ABSTRACT

One of the primary concerns in coal utilization is the emission of volatile air toxics, especially mercury. This project deals with mercury adsorption on specially modified activated carbons: Darco TRS and Darco FGD. Modification of the activated carbons was performed with CO₂ at different temperatures and times. Modification experiments show that the specific surface area of Darco TRS increases after CO₂ treatment, and the optimum temperature and time for that process is 600°C, 5 hrs. In contrast, the specific surface area of Darco FGD decreased during modification, except in the process performed at 600°C in which the BET surface area determined by CO₂ adsorption slightly increased. Mercury adsorption tests were performed at 25°C, 75°C, and 150°C for Darco TRS and at 75°C and 150°C for Darco FGD. It was found that modification doubled mercury sorption capacities of these activated carbons. Also, results obtained in these experiments show that increases in temperature result in significant reductions of Hg sorption capacities. For Darco FGD, results obtained in mercury sorption experiments show that modifications performed with CO₂ at 550°C for 5 hrs, 600°C for 2, 5, and 18 hrs, and 650°C for 5 hrs increase the mercury sorption capacities by 50%. The best adsorbent at 75°C was Darco FGD modified at 600°C for 5 hrs. On the other hand, the sorbent modified at high temperature (675°C) for 18 hrs shows lower mercury capacity than untreated carbon. Presence of SO₂ in the gas mixture slightly improves the Hg sorption capacity of Darco FGD sorbent, but changes in the sorption capacity for Darco TRS activated carbon is negligible.
EXECUTIVE SUMMARY

Using coal in electric utility power plants has stimulated considerable research to minimize emissions of pollutants. From the environmental protection point of view, it is important to reduce air toxics present in effluents, e.g., mercury. The toxicity of mercury has led to emission limitations in the 1990 Clean Air Act amendments for municipal waste combustors. Soon, coal-burning utilities also will be regulated. Although Hg emissions from coal-burning utilities are typically less concentrated than from waste combustors, the large quantities of coal burned produce a significant fraction of anthropogenic Hg emissions; therefore, it is important to reduce mercury deposition and to study all ways for reducing emissions of combustion-generated mercury. On the other hand, there is a primary need to increase the utilization of Illinois coal resources by developing new gas cleanup techniques.

The goal of this project is to evaluate the performance of activated carbon sorbents in mercury adsorption. The samples of Darco TRS and Darco FGD sorbents were obtained from American Norit Company, Inc. These samples are thermally activated from lignite coal and wood, respectively.

The work conducted during this year includes (1) modifying Darco TRS and Darco FGD activated carbons with carbon dioxide at different temperatures for different times, (2) determining the surface areas of the modified sorbents, (3) determining mercury sorption on as-received and modified activated carbons, and (4) evaluating SO₂ effects on mercury sorption.

Modification experiments show drastic increases of the specific surface area of Darco TRS activated carbon. The optimum temperature and time for this process seems to be 600°C and 5 hrs. Since both CO₂ and N₂ BET surface area increased, it may be concluded that this modification developed a new surface rich in micro- and macropores. The modification process of Darco FGD activated carbon yielded a decrease in the specific surface area, except for the treatment performed at 600°C for 5 hrs.

The adsorption of nitrogen on both activated carbons shows the same tendency: the modification of activated carbons Darco TRS and Darco FGD leads to increased adsorption and, therefore, to development of micro- and mesoporosity in such a way that not modified (as-received) activated carbons have almost exclusively micropores. Also, as-received carbons do not show hysteresis loops, whereas other sorbents show hysteresis loops which indicates opening the pores. Modification of both activated carbons at 600°C for 2 hrs yields the highest nitrogen adsorption, which suggests that the modification at these particular conditions causes
opening of all the pores with a very wide distribution of pore sizes.

In reviewing results obtained thus far, it is believed that the mechanism of CO₂ interaction with these two activated carbons is quite different. It is suggested that CO₂ gasifies the surface of Darco TRS carbon, and this gasification yields the formation of new micro- and macropores. In contrast, CO₂ may decompose on the Darco FGD carbon leaving the carbon, which may plug the existing pores. Additionally, during the treatment of that carbon with CO₂, oxygen was detected in the exiting gases from the reactor. To confirm this idea, more experiments will be performed using the thermogravimetric technique.

