ADSORPTION OF MERCURIC CHLORIDE FROM SIMULATED INCINERATOR EXHAUST GAS BY MEANS OF SORBALITTM PARTICLES

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Key Words: Adsorption, Mercuric Chloride, SorbalitTM, Heavy Metal Control, Waste Incineration

In this work the attention was focused on the use of SorbalitTM, a mixture of impregnated activated carbon and Ca(OH)₂, for adsorption of mercuric chloride from flue gas of municipal solid waste incinerators. The study was performed in an apparatus at laboratory scale in which simulated flue gas at a given temperature and HgCl₂ concentration flowed through a fixed bed of adsorbent material. The experimental results showed that the adsorbate loading at saturation depends on temperature in an unusual fashion: the saturation adsorbate loading decreases with T for $70^{\circ} \leq T \leq 150^{\circ} \text{C}$, but then increases for $150^{\circ} \leq T \leq 250^{\circ} \text{C}$. This result was interpreted by assuming that for $T \leq 150^{\circ} \text{C}$ a process of physical adsorption takes place, while for $T \geq 150^{\circ} \text{C}$ the results fall in a "transition zone" between physical adsorption and chemical adsorption. The Langmuir parameters were evaluated for the "low" temperature results, and the differential equations modeling the adsorption phenomenon were integrated, leading to the evaluation of a kinetic parameter describing the breakthrough curves experimentally determined.

Introduction

Gaseous emissions of mercury compounds from anthropic activities can determine severe injuries to the ecosystem. An increasing awareness is being addressed to this problem, and in the last ten to fifteen years the need of keeping under control mercury emissions has been the object of a great deal of attention, both for regulatory agencies worldwide and for the scientific community. The main sources of anthropic mercury emissions to the atmosphere are exhaust gases from coal combustion and municipal solid waste (MSW) incineration; such emissions, in the last years, reached and overcame natural mercury emissions (Pacyna and Munch, 1991). In particular for what concerns MSW incinerators, the European Union has set a limit of $50 \mu\text{g}/\text{Nm}^3$ (based on 11% oxygen) for atmospheric mercury emissions, while in the United States there are expected guidelines fixing such limit at $100 - 130 \mu\text{g}/\text{Nm}^3$ (based on 7% oxygen) (Krishnan *et al.*, 1994).

In order to minimize the environmental damages and to meet the air quality standards, flue gases from MSW incinerators and coal burning power plants have to be treated to reduce mercury emissions (Tseng

et al., 1990; Volland, 1991). Cleanup technologies available to control mercury emissions include wet scrubbing (Nakazato, 1990) and adsorption on dry sorbents (Fouhy, 1992; Thielen and Siepenbush, 1992). Processes based on the adsorption on dry sorbents do not pose the problem of the treatment and inertization of waste liquid streams, and therefore are very attractive both for small and large combustors, such as those used for incineration of hospital wastes or of urban wastes, respectively. These processes are accomplished either by injecting the sorbent into the exhaust gas, or by using multistage fixed beds for selective adsorption of acid gases, mercury and dioxins. At the moment, a growing demand exists for dry technologies capable of controlling, together with acid gases, also mercury emissions.

The relevant role that adsorption phenomena have on removal of mercury compounds was ascertained in a full scale study by Tseng *et al.* (1990), who conducted extensive measurements in USA. The authors indicated that high Hg removal efficiencies (95% and higher) are reached if the MSW incinerators are equipped with a spray dryer of alkaline compounds followed by a fabric filter. They showed that two elements are critical for such reduction, namely that bag filters, instead than electrostatic precipitators, are installed for particulate removal, and that the temperature at which the filters are operated is

* Received on January 29, 1996. Correspondence concerning this article should be addressed to A. Lancia.

lower than 200°C. Such observations could be interpreted by considering that bag filters allow enough time for contact between the gas phase and the layer of solid material deposited on the filter tissue, and that the adsorption phenomenon is strongly sensitive to temperature.

