

Mercury Speciation as a Function of Flue Gas Chlorine Content and Composition in a 1 MW Semi-Industrial Scale Coal-Fired Facility

Paper # 28

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ABSTRACT

The complicated chemistry and multiple mechanisms affecting mercury speciation and control make it necessary to investigate these processes at conditions relevant to full-scale boilers. Experiments were performed in a 1MW semi-industrial-scale, coal-fired facility, representative of a full-scale boiler. Southern Research Institute's *spike and recovery system and procedures* were used to obtain real-time mercury-speciation measurements, with less than 5% uncertainty in the measured values. The focus of this work was on solutions for Powder River Basin (PRB) sub-bituminous coals and high-burnout conditions, where the fly ash contained relatively little unburned carbon. The relationship of mercury oxidation with chlorine concentration was investigated in conjunction with other associated parameters of importance, such as unburned carbon, minerals in ash, and flue-gas composition. The impact of chlorine content was independently evaluated by injecting chlorine through the burner, while firing PRB coal. The concentration of oxidized mercury at the baghouse inlet and outlet increased as chlorine was added to the flue gas. For the high-efficiency (low UBC) conditions investigated in this work, ash composition was found to be more important than chlorine content. The addition of high-iron bituminous ash, either through direct ash injection or through coal blending, was found to significantly increase mercury oxidation before and within the pilot combustor's baghouse, while firing PRB coal. For certain pilot-scale conditions, blending a small amount of high-iron bituminous coal (<10% by mass) with PRB sub-bituminous coal, resulted in oxidized fractions of mercury of >50% before the particulate collection device and >95% at the outlet of a baghouse. Work continues at Southern Research Institute to elucidate the mechanisms observed for Hg-oxidation enhancement by coal-blending and other adjustments to the flue-gas composition. A greater understanding of these mechanisms will allow the design of Hg-mitigation strategies with high-certainty of the desired result.

INTRODUCTION

The predominant forms of mercury in coal-fired flue gas are elemental (Hg^0) and oxidized (HgCl_2)¹⁻³. The percentage of oxidized mercury in the stack effluent of a particular power plant depends on many variables associated with the coal type, combustion efficiency, and the pollution control equipment used. Essentially all of the mercury entering the furnace with the coal is vaporized and exists in the elemental form until the flue gases cool below 1000 °F¹⁻³. The oxidation of mercury in coal-fired boiler systems is kinetically limited¹⁻³. The mercury content of coal is small, and hence, so is the concentration of mercury in flue gas. The trace nature of mercury in flue gas adds complexity to the system of kinetically-controlled reactions that determine the fate of mercury speciation in coal-fired boilers. Because the concentration of mercury is very small in flue gas, any favorable mercury-oxidation reaction does not have the ability to promulgate itself. In virtually every conceivable competitive reaction, the competing gas component, much in excess of mercury, dominates. On the other hand, where the formation of mercuric compounds is thermodynamically favored, bulk and pore diffusion limitations dominate, unless the oxidant is in vast abundance compared with mercury.

In addition to the trace nature of mercury in coal-fired boilers, favorable reactions for mercury oxidation have short temperature/time windows. Consequently, the extent of mercury oxidation is highly dependent on catalytic processes. Heterogeneous catalysis not only enhances the direct mercury oxidation reactions, but also makes available gas components (such as Cl) that are otherwise scavenged by competing gas species present at much higher concentrations. The combination of factors affecting mercury speciation in coal-fired boilers makes it extremely difficult to design a cost-effective strategy for mercury control. The present work attempts to obtain an understanding of the mechanisms governing mercury speciation in flue-gas environments that exist in full-scale utilities. A correct and more complete understanding of Hg-speciation will allow direct design and development of Hg-mitigation technologies and processes with assurance of the desired result.

A system of reactions, which include significant chlorine-speciation reactions, has been proposed to describe homogeneous Hg-oxidation⁴. This set of governing reactions allows direct oxidation of Hg^0 to HgCl and HgCl to HgCl_2 by the following four chlorine species with different reaction rates: Cl, Cl_2 , HCl, and HOCl ⁴. This system of equations has been shown to effectively predict mercury speciation for specific homogeneous systems². However, the homogeneous model alone consistently under predicts the oxidation of mercury from coal-fired boilers⁵. Hence, it is important to identify and describe the heterogeneous reactions that dominate the mercury-oxidation process.

Benchscale work has identified several components of flyash that may play an important role in heterogeneous Hg-oxidation reactions⁶⁻⁷, particularly unburned carbon (UBC) and iron⁷. Niksa et. al.⁸ suggested a possible mechanism whereby UBC can catalyze mercury oxidation, as follows:



Chun et. al.⁷ performed benchscale Hg-oxidation experiments over different coal flyash and found that coal ash high in iron was particularly effective at catalyzing the mercury oxidation reaction. In analogy to Equ.1 and to other chlorine speciation catalysis enhanced reactions, the iron enhanced mercury oxidation reaction may be represented by:



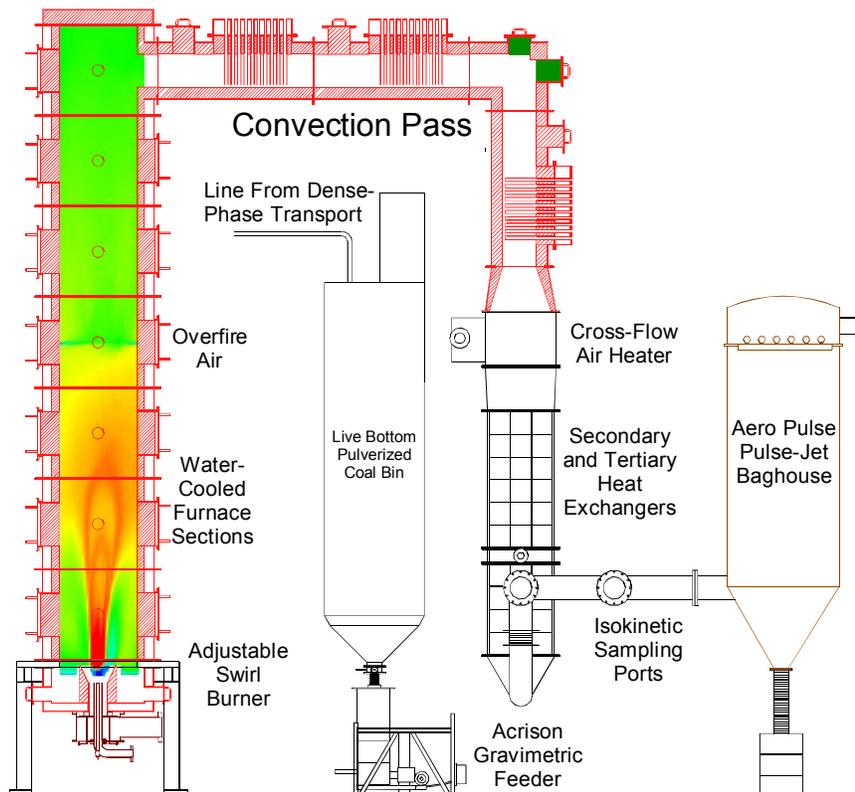
where FeCS = an iron catalytic site. In both equations 1 and 2 above, HCl is the chlorine species of focus, because this is the predominant form of chlorine in flue gas in all coal-fired boilers. In fact, nearly all chlorine passing through the burner is converted to HCl and remains in that form through the stack exit, as confirmed by experiments¹, thermodynamic equilibrium predictions¹, and kinetic modeling². On the other hand, Cl (attached to the catalytic site) is the most likely candidate for mercury oxidation. Indeed, Cl is considered the form of chlorine that is most responsible for mercury oxidation in coal-fired boilers⁹.

In addition to the specific heterogeneous reaction mechanisms suggested in the literature, SO_x and NO_x have been implicated in terms of having an effect on mercury oxidation³. Hence, the present work focuses on the effects of UBC and iron in ash and the importance of chlorine and other acid gases on mercury speciation. Experiments were conducted in a 1MW semi-industrial scale coal-fired facility. Therefore, the mechanisms elucidated are believed to be applicable to full-scale units.