Mercury adsorption experiments on Darco TRS activated carbons (as-received and modified) were performed at three different temperatures, 25°C, 75°C, and 150°C, and on Darco FGD at 75°C and 150°C. The results obtained in these tests clearly indicate that modification of activated carbon surfaces with carbon dioxide increases the sorption capacity of Hg by 20 to 40%. The best Darco TRS sorbent for mercury sorption at 25°C and 75°C were those modified at 600°C for 5 hrs, whereas for the test performed at 150°C, the highest activity was shown by the carbon modified at 600°C for 18 hrs. Generally, each modified activated carbon shows higher mercury capacity than as-received sorbents. Also, the results obtained in these experiments show that increases in temperature result in significant reductions of Hg sorption capacity. These observations are confirmed by the calculations of Hg⁰ capacity at 75°C of the adsorbent.

For Darco FGD, the results obtained in mercury sorption experiments show that modifications performed with CO₂ at 550°C for 5 hrs, 600°C for 2, 5, and 18 hrs, and 650°C for 5 hrs, increase the mercury sorption capacities by 10 to 50%. The best adsorbent at 75°C was Darco FGD modified at 600°C for 5 hrs. On the other hand, the sorbent modified at high temperature (675°C) for 18 hrs shows lower mercury capacity than untreated carbon.

The presence of SO₂ in the gas mixture slightly improves Hg sorption capacity of Darco FGD sorbent, but changes in the sorption capacity for Darco TRS activated carbon is negligible. However, when Darco TRS was modified at 600°C for 5 hrs, the mercury sorption slightly increased when compared with unmodified carbon. At this moment, it is hard to explain this phenomenon. This requires additional experiments together with identification of the mercury species present on the activated carbon surface. However, we may suggest that HgS may be formed at these conditions and relocated to other sites at the surface leaving the adsorption-active site free, ready to adsorb another molecule of mercury.
OBJECTIVES

The goal of this project is to effectively remove elemental mercury emitted from coal-burning utilities. The major objectives of this project are to:

1. determine the ability of using different activated carbon-based sorbents for gas-phase elemental mercury adsorption,

2. determine the optimum condition for sorption of mercury on activated carbons,

3. evaluate the effect of activated carbons modification with CO₂ on mercury adsorption,

4. determine the effect of SO₂ on mercury sorption, and

5. determine the mechanism and the rate of mercury adsorption on activated carbons.

INTRODUCTION AND BACKGROUND

Using Illinois coal in electric utility power plants has stimulated considerable research to minimize emissions of pollutants. From the environmental protection point of view, it is important to reduce air toxics present in effluents, e.g., mercury. The toxicity of mercury has led to emission limitations in the 1990 Clean Air Act amendments for municipal waste combustors (MWCs). Soon, coal-burning utilities also will be regulated. Although Hg emissions from coal-burning utilities are typically less concentrated than from MWCs, the large quantities of coal burned produce a significant fraction of anthropogenic Hg emissions; therefore, it is important to reduce mercury deposition and to study all ways for reducing emissions of combustion-generated mercury.

Mercury compounds in combustion gases are found in various inorganic forms, such as elemental mercury (Hg⁰), mercurous chloride (Hg₂Cl₂), and mercuric chloride (HgCl₂). They also can be found in various organic forms, such as methylmercury chloride ([CH₃]₂HgCl) and dimethylmercury ([CH₃]₂Hg). From the emission standpoint, the oxidized forms of Hg(II) are most significant because these forms have very high solubility and pose great life threatening hazards by entering biospheric cycles. As measured by Bergstrom and supported by Metzger and Braun, their levels of concentration are:

\[ \text{HgCl}_2 > \text{Hg}_2\text{Cl}_2 > \text{Hg}^0 \]
Other pollutants in the flue gas also affect the speciation of Hg. Schager⁴ pointed out that NO₂ and HCl increase oxidation of Hg, while SO₂ reduces it. Common reaction products found were HgO and HgCl₂, which comprised more than 50% of the Hg compounds. Similar results were presented by Hall et al⁵. They showed that elemental Hg is easily oxidized to HgCl₂ in the presence of O₂ and HCl. This is supported by Meji⁶ who found that Hg⁰ concentrations in coal-fired power plants decrease with increasing HCl concentrations due to the formation of HgCl₂.

