

Sorption of mercury species by activated carbons and calcium-based sorbents: effect of temperature, mercury concentration and acid gases

Bench-scale studies of mercury/sorbent reactions were conducted to understand mechanistic limitations of field-scale attempts to reduce emissions of mercury from combustion processes. The effects of temperature (60 to 140°C), sulfur dioxide (SO₂, 1000 ppm), hydrogen chloride (HCl, 50 ppm), and water vapor (5% molar) on the capture of elemental mercury (Hg⁰, 8 to 40 ppb) by two thermally activated carbons, and on the capture of mercuric chloride (HgCl₂, 11 to 73 ppb) by two calcium (Ca)-based sorbents were examined in a fixed-bed, bench-scale system. Capture of mercury species is affected by sorbent site activity. HgCl₂ is quickly adsorbed by the alkaline sites of Ca-based sorbents; sorption in combustors will likely be kinetically limited. Hg⁰, however, is more effectively removed by activated carbons; here the number of active sites appears to limit removal from flue gas. SO₂ and HCl were found to either enhance or reduce sorption depending on the species of mercury. Enhancement of Hg⁰ capture by activated carbon is associated with formation of active carbon-chlorine or carbon-sulfur sites while reduced capture of HgCl₂ is due to loss of alkaline sites through Ca-SO₂ and Ca-HCl reactions.

Introduction

Title III of the 1990 Clean Air Act Amendments (CAAA) requires the US 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 (Langley 1973; Westoo 1973).

Mercury, present in hazardous/municipal wastes and in coal (Billings *et al.* 1973), is readily volatilized during combustion and incineration processes (Klein *et al.* 1975). Mer-

Behrooz Ghorishi

ARCADIS Geraghty & Miller, Durham, NC, USA

Brian K. Gullett

US Environmental Protection Agency, National Risk Management Research Laboratory, Air Pollution Prevention and Control Division (MD-65), Research Triangle Park, NC, USA

Keywords – Elemental mercury; mercuric chloride, calcium-based sorbent, activated carbon, air pollution, emissions

Corresponding author: Dr. Brian K. Gullett, USEPA, NRMRL, APPCD, MD-65, Research Triangle Park, NC 27711, USA

Received 20 January 1998, accepted in revised form 19 April 1998

cury is the most volatile among various trace metals, and major portions of it can pass through existing particulate control devices (Klein *et al.* 1975).

Mercury control measures must account for differences in system specific speciation and concentration. Mercury in flue gas from a simulated municipal waste combustor (MWC) is found mainly as mercuric chloride (HgCl₂) due to the relatively high hydrogen chloride (HCl) concentration in MWCs (Hall *et al.* 1990), although this is not always the case. Measurements (Chang & Offen 1995) have found a majority of elemental mercury (Hg⁰) in one sampled MWC. This may be due to a reduction of HgCl₂ to Hg⁰ across a wet scrubber (WS) in the presence of sulfur dioxide (SO₂) (Evans & Nevitt 1997). Unlike MWCs, Hg⁰ is the prevailing form of mercury

in emissions from coal combustion processes (Devito *et al.* 1993), although exceptions have been noted (Laudal *et al.* 1996). In a recent pilot-scale coal combustion test program, Laudal *et al.* (1996) showed 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 HgCl_2). Speciation research is on-going to determine the conditions that favor formation of oxidized mercury in coal/waste combustion processes (Dunham *et al.* 1997; Carey *et al.* 1997; Livengood & Mendelsohn 1997; Senior *et al.* 1997). The importance of the form of mercury species lies in the fact that the oxidized forms of mercury seem to be more easily controlled via solid adsorption (Krishnan *et al.* 1994, 1996; Lancia *et al.* 1997). Also, HgCl_2 is water soluble and can be easily removed in WSs. Thus, altering or shifting the mercury species profile to HgCl_2 in facilities equipped with WS or lime injection systems enhances the control of mercury.

Sorbents that can react with mercury shift the metal from the vapor phase to the particulate (sorbent) phase, facilitating 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 and 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 evaluation of the adsorption kinetics and sorbent capacity of many different solid sorbents (Korpiel & Vidic 1997; Vidic & McLaughlin 1996; Otani *et al.* 1988; Metzger & Braun 1987; Lancia *et al.* 1993, 1996, 1997; Karatza *et al.* 1996a,b; Dunham *et al.* 1997; Carey *et al.* 1997; Meij 1991; Krishnan *et al.* 1994, 1996). Past research has identified two different classes of sorbents to be effective in mercury removal: activated carbons and calcium (Ca)-based sorbents (Vidic & McLaughlin 1996; Lancia *et al.* 1993, 1996, 1997; Karatza *et al.* 1996a,b; Dunham *et al.* 1997; Carey *et al.* 1997; Meij 1991; Krishnan *et al.* 1994, 1996). The effectiveness of these sorbents is dependent on the types of mercury species that exist in the coal/waste flue gases. Activated carbons have been found to be efficient Hg^0 and HgCl_2 sorbents (Vidic & McLaughlin 1996; Karatza *et al.* 1996b; Krishnan *et al.* 1994), and Ca-based sorbents (in addition to activated carbons) are effective HgCl_2 sorbents (Krishnan *et al.* 1996; Lancia *et al.* 1993). Most typically, these sorbents are injected into flue gas ducts at low temperatures or into the acid gas spray dryers.

Initial research on mercury sorption by sorbents has been

prompted by efforts to comply with MWC emission guidelines and regulations. Typical MWC concentrations of total mercury are on the order of 50 ppb and sorbent/mercury mass ratios of 500/1 are sufficient to meet emission requirements. However, concentrations of total mercury in coal combustors are typically over an order of magnitude lower than MWCs, around 1 ppb. Similar applications of sorbent injection technology for mercury control in coal-fired utilities require sorbent/mercury ratios of nominally 5 000/1 (Chang & Offen 1995). Since the predominant form of mercury in coal combustion is Hg^0 , activated carbon is typically used for emission control. More recent research on mercury control has attempted to apply the MWC-related results to coal-fired utilities, despite large differences in predominant species type and concentrations.

The effect of mercury concentration on adsorption by sorbents has typically shown an increase in adsorptive capacity at higher concentrations (Carey *et al.* 1997; Vidic & McLaughlin 1996; Karatza *et al.* 1996a). Comparative tests for Hg^0 and HgCl_2 sorption under identical conditions remain to be undertaken as does optimization of sorbent choice to mercury species.

Studies with activated carbons concluded that low reaction temperature (23 vs. 140°C; Krishnan *et al.* 1994) promotes Hg^0 adsorption (Vidic & McLaughlin 1996; Karatza *et al.* 1996a,b; Krishnan *et al.* 1994). As with concentration effects, comparative studies on the effect of temperature on Hg^0 and HgCl_2 uptake by activated carbons and Ca-based sorbents have not been reported.

Acid gases (SO_2 and HCl) present in flue gas influence mercury speciation and are also believed to influence the adsorption mechanism of Hg^0 and HgCl_2 by both activated carbons (Carey *et al.* 1997) and Ca-based sorbents (Krishnan *et al.* 1996). Carey *et al.* (1997) showed that the adsorption capacity of a lignite-coal-based activated carbon for both Hg^0 and HgCl_2 increases as the SO_2 concentration decreases and the HCl concentration increases. No explanations are currently available for the opposite effect of these two similar acid gases, suggesting the need for an investigation of HCl and SO_2 influences on Hg^0 and HgCl_2 uptake by activated carbon and Ca-based sorbents.

Sorbent-specific factors are also noted to affect mercury sorptive capacity. A study conducted using two thermally activated carbons indicated that the total surface area has a strong effect on Hg^0 adsorption capacity (Krishnan *et al.* 1994). A bituminous-coal-based activated carbon with twice the surface area as a lignite-coal-based activated carbon captured approximately 4 times higher amounts of Hg^0 . In addition to

different physical properties (total surface area and pore size distribution), these two activated carbons had different chemical characteristics, leaving open the question of the effect of physical and chemical characteristics on sorptive capacity.