EXPERIMENTAL

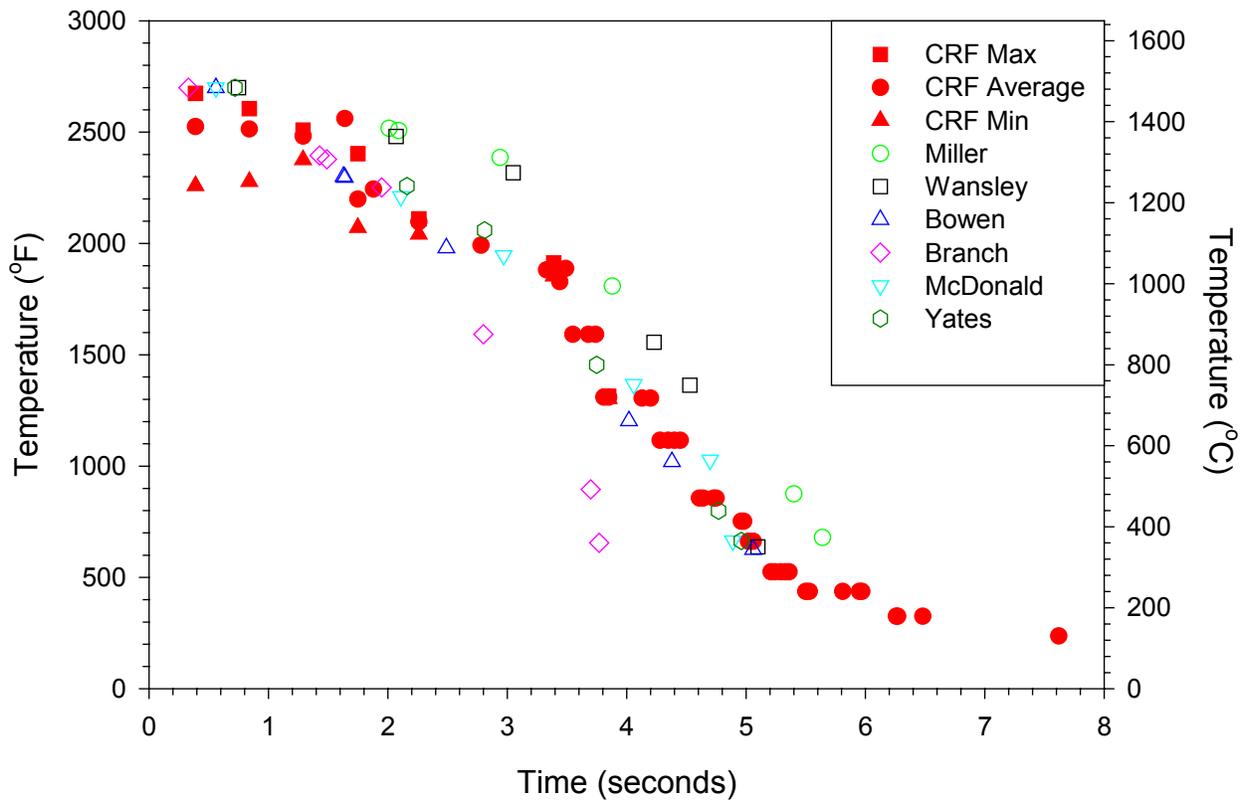
The Combustion Research Facility (CRF) at Southern Research Institute (SRI) in Birmingham, AL, is a 1-MW_t semi-industrial-scale, coal-fired facility, which mimics the thermal profile of a full-scale boiler from the burner through the economizer. Figure 1 shows a two-dimensional sketch of this facility.

Figure 1. Combustion Research Facility (CRF).



In this work, mercury speciation was measured at the inlet and outlet of an Aero-Pulse pulse-jet baghouse, which uses full-scale Ryton-bags. As shown in Fig. 2, the temperature/time history of the CRF mimics that of full-scale power plants from the burner through the economizer. The data in Fig. 3 illustrate the range of temperature/time histories for all experiments performed in the CRF, in this investigation. Two different baghouse temperature conditions were explored, a high (Inlet = 337 °F Outlet = 300 °F) and a low (Inlet = 280 °F Outlet = 260 °F) condition. The baghouse temperature was adjusted by changing the rate of cooling in the last set of heat exchangers, the inlet temperature of which was fairly constant and was always below 550 °F. Several hours were allowed between each change in baghouse temperature to allow the system to reach steady state. The residence time from the burner to the baghouse (identified in Fig. 3) changed by less than a quarter-second across the range of coal-blends and baghouse temperature conditions.

Figure 2. Combustion Research Facility (CRF) temperature/time histories compared with those of full-scale Southern Company coal-fired power plants.

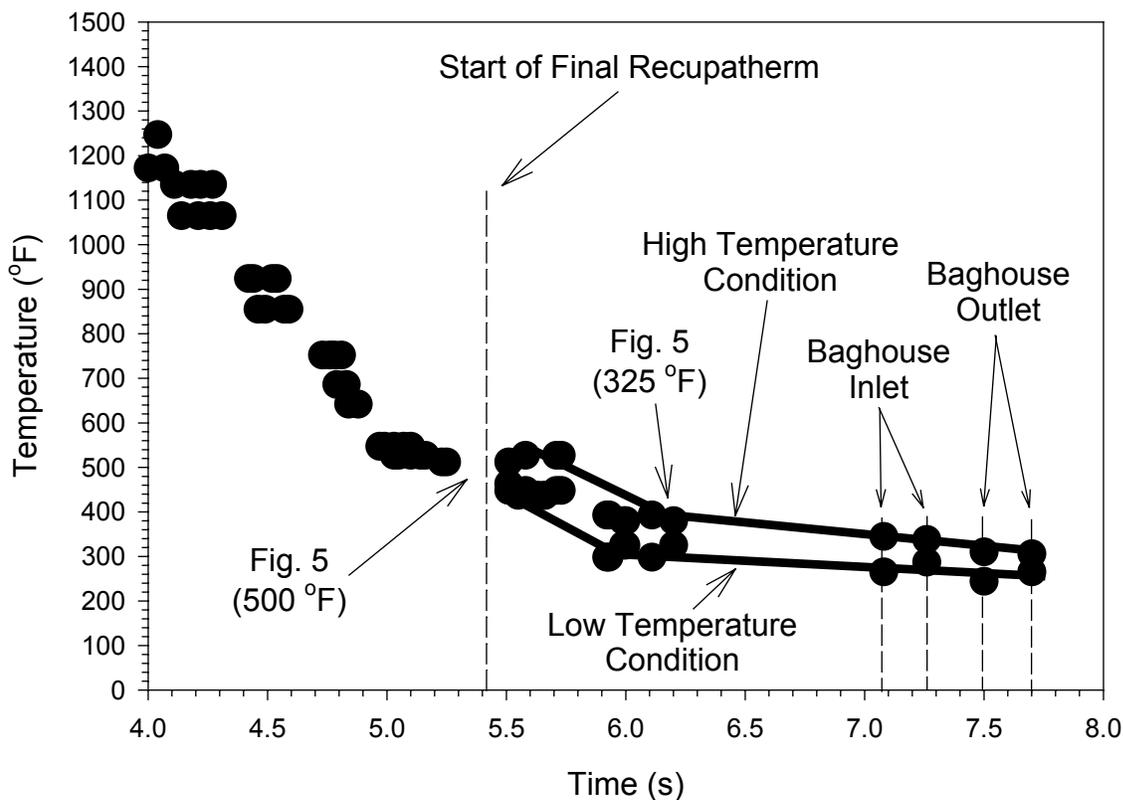


An extractive continuous-emissions monitoring (CEM) system measured the concentrations of CO, CO₂, NO_x, SO₂, and O₂ in the flue gas, just ahead of the baghouse. In addition, manual measurements of chlorine and moisture were obtained throughout the testing.

Mercury monitoring was performed with an advanced and improved version of the PS Analytical 10.665 Stack Gas Analyzer. The PSA monitor has been customized to use an APOGEE Scientific QSIS probe for sampling flue gas. The QSIS probe is designed to pull a large volume of flue gas through the core, or center, of a probe designed as an annulus at a high and turbulent velocity, thus scouring clean the walls of this core tube. The inner wall of the

annulus contains a section with a porous frit through which a small sample of flue gas is drawn. The excess flue gas is directed back into the duct, downstream of the sample inlet. In this way, the QGIS probe allows a sample to be drawn from the duct without pulling it through an ash layer, thereby minimizing alteration of the gas sample – especially capture or oxidation of the vapor phase mercury by or on the particulate. Southern Research also developed an advanced *spike and recovery* system to validate the correctness of the mercury-speciation numbers measured and correct for errors that occur. As a result of these and other modifications, Southern Research Institute believes it can now measure mercury speciation within a maximum uncertainty of 5%. Accurate and precise mercury speciation measurements are key to a fundamental mercury speciation and capture investigation.

Figure 3. Temperature profile during mercury measurements.



