MERCURY REMOVAL FROM COMBUSTION FLUE GAS BY USING OF ACTIVATED CARBON

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INTRODUCTION

The production of residues increases at such fast rates that their safe elimination becomes an important and updated problem. With a population of approximately 10 million, Portugal annually produces about 4 million tons of municipal solid wastes, and about 22% of this amount is incinerated [1].

The elimination of residues through the incineration and co-incineration represents a viable technical solution. This can reduce the initial volume of the wastes and offers the possibility of its energetic valorization.

The emission of hazardous pollutants in flue gases to the atmosphere resulting from the incineration process is the topic of main controversy against this technique. Hence measures have to be taken to reduce the impact of such emissions. The use of activated carbons (AC) is one of the options generally utilized for flue gas cleaning. Activated carbons can remove heavy metals, mercury and dioxins [2 - 4].

AC production technologies are expensive, so the search for new and low cost precursors and manufacturing methods are necessary. Agricultural and industrial residues can be alternative raw materials to the traditional feedstock, mostly mineral coal.

This paper reports the results of a research study on the mercury removal from flue gases, through reactive adsorption.

Two different activated carbons were tested to determine their efficiency for Hg adsorption. The first was an activated carbon prepared at INETI, from Paper Industry Wastes (ACPIW) following a chemical activation process with KOH. The second was commercially obtained from NUCON International, Inc. which has a commercial name Mersorb®, impregnated with elemental sulphur [5].

METHOD OF ACTIVATED CARBON´S PREPARING

In an attempt to produce economical and effective sorbents for the control of mercury emissions from flue gases resulting from combustion process, residues from various industries were tested. The most encouraging results were obtained with wastes coming from Paper Industry.

The ACPIW (Activated Carbon from Paper Industry Wastes) was prepared by chemical activation process with potassium hydroxide. The precursor previously crushed and dried was mixed with a solution containing the activating reagent. The mixture was dried at 110 ºC for 12 hours and put inside a basket made of stainless-steel. The basket was placed inside a cylinder-shaped reactor with a height of 1.85 m and 0.1 m diameter. An inert atmosphere was created in the interior of the reactor by continuous passing of a nitrogen flow. Then, the mixture

was heated at a rate of 10 ºC/min up to the process temperature at which it was held for 1 hour. After the activation process, the sample was cooled under N_2 flow and washed firstly with HCl and after with distilled water. The washed activated carbon was dried and characterised using physical adsorption of gases (N_2 at 77K and CO_2 at 273K). The results of this characterization are given in the Table 2.

MATERIALS USED

1. Fuels

Two different fuels separately and in mixture by 50:50% in weight, were used in a Fluidized Bed Combustor (FBC). The fuels were coal Carbocol, from Colombia and the commercially available sewage sludge, Biogran®.

Biogran® is supplied in form of grains with a diameter between 1.0 to 6.0 mm, with a dense texture adequate to be used, as received, in FBC systems.

The data on the proximate and elemental analyses of both, Carbocol and Biogran® are given in Table 1.

Table 1. Characterization of the fuels used

A. Proximate analysis (Wt%)		
	Carbocol	**Biogran®**
Moisture, (a.r.), %	3.6	8.0
Ashes, at 750ºC, (a.r.), %	7.5	34.0
Volatile matter, %, (d.b.)	36.6	50.0
Fixed Carbon, %, (d.b.)	52.3	8.0
B. Elemental analyses (Wt%, d.b.)		
Carbon	74.7	33
Hydrogen	5.1	4.8
Nitrogen	1.4	4.2
Sulphur	0.6	0.8
Chlorine	0.03	0.1
Superior Heating value, MJ/kg	29.5	13.9
Lower Heating value, MJ/kg	28.4	12.9
Mercury (a.r.), ppm	0.04	2.24

(a.r.) - as received; (d.b.) - dry base

2. Activated carbons

Two different activated carbons were tested to determine their Hg adsorption efficiency in flue gases. The first was the ACPIW, an activated carbon prepared at INETI following a process described above and the second was commercially obtained from NUCON International, Inc with a commercial name Mersorb®, impregnated with elemental sulphur. The main properties of both are given in Table 2.

Table 2. Properties of the activated carbons used

	ACPIW	MERSORB®
Specific surface area (by N_2 BET test method), m^2/g	573	1000
Volume of micropores (DR method), cm^3/g	0.24	0.39
Average width of the pores (DR method), nm	1.03	1.16
Impregnation reagent	----	Sulphur
Form	powder	pellets with a diameter of 1.5 mm

EQUIPMENTS AND TESTING METHODS USED

1) Pilot scale Fluidized Bed Combustor

The combustion tests were performed on a 90th kW atmospheric fluidised bed system [6]. The combustor height is 5 meters. It is square in cross section with each side being 30 cm. Its interior is made of refractory stainless steel and its exterior is well insulated with high temperature-resistant ceramic fibres. There are two heat exchangers: one placed in the bed region and the other in the upper part. The primary air enters through a distributor plate that has a form of inverted pyramid. The secondary air is supplied at different heights in the freeboard.
There are several openings for the fuel feeding, including a screw feeder, placed 50 cm above the distributor plate and which is connected to a silo with a weight cell. Most of elutriated particles are captured in the first cyclone. There is a second cyclone, which serves to increase the overall efficiency of collecting solid particles. The gases following the cyclones flow through a stack, in which it is possible to obtain samples for analysis.

