Modeling of Mercuric Chloride Removal in Ductwork and Fabric Filter by Raw Activated Carbon Injection

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Abstract

Based on previous experimental adsorption kinetic and equilibrium data for mercuric chloride (HgCl_2) adsorption onto raw activated carbon (AC), a comprehensive model was formulated for its removal in the ductwork and fabric filter by raw AC injection in coal combustion flue gas. Various factors that can impact the performance and sorbent utilization were investigated, including inlet HgCl_2 concentration, sorbent loading, particle size, external and internal mass-transfer considerations, residence time, filtration time, injection mode, and pressure drop. Despite these considerations, in-flight removal of HgCl_2 in the ductwork was found to be almost negligible. For the removal in fabric filter, the effect of particle size was found to be significant, particularly for continuous sorbent injection. On the other hand, a discontinuous injection mode delivering the same amount of sorbent in 10% of a cleaning cycle resulted in higher removal performance and sorbent utilization. However, at the end of the cleaning cycle, most of the sorbent capacity was not used ($< 0.2\%$). The pressure drop across the filter cake built by fly ash and sorbent was found to be manageable within typical operating limits.

Keywords: Sorbent injection, HgCl_2 adsorption, in-flight capture, fabric filter, external mass transfer, internal mass transfer

1 Introduction

The recent Mercury and Air Toxic Standard (MATS) rule limits the emissions of mercury (Hg) from power plants across the United States.[1] Under the MATS rule, the U.S. Environmental Protection Agency (U.S. EPA) started to reduce the mercury emissions from coal-fired power plants in 2015. Existing electric utility generating units (EGU) would limit their emissions below 0.18-18.14 g/GWh while newer EGUs would have stricter standards of limiting their emissions below 0.04-18.14 g/GWh depending on the type of fuel the EGU utilizes.[2] Activated carbon injection has shown promise in controlling gaseous mercury emissions in the particulate matter control devices (PMCDs).[3-4] Previous model results suggest that the removal of oxidized mercury (Hg(2+)) in an entrained flow, using powdered activated carbon (PAC) sorbent is insignificant due to the mass-transfer resistance associated with the sorbent and its short residence time.[5-6] It was also demonstrated through the U.S. Department of Energy's (U.S. DOE) Field Test Program that the in-flight removal of mercury vapor with short residence times was insignificant.[7] In contrast, the removal of mercury in the PMCDs such as fabric filter (FF) and electrostatic precipitator (ESP) was reported to be significant.[6-8]

It has been reported that raw activated carbon (AC) does not physically adsorb elemental mercury (Hg(0)) vapor in a typical post-combustion temperature window (e.g. 60-170 °C).[5-9] Halogenated AC has shown good potential to increase the removal of both Hg(0) and Hg(2+) species.[10-11] However, little has been reported about the capture performance of each mercury species by AC sorbent in terms of the physical and chemical properties of AC such as surface area, porosity, reactions kinetics, and adsorption kinetics and equilibrium. Since a typical mercury concentration in coal combustion flue gas is on the order of ppb, a minimum AC

sorbent to mercury mass ratio must be much higher than its stoichiometric ratio (e.g., $\sim >10,000:1$) to achieve $>90\%$ removal with a typical AC sorbent of a $\sim 20\text{-}\mu\text{m}$ diameter.[12-13] However, it is also difficult to find previous systematic studies about the effects of sorbent particle size, surface area, pore diameter and adsorption equilibrium and kinetics that can greatly impact on mercury capture performances in the ductwork and PMCDs.

Depending on a level of coal combustion, some unburned carbon remains in fly ash often as a consequence of low- NO_x combustion systems. It has been reported that the mercury removal performances by fly ash carbons greatly vary with respect to various parameters such as surface area, carbon content, chlorine content in coal, coal types, surface functionalities on carbon.[14-16] One of the previous studies predicted that $< 5\%$ of mercury could be adsorbed by unburned carbon fly ash.[15] Despite the wide performance variations, there is a consensus that the adsorption capacity of fly ash carbons are generally limited. A previous study reported that the capacity for HgCl_2 is ~ 10 times smaller than that of raw AC.[14-17]

In this study, the removal of mercuric chloride (HgCl_2) as a model oxidized mercury species in the ductwork and fabric filter using a raw AC sorbent (i.e. Norit America's DARCO-HG) has been systematically studied by taking into account the physical parameters of the raw AC sorbent, the physical adsorption equilibrium and kinetics for HgCl_2 , inlet HgCl_2 concentrations, sorbent injection loadings, and external/internal mass transfer. The impacts of these considerations on capture performances in the ductwork and filter cake are demonstrated. A consideration of the pressure drop across the filter cake is also presented for the sorbent injection in a typical range of fly ash loadings. Previous studies have shown the effects of flue gas constituents on the adsorption capacity of HgCl_2 onto activated carbon.[18-19] SO_2 was reported to have a negative effect on the sorption as it reacts with basic sites on AC. HCl helped

in increasing the sorption capacity while NO_2 helped in promoting the negative effect of SO_2 on the sorption capacity of HgCl_2 onto carbon. However, these effects have not been quantified for the adsorption of HgCl_2 and thus have not considered in this study.

