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PREPARATION AND CHARACTERIZATION OF CARBON-ENRICHED COAL  
FLY ASH.

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## **Abstract**

Carbon-enriched fractions have been obtained from two coal fly ash (FA) samples. The FA came from two pulverized-coal fired power stations (Lada and Escucha, Spain) and were collected from baghouse filters. Sieving was used to obtain carbon-enriched fractions, which were further subjected to two beneficiation processes: acid demineralization using HCl and HF, and oil agglomeration using soya oil-water. Yield in weight after sieving, unburned carbon content, and several physicochemical characteristics of the obtained fractions were used to compare the performance of the beneficiation methods. Low carbon concentration was obtained by sieving, particularly in the case of Escucha FA. However, after acid demineralization or oil agglomeration, fractions containing unburned carbon in a range of 63 to 68% were obtained. These fractions showed differences in mineral phase composition and distribution depending on the FA and on the beneficiation method used. The textural properties of the obtained fractions varied as a function of their carbon content and the beneficiation method used. However, no significant differences in morphology of the carbonaceous particles were found.

Keywords: Coal fly ash; Separation; Characterization.

## 1. - Introduction

Fly ash (FA) is the main by-product of coal combustion. In the European Community (EC-15) electric power stations generate 55 million metric tons (ECOBA, 2003) of coal combustion by-products, 44 million tons of which corresponds to fly ash. About 50% of this annual production is used in the cement industry, given that FA contains large amounts of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  and because of its pozzolanic property after reacting with lime and water. However,  $\text{NO}_x$  emissions reduction, through the installation of low  $\text{NO}_x$  burners, often results in higher unburned carbon contents, and therefore in a decreased marketability of some ashes. According to ASTM C618, a loss-on-ignition (LOI) greater than 6% renders FA unusable for cement or concrete manufacture. It is generally accepted that the unburned carbon tends to adsorb the air-entrainment reagents that are added to the cement to prevent crack formation and propagation. The problems derive not only from higher levels of unburned carbon, but also from the increased variability of the carbon content.

On the other hand, its content in water-soluble heavy metals makes coal FA unsuitable for agricultural uses. The complex, heterogeneous and variable composition of coal FA is the main reason why its bulk utilization has limited potential (Vassilev et al., 2004). Additional uses for coal FA would include a previous step of separation and beneficiation. Usual methods for carbon concentration are sieving, froth flotation (Brown et al, 1999) or agglomeration. Other methods are triboelectrostatic separation (Gray et al., 2002), carbochlorination (Yang et al., 2003 ) incipient fluidization or density separation (Furuya et al., 1987 )

Synthesis of zeolitic products by hydrothermal alkaline treatment (Querol et al.1997, 2001) and use of the carbonaceous part as a precursor for the development of activated carbons (Zhang et al., 2003; J.J. Li et al., 2006; Zhao et al.,2005) are interesting ways of recycling fly ash . An extensive review on FA utilization as a low-cost adsorbent has recently been carried out by Wang and Wu (2006).

Related scientific literature concerning uses of unburned carbon has been growing in volume over the past number of years. There are references dealing with the use of unburned carbon as an adsorbent for the treatment of wastewater from dyeing (Graham et al., 1996; Wang et al., 2005), mercury adsorption (Maroto-Valer et al., 2005), and the fabrication of automotive brake composites (Malhotra et al., 2000). The unburned coal used in the adsorption processes undergoes an activation step (Baltrus et al., 2001).

The aim of our research is to develop value-added products from coal fly ash. We have studied the fly ash obtained from the combustion of both a bituminous coal and a lignite-bituminous coal blend on the basis of an integral reutilization. In a previous work we demonstrated the potential of using carbon fly ash in nitric oxide removal (Rubio et al., 2006). In the present study we have obtained carbon-enriched fractions using several methods and a detailed characterization of their physical and chemical properties has been carried out. The influence of beneficiation method and type of burned coal on the characteristics of the obtained fractions are also considered. Work is in progress to assess the capacity of these carbon enriched-fractions for use in flue gas cleaning.

