

# **Mercury Control in Municipal Waste Combustors and Coal-fired Utilities**

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## ABSTRACT

Control of mercury (Hg) emissions from municipal waste combustors (MWCs) and coal-fired utilities has attracted attention due to current and potential regulations. Among several techniques evaluated for Hg control, dry sorbent injection (primarily injection of activated carbon) has shown promise for consistently removing high levels of Hg from MWC or coal flue gas. However, the performance in terms of amount of Hg removed per amount of sorbent varies widely between the MWC and coal-fired applications and from unit to unit.

In this study, we have conducted bench-scale experiments under conditions simulating MWCs and coal-fired units to study Hg capture by dry sorbents. The effect of reaction temperature on the capture of different Hg species [ $\text{Hg}^0$  and  $\text{Hg(II)}$ ] by various types of dry sorbents was the focus of bench-scale tests. An attempt has also been made in this study to compare the bench-scale results with results obtained from pilot studies and to explain disparities in fuel- and unit-specific performance. Our investigations showed that the reaction temperature and Hg species strongly affect Hg control. The results obtained in this suggested the two following mechanisms for Hg capture:

- i) Capture of  $\text{Hg}^0$  by activated carbons is limited by sorption kinetics, and
- ii) Capture of mercuric chloride ( $\text{HgCl}_2$ ) by activated carbons is limited by collision with carbon particles.

## INTRODUCTION

Title III of the 1990 Clean Air Act Amendments (CAAA) requires the U.S. Environmental Protection Agency (EPA) to submit a study on 189 hazardous air pollutants (HAPs). This study would include emissions and a risk (to public health) assessment of the 189 HAPs. Among the 189 HAPs, mercury (Hg) has drawn special attention because of concerns that ingestion of fish containing certain forms of Hg (like methyl mercury) could be harmful to human health.

An EPA “mercury” report to Congress<sup>1</sup> cites the largest emitters of Hg as coal-fired utilities, medical waste incinerators (MWIs), municipal waste combustors (MWCs), chlor-alkali plants, copper and lead smelters, and cement manufacturers. These sources account for 90 to 100 percent of anthropogenic Hg emissions. Utility boilers account for 24 percent of the total anthropogenic Hg emissions of which more than 90 percent are attributable to coal-fired utility boilers. MWIs and MWCs together account for nearly 60 percent of the anthropogenic Hg emissions. Because of intended, proposed, or existing regulations, control of Hg emissions from these sources needs to be studied.

There are several methods for controlling Hg emissions in MWCs and MWIs either in use or currently being tested. These include a variety of chemical, adsorption, and absorption techniques.<sup>2</sup> Primarily, dry sorbent injection (DSI) followed by a fabric filter (FF) or electrostatic precipitator (ESP), a spray dryer (SD) followed by a FF or ESP, and wet scrubbing (WS) have been tested as Hg control methods. The sorbents tested in the DSI/FF process to control Hg emissions include calcium-based sorbents and activated carbons. Varying levels of Hg control in MWCs using these technologies have been reported.<sup>3-5</sup> All tests showed that flue gas desulfurization (FGD) units (SD/FF and WS systems) with addition of DSI (injection of activated carbon) lead to consistently high (> 90 percent) Hg removal in MWCs.

Adoption of control strategies from MWCs, primarily DSI (injection of activated carbon), has not met with similar success in coal-fired utilities. A coal-fired pilot-scale study<sup>6</sup> showed that high Hg removal at 120 °C required a carbon:Hg ratio of 3,000:1. The amount of carbon:Hg for similar levels of removal in MWCs has been shown to be an order of magnitude lower. A similar result, showing the need for high carbon:Hg ratios in coal-fired utilities, was obtained from pilot-scale studies<sup>7</sup> at the University of North Dakota’s Energy and Environmental Research Center

(UNDEERC).

At a carbon:Hg ratio of 3,000:1 and an activated carbon cost of \$ 1.125/kg, our estimates indicate that the material cost would be approximately \$ 500,000 per year for a 500 MW coal-fired power plant. Chang et al. (Reference 6) report an annual cost of carbon injection of \$ 100,000 - \$ 1 million for Hg control in a 500 MW coal-fired plant. Another estimate<sup>8</sup> suggests that controlling 50 percent of the Hg emitted by U.S. utility power plants could range from \$ 1 billion to \$ 10 billion per year. These estimates can vary depending on equipment, installation, and disposal costs. The significant additional costs associated with Hg removal in coal-fired utilities emphasize the need for process optimization.

The concentration and speciation of Hg found in flue gas from a coal-fired utility is quite different than that of a MWC. Typically, the total Hg concentration in coal systems is at least an order of magnitude lower than that found in a MWC flue gas. Differences in the flue gas composition [particularly the higher hydrogen chloride (HCl) concentration in a MWC] lead to different equilibrium speciation of Hg between elemental mercury ( $\text{Hg}^0$ ), mercuric chloride ( $\text{HgCl}_2$ ), and mercuric oxide ( $\text{HgO}$ ).<sup>9</sup> These differences lead to uncertainties in applying Hg removal experience in MWCs to Hg capture in coal-fired utilities. Therefore, in order to optimize the Hg removal process in coal-fired utilities, the effects of Hg concentration, Hg species, and other process conditions must be understood.

In this paper, we discuss our bench-scale results obtained for Hg control under MWC and coal-fired conditions. In the former case, capture of roughly 30 ppb of inlet Hg by different types of sorbents was studied at 100 and 140 °C. In the latter case, capture of lower concentrations (1-2 ppb Hg) of Hg by the same sorbents was studied. Capture of different species of Hg ( $\text{Hg}^0$  and  $\text{HgCl}_2$ ) was studied in both the MWC and the coal-fired situations. Finally, the understanding of  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture obtained from our bench-scale efforts is extended to interpret the pilot-scale studies of UNDEERC.

## **SORBENTS**

Activated carbons PC-100 and FGD (both manufactured by American Norit Company, Inc.) were the sorbents used in this study to test capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$ . The precursors for PC-100 and FGD are bituminous coal and lignite, respectively. These activated carbons have

been used in field studies<sup>10</sup>. The significant differences in their physical characteristics are their surface areas ( approximately 1,000 m<sup>2</sup>/g for PC-100 versus approximately 500 m<sup>2</sup>/g for FGD) and particle diameters (17.55 μm for PC-100 versus 6.8 μm for FGD). The details of their pore size distributions are given in an earlier study.<sup>11</sup>

## **EXPERIMENTAL PROCEDURES**

A fixed-bed arrangement was used in all the sorption tests for both Hg<sup>0</sup> and HgCl<sub>2</sub>. There were, however, minor differences in the operational procedures and analysis in the sorption tests.

