Influence of the Type of Ash on the Insulating Capacity of Fly Ash Mortars Used for Passive Protection against Fire

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1.INTRODUCTION

The protection of the environment should be promoted by the recovery (reuse or recycling) of waste materials. In many cases, recycled materials must compete with low-cost products. However, when the properties of the waste make its use possible in specific, high added value applications, these products can successfully compete with products made from primary materials, and reduce the environmental costs of waste disposal.

Fly ash from the combustion of coal in power plants and biomass combustion ash have physical and chemical properties which make them suitable, in principle, for recycling as insulating materials.

The quantity of coal ash annually produced worldwide in large power stations probably exceeds 550 Mt[1]. On average, about 50% of these residues are utilized (with large variation from country to country) as additives in cement and concrete production or in civil construction. Thus, these by-products (coal combustion by-products; CCBs) can be either a valuable resource or a troublesome waste material incurring significant disposal costs.

This study continues along the lines of other studies by this research group[2, 3] to search for new ways of re-using coal combustion fly ashes, as well as other types, in manufacturing new insulating and fire-retardant products for use in fireproof doors and firewalls.

Throughout the project that this study forms a part of, we have studied different fly ashes from the combustion of pulverized coals from several Spanish power plants, biomass combustion ashes and co-combustion ashes. Ash and slag from the gasification of coal and biomass have also been tested. So far no big differences in behaviour between mortars prepared in identical conditions using different coal fly ashes have been found; thus, in this article, we show the results obtained using two types of ashes that show extreme behaviours: a high-silica ash, representative of the

combustion of high-quality pulverized coal from a power station, and the ash obtained from the combustion of the solid waste from the manufacture of olive oil.

The water content of the products developed in this study is very important given that this is what produces the formation of an evaporation plateau of about 373 K on the side not exposed to the fire as a result of an evaporation/condensation front that runs through the material, from the exposed side at high temperatures toward the cold, unexposed area; this provides the material with greater resistance to fire.

The aim of this article is to demonstrate the influence of the ash type and of certain additives with a high water content on the insulating capacity of certain mortars composed mainly (> 70 wt%) of ashes from coal and biomass combustion with a view toward their possible use in fireproof doors and firewalls.

At the same time, we aim to find a methodology that allows us to correlate the data from the fire-resistance tests as defined in this article to the thermal behavior of the material observed using differential scanning calorimetry techniques.

2.EXPERIMENTAL

2.1 MATERIAL

2.1.1. ASHES

In this study two types of ashes were used: Fly ashes (FA) from the combustion of a Colombian coal in the Los Barrios power station (Cadiz, Spain), a conventional class-F (ASTM) ash; and ash from the combustion of the residual biomass present in the waste from the olive oil extraction process (BFA) at a Spanish olive oil company (Aceites Pina, S.A., Cordoba, Spain). The chemical composition of both types of ashes is shown in Table 1.

We used Portland Cement (OPC) and gypsum (G) as the binders for the mortars.

Parameter	FA(%)	BFA (%)
Moisture		6.1
Loss on ignition	3.5	21.7
CaO	8.38	8.78
MgO	1.86	4.01
Fe_2O_3	2.39	1.07
Al_2O_3	34.4	0.51
SiO_2	45.3	12.73
MnO_2	0.05	
TiO_2	1.4	
K_2O	0.57	32.04
Na_2O	0.4	0.81
SO_3	0.46	

Table 1. Chemical composition of the ashes tested.

2.1.2 ADDITIVES

We studied exfoliated vermiculite and $MgCl_2.6H_2O$ as additives. Vermiculite is a hydrated silicate comprising magnesium, aluminium and iron and it has a flaky structure. As previous papers by this research group[2, 3] mention, vermiculite is usually added to mortars used for fire protection. The vermiculite used in this study is a commercial vermiculite and we studied the influence of its particle size. To do so, we used both unground vermiculite (VER2, 84.9% > 1.41 mm) and finely ground vermiculite (VER1 100% < 1.05 mm, sieved).