Mercury emission in MWCs can be limited by source preparation, product substitution, and flue gas clean up. Cleaning strategies include injection of activated carbon. In addition, flue gas cleaning operations of a spray dryer/fabric filter (SD/FF) may be effective in achieving mercury removal. Combustors with SD/FF controls remove about 95% of the Hg when the flue gas temperatures through the FFs are below 140°C⁶. Current technologies for combustor emission control also include spray dryer absorbers with activated carbon injection followed by a fabric filter. Recent results from testing a 400 ton/day mass burn plant in Stanislaus County (California) show that the average removal of Hg is about 95% with activated carbon injection and an SD/FF system⁷.

While activated carbon seems to be successful as a Hg sorbent, Bergstrom² found little Hg removal from an MWC pilot plant after injection of CaO prior to a fabric filter. Only when fly ash was recycled (presumably containing unburned C) and injected with the CaO, did significant reduction (87%) in Hg occur. Studies of the abilities of various sorbents on a fabric filter to remove Hg from flue gas showed that activated carbon and fly ash retain significant amounts of Hg compounds⁸.

Additionally, Metzger & Braun³ found that metallic mercury is only partially absorbed by activated carbon while mercury(II) chloride is completely absorbed at temperatures up to 200°C. However, 5% iodized activated carbon completely absorbs all Hg and HgCl₂ from 20 to 180°C.

It is well established that when the carbonized material is activated with carbon dioxide, the constrictions of the micropores are progressively eliminated and the final porous texture of the carbon is developed as a function of the extent of activation⁹-¹². Therefore, the activation with carbon dioxide results in increasing surface area and pore volumes as well.
EXPERIMENTAL PROCEDURES

Materials
The activated carbon samples (Darco TRS and Darco FGD) were obtained from the American Norit Company, Inc. at Atlanta, Georgia. These sorbents are thermally activated from lignite coal and wood, respectively.

Modification of Activated Carbons
A standard quartz-made plug-flow reactor (20 mm-OD and 40 cm-length) was used in performing the modification process. A 3 g sample of activated carbon was placed into the reactor, which was heated to the desired temperature by a Lindberg model 847 furnace equipped with an OMEGA temperature regulator. The carbon dioxide flow (50 mL/min) was controlled by a Sierra Side-Track mass flow controller.

Activated Carbons Surface Purity Measurements
Determination of activated carbons purity was performed by GC analysis of an effluent from the plug-flow reactor filled with 1 g of the sample and heated in the flowing helium from room temperature (25°C) to 500°C. A gas chromatograph equipped with a thermal conductivity detector and a 3 meter column filled with a Porapak Q packing material was used for analysis that was performed at 150°C.

BET Surface Area Measurements
Surface area measurements of as-received and modified activated carbons were made using CO₂ and N₂ gases. The Quantachrome BET analyzer was used for a BET single point CO₂ gas adsorption and the Quantachrome NOVA analyzer was employed for the BET N₂ single and multipoint gas sorptions. Prior to the measurements in both apparatus, the activated carbon samples were degassed at 200°C for 20 hrs.

Mercury Sorption Experiments
Mercury sorption experiments were performed in the apparatus shown in Figure 1. The main part of this system is a glass-made fixed-bed reactor which is 2 cm in diameter and 14 cm in height and a Buck 400A Mercury Analyzer with digital output connected to a chart recorder. The gas containing mercury passes through the absorption cell. The mercury vapor, which is in atomic form, absorbs the 253.7 nm radiation emitted from the light source (flameless atomic absorption). The change in energy transmitted through the cell is detected by a UV-sensitive phototube. A narrow bandpass filter in front of the phototube permits transmission of only 253.7 nm radiation and limits the analyzer sensitive to UV energy only.

To facilitate tubing connection and disconnection, threaded glass fittings and Swagelok connectors are used at both inlet and outlet ends of the reactor.
To preheat the incoming feed gas to a preselected operating temperature equal to that maintained in the fixed-bed reactor, the gas-transfer line is wrapped with heating tapes. A thermocouple is placed at the end of the preheating section, and its reading is fed back to a temperature controller (Omega), which regulates the temperature of the heating tapes. The reactor effluent gas is then piped in Teflon tubing to the gas-analysis section. In the beginning of each experiment, mercury concentration in the feed gas will be determined by directing the untreated feed gas into the gas-analysis section.