### Hg<sup>0</sup> sorption (MWC simulation)

Figure 1 is the schematic of the bench-scale apparatus used to study capture of Hg<sup>0</sup> by PC-100 and FGD. Approximately 100 mg of either PC-100 or FGD was placed in a glass reactor (inside the furnace) and heated to the desired reaction temperature of 100 or 140 °C. Pure nitrogen (N<sub>2</sub>) carried the Hg<sup>0</sup> vapors through the By-Pass where the inlet Hg<sup>0</sup> concentration was measured by an on-line detector (Ametek, model 400). The effect of flue gas constituents, such as HCl, sulfur dioxide (SO<sub>2</sub>), and water (H<sub>2</sub>O), on the capture of Hg species should also be assessed; however, this work was limited in scope to the effect of Hg concentration and species in an inert atmosphere. Upon establishing a baseline of 30 ppb, the N<sub>2</sub>/Hg<sup>0</sup> stream was switched to flow through the reactor. The percentage Hg<sup>0</sup> captured was obtained by recording the drop in Hg<sup>0</sup> concentration measured by the on-line analyzer.

### Hg<sup>0</sup> sorption (Coal-fired simulation)

The significantly lower concentrations of Hg<sup>0</sup> in the coal-fired simulation (2-3 ppb) were near the detection limit of the on-line Hg<sup>0</sup> analyzer (Figure 1). Therefore, the Hg<sup>0</sup> analyzer was used to provide only an estimate of the Hg<sup>0</sup> concentration in the gas stream. Since accurate on-line analysis of Hg<sup>0</sup> in the gas stream was not possible, the sorbents were removed and analyzed for total Hg by x-ray fluorescence (XRF). Therefore, batch experiments were performed (different exposure times of sorbent to Hg<sup>0</sup>).

Typically 100 mg of activated carbon was placed (stage 1) in the reactor (see Figure 1) followed by two 100 mg plugs of PC-100 which served as breakthrough traps (stages 2 and 3). Similar to testing in the MWC simulation, the N<sub>2</sub>/Hg<sup>0</sup> stream is switched through the reactor after establishing a baseline of roughly 1 ppb. At the end of a fixed duration (8, 12, or 24 h), the N<sub>2</sub>/Hg<sup>0</sup>

stream is diverted away from the reactor, and the three stages are analyzed separately for total Hg content using XRF.

The percentage Hg<sup>0</sup> capture by PC-100 or FGD after exposure to Hg<sup>0</sup> for time t,  $\emptyset_t$  was calculated as:

$$\emptyset_t = [\beta_1/(\beta_1 + \beta_2 + \beta_3)]*100 \quad (1)$$

where  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$  are the total Hg measured (ppmw using XRF) in each of the three sequential reactor stages. In all of our experiments, the fraction of total Hg capture in stage 3,  $\beta_3/(\beta_1 + \beta_2 + \beta_3)$ , was less than 0.1, indicating little, if any, Hg<sup>0</sup> breakthrough.

#### HgCl<sub>2</sub> sorption (MWC and Coal-fired situation)

The schematic for studying HgCl<sub>2</sub> capture shown in Figure 2 is similar to that used for studying Hg<sup>0</sup> capture. However, in the present study, there is no on-line analyzer for HgCl<sub>2</sub>. Therefore, the procedure for studying HgCl<sub>2</sub> sorption is identical to the coal-fired Hg<sup>0</sup> simulation. The fraction of HgCl<sub>2</sub> captured by FGD or PC-100 is obtained as described earlier [from equation (1)].

The methodology and accuracy of the XRF technique used to measure total Hg in FGD and PC-100 have been given earlier.<sup>9,12</sup>

## **RESULTS**

### MWC simulation

Figure 3 shows the instantaneous capture of HgCl<sub>2</sub> [30 ppb in N<sub>2</sub> (MWC simulation)] by 100 mg of activated carbons FGD and PC-100 at two temperatures -- 100 and 140 °C. Both sorbents show relatively high capture (> 80 percent) of incoming HgCl<sub>2</sub> at 100 °C. Even up to 5 h of reaction time, PC-100 captures more than 80 percent of the incoming HgCl<sub>2</sub> at 100 °C, and FGD approximately 85 percent. Higher temperatures reduce the percentage capture of incoming HgCl<sub>2</sub> for both the sorbents, although the effect of temperature on HgCl<sub>2</sub> capture by FGD is more pronounced.

The capture of 30 ppb of Hg<sup>0</sup> (MWC simulation) by 100 mg of FGD and PC-100 at the two temperatures -- 100 and 140 °C -- is shown in Figure 4. PC-100 captures nearly all of the incoming Hg<sup>0</sup> (at both temperatures) in the initial time period (less than 2 h of exposure to the Hg<sup>0</sup>/N<sub>2</sub> stream). FGD captures far lower percentages of incoming Hg<sup>0</sup> at both temperatures when

compared to PC-100. Similar to the results seen in Figure 3, increasing the temperature causes a reduction in the capture of  $\text{Hg}^0$  by FGD, but has very little effect on the capture of  $\text{Hg}^0$  by PC-100.

Depending on the manufacturing process [activation with nitrous oxide ( $\text{N}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), or  $\text{ZnCl}_2\text{-NH}_4\text{Cl-CO}_2$ ; or heat-treated at  $900\text{ }^\circ\text{C}$ ], activated carbon acquires properties of a solid base.<sup>13</sup> Reactions of gaseous oxygen ( $\text{O}_2$ ) with the surface of active carbon at temperatures below  $100\text{ }^\circ\text{C}$  produce  $\text{O}_2$  complexes which, on hydration, can form hydroxyl or other basic groups.<sup>14</sup> The large internal surface areas of PC-100 and FGD may provide sufficient basic active sites to capture the acidic  $\text{HgCl}_2$ .

From Figures 3 and 4, higher percentages of incoming  $\text{HgCl}_2$  compared to incoming  $\text{Hg}^0$  are captured by FGD and PC-100 at both temperatures. In a previous investigation,<sup>9</sup> we showed the likelihood of different active sites for the capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$  in activated carbons. Assuming similar access to sorption sites for  $\text{Hg}^0$  and  $\text{HgCl}_2$  and based on our discussion above, it appears that the sites for  $\text{Hg}^0$  capture are far fewer than those for  $\text{HgCl}_2$  capture or the sorption of  $\text{Hg}^0$  requires a higher activation energy.

#### Coal-fired simulation

Figure 5 shows capture of  $\text{HgCl}_2$  (approximately 1 ppb  $\text{HgCl}_2$  in  $\text{N}_2$ ) by 100 mg of FGD and PC-100 at 100 and  $140\text{ }^\circ\text{C}$ . High amounts ( $> 80$  percent) of incoming  $\text{HgCl}_2$  are captured by PC-100 at both temperatures. FGD captures lower amounts at both temperatures when compared to PC-100. Increasing the temperature has very little effect on the capture of  $\text{HgCl}_2$  by PC-100; whereas, it causes a decrease in the capture of  $\text{HgCl}_2$  by FGD.

