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Artificial Additions for Cement: Reproduction in Laboratory of Fluidized Bed Ash

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Abstract

This paper presents a experimental laboratory simulation of wastes that will be produced as a result of the implementation of a CIRCULATING FLUIDIZED BED (CFB) STEAM GENERATOR that is being built in the town of Rio Turbio in the province of Santa Cruz (Argentina).

For this analysis, the information published in the environmental impact study conducted by the Grupo Isolux Corsán SA and Others - JV (2008) was used. The design data associated with the operation of the plant was extracted from said document.

This power plant will use raw coal as fuel, thus introducing into the reactor a significant proportion of sterile (an inert material that is extracted with coal composed mainly of clay). Based on fuel and plant operation characteristics, it is expected as a residue of the combustion process a potentially reactive material that could be used as an artificial admixture for cement.

Time and temperature needed to generate the specified chemical composition for the residue were the most important parameters in the experimental simulation. In order to achieve expected crystallographic structure of these ashes, the assessment of the cooling method was critical.

The results of chemical composition and XRD show that, in principle, laboratory simulation can produce ashes similar to those expected to be produced at the power plant. Additionally, from the evaluation of the simulated-ashes characteristics, it seems possible to use the real residue from the steam generator as a pozzolanic admixture for cement.

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Keywords: Portland cement; pozzolan; laboratory simulation; coal; waste.

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1. Introduction

According to the Environmental Impact Study of the Thermal Power Plant which is currently under construction in Rio Turbio (Argentina) and considering a steady-state operation thereof at 100% capacity, 30 tn/h of bottom ash and 41.25 tn/h of fly ash will be generated (Grupo Isolux Corsán S.A. y Otros – UTE, 2008). This large volume of waste, estimated to be created when the power plant begins its operation, will present a challenge from the environmental point of view for the effective disposal of the ash.

The cement industry is continually evaluating the replacement of component materials, totally or partially, to reduce the environmental impact of their production process. In this context, it is well known the incorporation of mineral additions in blended cements generation. (M.F. Carrasco, G. Menéndez, V. Bonavetti, E.F. Irassar, 2005)

Within mineral admixtures can be found the pozzolans. They are siliceous or silico-aluminous natural materials which, by themselves, do not possess significant cementitious ability. However, finely ground and in the presence of water, they chemically react with one of the products of the cement hydration (calcium hydroxide), at room temperature, to form compounds with cementitious properties. These characteristics may occur in the just ground source material as in volcanic ash and some diatomaceous earths, or develops after a moderate calcination in the case of some clays. (Giovambattista, 2011)

One of these pozzolanic materials is metakaolin (MK), which finely divided chemically reacts with calcium hydroxide formed in cement hydration to generate cementitious compounds by modifying the microstructure of the paste. Added to the positive environmental impact involving partial replacement of cement by MK, the workability, some mechanical properties and the durability of concrete improves. (Sabir, B.B., Wild, S., Bai, J., 2001)

MK is a type of pozzolan which can be produced by thermal treatment of the kaolinite at temperatures between 600 and 900 °C. (Rashad, 2013) In this context, the calcination of kaolinitic clays that come with the coal used as fuel in Fluidized Bed Thermal Power Plants produces MK as a major component of the ash generated in the combustion process. Kaolinite is a mineral clay composed mainly of hydrated aluminum silicate ($2H_2O.Al_2O_3.2SiO_2$) and its structure consists of octahedral sheets of alumina and tetrahedral silica alternately stacked with a theoretical composition of 46.54% SiO_2, 39.5% Al_2O_3 and 13.96% H_2O. During heat treatment, kaolinite recrystallized as mullite (Al_6Si_2-O_{13}) or as spinel ($MgAl_2O_4$) and amorphous silica. (Rashad, 2013)

Under normal environmental conditions, the kaolin is stable. However, when it is heated at temperatures between 600 and 900 ° C, it loses 14% of its mass in hydroxylic bonds. This heat treatment (calcination) breaks the kaolin structure in a way such that the layers of alumina and silica lose their narrow long-range order. As a result of this dehydroxylation and subsequent reorganization, MK becomes a highly reactive transitional phase, an amorphous structure with latent hydraulic and pozzolanic reactivity, suitable for use in cementitious applications. (Rashad, 2013)

The main purpose of this work focuses on the evaluation of the feasibility of using the ashes generated in the thermal power plant based on a Fluidized Bed Combustor which is close to its commissioning in the city of Rio Turbio (Argentina). The possibility of incorporating this waste to the cement is an attractive alternative that deserves evaluation. Since the plant has not entered into operation yet, it was necessary to synthesize this residue at the laboratory for this study.

