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Behaviour of the elements introduced with the fuels in their distribution and immobilization between the coal–petroleum coke IGCC solid products ☆

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Abstract

In this research on the solid products of the Elcogas IGCC plant (Puertollano, Spain) the influence of the two fuels, coal and pet coke, on the composition of the fly ashes and slag is demonstrated and how the majority of the elements are provided by the coal and only some as V, Ni and Mo are provided by the pet coke.

The different nature of slag and fly ashes is highlighted and how the different elements are distributed between them that in general follow the indications of the mathematical models.

The passage of the elements into gaseous phase is calculated.

The fly ashes are some products of very fine granulometry that present problems of solubilization of a series of elements and therefore of deposition. Their inertization has been investigated by calcination at 1000 °C and with additives. Some good results have been obtained.

Keywords: IGCC; Trace elements; Inertization

1. Introduction

At the present time the most promising clean coal technology applied for electrical energy generation is gasification, especially integrated gasification in combined cycle due to the possibility of a better and simpler gas purification and the higher energetic efficiency of this technology.

All the technologies that use solid fuels, apart from gas emissions produce solid residues, slag (S) and fly ashes (FA) that must be stored or used because they are produced in a very large amount. These products may have a contaminant effect on the environment, especially the fly ashes due to their fine grain size. It is important that these products comply with Directive 1999/31/EC especially to be classified as inert landfilling material that can be deposited at a lower cost, in any case as non-hazardous material, thereby avoiding entering into the classification of hazardous materials.

The classical coal combustion has been researched during many years with respect to the possible contaminant problems of solid products or their use [1–5], and also the coal combustion with blending of solid wastes as tyre scraps [6,7], biomass, [8,9]. Combined cycle gasification is much more recent and less studied. The potential contamination of its products (slag, flying ashes and gas) on the environment is completely different from the impact of combustion power stations due to the reductive atmosphere that operates in these processes causing the formation of the elements in different species that are more

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sensitive to solubilization in water and other solutions, [10–14].

The IGCC installed by Elcogas in Puertollano has provided the samples to carry out this research. Elcogas uses coal from the Puertollano mine characterized by a high content of trace metals, especially Zn and Pb [7] that is blended with a petroleum coke coming from the refinery also located in Puertollano and that completely modifies the content in some minor elements such as vanadium, nickel and molybdenum. The blend is 50% coal/50% petroleum coke and 2.5% of limestone is added as fluxing agent. This plant uses an entrained flow gasifier that works with dry feed and gasifies with O_2 at 25 bar and 1400°–1600°, the slag is collected in the bottom of the chamber and is granulated with water and the gaseous current is cooled in three stages, 1550–800 °C, 800–400 °C, 400–235 °C. The gaseous current is filtered through ceramic candle filters at 235–250 °C and the gas passes with a particle load <3 mg/Nm^3. This gas has been considered in our research as "gas" to carry out a mass balance and that it is not really a gas because it even contains some solid particles. Then in the industrial circuit, this gas is washed to eliminate acid gases and impurities, after which it is treated in a hydrolysis process to hydrolyze the COS; finally it is desulphurized by a Claus process [15].

The tendency of the different elements to pass slag, fly ashes or gas has been modelled by several authors such as Thompson, Argent and Diaz-Somoano [11,16,17] who predict the distribution of the different elements among slag, fly ashes and gas and in this research the validity of these predictions is checked mainly for the considered case of Elcogas.

The Elcogas fly ashes are sold to cement companies for construction proposes, for which reason these are not really hazardous materials but by-products. In the case that FA were wished to be used as landfilling material, due to their high solubility in some elements [12,18], they could be classified as hazardous and then they should be stored with special precautions. The recovery of some of these easily solubilizable metals such as Ge [18] has been investigated.

Directive 1999/31/EC on the dumping of solid residues, specifies in its annex the classification of the materials as inert, not hazardous and hazardous. From the economic point of view, the transformation of the fly ashes in to an inert material is the most appropriate.

2. Experimental

Three series of samples were received that correspond to three different run periods over time. Each of these series is composed of coal, pet coke, limestone, slag, fly ashes and fine slag (the fine slag is not considered in this research because it is recirculated blended with the initial fuel due to its high carbon content of about 50%).

The mineralogical and chemical characterization was carried out, the relationship between the content of the elements of the different samples was established and the balance of each element used, the mass balance of the incoming and outgoing products and the analysis of the same by the considered elements was calculated.

The original fly ashes and their products after thermal treatments with and without additives to obtain their inertization, was leached with water in a ratio of 1 solid part per 10 water parts, for 24 h by means of agitation with turbine and in a thermostat at 25 °C to investigate their classification with respect to Directive 1999/31/EC. The liquid phase was separated from the leached solid by centrifugation and filtration and the extract was analyzed.

The crystalline phases were determined by X-ray diffraction (Philips PX-1710 diffractometer, equipped with a graphite monochromator and an automatic divergent slip and operating at 40 kV) using the X-ray line Cu Kα.

The microscopic study was performed using a scanning electron microscope, Hitachi S-570, with a Kevex 3500 microanalizer (10 mm^2 detection area) operating at 20 kV.

The chemical analysis was performed using a X-ray fluorescence equipment (Philips PW2540 VCR), A.A. Spectrometer Varian 220 FS, an ICP-AES Varian Vista MPX, an ICP-MS apparatus and a Ionic chromatograph Vertex Dionez 600.

The size analysis was carried out by sieving and also using a Micromeritics Sedigraph 0500.

3. Results and discussion

3.1. Distribution of elements in used fuels and combustion products

3.1.1. Distribution of elements in coal and pet coke

The characteristics of the fuels used regarding ashes and their S, H and N content C are given in Table 1.

As the fuel blend is approximately 50% coal/50% pet coke it is deduced from the table that almost all the solid residue of the gasification is supported by the coal, while the majority of C and S are supported by pet coke that in this way compensates the low calorific power of coal by its high ash content.

The coal, as supplier of elements (different from C and H), is the main provider of almost all of them except calcium that is mainly supported by the limestone added as fluxing agent and S, V, Ni and Mo that are principally contributed by the petroleum coke.

The variability of the coal is low as can be observed in Table 1 whereas the variability of the pet coke is higher as highlighted by its percentage of ashes. The relationship between the elements content of pet coke and coal varies according to the composition of the different pet coke (mainly in V, Ni and Mo).

The mineralogy of the coal is presented in Fig. 1 that shows its X-ray diffractogram which show that the main crystalline phases are formed by Quartz (Q), Kaolinite (K) Mica (M) and some Ankerite (Ak) and Siderite (Sd)