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Project Title: **REMOVAL OF ILLINOIS COAL-BASED VOLATILE TRACE  
MERCURY**

ICCI Project Number: 96-1/2.4A-1  
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ABSTRACT

Mercury, present as traces in Illinois coal, is readily volatilized during coal combustion. Mercury is the most volatile among various trace metals, and major portions of it can pass through existing particulate control devices. A sorbent that can react with this metallic species can effectively shift the metal from the vapor phase to the particulate (sorbent) phase, facilitating its removal. Past research has identified activated carbons and calcium-based sorbents to be effective in reducing mercury emissions.

This research project examined the interaction of sorbents with mercury and investigated the effect of process conditions on its capture. This research was a continuation of an earlier effort for ICCI (ICCI project number: 95-1/2.4A-1). Tests were conducted in two tasks. Task I studied mercury capture in a bench-scale, fixed-bed reactor in a simulated coal combustion environment. Two types of sorbents (an activated carbon and calcium hydroxide), and capture conditions (bed temperature and mercury concentration) were examined in order to optimize reduction of mercury emissions. Of interest was the effect of sulfur dioxide (SO<sub>2</sub>, 1000 ppm range) and hydrogen chloride (HCl, 50 ppm range) on the capture of mercury species (elemental mercury and mercuric chloride) by the sorbents. The presence of HCl and SO<sub>2</sub> in the simulated flue gas drastically enhanced the Hg<sup>0</sup> capture capability of a thermally activated carbon. This enhancement might have been effected through reaction of HCl and SO<sub>2</sub> with this sorbent and creation of active chlorine and sulfur sites.

In Task II, also in a bench-scale, fixed-bed reactor, residues produced during combustion of high sulfur Illinois coal in four different full-scale power plants were evaluated with respect to their mercury capture capabilities. Two different species of mercury, mercuric chloride (HgCl<sub>2</sub>) and elemental mercury (Hg<sup>0</sup>), were examined. This task explored the potential utilization of Illinois coal combustion residues as mercury species sorbents. Among the Illinois coal combustion residues, scrubber sludge (calcium sulfate type) samples exhibited considerable (40%-50%) HgCl<sub>2</sub> removal capabilities. Statistical calculations revealed that this activity is related to the presence of calcium in these samples. A coal fly ash sample obtained from an Illinois coal power plant (designated as 3PF) was the only combustion residue sample that exhibited both Hg<sup>0</sup> and HgCl<sub>2</sub> removal capability. The characteristics of this sample resembled those of a mixture of a typical fly ash and calcium sulfate.

## EXECUTIVE SUMMARY

The Air Pollution Prevention and Control Division (APPCD) of the United States Environmental Protection Agency (EPA) has conducted co-funded research in conjunction with the Illinois Clean Coal Institute (ICCI) to evaluate the reduction of volatile trace mercury by dry sorbent injection. Title III of the Clean Air Act Amendments (CAAA) places limitations on emissions of various air toxics. Among these, mercury present in Illinois coals, poses the most serious challenge to control technologies because of its high volatility. For coal-fired utilities, reduction of this metal is critical in complying with the emission standards set forth by the CAAA. Injection of dry sorbents under suitable conditions is a possible option for controlling mercury emissions. The research described here developed control strategies to reduce air toxics emissions in utilities using Illinois coals.

The objectives of the proposed research were to conduct bench-scale studies to identify cost-effective sorbents and examine effects of process parameters to develop optimum reaction conditions for removing mercury in a simulated combustion environment. Control technology experiences gathered at our laboratories and from Municipal Waste Combustors (MWCs) were used to identify sorbents and capture conditions. The parametric investigation conducted in our laboratories with these sorbents allows optimization of the process for mercury capture in coal combustors using Illinois coal. The research was performed over a twelve-month period and consisted of two Tasks.

Task I involved bench-scale testing of different sorbent types and capture conditions to identify optimal removal conditions for mercury from coal combustion flue gases. It was determined that the presence of acid gases (sulfur dioxide and hydrogen chloride) drastically enhance elemental mercury capture in a thermally activated carbon and significantly inhibit mercuric chloride capture in calcium hydroxide. Temperature and mercury concentration were two important sorption parameters. Combustion residues produced from burning high sulfur coals may have intrinsic properties capable of reducing mercury emissions. As part of this research in Task II, we examined mercury capture properties of different residue samples generated during combustion of high sulfur Illinois coal. Scrubber sludge (calcium sulfate type) samples exhibited considerable mercuric chloride removal capabilities. Statistical calculations revealed a strong positive correlation between the amount of calcium in the residue samples and mercuric chloride uptake. Higher percentages of calcium in these samples (such as scrubber sludge) led to a higher capture of mercuric chloride. On the other hand, the statistical calculations showed a strong negative correlation between mercuric chloride capture and the amount of aluminum, silicon, and iron in the residue samples. Higher percentages of these elements in the samples (such as fly ashes) led to a lower capture of mercuric chloride. Few combustion residue samples exhibited measurable elemental mercury capture. Statistical calculations, based on these limited results, indicated a strong positive correlation between concentration of bromine (Br) in the residue samples and elemental mercury capture. One may hypothesize that this capture can be effected through formation of Hg-Br bonds. Task II results may provide utility industries using Illinois coals strategies for reducing emissions of mercury, and means by which to utilize Illinois coal combustion residues.

## OBJECTIVES

The specific goals of the research were to study removal of volatile trace mercury from the flue gases using dry sorbent injection. Tests were performed under simulated combustion environments to identify the sorbent type and injection conditions most effective in reducing mercury emissions. These tasks were performed to meet the objectives:

- Perform bench-scale tests to study breakthrough capture of different species of mercury, elemental mercury ( $\text{Hg}^0$ ) and mercuric chloride ( $\text{HgCl}_2$ ), by an activated carbon and a calcium-based sorbent. Various capture conditions, including effect of  $\text{SO}_2$  (1000 ppm range) and HCl (50 ppm range) were examined.
- Evaluate mercury capture by different combustion residues produced from burning Illinois coals in different full-scale power plants.

## INTRODUCTION AND BACKGROUND

Metallic air toxics in flue gases are found in elemental or various oxidized forms and exist in the solid, aerosol, or vapor state. These compounds originate from the raw coal and are typically enriched in the fine particles (Markowski and Filby, 1985). The form and size distribution of each metal is a function of metal- and system-specific properties. For example, various concentrations of chlorine or sulfur have been shown to significantly affect the expected equilibrium product distribution (Linak and Wendt, 1993). Trace metals in flue gas streams are generally classified into three groups, based on their volatility and partitioning in the flue gas (Benson et al. 1993). Such a classification is not rigorous, and some species are placed in different classes by different references. Class I metals are the least volatile and are distributed between bottom ash and fly ash; Class II metals are more volatile, and are enriched in the fly ash; and Class III metals are the most volatile, and tend to escape with the vapor phase.

While particulate collection devices such as electrostatic precipitators and baghouses collect most of the metallic emissions, highly volatile metals (Class III) may form submicrometer aerosol fumes which are difficult to effectively collect. These submicrometer particles are particularly susceptible to human inhalation, resulting in significant health concerns. Mercury is considered Class III metals, and hence is of highest concern because it can be found at unacceptable levels in emissions from coal-fired utilities.

Without additional modifications, conventional flue gas desulfurization systems in MWCs are capable of removing mercury emissions to some extent (White et al., 1993). Limited tests performed by White and co-workers without specific control for mercury emissions showed a reduction in mercury emissions ranging from 24 to 76%.

If a sorbent can react with mercury species, then they will shift from the aerosol phase to the

large sorbent particle phase which can be collected effectively by a particulate control device.

To reduce mercury emissions in MWCs, injection of activated carbon has been shown to be a promising technology (White et al., 1993; Clarke, 1992). Nevertheless, several problems still exist, both economic and technical, concerning removal of mercury from flue gases.

The control of mercury emissions has been found to be strongly dependent on the form of mercury. Pilot-scale data (Schager, 1991) where activated carbon injection technology was used, showed the oxidized form to be more easily captured than elemental mercury ( $\text{Hg}^0$ ). Similar results were observed at the Electric Power Research Institute's High Sulfur Test Center's (HSTC) 4 MW pilot wet FGD system and at the MWC Sysav tests (Volland, 1991).

The ability to control mercury emissions varies with operating conditions. For instance, the presence of sulfur dioxide ( $\text{SO}_2$ ) has been associated with decreased mercury capture (Schager, 1991). The type of coal has also been found to affect different levels of mercury capture (Felsvang, 1992; 1993). The chlorine content in coal, capable of forming the less volatile and more water soluble mercuric chloride ( $\text{HgCl}_2$ ), is thought to be the factor for differences in mercury capture (Felsvang et al., 1993; DeVito et al., 1993).

For capture of metals, past pilot-scale work in the PI's laboratory (Gullett and Raghunathan, 1993) studied the effect of various dry sorbent injection processes in the emissions of coal-based metallic air toxics, including mercury. These tests involved furnace injection of four sorbents: hydrated lime, limestone, kaolinite and bauxite. Flue gas sampling was carried out using a mercury train and a size-classifying metals train. Without sorbent injection (baseline) almost all the mercury fed (as trace in coal) ended up in the vapor phase. However, both the calcium-based sorbents were effective in capturing mercury, reducing their vapor phase emissions substantially; kaolinite and bauxite had little effects. These results indicate that, for metal capture, simply providing additional surface, through sorbent injection, for metal condensation is not sufficient; a chemical affinity between the sorbent and the metal is necessary. However, little is known on the effect of other reaction parameters such as sorbent injection temperature, gas phase species (including  $\text{HCl}$  and  $\text{SO}_2$ ) and composition; and other kinetic variables.

