

Evaluation of the Impact of Chlorine on Mercury Oxidation in a Pilot-Scale Coal Combustor — The Effect of Coal Blending

Paper # 83

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ABSTRACT

Coal-fired power plants are a major source of mercury (Hg) released into the environment and the utility industry is currently investigating options to reduce Hg emissions. The EPA Clean Air Mercury Rule (CAMR) depends heavily on the co-benefit of mercury removal by existing and new wet flue gas desulfurization (FGD) scrubbers. The split (speciation) between chemical forms of mercury (Hg) species has a strong influence on the control and environmental fate of Hg emissions from coal combustion. The high-temperature coal combustion process releases Hg in elemental form (Hg^0). A significant fraction of the Hg^0 can be subsequently oxidized in the low-temperature, post-combustion environment of a coal-fired boiler. Relative to Hg^0 , oxidized Hg (Hg^{2+}) is more effectively removed by air pollution control systems (APCS). For example, the water-soluble Hg^{2+} is much more easily captured than insoluble Hg^0 in FGD units. Selective catalytic reduction (SCR) technology widely applied for reducing NO_x emissions from power plants also affects the speciation of Hg in the coal combustion flue gases. Recent full-scale field tests conducted in the U.S. showed increases in Hg oxidation across the SCR catalysts for plants firing bituminous coals with sulfur (S) content ranging from 1.0 to 3.9%. However, plants firing subbituminous Powder River Basin (PRB) coals which contains significantly lower chlorine (Cl) and sulfur (S) content and higher calcium (Ca) content than those of the bituminous coals, showed very little change in mercury speciation across the SCR reactors. A field study conducted by EPRI showed blending of PRB coal with a bituminous coal (60% PRB/40% bituminous) resulted in increased Hg^{2+} from 45% at the SCR inlet to 93% at the outlet. Coal blending appears to be a potentially cost effective approach for increasing Hg oxidation for PRB coal-fired SCR systems.

A study has been undertaken to investigate the effect of blending PRB coal with an Eastern bituminous coal on the speciation of Hg across an SCR catalyst. In this project, a pilot-scale (1.2 MW_t) coal combustor equipped with an SCR reactor for NO_x control was used for evaluating the

effect of coal blending on improving Hg oxidation across an SCR catalyst. Several parameters such as the ratio of PRB/bituminous coal blend and the concentrations of hydrogen halides (HCl, HBr, and HF) and halogens (Cl₂ and Br₂) in the flue gas were evaluated to determine their effects on the oxidation of Hg⁰ under typical SCR NO_x emission control conditions. The objective of this project was to evaluate the effectiveness of firing PRB/bituminous coal blends to enhance mercury oxidation in a coal fired power plant equipped with an SCR system.

INTRODUCTION

In March 2005, the EPA promulgated the Clean Air Mercury Rule (CAMR) to reduce the emission of mercury from coal-fired power plants [1]. Coal-fired power plants are a major anthropogenic source of mercury emissions in the U.S. [2]. There are several control options for mercury emissions from coal-fired boilers. Mercury may be captured as a co-benefit of particulate matter (PM) controls, NO_x controls, and SO₂ controls, as well as through mercury-specific control technologies, such as activated carbon injection. Available data show that the use of existing pollution control equipment can also be used to control mercury emissions. It is known that mercury in its oxidized state (Hg²⁺) is highly water soluble and thus would be expected to be captured in plants with wet FGD systems. One of the main obstacles with this approach is converting the elemental mercury into the water-soluble mercuric chloride form. Selective catalytic reduction (SCR) has been shown as a method of oxidizing mercury in some coal-fired boilers and results in increased mercury removal in the downstream wet FGD system. The degree of this co-benefit varies with the type of coal being burned and the specific control technology configuration.

Blending of coals of different ranks at pulverized coal-fired power stations is becoming increasingly common as electric utilities attempt to save costs, meet SO₂ emission limits and improve the combustion conditions in their plants. Many plants have begun to blend low-sulfur Powder River basin (PRB) coal with Eastern bituminous coals to reduce SO₂ emissions. Little data exists on the effect of blending on Hg speciation. One report by Laudal et al. [3] showed that the overall Hg oxidation was greater than 99% at a plant that blended 40% PRB with 60% bituminous coal (on a heat input basis) and operated an SCR unit. The goal of the current study was to examine the oxidation of mercury using blends ranging from 10% PRB to 40% PRB with the balance being Eastern bituminous coal, and compare those results to mercury oxidation when firing pure bituminous and pure PRB fuel.

