

# A PILOT SCALE PLANT APPLICATION FOR THE REMOVAL OF ELEMENTAL MERCURY BY ACTIVATED CARBON

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## Abstract

Mercury emissions are major environmental and regulatory concerns due to the toxic nature of mercury and the significant ever increasing amounts of this pollutant released into the atmosphere by various natural and anthropogenic sources. Cleanup technologies available to control mercury emissions include wet scrubbing and adsorption on dry sorbents. The latter does not pose any problem of treating and inertizing liquid waste streams thus being very attractive for both small and large combustors such as those used for the incineration of hospital wastes or urban wastes, respectively. Particularly, activated carbon adsorption is a technology that offers a great potential for the control of gas-phase mercury emissions. This research group has already carried out several studies on mercury adsorption, both in metallic and divalent form, on a laboratory scale apparatus, by using activated carbon, even impregnated. This time a new pilot-scale apparatus, in which a spray-dryer reactor, used in this research as a column with cyclone effect, is used to adsorb metallic mercury. The simulated flue gas is obtained by evaporating liquid mercury (reagent grade  $\text{Hg}^0$  from BDH) contained in a thermostated glass saturator into an air stream. The solid sorbent is powdered activated carbon, injected in column to be available for the gas phase. The exhaust gas exiting from the reactor is then forced to pass through a fabric filter.

The main purpose of the present paper is the study of metallic mercury adsorption phenomena by using a commercially available activated carbon (Norit DARCO FGD). The experimental results have been obtained by varying the following parameters in the indicated range: reactor temperature ( $T_r$ , 80 to 120°C); initial mercury concentration ( $c_{\text{Hg}}^{\text{in}}$ , 100 to 200  $\mu\text{g}/\text{m}^3$ ); carbon flowrate ( $M_c$ , 15.5 to 110.0 g/h) while the initial total gas flowrate was kept constant ( $Q_t = 52.30 \text{ m}^3/\text{h}$ ).

The main results obtained in this study show that mercury adsorption efficiency is higher at lower temperature, and that mercury removal efficiency up to 80% can be obtained for carbon concentrations in the range 0.3 to 2.1  $\text{g}/\text{m}^3$ . Moreover, the exhaust gas flowrate after fabric filter crossing, reaches mercury concentrations close to zero, in any case below the law imposed emission limits.

## Introduction

Gaseous mercury is one of the HAP (*Hazardous Air Pollutant*) in combustion flue gas that raises widespread concern throughout the world. Depending upon the combustion conditions and flue gas chemistry, mercury compounds may be emitted as bound particulate ( $\text{Hg}^{\text{p}}$ ), as oxidized mercury ( $\text{Hg}^{2+}$ ) or in the vapor state ( $\text{Hg}^0$ ), due to their high volatility. According to previous studies, combustion facilities such as coal-fired power plant, municipal solid waste incinerators (MSWI), ferrous or non-ferrous smelter, hazardous waste combustor (HWC) and so on are considered as the major anthropogenic sources of mercury to the atmospheric environment [1]. In particular, MSWI are considered the main anthropogenic