In each experiment, the reactor was loaded with 0.2 g of activated carbon and heated to the test temperature. At the same time, the permeation tube with Hg was loaded into the glass tube and placed into the furnace at 50°C. Helium flow (30 mL/min) was maintained by a Sierra mass flow controller.

**Effect of SO₂ on mercury sorption on activated carbons**
The effect of SO₂ on mercury sorption on activated carbons was determined using the apparatus described above. SO₂ (2% in He) was introduced into the Hg/He mixture before entering the reactor with sorbent. The gas leaving the reactor was analyzed for the presence of elemental mercury using the apparatus described above.

**RESULTS AND DISCUSSION**

**Effect of Carbon Dioxide Modification on the Surface Areas of the Activated Carbons**
The modification process was performed in the temperature range of 500°C to 675°C for 2 hrs, 5 hrs, and 18 hrs. The complete set of surface areas of as-received and modified activated carbons is shown in Table 1.

<table>
<thead>
<tr>
<th>Modfic. Conditions</th>
<th>DARCO TRS CO₂</th>
<th>DARCO TRS N₂m²/g</th>
<th>DARCO FGD CO₂</th>
<th>DARCO FGD N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmodified</td>
<td>266.23</td>
<td>257.46</td>
<td>540.25</td>
<td>519.60</td>
</tr>
<tr>
<td>500°C, 5 hrs</td>
<td>335.34</td>
<td>429.90</td>
<td>521.67</td>
<td>538.21</td>
</tr>
<tr>
<td>550°C, 18 hrs</td>
<td>635.57</td>
<td>529.29</td>
<td>323.20</td>
<td>390.54</td>
</tr>
<tr>
<td>600°C, 2 hrs</td>
<td>524.70</td>
<td>467.82</td>
<td>568.92</td>
<td>486.56</td>
</tr>
<tr>
<td>600°C, 5 hrs</td>
<td>763.95</td>
<td>432.10</td>
<td>608.05</td>
<td>481.40</td>
</tr>
<tr>
<td>600°C, 18 hrs</td>
<td>625.87</td>
<td>418.82</td>
<td>597.56</td>
<td>452.97</td>
</tr>
<tr>
<td>650°C, 5 hrs</td>
<td>610.23</td>
<td>442.80</td>
<td>500.87</td>
<td>420.81</td>
</tr>
<tr>
<td>675°C, 18 hrs</td>
<td>296.82</td>
<td>456.64</td>
<td>464.63</td>
<td>364.90</td>
</tr>
</tbody>
</table>
Activated carbons have a polymeric character, consisting of macromolecules of different sizes. The physical structure of this assembly of molecules is a "sponge-like" structure, containing interconnecting pores of different shapes and sizes and generally lacking the ordered regularity normally associated with crystalline lattices. The CO$_2$ adsorption areas are all larger because internal pore area in pores with diameter < 20 Å are included in the measurement. These pores are inaccessible for nitrogen.

Even though the samples initially are quite different in surface area or in nature of their porosity, Darco TRS has both CO$_2$ and N$_2$ specific surface areas smaller than Darco FGD activated carbon. However, the values of CO$_2$ and N$_2$ surface areas are quite similar for each activated carbon suggesting that the micropores become equally accessible to both nitrogen and carbon dioxide. However, their behavior in the modification process is different. The specific surface area of Darco TRS activated carbon increases during modification; however, the surface area of Darco FGD decreases after modification at the same conditions. The highest CO$_2$ surface area for Darco TRS was obtained after treatment at 600°C for 5 hrs, but the highest value of N$_2$ surface area was observed after modification at 550°C for 18 hrs. The small increase in surface area of Darco FGD activated carbon is only observed after modification at 600°C for 2 and 5 hrs; at other temperatures, the surface area of this activated carbon decreases.