In the MWC simulation (see Figure 3), PC-100 shows a high capture ( $> 90$  percent) of incoming  $\text{HgCl}_2$  at both temperatures for initial time periods (less than 2 h), but shows a steady decline in the capture percentage with increasing exposure time. On the other hand in the coal-fired simulation (see Figure 5), such a decline with exposure time is not evident for PC-100. This may be on account of the faster rate of depletion of basic active sites for  $\text{HgCl}_2$  capture in the MWC simulation.

The capture of low concentration  $\text{Hg}^0$  (approximately 1 ppb in  $\text{N}_2$ ) by 100 mg of PC-100 and FGD at 100 and  $140\text{ }^\circ\text{C}$  is shown in Figure 6. Here too, PC-100 captures a higher fraction of

incoming  $\text{Hg}^0$  than FGD at both temperatures. Temperature is seen to have a marginal effect on the capture of low concentration  $\text{Hg}^0$  by PC-100, similar to the other cases discussed before.

From Figures 5 and 6, it is clear that PC-100 captures a higher fraction of incoming  $\text{HgCl}_2$  than  $\text{Hg}^0$  at both temperatures. This is similar to the MWC simulation (see Figures 3 and 4). On the other hand, FGD is seen to capture similar levels of  $\text{HgCl}_2$  and  $\text{Hg}^0$  for the coal-fired simulation (see Figures 5 and 6), unlike the MWC simulation (Figures 3 and 4).

## DISCUSSION

Some of the results obtained in our study are summarized in Tables 1 and 2. The results shown in Tables 1 and 2 are for percent Hg capture by 100 mg of sorbent (PC-100 and FGD, respectively) exposed to a flow of Hg ( $\text{Hg}^0$  or  $\text{HgCl}_2$ ) in  $300 \text{ cm}^3/\text{min N}_2$  for 6 h.

A few of the main conclusions that can be drawn from Tables 1 and 2 are:

- i) PC-100 captures more  $\text{Hg}^0$  than FGD at both temperatures and concentrations (i.e., MWC and coal-fired simulations) during 6 h of exposure.
- ii) A larger percentage of incoming  $\text{Hg}^0$  is captured in a coal-fired situation by both activated carbons at both temperatures.
- iii) Lower percentages of  $\text{HgCl}_2$  are captured in a coal-fired simulation (compared to capture under a MWC simulation) by both activated carbons at both temperatures.
- iv) In the MWC simulation  $\text{HgCl}_2$  is removed more easily than  $\text{Hg}^0$ . In the lower Hg concentration coal simulations, the reverse is true: equal or greater amounts of  $\text{Hg}^0$  than  $\text{HgCl}_2$  were removed.

In a past study,<sup>9</sup> the capture of roughly 30 ppb  $\text{Hg}^0$  or 30 ppb  $\text{HgCl}_2$  by fresh PC-100 was compared with PC-100 exposed to heat ( $140 \text{ }^\circ\text{C}$ ). This study showed that the capture of  $\text{Hg}^0$  by heat-treated PC-100 was roughly 50 percent lower than that captured by fresh (or untreated) PC-100. Since heat treatment causes loss of internal pore structure and surface area, these experiments suggest that  $\text{Hg}^0$  capture is limited by capture on surface-bound active sites. For  $\text{HgCl}_2$ , there was no difference in the capture, suggesting that capture is not mediated by active sites. Since PC-100 has roughly twice the specific surface area of FGD and likely twice the number of active sites, it follows that PC-100 will be more effective at  $\text{Hg}^0$  capture than FGD, as per conclusion i).



The coal-fired simulation (with 1/30th of the  $\text{Hg}^0$  concentration of the MWC simulation but the same amount of activated carbon) has an activated carbon active site/ $\text{Hg}^0$  ratio 30 times higher than that of the MWC simulation. Since  $\text{Hg}^0$  capture is limited by the availability of active sites this should result in a significantly higher capture of  $\text{Hg}^0$  in the coal-fired simulation. Tables 1 and 2 show higher capture percentages at all temperatures, but not as high as expected if reaction is limited by the number of available sites. This suggests that capture of  $\text{Hg}^0$  in the coal-fired simulation may be limited by an additional rate limiting step other than site availability.

From Tables 1 and 2, both PC-100 and FGD capture similar amounts of  $\text{HgCl}_2$  in the coal-fired simulation despite large differences in their surface areas and, likely, active site population. This suggests that there must be sufficient active sites for  $\text{HgCl}_2$  capture on both PC-100 and FGD such that site availability does not limit sorption. These sites are likely basic in nature; previous work<sup>9</sup> has shown that activated carbons and lime-based sorbents both have high capture of acidic  $\text{HgCl}_2$  despite large differences in surface area. These abundant basic sites are most likely functional groups including oxygen as the proton acceptor.

With the number of active sites not limiting capture, a possible controlling mechanism for  $\text{HgCl}_2$  capture may be mass transport of  $\text{HgCl}_2$ . This mechanism involves transport of  $\text{HgCl}_2$  from the flowing bulk fluid to the surface of the carbon particle, and from the surface to the active sites via diffusion.

At the ultra-low Hg concentrations tested in the coal-fired simulation, the probability of Hg in a flowing stream contacting a stationary carbon particle increases with Hg concentration. For instance, consider two situations where the concentration of Hg in the gas phase are 2 and 4 molecules per unit area. Further, assume that the probability of a Hg molecule colliding with the carbon particles in that unit area is 0.1. Our calculations show that the probability of at least one molecule colliding with a carbon particle is 0.19 and 0.344, for the lower and higher concentrations, respectively. Increasing the number of molecules to six per unit area increases the probability of at least one molecule colliding with a carbon particle to 0.47. That is, as the concentration of the Hg species increases in the gas stream, the probability of collision increases asymptotically. Since the sites available for  $\text{HgCl}_2$  capture are abundant and assuming that intraparticle diffusion resistance is linear with concentration, *a likely controlling mechanism for*

*HgCl<sub>2</sub> capture is the rate of gas/solid contact.* Conclusion iii) of our study, which states that less HgCl<sub>2</sub> is captured at the lower HgCl<sub>2</sub> concentration, supports this argument.