The *spike and recovery system* is a first of its kind prototype provided by PS Analytical. The adaptation of this *spike and recovery system* to allow spiking at the tip of the APOGEE Scientific QGIS probe was performed by Southern Research personnel. The spike of mercury is introduced into the tip of the APOGEE Scientific QGIS probe far enough downstream from the inlet to prevent losses to the duct and far enough upstream of the porous annulus to allow complete mixing before the sampled gas is pulled through the porous frit. A relatively small quantity of air is used to carry the mercury spike to the probe. Therefore, dilution is insignificant, and the general flue-gas composition is undisturbed. The main impact of the spike is simply to increase the concentration of mercury in the sampled gas. This is significant, since mercury-oxidation processes that interfere with speciation measurements can involve three and four component interactions of flue-gas species on catalytic ash sites¹⁰. The concentration of mercury in the spike stream is generated by controlling the flow rate, pressures and temperatures

of air in and through a mercury reservoir chamber. In addition, SRI uses a parallel Hg-source for the *spike and recovery* system, involving permeation tubes, allowing a check on the source calibration. High-precision mass flow controllers are used to obtain the precise metering needed for high-certainty calibrated spikes. Southern Research believes that *spike and recovery* provides a greater level of confidence in the resulting mercury speciation than any other method currently in use. A schematic of the monitoring system is presented in Fig. 4, including spike location, gas-conditioning system, and calibrated spike source.

Figure 4. Mercury monitoring system, including spike and recovery.

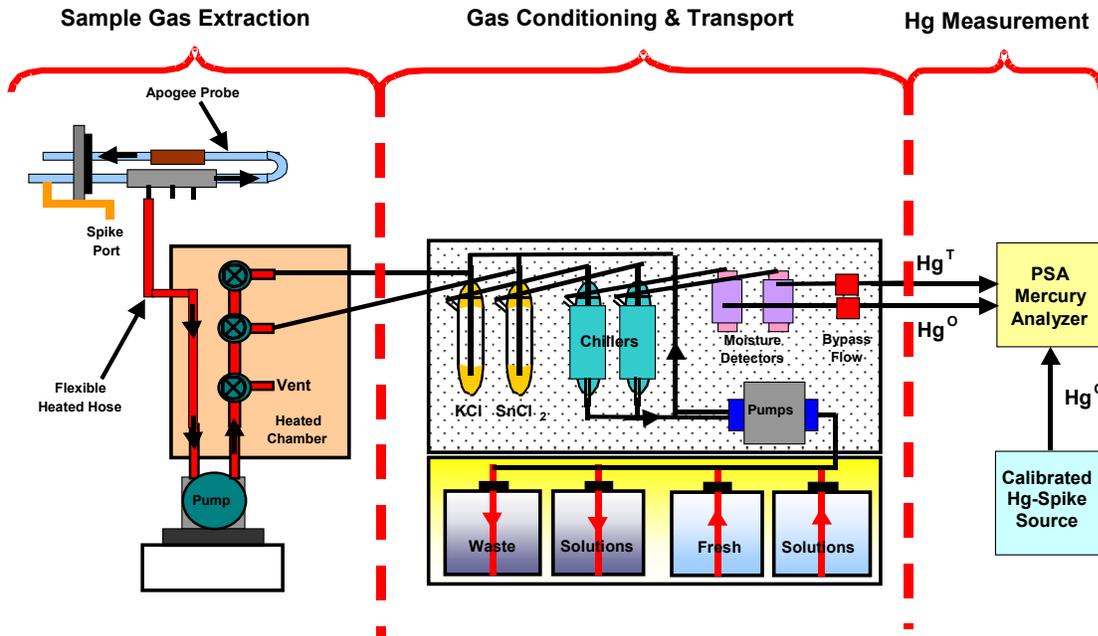


Figure 5 illustrates the use of the spike and recovery system for establishing total and oxidized mercury concentrations in the flue gas, while first burning natural gas (time 0:00 to 5:00) and then Black Thunder, a Powder River Basin (PRB) coal. As shown, the *spike recoveries* are observed on top of the measured initial mercury concentrations for both fuels. The mercury speciation data were obtained well upstream of the baghouse. The residence times at the actual sampling points (temperature locations) are marked on Figure 3. Table 1 contains the Hg-speciation measurements of the PRB flue gas, after correction using the *spike recoveries* shown in Table 2 (explained below).

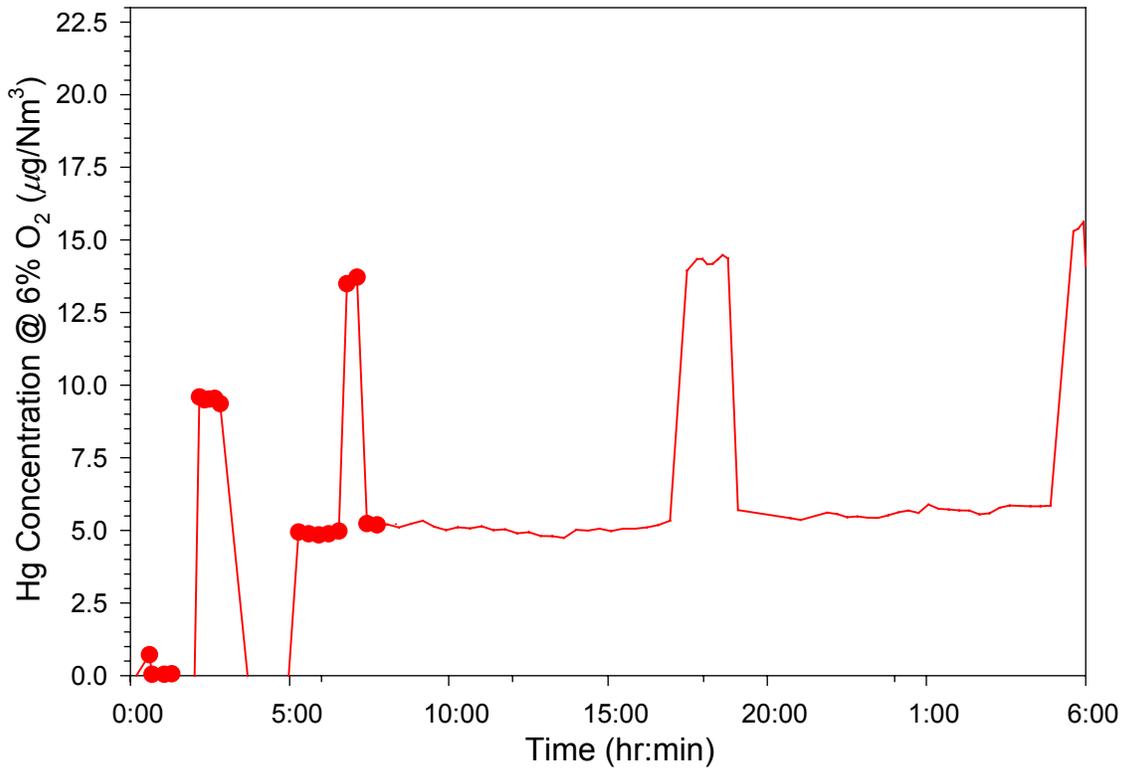
Table 1. Location and speciation of Hg-measurements, while firing PRB coal.

Location	Temperature (°F)	Hg ^o (µg/Nm ³)	Hg ^T (µg/Nm ³)	Elemental Fraction %
After Recupatherm 1	500	7.4 +/- 0.93	8.4 +/- 1.1	88.1 +/- 1.5
After Recupatherm 2	325	6.5 +/- 0.44	8.0 +/- 0.70	81.3 +/- 1.0

- The mercury concentrations were measured with 6% oxygen in the flue gas.

The percentage of elemental mercury was measured directly (i.e., the population of individual measurements of Hg° and Hg^{T} , taken one after the other, were used to obtain the average and standard deviation for the elemental fraction), not calculated from the other values in the table.

Figure 5. Mercury speciation data taken with an advanced and customized Hg-speciation semi-continuous monitor, and validated with *spike and recovery* for quality assurance.



As shown in Table 2, the recoveries of the elemental-mercury spike are consistently lower than the recoveries of total mercury. This is due to undesired oxidation in the sampling lines and uptake of mercury in the KCl impingers. On the other hand, the stannous chloride (total Hg) impingers scavenge a significant quantity of CO_2 , thus artificially raising the concentration of mercury in the sample gas.

Table 2. Spike recoveries while firing PRB coal.

Sample Type	Temperature (°C)	Recovery 1 (µg/Nm ³)	Recovery 2 (µg/Nm ³)	Recovery 3 (µg/Nm ³)	Ave Recovery /Spike (%)
Hg°	163	8.30	8.78	8.06	86.4
Hg^{T}	163	10.96	11.13	10.80	113.0
Hg°	260	7.91	8.24	7.81	82.4
Hg^{T}	260	11.59	11.64	11.06	117.8

- The Hg° spike injected into the tip of the sampling probe was $\sim 9.7 \mu\text{g}/\text{Nm}^3$.

