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ScienceDirect
Journal of the European Ceramic Society 26 (2006) 3783–3787
www.elsevier.com/locate/jeurceramsoc

The role of a coal gasification fly ash as clay additive in building ceramic

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Received 26 June 2005; received in revised form 23 December 2005; accepted 6 January 2006
Available online 28 February 2006

Abstract

The clean coal integrated gasification in combined cycle (IGCC) technology of electrical power generation is different than conventional process in combustible treatment which generates inorganic wastes in the form of glassy slag and fly ash with singular properties. We have studied the fly ash coming from ELCOGAS IGCC power plant as additive to clays for building ceramic fabrication.

The addition of this new kind of fly ash to a clay of medium plasticity to elaborate pressed specimens, that were baked at 900 °C, improves the sintering of the paste and consequently an improvement of absorption, saturation and mechanical properties of the fired bodies, with no negative effects on shrinkage, colour alteration or efflorescence. In contrast, this fly ash does not mend the excessive firing shrinkage when added to a clay of a high plasticity index.

Keywords: Sintering; Pressing; Waste Material

1. Introduction

The integrated gasification in combined cycle (IGCC) power plant of ELCOGAS S.A. in Puertollano, Ciudad Real (Spain) is the first IGCC plant implanted in Spain and the second one in Europe.[1] It has been designed to produce electricity by gasification of a mixture of coal and petroleum coke. The gasification results in a synthesis gas coming from the organic fraction of combustible mixture. This gas is subsequently depured and then burned with high efficiency in a combined cycle electricity-generating unit. After burning, the inorganic fraction of coal remains as solid wastes in the form of vitrified slag and fly ashes.

Several studies on the Puertollano IGCC fly ash have been reported focused on a general characterisation,[2] the speciation of mayor and trace elements, the recovery of germanium and zeolites synthesis.[3–5]

Similarly to most of conventional fly ash,[6] the pozzolanic activity of this fly ash and its suitability to be used as concrete additive has been assessed,[7] being at present recycled for that use. Nevertheless other applications must be investigated to valorise this residue providing that small changes in their properties could unable this fly ash to meet the requirements of the cement and concrete application.

Several authors have reported the recycling of conventional coal combustion fly ash or incinerated sewage ash in building ceramics[8–12] and the utilization of the Puertollano IGCC slag as grog material in red mud bricks.[13] Now, we give and discuss the results of the investigation on the recycling of this new kind of fly ash in building ceramics with the aim of evaluate the role played by IGCC fly ash in the ceramic process when added to clays of different rheological behaviour.

2. Materials and methods

IGCC fly ash (**#FA**), and two different clays from the area of Talavera de la Reina in Toledo (SPAIN) were utilized in this work. (**#LT**) is a clay of medium plasticity which is used in a brick facility for indoors use, and here taken as standard, and (**#A10**) clay of higher plasticity. Six mixtures (Table 1) were selected to perform the batches containing LT or A10 clays with fly ash added to be compared to the 100% LT clay taken as standard. The nomenclature of mixtures indicates first, the name of the clay (**LT** or **A10**), and then the fly ash (**FA**) followed by

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doi:10.1016/j.jeurceramsoc.2006.01.011

Table 1
Chemical composition of mayor elements

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	LOI
A10	51.49	24.02	6.54	0.07	2.13	2.05	0.38	2.96	0.69	0.38	9.21
LT	62.03	18.78	4.69	0.07	1.50	1.22	1.11	3.90	0.59	0.24	5.65
FA	54.35	23.22	3.84	0.028	0.65	3.5	0.6	3.9	0.67	0.5	3.47

a number indicating the content of fly ash as percentage in the batch.

Specimens of 40 mm diameter and 1 cm height were prepared by uniaxial pressing in a die at 20 Mpa/s for 20s. For a better dimensional homogeneity all pellets were composed of 25 g of mixture with 5% of distilled water added. Samples were dried at 110 °C and fired in an electric furnace at with controlled rate of heating at 100 °C/h, up to 900 °C, soaked for 5 h and then left in the furnace to cool down to room temperature.

