

## COMBINED MERCURY AND SULFUR OXIDES CONTROL USING CALCIUM-BASED SORBENTS

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### Abstract

The capture of elemental mercury ( $\text{Hg}^0$ ) and mercuric chloride ( $\text{HgCl}_2$ ) by three types of calcium (Ca)-based sorbents was examined in this bench-scale study under conditions prevalent in coal-fired utilities. Ca-based sorbent performances were compared to that of an activated carbon. Mercury capture of about 40% (nearly half that of the activated carbon) was achieved by two of the Ca-based sorbents. The presence of sulfur dioxide ( $\text{SO}_2$ ) in the simulated coal combustion flue gas enhanced the capture of  $\text{Hg}^0$  from about 10 to 40%. Increasing the temperature in the range of 65-100°C also caused an increase in the  $\text{Hg}^0$  capture by the two Ca-based sorbents. Mercuric chloride ( $\text{HgCl}_2$ ) capture exhibited a totally different pattern. The presence of  $\text{SO}_2$  inhibited the  $\text{HgCl}_2$  capture by Ca-based sorbents from about 25 to less than 10%. Increasing the temperature in the studied range also caused a decrease in  $\text{HgCl}_2$  capture. Upon further pilot-scale confirmations, the results obtained in this bench-scale study can be used to design and manufacture more cost-effective mercury sorbents to replace conventional sorbents already in use in mercury control.

## 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 these compounds, mercury has drawn special attention due to its increased levels in the environment and the well documented food chain transport and bioaccumulation of this specie and its compounds such as methyl mercury.<sup>1,2</sup> An EPA report to Congress cites the largest emitters of mercury as coal-fired utilities, medical waste incinerators (MWIs), municipal waste combustors (MWCs), chlor-alkali plants, copper and lead smelters, and cement manufacturers.<sup>3</sup> These sources are estimated to account for over 90% of all anthropogenic mercury emissions. Utility boilers account for nearly 25% of the total anthropogenic emissions, of which more than 90% are attributed to coal-fired utility boilers.

Mercury, a trace constituent of coal<sup>4</sup>, is readily volatilized during coal combustion.<sup>5</sup> Mercury is the most volatile trace metal, and major portions of it can pass through existing particulate matter (PM) control devices.<sup>5</sup> A sorbent reacting with this metallic species can effectively convert the vapor to a sorbed liquid or solid phase, facilitating its removal with sorbent particles in a PM control device. Mercury control processes which use adsorption on dry sorbents do not pose the problem of the treatment and stabilization of a waste liquid stream and, therefore, seem very attractive for coal combustors.

Several methods of controlling mercury emissions are in either commercial use or development for MWCs and MWIs.<sup>6</sup> Dry sorbent injection (DSI) of activated carbon, followed by fabric filtration (FF) has shown consistently high (>90%) mercury removal in MWC applications. Spray drying (SD) followed by FF, and wet scrubbing (WS) have both been successfully applied for acid gas control, and have been found to remove substantial (60-90%) amounts of mercury in MWCs. However, all three technologies have been less successful in removing mercury from coal-fired flue gases.<sup>7</sup>

There are primarily three reasons suspected for the observed differences in mercury capture between

MWC and coal-fired cases: (a) the differences in the mercury components (species) present in the two flue gases, (b) mercury species concentrations, and (c) composition of the two flue gases. On account of the larger concentrations of hydrogen chloride (HCl) present in a MWC flue gas, mercury is thought to exist primarily as mercuric chloride ( $\text{HgCl}_2$ ).<sup>8</sup> Recent pilot plant studies on coal-fired flue gas indicate that for some Ohio coals, a considerable portion of mercury vapor may be  $\text{HgCl}_2$ . However, the same study indicated that elemental mercury ( $\text{Hg}^0$ ) vapor concentration may actually increase across a wet limestone scrubber, presumably due to the reduction of  $\text{HgCl}_2$  vapor entering the scrubber.<sup>9</sup> The lower concentration of HCl in a coal-fired flue gas is believed responsible for a portion of the mercury to exist as  $\text{Hg}^0$ .

Another difference in the two types of flue gases is their total mercury concentrations. The total mercury concentration in a MWC flue gas is typically several orders of magnitude higher than the mercury concentration in a coal-fired flue gas. The typical mercury concentration observed in coal combustion flue gas (2-3 ppb)<sup>10</sup> was simulated throughout this study. The third difference between MWC and coal-fired systems is the composition of the flue gases. Sulfur dioxide ( $\text{SO}_2$ ) is present at higher concentration in coal combustion flue gases and is believed to influence the capture of mercury by different sorbents and emission control devices. The effect of  $\text{SO}_2$  on mercury capture was investigated in this study.

Pilot-scale studies have shown that, to achieve high removals of mercury in coal-fired power plants, activated carbon to mercury (by weight) ratios of around 3000/1 were required.<sup>11,12</sup> At an activated carbon cost of \$1.125 /kg, the material cost would be approximately \$500,000 per year for a 500 MW power plant. Chang et al.<sup>11</sup> arrived at an annual cost of \$100,000 to \$1 million for mercury control in a 500 MW power plant. A recent study by Chang and Offen<sup>7</sup> estimates that removing 50% of the mercury emitted in flue gas by U.S. power plants could range from \$1 billion to \$10 billion per year. Therefore, bench-scale efforts to study process parameters and sorbent types for mercury control in coal-fired flue gas are needed to develop effective and economic mercury capture technology. In addition, improvement of mercury control using existing technologies for  $\text{SO}_2$  and fine PM control would appear to be prudent. Therefore this study focuses on improving the existing  $\text{SO}_2$

control sorbents for a potentially combined mercury and SO<sub>2</sub> control.

Bench-scale results from laboratories at the Air Pollution Prevention and Control Division (APPCD) of the U.S. Environmental Protection Agency (EPA) showed that Ca-based sorbents were effective in controlling HgCl<sub>2</sub> under MWC operating conditions (in the absence of SO<sub>2</sub>)<sup>13</sup>. It was found that calcium oxide (CaO) and calcium hydroxide [Ca(OH)<sub>2</sub>] were effective in capturing HgCl<sub>2</sub> at 100°C. At 140°C, however, the Ca-based sorbents were found to be less efficient in capturing HgCl<sub>2</sub>. Also, during the Hg<sup>0</sup> capture experiments, only activated carbons exhibited significant capture at both 100 and 140°C in the absence of SO<sub>2</sub>. Pilot-scale tests showed that injection of Ca-based sorbents into a furnace reduced total mercury emissions at the outlet of the furnace.<sup>14</sup> Stouffer et al. have shown that, in an air toxics control pilot plant, high system HgCl<sub>2</sub> removal can be achieved with the injection of hydrated lime as the sorbent.<sup>15</sup> At 93°C, removals of HgCl<sub>2</sub> from the gas were about 55 and 85% at Ca/Hg weight ratios of 5,000 and 100,000, respectively. The corresponding Hg<sup>0</sup> removals ranged only from 10 to 20%, even at Ca/Hg weight ratios as high as 300,000.

