Mercury Control by Injection of Activated Carbon and Calcium-Based Sorbents

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ABSTRACT

Injection of activated carbon is among the technologies used for control of mercury (Hg) emitted during municipal waste combustor (MWC) operation. Depending on the form of Hg present and amount of activated carbon injected, varying levels of control have been achieved in field units. However, under favorable laboratory conditions, we have found that calcium (Ca)-based sorbents can be as effective as some of the activated carbons in controlling Hg emissions.

This paper compares the capture of both elemental mercury (Hg°) and mercuric chloride ($HgCl_2$) vapor by different types of commercially available activated carbons and Ca-based sorbents, including quicklime (CaO) and hydrated lime [$Ca(OH)_2$]. Comparisons were made at two temperatures in bench-scale reactors, with other conditions remaining identical. Our results showed that, at the lower temperature (100 °C), Ca-based sorbents capture incoming $HgCl_2$ as well as the activated carbons. At the higher temperature (140 °C), activated carbons showed relatively higher capture of $HgCl_2$ than Ca-based sorbents. However, only activated carbons exhibited significant capture of Hg° at either temperature. Because field measurements as well as equilibrium predictions show that Hg exists in MWC flue gas primarily as $HgCl_2$, the results indicate the possibility of injecting CaO or $Ca(OH)_2$ along with activated carbons to reduce operating costs in controlling Hg emissions.

INTRODUCTION

Emissions of Hg vapor from MWCs and coal-burning utilities may present significant health and environmental hazards. The Clean Air Act Amendments of 1990 (Title III, Section

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112[b][1]) require major sources to use maximum available control technology (MACT) to reduce Hg emissions. Existing flue gas desulfurization systems have been shown to control Hg emissions to some extent in both MWCs and coal combustors (1,2). To achieve higher Hg removal efficiencies, however, additional systems, such as an activated carbon sorption process (1,2), may be required.

Hg is known to exist in flue gas as either Hg° or an oxidized form [$HgCl_2$ or mercuric oxide (HgO)] (3). Figure 1 shows the equilibrium concentration of Hg species at 7.7% oxygen (O_2), 7.7% carbon dioxide (CO_2), 4% water vapor (H_2O), 400 ppm sulfur dioxide (SO_2), 19.5 ppb Hg, and the balance nitrogen (N_2). The results have been obtained by employing the thermodynamic code CET89 (4). As is seen, for all three concentrations of hydrogen chloride (HCl), Hg° exists at the higher temperatures typically found in the combustor or economizer of a MWC or power plant. At lower temperatures, Hg exists only as $HgCl_2$. At higher temperatures, negligible amounts of HgO are formed. Similar equilibrium distributions of Hg species were obtained by Schager (5) and Lancia et al. (6). Also, it can be seen from Figure 1 that, in flue gases with relatively higher HCl concentration, $HgCl_2$ exists at relatively higher temperatures. Moreover, the results in Figure 1 show that, even in MWC flue gases with low HCl concentrations, Hg exists primarily as $HgCl_2$.

Injection of activated carbon either upstream or downstream of a spray dryer (SD) has been shown to reduce Hg emissions in both MWCs (1) and coal-fired utilities (2). Typically, these activated carbon processes operate at injection temperatures of 100-200 °C. Provided that equilibrium is attained rapidly by the Hg species prior to contacting activated carbon, $HgCl_2$ would be the dominant species at temperatures below 500 °C (see Figure 1). Non-attainment of equilibrium by the different Hg compounds would imply the presence of Hg° at 100-200 °C. The control of Hg emissions has been found to be strongly dependent on the form of Hg. Several tests have shown that relatively low amounts of Hg° are captured compared to the oxidized forms (5,7). Therefore, it is necessary to understand the sorption process as well as the mechanism of capturing both $HgCl_2$ and Hg° by activated carbons at these temperatures.

In previous investigations (8,9), we studied the sorption of Hg° by three activated carbons, namely PC-100, FGD, and HGR. The first two are thermally activated, while HGR is activated by elemental sulfur (S) impregnation. Our results showed that specific locations (active sites) in PC-100 and FGD cause sorption of Hg°. However, upon exposure to heat

(140 °C in N_2) prior to $Hg°$ sorption tests, the active sites were found to be either deactivated or destroyed, thus leading to significantly lower capture of $Hg°$. Sorption of $Hg°$ in HGR at 140 °C occurs primarily through the reaction of S and $Hg°$ while at 23 °C, sorption occurs in non-S sites residing on the external surface. Heating HGR did not cause a loss in its sorption capacity, unlike PC-100 and FGD. In addition to tests studied by Jozewicz et al. (8) and Krishnan et al. (9), previous studies by Gullett and Jozewicz (10) explored the effect of surface area and porosity of activated carbons on $Hg°$ capture. Unlike the studies on sorbent reactivity towards $Hg°$, there is very little laboratory data in the literature on the capture of $HgCl_2$ by activated carbons. Therefore, experiments were performed as part of this study to quantify and understand sorption of $HgCl_2$ by activated carbons. Sorption of $Hg°$ by these sorbents under identical conditions was also studied for comparison with the capture of $HgCl_2$.

Although activated carbons are injected in the temperature window of 100-200 °C with the specific intent of Hg capture, injection of CaO or $Ca(OH)_2$ to remove SO_2 emissions may also capture Hg vapor from MWC flue gas. For instance, Hg reduction by injection of $Ca(OH)_2$ was observed by Gullett and Raghunathan (11) in their pilot-scale unit. However, the species of Hg captured by $Ca(OH)_2$ in their study are unknown, as are the conditions where capture occurred in their unit (e.g., temperature). Lancia et al. (6) investigated adsorption of $HgCl_2$ on $Ca(OH)_2$ particles in a simulated MWC and observed high removal efficiencies of $HgCl_2$ by $Ca(OH)_2$ particles. As part of this study, we investigated the capture of both $Hg°$ and $HgCl_2$ by CaO and $Ca(OH)_2$ at two temperatures (100 and 140 °C) to determine the feasibility of injection of CaO or $Ca(OH)_2$ in controlling total Hg emissions.

