

**LABORATORY DUCT INJECTION OF A ZEOLITE-BASED
MERCURY SORBENT**

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Laboratory Duct Injection of a Zeolite-Based Mercury Sorbent

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ABSTRACT

The measurement and control of mercury emissions from utility power plants continue to be the subjects of much study. In a program funded by the Department of Energy, Physical Sciences Inc. (PSI) is developing a mercury sorbent using a zeolite material with a proprietary agent for improved capture of elemental as well as oxidized mercury.

Previous research at PSI has shown the feasibility of using zeolites for mercury capture. Results of this work showed that a treated zeolite sorbent performed as well as a treated activated carbon in removing total mercury from the flue gas, and that treating the zeolite improved elemental mercury capture compared to the untreated zeolite.

In the current work two types of treated zeolite sorbent and one type of activated carbon were injected into flue gases from combustion of a Pittsburgh seam bituminous coal with the purpose of evaluating sorbent efficiency under conditions that approximate full-scale utilities with electro-static precipitators. The gas temperatures and residence times were similar to those found in power plant flue gas ducts and were in the range of 130 to 200°C and 2 s, respectively. The mercury concentration varied in the range of 30 to 60 $\mu\text{g}/\text{m}^3$. As in the previous fixed bed work, mercury concentration and speciation were measured using the modified Ontario Hydro Method. The mercury removal efficiencies in the experiments were zeolite sorbent was used varied in the range of 45 to 92% for sorbent to Hg ratios in the range of 5,000 to 96,000. When no sorbent was injected, ash did remove some mercury, but in the presence of sorbent the role of ash in mercury removal appeared to diminish, presumably due to the higher reactivity of the sorbent with respect to the ash.

INTRODUCTION

Mercury is one of the 11 toxic metals recognized by the Title III of the Clean Air Act Amendments as Hazardous Air Pollutants and has received special attention because of its high toxicity and bioaccumulation. It has been estimated that the global emissions of mercury from all sources is approximately 6,000 tons per year and that emissions from power generation account for almost 40% of that total.¹ In the United States 21% of the total mercury emissions are attributed to coal-fired utility boilers.²

Even though the concentrations of Hg in coal are relatively low at 0.012 to 3.3 ppmw, releases to the environment can be considerable due to the large amounts of coal that are burned. Mercury concentrations in the flue gas streams of coal fired power plants have been reported at levels between 1 and 120 $\mu\text{g}/\text{m}^3$ with emissions from the plant of 0.5 to 6 kg/day,^{3,4} while typical

values are in the range of 1 to 10 $\mu\text{g}/\text{m}^3$. The forms of mercury vapor in power plant flue gases are elemental Hg and oxidized Hg (probably HgCl_2 , and in some cases, HgO), with elemental mercury being the predominant form.⁵⁻⁹

Since mercury is very volatile, only a small amount is removed along with the fly ash in the particulate control devices such as electrostatic precipitators or baghouses, and the rest comes out to the atmosphere along with the flue gases. Generally, HgCl_2 can be removed from the flue gases easier than elemental Hg, either through wet scrubbing, dry injection or fixed bed using activated carbon.⁶⁻⁹ However, removal of elemental mercury is more challenging, since it is practically insoluble in water and can be removed to a certain extent with expensively treated activated carbons. Bench-scale tests conducted with elemental mercury showed generally low removals using untreated activated carbon and increased removals with carbons treated with sulfur and other additives. This work also showed the potential for high mercury removals using mineral sorbents such as zeolites.⁹⁻¹⁴

A problem related with the use of activated carbon as mercury sorbent in coal-fired utility boilers is the deterioration of the quality of fly ash. Coal fly ash has potential commercial value in the cement making process and in the plastics industry, but limits of carbon content are imposed to prevent degradation of the final product. For example, concrete used in areas with frequent periods of freezing weather is deliberately mixed with air bubbles to provide space for expansion and contraction of the other components. The excess carbon in the ash used in the cement actually absorbs the air, which produces a less durable material. The plastics industry requires filler materials for its products and would consider the use of coal fly ash that is low in carbon and of consistent quality. Therefore, in addition of being expensive, activated carbons that can be used for removing elemental mercury may lower the selling value of the ash.

