



MERCURY TRANSFORMATIONS IN COAL COMBUSTION FLUE GAS

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Project Description

Fundamental research focused on transformations of mercury during coal combustion (Program Area 1 of the CATM program), with a heavy emphasis on the conversion of elemental mercury (Hg^0) to oxidized or particulate forms or species that form in coal combustion flue gas as a result of complex interactions with fly ash, chlorine, and nitrogen oxide (NO_x). Gas–solid (heterogeneous) and gas–gas (homogeneous) reactions and interactions were examined by collecting data from bench- and pilot-scale research facilities. Coal combustion flue gases derived from lignite, subbituminous, and bituminous coals having varied mercury and chlorine concentrations were studied. Rates of mercury species formation were determined, and reaction rates (kinetics) were determined using a specially designed time–temperature entrained-flow reactor (EFR). A fundamental understanding of mercury–flue gas–fly ash interactions is being used to accelerate the development of mercury control technologies.

Goal

The overall goal of this project was to develop a fundamental understanding of Hg transformations in flue gas. Specific objectives to accomplish this goal included investigating the impacts of NO_x on the conversion of Hg^0 to both $\text{Hg}^{2+}(\text{g})$ and $\text{Hg}^{2+}(\text{p})$; conducting time–temperature-resolved experiments of mercury transformations (oxidation of Hg^0 to both Hg^{2+} and $\text{Hg}[\text{p}]$) for two different coals using an EFR in a slipstream to a pilot-scale combustion system, with chlorine injection; and determining the mass transfer–capacity limit relationships to quantify and compare the reactivities of the different fly ashes with mercury in the flue gas.

Rationale

A critical review in 2003 [1] revised an original assessment [2] that coal combustion is the primary source of anthropogenic mercury emissions in the United States, accounting for 48 tons/yr of total point-source mercury emissions. Knowledge of mercury physical and chemical transformation in coal combustion flue gas is imperative for understanding the transport and fate of mercury released into emission control systems and the atmosphere. The current knowledge of mercury transformation in coal combustion flue gas is based largely on experimental investigations of mercury reactions in simulated flue gases and on the interpretations of field test data [3, 4]. Hg exists primarily as gaseous Hg^0 and as inorganic mercuric

compounds, Hg^{2+}X (where X may be Cl_2 , $[\text{NO}_3]_2 \cdot \text{H}_2\text{O}$, SO_4 , O), in coal combustion flue gas. Hg emissions from coal-fired boilers can be classified, based on the capabilities of currently available analytical methods for determining Hg speciation, into three main forms: gaseous Hg^0 ; gaseous oxidized mercury, Hg^{2+} ; and particle-associated mercury, $\text{Hg}(\text{p})$ [3, 4]. Total mercury ($\text{Hg}[\text{tot}]$) concentrations in coal combustion flue gas generally range from 5 to 10 $\mu\text{g}/\text{m}^3$; however, Hg^0 , Hg^{2+} , and $\text{Hg}(\text{p})$ concentrations are much more variable, depending on the coal composition, combustion conditions, and flue gas quench rate. Each Hg form has distinctive physical and chemical properties; therefore, their emission, transport, and deposition characteristics are different. Hg^0 is the most abundant and persistent form in the atmosphere because of its high volatility, chemical inertness, and very low water solubility [5–9]. Relative to Hg^0 , Hg^{2+} and $\text{Hg}(\text{p})$ are less volatile as well as more water-soluble and chemically reactive. Thus Hg^{2+} and $\text{Hg}(\text{p})$ are more effectively captured in conventional pollution control systems and are more likely to deposit locally or regionally. Hg emission control strategies and transport/deposition models for coal-fired boilers can be improved by identifying the fundamental mechanisms involved in Hg–flue gas–fly ash interactions that transform Hg^0 to Hg^{2+} and $\text{Hg}(\text{p})$.

Results are presented in this annual report for work performed in testing the injection of nitrogen oxide or NO_x into coal combustion flue gas to observe impacts on Hg^0 conversion. Also, kinetic constraints on Hg^0 conversion when subbituminous coal is burned with chlorine spiking were examined and are discussed.

