perspective of standardised manufacturing and potentially higher productivity.

Another aspect that merits attention is the possibility of producing different qualities of concrete (measured in terms of mechanical strength, for instance) by modifying conditions such as the nature of the alkali activator used. Activators containing a certain amount of soluble silica are able to improve ash reactivity or even stimulate the formation of a more polymerized (silica-rich) and consequently more compact and mechanically stronger final product. This finding is of particular importance, for it means that materials, prices and other factors can be adapted to the needs of the precasting industry.

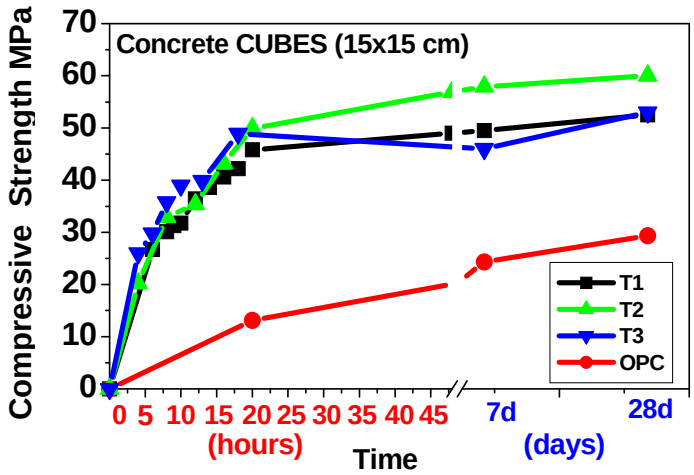


**Figure 3.** Mechanical strength of concrete specimens found in trials 1, 2 and 3.

Finally, attention should be drawn to the adaptability of the material to the existing industrial facilities (the railroad sleepers studied were manufactured without significantly changing the conventional process). Moreover, this new material was used in sleeper manufacture because of

the improvements afforded in product performance. Shrinkage, for instance, was negligible compared to the values recorded in Portland cement concrete, while an exceptionally good bond formed between de new material and the prestressed steel. While concrete sleepers made with Portland cement fail under a load of 46 tonnes (equivalent to a strength of 80 MPa in cubic specimens), these activated fly ash concrete sleepers withstood loads of up to 50 MPa.

Figure 4 shows photographs of industrial scale monoblock railway sleeper manufacture using the trial 3 dosage (see Table 1). The railway sleepers were manufactured with no need to significantly alter the manufacturing stream in place at the plant. The most notable change affected curing temperature, raised from 50 to 85-90 ºC, which entailed building a pressurised steam injection tunnel (see Figure 4).

**Figure. 4.** Photographs of the industrial scale manufacture of monoblock railway sleepers with (OPC-free) alkali-activated fly ash concrete

The sleepers were subjected to the mandatory static and dynamic tests. The values obtained met both Spanish and European code requirements. The ***static test*** consisted of applying a static load to the section studied to determine the load at first cracking. The ***dynamic test*** consisted of applying a steadily rising pulsating load to simulate exceptional impact and determine, as in the static test, the loads under which characteristic cracking appeared. The findings are given in Table 2.

**Table 2.** Results for monoblock railway sleepers made with Portland cement-free, alkali-activated fly ash concretes

| | | Code value | | AAFA sleeper |
|---|---|---|---|---|
| | | **RENFE*** | **UIC**** | |
| **Static test** | **1st crack** | 13 t | 15 t | 42.57 t |
| | **Failure** | 28.6 t | 33 t | 59.47 t |
| **Dynamic test** | **1st crack > 0.05 mm** | 195 kN | 228 kN | 350 kN |
| | **Failure** | 286 kN | 334 kN | 390 kN |

* Spanish national railway system
** International Union of Railways

## 3. Manufacture of lightweight matrices in place of traditional cores in sandwich panels

All materials play an important role in construction today. Hence the future of the construction industry is highly conditioned by the development of new materials and the use of new construction methods, as well as by the application of building codes with increasingly demanding structural safety, fire protection, and acoustic and thermal insulation provisions. All the foregoing calls for properties very difficult to obtain with conventional metals, fired clay products, polymers and concrete.

The development of composites or materials containing a combination of different types of elements, and consequently exhibiting the full range of their respective properties, has acquired considerable importance in recent years in an attempt to meet these new needs.

Generally speaking, a composite is defined to be a multi-phase material that conserves a significant portion of the properties of its constituent phases, which are combined as optimally as possible. Further to the principle of combined action, the properties sought are best obtained when a composite containing two or more materials is designed on the grounds of the scientific information available.