2) The stack gas sampling set-up

The sampling of stack gases and their laboratorial analysis were carried out in accordance with the Standard Test Method for Elemental, Oxidized, Particle-bound and Total mercury in flue gases produced in coal-fired stationary sources, known as Ontario Hydro Method [7].
A flue gas sample is withdrawn from the stack with a probe and passes through a glass fibre filter located in the heated box, where the particulate matter is retained. A condensing/absorbing system of eight impingers immersed in an ice bath is connected to the hot box. The first,

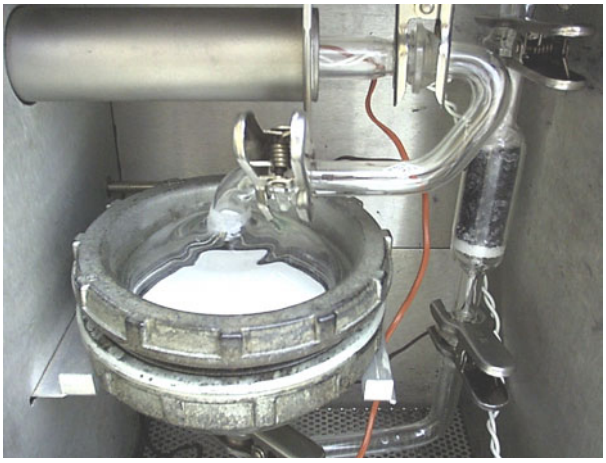

Figure 1. The interior of the hot box, with the adsorption reactor in operating position.

second and third impingers contain aqueous potassium chloride solution to trap oxidized Hg. The fourth one contains an aqueous solution of nitric acid with hydrogen peroxide. The fifth, sixth and seventh impingers contain an aqueous solution of potassium permanganate with sulphuric acid. The elemental Hg is collected in these four impingers. The eighth impinger contains silica gel to trap the moisture from flue gases. A gas meter measures the volume of gas sample.
After the sampling is performed, the system is disassembled and the solutions, as well as particulate matter collected on the filter, are analysed.
The adsorbents are placed into a fixed bed adsorption reactor with a cylindrical form, made from borosilicate glass. The reactor is placed in the interior of the flue gas sampling set-up´s hot box, as shown in Figure 1.
An advanced Hg analyser LECO AMA 254 is used to measure Hg concentration in the samples collected. This instrument is a single purpose atomic absorption spectrophotometer for mercury determination.

RESULTS

1) Hg emissions with flue gases

To establish a baseline of the Hg emission levels with flue gases resulting from each fuel used, three combustion tests were performed: one with coal only (designated as C), the other with Biogran® just (designated as B), and finally the mixture of the two fuels (designated as M).
The sampling of flue gases and their analysis were performed in each run as described above. The results obtained are presented in Figure 2.

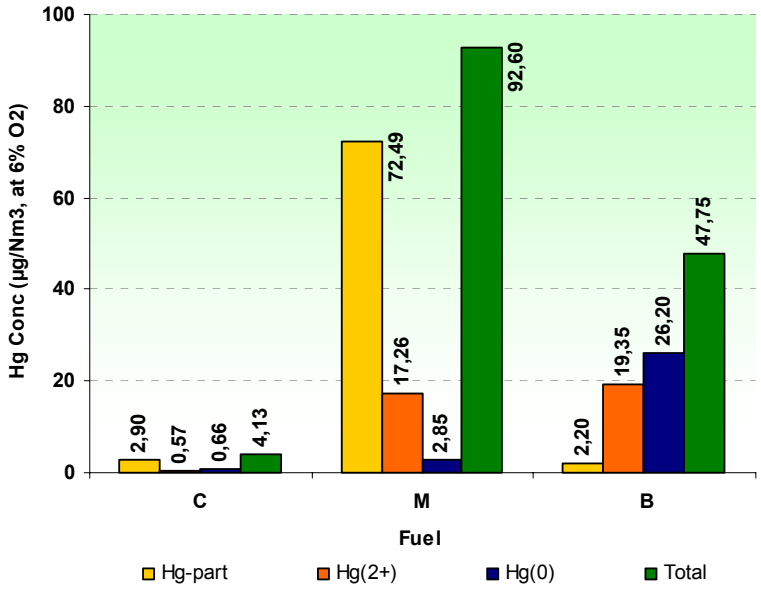

Figure 2. Mercury emission levels in flue gases resulting from various fuels.
Legend: Hg(part) - particle-bound mercury; Hg(0) - elemental mercury; Hg(2+) - oxidized mercury; Hg(t) - total mercury.

