An Experimental Study on Mercury Sorption by Activated Carbons and Calcium Hydroxide

Behrooz Ghorishi
Acurex Environmental Corporation
4915 Prospectus Drive
Durham, NC 27713

Brian K. Gullett
U.S. Environmental Protection Agency
Air Pollution Prevention and Control Division (MD-65)
Research Triangle Park, NC 27711
INTRODUCTION

Title III of the 1990 Clean Air Act Amendments (CAAAs) requires the U.S. Environmental Protection Agency (EPA) to submit a study on 189 hazardous air pollutants (HAPs) from industrial sources. This study will include an emission and risk (to public health) assessment of the HAPs. Among the 189 HAPs, mercury has drawn special attention due to its increased levels in the environment and well-documented food chain transport and bioaccumulation.¹ ²

Mercury, present in hazardous/municipal wastes and in coal³, is readily volatized during combustion and incineration processes.⁴ Mercury is the most volatile among various trace metals, and major portions of it can pass through existing particulate control devices.⁴ A sorbent that can react with mercury can effectively shift this metal from the vapor phase to the particulate (sorbent) phase, facilitating its removal. Mercury control processes which use adsorption on dry sorbents do not pose the problem of treatment and stabilization of the waste liquid stream and, therefore, seem very attractive for coal combustors and hazardous/municipal waste incinerators. The need to develop mercury control technologies and the attractive features of adsorption processes on dry sorbents led researchers to focus their efforts on the evaluation of the adsorption kinetics and sorbent capacity of many different solid sorbents. Past research has identified two different classes of sorbents to be effective in mercury removal: activated carbons and calcium-based sorbents.⁵ ⁷

An important scientific issue that needs to be addressed is the chemical form in which mercury is released from combustion systems. Previous investigations conducted in EPA laboratories⁶ ⁷ have indicated that mercury control strategies are dependent upon the type of mercury species that exist in the coal/waste combustion flue gases. These studies have shown the relative ease of controlling oxidized mercury (specifically mercuric chloride, HgCl₂) as opposed to elemental mercury (Hg⁰). Hall et al.⁸ showed that, in a simulated municipal waste combustor (MWC), flue gas mercury is mainly found as HgCl₂. They postulated that HgCl₂ is the most favorable mercury species due to relatively high hydrogen chloride (HCl) concentration in MWCs. On the other hand, Hg⁰ is the prevailing form of mercury in emissions from coal combustion processes.⁹ However, recent pilot-scale coal combustion test results have indicated that combustion of certain types of coal (Blacksville, a bituminous coal from the Pittsburgh No. 8 seam) can lead to a flue gas mercury species profile dominated by oxidized mercury (most probably HgCl₂).¹⁰ Research in this area is on-going to determine the conditions that favor formation of oxidized mercury in coal combustion processes.

The presence of both Hg⁰ and HgCl₂ in combustion flue gases justifies a comprehensive research study on the adsorption of both these species by solid sorbents. As mentioned, preliminary investigations found activated carbons to be efficient Hg⁰ sorbents,⁶ and calcium-based compounds to be effective HgCl₂ sorbents.⁷ The activated carbon studies⁶ were focused on determining the effect of temperature (23 vs. 140°C) on the adsorption of Hg⁰ on two different kinds of thermally activated carbons (FGD and PC-100, Norit Americas Inc.) in a fixed-bed reactor system. It was concluded that surface area and temperature have a strong effect on the Hg⁰ adsorption capacity of the activated carbons. PC-100, with twice the specific surface area compared to that of FGD, captured about four times the amount of Hg⁰ captured by FGD. Both thermally activated carbons exhibited almost double the adsorption capacity at 23°C compared to that at 140°C. This study reports on the continuation of that investigation⁶ with emphasis on obtaining Hg⁰ breakthrough sorption curves. Systematic tests were conducted in which the
effects of temperature, inlet Hg\(^0\) concentration, and the presence or absence of sulfur dioxide (SO\(_2\)) were investigated. The adsorption of Hg\(^0\) was studied by varying the temperature in the range of 60-140°C and the Hg\(^0\) concentration in the gas stream in the range of 8-40 ppb (65-327 μg/dscm). The selected concentration range was higher than that observed in coal-fired units (1-20 μg/dscm).\(^6\) SO\(_2\) is believed to be an important flue gas species influencing the capture of mercury compounds by activated carbons and calcium-based sorbents.\(^7\) The effect of this species was studied at a concentration of 1000 ppm (2.6 g/dscm).