In flue gas from MSW incinerators mercury is mainly present as HgCl_2 (Hall *et al.* 1990; Lancia *et al.* 1993), since there is a relatively high concentration of HCl; on the other hand, elemental mercury is the prevailing form in emissions from coal combustion processes, due to the reducing properties of SO_2 (Schager, 1990). The study of adsorption of mercury in the elemental form was performed by Otani *et al.* (1986; 1988), Henning *et al.* (1988), Schager (1990), Gullett and Jozewicz (1993), and by Krishnan *et al.* (1994). Otani *et al.* (1986) studied the behavior of elemental mercury in the gas phase and its adsorption on different porous solids, such as flyash and activated carbon. They found a higher adsorption capacity for activated carbon than for flyash. Later, the same group (Otani *et al.*, 1988) showed that impregnating porous solids with sulfur enhances the adsorption capacity; they also pointed out to the links existing between adsorption capacity and superficial properties of the solid, including the concentration of the impregnating species. These results were confirmed by Henning *et al.* (1988), who used activated carbon impregnated with sulfur or KI.

Schager (1990) compared adsorption of elemental and oxidized mercury on different sorbents, finding that oxidized mercury is more easily adsorbed than elemental mercury. Specifically, he measured the adsorption capacity with regard to oxidized mercury exhibited by different materials, such as activated carbon, fly ash and calcium compounds (CaO , CaSO_4), and found that the highest adsorption capacity is exhibited by activated carbon, while the lowest is shown by calcium compounds.

Gullett and Jozewicz (1993) tested six carbons with different physical characteristics. They found that the adsorption capacity spans over a wide range, and in general that the lower the temperature, the higher the adsorption capacity. Furthermore, they found that the adsorption capacity is exponentially related to surface area.

Krishnan *et al.* (1994) studied the effect of temperature on the adsorption of elemental mercury on two kinds of thermally activated carbons and on one kind of sulfur impregnated carbon. They found that the surface area has a strong effect on the adsorption capacity of all the sorbents tested, and that while both thermally activated carbons exhibit an almost double adsorption capacity at 23°C with respect to that at 140°C, sulfur impregnated carbon is almost temperature insensitive. They also used desorption tests to reach a deeper insight of the physics

of the process, and suggested that, while physical adsorption is the prevailing mechanism for capture by thermally activated carbon at low temperature, chemisorption is the prevailing one in other cases.

The adsorption of oxidized mercury was studied by Schager (1990), whose results are described above, by Lancia *et al.* (1993) and by Karatza *et al.* (1995, 1996a, b). Lancia *et al.* (1993) studied the influence of temperature on adsorption of mercuric chloride by calcium hydroxide. They found that the lower the temperature, the higher the adsorption capacity. Karatza *et al.* (1995) evaluated the mercuric chloride adsorption capacity showed by flyash collected in a full scale MSW incinerator. They showed that at a relatively low temperature (150°C) the flyash samples considered are suitable sorbents for mercuric chloride removal, and that the adsorption capacity decreases when temperature increases. Karatza *et al.* (1996a, b) studied the adsorption of mercuric chloride on activated carbon and on the same carbon impregnated with Na_2S , again considering the dependence on temperature. They found that impregnation of the carbon with Na_2S strongly enhances the adsorption capacity and that the adsorption process is exothermic both for "raw" carbon and for Na_2S impregnated carbon.

The scope of the present work is to study adsorption of mercuric chloride on a reagent expressly designed to control the emissions of both acid gas and mercury (SorbalitTM, produced by Maerker Zementwerk gmbh of Harburg, Germany) made of 95% of $\text{Ca}(\text{OH})_2$ and 5% of impregnated activated carbon). This sorbent is intended for injection in the exhaust gas line and subsequent collection (together with fly-ash) on a bag filter, where good conditions for gas-solid contact are realized (Blumbach and Nethe, 1992). The experiments were performed in an apparatus at laboratory scale in which simulated flue gas containing HgCl_2 was contacted with a fixed bed of adsorbent material. Breakthrough curves and adsorbate loadings for the material tested were obtained at different temperatures in the range of 70 – 250°C, while the HgCl_2 concentration in the inlet gas stream was varied in the range of 500 – 7000 $\mu\text{g}/\text{m}^3$: these intervals were selected since they include those of interest for MSW incinerators equipped with bag filter. The possibility of using Langmuir isotherms to describe the physical adsorption phenomena was tested, and a model based on the assumption of kinetic control was used to evaluate the kinetic parameters of the process.