Since the turbulent calcination state in the power-plant fluidized bed is not experimentally available, static, laboratory-scale conditions were used to generate ashes with identical characteristics of those at the bottom of the thermal power plant. To recreate said conditions, the available operating data of the thermal power plant, the theoretical basis of operation of fluidized bed combustors with incorporation of sand as inert to achieve entrainment of particles and the principles of coal combustion reactions were employed. (Basu, 1999)

According to the analysis of the ash production process in the thermal power plant, and considering that the study is focused on evaluating the use of waste as mineral additions, it was established that the reproduction depends mainly on the cooling of ashes simulation methodology: a heat exchanger and subsequent water-spraying were used, with temperature and calcination time as the main parameters.

As noted above, to increase the reactivity of the pozzolan it is necessary to modify the crystal structure through dehydroxylation, by strict control of parameters such as calcination temperature and times (L. B. Beltramini, M.F. Carrasco, R. Grether, M. Suarez y A. Guilarducci, 2010). The amorphicity of the sample obtained has a direct influence on the reactivity of the ash used as addition.

2. Experimental Procedure

For the reproduction of the ashes in the laboratory, materials were used with the characteristics (chemical composition and fineness) given in the Environmental Impact Assessment (Grupo Isolux Corsán S.A. y Otros – UTE, 2008). Consequently, untreated coal from Rio Turbio and limestone (purity 89% $CaCO_3$) in the proportions established for the operation of the thermal power plant were employed.

In order to find an optimal time-temperature ratio for playback of ashes in a static manner, 875 °C was adopted as the calcination temperature, corresponding to the central value within the range of operation of the thermal power plant (850-900 °C) and tests were performed at different residence times for the sample in an electric oven. The choice of different times studied is based on homogeneity of calcinig process at the Plant due to the combination of three main variables: time, turbulence and temperature. If one of these factors is reduced (for instance, eliminating the turbulence during static calcination) the other parameters should be increased to achieve the same degree of theoretical combustion (90%). To define the cooling system of the ashes, it was necessary to conduct a thorough review of the EIA considering each of the remarks made in relation to the operation of the thermal power plant and the entire process by which untreated carbon becomes ashes. The importance of this definition is that this process determines the crystal structure of the ashes and thus defines the reactivity thereof as further mineral addition for portland cement.

With the intention to reproduce the conditions of cooling of the ashes in thermal power plant, a cooling device was designed and built, mimicking the operating conditions.

To confirm the adequacy of the residence time of the sample in the electric furnace, tests of calcination loss (IRAM 1654:1968) were performed to the laboratory-made ash. This test corroborates one of the most important aspects: the efficiency of combustion.

With regard to the chemical characterization of the ashes, Energy Dispersive X-ray Analysis (EDXA) for determining the composition of oxides and X-Ray Diffraction (XRD) to evaluate the crystallinity of the sample were carried out.

Additionally, the reactivity of the material was evaluated by determining the Fixed Lime parameter (M. I. Sánchez de Rojas, M. Frías, J. Rivera, M. J. Escorihuela y F. P. Marín, 2001). This parameter is obtained by measuring the difference of the concentration of CaO of the initial saturated solution and that of the lime present in the solution in contact with the sample at different test times.

3. Results and Discussion

Figure 1 shows the results of loss on ignition for various calcinations performed to evaluate the optimum time for reproduction of the ashes.

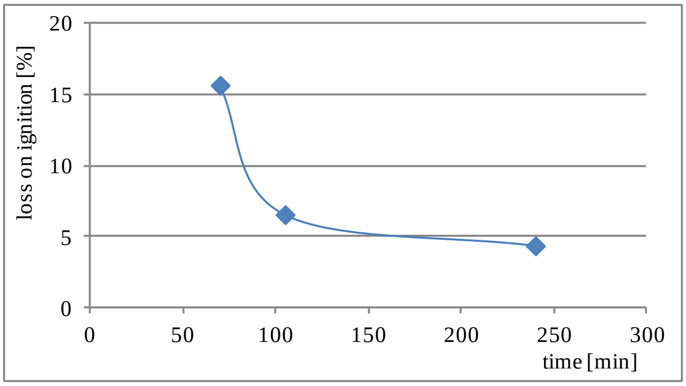


Fig.1. Evolution of the loss on ignition as a function of residence time in the furnace at 875 ° C for a # 600µm sample.