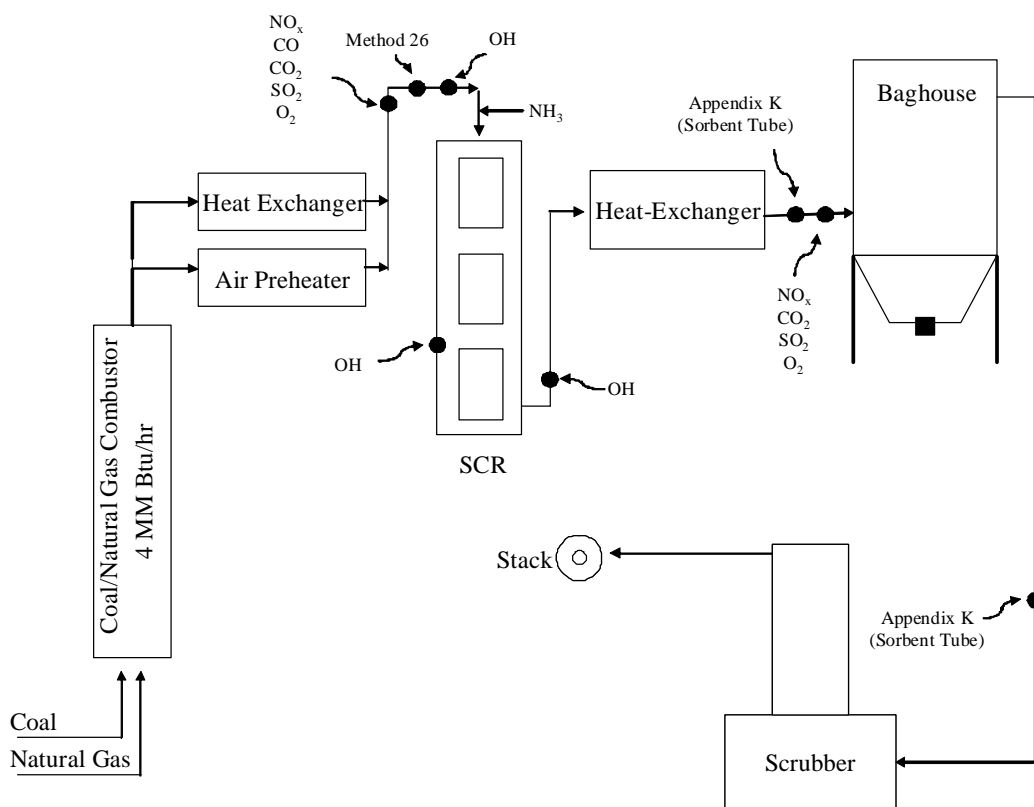
The results presented here focused on the effect of Cl concentration on the oxidation of Hg across the SCR unit. In a full-scale power plant, oxidation will occur across the air pre-heater. Additional tests to evaluate the air pre-heater on Hg oxidation were not performed because the air pre-heater on the pilot plant is not representative of that at a full-scale power plant.

EXPERIMENTAL APPROACH

The multi-pollutant control research facility (MPCRF), located at EPA's Research Triangle Park campus, was used for the PRB and bituminous coal blending speciation tests. The MPCRF is a 4 MM Btu/hr (1.2 MW_e) multi-fuel combustor that can fire pulverized coal, fuel oil, or natural gas. A schematic of the facility is shown in Figure 1. The facility consists of the combustor, a series

of heat exchangers to simulate the convective section, a selective catalytic reduction (SCR) unit, a fabric filter, and a lime slurry wet scrubber. The MPCRF is equipped with two sets of continuous emissions monitors (CEMs) for measuring different flue gas species including sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), carbon dioxide (CO_2), and oxygen (O_2). These measurements were taken at the inlet to the SCR and prior to the inlet of the baghouse. NO_x measurements were taken at the inlet and outlet of the SCR to determine the NO_x reduction efficiency.

Figure 1. Schematic of Multi-Pollutant Control Research Facility with Sampling Locations Shown



A low-sulfur PRB coal from the North Antelope seam located in Wyoming was used as the baseline coal in these tests. A medium sulfur Eastern bituminous coal (Pittsburgh #8) was used to increase the amount of chlorine in the fuel blends. The effect of the SCR unit on Hg speciation was tested at four different PRB/bituminous blending ratios, 60%/40%, 70%/30%, 80%/20%, and 90%/10%. Along with the two baseline tests of 100% PRB and 100% of bituminous, as well as one repeated blend test, a total of seven tests were conducted for this study.

The separate coal blends were prepared in batches by calculating the amount of coal required to obtain the specific blends. The blended coal batches were calculated based on the as-received heating value for the two coals. The coal was then weighed and placed in a roll-off container for

blending. A front-end loader was used to blend the coal together prior to being pulverized in a hammermill. Samples were taken for each blend after pulverization and sent for proximate and ultimate analysis by an outside laboratory. The analysis results for the blends and baseline coals are shown in Table 1. Neutron activation analysis (NAA) was used to determine the iodine (I), bromine (Br), and chlorine (Cl) content of the coal and are shown in Table 2. The chlorine in the coal and coal blends ranged from 973 ppm for the bituminous coal to 35 ppm for the PRB. Bromine was 13.4 ppm for the bituminous coal and 1.7 ppm for the PRB. Iodine was present in concentrations less than 2 ppm for all the fuel blends.

