

## Evaluation of Fly Ash Reactivity from Incineration of Hazardous Waste in Lime Pastes

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The annual global production of fly ash is estimated at about 780 million tons per year and has been used successfully in the cement industry for more than 50 years, mainly as a mineral additive in Portland cement and also as a component of mixed cement. In this work, the ash reactivity from hazardous waste as supplementary cement material was evaluated. For this, the ashes reactivity in lime pastes was analyzed, centered on thermogravimetric tests as a characterization technique to determine the phases present. Part of the ashes of hazardous waste was pretreated, in order to eliminate chlorides and sulfates from the incineration process. The ashes were characterized by means of DRX and FRX, finding low content of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the ashes of hazardous residues. The pastes were prepared according to the ASTM C-305 standard, using a water/lime ratio of 0.4. The hydration process was stopped with acetone at the ages of 1, 3, 7, 14, 28 and 56 days. It can be concluded that only mixtures of untreated hazardous waste ash are more attractive to be used as replacements in the production of construction inputs.

### 1. Introduction

The annual production of fly ash is estimated at about 780 million tons per year, and has been used in the cement industry for more than 50 years. Fly ash is the most used and appropriate material waste in geopolymerization processes due to the large production worldwide (Gul et al., 2014; Geng et al., 2017). These are byproducts derived from the combustion processes of different materials and collected by means of mechanical and electrostatic separators. Fly ash is generally composed of soluble salts, heavy metals, and in some cases, can contain polychlorinated dioxins and furans and is classified as a hazardous waste in many countries (Huber et al. 2016; Jiao et al. 2016; Purgar et al. 2016). Currently, in developing countries, these ashes are taken to sanitary landfills, this implies high costs and in some cases the use of cement must be required in order to reduce the danger of these, and according to Huber et al. (2016) can cause CO<sub>2</sub> emissions of up to 500 kg CO<sub>2</sub>/Mg fly ash. The fly ash is composed according to Feng et al. (2015) by amorphous silica and alumina, but this composition depends on the type of incinerated material, Toniolo and Boccaccini (2017) argue that they present a sphericity and favorable size that improves workability and makes a suitable material for the production of geopolymers. One of the main disadvantages of fly ash from the incineration of hazardous waste is the amount of salts that can be contained. According to Wongpromrat and Anantpinijwatna (2018), chloride-induced steel corrosion can cause structures to lose durability in terms of mechanical strength, fatigue and flexural strength. Likewise, the smooth concrete is cracked and can no longer withstand mechanical force.

Therefore, some authors have worked on washing the ashes using one step and two washing steps as pretreatment in different types of ashes (Colangelo et al. 2012). The prewashing of ashes has been proposed as a granular material bonded to the cement in the manufacture of the sub-base layer for the construction of roads. In the same way, Colangelo et al. (2012) have carried out full cost analysis of the process, which took into account the stabilization of the cement, the previous treatment of the washing and the elimination of salts, less the benefits of the reuse of the material and compared with the load by the simple elimination without treating the fly ash, resulting in the economically viable process. The aim of this study is to evaluate the reactivity of fly ash from the incineration of hazardous residues in lime pastes, as well as to determine whether

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a different behavior in the reactivity and formation of calcium-silicate-hidrite (C-S-H) gels is observed with a previous wash treatment to the ash.

## 2. Materials and experimental procedure

### 2.1 Materials

Ashes from a hazardous waste incineration plant were used to determine their reactivity as a supplementary material for cement. These ashes are named HA (hazardous ashes) through the text. Part of these ashes were treated to remove some metals, chlorides and sulphates associated to the kind of wastes. Some chlorides and sulphates are also generated in the incineration process. The treatment consisted in washing the ashes with deionized water according to the procedure explained by Colangelo et al. (2012). A deionized-water/ash from 5/1 ratio was used in this treatment (ASTM, 2015). After the washing process, the material rested for 24 hours and then it was centrifuged, using a speed of 10000 rpm for one hour to sediment the ashes (Kreuter, 1996). The precipitated material was put in an oven at 75 ° C for one week, to eliminate the moisture. The sample was then crushed and sieved. The treated ashes are called THA in this text.

Table 1 presents the chemical composition of HA and THA. These results were obtained using X-ray fluorescence (XRF). The equipment used is from the brand Thermo wavelength.