Most composites comprise two phases, a continuous matrix and a disperse phase that surrounds or envelops the matrix.

Sandwich panels are presently manufactured for any number of applications. As a rule, they provide acoustic and thermal insulation. The success of these panels can be attributed primarily to the following properties:

- high bearing capacity, light weight
- excellent and durable thermal insulation
- good heat and humidity barrier
- excellent water repellence
- weather- and aggressive environment-resistant skins
- rapid installation with no need for complex hoisting equipment
- economical production
- fire resistance in panels with mineral wool cores.

Standard sandwich panels are three-layered (as shown in Figure 5). The rigid surfaces (skins), which have a fairly high modulus of elasticity, are held apart by a thick, lightweight core with sufficient bending stiffness to withstand most stress. The core also serves as thermal insulation. Each component is relatively weak and flexible taken by itself, but the combined panel comprises a rigid, strong, lightweight structure.

A number of materials may be used for the skin: fibreglass- and carbon fibre-reinforced epoxy resin (the resins are usually unsaturated polyesters and vinyl esters). Other materials commonly used include wood, unreinforced polymers and metal (normally galvanised sheet steel and aluminium or, for specific purposes, copper). The surface elements range from 0.25 to 12.7 mm thick.

The core has two structural functions. First, it separates the two skins and resists deformation perpendicular to the plane of these two surfaces. And second, it affords some degree of shear strength along the planes perpendicular to the skin.

The core may consist of either organic or inorganic materials. The organic materials most often used include rigid expanded polyurethane and extruded polystyrene. The drawback to both these materials is that they generate toxic fumes when ignited. Organic matrices cannot therefore generally be used for applications in which temperatures of over 200 ºC are reached.

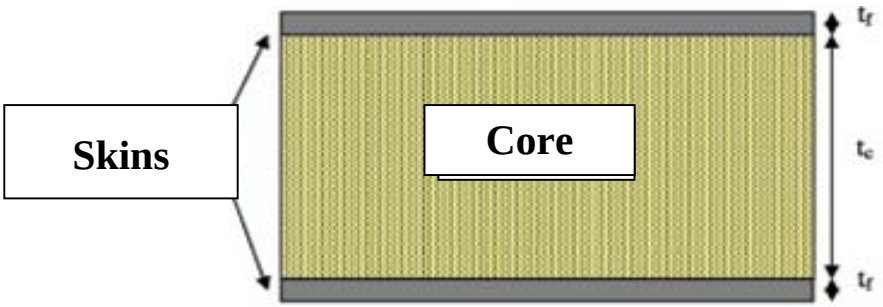


***Figure 5.*** *Sandwich panel*

The most common inorganic cores include mineral wool and fibreglass, both of which are non-flammable and chemically inert. The drawback is that they cannot withstand loads. Other possible materials include synthetic rubber and cement.

The present study explored the possibility of manufacturing these cores with alkali-activated fly ash, using a series of air-entraining admixtures to lower the density of this material. The procedure followed is described below.

Three air-entraining admixtures, A, B and C, were initially tested at a dosage of 1 %wt. In all three cases the activating solution used was an 8-M NaOH (85 %wt) and Wg (15 %wt) mix, denominated N8W15. The pastes were mixed with the air-entraining product and poured into a mould holding three 4x4x216-cm prismatic specimens. The material was subsequently cured in a kiln for 20 hours at 85 ºC and very high humidity. After removal from the mould the next day, the specimens were tested for density and mechanical strength.

Admixture A led to segregation, i.e., it generated porosity on the surface only, and was consequently ruled out. Admixture B yielded a material with a density of 1 000 kg/m$^3$ and compressive strength values of 7.2±2.7 MPa (see Table 3). This admixture reacted very rapidly with the paste, however, reducing its workability and causing homogenisation problems. The material obtained with admixture C, by contrast, had evenly distributed pores, a density of 603.5 kg/m$^3$ and a compressive strength of 2.0±0.11 MPa.

**Table 3.** Lightweight materials

| Admixture A | Admixture B | Admixture C |
|---|---|---|
| | | |
| Segregation<br>Surface porosity<br>Poor homogenisation | Very rapid, uncontrolled reaction<br>Homogenisation problems | Reaction after 1 hour<br>Evenly distributed pores |

Manufacture of large (40 x 40 x 6-cm) core panels was undertaken with admixture C. Here also the paste was poured into a mould and cured in a kiln at 85 ºC for 1 hour. When a suitable consistency was reached, it was floated and returned to the kiln for a further 19 hours. Figure 6 depicts the mould used and the material generated.