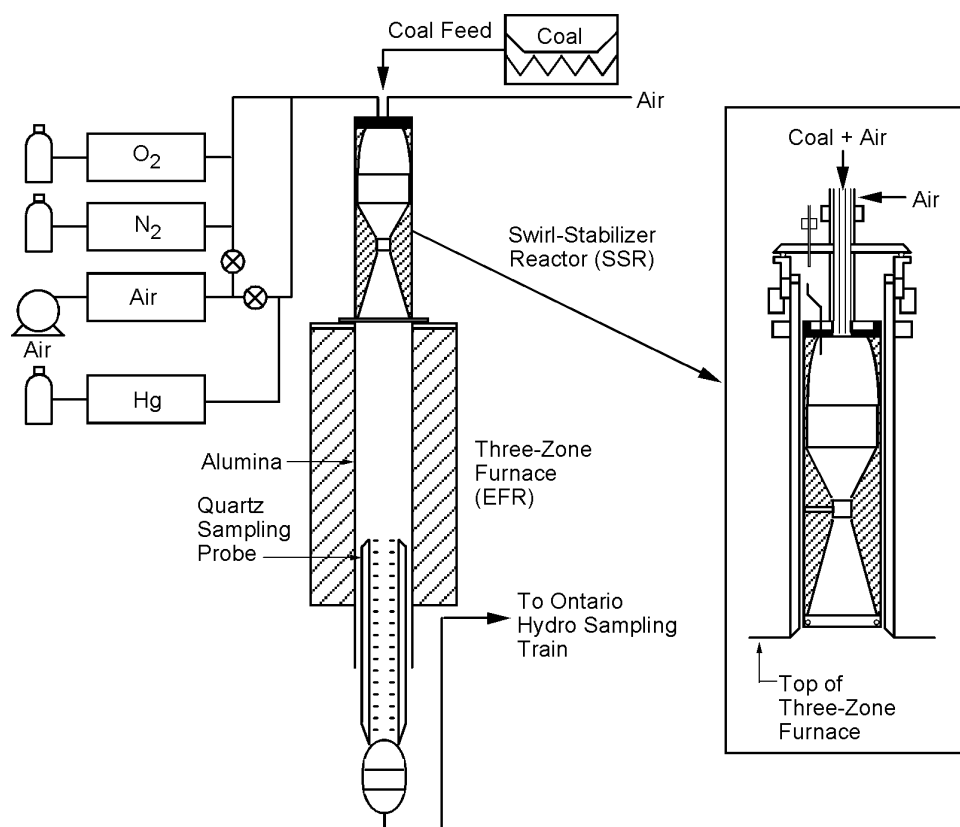
To address the issues of cost, high removal efficiency and fly ash quality after sorbent injection, a variety of sorbents, other than carbon based, have been tested over the years, with zeolites being one of them. Zeolites are aluminosilicate materials that have extensively been used as adsorbents for gas separation and purification, and they are also used as ion exchange media for water treatment and purification. They have open crystalline structures constructed from tetrahedra of the form TO_4 ($\text{T} = \text{Si}, \text{Al}$) and also contain non-framework cations. Zeolites can reversibly adsorb water and other molecules and exchange the non-framework cations.

The performance of a natural zeolite as mercury sorbent was assessed in earlier work at PSI using the flue gases from combustion of coal. Two different forms of this zeolite were used, plain zeolite and zeolite treated with a proprietary agent. Experiments both in fixed bed and injection mode were performed at temperatures in the range of 150 to 230°C. Data indicated that the treated zeolite removed both elemental and oxidized mercury and performed well in comparison to activated carbon. Leachability tests on this material showed that the sorbent can be safely disposed of in a landfill if sale of the ash is not an option. This paper presents additional mercury removal data from treated and untreated zeolite and also activated carbon.

EXPERIMENTAL APPARATUS

To determine the ability of each sorbent to capture mercury under realistic conditions, the mercury-containing gas stream was to be generated by the combustion of coal in PSI's electrically heated Entrained Flow Reactor (EFR), shown schematically in Figure 1. This apparatus, which can achieve a maximum gas temperature of 1723 K, has been used extensively on many of PSI's combustion research projects. Fuel, air, and any other desired gases are injected into the reactor through an alumina venturi that serves as a mixing section on the top of the EFR. The combustion section is an externally heated ceramic tube that is 8.57 cm in internal diameter and 158 cm in length. Gas sampling can be performed at the bottom of this section through one of several types of sampling devices that are available to meet the requirements of the research program.

Figure 1. PSI entrained flow reactor.



Coal was burned in the EFR to more closely approach the conditions found in power plant flue gases. For this program, a bituminous coal, Pittsburgh seam, was used. The mercury content of the coal as determined by Neutron Activation Analysis is 0.11 ppm.

A device consisting of a temperature controlled permeation tube with a carrier gas flow of oxygen regulated by a mass flow controller was employed to inject additional mercury into the axial air stream at the top of the EFR. Using this technique, the presence of mercury was assured at the exit of the reactor while still utilizing the combustion of coal to ensure the presence of any

flue gas constituents, for example sulfur or chlorine, that may interfere with or accelerate the reaction of the mercury with the sorbent in the fixed bed. Table 1 shows the approximate composition of the gas stream exiting the furnace.