The specimens coming from the mixtures LTFA50, A10FA50 and FA100 resulted in defective bodies after firing, so only mixtures LT100, LTFA10 and LTFA20 were further analyzed.

Comparative measures on the processing parameters and the final products properties were performed: drying loss and shrinkage in green bodies and firing weight loss and shrinkage, water absorption, water suction, saturation coefficient, radial compression resistance and XRD analysis on fired specimens were tested.

Several analytical methodologies has been carried out including chemical analysis by X-ray fluorescence (XRF) on powder pressed pellets; mineralogical analysis by powder X-ray diffractometry (XRD); particle size analysis was performed by wet Sedigraph method in water; thermal data were obtained by differential thermal analysis (DTA) in air atmosphere scanned at 10 °C/min, and sintering behaviour by hot stage microscopy (HSM) scanned at 5 °C/min. The sintering curve shows the changes of the shape of a small cylindrical specimen of 2 mm × 4 mm made of pressed powder of sample while the temperature increases. The initial height of the specimen is taken as 100% and shrinkage or expansion are measured as percentage values below or above 100% respectively.

The Atterberg limits were determine to evaluate the plasticity of the raw clays and the clay–fly ash mixtures.[14,15] The efflorescence test and the water absorption of final products were evaluated according to Spanish standards.[16,17] After the water absorption test, the same samples were kept for 5 h in boiling water to calculate the saturation coefficient.[18] This parameter gives an indirect measure to evaluate the freeze resistance of ceramic materials.[19] Mechanical behaviour was monitored by diametrical compressing failure test[20] at a speed of 0.2 mm/min.

3. Results and discussion

Table 2 shows the chemical composition of the raw materials. Among minor elements, quantities below 1% of Zn, Ni, V and Pb were detected in a semiquantitative XRF analysis. As can it be seen, IGCC fly ash do not differ in composition to that of clays. This fly ash is classify according to ASTM classification[21] as Class F accounting the low content of calcium oxide and slightly

Table 2
Composition of batches

Mixture	Clay (%)	Fly ash (%)
LT100 (standard)	100.0	0.0
LTFA10	90	10
LTFA20	80	20
LTFA50	50	50
A10FA50	50	50
FA100	0	100

acidic character (pH 6.3 in water suspension L/S = 10/1). The particle size curves (Fig. 1) show that LT clay is larger particle size than that of clay A10 and fly ash is the finest of the raw materials. The diffraction pattern of the two clays (Fig. 2) only differ in the higher intensity of quartz reflection peaks in LT clay in agreement with the higher content of SiO_2 and larger particle size of this clay. IGCC fly ash diffractogram (Fig. 3) is characteristic of a glassy material and only very low intensity peaks of sulphides (pyrrotite and galene) are detected. In contrast to conventional fly ash mineralogy,[22] quartz, lime or mullite are not found.

The thermal DTA curve of IGCC fly ash (Fig. 4) shows the exothermic peaks at 450 and 700 °C due to oxidation processes. The clays curve show an endotherm from the dehidroxilation of the clay minerals and an exothermic at higher temperature due to the growth of new mineral phases during the sinterization.

The Plasticity of clays and mixtures is shown in Fig. 5. It is clear from the data that the addition of fly ash have a small effect on the plasticity of clays, being necessary a 50% of fly ash to achieve a small reduction of plasticity of the A10 clay. Only the mixtures based on clay LT are situated within the limit of the square of suitability of pastes.

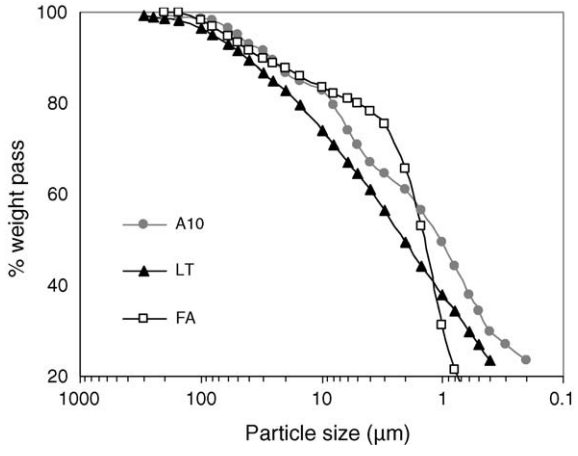

Fig. 1. Particle size of clays and fly ash.