A fundamental understanding of mercury capture by sorbents is essential in optimizing processes for mercury reduction. Bench-scale experiments have been performed to this extent to study  $\text{Hg}^0$  capture by different activated carbons in the PI's laboratories (Gullett and Jozewicz, 1993; Jozewicz et al., 1993; Krishnan et al., 1994). The results obtained from these studies indicate the importance of physical, structural, and chemical properties of the individual activated carbon. The other parameters of significance were the capture temperature and inlet  $\text{Hg}^0$  concentration. Recently several sorbents, including activated carbons and calcium hydroxide, were evaluated with respect to  $\text{HgCl}_2$  and  $\text{Hg}^0$  capture in the PI's laboratories. Preliminary results indicate the importance of reaction temperature and sorbent type on  $\text{HgCl}_2$  and  $\text{Hg}^0$  reduction.

Bench-scale experiments have been performed to obtain fundamental understanding of capture of mercury by activated carbons and calcium-based sorbents in the presence of low concentrations (100 ppm) of sulfur dioxide. Some of the important findings are listed below:

- Capture of  $\text{Hg}^0$  was found to depend strongly on the sorbent type and reaction conditions.
- Unlike the high capture of total mercury (approx. 90%) seen by investigators at the Camden county MWC (White et al., 1993), the same activated carbons showed much lower capture of  $\text{Hg}^0$  under similar conditions.
- In agreement with other investigators, preliminary results indicate that  $\text{HgCl}_2$  is more readily captured than  $\text{Hg}^0$ .
- Thermodynamic equilibrium predictions show that mercury exists mainly as  $\text{Hg}^0$  and  $\text{HgCl}_2$ . Altering  $\text{HCl}$  concentration shifts the equilibrium distribution. Unlike  $\text{HCl}$ ,  $\text{SO}_2$  was found not to influence the equilibrium distribution.
- Condensation of water vapor present in the simulated flue gas may increase mercuric chloride sorption of activated carbons.
- Presence of  $\text{SO}_2$  enhanced the capture of elemental mercury by calcium-based sorbents. This may be due to the creation of active sulfur (S) sites and subsequent chemisorption of  $\text{Hg}^0$  by these sorbents.
- Presence of  $\text{SO}_2$  inhibited the capture of mercuric chloride by calcium-based sorbents. This may be due to the competition of  $\text{SO}_2$  with  $\text{HgCl}_2$  for the sorbent alkaline sites.
- One type of coal fly ash (very high carbon content) exhibited comparable  $\text{Hg}^0$  and  $\text{HgCl}_2$  sorption activity to an activated carbon (FGD), indicating its potential effectiveness as a mean of mercury control in coal-fired utility boilers

Some important findings from pilot-plant tests are:

- For uncontrolled emissions, nearly all the mercury evolved from coal combustion was found in the vapor phase.
- Injection of limestone and hydrated lime was effective in capturing mercury, while kaolinite and bauxite sorbents had little effect.
- High temperature (1000-700°C)/in-flight (residence time of around 2 seconds) capture of mercury can be effected through injection of calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ].

## EXPERIMENTAL PROCEDURES

Figure 1 illustrates the schematic of the bench-scale apparatuses used to study capture of elemental mercury and mercuric chloride. 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 generated  $\text{HgCl}_2$  or  $\text{Hg}^0$  vapor was carried into the main system by a nitrogen stream

where it mixed with the simulated flue gas in the manifold. A three-way valve placed before the manifold diverted the mercury-laden stream away from the manifold when desired. The first three-way valve placed after the manifold was used to direct flow to and away from the fixed-bed reactor. The tested sorbents were placed in the reactor which was maintained at the desired system temperature. A furnace kept at 850°C was placed on-line to convert any oxidized Hg ( $\text{Hg}^{++}$ ) to  $\text{Hg}^0$ . According to the thermodynamic predictions, the only mercury species at this temperature is  $\text{Hg}^0$ . The presence of the furnace enabled on-line detection of non-adsorbed  $\text{HgCl}_2$  as  $\text{Hg}^0$  by the on-line ultraviolet  $\text{Hg}^0$  analyzer thus providing actual  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture by the fixed-bed of sorbents.

Prior to the  $\text{Hg}^0$  analyzer, water vapor was removed from the flue gases. NAFION® gas sample dryers (Perma Pure Inc.) were used to selectively remove water vapor from the effluent of the fixed-bed reactor. Repeated quality checks have indicated that this system has no affinity toward adsorption of elemental mercury and acid gases present in the flue gas.

Continuous on-line UV  $\text{Hg}^0$  analysis was performed with Buck 400A analyzers. The UV elemental mercury analyzer responded to sulfur dioxide concentrations as well as elemental mercury. For instance, a gas stream consisting of 200 ppm  $\text{SO}_2$  and 3 ppb  $\text{Hg}^0$  produced a  $\text{SO}_2$  to  $\text{Hg}^0$  signal response in the  $\text{Hg}^0$  analyzer equal to a ratio of approximately 8 to 18 in strength. Considering this, the analysis should account for changes in  $\text{SO}_2$  and  $\text{Hg}^0$  signal in the UV analyzer. This was accomplished by placing a sulfur dioxide analyzer on-line after the  $\text{Hg}^0$  analyzer. The  $\text{SO}_2$  analyzer was incapable of detecting mercury in the range of this study (8 to 80 ppb). By subtracting the  $\text{SO}_2$  signal obtained using the  $\text{SO}_2$  analyzer ( $\text{SO}_2$  signal corresponding to the mercury analyzer) from the total response of the mercury analyzer, the change in mercury concentration was obtained.

Baseline measurements of  $\text{Hg}^0$  in the by-pass mode (no fixed-bed reactor) revealed a major interference caused by HCl in the on-line  $\text{Hg}^0$  analysis system. Repeated tests confirmed that HCl reacted with  $\text{Hg}^0$  in the gas-phase and at the outlet of the furnace (most probably at a temperature range of 600°C), thus converting portions of  $\text{Hg}^0$  back to  $\text{HgCl}_2$ , which is not detectable by the on-line  $\text{Hg}^0$  analyzer. This interference undermines the usage of the furnace as the ionic mercury thermal converter. Two different procedures were adopted to overcome the interferences caused by HCl. In the first procedure, fixed-beds of different alkaline materials were placed downstream of the fixed-bed reactor and upstream of the furnace, to selectively scrub HCl from the simulated flue gas. This procedure was unsuccessful since all the conventional alkaline materials tested [ $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Mg}(\text{OH})_2$ ] were also effective in removing  $\text{HgCl}_2$  from the flue gas, thus making this procedure a non-selective removal system. This is not surprising, however, since  $\text{HgCl}_2$  (an acid gas) has similar acidic properties as HCl; an alkaline material that removes one effectively, should also be relatively effective in removing the other one. In the second procedure, a non-thermal method was adopted to convert ionic mercury to  $\text{Hg}^0$ . The objective was to avoid the temperature window of 600°C, which may be the optimum region for conversion of  $\text{Hg}^0$  to  $\text{HgCl}_2$  in the presence

of HCl. It has been reported that a saturated solution of stannous chloride ( $\text{SnCl}_2$ ) has the potential to convert ionic mercury to  $\text{Hg}^0$  at room temperature. An impinger of a saturated solution of  $\text{SnCl}_2$  in water was installed parallel to the furnace (thermal converter). Baseline  $\text{Hg}^0$  concentration was established using the furnace while flowing a known concentration of  $\text{HgCl}_2$  through the system. The flow of the flue gas was then directed away from the furnace and into the impinger and the on-line  $\text{Hg}^0$  analyzer. At best only 50% of the incoming  $\text{HgCl}_2$  was recovered, indicating that the  $\text{SnCl}_2$  solution was incapable of converting all the ionic mercury to  $\text{Hg}^0$ . This procedure can not be considered as a viable method to reduce ionic mercury. Since both these procedures were unsuccessful in eliminating HCl interferences in the on-line mercury analysis system, an off-line method was adopted. In this method, the sorbents were exposed to the mercury species ( $\text{HgCl}_2$  and  $\text{Hg}^0$ ) laden flue gases for a period of 24 hours and subsequently the amount of mercury adsorbed on the sorbent was determined using X-Ray Fluorescence (XRF) technique.

## RESULTS AND DISCUSSION

The results of each task are discussed separately in this section.

### Task I: Effects of $\text{SO}_2$ and HCl on mercury species capture

The bench-scale setup (Figure 1) was used to study the effects of two coal combustion acid gases on the mercury species capture. Typical coal combustion  $\text{SO}_2$  (1000 ppm) and HCl (50 ppm) concentrations were used throughout this study to simulate the coal combustion conditions. Previous investigations conducted for ICCI (Gullett et al., 1996) identified activated carbons as efficient  $\text{Hg}^0$  sorbents and calcium-based compounds as efficient  $\text{HgCl}_2$  sorbents. Hence, the focus of this study was on evaluating the effects of acid gases on the removal of  $\text{Hg}^0$  by an activated carbon (FGD, Norit Americas Inc.) and  $\text{HgCl}_2$  by calcium hydroxide [ $\text{Ca}(\text{OH})_2$ ]. The primary factors affecting the sorption of mercury species are the bed temperature and the inlet mercury concentration. Prior to the acid gases studies, a preliminary investigation was conducted to obtain the temperature/mercury concentration behavior of the sorbents under the baseline (no acid gases) conditions. Following the baseline tests, the effect of acid gases was studied by adding these compounds to the baseline conditions on an individual basis and combined (synergistic/antagonistic effects). Results are discussed separately for  $\text{HgCl}_2$  and  $\text{Hg}^0$ .

