

## Adsorption of Mercury Chloride onto Activated Carbon on a New Pilot Scale Plant

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A commercially available activated carbon (Norit Darco FGD) has been used to perform experimental runs aimed to study the divalent mercury adsorption phenomena. The authors have already investigated about this topic, carrying out several studies on mercury adsorption, both in metallic and divalent form, by using activated carbon, on a laboratory scale apparatus. However this time their studies are focused on adsorption of divalent mercury chloride vapors onto a solid carbon phase dispersed in a continuous phase; so a new pilot scale plant necessitates. The new layout has permitted to investigate phenomena involved varying the following parameters: first of all the temperature reactor (from 120 °C to 135 °C), then the initial mercury concentration ( $C_{Hg}^{in}$ , 1000 to 2000  $\mu\text{g}/\text{m}^3$ ), finally the initial total gas flowrate (27.8 to 62.3  $\text{m}^3/\text{h}$ ). The carbon flowrate has been kept constant to 6 g/h value. Results obtained are very encouraging, as the activated carbon efficiency reaches up to 80% value.

### 1. Introduction

Incineration of municipal solid wastes (MSW) is regarded as an important source of Hg into the atmosphere. As a matter of fact, during combustion, most of mercury (up to 98%) is readily volatilized and can pass even through particulate control devices in the vapor phase. Mercury is present in the combustion flue gas either as elemental mercury ( $\text{Hg}^0$ ) or, in the oxidized form, as mercuric oxide ( $\text{HgO}$ ), mercuric chloride ( $\text{HgCl}_2$ ) and mercurous chloride ( $\text{Hg}_2\text{Cl}_2$ ). In flue gas from MSW incinerators mercury is mainly found as  $\text{HgCl}_2$  since there is a relatively high concentration of HCl; while elemental mercury is the prevailing form in emissions from coal combustion processes, due to the reducing properties of  $\text{SO}_2$  (Lancia et al. 1997). Among the mercury removal treatments available, dry adsorption processes give the advantage that there is no need to treat and stabilize any waste liquid streams; therefore they seem very attractive for coal combustors and hazardous/municipal waste incinerators. Moreover, mercury control devices must consider system-specific differences in terms of concentration and speciation ( $\text{Hg}^0$  or  $\text{Hg}^{2+}$ ) existing between coal combustors and waste incinerators. The best available technology (BAT) to reduce these emissions is considered to be fabric filters in combination with dry or wet adsorption methods. Particularly, activated carbon adsorption is a technology that offers a great potential for the control of gas-phase mercury emissions (Yan et al., 2004).

In the last two decades, the need to develop effective mercury control technologies and the attractive features of adsorption processes led researchers to focus their efforts on the evaluation of the adsorption kinetics and sorbent capacity of many different solid sorbents, particularly activated carbons (ACs). It has

been demonstrated that several factors potentially affect the efficiency of these sorbents in mercury removal from flue gas; these include the mercury speciation in flue gas; the flue gas composition and process conditions (e.g., flue gas temperature, particulate control equipment). These studies showed that: the elemental mercury is more difficult to be adsorbed than the oxidized form (Schager, 1990; Chang and Offen 1995; Karatza et al., 1996a, 1996b); the sorbent adsorption capacity spans over a wide range by changing the ACs (Ghorishi and Gullett, 1998; Yan et al., 2004; Karatza et al., 1996a, 1996b, 1996c) and, in general, the lower the temperature and  $\text{SO}_2$  concentration the higher the adsorption capacity (Gullett and Jozewicz, 1993; Krishnan et al., 1994; Karatza et al., 1998; Presto and Granite, 2007).