Table 1. Ultimate and Proximate Analysis for Coal Samples (as-received basis)

Sample	100% BIT	65%/35% (PRB/BIT)	70%/30% (PRB/BIT)	74%/26% (PRB/BIT)	79%/21% (PRB/BIT)	91%/9% (PRB/BIT)	100% PRB
Proximate							
Moisture	2.63	19.43	18.42	21.32	23.88	27.38	31.37
Volatile	35.02	31.63	33.29	31.49	34.91	39.78	32.72
Ash	6.06	6.16	6.49	5.69	4.95	3.81	4.04
Fixed Carbon	56.29	42.78	41.8	41.5	36.26	29.03	31.87
Ultimate							
Carbon, %	76.80	59.58	57.04	58.82	54.58	51.3	51.02
Hydrogen, %	5.36	6.0	4.71	5.93	5.61	5.93	5.95
Nitrogen, %	1.79	1.05	0.97	0.97	0.98	0.91	<0.5
Sulfur, %	1.40	0.63	0.54	0.48	0.43	0.30	0.25
Oxygen, %	8.49	26.55	30.23	28.09	33.43	37.75	38.74
Fluorine, ppm	94	52	N/A	52	72	88	63
Heating Value, Btu/lb	13,852	10,202	9,891	9,650	9,378	8,733	8,201
Hg, ppb (dry)	134	52	66	28	86	37	42

Table 2. Neutron Activation Results for Coal Samples

Sample	Iodine (ppm)	Bromine (ppm)	Chlorine (ppm)
100% Bit	1.9	13.4	973
65%/35% (PRB/BIT)	0.8	5.0	337
70%/30% (PRB/BIT)	0.9	3.6	270
74%/26% (PRB/BIT)	0.6	3.6	237
79%/21% (PRB/BIT)	<0.5	2.9	154
91%/9% (PRB/BIT)	<0.5	1.9	101
100% PRB	<0.5	1.7	35

The facility is designed to be pre-heated on natural gas until the temperature exceeds 2000 °F at which time the facility can be switched over to coal. During these tests, the facility was switched over to coal in the afternoon prior to a test day. It takes about one hour for the flue gas temperature to stabilize once the unit is fired on coal. The ammonia injection system was then turned on about one hour after being switched to coal. Once a test day had finished the unit was then switched back to natural gas to maintain temperature in the unit.

The SCR unit consists of three full length sections of honeycomb SCR catalyst elements (each section containing nine honeycomb catalyst elements of 1190 mm length and 150 mm square cross-section). Each section of the SCR catalyst is equipped with a flow straightener, a soot blower, and the catalyst. The SCR was operated at a temperature of approximately 700-740 °F, with a space velocity of 1900 h⁻¹. A NH₃/NO_x ratio of 0.9-1 was used for these tests. Anhydrous ammonia was metered using a mass flow controller and was injected into the flue gas duct about 4 feet prior to the SCR unit, which was designed to achieve 5% RMS deviation of NH₃ concentration (i.e., reasonably well-mixed conditions simulating commercial practice). Ammonia slip was not measured during these tests. Flue gas flow rates were measured at the outlet of the SCR using a pitot tube. The SCR unit was designed with sample ports located between each catalyst section. Soot blowers were used to clean the catalyst prior to the start of a test day and approximately twelve hours into a test.

The catalyst that was used in this system was manufactured by Cormetech. The catalyst samples tested in the EPA pilot combustor were extracted from a full-scale 300 MW unit after approximately 15,000 hours in DeNO_x service firing low sulfur Eastern bituminous fuel. The DeNO_x activity compared to fresh catalyst was estimated by Cormetech to have a 0.8-0.9 K/Ko value. A used catalyst was selected to minimize the amount of time required for the catalyst to be saturated with mercury, as new catalysts tend to adsorb mercury for a period after being installed.

Several sampling locations were used during these tests and are noted in Figure 1. The primary speciated mercury measurement was made using the Ontario Hydro (OH) method. The method was modified in that an in-stack filter was used in place of the standard hot box filter. Two OH impinger trains per day were pulled at the inlet and outlet of the SCR unit with a total sampling time of approximately 1.5 hours per train. During the 100% bituminous test and the 70% PRB/30% bituminous test an additional OH train was pulled after the second catalyst section. All OH trains were recovered and analyzed by the EPA's in-house contractor.