The sorption of $Hg°$ and $HgCl_2$ by PC-100, FGD, HGR, CaO, and $Ca(OH)_2$ at two temperatures is investigated in this study. Also, sorption of $Hg°$ and $HgCl_2$ by fresh and heat treated activated carbons has been investigated in an effort to identify the active sites participating in capturing $Hg°$ and $HgCl_2$.

SORBENT CHARACTERISTICS

Of the five types of sorbents tested for $Hg°$ and $HgCl_2$ capture, three (PC-100, FGD, and HGR) are activated carbons. PC-100 and FGD are thermally activated carbons while HGR is sulfur-activated with roughly 7% (by weight) S. Details on their physical characteristics (pore size distributions, particle size ranges, pore volumes, and surface areas) and a chemical analysis of each are given in an earlier publication (9). Reagent-grade

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hydrated lime supplied by Fischer Scientific was the source for $Ca(OH)_2$. Approximately 1 g of the Yorktown hydrated lime was calcined at 1,000 °C for 1 h in a flow of N_2 to produce CaO used in our experiments. The Brunauer-Emmett-Teller (BET) surface areas of $Ca(OH)_2$ and CaO were 13 and 27 m^2/g, respectively. Compared to surface areas of 1000 m^2/g for PC-100 and HGR, and 500 m^2/g for FGD, the Ca-based sorbents have an insignificant surface area.

EXPERIMENTAL APPARATUSES AND PROCEDURES

Hg° Capture Studies

The setup used for studying Hg° capture has been described in detail elsewhere (8,9,10). In these experiments, approximately 100 mg of the sorbent was placed between glass wool supports in a glass reactor. A flow of 200 cm^3/min of N_2 containing 30 ppb Hg° was the inlet stream. An online ultraviolet (UV) detector (Ametek, Model 400) recorded the Hg° concentration. The calibration of the UV detector and the experimental procedures have also been explained elsewhere (8,9,10). Because an online analyzer is used to measure breakthrough Hg° concentration, a simple mass balance yields the percentage of Hg° captured by the sorbent.

$HgCl_2$ Capture Studies

Figure 2 shows the schematic diagram of the apparatus used for studying $HgCl_2$ capture. A diffusion vial filled with $HgCl_2$ powder is the source of a constant supply of gaseous $HgCl_2$. The carrier gas is pure N_2 flowing at 200 cm^3/min. Depending on the temperature of the furnace encasing the diffusion vial, varying levels of $HgCl_2$ concentration in the carrier gas can be obtained. In all our experiments, the $HgCl_2$ concentration in the N_2 stream was approximately 30 ppb.

While the reactor containing the sorbent is being heated, the $HgCl_2/N_2$ stream bypasses the reactor. Once the desired conditions have been obtained, the three-way valve is switched to direct flow through the reactor. At the end of a fixed duration experiment, the three-way valve is used to divert flow away from the reactor, and each stage of the reactor is analyzed for total Hg content. Unlike experiments performed to study Hg° capture, there is no online analyzer for $HgCl_2$; hence, batch operations were necessary.

In our experiments to study $HgCl_2$ capture, three stages of sorbent were used. The first stage, containing the sorbent under study, was exposed to 30 ppb $HgCl_2$ in N_2. The second

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and the third stages always contained activated carbon, PC-100, because PC-100 showed the highest capture of $HgCl_2$. Approximately 100 mg of sorbent was loaded in each stage and was supported by glass wool. The latter two stages ensured that all the generated $HgCl_2$ was captured. At the end of a run, each stage was analyzed for total Hg. Analysis of the three stages is necessary to obtain an accurate generation rate of $HgCl_2$ vapor from the diffusion vial such that the $HgCl_2$ capture efficiency of the sorbent being evaluated (first stage) can be obtained. The $HgCl_2$ captured is obtained from

$$\Phi_t = [\alpha_1/(\alpha_1 + \alpha_2 + \alpha_3)] \times 100 \qquad (1)$$

where Φ_t is the cumulative percentage of incoming $HgCl_2$ captured by the sorbent being evaluated (Stage 1) in time t. Here, α_1, α_2, and α_3 are the amounts of Hg measured by x-ray fluorescence (XRF) (ppmw) in Stages 1, 2, and 3, respectively.

XRF was employed to quantitatively determine total Hg in each of the three stages. Standards were prepared for each sorbent (the three activated carbons and two Ca-based sorbents) tested in this study by doping with known concentrations of Hg solution to provide samples ranging from 10 to 1,000 ppm of Hg by weight. The calibration of the XRF machine (Siemens, Model SRS303) was undertaken for each sorbent in the 10 to 1,000 ppm range using these standards. A linear correlation for each sorbent was obtained in the 0 to 100 and 100 to 1,000 ppm ranges. The strength of the XRF signals obtained from the analysis of sorbents from our experiments were matched with these correlations to obtain $HgCl_2$ concentrations.

In some of our Hg° experiments, the activated carbon samples were analyzed at the end of the run employing XRF. Figure 3 compares the concentration of Hg° obtained by the online UV analyzer with that obtained from the XRF analysis. A very close match is seen between the two methods of analysis, indicating the reliability of the XRF technique to measure Hg in samples. Periodically, samples used for calibrating the XRF machine were also analyzed through cold vapor atomic absorption (CVAA) as a further measure of data quality. Results obtained from the CVAA analysis showed that the samples used for calibrating the XRF instrument were within 10% of the XRF value.

RESULTS

Figure 4 shows the percentage of incoming $HgCl_2$ (30 ppb) captured by PC-100, FGD, HGR, $Ca(OH)_2$, and CaO at 100 and 140 °C.

All five sorbents show relatively higher capture (>80 %) of $HgCl_2$ at 100 °C (see Figure 4) than at 140 °C (<80%). Activated carbons PC-100 and HGR show comparatively smaller decreases in $HgCl_2$ captured at 140 °C, whereas activated carbon, FGD, and the two Ca-based sorbents show significant decreases in $HgCl_2$ captured. Lancia et al. (6) also observed lower $HgCl_2$ capture by $Ca(OH)_2$ particles at higher temperatures (95% at 100 °C versus 80% at 150 °C). Because their experimental conditions were different from ours (that is, sorbent loading, face velocity, $HgCl_2$ concentration, and particle physical characteristics), a direct comparison of the capture efficiencies cannot be made.

