Use of zeolitised fly ashes in fire resistant plates

Carlos Leiva[1], Luis F. Vilches[1], Xavier Querol[2], Jose Vale[1]. and Constantino Fernández Pereira[1]*

1) University of Seville, School of Industrial Engineering, Department of Chemical and Environmental Engineering, Camino de los Descubrimientos s/n E-41092, Seville, Spain.
2) Institute of Earth Sciences “Jaume Almera”, CSIC, c/ Lluis Solé Sabaris, s/n 08028, Barcelona, Spain
[*]Corresponding author. Tel.:+34-954487271; fax: +34-9554461775. E-mail address: pereira@esi.us.es

Abstract

In this study, the application of some zeolitised fly ashes to make insulating plates with fire-resistant properties by means of simple, low-cost molding and curing methods has been analyzed. The plates, with a weight composition of 60% zeolitised fly ashes, 30% gypsum 9.5% vermiculite and 0.5% glass fiber, present a great capacity for water retention and, consequently, when they were subjected to fire tests, showed excellent insulating properties, better than those shown by other tested commercial products (gypsum). Mechanical properties with regard to compressive and bending strength have been measured and an environmental study was carried out. The plates developed with zeolitised fly ashes could potentially be useful as a component in construction materials for passive fire protection in doors and firewalls for buildings and industrial installations.

Keywords: zeolitised fly ashes, fire resistance, plates

1. Introduction

Synthetic zeolites may be obtained from coal fly ashes. Many patents and technical papers have proposed different hydrothermal activation methods to synthesize zeolites from fly ashes (ZFA). All the methods developed are based on the dissolution of aluminum–silicate phases from coal fly ashes in an alkaline solution (mainly NaOH and KOH solutions) and the subsequent precipitation of the zeolitic material [1], in which large cavities and channels exist where water molecules and cations can be absorbed. This property explains the high capacity of cationic exchange and hydration of zeolites.

The classic alkaline conversion of fly ash implies the attack of the ash with an alkaline solution using a determined activation solution/fly ash ratio, with alkali concentration, temperature, and reaction time to obtain different zeolite species. The zeolite contents of the resulting material varied widely depending mainly on the activation solution/fly ash ratio and the reaction time.

Zeolites are crystalline aluminum-silicates, containing group I or II elements as counterions of the negative charge of the aluminate group. Their structure is made up of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked to each other at the corners by sharing their oxygens[2].

As a consequence of their peculiar structural properties, zeolites have a wide range of industrial applications [3]. Thus, for example zeolites have been applied as a mineral admixture in concrete production for more of ten years in China [4]. In a related line, other application of zeolites could be as principal component of fire resistance plates used for buildings and other constructions due to their water storage properties [5].

Fire resistance is the property of a material or an assembly to withstand fire or give protection from it. Some of the commercial products used for thermal insulation or passive fire protection in buildings and industrial installations have a chemical composition and chemical properties similar to those found in some ash- and slag-based products. The results of previous studies of our research group [6-9] most of them on ash products conformed as plates support this fact.

In the present study, plates made using simple methods and comprised mainly of ZFA were subjected to different thermal and mechanical tests with the aim of analyzing their fire-resistance behavior, and their mechanical properties.

2. Materials and methods

2.1 Materials

For this study, fly ashes from the combustion of coal in Narcea Power Plant in the North of Spain (FA) were used. The chemical and mineralogical composition of ash is shown in Table 1. The fly ash is a conventional class-F (ASTM) ash showing a relative low mullite level.