1. Experimental Apparatus and Technique

The apparatus used for the experiments of HgCl_2 adsorption is sketched in Fig. 1. In this apparatus the simulated flue gas, at the required

Fig. 1 Sketch of the experimental apparatus

temperature and HgCl_2 concentration, was produced, and the mercuric 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 the nitrogen stream was kept constant 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 ID and 60 mm high, and was kept into a thermostated oven equipped with a PID temperature controller.

SorbalitTM, a mixture of calcium hydroxide (95%) and impregnated activated carbon (5%) was used as adsorbing material. Relevant physical properties of SorbalitTM are reported in Table 1. The adsorbing bed was made of about 12 mg of adsorbing particles mixed with 3.0 g of 100 μm glass beads acting as inert, 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. Furthermore, in order to avoid losses of powder in the gas stream, a downward flow was used in the reactor.

The experiments were conducted varying the temperature of the adsorbing bed (*T*) from 70 – 250°C and the HgCl_2 concentration in the inlet stream to the bed (*c*₀) from 500 – 7000 $\mu\text{g}/\text{m}^3$, while the gas molar flow rate (*G*) was kept fixed in all runs at about 1.87×10^{-3} mol/s. Before each run the gas line was saturated for about two hours with a gas with the same concentration and temperature as those to be used in

Table 1 Characteristics of SorbalitTM

Composition	[w/w]	$\text{Ca}(\text{OH})_2$	95%
		Brown coke	5%
Mean particle diameter, <i>d</i>	[μm]		90
Bulk density	[kg/m^3]		390
BET specific surface area, <i>s</i>	[m^2/g]		20

the experiments; this procedure had to be adopted since the ducts upstream the junction *N* are made of stainless steel, which can adsorb HgCl_2 vapors (Schager, 1990). The HgCl_2 concentration in the gas streams entering and exiting the reactor was determined by absorbing the gas by means of gas washing bottles for about 1 min. An aqueous solution containing KMnO_4 acidified by H_2SO_4 was used (Wilshire, 1993), and the samples were analyzed by means of Cold Vapor Atomic Absorption (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.

In each experimental run the outlet HgCl_2 concentration from the reactor (*c*_{out}) was evaluated at different times, until saturation was reached (*c*_{out} = *c*₀). The longest saturation time found was about four hours; therefore, in order to be sure that the saturation of the solid had been reached, it was decided to continue each experiment for a time much longer than the saturation time, namely ten hours. After each run the total adsorbate loading at saturation (ω^*) was measured by leaching the bed material with aqua regia ($\text{HNO}_3 + 3\text{HCl}$) and then by analyzing the solution by means of CVAA, and an error not larger than 8% was found in the mercury material balance.

2. Results

Adsorption of mercuric chloride on SorbalitTM particles was experimentally studied by determining breakthrough curves and adsorbate saturation loadings for the system. Breakthrough curves, which depend on both temperature and mass transfer characteristics of the bed, give the ratio of the outlet to the inlet HgCl_2 concentration (*c*_{out}/*c*₀) as a function of time. This ratio starts from 0 and grows with time, until the adsorbing bed becomes saturated and it is *c*_{out}/*c*₀ = 1. On the other hand adsorbate loadings at saturation give the mass of adsorbed HgCl_2 per unit mass of sorbent, and depend on HgCl_2 gas phase concentration and temperature. Since SorbalitTM is mainly intended for HgCl_2 capture in bag filters, the temperature range of interest for bag filters operation (150° – 250°C) was selected for a detailed experimental analysis. In Fig. 2 the breakthrough curves are reported for the three temperatures of 150°, 200°, and 250°C, with two different inlet HgCl_2 con-

Fig. 2 Breakthrough curves for different bed temperatures and HgCl_2 inlet concentrations

Fig. 3 Total adsorbate loading curves for different bed temperatures and HgCl_2 inlet concentrations

centrations for each temperature. The figure shows that the time necessary for saturation is on the order of several hours, depending on the experimental conditions, and that the higher the temperature the higher the saturation time, while the higher the inlet HgCl_2 concentration, the shorter the saturation time.