Table1. Flue gas composition from the combustion of Pittsburgh coal in the EFR.

Constituent	Volume %
CO ₂	16.14
H ₂ O	6.07
O ₂	3.73
N ₂	74.6
SO ₂ (ppm)	1293
HCl (ppm)	70
Total Hg*	30-60 µg/m ³

* With addition of elemental mercury.

Once the flue gas exited the furnace, it entered a quartz tubular reactor. The top part of the reactor is a tube 1/2 in. in diameter into which sorbent is injected. The flue gases are cooled to about 250°C with air blown at the outside of this section. The main section of the reactor is a 1.75 in. in diameter tube, 16 in. long and was kept at 130 to 200°C using insulation and a heating tape.

To ensure that no additional mercury removal took place downstream the reactor, the flue gases passed through a series of particulate removal devices, starting with an impactor. We designed and built the impactor by modifying a glass impinger to allow for the removal of large particles, which were mainly ash particles and sorbent agglomerates. Two glass cyclones were subsequently used to remove particles in the range of 15 to 20 µm. The remaining particles were removed by a Whatman 934 AH Glass Microfiber Filter placed in a Pyrex filter holder assembly. The assembly was placed in a temperature-controlled box adjusted to 150°C. This apparatus is shown in Figure 2.

After leaving the filter assembly, the gas stream passed into a series of impingers designed to collect any mercury left in the flue gases and determine the mercury species. For this setup we used the Ontario Hydro Method which in recent testing has achieved good results in measuring total mercury and has shown the most promise for the determination of mercury species. Figure 3 shows a schematic of this system.

The sorbent injection system consisted of a syringe with the sorbent loaded on driven by a syringe pump into a tube. The air flowing in the tube was used to carry the sorbent. The injection rate was controlled by the speed of the syringe pump. Two types of treated zeolite were used and also untreated zeolite with particle size in the range of 1 to 5 µm. In addition, a high-surface-area activated carbon, CL-213, from Barneby and Sutcliffe was used as a comparison.

Figure 2. Particulate collection apparatus for sorbent injection experiments.

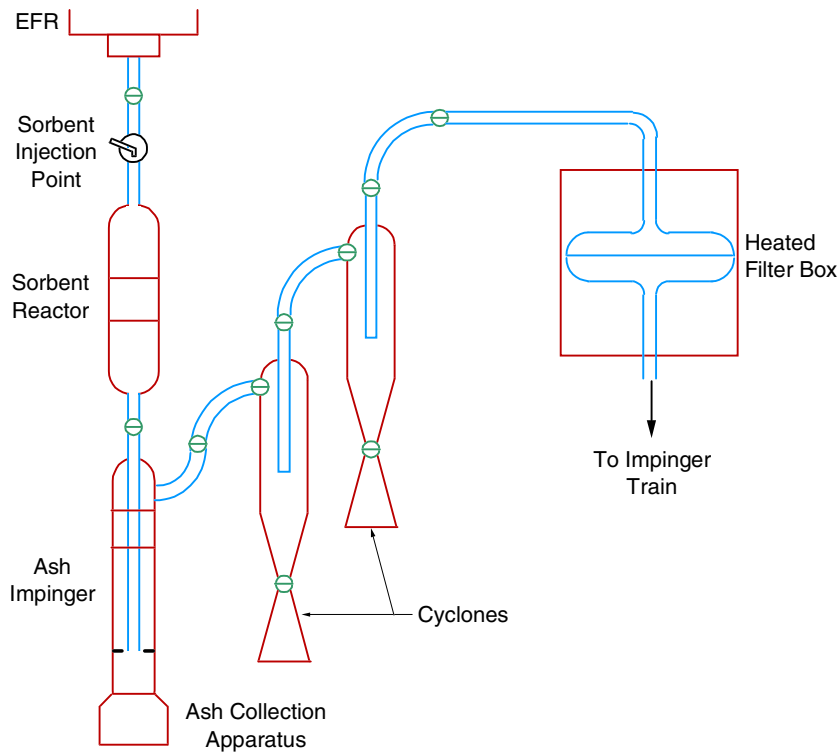
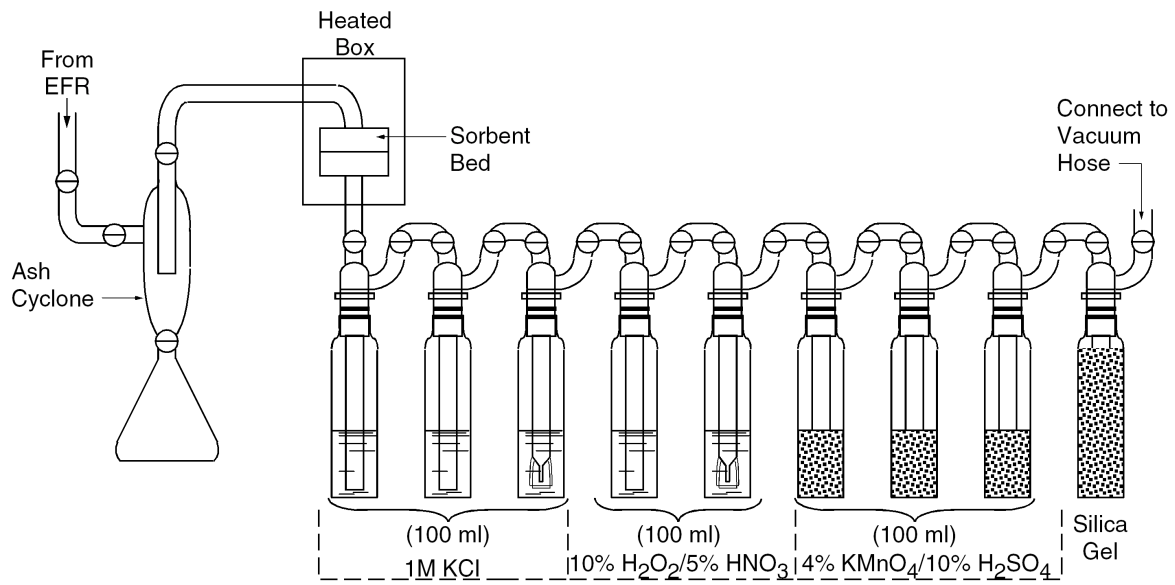