The data in Figure 4 are replotted in Figures 5 and 6 to compare Hg° versus $HgCl_2$ capture at 140 and 100 °C, respectively. Figures 5 and 6 show that all three activated carbons show relatively higher capture of $HgCl_2$ compared to Hg°. Activated carbon PC-100 after 4 h of exposure (at 140 °C) shows close to 90% capture of incoming $HgCl_2$ compared to approximately 80% capture of Hg°. However, for longer exposures, PC-100 continues to capture 90% of incoming $HgCl_2$, whereas the percentage of Hg° captured decreases continuously. The difference between Hg° and $HgCl_2$ captured by the other activated carbons is far greater than that of PC-100. For instance, only 20% of incoming Hg° is captured by FGD (at 140 °C) compared to roughly 60% of $HgCl_2$ after 4 h of exposing FGD to each Hg species. At the same conditions, HGR captures 60% of incoming Hg° compared to over 90% of $HgCl_2$ (see Figure 5).

DISCUSSION

Depending on the manufacturing process (activation with nitrous oxide (N_2O), ammonia (NH_3), or $ZnCl_2$-NH_4Cl-CO_2, or heat-treated at 900 °C), activated carbon acquires properties of a solid base (12). Reactions of gaseous O_2 with the surface of active carbon at temperatures somewhat below 100 °C produce O_2 complexes which on hydration can form hydroxyl or other basic groups (13). The large internal surface areas of the activated carbons may provide sufficient basic sites to capture the acidic $HgCl_2$ by a chemical reaction.

In a previous investigation (9), we observed that sorption of Hg° by thermally activated carbons PC-100 and FGD occurred via a combination of physisorption and chemisorption at specific active sites. These active sites were either deactivated or destroyed when the activated carbons were exposed to a flow of N_2 at 140 °C for 4 h (heat-treated) resulting in lower sorption of Hg°. In the current study, we compared the sorption of $HgCl_2$ with sorption of Hg° by fresh and heat-treated PC-100. Figure 7 shows the amount of Hg (Hg° and $HgCl_2$) sorbed by 100 mg of fresh and heat-treated PC-100 after 4 h of exposure to 30 ppb of either Hg° or $HgCl_2$ at 140 °C. The result is expressed as milligrams of Hg per gram of PC-100. Figure 7 shows that heat-treatment lowers the sorption of Hg° (roughly by 50%), but does not affect sorption of $HgCl_2$. This is indicative of different sorption sites for Hg° and $HgCl_2$, which likely leads to the differences in Hg° and $HgCl_2$ sorption seen in Figures 5 and 6. The basic sites causing the capture of $HgCl_2$ are not affected by heat treating the activated carbon. On the other hand, the oxygen functional groups suspected of capturing Hg° (9) are either depleted or deactivated.

$Ca(OH)_2$ captures high amounts of incoming $HgCl_2$ at 100 °C and moderate amounts at 140 °C (see Figures 4, 5, and 6). At 100 °C, $Ca(OH)_2$ captures close to 90% of incoming $HgCl_2$. Compared to the activated carbons, $Ca(OH)_2$ used in this study has very little surface area [500 to 1,000 m^2/g for the activated carbons compared to 13 m^2/g for $Ca(OH)_2$]. Despite the comparative lack of an internal structure, $Ca(OH)_2$ captures similar amounts of $HgCl_2$ as the three activated carbons at 100 °C. At 140 °C, $Ca(OH)_2$ captures $HgCl_2$ in amounts similar to activated carbon, FGD. In the experiments of Lancia et al. (6), similar removals of $HgCl_2$ by $Ca(OH)_2$ were observed. At both temperatures, however, we found $Ca(OH)_2$ to capture negligible amounts of Hg° (see Figures 5 and 6). Tanabe et al. (14) have classified CaO to be a solid superbase. Therefore, in spite of the lack of a large surface area like activated carbons, the superbasic property of $Ca(OH)_2$ [assuming $Ca(OH)_2$ to have superbasic properties similar to CaO] causes high capture of $HgCl_2$. The superbasic property of the Ca-based sorbents, however, does not lead to capture of Hg° to the extent of the activated carbons.

Thermodynamic predictions obtained in this study as well as studies of Hall et al. (3, 15) and Schager (5) suggest that Hg would most likely be present as $HgCl_2$ in a MWC flue gas. Bloom et al. (16), based on measurements from actual coal combustor sites, report that much of the Hg in flue gas appeared to be in the oxidized form. From the high percentage of

$HgCl_2$ capture by CaO and $Ca(OH)_2$ seen in this study, injection of Ca-based sorbents would likely prove beneficial in capturing high amounts of total Hg in a MWC under favorable conditions.

Dry scrubbing by spray dryer absorption (SDA) is used in several hundred MWCs and hazardous waste incinerators (HWIs) (17, 18). Spray dryer plus fabric filter (SD/FF) systems have shown moderate to high removals of Hg (19). Felsvang et al. (19) report 30 to 50% Hg removal by SDA systems in MWCs. Gullett and Raghunathan (11) have also shown that injection of $Ca(OH)_2$ can control Hg emissions in a coal-fired pilot-plant study. Data obtained from the U.S. Environmental Protection Agency's (EPA's) Biomedical Waste Incineration (BWI) study (20) show, however, that dry $Ca(OH)_2$ injection/FF- or SD/FF-equipped plants do not control Hg. Tests at Camden County MWC (1) have shown Hg control ranging from 20 to 90 % without carbon injection. To achieve consistently high Hg control, activated carbon injection was necessary. Factors which could probably affect Hg control by dry $Ca(OH)_2$ injection are the process conditions -- temperature, Hg species, and physical characteristics of $Ca(OH)_2$. Although equilibrium calculations predict Hg to be present as $HgCl_2$ in a BWI flue gas, the apparent contradictions posed by the EPA BWI study (20) emphasize the need for field speciation.