In the study reported here, a laboratory-scale, fixed-bed apparatus was used to study the effect of temperature (60 to 140°C), inlet Hg^0 concentration [8 to 40 ppb (65 to 327 $\mu\text{g}/\text{dscm}$)], inlet HgCl_2 concentration [11 to 73 ppb (122 to 809 $\mu\text{g}/\text{dscm}$)], SO_2 [0 to 1000 ppm (0 to 2.6 g/dscm)], HCl [0 to 50 ppm (0 to 0.75 g/dscm)], and water vapor (5%, molar) on Hg^0 uptake by two different thermally activated carbons and HgCl_2 uptake by Ca-based sorbents. The fixed-bed experiments simulate baghouse conditions in which flue gas penetrates a filter cake (i.e. fixed-bed) of sorbent (injected upstream) and fly ash at temperatures less than 150°C. The focus of the study was to answer the following questions:

- Under identical operating conditions, how do the rates and capacities of Hg^0 uptake by thermally activated carbons and HgCl_2 uptake by Ca-based sorbents compare?

- What is the effect of Hg^0 and HgCl_2 concentration on reaction? How influential is the effect of temperature on the fixed-bed adsorption of mercury species?
- How important are the effects of physical and chemical characteristics of sorbents on their Hg^0 and HgCl_2 uptake?
- What are the effects of acid gases (HCl and SO_2) and water vapor on sorbent reaction with Hg^0 and HgCl_2 ?

Addressing these sorbent- and condition-specific questions through bench-scale simulations will provide mechanistic and kinetic information for reaction modeling (Karatza *et al.* 1996a; Carey *et al.* 1997; Rostam-Abadi *et al.* 1997), sorbent development, and optimization of reaction conditions in field applications.

Experimental procedure

A schematic of the experimental apparatus used to study the capture of Hg^0 and HgCl_2 is shown in Fig. 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

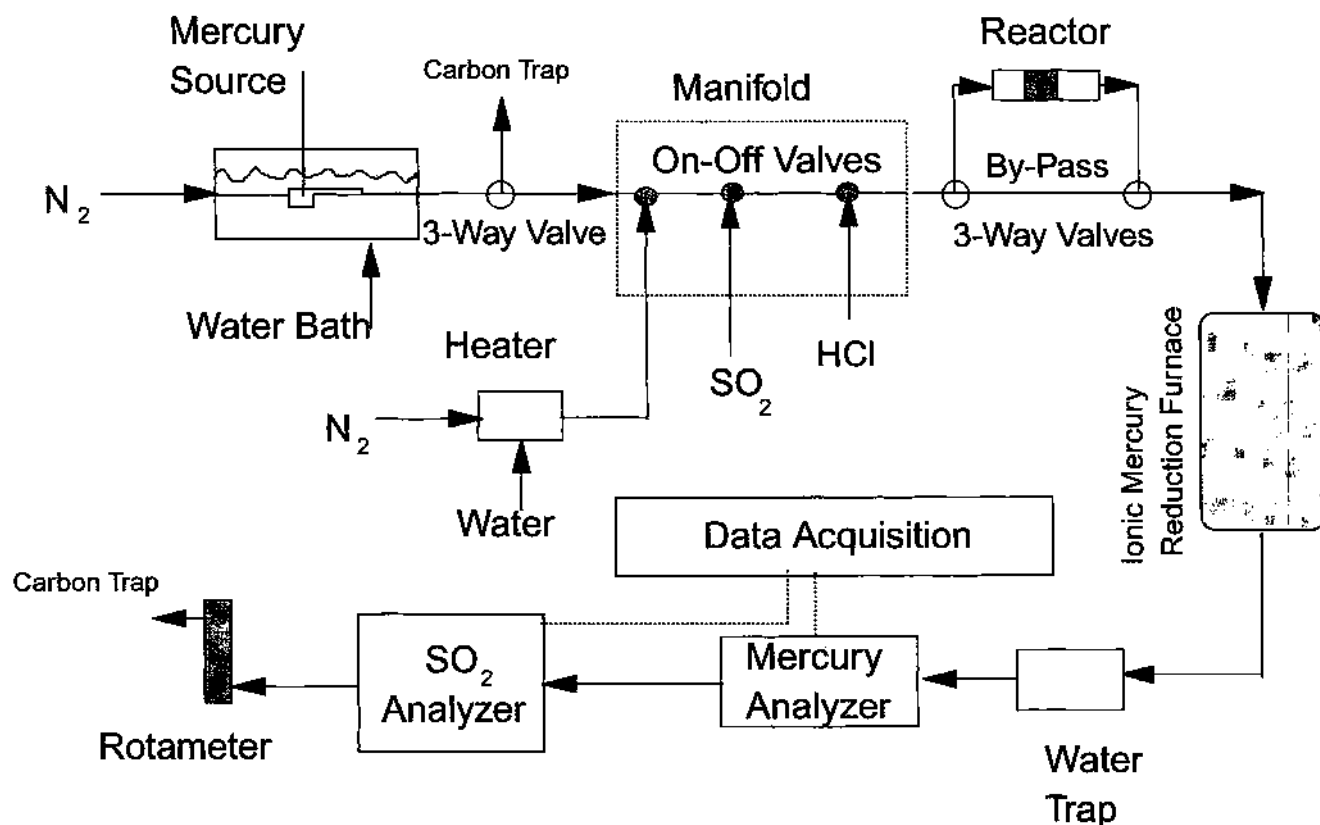


Fig. 1. Schematic of the bench-scale fixed-bed reactor setup.

Inc.; Santa Clara, CA, USA) 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. The mercury vapor generated was carried into a manifold by a nitrogen stream where it mixed with SO_2 , HCl , and water vapor (as required by each particular experiment) at a constant total system flow rate of $350 \text{ cm}^3/\text{min}$ (at standard temperature and pressure; STP). A three-way valve placed before the manifold (Fig. 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 and 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 (Krishnan *et al.* 1995). Quality control experiments, in the absence of HCl in the simulated flue gas, also showed that all the HgCl_2 can be recovered as Hg^0 across this furnace. 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_2 as well as Hg^0 , resulting in additive signals. For example, a gas stream consisting of $1\,000 \text{ ppm}$ SO_2 and 15 ppb Hg^0 produced a SO_2/Hg^0 signal ratio of $8/18$. Signal effects due to SO_2 were corrected by placing an on-line SO_2 analyzer (UV) downstream of the Hg^0 analyzer and subtracting the measured SO_2 signal from the total response of the mercury analyzer (the SO_2 analyzer was incapable of responding to mercury in the concentration range used in this study). Prior to the Hg^0 UV analyzer, water vapor was selectively removed from the gas via NAFION[®] gas sample dryers (Perma Pure Inc.; Toms River, NJ, USA). Repeated quality checks have indicated that this system has no affinity toward adsorption of Hg^0 or acid gases present in the gas.

In each test, the fixed-bed was exposed to the mercury-laden gas for 7 hours or until 100% breakthrough (saturation) was achieved (whichever came first). During this period the exit concentration of mercury was continuously monitored. The instantaneous removal of Hg^0 or HgCl_2 at any time (t) was obtained as follows:

$$100 * [(\text{mercury})_{\text{in}} - (\text{mercury})_{\text{out}}] / (\text{mercury})_{\text{in}} = \text{instantaneous removal at time } t (\%) \quad [1]$$

The specific amount of mercury species uptake q , cumulative removal up to time t ; weight mercury species/weight sorbent was determined by integrating and evaluating the area under the removal curves. Selected experiments conducted during this test program were run in duplicates and indicated a range of $\pm 10\%$ about the mean in the experimental results.

The presence of HCl (50 ppm) in the simulated flue gas created a major interference in the on-line mercury analysis system. Repeated tests confirmed that HCl reacts with Hg^0 in the gas phase and at the outlet of the mercury reduction furnace during the natural cool-down period, thus converting portions of Hg^0 back to HgCl_2 , which is not detectable by the on-line Hg^0 analyzer. This interference undermined the use of the furnace as an ionic mercury converter. An off-line method was adopted to study the effect of HCl on Hg^0 and HgCl_2 adsorption. In this method, a selected carbon- and Ca-based sorbent was exposed (in the fixed-bed reactor) to the mercury-laden flue gas for a period of 24 hours and subsequently the amount of mercury adsorbed on the sorbent was determined using X-ray fluorescence (Siemens SRS 303 XRF analyzer). Selected tests in the off-line test program were run in duplicates and indicated a range of $\pm 13\%$ about the mean in the experimental results.