*Table 1. Chemical composition of the ashes obtained by means of XRF.*

Compound	HA (%)	THA (%)
SiO <sub>2</sub>	0.72	2.22
TiO <sub>2</sub>	0.05	0.24
Al <sub>2</sub> O <sub>3</sub>	0.07	0.57
Fe <sub>2</sub> O <sub>3</sub>	0.04	0.13
MnO	N.D.	0.03
MgO	0.02	0.20
CaO	0.44	2.93
Na <sub>2</sub> O	3.73	4.51
K <sub>2</sub> O	0.37	0.37
P <sub>2</sub> O <sub>5</sub>	0.04	0.25
SO <sub>3</sub>	1.32	3.25
Cl	4.27	3.23
ZnO	0.08	0.30
Cr <sub>2</sub> O <sub>3</sub>	N.D.	0.02
CuO	N.D.	0.04
PbO	0.02	0.10
PPI (105°-1000°C)	88.79	81.58
SrO	-	-

A change in chemical composition can be found in THA, when it is compared to HA. A loss in chlorides and sulfates is noticed. This new composition can be attributed to the washing and centrifugation process employed for the material (Colangelo et al. 2012; Rada 2017).

### 2.2 Mineralogical composition of ashes

X-ray diffraction (XRD) test were carried out to determine the mineralogical phases present in HA and THA, before they were mixed with the lime and at 56 days of hydration when a replacement of 40% was used. The equipment used was a Miniflex-Rigaku X-ray diffractometer working on Bragg-Brentano geometry with Cu-Ka1.2 wavelengths (1.54051 y 1.54433 Å). The angular range used was of  $2\theta = 6-80^\circ$ , using a  $0.02^\circ$  step ( $2\theta$ ) and an acquisition time of 2 s per step.

### 2.3 Paste preparation

Lime pastes were prepared according to ASTM C305 standard. A 0.5 water/(lime-ash) ratio was used. This amount of water was considered to guarantee complete hydration of the pastes (Suwimol y Daungruedee, 2008). Substitutions of 10, 20, 30 and 40% by weight of the lime were done for both ashes. The nomenclature in this document is the name of the ash followed by a number, which represents the percentage of replacement. For example HA1, indicates that 10% of lime has been replaced by HA.

The curing process, after paste preparation, was done in water at 25 °C. Contact between material and water was avoided using hermetic plastic bags. This is important to consider, to conserve the quantity of water in the

material. At different ages (1, 3, 7, 28, 56 days) the hydration process was arrested using acetone and then the samples were put into an oven at 60 °C.

## 2.4 Thermogravimetric analysis (TGA)

Thermogravimetric tests were run in a TGA-5500 Discovery device from TA Instruments. The heating temperatures were between 30 and 600 °C, with a heating rate of 10 °C min<sup>-1</sup> and nitrogen was used as purge gas.

## 3. Results and discussion

### 3.1 Mineralogical composition of ashes

Figure 1 presents the main phases present in HA and in THA. These phases were obtained by XRD.

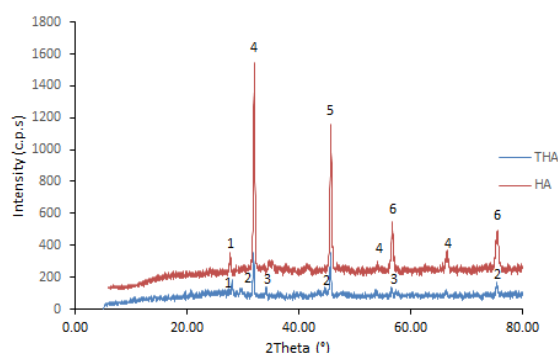


Figure 1: XRD results of ashes before hydration. (1) SiO<sub>2</sub>, (2) NaCl, (3) Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, (4) CaO, (5) PbO, (6) Fe<sub>2</sub>O<sub>3</sub>,

As it can be noticed from Figure 1, a change in mineralogical composition can be determined after the washing process. HA presents SiO<sub>2</sub>, CaO, PbO and Fe<sub>2</sub>O<sub>3</sub>, while THA presents SiO<sub>2</sub>, NaCl and Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>. According to ASTM C618 none of these ashes corresponds to any classification of fly ash used as supplementary material for cements. SiO<sub>2</sub> is the only component, present in the ashes, useful for cementitious materials. The presence of Ca<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> in THA could be interesting, as it is a phase that contains many of the basic elements of cements. On the other hand, the presence of CaO could also have an effect in hydration process, because the importance of this compound in cement production. It is also important to evidence high crystallinity of both ashes, although it could be said that THA is less crystalline than HA. This can be observed as the peaks of THA are less pronounced and at the beginning of this curve, around SiO<sub>2</sub>, there is shape like a little wave. A low crystallinity of ashes is desirable, because it means that the material can react with hydrated phases of cement (potlandite) to produce C-A-S-H. From the XRD and XRF results of these ashes, it is possible to discard both ashes as replacement for cement. Nevertheless, it is important to continue analyzing these materials, because they represent an environmental issue and it is necessary to find a way to use them.