**Figure 6.** Moulds and physical appearance of the panels manufactured

Subsequent studies were conducted to optimise the percentage of sodium silicate added to the alkaline solution and the dosage of air-entraining admixture. The 40x40x6-cm panels, obtained with solution DW15 [10-M NaOH (85 %) + waterglass (15 %)] and 1.2 % (by fly ash mass) admixture, exhibited a density of ≈400-450 kg/m$^3$ and compressive strength of ≈2 MPa.

***4- Development of a fire-resistant cover***

The primary purpose in studying this final application was to establish the fundamentals for developing a series of new alkali-activated fly ash-based inorganic materials usable as a fire-resistant coating for fibreglass or carbon fibre matrices.

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Despite their lower density, sheets of fibreglass- or carbon fibre-reinforced polymeric resin can develop strength similar to the values characteristic of steel. The main drawback to such materials is their low resistance to high temperatures and their combustibility when directly

exposed to a flame. The data in Table 4 show that fibreglass and carbon fibre deteriorate after 8 to 20 seconds of direct exposure to a flame.

The interaction between fire and these materials can be essentially described in terms of the following two factors.
***Reaction to fire*** is the relative capacity of materials to favour the initiation or propagation of a fire, i.e., their contribution to fire as laid down in the existing legislation [to determine a material's reaction to fire, its ignitability is tested "by direct impingement of flame"]. The procedure consists of holding the sample in a vertical position in a Bunsen burner flame (Spanish, European and international standard UNE-EN-ISO 11925-2).
***Fire resistance*** (or fire rating) is the capacity of a material to retain its bearing capacity, integrity and stability for a given amount of time (property generally required of structural members).

These two factors (**reaction to fire** and **fire resistance**) should always be considered separately, because a product that reacts well to fire may not be fire-resistant. This is the case of self-extinguishing products, for instance (inasmuch as they generate no flame they meet reaction to fire requirements, but since they are deteriorated and consumed in the process, they fail to remain intact long enough to comply with fire resistance provisions).

In the present study, these glass or carbon fibre-reinforced resin specimens were coated with an alkali-activated fly ash slurry prepared with different alkaline activators in the presence or absence of filler. The effect of the thickness of the layer of slurry was also studied.

These materials were exposed directly to flame as specified in standard UNE-EN-ISO 11925-2: the coated samples were placed underneath an extractor hood and held with tongs in a vertical position in contact with a Bunsen burner flame.

The main findings are summarised in Table 4.

-***Material 1*** was a carbon fibre-reinforced resin coated with a 6-M NaOH-activated fly ash slurry**.** The photography in Table 4 shows the specimen after the test, which lasted 8 minutes. At longer times, the sample first began to smell and then to smoke profusely, but the flame was not propagated.

***Material 2*** was a carbon fibre-reinforced resin coated with a layer of slurry consisting of 80 % FA + 20 % cement + solution DW15. In this case the test time was shorter, just 4 minutes, and concluded when the sample began to smoke and give off an unpleasant odour due to the decomposition of the substrate. The area exposed to the flame cracked profusely, but the flame was not propagated.

-***Material 3*** was coated with 80 % fly ash + 10 % OPC + 10 % filler + activator. In this case the small proportion of filler added to the mix lengthened fire resistance considerably, from 4 to 40 minutes where the resin was slurry-coated. The coating was 3 to 5 mm thick. The flame was not propagated to the rest of the specimen in this case either.

In light of the results of the third test, where a thicker layer improved fire resistance substantially, the other materials were also tested to determine whether several layers of slurry would enhance fire resistance. This hypothesis was not confirmed, however, very likely because applying more than one layer of paste to the substrate greatly reduced bonding effectiveness.

**Table 4**. Fire protection tests

| Material | Exposure time | Results | Material | Exposure time | Results |
|---|---|---|---|---|---|
| Fibreglass + epoxy resin | 8 seg. | | FA | 8 min. | |
| Carbon fibre + epoxy resin | 20 seg. | | FA + 20C | 4 min. | |
| | | | FA + 10C+ 10Filler | 40 min. | |

This study showed that the improvements achieved with an alkali-activated fly ash or alkaline inorganic polymer coating included the following.

-The primary advantage obtained with the use of this type of coating is non-propagation of the flame.
-The resin ignites where the flame is applied but the flame is not propagated upward. The flame disappears when the resin is consumed.
-The most promising results were obtained with material 3, probably because the presence of a filler afforded a better bond between the slurry and the substrate, while also lowering the internal stress in the slurry itself.

**Acknowledgments**

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