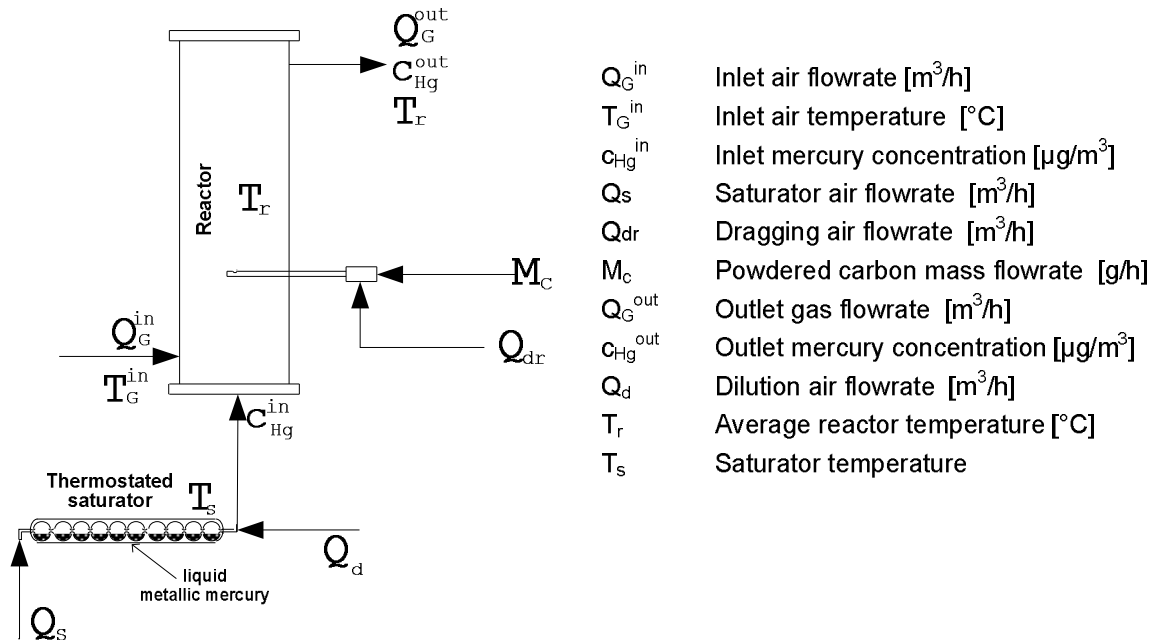
elemental mercury source (12 tons/year, [2]), since mercury is a trace element in MSW (0.5-4 mg of Hg/kg; [3, 4]). The difficulties in the removal caused by insolubility in water and poor reactivity with other species have made the  $\text{Hg}^0$  a major target of research in the field of gaseous mercury removal. In order to reduce the global emission of mercury, a cost-effective mercury emission control technology is required. Cleanup technologies available to control mercury emissions include wet scrubbing (alkaline solutions in wet FGD processes for a combined removal of  $\text{SO}_2/\text{Hg}$  [5]), and adsorption on dry sorbents. The latter requires neither treatment nor inertization of liquid waste streams and is very attractive for both small and large combustors such as those used for the incineration of hospital wastes or urban wastes, respectively. Sorbent injection methods have already been applied to incinerators or power plants [6, 7] to remove gaseous mercury in developed countries, because they can remove  $\text{Hg}^0$  as well as oxidized mercury. However, since the removal characteristics of gaseous mercury within flue gas by sorbent injection are largely affected by the composition of flue gas and the operational conditions, it is difficult to predict the characteristics of its removal. Activated carbon (AC) is a representative sorbent for mercury removal in flue gas; however, virgin ACs show poor removal of mercury compounds. For this reason, chemically treated activated carbons are often employed for mercury control. The use of activated carbon having large surface area can enhance the physical adsorption of mercury. Meanwhile, impregnation of activated carbon with elements such as sulfur, iodine, chlorine, and bromine can promote the chemical adsorption of mercury. These elements are known as providers of active sites for mercury bonding on a carbon surface [8]. However, despite the large amount of work carried out to evaluate the best operating conditions to capture the mercury present in the flue gas from MSW incinerators, the kinetic and thermodynamic values which characterize the adsorption, are not well known.

This research group has already carried out several studies on mercury adsorption, both in metallic and divalent form, on a laboratory scale apparatus, by using activated carbon, even impregnated [9, 10]. This time, a new pilot-scale apparatus with a continuous spray-dryer reactor, used in this research as a column with cyclone effect, is used in stationary conditions to adsorb metallic mercury by using a commercially available activated carbon (Norit DARCO FGD), injected in column to be available for the gas phase. The simulated flue gas is obtained by evaporating liquid mercury (reagent grade  $\text{Hg}^0$  from BDH) contained in a thermostated glass saturator into an air stream. The experimental results are reported as mercury loading and removal efficiency as a function of carbon concentration, showing that the adsorption mechanism is most likely a physical adsorption, and that depending on operating conditions removal efficiency up to 80% can be achieved.