Approach

Tests were performed using three reactors: a 580-MJ/hr pulverized coal (pc)-fired combustion test facility; a bench-scale (42 MJ/hr) downfired conversion and environmental process simulator (CEPS) combustion furnace with provisions for burning fuel under controlled conditions of temperature, atmosphere, and residence time; and a portable EFR which is a slipstream apparatus. Both combustion furnaces have capabilities for introducing added gases and solids (spiking) and for sampling gases and solids for analysis through various stages of combustion and gas cooling. Methods were developed for determining overall rates of transformation of total gaseous Hg ($\text{Hg}[\text{g}] = \text{Hg}^0 + \text{Hg}^{2+}$) to $\text{Hg}(\text{p})$ and Hg^0 to Hg^{2+} and/or $\text{Hg}(\text{p})$ using the portable bench-scale EFR and an on-line Hg analyzer attached to slipstreams from the 580- and 42-MJ/hr pc-fired combustion systems. The EFR was used to investigate Hg transformations under controlled residence time and temperature conditions.

Coal Characteristics, Combustion Testing, and Analyses

This report focuses primarily on tests involving subbituminous coals from the Absaloka and Belle Ayr Mines and lignitic coal from the Falkirk Mine in North Dakota. Detailed information on the composition of these coals can be found elsewhere [10], but basically they all have fairly low ash and sulfur, with less than 0.1 ppm mercury contents, and about 80% of their precontrol device flue gas mercury content existing as an elemental form. Spike testing in the CEPS (42 MJ/hr) involved injecting NO_2 gas through access ports along the CEPS radiant furnace or convective pass sections during combustion of Absaloka and Falkirk coals. A cylinder of certified working-class-grade NO_2 (5045 ppmv NO_2 in N_2) was used as an NO_2 injection source. NO_2 injection concentrations, ranging from about 80 to 200 ppmv, were controlled using a calibrated flowmeter. Concentrations of major flue gas components (O_2 , NO , NO_x , SO_2 , CO , and CO_2) were measured at the furnace outlet of the combustion system using on-line analyzers. Hg speciation analyses were conducted at the baghouse inlet using the Ontario Hydro (OH) method [11]. An on-line Hg analyzer, Semtech Mercury 2000 or Tekran 2537A, was used to measure Hg^0 and gaseous $\text{Hg}(\text{tot})$ concentrations at the baghouse inlet and outlet locations on the combustor. The Semtech Mercury 2000 and Tekran 2537A instruments, described by Laudal et al. [12], use Zeeman-modulated cold-vapor atomic absorption spectrometry and gold amalgamation cold-vapor atomic fluorescence spectroscopy, respectively, to measure Hg^0 concentrations. Fly ash sampling components of a U.S. Environmental Protection Agency (EPA) Method

29 sampling train, a glass nozzle and probe, and quartz-fiber filter maintained at the flue gas temperature were used at the baghouse inlet location to obtain particle-free gas samples for analysis. After particle filtration, a proprietary flue gas-conditioning system was used to remove acid gases and reduce any Hg^{2+} present to Hg^0 for subsequent $\text{Hg}(\text{tot})$ measurement. Even though $\text{Hg}(\text{p})$ concentrations were not determined on-line, the nearly continuous monitoring of Hg^0 and $\text{Hg}(\text{tot})$ concentrations was sufficient to evaluate whether NO_2 or HCl additions into the coal combustion flue gases effectively promoted the conversion of Hg^0 to Hg^{2+} or $\text{Hg}(\text{p})$. Flue gas atomic chlorine (Cl) was measured at the baghouse inlet using EPA Method 26A. Hg and Cl mass balances were calculated from the average coal Hg and Cl concentrations, coal feed rates, average flue gas flows, and measured flue gas $\text{Hg}(\text{tot})$ and Cl concentrations. Mass balance closures of 75%–125% were considered acceptable based on experience with the OH method and EPA Method 26A.

A slipstream from either one of the combustion test furnaces was used to provide flue gas to a portable bench-scale EFR, shown schematically in Figure 1. The reactor, made of stainless steel, is 122 cm long with an internal diameter of 6.35 cm. The inner side of the reactor was polished to minimize wall effects. Ten sampling ports, at intervals of 12.7 cm, are situated along the reactor as indicated in Figure 1. Different-sized nozzles were used to isokinetically extract coal combustion flue gas from the combustion unit into the EFR. Electric heating tapes, combined with a temperature controller, were used to heat the reactor, thus enabling flue gas to be maintained isothermally at 400°, 275°, and 150°C. Ports in the reactor were used to sample flue gas from the EFR at points corresponding to 0, 0.5, 1, 3, 5, and 7 s of residence time in the reactor.