## **COMPARISON WITH FIELD RESULTS**

The field studies at the University of North Dakota<sup>10</sup> include capture of Hg<sup>0</sup> and HgCl<sub>2</sub> by lignite activated carbon (lignite AC), FGD, an iodated activated carbon (iodated AC), and PC-100. Here, the particle size of FGD and iodated AC are approximately the same. Three types of coal were fired in three separate cases which led to different Hg speciation in the flue gas. Table 3 summarizes the Hg speciation results of this study.<sup>10</sup> The following discussion highlights the three coal cases, extends our findings to these field results, and compares our capture results for PC-100 and FGD with theirs.

### **Absaloka Case**

Miller et al. (Reference 10) found that FGD at 3000:1 carbon:Hg ratio (by weight) performed similarly as iodated AC at a weight ratio of 1200:1 (carbon:Hg). Absaloka coal flue gas has more Hg<sup>0</sup> than Hg<sup>++</sup> (see Table 3). Hg<sup>++</sup> represents the oxidized form of Hg and, based on our thermodynamic calculations,<sup>9</sup> HgCl<sub>2</sub> is the most likely form. As per our conclusions (from bench-data), iodated AC, which has special sites for Hg<sup>0</sup> capture, should perform better than FGD at similar carbon:Hg ratios and perhaps perform equally as well as FGD at the lower carbon:Hg ratio. Their speciation data also showed that Hg<sup>0</sup> was removed far better by iodated AC than FGD at the lower carbon:Hg ratios, in agreement with our findings.

### **Comanche Case**

The results<sup>10</sup> for the Comanche case show higher capture of total Hg at 3000:1 FGD:Hg ratio than 1200:1 iodated AC:Hg ratio. Here most of the Hg is oxidized and therefore, according to our bench-scale findings, capture should be limited by collision of Hg<sup>++</sup> with carbon. At the lower ratio for iodated AC, the probability of collision decreases and hence the lower capture seen. Also, iodated AC is seen to capture a higher fraction of Hg<sup>0</sup> than FGD, confirming the hypothesis of sorption kinetics limiting the capture of Hg<sup>0</sup>.

### **Blacksville Case**

At 121 °C, FGD at a 3000:1 carbon:Hg ratio captures nearly 90 percent of total Hg.<sup>10</sup> At the same temperature, lignite AC at 1200:1 ratio captures less than 80 percent of total Hg.<sup>10</sup>

Blacksville coal-fired flue gas has more  $\text{Hg}^{++}$  than  $\text{Hg}^0$  (see Table 3). The larger amounts (or number) of FGD particles (due to similar particle sizes and assuming similar densities) would increase the probability of collision with the  $\text{Hg}^{++}$  molecules leading to higher capture. The results of Miller et al. (Reference 10) also show that, even at the lower carbon:Hg weight ratio, iodated AC captures a higher fraction of  $\text{Hg}^0$  than FGD. Also, FGD captures a higher fraction of incoming  $\text{Hg}^{++}$ , in agreement with our conclusions.

#### PC-100 versus FGD

Field data<sup>10</sup> show that, at an identical carbon:Hg weight ratio (3000:1), FGD captures a greater percentage of  $\text{Hg}^{++}$  than PC-100 and PC-100 captures a higher fraction of  $\text{Hg}^0$  than FGD. At equivalent Hg concentrations, the total mass feed rate of carbon is the same and the number of FGD particles is higher than PC-100 due to FGD's smaller particle diameter (about 5  $\mu\text{m}$  versus 20  $\mu\text{m}$  for PC-100). The number of FGD to PC-100 particles in the field study is approximately equivalent to the inverse of their volumetric ratio, or 64:1 (assuming similar densities for the two carbons). The larger number of FGD particles increases the probability of collision with  $\text{Hg}^{++}$  and offers an explanation for the higher  $\text{Hg}^{++}$  capture observed by Miller et al. (Reference 10).

Since PC-100 has a larger surface area than FGD (approximately 1000 and 500  $\text{m}^2/\text{g}$ , respectively) it has more active sites to adsorb  $\text{Hg}^0$ . Despite the larger number of FGD particles, PC-100 performs better for  $\text{Hg}^0$  capture,<sup>10</sup> confirming our theory of sorption limitation for  $\text{Hg}^0$ .

These similarities between our bench-scale results and field data<sup>10</sup> lend support to use of bench-scale methods as a means of predicting full-scale performance. The effect of varying flue gas constituents on Hg speciation and sorbent performance may further enhance the predictive capability of bench-scale simulations.

#### **SUMMARY AND CONCLUDING REMARKS**

Bench-scale tests were performed in this study to assess the capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$  by two types of activated carbons, PC-100 and FGD. The test conditions included variation of Hg ( $\text{Hg}^0$  and  $\text{HgCl}_2$ ) concentration and reaction temperature. The higher Hg concentration corresponded to conditions in a MWC and the lower Hg concentration to conditions prevalent in a coal-fired flue gas.  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture by the two activated carbons was studied at 100 and

140 °C.

Among our main findings were:

- i) PC-100 captures more  $\text{Hg}^0$  than FGD at both temperatures and concentrations (i.e., MWC and coal-fired simulations).
- ii) A larger percentage of incoming  $\text{Hg}^0$  is captured in a coal-fired simulation by both activated carbons at both temperatures.
- iii) Lower fractions of  $\text{HgCl}_2$  are captured in a coal-fired simulation (compared to capture under MWC simulation) by both activated carbons at both temperatures.
- iv) Unlike the MWC simulation, a higher fraction of incoming  $\text{HgCl}_2$  is not necessarily removed (compared to  $\text{Hg}^0$  capture) for the coal-fired simulation. That is,  $\text{HgCl}_2$  may not necessarily be removed with greater ease than  $\text{Hg}^0$  by activated carbon injection in a coal-fired simulation.

These results along with our past efforts<sup>9</sup> suggested two mechanisms for Hg capture:

- i) Capture of  $\text{Hg}^0$  by activated carbons is limited by sorption kinetics, and
- ii) Capture of  $\text{HgCl}_2$  by activated carbons is limited by collision with carbon particles.

The conclusions arrived at from this study were compared with and are in agreement with field data.<sup>10</sup> Control of Hg in coal-fired combustors is challenging due to the low concentrations of Hg species in the flue gas. Specifically, control of  $\text{Hg}^0$  is limited by reactivity of the sorbent (that is, type and number of active sites for  $\text{Hg}^0$  capture) and control of  $\text{HgCl}_2$  is limited by collision probability with the sorbent. A control strategy would therefore need accurate speciation of Hg in the flue gas. If  $\text{HgCl}_2$  is the dominant species, total Hg control may be achieved by injecting larger amounts of an inexpensive sorbent with ‘basic’ sites. On the other hand if  $\text{Hg}^0$  is the major Hg species, then the injected sorbent must have sufficiently active sorptive sites for  $\text{Hg}^0$  capture.