## 2. - Experimental

Two FA types (F type), from two pulverized-coal fired power stations were examined in this study. The power stations are located in the north (Lada, 505MW) and the east (Escucha, 160 MW) of Spain. The coal burned in Lada is bituminous, while in Escucha a blend of 70% lignite-30% bituminous coal is used.

A preliminary fly ash screening was performed from 10 kg of sample. In this way, six fractions were obtained: <100 $\mu\text{m}$ , 100-200  $\mu\text{m}$ , 200-300  $\mu\text{m}$ , 300-400  $\mu\text{m}$ , 400-500  $\mu\text{m}$  and >500  $\mu\text{m}$ . The unburned carbon content (LOI) of each fraction was determined by thermogravimetric analysis (TGA): 20 mg of each sample was heated in a temperature ramp of 20°C. min<sup>-1</sup> under air as purge gas, in a simultaneous TG-DSC from TA-Instruments (TA-DSC 2960). The samples were heated in air until they reached constant weight.

The information obtained in this preliminary study was used to determine the carbon-enriched fractions as a function of weight percentage and unburned coal content:

Dp>100 $\mu\text{m}$  for Lada FA and Dp>200 $\mu\text{m}$  for Escucha FA. In this way, two different fractions were obtained from 150 kg of each as-received FA (L-AR and E2-AR); two carbon-enriched fractions (L-EN, E2-EN), and two rejected fractions (L-RJ and E2-RJ). The carbon-enriched fractions were used as feed for subsequent acid digestion and oil agglomeration to further increase their carbon-content.

L-EN and E2-EN were partially demineralized according to Bishop's method (Bishop and Ward, 1958). The samples were initially treated with HCl 5N at 55°C for 45 min, after which they were filtered and washed with water to eliminate all chloride. After

drying, the samples were treated with HF 5N at 55°C for 45 min. The resulting cake was treated with concentrated HCl (38% wt.) at 55°C for 45 min. Finally, the samples were filtered, washed with water, and dried.

This acid-treated samples were named L-EN-D and E2-EN-D. Another part of L-EN and E2-EN was oil agglomerated in Waring blender equipment (Alonso et al, 1999). In a typical experiment, 400 cc of distilled water and 16 g of sample were placed in the blender and mixed at 11,000 rpm for 5 min, to disperse the particles. Then, 2 % vegetable oil (soya bean frying oil) was added, and mixing was continued at the same speed for 60 sec. to produce agglomerates. After recovery, the agglomerates were filtered, washed with ethanol, perchloroethylene and ethyl ether to extract the oil. The agglomerates were then washed with water and dried overnight at 50°C. Thus, two samples, L-EN-AG and E2-EN-AG, were obtained. A part of these samples was heated at 550°C in N<sub>2</sub> atmosphere. Two thermal-treated samples were thus obtained, namely L-EN-AG-T and E2-EN-AG-T.

The origin and treatments of all samples studied can be seen in the Figure 1.

Major and minor element composition was obtained for the carbon-enriched samples as well as for their parent fly-ash by inductively coupled plasma in a Ultratrace-2000 from JOBIN-YVON, on dissolution by acid digestion using LiB<sub>4</sub> and further HCl attack.

Powder X-ray diffraction (XRD) was used for phase mineral characterization. XRD profiles were obtained using CuK $\alpha$  radiation, range 2-theta from 3° to 80°, step 0,05° and step time 5 sec. In order to compare fractions, the X-axis is presented from 20 to 40°. The diffractograms were recorded with a DS-8 Advance instrument from Brucker.

Elemental analyses were performed for C, H, N, O and S in a Flash 1112 analyser from Thermo-Finnigan.