Moreover, studies devoted to reach a deeper insight of adsorption phenomena onto different ACs, often opportunely modified to increase their adsorption capacity, suggest the following: the higher the specific surface the higher the adsorption capacity (Yan et al., 2004, Karatza et al., 2011). Oxygen surface complexes, lactone and carbonyl groups (Di Natale et al. 2011, Karatza et al., 2013) are the favourite active sites for  $\text{Hg}^0$  capture (Li et al., 2003). Some additives e.g.,  $\text{Na}_2\text{S}$ ,  $\text{CuCl}_2$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{MnO}_2$  and  $\text{CuCoO}_4$ , added to the carbon by impregnation process, may have a positive effect on the metal mercury capture (Karatza et al., 1996c, Karatza et al., 2011; Lee et al., 2008; Mei et al., 2008).

Despite the large amount of work carried out to evaluate the best operating conditions to capture the mercury present in the flue gas, the kinetic and thermodynamic values which characterize adsorption are scarce, and the studies on mercury desorption by exhaust sorbents are lacking. It is worth noticing that mercury desorption is relevant either to recover the mercury and to detoxify the adsorbing material in order to avoid its stabilization before landfilling or to allow its reuse.

The main goal of the present article is to investigate the divalent mercury adsorption behavior by using a commercially available activated carbon in a pilot plant scale apparatus, with determining the adsorption efficiency at different temperatures and gas flowrates.

## 2. Materials and methods

The experimental apparatus used for mercury adsorption experimental runs is sketched in Figure 1. It consists of a column reactor with cyclone effect (gaseous phase fed tangentially at the bottom of the vessel), equipped for divalent 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 synthetic gas is realized through the injection of a liquid mercury solution, which is atomized in a nozzle. A commercially available activated carbon (Norit DARCO FGD) was used as a sorbent in powdered form. FGD carbon has a bulk density of  $510 \text{ kg/m}^3$ , a surface area of  $600 \text{ m}^2/\text{g}$ . 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. The result is that a solid carbon phase is dispersed in a continuous gaseous phase.

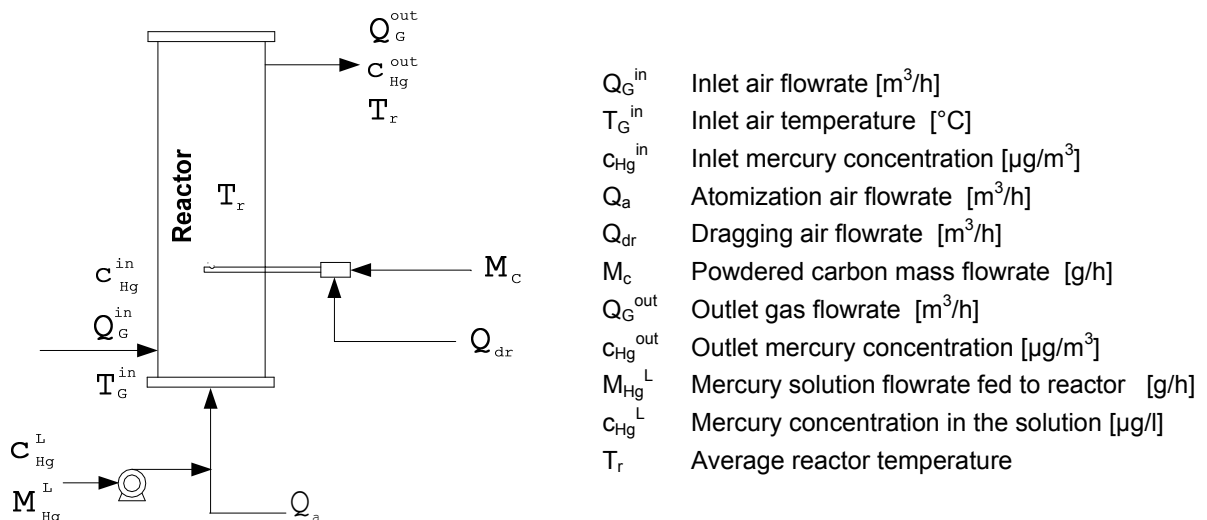


Figure 1: Overall reaction rate as a function of catalyst concentration;  $p_{\text{O}_2}=21.3 \text{ kPa}$