Sorbents

The capture of Hg^0 was investigated using two different thermally activated carbons, commercially named FGD and PC-100. The capture of HgCl_2 was investigated using two different Ca-based sorbents: $\text{Ca}(\text{OH})_2$ and "modified Advacate" (a mixture of $\text{Ca}(\text{OH})_2$, fly ash, and a surfactant). FGD, manufactured by Norit Americas Inc. (Atlanta, GA, USA), is a lignite-coal-based activated carbon. Information about the total surface area and average pore size diameter of FGD (and other sorbents) was obtained using a Micromeritics ASAP 2600 based on nitrogen adsorption/desorption with the Brunauer-Emmett-Teller (BET) method (Table 1). PC-100, also manu-

Table 1. Physical characteristics of the studied sorbents.

Sorbent	Total surface area (m^2/g)	Average pore diameter (nm)	Particle size (μm)
FGD	500	3.2	<30
PC-100	900	1.8	<30
$\text{Ca}(\text{OH})_2$	13	33.4	NM
Modified advacate	91	21.2	NM

NM: not measured.

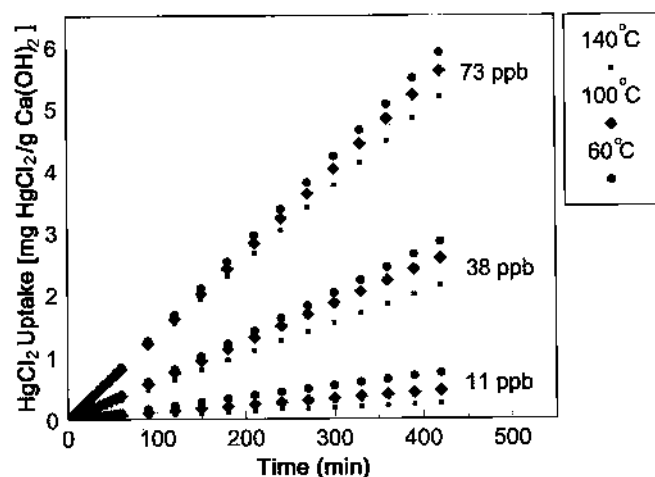


Fig. 2. Effects of bed temperature and inlet HgCl_2 concentration on HgCl_2 uptake by Ca(OH)_2 (baseline conditions).

factured by Norit Americas Inc., is a bituminous-coal-based activated carbon. 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 (see Table 1). The Ca(OH)_2 used in HgCl_2 removal studies was a reagent grade Ca(OH)_2 (Sigma Inc.; St. Louis, MO, USA) containing 97.6% Ca(OH)_2 and 1.8% calcium carbonate (CaCO_3). A detailed description of the modified Advacate is given elsewhere (Krishnan *et al.* 1996). This sorbent is a 3:1 mixture of a fly ash (Clinch River fly ash) and Ca(OH)_2 with a surfactant as an additive. Modified Advacate [25% Ca(OH)_2] has a much higher total surface area (7 times higher) and slightly lower average pore diameter than Ca(OH)_2 .

Results

HgCl_2 Capture by Ca-Based Sorbents

The effects of temperature and inlet concentration on the HgCl_2 uptake by Ca(OH)_2 , obtained under the baseline conditions (nitrogen and HgCl_2 only), are shown in Fig. 2. During the run, HgCl_2 uptake (q) increased linearly as time of exposure progressed; i.e. the instantaneous removal was constant throughout the duration of test. Increasing the HgCl_2 concentration and decreasing the bed temperature increased the HgCl_2 uptakes. Inlet HgCl_2 concentration had a much more pronounced effect on long-exposure time uptakes than the bed temperature. Results of the same set of experiments performed using modified Advacate as the sorbent are shown in Fig. 3 (in comparison to Ca(OH)_2 at a bed temperature of 100°C). Considering the experimental variability ($\pm 10\%$),

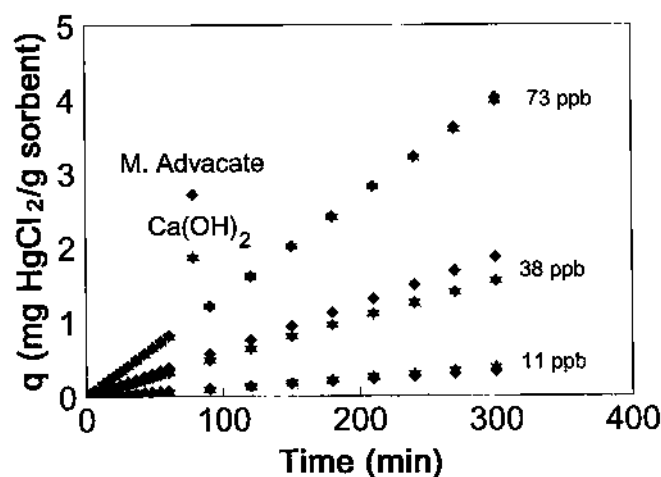


Fig. 3. Comparison between Ca(OH)_2 and modified Advacate; uptake of HgCl_2 (100°C).

results presented in Fig. 3 show identical HgCl_2 capture capabilities of Ca(OH)_2 and modified Advacate (contains 25% Ca(OH)_2).

Since both Ca-based sorbents showed identical HgCl_2 removal capabilities, the effect of adding 1 000 ppm SO_2 to the inlet gas was studied using Ca(OH)_2 as the sorbent (to minimize program costs), while keeping the total flow through the fixed-bed constant. Fig. 4 shows the effect of SO_2 at a constant inlet HgCl_2 concentration of 38 ppb for the three studied temperatures. At the low temperature (60°C), SO_2 had no effect. However, at higher temperatures the presence of SO_2 drastically reduced the sorption capacity of Ca(OH)_2 . In the presence of SO_2 and at 100°C , the saturation capacity ($0.7 \text{ mg HgCl}_2/\text{g Ca(OH)}_2$) was achieved after 5 hours of exposure; at 140°C , the saturation capacity ($0.1 \text{ mg HgCl}_2/\text{g Ca(OH)}_2$) was achieved after only 1 hour of exposure.

XRF results of the effect of HCl on HgCl_2 capture by Ca(OH)_2 are shown in Table 2. Five runs at different gas conditions were performed to deduce the effect of HCl in the presence and absence of SO_2 . As expected, the XRF analysis of the exposed sorbent in the blank run (#1a) revealed no solid-phase mercury (detection limit of $0.02 \text{ mg mercury/g sorbent}$). In the "baseline" test (run #2a) the sorbent [Ca(OH)_2], exposed to a flow of N_2 and 73 ppb HgCl_2 revealed a solid-phase mercury concentration of $6.03 \text{ mg mercury/g Ca(OH)}_2$, the highest solid-phase mercury concentration observed during this test program. The effect of added HCl (run #3a) and, to a higher extent SO_2 (run #4a), was to significantly decrease the amount of captured HgCl_2 by the sorbent. The effect of combined HCl and SO_2 was very close to the effect of SO_2 alone.

