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

ABSTRACT

This work evaluates the behavior of thallium in a 50MW 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.

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 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 behaviour 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.

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. Figure 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 ºC for 1 hour. After that, the temperature was increased to 500ºC and this temperature was maintained for 2 hours. 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 equation (1) by well tried calculation methods [3, 11]

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

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 contents and ash yield of the combustible blends (CMA-CMD) can be considered statistically the same with an average Tl concentration of 0.76 µg g^{-1}, which represents 1.16 µg g^{-1} if it is referred to the ashes. Worthy of note is that the total ash yield of the combustible material has values as high as 65% because of the nature of the combustible blend which is a mixture of coal with a high proportion of coal waste. The characteristics of the plant made it possible to burn wastes from old disposal sites and recover the combustible material present in those wastes.

According to the data in Table 2, the Tl content of the ashes is of same order of magnitude in all the cases. It can be seen that the Tl concentrations in all the solid by-products sampled from the strippers, the cyclone and the electrostatic precipitator are between 0.93 and 1.70 µg g^{-1}. The average value is 1.20 µg g^{-1} and the standard deviation when all the samples are compared is 0.20 µg g^{-1}. Although broadly speaking this can be considered a relatively homogeneous distribution of Tl among the solid by-

products, it might be worth while to study the data more deeply to see if the small differences observed *i.e.* 0.93-1.70, are related to different characteristics and variations in major element composition of the ashes. Although the results under discussion point to the indiscriminate distribution of Tl, the mineral composition of the ashes and its relationship with the Tl content was evaluated more closely using the analysis of major elements that constitute the mineral matter. The ash composition of the whole samples taken from the power plant was analyzed for content in Si, Al, Ca, Mg, Fe, Na. K, Ti and P, and the results are reported as oxides in the raw sample (Table 2). These analyses are relatively uniform, but nevertheless some differences stand out. The most remarkable of these differences are related to calcium content. Limestone was added to the fuel blend to assist in S capture and this is the origin of the relatively high CaO in the ashes. Proportionally more CaO has been carried over into the fly ashes than to the bottom ashes, although the difference is not great. This can be attributed to physical fractionation in the gas stream.

Most of the remaining major elements are derived from clay minerals which are present in the coals and the associated mudrocks. The high percentages of ash in the coal blends is a consequence of the importance of the clay minerals in this fuel. The ratio of alumina to silica in the ash samples is not constant, but again the differences are small. The Al_2O_3/SiO_2 ratio is higher in the ash samples from the electrostatic precipitator, in particular in samples FA 10, FA11, FA14 and FA15. In view of the clay mineralogy of the coals and mudrocks in this coalfield [12] the higher ratio probably reflects a marginally higher kaolinite contribution to those ash samples. This is supported by the lower value of the K_2O/Al_2O_3 ratio consistent with a decrease in the proportion of illite in the same samples. Illite and kaolinite are intimately associated in the mudrocks and to some extent in the coals, but small amounts of disseminated kaolinite occur in the coals independently of the illite. It is therefore possible to interpret the changes in the two ratios, not only in terms of clay proportions, but more importantly in terms of where

the clays originated from and how the combustion products were fractionated, presumably as a function of grain size. The ash derived from the clays formed within the coal can be expected to be more fine grained, at least initially, because of the disseminated nature of the clay within the coal. A higher ratio in the final ash might therefore indicate a greater contribution from the coal itself.

The relationship between the Tl concentration in each solid phase and different key properties such as carbon content and surface area was also investigated. The loss on ignition (LOI) values (Table 2), serve to provide an estimate of the unburned carbon content of the ash samples. The unburned carbon content is the carbonaceous matter on to which adsorption phenomena may occur, although it is important to bear in mind that adsorption is also related to surface area. Figure 2 shows the thallium content as a function of surface area of the ashes, which in turn depends on the carbon content (Figure 3). There is a clear relationship between LOI and surface area. Although not studied in this work, this indicates that the variation in surface area for these ashes is due to the different carbonaceous contents. The relationship between surface area and Tl content can be inferred from Figure 2. The correlation is significant at the 95% level, although it is lower than for other volatile elements such as Hg previously studied in the same power plant [13]. The particle size and particle morphology observed by SEM differ considerably at different sampling points. following the same tendency as the surface area of the samples. The particle size of the ashes decreases from the first to the last hoppers, while the homogeneity in shape increases. To illustrate these changes, Figure 4 shows SEM images of a representative selection of ashes (FA1, FA8, F17, and FA 15). Sample FA1 is one of the ashes taken from the heat recovery area FA8 was taken from the hoppers of the air heater; F17 from one of the first 4 hoppers in the electrostatic precipitator and FA 15 from one of the last 4 hoppers in the electrostatic precipitator (Figure 1). It was observed that the particle size decreased from the ashes from the heat recovery area to the ashes from the air heater and the

