

Insulating capacity of fly ash pastes used for passive protection against fire

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Abstract

This study deals with the possibilities of recycling different combustion sub-products into usable products for passive protection against fire. We studied conventional combustion fly ashes from different types of pulverized coal in thermal power plants, which have a long tradition of applicability in construction, and ashes from new energy production processes based on other fuels, such as biomass, in an effort to find new applications for them. In order to be able to carry out this study, we developed a methodology that allows us to (1) predict the insulating behaviour of pastes comprising ashes, binders and other additives, (2) know what contributions each of the components makes and (3) considerably reduce the time required to test potential products with fire-resistant properties.

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1. Introduction

Within any residue management strategy, recycling is an economically attractive option when there are large amounts of residue that can be recovered in specific applications with a high added value and, at the same time, a reduction in the cost of the residue management and dumping.

Fly ashes (FA) from the combustion or gasification of coal or biomass, are residues that have some physico-chemical properties that make them very attractive for their use as basic components of recycled materials with insulating properties. In this regard, our group previously studied the properties of products made up of coal combustion fly ashes (class F, according to ASTM regulations) and other residues [1–3] with a

view toward their possible use in the elaboration of insulating and fire-resistant products that might be used in passive protection against fire.

There are many particular characteristics of ashes and slags that can significantly affect the properties of the insulating materials made with these sub-products. Among them, the following are worth noting: the chemical composition, pozzolanic activity, grain-size distribution, morphology and mineralogy.

Passive protection against fire can be understood as a set of well-thought-out construction measures that are taken in order to lessen the possibility of a fire starting, prevent it from spreading and ensure the stability of a building until the fire is under control or has been put out. In the field of passive fire protection, compartmentalization consists of establishing physical limits for a certain space so that a fire can be contained within it. Creating fire resistant divisions or partitions allows us to set up an effective barrier between the fire and the elements we want to protect, thus preventing the fire from

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spreading to other areas. Among the most widely-adopted solutions for protection are fire doors and screens using plates or panels.

For the manufacture of the fireproof core of fire resistant doors and screens, insulating and fire-resistant materials with different characteristics are usually used, including a large number of materials comprised of insulators based on different silicic compounds, e.g. fly ashes, which can be reinforced by fibres and different absorbent additives that yield high porosity and good thermal stability at high temperatures.

When the surface of a porous medium with a water content in its different forms (free, adsorbed, crystallized, etc.) is exposed to a real or simulated fire by means of exposure to a normalized temperature [4], part of the water evaporates, which generates overpressure in the pores of the material. Consequently, the evaporated water is transported from the exposed surface as a result of a pressure gradient to the interior of the material, which is cooler, and the water condenses again. A liquid film is thus formed which is progressively displaced toward the unexposed part. Thus, the water content of the material causes an evaporation plateau to appear at around 100 °C in the temperature profile of the unexposed side (temperature vs. time) since the pressure gradients do not significantly influence the saturation pressure of the liquid water in the interphase [5]. This phenomenon is represented in Fig. 1 for an insulating plate.

Due to current and future use of coal and different forms of biomass and to the foreseeable development of biomass as a source of energy through combustion or gasification, in the immediate future it will be necessary to progress in technological advances that will allow for a massive application of ashes and slags produced using the above-mentioned processes.

This study was done with the aim of developing a simple methodology for defining the possibilities for recycling the type of waste in question in applications with strict insulating requirements like passive protec-

tion against fire. The method allows us to analyze the insulating capacity of pastes comprised mainly of ashes or slags, by means of the correlation between the heat flow absorbed by the samples, measured using Differential Scanning Calorimetry (DSC), and the evaporation plateau interval for samples exposed to temperatures according to fire-resistance test regulations.

As Fig. 1 shows, the longer the evaporation plateau interval, the greater the insulating capacity—measured in time (generally expressed in minutes)—necessary for the material to reach a certain temperature indicated in the fire-resistance regulations [4]. The methodology developed in this study is intended to yield a first optimization of the insulating capacity of these products by studying the contribution of different components of the products to that capacity.