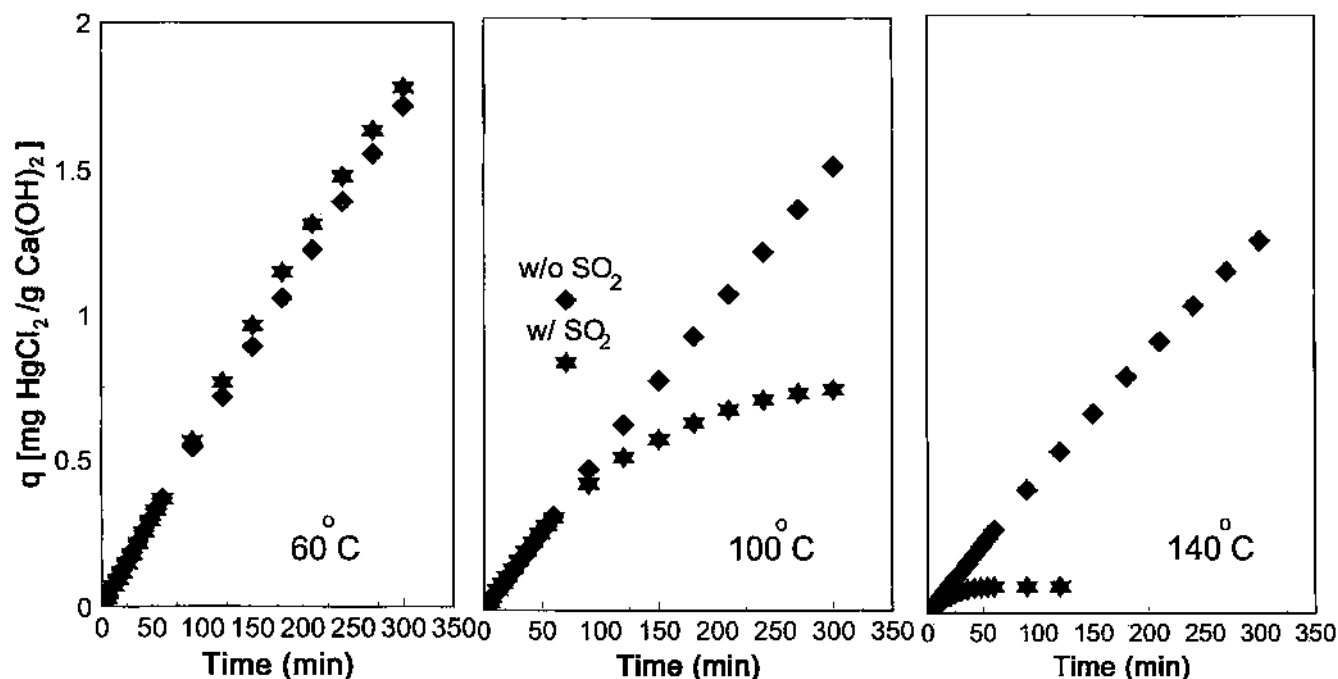


Fig. 4. Effect of SO_2 (1 000 ppm) on HgCl_2 uptake by $\text{Ca}(\text{OH})_2$ (inlet HgCl_2 concentration of 38 ppb). w/ with SO_2 ; w/o without SO_2

Hg^0 Capture by Activated Carbons

The effects of temperature and inlet concentration on the Hg^0 uptake by the FGD are shown in Fig. 5. Unlike HgCl_2 capture by $\text{Ca}(\text{OH})_2$, during a typical 5-h run the sorbent (FGD) reached its saturation capacity, indicating that the available active sites for capturing Hg^0 are limited. Comparison between Figs. 2 and 5 reveals a one order of magnitude higher uptake of HgCl_2 by $\text{Ca}(\text{OH})_2$ than Hg^0 by FGD. Results of duplicate tests for PC-100 in comparison to FGD are presented in Fig. 6 (bed temperature of 100°C). PC-100 also consistently exhibited higher Hg^0 uptakes than FGD at temperatures of 60 and 140°C (not shown here).

The effect of SO_2 on Hg^0 capture by FGD was studied by adding 1 000 ppm SO_2 to the N_2/Hg^0 (40 ppb) stream while

keeping the total gas flow constant through the bed. The highest inlet Hg^0 concentration was chosen to minimize the interferences of SO_2 in the Hg^0 analyzer discussed previously. Fig. 7 shows the effect of SO_2 on Hg^0 capture 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.

The effect of HCl on Hg^0 capture by FGD was studied using the off-line method (XRF analysis). In the fixed-bed reactor (Fig. 1), five experiments were conducted under different flue gas conditions with 1 g of FGD (100°C , flowrate of $300\text{ cm}^3/\text{min}$; 24 h). Results are shown in Table 3. Run #1b (the blank run) revealed an absence of any detectable mercury. In run #2b (the baseline run), the FGD was exposed to a flow of 40 ppb Hg^0 in N_2 . Subsequent XRF analysis revealed a solid-phase mercury concentration of 0.187 mg mercury/g FGD, the lowest solid-phase concentration observed during the Hg^0 test program (see Table 3). Unlike HgCl_2 capture by $\text{Ca}(\text{OH})_2$, FGD was least active toward adsorption of Hg^0 when no acid gas compounds were present. The effect of added HCl (run #3b) and, to a lesser extent, SO_2 (run #4b) was to significantly increase the amount of Hg^0 in the sorbent. The effect of combined HCl and SO_2 was to increase Hg^0 sorption even

Table 2. Effect of HCl (50 ppm) on the HgCl_2 (73 ppb) capture by 1 g $\text{Ca}(\text{OH})_2$ in the absence and presence of SO_2 (1 000 ppm). Exposure time was 24 h, bed temperature was 100°C , flowrate was $300\text{ cm}^3/\text{min}$.

Run #	Flue gas component	Solid-phase mercury concentration mg mercury/g $\text{Ca}(\text{OH})_2$
1a	N_2 (blank)	0
2a	$\text{N}_2 + \text{HgCl}_2$ (baseline)	6.03
3a	$\text{N}_2 + \text{HgCl}_2 + \text{HCl}$	3.09
4a	$\text{N}_2 + \text{HgCl}_2 + \text{SO}_2$	1.28
5a	$\text{N}_2 + \text{HgCl}_2 + \text{HCl} + \text{SO}_2$	1.78

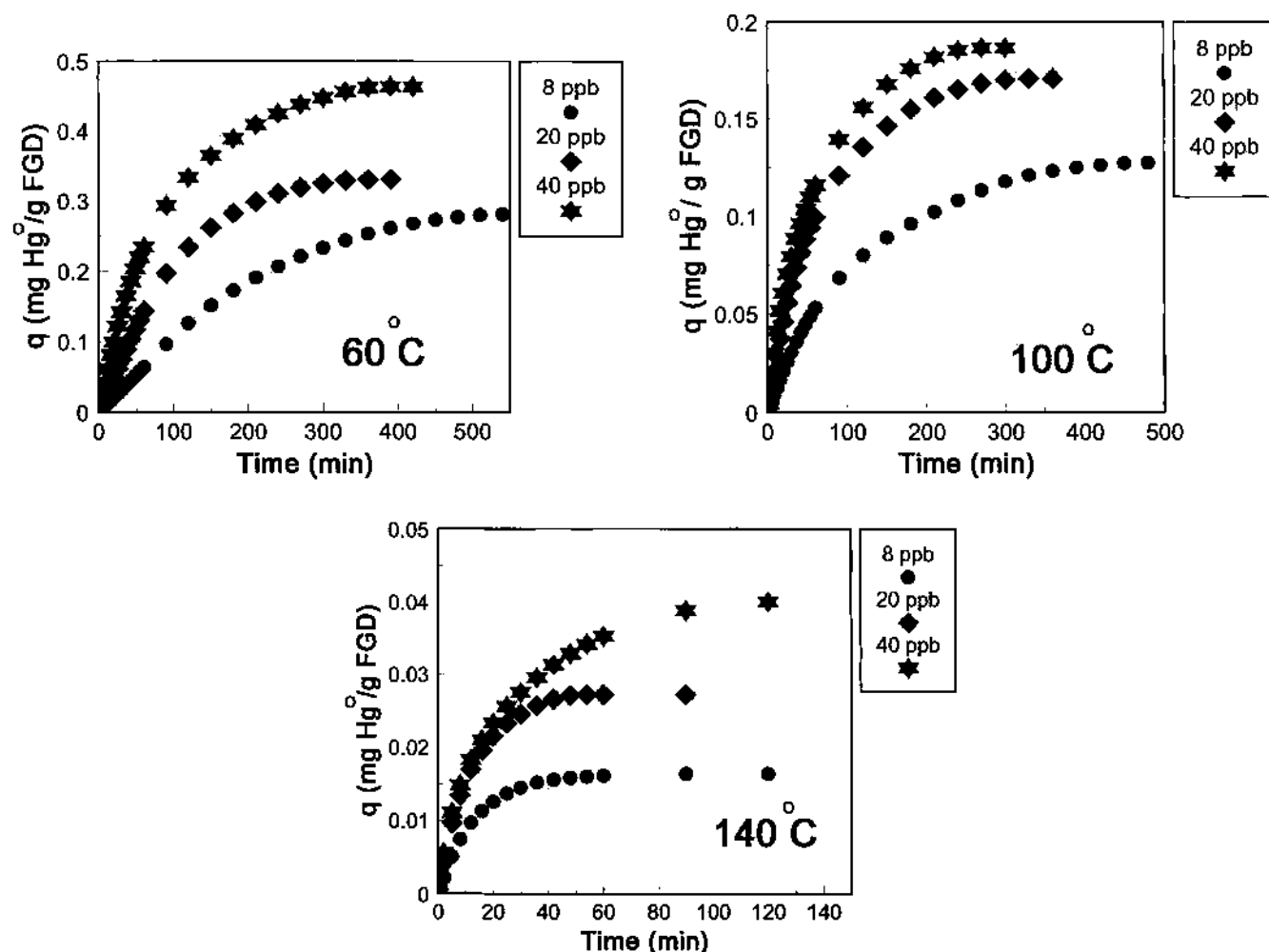


Fig. 5. Effects of bed temperature and inlet Hg⁰ concentration on Hg⁰ uptake by activated carbon, FGD (baseline conditions).

more.

