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Enrichment of thallium in fly ashes in a Spanish circulating fluidized-bed combustion plant

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HIGHLIGHTS

- Thallium behavior in a circulating fluidized bed combustion plant is assessed.
- Thallium is mainly retained in the ashes in a circulating fluidized bed combustion plant.
- In fluidized bed combustion it may be expected that emission of thallium in gas phase would be low.

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ABSTRACT

This work evaluates the behavior of thallium in a 50 MW industrial circulating fluidized-bed combustion plant (CFBC), focusing on the distribution of this element among the bottom and fly ashes separated by the solid retention devices in the plant. The results show that thallium species are mainly retained in the solid by-products and are not emitted to air with flue gases in significant amounts, proving that this technology is a more effective means of preventing thallium emissions than pulverized coal combustion technology (PCC). The mass balance of the thallium content in the solids shows that this element was retained in the ashes separated by the different devices installed in the plant. An evaluation of the ash fractions taken from the strippers, the heat recovery area, the hoppers in the air heater and the electrostatic precipitator, shows that thallium was relatively homogeneously distributed in all the ash samples, independently of their composition, but is slightly related to surface area, which in turn is dependent on particle size and unburned carbon content.

1. Introduction

Thallium is a toxic element that occurs in two oxidation states; Tl(I) and Tl(III), the latter being more toxic. Thallium toxicity could pose a serious health problem because its compounds remain in the air, water, and soil for a long time and do not decompose. Eventually Tl enters the food chain, accumulating in fish and shellfish [1–3]. The main sources of Tl release to the environment are industrial processes, where Tl is present as an impurity in the raw materials. The data available at present indicate that power-generating plants are one of the main sources of Tl emissions to the atmosphere [2,4].

Thallium concentrations in most coals range from 0.5 to 3 $\mu g\ g^{-1}$ and it has been calculated that about half of this is emitted into the atmosphere [5]. Emissions of Tl in the flue gases of coal-fired power-generating plants can amount to 700 $\mu g\ m^{-3}$. A number of studies performed on conventional pulverized coal combustion power plants (PCC) have found that Tl volatilizes at the high temperatures of the boiler and condenses on the surface of the fly ash particles, which are mainly enriched in particles of small size and high surface area [6,7], in the cooler parts of the system. It is thought that Tl in ashes is mainly present in the form of sulphates [8]. As a result of the evaporation and condensation of the thallium species, Tl could be as much as 2–10 times more concentrated in the fine fly ash fractions than it was in the coal before combustion [9,10]. The concentrations of Tl reported to be emitted on airborne fly ash from coal-burning power plants range from 29 to 76 $\mu g\ g^{-1}$. The highest concentrations have been found on

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particles with a size of less than 7 μm in diameter. Such particles are the most dangerous; they are able to pass through conventional particle retention devices in power-generating plants, after which they remain suspended in the atmosphere. They may even end up being deposited in the lower respiratory tract [9].

In modern industrial societies ways must be found to obtain energy from coal with minimum production of pollutants. The reduction of greenhouse gas emissions from energy production using coal must be accomplished with the reduction of other toxic pollutants such as thallium. Although the behavior of Tl, and other toxic trace elements, has been studied in PCC, less attention has been paid to trace element behavior in some of the less commonly used but more efficient and cleaner coal combustion technologies. This is the case with fluidized-bed combustion (FBC), which nowadays is a highly developed energy-producing technology. The advantages of this technology are its ability to co-combust different solid combustibles, including biomass and wastes, and its capacity to avoid emissions of NOx and SO_2. However, probably the most important advantage of FBC nowadays is that this technology is compatible with processes for capturing CO_2. Previous studies have demonstrated that volatile toxic elements can be captured in fly ashes more efficiently in FBC than in PCC, though literature on Tl behavior during coal combustion in FBC is still scarce. The aim of the present work is to estimate the distribution of Tl among the solid by-products of a CFBC plant to evaluate the likely emissions to the air and to establish the relationships between fly ash characteristics, mineral components and thallium retention.