lowest values were presented by the ashes from the electrostatic precipitators. It was found that particles in the fly ashes from the heat recovery area and the air heater were about 100 µm, while particles from the first two hoppers of the electrostatic precipitators were smaller than 50 µm. In the last two hoppers the size of the particles was smaller, and aggregates of less than 20 µm were observed.

For purposes of comparison of these by-products with the ashes from PCC plants which have been studied in greater depth, the relative enrichment factor (RE) values for all the ashes analyzed are shown in Figure 5. The RE factor (Equation 1) is a method of comparison that facilitates understanding of the behavior of trace elements in a combustion process. In this case, it can be observed that the RE values are similar and are all > 1. This confirms a similar distribution of Tl among the ashes in this power plant and also shows that the ashes act as a sink for Tl. The increase in carbon content and surface area may not be the only characteristic of fly ashes that usually influences distribution of trace elements among the combustion by products, especially when evaluating ash fractions of different characteristics as in this case. Temperature, contact time and other variables related to the design of the electrostatic precipitator also may play a role.

The results of a mass balance performed over the three days of sampling with respect to the input and output of thallium in all the solid by-products, are presented in Table 3. It can be seen that the input and output of thalium was similar. It should be pointed out that due to the limitations of sampling in a power plant the calculated output of thallium is higher than the input. However, the difference is within the order of uncertainly for this kind of balance, the possible error being of the order of 5% which is a very satisfactory result for an industrial study.

From the results presented above it can be inferred that the Tl present in coal can be captured efficiently in the ashes of a FBC power plant. Although broadly speaking Tl is homogeneously distributed among the ashes, segregation in ashes with a high surface

area could take place, although this segregation would not be as great as in the case of other volatile toxic elements such as mercury [13]

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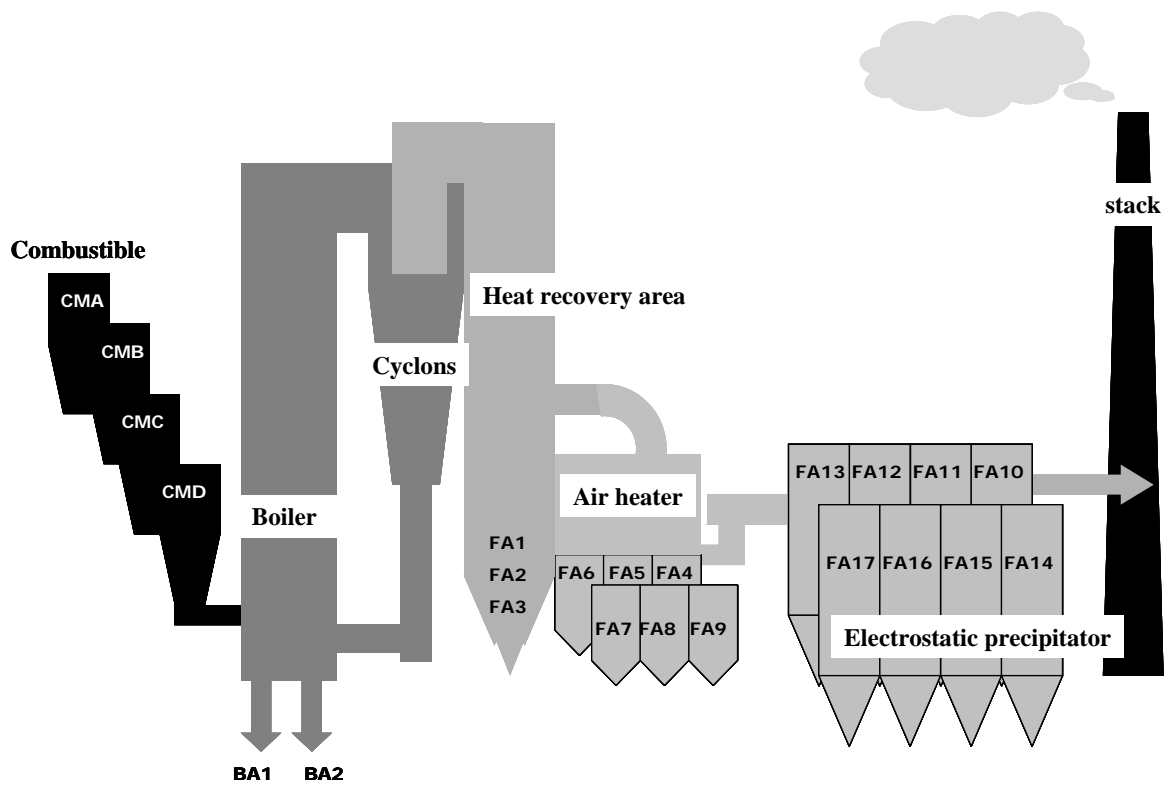
Figure 1.-Schematic diagram of the sampling points in the CFBC plant facility