## Materials and Methods

The experimental apparatus used for mercury adsorption experimental runs is sketched in Figure 1. It consists of a spray-dryer reactor, used as a column with cyclone effect (gaseous phase fed tangentially at the bottom of the vessel), equipped for metallic mercury adsorption. In detail, a stainless steel cylindrical reactor (height: 2.6 m, diameter: 0.36 m) is used to contact the synthetic gas (air + mercury) with the carbon flowrate injected in the column. The gas stream was obtained by evaporating liquid mercury contained in a thermostated glass saturator into a gaseous air stream. The saturator was made of a horizontally placed string of 10 empty glass spheres 30 mm ID, connected by short and narrow glass tubes (about 1 mm ID, 5 mm long), into which about 350 g of liquid mercury (reagent grade  $\text{Hg}^0$  from BDH) were deposited. This device allowed both a relatively large gas-liquid contact area (over the spheres) and a good mixing of the gas (in the tubes). The mass flow rate of the gaseous stream into the saturator  $Q_s$  was kept constant by a hot wire flow rate controller, and the  $\text{Hg}^0$  concentration in the gas stream fed to the reactor was controlled by varying the temperature of

the saturator and by diluting the saturated stream with an air dilution stream  $Q_d$ , the flow rate of which was controlled by another hot wire flow rate controller. A commercially available activated carbon (Norit DARCO FGD) was used as sorbent in powdered form. FGD carbon has a bulk density of  $510 \text{ kg/m}^3$ , a surface area of  $600 \text{ m}^2/\text{g}$ , and removes elemental mercury most likely according to a physical adsorption mechanism [11]. The carbon is introduced in the reactor through a proper designed device, a vibrating tank from which by means of a *Venturi effect* the carbon is injected in the reaction vessel.

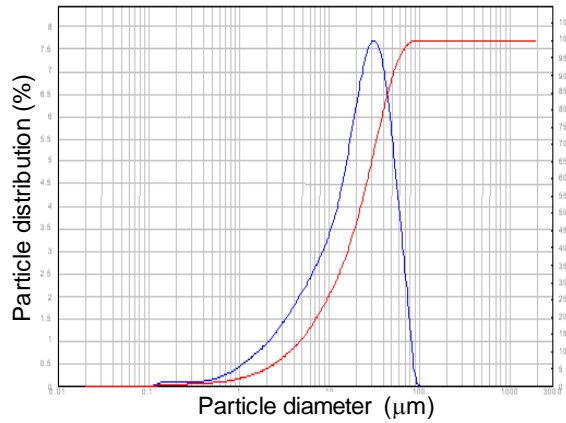


**Figure 1.** Reactor equipped for metallic mercury adsorption.

The carbon particle size distribution was characterized by means of a laser particle size analyzer (Malvern Mastersizer 2000) and is reported in Figure 2. The carbon powder had a relatively broad size distribution ( $0.1\text{--}80 \mu\text{m}$ ) with a *Sauter mean diameter*  $D_{32}=8.2 \mu\text{m}$ . The activated carbon adsorption capacity has been previously tested by the same research group in a laboratory scale fixed bed apparatus, whose characteristics together with the used experimental procedures and results are reported elsewhere [9]. It was observed that FGD carbon saturation at  $100^{\circ}\text{C}$  is relatively rapid, showing 50% mercury capture efficiency after about 1–2 min and 20% efficiency after about 5–10 min of operation.

Adsorption experiments carried out in the new pilot plant were conducted at different reactor temperature ( $T_r=80, 100$  and  $120^{\circ}\text{C}$ ), for three  $\text{Hg}^0$  concentrations in the inlet stream before the injection into the reactor ( $c_{Hg}^{in}=100, 150, 200 \mu\text{g}/\text{m}^3$ ), at different solid carbon mass flowrate ( $M_c=15.5, 62.7, 110.0 \text{ g}/\text{h}$ ), while the total gas flowrate was kept constant at the value  $Q_t=52.30 \text{ m}^3/\text{h}$ , where  $Q_t=Q_G^{in}+Q_{dr}+Q_s+Q_d$  (see Fig. 1)

The  $\text{Hg}^0$  concentration in the outlet gas stream from the reactor ( $c_{Hg}^{out}$ ) was continuously determined, as a function of time, by using the mercury continuous analyzer MONITOR 2000 by Seefelder Messtechnik. The remaining flue gas exiting the reactor ( $Q_G^{out}$ ) was forced to pass through a fabric filter in Terylene™ (Dalamat) and subsequently discharged to the environment.