### *Effects of temperature, concentration, and acid gases on $\text{HgCl}_2$ capture by $\text{Ca}(\text{OH})_2$ :*

As mentioned, the efficient and cost effective sorbents for  $\text{HgCl}_2$  capture are calcium-based compounds.  $\text{Ca}(\text{OH})_2$  was chosen as the  $\text{HgCl}_2$  sorbent. A detailed description of  $\text{Ca}(\text{OH})_2$  is included elsewhere (Gullett et al., 1996). Briefly, calcium hydroxide (reagent grade, Sigma Inc.) is 97.6%  $\text{Ca}(\text{OH})_2$  and 1.8%  $\text{CaCO}_3$ . It has a total surface area (external and pore) of  $13 \text{ m}^2/\text{g}$  and an average pore diameter of 33.4 nm. During the baseline tests, 20 mg of

$\text{Ca}(\text{OH})_2$  was used in the fixed-bed reactor. Empty reactor results indicated no removal of  $\text{HgCl}_2$ .

$\text{HgCl}_2$  capture by  $\text{Ca}(\text{OH})_2$  was evaluated under the baseline conditions ( $\text{N}_2$  and  $\text{HgCl}_2$  only) as a function of the two primary parameters: bed temperature (60, 100, 140°C) and inlet  $\text{HgCl}_2$  concentration (11, 38, 73 ppb, or 90, 311, 597  $\mu\text{g}/\text{dscm}$ ). The studied temperature range was chosen to reflect the conditions in the air pollution control systems of coal-fired utility boilers. The chosen concentration range reflects the very high end of those encountered in coal-fired utility boilers. It was determined that optimum baseline/ $\text{SO}_2$  comparisons can be made under these relatively high  $\text{HgCl}_2$  concentrations (very low  $\text{SO}_2$  interferences in the mercury analyzer, cf. Experimental Procedure). The baseline results are shown in Figure 2. This figure shows that during an exposure time of 5 hours,  $\text{Ca}(\text{OH})_2$  never reached its maximum capacity. A number of these tests were run overnight at exposure times of greater than 24 hours; maximum capacities were never reached. This observation may indicate an abundance of  $\text{HgCl}_2$  adsorption sites on  $\text{Ca}(\text{OH})_2$ . Considering the acidic nature of gaseous  $\text{HgCl}_2$ , these sites can be hypothesized to be alkaline. Figure 2 shows that the inlet  $\text{HgCl}_2$  concentration (or its partial pressure) is an important parameter in determining the amount captured. After 5 hours of exposure, increasing the concentration of  $\text{HgCl}_2$  by a factor of 6.6 (from 11 to 73 ppb), increased the captured amount by a factor of 10. The bed temperature was a less important factor in  $\text{HgCl}_2$  capture; increasing the temperature from 60 to 140°C, decreased the captured amount by a factor of 1.4. From findings in adsorption processes, we know that a rise in partial pressure and a fall in temperature results in an increase in the amount of material adsorbed. The temperature and concentration trends observed here, indicate that the process is an adsorption (physical and/or chemical) controlled process and what determines the rate of  $\text{HgCl}_2$  capture is how fast these molecules at the vicinity of the sites are captured physically and/or chemically.

The effect of  $\text{SO}_2$  on the  $\text{HgCl}_2$  capture by  $\text{Ca}(\text{OH})_2$  was studied by adding 1000 ppm  $\text{SO}_2$  to the  $\text{N}_2/\text{HgCl}_2$  stream, while keeping the total flow through the fixed-bed constant. The results are shown in Figure 3. This figure shows the effect of  $\text{SO}_2$  at a constant inlet  $\text{HgCl}_2$  concentration of 38 ppb for the three studied temperatures. At the low temperature (60°C),  $\text{SO}_2$  had no effect. However, increasing the temperature drastically reduced the sorption capacity of  $\text{Ca}(\text{OH})_2$  in the presence of  $\text{SO}_2$ . It appears that  $\text{Ca}(\text{OH})_2$  and  $\text{SO}_2$  may react at the higher temperatures, leading to destruction of the available active (alkaline) sites needed for  $\text{HgCl}_2$  capture. The presence of  $\text{SO}_2$  limited the capture of  $\text{HgCl}_2$  by  $\text{Ca}(\text{OH})_2$  to no more than 0.5-1 mg  $\text{HgCl}_2/\text{g Ca}(\text{OH})_2$ . This number probably represents the maximum number of available active sites when  $\text{SO}_2$  is present in the flue gas stream at a concentration of 1000 ppm.

The effect of  $\text{HCl}$  was studied using the off-line method (XRF technique). In the fixed-bed system (Figure 1), about one gram of  $\text{Ca}(\text{OH})_2$  was exposed to the  $\text{HgCl}_2$  laden flue gas at a bed temperature of 100°C for a total exposure time of 24 hours at a total system flowrate



of 350 cm<sup>3</sup>/min. Six runs at different flue gas conditions were performed to deduce the effect of HCl in the presence and absence of SO<sub>2</sub> (Table 1). Run #1a was the blank run in which the fixed-bed of Ca(OH)<sub>2</sub> was exposed to a stream of N<sub>2</sub>. As expected, the XRF analysis of the exposed sorbent revealed no peak for mercury. It should be noted that the presence of mercury in solid samples (sorbents) is detected by XRF technique as a single peak with a measurable intensity (in Kilo count per second per gram of sorbent, Kc/s/g) which is directly proportional to the mercury concentration in the sorbent. In run #2a (the baseline run), the sorbent was exposed to a flow of 73 ppb HgCl<sub>2</sub> in N<sub>2</sub>. XRF analysis of the exposed sorbent revealed a mercury intensity of 0.3768 Kc/s/g; the highest intensity observed during the off-line HgCl<sub>2</sub> test program. This observation suggests that Ca(OH)<sub>2</sub> is active toward adsorption of HgCl<sub>2</sub> when no other species is present in the flue gas. This is also in agreement with the on-line HgCl<sub>2</sub> capture studies discussed above.

Runs #3a and #4a were duplicates in which the sorbent was exposed to a flow of 73 ppb HgCl<sub>2</sub> and 50 ppm HCl. Mercury intensities of 0.2061 and 0.1797 Kc/s/g were obtained indicating an experimental variation of 13% which is considered to be acceptable precision. As indicated by the intensities (directly proportional to the solid-phase concentration), the presence of HCl inhibits the HgCl<sub>2</sub> capture capability of Ca(OH)<sub>2</sub> by a factor of about two. Run #5a was designed to once again illustrate the effect of SO<sub>2</sub> on the capture of HgCl<sub>2</sub> by Ca(OH)<sub>2</sub>. In the on-line HgCl<sub>2</sub> studies performed previously, it was determined that SO<sub>2</sub> at a concentration range of 1000 ppm (typical of Illinois coal) can drastically decrease the sorption capability of Ca(OH)<sub>2</sub> at a bed temperature range of 100-140°C (Figure 3). In run #5a (Table 1), the sorbent was exposed to a flow of N<sub>2</sub>, 73 ppb HgCl<sub>2</sub>, and 1000 ppm SO<sub>2</sub>. The presence of SO<sub>2</sub> inhibited the HgCl<sub>2</sub> capture by a factor of about 5. It appears that SO<sub>2</sub> at a concentration range of 1000 ppm was a more influential inhibitor than HCl at a concentration range of 50 ppm. Finally in run #6a, the sorbent was exposed to both SO<sub>2</sub> and HCl simultaneously. Considering the experimental variability of about 13%, the results of run #6a indicate the prevailing inhibition effect of SO<sub>2</sub> on the HgCl<sub>2</sub> capture by Ca(OH)<sub>2</sub> and the fact that inhibition effects of HCl and SO<sub>2</sub> are not additive.

Previous on-line studies indicated that at a flue gas composition of 73 ppb HgCl<sub>2</sub> and 1000 ppm SO<sub>2</sub> in N<sub>2</sub> and a temperature of 100°C, Ca(OH)<sub>2</sub> reached its HgCl<sub>2</sub> saturation capacity of 1.28 mg HgCl<sub>2</sub>/g Ca(OH)<sub>2</sub> after 5 hours of exposure (Figure 3). This value is indicated in the fourth column in Table 1. Using the linear proportionality between solid-phase mercury concentration and intensities, the captured amounts of HgCl<sub>2</sub> during the remaining five runs were calculated and included in Table 1. In summary, these studies indicate that presence of 50 ppm HCl in the simulated flue gas can decrease the HgCl<sub>2</sub> sorption capability of Ca(OH)<sub>2</sub> by half. The inhibition effect of 1000 ppm SO<sub>2</sub> is even more drastic (factor of five), and essentially controls the uptake of HgCl<sub>2</sub>. The inhibition effects of these acid gases are not additive. Based on these results one may conclude that the optimum region for the control of HgCl<sub>2</sub> by injection of Ca(OH)<sub>2</sub> is downstream of the acid gas removal devices.

**Table 1. Effect of HCl (50 ppm) on the HgCl<sub>2</sub> (73 ppb) capture by Ca(OH)<sub>2</sub> in the absence and presence of SO<sub>2</sub> (1000 ppm)**

Run #	Flue gas component	Normalized XRF Hg intensity (Kilo count/sec/g)	Solid-phase mercury concentration [mg HgCl <sub>2</sub> / gCa(OH) <sub>2</sub> ]
1a	N <sub>2</sub> (blank)	0	0
2a	N <sub>2</sub> + HgCl <sub>2</sub> (baseline)	0.3768	6.03
3a	N <sub>2</sub> + HgCl <sub>2</sub> + HCl	0.2061	3.30
4a	N <sub>2</sub> + HgCl <sub>2</sub> + HCl (duplicate)	0.1797	2.88
5a	N <sub>2</sub> + HgCl <sub>2</sub> + SO <sub>2</sub>	0.080	1.28
6a	N <sub>2</sub> + HgCl <sub>2</sub> + HCl + SO <sub>2</sub>	0.1115	1.78

***Effects of temperature, concentration, and acid gases on Hg<sup>0</sup> capture by FGD:***

As mentioned, activated carbons are efficient sorbents for Hg<sup>0</sup> capture. Activated carbon DARCO®FGD (Norit Americas Inc.) was chosen as the Hg<sup>0</sup> sorbent. A detailed description of this compound is included elsewhere (Gullett et al., 1996). Briefly, FGD is a lignite-coal-based activated carbon with a total carbon content of around 70%, total surface area (external and pore) of 575 m<sup>2</sup>/g, and an average pore diameter of 3.2 nm. During the baseline tests, 20 mg of FGD was diluted by 2 g sand in the fixed-bed to prevent any potential channeling of the flue gases. Baseline results indicated no removal of Hg<sup>0</sup> by sand and empty reactor.