N<sub>2</sub> adsorption isotherms were performed in an Autosorb-1 from Quantachrome. Prior to the analysis, samples were outgassed at 250°C under vacuum up to 10<sup>-5</sup> mm Hg.

Analyses of mercury porosimetry were carried out in a Poremaster from Quantachrome. Morphological examination of the samples (coated with a gold layer) was carried out by means of scanning electron microscopy (SEM) in a Hitachi S-3400N at several magnifications. In some cases secondary electron images were obtained of samples embedded in a polished cross section resin.

### **3.-Results and discussion**

#### 3.1. Chemical and mineralogical characterization

As-received FA from Lada (L-AR) contains significant higher amount of unburned coal than FA from Escucha (E2-AR). Unprocessed coal ash typically contains a mixture of small mineral and larger char particles. The results of size screening (Table 1) indicate that in Escucha FA, the unburned coal is present as coarser grains than in Lada FA. For this reason the bulk of Lada FA was sieved at 100µm whereas FA from Escucha was sieved at 200µm. In this way a carbon rich fraction of size >100µm (L-EN) was obtained from Lada FA and a carbon-rich fraction of size >200µm (E2-EN) was obtained from Escucha FA. The fractions of size <100µm and <200µm were named L-RJ and E2-RJ, respectively. The yield in weight of E2-EN and its unburned carbon content was poorer (2.17 % by weight, LOI 15.11%) than in the case of L-EN (4.96 % by weight, 31.67% LOI). It is obvious that sieving is not a satisfactory method for screening unburned carbon concentration in the case of Escucha FA.

Acid treatment and oil agglomeration increase the carbon content remarkably in both EN fractions, as shown in Table 3. This increase is very significant for the E2-EN fraction as its LOI is raised from 15.11% to 67.63% after demineralization and to 69.68% after agglomeration. The LOI of the L-EN fraction increases from 31.67% to 67.61% after demineralization and to 73.76% after agglomeration.

Mineral phases of as-received FA can be observed in Figure 2. XRD profiles show that major mineral phases are mullite, quartz, lime and aluminosilicate glass. Escucha FA also contains significant amounts of magnetite. The amorphous peak at around  $\theta = 24^\circ$  could correspond to a carbon signal, but the main contribution to this peak comes from the amorphous part of the mineral matter.

FA chemical composition varies depending upon the type of coal used, combustion conditions, and air pollution control devices. The two FA types studied in this work are of F class ( $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$ ,  $\text{CaO} < 5\%$ ), though it was expected that Escucha FA would be C class. (Escucha power station burns a 70% lignite-30% bituminous blend).

The chemical composition of the studied samples is given in Table 3. L-EN and E2-EN fractions are very similar to the as-received ones (L-AR and E2-AR). It appears that the granulometric separation does not involve a segregation of inorganic species. Some differences appear if the chemical composition of samples L-EN-D and E2-EN-D is compared to L-EN and E2-EN: after demineralization there is a decrease in Ca content in both FA samples, and in iron content in E2-EN-D. The iron in L-EN and E2-EN samples comes from magnetite and are associated with mullite or complex aluminium silicates in the vitreous phase of the inorganic matter. Both are solubilized in HCl and FH.

The chemical composition of inorganic matter in FA enriched by oil agglomeration (L-EN-AG and E2-EN-AG) is also shown in Table 3. It is possible to see that the agglomeration process involves a segregation of iron species. The technique of oil agglomeration employs the

difference in surface properties of unburned carbon and the inorganic part of FA. The unburned carbon particles are hydrophobic and are preferentially wet by the oil, and the hydrophilic mineral matter is retained in the aqueous phase. In view of the results obtained by ICP, it can be deduced that iron-containing compounds (mainly magnetite) are in the form of discrete particles or in carbonaceous particles with high inorganic content, and have been retained in the aqueous phase. Moreover, the high specific gravity of magnetite (5.17 g/cc) can lead to these particles being rejected.

