

ARSENIC AND SELENIUM CAPTURE BY FLY ASHES
AT LOW TEMPERATURE

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ABSTRACT

Arsenic and selenium compounds may be emitted to the environment during coal conversion processes, although some these compounds are retained in the fly ashes, in different proportions depending on the characteristics of the ashes and process conditions. The possibility of optimizing the conditions to achieve better trace element retention appears an attractive, economic option for reducing toxic emissions. This approach requires a good knowledge of fly ash characteristics and a thorough understanding of the capture mechanism involved in the retention. In this work the ability of two fly ashes, one produced in Pulverized Coal Combustion and the other in Fluidized Bed Combustion, to retain arsenic and selenium compounds from the gas phase in coal combustion and coal gasification atmospheres was investigated. In order to explore the possible simultaneous retention of mercury, the influence of the unburned coal particle content was also evaluated. Retention capacities between 2-22 mg g⁻¹ were obtained under different conditions. The unburned coal particle content in the fly ash samples does not significantly modify retention capacities.

Keywords: Fly ash, unburned carbon, mineral matter, arsenic and selenium.

INTRODUCTION

Fly ashes constitute most of the waste generated in coal-fired plants (1). Fly ashes are fine particles of aluminosilicate glass, quartz, mullite, hematite, ferrite, and anhydrite or lime in different stages of transformation depending on their origin. They may also contain a variable but small proportion of organic matter (unburned). The proportion and characteristics of the fly ashes depend not only on the nature, mineral matter content and composition of the coal, but also on the coal combustion technology and process conditions employed.

Some of the components of the mineral matter in coal are volatilized during coal combustion and gasification. As a consequence, energy generation from coal is one of the anthropogenic sources of trace element emissions. It has been proved that some of the gaseous species produced from trace element evaporation condense or react on the surface of the fly ashes present in the flue gases. This may occur in the gas stream and in the particle control devices at different temperatures. The elements are either partially or totally retained in the particles, leading to a reduction in the amount of trace elements emitted to the atmosphere in gas phase. However, the emission of elements concentrated in smaller size particles that are not retained by the particle control devices, cannot be avoided (2-5).

Although arsenic and selenium are essential trace elements for humans and animals, they have also been linked to harmful toxicological impacts. Concentrations of arsenic in coal may reach $100 \mu\text{g g}^{-1}$, whereas selenium is generally present in concentrations lower than $2 \mu\text{g g}^{-1}$. The proportion of these species retained in fly ashes during coal combustion and gasification processes may vary in different power stations. In general terms a high fraction of the arsenic originally present in coal is captured in fly ash particles as a result of a condensation process or due to a reaction with some of

the fly ash components, whereas selenium escapes in gas phase in larger proportions (3). Any improvement to the process that would entail a more efficient capture of arsenic and selenium by fly ashes would be a significant step forward. This may be achieved by favouring trace element and ash interactions, or by reusing the fly ashes as a sorbent during the actual process. Recycling fly ashes or some of their components as sorbents, mainly for the capture of mercury (6-8) and to a lesser extent arsenic and selenium, has been studied previously (9), and the possible capture of mercury on unburned particles in fly ashes has been contemplated. For arsenic and selenium, however, the principal means of capture have been the major inorganic components (10-11). Although the retention mechanisms are not yet completely understood, previous works on arsenic and selenium retention using different solid sorbents (12-15) provide a good basis for understanding the interaction of these elements with the components of fly ashes.

The aim of this study was to ascertain the ability of different fly ashes to retain arsenic and selenium species from coal combustion and gasification flue gases at low temperature and to identify the components involved in this retention. The ultimate aim will also try to identify the conditions which would optimize this retention and assessing the possibility of reusing fly ashes as sorbents.

EXPERIMENTAL SECTION

Two fly ash samples (CTP and CTA), were studied. CTP was taken from a fluidized bed combustion plant (La Pereda, Asturias, Spain) which burns a mixture of coal wastes and bituminous coals of high ash content and employs limestone in its bed. CTA was sampled from a pulverized coal power plant (Anllares, Leon, Spain), which burns high rank coals. Fractions rich in unburned coal particles were separated by size

fractionation and oil agglomeration. Oil agglomeration experiments were conducted in a commercial seven speed Waring blender, using domestic oils as agglomerants following a method previously developed (16-17). The oil agglomerates obtained from the fly ashes were filtered, washed with ethanol, perchloroethylene and ethyl ether to extract the oil, water-washed and dried overnight at 50°C.