The concentrations of chlorine (Cl) and sulfur (S) in the exposed FGD were determined using the XRF technique; results are summarized in Table 4. Cl concentration in FGD doubled upon exposure to HCl (sample #2); the additional presence of SO₂ (sample #3) decreased the Cl concentration, but it was still elevated from baseline levels (sample #1). S concentration in FGD also doubled upon exposure to SO₂ (sample #5). Presence of HCl had no effect on S uptake.

The effect of water vapor (5% mole) on Hg⁰ uptake by FGD at 140 and 100°C is shown in Fig. 8. At 60°C, water vapor condensed on the surface of FGD, leading to a partial blockage of the system gas flow and resulting in pressure fluctuations; on-line Hg⁰ measurement was not possible at this temperature. Note that the homogeneous dew point of 5% water vapor in air is below 60°C, but that the actual dew

point above hygroscopic solids (such as activated carbon) can be significantly higher, favoring condensation of water vapor at the solid surface.

Discussion

Results presented in Fig. 2 show that Ca(OH)₂ did not reach its HgCl₂ saturation capacity during the exposure period, indicating an abundance of HgCl₂ adsorption sites on Ca(OH)₂. On the other hand, the available active sites for capturing Hg⁰ by a lignite-coal-based activated carbon (FGD) are limited (Fig. 5). Note that, in a previous investigation (Krishnan *et al.* 1996), tests using Ca(OH)₂ showed that no Hg⁰ was captured, indicating an apparent lack of Hg⁰-specific sites in the Ca-based sorbent. The same investigation also revealed that FGD is a much more efficient HgCl₂ sor-

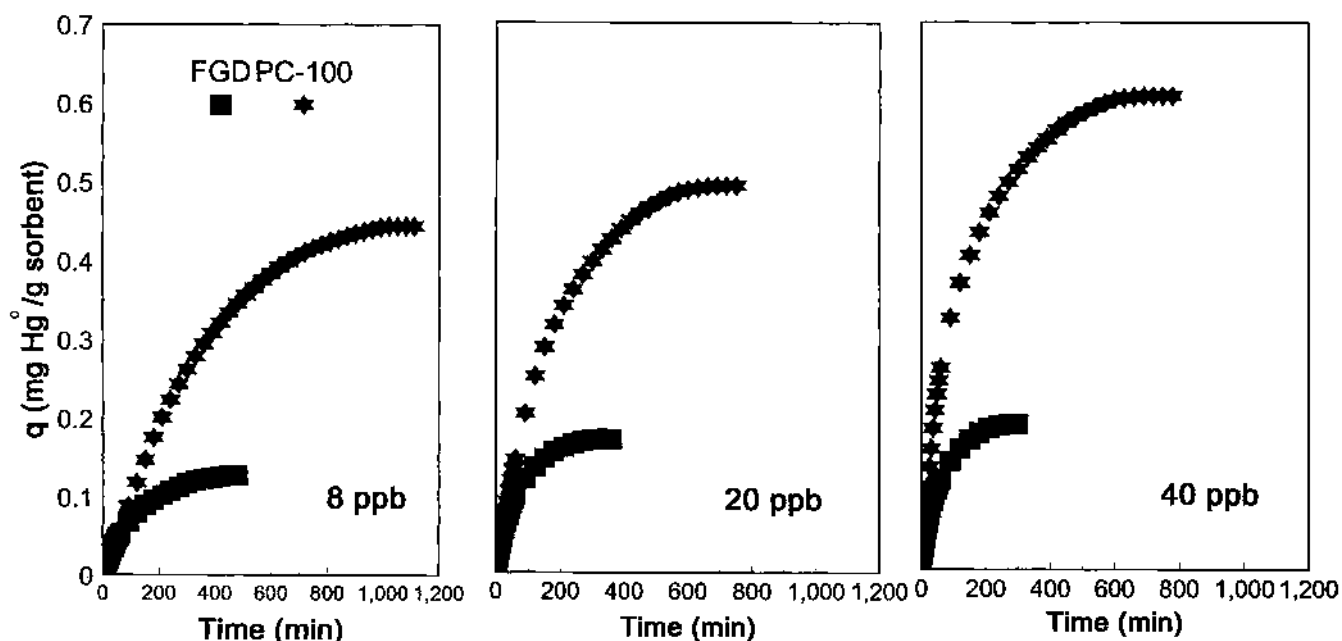


Fig. 6. Uptake of Hg^0 by activated carbons, FGD and PC-100 (bed temperature of 100°C , baseline conditions).

bent than $\text{Ca}(\text{OH})_2$. Karatza *et al.* (1996a) also showed that commercially available activated carbons have HgCl_2 adsorption capacity of more than 1% of activated carbon's weight, a more than 1 order of magnitude higher HgCl_2 uptake than Hg^0 uptake by carbon-based sorbents. While studies con-

ducted by Carey *et al.* (1997) showed that removing Hg^0 from flue gas using a thermally activated carbon is, in general, not much more difficult than HgCl_2 , converse results were obtained in this and previous investigations (Lancia *et al.* 1997; Krishnan *et al.* 1996). In summary, most indications are

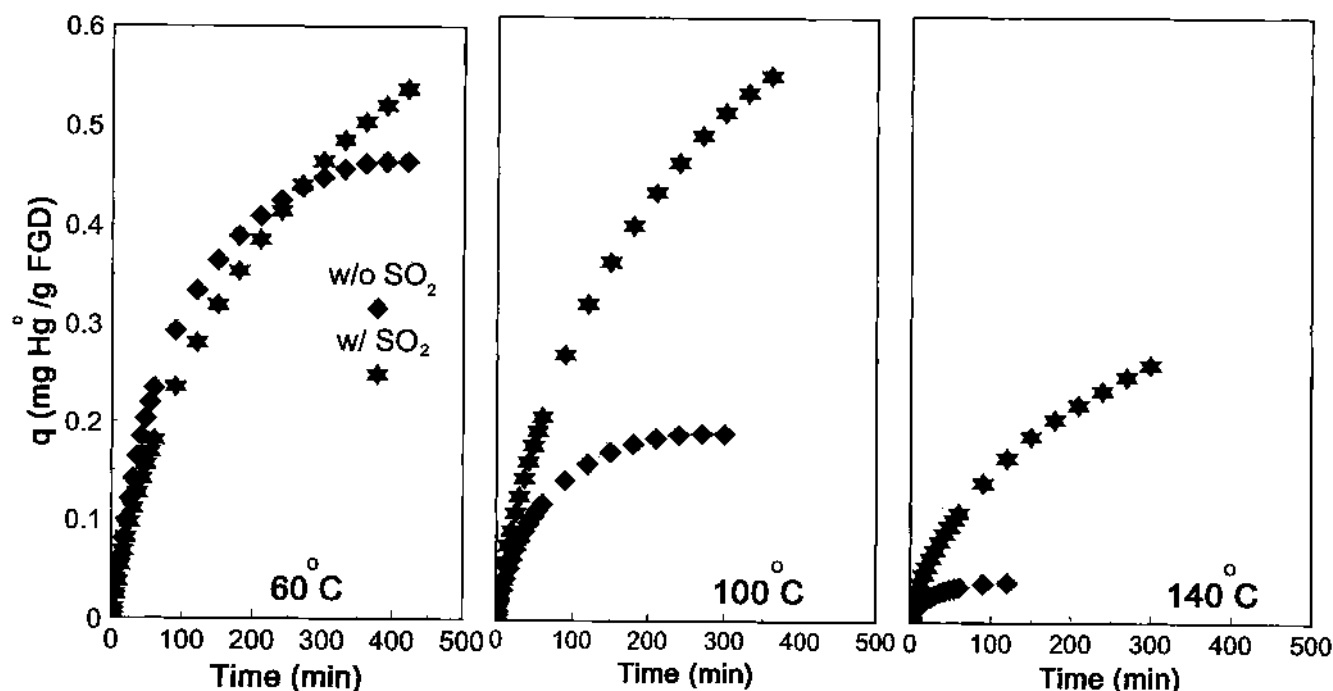


Fig. 7. Effect of SO_2 (1 000 ppm) on Hg^0 uptake by activated carbon, FGD (inlet Hg^0 concentration of 40 ppb). w/ with SO_2 ; w/o without SO_2

Table 3. Effect of HCl (50 ppm) on the Hg^0 (40 ppb) capture by activated carbon, FGD, in the absence and presence of SO_2 (1 000 ppm). Exposure time was 24 h, bed temperature was 100°C, flowrate was 300 cm^3/min .