Considering the above observations, a potential method of cost reduction in controlling mercury emissions in coal-fired utilities (low mercury concentration) would be to utilize the cheaper Ca-based sorbents. This paper reports results of experiments to study Hg<sup>0</sup> and HgCl<sub>2</sub> capture by several Ca-based sorbents and their performance compared with a lignite-coal-based activated carbon (DARCO® FGD, Norit Americas Inc.). Hg<sup>0</sup> and HgCl<sub>2</sub> concentrations were roughly 2 to 3 ppb in a simulated flue gas in order to replicate conditions (as close as possible) prevalent in a coal-fired flue gas.<sup>10</sup> Among the Ca-based sorbents evaluated in this study were reagent grade hydrated lime (calcium hydroxide), a mixture of fly ash and hydrated lime (advanced silicate -- Advacate), and a modified Advacate. More details on the sorbents tested in this study are given in the next section. Capture of Hg<sup>0</sup> and HgCl<sub>2</sub> by these sorbents was studied as a function of system temperature and SO<sub>2</sub> present in the simulated flue gas.

## Sorbents

The capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$  by five types of sorbents was studied in this investigation. Of the five, the three Ca-based sorbents were hydrated lime, Advacate, and a modified Advacate.  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture by Clinch River Fly Ash (CRFA) and an activated carbon (FGD) was also measured for comparison. Preparations of Advacate and modified Advacate are discussed below.

### Preparation of Advacate and Modified Advacate

Advacate was prepared in a pressure hydrator at  $150^\circ\text{C}$  by mixing a 3/1 ratio (by weight) of CRFA to hydrated lime. The modified Advacate was prepared by addition of a chemical agent during this process. The entire reaction time in the pressure hydrator was 1 h. After preparation of the sorbents, they were placed in a vacuum oven at  $165^\circ\text{C}$  for 24 h before use. Several batches of Advacate and modified Advacate were prepared, and their physical characteristics were studied using nitrogen ( $\text{N}_2$ ) sorption. Very similar physical characteristics were obtained for different batches of each, indicating their reproducibility. The following subsection describes, in detail, the structural properties and chemical compositions of the studied sorbents.

### Structural Properties/Chemical Compositions of the Sorbents

Information about the internal pore structure (total and incremental volume and surface area) of the three Ca-based sorbents was determined by a Micromeritics ASAP 2600 using  $\text{N}_2$  adsorption/desorption with a Brunauer-Emmett-Teller (BET) method. BET analyses on the three Ca-based sorbents (hydrated lime, Advacate, and modified Advacate) obtained from  $\text{N}_2$  sorption are shown in Figure 1. Of the three, hydrated lime had the lowest internal pore volume and surface area. Advacate, containing only 25% of hydrated lime by weight, had a higher surface area than hydrated lime. Modified Advacate had the highest surface area among the three. A bimodal pore size distribution was seen for the three Ca-based sorbents with most of the pore diameters being

approximately 15 to 50 nm. The total pore volume of modified Advacate was over five times that for hydrated lime and three times the pore volume of Advacate. The internal pore structure of the studied activated carbon (FGD) is shown in Figure 2. Bimodal pore size distribution was not observed in the case of FGD. Unlike Ca-based sorbents, pores with diameters less than 5 nm were the significant contributors to the total pore area and volume in FGD, causing the average pore diameter in FGD to be considerably lower than that of Ca-based sorbents. Structural properties and chemical composition of the studied sorbents are summarized as:

**Hydrated lime:** The Hydrated lime used in this research was reagent grade (Sigma Inc.) containing 97.6%  $\text{Ca}(\text{OH})_2$  and 1.8% calcium carbonate ( $\text{CaCO}_3$ ). This material has a total surface area of  $13.0 \text{ m}^2/\text{g}$  and an average pore diameter of 33.4 nm.

**Clinch River Fly Ash (CRFA):** This material is a fly ash obtained from the Clinch River Virginia power plant. This power plant uses a local bituminous coal. The mineral content of this fly ash is: 5.2%  $\text{CaO}$ , 51.6%  $\text{SiO}_2$ , 24.7%  $\text{Al}_2\text{O}_3$ , 0.5%  $\text{Na}_2\text{O}$ , 1.8%  $\text{MgO}$ , 3.3%  $\text{K}_2\text{O}$ , 7.8%  $\text{Fe}_2\text{O}_3$ , and 1.4%  $\text{TiO}_2$ . CRFA has a total surface area of  $2.3 \text{ m}^2/\text{g}$  and an average pore diameter of 8.1 nm.

**Advacate:** A reaction product of a 3/1 mixture of CRFA and hydrated lime. As prepared for this study, it had a total surface area of  $30.9 \text{ m}^2/\text{g}$  and an average pore diameter of 21.2 nm.

**Modified Advacate:** Advacate prepared with an additional chemical agent. Modified Advacate for this study had a total surface area of  $91.4 \text{ m}^2/\text{g}$  and an average pore diameter of 22.2 nm.

**FGD:** A trademark for an activated carbon known as “DARCO® FGD” manufactured by Norit Americas Inc. FGD is a lignite-coal-based activated carbon manufactured specifically for the removal of heavy metals. It has a total surface area of  $575 \text{ m}^2/\text{g}$  and an average pore diameter of 3.2 nm. More information about physical characteristics and mercury capture performance of FGD can be found elsewhere.<sup>16</sup> Table 1 summarizes the physical properties of the studied sorbents.

## Experimental Apparatus and Procedures

Figure 3 is a schematic of the experimental apparatus used to study capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$ . Pure  $\text{HgCl}_2$  powder in a diffusion vial was the source of  $\text{HgCl}_2$  vapor, and pure  $\text{Hg}^0$  liquid in a permeation tube was the source of  $\text{Hg}^0$  vapor. The relative concentration of  $\text{HgCl}_2$  or  $\text{Hg}^0$  vapor in the gas

stream was varied by adjusting the water bath temperature. The generated  $\text{HgCl}_2$  or  $\text{Hg}^0$  vapor was carried into the main system by a nitrogen ( $\text{N}_2$ ) stream where it was mixed with water vapor ( $\text{H}_2\text{O}$ ), air, sulfur dioxide ( $\text{SO}_2$ ), and carbon dioxide ( $\text{CO}_2$ ) in the manifold. The composition of the simulated flue gas and the total system flow rate was kept constant throughout these studies as follows: 2-3 ppb  $\text{HgCl}_2$  or  $\text{Hg}^0$ , 5%  $\text{H}_2\text{O}$ , 7%  $\text{O}_2$ , 10%  $\text{CO}_2$ , 173 ppm  $\text{SO}_2$ , and balance of nitrogen, total system flow:  $300 \text{ cm}^3/\text{min}$

A 3-way valve placed before the manifold (Figure 3) diverted the  $\text{Hg}^0$  or  $\text{HgCl}_2$  in the  $\text{N}_2$  stream away from the manifold when desired. The first 3-way valve placed after the manifold was used to direct flow to or away from the fixed-bed reactor. The sorbent to be tested (approximately 0.1 g) was placed in the constant temperature reactor. A furnace kept at  $850^\circ\text{C}$  was added downstream of the reactor to convert any oxidized mercury vapor to  $\text{Hg}^0$ . According to thermodynamic predictions, the only Hg specie at this temperature is  $\text{Hg}^0$ .<sup>13</sup> The presence of the furnace enabled detection of non-adsorbed  $\text{HgCl}_2$  as  $\text{Hg}^0$  by the on-line ultraviolet (UV)  $\text{Hg}^0$  analyzer, thus providing actual, continuous  $\text{Hg}^0$  or  $\text{HgCl}_2$  capture data by the packed bed of sorbent. Prior to the mercury analyzer, an ice bath served as a water trap. Quality control experiments had previously indicated no loss of  $\text{Hg}^0$  or  $\text{SO}_2$  in the water trap.