Parameter	%	Parameter	%
Loss on ignition	3.5	Mullite	3.8
CaO	4.2	Quartz	6.6
MgO	2.7	Cristobalite	<0.3
Fe_2O_3	7.0	Anhydrite	0.2
Al_2O_3	23.0	Calcite	<0.3
SiO_2	54.3	Lime	0.7
MnO	0.09	Hematite	<0.3
TiO_2	1.1	Magnetite	1.5
K_2O	3.9	Feldspar	0.2
Na_2O	0.8	Ettringite	<1.0
SO_3	0.2	Glass	87.0
P_2O_5	0.2		

Table 1. Major oxides and mineral content of the fly ash (wt%)

Conventional synthesis procedures—2 M NaOH for the activation solution, a solution/fly ash ratio of 2 $L \cdot kg^{-1}$, T=150ºC, and t=24 h—were used to obtain NaP1-rich products at pilot plant scale. Details of the methodology have been reported elsewhere [3]. The content of NaP1 zeolite in the ZFA has been 55%.

Gypsum (G) was used as the binder for the pastes. Glass fiber 2-4 cm long and 20-50 microns in diameter was used to improve the mechanical resistance to bending and fissuring in the mortar.

Vermiculite (V), a component usually added to mortars used for fire protection[6], was also used as an additive. Vermiculite is a hydrated silicate comprising magnesium, aluminum and iron that has a flaky structure. The vermiculite used in this study is a commercial product (VERLITE), having 84.9% of particles with a diameter below 1.41 mm-size.

2.2 Plate preparation

Our goal was to come up with a product comprised mainly of zeolitised fly ashes. The final composition of the plates was obtained using an optimization process in which two main objectives were taken into account: (1) an improvement in the insulating properties and (2) the need for certain minimal mechanical properties, defined by what the products were ultimately expected to be used for. In order to compare the insulating and mechanical properties of the ZFA plates, fly ash (FA) and commercial gypsum (G) plates have been manufactured.

The composition of the plates is shown in Table 2.

Plate	ZFA	FA	G	V	G-F	Water/solids Ratio
ZFA-P	60	-	30	9.5	0.5	0.7
FA-P	-	60	30	9.5	0.5	0.4
G-P	-	-	100	-	-	0.4

Table 2. Composition (wt%) of the plates

The solid components shown in the above table were placed in a planetary mixer and were mixed until a homogeneous mixture was achieved. Then water was added to the mixture and again was mixed until a homogeneous paste was obtained. Table 2 shows that ZFA plates need more water due to the high absorption capacity of the zeolites.

The paste obtained was placed in moulds 2 cm thick, 28 cm high and 18 cm wide to be conformed as a plate (Figure 1). The plates were taken out of the moulds after 24 hours and left to cure at ambient temperature for more than 28 days (average temperature: 20ºC; average relative humidity: 45%). The plates were used to make test pieces of different shapes and sizes which were used in the mechanical tests.

Figure 1. Plate for fire resistance test

2.3 Insulating properties

The standard fire-resistance test described in Spanish regulation EN-UNE 1363-1[10], which is similar to other widely-used international standards, has been used. To simulate the conditions of exposure to fire, the regulation requires that one of the sides of the protective material be exposed to heat according to a standard temperature curve defined by the equation: $T=20 + 345\cdot\log_{10}(8t+1)$, where T is the oven temperature for the tests in °C and t is the time in minutes from the beginning of the test.

To study the insulating capacity of the plates, a special oven was used so that the molded plates could be subjected to the standard fire resistance test mentioned above. This furnace allowed us to record the surface temperature of the exposed surface (hot surface, T_{in}) of the plate by means of an S-type thermocouple inside the oven, which was used to regulate the temperature of the oven by means of a proportional controller in order to produce the standard temperature curve. On the unexposed surface (cold surface, T_{out}), the temperature was registered by means of a Pt-100 probe with a stainless steel contact surface[7].

In order to analyze the insulating capacity of the plates in a way similar to that recommended by the Spanish standards, the time necessary for T_{out} to reach 180ºC (t_{180}) has been considered as a reference value for studying this property.

2.4 Physicochemical and mechanical properties

With the aim of characterizing the physical and mechanical properties of the product, the following tests were carried out:

2.4.1. Thermogravimetry

Samples of 300-400 mg for the thermogravimetric measurements (TG-SDTA) were taken from the surface of the test plates. A heating rate of 10°C/min was chosen, using N_2 as the purging gas.

