FINAL TECHNICAL REPORT
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Project Title: **MERCURY ADSORPTION IN SIMULATED FLUE GAS**
OF COAL- FIRED BOILERS BY OXIDATION

ICCI Project Number: 96-1/2.4A-3
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ABSTRACT

It has been reported that a large portion of mercury in coal cannot be removed by conventional flue gas cleanup equipment. However, oxidized mercury can be captured more easily by sorbents than elemental mercury. The objective of this project is to convert elemental mercury to oxidized mercury by using oxidants prior to sorption.

Equilibrium calculations of mercury forms based on the thermodynamic data were performed using the STANJAN computer program. Thermodynamic data of common mercury species was gathered and data files were created. Properties of an Illinois coal were used in the equilibrium calculations of coal combustion. The reactants and their concentrations, and conditions of combustion were specified in the calculations. Six oxidants were preselected and their thermodynamic data was incorporated in the calculations. The specific coal combustion products, including mercury species and their concentrations, were determined from the equilibrium calculations. Based on these calculations, promising oxidants for mercury oxidation were selected for detailed bench-scale mercury adsorption tests. Equipment required for upgrading the existing bench-scale adsorption facility were procured. Two activated carbon samples were selected for sorption tests. Base case (without any oxidants) and preliminary tests for mercury adsorption using the bench-scale adsorption facility were initiated. Several preliminary mercury oxidation tests, including a base case (no sorbent or oxidant) and oxidant screening tests (oxidant present, no sorbent) were completed and the $KMnO_4$ scrubbing solutions were submitted for mercury concentration analysis.

All parametric oxidation/adsorption tests using the preselected oxidants and two activated carbon samples have been completed. Testing was conducted over a range of oxidation reactor temperatures, test duration times and oxidant type. Both nitrogen and nitrogen with approximately 1500 ppm SO_2 present were used as the carrier gas. All activated carbon samples were analyzed for mercury content using Cold Vapor Atomic Absorption Spectroscopy (CVAAS).

With the exception of hydrogen peroxide and chlorine, little oxidation activity was observed with the evaluated oxidants. Under the most favorable conditions (hydrogen peroxide and 260 °C), approximately 20% of the elemental mercury entering the reactor was oxidized and adsorbed, compared with a baseline level of 7% at the same conditions.

EXECUTIVE SUMMARY

Mercury is found to be the most volatile trace metal in coal that cannot be effectively removed by conventional flue gas cleanup systems. However, it has been reported that oxidized mercury showed much higher removal potential than elemental mercury. The objective of the project was to convert elemental mercury to oxidized mercury using oxidants to improve the removal efficiency of total mercury.

The thermodynamic data of the major components of coal, combustion gases, common mercury species, and flue gas was gathered and data files were created using Stanford University's STANJAN computer software. The properties of an Illinois coal (IBC-106) were used in the equilibrium calculations. Theoretical calculations of mercury species under coal-fired flue gas conditions using the STANJAN program were performed. Six oxidants were preselected and included in the equilibrium calculations. The preselected oxidants included chlorine, ozone, hydrogen peroxide, calcium oxide, iron oxide (Fe_2O_3), and sodium perchlorate. Chlorine was found to be the most reactive oxidant. The other five oxidants showed very little effect on mercury oxidation. The existing bench-scale adsorption facility was upgraded to include a furnace and a reactor chamber.

Two base case tests (with no oxidant or sorbent) using the bench-scale adsorption facility were performed with standard $KMnO_4$ impingers downstream of the oxidation reactor. The $KMnO_4$ impinger solutions were analyzed to determine the actual mercury concentration in the gas stream at the oxidation reactor inlet for comparison with the stated permeation rate for the elemental mercury permeation tube in an effort to account for potential dropout. Mercury adsorption percentages presented in this report are based on the actual feed concentration determined from the impinger solution analysis.