Halogen measurements were taken at the inlet of the SCR once per test condition using EPA Method 26. Sorbent tubes were used to obtain total mercury concentrations at the inlet and outlet of the baghouse. Sorbent tube measurements at the inlet to the baghouse were biased due to the flyash buildup in the front section of the tube and the results are not reported.

Flyash samples were collected from the baghouse hopper twice during each run. These samples were used to measure loss on ignition (LOI) and Hg uptake by the ash. These results are shown in Table 3. The total mercury concentration in the sorbent tubes and in the flyash was determined using the thermal decomposition method specified in Appendix K of the Clean Air

Mercury Rule. An Ohio Lumex model RA-915+ was used for the analysis. The high LOI in the ash is a result of slag tubes that were installed in the radiant section of the furnace.

Table 3. Baghouse Hopper Ash Hg and LOI of Ash

Test Conditions (PRB/BIT Ratio)	Average LOI, %	Hg in ash, µg/kg
100% Bit	21	2960
65%/35%	12.5	2590
70%/30%	11.9	2210
74%/26%	15.3	2000
79%/21%	15.1	1600
91%/9%	16.5	1560
100% PRB	13.7	1725

The operating conditions for the tests are shown in Table 4. The SCR inlet temperature ranged from a high of 740 °F to a lower limit of 700 °F. The SCR outlet temperature was roughly 60-70 °F lower than the inlet temperature due to heat loss across the catalyst section, and ranged from 630 to 670 °F. The SCR inlet NO_x concentration ranged from 530 to 625 ppm, with a greater than 90% reduction in NO_x achieved across the SCR. Sulfur dioxide ranged from a high of 990 ppm for the 100% bituminous test to 153 ppm for the 100% PRB test. Excess oxygen concentrations in the flue gas were in the 5-6 % range.

Table 4. Operating Conditions for the Coal Blending Tests

PRB/BIT Ratio	SCR Inlet					SCR Outlet				
	NO _x ppm	SO ₂ ppm	CO ₂ %	O ₂ %	Temperature °F	NO _x ppm	SO ₂ ppm	CO ₂ %	O ₂ %	Temperature °F
0%/100%	625	990	14.7	5.1	725	65	988	14.4	5.0	660
65%/35%	570	457	13.7	6.7	700	28	432	13.5	6.6	630
70%/30%	575	421	14.6	5.4	720	42	400	14.2	5.6	660
74%/26%	530	365	14.1	6.2	740	32	349	14.2	5.6	670
79%/21%	545	263	14.3	5.9	710	13	175	13.6	6.3	650
91%/9%	530	169	13.5	6.8	730	10	77	13.1	7.1	665
100%/0%	580	153	15.8	4.7	725	48	126	15.1	5.0	665

RESULTS AND DISCUSSION

Mercury concentration data from the coal blending tests are shown in Table 5. Elemental mercury (Hg⁰), oxidized mercury (Hg²⁺), and total mercury (Hg^T) are shown for the SCR inlet and SCR outlet. Two OH sampling trains were pulled during each test day. No particulate-bound mercury was detected as the temperature of the in-stack filter was above 600 °F. Mercury

speciation results for the tests are shown in Figure 2. The amount of Hg^{2+} is shown as an average of the two runs for each coal blend at the SCR inlet and outlet. The percentage of Hg^{2+} is higher at the SCR outlet than at the SCR inlet for all of the test cases except for the 100% PRB run where the inlet and outlet oxidized concentrations were similar.

The percent oxidized mercury for the SCR inlet and SCR outlet is shown in Figure 3. The SCR inlet Hg^{2+} concentration is highest for the 100% bituminous coal run at about 27%. At the SCR outlet the Hg^{2+} concentration increases to 84%. The net increase in Hg oxidation across the SCR unit decreases with a corresponding decrease in the percent bituminous coal. The net oxidation across the SCR for the PRB coal is slightly negative. It is clear that a higher degree of oxidation is obtained with the higher rank bituminous coal and corresponding higher chlorine content. An abrupt drop occurs when reducing bituminous blend fraction from 70% PRB/30% bituminous to 80% PRB/20% bituminous. The amount of Hg^{2+} was near 55% for the 70/30 blend and drops to 20% for the 80/20 blend. Similar lower Hg^{2+} results were obtained for the 90/10 blend tests.