Run #	Flue gas component	Solid-phase mercury concentration mg mercury/g FGD
1a	N_2 (blank)	0
2a	$\text{N}_2 + \text{Hg}^0$ (baseline)	6.03
3a	$\text{N}_2 + \text{Hg}^0 + \text{HCl}$	3.09
4a	$\text{N}_2 + \text{Hg}^0 + \text{SO}_2$	1.28
5a	$\text{N}_2 + \text{Hg}^0 + \text{HCl} + \text{SO}_2$	1.78

that it is more difficult to control Hg^0 emissions and, in those situations where HgCl_2 is the dominant flue gas mercury species, pre-baghouse injection of hydrated lime may be considered an effective mercury control strategy.

Figs. 2 and 5 depict the effect of bed temperature and mercury concentration on HgCl_2 and Hg^0 uptakes by $\text{Ca}(\text{OH})_2$ and FGD, respectively. Increasing the adsorbate (mercury species) concentration and decreasing the bed temperature increased the uptakes. These results are in agreement with other investigations (Carey *et al.* 1997; Vidic & McLaughlin 1996; Karatza *et al.* 1996; Lancia *et al.* 1996; Karatza *et al.* 1996b). 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 HgCl_2 or Hg^0 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 HgCl_2 or Hg^0 concentration in the vicinity of the surface is very close to the bulk concentration. Moreover, the observed increases in uptakes with decreased temperature do not support an external mass transfer hypothesis, since mass transfer increases in proportion to the 1.5 power of absolute temperature.

Fig. 2 shows that the inlet HgCl_2 concentration had a much more pronounced effect on long-exposure time uptake by $\text{Ca}(\text{OH})_2$ than the bed temperature. On the other hand, Hg^0 capture by FGD was influenced more by the bed temperature (see Fig. 5; note the ordinate scale). A modeling/mechanistic study needs to be performed to shed light on these effects and reveal the underlying reason(s) why bed temperature is the influential Hg^0 sorption parameter and concentration is the important HgCl_2 capture parameter. Understanding the fundamental effects of these two important combus-

Table 4. Concentration (wt%) of chlorine (Cl) and sulfur (S) in simulated-flue-gas exposed activated carbon, FGD. Exposure time was 24 h, bed temperature was 100°C, flowrate was 300 cm^3/min .

Sample #	Flue gas component	Element	Concentration (wt%)
1	N_2 (blank)	Cl	0.226
2	$\text{N}_2 + \text{Hg}^0 + \text{HCl}$	Cl	0.547
3	$\text{N}_2 + \text{Hg}^0 + \text{HCl} + \text{SO}_2$	Cl	0.355
4	N_2 (blank)	S	0.856
5	$\text{N}_2 + \text{Hg}^0 + \text{SO}_2$	S	1.819
6	$\text{N}_2 + \text{Hg}^0 + \text{HCl} + \text{SO}_2$	S	1.733

tion parameters will help operators to determine the performance of $\text{Ca}(\text{OH})_2$ and FGD in field applications where a broad range of $\text{Hg}^0/\text{HgCl}_2$ concentrations and baghouse temperatures may be encountered.

Fig. 3 illustrates a comparison between HgCl_2 uptakes by two different Ca-based sorbents: $\text{Ca}(\text{OH})_2$ and modified Advacate. Modified Advacate has 7 times higher total surface area and 0.6 times lower average pore diameter than those for $\text{Ca}(\text{OH})_2$, a totally different pore size distribution (Krishnan *et al.* 1996). Both Ca-based sorbents exhibited identical HgCl_2 capture capabilities. This observation may once again indicate the abundance of active sites for capturing HgCl_2 in $\text{Ca}(\text{OH})_2$ (modified Advacate is 25% $\text{Ca}(\text{OH})_2$). It may also be concluded that a pore diffusion process is not the controlling mechanism in the removal of HgCl_2 , since modified Advacate with a different pore size distribution and total surface area exhibited the same uptakes as $\text{Ca}(\text{OH})_2$.

Fig. 6 illustrates a comparison between Hg^0 uptakes by two different thermally activated carbons: FGD (lignite-coal-based) and PC-100 (bituminous-coal-based). PC-100 has

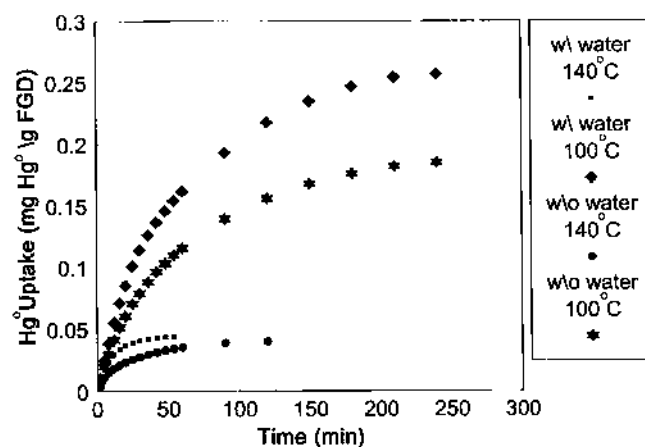


Fig. 8. Effect of water vapor (5% mole) on Hg^0 uptake by activated carbon, FGD (inlet Hg^0 concentration of 40 ppb).

approximately 2 times higher total surface area and 0.56 times lower average pore diameter than FGD. PC-100 consistently exhibited higher Hg^0 uptakes (3 to 4 times higher) than FGD. These results are in agreement with a previous investigation (Krishnan *et al.* 1994) indicating the influential effect of activated carbon's total surface area in adsorption of Hg^0 . Unlike the HgCl_2 adsorption by the Ca-based sorbents, pore size distribution and total surface area are important parameters when adsorption of Hg^0 by activated carbons is considered. In this case, pore diffusion may be an important mechanism which should be considered in any modeling studies.

The effects of SO_2 on HgCl_2 uptake by $\text{Ca}(\text{OH})_2$ and Hg^0 uptake by FGD are shown in Figs. 4 and 7, respectively. Dissimilar behaviors were observed. At higher temperatures (100 to 140°C), the presence of SO_2 inhibited the capture of HgCl_2 by $\text{Ca}(\text{OH})_2$ and enhanced the capture of Hg^0 by FGD. It appears that $\text{Ca}(\text{OH})_2$ and SO_2 react at higher temperatures, leading to the destruction of the available (possibly alkaline) sites needed for HgCl_2 capture. On the other hand, at a higher temperature, SO_2 reacted with the activated carbon, FGD, and created active sulfur sites, which are considered to be very active in capturing Hg^0 (Korpiel & Vidic 1997; Krishnan *et al.* 1994). The activity of FGD in the presence of SO_2 at higher temperatures resembles that of sulfur-impregnated (chemically impregnated) activated carbon studied by Krishnan *et al.* (1994). Note, however, that in a study conducted by Carey *et al.* (1997), an increase in SO_2 concentration was found to inhibit the capture of Hg^0 by a lignite-coal-based activated carbon. Carey *et al.* (1997) results seems to be in disagreement with the results obtained in this study.

The effect of SO_2 on Hg^0 uptake was also studied using a bituminous-coal-based activated carbon (PC-100). 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. The elemental compositions of FGD and PC-100 were determined using the Siemens SRS XRF analyzer. The concentration of Ca in the FGD and PC-100 activated carbons (fresh) was the noticeable distinction: 1.82 wt% in FGD as opposed to 0.13 wt% in PC-100. As discussed, the presence of SO_2 enhanced the Hg^0 capture by FGD (and not PC-100), possibly through a sulfur site generation mechanism. This observation may be attributed to the higher concentration of Ca (SO_2 adsorbent) in FGD. A comprehensive

understanding of the chemical nature (active sites) of these activated carbons and their influence on Hg^0 capture remains to be developed. It appears that only specific activated carbons with high Ca contents may have enhanced Hg^0 sorption capabilities in the presence of SO_2 . This is an important factor in selection of activated carbon for control of Hg^0 in coal/waste combustion processes.