To sum up, with the proposed method we hope to reduce the time necessary for experimentation by selecting pastes that are promising with respect to their insulating properties and rejecting those that are not, thus avoiding the long process of test piece preparation, setting and curing and the carrying out of the fire-resistance test.

2. Experimental

Materials and test methods are examined in the following Section 2.1 and 2.2 respectively.

2.1. Material

The products dealt with in this study are made up of three types of material:

- Ashes from coal and biomass combustion, coal-biomass co-combustion and fuel gasification.
- Two binders (ordinary Portland cement and gypsum).
- Several water-absorbent additives.

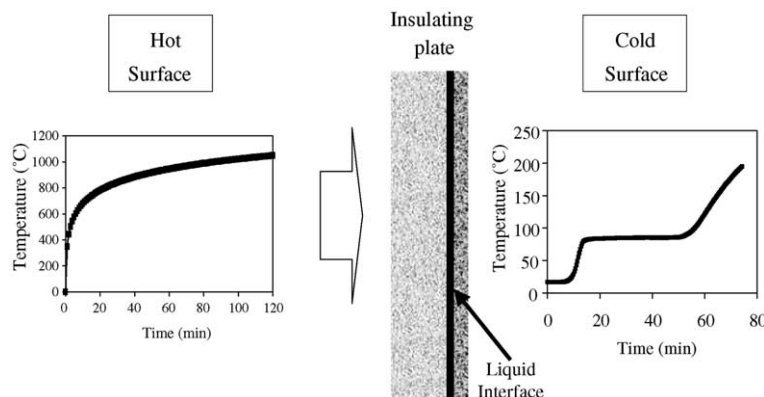


Fig. 1. Model of fire exposure in an insulating plate.

We used ashes produced by different fuels in different processes and conditions of energy exploitation. We thus hoped to have at our disposal ashes with very different chemical, pozzolanic, morphological and mineralogical properties in order to use the proposed methodology to evaluate a wide range of potential components.

All the pastes tested were made up of more than 70 wt% of ashes and the rest of the components were binders and additives, except in the samples containing rice husk, which had a lower percentage of ashes, and in the binder blanks. The additives used comprised certain silicates and other hydroabsorbent chemicals, which increase the insulating capacity and contribute to a greater mechanical resistance in the products manufactured. Table 1 shows where the ashes came from and which binders and types of additives were used.

The ashes, binders and additives were mixed with the water in a planetary mixer until a paste was obtained. In all of the cases, the water was added at a water-(ash + binder) ratio of 0.4 and during the mixing the additives were included in different proportions, depending on the ash + binder mass. After mixing, the mortars were left to set for 28 days at room temperature; the samples were taken out of the moulds two days after their preparation. The weight composition of the different pastes tested is shown in Table 2.

2.2. Test methods

The pastes corresponding to the compositions described above underwent different thermal and mechanical tests. A diagram of the experimental set-up for the measurement of the insulating capacity is shown in Fig. 2. 200-mm-high, 50-mm-diameter cylinders were placed in an oven and subjected to a heating program that provides a fire resistance temperature curve in accordance with that indicated by Spanish regulations, and which corresponds to the expression:

$$T = 20 + 345 \cdot \log(8t + 1) \quad (1)$$

where T represents the temperature in °C and t the time in minutes.

Table 2
Composition (wt%) of the pastes

Sample	Ash	Binder	Additive
1/B1	80	20	–
1/B1/A1	75	12	13
1/B2	80	20	–
1/B2/A1	75	18	7
1/B2/A2	74	18	8
1/B2/A3	74	18	8
1/B2/A4	73	18	9
2/B2	80	20	–
3/B2	80	20	–
4/B1	80	20	–
4/B2	80	20	–
5/B2 (1)	5	95	–
5/B2 (2)	40	60	–
4/5/B2	75/5	20	–
6/B2	80	20	–
7/B1	80	20	–
B2	–	100	–
B2/A2	–	90	10

In order to measure the temperature in the centre of the cylinder (T_{in}), a 3 mm-diameter type K thermocouple was used (Fig. 2 shows the sample set). A ceramic type S thermocouple whose diameter was 3.5 mm was used to measure the temperature outside the cylinder (T_{out}). The thermocouples were connected to a data acquisition system that registers both temperatures. The cylinders were insulated at their bases by means of a ceramic, 0.2 W/m · K (at 1000 °C) conductivity fibre, so only a symmetric heat flow of radial component would be expected.