The total adsorbate loading (ω_{tot}) was determined from the experimental breakthrough curves. Figure 3 reports ω_{tot} as a function of time, for the same experimental conditions of the breakthrough curves of Fig. 2. Figure 3 shows that ω_{tot} starts from zero and increases with time to reach the saturation value (ω^*), the value of which was determined by means of

Fig. 4 Saturation adsorbate loadings versus HgCl_2 concentration for different bed temperatures

the procedure outlined in the previous section. Similarly to the results reported in Fig. 2, Fig. 3 shows that, as c_0 increases, saturation is approached in a shorter time, even though at a higher adsorbate loading. Furthermore, Fig. 3 shows that the higher the temperature the higher the value of ω_{tot} .

In order to have a broader picture of the SorbalitTM adsorption capacity for mercuric chloride, some experiments were carried out to obtain such values varying temperature and HgCl_2 gas phase concentration in wider ranges than those reported in Figs. 2 – 3. In Fig. 4 there are reported values of ω^* obtained for different concentrations of HgCl_2 in the gas stream (c^*) at $T = 70^\circ, 90^\circ, 150^\circ, 200^\circ$, and 250°C . Such figure shows that at all the temperatures considered the adsorption process is a favorable one, since the slope of the curve of ω^* vs. c^* decreases when c^* increases. Furthermore, and more unexpectedly, the data reported in Fig. 4 show a rather unusual dependence of ω^* on T . It can be observed that in the temperature range of $70^\circ - 150^\circ\text{C}$ ω^* decreases with T , while in the range of $150^\circ - 250^\circ\text{C}$ ω^* increases with T .

3. Discussion

The experimental results of Fig. 4 clearly show that the adsorbate loading at saturation depends on the gas phase concentration, and therefore that the phenomenon under consideration is an adsorption process, rather than a gas-solid reaction leading to the formation of a chemical compound. On the other hand, the unusual growth of ω^* with temperature for $T > 150^\circ\text{C}$ cannot be easily justified only on the basis of adsorption theory, since adsorption phenomena are intrinsically exothermic.

With the aim of clarifying the dependence of ω^* on T , some general considerations on the nature of the adsorbate-adsorbent bonds are in order. The intensity of these bonds lies in a range which on the low side is limited by physical adsorption, with only van der Waals interactions occurring, and on the high side by the formation of a true chemical compound, with strong (ionic or covalent) bonds between adsorbate and adsorbent. The situation in which adsorbate and adsorbent interact forming bonds the intensity of which lies between those two extremes is generally referred to as chemical adsorption, or *chemisorption*. Both physical adsorption and chemisorption are exothermic processes, and therefore are favored by low temperatures; however the higher activation energies which characterize chemisorption require relatively high temperatures to take place.

For a given couple adsorbate-adsorbent it may well happen that at low temperature physical adsorption is prevalent, being the kinetic of chemisorption so slow to prevent its actual occurrence, while at high temperature the amount physically adsorbed becomes negligible and the chemisorption kinetics are fast enough to reach conditions of thermodynamic equilibrium. At intermediate temperatures between "low" and "high" a progressive change from physical adsorption to chemisorption occurs. In this range the adsorbate loading increases with temperature since the chemisorption kinetics become faster and faster, according to the plot qualitatively sketched in Fig. 5 (Carrà and Morbidelli, 1983).

The experimental results reported in Fig. 4 can be interpreted by assuming that for $T < 150^\circ\text{C}$ a process of physical adsorption occurs, while for higher temperatures the experiments fall in the transition zone, and therefore ω^* grows with T . Experimental data obtained at temperatures higher than 150°C , and therefore falling in the transition zone, cannot be strictly considered equilibrium data; rather they are data corresponding to a situation in which, given the time scale chosen for the experiments, the HgCl_2 adsorption rate exhibited by Sorbalit becomes so low to be practically unnoticeable. Therefore, the discussion will be limited to the data relative to the low temperature zone, in which a thermodynamic approach is possible.