The results obtained in our study indicate that Ca-based sorbents like CaO and $Ca(OH)_2$ are effective in controlling only $HgCl_2$ and that activated carbons are needed to control $Hg°$. Therefore, high removal of Hg is possible by application of Ca-based sorbents [similar to results of Felsvang et al. (19) and Gullett and Raghunathan (11)] in flue gases containing a significant portion of $HgCl_2$ and at temperatures below 140 °C. In situations where both $Hg°$ and $HgCl_2$ are present in significant fractions, CaO or $Ca(OH)_2$ may be injected along with activated carbons. Such processes where hydrated lime is injected along with activated carbon (the "Alka/Sorb" and "Sorbalit" processes) are used for treating waste-to-energy, HWI, and BWI combustion gases (20,21). Careful sampling of the Hg compounds in a flue gas, accompanied by the results obtained from bench-scale tests of the type reported in this study, would allow sorbent selection for optimum control of Hg from flue gases where the bulk of Hg capture occurs in baghouses or electrostatic precipitators (ESPs).

A possible cost optimization in controlling Hg emissions if $HgCl_2$ sorption by activated carbons leads to lower $Hg°$ sorption would be to carefully "stage" the injection of Ca-based sorbents and activated carbons. By injecting Ca-based sorbents before activated carbon,

most of the HgCl$_2$ would be captured, leaving only Hg° to be captured by activated carbon. Therefore, only limited amounts of activated carbon would be necessary to capture the remaining Hg, leading to potential cost reduction.

SUMMARY AND CONCLUDING REMARKS

Thermodynamic predictions obtained from this study, as well as others including field data, have shown that Hg exists primarily as Hg° and HgCl$_2$. The capture of Hg° and HgCl$_2$ at 100 and 140 °C by three types of activated carbons and two Ca-based sorbents was investigated in this study.

In general, all five sorbents studied here showed higher capture of HgCl$_2$ at 100 °C. The effect of temperature on HgCl$_2$ capture was significant for activated carbon FGD and the two Ca-based sorbents, CaO and Ca(OH)$_2$. Lowering the temperature had only a small effect on HgCl$_2$ capture by activated carbons PC-100 and HGR.

Of the two species of Hg investigated, HgCl$_2$ was found to be captured with greater efficiency than Hg° by all the sorbents studied. Since HgCl$_2$ is acidic, it is captured by the basic sites in the activated carbons. The basic sites in activated carbon arise due to the manufacturing process. Despite the lack of surface area in CaO and Ca(OH)$_2$ compared to the activated carbons, similar amounts of HgCl$_2$ were captured by both. This is because CaO is a solid superbase and the mechanism is not surface-limited.

The active sites where Hg° and HgCl$_2$ are sorbed in activated carbons were found to be different. This was concluded based on our studies comparing sorption of Hg° and HgCl$_2$ by fresh and heat-treated PC-100. Whereas the sorption of Hg° decreased on heat-treating PC-100 (possibly due to loss of oxygen-related functional groups), HgCl$_2$ sorption was unaffected.

The high percentage capture of HgCl$_2$ by CaO and Ca(OH)$_2$ indicates that, where HgCl$_2$ is present in significant amounts in MWC flue gas, dry injection of CaO or Ca(OH)$_2$ could possibly control Hg emissions at favorable process conditions. Where both Hg° and HgCl$_2$ exist in significant fractions, staged injection (Ca-based followed by activated carbon) may reduce Hg removal costs. Staging would eliminate competition for HgCl$_2$ between Ca-based sorbents and activated carbons. Future bench-scale experiments are planned to investigate simultaneous sorption of Hg° and HgCl$_2$ by activated carbons to study the feasibility of such a process.