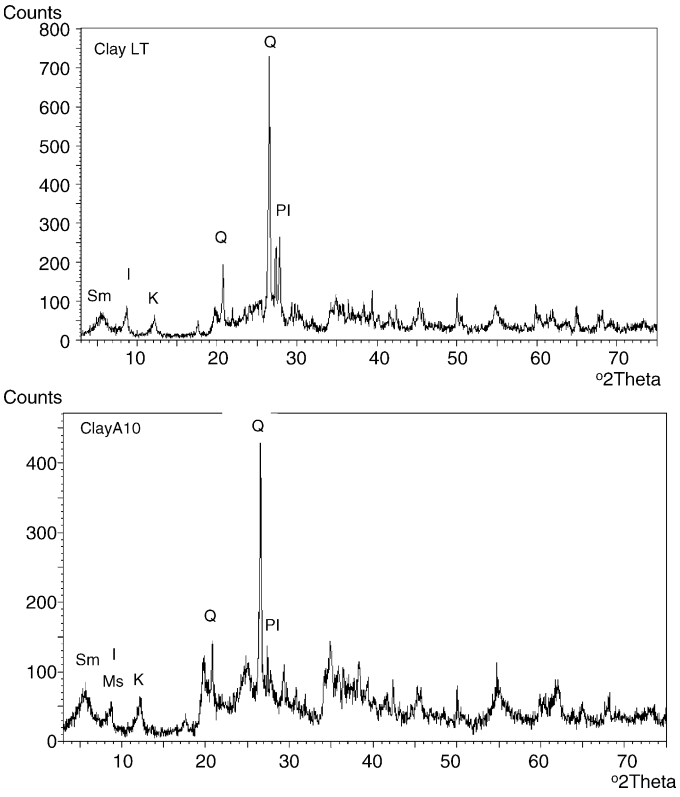

Fig. 2. Mineralogy of clays: Sm: smectite; Ms: muscovite; K: kaolinite; I: illite; Q: quartz; Pl: plagioclase.

The sintering curves of raw materials and mixtures (Fig. 6) reveal a different tendency depending on the clay: mixture of LT with 50% of fly ash (LTFA50) has identical trace than LT clay (LT100) on contrast to the curves of mixtures FA-A10, with traces closer to that of fly ash 100% (FA100). This behaviour contrast to the usual lower shrinkage of pastes reported with conventional fly ash.[23]

Table 3 summarizes the result of the analysis on fired final products of the LT standard batch and LTFA10 and LTFA20 mixtures.

The differences between the standard and the fly ash added specimens in weight loss and shrinkage on firing may be considered negligible. As for the water the absorption and the saturation

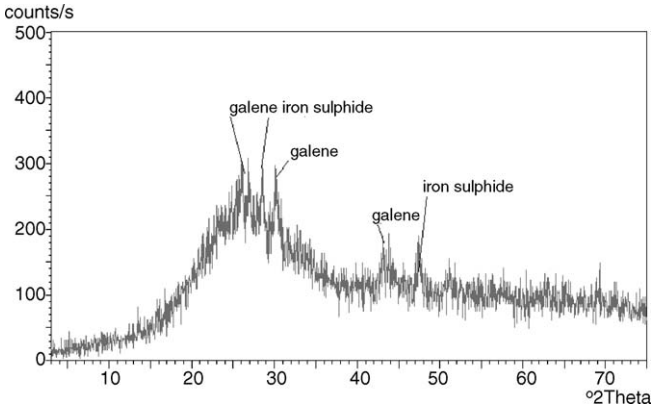

Fig. 3. Mineralogy of fly ash.