Two activated carbon samples were used as the sorbents for the mercury adsorption tests. Removal of mercury using oxidants was carried out under different test conditions. The amount of mercury captured by the sorbents was determined using Cold Vapor Atomic Absorption Spectroscopy (CVAAS). Due to potentially wide variations in mercury concentration in a given carbon sample, the total carbon sample for each test was divided and duplicate analyses performed to yield a total mercury concentration for a given test.

Based on reported results from various field tests investigating the use of various additives as a means of improving mercury control, the oxidants chosen for the bench-scale phase of the project were modified and include: sulfur dioxide (SO_2), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), chlorine (Cl_2), and hydrogen sulfide (H_2S). All parametric oxidation/adsorption tests using the preselected oxidants and both of the activated carbon samples have been completed. Testing was conducted over a range of oxidation reactor temperatures, test duration times and oxidant type. Both nitrogen and nitrogen with approximately 1500 ppm SO_2 present were used as the carrier gas. Over the range of reactor temperatures tested, hydrogen peroxide was found to be the most active oxidant, followed by chlorine. For the most active conditions (H_2O_2 as the oxidant, 260 °C reactor temperature), approximately 20% of the inlet mercury was oxidized and adsorbed, compared with approximately 7% at the same operating conditions with no oxidant present.

The other oxidants (SO_2, H_2S, and HCl) showed minimal oxidation activity.

Testing was also conducted in an effort to determine the effect of sorbent type on mercury adsorption. Two Calgon activated carbons, one a standard type and one modified with potassium iodide, were used for the comparison testing. Due to unresolved operational and/or analytical problems with the sorbent comparison samples, however, no definitive comparison between the two activated carbons was possible.

OBJECTIVES

The ultimate goal of this work was to enhance mercury removal by converting elemental mercury to oxidized mercury using oxidants under simulated flue gas conditions. The specific objectives of the work were to:

1. identify the mercury speciation under coal combustion and flue gas conditions through equilibrium calculations;
2. select oxidants and reaction conditions which can promote oxidation of elemental mercury;
3. perform bench-scale mercury oxidation and sorption tests;
4. correlate mercury removal with conditions of mercury oxidation.

INTRODUCTION AND BACKGROUND

Mercury has been found to be the most volatile trace metal in coal that cannot be effectively removed by conventional flue gas cleanup systems. A large portion of mercury escapes as gaseous phase or with the fine particulates in the flue gas. An alternative is to use a sorbent to capture mercury. Various sorbents have been tested. The most promising sorbent for mercury removal is activated carbon.

Field and pilot-scale data have shown that a considerable portion (as high as 50% for certain subbituminous coals) of the mercury from coal combustion is elemental mercury. Oxidized mercury typically exhibits much higher removal by conventional flue gas cleanup devices than elemental mercury. Therefore, converting elemental mercury to oxidized mercury would be beneficial to mercury removal.

EXPERIMENTAL PROCEDURES

Thermodynamic Calculations
The first phase of this project consisted of computer simulations to determine the mercury species which are most likely to exist in coal-fired flue gas conditions. This was done through theoretical calculations which were based on thermodynamic data of common mercury species and other components in coal-fired flue gas. STANJAN version 3.95, courtesy of Stanford University, was utilized to perform these calculations. Thermodynamic data for all likely mercury species was obtained from the JANAF thermochemical property tables.

Properties of an Illinois coal sample IBC-106 were used in the equilibrium calculations. IBC-106 was selected because of its relatively high mercury content as compared to other Illinois basin coal samples. Oxidants which have the potential to promote oxidation of elemental mercury were preselected and included in the theoretical calculations. Six oxidants were preselected for evaluation. These oxidants included chlorine, ozone,

hydrogen peroxide, calcium oxide, iron oxide, and sodium perchlorate. Based on the equilibrium calculations, the oxidants which show a relatively high degree of conversion of elemental mercury to oxidized mercury would then be selected for adsorption tests.