The original fly ashes and the separated fractions were characterized by various methods. Atomic absorption spectrometry (AAS) was used to determine the elemental composition, including total CaO. Free CaO was determined by the Standard method UNE-EN 451-1. A morphological study was carried out by Scanning Electron Microscopy (SEM) and the BET surface area was determined by volumetric adsorption of nitrogen at 77K. Thermodynamic equilibrium calculations using HSC-Chemistry 5.1 software were employed to predict the composition of the chemical species in the gas phase and any possible reactions with the fly ash components.

The experimental device used for the retention experiments consisted of a quartz reactor fitted with an internal and external tube and heated in two furnaces (Figure 1). The trace elements in the gas phase were obtained from the evaporation of As_2O_3 and Se at 250°C and 400°C respectively. The sorbent and element source were placed inside the same internal tube but heated separately in the two furnaces. The temperature of the sorbent bed was 120°C. Synthetic gas mixtures, typical of coal combustion (64% CO, 3.7% CO₂, 20.9% H₂, 4.0% H₂O 1.0% H₂S balanced with N₂), and gasification processes (15% CO₂, 9.2% O₂, 0.2% SO₂, 6.6% H₂O balanced with N₂), were passed through the reactor. These gas mixtures carried the element compound in vapor phase through the sorbent bed at a flow rate of 0.5 L min⁻¹. The sorbent bed was prepared by mixing 1 g of fly ash with 3 g of sand homogenate by shaking. The bed was 2.5 cm in diameter and 1.1 cm in height. The amount of element condensed in the reactor before it

reached the sorbent bed was determined by carrying out a blank experiment, cleaning the reactor using HNO_3 , and analyzing the element in solution. The element not retained in the sorbent was captured in impingers containing HNO_3 0.5N. The quantity of element retained in the sorbent was analyzed by ICP-MS (As) and HG-ICP-MS (Se) (18), after dissolution in a microwave oven. Sorption capacity (milligrams of element per g of sorbent) and efficiency (percentage of element retained) were then evaluated. To determine maximum retention capacity (MRC), a series of experiments were conducted, in which the quantity of the element source was gradually increased until the sorbent was saturated. Post-retention fly ashes were analyzed by laser ablation, inductively coupled plasma mass spectrometry (LA-ICP-MS) and Scanning Electron Microscopy coupled to Energy Dispersive X-ray analysis (SEM-EDX). Desorption experiments were carried out in the same conditions as adsorption, at the same temperature and using the same gas composition (combustion and gasification). They were performed on the samples of sorbent post retention obtained when the MRC was attained. Desorption in each case was evaluated in a test carried out for the same duration of time necessary to obtain the MRC for each element.

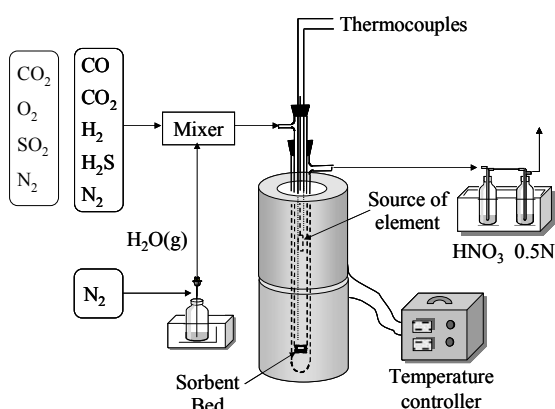


Figure 1. Schematic diagram of the experimental device.