Hg<sup>0</sup> capture by FGD was evaluated under the baseline conditions as a function of the two primary parameters: bed temperature (60, 100, 140 °C) and inlet Hg<sup>0</sup> concentration (8, 20, 40 ppb or 65, 164, 327 µg/dscm). The baseline results are shown in Figure 4. Unlike HgCl<sub>2</sub> capture by Ca(OH)<sub>2</sub>, during a typical 5 hour run, the sorbent (FGD) reached its saturation capacity, indicating that the available active sites for capturing Hg<sup>0</sup> in the activated carbon are limited. Considering that activated carbon may be a much better sorbent than Ca(OH)<sub>2</sub>, due to its higher surface area, the comparison between Hg<sup>0</sup> and HgCl<sub>2</sub> results (Figures 2 and 4) suggests the degree of difficulty in controlling Hg<sup>0</sup>, and the fact that the sites needed for Hg<sup>0</sup> capture are less abundant than those needed to capture HgCl<sub>2</sub>. It should be noted that the baseline tests conducted with Ca(OH)<sub>2</sub> as the Hg<sup>0</sup> sorbent yielded no capture, indicating its ineffectiveness due to lack of Hg<sup>0</sup> active sites.

From Figure 4 it is apparent that, unlike HgCl<sub>2</sub> capture by Ca(OH)<sub>2</sub>, the amount of captured Hg<sup>0</sup> was much more influenced by the bed temperature than the inlet concentration. Increasing the temperature decreased the amount captured, the rate of capture (kinetic), and the time needed to reach the maximum capture (equilibrium). Increasing the inlet Hg<sup>0</sup>

concentration increased the amount captured, the rate of capture, and the time needed to reach the maximum capture. Similar to the  $\text{HgCl}_2$  case, the temperature and concentration trends suggest that the process is adsorption controlled.

The effect of  $\text{SO}_2$  on  $\text{Hg}^0$  capture by FGD was studied by adding 1000 ppm  $\text{SO}_2$  to the 40 ppb  $\text{Hg}^0$  in  $\text{N}_2$  stream while keeping the total flow through the fixed-bed constant. Figure 5 shows the effect of  $\text{SO}_2$  at a constant inlet  $\text{Hg}^0$  concentration of 40 ppb for the three studied temperatures. Similar to the  $\text{HgCl}_2$  case, at the lower end of the temperature range ( $60^\circ\text{C}$ ),  $\text{SO}_2$  had basically no effect on the  $\text{Hg}^0$  uptake by FGD. However, increasing the temperature drastically increased the  $\text{Hg}^0$  capture capabilities of FGD in the presence of  $\text{SO}_2$ . It appears that at higher temperatures,  $\text{SO}_2$  reacted with FGD and created sulfur (S) sites, which are considered to be very active in capturing  $\text{Hg}^0$  (Krishnan et al., 1994). The activity of FGD in the presence of  $\text{SO}_2$  at higher temperatures resembled that of sulfur impregnated activated carbon studied by Krishnan et al. (1994). These results may indicate that, in Illinois coal-fired utility boilers, optimum capture of  $\text{Hg}^0$  can be obtained by injecting activated carbon prior to the  $\text{SO}_2$  removal system.

The effect of HCl was studied using the off-line method (XRF analysis). In the fixed-bed system (Figure 1), about 0.1 gram of activated carbon, FGD, was exposed to the  $\text{Hg}^0$  laden flue gas at a bed temperature of  $100^\circ\text{C}$  for a total exposure time of 24 hours at a total system flowrate of  $300\text{ cm}^3/\text{min}$ . Similar to the  $\text{HgCl}_2$  studies, 6 runs at different flue gas conditions were performed to deduce the effect of HCl on  $\text{Hg}^0$  uptake by FGD in the presence and absence of  $\text{SO}_2$  (Table 2). Run #1b was the blank run in which the fixed-bed of FGD was exposed to a stream of  $\text{N}_2$  and, as expected, no mercury peak was detected. It should be noted that the detection limit of the XRF technique is around 20 ppm (0.02 mg/g). In run #2b (the baseline run), the sorbent (FGD) was exposed to a flow of  $\text{N}_2$  and 40 ppb  $\text{Hg}^0$ . Subsequent XRF analysis of the exposed sorbent revealed a mercury intensity of 0.3263 (Table 2), the lowest intensity observed during the  $\text{Hg}^0$  test program. This observation suggests that, unlike  $\text{HgCl}_2$  capture by  $\text{Ca}(\text{OH})_2$ , FGD is least active toward adsorption of  $\text{Hg}^0$  when no other acid gas species is present in the flue gas. This is also in agreement with the on-line  $\text{Hg}^0$  capture studies discussed above.

Runs #3b and #4b were duplicates in which the sorbent was exposed to a flow of  $\text{N}_2$ , 40 ppb  $\text{Hg}^0$ , and 50 ppm HCl under identical conditions as runs #1b and #2b. Mercury intensities of 1.5562 and 1.4923 Kc/g/s were obtained, indicating an experimental variability of about 4%. As indicated by the intensities, unlike  $\text{HgCl}_2$  capture by  $\text{Ca}(\text{OH})_2$ , the presence of HCl enhanced the  $\text{Hg}^0$  capture capability of FGD by a factor of about 5. It appears that HCl reacted with FGD under these conditions and created chlorine (Cl) sites, which may be considered to be very active in capturing  $\text{Hg}^0$ . Run #5b was designed to once again deduce the effect of  $\text{SO}_2$  on the capture of  $\text{Hg}^0$  by FGD. In the on-line studies performed previously, it was determined that  $\text{SO}_2$  at a concentration range of 1000 ppm, can enhance the sorption capability of FGD at a bed temperature range of  $100\text{-}140^\circ\text{C}$  (Figure 5). In run #5b (table 2),

the sorbent was exposed to a flow of 40 ppb  $\text{Hg}^0$  and 1000 ppm  $\text{SO}_2$  in  $\text{N}_2$ ; the presence of  $\text{SO}_2$  enhanced the  $\text{Hg}^0$  capture by a factor of about 3. It appears that HCl at a concentration range of 50 ppm had a more pronounced enhancement effect on the  $\text{Hg}^0$  uptake than 1000 ppm  $\text{SO}_2$ , suggesting that the "Cl sites" created in the presence of HCl may be more active (or more abundant) than the "S sites" created in the presence of  $\text{SO}_2$ .

Finally in run #6b, the sorbent (FGD) was exposed to both  $\text{SO}_2$  and HCl simultaneously. Under these conditions, the enhancement effect was the highest at a factor of about 6, indicating that both created active sites were instrumental (but not additive) in capturing  $\text{Hg}^0$  simultaneously. Previous on-line studies indicated that under the baseline conditions (run #2b, table 2), and at a fixed-bed temperature of  $100^\circ\text{C}$ , FGD reached its elemental mercury saturation capacity of 0.187 mg  $\text{Hg}^0/\text{g}$  FGD after about 5 hours of exposure. This value is indicated in the fourth column in Table 2. Using the linear proportionality between solid-phase mercury concentration and intensities, the captured amounts of  $\text{Hg}^0$  during the remaining five runs were calculated and included in this table.

**Table 2. Effect of HCl (50 ppm) on the  $\text{Hg}^0$  (40 ppb) capture by activated carbon, FGD, in the absence and presence of  $\text{SO}_2$  (1000 ppm)**

Run #	Flue gas component	Normalized XRF Hg intensity (Kilo count/sec/g)	Solid-phase mercury concentration (mg $\text{Hg}^0/\text{g}$ FGD)
1b	$\text{N}_2$ (blank)	0	0
2b	$\text{N}_2 + \text{Hg}^0$ (baseline)	0.3263	0.187
3b	$\text{N}_2 + \text{Hg}^0 + \text{HCl}$	1.5562	0.892
4b	$\text{N}_2 + \text{Hg}^0 + \text{HCl}$ (duplicate)	1.4923	0.855
5b	$\text{N}_2 + \text{Hg}^0 + \text{SO}_2$	0.9586	0.549
6b	$\text{N}_2 + \text{Hg}^0 + \text{HCl} + \text{SO}_2$	1.8712	1.072

It was hypothesized that exposing FGD to the acid gases (HCl and  $\text{SO}_2$ ) creates active Cl and S sites. Analysis of these elements in the exposed sorbent could potentially provide some evidence for this hypothesis. The concentrations of Cl and S in the exposed FGD were determined using the XRF technique; results are summarized in Table 3. The concentration of chlorine in FGD exposed to  $\text{N}_2$  was 0.226%. This is the background amount of chlorine present in activated carbon, FGD (sample #1). The Cl concentration in FGD exposed to HCl and  $\text{Hg}^0$  for 24 hours, increased to 0.547%; a 2.4 fold increase in chlorine concentration. The increased concentration (or number) of chlorine atoms might then have been instrumental in capturing  $\text{Hg}^0$  (see Table 2). The presence of  $\text{SO}_2$  in the flue gas decreased the chlorine uptake by FGD (sample #3), however it created sulfur sites (sample #5) which were

hypothesized to be active in capturing  $\text{Hg}^0$ . The concentration of sulfur (S) in FGD exposed to  $\text{N}_2$  was 0.856%. This is the background amount of sulfur present in activated carbon, FGD (sample #4). The sulfur concentration in FGD exposed to  $\text{SO}_2$  and  $\text{Hg}^0$  for 24 hours increased to 1.819%; a 2.1 fold increase in sulfur concentration (sample #5). The presence of HCl apparently did not have any effect on the sulfur uptake by FGD (sample #6). In summary, it appears that the presence of acid gases in the simulated flue gas creates active sites that are instrumental in capturing elemental mercury. Based on these results, one may conclude that the optimum region for the control of  $\text{Hg}^0$  by injection of activated carbon, FGD, is upstream of the acid gas removal systems.