2 Kinetic Model for HgCl_2 Adsorption onto Raw AC

2.1 Model assumptions

Physical adsorption is considered a main mechanism for HgCl_2 adsorption onto raw AC for sorbent injection after air preheater at $\sim 120\text{-}160^\circ\text{C}$. [19] The adsorption kinetics was based on the Langmuir theory for this study as the experimental adsorption kinetic data best fit this theory. [20-21] In a post-combustion entrained flow after sorbent injection, the adsorption of HgCl_2 onto sorbents comprises of mainly three steps: (1) the external mass transfer of bulk phase HgCl_2 to the outer surface of the sorbent; (2) the internal mass transfer due to pore diffusion inside the sorbent particle; and (3) the surface adsorption of HgCl_2 onto the inner pore surface of the sorbent. In this study, the adsorption of HgCl_2 onto AC sorbent has been modeled using the following assumptions:

- 1) The flue gas in the ductwork and filter cake follows plug flow;
- 2) The axial diffusion is negligible;
- 3) The sorbent particles are spherical in shape and have a uniform particle size;
- 4) The adsorption process is isothermal since HgCl_2 is present in trace amounts;
- 5) The properties of the sorbent used are constant; and
- 6) The adsorption of HgCl_2 on the inner walls of the ductwork is negligible.

2.2 Model equations

2.2.1 In-flight model

The intrinsic HgCl_2 adsorption kinetic expression is given by the Langmuir theory in eq.

1. All of the symbols used in the equations are summarized in the nomenclature section.

$$r_A = \rho_p \frac{dq}{dt} = \rho_p \left(k_1 (q_{\max} - q) C - k_2 \left(= \frac{k_1}{K} \right) q \right) \quad (1)$$

At equilibrium ($r_A = 0$), the kinetic rate expression leads to the following Langmuir isotherm.

$$q^* = q_{\max} \frac{KC^*}{1 + KC^*} \quad (2)$$

The two parameters of ($q_{\max}$) and K obtained from the Langmuir isotherm given in eq. 2 are used in the Langmuir kinetic expression shown in eq. 1.

A shell mole balance is formulated to describe the adsorption of HgCl_2 inside the sorbent particle. The expression is given as

$$\epsilon_p \frac{\partial C}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_e \frac{\partial C}{\partial r} \right) - r_A \quad (3)$$

The local adsorption rate given in eq. 1 is coupled with the adsorption kinetic expression in eq. 3 in order to calculate the concentration of HgCl_2 inside the pore.

Then a mole balance inside the ductwork is taken to describe the in-flight adsorption of HgCl_2 in an entrained flow as shown in eq. 4.

$$\frac{\partial C_B}{\partial t} = -r_{A,obs} \frac{m_{AC}}{\rho_p} \quad (4)$$

The observed adsorption rate expression at the external surface of the sorbent ($r = R_p$) is calculated by taking a volume average of the local HgCl_2 adsorption rate inside the pores over the entire sorbent particle. This expression is denoted as

$$r_{A,obs} = \frac{3}{R_p} D_e \left. \frac{\partial C}{\partial r} \right|_{(r=R_p,t)} \quad (5)$$

Then the observed adsorption rate is coupled with the mole balance in eq. 4 to predict the bulk-phase HgCl_2 concentration.

The set of eqns. (1), (3), and (4) has the following initial conditions (ICs) and boundary conditions (BCs).

Initial conditions (ICs):

$$q(r, t = 0) = 0; C(r, t = 0) = 0; C_B(t = 0) = C_B^{in} \quad (6)$$

Boundary conditions (BCs):

$$\left. \frac{\partial q}{\partial r} \right|_{(r=0,t)} = 0; \left. \frac{\partial C}{\partial r} \right|_{(r=0,t)} = 0; \left. \frac{\partial C}{\partial r} \right|_{(r=R_p,t)} = \frac{k_g}{D_e} (C_B(t) - C(r = R_p, t)) \quad (7)$$

By solving the coupled governing equations comprised of eqns. (1), (3), (4) with ICs and BCs in eqns. (6) and (7), the profiles of $q(r, t)$, $C(r, t)$ and $C_B(t)$ can be obtained.

The governing equations (eqns. (1), (3), (4)), and the ICs and BCs given in eqns. (6) and (7) are normalized with the following dimensionless variables.

$$\gamma \equiv \frac{C}{C_B^{in}}; \gamma_B \equiv \frac{C_B}{C_B^{in}}; \phi \equiv \frac{q}{q_{\max}}; \xi \equiv \frac{r}{R_p}; \tau' \equiv \frac{t}{\frac{\varepsilon_p R_p^2}{D_e}} \quad (8)$$

The normalized governing equations with the ICs and BCs are given in eqns. (9)-(13).