RESULTS AND DISCUSSION

The characteristics of the fly ashes and the selected fractions obtained after size fractionation and oil agglomeration are given in Tables 1-2. The fractions were selected on the basis of a previous size fractionation study (19) from which it was concluded that in the CTA sample unburned coal particles are concentrated in the fractions of large particle size. Three samples obtained from CTA were studied. One was the original fly ash and the second the size fraction with the highest loss on ignition (LOI). This was the size fraction separated from the raw fly ash sample by sieving to a size of more than 150 μ m size and is designated in the work as CTA>150 μ m. The third fraction was obtained by agglomerating the CTA>150 sample with a vegetable oil (CTA>150 agl). The LOI value of CTA>150 was 22.4%, this concentration reaching 73 % when CTA>150 was agglomerated using a 5% vegetal oil emulsion (19). In the preliminary size fractionation study for the CTP sample it was observed that the unburned particles were homogeneously distributed among the different particles, all of which had similar LOI values. For this reason only the raw CTP sample was used in this work.

Table 1. -Ash content and BET surface area in different fly ash samples

Sample	Ash content (%)	Surface Area (m^2g^{-1})
CTA orig.	94.3	1.6
CTA>150	77.6	4.2
CTA>150 agl.	27.0	5.8
CTP orig.	96.2	6.7

The ash content and surface area of the four samples studied in the retention experiments are presented in Table 1. An increase in the surface area of the CTA fractions is observed as the unburned coal particle content increases. Although the

differences in surface area are not significant when compared to porous materials, they can be used for evaluating the properties with other similar fly ashes that are studied for mercury capture (20). As regards their morphology, it was confirmed by SEM, that fly ashes from a coal-pulverized power plant (CTA) are formed mainly by microspheres, while the fly ash particles from a fluidized bed boiler (CTP), are irregular in shape.

Table 2. Elemental composition for the different fly ash samples.

% (db)	CTA orig.		CTA >150		CTA >150 agl.		CTP orig.	
	FA	HTA	FA	HTA	FA	HTA	FA	HTA
SiO ₂	53.3	56.5	43.2	55.7	15.7	58.2	52.1	54.2
Al ₂ O ₃	25.6	27.2	20.4	26.3	6.75	25.0	21.9	22.8
Fe ₂ O ₃	5.87	6.23	5.14	6.63	1.53	5.67	5.97	6.21
MgO	1.82	1.93	1.27	1.64	0.52	1.92	1.39	1.44
Na ₂ O	0.72	0.76	1.87	2.41	0.23	0.85	0.63	0.66
K ₂ O	3.37	3.57	3.18	4.10	0.99	3.65	2.98	3.10
TiO ₂	<1	<1	<1	<1	0.41	1.50	<1	<1
SO ₃	0.31	0.32	0.17	0.22	0.14	0.52	5.12	5.32
CaO _{total}	2.09	2.22	1.25	1.61	0.73	2.70	6.36	6.61
CaO _{free}	0.11	0.12	0.04	0.05	0.05	0.18	1.06	1.10

The composition of the inorganic components of the fly ash and fraction samples is shown in Table 2. This composition is calculated using two different formats; i) percentages of oxides in the samples (FA) and ii) percentages of oxides in the ashes of these samples obtained at 815 °C by the the ISO standard method (HTA). By comparing the compositions of the HTAs it is possible to balance the differences in the relative proportions of each component, whereas a comparison of the FAs compositions would make it possible to contrast the absolute concentration in the samples. The composition of the HTAs of the three CTA fractions may be considered similar, the only exception

being the high Na content in CTA >150, and the higher proportion of free CaO in the original CTP. From an evaluation of the ash composition of the original CTA and CTP samples, the most remarkable difference was found to be the higher total CaO content in CTP. Bearing in mind that arsenic and selenium may interact with the CaO particles, as previously suggested (9,12-15), special attention should be paid to the free CaO content (21), which is significantly higher in the CTP sample. Arsenic capture by limestone has been observed and attributed to a chemical reaction between CaO and As₂O₃ resulting in Ca AsO₄ (12).

According to thermodynamic equilibrium data, in conditions similar to the experiments, As₄O₁₀(g) is the most stable species in combustion conditions, whereas As₄(g) is the thermodynamically stable species in the gasification atmosphere. For selenium compounds, SeO₂(g) can be expected to be the species present in a combustion atmosphere, whereas H₂Se(g) will form in a coal gasification atmosphere. Although different species were predicted for both elements and atmospheres at the evaporation temperatures, in all cases the speed of evaporation was similar and independent of the compound finally formed.