Figure 3. Modified Ontario Hydro method for capture of mercury species in the sample gas stream of the EFR.



Mercury mass balance closure was determined for all runs by adding the mercury from each of the analyzed samples and dividing by the sum of the theoretical mercury from the combustion of the coal and the added mercury from the permeation tube as determined by the Jerome analyzer.

The normal operating conditions were:

- Coal flow rate: 1.7 g/min
- Furnace temperature: 1700 K
- Equivalence ratio: 1.2
- Mercury reactor residence time: 2 s
- Mercury reactor temperature: 130 to 230°C.
- Mercury concentration: 30 to 60 $\mu\text{g}/\text{m}^3$

SAMPLE ANALYSIS

For each run, there were two solid samples: one designated as cyclone ash which consisted of all ash from the particulate capture devices and connecting tubes, and the second designated as filter ash. These samples were first digested using an HF microwave digestion procedure and then analyzed by AA. The analytical laboratory was also sent a sample of Standard Reference Material #1633b, Coal Fly Ash from National Institute of Standards & Technology (NIST). Their analysis of this material was 82% of the certified value for mercury.

The liquid samples for the runs consisted of four samples: three impinger samples from the Ontario Hydro train, KCl, $\text{H}_2\text{O}_2/\text{HNO}_3$, and KMnO_4 , and one sample consisting of the nitric acid rinse of all the glassware prior to the heated filter box. These samples were analyzed according to the procedures for Ontario Hydro method. In addition to these samples, blanks and spiked samples of each impinger solution were analyzed by the laboratory.