$$\frac{\partial \phi}{\partial \tau'} = \frac{\varepsilon_p R_p^2}{D_e} \left[k_1 (1 - \phi) \gamma C_B^{in} - k_2 \left(= \frac{k_1}{K} \right) \phi \right] \quad (9)$$

$$\xi^2 \frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial \gamma}{\partial \xi} \right) - \frac{\rho_p \xi^2 q_{\max} R_p^2}{D_e C_B^{in}} \left[k_1 (1 - \phi) \gamma C_B^{in} - k_2 \left(= \frac{k_1}{K} \right) \phi \right] \quad (10)$$

$$\frac{\partial \gamma_B}{\partial \tau} = - \frac{3 m_{AC} \varepsilon_p}{\rho_p} \frac{\partial \gamma}{\partial \xi} \bigg|_{(\xi=1, \tau)} \quad (11)$$

ICs

$$\phi(\xi, \tau = 0) = 0; \gamma(\xi, \tau = 0) = 0; \gamma_B(\tau = 0) = 1 \quad (12)$$

BCs

$$\frac{\partial \phi}{\partial \xi} \bigg|_{(\xi=0, \tau)} = 0; \frac{\partial \gamma}{\partial \xi} \bigg|_{(\xi=0, \tau)} = 0; \frac{\partial \gamma}{\partial \xi} \bigg|_{(\xi=1, \tau)} = \frac{k_g R_p}{D_e} \left(\gamma_B(\tau) - \gamma(\xi=1, \tau) \right) \quad (13)$$

2.2.2 Filter cake model

A detailed description about our filter cake model is given in our previous study.[22] The dimensionless normalized variables, governing equations, and ICs and BCs used in the filter cake model are given in eqns. (14)-(19).

$$\gamma \equiv \frac{C}{C_B^{in}}; \gamma_B \equiv \frac{C_B}{C_B^{in}}; \phi \equiv \frac{q}{q_{\max}}; \xi \equiv \frac{r}{R_p}; \tau \equiv \frac{u}{L_F} t; \lambda \equiv \frac{z}{L_F} \quad (14)$$

$$\frac{\partial \phi}{\partial \tau} = \frac{L_F}{u} \left[k_1 (1 - \phi) \gamma C_B^{in} - k_2 \left(= \frac{k_1}{K} \right) \phi \right] \quad (15)$$

$$\frac{\varepsilon_p u \xi^2 R_p^2}{L_F D_e} \frac{\partial \gamma}{\partial \tau} = \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial \gamma}{\partial \xi} \right) - \frac{\rho_p \xi^2 q_{\max} R_p^2}{D_e C_B^{in}} \left[k_1 (1 - \phi) \gamma C_B^{in} - k_2 \left(= \frac{k_1}{K} \right) \phi \right] \quad (16)$$

$$\varepsilon_b \frac{\partial \gamma_B}{\partial \tau} + \frac{\partial \gamma_B}{\partial \lambda} = - \frac{3(1 - \varepsilon_b) D_e L_F}{R_p^2 u} \frac{m_{AC}}{m_{Ash} + m_{AC}} \frac{\partial \gamma}{\partial \xi} \bigg|_{(\lambda, 1, \tau)} \quad (17)$$

ICs:

$$\phi(\lambda, \xi, \tau = 0) = 0; \gamma(\lambda, \xi, \tau = 0) = 0; \gamma_B(\lambda, \tau = 0) = 0 \quad (18)$$

BCs:

$$\left. \frac{\partial \phi}{\partial \xi} \right|_{(\lambda, \xi=0, \tau)} = 0; \left. \frac{\partial \gamma}{\partial \xi} \right|_{(\lambda, \xi=0, \tau)} = 0; \left. \frac{\partial \gamma}{\partial \xi} \right|_{(\lambda, \xi=1, \tau)} = \frac{k_g R_p}{D_e} (\gamma_B(\lambda, \tau) - \gamma(\lambda, \xi=1, \tau)); \gamma_B\left(\lambda = \frac{L(\tau)}{L_f}, \tau\right) = 1 \quad (19)$$

Darcy's law is used to express the pressure drop across the filter cake. The pressure drop is given as the sum of two terms, one of which is related to the clean filter medium, ΔP_f , while the other one is related to the dust cake itself, ΔP_c . [23]

$$\Delta P = \Delta P_f + \Delta P_c \quad (20)$$

The pressure drop across the clean fabric is given by

$$\Delta P_f = S_E \times V \quad (21)$$

where S_E is the resistance due to the fabric and V is gas velocity. The pressure drop due to the dust is given by

$$\Delta P_c = K_2 \times C_i \times V^2 \times t \quad (22)$$

where K_2 is the specific cake coefficient; C_i is the inlet dust concentration; and t is filtration time. The ΔP_c term is especially important as it is generally larger in magnitude than the first term, ΔP_f . K_2 depends on the type of a dust, mean particle diameter of dust and is a measure of how fast the dust accumulates in the filter cake. It is found experimentally. [24]

2.3 Parameters used in the model

The HgCl_2 adsorption model was applied to DARCO-HG AC sorbent. Table 1 lists the physical properties of the sorbent and diffusion coefficient values. The Langmuir adsorption equilibrium and intrinsic kinetic parameters were obtained from our previous study. [21] Another dataset for the DARCO-G60 AC sorbent reported in a previous study is also shown in Tables 1

and 2 for a comparison of modeling results.[20] The effective diffusivity inside the pores of the sorbent (D_e) and the gas-phase mass transfer coefficients (k_g) were calculated to be 9.05×10^{-8} m²/s and 2.12 m/s, respectively.