A previous investigation\(^7\) illustrated the relative ease of removal of HgCl\(_2\) as compared to Hg\(^0\). It was concluded that calcium-based sorbents --calcium hydroxide [Ca(OH)\(_2\)] and mixtures of Ca(OH)\(_2\) and fly ash-- can potentially be very cost effective in adsorbing HgCl\(_2\) from simulated flue gases. A comprehensive, systematic study on the control of HgCl\(_2\) by activated carbons has been conducted by Karatza et al.\(^1\), concluding that at a temperature of 150°C and gas-phase HgCl\(_2\) concentration of 1000 μg/dscm a thermally activated carbon can capture a mass of HgCl\(_2\) greater than 1% of its weight. The investigation presented here reports on the continuation of a previous study\(^7\); it focuses on a systematic study on the effect of temperature (60-140°C), HgCl\(_2\) concentration [11-73 ppb (122-809 μg/dscm)], and SO\(_2\) (1000 ppm) on the HgCl\(_2\) capture by Ca(OH)\(_2\).

In summary, the scope of the present work was to study adsorption of Hg\(^0\) by thermally activated carbons and HgCl\(_2\) by Ca(OH)\(_2\). While the focus of the previous investigations\(^6,7\) was mainly on a screening type of comparison between these sorbents, this work investigates the fundamental and quantitative dependence of the adsorption capacity of sorbents and mercury removal on sorption parameters such as temperature, gas-phase mercury species concentration, and flue gas species (SO\(_2\)). The experiments were performed in a laboratory-scale, fixed-bed apparatus, in which the inlet gas containing nitrogen, Hg\(^0\) or HgCl\(_2\), and, on occasions, SO\(_2\) were contacted with sorbents.

**EXPERIMENTAL PROCEDURE**

A schematic of the experimental apparatus used to study the capture of Hg\(^0\) and HgCl\(_2\) is shown in Figure 1. Pure HgCl\(_2\) powder contained in a diffusion vial was the source of HgCl\(_2\) vapor, and pure Hg\(^0\) liquid in a permeation tube (VICI Metronics Inc.) was the source of Hg\(^0\) vapor. The concentration of HgCl\(_2\) or Hg\(^0\) in the gas stream was controlled by adjusting the water bath temperature. A detailed description of the calibration of the mercury generation system and its quality control checks has been reported elsewhere.\(^6,7\) The mercury vapor generated was carried into a manifold by a nitrogen stream where it mixed with SO\(_2\) (in the SO\(_2\) studies only) at a constant total system gas flow rate of 350 cm\(^3\)/min (at standard temperature and pressure). A three-way valve placed before the manifold (Figure 1) diverted the mercury-laden nitrogen stream away from the manifold when desired. The first three-way valve placed after the manifold was used to direct flow to or away from the fixed-bed reactor. The sorbent to be studied (approximately 0.02 g diluted with 2 g inert glass beads; bed length of approximately 2 cm) was placed in the reactor which was maintained at the desired bed temperature by a temperature controller. A furnace kept at 850°C was placed downstream of the reactor to convert any oxidized mercury (Hg\(^++\), as in HgCl\(_2\)) to Hg\(^0\). According to thermodynamic predictions, the only mercury species that exists at this temperature is Hg\(^0\).\(^12\) The presence of the furnace enabled detection of non-adsorbed HgCl\(_2\) as Hg\(^0\) by the on-line ultraviolet (UV) Hg\(^0\) analyzer, thus providing actual, continuous Hg\(^0\) or HgCl\(_2\) capture data by the fixed-bed of sorbent. The UV Hg\(^0\) analyzer used in this study
responded to SO\textsubscript{2} as well as Hg\textsuperscript{0}. For instance, a gas stream consisting of 1000 ppm SO\textsubscript{2} and 15 ppb Hg\textsuperscript{0} produced a SO\textsubscript{2}/Hg\textsuperscript{0} signal ratio of 8/18. Contributions from SO\textsubscript{2} were corrected for by placing a SO\textsubscript{2} analyzer (UV) on-line downstream of the Hg\textsuperscript{0} analyzer. The SO\textsubscript{2} analyzer was incapable of responding to mercury in the concentration range used in this study. By subtracting the SO\textsubscript{2} signal measured by the SO\textsubscript{2} analyzer from the total response of the mercury analyzer, the mercury concentration was obtained.