There are various applications for magnesium compounds with regard to fire retardant materials. Magnesium oxychloride cement (Sorel cement) is an aerogel material whose main crystal phase is $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$. Because of its light weight, strength, quick hardening, fire resistance and easy processing, Sorel cement has great potential in the field of prefabricated fire-resistant products.

Other magnesium-containing elements of passive protection against fire that do not contain magnesium oxychloride cement are described in the bibliography. A blend containing MgO and fly ash has been used for lightweight partition wallboard[4]. Also a fire resistant cement blend containing alumina cement, fly ash, perlite, $Mg(OH)_2$ and methylcellulose has been patented to be used as fire resistant strong inorganic sheet material[5]. Magnesium hydroxide is a metal hydrate that decomposes endothermically, accompanied by the formation of water and for this reason is used as a flame retardant in polymeric products. Magnesium-containing foamed materials have also been described. A low cost foam material made of magnesium oxide, which also contains a magnesium chloride solution and a high proportion (80-20%) of powdered coal ash used as filler has been patented by Zhu et al[6].

The analysis of the decomposition process for magnesium chloride hexahydrate salt by heat is not completely defined; however, according to Esmail et al.[7], when the compound is subjected to high temperatures, three stages can be observed: first, water loss, which yields magnesium chloride dihydrate; second, its transformation into a monohydrate; and third, the decomposition of the monohydrate into magnesium oxide and hydrochloric acid.

2.1.3 BLENDS TESTED

The list of the compositions of the mortars tested is shown in Table 2.

The ashes and the binders were mixed with the water in a planetary mixer, in a proportion of 4 to 1. In all of the mixtures, the water-mortar proportion was kept constant and equal to 0.4 and during the mixing the additives were included in different proportions, depending on the mortar mass (ash+binder), which are shown in Table 2. After mixing, the mortars were left to set for 28 days at ambient temperature; the samples were taken out of the moulds two days after preparation.

2.2. TEST METHODS

The compositions described above underwent the following tests:

2.2.1. MEASUREMENT OF INSULATING CAPACITY

A diagram of the experimental set-up for the measurement of the insulating capacity is shown in Figure 1. 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 responds to the expression

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

where T represents the temperature in ºC and t represents the time in minutes.

Notation	Ash (wt% mortar)	Binder (wt% mortar)	Water (water/mortar)	Additive (additive/mortar)
M1	FA (80%)	OPC (20%)	0.4	-
M2	FA (80%)	G (20%)	0.4	-
M3	BFA (80%)	OPC (20%)	0.4	-
M4	BFA (80%)	G (20%)	0.4	-
M1-A1	FA (80%)	OPC (20%)	0.4	$MgCl_2.6H_2O$ (5/100)
M1-A2	FA (80 %)	OPC (20%)	0.4	$MgCl_2.6H_2O$ (10/100)
M1-A3	FA (80%)	OPC (20%)	0.4	$MgCl_2.6H_2O$ (12/100)
M2-B1	FA (80%)	G (20%)	0.4	VER1 (5/100)
M2-B2	FA (80%)	G (20%)	0.4	VER1 (7.5/100)
M2-B3	FA (80%)	G (20%)	0.4	VER1 (10/100)
M2-C1	FA (80%)	G (20%)	0.4	VER2 (7.5/100)

Table 2. Composition of the mortars tested

In order to measure the temperature in the center of the cylinder (T_{in}), a type K thermocouple 3 mm in diameter was used (the samples set with the thermocouple in the center of the cylinder). A ceramic type S thermocouple 3.5 mm in diameter 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 1000ºC) conductivity fiber, so only a symmetric heat flow of radial component would be possible.

In order to analyze the insulating capacity of mortars in a similar way to that presented in the Spanish standards regarding resistance to fire, we considered the time necessary for T_{in} to reach 400ºC, as well as the duration of the evaporation plateau mentioned above, as reference values for studying this property. The T_{in} = 400ºC criterion serves as a reference for the insulating properties of the ashes and binders and the duration of the evaporation plateau allows us to evaluate the contribution to insulation by the additive.