Table 5. Hg Speciation Results from the SCR Inlet and SCR Outlet

PRB/BIT Ratio	SCR Inlet				SCR Outlet			
	Hg^0 $\mu\text{g}/\text{m}^3$	Hg^{2+} $\mu\text{g}/\text{m}^3$	Hg^T $\mu\text{g}/\text{m}^3$	Ox Hg %	Hg^0 $\mu\text{g}/\text{m}^3$	Hg^{2+} $\mu\text{g}/\text{m}^3$	Hg^T $\mu\text{g}/\text{m}^3$	Ox Hg %
100% Bit - Sample 1	8.99	3.64	12.63	28.8	2.22	10.34	12.55	82.3
100% Bit - Sample 2	9.64	3.36	13.01	25.9	2.10	12.23	14.33	85.3
65%/35% - Sample 1	5.86	1.12	6.98	16.0	2.87	4.68	7.55	61.9
65%/35% - Sample 2	6.56	0.72	7.28	9.8	3.10	4.95	8.05	61.5
70%/30% - Sample 1	7.70	2.03	9.74	20.9	4.62	5.26	9.88	53.3
70%/30% - Sample 2	5.09	1.71	6.80	25.2	3.07	4.03	7.10	56.8
74%/26% - Sample 1	4.73	1.11	5.83	19.0	2.80	3.13	5.93	52.7
74%/26% - Sample 2	8.38	0.36	8.74*	4.1	7.08	1.23	8.31*	14.8
79%/21% - Sample 1	6.36	0.32	6.68	4.8	5.50	0.52	6.02	8.7
79%/21% - Sample 2	5.51	0.46	5.97	7.6	3.98	1.89	5.87	32.2
91%/9% - Sample 1	5.09	0.23	5.32	4.3	4.28	1.04	5.31	19.5
91%/9% - Sample 2	5.23	0.27	5.50	4.9	3.71	0.94	4.65	20.2
100% PRB - Sample 1	5.52	0.37	5.90	6.4	6.36	0.15	6.51	2.2
100% PRB - Sample 2	5.89	0.40	6.30	6.4	5.89	0.21	6.10	3.4

*This run has been omitted from the data set due to facility problems during the sampling period.

Sorbent tube traps were used to characterize the total amount of Hg that was getting through the baghouse. The Hg^T (post-baghouse) for each test condition is shown in Table 6. The initial intent of these tests was to characterize Hg removal through the entire system including the scrubber. However, little to no Hg passed through the baghouse due to adsorption on unburned carbon in the ash due to the high LOI of the ash. Initial sorbent traps on the outlet of the scrubber were collected, but this sampling location was discontinued when the results showed that the total Hg concentrations at the FGD inlet were below the detection limit.

Figure 2. Mercury Speciation Results for Different Coal Blend Combinations

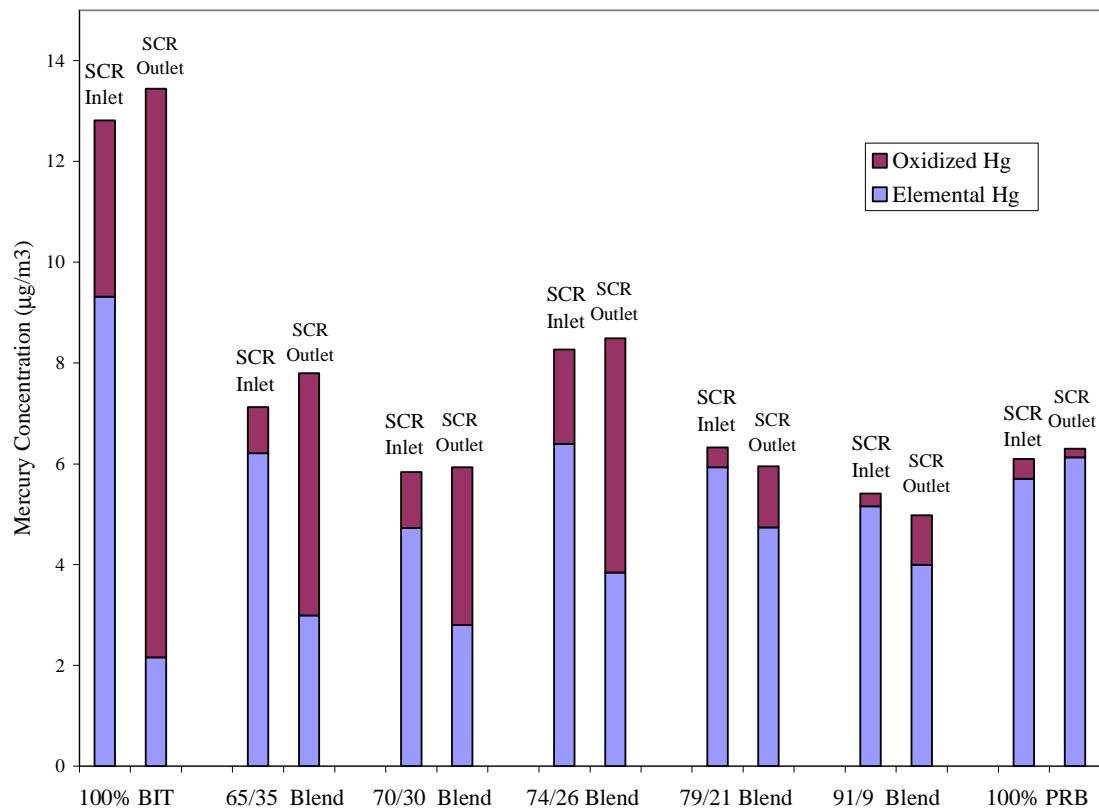


Figure 3. Percent Oxidized Mercury for SCR Inlet and SCR Outlet for Different Coal Blend Combinations