In each test, the fixed-bed was exposed to the mercury-laden flue gas for 24 hours or until 100% breakthrough (saturation) was achieved (whichever came first). During this period the exit concentration of mercury was continuously monitored. The percent removal of Hg\textsuperscript{0} or HgCl\textsubscript{2} at any time was obtained as follows: percent removal = 100*[\text{in}-(\text{in}-(\text{out})]/(\text{in})]. The amount of mercury species uptake at any time (q, weight mercury species/weight sorbent) was determined by integrating (in time) and evaluating the area under the removal curves. Selected experiments conducted during this test program were run in duplicates and indicated a variation of ±10% in the experimental results.

**SORBENTS**

The capture of Hg\textsuperscript{0} was investigated using two different thermally activated carbons: FGD and PC-100. The capture of HgCl\textsubscript{2} was investigated using Ca(OH)\textsubscript{2}. FGD, manufactured by Norit Americas Inc., is a lignite-coal-based activated carbon with a bulk density of 0.51 g/cm\textsuperscript{3}, ignition temperature of 450°C, and particle size greater than 400 mesh (less than 30 \mu m). Information about the total surface area and average pore size diameter of FGD (and other sorbents) was obtained by using a Micromeritics ASAP 2600 based on nitrogen adsorption/desorption with the Brunauer-Emmett-Teller (BET) method. FGD has a total surface area of 500 m\textsuperscript{2}/g and an average pore diameter of 3.2 nm. PC-100, manufactured by Norit Americas Inc., is a bituminous-coal-based activated carbon with a bulk density of 0.52 g/cm\textsuperscript{3}, ignition temperature of 450°C, and a particle size greater than 400 mesh (less than 30 \mu m). PC-100 has a total surface area of 900 m\textsuperscript{2}/g and an average pore diameter of 1.8 nm. It has nearly twice the surface area of FGD; most of this surface area is due to its smaller pores than those of FGD as indicated by PC-100's smaller average pore diameter. The Ca(OH)\textsubscript{2} used in the HgCl\textsubscript{2} removal studies was a reagent grade Ca(OH)\textsubscript{2} (Sigma Inc.) containing 97.6% Ca(OH)\textsubscript{2} and 1.8% calcium carbonate (CaCO\textsubscript{3}). It has a total surface area of 13 m\textsuperscript{2}/g and an average pore diameter of 33.4 nm.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**HgCl\textsubscript{2} Capture by Ca(OH)\textsubscript{2}**

The effects of temperature and inlet concentration on the HgCl\textsubscript{2} uptake by Ca(OH)\textsubscript{2}, obtained under the baseline conditions (nitrogen and HgCl\textsubscript{2} only), are shown in Figure 2. During the 24 hours of exposure, HgCl\textsubscript{2} uptake (q) increased linearly as time of exposure progressed; Ca(OH)\textsubscript{2} did not reach its saturation capacity under the baseline conditions. This observation may indicate an abundance of HgCl\textsubscript{2} adsorption sites on Ca(OH)\textsubscript{2}. Considering the acidic nature of gaseous HgCl\textsubscript{2}, these sites can be hypothesized to be alkaline. Note that, for the sake of comparison to the Hg\textsuperscript{0} data, the results were truncated to show the first 5 hours of exposure; further uptakes up to 24 hours can be obtained by extending the lines.

The percent removals [constant during the exposure period; measured (HgCl\textsubscript{2})\textsubscript{out} was constant] of incoming HgCl\textsubscript{2} by the fixed-bed of Ca(OH)\textsubscript{2} as a function of temperature and inlet concentration are shown in Figure 3. Increasing the HgCl\textsubscript{2} inlet concentration and decreasing the bed temperature
increased the percent removals. The bed temperature had a strong effect on the percent removals at the lowest concentration (11 ppb) tested, and the inlet concentration influenced percent removals more strongly at the highest temperature (140°C) tested.