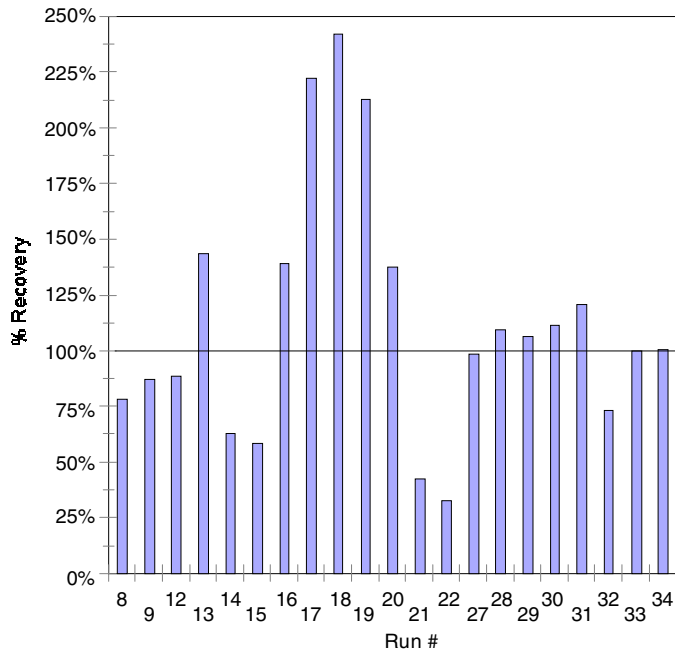
RESULTS

Mass Balance Closure

The mercury concentration results of the liquid and solids analyses were compared to the theoretical mercury input for each run to determine a mercury mass balance closure. The theoretical mercury input is defined as the sum of the injected mercury and the mercury contained in the amount of coal burned during the run. A plot of the results for runs for which data will be presented in this paper is shown in Figure 4.

Note that in Run 14, the mercury balance closure drops to 67%, then a few runs later peaks at almost 250% then drops back down to approximately 30% in Run 22. After discovery of this trend, it was noted that the mercury permeation tube needed to be monitored more consistently. Accordingly, the injected mercury rate was measured at the furnace injection point for subsequent runs using the Jerome Mercury Analyzer. Following the institution of this procedure, the mercury mass balance closure returned to an acceptable level as demonstrated in Runs 27 to 34.

Figure 4. Mercury mass balance closure for laboratory sorbent injection experiments.



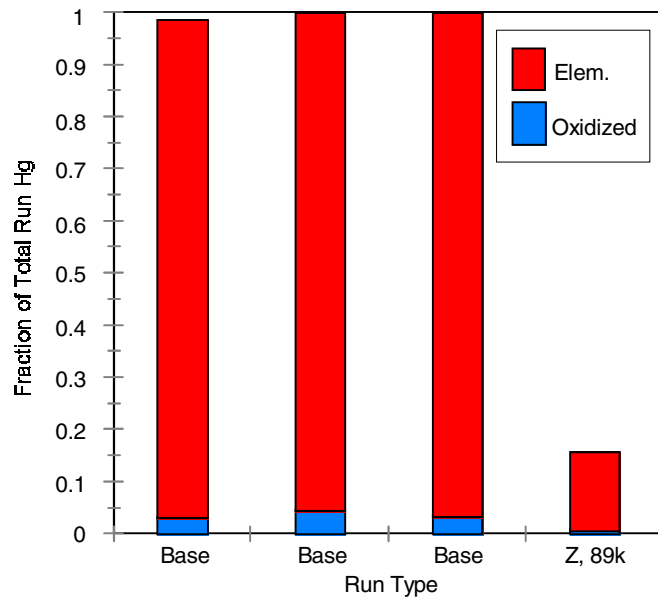
Baseline Runs

In order to characterize the experimental apparatus and explain experimental data, three types of baseline runs were conducted. In all cases additional mercury was added to the system.

- (A) No coal combustion took place and no sorbent was injected. The purpose of these experiments was to determine the amount of mercury that may be lost while flowing through the furnace.
- (B) No coal combustion took place but treated zeolite was injected. The purpose of these experiments was to determine the amount of mercury captured by the treated zeolite when no coal combustion products are present.
- (C) Coal combustion took place but no sorbent was injected. The purpose of these experiments was to measure the amount of mercury removed by the fly ash alone.

Figure 5 shows results from baseline types A and B, in which the amount of mercury exiting the system (downstream of the filter assembly) and mercury speciation are plotted. For baseline A runs, over 98% of the total amount of mercury injected is recovered in the impingers at the end of the baseline A runs. This indicates that there is no substantial amount of mercury lost or unaccounted for while flowing through the furnace. Also for these runs, greater than 95% of the mercury is collected as elemental mercury. It is unknown why 5% or less of the mercury in the three baseline runs was collected as oxidized mercury. It may be possible that some of the elemental mercury was removed in the potassium chloride impingers or that some oxidation may

Figure 5. Mercury speciation for runs without coal combustion, baselines type A and B.



have occurred while the mercury was in the furnace. Note that based on baseline A, 95% of the mercury in the gas was expected to be elemental in these experiments.

Baseline type B consists of a run in which treated zeolite sorbent was injected into the sorbent reactor at 130°C (266°F), with no coal combustion taking place. As shown in Figure 5, only 15% of the total mercury was recovered in the Ontario Hydro train, while the rest was removed by the sorbent. Of the remaining 85%, 61% was captured in flight, and 24% was captured on the filter sorbent. The sorbent:Hg ratio was 89,000 for this run and the run shows an 85% reduction in elemental mercury under these conditions. The mass balance closure for these baseline runs was excellent, ranging from 98 to 110%.