Table 1. Average temperatures of ashes at the sampling points

		Tª ºC
BA1-BA2	Strippers	330
FA1-FA3	Heat recovery area	320
FA4-FA9	Air heater hoppers	133
FA10-FA17	Electrostatic precipitator	145

Table 2.- Thallium content (**μg g^{-1}**), ash yield and LOI of coal and ashes (%wt), surface area (s.a) and major elemental composition (expresed as oxides) of the ashes of each product.

	μg g^{-1}	% wt	% wt	m^2 g^{-1}	% wt								
Sample	Tl	ash	LOI	s.a	Na$_2$O	MgO	Al$_2$O$_3$	SiO$_2$	P$_2$O$_5$	K$_2$O	CaO	TiO$_2$	Fe$_2$O$_3$
CMA[1]	0.75	64.7			0,82	1,42	25,8	50,4	0,11	3,88	5,64	0,91	5,95
CMB[1]	0.74	65.0			0,83	1,40	26,6	52,6	0,11	4,11	6,71	0,91	6,40
CMC[1]	0.77	65.5			0,81	1,48	28,6	54,8	0,14	4,35	7,07	0,96	6,49
CMD[1]	0.78	65.3			0,84	1,47	26,9	51,9	0,12	4,06	5,79	0,92	6,25
BA1	1.20				0.80	1.39	25.8	52.0	0.12	4.08	6.54	0.89	5.85
BA2	0.93				0.80	1.29	25.8	49.0	0.11	3.82	8.24	0.84	5.38
FA1	0.95		1.30	3.28	0.78	1.30	24.9	46.5	0.11	3.68	10.7	0.80	5.41
FA2	0.93		1.39	2.71	0.83	1.30	24.8	45.9	0.11	3.67	10.8	0.78	5.24
FA3	1.20		1.47	3.55	0.88	1.30	24.9	47.1	0.12	3.95	10.6	0.82	5.57
FA4	1.30		1.35	3.73	0.86	1.30	26.0	48.7	0.12	4.00	8.33	0.85	5.63
FA5	0.99		1.38	2.84	0.76	1.29	25.2	45.0	0.11	3.54	10.7	0.77	5.15
FA6	1.10		1.33	3.21	0.80	1.29	25.8	46.7	0.12	3.86	10.4	0.82	5.42
FA7	1.20		1.27	3.56	0.84	1.29	25.2	46.6	0.11	3.75	10.4	0.80	5.41
FA8	1.00		0.99	2.81	0.80	1.29	24.8	46.3	0.11	3.77	11.3	0.79	5.33
FA9	0.99		1.40	4.06	0.85	1.24	25.4	47.0	0.11	3.89	9.99	0.83	5.35
FA10	1.30		5.68	9.51	0.85	1.41	26.0	43.8	0.13	3.14	9.68	1.08	7.84
FA11	1.20		5.81	8.95	0.78	1.39	25.6	43.2	0.12	3.15	9.54	0.99	7.04
FA12	1.70		3.97	7.35	0.79	1.32	24.8	44.9	0.11	3.59	9.93	0.88	6.29
FA13	1.20		2.70	5.47	0.79	1.29	24.7	46.1	0.12	3.81	10.1	0.87	6.06
FA14	1.30		5.30	10.0	0.79	1.43	25.6	43.5	0.13	3.17	9.51	1.07	8.02
FA15	1.30		5.78	9.79	0.87	1.40	25.8	45.2	0.13	3.34	9.58	1.03	7.26
FA16	1.30		4.44	7.37	0.80	1.33	24.6	45.7	0.11	3.70	10.8	0.86	6.05
FA17	1.40		2.45	5.04	0.78	1.30	25.4	45.4	0.11	3.64	9.53	0.83	5.84