The results show that when the coal was burned alone, the concentrations of all Hg species were relatively low, because of the low Hg concentration in the coal.
The sum of the elemental Hg and oxidized Hg concentrations in test with the Biogran® is approximately the double of that obtained in the test with the mixture.
The total Hg concentration captured is found to be higher in the case of the combustion of the mixture than that of the Biogran® alone. This fact can be probably explained by elutriation of fine coal particles, probably due to attrition during the burning process, which are then captured in cyclones and on the filter. These fine particles on the filter are believed to absorb mercury prior to passing the gases through solutions.

2) Hg emission levels when an activated carbon is used

To determine mercury removal efficiency of the selected activated carbons, three combustion tests were performed which were: a) the mixture of the two fuels with Mersorb®, b) Biogran® alone with Mersorb®, c) the mixture with ACPIW. The mercury emission levels measured in these tests are presented in Figure 3.

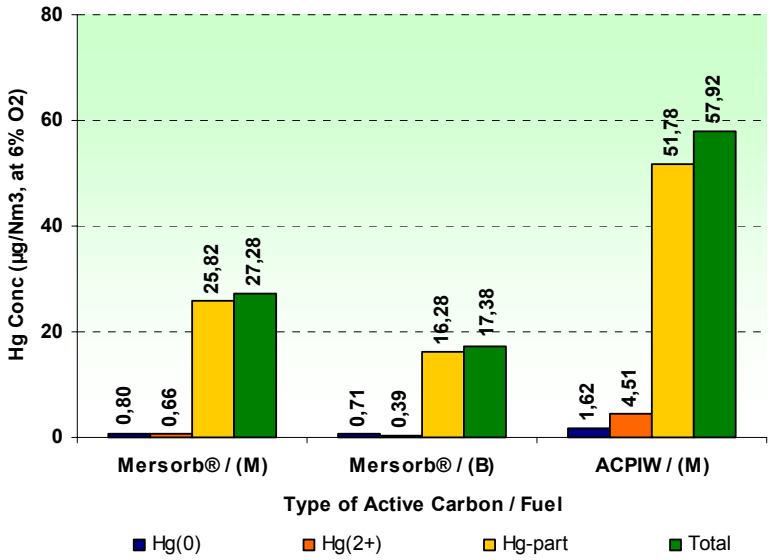

Figure 3. Mercury emission levels in flue gases when an activated carbon is used.
Legend: Hg(part) - particle-bound mercury; Hg(0) - elemental mercury; Hg(2+) - oxidized mercury; Hg(t) - total mercury; M - mixture of Biogran® and coal; B - Biogran®.

The results show that the concentrations of the oxidized and elemental mercury are very low in flue gases after going through an activated carbon fixed bed. To calculate Hg removal efficiency (% Ads), only the concentrations of these two mercury forms were used because the particle-bound mercury was trapped on the filter, placed before the adsorption reactor. Hence, the following formula was used:

$$\% Ads = \{[C(Hg^{2+} + Hg^{0})_{w/o\ a\ c} - C(Hg^{2+} + Hg^{0})_{with\ a\ c}] / C(Hg^{2+} + Hg^{0})_{w/o\ a\ c}\} 100$$

where $C(Hg^{2+} + Hg^{0})_{w/o\ a\ c}$ is the sum of the oxidized and elemental mercury concentrations in the flue gases produced during the tests performed without AC and $C(Hg^{2+} + Hg^{0})_{with\ a\ c}$ is the sum of the same species obtained during the tests performed with use of adsorbents.

The Mersorb® was found to have mercury adsorption efficiency of about 97.6% and 92.7% when the Biogran® was used alone and in a mixture with the coal, respectively. The ACPIW had a lower adsorption efficiency being about 69.5%, when the mixture referred to above was used as fuel.

These values were obtained at the temperature of 110 ºC, which is similar with the current operating temperatures for most ESP and baghouses used as Hg removal devices. Residence time of the flue gas in the adsorption reactor was about 0.07 s.

CONCLUSIONS

The ACPIW was prepared using wastes coming from Paper Industry and was tested, as well as Mersorb®, the commercial AC, regarding their mercury removal efficiency.

As expected, the Mersorb®, impregnated with sulphur, has shown greater mercury adsorption efficiency than the ACPIW, an untreated activated carbon for the specific application of Hg capture. Therefore, ACPIW should be improved by the impregnation or other treatment. This task is the aim of the on-going work.

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