### 3.2 Thermogravimetric analysis

Figure 2 presents the evolution in time (from one day until 56 days) of hydration of lime pastes with different percentages of replacement using THA.

Figure 2a presents the evolution of phases in lime pastes with 10% of THA. The peak near 440 °C presents an increment with time. This peak corresponds to the degradation of portlandite, which is normal to appear and to increase, because this is the main phase in lime. There is no evidence of the appearance of any other peak. This condition indicates that there is no reaction between the ash and the lime. Figure 2b, which presents the DTG results for 20% of THA in lime pastes, shows the same peak of portlandite with a similar behavior of the Figure 2a. These curves present a little peak around 100 °C in day 3. This is the temperature, where C-S-H can degrade. It seems that C-S-H is forming from the reaction of THA with lime during the hydration process. C-S-H is the most important hydrated phase of cementitious materials, because it is the responsible of the mechanical resistance and the hardness of the material. Figure 2c corresponds to the effect of time in the hydration of lime with 30 % of THA and has the same behavior of Figure 2b. The peak at around 100 °C seems to be higher than the one in Figure 2b. This peak appears since day 1, but it is higher at 28 and 56 days. Figure 2d shows the evolution with time of the hydration of lime pastes with 40% of THA. As it can be

noticed, the behavior of this figure is similar to the behavior of Figure 2a. The only peak that can be detected when 40% of lime is replaced by THA is the one associated to portlandite.

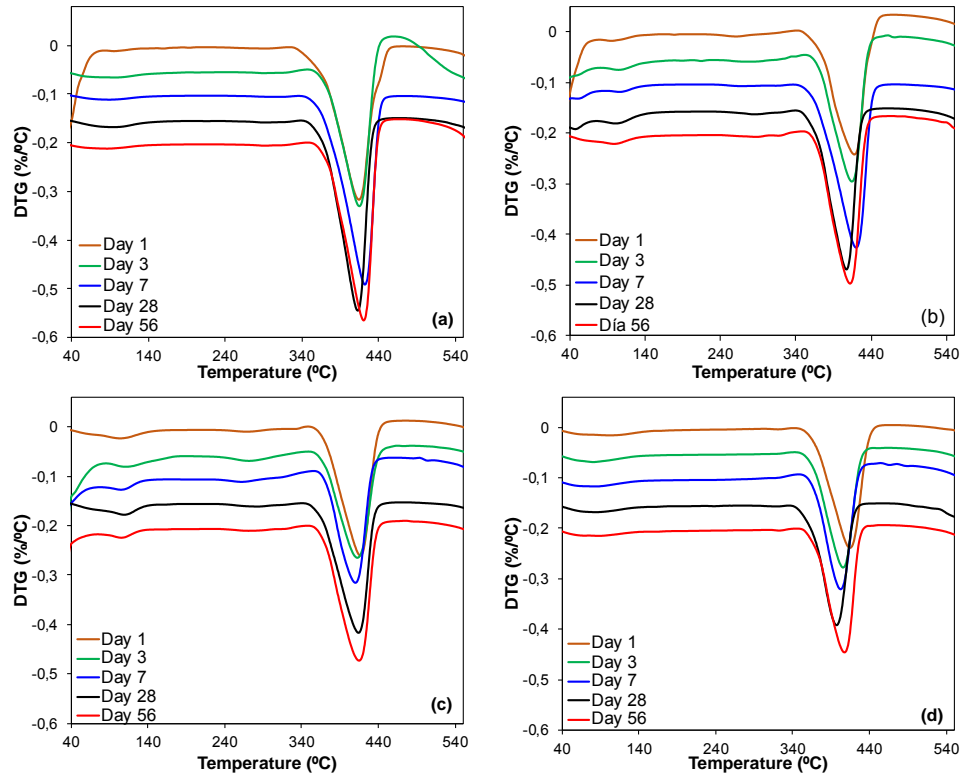


Figure 2: DTG results of the evolution in time for different percentages of THA in lime pastes: (a) 10%; (b) 20%; (c) 30% and (d) 40%.