To calculate the pressure drop across the filter cake, a dust velocity of 0.02 m/s was taken.[23] Typically, activated carbon sorbent loading is ~1-5% of the fly ash loading.[25] This way, the fly ash loading was calculated to be 10 g/m³. The value of the specific cake resistance, K_2 , was calculated to be 1×10^5 s⁻¹ (=10 inches of H₂O/fpm/(lb/ft²)) and 0.63×10^{-8} s⁻¹ (=6.25 inches of H₂O/fpm/(lb/ft²)) based on the dust velocity and the mass mean diameter of fly ash dust of 10 μm and 20 μm, respectively.

3 Results and Discussion

The model was solved by using COMSOL Multiphysics (version 4.4). The in-flight HgCl₂ removal performance of the sorbent was assessed by using two parameters. The first one was normalized average HgCl₂ uptake $\left(\frac{q_{avg}}{q_{max}} \right)$ as an indicator for the sorbent utilization. It was calculated by

$$q_{avg}(t) = \frac{[C_B^{in} - C_B(t)]}{m_{AC}} \quad (23)$$

The other performance parameter was HgCl₂ removal represented by normalized bulk-phase HgCl₂ concentration $\gamma_B(\tau) = \frac{C_B(t)}{C_B^{in}}$. In a typical power plant, the in-flight residence time of a sorbent after air preheater is estimated to be ~1.5-2 s until the sorbent particles are collected at PMCDs.[26] Therefore, in this study, all simulations have been run for ≤ 5 s.

On the other hand, for the study of HgCl_2 capture in a fabric filter, the average HgCl_2 uptake was modified for the capture in the filter cake by

$$q_{avg}(t) = \frac{\int_0^t (C_B^{in} - C_B^{out}(t)) dt}{m_{AC} t} \quad (24)$$

The normalized HgCl_2 concentration at the outlet of the filter cake was determined by

$$\gamma_B(\lambda = 0, \tau) = \frac{C_B^{out}(z = 0, t)}{C_B^{in}} \quad (25)$$

The operating conditions listed in Table 3 were selected as a base case and were used to study the effects of different factors. In the base case, a sorbent injection loading of 0.1 g/m^3 was chosen since most power plants cannot allow for the loading greater than 0.16 g/m^3 ($=10 \text{ lb/MMacf}$).[7]

3.1 In-flight HgCl_2 removal study

3.1.1 Effects of sorbent particle size and inlet HgCl_2 concentration

The HgCl_2 removal efficiency and sorbent utilization as a function of in-flight residence time for different particle sizes ranging from 10 to 30 μm and varying inlet HgCl_2 concentrations ranging from 1 ppbv ($=11 \mu\text{g/dscm}$) to 5 ppbv ($=55 \mu\text{g/dscm}$) for raw AC sorbent are shown in Figure 2(a) and 2(b), respectively. It is evident that HgCl_2 removed in the ductwork is $< \sim 0.5\%$ up to 5-s residence time for all the particle sizes and inlet HgCl_2 concentrations at the baseline sorbent injection loading of 0.1 g/m^3 . Although it is difficult to find experimental data obtained for the in-flight removal of HgCl_2 under well-controlled settings in the literature, a previous paper taking into account the adsorption kinetics and equilibrium for another PAC sorbent also reported that the removal under similar conditions was negligible.[5] As the sorbent particle size

increases from 10 to 30 μm , the internal mass-transfer resistance increases and thus HgCl_2 removal efficiency decreases from ~ 0.5 to 0.25% . It is seen that a variation in the inlet HgCl_2 concentrations does not affect the HgCl_2 removal efficiency. This suggests that the external mass-transfer resistance derived from the HgCl_2 concentration difference in the bulk gas phase is not critical to HgCl_2 removal in the ductwork. Since the sorbent has a very short residence time in the duct, the in-flight capture of HgCl_2 is negligible.

From Figure 2(b), it can be seen that the sorbent utilization of DARCO-HG is very small as $\sim < 0.005\%$ of the maximum sorbent capacity was utilized. Although a variation in sorbent particle sizes and inlet HgCl_2 concentrations does play a role in the sorbent utilization, these effects are noted insignificant. The sorbent utilization decreases from ~ 0.0048 to 0.0026% with an increase in sorbent particle size from 10 to 30 μm . The sorbent utilization increases with an increase in the inlet HgCl_2 concentration as the sorbent can adsorb more HgCl_2 .