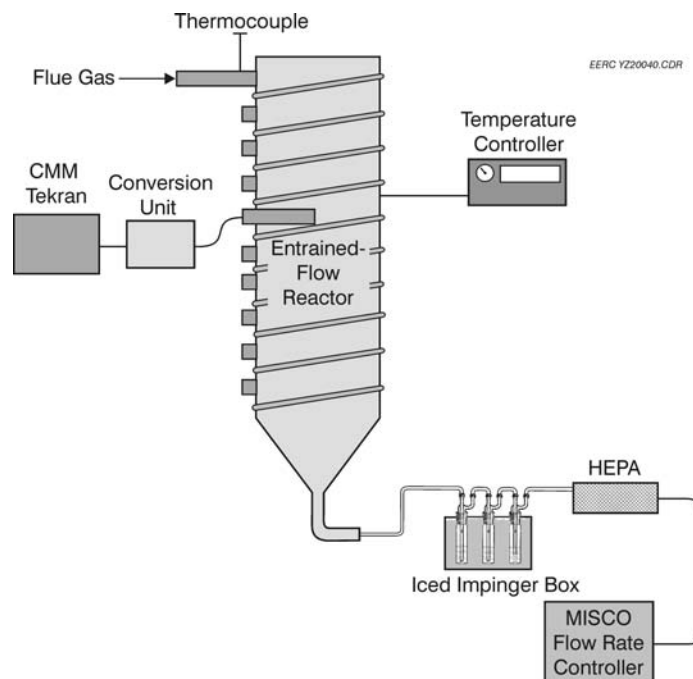


Figure 1. Schematic Diagram of the Entrained-Flow Reactor

Progress

Average Hg mass balances for the Absaloka and Falkirk baseline combustion tests were acceptable at 88%, and 76%, respectively. Hg(p) was insignificant (<1%) in all three flue gases. Hg⁰ was predominant in both the Absaloka and Falkirk flue gases: comprising about 80% of the mercury form in the flue gas.

Prior to injecting NO₂ into coal combustion flue gases, NO₂ was injected into air in the CEPS combustion system. On-line NO measurement results were subtracted from those for NO_x to estimate NO₂ concentrations. NO₂ injections were within ±5% of the intended injection concentration. Quantifying NO₂ in a similar manner during coal combustion was impeded because of the large variability in NO and NO_x concentrations (±150 ppmv) relative to the 80–190 ppmv NO₂ injections. Nevertheless, semiquantitative NO and NO₂ measurements made during NO₂ injections into the coal combustion flue gases suggested that most of the NO₂ was converted to NO when NO₂ was injected at ≥815 °C, whereas most of the NO₂ was stable in the postcombustion flue gas environment when injected at ≤475 °C. The NO₂ injection concentrations used in this investigation, 80–190 ppmv, are consistent with those used in bench-scale investigations of NO_x–fly ash–Hg⁰ interactions [13–16].

Hg speciation results in Figure 2, an average of triplicate OH method measurements at the baghouse inlet (195 °C), indicate that the injection of 80 ppmv NO₂ at 440 °C into the Absaloka flue gas did not significantly affect Hg speciation. The quartz-fiber filter component of the three OH sampling trains created a 195 °C fixed bed (average loading = 2.60 g/cm²) of Absaloka fly ash during the 1.5-hr sampling periods. In comparison, Lee et al. [17] found that approximately 30% of a 40 ppbv Hg⁰ spike in a simulated 300 °C flue gas containing 200 ppmv NO_x (~10% NO₂ and 90% NO) was converted to Hg²⁺ downstream from a 250 °C fixed bed (0.25 g) of Absaloka fly ash.