It should be noted that the  $\text{Hg}^0$  research apparatus is made of Teflon™. The  $\text{HgCl}_2$  apparatus is made of quartz and avoids the use of Teflon™, which is known to adsorb  $\text{HgCl}_2$ .

The UV  $\text{Hg}^0$  analyzer responded to  $\text{SO}_2$  concentrations as well as to  $\text{Hg}^0$ . For instance, a gas stream consisting of 173 ppm  $\text{SO}_2$  and 3 ppb  $\text{Hg}^0$  produced a  $\text{SO}_2/\text{Hg}^0$  signal ratio of 8/18. Contributions from  $\text{SO}_2$  were accounted for by placing a  $\text{SO}_2$  analyzer (UV) on-line downstream of the  $\text{Hg}^0$  analyzer. The  $\text{SO}_2$  analyzer was incapable of responding to mercury in the concentration range used in this study. By subtracting the  $\text{SO}_2$  signal measured by the  $\text{SO}_2$  analyzer from the total response of the mercury analyzer, the mercury concentration was obtained.

In addition to sorbents, other parameters studied in this investigation were packed bed temperature

and the presence of SO<sub>2</sub>. The two studied temperatures were 100 and 65°C. These temperatures are typically observed in the air pollution control system of coal-fired utility boilers. The effect of SO<sub>2</sub> was studied by performing two sets of packed bed experiments -- in the absence of SO<sub>2</sub> and in the presence of 173 ppm SO<sub>2</sub>. This relatively low level of SO<sub>2</sub> was selected to minimize UV interference with Hg<sup>0</sup> detection, and to be consistent with the previous activated carbon sorption experiments. For the same reasons, UV monitor interference and consistency with activated carbon data, the experiments reported here have been limited to simulated flue gas with no nitrogen oxides, HCl, and only 5% moisture. The effects of temperature and SO<sub>2</sub> on Hg<sup>0</sup> and HgCl<sub>2</sub> capture by different sorbents were studied independently. In each test, the packed bed was exposed to the simulated flue gas for 30 minutes during which the exit concentration of mercury was continuously monitored. The percent removal of Hg<sup>0</sup> or HgCl<sub>2</sub> was obtained according to: percent removal = 100 (mercury<sub>in</sub> - mercury<sub>out</sub>)/mercury<sub>in</sub>. It should be noted that each set of parameters was run in duplicate. If the duplicates did not meet the precision goal (the data quality indicator) of ±10%, the parameters were tested a third time.

## Results and Discussions

### Capture of Elemental Mercury

Figure 4 shows the effect of SO<sub>2</sub> on Hg<sup>0</sup> capture performance of the Ca-based sorbents as compared to the activated carbon (FGD) and CRFA at 100°C. Removals presented in Figure 4 (and Figure 7) are obtained by averaging the removal data acquired during the exposure period (30 minutes). Of the five, FGD showed the highest capture of Hg<sup>0</sup> during the 30 minutes of exposure (constant during this period). Both CRFA and hydrated lime exhibited insignificant capture of Hg<sup>0</sup> (approximately 5%). Among the Ca-based sorbents, it is seen that Hg<sup>0</sup> capture increases as the total surface area and cumulative pore volume increases (Figure 1 and Table 1). The presence of SO<sub>2</sub> significantly increased the capture of Ca-based sorbents, especially Advacate and modified Advacate. The insignificant Hg<sup>0</sup> capture by the Ca-based sorbents in the absence of SO<sub>2</sub> indicated the lack of any interaction (physical or chemical) between the Hg<sup>0</sup> and the Ca-based sorbents. The enhancement effect of SO<sub>2</sub> at 100°C



may indicate that the reaction of  $\text{SO}_2$  and sorbents created active sulfur (S) sites for the adsorption of  $\text{Hg}^0$ , possibly through formation of Hg-S bonds (chemisorption). Conversely, the lack of significant improvement in  $\text{Hg}^0$  capture for hydrated lime with  $\text{SO}_2$  present (Figure 4) indicates the need for a fine pore structure as well as  $\text{SO}_2$ . If indeed, the major  $\text{Hg}^0$  capture mechanism is chemisorption by  $\text{SO}_2$ -generated active sites, then decreasing the system temperature should decrease the overall rate of “active site generation and chemisorption” leading to a decrease in  $\text{Hg}^0$  capture.

The effect of temperature (65 vs 100°C) on  $\text{Hg}^0$  capture by Advacate and modified Advacate in the presence of  $\text{SO}_2$  is illustrated in Figure 5. This figure shows  $\text{Hg}^0$  capture throughout the 30 minutes of exposure. The observed higher captures at higher temperature support the chemisorption theory of  $\text{Hg}^0$  capture by the Ca-based sorbents in the presence of  $\text{SO}_2$ .

The capture of  $\text{SO}_2$  by the five sorbents during the  $\text{Hg}^0$  tests was also monitored at 100°C (Figure 6). All three Ca-based sorbents showed higher captures of  $\text{SO}_2$  than activated carbon (FGD), which was expected because of their alkaline nature. After approximately 10 minutes of exposure to the simulated flue gas, the  $\text{SO}_2$  reaction rate (change of percent removal with time) showed diminishing removal with increasing time. One explanation is that the reaction of  $\text{SO}_2$  with Ca-based sorbents may lead to pore mouth closure, thus blocking the access of  $\text{SO}_2$  to the interior of the Ca-based sorbents. This would occur within the first 10 minutes of exposure of sorbent to flue gas. One may speculate that since all three Ca-based sorbents had the same average pore diameter (20-30 nm), they should exhibit the same monotonically decreasing  $\text{SO}_2$  capture pattern.

In summary,  $\text{Hg}^0$  can be captured by previously reacted mixtures of fly ash and hydrated lime (Advacate and modified Advacate) when  $\text{SO}_2$  is present in the flue gas. Based on this observation, one may conclude that, in terms of  $\text{Hg}^0$  control, the optimum region for injection of Ca-based sorbents is upstream of  $\text{SO}_2$  control systems in which a higher concentration of  $\text{SO}_2$  is present, and flue gas temperatures are higher. In this way, both  $\text{SO}_2$  and  $\text{Hg}^0$  emissions may be controlled for approximately the cost of  $\text{SO}_2$  control by sorbent injection alone. Modifying sorbents to increase the total surface area and fine pore structure increases  $\text{Hg}^0$  uptake in the presence of  $\text{SO}_2$  for the sorbents

studied.