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Table 1. Hg capture (%) comparison by activated carbon PC-100 at 6 h exposure and two isothermal reaction temperatures (from results shown in Figures 3, 4, 5, and 6).

Hg Species	30 ppb (MWC simulation)		1 ppb (coal-fired simulation)	
	100 °C	140 °C	100 °C	140 °C
Hg <sup>0</sup>	67%	70%	85%	85%
HgCl <sub>2</sub>	90%	90%	50%	45%

Table 2. Hg capture (%) comparison by activated carbon FGD at 6 h exposure exposure and two isothermal reaction temperatures (from results shown in Figures 3, 4, 5, and 6).

Hg Species	30 ppb (MWC simulation)		1 ppb (coal-fired simulation)	
	100 °C	140 °C	100 °C	140 °C
Hg <sup>0</sup>	35%	20%	50%	30%
HgCl <sub>2</sub>	85%	55%	50%	25%

Table 3. Flue gas Hg speciation for the three types of coal used by Miller et al. (Reference 10). The sampling temperatures are about 121 °C.

Hg Species	Absaloka		Comanche		Blacksville	
	Conc. (ppb)	Fraction	Conc. (ppb)	Fraction	Conc. (ppb)	Fraction
Hg <sup>0</sup>	0.16	0.67	0.16	0.31	0.08	0.15
Hg <sup>++</sup>	0.08	0.33	0.36	0.69	0.44	0.85

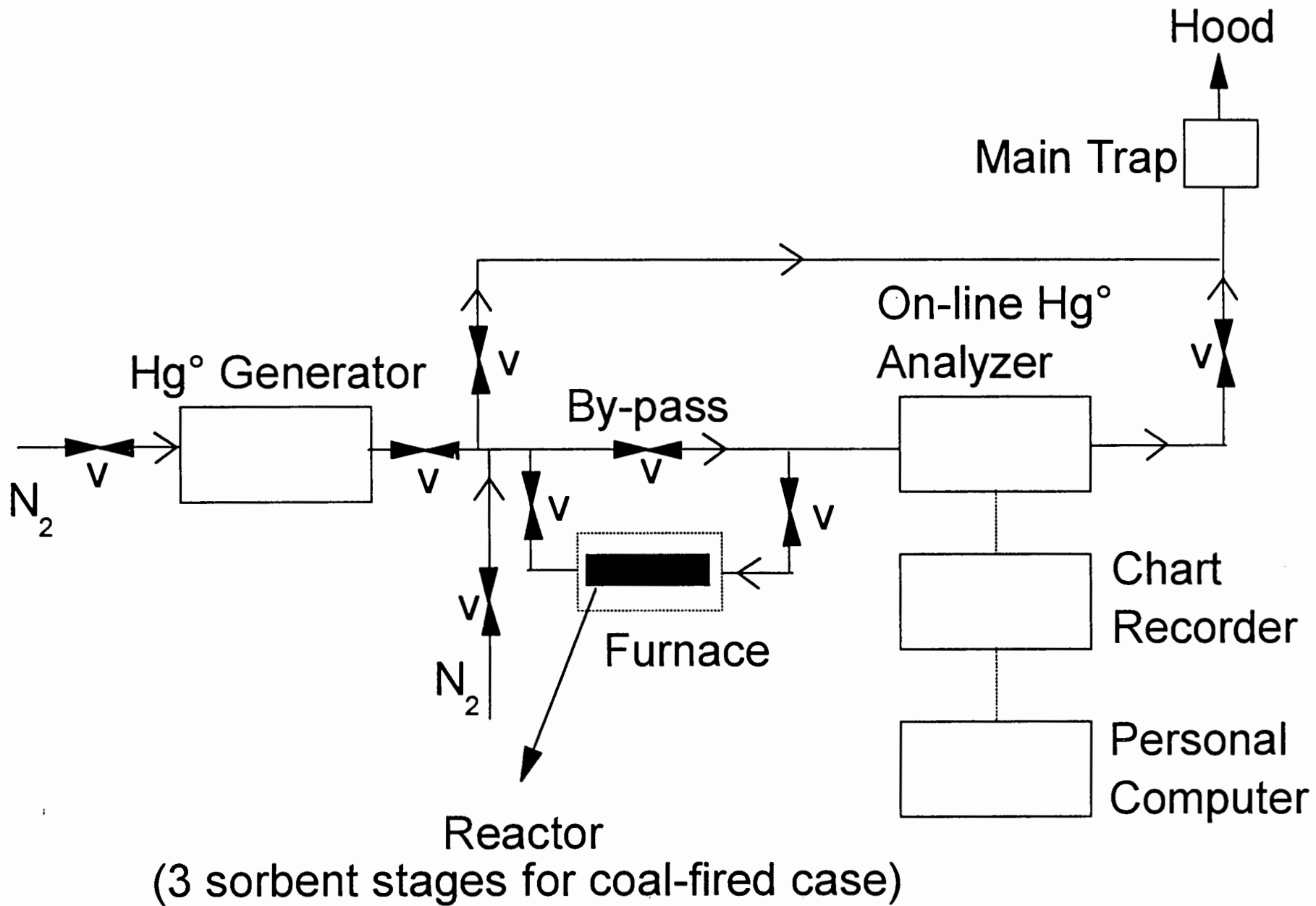


Figure 1. Schematic of bench-scale apparatus used to study  $\text{Hg}^\circ$  capture (v: valve).