The process that occurs when gaseous HgCl_2 contacts the SorbalitTM can be described as a condensation process on the adsorbent surface, the rate of which can be expressed as the difference between the rates of adsorption (condensation) and desorption (evaporation). The former is proportional to HgCl_2 concentration in the gas phase and to the difference between the total available surface area, which is constant and naturally does not depend on T , and the occupied surface area. The latter is proportional to the occupied surface area; hence the

Fig. 5 Qualitative sketch of the dependence of the saturation adsorbate loading on the bed temperature

Table 2 Thermodynamic equilibrium constants at different temperatures for SorbalitTM

$T [^\circ\text{C}]$	$K [\text{m}^3/\text{g}]$
70	636
90	213
150	73

overall rate of the process is expressed by the following equation:

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

where c is the HgCl_2 concentration in the gas phase, ω is its concentration as adsorbate on the solid, $\omega_{\max}$ is the asymptotic adsorbate concentration, and k_1 and k_2 are the kinetic constants of the adsorption and of the desorption process, respectively. At equilibrium ($r=0$) such rate equation leads to the Langmuir isotherm:

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

where K is the equilibrium constant, related to the kinetic parameters by the equation:

$$K = k_1/k_2 \quad (3)$$

Physical equilibrium data ($70^\circ\text{C} \leq T \leq 150^\circ\text{C}$) of Fig. 4 were used to evaluate the Langmuir parameters (K and $\omega_{\max}$) using a non-linear regression technique. The best estimate for $\omega_{\max}$ is 3.04×10^{-2} , while for K , which depends on T , the best estimates are reported in Table 2. The Langmuir isotherms obtained on the

Fig. 6 Arrhenius plot for the equilibrium constant K

basis of the values of Table 2 are also included in Fig. 4 (continuous lines). The values reported in Table 2 show that K decreases when the temperature increases. In particular, it is possible to hypothesize that K has a dependence on temperature of the Arrhenius kind, according to the following equation (Carrà and Morbidelli, 1983):

$$K = K_0 e^{-\Delta H_{ads}/RT} \quad (4)$$

where K_0 is the preexponential factor and ΔH_{ads} is the heat of adsorption. The values of K_0 and ΔH_{ads} , obtained by a nonlinear regression, are $1.1 \times 10^{-2} \text{ m}^3/\text{g}$ and 30.8 kJ/mol , respectively. In Fig. 6 the values of K , together with the continuous lines obtained using Eq. (4) with $K_0 = 1.1 \times 10^{-2} \text{ m}^3/\text{g}$ and $\Delta H_{ads} = 30.8 \text{ kJ/mol}$, are reported in the form of an "Arrhenius" plot.

The values of the kinetic constants of the adsorption and desorption processes k_1 and k_2 can be evaluated from the experimental breakthrough data, considering a balance on HgCl_2 adsorbed in the bed. Indicating the axial coordinate in the bed with x , it is:

$$V \frac{\partial c}{\partial x} + \varepsilon \frac{\partial c}{\partial t} + \rho_b \frac{\partial \omega}{\partial t} = 0 \quad (5)$$

where ε is the external void fraction of the bed, ρ_b is the bulk density of the adsorbent particles and V is the superficial velocity of the gas, which is assumed constant along the reactor. Such balance equation has to be associated to a constitutive equation for the rate of accumulation on the solid: neglecting the diffusional resistances and considering Eq. (1), the constitutive equation can be expressed as follows:

○ $c_0 = 1.10 \text{ mg/m}^3$; △ $c_0 = 3.56 \text{ mg/m}^3$; ◇ $c_0 = 6.75 \text{ mg/m}^3$; □ $c_0 = 6.92 \text{ mg/m}^3$

Fig. 7 Comparison between model and experimental HgCl_2 outlet concentration at 150°C

$$\frac{\partial \omega}{\partial t} = k_1(\omega_{max} - \omega)c - k_2\omega \quad (6)$$

Eqs. (5) and (6) have to be integrated subject to the following boundary conditions:

$$\begin{cases} t = 0; & 0 \leq x \leq L; & c = 0; & \omega = 0 \\ t \geq 0; & x = 0; & c = c_0 \end{cases} \quad (7)$$

The system of Eqs (5)–(7) with the boundary conditions (7) was solved using the analytical method proposed by Rhee *et al.* (1986). Using the Langmuir parameters K and ω_{max} previously determined, the HgCl_2 concentration profiles in the gas phase can be obtained as a function of time. The only parameter in the model is k_1 , being k_2 related to it by Eq. (3). This parameter was estimated for the experiments performed at 150°C by fitting model calculations to experimental breakthrough curves, and the value of $0.45 \text{ m}^3/\text{g s}$ was obtained. From this it followed $k_2 = 6.16 \times 10^{-3} \text{ s}^{-1}$. It is interesting to observe that, according to the physical meaning of k_1 , its value has to be independent on the inlet HgCl_2 concentration to the adsorbing bed. Such result is confirmed by Fig. 7, which for the runs carried out at $T = 150^\circ\text{C}$ reports a comparison between the experimental values of c_{out} and the calculated ones, evidencing a good agreement between model and experiments.