### Capture of Mercuric Chloride

Figure 7 depicts the effect of  $\text{SO}_2$  on  $\text{HgCl}_2$  capture performance of the three Ca-based sorbents as compared to the activated carbon (FGD) and Clinch River Fly Ash (CRFA) at  $100^\circ\text{C}$ . Similar to  $\text{Hg}^0$ , FGD captured the highest fraction of incoming  $\text{HgCl}_2$  (constant removal during the exposure period), with the three Ca-based sorbents and CRFA showing from 10 to 20%  $\text{HgCl}_2$  capture in the absence of  $\text{SO}_2$ . Unlike the  $\text{Hg}^0$  case, the presence of  $\text{SO}_2$  inhibited the  $\text{HgCl}_2$  capture by Advacate and modified Advacate, indicating that perhaps  $\text{HgCl}_2$  is not attracted to the sites preferred by  $\text{Hg}^0$ , and has affinity for  $\text{SO}_2$  capture sites. The  $\text{SO}_2$  inhibition effect may also confirm the earlier conclusion that the presence of  $\text{SO}_2$  caused a blockage of pores in Advacate and modified Advacate, and therefore limited the access of  $\text{HgCl}_2$  to the interior structure of the sorbents. One may also attribute the  $\text{SO}_2$  inhibition effect to the competition of  $\text{SO}_2$  with  $\text{HgCl}_2$  (both acid gases) for the alkaline sites located inside the pores or on the external surface of the sorbent.

Figure 8 illustrates the effect of temperature on  $\text{HgCl}_2$  capture by Advacate and modified Advacate in the absence of  $\text{SO}_2$  (optimum condition), throughout the 30 minutes of exposure. Unlike the  $\text{Hg}^0$  case, decreasing the temperature caused an increase in  $\text{HgCl}_2$  capture by these sorbents. The effect of temperature may be explained by a physisorption mechanism through which the  $\text{HgCl}_2$  molecules are adsorbed by the sites.

An interesting observation can be made by comparing Figure 8 (effect of temperature on  $\text{HgCl}_2$  capture) to Figure 5 (effect of temperature on  $\text{Hg}^0$  capture). Unlike  $\text{Hg}^0$ ,  $\text{HgCl}_2$  capture increased (with time) at the lowest studied temperature ( $65^\circ\text{C}$ ). The reason may be outlined as follows.

At lower temperatures, water vapor present in the simulated flue gas may condense on the surface of Advacate and modified Advacate. It should be noted that the homogeneous dew point of 5% water vapor in air is below  $65^\circ\text{C}$ , but that the actual dew point above hygroscopic solids (such as calcium

silicates) can be significantly higher, favoring condensation of water vapor at the solid surface. If water vapor molecules were to condense on the sorbent sites, they could readily dissolve the incoming  $\text{HgCl}_2$  molecules but not the insoluble  $\text{Hg}^0$  molecules. As the time of exposure progresses, an increasing number of water vapor molecules condense, thus the capture percentage of  $\text{HgCl}_2$  increases. This dissolution effect, yet to be proven for these sorbents, may be very important in practical situations where the concentration of water vapor is likely higher than for these bench-scale simulations.

## Conclusion

The capture of elemental mercury ( $\text{Hg}^0$ ) and mercuric chloride ( $\text{HgCl}_2$ ), the mercury species identified in coal flue gas, by three types of calcium-based sorbents differing in their internal structure, was examined in a packed-bed, bench-scale study under simulated flue gas conditions for coal-fired utilities. The results obtained were compared with  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture by an activated carbon (FGD) under identical conditions. Tests were conducted with and without  $\text{SO}_2$  to evaluate the effect of  $\text{SO}_2$  on  $\text{Hg}^0$  and  $\text{HgCl}_2$  control by each of the sorbents.

The Ca-based sorbents showed insignificant removal of  $\text{Hg}^0$  in the absence of  $\text{SO}_2$ . However, in the presence of  $\text{SO}_2$ ,  $\text{Hg}^0$  capture was enhanced for the three Ca-based sorbents. It was postulated that the reaction of hydrated lime with  $\text{SO}_2$  would result in pore mouth closure as evidenced by the sharp drop in the  $\text{SO}_2$  removal rate after the initial 10 minutes of exposure. Despite the loss of internal surface area, the relatively high uptake of  $\text{Hg}^0$  observed for these sorbents in the presence of  $\text{SO}_2$ , suggests that  $\text{Hg}^0$  and  $\text{SO}_2$  do not compete for the same active sites, and the sites for  $\text{Hg}^0$  capture are influenced positively by the presence of  $\text{SO}_2$ . Moreover, the capture of  $\text{Hg}^0$  in the presence of  $\text{SO}_2$  increased with sorbent surface area and internal pore structure.

Conversely, the three Ca-based sorbents showed decreased removal of  $\text{HgCl}_2$  in the presence of  $\text{SO}_2$ . In the absence of  $\text{SO}_2$ , roughly 25% of the incoming  $\text{HgCl}_2$  was captured. The alkaline sites in the Ca-based sorbents were postulated to be instrumental in the capture of acidic  $\text{HgCl}_2$ .  $\text{SO}_2$  not only

competed for these alkaline sites but also, as mentioned, likely closed pores with subsequent reduction in accessibility of the interior of the Ca-based sorbent particles to the  $\text{HgCl}_2$  molecules.

It was hypothesized that the capture of  $\text{Hg}^0$  in the presence of  $\text{SO}_2$  may occur through a chemisorption mechanism, while the nature of the adsorption of  $\text{HgCl}_2$  molecules may be explained through a physisorption mechanism. The effect of temperature studies further confirmed this hypothesis. Increasing the system temperature caused an increase in  $\text{Hg}^0$  uptake by the sorbents in the presence of  $\text{SO}_2$ . However, the increase in temperature resulted in a significant decrease in the  $\text{HgCl}_2$  uptake in the absence or presence of  $\text{SO}_2$ . Increased sorbent surface area and internal pore structure had no observable effect on  $\text{HgCl}_2$  capture in the presence of  $\text{SO}_2$ .

With the relatively large quantities of Ca needed for  $\text{SO}_2$  control at coal-fired boilers, the above results suggest that Ca-based sorbents, modified by reaction with fly ash, can be used to control total mercury emissions and  $\text{SO}_2$  cost-effectively. The most effective Ca-based sorbents are those with significant surface area (for  $\text{SO}_2$  and  $\text{HgCl}_2$  capture) and pore volume (for  $\text{Hg}^0$  capture).

Sorbents injected upstream of a fabric filter should perform as indicated by the fixed-bed reactor simulation in this study. Confirmation of these results on a 50 cfm (0.024 m/s) pilot plant is anticipated later this year.