2. Experimental

The study was performed using samples taken from a 50 MW industrial circulating fluidized-bed combustion (CFBC) plant in La Pereda, Spain. The boiler was fed with a blend of 36–40 wt% bituminous coal, 51–56 wt% coal wastes obtained from disposal sites (Villallana and Batán), and around 6 wt% limestone. Representative samples of each stream were obtained over a period of three days. Sampling was carried out continuously for 6 h every day, with around 2 kg of sample being taken every 30 min. Each sample was homogenized to form a single sample representative of the sampling point. Fig. 1 presents a schematic diagram of the CFBC facility and the sampling points of the coal blends (CM), bottom ashes (BA), and fly ashes (FA). Of the total quantity of ash collected, 56% was bed ash and 44% was fly ash. A total of 15% of the fly ash had amassed in the hoppers of the heat recovery area of the plant, 20% had accumulated in the hoppers of the air heater, and 65% in the electrostatic precipitator (ESP). Inside the ESP unit, the bulk of the fly ash had accumulated in the precipitator fields in the following proportions: 40% in the first field; 22% in the second field; 2% in the third field, and 1% in the fourth field. The temperatures of the ashes sampled over the three sampling days are presented in Table 1.

Analysis of Tl was carried out by ICP-MS on the solution obtained after elimination of the carbon material. The ashes for the analysis were obtained by burning this carbon material in a furnace at 300 °C for 1 h. After that, the temperature was increased to 500 °C and this temperature was maintained for 2 h. 50 mg of the ashes obtained were then digested in a microwave oven using 1 mL of HNO3 plus 2 mL of HF. The solution was diluted to 50 mL with ultrapure water and analyzed in the ICP equipment.

The thallium enrichment values for the fly ashes were calculated using Eq. (1) by well tried calculation methods [3,11]

$$RE = (\text{Tl concentration in ash}/\text{Tl concentration in coal})\,(\text{percentage of ash in coal}/100) \quad (1)$$

Ash yield and loss on ignition (LOI) were determined by combustion in air at 815 °C. The Brunauer–Emmett–Teller (BET) surface area was determined by volumetric adsorption of nitrogen at 77 K. The ash composition for all of the samples taken from the power plant was analyzed by X-ray fluorescence (XRF) of the fused ashes. Particle size and morphology were estimated by scanning electron microscopy (SEM).

3. Results and discussion

The data for ash yield, LOI, surface area and Tl concentration of all the samples studied are presented in Table 2. All data refer to the sample air-dried. The limestone additive does not contain significant concentrations of Tl and all the input of this element to the CFBC plant originates from the combustible materials. The thallium

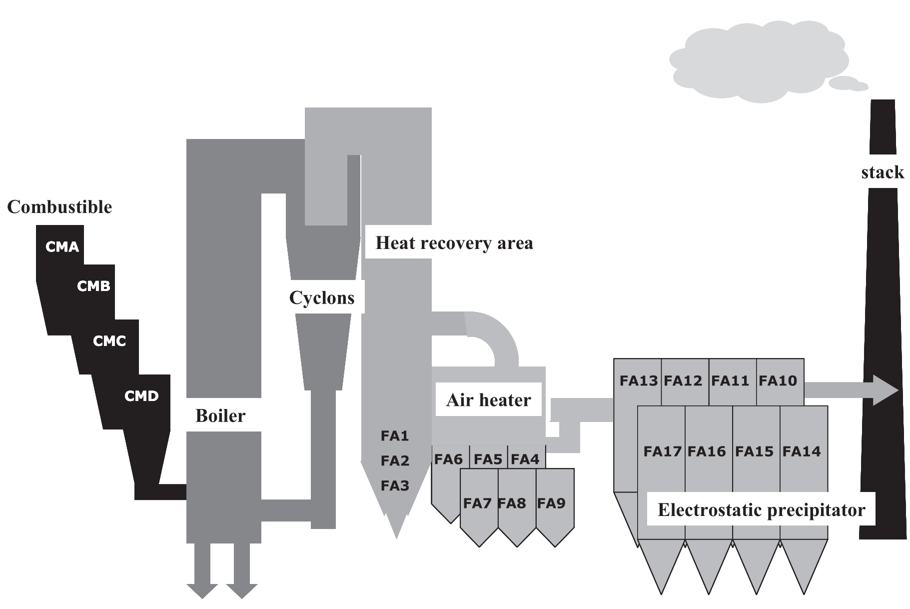

Fig. 1. Schematic diagram of the sampling points in the CFBC plant facility.