According to Figure 2 it can be said that THA in 20% and 30% generates chemical effects in lime pastes, producing a new phase, which could probably be related to C-S-H. Figure 3 presents the evolution from one day until 56 days of lime pastes hydration with replacements of HA of 10%, 20%, 30% and 40%.

Figure 3a shows the effect of 10% of HA in lime pastes from one day until 56 days of hydration. It can be seen from the different curves in this figure that only portlandite is detected. In Figure 3b, which represents the behavior with time of 20% of HA, another peak is found. This peak appears at around 100 °C and is more evident at 1, 7 and 56 days. As it was explained before, at 100 °C takes place the degradation of C-S-H. The appearance of this peak, can also be observed in Figure 3c, which presents the evolution with time of lime paste with 30% of HA. In Figure 3c this peak can be found between one day and 28 days. At 56 days this peak is not detected, probably because a new reaction takes place. The results of phases obtained in lime pastes with 40% of HA are presented in Figure 3d. The peak of portlandite can be found, as in the other curves, and the peak associated to C-S-H is also observed at the 5 different ages. Figure 3d presents the highest peaks at 100 °C. It can be noticed that this peak is better defined in this Figure 3d, than in the others. HA has a chemical effect more evident when it is used in higher contents as 40%.

From the curves presented before it is not possible to conclude anything in a specific way. It seems that the use of THA at 20% and 30% of replacement produces a beneficial effect, because a new phase appears. The same phenomenon is observed in THA, especially, when 40% of lime is replaced. Until this part of the work it seems that the little peak around 100 °C corresponds to C-S-H, but it not possible to assure that. To corroborate the results obtained by TGA, XRD were carried out at 56 day of hydration.

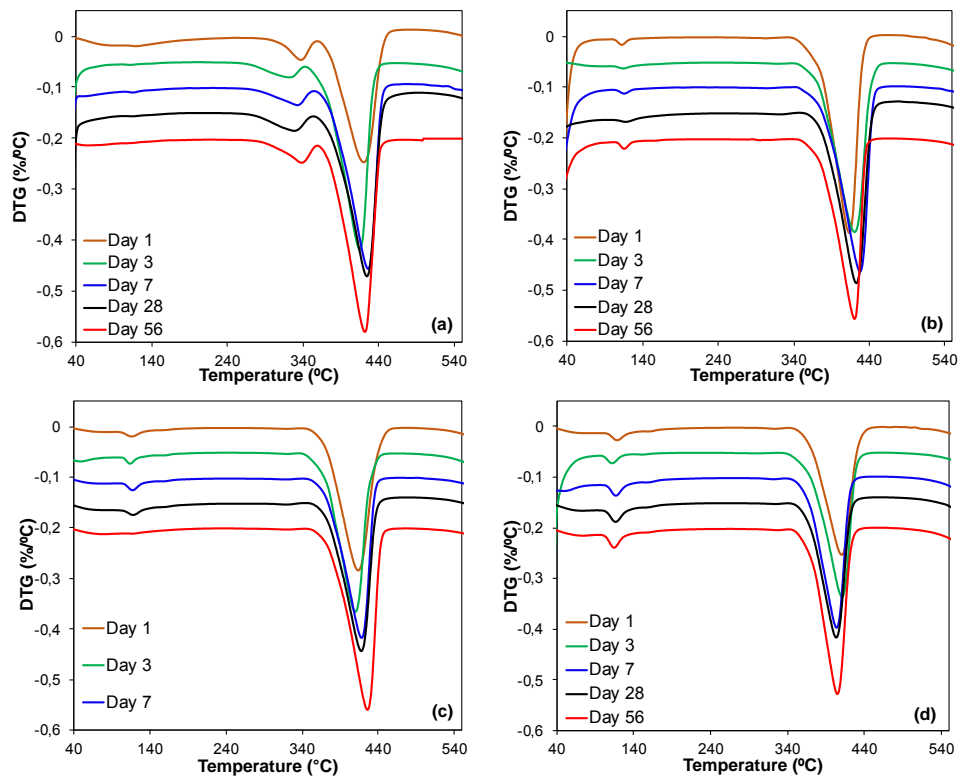


Figure 3: DTG results of the evolution in time for different percentages of HA in lime pastes: (a) 10%; (b) 20%; (c) 30% and (d) 40%.