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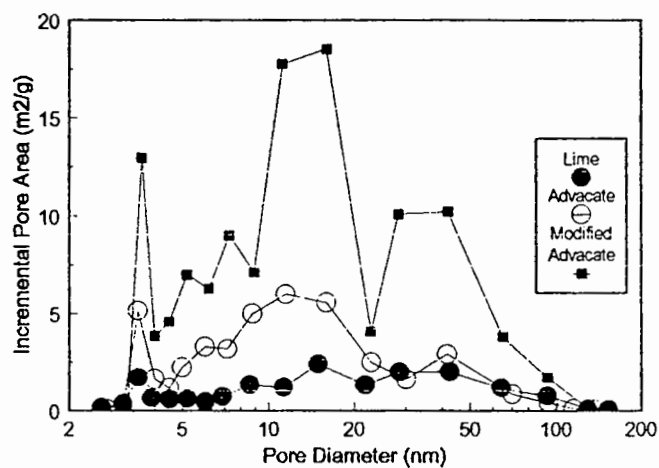
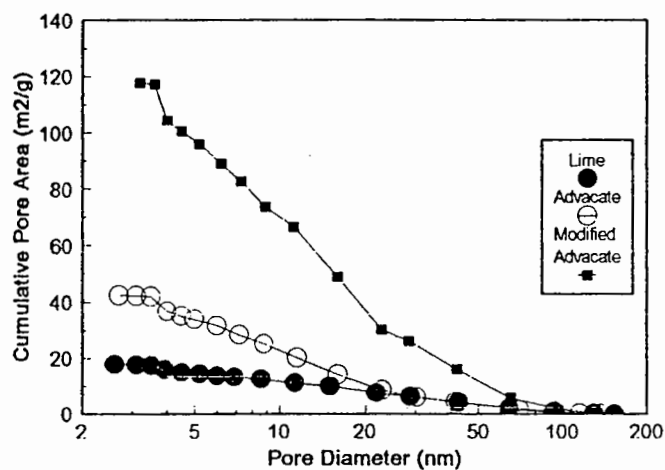
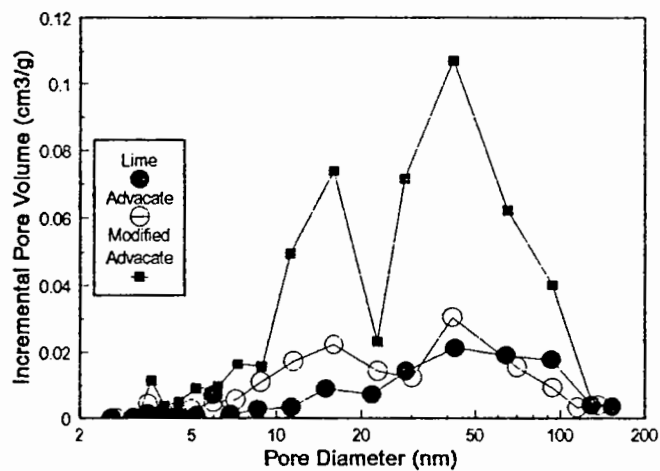
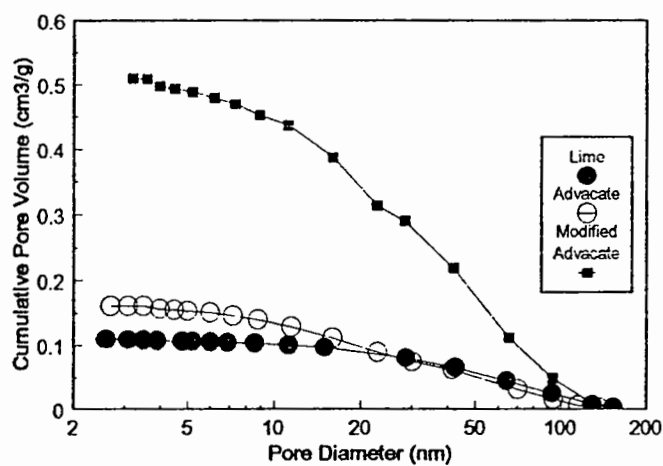
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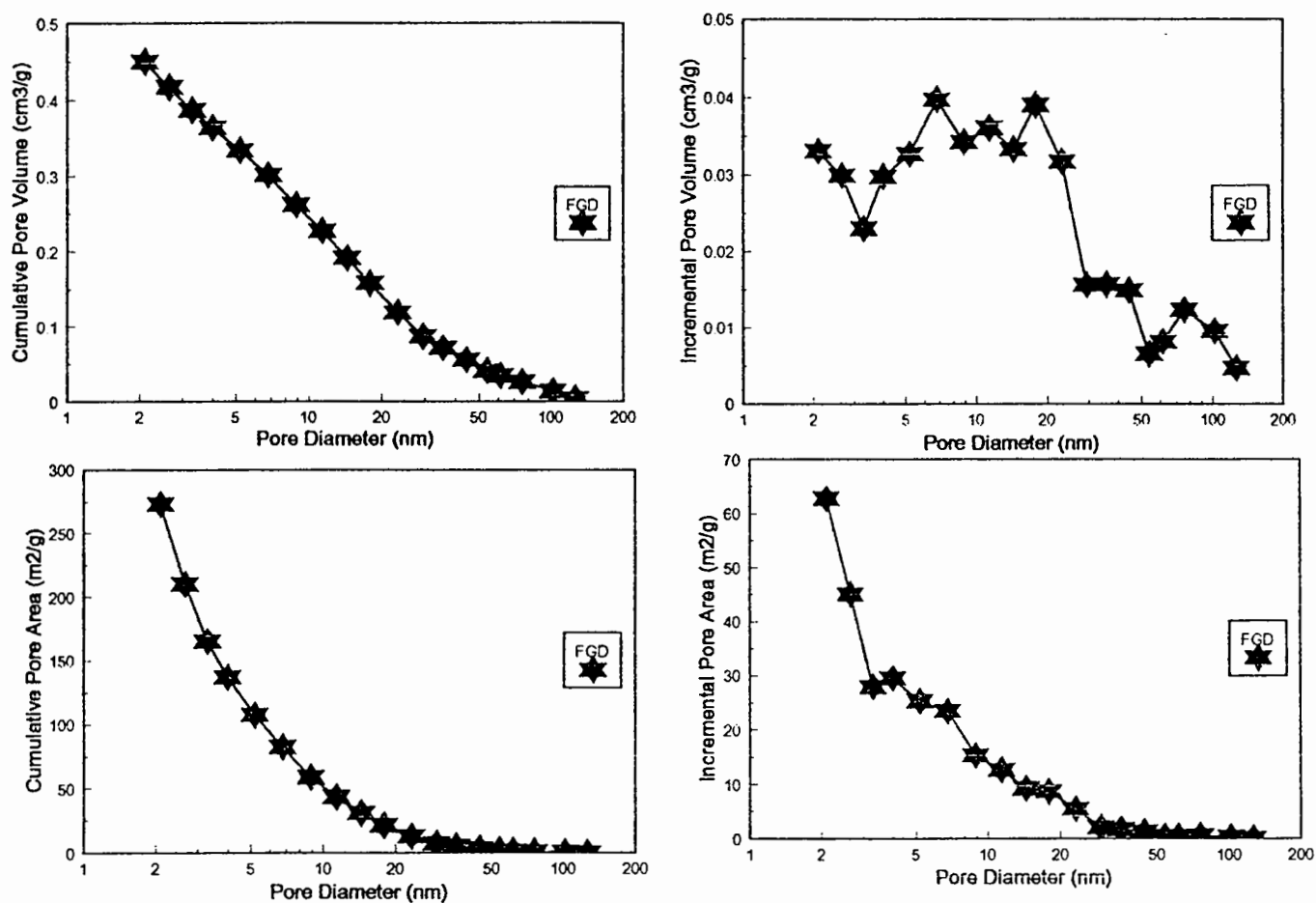
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**Table 1.** Total Surface Area and Average Pore Diameter of Sorbents