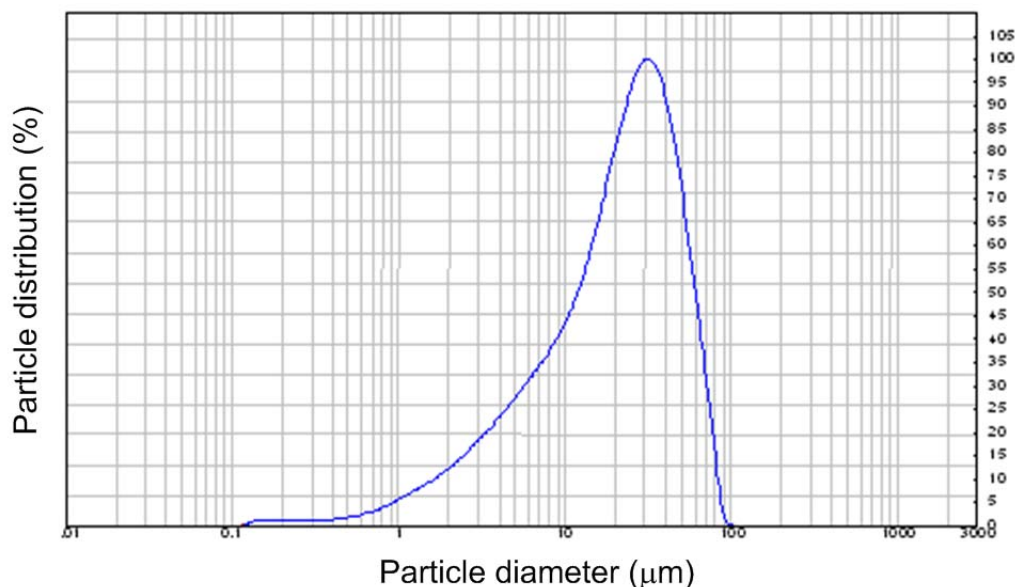


Figure 2: Particle size distribution for Darco Norit FGD carbon

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 (0.1–80  $\mu\text{m}$ ) 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 (Karatzas et al., 2006). 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 pilot plant were conducted at different reactor temperature ( $T_r=120, 130, 135 \text{ }^{\circ}\text{C}$ ), for three total gas flowrate  $Q_t$  ( $Q_t= 27.8, 46.1$  and  $52.3 \text{ m}^3/\text{h}$ ), where  $Q_t=Q_G^{in}+Q_d+Q_a$  (see Figure 1), at different  $\text{Hg}^0$  concentrations in the inlet stream ( $c_{\text{Hg}^0}^{in}=1000$  and  $2000 \mu\text{g}/\text{m}^3$ ), while the solid carbon mass flowrate was fixed to the value  $M_c=6.0 \text{ g}/\text{h}$ .

The  $\text{Hg}^0$  concentration in the outlet gas stream from the reactor ( $c_{\text{Hg}^0}^{out}$ ) was continuously determined, as a function of time. The  $\text{Hg}^0$  concentration in the outlet gas stream from the reactor was determined, as a function of time, by absorbing the gas by means of gas washing bottles for about 1 min.

A  $\text{KMnO}_4$  aqueous solution acidified by  $\text{H}_2\text{SO}_4$  (Wilshire et al., 1993) was used, and the samples were analyzed by means of Cold Vapor Atomic Absorption (CVAA), using  $\text{NaBH}_4$  as reducing agent.

Such procedure was considered accurate, since no mercury was found in the gas exiting the washing bottle when another bottle was placed in series to the first.

### 3. Results and discussion

A typical response of an elemental mercury capture test in the 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 initial mercury concentrations ( $c_{\text{Hg}^0}^{in}=1000$  and  $2000 \mu\text{g}/\text{m}^3$ ), at the temperature  $T_r=130 \text{ }^{\circ}\text{C}$ , for the fixed carbon mass flowrate  $M_c=6.0 \text{ g}/\text{h}$  and a carbon concentration  $c_c=0.10 \text{ g}/\text{m}^3$ , 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 about 15 minutes.

