

A Comparison among Different Sorbents for Mercury Adsorption from Flue Gas

Dino Musmarra^a, Despina Karatza^a, Amedeo Lancia^b, Marina Prisciandaro^c, Giuseppe Mazziotti di Celso^d

^aDipartimento di Ingegneria Civile, Design, Edilizia e Ambiente, Seconda Università degli Studi di Napoli, Real Casa dell'Annunziata, Via Roma 29, 81031 Aversa (CE), Italy

^bDipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università di Napoli "Federico II", P.le Tecchio 80, 80125 Napoli, Italy

^cDipartimento di Ingegneria Industriale e dell'Informazione e di Economia, Viale Giovanni Gronchi 18, 67100 L'Aquila, Italy

^dDipartimento di Scienze degli Alimenti, Università degli Studi di Teramo, Via Carlo R. Lerici, 64023 Mosciano S. Angelo (TE), Italy

marina.prisciandaro@univaq.it

The adverse effects of mercury on human health are a well-known problem, as mercury is a persistent toxic pollutant. Among the anthropogenic sources, the coal fired utility boilers, the combustion of municipal solid waste (MSW) and the cement production process are the main sources of mercury emission. The problem of mercury abatement is particularly tricky, because during combustion up to 98% of mercury is rapidly volatilized without being captured by means of particulate control devices.

The present work is focused on the removal of mercury compounds in flue gas by dry adsorption process on solid sorbents, which is considered a BAT (Best Available Technology) for mercury pollution control. In this paper, a comparison among different commercial solid sorbents (i.e. several commercial activate carbons) used by this research group to adsorb metallic and divalent mercury from combustion flue gas is presented. The tested activated carbon are HGR carbon and Darco G60 carbon, impregnated or not. The comparison is carried out in terms of isotherm curves, for the temperatures ranging from 90°C to 200°C, which is an interval typical of the exhaust gas treatment line downstream an industrial combustor.

1. Introduction

Mercury emissions can cause serious problems to human health. This is the reason why European Commission in 2006 established strict mercury concentration limits in some aquatic food (European Commission, 2006) reserved to human consumption, where mercury most efficiently accumulates (Pavlish, 2009). Mainly, mercury emissions can be found in exhaust gas from coal fired utility boilers (Uddin et al., 2008; Granite et al., 2000; Mazziotti di Celso et al., 2013), from the combustion of municipal solid waste (MSW) (Serre and Silcox, 2000; Jurng et al., 2002) and from the cement production process (Zheng et al., 2012; Prisciandaro et al., 2003).

Among these three processes, the highest values are imputed to MSW, as showed by Pacyna et al. (2006), who declared from 200 to 1000 $\mu\text{g of Hg}/\text{Nm}^3$ mercury concentrations in exhaust gas, while in coal fired utility boilers and cement production process they varies between 5 and 20 $\mu\text{g of Hg}/\text{Nm}^3$ (Zheng et al., 2012). In addition, not only mercury emission values, but also mercury species have to be considered: elemental mercury (Hg^0) is very hard to remove, due to its insolubility in water, low melting point and scarce reactivity with other species. Owing to these features, elemental mercury treatment has been widely studied in literature (Zheng et al., 2012; Karatza et al., 2011; Yao et al., 2014). Anyway in the flue gases from MSW incinerators, mercury is mainly found as HgCl_2 , due to the relatively high concentration of HCl (Heidel et al., 2014), while elemental mercury is the prevailing form in emissions from coal combustion processes (Pacyna et al., 2006).

The removal of Hg^0 and $HgCl_2$ is still a topical research. Many authors proposed different cleanup technologies, like mercury capture by means of sorbent injection (Pavlish et al., 2003; Yang et al., 2007; Karatza et al., 1996, 1998; Lancia et al., 1996): this is a promising one, which permits to incisiveness remove elemental mercury, with the main drawbacks due to the excessive amount of sorbent required, which is expensive, and the hard loading of particulate to the filter baghouse (Bustard et al., 2004).