Oxidation/Adsorption Testing
An existing bench-scale adsorption facility originally consisted of a gas preheater, a bubbler for elemental mercury, and a sorbent bed which is surrounded by an electric furnace. This facility was upgraded to include mercury permeation tubes as the mercury source, various oxidant permeation tubes and a reactor in which oxidation of the elemental mercury takes place.   The reactor is surrounded by a separate electric furnace which is used to control the temperature of oxidation.   Each furnace is equipped with a programmable controller to maintain temperature. Carrier gas flows are maintained with ball float rotameters. A schematic of the bench-scale adsorption facility is shown in Figure 1.
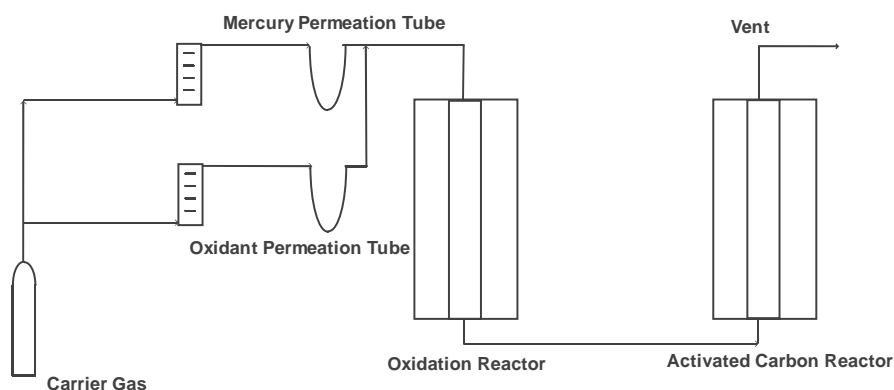

Figure 1. **Bench-Scale Adsorption Facility Schematic**

For a typical oxidation/adsorption test, the following procedure was followed:

1. Turn on mercury permeation tube and oxidant permeation tube temperature baths. The permeation tubes are located in U-shaped holders in the constant temperature baths. Carrier gas is introduced in one leg of the holder and exits the opposite leg. The bath temperatures are set based on the certified temperature for a given permeation tube.

2. Preheat oxidation furnace to desired temperature.

3. Load preweighed sample of activated carbon into glass tube. Typically, 10 grams of

activated carbon were used for each test. A fritted disc was installed in the glass tube at the midpoint to serve as a support for the activated carbon. The tube was then tapped to settle the activated carbon and minimize any gas bypass. The glass tube was then installed in the sorbent bed furnace, the furnace turned on to preheat, and the inlet and outlet gas lines connected to the glass tube. A sorbent bed temperature of 60 °C (150 °F) was used for all of the sorbent tests. A thermocouple was located in the activated carbon bed to monitor bed temperature.

4. Once furnace and permeation tube bath temperatures have stabilized, initiate gas flows. Two ball float rotameters were used to control flow to the permeation tubes. Gas flow was split 50/50 between the oxidant and mercury permeation tubes and total gas flow for the tests was 100 ml/min.

5. Once test is complete, shut off gas flows, turn off sorbent bed furnace and remove activated carbon sample. If a follow-up test is to be conducted, reset oxidation reactor furnace to desired temperature and load new activated carbon sample into glass tube. Activated carbon samples were stored under refrigeration until CVAAS analysis to prevent sample degradation.

Two activated carbon samples were used as sorbents, both supplied by Calgon. The first sorbent (identified as AC1) was a Type HGR-LH potassium iodide impregnated carbon. Some studies have indicated that potassium iodide-modified activated carbons have higher adsorption potential for mercury. The second sample (identified as AC2) was a standard Calgon Centaur 4x6 activated carbon. The majority of the oxidation/adsorption tests were conducted with the HGR-LH modified activated carbon.