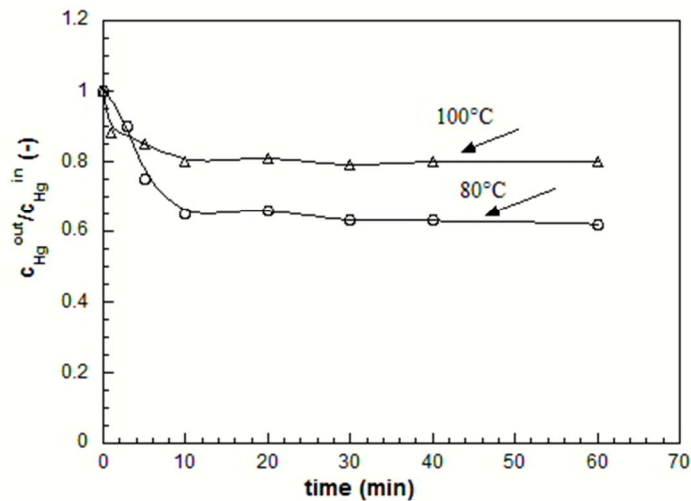
**Figure 2.** Particle size distribution for Darco Norit FGD carbon.

### Results and discussion

A typical response of an elemental mercury capture test in the new experimental apparatus is reported in Figure 3, which shows the outlet mercury concentration, referred to its initial value, as a function of time for two different tested temperature values ( $T_r=80$  and  $100^\circ\text{C}$ ), for the fixed carbon mass flowrate  $M_c=15.5$  g/h and carbon concentration  $c_c=0.30$  g/m<sup>3</sup>, defined as follows:

$$c_c = \frac{M_c}{Q_t} \quad (1)$$

The analysis of the figure clearly shows that the steady state condition is reached in a time which depends on the experimental conditions, but it is of the order of few minutes.

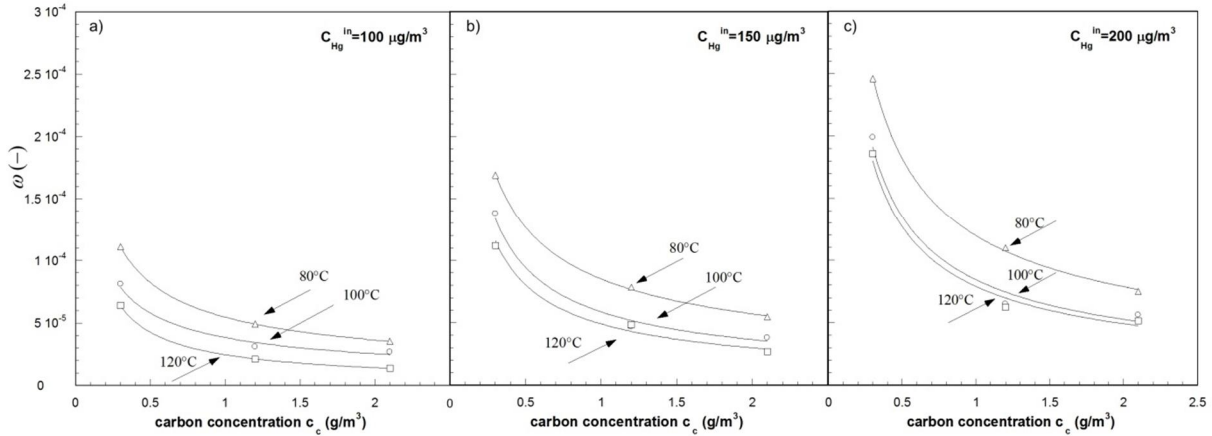


**Figure 3.** Outlet mercury concentration as a function of time;  
 $c_{Hg}^{in} = 200$   $\mu\text{g}/\text{m}^3$ ,  $Q_t = 52.30$   $\text{m}^3/\text{h}$ ,  $M_c = 15.5$   $\text{g}/\text{h}$ ;  $c_c = 0.30$   $\text{g}/\text{m}^3$ ;  
 $\circ$ :  $T_r = 80^\circ\text{C}$ ;  $\triangle$ :  $T_r = 100^\circ\text{C}$ .