The elemental analyses of the as-received FA and its fractions are reported in Table 2. The low hydrogen content observed in demineralized and agglomerated samples indicates that carbonaceous particles have undergone a complete devolatilization. The observed differences between carbon content and LOI are attributable to the presence of Ca-containing species which oxidize below 1000°C (Baltrus et al, 2001).

### 3.2. Morphology

A general view of as-received FA is shown in Figure 3. A higher amount of discrete inorganic particles are observed in Escucha FA. Different glassy spheres, spheroids and agglomerates predominantly constitute the studied fly ash. The advanced fusion stage (spheres) of the inorganic species caused by the high temperatures reached during combustion can be observed. In the carbon-rich fractions obtained by sieving (L-EN and E2-EN), sponge-like carbon particles (Figures 3c and 3d) can be observed, as well as char particles with parallel slits (Figures 3e and 3f), showing a burning pattern typical of ordered aromatic structures (Milenkova et al. 2003). Anisotropic porous material is the most important contributor to the unburned carbon particles in Lada and Escucha FA. The similarities in morphology observed when comparing the two FA types indicate that the unburned carbon in Escucha FA probably originates from the

bituminous coal present in the burning blend. The lignite was more reactive and burned away completely. This observation is consistent with the lower LOI value shown by the as-received Escucha FA.

At a higher degree of magnification (Figure 4a and 4b) it is possible to see the slits and interstices of char particles filled with small inorganic spheres that still remain in the agglomerated fractions (Figures 4e and 4f). These spheres have been almost completely removed after demineralisation. (Figure 4c and 4d). However the ash values of L-EN-D and E2-EN-D are of the same order as those of L-EN-AG and E2-EN-AG, indicating that parts of minerals treated by acids remain unsolubilized. Some salt formation (needles) can be also observed in the demineralized samples as a consequence of chemical leaching (Vassilev and Vassileva, 2005).

Backscattered electron images (Figure 5) of unburned carbon particles embedded in polished resin (cross section) show the presence of fused inorganic matter dispersed within the carbon matrix, with no appreciable differences between the Lada and Escucha agglomerated fractions. In these images, dark areas are composed of carbon structures, whereas brighter, small spheres and aggregates correspond to inorganic matter. This inorganic matter is part of the original mineral matter in the coal, and further removal appears to be difficult.

### 3.3. Thermal analysis

Thermogravimetric experiments described the evolution of each sample in a temperature ramp of  $20^{\circ}\text{C}\cdot\text{min}^{-1}$  performed under air as purge gas. Figure 6 shows the thermograms and heat flow curves (arbitrary units) obtained by the simultaneous differential scanning calorimeter. In this way, it is possible to obtain, not only the loss-on-ignition of fly ash, but also the exothermic curves of carbonaceous matter

combustion. As expected, the enriched-agglomerated samples have a higher LOI than the enriched ones. The enriched samples lose weight steadily with the temperature program, but EN-AG samples show a first mass loss in a step between 250° and 500°C. It is clearly seen in the heat flow profiles that there is an early combustion of carbonaceous matter in that range of temperatures in agglomerated samples. This implies that the samples could contain a sort of residual material from the agglomeration oil, in spite of exhaustive solvent extraction after the process. On the other hand, Figure 6 gives a clear comparison of carbonaceous matter structure for both fly ashes: under these experimental conditions, samples from the Lada plant start combustion at 600°C, whereas Escucha samples start loss of weight at 500°C. These results indicate that the carbonaceous matter from the Escucha seam is more reactive than that of the Lada FA, probably owing to differences in rank between the coals burned in the two electric power stations.

#### 3.4 Textural characterization

Nitrogen isotherms of as-received and carbon-enriched fly ashes are depicted in Figures 7 and 8. They are Type II according to BDDT classification (Brunauer et al, 1940), typical of macroporous solids.