RESULTS AND DISCUSSION

Thermodynamic Calculations

Thermodynamic data for common mercury species, such as $Hg(g)$, $Hg(l)$, $Hg_2Cl_2(g)$, $Hg_2Cl_2(s)$, $HgCl_2(g)$, $HgCl_2(s)$, $HgO(g)$, $HgO(s)$, etc. was gathered from the JANAF Thermochemical Tables. The data was input into the STANJAN software and data files were created. Properties of IBC-106 coal were also input in the calculations. A 20% excess air was assumed in the coal combustion calculations. All oxidant calculations were performed at a minimum of two temperatures, 1900K and 1000K (2960 °F and 1340 °F). Additional temperature calculations within this range were also performed for some of the oxidants. Of the six oxidants (chlorine, ozone, hydrogen peroxide, calcium oxide, iron oxide (Fe_2O_3), and sodium perchlorate), chlorine is (thermodynamically) the most reactive oxidant.

General Observations
In the presence of either gas or liquid oxidants, most of the mercury exists in the flue gas as elemental mercury rather than mercuric oxide. As the flue gas temperature decreases (calculations performed at 1500, 1200, 900, 600, and 300K), the concentration of elemental mercury increases and the concentration of mercuric oxide decreases. No solid or liquid mercury species are formed even when the gas temperature is near typical flue gas temperature.

Effect of Chlorine
Independent of chlorine concentration (3E-04 to 3E-08 lb mole of the coal), essentially all (>99%) of the mercury present in the coal reacts with chlorine to form the solid/liquid phase of mercuric chloride (the program only differentiates between gaseous and solid/liquid phases). Trace amounts exist as elemental Hg, HgO, and Hg_2Cl_2. These concentrations were typically less than 0.1% of the total mercury present in the coal.

Effect of Solid Oxidants
For each of the solid oxidants tested ($NaClO_4$, CaO, and Fe_2O_3), and regardless of temperature, essentially no mercury oxidation occurred. Trace amounts (0.05% or less of the total mercury present) of solid/liquid elemental Hg and solid HgO were formed.

Effect of Coal Sulfur
The effect of sulfur on mercury speciation was not able to be determined from the equilibrium calculations because of the lack of the thermodynamic data for mercuric sulfide.

Oxidation/Adsorption Testing

Operational Parameter Effects
32 bench-scale tests were conducted during the course of the program. These tests included 1) base tests, where no sorbent or oxidant were present, to determine the amount of elemental mercury present in the gas stream; 2) baseline tests, where only an activated carbon sample was present, to determine the amount of elemental mercury adsorption; and 3) oxidation/adsorption tests, where both oxidant and sorbent were present. A summary of the tests and test conditions is shown in Table 1. For each test, the test ID (AC1 or AC2), test duration, oxidant type, activated carbon sample weight, oxidation reaction temperature, mercury concentration via CVAAS, and % adsorbed mercury are given. The mercury concentrations presented in Table 1 are on a 1 μg basis. The % adsorbed mercury values are based on the average mercury flow rate, test duration, mercury concentration, and sample weight.

For each test, the total gas flow was 100 ml/min. Corresponding oxidant concentrations were as follows: Cl_2 - 145 ppm, H_2S - 73 ppm, and HCl - 90 ppm. For H_2O_2, half of the carrier gas was bubbled through a 30% H_2O_2 solution heated to 70 °C.

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Table 1. Summary of Oxidation/Adsorption Bench-Scale Tests