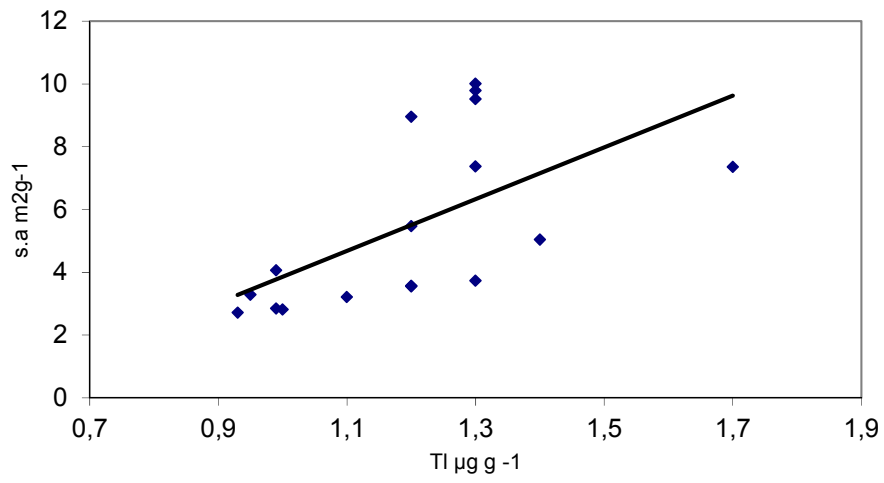1. Composition of the ashes of these coals.

Figure 2.- Relationship between thallium and the surface area for all the ashes.

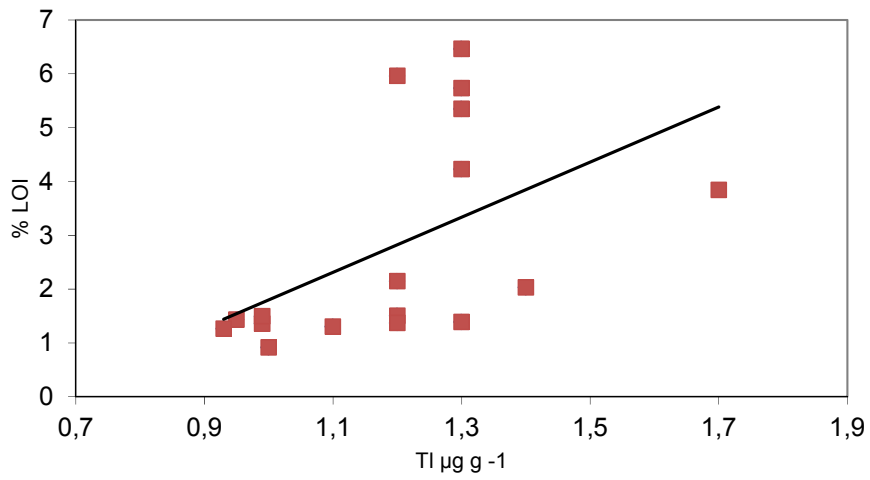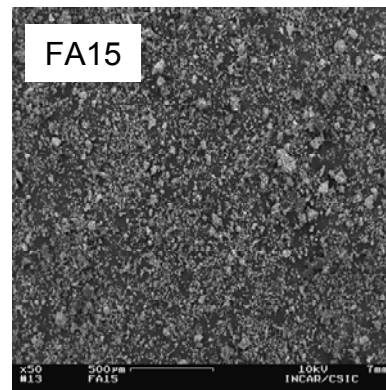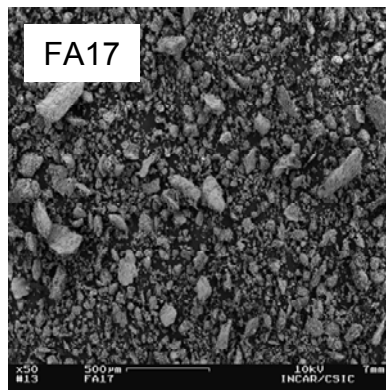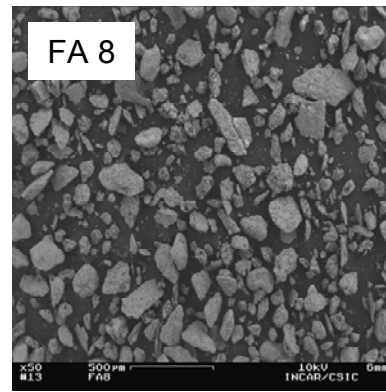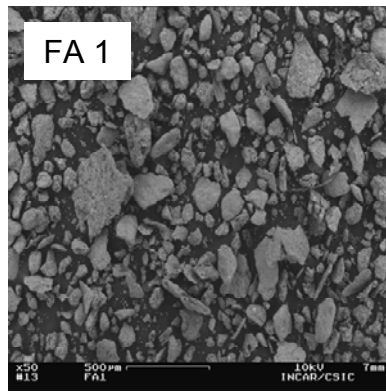Figure 3.- Relationship between thallium and LOI for all the ashes