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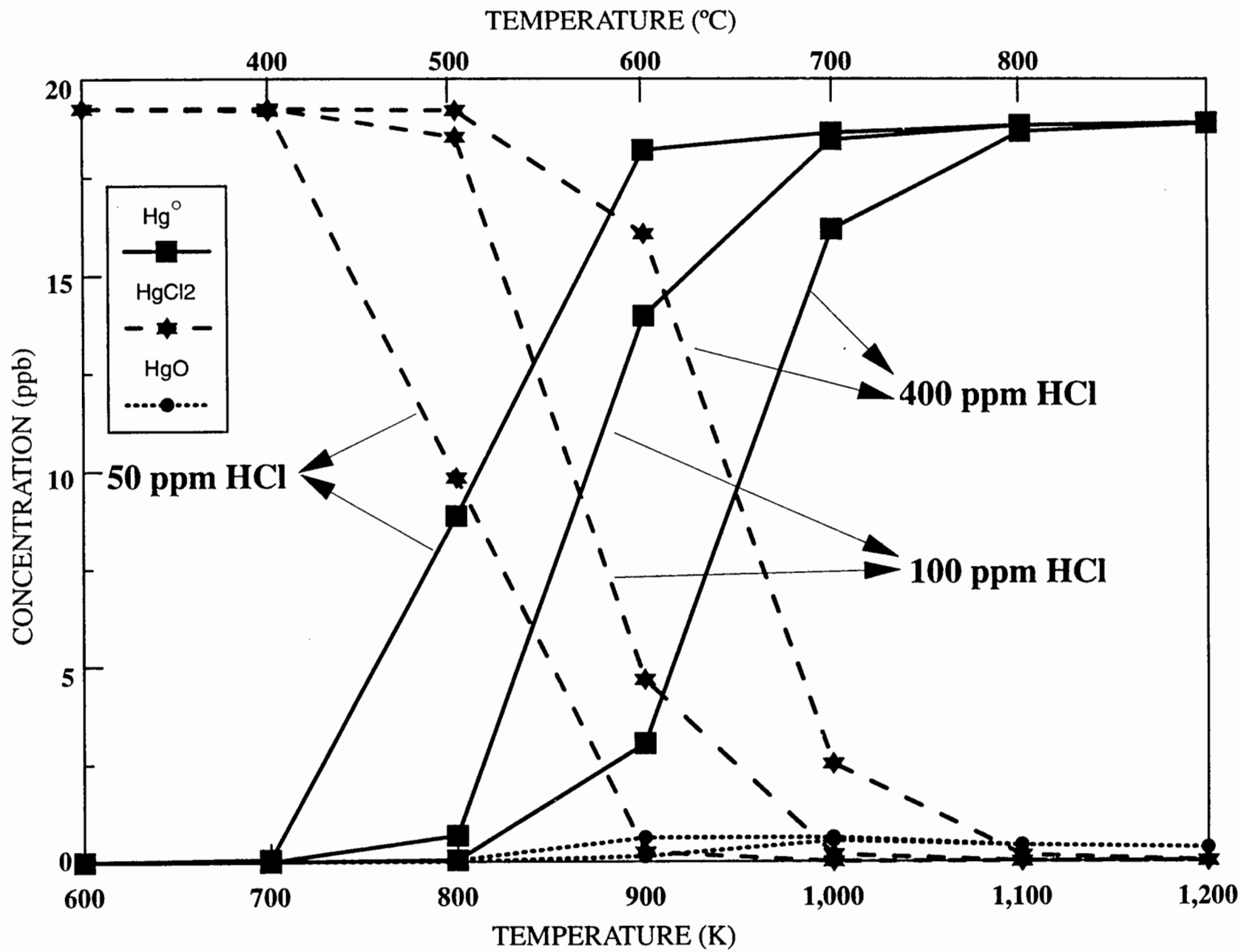
Figure 1. Equilibrium prediction of Hg species as a function of HCl concentration in flue gas. The flue gas consisted of 7.7% O_2, 7.7% CO_2, 4% H_2O, 400 ppm SO_2, 19.5 ppb Hg, and the balance N_2.
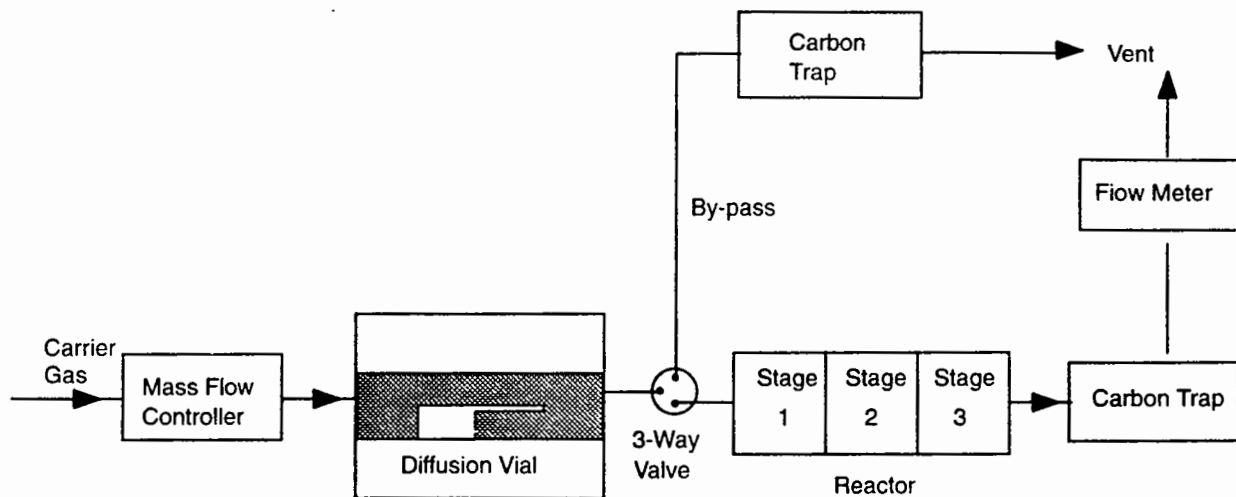
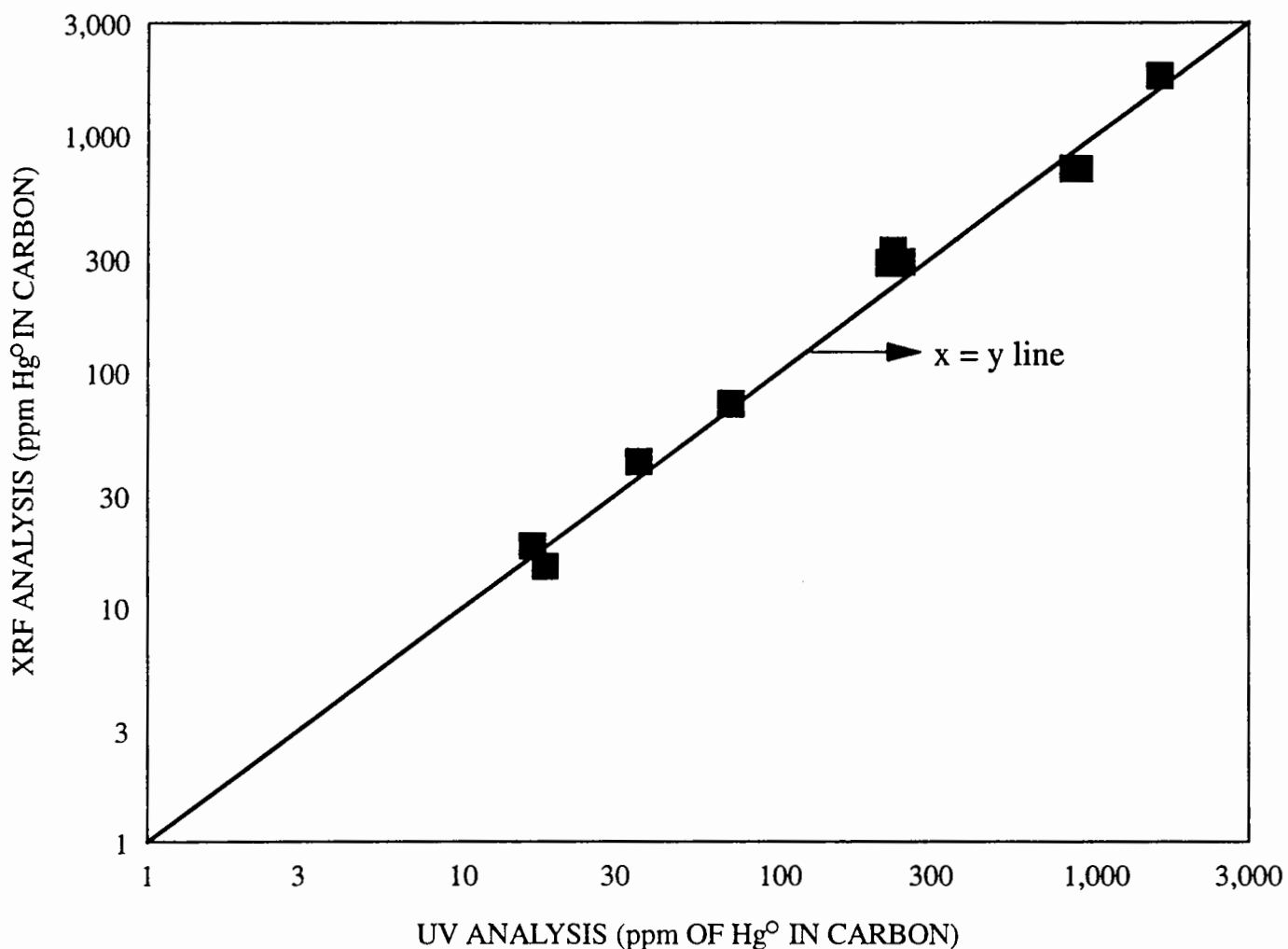Figure 2. Schematic diagram of experimental apparatus used to study $HgCl_2$ capture.