In adsorption processes, a rise in partial pressure and a fall in temperature result in an increase in the amount of the material adsorbed (adsorbate). The temperature and the concentration (partial pressure) trends observed here suggest that the process is an adsorption (physical and/or chemical) controlled process and that the rate of HgCl₂ capture is determined by how fast molecules in the vicinity of the active sites are being adsorbed. This indicates that the capture process is not controlled by an external (boundary layer) mass transfer mechanism; boundary layer mass transfer is fast and the HgCl₂ concentration in the vicinity of the surface is very close to the bulk concentration. Moreover, the observed effect of temperature on the amount captured (or percent removed) does not support an external mass transfer hypothesis, since the mass transfer rate is proportional to the 1.5 power of absolute temperature.

The effect of SO₂ on HgCl₂ capture by Ca(OH)₂ was studied by adding 1000 ppm SO₂ to the nitrogen/HgCl₂ stream, while keeping the total flow through the fixed-bed constant. The results are shown in Figure 4. This figure shows the effect of SO₂ at a constant inlet HgCl₂ concentration of 38 ppb for the three studied temperatures. At the low temperature (60°C), SO₂ had no effect. However, increasing the temperature drastically reduced the sorption capacity of Ca(OH)₂ in the presence of SO₂. It appears that Ca(OH)₂ and SO₂ may react at higher temperatures, leading to the destruction of the available (alkaline) sites needed for HgCl₂ capture. In the presence of SO₂ and at 100°C, saturation capacity [0.7 mg HgCl₂/g Ca(OH)₂] was achieved after 5 hours of exposure; at 140°C, saturation capacity [0.1 mg HgCl₂/g Ca(OH)₂] was achieved after only 1 hour of exposure. Note that in the absence of SO₂, saturation capacities were never achieved during the 24 hours of exposure.

Hg₀ Capture by Activated Carbons
The effects of temperature and inlet concentration on the Hg₀ uptake by activated carbon, FGD, under the baseline conditions, are shown in Figure 5. Unlike HgCl₂ capture by Ca(OH)₂, during a typical 5-hour run the sorbent (FGD) reached its saturation capacity, indicating that the available active sites for capturing Hg₀ in the activated carbon are limited. The comparison between Hg₀ and HgCl₂ uptake results (Figures 2 and 5) suggests that it is more difficult to control Hg₀ emissions. It should be noted that in a previous investigation the baseline tests conducted using Ca(OH)₂ showed that no Hg₀ was captured, indicating the ineffectiveness of Ca(OH)₂ (lack of active sites) in capturing Hg₀.

From Figure 5 it is apparent that the amount of Hg₀ captured is influenced more by the bed temperature than by the inlet concentration (note the ordinate scales). Increasing the temperature reduced the saturation capacity and the time needed to reach the saturation capacity. Increasing the inlet Hg₀ concentration increased the saturation capacity, and the initial rate of Hg₀ uptake (slope of tangent at the origin). Similar to the HgCl₂ case, the temperature and concentration trends suggest that the process is active site adsorption controlled.

The same set of tests were performed using PC-100 as the activated carbon sorbent. Results for PC-100 in comparison to FGD are presented in Figure 6 (bed temperature of 100°C). PC-100 also consistently exhibited higher saturation capacity than did FGD at temperatures of 60° and 140°C (not presented
here). It should be noted that PC-100 exhibited the same temperature and concentration trends as those of FGD: higher Hg\(^0\) captures at lower temperatures and higher inlet concentrations.

The effect of SO\(_2\) on Hg\(^0\) capture by FGD was studied by adding 1000 ppm SO\(_2\) to the nitrogen/Hg\(^0\) (40 ppb) stream while keeping the total gas flow through the fixed-bed constant. The highest inlet Hg\(^0\) concentration was chosen to minimize the interference of SO\(_2\) in the Hg\(^0\) analyzer discussed previously. Figure 7 shows the effect of SO\(_2\) on Hg\(^0\) uptake at a constant inlet Hg\(^0\) concentration of 40 ppb for the three studied temperatures. At the lowest temperature tested (60°C), SO\(_2\) had essentially no effect on the Hg\(^0\) uptake by the FGD; however, increasing the temperature increased the Hg\(^0\) capture by the FGD. It appears that at higher temperatures, SO\(_2\) might have reacted with the FGD and created active sulfur (S) sites, which are considered to be very active in capturing Hg\(^0\).\(^6\) The activity of FGD in the presence of SO\(_2\) at higher temperatures resembled that of sulfur-impregnated (chemically impregnated) activated carbon studied by Krishnan et al.\(^6\) Based on these observations, one may consider injecting this activated carbon upstream of the acid gas removal devices of the full-scale combustion systems in order to take advantage of the enhancement effect of SO\(_2\) on Hg\(^0\) capture.