Better performances can be obtained with adsorption technique onto active carbons (Musmarra et al., 2013). Particularly, active carbons with a large surface area allow mercury physical adsorption. Furthermore when they are impregnated with sulfur, iodine, chlorine or bromine, active carbons have demonstrated to be very efficient as regard mercury abatement. This remarkable behavior is due to the ability to activate, on the carbon surface, a lot of sites, where very strong chemical bounds with mercury are established (Choi et al., 2009). However, at the moment, in spite of the engagement of the scientific community, kinetic and thermodynamic mechanisms which lay the foundations for active carbon adsorption are not well known.

In this paper a comparison of mercury adsorption results obtained by using different commercial sorbents, impregnated or not, is reported. In particular experimental runs were performed with the following commercial activated carbons: HGR (from Calgon-Carbon Corp.) (Karatza et al., 2000), and Darco G60 (from BDH) alone (Karatza et al., 1996a) and impregnated with Na_2S in different percentage (Karatza et al., 1996b). The study was carried out in an apparatus at laboratory scale, in which simulated flue gas containing Hg^0 and $HgCl_2$, separately, was contacted with the above mentioned active carbons. Experiments were performed at a temperature of interest in the removal process (90–200°C) and with the concentration of Hg^0 and HCl_2 in the gas stream varying in the range of 1–7 mg/m^3 . Finally, equilibrium data were fitted with Langmuir isotherm, to obtain Langmuir parameters.

2. Experimental

In Figure 1 the apparatus used for the experiments with elemental mercury is sketched. A simulated flue gas, at the required temperature and Hg^0 concentration, was produced and mercury adsorption on fixed bed was carried out. The simulated flue gas was obtained by evaporating the liquid mercury contained in a thermostated glass saturator into a stream of pure nitrogen. 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 Hg^0 from BDH) were deposited. This design allowed both a relatively large gas-liquid contact area (in the spheres) and a good mixing of the gas (in the tubes). The mass flow rate of nitrogen into the saturator was kept constant by a hot wire flow rate controller. The Hg^0 concentration in the gas stream fed to the reactor was controlled by varying the temperature of the saturator and by diluting in the junction N the saturated stream with one of pure nitrogen, whose flow rate was controlled by another hot wire flow rate controller.