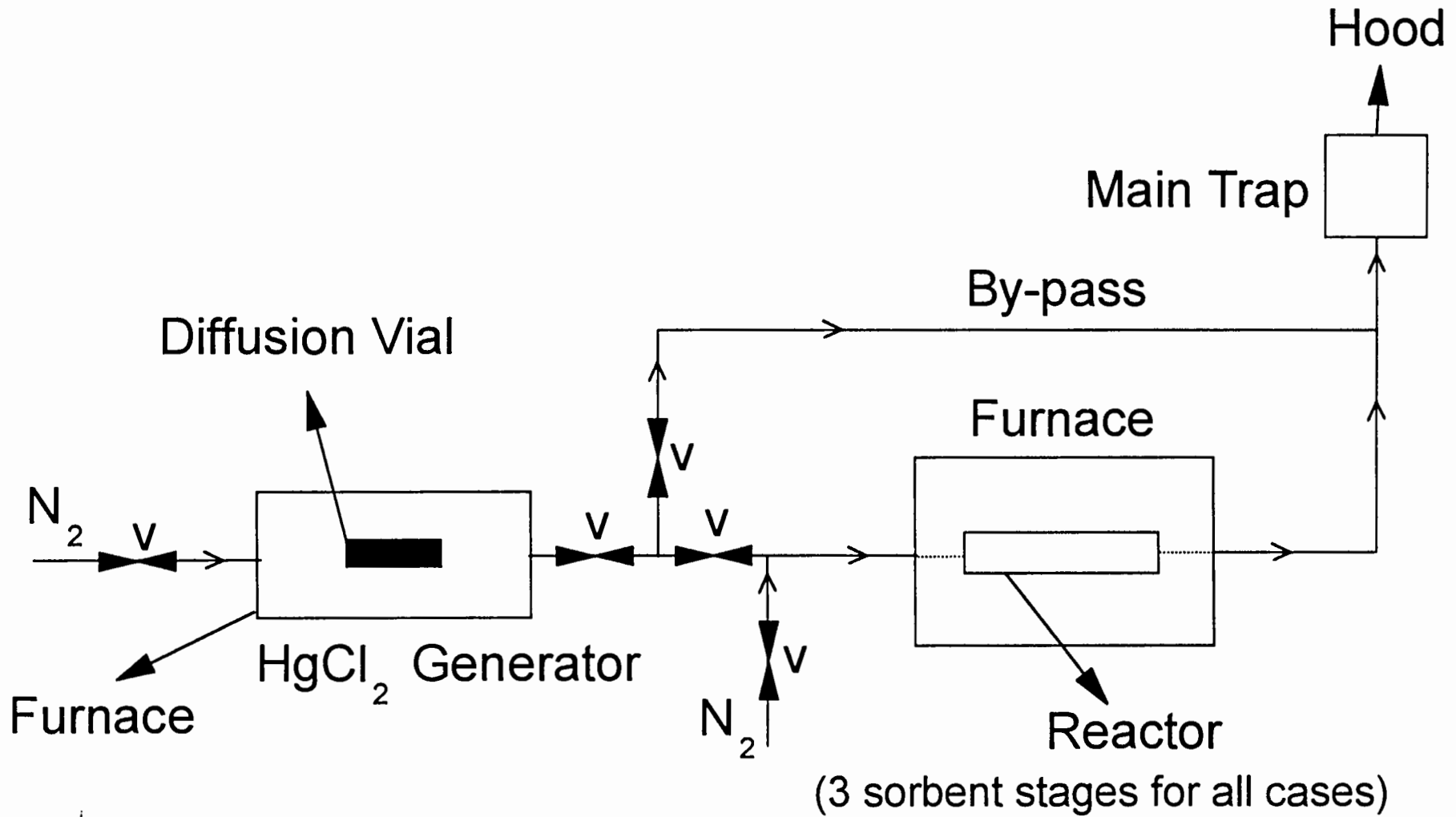


Figure 2. Schematic of bench-scale apparatus used to study  $\text{HgCl}_2$  capture (v: valve).

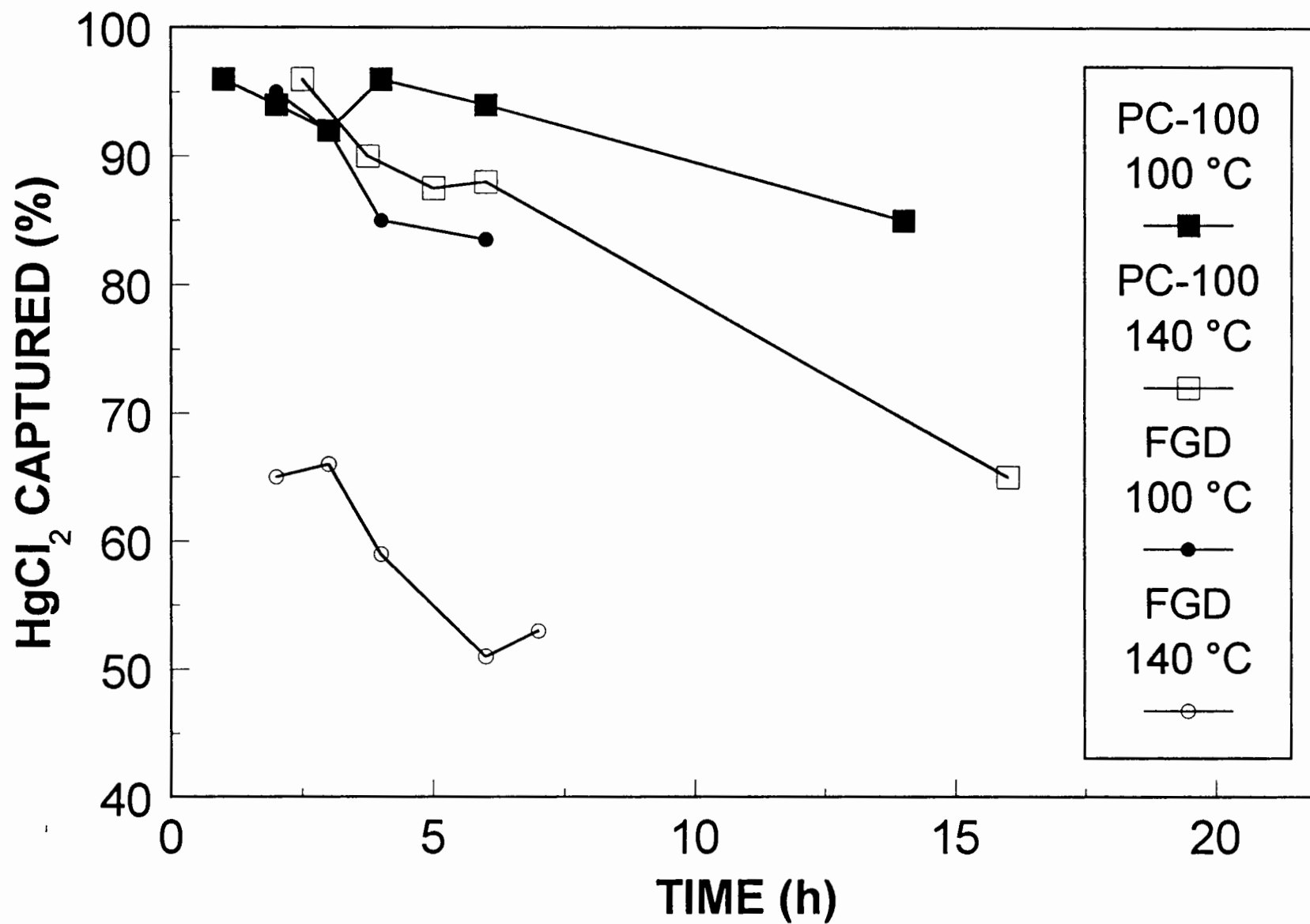


Figure 3. MWC case: Capture of HgCl<sub>2</sub> (30 ppb in N<sub>2</sub>) at 100 and 140 °C by 100 mg of FGD and PC-100