The mechanism of the modification process with CO$_2$ seems to be quite different for those two activated carbons used in this study. For Darco TRS it brings drastic changes in the porous structure, especially in the micro- and macropores which are "detected" by both carbon dioxide and nitrogen molecules. It may be suggested that carbon dioxide likely causes slow gasification of the carbon surface that yields good pores development. However, Darco FGD activated carbon’s surface interaction with CO$_2$ generally yields in decreasing the pore structure, which may be caused by decomposition of carbon dioxide and surface deposition of carbon particles resulting in plugging the existing pores. Also, oxygen, which probably is formed in CO$_2$ decomposition, may burn the activated carbon surface. This burn-off process will decrease the porous structure of the Darco FGD activated carbon. We have some evidence supporting this mechanism. The GC analysis of the gaseous products formed during the modification of FGD activated carbon at 675°C shows approximately 8% oxygen in the concentration. Since no oxygen is entering the reactor (CO$_2$ is flowing through the oxygen trap), the only possibility is that oxygen is formed during the modification process.
**Activated Carbon Surface Purity Determination**

In order to determine whether Darco TRS and Darco FGD carbons were chemically impregnated, the desorption GC spectra were taken under flowing helium. It was found that no desorption products were detected in the ambient - 500°C range, confirming that the activated carbons were not chemically impregnated.

**Nitrogen Adsorption Isotherms on Modified Activated Carbons**

Figures 2 and 3 show the adsorption isotherms of N₂/77 K for the activated carbons Darco TRS and Darco FGD, respectively. All these isotherms cover the relative pressure range to 0.20 and correspond to type I of the BDDT classification.

The adsorption of nitrogen on both activated carbons shows the same tendency: the modification of activated carbons Darco TRS and Darco FGD leads to increased adsorption, and therefore, to development of micro- and mesoporosity in such a way that not modified (as-received) activated carbons have almost exclusively micropores. Also, as-received carbons do not show hysteresis loops, whereas other sorbents show hysteresis loops which indicates opening the pores. Modification of both activated carbons at 600°C for 2 hrs yields in the highest nitrogen adsorption, which suggests that modification at these particular conditions causes opening of all the pores with a very wide distribution of pore sizes.

**Experiments with Empty Reactor**

Baseline tests were carried out in order to establish a performance baseline against which the results of the sorbents' activities could be compared. Figure 4 presents the results of these tests. First, mercury concentration in the stream bypassing the reactor was monitored for 2 hrs. This is a baseline for Hg. In the next experiment, helium with mercury was flowing through the empty reactor. At the beginning, the concentration of Hg drops and, after approximately 1 hour, returns to the initial value. In this experiment, stainless fittings were used as connectors between teflon tubes and the reactor. However, mercury seems to react with some components of the fitting material; therefore, stainless fittings were replaced with Teflon fittings and a similar experiment was carried out for 2 hrs. Figure 1 shows that Hg concentration is constant and similar to that obtained when gas did not flow through the reactor.

Figure 5 shows the results of another experiment in which the adsorption of Hg in an empty reactor and in a reactor loaded with glass wool was determined. The decrease in the gas phase concentration of mercury was negligible for this experiment, indicating that wall effects are not important and that glass wool is nonadsorptive to Hg.
Mercury Sorption on Darco TRS Activated Carbon

Figures 6, 7, and 8 present the effect of modification on the mercury adsorption. The experiments were performed at three different temperatures: 25°C, 75°C, and 150°C. The results obtained in these tests clearly indicate that modification of activated carbon surfaces with carbon dioxide increases the sorption capacity of the solid. The best adsorbent for mercury sorption at 25°C and 75°C was the carbon modified at 600°C for 5 hrs; whereas, for the test performed at 150°C, the highest activity was shown by the carbon modified at 600°C for 18 hrs. However, each modified activated carbon shows higher mercury capacity than an as-received sorbent. Also, the results obtained in these experiments show that increases in temperature result in significant reductions in sorptive capacity. These observations are confirmed by the calculations of Hg⁰ capacity of the adsorbent used in this part of the research. The Hg⁰ capacity is determined as the amount of mercury sorbed at 75°C until the outlet Hg⁰ concentration returned to the baseline value (0.03 ppm). The capacities are determined by integration of the concentration - time values determined by the mercury analyzer:

\[ \int (Hg_i - Hg_t) \, dt \]

where Hgᵢ and Hgₜ are the mercury concentrations at the baseline and at the time, t, respectively. The results that are shown in Figure 9 indicate that there is considerable variation in Hg capacities among these sorbents. Thus our results clearly demonstrate that modification at different conditions of Darco TRS activated carbon results in sorbents that have different mercury sorption capacities. We assume that modification with carbon dioxide of Darco TRS activated carbon brings drastic changes in the porous structure, especially in the micro- and macropores that are detected by both CO₂ and N₂ BET surface areas. Also, we suggest that CO₂ likely causes slow gasification of the carbon surface that yields good pore development.