Sorbent	Total Surface Area (m <sup>2</sup> /g)	Average Pore Diameter (nm)
Hydrated Lime	13.0	33.4
Advacate	30.9	21.2
Modified Advacate	91.4	22.2
Clinch River Fly Ash (CRFA)	2.3	8.1
Activated Carbon (FGD)	575	3.2



**Figure 1. Internal Pore Structure Characteristics of Lime, Advacate, and Modified Advacate Obtained from Nitrogen Sorption**



**Figure 2. Internal Pore Structure Characteristics of DARCO FGD Obtained from Nitrogen Sorption**



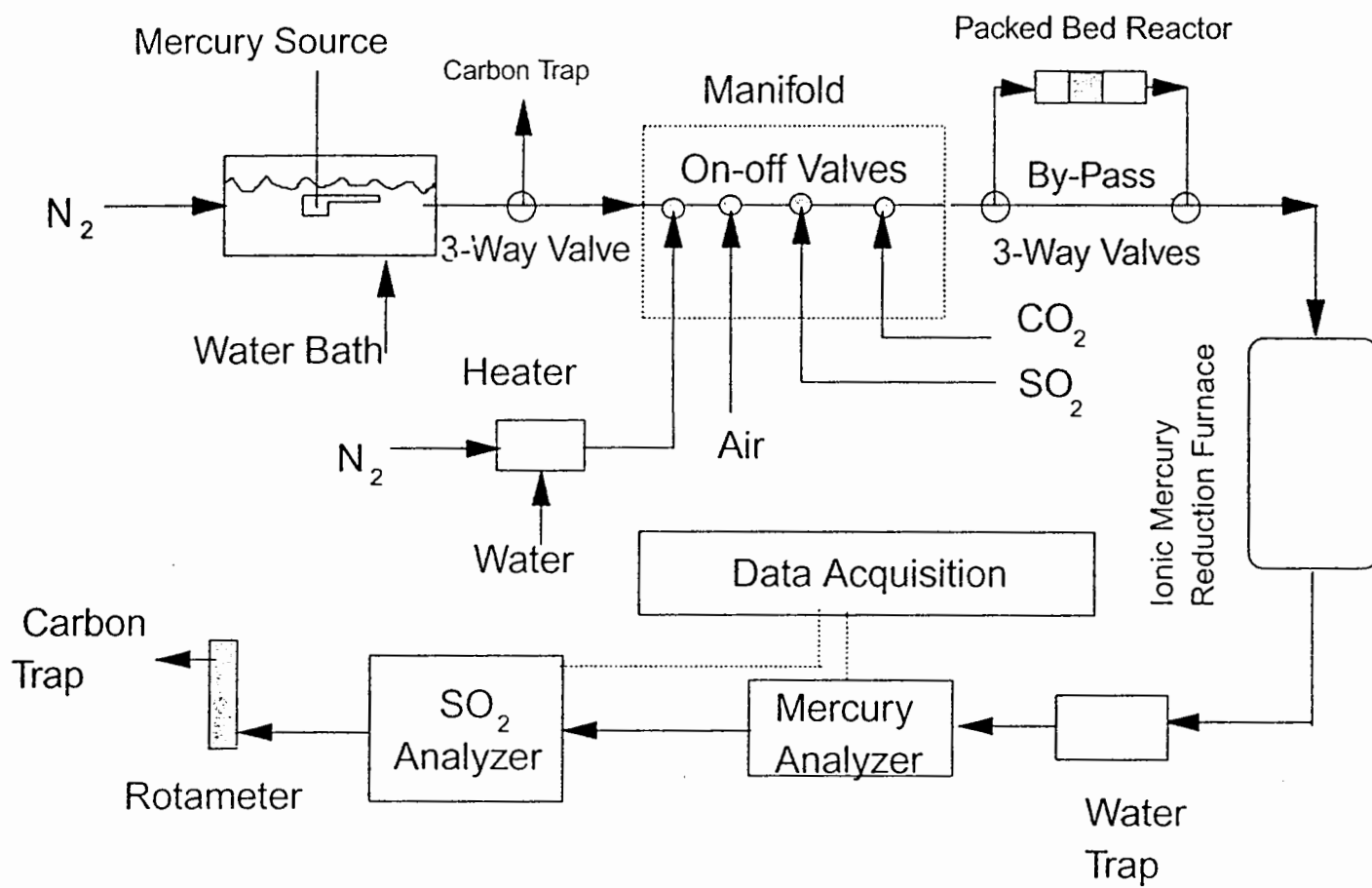
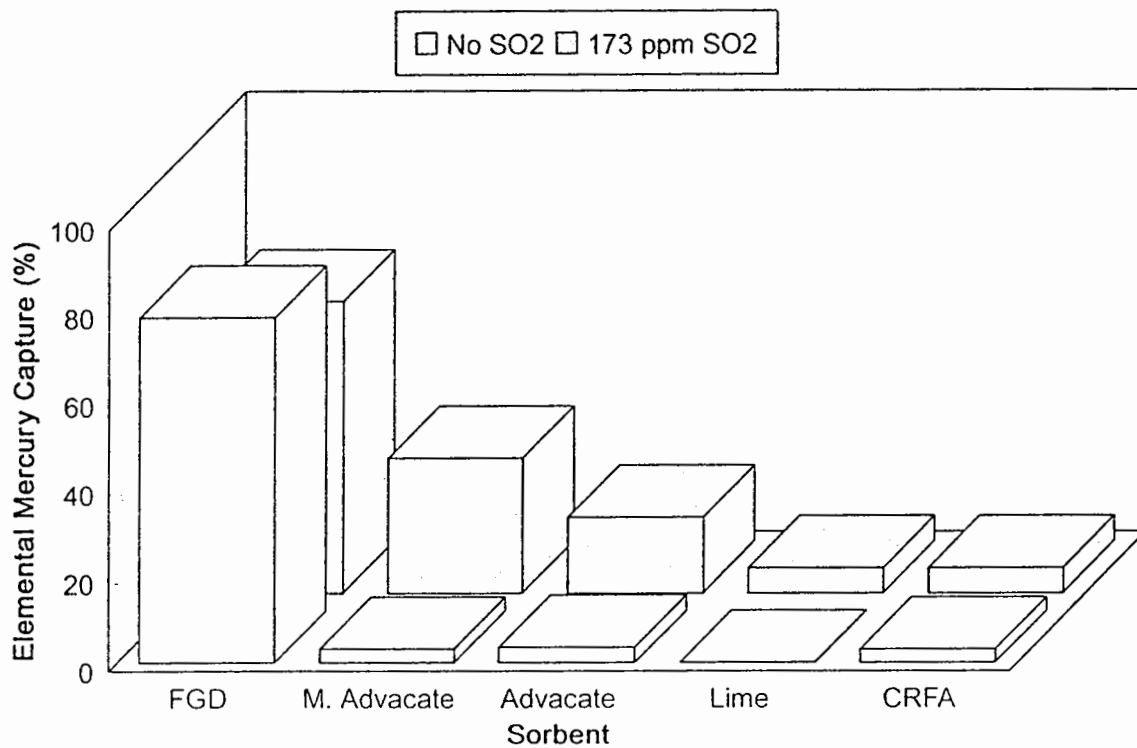
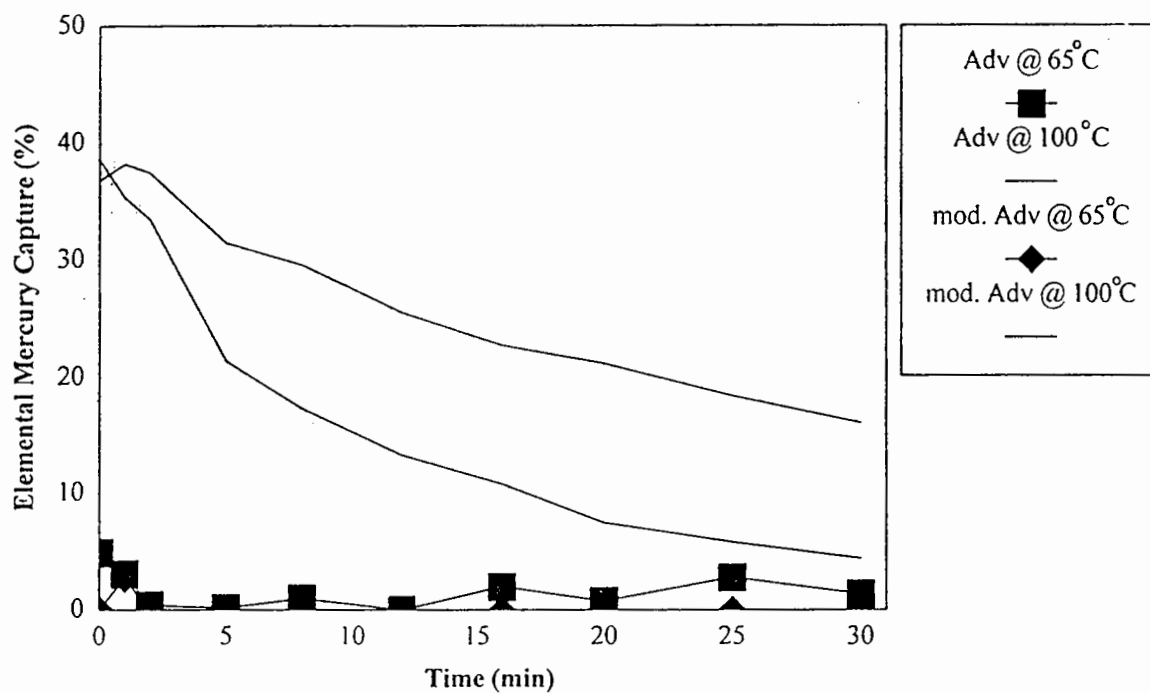