The experimental procedure was designed to evaluate the retention capacities of different fly ashes and fly ash fractions, using higher concentrations of arsenic and selenium species than those usually found in a coal. The element retained was determined by analyzing the fly ash post-retention after passing different amounts of arsenic or selenium through the fly ash sorbent bed. Evaluation of the retention of arsenic and selenium using sand as the inert material in the bed (Tables 3-4) has demonstrated that the capture of arsenic in combustion and gasification and selenium in gasification is negligible. In the case of Se in combustion a considerable amount is

condensed, the quantity retained in sand being 30% of the quantity retained when the bed contains sand + fly ash.

Table 3. Retention of arsenic in the sand and fly ashes in the two gas atmospheres at 120°C

Sorbent	combustion		gasification	
	MRC mg g⁻¹	%E	MRC mg g⁻¹	%E
sand	0.04	0.05	0.05	0.06
CTA orig.	2.8±0.1	12±4	2.1±0.1	12±4
CTA >150	3.5±0.1	13±6	2.9±0.1	15±6
CTA >150 agl.	4.2±0.1	18±9	3.8±0.1	18±5
CTP orig.	5.3±0.1	17±6	4.5±0.1	21±5

Table 4. Retention of selenium in the sand and fly ashes in the two gas atmospheres at 120°C

Sorbent	combustion		gasification	
	MRC mg g⁻¹	%E	MRC mg g⁻¹	%E
sand	4.7	9.7	0.06	0.08
CTA orig.	15.6±0.3	27±6	17.4±0.3	34±4
CTA >150	16.5±0.3	26±4	18.4±0.3	36±2
CTA >150 agl.	17.7±0.2	31±4	19.3±0.3	37±4
CTP orig.	17.8±0.3	38±5	21.5±0.4	35±6

The quantity of element retained in fly ashes (mg ret/g sorbent) was plotted against the quantity of element passed through the sorbent (mg gas/g sorbet). If the curve is fitted onto two straight lines, two parameters can be inferred. One is efficiency, defined as the percentage of element retained (%E) and the other the maximum retention capacity (MRC). Efficiency was estimated as the slope value of the line

corresponding to the unsaturated sorbent. MRC corresponds to the saturation level of the sorbent (Figures 2-3). The values for %E and MRC are presented in Tables 3-4. Each value was calculated as the average of several determinations (between 4 and 8) and the confidence limit of the results is given as the standard deviation. It can be observed that the retention of arsenic in both atmospheres is similar, retention decreasing slightly in the gasification atmosphere. However, in the case of Se, the MRC is slightly higher in the gasification atmosphere. The kinetics of the adsorption process does not significantly differ for either atmosphere despite the fact that different species were predicted in each case.

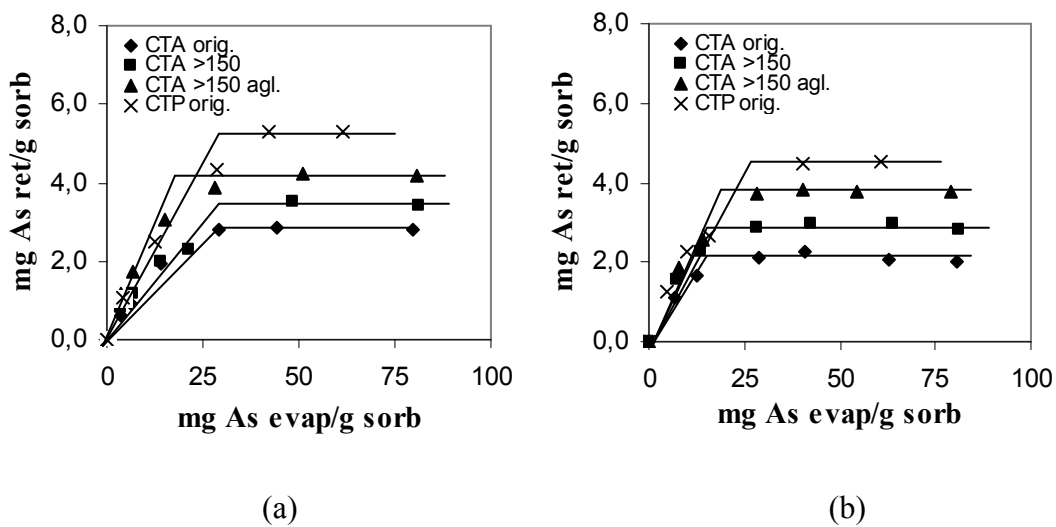


Figure 2. Arsenic retention in fly ashes in (a) the combustion and (b) the gasification atmosphere.