Conclusion

HgCl₂ adsorption on Sorbalit™, a mixture of Ca(OH)₂ and impregnated activated carbon was studied, and it was proved that Sorbalit™ is a suitable sorbent for control of HgCl₂ emissions from MSW incinerators. Adsorption of HgCl₂ on Sorbalit™ is a favorable process in the temperature range of 70° – 250°C, and the main feature of this process is the rather unusual dependence of the adsorbate loading on temperature: in the temperature range of 70° – 150°C the adsorbate loading decreases with *T*, while in the range of 150° – 250°C it increases with *T*. This result was interpreted by assuming that for *T* ≤ 150°C a physical adsorption occurs, while the results relative to higher temperatures fall in a “transition zone” between physical adsorption and chemical adsorption, in which the adsorbate loading can in fact grow with temperature.

A thermodynamic approach was used to discuss the “low” temperature results (*T* ≤ 150°C). In this way it was possible to obtain the parameters of the Langmuir isotherms and the kinetic constants of adsorption and desorption. On the other hand no quantitative approach was attempted for the “high” temperature results. Nevertheless these results appear to be quite relevant from a practical point of view, since they indicate that, if Sorbalit™ is used, it is possible to operate the bag filters installed downstream MSW incinerators at higher temperature, and therefore to reduce the corrosion problems which often are linked to the use of these devices.

Appendix

The estimation of the relative rates of internal diffusion, external diffusion and adsorption itself can be made by comparing the experimentally observed relaxation time with the estimated values for the external and internal diffusion time. While from the top two plots of Fig. 3 it appears that the relaxation time is in the order of 10³ s, the two diffusion times can be evaluated as:

$$t_D \approx \frac{d^2}{D} \quad (A1)$$

where *t_D* is the (internal or external) diffusion time, *d* is a characteristic length, and *D* is the appropriate value of the diffusivity. For what concerns the external diffusion time (*t_{Dext}*), it is:

$$t_{Dext} \approx \frac{\delta^2}{D_{HgCl_2}} \quad (A2)$$

where *D_{HgCl₂}* is the gas phase diffusivity of HgCl₂ in N₂ and *δ* is the thickness of the (external) mass transfer boundary layer. For what concerns *D_{HgCl₂}*, Perry and Chilton (1973) report that the value of Hg⁰ diffusivity in N₂ is 1.3 × 10⁻⁵ m²/s at *T* = 273 K. Considering an exponent of 1.75 for the dependence on temperature, this corresponds to *D_{Hg⁰}* = 2.8 × 10⁻⁵ m²/s at *T* = 423 K = 150°C, a value that can be taken as a fair approximation of the order of magnitude of *D_{HgCl₂}*. In turn *δ* can be estimated from the Sherwood number (*Sh*) once the Reynolds number (*Re*) is known. In the present

situation for the Reynolds number one has:

$$Re = \frac{GMd_r}{S\mu} \quad (A3)$$

where *M* is the molar weight of the gas, *d_r* the reactor internal diameter, *S* is the reactor section area and *μ* is the gas viscosity (*μ* = 2.3 × 10⁻⁵ kg/m s at *T* = 150°C and *p* = 1 atm), so that it is *Re* = 3.33. Given this low value of *Re* it is reasonable to expect *Sh* ≈ 2, and therefore *δ* ≈ *d*/2 = 45 μm, which leads to *t_{Dext}* ≈ 10⁻⁴ s.