It is typical for class C carbons to have a surface area in the range of 300 m<sup>2</sup>/g to 400 m<sup>2</sup>/g, whereas carbons from class F ashes have surface areas which are typically in the range of about 30 to 70 m<sup>2</sup>/g . The surface areas obtained for the carbon-enriched samples studied in this work are shown in Table 5. The obtained areas oscillate between 60 and 220 m<sup>2</sup>/g on a dry and ash-free basis. However, the authors prefer to consider surface area data on a moisture-free basis, even with the understanding that the surface area of the inorganic fraction contributes only 07-08 m<sup>2</sup>/g (Kulaots et al 2004). It seems

more realistic to consider the samples as a whole since, in their assessment as adsorbents/catalysts, the samples are used in this way.

The increase in surface area is significant for the demineralized samples. Not only does carbon enrichment of these samples contribute to this effect, but also the enlargement of the existing pore by wall collapse. The removal of microspheres of inorganic matter that fills the slits of the carbon particles may also contribute to giving better accessibility to the porous system. The removal of mineral matter after demineralization can be clearly seen in the SEM images (Figure 4c and 4d). Surprisingly, BET values reported for agglomerated samples having a carbon content of the same order as that of demineralized samples were much lower than expected. This fact could have two possible explanations: a) the agglomeration process removed discrete mineral particles, but the mineral matter remaining in the carbonaceous particles is arranged in such a way as to block the entrance to the porous system of the particle. b) Some of the remaining oil was responsible for blocking the pore entrance. SEM backscattered electron images (Fig 5) demonstrate that inorganic matter is not responsible for the low surface area values of L-EN-AG and E2-EN-AG. A significant fraction of inorganic matter is encapsulated by the carbonaceous particle, and the outer particle surface is almost entirely free from inorganic matter.

On the other hand, the weight loss at temperatures between 300° and 400°C (L-EN-AG 2.4% and E2-EN-AG 3.8%) observed for the agglomerated samples (Figure 6) could be attributed to remaining oil. These weight losses can be related to the peaks that appear at the same temperatures showing an exothermic heat flow. Moreover, this is consistent with the very significant increase in surface areas of L-EN-AG and E2-EN-AG after heating at 550°C (Table 5, samples L-EN-AG-T and E2-EN-AG-T), as was expected. The increase in surface area is higher in the case of E2-EN-AG, which is consistent with the higher amount of oil retained in

this sample. Additionally, Hg porosimetry data reported in Table 7 indicates oil adsorption during the agglomeration process: unexpected low values of porosity for agglomerated samples and significant increase after heating.

The high density values, as well as low surface area and porosity, could be attributed to the existence of anisotropic carbon particles. It is surprising to find these values in Escucha samples, which would be expected to have more disordered and porous carbon particles.

(Baltrus et al 2001, Vassilev et al 2004). The morphological observations by SEM, however, indicate that the carbon particles in Escucha FA mainly originate from the bituminous coal in the blend.

#### **4.- Conclusions**

Carbon-enriched fractions were obtained from two FA types through a combination of sieving followed by acid leaching (HCl and HF) or oil agglomeration. Low carbon concentration was obtained by sieving, particularly in the case of Escucha FA. However, after acid demineralization or oil agglomeration, fractions containing unburned carbon in a range of 63% to 68% were obtained. These fractions showed differences in mineral phase composition and distribution depending on the FA and on the beneficiation method used. Sieving does not significantly change the chemical composition of FA, but the acid treatment removes mainly glass, as well as calcium minerals and iron oxide species (magnetite). The agglomerated samples also show a decrease in iron content.

Both concentration methods lead to changes in the porous texture of the samples studied.

The agglomeration process causes a blocking of the pore entrance, owing to the oil remaining in the carbon particles, whereas the HCl and HF treatment significantly increases the surface area of the samples.

From a morphological point of view, no significant differences were found between the carbonaceous particles from Lada and Escucha FA.

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