**Table 3. Concentration (%wt) of chlorine (Cl) and sulfur (S) in the exposed FGD to the simulated flue gas.**

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

Task II: Performance Evaluation of Illinois Coal Combustion Residues:

In this Task,  $\text{HgCl}_2$  and  $\text{Hg}^0$  capture capabilities of nine different Illinois coal combustion residues were evaluated. The samples were obtained from the Illinois Basin Coal Combustion Residues Sample Program (CRSP). Table 4 summarizes the sample designations. Power plant #1 is located in southern Illinois and burns Herrin (No. 6) coal which is mined in southern Illinois. The coal is combusted in pulverized coal combustion (PCC) and cyclone boilers. Power plant #2 is located near the Illinois-Indiana border. It burns Springfield (No. 5) and Herrin (No. 6) coals that are combusted in PCC boilers. This plant has two wet limestone scrubber units; one utilizes an inhibited oxygen cycle and the other employs a forced-oxidation cycle. Power plant #3 is located in central Illinois and burns Herrin (No. 6) and Springfield (No. 5) coals which are mined in southern and central Illinois, respectively. This plant uses a fluidized-bed combustion technology. Power plant #4 is located in central Illinois and burns Springfield (No. 5) coal. The coal is combusted in one PCC boiler and two cyclone boilers. A wet limestone scrubber utilizing a forced-oxidation cycle has been installed on the PCC unit. The scrubber sludge sample from this power plant is not fixated.

**Table 4. Illinois coal combustion residue designations**

Sample ID #	Power Plant #	Sample Type
1PPB	1	Bottom Ash (PCC Boiler)
1PCB	1	Bottom Ash (Cyclone Boiler)
2PPF	2	Fly Ash
2PPB	2	Bottom Ash
2PPS	2	Scrubber Sludge (inhibited oxygen cycle)
3PF	3	Fly Ash
4PPF	4	Fly Ash
4PPB	4	Bottom Ash
4PPIS	4	Scrubber Sludge (forced-oxidation cycle)

HgCl<sub>2</sub> sorption evaluation of the residue samples were conducted in the fixed-bed reactor setup (Figure 1) under the following conditions: 73 ppb HgCl<sub>2</sub>, 10% carbon dioxide, 7% oxygen, 5% water vapor, 173 ppm sulfur dioxide, and balance N<sub>2</sub>; total system flowrate of 350 cc/min, fixed-bed temperature of 100 °C, and 0.1 gram of sorbent. Of the nine samples (Table 4), four exhibited considerable mercuric chloride removal capabilities; they are 2PPS, 4PPIS, 1PPB, and 3PF. These results in comparison to the activated carbon (FGD) and Ca(OH)<sub>2</sub> are shown in Figure 6. FGD and Ca(OH)<sub>2</sub> exhibited better performances than these samples. Sample # 2PPS exhibited a relatively good HgCl<sub>2</sub> capture capability; initially it removed about 50% of incoming HgCl<sub>2</sub> with a slow decrease (note the log scale of the time axis) to a value of 25% after 240 minutes of exposure. Sample # 2PPS is a scrubber sludge sample from power plant #2, which uses a limestone wet scrubber. One may relate the HgCl<sub>2</sub> removal activity of this sample to the presence of calcium compounds in this sludge. The other scrubber sludge sample (4PPIS) also exhibited considerable HgCl<sub>2</sub> removal capability (Figure 6). The HgCl<sub>2</sub> capture capabilities of the remaining five samples in comparison to FGD and Ca(OH)<sub>2</sub> are shown in Figure 7. As indicated, only sample #4PPB (a bottom ash) exhibited some HgCl<sub>2</sub> capture. Most of these samples were exhausted after 10-50 minutes of exposure to the HgCl<sub>2</sub> laden flue gas.

Hg<sup>0</sup> sorption evaluation of the residue samples were conducted in the fixed-bed reactor setup (Figure 1) under the following conditions: 40 ppb Hg<sup>0</sup>, 10% carbon dioxide, 7% oxygen, 5% water vapor, 173 ppm sulfur dioxide, and balance N<sub>2</sub>; total system gas flowrate of 350 cc/min, fixed-bed temperature of 100 °C, and 0.1 gram of sorbent. Of the nine samples (Table 2), only two exhibited measurable Hg<sup>0</sup> removal; they are 3PF and 2PPS. These results in comparison to the activated carbon (FGD) and Ca(OH)<sub>2</sub> are shown in Figure 8. Sample

3PF initially removed about 13% of the incoming  $\text{Hg}^0$ ; this removal decreased as time of exposure progressed. The sample was exhausted after 20 minutes of exposure. Both  $\text{Ca}(\text{OH})_2$  and 2PPS showed negligible (3-4%)  $\text{Hg}^0$  removal.

To correlate the chemical composition of the residue samples to their  $\text{Hg}^0$  and  $\text{HgCl}_2$  removal capabilities, the elemental compositions of these samples were quantified. The residue samples were analyzed for their elemental composition using a Siemens 303 X-Ray Fluorescence (XRF) analyzer. Table 5 outlines the elemental compositions of the residue samples. Based on these data the samples can be categorized as follows:

Category 1: Calcium Sulfate ( $\text{CaSO}_4$ ) type- 2PPS and 4PPIS (scrubber sludge samples) both contained predominantly calcium (24% wt) and sulfur (18% wt). These samples also exhibited considerable  $\text{HgCl}_2$  removal. Thus, there seems to be a correlation between presence of calcium and  $\text{HgCl}_2$  removal capability. Statistical calculations confirmed a strong positive correlation between the amount of Ca in the residue samples and  $\text{HgCl}_2$  uptake. Higher percentages of Ca in these samples led to higher capture of  $\text{HgCl}_2$ . Scrubber sludge samples can be used as  $\text{HgCl}_2$  sorbents.

Category 2: Fly ash type- 2PPB, 4PPB, 1PCB, 2PPF, and 4PPF contained elevated levels of silicon (20%-30%) and aluminum (6.5%-11%) and low levels of calcium (2.4%-4.2%) and trace levels of sulfur (0.02%-1.0%). These samples, consequently, did not exhibit considerable  $\text{HgCl}_2$  removal. Statistical calculations showed a strong negative correlation between the  $\text{HgCl}_2$  uptake and the amount of aluminum (Al), silicon (Si), and iron (Fe) in the residue samples. Higher percentages of Al, Si, and Fe in these samples (fly ash type) led to a lower capture of  $\text{HgCl}_2$ . These fly ash type samples were also not active toward  $\text{Hg}^0$  adsorption. Carbon content of these samples was not measured, however visual inspection revealed that these fly ashes contain very low amounts of carbon. It is believed that,  $\text{Hg}^0$  removal may be correlated to the carbon content of the sorbents. Lack of  $\text{Hg}^0$  removal activities of these samples may be related to the low amount of their carbon content.

Category 3: Calcium/fly ash type- 3PF is in this category. It has characteristics of both calcium-based and fly ash-based materials. 3PF contained 19.5% calcium, 12.8% silicon, 4.3% aluminum and 6.4% sulfur. 3PF was the only sample that exhibited some  $\text{Hg}^0$  capture capabilities. Further review of the XRF analysis revealed that unlike the other residue samples, 3PF contains bromine (Br) at a low concentration of 8.5 ppm (0.00085 wt%). It was previously shown that the presence of chlorine (Cl) on activated carbon enhances capture of  $\text{Hg}^0$ . In this case, Br (a halogen element) might have been instrumental in the adsorption of  $\text{Hg}^0$ . Statistical calculations, based on the limited  $\text{Hg}^0$  data, also indicated a strong positive correlation between concentration of Br in the residue sample and  $\text{Hg}^0$  capture. Sample 3PF also showed considerable  $\text{HgCl}_2$  removal (due to the presence of Ca). Further investigation of this potentially useful combustion residue is needed to understand its  $\text{Hg}^0$  and  $\text{HgCl}_2$  removal capabilities.