Results obtained by the adsorption runs are reported in the following Figures 4 a-b-c and 5 a-b-c in terms of adsorbate loading ( $\omega$ ) and removal efficiency ( $\eta$ ), defined by the following equations:

$$\omega = \frac{10^{-6}(c_{Hg}^{in} - c_{Hg}^{out})Q_t}{M_c} \quad (2)$$

$$\eta = \frac{(c_{Hg}^{in} - c_{Hg}^{out})}{c_{Hg}^{in}} 100 \quad (3)$$



**Figure 4 a-b-c.** Adsorbate loading versus carbon concentration at the fixed initial mercury concentration;

a)  $c_{Hg}^{in} = 100 \mu\text{g}/\text{m}^3$ ; b)  $c_{Hg}^{in} = 150 \mu\text{g}/\text{m}^3$ ; c)  $c_{Hg}^{in} = 200 \mu\text{g}/\text{m}^3$ .  
 $\Delta$ : 80°C;  $\circ$ : 100°C;  $\square$ : 120°C.

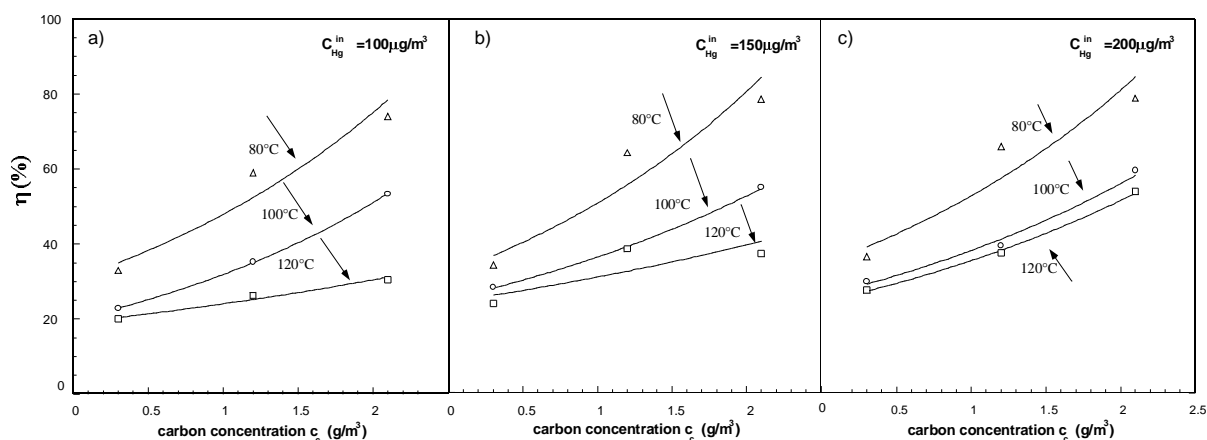
In details, Figures 4 a-b-c reports the adsorbate loading ( $\omega$ ) as a function of carbon concentration ( $c_c$ ) for three different initial mercury concentrations, *e.g.*  $c_{Hg}^{in} = 100 \mu\text{g}/\text{m}^3$  (Fig 4a),  $c_{Hg}^{in} = 150 \mu\text{g}/\text{m}^3$  (Fig 4b) and  $c_{Hg}^{in} = 200 \mu\text{g}/\text{m}^3$  (Fig 4c), respectively.

As can be noted, for a fixed mercury concentration level (each of the Figure 4a, 4b and 4c) and for every tested temperature, the adsorbate loading continuously decreases with increasing carbon concentration. This behavior is expected because for each temperature, the driving force of the process, expressed by the difference between inlet and outlet mercury concentration at the numerator of Eq. (2), decreases while the carbon mass flowrate increases, thus reducing  $\omega$ . Moreover, the comparison among the three tested temperatures indicates that adsorbate loading is promoted by the lower temperature, thus confirming that the adsorption is mainly of the physical kind. Moreover, the comparison among Figs 4a, 4b and 4c shows that by increasing the initial mercury concentration from 100 (Fig. 4a) to 200  $\mu\text{g}/\text{m}^3$  (Fig. 4c), other conditions being equal, the adsorbate loading gained for each temperature increases as expected.