Results obtained by the adsorption runs are reported in the following figures in terms of removal efficiency ( $\eta$ ), defined by the following equation:

$$\eta = \frac{(c_{Hg}^{in} - c_{Hg}^{out})}{c_{Hg}^{in}} 100 \quad (2)$$

Figure 4 shows the removal efficiency ( $\eta$ ) as a function of carbon concentration  $c_c$  for the reactor temperature  $T_r=130\text{ }^\circ\text{C}$ , for the two tested initial mercury concentrations  $c_{Hg}^{in}=1000$  and  $2000\text{ }\mu\text{g}/\text{m}^3$ . The analysis of the figure shows that at a fixed temperature and initial mercury concentration, the removal efficiency increases with increasing the carbon concentration from  $0.10$  to  $0.22\text{ g}/\text{m}^3$ , since in Eq(2) 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 can be noted that for a fixed carbon concentration, when  $c_{Hg}^{in}$  doubles from  $1000$  to  $2000\text{ }\mu\text{g}/\text{m}^3$ , efficiency grows but less than 10 percent.

Figure 5 shows the removal efficiency ( $\eta$ ) as a function of reactor temperature  $T_r$  at the fixed carbon concentration  $c_c=0.13\text{ g}/\text{m}^3$ , for the two tested initial mercury concentrations  $c_{Hg}^{in}=1000$  and  $2000\text{ }\mu\text{g}/\text{m}^3$ . The analysis of the figure shows that for a fixed initial mercury concentration, carbon removal efficiency decreases with temperature growing, indicating that mercury adsorption is promoted by the lower temperature, and confirming that the adsorption is mainly of the physical kind. Once again, the effect of an increase in the initial mercury concentration is that of improving the efficiency, but not very intensely (see Figure 4).

#### 4. Conclusions

In this paper, the experimental results obtained in a pilot plant for the adsorption of divalent mercury onto FGD activated carbon are reported. The results show that adsorption is favourably 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  $0.10\text{--}0.22\text{ g}/\text{m}^3$ , and the efficiencies increased with increasing carbon concentration for each tested temperature. In conclusions, the reactor column with cyclone effect and activated carbon injection may be considered a reliable treatment, allowing the respect of the law imposed limits as for mercury emissions.

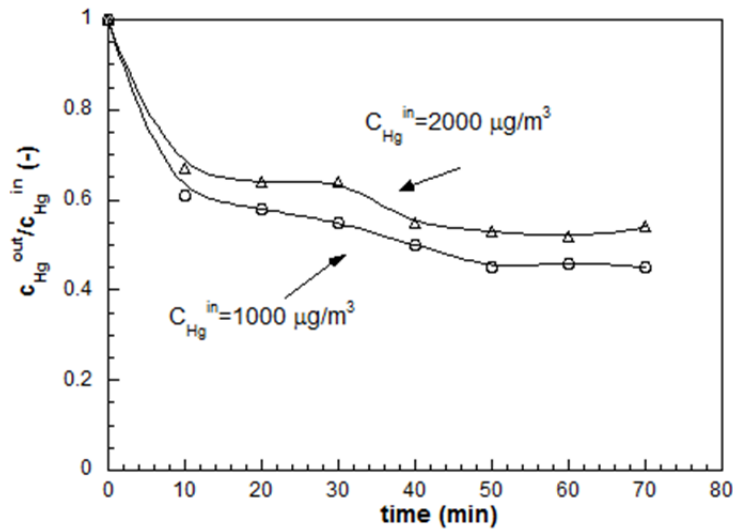


Figure 3: Outlet mercury concentration as a function of time;  $T_r=130\text{ }^\circ\text{C}$ ,  $Q_t=62.3\text{ m}^3/\text{h}$ ,  $M_c=6.0\text{ g}/\text{h}$ ;  $c_c=0.10\text{ g}/\text{m}^3$ ;  $\circ$ :  $c_{Hg}^{in}=1000\text{ }\mu\text{g}/\text{m}^3$ ;  $\square$ :  $c_{Hg}^{in}=2000\text{ }\mu\text{g}/\text{m}^3$