In comparison to SO_2 , HCl was found to, qualitatively, have similar effects on HgCl_2 uptake by $\text{Ca}(\text{OH})_2$ (Table 2) and Hg^0 uptakes by FGD (Table 3). Results in Table 2 indicate that the presence of 50 ppm HCl in the flue gas can decrease the HgCl_2 sorption capability of $\text{Ca}(\text{OH})_2$ by half. The inhibition effect of 1 000 ppm SO_2 is even more drastic (factor of 5), and essentially controls the uptake of HgCl_2 . The inhibition effect of acid gases on HgCl_2 adsorption is thus an important factor which needs to be considered in full-scale facilities. Above-stoichiometric (reaction with SO_2 and HCl) injection rates of $\text{Ca}(\text{OH})_2$ are needed to achieve any HgCl_2 capture in coal/waste combustion facilities if such injection is being implemented upstream of fabric filters (simulated by the fixed-bed reactor). One also needs to consider that, typically, coal combustion flue gases contain a higher concentration of SO_2 and a lower concentration of HCl than waste combustion flue gases. If indeed the inhibition effect of SO_2 is more drastic than HCl, higher injection rates of $\text{Ca}(\text{OH})_2$ will be needed in coal combustion processes.

Results in Table 3 show that HCl can react with FGD and create chlorine (Cl) sites; these sites are instrumental in capturing Hg^0 through formation of Cl-Hg bonds in the solid phase. The enhancement effect of HCl on Hg^0 capture by FGD was also observed by Carey *et al.* (1997). Similar to HCl, and as previously discussed (Fig. 7), one can conclude that the reaction of SO_2 and FGD (run #4b, Table 3) may create active sulfur (S) sites which are effective in capturing Hg^0 through formation of solid-phase S-Hg bonds. Despite a lower gas-phase concentration, HCl had a more pronounced enhancement effect on Hg^0 capture, suggesting that the Cl sites are more active than S sites. Run #5b shows that both types of active sites are instrumental (but not additive) in capturing Hg^0 simultaneously.

It was hypothesized that exposing FGD to the acid gases, HCl and SO_2 , creates active Cl and S sites. Analysis of these elements in the exposed sorbent could potentially provide some evidence for this hypothesis. Concentrations of Cl and S in the exposed FGD sorbent are summarized in Table 4. A 2.4-fold increase in Cl concentration was observed in the FGD sample exposed to 50 ppm HCl for 24 hours. The increased concentration (or number) of Cl atoms have then

been instrumental in capturing Hg^0 (see Table 3) through formation of Cl-Hg bonds. A 2.1-fold increase in S concentration was observed in the FGD sample exposed to 1 000 ppm SO_2 for 24 h. The increased SO_2 concentration in FGD enhanced its Hg^0 capture capability through formation of Hg-S bonds. In summary, it appears that the presence of acid gases in the simulated flue gas creates active sites that are instrumental in capturing Hg^0 . Based on these results, one may conclude that the optimum region for the control of Hg^0 by injection of activated carbon, FGD, is upstream of the acid gas removal system where the activated carbon is exposed to high levels of SO_2 and HCl.

Fig. 8 shows that the presence of water vapor at 100°C slightly enhanced the Hg^0 capture by FGD; this enhancement effect was not as significant as that exhibited by SO_2 and was not observed at 140°C . This enhancement may be due to partial condensation of water molecules onto active sites changing the site polarity and, hence, affinity to Hg^0 .

Conclusion

The effects of bed temperature, mercury concentration, presence of acid gases (HCl and SO_2), and presence of water vapor on the capture of Hg^0 and HgCl_2 by thermally activated carbons (FGD and PC-100) and Ca-based sorbents ($\text{Ca}(\text{OH})_2$ and mixture of $\text{Ca}(\text{OH})_2$ and fly ash) were examined in a fixed-bed, bench-scale system. Sorption studies indicated an abundance of HgCl_2 adsorption sites in Ca-based sorbents. Increasing the HgCl_2 concentration increased its uptake and increasing the bed temperature decreased this uptake. Gas-phase HgCl_2 concentration had a very strong effect in its adsorption, while bed temperature had a small influence on such adsorption. The observed temperature and concentration trends suggests 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. Mixtures of $\text{Ca}(\text{OH})_2$ and fly ash with 7 times higher surface area than $\text{Ca}(\text{OH})_2$ and a totally different pore size distribution exhibited identical HgCl_2 capture to that of $\text{Ca}(\text{OH})_2$. The presence of acid gases (1 000 ppm SO_2 and 50 ppm HCl) drastically decreased the uptake of HgCl_2 by $\text{Ca}(\text{OH})_2$. The inhibition effect of SO_2 was more drastic than

HCl, and essentially controlled the HgCl_2 uptake. It was hypothesized that the inhibition effect is due to a competition between these acid gases and HgCl_2 for the available alkaline sites.

Sorption studies further indicated that the available active sites for capturing Hg^0 in the activated carbons are limited, suggesting that it is more difficult to control Hg^0 emissions. Increasing the Hg^0 inlet 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. Unlike HgCl_2 capture by $\text{Ca}(\text{OH})_2$, bed temperature had a very strong effect on the Hg^0 adsorption by the activated carbons, and gas-phase Hg^0 concentration had a small influence on such adsorption. PC-100, with twice the surface area of FGD, consistently exhibited higher saturation capacities (3 to 4 times higher) than FGD. The presence of acid gases had a positive effect on the capture of Hg^0 by a lignite-coal-based activated carbon (FGD) and had no influence on Hg^0 capture by a bituminous-coal-based activated carbon (PC-100). This difference was related to a higher concentration of Ca (acid gas sorbent) in FGD. It appears that adsorption of these acid gases by FGD creates active S and Cl sites, which are instrumental in capturing Hg^0 , through formation of S-Hg and Cl-Hg bonds in the solid phase (chemisorption). Based on these results, it may be concluded that the optimum region for the control of Hg^0 by injection of activated carbon is upstream of the acid gas removal system.

Acknowledgments

This work was co-sponsored by the Illinois Department of Commerce and Community Affairs through the Illinois Coal Development Board and the Illinois Clean Coal Institute (ICCI) (Project Manager: Ken Ho). This work and use thereof are subject to the disclaimer statement of the ICCI, available upon request. The authors acknowledge the logistical support of Richard Valentine (EPA/APPCD), experimental assistance from Lisa Adams and Hamid Bakhteyar and technical assistance from Wojciech Jozewicz (ARCADIS Geraghty & Miller).

References

- Billings, C. E., Sacco, A. M., Matson, W. R., Griffin, R. M., Coniglio, W. R. & Harley, R. A. (1973) Mercury Balance on a Large Pulverized Coal-

- Fired Furnace. *Journal of Air Pollution Control Association* 23, 773.
Carey, T. R., Hargrove, O. W., Richardson, C. E., Chang, R. & Meserole, F.