However, with *spike and recovery* these errors can be observed and corrected. In this case (see Table 2), the spike recoveries were all within 20% of the expected value. Hence, a simple linear correction factor was used. As partially apparent in the data of Table 2, the difference in recoveries between expected and actual values was systematic, not random. In addition, as apparent in Fig. 5, there was little variation of the measured data for the flue-gas measurements or the spike-recoveries themselves. Using the *spike and recovery system* to correct for the systematic error has allowed mercury speciation measurements with less than 5% uncertainty for all of the data presented in this paper. This estimate of maximum uncertainty is the standard deviation of corrected values added to the variance observed with fluctuations in CRF operational parameters.

Tables 3-5 contain the analysis (including Hg and Cl) of the Black Thunder Powder River Basin Coal (PRB) and two bituminous coals, Choctaw America and Blacksville, used in this work. The PRB coal is the same coal used to obtain the data in Fig. 5. As shown in Tables 3 and 4, both PRB and Choctaw America are low chlorine coals. Blacksville is a higher chlorine coal (see Table 5). Choctaw America was chosen to blend with PRB for two reasons. First, it is a low chlorine coal, so the importance of other parameters could more easily be examined without interference of chlorine. Second, it has a high iron content. As shown in Table 6, Blacksville has an even higher iron content than Choctaw America, which is the primary reason for choosing this coal to blend.

Table 3. Black Thunder PRB Sub-bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	14.00	% Carbon	74.55	Hg ($\mu\text{g/g}$)	0.07 – 0.08
% Ash	5.92	% Hydrogen	4.78		
% Volatiles	37.57	% Nitrogen	1.03	Cl (%)	0.0130
% Fixed C	42.70	% Sulfur	0.37		
HV (Btu/lb)	9,969	% Oxygen	19.27		

Table 4. Choctaw America HvA Bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	2.04	% Carbon	85.39	Hg ($\mu\text{g/g}$)	0.08 – 0.10
% Ash	4.19	% Hydrogen	5.16		
% Volatiles	31.76	% Nitrogen	2.04	Cl (%)	0.0127
% Fixed C	62.01	% Sulfur	0.96		
HV (Btu/lb)	14,019	% Oxygen	6.45		

Table 5. Blacksville HvA Bituminous coal analysis.

Proximate Analysis (as rec.)		Ultimate analysis (daf)		Hg and Cl Analysis (as rec.)	
% Moisture	4.03	% Carbon	84.00	Hg ($\mu\text{g/g}$)	0.09
% Ash	8.49	% Hydrogen	5.40		
% Volatiles	37.01	% Nitrogen	1.67	Cl (%)	0.0580
% Fixed C	50.47	% Sulfur	3.10		
HV (Btu/lb)	13,299	% Oxygen	5.84		

Table 6. Mineral analysis of parent coals

Species	Black Thunder	Choctaw America	Blacksville
% Li ₂ O	0.01	0.06	0.03
% Na ₂ O	1.4	1.1	1.0
% K ₂ O	0.50	2.0	2.9
% MgO	4.3	1.1	1.0
% CaO	22.0	2.5	4.6
% Fe ₂ O ₃	6.0	13.8	21.1
% Al ₂ O ₃	15.4	31.4	21.3
% SiO ₂	35.4	42.6	41.6
% TiO ₂	1.3	1.3	1.2
% P ₂ O ₅	0.70	0.16	0.08
% SO ₃	11.5	2.8	4.8

RESULTS AND DISCUSSION

Many different parameters are altered when coal-blend and firing conditions are changed. However, the coal mercury content was fairly consistent (see Tables 3-5), and operation of the CRF was stable. Therefore, the main differences in conditions fall within two broad categories, flue-gas composition and flyash properties. The likely parameters of importance are UBC, iron and calcium content, availability of catalytic material, total flue-gas chlorine content, moisture, SO₂, NO_x, and surface area. The other large-volume benign parameters (i.e., O₂, CO/CO₂, etc.) were visually examined for a correlation with Hg-oxidation in plots similar to those shown in the remainder of this paper, but none were found. Of the likely parameters, NO_x and moisture were found not to have any observable correlation to mercury oxidation in this work. The remaining likely parameters were examined, and their relationship to mercury oxidation is illustrated and discussed in this section.

Figure 6 compares the relationship between Hg-speciation and chlorine when the flue gas HCl is varied either by injecting chlorine through the burner while firing PRB coal or by blending PRB with higher chlorine bituminous coals. All data presented in this and all remaining figures are corrected to 8% oxygen in the flue gas, which was the average oxygen level in the flue gas at the baghouse inlet. Thus all of the values presented are directly comparable, one to another. In Fig.6, the vertical axis is the fraction of gas-phase elemental mercury found at either the baghouse inlet or outlet divided by the total gas-phase mercury found at the baghouse inlet. The mass balance on coal-mercury suggests that the majority of mercury at the baghouse inlet was in the gas-phase for all blend conditions. It was assumed that any elemental mercury captured in the baghouse would have been first oxidized. It was also assumed that reduction of mercury from the oxidized to elemental form across the baghouse was insignificant. The conventions described for Hg^o/Hg^T at the inlet and outlet of the baghouse, shown in Fig. 6, were also used for all remaining graphs in this paper.

As shown (see Fig. 6), chlorine injection through the burner of the CRF decreased the fraction of elemental mercury at the inlet and outlet of the baghouse. However, the elemental mercury fraction at the inlet and outlet of the baghouse during coal blending (with the same concentration of HCl in the flue gas) is much less than that observed while firing PRB coal only. This step change in Hg-oxidation between 100% PRB and PRB/bituminous blends, suggests a

change of controlling Hg-oxidation mechanisms. The values in Fig. 6 are not significantly affected by differences in furnace exit oxygen (FEO) levels, which has an effect on UBC.

Figure 6. Effect of flue-gas chlorine on Hg-oxidation at the baghouse inlet and outlet for several different levels of furnace exit oxygen (FEO).