Test ID	Test Duration, hrs	Oxidant	Sample Wgt., g	Oxidation Reactor Temp., °F	Hg Conc., μg/g	Adsorbed Hg, %
AC1-01	20	none	10.08	350	10.9	8.52
AC1-02	21	none	10.09	500	9.5	7.05
AC1-03	20.5	Cl_2	10.09	350	NA	NA
AC1-04	20	Cl_2	10.04	500	NA	NA
AC1-05	20	H_2S	8.86	350	21.4	14.7
AC1-06	20	H_2S	8.84	500	10.6	7.24
AC1-07	6	H_2S	9.02	500	5.1	11.76
AC1-08	20	Cl_2	10.02	350	15.9	12.31
AC1-09	20.25	Cl_2	10.05	500	18.8	14.43
AC1-10	6	Cl_2	9.9	500	6.9	17.56
AC1-11	21	H_2O_2	10.08	350	18.2	13.55
AC1-12	20	H_2O_2	9.98	500	25.3	19.56
AC1-13	6	H_2O_2	10.00	500	5.6	14.36
AC1-14	20.25	HCl	10.09	350	9.3	7.17
AC1-15	20	HCl	9.98	500	11.6	8.97
AC1-16	20	HCl	9.94	644	16.6	12.81
AC1-17	6	HCl	9.99	500	6.1	15.79
AC1-18	20	SO_2	10.08	500	8.2	6.44
AC1-19	22	SO_2	10.02	644	9.0	6.34
AC1-20	6	SO_2	10.02	500	1.5	3.83
AC1-21	20	H_2O_2	9.98	644	8.5	6.59
AC1-22	20.5	Cl_2	10.04	644	0.2	0.13
AC1-23	21.5	Cl_2	10.01	500	0.1	0.05
AC1-24	6	Cl_2	10.08	500	0.1	0.03
AC1-25	21	SO_2+Cl_2	NA	500	NA	NA
AC1-26	20	SO_2+Cl_2	10.1	644	1.0	0.80
AC2-21	20	H_2O_2	9.67	644	5.1	3.84
AC2-22	20	Cl_2	9.62	644	0.8	0.6
AC2-23	20	Cl_2	9.62	500	0.5	0.37
AC2-24	6	Cl_2	9.68	500	0.2	0.48

In addition to the tests listed Table 1, two tests were conducted using standard KMnO$_4$ gas sampling train impingers instead of activated carbon samples. These tests were conducted without oxidant in an effort to determine the amount of elemental mercury present in the gas stream. Over a 20 hour test period, the total mercury collected averaged 1290 μg, or an hourly feed rate of 64.5 μg/hr.

Tests AC1-03 and AC1-04 did not yield acceptable results due to an operational problem with the carrier gas flow rate during the test. Tests AC1-01 and AC1-02 represent baseline adsorption tests to determine the amount of elemental mercury adsorbed by the HGR-LH activated carbon (AC1). Similar baseline adsorption levels were seen with the Centaur carbon (AC2). As can be seen, adsorption levels during most of the oxidation/adsorption tests were typically close to or slightly above baseline levels, indicating little oxidation activity. Exceptions to this observation include hydrogen peroxide, chlorine, and hydrogen sulfide, although the oxidation activity for hydrogen sulfide decreased with increasing oxidation temperature, contrary to the other oxidants. The data from Table 1 for AC1 is shown graphically in Figures 2 through 4. Figure 2 shows the effect of oxidation temperature on mercury adsorption as a function of oxidant type, Figure 3 shows the effect of test duration, and Figure 4 shows the percentage of the feed mercury adsorbed on the carbon as a function of oxidation temperature.
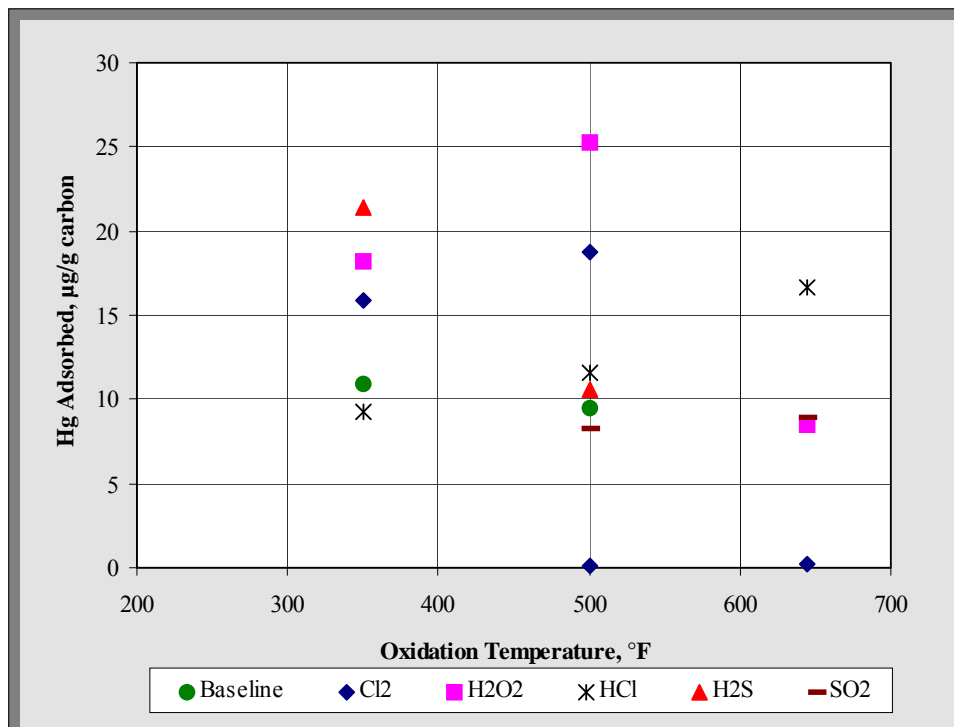