- B. (1997) Performance of Activated Carbon for Mercury Control in Utility Flue Gas Using Sorbent Injection. In: *Proceedings of the First EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium (the "Mega" Symposium)*, August 25–29, 1997, Washington, DC, USA.
- Chang, R. & Offen, G. R. (1995) Mercury Emission Control Technologies; An EPRI Synopsis. *Power Engineering*, November, 51–57.
- Devito, M. S., Tunari, P. R., Carlson, R. J. & Bloom, N. (1993) Sampling and Analysis of Mercury in Combustion Flue Gas. Presented at the *EPRI's Second International Conference on Managing Hazardous Waste Air Pollutants*, July 13–15, 1993, Washington, DC, USA.
- Dunham, G. E., Miller, S. J., Chang, R. & Bergman, P. (1997) Mercury Capture by an Activated Carbon in a Fixed-Bed Bench-Scale System. Paper 97-WA72A.03. Presented at the *Air & Waste Management Association's 90th Annual Meeting & Exhibition*, June 8–13, 1997, Toronto, Ontario, Canada.
- Evans, A. P. & Nevitt, K. D. (1997) Mercury Speciation Measurements on a 10 MWe Coal-Fired Boiler Simulator. Paper 97-WA72B.07 Presented at the *Air & Waste Management Association's 90th Annual Meeting & Exhibition*, June 8–13, 1997, Toronto, Ontario, Canada.
- Hall, B., Lindqvist, O. & Ljungstrom, E. (1990) Mercury Chemistry in Simulated Flue Gases. Related to Waste Incineration Conditions. *Environmental Science & Technology* 24, 108.
- Karatza, D., Lancia, A., Musmarra, D., Pepe, E. & Volpicelli, G. (1996a) Removal of Mercuric Chloride from Flue Gas by Sulfur Impregnated Activated Carbon. *Hazardous Waste & Hazardous Material* 13, 95.
- Karatza, D., Lancia, A., Musmarra, D. & Pepe, E. (1996b) Adsorption of Metallic Mercury on Activated Carbon. *Twenty-sixth Symposium (International) on Combustion*, The Combustion Institute, July 28–Aug 2, 1996, Pittsburgh, USA, PA, p. 2439.
- Klein, D. H., Andren, A. W., Carter, J. A., Emery, J. E., Feldman, C., Fulkerson, W., Lyon, W. S., Ogle, J. C., Talmi, Y., Van Hook, R. I. & Bolton, N. (1975) Pathways of 37 Trace Elements Through Coal-Fired Power Plant. *Environmental Science & Technology* 9, 973.
- Korpiel, J. A. & Vidic, R. D. (1997) Effect of Sulfur Impregnation Method on Activated Carbon Uptake of Gas-Phase Mercury. *Environmental Science & Technology* 31, 2319–2325.
- Krishnan, S. V., Gullett, B. K. & Jozewicz, W. (1994) Sorption of Elemental Mercury by Activated Carbons. *Environmental Science & Technology* 28, 1506.
- Krishnan, S. V., Gullett, B. K. & Jozewicz, W. (1995) Mercury Control by Injection of Activated Carbon and Calcium-Based Sorbents. Presented at the *Solid Waste Management Thermal Treatment & Waste-To-Energy Technologies Conference*, USEPA/AEERL and A&WMA, April 18–21, 1995, Washington, DC, USA.
- Krishnan, S. V., Bakhreyar, H. & Sedman, C. B. (1996) Mercury Sorption Mechanisms and Control by Calcium-based Sorbents. Presented at the *89th Air & Waste Management Association Annual Meeting*, June 23–28, 1996, Nashville, TN, USA.
- Lancia, A., Musmarra, D., Pepe, E. & Volpicelli, G. (1993) Adsorption of Mercuric Chloride Vapors from Incinerator Flue Gases on Calcium Hydroxide Particles. *Combustion Science and Technology* 93, 277.
- Lancia, A., Musmarra, D. & Pepe, E. (1996) Adsorption of Mercuric Chloride from Simulated Incinerator Exhaust Gas by Means of Sorbalit™ Particles. *Journal of Chemical Engineering Japan* 29, 939.
- Lancia, A., Musmarra, D., Pepe, E. & Volpicelli, G. (1997) Control of Emissions of Metallic Mercury from MSW Incineration by Adsorption on Sorbalit™. *The 1997 International Conference on Incineration and Thermal Treatment Technologies*, May 12–16, 1997, Oakland, CA, USA.
- Langley, D. G. (1973) Mercury Methylation in an Aquatic Environment. *Journal of Water Pollution Control* 45, 44.
- Laudal, D. L., Heidt, M. K., Brown, T. D., Nott, B. R. & Prestho, E. P. (1996) Mercury Speciation: A Comparison Between EPA Method 29 and Other Sampling Methods. Presented at the *89th Air & Waste Management Association Annual Meeting*, June 23–38, 1996, Nashville, TN, USA.
- Livengood, C. D. & Mendelsohn, M. H. (1997) Enhanced Control of Mercury Emissions Through Modified Speciation. Paper 97-WA72A.01 Presented at *Air & Waste Management Association's 90th Annual Meeting & Exhibition*, June 8–13, 1997, Toronto, Ontario, Canada.
- Meij, R. (1991) A Sampling Method Based on Activated Carbon for Gaseous Mercury in Combustion Flue Gases. *Water, Air, and Soil Pollution* 56, 117.
- Metzger, M. & Braun, H. (1987) In-Situ Mercury Speciation in Flue Gas by Liquid and Solid Sorption Systems. *Chemosphere* 16, 821–832.
- Otani, Y., Emi, H., Kanaoka, C., Uchijima, I. & Nishino, H. (1988) Removal of Mercury Vapor from Air with Sulfur-Impregnated Adsorbents. *Environmental Science & Technology* 22, 708–711.
- Rustam-Abadi, M., Chen, S. G., Hsi, H.-C., Rood, M., Chang, R., Carey, T., Hargrove, B., Richardson, C., Rosenhoover, W. & Meserole, F. (1997) Novel Vapor Phase Mercury Sorbents. In: *Proceedings of the First EPRI-DOE-EPA Combined Utility Air Pollutant Control Symposium (the "Mega" Symposium)*, August 25–29, 1997, Washington, DC, USA.
- Senior, C. L., Bool, L. E., Huffman, G. P., Huggins, F. E., Shah, N., Sarofim, A., Olmez, I. & Zeng, T. (1997) A Fundamental Study of Mercury Partitioning in Coal-Fired Power Plant Flue Gas. Paper 97-WA72B.08 Presented at the *Air & Waste Management Association's 90th Annual Meeting & Exhibition*, June 8–13, 1997, Toronto, Ontario, Canada.
- Vidic, R. D. & McLaughlin, J. B. (1996) Uptake of Elemental Mercury Vapors by Activated Carbons. *Journal of Air & Waste Management Association* 46, 241–250.
- Westoo, G. (1973) Methylmercury as Percentage of Total Mercury in Flesh and Viscera of Salmon and Sea Trout of Various Ages. *Science* 181, 567.

Letters to the Editor

Dear Sir,

We read the paper titled "An empirical approach to the performance assessment of solid waste landfills" by W. B. Nixon, R. J. Murphy and R. I. Stessel (*Waste Management & Research* 15, 607-626) with great interest. The paper is a useful discussion of the use of landfill models in assessing pollution potential. The real strength of the paper lies in its foundation on an existing data base. Our interest in the paper concerns the applications of the existing models in the context of low-income, developing countries since we are currently researching the development of appropriate landfill guidelines for low- and middle-income countries. The following comments and questions on the paper are presented for discussion:

General comment

The paper is proposed as a contribution to the development of models and methods "to simulate or assess the probability, magnitude and potential consequences of the leakage of aqueous environmental contaminants from solid waste landfills and similar facilities". Consequently, a succinct and useful account of the previous models is provided in the paper. One of the key criticisms made of the previous model was that different models are likely to yield a different assessment of the same facility. The issue of inter-model reliability was implied. The other criticisms was the use of subjective elements by the previous model builders. At this stage, the readers' expectations were raised to see if the author would answer the criticism raised against the previous work. A possible outcome of the paper may have been the proposed changes in one or few of those models. Upon completing a careful reading of the paper the question remains: Have the authors answered the criticism raised on the previous models? With all due respect, and in spite of the some good work, it is hard to conclude that we are better off in terms of predicting landfill failures more objectively. It is also questionable whether the study has increased the reliability of the previous models. No new model was proposed. Some of the data analysis and its basis could be improved.

Specific comments

1. The paper used the secondary data from 500 landfills "to determine the correlation between a magnitude of observable parameters and the *actual* performance of these landfills". It claims that, as a result of the study, the "existing models may be refined" without any mention of how.
2. In Section 3.1, it appears that the performance parameters were taken from the previous models. It is not clear whether the sum of all the parameters from the previous models was selected or only a selection taken. Even if all the parameters were selected; the possibility remains that some 'other' parameters may have been missed. If a selection was made; there is no justification or explanation provided about the rationale for selection. Is this not the use of subjective judgments? Is it not the case, therefore, that selection criteria applied by another researcher would produce a separate set of parameters? Further, it appears that, for a number of parameters, it is not clear how they are related to the potential consequences of the leakage.
3. The parameters were then "correlated with ground water, surface water and soil sampling and testing results as evidence of long-term performance". However, it appears that some of the "parameters of interest" were not in the data base and were collected from other sources. It is not clear whether this 'outside' data used was compatible with the data base parameters used.
4. It could be deduced that bivariate correlations were used to understand the correlation. It was neither explained nor justified why a bivariate analysis was used where a multivariate technique would have been more suitable because many variables were likely to interact. There is no explanation of the effect of other factors influencing the relationship between the two factors being studied.
5. In Section 3.3, the basis for selection of the 31 parameters was not mentioned. Is not this again the use of subjective judgment which was a key criticism of the previous study?