Table 2 compares the isothermal (75°C) sorption capacity of Darco TRS activated carbon (as received and modified at different conditions) with both CO₂ and N₂ BET surface areas. There appears to be a relationship between Hg sorption capacity and CO₂ surface area; higher surface areas improve sorptive capacity. For N₂ BET, the effect of surface area is negligible.

Mercury Sorption on Darco FGD Activated Carbon

The experiments with mercury sorption on Darco FGD activated carbon are shown in Figures 10 and 11. This sorbent was not
Table 2. Comparison of Hg sorption capacity with surface areas of as-received and modified TRS carbons

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Hg sorption capacity</th>
<th>CO₂ surface area</th>
<th>N₂ surface area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg Hg/g carbon</td>
<td>m²/g</td>
<td>m²/g</td>
</tr>
<tr>
<td>as received</td>
<td>1.5</td>
<td>266.23</td>
<td>257.25</td>
</tr>
<tr>
<td>500°C, 5 hr</td>
<td>1.8</td>
<td>335.34</td>
<td>429.90</td>
</tr>
<tr>
<td>550°C, 18 hr</td>
<td>1.4</td>
<td>635.57</td>
<td>529.29</td>
</tr>
<tr>
<td>600°C, 2 hr</td>
<td>2.2</td>
<td>524.70</td>
<td>467.82</td>
</tr>
<tr>
<td>600°C, 5 hr</td>
<td>3.9</td>
<td>763.95</td>
<td>432.10</td>
</tr>
<tr>
<td>600°C, 18 hr</td>
<td>3.3</td>
<td>625.87</td>
<td>418.82</td>
</tr>
<tr>
<td>650°C, 5 hr</td>
<td>2.7</td>
<td>610.23</td>
<td>442.80</td>
</tr>
<tr>
<td>675°C, 18 hr</td>
<td>3.3</td>
<td>296.82</td>
<td>456.64</td>
</tr>
</tbody>
</table>

tested at 25°C due to the excessive amount of time (days) required to return the Hg concentration to the baseline value; therefore, the experiments were performed at 75°C and 150°C only.

The results obtained in these experiments show that modifications performed with CO₂ at 550°C for 5 hrs, 600°C for 2, 5, and 18 hrs, and 650°C for 5 hrs increase the mercury sorption capacities. The best adsorbent at 75°C was Darco FGD modified at 600°C for 5 hrs. On the other hand, the sorbent modified at high temperature (675°C) for 18 hrs shows lower mercury capacity than untreated carbon.

The mercury capacity for each tested sorbent was calculated the same as for Darco TRS activated carbon. The results of these calculations are presented in Figure 12, which shows that for the reactions performed at 75°C, the highest Hg capacity was observed for sorbents modified at 600°C and 650°C for 5 hrs.

As for Darco TRS activated carbon, we compared the calculated Hg capacity with both CO₂ and N₂ surface areas of Darco FGD as-received and modified samples. The results are presented in Table 3.

For this activated carbon, there appears to be a relationship between mercury sorption and CO₂ surface area; higher surface area improves sorptive capacity of modified Darco FGD activated carbon.

**Effect of SO₂ on mercury sorption on activated carbons**

Figures 13 and 14 show the effect of the presence of SO₂ on mercury sorption at 75°C on as-received Darco FGD and Darco TRS, respectively. As may be seen on these figures, the
Table 3. Comparison of Hg sorption capacity with surface areas of as-received and modified TRS carbons

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Hg sorption capacity mg Hg/g carbon</th>
<th>CO₂ surface area m²/g</th>
<th>N₂ surface area m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>as received</td>
<td>9.0</td>
<td>540.25</td>
<td>519.60</td>
</tr>
<tr>
<td>500°C, 5 hr</td>
<td>9.9</td>
<td>521.67</td>
<td>538.21</td>
</tr>
<tr>
<td>550°C, 18 hr</td>
<td>9.2</td>
<td>323.20</td>
<td>390.54</td>
</tr>
<tr>
<td>600°C, 2 hr</td>
<td>9.2</td>
<td>568.92</td>
<td>486.56</td>
</tr>
<tr>
<td>600°C, 5 hr</td>
<td>12.3</td>
<td>608.05</td>
<td>481.40</td>
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<tr>
<td>600°C, 18 hr</td>
<td>11.8</td>
<td>597.56</td>
<td>452.97</td>
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<tr>
<td>650°C, 5 hr</td>
<td>12.1</td>
<td>500.87</td>
<td>420.81</td>
</tr>
<tr>
<td>675°C, 18 hr</td>
<td>9.0</td>
<td>464.63</td>
<td>364.90</td>
</tr>
</tbody>
</table>