3.1.2 Effects of sorbent loading and external/internal mass transfer

The in-flight HgCl_2 removal efficiency and sorbent utilization with respect to sorbent loading and external/internal mass transfer are shown in Figure 2(c) and (d), respectively. Although the removal is insignificant, the effect of sorbent loading is pronounced. When the sorbent loading increases from 0.1 g/m^3 ($=6.2 \text{ lb/MMcf}$) and 1 g/m^3 ($=62 \text{ lb/MMcf}$), the HgCl_2 removal efficiency almost proportionally increases from $\sim 0.4\%$ to $\sim 3.4\%$.

On the other hand, external mass transfer is found to play an insignificant role as the HgCl_2 removal efficiency is almost identical in the presence and absence of an external mass-transfer consideration. When external mass-transfer is taken into account, the Ranz and Marshall equation in eq. (26) is used for the mass-transfer coefficient (k_g) in eqns. (7) and (13).

$$Sh = 2 + 0.6(Re_d)^{1/2} (Sc)^{1/3} \quad (26)$$

When it is not considered for the case of excluding external mass transfer, the surface concentration was set to the bulk-phase concentration (i.e. $C(R_p, t) = C_B(t)$). The external mass-transfer resistance is found to be insignificant and can thus be ignored.

The role of internal mass transfer comprising pore diffusion and surface adsorption is more pronounced for the in-flight capture. The internal pores provide the surface area and pore volume required for the adsorption and transport of $HgCl_2$ inside AC. When the internal surface area is reduced, the maximum adsorption capacity in the Langmuir adsorption kinetics in eq. (1) is also reduced. The pore size governs the pore diffusion of $HgCl_2$ and determines the effective diffusivity via the Knudsen diffusivity in the model. The pore diffusion of $HgCl_2$ inside DARCO-HG is primarily governed by the Knudsen diffusion. In order to examine the effect of pore diameter and maximum adsorption capacity, the model predictions using DARCO-HG were compared with those using DARCO-G60. The parameters obtained for DARCO-G60 in Tables 1 and 2 were used to predict the $HgCl_2$ removal and sorbent utilization. When the reduced effectivity diffusivity (D_{eff}), maximum adsorption capacity (q_{max}), and adsorption equilibrium constant (K) were used for DARCO-G60, $HgCl_2$ removal decreased from ~0.35% (DARCO-HG) to ~0.30% (DARCO-G60) for a short residence time of 5 s given in Fig. 2(c). The corresponding sorbent utilization in Fig. 2(d) shows that DARCO-G60 is better utilized for the in-flight removal since the maximum adsorption capacity (0.0387 g $HgCl_2$ /g sorbent for DARCO-G60) is less than that of higher surface area sorbent (0.055 g $HgCl_2$ /g sorbent for DARCO-HG). It is also seen that better sorbent utilization can be achieved at low sorbent loading, high porosity, and no external mass transfer. However, it should be noted that these effects on the in-flight removal is negligible.

3.1.3 Effects of particle size, sorbent loading and residence time

The local HgCl_2 concentration profile inside the sorbent as a function of the radius of the particle with different sorbent particle sizes varying from 10 to 30 μm and in-flight residence times varying from 2 to 5 s is shown in Figure 3(a). It is clearly shown that a variation in the residence times from 2 to 5 s makes almost no difference in the HgCl_2 concentrations inside the sorbent with the different particle sizes. This indicates that the residence times are too short to result in different local HgCl_2 concentrations inside the sorbent.

Figure 3(b) shows the local HgCl_2 concentration profiles with respect to sorbent loading ranging from 0.1 to 1 g/m^3 and residence time varying from 2 to 5 s. The result suggests that even the 10-time difference in the sorbent loadings has an insignificant impact on the local HgCl_2 concentration profiles.

3.2 Fabric filter HgCl_2 removal study

3.2.1 Effects of sorbent particle size and external/internal mass transfer

Figure 4(a) and (b) show the HgCl_2 removal efficiency and sorbent utilization as a function of filtration time in terms of sorbent particle size, external, and internal mass transfer. The results show that the sorbent particle size plays a major role in HgCl_2 removal efficiency on FF. For example, a smaller sorbent with a 10- μm diameter shows a ~90% HgCl_2 removal efficiency at 40 min while a larger sorbent with a 30- μm diameter shows ~70% removal. A smaller particle has less resistance to adsorption when compared to a larger sorbent. The result also estimates that it takes ~60 min to achieve 90% HgCl_2 removal when the sorbent with a 20- μm diameter is continuously injected at 0.1 g/m^3 .

The sorbent utilization for a smaller particle is found to be better compared to a larger one. However, it needs to be noted that the adsorption capacity of a small sorbent is small compared to the capacity of the large one. To study the effect of internal mass transfer, two sorbents with different surface areas were compared. The internal pores required for adsorption was found to be an important factor with the smaller surface area sorbent showing lower HgCl_2 removal efficiency.