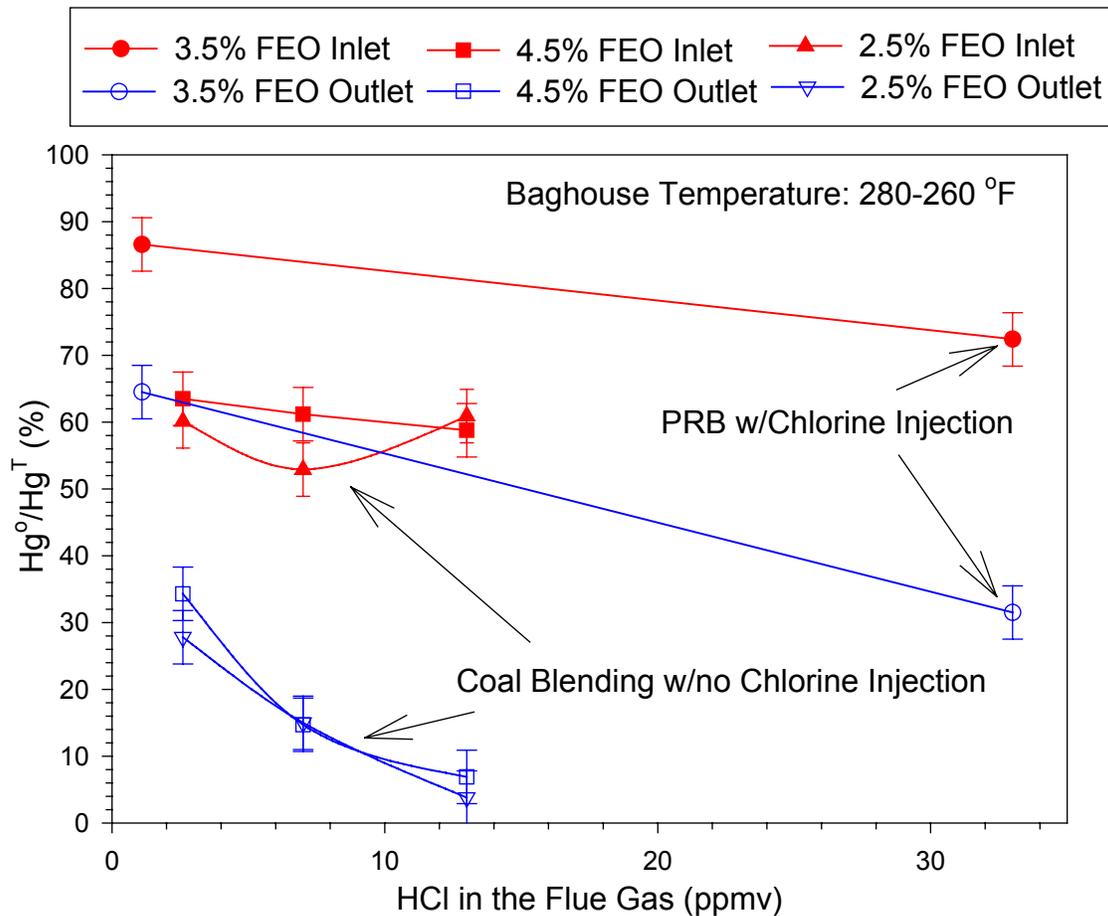


Figure 7 illustrates the extent of mercury oxidation at the inlet of the baghouse for 3 different coal blends at two different FEO levels. For comparison, a line is drawn in Fig. 7 at ~ 86.6%, representing the fraction of mercury in the elemental form for 100% PRB at 3.5% FEO and approximately 1 ppm HCl. The differences in elemental mercury fraction between different coal blends is small compared with the step decrease in elemental mercury between the 100% PRB case and the coal blend cases, which is about 30%. In general, lower FEO corresponds with higher UBC, but there is very little difference in the fraction of elemental mercury between the 4.5% FEO (UBC: 0.72-0.34) and 2.5% FEO (UBC: 1.45-0.33) data. Flue gas chlorine is also indicated on Fig. 7 (from coal chlorine). It is apparent that oxidation was not dominated by chlorine content in the flue gas. In addition to the variables listed in Fig. 7, the ash composition (i.e., iron and calcium content) differed for each blend.

At the baghouse outlet (see Fig. 8), the extent of mercury oxidation was much greater, indicating significant capture by the ash and/or catalytic enhancement of mercury oxidation through the baghouse filter cake. Again, the elemental mercury fraction for 100% PRB coal is much higher than all of the coal blend results. This step decrease in elemental mercury at the

front and back of the baghouse suggests that there was a change in mechanisms controlling mercury oxidation between 100% PRB firing and all coal-blend conditions.

Figure 7. Mercury speciation at the baghouse inlet (@280 °F) for different blends of PRB and bituminous coals (BV = Blacksville, CA = Choctaw America)

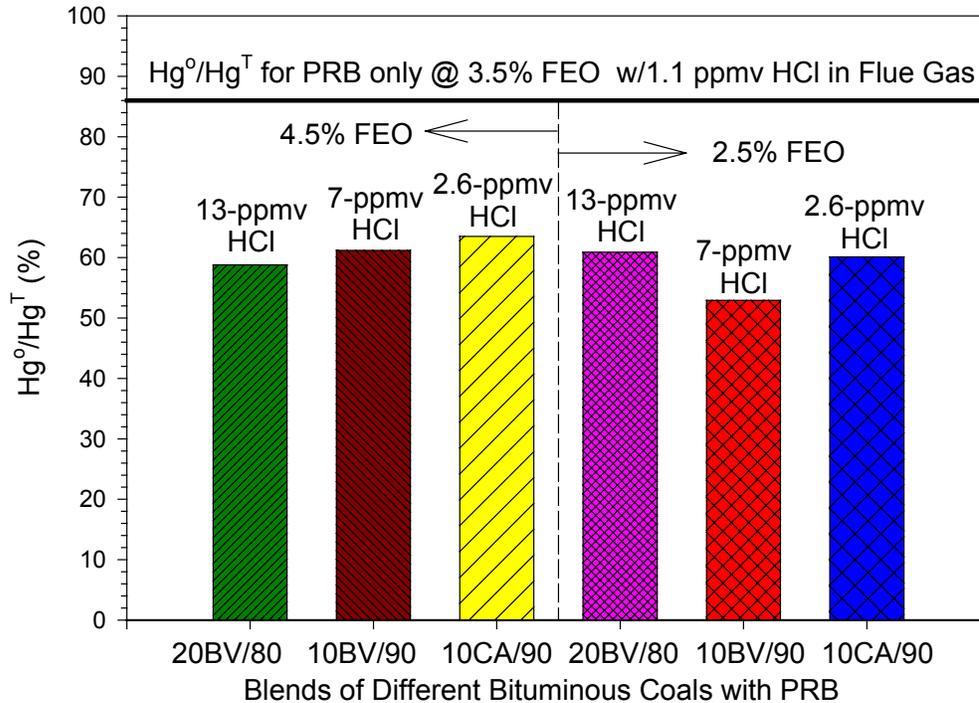
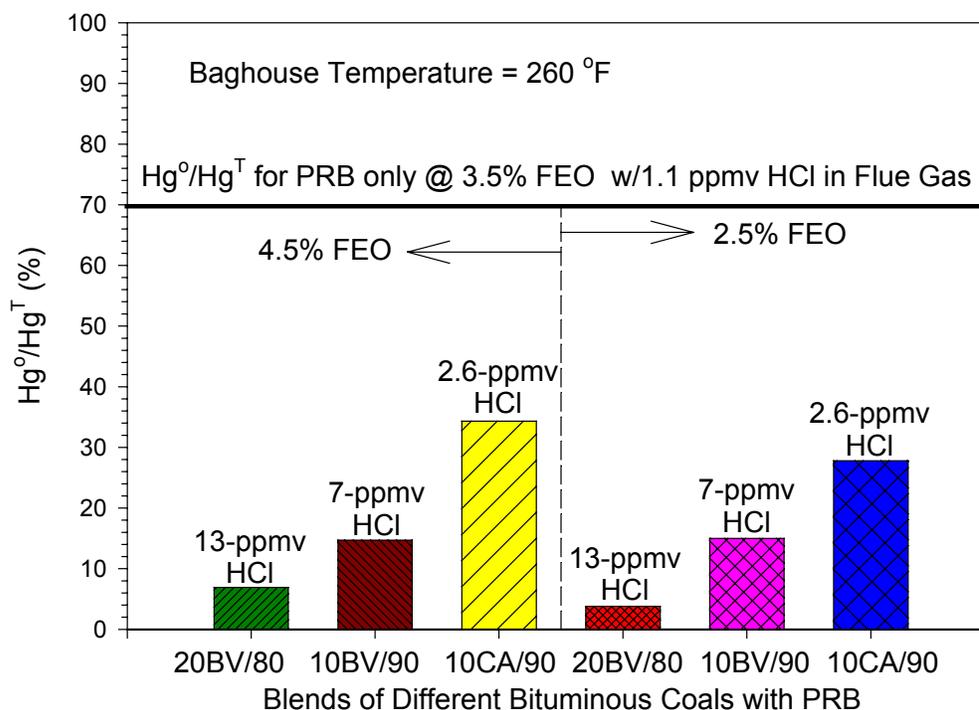


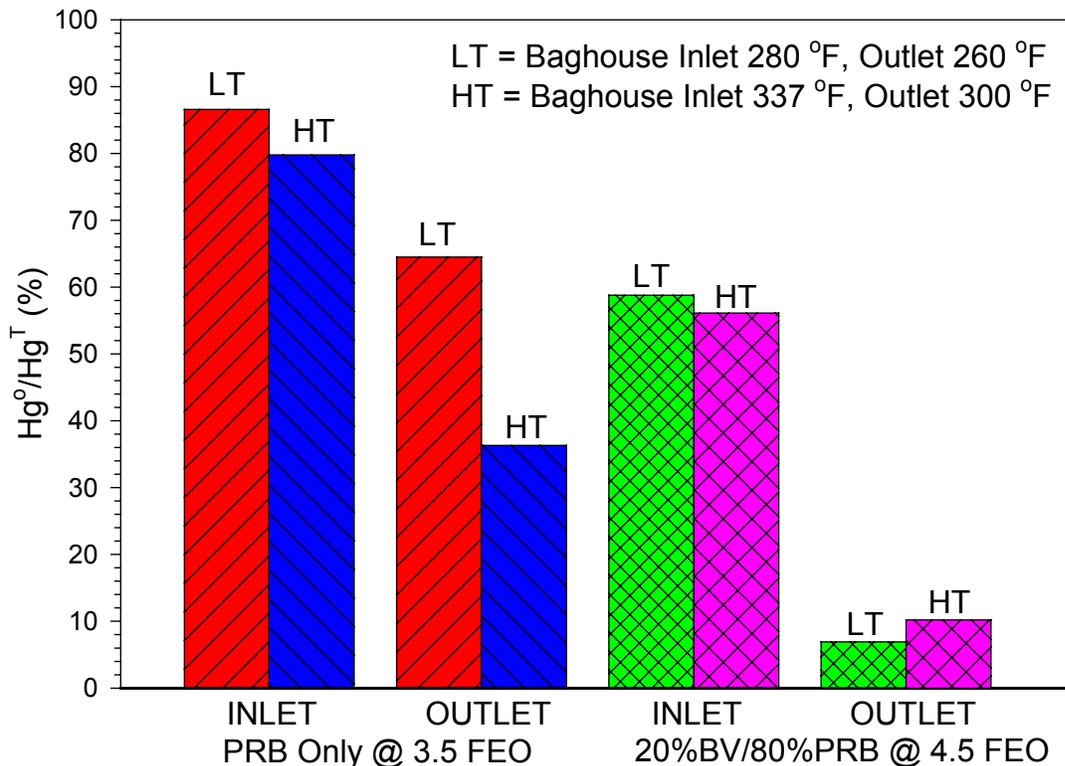
Figure 8. Mercury speciation at the baghouse outlet (@260 °F) for different blends of PRB and bituminous coals.