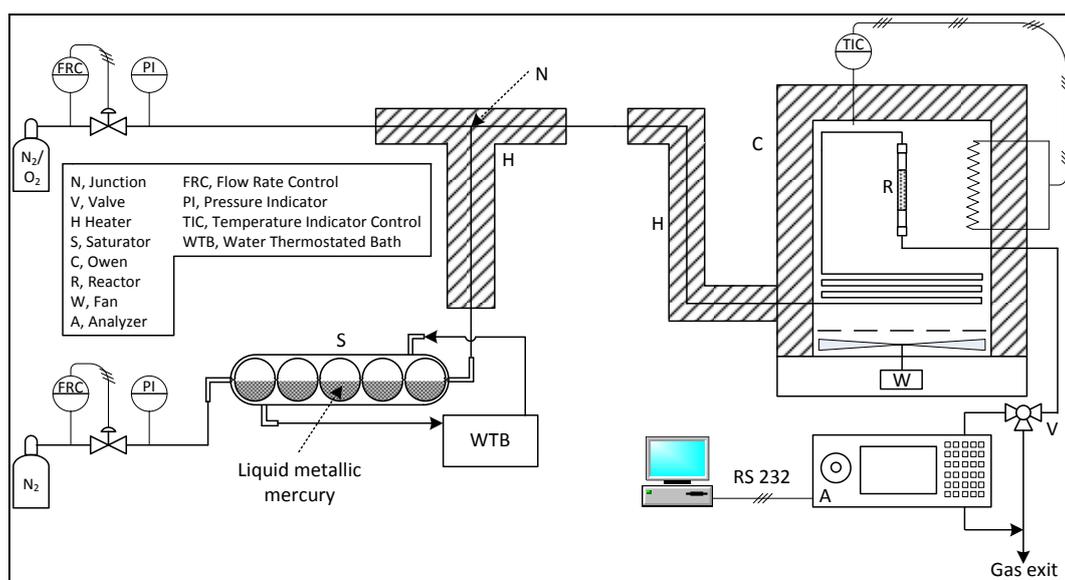


Figure 1 – Experimental apparatus for elemental mercury

The diluted stream was fed to a glass reactor containing the sorbent. The reactor was 35 mm ID and 60 mm high, and was kept in a thermostated oven equipped with a PID temperature controller. The adsorbing bed was made of adsorbing particles (10 – 30 mg) mixed with 100 μm glass beads (5 g) as inert, and its length (L) was 6 mm. This arrangement was chosen in order to avoid channeling, while keeping a small reactive surface. Figure 2 shows the apparatus used for the experiment of HgCl_2 . The simulated flue gas, at the required temperature and HgCl_2 concentration, was produced and the mercury chloride adsorption on fixed bed was carried out. The simulated flue gas was obtained by sublimating reagent grade solid HgCl_2 contained in a stainless steel (AISI 316) cylindrical saturator into a stream of pure nitrogen. The saturator was kept at a fixed temperature by a heating tape driven by a PID temperature controller and the mass flow rate of nitrogen stream was measured by a hot wire flow rate controller. The HgCl_2 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 a stream of pure nitrogen in the junction N. The diluted stream was fed to a glass reactor containing the sorbent. The reactor was 8.85 mm I.D. and 60 mm high, and was kept into a thermostated oven equipped with a PID temperature controller. The bed was made of 12 mg of adsorbing particles mixed with 3.0 g of inert glass beads of the same size, and its length (L) was 40 mm. This arrangement was chosen with the aim of operating with a bed long enough to avoid channeling, while keeping a small reactive surface.

For both experimental apparatuses a downward flow was used in the reactor, in order to avoid losses of powder in the gas stream.

Different commercially activated carbon was used as sorbent: HGR by Calgon-Carbon Corp., Darco G60 from BHD alone and impregnated with Na_2S , too. Tab. 1 reports the physical characteristics of the adsorbing materials.

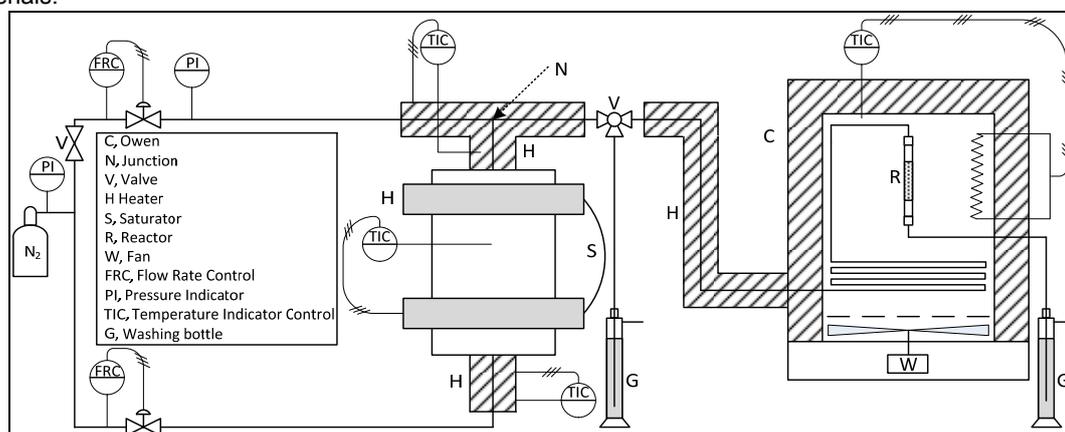


Figure 2 – Experimental apparatus for mercury chloride

The two impregnated activated carbons were obtained by sinking the raw activated carbon into concentrated aqueous solutions of Na_2S and then by drying the filtered solid. Namely, the two solutions used had 5% and 15% (w/w) concentrations of Na_2S and, correspondingly, the impregnated carbons had Na_2S content of 7.8% and 18.7% (w/w). As reported in Table 1 the impregnation process considerably reduces the surface area of the solid and increases its bulk density.