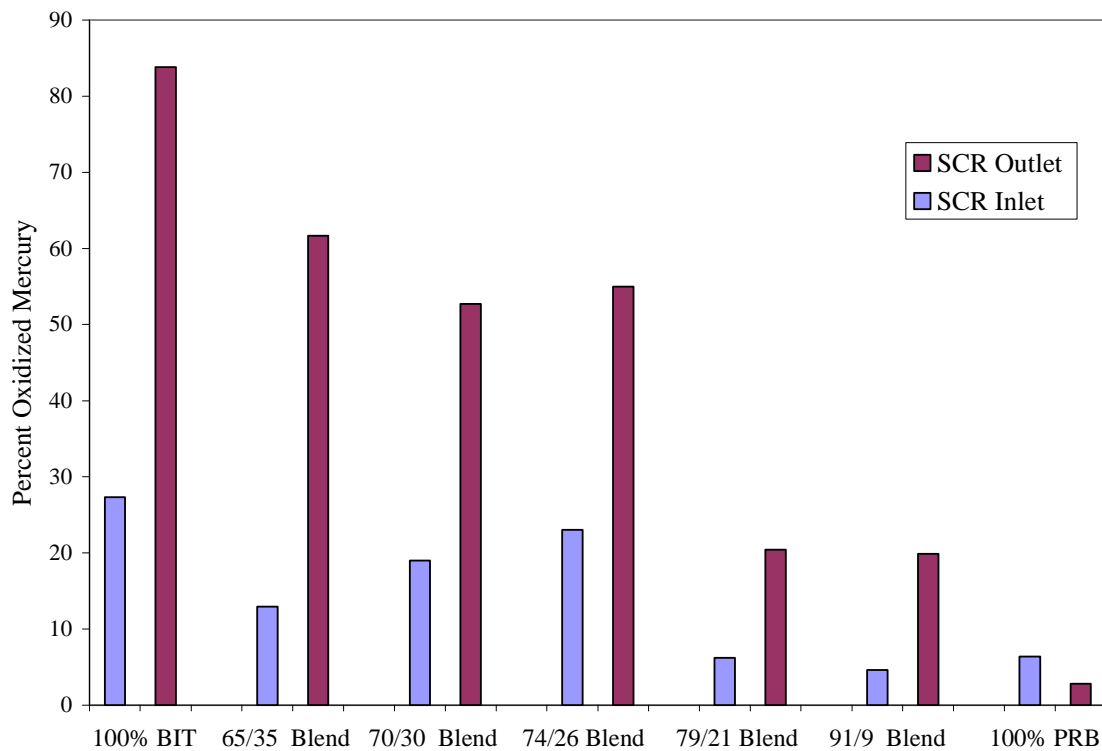


Table 6. Sorbent Tube Results (post-baghouse)

PRB/BIT Ratio	Hg ^T – Sample 1 (µg/m ³)	Hg ^T – Sample 2 (µg/m ³)
100% BIT	<0.1	<0.1
65%/35%	1.6	<0.1
70%/30%	0.18	0.15
74%/26%	0.20	0.13
79%/21%	<0.1	<0.1
91%/9%	<0.1	0.20
100% PRB	0.10	0.10