With the aim of measuring the energy absorbed by the test probes, we used the differential scanning calorimetry (DSC) technique. Thus, 5-mm-diameter, 3-mm-thick samples placed in non-hermetic aluminium containers, were subjected to a heating program of 2 °C/min in a TA DSC 2920 Instrument, from 30 °C to 400 °C, using nitrogen as purging gas.

3. Results and discussion

To describe the methodology employed, Fig. 3 shows the temperature profile obtained using the gypsum

Table 1
Materials used: ashes, binders and additives

Ash origin		Binders		Additives	
1	Pulverised coal combustion in Power Station 1	B1	Portland cement	A1	Magnesium-based hydroabsorbent
2	Pulverised coal combustion in Power Station 2	B2	Gypsum	A2	Hydrated ferromagnesian aluminium silicate (Granulometry 1)
3	Pulverised coal combustion in Power Station 3			A3	Hydrated ferromagnesian aluminium silicate (Granulometry 2)
4	Olive oil pomace combustion in a fixed grate furnace			A4	Silica-based hydroabsorbent
5	Rice husk combustion in a fixed grate furnace				
6	Coal-olive oil pomace co-combustion in a fixed grate furnace				
7	Coal and petroleum coke gasification in an IGCC plant				

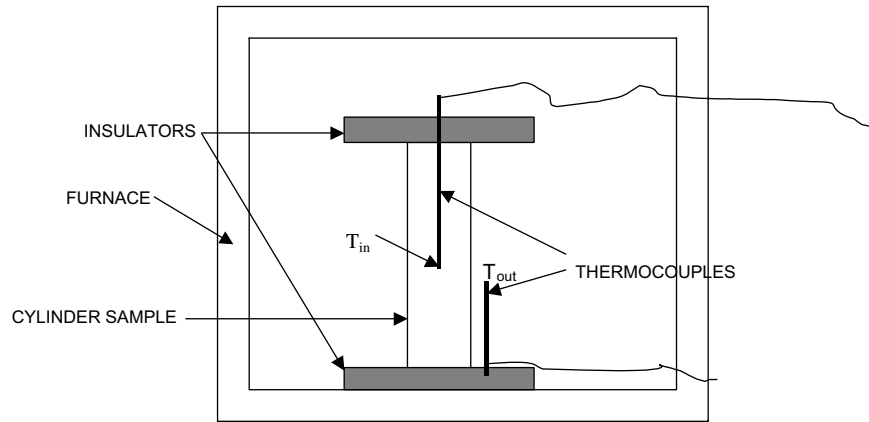


Fig. 2. Experimental set-up for fire resistance test.

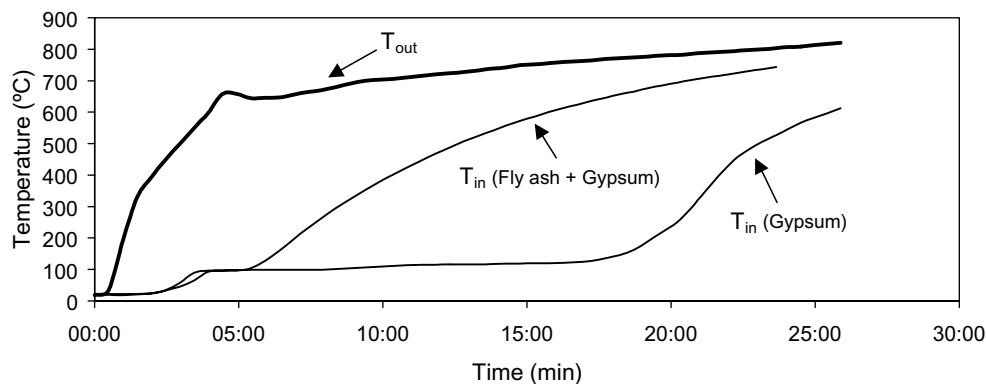


Fig. 3. Fire-resistance test results of some test probes.