Figure 4 presents the TG (Figure 4a) and DTG (Figure 4b) curves for different percentages of replacement of HA at 56 days. EI behaviour for this ash is similar to the one presented in THA. It can be noticed that, in general, when the percentage of replacement increases, there is higher reactivity of the sample.

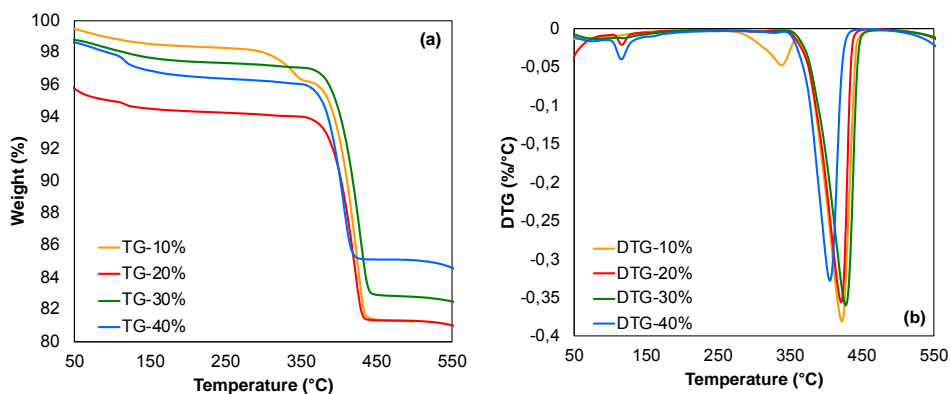


Figure 4: DTG results of the evolution at 56 day of HA in lime pastes: (a) TG and (b) DTG

### 3.3 XRD of hydrated samples at 56 days

Figure 5 presents the results of lime with 40% of HA and 40% of THA in lime pastes at 56 days of hydration. It can be noticed that new phases are obtained, when this figure is compared to Figure 1. This is normal, because now the ashes are mixed with lime and water. The main phase found in both curves is portlandite, the main component of lime. Both curves present portlandite,  $\text{SiO}_2$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Ca}_2\text{SiO}_4$  [belite,] and  $\text{Ca}_3\text{SiO}_5$  [alite]. The presence belite and alite is important and significant. These two phases appear after the reaction of lime with the ashes. When these phases react with water produce portlandite and C-S-H. So, it is more viable that the peak in DTG curves at 100 °C is C-S-H. The absence of C-S-H in XRD results can be explained, because this not a crystalline phase.

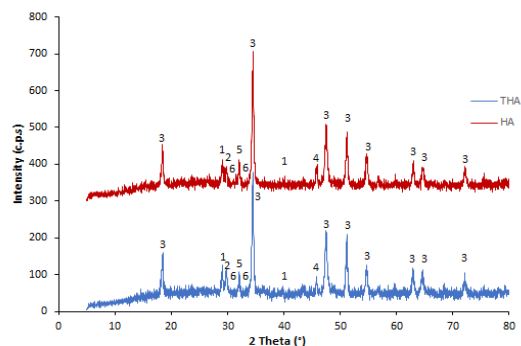


Figure 5: XRD results of samples with 40% of ash at 56 day of hydration. (1)  $\text{SiO}_2$ , (2)  $\text{Fe}_3\text{O}_4$ , (3)  $\text{Ca}(\text{OH})_2$  [Portlandite, CH], (4)  $\text{Al}(\text{OH})_3$ , (5)  $\text{Ca}_2\text{SiO}_4$  [Belite,  $\text{C}_2\text{S}$ ], (6)  $\text{Ca}_3\text{SiO}_5$  [Alite,  $\text{C}_3\text{S}$ ]

#### 4. Conclusions

It was possible to demonstrate that both ashes present portlandite as the main phase, because it is the most important component of lime. The two mixtures after 56 days of hydration also show the formation of belite and alite, which is evident in the thermogravimetric analyses of the temperature in the range between 50 and 150 °C. Likewise, it was found that as the hydration time passes other types of phases that could be C-S-H associations are formed. Therefore, it is shown that these ashes could be applied to mixtures with cement in the preparation of low-performance inputs, however it is necessary to first perform leaching tests and TCLP on monoliths in order to evaluate the release of metals that may produce problems to health or the environment.

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