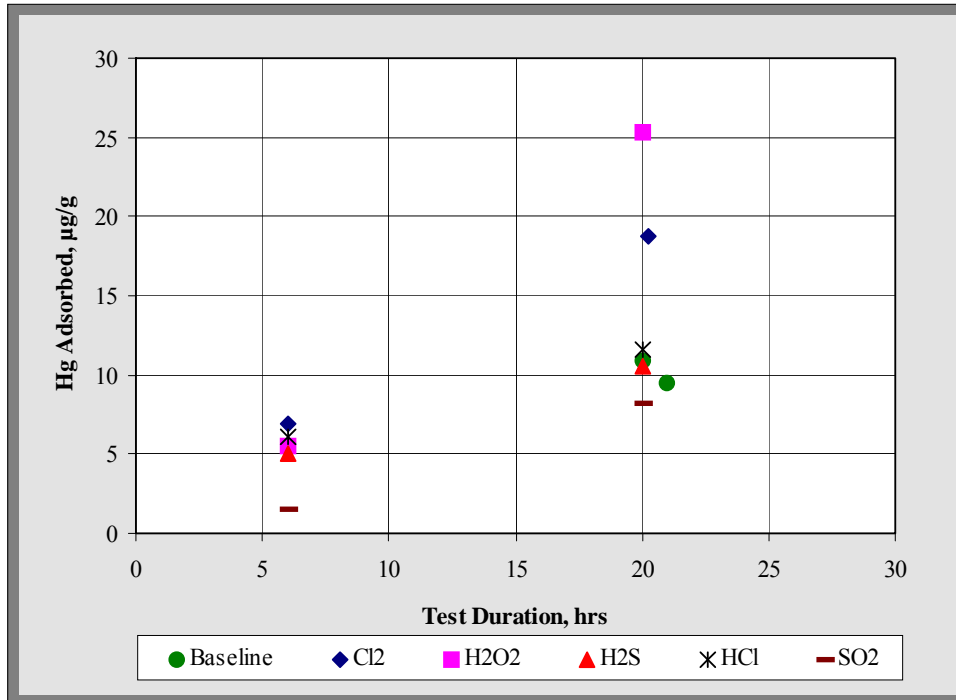**Figure 2. Effect of Oxidation Temperature on Hg Adsorption - AC1**