3.2.2 Effects of sorbent loading and external/internal mass transfer

The temporal removal of HgCl_2 and sorbent utilization with respect to sorbent loading and external/internal mass transfer are shown in Figure 4(c) and (d), respectively. Sorbent loading and filtration time are the most important factors affecting the HgCl_2 removal efficiency in FF. As a case study, the HgCl_2 removal performances are compared for continuous and discontinuous sorbent injection methods introducing the same amount of the raw AC sorbent during a cleaning cycle. By injecting a 10-time higher sorbent loading (i.e. 1 g/m^3) in 10% of a cleaning time (i.e. 9 min), a HgCl_2 removal efficiency of ~90% can be achieved within the first 10% of the filtration time. If the same amount of sorbent is used at a lower sorbent loading (i.e. 0.1 g/m^3), the same ~90% HgCl_2 removal can be achieved after ~66% of the entire filtration time. As shown in Figure 4(d), while a continuous sorbent loading at 0.1 g/m^3 can utilize ~0.15% of the total adsorption capacity, a discontinuous loading at 1 g/m^3 can achieve ~0.20%.

The role of external mass transfer is also found to be insignificant in FF. This shows that the external mass-transfer resistance estimated by the Ranz and Marshall equation is diffusion limited and insignificant under FF conditions. However, the effect of internal mass transfer is significant as can be seen in Figure 4 (c-d). In the case of discontinuous loading, it is seen that

HgCl₂ removal efficiency decreases after sorbent injection is cut-off for smaller surface area sorbent. This is because the desorption of HgCl₂ from the sorbent is significant. This is not evident in DARCO-HG as the equilibrium constant is relatively higher.

3.2.3 Effects of sorbent particle size and continuous/discontinuous injection

An additional case study is conducted for continuous and discontinuous injection in terms of sorbent particle size by taking into account external and internal mass transfer. The effect of the sorbent particle size on the removal is much more pronounced for continuous injection as shown in Figure 5(a). When the particle diameter varies from 10 to 30 μm , the HgCl₂ removal efficiency for continuous injection varies noticeably. For example, a 90% HgCl₂ removal efficiency is achieved at ~40 min for a continuous injection of 10- μm particles while it takes ~78 min to achieve the same 90% removal with 30- μm particles. On the other hand, the removal for discontinuous injection is less sensitive to the particle size. This difference is attributed mainly to the sorbent injection loading (m_{AC}) in eq. (17). When discontinuous injection is used, the thick sorbent layer accumulated on the filter cake as a result of high loading during an initial filtration period significantly removes HgCl₂, thus leading to less dependence on the particle size.

Figure 5(b) shows better sorbent utilization for continuous injection up to later filtration phase as a result of low continuous loading. However, if longer filtration time is allowable, discontinuous injection shows better utilization. This will be governed by allowable pressure drop across the filter cake, and is discussed in the next section.

3.2.4 Pressure drop across the filter cake

Figure 6 shows the pressure drop across the filter cake in terms of fly ash particle size and cake thickness as a function of filtration time. Typically, fabric filters have an operating pressure drop ranging between 871 Pa (=3.5 inches of H₂O) and 2,240 Pa (=9 inches of H₂O) with an average operating pressure drop of ~1,593 Pa (=6.4 inches of H₂O).[23] In practice, a typical sorbent loading is ~1-5% of fly ash loading and a typical fly ash loading is ~10 g/m³. [25] Using Darcy's law, the pressure drop can be estimated for the filter cake. The particle size distribution of fly ash is reported to range from 5 µm to as big as 100 µm with an average particle size of ~10-20 µm comparable to the size of raw AC.[27] Therefore, in this study, the pressure drop is estimated using fly ash particles with 10- and 20-µm diameters injected at 10 g/m³. As shown in Figure 6, the pressure drop is sensitive to the particle size. For a dust diameter of 10 µm, an average cleaning cycle based on the average pressure drop could be close to ~70 min while for 20-µm dust particles, an average cleaning cycle can last up to 90 min, which is used in this study. The filter cake thickness was estimated to be ~1.5 mm for a filtration time of 90 min.

4 Conclusions

A detailed case study on the adsorption of HgCl₂ by DARCO-HG sorbent was performed. The modeling results showed that the in-flight capture of HgCl₂ was almost negligible with an HgCl₂ removal efficiency of ~<0.5% at 140 °C. The sorbent utilization was <0.005% of the maximum adsorption capacity of the raw AC. Among the parameters studied, high sorbent loading, maximum adsorption capacity (as a driving force for adsorption kinetics) and residence time were found to play a role in HgCl₂ removal efficiency. However, there seems to be no

practical solution to increase mercury removal in the ductwork. Most HgCl_2 removal could be achieved in fabric filter. For the removal in FF, particle size significantly influenced the removal performance for continuous injection whereas it did not show an advantage for discontinuous injection using the same amount of sorbent over the same cleaning cycle. The sizable filter cake thickness promptly piled from discontinuous injection could compensate for the sensitivity of particle size. Most pressure drop across the filter cake was derived from fly ash loading and size, which can determine the cleaning cycle and sorbent loading required to meet the performance goal.