**Table 5. Elemental compositions of Illinois coal combustion residues (wt%)**

Element	Sample Identification (see Table 4)								
	2PPS	4PPIS	4PPF	2PPF	4PPB	2PPB	1PPB	1PCB	3PF
Na	0.043	0.025	0.812	1.01	0.536	0.430	0.548	0.283	0.457
Mg	0.544	0.094	0.499	0.634	0.402	0.496	0.536	0.503	3.54
Al	0.174	0.047	8.22	11.2	6.55	8.4	7.34	7.93	4.35
Si	1.190	0.412	30.8	25.1	26.2	21.4	27.9	20.4	12.8
P	0.013	0.025	0.061	0.057	0.043	0.061	0.061	0.070	0.048
S	18.4	18.4	0.696	1.04	0.142	0.330	0.248	0.028	6.4
K	0.070	0.019	1.42	1.86	1.12	1.58	1.25	1.47	1.01
Ca	24.9	24.2	3.19	2.46	3.81	3.34	4.2	3.8	19.5
Ti	0.024	0.004	0.348	0.451	0.278	0.346	0.289	0.032	0.114
Mn	0.010	0.006	0.041	0.033	0.046	0.037	0.056	0.046	0.043
Fe	0.151	0.057	8.34	8.35	7.24	7.5	7.3	7.56	4.71
Cu	0.001	0.001	0.006	0.016	0.004	0.008	0.005	0.005	0.005
Sr	0.025	0.009	0.018	0.027	0.012	0.021	0.014	0.016	0.031

### CONCLUSION AND RECOMMENDATIONS

- Calcium hydroxide [Ca(OH)<sub>2</sub>] contains abundant sites capable of capturing HgCl<sub>2</sub> and lacks the necessary active sites for the removal of Hg<sup>0</sup>.
- Inlet HgCl<sub>2</sub> concentration is an important parameter in determining the rate and the amount captured by Ca(OH)<sub>2</sub>.
- Reaction of SO<sub>2</sub> and Ca(OH)<sub>2</sub> at higher temperature ranges (100-140°C) destroys the majority of HgCl<sub>2</sub> adsorption sites.
- Thermally activated carbon (FGD) contains a limited number of active-sites capable of capturing Hg<sup>0</sup>.
- System temperature is an important parameter in determining the rate and the amount of Hg<sup>0</sup> captured by FGD.
- Reaction of SO<sub>2</sub> and FGD at higher temperatures (100-140°C) creates sulfur (S) sites that are very active in capturing Hg<sup>0</sup>.
- The presence of 50 ppm HCl in the simulated flue gas can inhibit the HgCl<sub>2</sub> sorption capability of Ca(OH)<sub>2</sub> by half. The inhibition effect of 1000 ppm sulfur dioxide is



even more drastic (factor of five), and essentially controls the uptake of  $\text{HgCl}_2$  by  $\text{Ca}(\text{OH})_2$ .

- The presence of 50 ppm HCl in the simulated flue gas enhances the  $\text{Hg}^0$  capture capability of FGD by a factor of five. This enhancement may be effected through reaction of HCl and FGD and creation of active chlorine (Cl) sites. HCl has a more pronounced enhancement effect on  $\text{Hg}^0$  uptake by FGD than  $\text{SO}_2$ .
- Among the Illinois coal combustion residues, scrubber sludge samples exhibited considerable mercuric chloride removal capabilities. This activity may be due to the presence of calcium compounds in these samples. Statistical calculations further confirmed this hypothesis.
- A fly ash sample from an Illinois coal power plant was the only combustion residue sample that exhibited combined  $\text{Hg}^0$  and  $\text{HgCl}_2$  removal capability. The  $\text{Hg}^0$  capture capability of this sample may be related to the presence of bromine (Br) which can potentially behave as an active site for the capture of  $\text{Hg}^0$ .

In terms of the control of mercury species in Illinois coal-fired utility boilers, optimum capture of elemental mercury may be obtained by injecting activated carbon (FGD) upstream of the acid gas removal devices, and optimum capture of mercuric chloride may be obtained by injecting hydrated lime [ $\text{Ca}(\text{OH})_2$ ] downstream of these devices. Scrubber sludge samples from Illinois coal power plants can be used to control mercuric chloride emissions. More research is needed to investigate the potential usage of combustion residue samples in elemental mercury control technologies. Future research should be directed toward an understanding of the effect of fly ash carbon content on elemental mercury removal.

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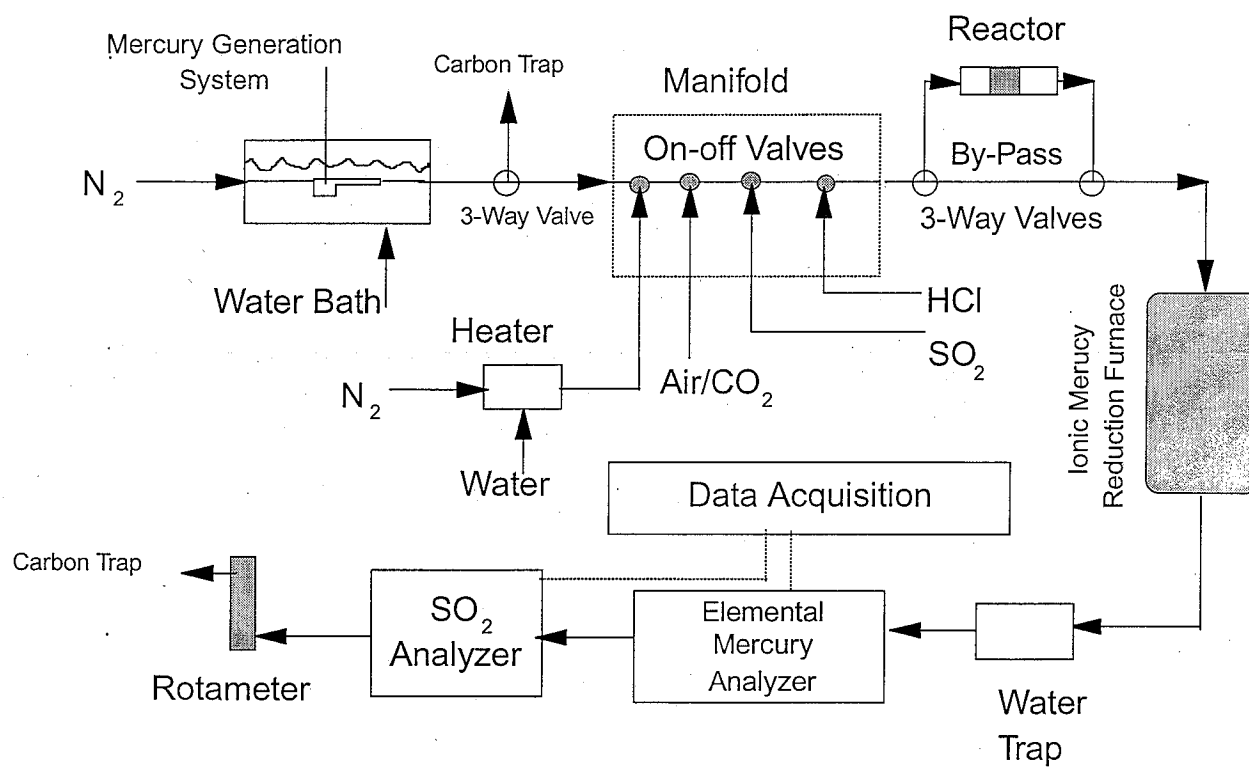


Figure 1. Schematic of the bench-scale, fixed-bed apparatus for studying  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture.

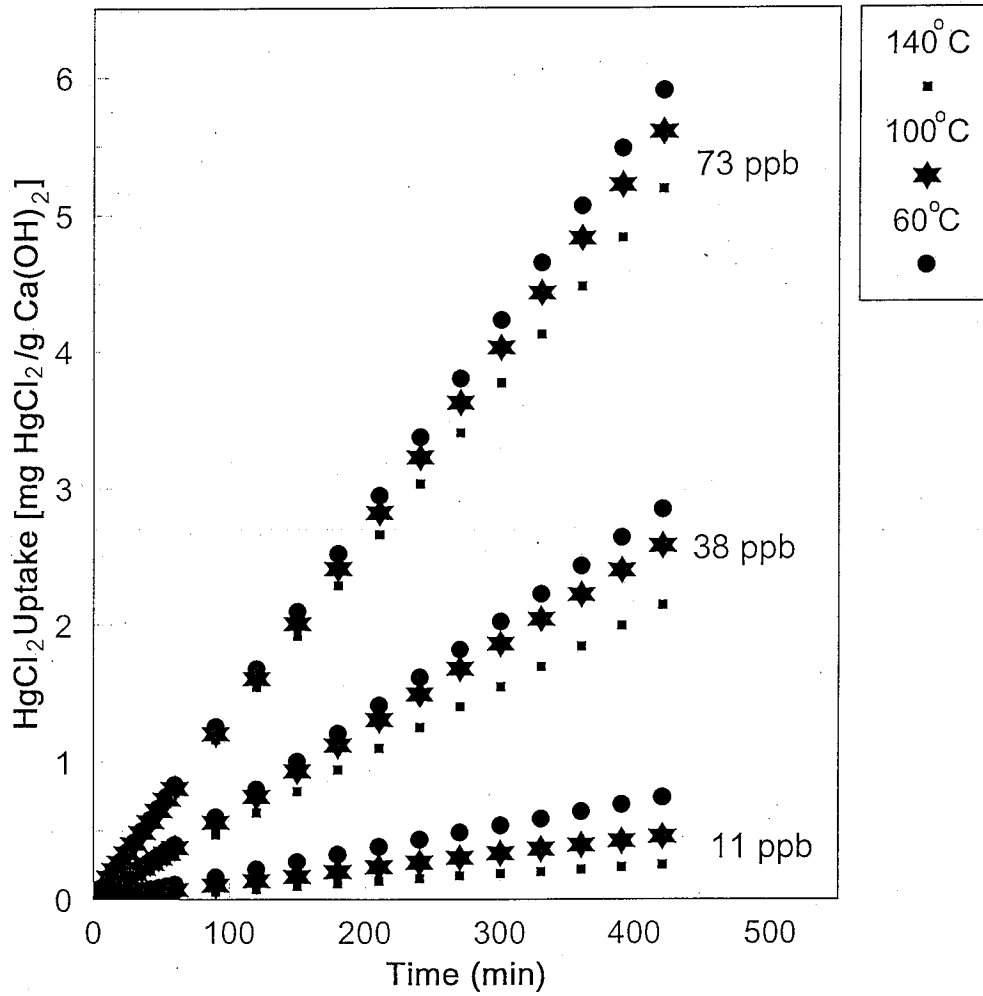


Figure 2. Effects of bed temperature and inlet HgCl<sub>2</sub> concentration on HgCl<sub>2</sub> uptake by Ca(OH)<sub>2</sub> (baseline conditions).