Figure 3. Comparison of methods of analysis of Hg^0 in activated carbon samples. Online UV (x-axis) vs. XRF (y-axis).
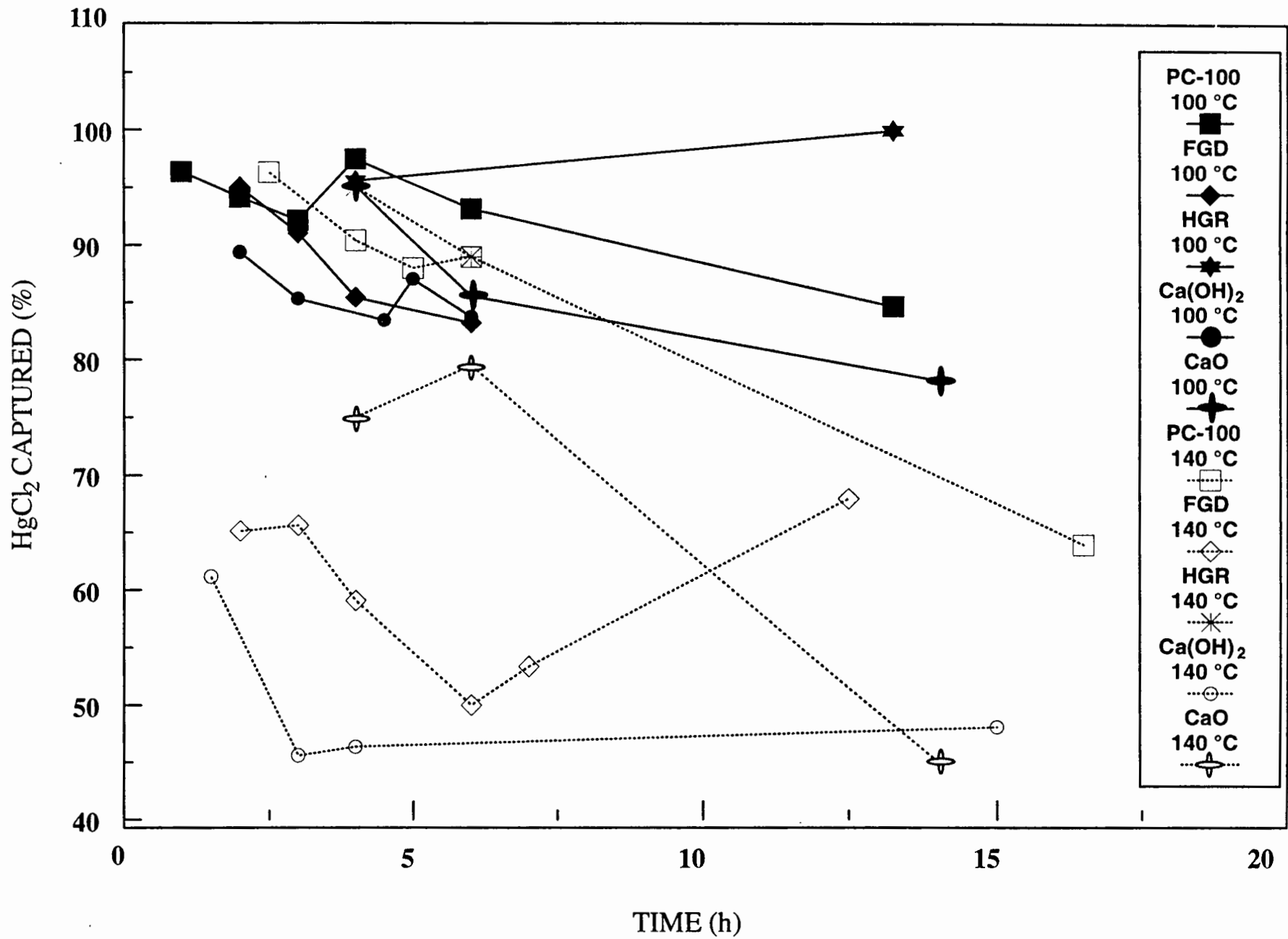
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Figure 4. Effect of temperature on first-stage capture of 30 ppb $HgCl_2$ by 100 mg of PC-100, FGD, HGR, CaO, and $Ca(OH)_2$. Flowrate of 200 cm³/min N_2.