Results from baseline C runs, “fly ash baseline” are shown in Figures 6 and 7. The amount of mercury removed per unit mass of ash was plotted against the mass of ash present in the present in the effluent stream, as shown in Figure 6. To account for variations in mercury concentration in the effluent stream between the runs the mass of ash was normalized with the amount of mercury present. It can be seen that ash removes mercury and the amount of mercury removed per unit mass decreases from 8 to 2 µg/g as the ash to mercury ratio present in the effluent gas increases from 500 to 4200.

Figure 7 shows speciation data for the fly ash baseline runs. The fraction of the total mercury recovered by the impingers ranges from 18 to 60%. The remaining mercury in the runs was captured by particulate with less than 2% being found in the filter ash for all runs. Most of the mercury recovered was elemental, with the average ratio of elemental to oxidized mercury being 3.2, for runs #15, 16, and 17 of Figure 7. In most of “fly ash baselines”, Figure 7, 9 to 17% of the initial amount of mercury is recovered as oxidized, while only 5% of the initial amount of

Figure 6. Mercury captured by fly ash for baseline type C runs.

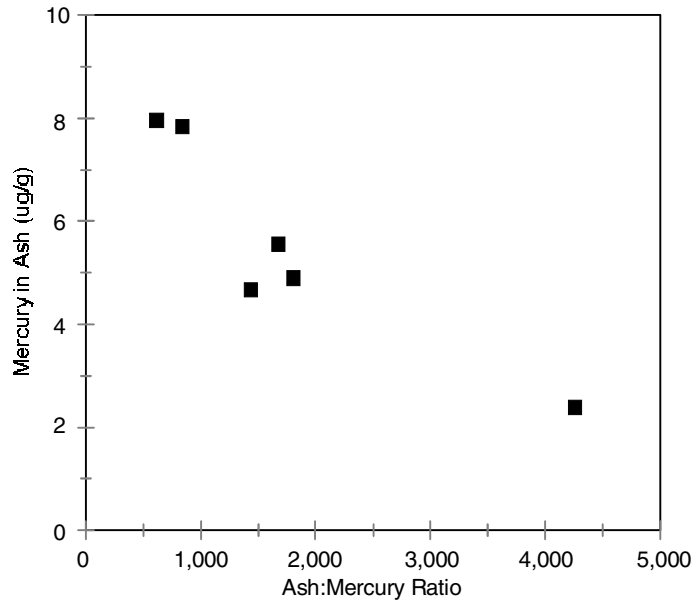
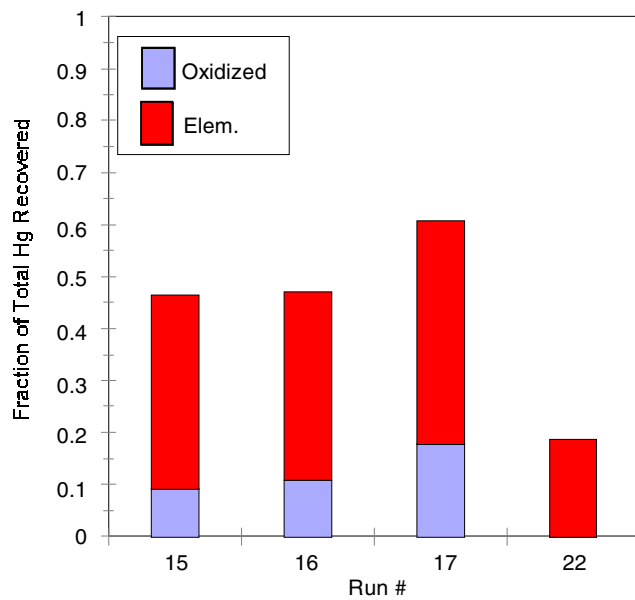


Figure 7. Speciation data for fly ash baseline runs.



mercury is recovered as oxidized in baseline type A runs, in which no fly ash is present. This is an indication oxidation of mercury takes places in the presence of flue gases and fly ash.

In previous work at PSI, which duplicated these conditions with the exception of no provision for in-flight capture of mercury, we demonstrated no mercury capture by the filter ash and 61% elemental and 38% oxidized mercury in the impingers with 91% mass balance. Comparing the

data in Figure 7 with the earlier data indicates that the Pittsburgh fly ash has removed 40% of the elemental and 75% of the oxidized mercury.

Sorbent Injection Data

Figure 8 shows a plot of mercury capture by activated carbon at both high and low temperatures as a function of sorbent:Hg ratio. This data shows that there is very little decrease in the mercury capture at the higher temperature in this range of sorbent ratios. For the low temperature data it also shows little increase in mercury capture with 70% increase in sorbent injected. This trend at the higher mercury capture levels that has been shown in other activated carbon injection work. Further reduction in mercury would require a substantial increase in the amount of sorbent injected.