2.4.2 Bending and compressive strength

The compressive (Rc) and bending (Rf) strength of the samples were also evaluated using a compressing test machine (Suzpecar, MEM-102/ 50 t)[11, 12]. The compressive strength tests were performed on 40-mm-high, 35-mm-diameter cylinders and the bending strength tests were done on 14-cm-high test probes with a 4 x 4 cm base.

2.4.3 Surface hardness

The potential applications of the plates in construction materials which might be subject to impact, caused us to analyze the surface hardness (D) of the material[13]. The principle of the method described in the regulations is related to the resistance given by the plate to the penetration of a Shore C durometer. The test was carried out twice on 2-cm-thick plates with a surface area of 28 x 18 cm.

2.4.4 pH

The pH was measured according to European standards[13]. A sample of 2 g was taken from the plate and was put into contact with 20 g of water. After 5 minutes, the pH of the solution was measured.

2.5. Environmental study

Given that ZFA, the main component of the product, has not been highly studied, an environmental study has been carried out to characterize the ash more completely in order to better evaluate its possible uses. The study involved subjecting the ash to the UNE-EN-12457 test[14]. Metal analysis in UNE-EN leachates was carried out using Inductively Coupled Plasma techniques.

3. Results and discussion

3.1. Physicochemical properties

The density of the ZFA-P plate (672 kg/m^3) falls within the density interval for low density boards [15] (600 - 800 kg/m^3), and is very low if it is compared with the density of FA-P and G-P plates (895 and 1510 kg /m^3 respectively). The TG-SDTA results for the ZFA-P are plotted in Figure 2. As the figure shows, the weight loss of the product up to approximately 250ºC (point A) is 12.5%, due to the evaporation of the free water and the chemically bounded water of gypsum and ZFA, as evidenced by the endothermic response of the SDTA curve from room temperature to 250°C. From 250°C to 650°C (point B) the curve is almost constant, the mass loss (2%) being due to the evaporation of the adsorbed water in the vermiculite[6]. From 650ºC in advance the mass loss is probably due to transformations undergone by some ZFA phases and the combustion of the unburned matter of the fly ashes [16].