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Nomenclature

C	HgCl_2 concentration inside the pore, $\text{g HgCl}_2/\text{m}^3$
C_B	HgCl_2 concentration in the bulk gas phase, $\text{g HgCl}_2/\text{m}^3$
C_B^{in}	inlet HgCl_2 concentration in the bulk gas phase, $\text{g HgCl}_2/\text{m}^3$
C_B^{out}	outlet HgCl_2 concentration in the bulk gas phase, $\text{g HgCl}_2/\text{m}^3$
C_i	inlet dust concentration, lb/ft^3

D_e	effective pore diffusion coefficient, m ² /s
D_p	sorbent particle diameter, m
K	equilibrium constant, $K=k_1/k_2$, m ³ /g HgCl ₂ .
k_1	adsorption rate constant, m ³ /(g·s)
k_2	desorption rate constant, 1/s
K_2	specific cake coefficient, 1/s
k_g	gas-phase mass-transfer coefficient, m/s
m_{AC}	sorbent injection loading in flue gas, g/m ³
m_{Ash}	fly ash concentration in flue gas, g/m ³
L	filter cake thickness, m
L_F	final cake thickness formed at a final filtration time (t_F)
ΔP	pressure drop across the filter cake, Pa
ΔP_c	pressure drop due to filter cake, Pa
ΔP_f	pressure drop due to filter, Pa
S_E	residual drag due to fabric, Pa/(m/s)
q	HgCl ₂ uptake onto sorbent, g HgCl ₂ /g sorbent
q_{avg}	average HgCl ₂ uptake onto sorbent, g HgCl ₂ /g sorbent
q_{max}	maximum HgCl ₂ adsorption capacity, g HgCl ₂ /g sorbent
R_p	radius of sorbent particle, m
r	radial distance inside sorbent, m

r_A	intrinsic HgCl_2 adsorption rate, g HgCl_2 adsorbed/(m^3 sorbent·s)
$r_{A,obs}$	observed HgCl_2 adsorption rate, g HgCl_2 adsorbed/(m^3 sorbent·s)
t	time, s
t_F	final filtration time, s
u	superficial gas velocity, m/s
V	gas velocity, m/s
z	axial filter cake thickness from fabric filter surface, m
*	equilibrium state

Greek letters

ε_b	bed porosity
ε_p	particle porosity
ρ_p	sorbent particle density, g/m^3
φ	in-flight dimensionless sorbent uptake, see eq. (8)
ξ	in-flight dimensionless radial distance, see eq. (8)
γ	in-flight dimensionless pore concentration, see eq. (8)
γ_B	in-flight dimensionless bulk concentration, see eq. (8)
τ'	in-flight dimensionless time, see eq. (8)
φ	filter cake dimensionless sorbent uptake, see eq. (14)
ξ	filter cake dimensionless radial distance, see eq. (14)
λ	filter cake dimensionless axial distance, see eq. (14)
γ	filter cake dimensionless pore concentration, see eq. (14)

γ_B filter cake dimensionless bulk concentration, see eq. (14)

γ_B^{out} filter cake dimensionless outlet bulk concentration

τ filter cake dimensionless time, see eq. (14)

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Figure Caption

Fig. 1. Schematic of post-combustion capture of mercury in a typical coal-fired power plant

Fig. 2. Effects of sorbent particle size and inlet HgCl_2 concentration on (a) HgCl_2 removal efficiency, (b) sorbent utilization as a function of in-flight residence time, where external and internal mass transfer resistances were considered for all cases (DARCO-HG, $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$). Effects of sorbent loading, internal mass transfer (int MT) and external mass transfer (ext MT) on (c) HgCl_2 removal efficiency and (d) sorbent utilization as a function of in-flight residence time (DARCO-HG, $C_{\text{B}}^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ } \mu\text{g/dscm}$), $D_{\text{p}} = 20 \text{ } \mu\text{m}$, $T = 140 \text{ }^\circ\text{C}$)

Fig. 3. (a) Effects of sorbent particle size and in-flight residence time on the HgCl_2 concentration inside the sorbent as a function of radius of the particle (DARCO-HG; C_{B}^{in} , 1 ppbv ($= 11 \text{ } \mu\text{g/dscm}$), $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$). (b) Effects of sorbent loading and in-flight residence time on the HgCl_2 concentration inside the sorbent as a function of radius of the particle (DARCO-HG, $C_{\text{B}}^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ } \mu\text{g/dscm}$), $D_{\text{p}} = 20 \text{ } \mu\text{m}$, $T = 140 \text{ }^\circ\text{C}$)

Fig. 4. Effects of sorbent particle size and internal (int MT)/external mass transfer (ext MT) on (a) HgCl_2 removal efficiency and (b) sorbent utilization for continuous sorbent injection (DARCO-HG, $C_{\text{B}}^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ } \mu\text{g/dscm}$), $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$). Effects of sorbent loading and internal (int MT)/ external mass transfer (ext MT) on (c) HgCl_2 removal efficiency and (d) sorbent utilization for continuous (CI) and discontinuous (DI) sorbent injection (DARCO-HG, $C_{\text{B}}^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ } \mu\text{g/dscm}$), $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$)

Fig. 5. Effects of sorbent particle size and loading on (a) HgCl_2 removal efficiency and (b) sorbent utilization when external and internal mass transfers were considered for continuous (CI)

and discontinuous (DI) sorbent injection (DARCO-HG, $C_B^{\text{in}} = 1$ ppbv ($= 11 \mu\text{g/dscm}$), $T = 140$ °C)