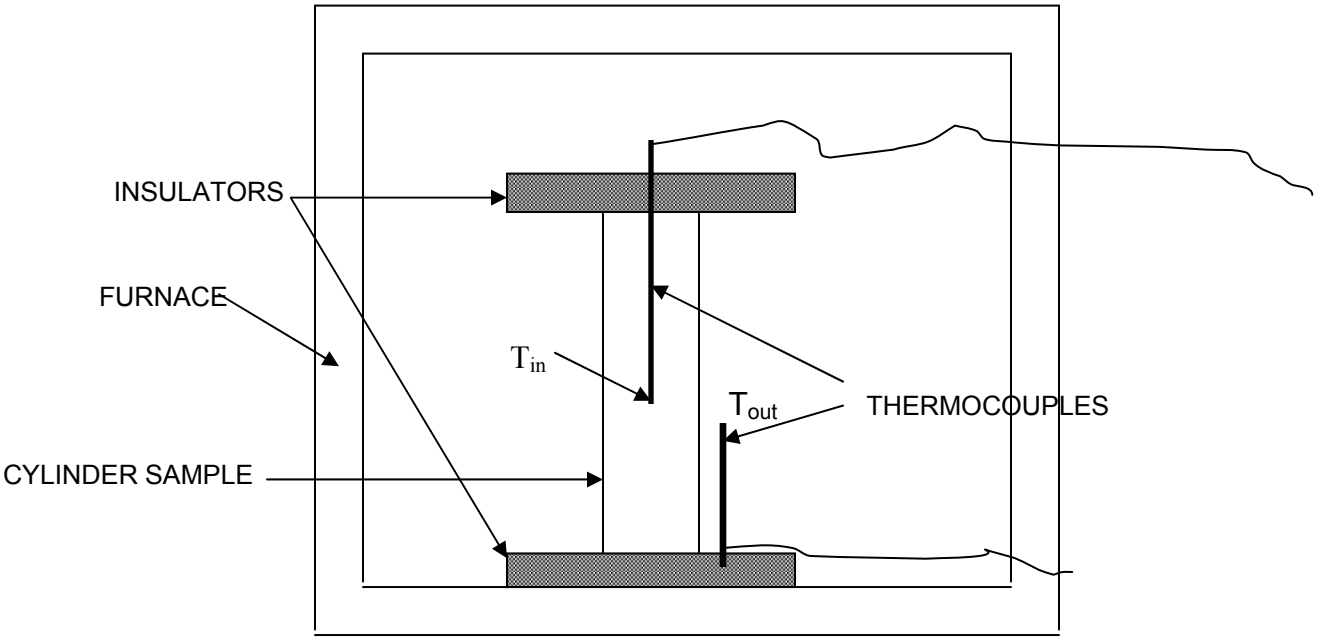

Figure 1. Experimental set up for fire resistance test.

At the same time, in order to optimize efforts in the study of the insulating behavior of types of ashes other than those used in this study, we analyzed the existence of a potential correlation between the insulating capacity and the energy absorbed by the mortars in samples on a small scale. We used the differential scanning calorimetry (DSC) technique to measure the energy absorbed. We used a TA DSC 2920 Instrument with 5-mm-diameter, 3-mm-thick samples placed in non-hermetic aluminum containers, which were subjected to a heating program of 2ºC / min from 30ºC to 400ºC, using nitrogen as a purging gas.

2.2.2 COMPRESSIVE STRENGTH

The compressive strength was measured according to the procedure indicated in the Spanish standards[9]. The compressive strength tests of the samples were performed on 40-mm-high, 35-mm-diameter cylinders with a compressing test machine (Suzpecar, MEM-102/ 50 t).