As far as the estimation of the internal diffusion time (*t_{Dint}*) is concerned, the particle diameter *d* and effective intraparticle diffusivity *D_{eff}* should be used. According to Satterfield and Sherwood the order of magnitude of *D_{eff}* may be estimated by means of the following equation:

$$D_{eff} = \frac{\varepsilon_p}{\tau} \left(\frac{1}{1/D_{HgCl_2} + 1/D_{Kn}} \right) \quad (A4)$$

where *ε_p* is the internal porosity, defined as the ratio between pore volume and particle volume, *τ* is the tortuosity factor, and the so called Knudsen diffusivity *D_{Kn}* (expressed in cm²/s) can be estimated by means of the following dimensional equation:

$$D_{Kn} = 9.700 r_p \sqrt{T/M_{HgCl_2}} \quad (A5)$$

In this equation *M_{HgCl₂}* is the HgCl₂ molecular weight (*M_{HgCl₂}* = 271.6 g/mol), and *r_p* is the effective pore diameter, expressed in cm. In turn *r_p* can be estimated as:

$$r_p = \frac{2\varepsilon_p}{\rho_p s} \quad (A6)$$

where *ρ_p* is the particle density.

The particle density of Sorbalit can be estimated from its bulk density (*ρ_b* = 390 kg/m³): assuming an external voidage of about 0.5 it is obtained *ρ_p* = 780 kg/m³; furthermore, taking the true density of Sorbalit *ρ_t* as equal to 2200 kg/m³, it is obtained *ε_p* = 0.65. These two values give *r_p* = 8.3 × 10⁻⁶ cm. In turn from *r_p* it is obtained *D_{Kn}* = 0.10 cm²/s, and eventually, taking a conservative estimate of *τ* = 10, it is obtained *D_{eff}* = 4.8 × 10⁻⁷ m²/s which gives *t_{Dint}* ≈ 10⁻² s.

The comparison between the experimentally evaluated relaxation time (≈ 10³ s) and the two estimated diffusion times (10⁻⁴ s and 10⁻² s for the external and the internal diffusion time respectively) indicates that the rate of the diffusional processes is much bigger than the adsorption rate, and therefore that the overall process is controlled by the kinetics of adsorption itself.

Nomenclature

<i>c</i>	= HgCl ₂ concentration	[g/m ³]
<i>d</i>	= particle size	[m]
<i>d_r</i>	= reactor internal diameter	[m]
<i>D</i>	= diffusivity	[m ² /s]
<i>D_{eff}</i>	= effective intraparticle diffusivity	[m ² /s]
<i>D_{Kn}</i>	= Knudsen diffusivity	[m ² /s]
<i>G</i>	= gas molar flow rate	[mol/s]
<i>k₁</i>	= kinetic constant of the adsorption reaction	[m ³ /g s]
<i>k₂</i>	= kinetic constant of the desorption reaction	[s ⁻¹]
<i>K</i>	= equilibrium constant	[m ³ /g]
<i>K₀</i>	= preexponential factor	[m ³ /g]
<i>L</i>	= length of the adsorbing bed	[m]
<i>M</i>	= molar weight	[g/mol]
<i>r</i>	= adsorption rate	[s ⁻¹]
<i>R</i>	= gas constant	[J/mol K]
<i>r_p</i>	= effective pore diameter	[m]
<i>Re</i>	= Reynolds number	[—]
<i>s</i>	= specific surface area	[m ² /kg]

S	= reactor section area	[m ²]
Sh	= Sherwood number	[—]
t	= time	[s]
T	= temperature	[K]
t_D	= diffusion time	[s]
t_{Dext}	= external diffusion time	[s]
t_{Dint}	= internal diffusion time	[s]
V	= superficial velocity	[m/s]
x	= axial coordinate in the bed	[m]

δ	= thickness of the mass transfer boundary layer	[m]
ΔH_{ads}	= heat of adsorption	[J/mol]
ε	= external void fraction	[—]
ε_p	= internal porosity	[—]
μ	= gas viscosity	[kg/m s]
ρ_b	= bulk density	[g/m ³]
ρ_p	= particle density	[kg/m ³]
ρ_t	= true density	[kg/m ³]
τ	= tortuosity factor	[—]
ω	= adsorbate loading	[gHgCl ₂ /g _{sorbent}]
ω_{max}	= asymptotic adsorbate concentration	[gHgCl ₂ /g _{sorbent}]

<Superscript>

*	= saturation value
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<Subscript>

0	= inlet
out	= outlet
tot	= total

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