Table 1 – Physical characteristics of the adsorbing materials

Material	Average diameter (μm)	BET surface area m^2/g	Bulk density kg/m^3
Darco G60	3.5	230	4.50×10^2
Darco G60 + 7.8% Na_2S	3.9	184	4.97×10^2
Darco G60 + 18.7% Na_2S	3.9	123	5.62×10^2
HGR	4.5	628	5.92×10^2

In the experimental runs the temperature of the adsorbing bed (T) was varied between 90 to 200°C, while the Hg^0 or HgCl_2 concentration (c_0) in the gas stream entering bed was changed from 1 to 7 mg/m^3 . The Hg^0 concentration in the gas stream out-flowing from the reactor was measured, as a function of time, by using the mercury continuous analyzer MONITOR 2000 by Seefeldler Messtechnik. The HgCl_2 concentration was determined by adsorbing the gas by means of gas washing bottles containing a KMnO_4 aqueous solution acidified by H_2SO_4 and then by analyzing the samples by means of Cold Vapor Atomic Adsorption (CVAA),

using 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. Besides, the quantity of mercuric chloride and elemental mercury adsorbed on the bed was measured by leaching after each run the bed material with aqua regia ($\text{HNO}_3 + 3\text{HCl}$) and then analyzing the solution by means of CVAA, and a difference not larger than 8% was found in the mercury material balance.

3. Results and Comments

The phenomenon investigated is an adsorption process: hence the adsorbate loading at equilibrium is a function of gas phase concentration. So, if the Langmuir isotherm is used to describe the sorbent-sorbate interaction, the rate of the process (r) can be expressed as the difference between the adsorption rate and the desorption rate, as stated by the following equation:

$$r = k_1(\omega_{\max} - \omega)c - k_2\omega \quad (1)$$

where c is the Hg^0 concentration in the gas phase, ω is its concentration as adsorbate on the solid, ω_{\max} is the asymptotic adsorbate concentration, and k_1 and k_2 are the kinetic constants of the adsorption and of the desorption reaction, respectively. At equilibrium ($r=0$) such rate equation leads to the Langmuir isotherm:

$$\omega^* = \omega_{\max} \frac{Kc^*}{1 + Kc^*} \quad (2)$$

where $K=k_1/k_2$ is the equilibrium constant. The equilibrium data showed in the following figures were used to evaluate Langmuir parameters as a function of the temperatures, using a non-linear regression. Table 2 shows Langmuir parameters for the adsorbing materials.

Table 2 – Langmuir parameters for the adsorbing materials

Material	ω_{\max} (-)	K m^3/g	T $^{\circ}\text{C}$
HGR	8.4×10^{-2}	581	120
	2.2×10^{-2}	421	150
	1.1×10^{-2}	200	200
Darco G60, Hg^0	6.9×10^{-4}	1202	90
	1.9×10^{-4}	668	120
	1.05×10^{-4}	420.8	150
Darco G60, HgCl_2	1.13×10^{-1}	594	120
	3.87×10^{-2}	477	150
	2.53×10^{-2}	168	200
Darco G60 + 7.8% Na_2S	1.62×10^{-1}	376	120
	1.06×10^{-1}	250	150
	3.97×10^{-2}	129	200

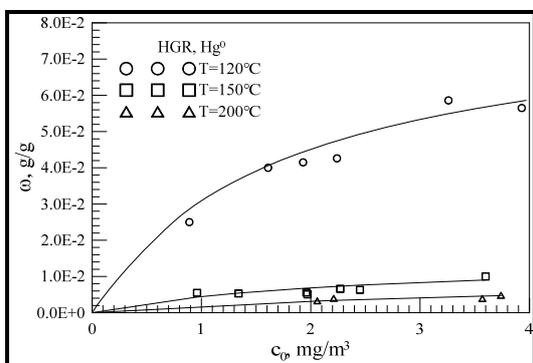


Figure 3 – Adsorption isotherms for HGR activated carbon at different temperatures.