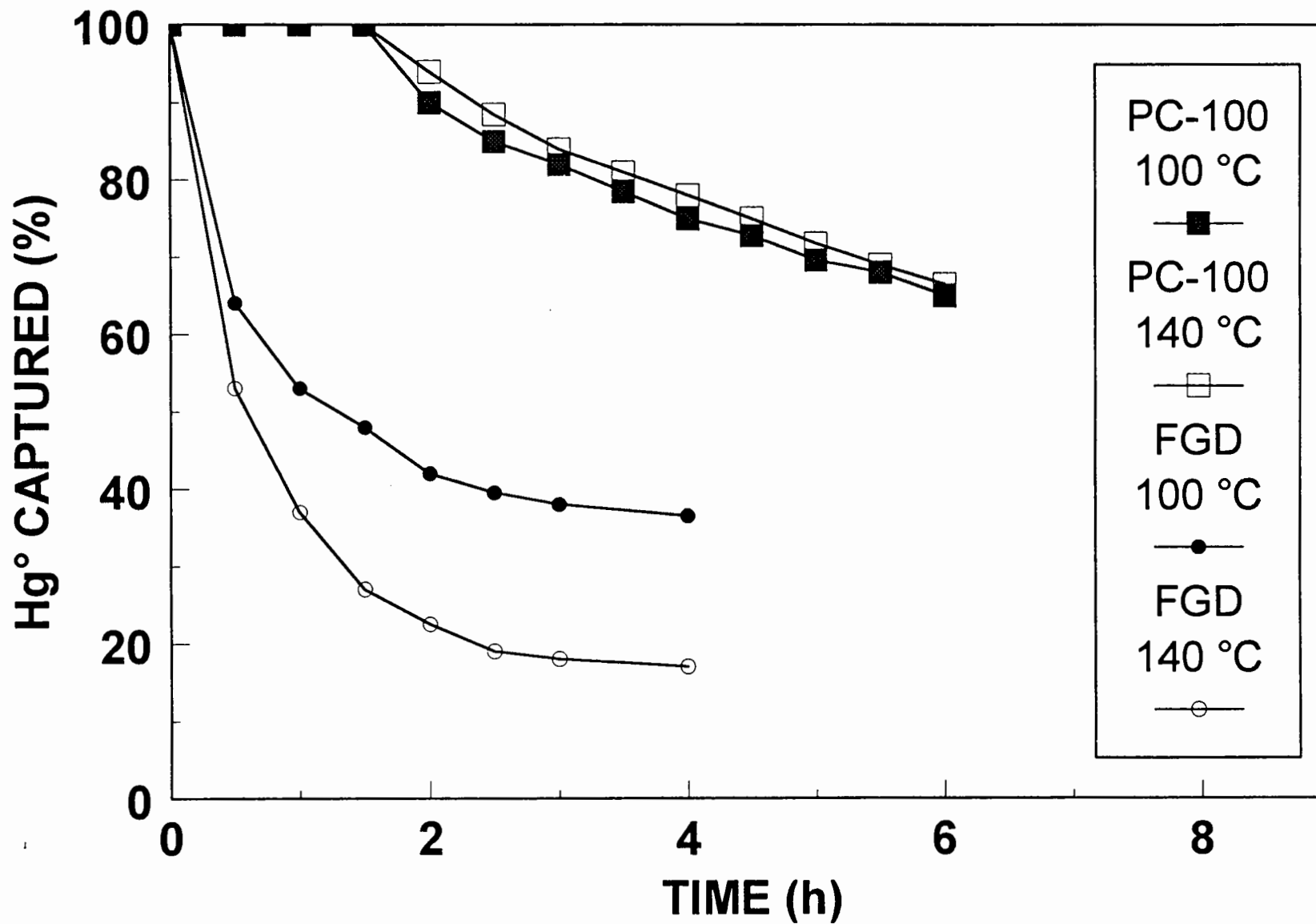


Figure 4. MWC case: Capture of Hg° (30 ppb in N<sub>2</sub>) at 100 and 140 °C by 100 mg of FGD and PC-100