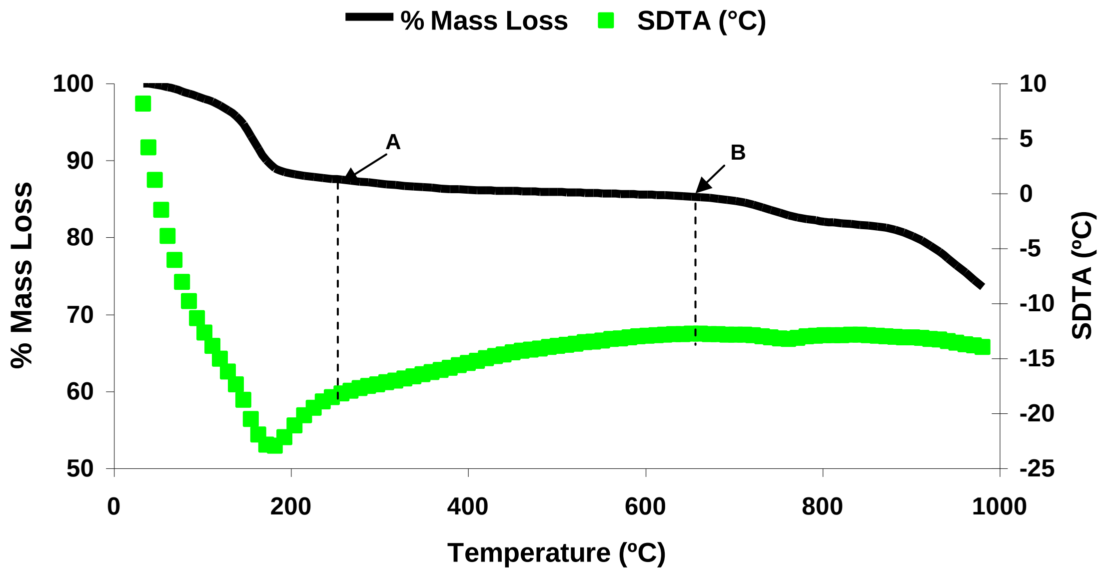

Figure 2. TG and SDTA curves of the ZFA-P

From the acid-base point of view, the ZFA-P can be classified as a normal board (pH value between 8.5 and 10) as the measurement gave a pH value of 9.7[13].

3.2 Insulating capacity of the plates

The insulating capacity of the plates were calculated by measuring the time necessary for the unexposed side to reach a temperature of 180°C (t_{180}) when the exposed side is subjected to the standard fire-resistance temperature. Figure 3 shows the results obtained with 20 mm-thick plates.

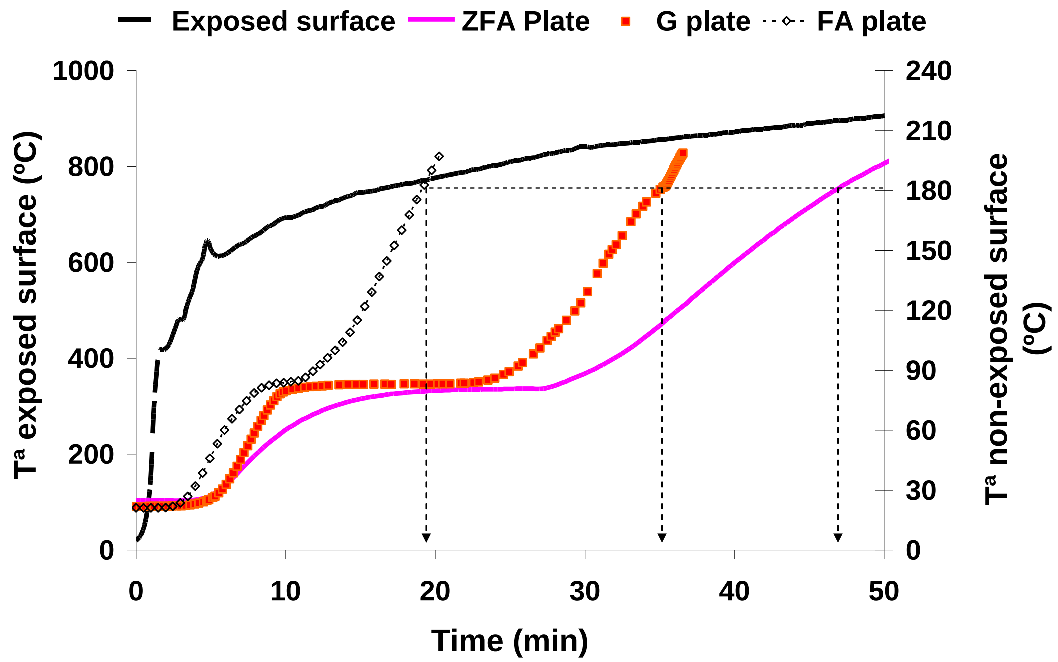

Figure 3. Fire test of the plates

The figure shows the insulation capacity of the product, with t_{180} values of over 46 min for thicknesses of 20 mm in the case of ZFA-P. This result is considerably better than that obtained for G-P (35.4 min), using the same test. The insulating capacity of the ZFA plates is higher than that presented by plates of the same dimensions, made with the same proportions studied here using coal fly ash (19.5 min) or biomass fly ash [17], instead of the zeolitised ash. This result implies that the zeolitisation of the fly ashes is the responsible for the increased insulating capacity. The developed product has a high capacity for water retention, supplied by some components of the ZFA, like NaP1. It also should be pointed out that no smoke was emitted from the plates at any time during the test.