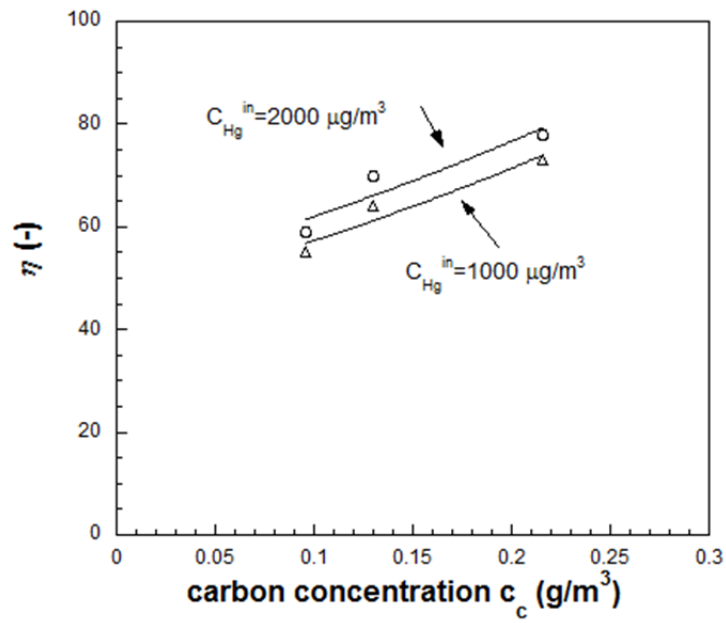


Figure 4: Efficiency vs. carbon concentration at  $T_r = 130$  °C;  $\square$ :  $C_{Hg}^{in} = 1000$  μg/m<sup>3</sup>;  $\circ$ :  $C_{Hg}^{in} = 2000$  μg/m<sup>3</sup>

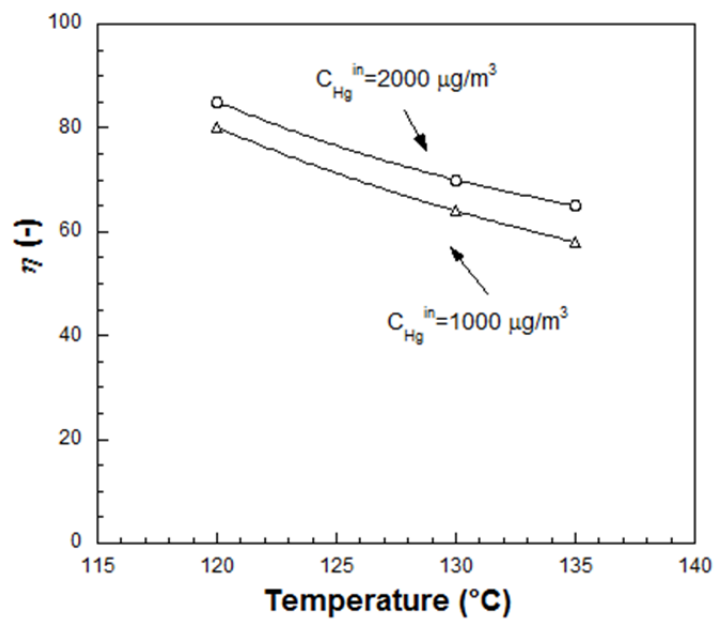


Figure 5: Efficiency vs. reactor temperature  $T_r$  at fixed carbon concentration  $c_c = 0.13$  g/m<sup>3</sup>.  
 $\Delta$ :  $C_{Hg}^{in} = 1000$  μg/m<sup>3</sup>;  $\circ$ :  $C_{Hg}^{in} = 2000$  μg/m<sup>3</sup>

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