The presence of SO₂ slightly improves Hg sorption capacity of Darco FGD sorbent, but changes in the sorption capacity for Darco TRS activated carbon is negligible. However, when Darco TRS is modified at 600°C for 5 hrs (Figure 15), the mercury sorption is slightly increased when compared with unmodified carbon. At this moment, it is hard to explain this phenomenon. This requires additional experiments, together with identification of the mercury species present on the activated carbon surface. However, we may suggest that HgS may be formed at these conditions and relocate to other sites at the surface leaving the adsorption active site free, ready to adsorb another molecule of mercury.

CONCLUSIONS AND RECOMMENDATIONS

1. The carbon dioxide modification process of Darco TRS and FGD activated carbons results in drastic changes of the porous structure of these carbons.

2. Large increases in specific surface area of Darco TRS activated carbon during the reaction with CO₂ may be caused by slow gasification with CO₂ resulting in formation of new micro and macropores.

3. The specific surface area of Darco FGD activated carbon generally decreases during the modification reaction. It may be suggested that CO₂ decomposes on the activated carbon surface, and the new carbon formed during this decomposition is plugging already existing pores.

4. Modification of Darco TRS activated carbon with carbon dioxide enhances the sorption capacity for mercury, and the sample modified at 600°C for 5 hr shows the larger sorption capacity for mercury.
5. Modification of Darco FGD with CO₂ in the temperature range 550°C to 650°C increases Hg sorption by 50%. On the other hand, the modification performed at high temperature (675°C) lowers the sorption capacity of this sorbent.

6. The mercury sorption capacity seems to be related to CO₂ BET surface area; higher surface areas improve mercury sorption capacity.

7. For N₂ BET measurements, the effect of surface area on mercury adsorption is negligible.

8. The presence of SO₂ in the gas slightly increases the mercury sorption on Darco FGD activated carbon; however, it does not show any effect of the process performed on Darco TRS carbon.

REFERENCES

3. Metzger M., Braun H., 1987, Chemos., 16(4), 821
Figure 1. Schematic diagram of the apparatus for mercury adsorption on activated carbons.
Figure 2. \( \text{N}_2/77k \) adsorption isotherms of activated carbon TRS after modification with \( \text{CO}_2 \)
Figure 3. N$_2$/77K adsorption isotherms of activated carbon Darco FGD after modification with CO$_2$. 

DARCO FGD 

600°C, 5 hrs 
550°C, 18 hrs 
650°C, 5 hrs 
--- x --- as-received 
600°C, 2 hrs 

\( p/p_0 \)

150 140 130 120 110 100 90 80 70 0
Figure 4. Plot of Hg concentration versus time for blank experiments (empty reactor) with different fittings
Figure 5. Effect of glass wool on mercury concentration in the blank tests
Figure 6. Mercury adsorption on as received and modified Darco TRS activated carbon at 25°C
Figure 7. Mercury adsorption on as received and modified Darco TRS activated carbon at 75°C
Figure 8. Mercury adsorption on as-received and modified Darco FGD activated carbon at 150°C
Figure 9. Darco TRS activated carbon—plot of sorption capacity of mercury at 75°C
Figure 10. Mercury adsorption on as-received and modified Darco FGD activated carbon at 75°C
Figure 11. Mercury adsorption on as-received and modified Darco FGD activated carbon at 150°C
Figure 12. Darco FGD activated carbon - plot of sorption capacity of mercury at 75°C
Figure 13. Effect of SO₂ on mercury sorption on as-received Darco TRS activated carbon at 75°C
Figure 14. Effect of SO₂ on mercury sorption on as-received Darco TRS activated carbon at 75°C
Figure 15. Effect of SO$_2$ on mercury sorption at 75°C on Darco TRS modified at 600°C for 5 hours