Fig. 6. Effects of fly ash particle mass-mean diameter (MMD) on pressure drop across the filter cake at fly ash loading of 10 g/m^3 and cake thickness as a function of filtration time for a dust velocity of 0.02 m/s

Table 1. Physical properties of raw AC and diffusivity values used in this study

Sorbent	Particle density, ρ_p (g/cm ³)	BET Surface area (m ² /g)	Pore volume, v_p (cm ³ /g)	Particle porosity, ϵ_p	d_{pore} (nm)	Knudsen diffusivity (m ² /s)	Effective diffusivity (m ² /s)
DARCO-HG	0.950	476	0.53	0.50	6.2	3.71×10^{-7}	9.05×10^{-8}
DARCO-G60[20]	0.450	230	Not available	0.60	3.7	2.21×10^{-7}	7.86×10^{-8}

Molecular diffusivity = 1.53×10^{-5} m²/s

Table 2. Langmuir adsorption equilibrium and kinetic constants used in this study

Sorbent	$q_{\max}$ (g HgCl ₂ /g sorbent)	K (m ³ /g HgCl ₂)	k ₁ (m ³ /(g·s))	k ₂ (1/s)
DARCO-HG	0.055	2.1×10^4	0.2	9.5×10^{-6}
DARCO-G60[20]	0.0387	4.77×10^2	0.2	4.19×10^{-4}

Table 3. Base case simulation parameters used for in-flight and fabric filter capture.

Parameter	Value
Inlet HgCl ₂ concentration	1 ppbv (=11 µg/dscm)
Sorbent injection loading	0.1 g/m ³ (=6.2 lb/MMcf)
Temperature	140 °C
Residence time in ductwork for in-flight capture	5 s
Filtration time for fabric filter capture	90 mins

Fig. 1
Schematic of post-combustion capture of mercury in a typical coal-fired power plant

Fig. 2

Effects of sorbent particle size and inlet HgCl_2 concentration on (a) HgCl_2 removal efficiency, (b) sorbent utilization as a function of in-flight residence time, where external and internal mass transfer resistances were considered for all cases (DARCO-HG, $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140^\circ\text{C}$). Effects of sorbent loading, internal mass transfer (int MT) and external mass transfer (ext MT) on (c) HgCl_2 removal efficiency and (d) sorbent utilization as a function of in-flight residence time (DARCO-HG, $C_{\text{B}}^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ }\mu\text{g/dscm}$), $D_p = 20 \text{ }\mu\text{m}$, $T = 140^\circ\text{C}$)

Fig. 3

(a) Effects of sorbent particle size and in-flight residence time on the HgCl_2 concentration inside the sorbent as a function of radius of the particle (DARCO-HG; C_B^{in} , 1 ppbv (= 11 $\mu\text{g}/\text{dscm}$), $m_{\text{AC}} = 0.1 \text{ g}/\text{m}^3$, $T = 140 \text{ }^\circ\text{C}$). (b) Effects of sorbent loading and in-flight residence time on the HgCl_2 concentration inside the sorbent as a function of radius of the particle (DARCO-HG, $C_B^{\text{in}} = 1 \text{ ppbv}$ (= 11 $\mu\text{g}/\text{dscm}$), $D_p = 20 \text{ }\mu\text{m}$, $T = 140 \text{ }^\circ\text{C}$)

Fig. 4

Effects of sorbent particle size and internal (int MT)/external mass transfer (ext MT) on (a) HgCl_2 removal efficiency and (b) sorbent utilization for continuous sorbent injection (DARCO-HG, $C_B^{\text{in}} = 1$ ppbv ($= 11 \mu\text{g/dscm}$), $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$). Effects of sorbent loading and internal (int MT)/external mass transfer (ext MT) on (c) HgCl_2 removal efficiency and (d) sorbent utilization for continuous (CI) and discontinuous (DI) sorbent injection (DARCO-HG, $C_B^{\text{in}} = 1$ ppbv ($= 11 \mu\text{g/dscm}$), $m_{\text{AC}} = 0.1 \text{ g/m}^3$, $T = 140 \text{ }^\circ\text{C}$)

Fig. 5.

Effects of sorbent particle size and loading on (a) HgCl_2 removal efficiency and (b) sorbent utilization when external and internal mass transfers were considered for continuous (CI) and discontinuous (DI) sorbent injection (DARCO-HG, $C_B^{\text{in}} = 1 \text{ ppbv}$ ($= 11 \text{ } \mu\text{g/dscm}$), $T = 140 \text{ } ^\circ\text{C}$)

Fig. 6

Effects of fly ash particle mass-mean diameter (MMD) on pressure drop across the filter cake at fly ash loading of 10 g/m^3 and cake thickness as a function of filtration time for a dust velocity of 0.02 m/s

Figure 1

Revised Figure 2

Revised Figure 3

Revised Figure 4

Revised Figure 5

Revised Figure 6