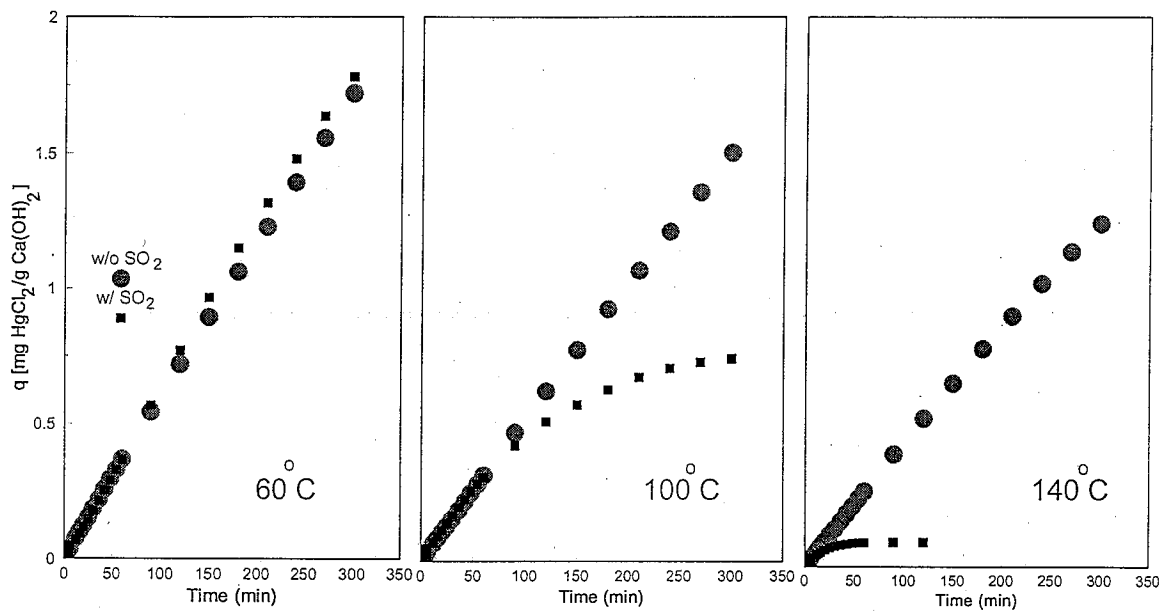


Figure 3. Effect of  $\text{SO}_2$  (1000 ppm) on  $\text{HgCl}_2$  uptake by  $\text{Ca(OH)}_2$  ( $\text{HgCl}_2$  concentration of 38 ppb).

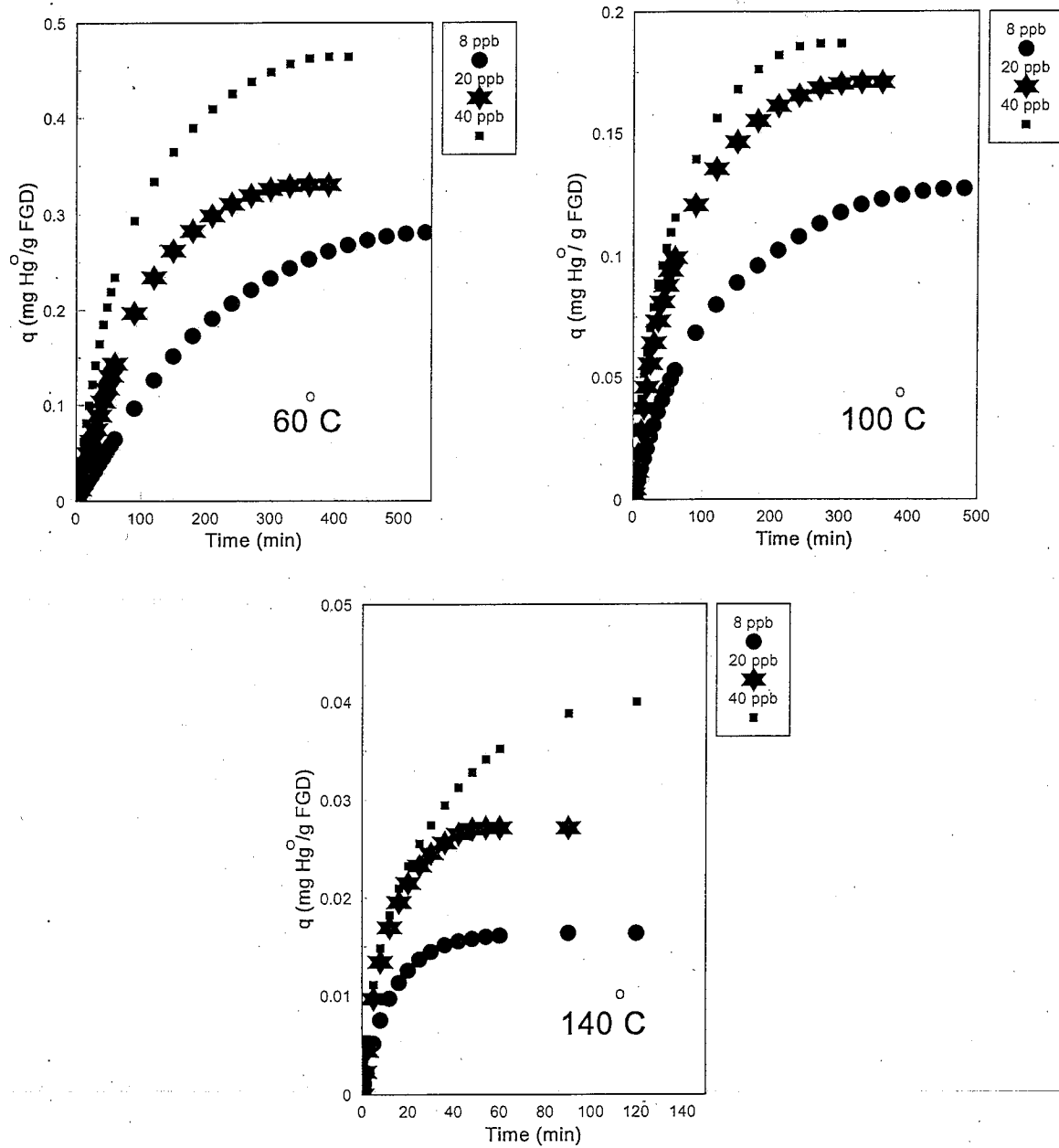


Figure 4. Effects of bed temperature and  $\text{Hg}^0$  concentration on  $\text{Hg}^0$  uptake by activated carbon, FGD (baseline conditions).

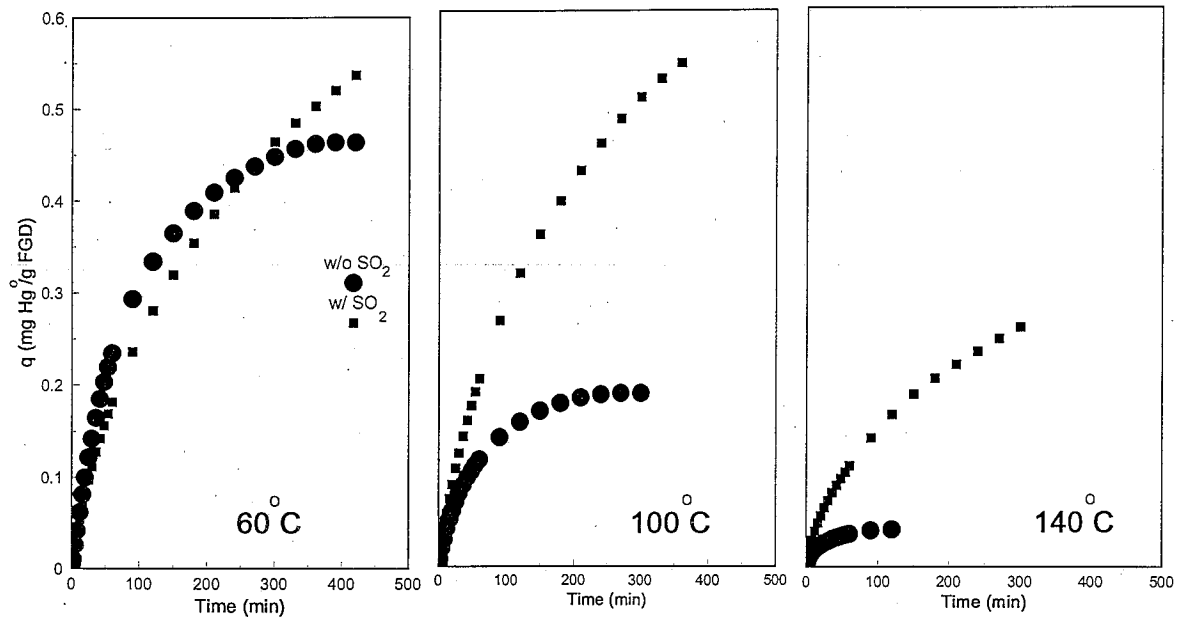


Figure 5. Effect of SO<sub>2</sub> (1000 ppm) on Hg<sup>0</sup> uptake by activated carbon, FGD (inlet Hg<sup>0</sup> concentration of 40 ppb).