Significant Hg-oxidation and/or removal occurred across the baghouse while firing PRB coal only (see Figs. 6-8). Apparently, the PRB ash in the baghouse filter cake promotes significant catalytic oxidation and/or sorption of elemental mercury. The extent of Hg-oxidation across the baghouse also correlates somewhat with flue-gas chlorine content (see Figs. 6 and 8) when the chlorine is varied by firing different blends. However, chlorine content and the extent of bituminous ash (high iron ash) in the blends are related. It is significant that the elemental mercury reduction across the baghouse increased from an Hg^0/Hg^T level of $\sim 30\%$ to $>90\%$ at the baghouse exit, when blending only 20% of Blacksville coal by mass with PRB coal. Unlike the baghouse inlet, the concentration of elemental mercury at the baghouse outlet was less for all coal blends while operating at 2.5% FEO. Therefore, it appears that increased UBC in the ash, during operation at 2.5% FEO, promoted oxidation and/or removal of elemental mercury across the filter cake.

Figure 9 illustrates the relationship of baghouse temperature with elemental mercury fraction at the inlet and outlet of the baghouse. The baghouse temperature was changed by adjusting the cooling rate in the final set of heat exchangers. Hence, the change in baghouse temperature affected the flue-gas temperatures upstream of the baghouse (see Fig.3), at the baghouse inlet, and at the baghouse outlet. In addition, using this method to adjust baghouse temperature avoided the convoluting effect of changing moisture content.

Figure 9. Effect of baghouse temperature on Hg-oxidation.



The small differences in Hg^0/Hg^T -ratio (at the baghouse outlet) were obtained one after the other, by raising and subsequently lowering the baghouse temperature. For example, the low temperature condition was measured, followed by immediate change in heat extraction from the flue gas and rapid increase in baghouse temperature. An immediate change in the Hg^0/Hg^T -ratio was observed and measured for several hours. Finally, heat extraction was altered to return to

the low-temperature condition, and the mercury ratio values returned to the low-temperature values previously measured. In this manner, errors associated with small operational differences from one run to another were eliminated. The standard deviations of the $\text{Hg}^{\circ}/\text{Hg}^{\text{T}}$ ratios directly measured in this work were less than $\pm 1\%$. Hence, while the differences observed as a function of temperature for the coal blend were not large, they were statistically relevant.

Figure 9 indicates, as shown in previous graphs, that significant reduction of Hg° occurs across the baghouse and that coal blends yield significantly more oxidation than PRB only. The higher temperature is slightly more effective at oxidizing mercury at the baghouse inlet, for 100% PRB. This effect (for 100% PRB) seems to be enhanced by the baghouse, as the elemental mercury fraction at the baghouse outlet for the higher temperature sample is approximately half the low-temperature value.

The difference between low- and high-temperature oxidation was smaller for the coal blend; i.e., the high-temperature condition did not increase mercury oxidation in the coal blend as it did with 100% PRB. This shift in temperature-dependent behavior is further indication that the mechanisms governing mercury oxidation are different between the 100% PRB case and the coal blends. While the differences in $\text{Hg}^{\circ}/\text{Hg}^{\text{T}}$ -ratio (at the baghouse outlet) were repeatable, they were very small. Therefore, the mercury oxidation effects of flue gas and/or fly ash may not be as dependent on temperature with blends as they seem to be with 100% PRB.

Figures 10-12 illustrate a lack of correlation of Hg-oxidation at the baghouse inlet with UBC, SO_2 , or iron/calcium ratio, at the low-temperature condition. This correlation absence was also observed for all ash and flue-gas components.

Figure 10. Influence of UBC on Hg-speciation.

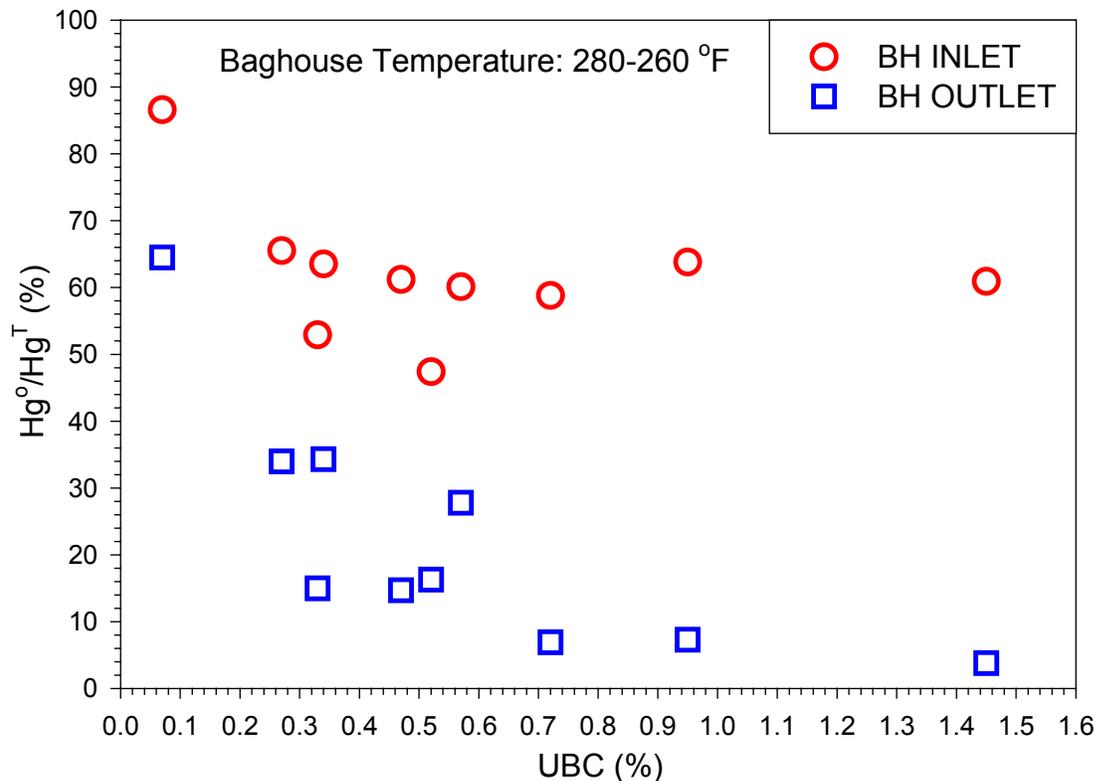


Figure 11. Influence of SO₂ on Hg-speciation.