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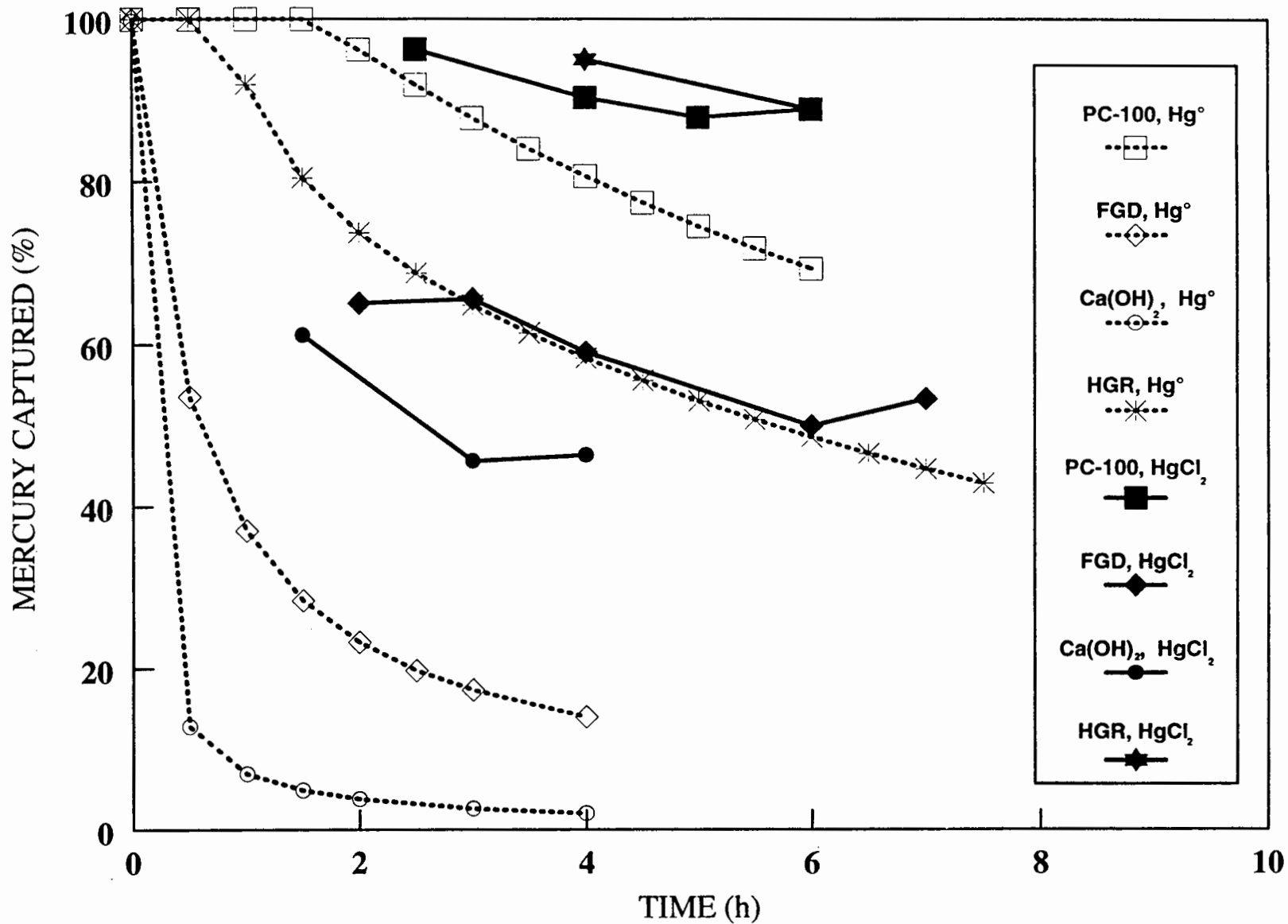
Figure 5. Comparison of capture of 30 ppb Hg° and 30 ppb $HgCl_2$ by 100 mg of PC-100, FGD, HGR, and $Ca(OH)_2$ at 140 °C. Inlet gas flowrate of 200 cm³ /min N_2.
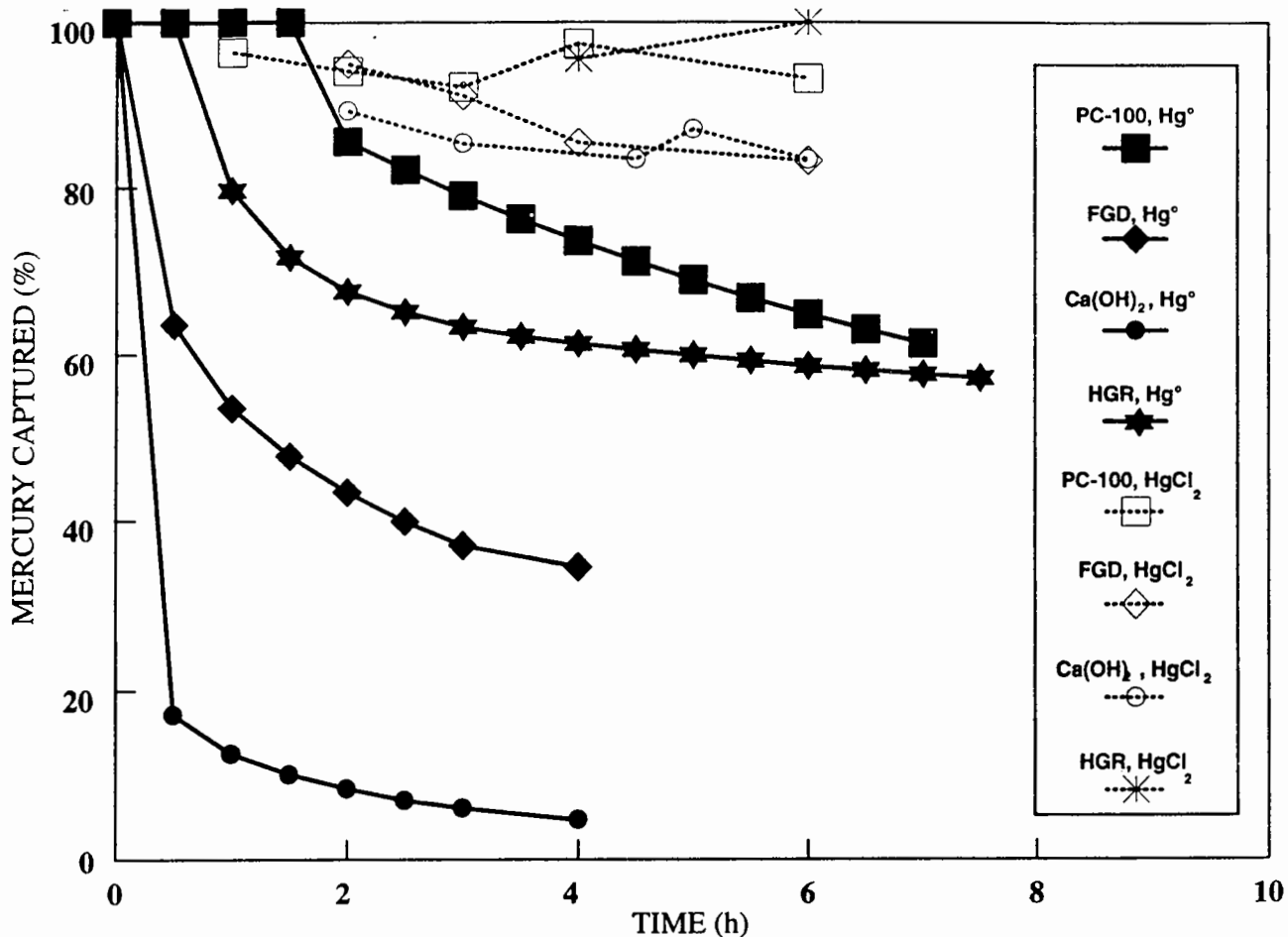
Figure 6. Comparison of capture of Hg° and HgCl$_2$ by 100 mg each of PC-100, FGD, HGR, and Ca(OH)$_2$ at 100 °C. Inlet gas flowrate of 200 cm ^{3}/min N$_2$ (30 ppb Hg° or HgCl$_2$).
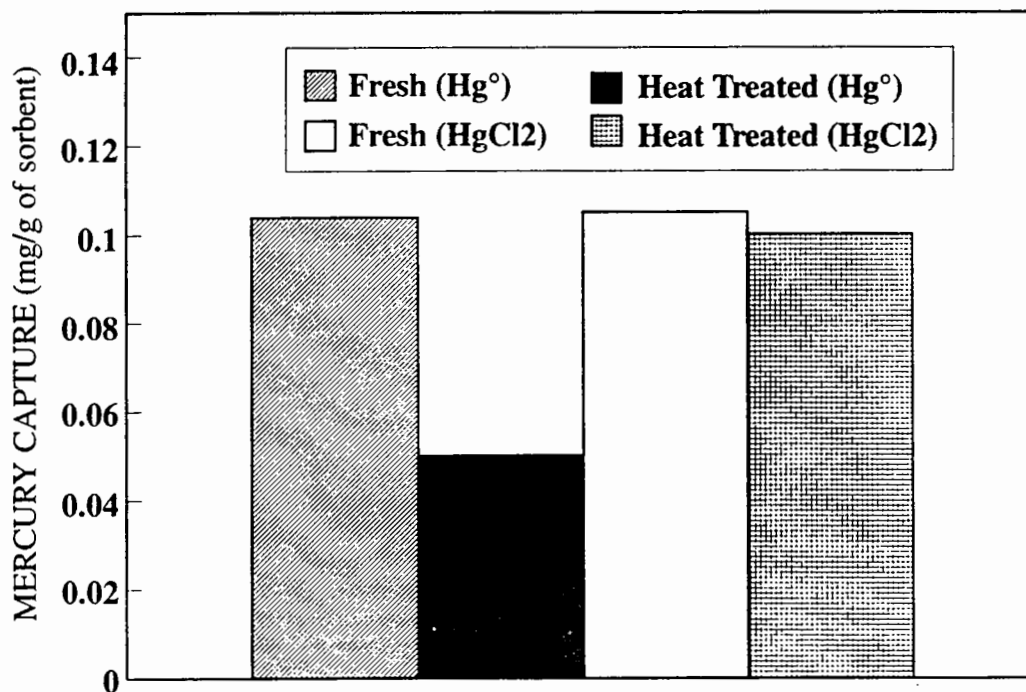