Figure 4.-SEM Images of some representative ashes using the same power of magnification
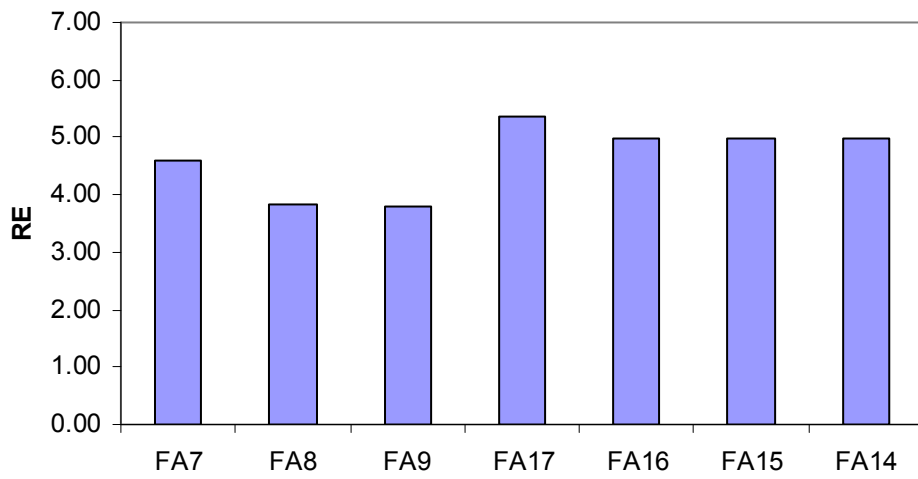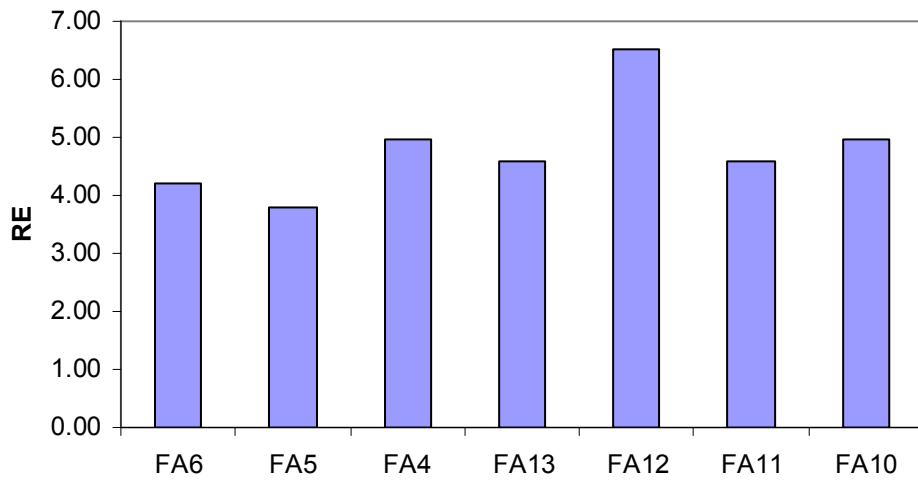
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Figure 5.-Enrichment factors of thallium in the fly ashes obtained from the hoppers of the electrostatic precipitators

Table 3.-Estimated balance of thallium in the solids of the plant

input	output					Tl_{out}/Tl_{in}
% wt	% wt					
CM	BA	FA stripper	FA cyclone	ESP	∑output	
48.3	14.8	11.5	2.9	21.3	50.5	1.05