From the plot in Figure 1, it can be determined that a calcination of 105 min at 875 °C allows obtaining a coal combustion efficiency greater than 90%. It is highlighted that this efficiency corresponds to the fineness established for the operation of the plant (maximum size of the ashes 9.5 mm).

In Figure 2, the comparison of carbon content estimation from EDXA tests and loss on ignition, for the milled sample to different finenesses are shown.

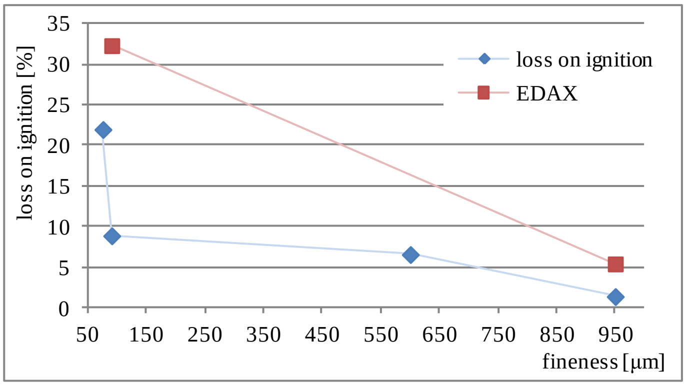


Fig.2. Evolution of carbon measured by loss on ignition and EDXA depending on the fineness of the sample calcined at 875 °C for 105min.

The analysis of Figure 2 may indicate that as the sample is smaller in size the result obtained in loss on ignition and EDXA tests show larger values, indicating that coal present inside the larger particles is exposed due to the milling process.

As a result of the static calcination and the heterogeneity of the ashes, darker particles (M1) and clearer particles (M2) of different sizes (all less than 9.5mm) were observed. An example of both types of samples (M1 and M2) is shown in Figure 3.

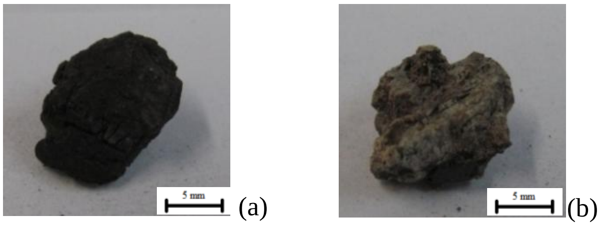


Fig.3. (a) sample M1– (b) sample M2.

For chemical characterization of the ashes, besides particle types M1 and M2, the milled sample (comprising a set of particles of different colors and sizes, ground in a mortar to # 90µm) was evaluated. Table 1 summarizes the results obtained in the tests and a comparison with theoretical values published in the EIA.

Table1.Chemical characterization of the ashes

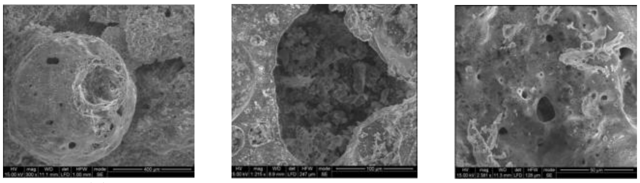
OXIDE (% wt)	THEORETICAL (%wt)	#90µm	M1 #9.5mm	M2 #9.5mm
Na_2O	0.6	1.48	1.52	0.78
MgO	1.4	2.11	8.2	1.75
Al_2O_3	26	24.42	31.4	25.98
SiO_2	57.9	48.92	34.13	49.98
SO_3	3.8	0.76	0.56	1.22
K_2O	1.2	0.66	0.43	0.61
CaO	3.1	9.86	4.19	8.82
TiO_2	1.4	2.58	1.16	3.88
Fe_2O_3	4.5	9.22	18.41	6.99
Carbon	-	32.32	5.66	5.15

Regarding the carbon content, in M1 and M2 samples Carbon accounts for 5-6% of the total mass, while in the milled sample represents more than 30%. The explanation for this variation is that very small particles of amorphous carbon after combustion appear in the grinding but are not detected in larger ash particles. That is because EDXA is a surface-analysis test, so when the sample is reduced to a smaller size through grinding a greater carbon content is detected.

From the analysis of Table 1 it can be indicated that the main components found in the sample generated are the same as in the expected power plant ash sample. In both cases the samples are mainly composed of silicon oxide and aluminum oxide.