Figure 3. Effect of Test Duration on Hg Adsorption - AC1
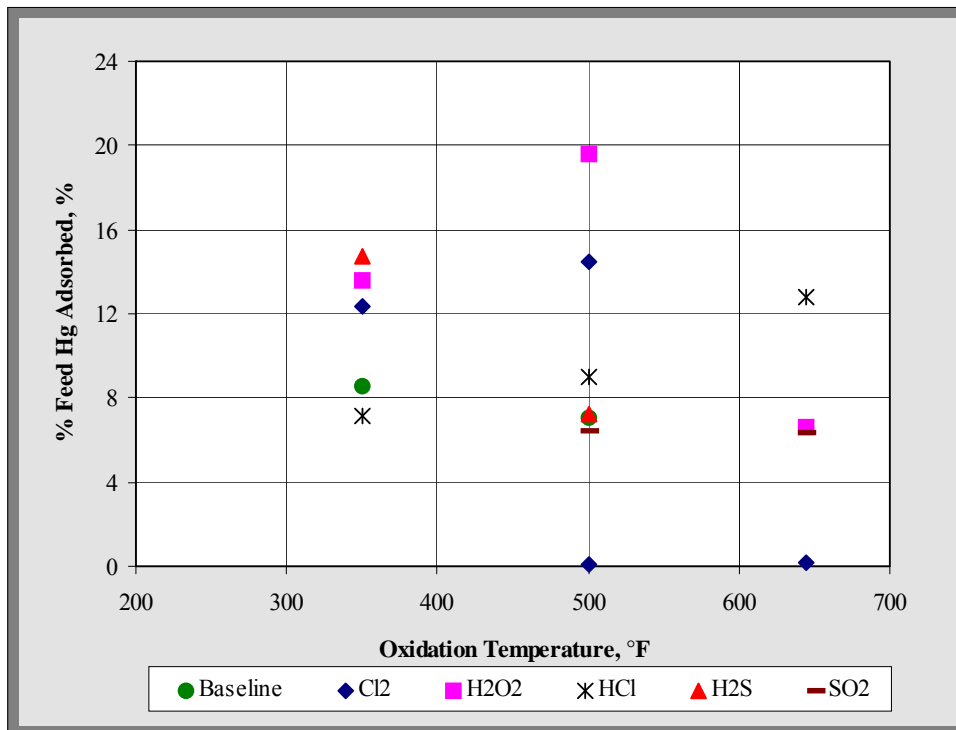

Figure 4. Percent Feed Hg Adsorbed vs. Oxidation Temperature

As can be seen in Figures 2 and 4, the oxidation activity for most of the oxidants tested was minimal, and that hydrogen peroxide was more reactive than chlorine. In addition, HCl appears to increase in activity with increasing temperature, whereas both hydrogen peroxide and chlorine appear to decrease in activity. It should be noted, however, that the oxidation tests at 644 °F for both chlorine and hydrogen peroxide were performed during a period where low concentrations were detected, regardless of oxidant or temperature. For example, tests AC1-25 and AC1-26, where chlorine was the oxidant with SO_2 present, were not included in these plots due to low concentrations. Further discussion of this problem is given in the following section. It should be noted that the tests, by and large, were conducted chronologically; however, no changes were made to the facility itself or the procedures used to conduct the tests and subsequent analyses.

The data in Figure 3 reflect the expected trend of increasing adsorption with increasing test duration, indicating that the carbon samples were not becoming saturated, although for most of the oxidants (hydrogen peroxide being the exception) the sorbents do not exhibit a constant adorption rate (i.e. 3.33 times as much adsorbed mercury at 20 hours as at 6 hours), rather they exhibit a decreasing adsorption capacity with time.