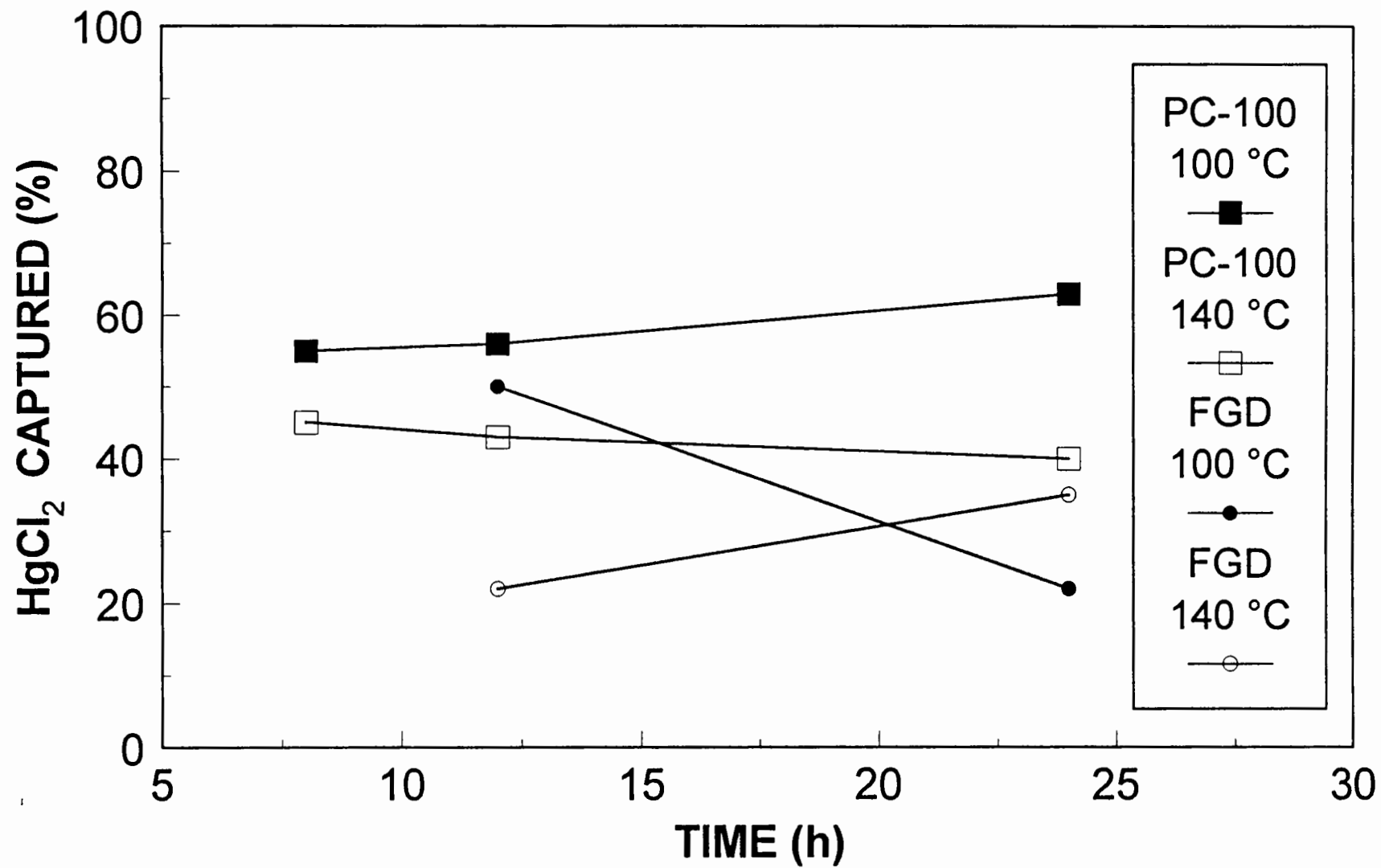


Figure 5. Coal-fired case: Capture of  $\text{HgCl}_2$  (1 ppb in  $\text{N}_2$ ) at 100 and 140 °C by 100 mg of FGD and PC-100

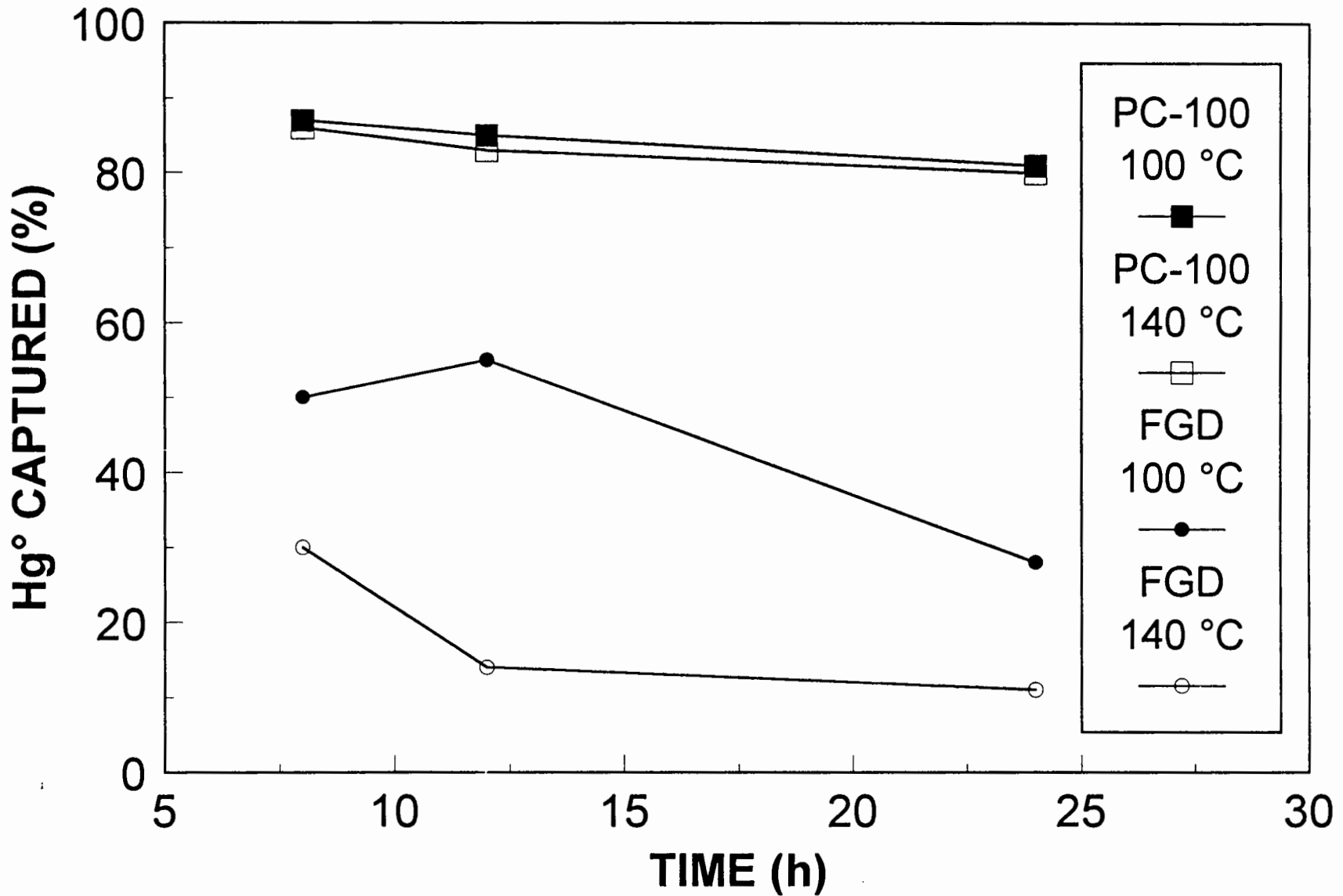


Figure 6. Coal-fired case: Capture of  $\text{Hg}^\circ$  (1 ppb in  $\text{N}_2$ ) at 100 and 140 °C by 100 mg of FGD and PC-100

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16. ABSTRACT <b>The paper gives results of a study of bench-scale experiments under conditions simulating municipal waste combustors (MWCs) and coal-fired utilities to study mercury (Hg) capture by dry sorbents. The effect of reaction temperature on the capture of different Hg species--Hg<sup>0</sup> and Hg(II)--by various types of dry sorbents was the focus of bench-scale tests. An attempt was also made in this study to compare the bench-scale results with results obtained from pilot studies and to explain disparities in fuel- and unit-specific performance. Our investigations showed that the reaction temperature and Hg species strongly affect Hg control. The results obtained in this study along with our past efforts suggested two mechanisms for Hg capture: (a) capture of Hg<sup>0</sup> by activated carbons is limited by sorption kinetics; and (b) capture of HgCl<sub>2</sub> by activated carbons is limited by collision with carbon particles. (NOTE: Control of Hg emissions from MWCs and coal-fired utilities has attracted attention due to current and potential regulations. Among several techniques evaluated for Hg control, dry sorbent injection--primarily injection of activated carbon--shows promise for consistently removing high levels of Hg from MWC or coal flue gas. However, the performance in terms of amount of Hg removed per amount of sorbent varies widely between MWC/coal-fired applications and from unit to unit.)</b>		
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Mercury	Stationary Sources	07B
Combustion	Municipal Waste Combustors	21B 14G
Wastes		
Utilities		21D
Coal		
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