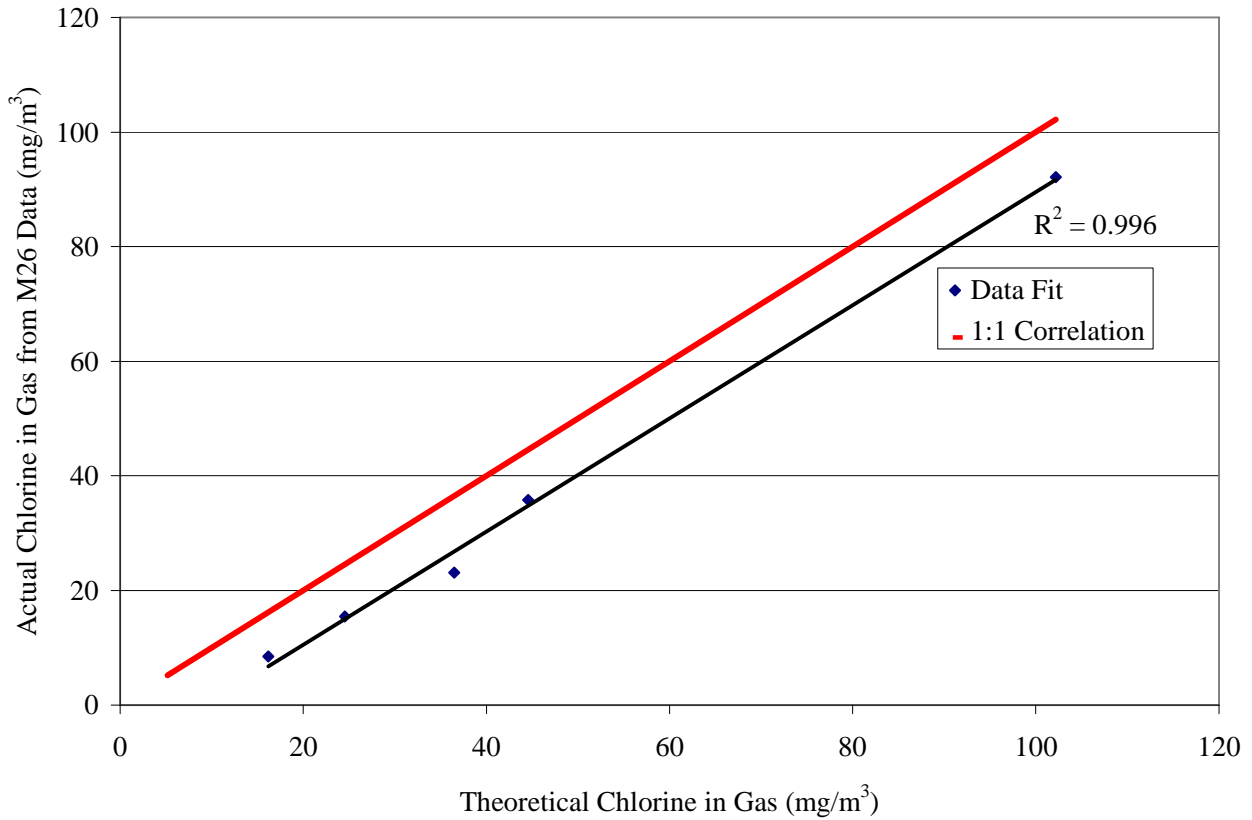
One of the main goals of this project was to determine the effect of halogen concentration on Hg oxidation. EPA Method 26 was used to characterize the halogens in the flue gas. Table 7 contains the Method 26 results for these tests. As shown in Table 7 nearly all of the chlorine in the coal was converted into hydrogen chloride (HCl). Bituminous coal had the highest Cl concentration (see Table 2) which translated into an HCl concentration of 60.8 ppm at the SCR inlet, while PRB had the lowest fuel Cl concentration which translates into an HCl concentration of below 5 ppm at the SCR inlet. Bromine and hydrogen bromide (HBr) were not detected in the flue gas at the SCR inlet, while hydrogen fluoride (HF) was present in concentrations of less than 5 ppm. It is therefore expected that the primary Hg oxidant is HCl. There is an excellent correlation for the HCl in the flue gas as a function of coal chlorine content, as shown in Figure 4. The one to one correlation is also shown in Figure 4 that indicates most of the chlorine is in the vapor phase and available for reacting with Hg. Based on the results from these tests it was determined that oxidation of Hg is highly dependent on the amount of chlorine in the coal and less so for the amount of bromine and fluorine.

Table 7. Method 26 Results for Coal Blending Tests

PRB/BIT Ratio	HCl (ppm)	Cl ₂ (ppm)	HBr (ppm)	Br ₂ (ppm)	HF (ppm)	F ₂ (ppm)
100% BIT	60.8	0.09	<0.1	<0.1	4.9	<0.05
65%/35%	23.6	0.07	<0.1	<0.1	3.8	<0.05
70%/30%	NS	NS	NS	NS	NS	NS
74%/26%	15.2	0.05	<0.1	<0.1	2.5	0.1
79%/21%	10.2	0.03	<0.1	<0.1	1.4	<0.05
91%/9%	5.6	0.03	<0.1	<0.1	1.7	<0.05
100% PRB	NS	NS	NS	NS	NS	NS

