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Environmental impact of a coal combustion-desulphurisation plant: Abatement capacity of desulphurisation process and environmental characterisation of combustion by-products

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Abstract

The fate of trace elements in a combustion power plant equipped with a wet limestone flue gas desulphurisation (FGD) installation was studied in order to evaluate its emission abatement capacity. With this aim representative samples of feed coal, boiler slag, fly ash, limestone, FGD gypsum and FGD process water and wastewater were analysed for major and trace elements using the following techniques: inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-atomic emission spectrometry (ICP-AES), ion chromatography (IC), ion selective electrode (ISE) and atomic absorption spectroscopy (AAS). Mass balances were established allowing to determine the element partitioning behaviour. It was found that, together with S, Hg, Cl, F, Se and As were those elements entering in the FGD plant primarily as gaseous species. The abatement capacity of the FGD plant for such elements offered values ranged from 96% to 100% for As, Cl, F, S and Se, and about 60% for Hg. The environmental characterisation of combustion by-products (boiler slag, fly ash and FGD gypsum) were also established according to the Council Decision 2003/33/EC on waste disposal. To this end, water leaching tests (EN-12457-4) were performed, analysing the elements with environmental concern by means of the aforementioned techniques. According to the leaching behaviour of combustion by-products studied, these could be disposed of in landfills for non-hazardous wastes.

Keywords: Desulphurisation; Coal combustion; Leaching; Gypsum; Fly ash; Slag

1. Introduction

Sulphur emissions from coal combustion have been the focus of great concern during the last decades due to their relation to the formation of acid rain, accelerated soil acidification and forest degradation. In order to comply with the air quality regulations established accordingly in this regard, and so to protect the environment, in many countries coal-combustion electricity-generating plants have switched from high- to low-sulphur coal or blending, together, or not, with the installation of flue gas desulphurisation (FGD) plants. Although not everywhere applied, the latter measure has been necessary in several countries for many years to fulfill regulations on sulphur emission abatement. In the near future it is also expected to increase worldwide implementation of FGD systems as regulations are becoming stricter.

Many types of FGD systems have been developed. These can be classified in two major groups, wet and dry processes, which are subdivided in several types depending on the specific chemical reactions taking place and the flow conditions employed. Among them, the wet limestone FGD process is by far the most widely used because of

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its high desulphurisation performance, reliability and low utility consumption (Kikkawa et al., 2002). In this system SO_2 is removed from the flue gas by absorption into limestone slurry as sulphate which in turn is extracted from the absorber as gypsum slurry and finally dewatered. The chemical reaction occurring in a wet limestone FGD process can be summarised as follows:

$$CaCO_3(s) + SO_2(g) + 1/2O_2(g) + 2H_2O(l) \rightarrow CaSO_4 \cdot 2H_2O(s) + CO_2(g) \quad (1)$$

The so-called FGD gypsum produced in this manner has found commercial application in the wallboard manufacture, besides it is also employed as a landfill material in mine reclamation. Other uses such as agricultural lime substitute, amendment for improving soil properties, construction material for roads, and waste stabilisation product have been suggested (Solem-Tishmack et al., 1995; Stehouwer et al., 1995; Payette et al., 1997; Chen et al., 2005; Chou et al., 2005). In spite of the proposed applications, most of this by-product ends up in landfills. Up to now, the FGD gypsum is regarded as environmentally friendly, but with increasing landfill closures and regulatory pressures on operating facilities to improve environmental conditions (Council Directive 1999/31/EC; Council Decision 2003/33/EC) its characterisation could change and therefore this by-product could come out as a new environmental issue to be faced by the coal combustion plants. It is worth noting that the limestone slurry used in the aforementioned desulphurisation technique acts as an scavenging system not only for sulphur but for other high volatile elements such as fluorine, chlorine, mercury, arsenic, selenium and boron present either in the gas emissions or condensed on the small particles escaping to the electrostatic precipitators (ESPs) (typically <1%) before entering in the FGD installation, and for trace elements (Cd, Cr, Cu, Ni, Pb, Zn, Ba, Mo) enriched also in these particles. Therefore, it is relevant to know the fate of trace elements in the coal-combustion power plants in order to assess the effectiveness of the wet limestone FGD process as well as the environmental characteristics of the coal combustion by-products, namely FGD gypsum, fly ash and boiler slag. Fly ash and boiler slag, likewise FGD gypsum, are usually disposed of, especially in the case of slag. As regards fly ashes, although their application in the concrete manufacture is clearly established, their destination to this use greatly depends on the producer country; thus in some countries, e.g. The Netherlands, most ashes find their way to such application as the cost of using them this manner is much lower than the cost of their landfilling (Reijnders, 2005), but in many others, e.g. Greece, disposal is still the main mode of dealing with them (Antiohos and Tsimas, 2004). This fact is sometimes caused by the special characteristics (high free lime and sulphur contents) of some fly ashes (class C fly ashes) that make them not so suitable for cementitious systems, but generally the reason lies in the high fly ash production that greatly surpasses the amounts required by the construction industry. Several other uses have been proposed for this by-product, including the synthesis of zeolites (Querol et al., 1997a,b), geopolymers (Swanepoel and Strydom, 2002; Bakharev, 2005) and fire-proof products (Vilches et al., 2002), but their commercial application is still very limited.

Whereas numerous researches have been devoted to evaluate the partitioning behaviour of trace element between the by-products arising from coal combustion in power plants, using different coal types as well as different combustion conditions (Querol et al., 1995a; Martinez-Tarazona and Spears, 1996; Yan et al., 1999; Vassilev et al., 2001, 2005; Pires and Querol, 2004; Spears and Martinez-Tarrazona, 2004; Li et al., 2005; among others), the studies concerning the final fate of trace elements in coal-combustion power plants equipped with a FGD facility are much more scarce (Meij, 1994; Yokoyama et al., 2000; Sandelin and Backman, 2001; Meij et al., 2002; Lee et al., 2006), besides most of these studies are either theoretical approaches or are mainly focused on the behaviour of mercury.

The objective of the present work is twofold: (a) to study the fate of trace elements in a combustion coal plant equipped with a wet limestone FGD installation, and so to evaluate its abatement capacity for hazardous element emissions, and (b) to assess the environmental characteristics of arisen by-products (FGD gypsum, fly ash and boiler slag) according to the Council Decision 2003/33/EC on waste disposal recently put in force.

2. Materials and methods

2.1. Sample collection and preparation

Samples of feed coal were collected from a Spanish coal-combustion power plant equipped with a wet limestone FGD installation for 7 days during which a 69 900 t stockpile of constant coal quality (H_2O, S, ash (wt.%): 18.01, 4.66 and 23.3, respectively) was consumed by the boiler. Collection was performed every two days, obtaining three different samples that were mixed and homogenised to give a single sample. The coal was a mixture of four local sub-bituminous coals and one imported sub-bituminous coal (<27%). The combustion by-products from the coal combustion plant-FGD installation were also collected simultaneously with feed coal. Thus, three different samples of the slag (composition: glass, quartz, mullite, magnetite, hematite and albite; C (wt.%): 0.35; LOI (wt.%): <1) from the ashers of the boiler and of the fly ash (composition: glass, quartz, mullite and magnetite; C (wt.%): 1.0; LOI (wt.%): 1.4) from the hoppers of the ESPs were collected, then mixed and homogenised. Likewise, different samples of the FGD gypsum together with the limestone and process water used in the desulphurisation process were collected. Moreover, the wastewater derived from the gypsum slurry filtration was sampled as well.

Representative splits of the coal, slag, fly ash and limestone were separated by riffling, splitting and then grinding