2.6. SETTING TIME

The setting time for the materials was determined according to Spanish standards[10] using a Vicat apparatus at ambient temperature. We used 35-mm-diameter, 40-mm-high cylinders to carry out these tests. The initial setting time (t_i) is when the Vicat

apparatus needle penetrates the sample to a point 5±1 mm from the base of the cylinder and the final setting time is the instant in which the Vicat needle gives no visible signal over the upper base of the cylinder.

3.RESULTS AND DISCUSSION

3.1. INFLUENCE OF ASH TYPE AND BINDER

3.1.1. INSULATING CAPACITY

Figure 2 shows the result of the insulating capacity of the mortars comprised exclusively of ashes and binders.

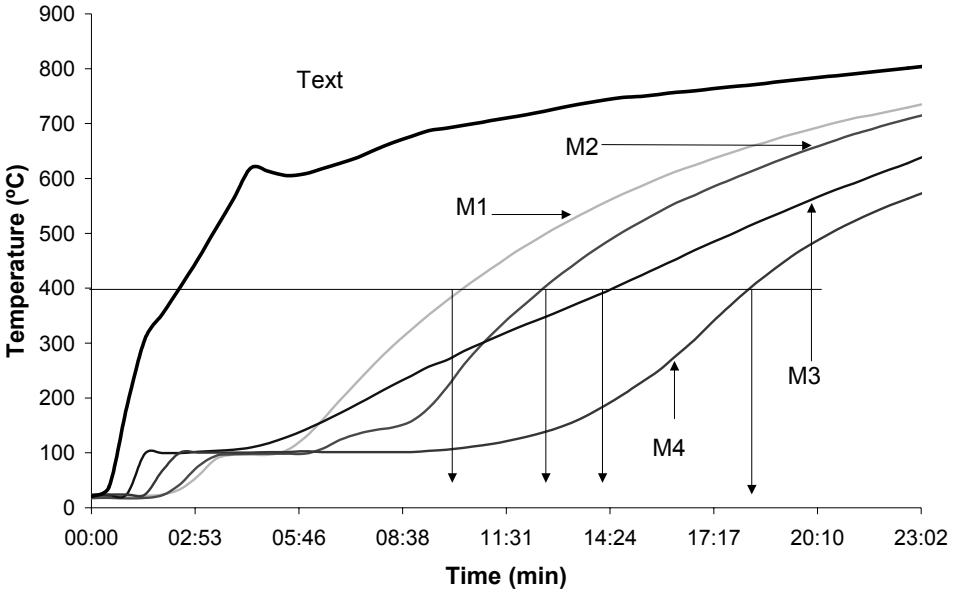

Figure 2. Measurement of insulating capacity.

As Figure 2 shows, the composition that presents the greatest insulating capacity is M4, due mainly to the duration of its evaporation plateau.

Likewise, Figure 3 shows the DSC carried out on each of the above-mentioned compositions. We can see the different endothermic reactions produced in these mortars. At about 75ºC we see the evaporation of the free water. Between 110 and 130ºC the water that is chemically bound evaporates; this occurs mainly in the mortars whose binder is gypsum ($CaSO_4.2H_2O$). The combination of these reactions yields the evaporation plateau in the tests when the insulating capacity is measured.

At the same time, from Figure 2 we can deduce that the insulating behavior of the BFA ashes is better than that of the FA ashes. We can also clearly observe that the duration of the evaporation plateau is influenced by the type of binder used. The materials with gypsum as a binder have a greater evaporation plateau because of the greater amount of water that gypsum contains in its composition.