When the retention capacities of the CTA fractions which have different unburned particle contents are compared, no significant variations are observed. The results suggest that the unburned material in the different fly ash samples does not greatly influence arsenic and selenium retention, and only a small increase in MRC and efficiency is observed when the unburned coal particle content rises. MRC always

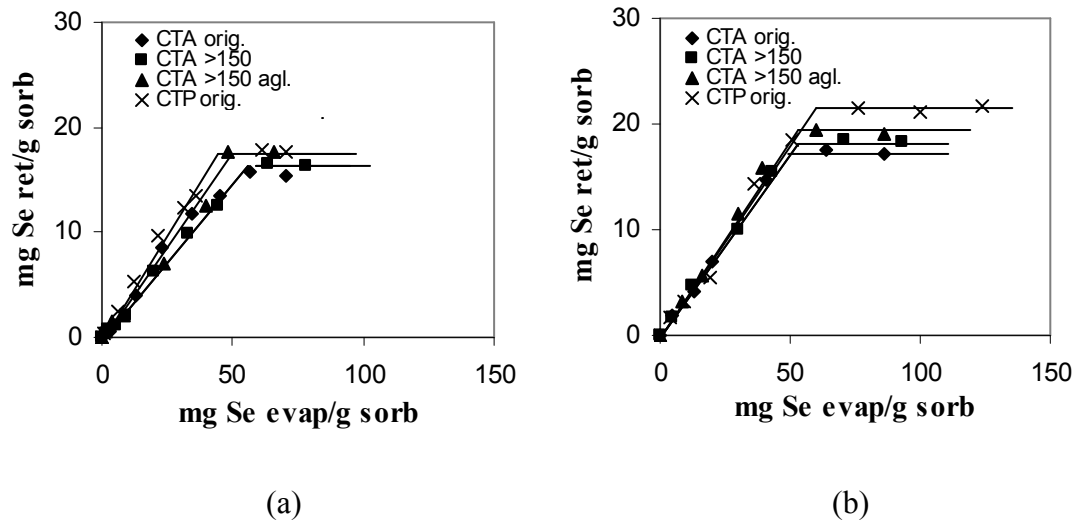


Figure 3. Selenium retention in fly ashes in (a) the combustion and (b) the gasification atmosphere.

shows a higher value in the CTP fly ash which is the one with the smallest unburned carbon content. Retention hardly increases with carbon material content in the same fly ash, although a high surface area, due to an increase in unburned carbon content (Table 1), favors the retention of these elements in both the combustion and gasification atmospheres.

Identification of As and Se relationships using the fly ash components after the retention experiments was carried out by both SEM/EDX and LA-ICP-MS. In spite of the low detection limits of SEM/EDX compared to LA-ICP-MS, the results obtained by the two techniques confirm the same associations (Figures 4-6). The LA-ICP-MS analysis showed relations between Ca-As and Fe-As in the CTA orig and CTP orig fly ashes post retention in the combustion and the gasification atmospheres. The relationships found were similar for both the CTA and CTP samples in both atmospheres. As an example, Figure 4 illustrate the relationships between As and Ca obtained for the CTA sample in the combustion and gasification atmospheres. Similar

relationships were obtained between As and Fe. Moreover, an analysis by SEM-EDX in the CTP orig sample corroborated the presence of relatively high quantities of arsenic in particles that have high proportions of Fe (Figure 5).