cylinders (B2) and those made of gypsum and coal combustion fly ashes (1/B2), when the different cylinders tested were exposed to temperatures stipulated in the fire-resistance test regulations. If we measure the insulating capacity according to the time it takes the interior of the cylinder to reach a certain temperature (e.g. 400 °C) [4], we see the influence of the slopes of the curves, before and after the evaporation plateau, which are associated with the thermal diffusivity values of the material when wet and when dry. But, as we can see, the parameter that has the greatest effect is the evaporation plateau interval, which is influenced by the type of ash, the binder used and, of course, the addition of water absorbent additives, all of which justifies studies on how to optimize the mixtures, such as the one carried out here.

Fig. 4 shows the results obtained in the DSC tests for the previous pastes (B2 and 1/B2). We can see how the absorption of energy by the pastes responds to the content and the chemical form in which water is present in them. This is shown by different peaks between 60 and 200 °C.

Table 3 shows the values for the energy absorbed in the DSC test and the evaporation plateau interval for

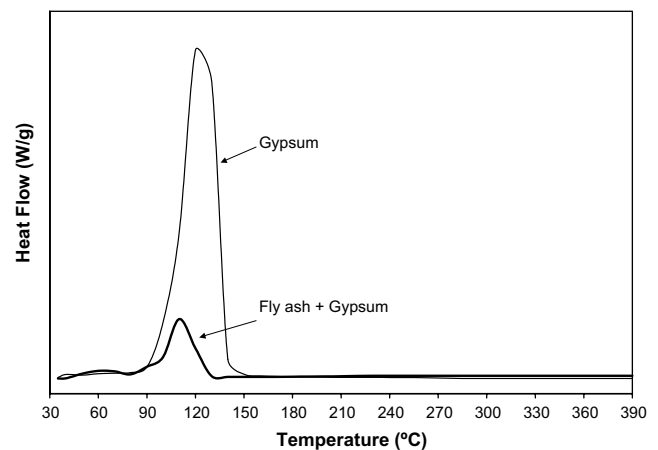


Fig. 4. DSC results of some pastes.

each of the compositions tested. The energy absorbed by the pastes in the DSC tests, E (in J/g), was obtained by integrating the area underneath the peaks (see Fig. 5), while the evaporation plateau interval was calculated, in accordance with the fire-resistance regulations [4], by measuring the time (T , in minutes) defined by the

Table 3

Energy absorbed in the DSC thermogram (E) and evaporation plateau intervals (T) of the pastes tested

Paste composition	E (J/g)	T (min)
1/B1	16.89	1.88
1/B1/A1	127.6	4.11
1/B2	76.62	2.82
1/B2/A1	105.9	4.08
1/B2/A2	89.2	3.70
1/B2/A3	44.85	3.15
1/B2/A4	15.79	1.85
2/B2	84.87	2.51
3/B2	68.9	2.08
4/B1	206.1	4.95
4/B2	250.8	8.15
5/B2 (1)	261.9	9.07
5/B2 (2)	184.9	7.20
4/5/B2	146.9	3.08
6/B2	165.5	6.55
7/B1	15.13	0.58
B2	468.7	12.47
B2/A2	301.3	8.85

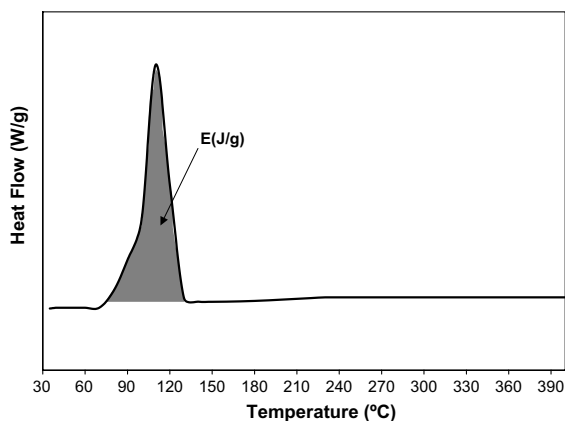


Fig. 5. Measurement of the energy absorbed in the DSC thermogram.

intersections of lines $t_{60} - t_{80}$ and $t_{200} - t_{115}$ with the horizontal line of 100 °C (see Fig. 6).