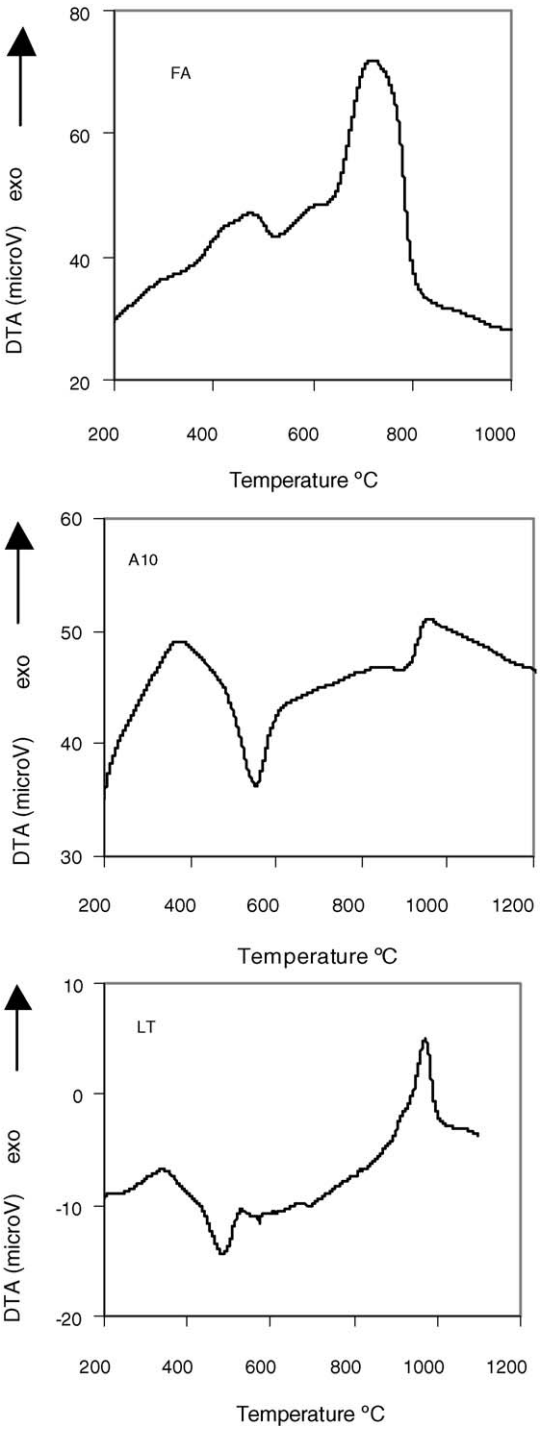

Fig. 4. DTA traces of fly ash FA and clays A10 and LT.

coefficient, it is clear a decrease in both values with increasing content of fly ash. The radial compression failure test gives (Table 3) an increase of mechanical resistance with growing content of fly ash in the batch.

The X-ray diffraction patterns of the samples LT100, LTFA10 and LTFA20 (Fig. 7) show that the peak corresponding the philosilicate muscovite, in LT clay, remains after firing at 900 °C in LT100 standard batch, but disappear in the batches with fly ash added. The rest of peaks correspond to the quartz from the

Table 3
Processing parameters and final product properties

	Drying loss (%)	Firing loss (%)	Radial shrinkage (%)	Water absorption (%)	Saturation coefficient	Radial compression failure resistance (N/mm^2)
LT100	3.08	5.67	−0.14	14.13	0.96	0.71
LTFA10	3.72	5.99	−0.18	12.7	0.91	1.33
LTFA20	4.87	5.35	0.47	10.38	0.78	2.20

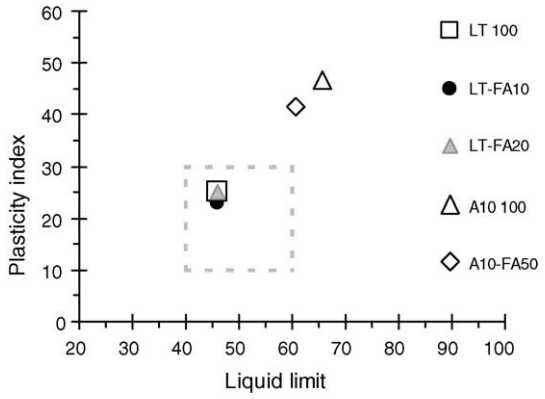

Fig. 5. Plasticity of clays and mixtures clay–fly ash.