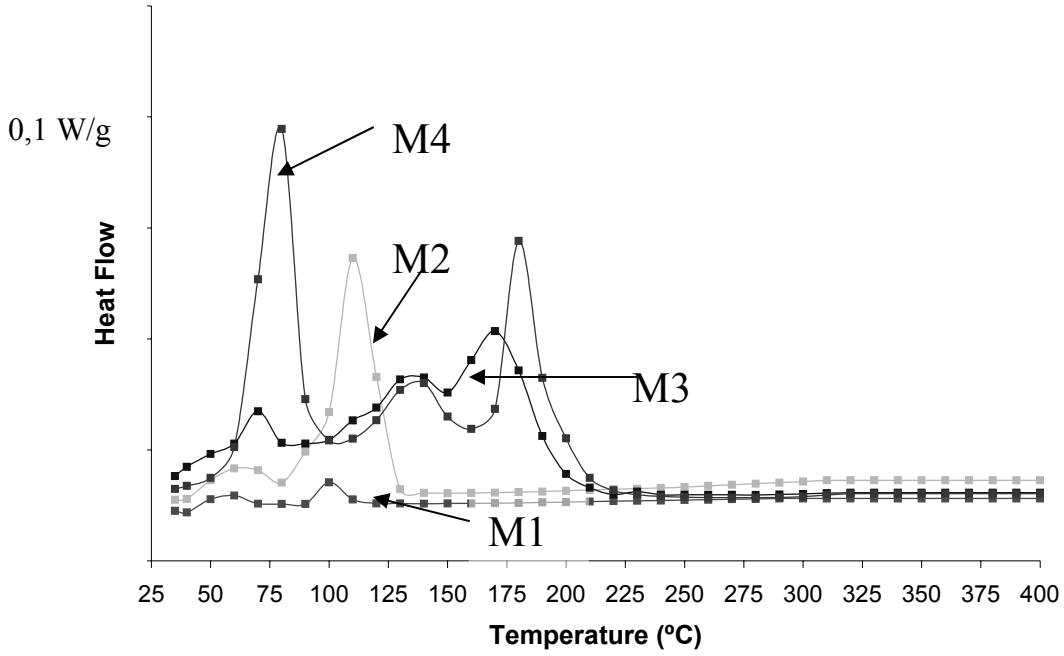

Figure 3. Heat flow of materials tested.

Table 3 shows the time (t_{400}), expressed in minutes, that it takes the inside of the cylinders (T_{in}) to reach 400ºC and the energy necessary to heat the sample from 30 to 400ºC (E). This latter value was calculated by integrating the curves obtained with the DSC between 30 and 400ºC (see Fig. 3). This value can be interpreted as an average heat capacity if it is divided by the temperature interval considered (370ºC).

Sample	M1	M2	M3	M4
t_{400} (min)	10:21	12:30	14:30	16:15
E (J/g)	344.8	476.0	547.2	587.0

Table 3. Time needed to reach 400ºC and energy employed to heat the sample, per unit of mortar mass

In the table above we can see the good correlation between the time needed to reach T_{in}= 400ºC and the energy absorbed per unit of mortar mass.

3.1.2 MECHANICAL PROPERTIES

Table 4 shows the values for the compressive strength of the mortars both before ($\sigma_c(0)$) and after ($\sigma_c(1)$) being subjected to the thermal test. As we can see, the use of OPC produces greater resistance than gypsum.

Furthermore, the mortars with BFA are more than twice as strong as the mortars comprised mainly of FA. This may be due, among other factors, to the greater density of the BFA mortars (1220-1370 kg/m^3) as compared to the FA mortars (1120-1170 kg/m^3).

SAMPLE	M1	M2	M3	M4
$\sigma_C(0)$ (MPa)	1.3	0.8	3.2	2.0
$\sigma_C(1)$ (MPa)	0.2	0.2	1.8	0.7

Table 4. Compressive strength (σ) of the mortars tested.

3.1.3. SETTING TIME

The setting time of the samples are given in the Table 5.

	M1	M2	M3	M4
t_i (hours)	1.2	0.3	5.0	4.41
t_f (hours)	19.3	2.2	41.7	38.3

Table 5. Setting time of mortars.

From the results, it can be seen that mortars containing gypsum require less setting time than those containing Portland cement. We can also see in Table 5 that the type of ash affects the setting time: biomass combustion ashes take longer to set.