The content of iron oxide (III) is greater in the sample generated in the laboratory with respect to the value indicated in the EIA, while the content of sulfur oxide (VI) is much higher compared to the EIA of the measured values in reproduction. These differences can be attributed to the difference in the combustion process employed against the expected operating conditions for the power plant.

Figure 4 shows photomicrographs of ashes obtained.



(a) (b) (c)

Fig.4.Photomicrographs. (a) mag 300x; (b) mag 1215x; (c) mag 2381x.

By looking at the morphology of the sample, it can be noted that it is very rough and with high pore content. Its surface shows an overlap of different layers of material.

In Figure 5 the diffractogram of ash generated in calcination at 875 °C for 105 minutes is shown. It is also detected more overlapping in all graphite oxides. The amounts are just the result of dividing the total by the number of compounds.

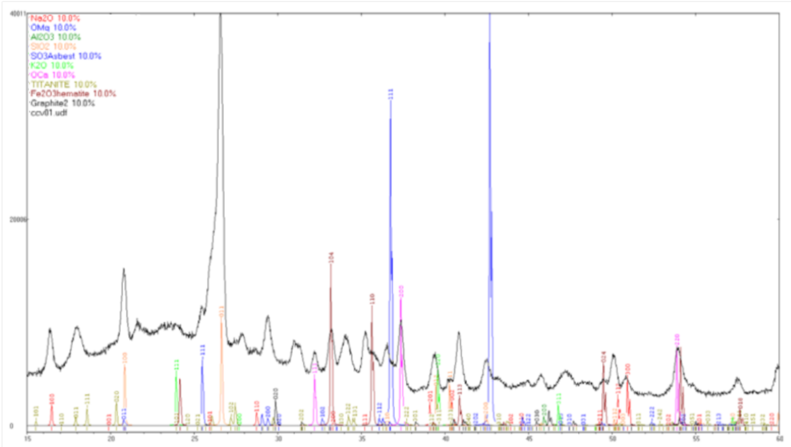


Fig.5. Diffractogram ash generated in laboratory.

Analyzing the diffractogram, it can be determined that the sample had a high degree of amorphicity.

With regard to the evaluation of the reactivity of the material by the method of fixed lime, in Figure 6 the evolution of consumption of [CaO] by the ash is shown.

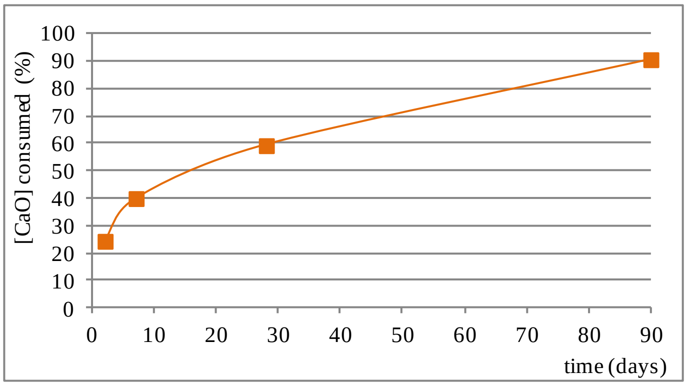


Fig.6. Fixed lime test results of ash # 75µm

It can be seen from these results that the ash has pozzolanic activity, this fact evidenced by the increasing consumption of [CaO] of the saturated solution in contact with it.

4. Conclusion

The main conclusion of the chemical analysis of the calcined material at 875 °C for 105 minutes is that the sample generated in the laboratory is similar to the residue that is estimated to be produced when the Rio Turbio thermal power plant starts working.

From the analysis of the chemical composition of the ash generated, it is possible to indicate that the sample consists of some kind of pozzolan mainly through the Al_2O_3:SiO_2:Fe_2O_3 amorphous structure which is not detectable by XRD but whose chemical composition corresponds to that detected by the electron microprobe.

Regarding the evaluation of the content of coal, as the sample size is smaller the loss on ignition test parameter is greater. In this regard, it is important that to be used as additions, ashes must be ground to a fineness of less than

75µm. Thus detecting this difference in carbon content should be taken into account for the analysis of the feasibility of using ashes as additions. That is, it should be considered that the ash does not exceed the limit of 10% of the carbon content that sets the standard IRAM 1668: 1969 for thinnesses employed.

The samples generated in the reproductive stage of bottom ash to be obtained during operation of the plant have pozzolanic activity, suggesting that its incorporation into cement as a mineral addition is possible, since the material obtained it could be classified as an artificial pozzolan.

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