Unlike FGD, the presence of SO\(_2\) did not have any effect on Hg\(^0\) capture by PC-100. This may be due to the inability of PC-100 to form sulfur-activated sites. One may relate this observation to the differences in chemical structure and composition of these two thermally activated carbons. FGD and PC-100 are lignite-coal-based and bituminous-coal-based activated carbons, respectively. Future efforts will be directed toward a comprehensive understanding of the chemical nature (active sites) of these activated carbons and its influence on Hg\(^0\) capture. These future studies will also help explain the observed higher activities of PC-100 as compared to FGD, since this may not be just a total surface area effect, as indicated by SO\(_2\) studies.

**CONCLUSION**

The effects of bed temperature, mercury concentration, and the presence of SO\(_2\) on the capture of Hg\(^0\) and HgCl\(_2\), the mercury species identified in coal/waste combustion flue gases, by thermally activated carbons (FGD and PC-100, Norit Americas Inc.) and a calcium-based sorbent [Ca(OH)\(_2\)] were examined in a fixed-bed, bench-scale system. Sorption studies indicated an abundance of HgCl\(_2\) adsorption sites in Ca(OH)\(_2\). Considering the acidic nature of gaseous HgCl\(_2\), these sites can be assumed to be alkaline. Increasing the HgCl\(_2\) inlet concentration increased its removal, and increasing the bed temperature decreased this removal. The observed temperature and concentration trends suggest that the process is adsorption controlled and that the rate of HgCl\(_2\) capture is determined by how fast molecules in the vicinity of the active sites are being adsorbed. The presence of SO\(_2\) drastically reduced the sorption capacity of Ca(OH)\(_2\) at a bed temperature range of 100-140°C. Sorption studies further indicated that the available active sites for capturing Hg\(^0\) in the activated carbons are very limited, suggesting that it is more difficult to control Hg\(^0\) emissions. Increasing the inlet Hg\(^0\) concentration and decreasing the bed temperature increased the saturation capacities of the activated carbons, the time needed to reach this capacity, and the initial rate of Hg\(^0\) uptake. PC-100, with twice the total surface area as that of FGD, consistently exhibited higher saturation capacity than that for FGD. The presence of SO\(_2\) drastically increased the Hg\(^0\) capture capabilities of FGD and had no influence on Hg\(^0\) capture by PC-100. These observations may be due to the differences in chemical structure and composition of these two thermally activated carbons.

**PEER-REVIEW**
Based on these observations, the optimum region for control of HgCl₂ by calcium-based sorbents may be considered to be downstream from acid gas (SO₂) removal devices. One may also consider injecting activated carbon (FGD) upstream of the acid gas removal devices of the full-scale combustion systems in order to take advantage of the enhancement effect of higher SO₂ levels on Hg⁰ capture.

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REFERENCES

Figure 1. Schematic of the bench-scale, fixed-bed reactor setup.
Figure 2. Effects of bed temperature and inlet HgCl$_2$ concentration on HgCl$_2$ uptake by Ca(OH)$_2$ (baseline conditions).
Figure 3. Effects of bed temperature and inlet HgCl₂ concentration on HgCl₂ removal by Ca(OH)₂ (baseline conditions).
Figure 4. Effect of SO₂ (1000 ppm) on HgCl₂ uptake by Ca(OH)₂ (inlet HgCl₂ concentration of 38 ppb).
Figure 5. Effects of bed temperature and inlet Hg\(^0\) concentration on Hg\(^0\) uptake by activated carbon, FGD (baseline conditions).
Figure 6. Uptake of Hg\(^0\) by activated carbons, FGD and PC-100 (bed temperature of 100°C, baseline conditions).
Figure 7. Effect of SO$_2$ (1000 ppm) on Hg$^0$ uptake by activated carbon, FGD (inlet Hg$^0$ concentration of 40 ppb).