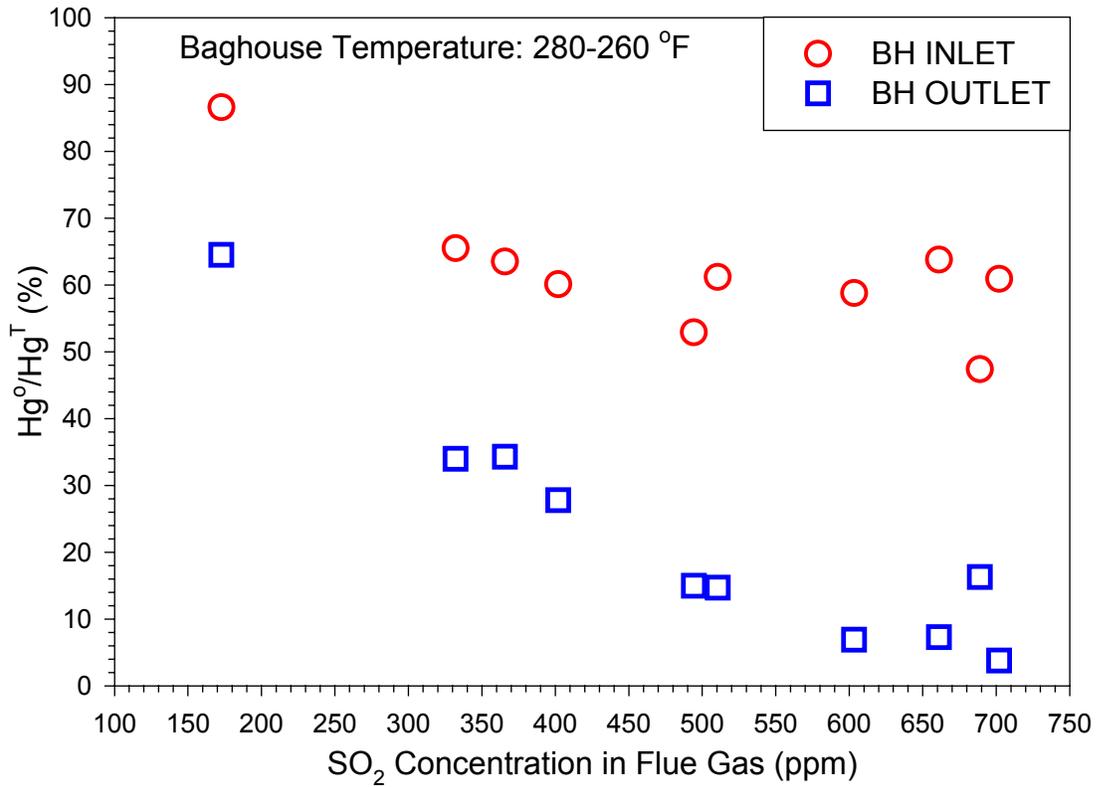


Figure 12. Relationship of ash Fe₂O₃/CaO ratio with Hg-speciation.

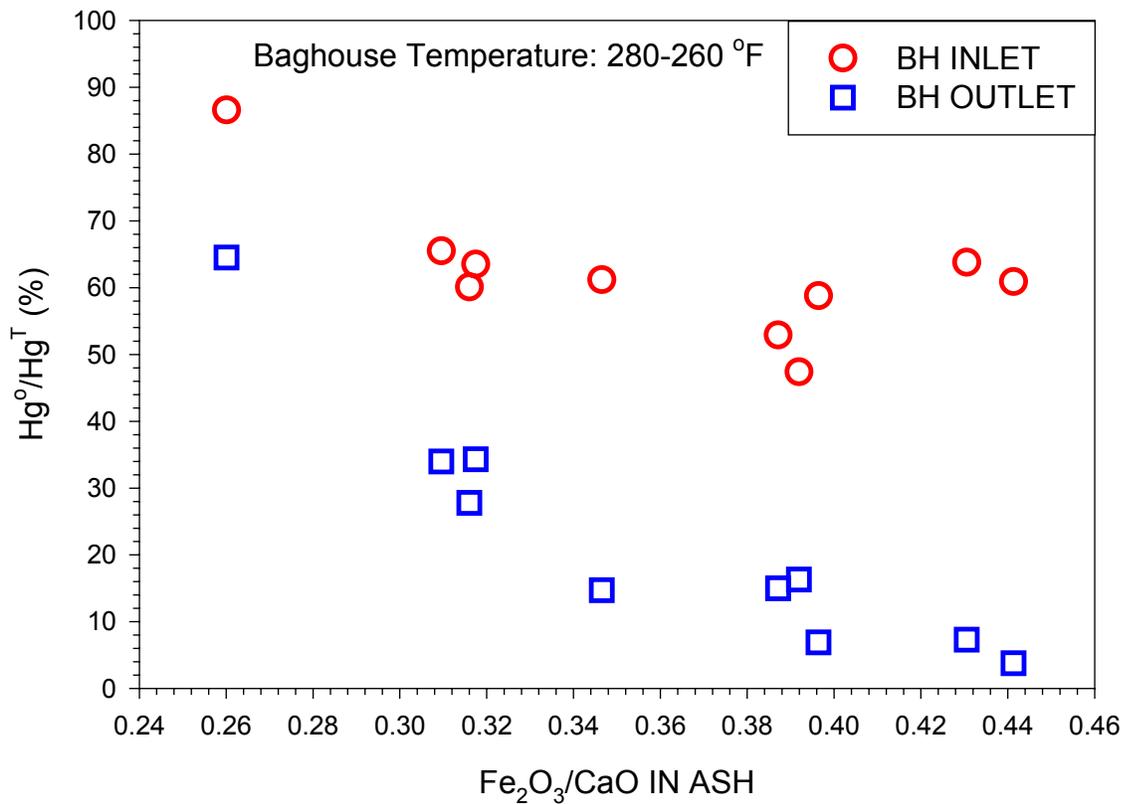


Figure 10 indicates a moderate correlation between Hg-oxidation and UBC, at the baghouse outlet, but this correlation is confounded by the association of UBC with other coal-blending parameters. As the amount of bituminous coal is increased in the blend, so does UBC, SO₂, iron, and chlorine. However, as shown in Fig. 8, lower FEO levels, which produces higher UBC, yielded less elemental mercury at the baghouse outlet. PRB generally produces low-UBC flyash, and the efficient operation of the CRF produced low UBC flyash values (< 1.5%) for all coal blends. However, for less efficient boilers and/or for those burning bituminous coals, UBC may play a more dominant role.

Figure 11 indicates a significant correlation of mercury oxidation (including any baghouse removal of Hg⁰) with SO₂ at the baghouse outlet. However, SO₂ also correlates with the increase in the fraction of bituminous coal in the blend, which in turn corresponds with the alteration of the flyash. Table 7 shows the mineral analysis, UBC, and LOI, for the PRB and four PRB/bituminous blends examined in this work. The elemental compositions are very similar. The PRB coal tested had a significant amount of iron in the ash. Although the two bituminous coals contained significantly more iron than PRB (see Table 6), the increase in total iron content of the blends was small. However, the form and availability of iron in PRB ash may be much different than in the bituminous coals. In addition, activity and availability of catalytic materials (such as iron) is more important than the elemental composition of the ash. Therefore, the relationship between mercury oxidation and the iron/calcium ratio was examined (see Fig. 12). This ratio is the best indication of the relative amount of bituminous coal iron in the ash, since both bituminous coals were higher in iron and lower in calcium than the PRB coal. As shown in Fig. 12, a smooth and significant correlation exists between the elemental mercury fraction at the baghouse outlet (again, measured relative to the Hg^I level at the inlet) and the addition of bituminous-coal iron to the flyash. Less than 5% of the mercury entering the baghouse exits in the elemental form for the highest iron/calcium ratios (see Fig. 12).

Table 7. Analysis of isokinetically sampled ash, for blends of PRB with bituminous coals.

Component	100% PRB	Blend 1	Blend 2	Blend 3	Blend 4
% Li ₂ O	0.01	0.02	0.02	0.02	0.02
% Na ₂ O	2.4	1.7	1.9	2.1	1.7
% K ₂ O	0.61	0.70	0.58	0.59	0.74
% MgO	5.3	3.8	4.2	4.4	4.0
% CaO	27.3	21.6	22.8	25.2	22.2
% Fe ₂ O ₃	7.1	9.3	7.9	7.8	8.7
% Al ₂ O ₃	18.2	20.6	21.2	20.7	21.3
% SiO ₂	29.6	34.5	31.2	29.9	34.1
% TiO ₂	1.7	1.6	1.6	1.8	1.6
% P ₂ O ₅	1.30	1.1	1.5	1.5	0.95
% SO ₃	3.7	4.3	5.1	4.8	3.4
% LOI	0.23	0.94	0.36	0.59	0.92
% UBC	0.04-0.07	0.72-1.45	0.33-0.47	0.27-0.57	0.51-0.53

The step change in Hg-oxidation between 100% PRB (the leftmost data point in each plot) and the coal blends has been observed in Figs. 6-12. The correlations in Figs. 10-12 suggest mechanisms responsible for this step change, because the 100% PRB data points seem to fall into line with the correlation for the coal blends (particularly for the baghouse outlet). This

suggests that UBC, SO₂, the added bituminous coal iron, or a combination of these parameters is responsible for the change in mechanisms observed between the 100%-PRB condition and all coal-blend conditions.

Heterogeneous Hg-oxidation mechanisms are associated with particulate material, which plays a more dominant physical role in the ash-cake coating bag surfaces than in the disperse phase. On the other hand, sulfur dioxide may play as dominant of a role in homogeneous mechanisms as in heterogeneous mechanisms. Nevertheless, the relationship of Hg-oxidation to bituminous ash in a dust cake and SO₂ in the flue gas are confounded by the fact that SO₂ and bituminous ash content are related for the coal blends investigated in this work. Hence, it was necessary to experimentally isolate these two parameters. This was done in part by directly injecting high-iron flyash into the baghouse, without adjusting the SO₂ concentration or any other parameters. Ash from the same Choctaw America coal used in this work was selected for this experiment. Its composition is provided in Table 8, along with a comparison of its internal surface area with that of PRB ash. As shown (see Table 8), the surface area is small and similar to PRB ash, while the iron content is high. However, as discussed above, the PRB coal investigated has a moderately high iron content as well (see Table 6). The impact of injected ash is a function of the *form and availability of the iron* as well. The UBC level, while relatively small for bituminous coal ash, is significantly higher than for the PRB ash (see Table 7).