3.2. EFFECT OF THE ADDITIVES

3.2.1 VERMICULITE

To study this additive we compared the behavior of mortar M2 without vermiculite to that of the same mortar after the addition of 7.5 g of vermiculite per each 100 g of mortar, and we used both ground and unground vermiculite. Figure 4 shows the measurements of the insulating capacity of the mortars tested.

Table 6 shows the different parameters measured in the mortars after the addition of vermiculite.

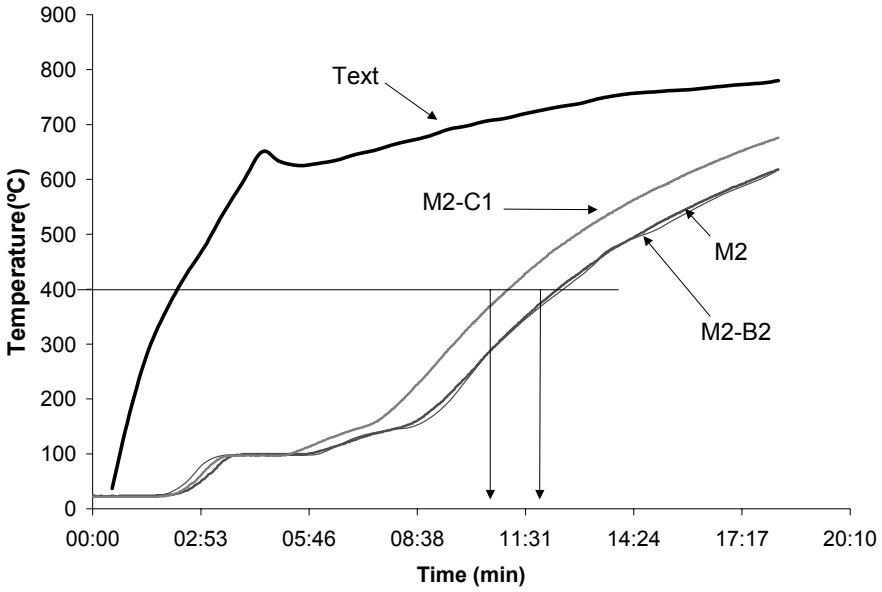

Figure 4. Measurement of the insulating capacity of mortars with vermiculite.

SAMPLE	M2	M2-B1	M2-B2	M2-B3	M2-C1
ADDITIVE	-	5/100 VER1	7,5 /100 VER1	10/100 VER1	7,5/100 VER2
t_{400} (min)	12:30	-	12:26	-	11:06
E (J/g)	476.0	473.6	480.3	492.2	421.4
$\sigma_c(0)$ (MPa)	0.8	0.9	2.0	1.8	1.6
$\sigma_c(1)$ (MPa)	0.2	0.4	0.3	0.1	0.2

Table 6. Properties of vermiculite mortars.

We can deduce from Figure 4 and Table 6 that the mortars with and without VER1 have a similar insulating capacity. However, the mortar with VER2 (unground vermiculite) has a slightly lower insulating capacity. This is probably due to the fact that the mortar is more porous, which allows the water that is retained in the mortar to evaporate with less energy, causing a shorter evaporation plateau.

The mechanical properties of the mortars with vermiculite are changed: their compressive strength is greater, especially in the case of VER1, which saw more than a 100% increase when vermiculite was added. However, a very great amount of VER1 seems to produce a decrease in the compressive strength, as occurred with M2-B3. The use of VER2 produces a mortar with a lower compressive strength than the corresponding mixture with VER1 in the same proportion, probably because the material is less dense and thus produces a more porous mortar. This creates preferential pathways for the breakage of the mortar and diminishes its compressive strength.