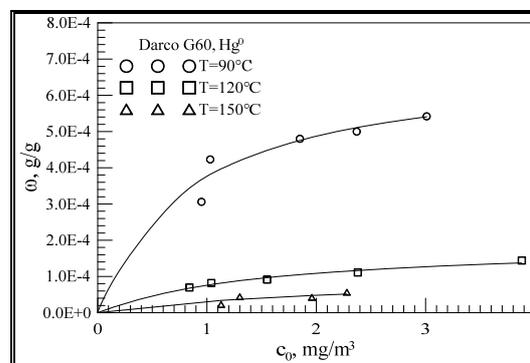


Figure 4 – Adsorption isotherms for Darco G60 activated carbon at different temperatures.

Figure 3 and 4 show isotherm curves for two different solids, HGR and Darco G60, both not impregnated, as a function of elemental mercury concentration, for three different temperatures. These isotherms are of favorable kind and they show, apart from solid sorbent, that the higher the temperature, the lower the adsorption capacity, confirming the exothermic nature of the adsorption process under consideration. However, looking at y-axis range, the behavior of HGR solid seems to be much more favorable than Darco G60 one, because its adsorption capacity is about two order of magnitude higher than Darco G60. This peculiarity is probably due to the surface area value of HGR, which is about three times as Darco G60 alone, as showed in Table 1.

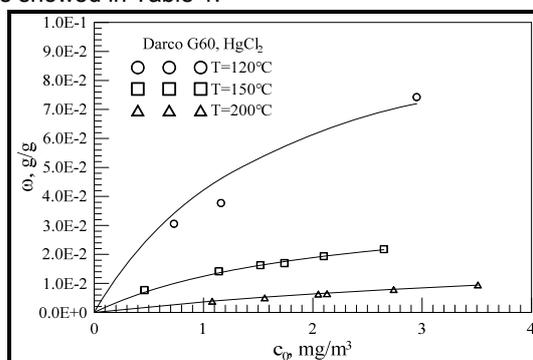


Figure 5 – Adsorption isotherms for Darco G60 activated carbon at different temperatures.

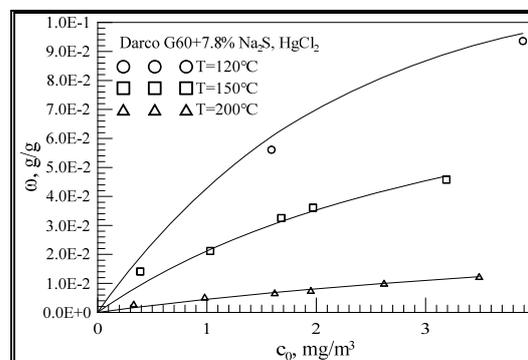


Figure 6 – Adsorption isotherms for Darco G60 impregnated with 7.8% Na_2S activated carbon at different temperatures.

Figure 5 and 6 make the comparison between isotherm curves for the same solid, Darco G60 is on the left, Darco G60 impregnated with 7.8% Na_2S on the right. The curves are still showed for three different temperature, but the mercury specie investigated is the chloride type. The comparison between results relative to raw carbon and those obtained for impregnated one indicates that the addition of Na_2S increases the adsorption capacity: this behavior is due to the formation of bonds between the adsorbate molecule and active sites distributed on the surface of the adsorbent, which favor the adsorption of mercury molecules. Finally, increasing the percentage of Na_2S until 18.7%, not relevant gains in terms of mercury adsorption were detected.

4. Conclusions

In this paper a comparison among different commercial solid sorbents, alone and impregnated, used in adsorption process, aimed to remove mercury compounds in flue gas, was showed. Results obtained demonstrated that adsorption process is always promoted in case of low temperature values. Furthermore HGR seems to be a more efficient solid sorbent in mercury removal than Darco G60. This last improves its performance, when impregnated with 7.8% Na_2S , due to formation of bonds between the adsorbate molecule and active sites, even if higher Na_2S percentage shows have poor effects in increasing adsorption process.

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