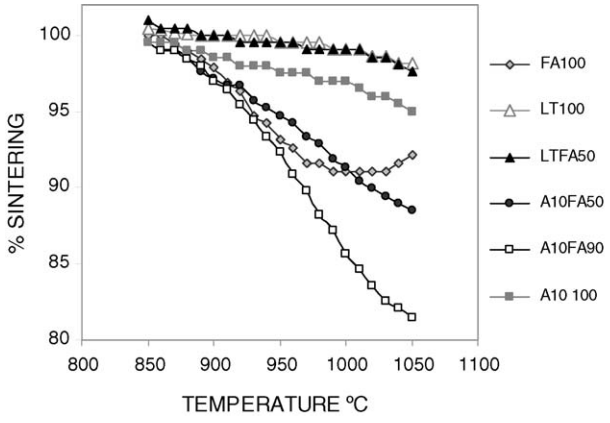

Fig. 6. Sintering curves of clays and mixtures clay–fly ash. Shrinkage as values below 100%.

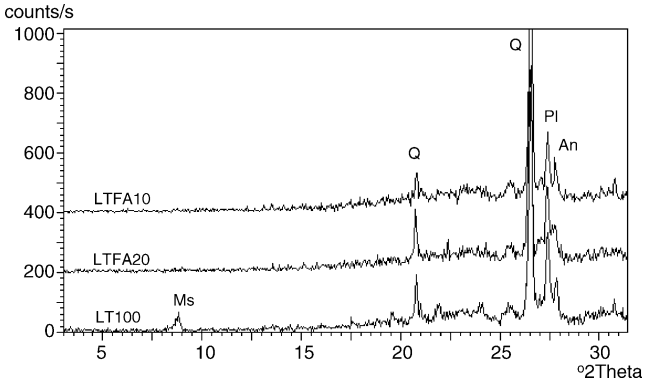

Fig. 7. XRD pattern of the standard and fly ash added ceramics baked at 900 °C. Ms: muscovite; Q: quartz; Pl: plagioclase; An: anorthite.

raw clay and an anorthite phase developed during the ceramic process.

Finally the efflorescence analysis of the three batches qualify the specimens as no efflorescent.

4. Conclusion

The glassy nature of IGCC fly ash, together with its small particle size and reducing character, determine that this waste do not act as a grog material in ceramic pastes, but as an active additive that improves the sintering process at usual temperatures of bricks manufacturing. The exothermic reaction of the fly ash at 750 °C is likely to be the reason of this behaviour.

The effect of the fly ash addition depends on the plastic characteristics of the clays. Fly ash added up to 20% to clays of medium plasticity promotes the formation of a liquid phase that make possible the thermal transformation of a muscovite phase at earlier temperatures than the standard bodies.

The better sintering in the fly ash specimens gives rise to the subsequent improvement of values of water absorption, saturation coefficient and mechanical strength in comparison to the standard paste without fly ash. The variation in the values of shrinkage on firing is negligible. As for the colour, fly ash containing ceramic show a slightly darker reddish coloration, and no efflorescence is observed. A higher content of fly ash in the mixture resulted in defective specimens that were no further measured.

The addition of IGCC fly ash to a very plastic clay, in absence of grog material inside the paste, produces a high shrinkage that results after firing in deformed ceramic bodies, with severe cracks and exfoliations.

Acknowledgement

Work carried out with a financial grant from the European Coal and Steel Community, Project ECSC 7220-PR145 (HIVALUE).

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