Figure 7. Effect of heat-treatment (exposing sorbent to a flow of N$_2$ at 140 °C for 4 h prior to capturing Hg) on Hg° and HgCl$_2$ capture by PC-100. Figure compares Hg° and HgCl$_2$ capture by 100 mg of fresh and heat-treated PC-100 after 4 h of exposure to 30 ppb Hg° or HgCl$_2$ in a flow of 200 cm^3/min N$_2$.

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1. REPORT NO. EPA/600/A-97/011	2.	3.

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16. ABSTRACT The paper compares the capture of both elemental mercury ($Hg^°$) and mercuric chloride ($HgCl2$) vapor by different types of commercially available activated carbons and calcium (Ca)-based sorbents, including quicklime (CaO) and hydrated lime, $Ca(OH)2$. Comparisons were made at two temperatures in bench-scale reactors, with other conditions remaining identical. (NOTE: Injection of activated carbon is among the technologies used for control of mercury (Hg) emitted during municipal waste combustor (MWC) operation. Depending on the form of Hg present and amount of activated carbon injected, varying levels of control have been achieved in field units. However, under favorable laboratory conditions, Ca-based sorbents can be as effective as some of the activated carbons in controlling Hg emissions.) Study results showed that, at the lower temperature (about 100 C), Ca-based sorbents capture incoming HgCl2 as well as activated carbons. At the higher temperature (140 C), activated carbons showed relatively higher capture of HgCl2 than Ca-based sorbents. However, only activated carbons exhibited significant capture of $Hg^°$ at either temperature. Because field measurements and equilibrium predictions show that Hg in MWC flue gas exists primarily as HgCl2, the results indicate the possibility of injecting CaO or Ca(OH)2 along with activated carbons to reduce operating costs.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Mercury (Metal)	Stationary Sources	07B
Activated Carbon	Mercuric Chloride	11G
Sorbents	Quicklime	
Calcium Oxides	Hydrated Lime	
Combustion	Municipal Waste Com-	21B
Wastes	bustion	14G

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