Sorbent Comparison
As mentioned above, two activated carbons were used during the oxidation/adsorption tests: AC1 - the HGR-LH potassium iodide-modified carbon, and AC2 - the standard Centaur 4x6 carbon. A graphical comparison of the two sorbents is given in Figure 5, which shows mercury adsorption as a function of oxidation temperature.
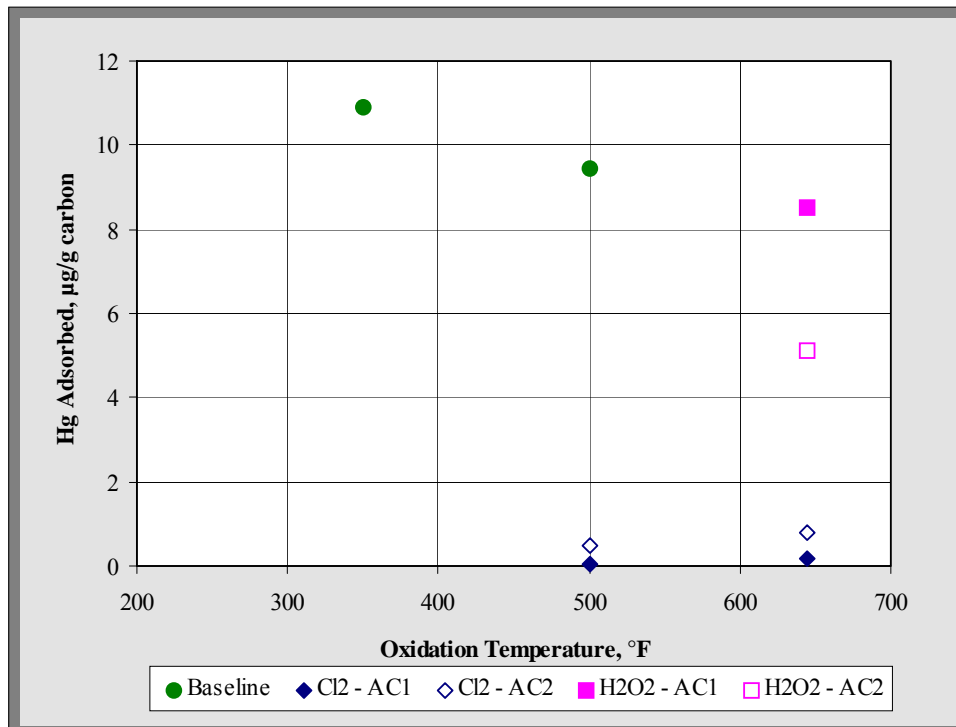

Figure 5. Effect of Oxidation Temperature - Sorbent Comparison

As can be seen, adsorption for each of the sorbents was much lower than baseline measurements, taken with no oxidant present. The cause for this is unknown, since the same operational and chemical analysis procedures were used for each test during the entire program. One possibility is variation in mercury flow from the permeation tube, although this is unlikely since 1) the permeation tube was still satisfactorily filled with mercury, and 2) the two impinger tests to measure mercury concentration in the gas were conducted over the span of several days, indicating that the permeation rate of the tube was fairly constant. As a result, no definitive comparison between the two carbons can be made.

CONCLUSION(S) AND RECOMMENDATION(S)

Theoretical thermodynamic calculations and bench-scale oxidation/adsorption tests were conducted in an effort to determine the physical parameters and chemical oxidants which are most conducive to the conversion of elemental mercury to one (or more) of its oxidized forms. Once oxidized, mercury may be more readily captured by conventional flue gas cleanup systems.

Based on the results from the work performed for this project the following conclusions and recommendations are offered:

- From a theoretical standpoint (thermodynamically), chlorine is the only viable oxidant of the oxidants investigated. Even at very low chlorine concentrations, essentially all of the mercury present in the coal is converted to mercuric chloride.

- Although the thermodynamic calculations indicated that the other oxidants exhibited very little oxidation activity, use of these oxidants in real-life systems has shown varying degrees of oxidation. This is most likely due to the effect of various physical phenomena (e.g., duct surfaces, flyash) which may aid in the oxidation of the mercury present in the flue gas.

- The bench-scale oxidation/adsorption tests indicated that, in addition to chlorine, hydrogen peroxide and hydrogen sulfide are potential oxidants, although the oxidation activity of hydrogen sulfide decreased with increasing oxidation reaction temperature, and that there is some question as to the validity of the test results for both hydrogen peroxide and chlorine at the higher oxidation temperatures. As with the thermodynamic calculations, the bench-scale tests do not entirely reflect actual implementation of these oxidants; rather, they offer information on the relative potential of the use of these oxidants in a real-life application.

- It is recommended that further bench-scale oxidation/adsorption testing, especially at higher oxidation temperatures, be considered. Some of the thermodynamic calculations indicated that good oxidation with chlorine is possible at higher temperatures than were achievable with the current equipment configuration.

DISCLAIMER STATEMENT

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