Figure 5 a-b-c shows the removal efficiency  $\eta$  as a function of carbon concentration  $c_c$  for three different initial mercury concentrations, *e.g.*  $c_{Hg}^{in} = 100 \mu\text{g}/\text{m}^3$  (Fig 5a),  $c_{Hg}^{in} = 150 \mu\text{g}/\text{m}^3$  (Fig 5b) and  $c_{Hg}^{in} = 200 \mu\text{g}/\text{m}^3$  (Fig 5c), respectively.

Each of the figures (5a, 5b and 5c) shows that at a fixed temperature, the removal efficiency increases with increasing the carbon concentration from 0.30 to 2.10  $\text{g}/\text{m}^3$ , since in Eq.(3) the initial  $\text{Hg}^0$  concentration is the same, while the outlet  $\text{Hg}^0$  concentration decreases while increasing the amount of carbon  $M_c$ , and thus carbon concentration (Eq. 2). Moreover, it is clear the adverse effect of a temperature increase. It is also possible noting that, while changing  $c_{Hg}^{in}$  from 100  $\mu\text{g}/\text{m}^3$  (Fig. 5a) to 200  $\mu\text{g}/\text{m}^3$  (Fig. 5c), the efficiency variation interval is almost the same for  $T_r=80^\circ\text{C}$  and  $100^\circ\text{C}$ , varying in the range 33-79% and in the range 23-60% for  $T_r=80$  and  $100^\circ\text{C}$ , respectively; while at  $T_r=120^\circ\text{C}$  the efficiency are higher

at higher mercury concentration (Fig. 5c), not far from to the values obtained at  $T_r=100^\circ\text{C}$ , while at lower mercury concentrations the efficiency are much lower, as namely  $\eta$  is in the range 20-30% for  $c_{\text{Hg}}^{\text{in}}=100\mu\text{g}/\text{m}^3$  (Fig. 5a) and in the range 24-37% for  $c_{\text{Hg}}^{\text{in}}=150\mu\text{g}/\text{m}^3$  (Fig. 5b).



**Figure 5 a-b-c.** Efficiency versus carbon concentration at the fixed initial mercury concentration; a)  $c_{\text{Hg}}^{\text{in}} = 100 \mu\text{g}/\text{m}^3$ ; b)  $c_{\text{Hg}}^{\text{in}} = 150 \mu\text{g}/\text{m}^3$ ; c)  $c_{\text{Hg}}^{\text{in}} = 200 \mu\text{g}/\text{m}^3$ .  $\Delta$ :  $80^\circ\text{C}$ ;  $\circ$ :  $100^\circ\text{C}$ ;  $\square$ :  $120^\circ\text{C}$ .

## Conclusions

In this paper, the experimental results obtained in a new pilot plant for the adsorption of metallic mercury onto FGD activated carbon are reported. The results show that adsorbate loading is favorably influenced by a decrease in temperature, thus confirming that the physical adsorption mechanism is the most likely. Moreover, mercury capture efficiencies up to 80% were obtained for carbon loadings in the gas in the range  $0.3\text{--}2.1 \text{ g m}^{-3}$ , and the efficiencies increased with increasing carbon concentration for each tested temperature. Moreover, after the fabric filter crossing, the exhaust gas in each test reached mercury concentrations very close to zero.

In conclusions, the reactor column with cyclone effect and activated carbon injection in conjunction with a fabric filter may be considered a reliable treatment, allowing the respect of the law imposed limits as for mercury emissions.

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## Nomenclature

$c$	concentration ( $\mu\text{g}/\text{m}^3$ )
$D_{32}$	Sauter mean diameter
$M$	mass flow rate (g/h)
$Q$	volumetric gas flowrate ( $\text{m}^3/\text{h}$ )
$T$	temperature (K)

## Greek symbols

$\eta$	efficiency (dimensionless)
$\omega$	adsorbate loading ( $\text{g}_{\text{Hg}}^0/\text{g}_c$ )

## Superscripts

*in* inlet  
*out* outlet

## Subscripts

*c* carbon  
*d* dilution  
*dr* dragging  
*G* gas  
*Hg* metallic mercury  
*r* reactor  
*s* saturator  
*t* total

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