Figure 8. Mercury captured by activated carbon at high and low temperatures.

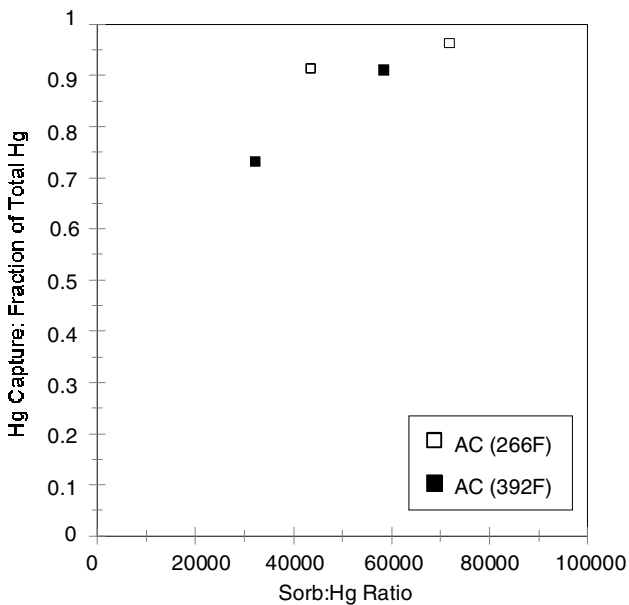


Figure 9 is a plot of mercury removal by the two types of treated zeolite sorbent at high and low temperatures as a function of sorbent:Hg ratio. Also included in the plot is the low temperature zeolite injection run with no coal combustion. A comparison of the high temperature data with the low temperature runs once again shows no difference in mercury capture with an increase in temperature. This effect was also noted in previous zeolite work at PSI. There does seem to be an increase in mercury capture with larger sorbent:Hg ratios for the zeolite sorbent with the more dramatic increase at ratios below 20,000. Mercury removal efficiencies were in the range of 45% to 92% depending on the zeolite type and the sorbent to mercury ratio.

Figure 10 shows the amount of mercury removed per unit mass of sorbent plotted against the sorbent to mercury ratio present in the effluent stream. As the sorbent to mercury ratio increases, the amount of mercury removed per unit mass of sorbent decreases for all sorbents. Strikingly, there are no great differences between the different sorbent runs. In these runs, part of the

Figure 9. Mercury captured by zeolite sorbent at high and low temperatures.

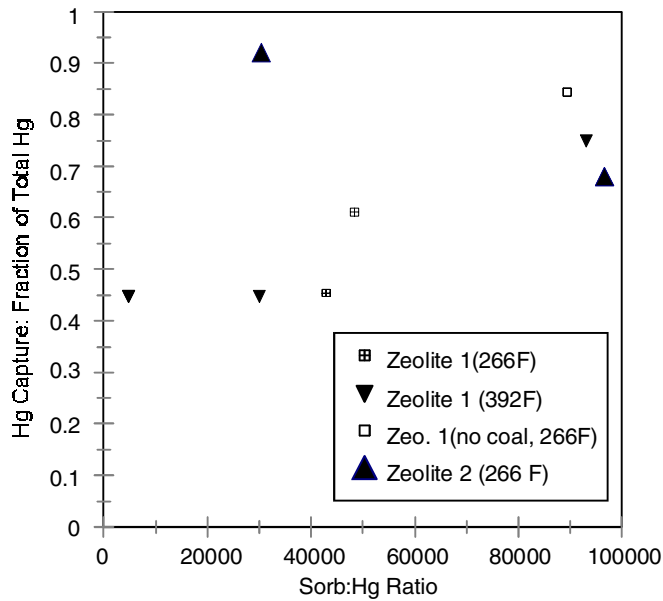
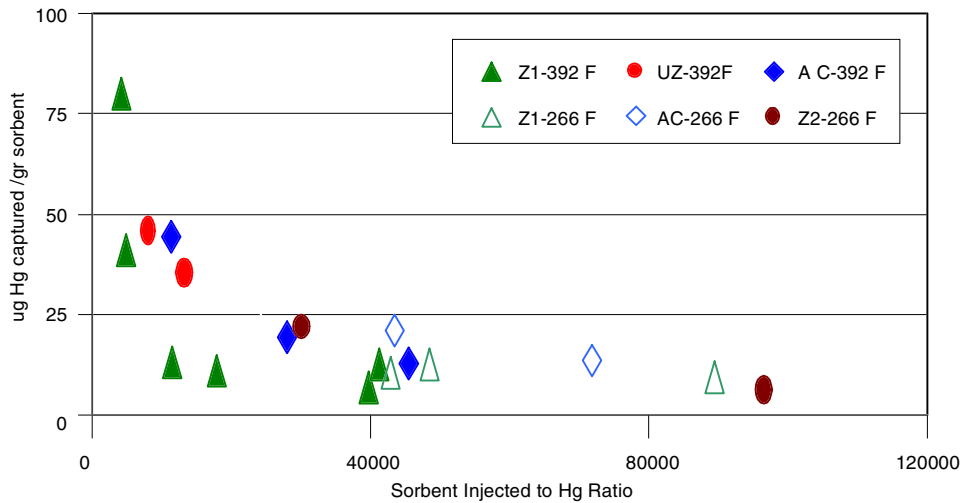