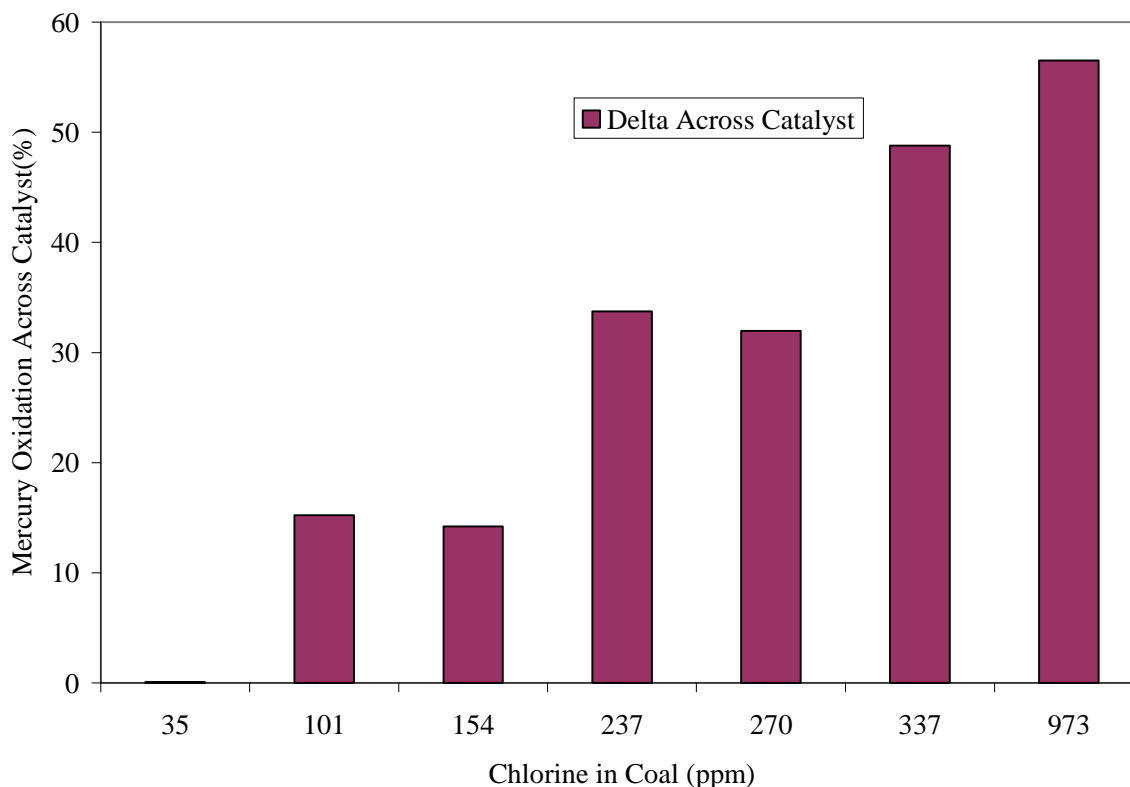
NS=No Sample

Figure 4. Gas-phase chlorine ($\text{HCl} + \text{Cl}_2$) versus theoretical chlorine concentration



The data from Figure 4 are shown Figure 5 as the absolute percentage change of oxidized mercury (SCR outlet minus SCR inlet) as a function of coal chlorine content. There is no net increase with the PRB coal alone as compared to 58% for the bituminous coal. A modest increase is achieved when adding 10 and 20% bituminous coal to the blend. Another distinct increase of 35% was achieved with the addition of 30% bituminous to the blend. By adding 40% bituminous to the blend the mercury oxidation approaches that of the pure bituminous coal alone. From this graph one may estimate expected levels of oxidized mercury at the SCR outlet as a function of coal chlorine content. Increasing the chlorine content three fold from 300 ppm to 900 ppm only nets an increase of roughly 30%, indicating that not all of the chlorine in the flue gas reacts with the available mercury. Laudal et al. [3] reported that for a 60/40 blend (543 ppm Cl) the amount of oxidized Hg at the exit of the SCR approached 99%.

Figure 5. Mercury Oxidation (absolute change) across the SCR as a Function of Coal Chlorine Content



SUMMARY

Coal blending tests were conducted to investigate the effect of blending PRB coal with an Eastern bituminous coal on the speciation of Hg across an SCR catalyst. Tests were conducted in which 100% bituminous coal and 100% sub-bituminous PRB were fired to examine the effect on mercury oxidation. Several blends were run with bituminous coal comprising the minority fraction. It was determined that a higher percentage of the total Hg was present as oxidized Hg at the SCR outlet as the chlorine in the coal increased. The other hydrogen halides such as HBr and HF do not appear to be in appreciable concentrations to have an impact on oxidation. A blend that contained at least 35% bituminous coal was necessary to obtain an oxidized Hg concentration of 60% oxidized Hg at the SCR outlet with 100% bituminous coal producing just under 90% oxidized Hg at the SCR outlet. Very little Hg passed through the baghouse due to the high LOI of the ash. Those power plants that are equipped with SCR and wet scrubbers may have an additional option of utilizing existing DeNO_x and SO₂ pollution control equipment to improve mercury control by adding an additional source of chloride to the fuel through fuel blending or other means.

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KEY WORDS

Mercury Control, Selective Catalytic Reduction, Coal Blending, Chlorine