3.6.5.$MgCl_2.6H_2O$

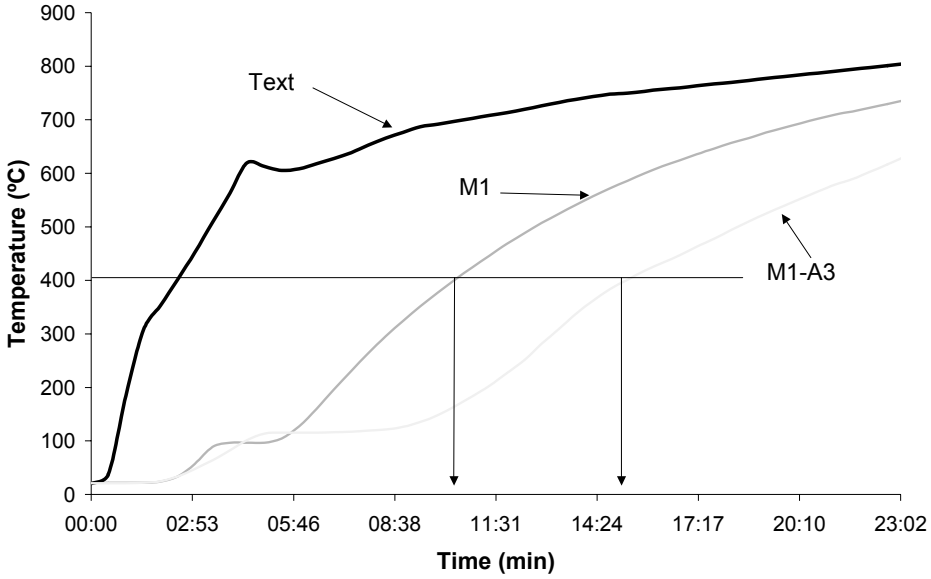

Figure 5. Measurement of the insulating capacity of mortars with $MgCl_2.6H_2O$

In studying this additive, we compared the change in the insulating capacity for mortar M1, with and without the additive. Figure 5 shows the results obtained for the insulating capacity of a mortar with the addition of $MgCl_2.6H_2O$, and we can see the great increase in the evaporation plateau.

SAMPLE	**M1**	**M1-A1**	**M1-A2**	**M1-A3**
ADDITIVE		5/100 $MgCl_2.6H_2O$	10/100 $MgCl_2.6H_2O$	12/100 $MgCl_2.6H_2O$
t_{400} (min)	12.5	-	-	13.45
E (J/g)	344.8	424.7	450.5	482.1
σ_c(0)(MPa)	1.3	1.0	0.9	0.6
σ_c(1)(MPa)	0.2	0.8	0.8	0.2

Table 7. Properties of mortars containing $MgCl_2.6H_2O$

Table 7 shows how the addition of $MgCl_2.6H_2O$ produces a considerable increase in the insulating capacity. We also see that, although this additive decreases the compressive strength, the resulting mechanical resistance is always adequate for the objectives of the product.

4. Conclusions

The conclusions that can be highlighted from this study are:

1. Mortars comprised mainly of BFA present a greater insulating capacity than those comprised mainly of FA when this property is measured in test conditions for fire resistance, probably as a consequence of greater water retention by the BFA ashes.

2. Mortars that use gypsum as a binder present a greater insulating capacity than those that have OPC as a binder as a result of the water content of gypsum.

3. There is a good linear correlation (R^2=0,95, for a number of samples equal to 7) between the insulating capacity of the mortars and the energy absorbed by small samples of the mortars in the DSC test. This methodology allows us to draw conclusions about the insulating capacity of other types of ashes. If this methodology is confirmed, it would allow is to save time and materials; we would be able to discard some ashes and other ingredients and would not have to prepare experiments on large test probes of mortar.

4. All of the mortars tested presented an acceptable compressive strength for the purposes of this product, though the mortars comprised of BFA presented greater compressive strength than those comprised of FA. What is more, the mortars that had OPC as the binding material presented greater compressive strengths than those that had gypsum as the binding material.

5. All of the mortars presented acceptable setting properties, though the use of BFA causes a considerable increase in the setting time.

6. The addition of additives seems to be a good way to improve the insulating capacity and the mechanical properties of the mortars tested.

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