Table 8. Analysis of Choctaw America coal ash injected into baghouse.

Mineral Analysis		Other Properties	
% Li ₂ O	0.06		
% Na ₂ O	1.4	LOI	4.2 %
% K ₂ O	2.0		
% MgO	1.2	UBC	3.51 %
% CaO	3.9		
% Fe ₂ O ₃	12.4	meso-pore	
% Al ₂ O ₃	33.0	N ₂ -BET	
% SiO ₂	43.1	Surface Area	2.32 m ² /g
% TiO ₂	1.8		
% P ₂ O ₅	0.38	<i>PRB Ash</i>	<i>PRB Ash</i>
% SO ₃	0.53	<i>Surface Area</i>	<i>2.02 m²/g</i>

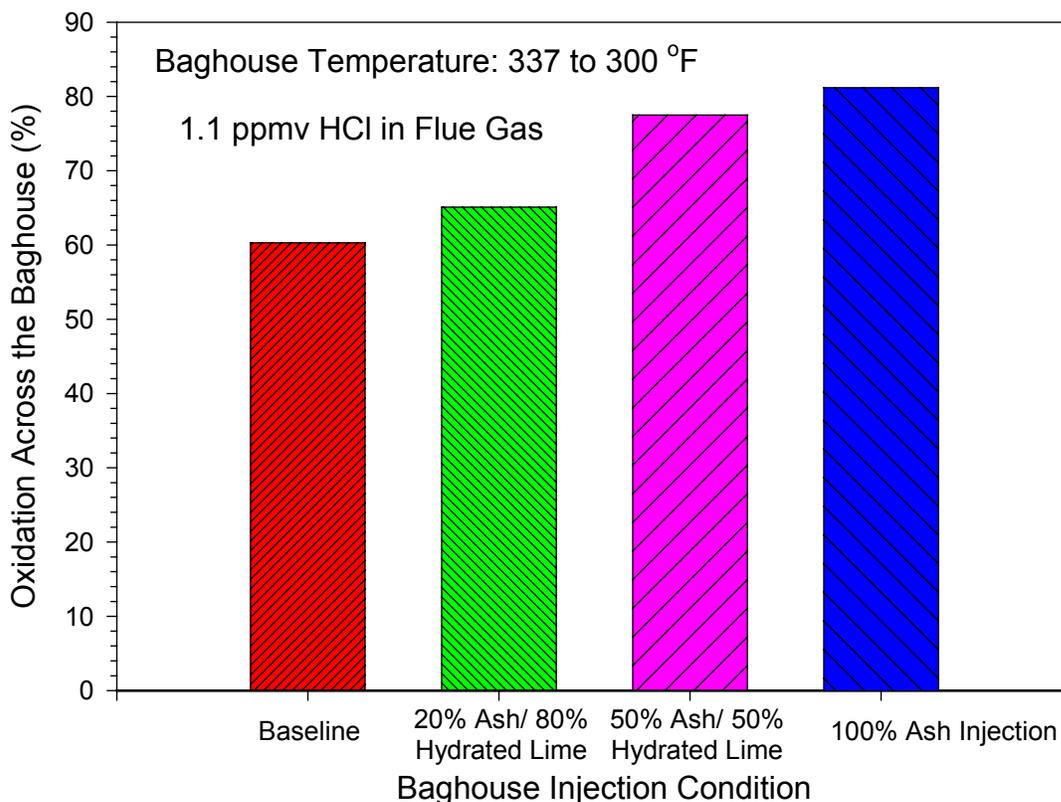
LOI = Loss On Ignition, UBC = Unburned Carbon

Figure 13 contains the results of the baghouse ash injection tests conducted at the high-temperature (337 °F to 300 °F) baghouse condition, which is most favorable for elemental-mercury removal (oxidation and/or sorption) by PRB flyash (see Fig.9). The baseline case of PRB-only was compared with three different baghouse injection conditions, 100% Choctaw ash, and two blends of Choctaw ash with hydrated lime, 20% Choctaw ash/80% hydrated lime and 50% Choctaw ash/50% hydrated lime. Particulate was injected into the baghouse at a rate approximately equal to the mass rate of flyash flowing into the baghouse from the furnace. The baghouse was pulsed down at the beginning of each new injection condition, to avoid excessive buildup of material or long transition times from a previous condition. Approximately the same mass rate of particulate was used for each baghouse injection condition.

Hydrated lime has a surface area (~18 m²/g) much greater than that of Choctaw ash (see Table 8). Therefore, the influence of ash composition could be distinguished from the mere

increase in mass loading or surface area. As shown in Fig. 13, the injection of 100% Choctaw ash significantly enhanced the oxidation of mercury across the baghouse. Hydrated lime was relatively benign in its effect on Hg-oxidation. As illustrated in Fig. 13, Hg-oxidation increased with increasing concentration of Choctaw ash. The hydrated lime acted merely to dilute the impact of injecting Choctaw ash. It is clear that the catalytic properties of the high-iron ash were important in the oxidation of mercury across the baghouse. It is likely that the bituminous ash iron and UBC were important catalytic components that promoted mercury oxidation in the baghouse. However, the extent of the influence of SO₂ on Hg-oxidation for the coal-blends investigated is uncertain. This will need to be examined further in subsequent experiments.

Figure 13. Oxidation of mercury across the baghouse while injecting ash and hydrated lime directly into the baghouse.



The high-temperature baghouse condition, used for the direct ash-injection tests was more favorable for baseline (PRB only) Hg-oxidation (see Fig. 9). However, the low-temperature condition was more favorable for enhancement of Hg-oxidation by the coal blends (see Fig. 9). Therefore, the impact of direct ash injection on Hg-oxidation at the lower temperature condition would likely be more dramatic.

CONCLUSIONS

Total chlorine content, injected independently through the burner or inherent in the coal, tends to increase mercury oxidation in the disperse phase, prior to the baghouse, and across (examined by total Hg⁰ reduction) the baghouse (ash cake and filter media). However, in terms

of differences observed between PRB sub-bituminous coals and bituminous coals in full-scale boilers, catalytic enhancement by the fly ash is a more important factor in determining the extent of mercury oxidation than the flue gas total chlorine content. PRB-ash (and possibly the bag fabric) captures and/or catalytically enhances the oxidation of mercury across the baghouse, which enhancement increases significantly (~30%) with small increases in temperature (~ $\Delta 40$ °F). The catalytic activity of low-UBC bituminous ash is greater than that for low-UBC PRB ash. UBC, even at the low levels investigated in this work, appeared to have some catalytic effects on mercury speciation, with the activity of relatively low-UBC bituminous ash being greater than the very-low-UBC PRB ash. For less efficient combustion conditions, UBC may play a more dominant role in Hg-oxidation. The iron content and form in bituminous ash seems to be an important component of its catalytic activity; elemental mercury reduction across the baghouse was observed to increase with addition of bituminous-ash iron, although the change to total iron in the ash was small. Hence, the catalytic activity and availability of iron appears to be important and differs between coal types. Sulfur dioxide may also play an important role in determining Hg-speciation.

These results suggest that coal blending may play an important role in mercury mitigation strategies of the future, but substantially more data are needed to confirm this hypothesis and understand the governing processes well enough to rely on such an approach as a compliance strategy. In this pilot combustor, and with these fuels, blending a small amount of bituminous coal (<10% by mass) with PRB sub-bituminous coal, resulted in oxidized fractions of mercury of >50% before the particulate collection device and >95% at the outlet of a baghouse. These results were achieved while maintaining UBC at reasonable levels.

ACKNOWLEDGMENTS

Southern Research Institute would like to thank our sponsors for supporting this work. Particularly, we would like to thank the U.S. Department of Energy for funding this work through cooperative agreement number DE-PS26-02NT41183, and to Barbara Carney for providing project management direction. We would also like to thank the Environmental Protection Agency, Tennessee Valley Authority, Southern Company, Arkansas Electric Cooperative Corp., Dairyland Power Cooperative, Dynegy Midwest Generation, Inc., MidAmerican Energy Co., and the Electric Power Research Institute for funding this work through a joint collaboration.

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KEY WORDS

Mercury, Speciation, Catalysis, Coal, Flyash, and Chlorine