Figure 10. Mercury captured in sorbent runs.

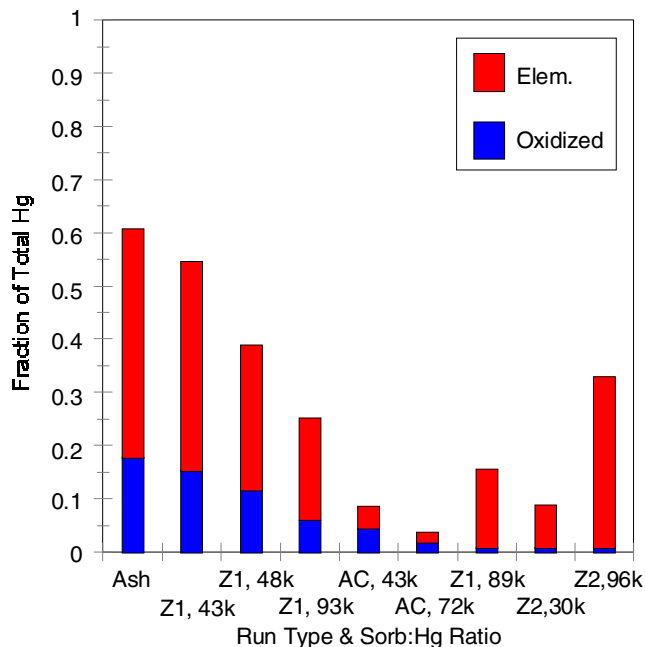


mercury is removed by the ash and part by the sorbent, but the relative amount is hard to estimate from these experiments. Simple mass balance calculations indicate that in the sorbent runs, the amount of mercury removed per unit mass of ash has to be less than what shown in Figure 6. This indicates that the reactivity of the sorbent is higher than that of the ash, therefore mercury is preferentially removed by the sorbent.

Figure 11 shows speciation data for the sorbent injection runs. Again is apparent that both in zeolite and activated carbon runs mercury oxidation takes place. The exact amount of mercury

that oxidizes and the fraction of the elemental and oxidized mercury that are removed cannot be easily deduced from these experiments.

Figure 11. Speciation data for sorbent injection runs.



Summary

Two types of treated zeolite sorbent and an activated carbon were injected into coal combustion flue gases in a laboratory reactor under various conditions. The flue gas was generated by the combustion of Pittsburgh seam coal and the mercury concentration of the stream was augmented with additional elemental mercury. The temperature of the flue gases was in the range of 130 to 200°C, the mercury concentration was in the range of 30 to 60 μm^3 and the residence times of the sorbent in the flue gases were about 2 s.

When there is no sorbent present, the Pittsburgh coal ash removes a significant portion of the mercury in-flight. In the presence of sorbent, mercury seems to be preferentially removed by the sorbent, presumably due to lower reactivity of the ash with respect to sorbent.

Examination of the speciation data for the sorbent injection runs shows a reduction in elemental mercury with increased sorbent:Hg ratios for both sorbents. In addition, the speciation results show that the fly ash removes both elemental and oxidized mercury with the most significant reduction occurring in the oxidized portion.

Mercury capture for each sorbent was displayed as a function of sorbent:Hg ratio for both high and low temperatures. The mercury capture varied in the range of 45 to 92% depending on the amount of sorbent injected and the type of sorbent. These data showed no difference in mercury capture with an increase in gas temperature in the sorbent reactor for all sorbents. At lower

sorbent:Hg ratios for the zeolite sorbent, an increase in mercury capture was evident with small changes in the ratio. However, this trend disappeared at the higher sorbent:Hg ratios for the activated carbon runs. This indicates that to achieve further reduction in vapor phase mercury would require a substantial increase in the amount of sorbent injected into the gas stream.

ACKNOWLEDGMENTS

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