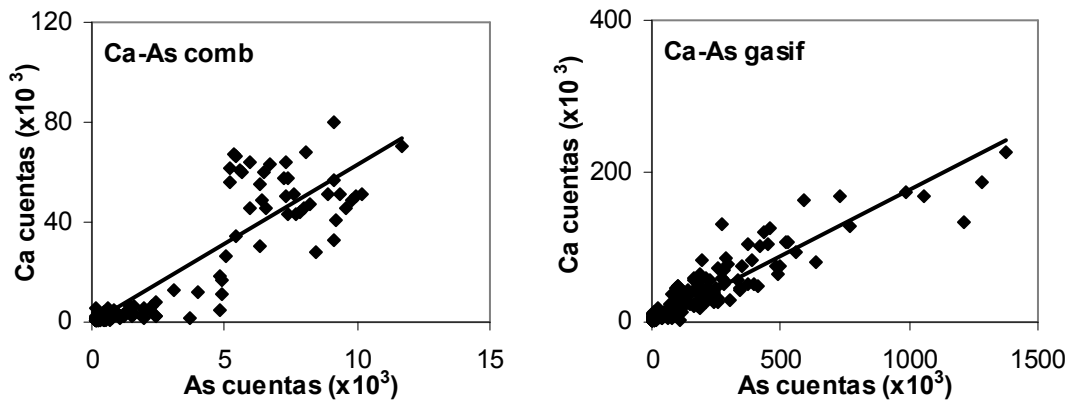


Figure 4. Relationships observed by LA-ICP-MS between arsenic and calcium in the combustion atmosphere and in the gasification atmosphere.

Counts

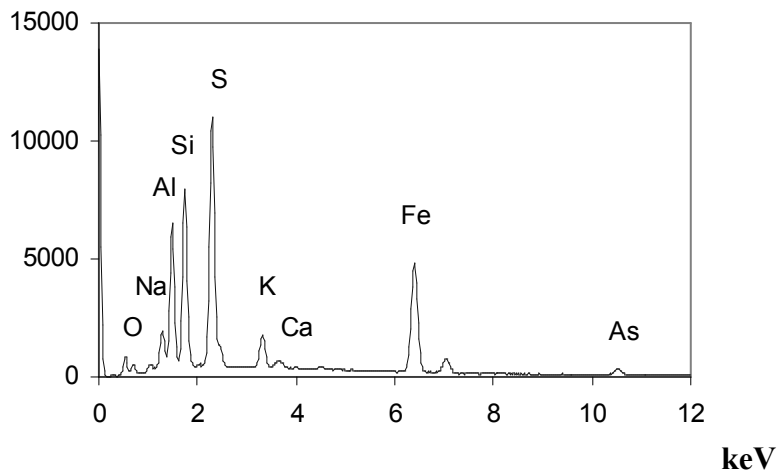


Figure 5. Analysis by EDX of post-retention fly ash CTP obtained in the gasification atmosphere

Se was not identified by SEM/EDX in any of the particles of fly ashes post retention in the combustion atmosphere. However, it was found in the fly ashes containing high quantities of Ca (CTP orig), after the experiments carried out in the gasification atmosphere. When the fly ashes were analyzed by LA-ICP-MS, no Ca-Se associations or Fe-Se associations were identified in either CTA or the CTP fly ashes post retention in the combustion atmosphere. Figure 6 shows an example of this non-correlation for the CTA sample. However, in the ashes obtained in the gasification atmosphere, relationships between Se and Ca and Fe were observed also in both cases.