Figure 3. Schematic of the Bench-Scale Packed Bed Reactor



**Figure 4. Effect of Sulfur Dioxide on Elemental Mercury Capture by the Sorbents at 100°C**



**Figure 5. Effect of Temperature on Elemental Mercury Capture by Calcium-Based Sorbents (Advacate and Modified Advacate) in the Presence of 173 ppm Sulfur Dioxide**

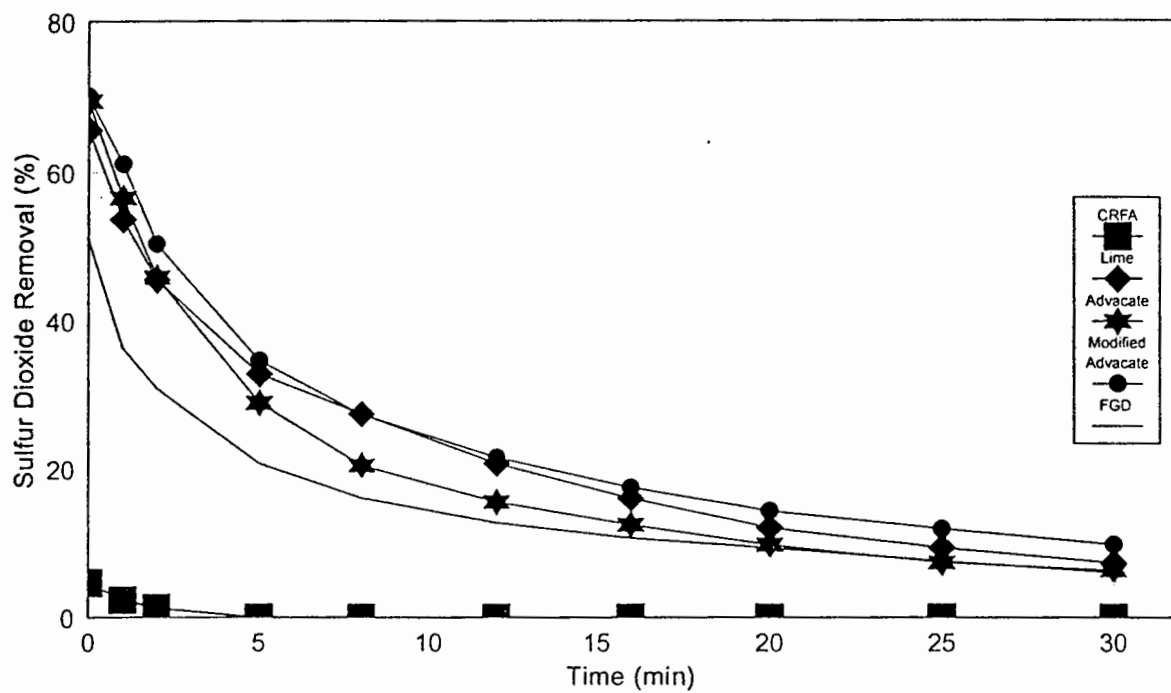
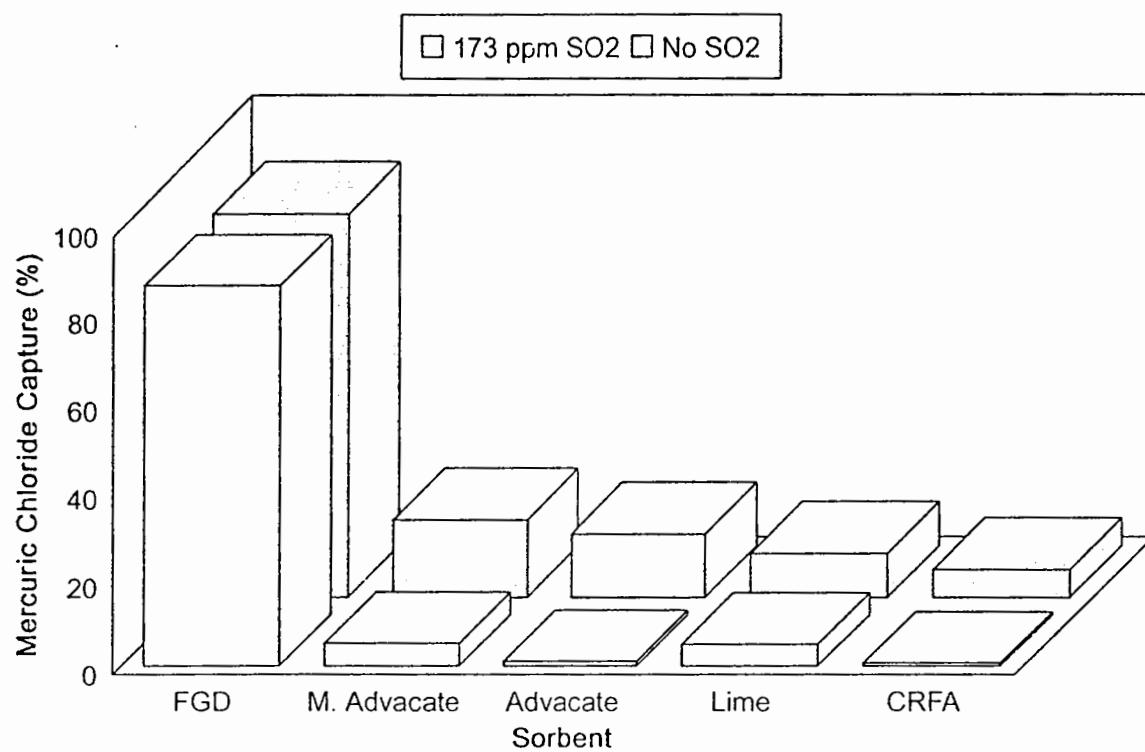
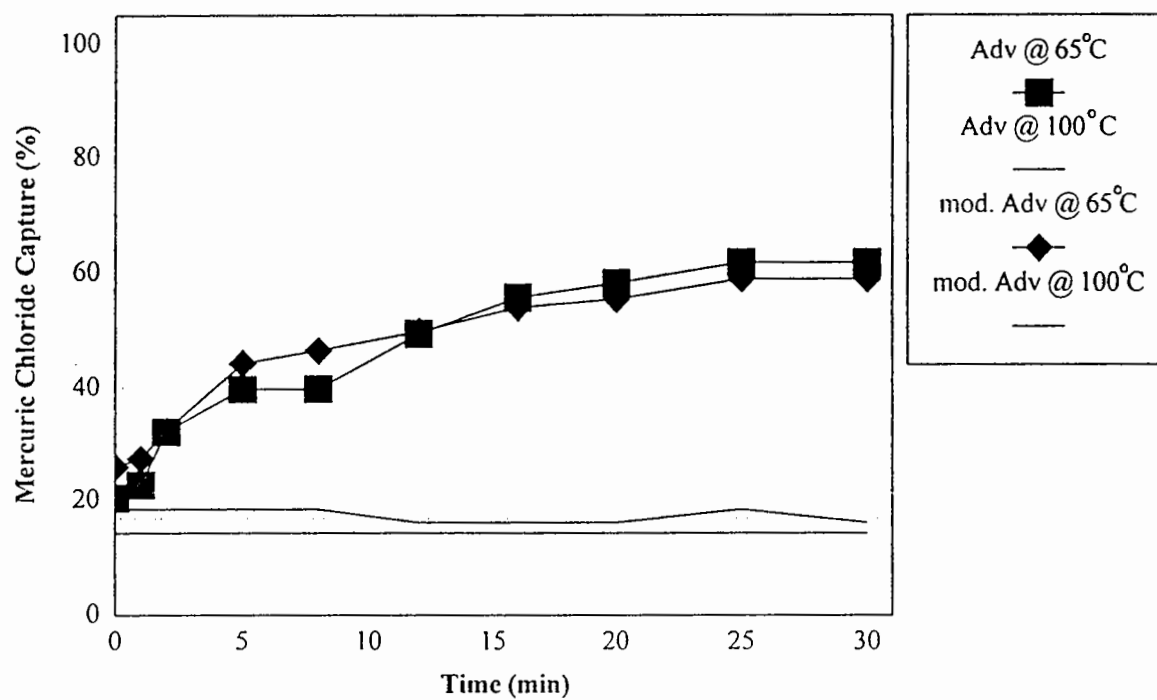


Figure 6. Capture Percentage of Incoming Sulfur Dioxide by the Sorbents at 100°C



**Figure 7. Effect of Sulfur Dioxide on Mercuric Chloride Capture by the Sorbents at 100°C**



**Figure 8. Effect of Temperature on Mercuric Chloride Capture by the Calcium-Based Sorbents (Advacate and Modified Advacate) in the Absence of Sulfur Dioxide**

NRMRL-RTP-P-184a			TECHNICAL REPORT DATA (Please read instructions on the reverse before completing)	
1. REPORT NO. EPA 600/A-98/053		2.		3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Combined Mercury and Sulfur Oxides Control Using Calcium-Based Sorbents		5. REPORT DATE		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) S. Behrooz Ghorishi (Acurex) and Charles B. Sedman (EPA)		8. PERFORMING ORGANIZATION REPORT NO.		
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16. ABSTRACT The paper gives results of an examination of the capture of elemental mercury (Hgo) and mercuric chloride (HgCl <sub>2</sub> ) by three types of calcium (Ca)-based sorbents in a bench-scale study under conditions prevalent in coal-fired utilities. Ca-based sorbent performances were compared to that of an activated carbon. Mercury capture of about 40% (nearly half that of the activated carbon) was achieved by two of the Ca-based sorbents. The presence of sulfur dioxide (SO <sub>2</sub> ) in the simulated coal combustion flue gas enhanced the capture of Hgo from about 10 to 40%. Increasing the temperature in the range of 65-100 C also caused an increase in the Hgo capture by the two Ca-based sorbents. HgCl <sub>2</sub> capture exhibited a totally different pattern. The presence of SO <sub>2</sub> inhibited the HgCl <sub>2</sub> capture by Ca-based sorbents from about 25 to < 10%. Increasing the temperature in the studied range also caused a decrease in HgCl <sub>2</sub> capture. Upon further pilot-scale confirmations, the results obtained in this bench-scale study can be used to design and manufacture more cost-effective mercury sorbents to replace conventional sorbents already in use in mercury control.				
17. KEY WORDS AND DOCUMENT ANALYSIS				
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
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