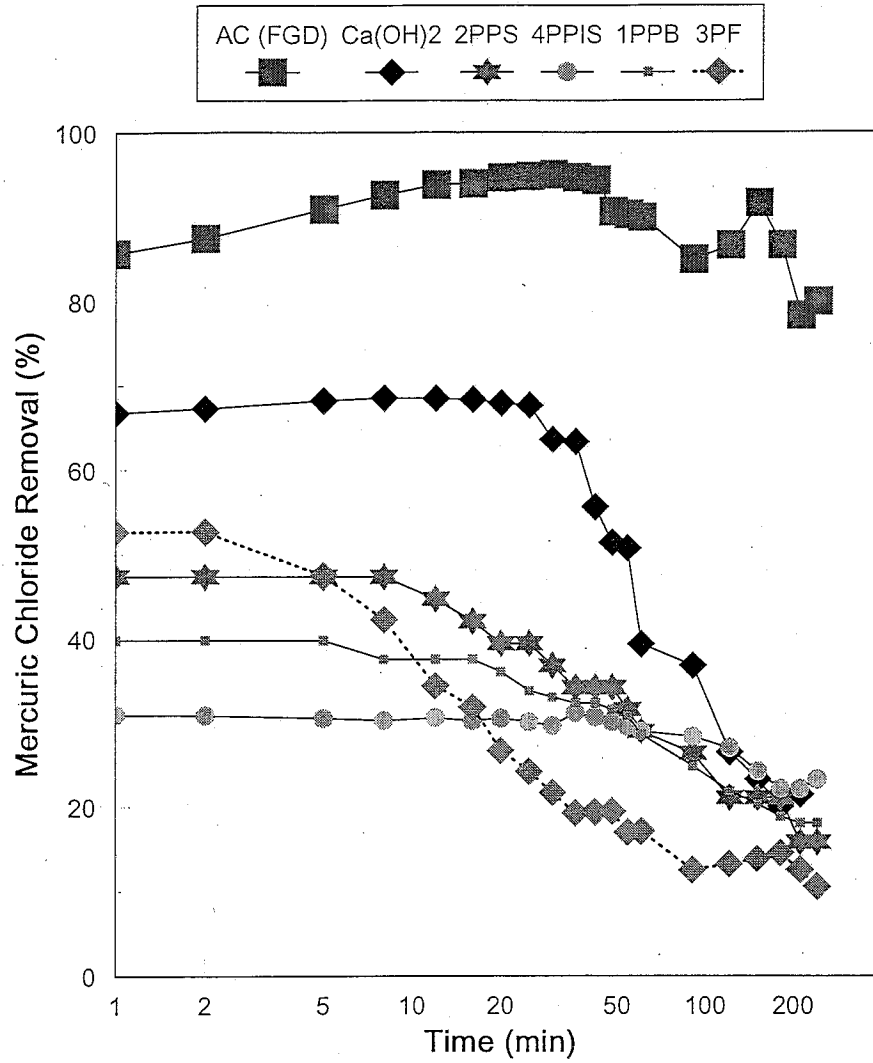


Figure 6.  $\text{HgCl}_2$  removal by four active Illinois coal combustion residues (see Table 4) in comparison to activated carbon, FGD and  $\text{Ca(OH)}_2$ .

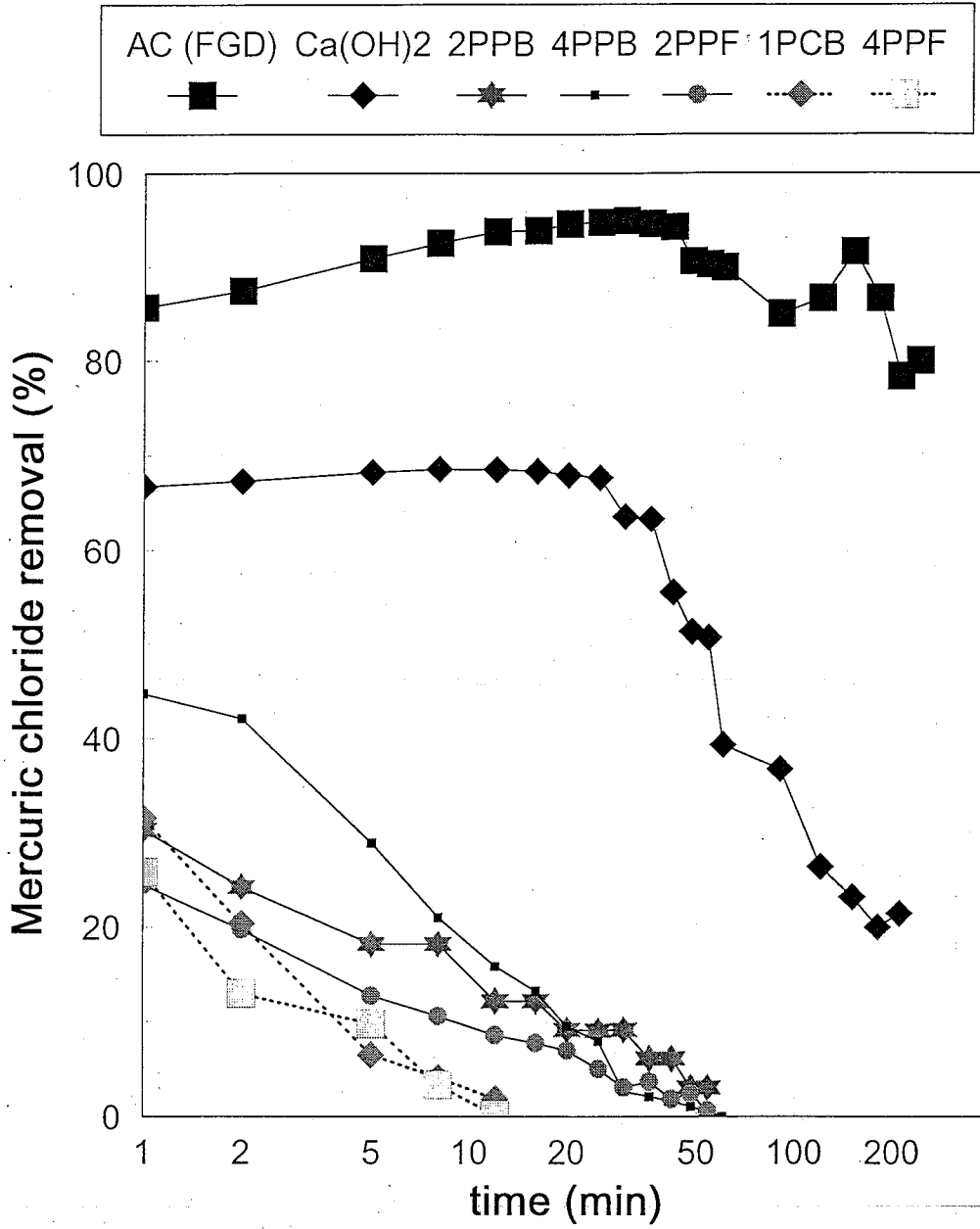


Figure 7.  $\text{HgCl}_2$  removal by five inactive Illinois coal combustion residues (see Table 4) in comparison to activated carbon, FGD and  $\text{Ca}(\text{OH})_2$

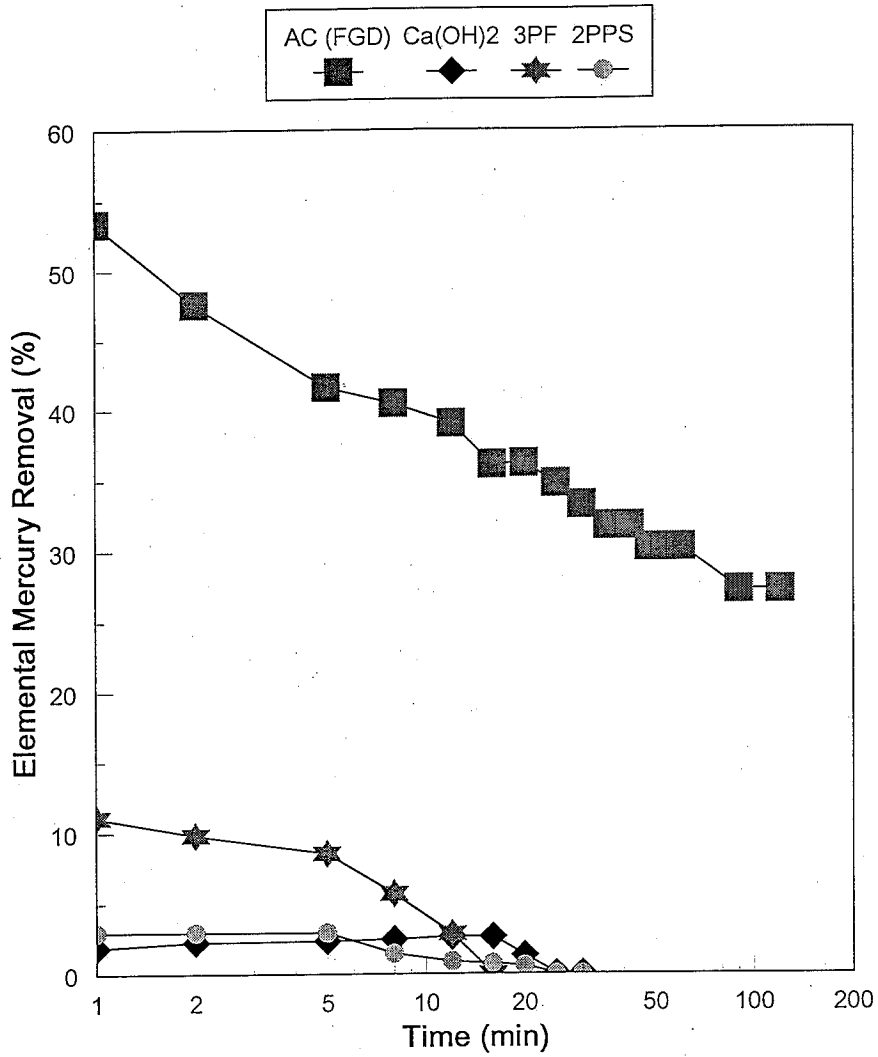


Figure 8.  $\text{Hg}^0$  removal by two Illinois coal combustion residues (see Table 4) in comparison to activated carbon, FGD and  $\text{Ca}(\text{OH})_2$ .