In order to demonstrate that the proposed methodology is good, we studied the relationship between the energy absorbed by the cylinders (E) and the evaporation plateau interval (T). When T is represented against E , an excellent linear correlation is obtained which has a correlation index of $R^2 = 0.9279$, for 18 samples analyzed, as is shown in Fig. 7.

In view of the good results obtained with regard to the insulating capacity of the different pastes studied, the potential of the methodology presented as a tool for prediction should be emphasized. The influence of the type of ash can be clearly observed; of all the ashes tested, those from olive oil pomace combustion in a fixed grate furnace had a particularly high insulating capacity. Also, this study shows that all the mortars made with coal combustion ashes from different power stations present very similar insulating properties when

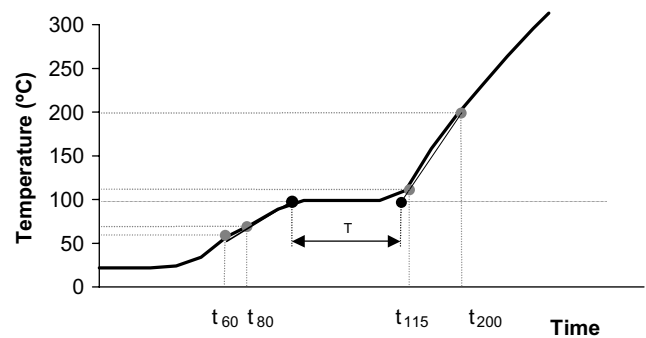


Fig. 6. Measurement of the evaporation plateau interval.

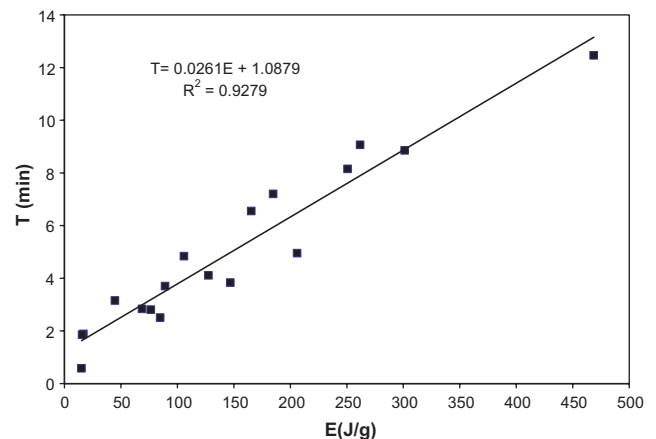


Fig. 7. Relationship between the DSC energy values and the evaporation plateau intervals.

used with the same binder. Furthermore, the use of gypsum instead of Portland cement is seen to increase the insulating capacity, probably as a consequence of the hydration water contributed by the calcium sulphate. Finally, replacing part of the ash in the pastes with the different additives tested may have a negative effect on the insulating properties of the pastes.

4. Conclusions

The possibilities of recycling different types of fly ashes in materials used for passive protection against fire, which have been demonstrated in previous papers, are clear and have once again been confirmed by this study. Furthermore, through the use of simple thermal analysis techniques, such as DSC, this study yields access to a methodology that translates into a considerable reduction in experimental effort with respect to analyzing the recycling of different types of ash in this field. Thus, we were able to analyze some of the new types of ashes that are being generated in the EU from the biomass combustion, coal-biomass co-combustion and biomass gasification. Likewise, with the methodology developed here, we can easily quantify the influence that the different

types of ashes and the other components have on the insulating capacity of the products that contain them and optimize the composition of the mixtures. Thus, for example, we can study the role of different water-absorbent additives used to achieve an increase in the evaporation plateau that these materials generate when they undergo the fire-resistance tests and, consequently, improve the insulating properties of the product.

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