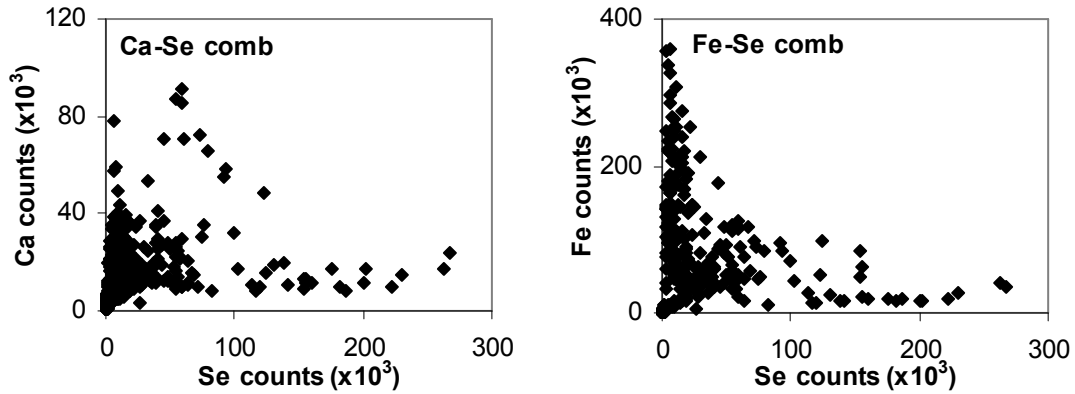
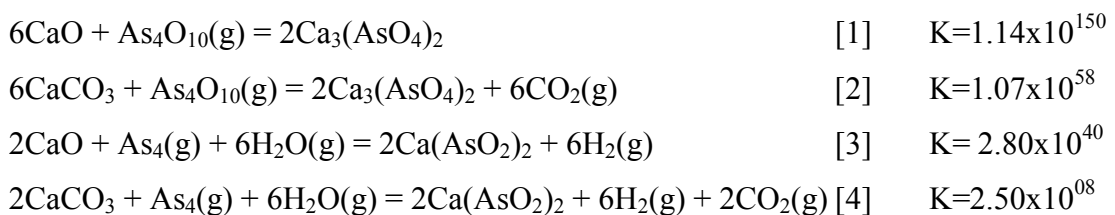
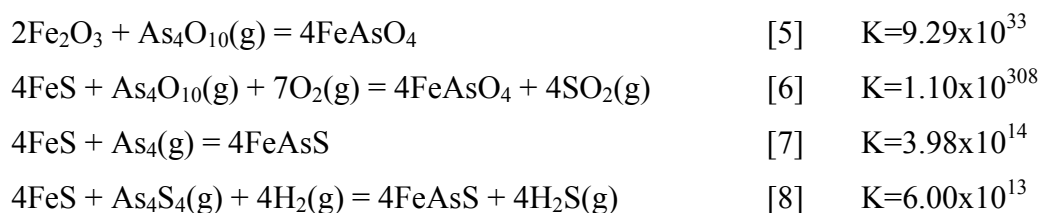


Figure 6. Relationships observed by LA-ICP-MS between selenium and calcium and iron in the combustion atmosphere.

Various studies, including some of our previous works, have suggested possible Ca and/or Fe interactions with As and Se (9,12-15). Ca might react with As in both atmospheres as follows [1-4]



Similarly, the following thermodynamic Fe-As interactions may occur [5-8]:



These possible reactions are supported by the SEM/EDX and LA-ICP-MS results and by the desorption behavior of arsenic in the post retention fly ashes. When desorption experiments in the combustion and gasification atmospheres were carried out, arsenic linkage remained stable and none of this element was seen to leave the fly ash, implying a strong association rather than physical adsorption (Table 5).

Table 5. Percentages of element lost in the desorption experiments

Sorbent	combustion		gasification	
	As	Se	As	Se
CTA orig.	4%	92%	1%	25%
CTP orig.	1%	93%	1%	27%

In the case of selenium, MRC was higher in the gasification atmosphere where the species in gas phase was H_2Se (Table 4). A number of Ca-Se and Fe-Se interactions may be predicted from thermodynamic equilibrium calculations for the gasification atmosphere, the following reactions being possible at 120°C [9-10]:



According to previously published works (13-14), a chemical reaction between CaO and SeO₂ resulting in CaSeO₃ is possible in a combustion atmosphere, but this reaction is not supported by results of this study. It should be considered that i) the losses of selenium in the combustion atmosphere after the thermal treatment at 120 °C were higher than 90% in all cases, and ii) the SEM/EDX and LA-ICP-MS analyses did not suggest any association between Se and Ca and Fe. However, in the gasification atmosphere after the same thermal treatment, only between 25-26% of the Se is desorbed, suggesting that the interactions in this atmosphere were stronger than in combustion (Table 5). Associations between Se and Ca and Fe were observed in the sorbents post retention in the gasification atmosphere by SEM/EDX and LA-ICP-MS. Therefore, in a combustion atmosphere physical adsorption is more likely than a chemical interaction, whereas in the gasification both chemical and physical adsorption may be responsible for Se capture in both fly ashes.

Although the differences between the MRC and %E results are not remarkable, the slightly higher values for CTP may be due to the higher Ca content. The carbonaceous material content in the fly ashes studied has no significant relation with arsenic and selenium retention. However some mineral matter compounds may lead to an increase in the retention of these elements.

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