3.3 Mechanical properties

Though the mechanical characteristics demanded for plates used in passive protection against fire are minimal, some properties have been studied to better characterize the product and also because mechanical properties are important in regard to the manufacturing process.

Table 3 shows the mechanical properties determined. As can be seen, the mechanical quality of the material is rather poor when is compared with that of similar products[15].

Parameter	Value
Rc	0.29 MPa
Rf	0.82 MPa
D	16 Shore C

Table 3. Mechanical properties of the plates

Thus, the Rc value of ZFA-P is very low when is compared with that of gypsum plates (14.12 MPa). The compressive strength of ZFA-P is also lower than that of FA-P (0.81 MPa).

Likewise, the Rf value obtained is a low value if it is compared with that of G-P (4.5 MPa), but is similar to the bending strength of FA-P plates (0.81 MPa). As expected, the contribution of the glass fiber had a very positive effect on the resistance to bending values.

The hardness of the material is also significantly lower than that of G-P (53 Shore C) and FA-P (26 Shore C) plates. After the thermal test, there was a clear decrease in the D value of the exposed side of the ZFA-P plates (6 Shore C units), while on the unexposed side the decrease was less pronounced (14 Shore C units).

3.4. Environmental study

In Spain there is no national legal implemented requirement for the re-use of waste materials in these types of products. Only some regional regulations exist for some combustion residues (some types of slag) used in other kind of applications.

As there is no much information on the environmental impact of materials as ZFA, a leachability study was carried out using the UNE-EN-12457 leaching test to compare the leachate concentrations with the limits stated by the EU waste landfill directive (EULFD)[18] in which three waste categories are defined, when waste landfill is considered: inert, non-hazardous and hazardous, depending on the concentration values of different parameters in an aqueous waste leachate. The leaching limit values shown in Table 4 apply for granular (not monolithic) waste acceptable at landfills for inert, non-hazardous and hazardous waste, calculated at a liquid to solid ratio of 10 L/kg for total release.

As can be seen, in no cases do the metals analyzed exceed the established limits for hazardous wastes, and only As goes beyond the limit for non-hazardous wastes. Besides As, the limits for inert wastes are exceeded by, Cr and Mo.

EULFD (mg/kg, dm)				
Element	**Inert Waste**	**Non-hazardous Waste**	**Hazardous Waste**	**ZFA**
As	0.5	2	25	24
Ba	20	100	300	<0.01
Cd	0.04	1	5	<0.03
Cr (total)	0.5	10	70	7.1
Cu	2	50	100	<0.03
Hg	0.01	0.2	2	<0.3
Mo	0.5	10	30	2.7
Ni	0.4	10	40	<0.1
Pb	0.5	10	50	<0.3
Sb	0.06	0.7	5	<0.2
Se	0.1	0.5	7	<0.4
Zn	4	50	200	0.7

Table 4. UNE-EN12457 leachability of ZFA. Criteria for waste acceptance at landfills for different wastes according to the EULFD

4. Conclusions

Although further research and development of the concept is still necessary, the insulating and mechanical properties of the product described in this paper form a good technological foundation for the manufacture of a fire-resistant product comprised mainly of zeolitised fly ashes that is beneficial both from technical and environmental standpoints.

The plates show a very good fire resistance, even better than other typical materials used in passive fire protection, like gypsum plasterboards. However, the mechanical properties of the plate are not good, so that it is necessary to improve them. Some ideas in regard to this include using other additives or decreasing the percentage of the zeolites in the product.

Not great environmental problems are expected for the plates, according to the leachability study carried out for the zeolitised ashes. Besides, from the environmental point of view it is necessary to remember that the potential uses of the plates in different constructive elements implies the need for the final product to be covered or protected by some material, at the very least a layer of some special paint. In that way, the plates will neither undergo direct contact with people nor exposure to the elements outdoors, and the risks associated with their use will be minimal.

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