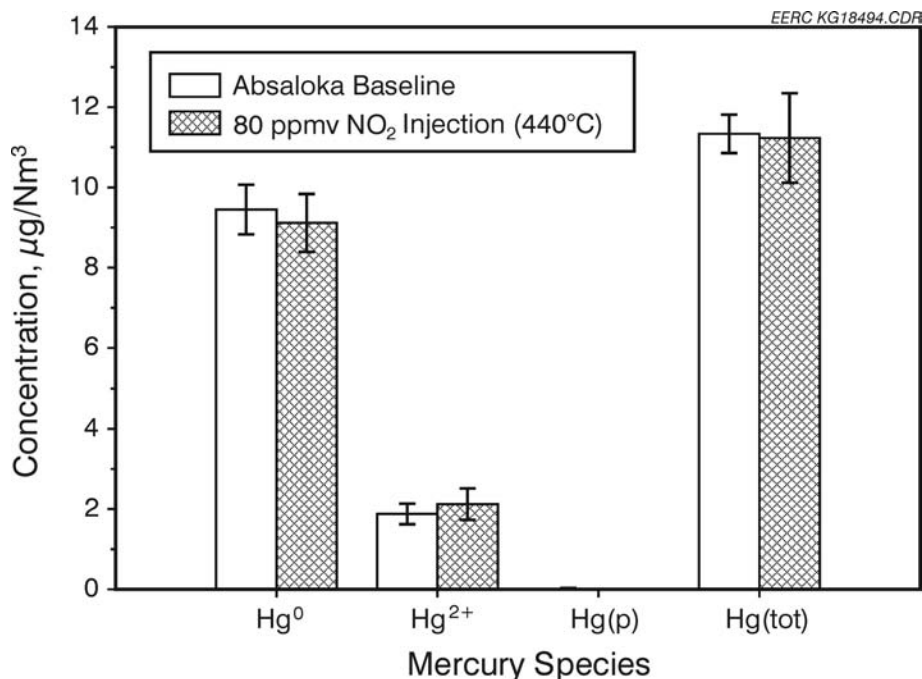


Figure 2. Mercury Speciation of Baseline and 80 ppmv NO₂-spiked Absaloka Flue Gases

NO₂ was also injected at higher concentrations of 100 and 190 ppmv into the Falkirk coal combustion flue gases while Hg⁰ and Hg(tot) concentrations were measured on-line, instead of using OH analyses. The Falkirk flue gas was appropriate for evaluating the effects of NO₂ injection on Hg speciation because of its relatively high Hg⁰ concentration. During the Falkirk NO₂ injection test, 100 ppmv NO₂ was injected at 880°C, and Hg⁰ and Hg(tot) were measured online at the baghouse inlet (180°C). 190 ppmv NO₂ was also injected at 475°C, and Hg⁰ and Hg(tot) were measured on-line at the baghouse inlet (180°C) and outlet (110°C).

On-line Hg⁰ and Hg(tot) measurement results for the Falkirk flue gas are presented in Figures 3 and 4 for the 100 and 190 ppmv NO₂ injections. Mercury mass balance calculations and comparisons to the corresponding OH results in Figure 2 indicate that the on-line Hg⁰ and Hg(tot) results are biased low by about 30%. Despite these biases, the on-line measurement results in Figures 3 and 4 are sufficient to detect variations in Hg⁰/Hg(tot) as a result of NO₂ injection. The results in Figures 3 and 4 indicate that NO₂ injection did not significantly affect the Hg speciation of Falkirk flue gas.

In summary, NO₂ injections into Absaloka and Falkirk coal combustion flue gases did not significantly affect Hg speciation, even though NO_x has been shown to be an important heterogeneous Hg⁰ reactant in simulated flue gases [13–16]. The lack of heterogeneous Hg⁰–NO_x reactions in the 42-MJ combustion system suggests that components of Absaloka and Falkirk combustion flue gases and/or fly ashes inhibit heterogeneous Hg⁰–NO_x reactions or the residence time–temperature conditions in the combustion system are much different relative to bench-scale flue gas simulators.

Kinetic Effects on Mercury Transformation

Time–temperature tests were performed for chlorine injection tests using the Absaloka coal and the EFR (Figure 1). The data show 0.052–0.132 μg/g of mercury and 4.3–50 μg/g of chlorine in the Absaloka coal. The low chlorine content in this coal suggests that chlorination of Hg⁰ may be limited. Flue gas components from the two coal combustion experiments are listed in Table 1. The fly ash was collected for elemental analyses, and the results are presented in Table 2. The loss on ignition (LOI) in the ash was also measured and is listed in Table 2, indicating complete coal combustion and low residual carbon levels in the fly ash.

During the Absaloka coal combustion test, in addition to the baseline test, 200 ppmv HCl was injected into the combustion zone while Absaloka coal was being burned. The purpose was to examine mercury chlorination in the flue gas. A mercury continuous emission monitor (Tekran 2537A) was used to measure mercury vapor concentration in the flue gas at the exit of the convective pass. Ash samples, including bottom ash deposited in the convective pass zone and fly ash in the flue gas, were collected for mercury analysis. In the baseline test, 6.95 μg/m³ total mercury vapor with 3.62 μg/m³ of Hg⁰ was measured in the flue gas at the convective pass outlet, indicating 47.9% mercury oxidation at temperatures higher than 440°C. The ash samples collected from the convective pass zone (bottom ash) and fly ash from the flue gas were analyzed for mercury content (see Figure 5) and revealed 0.0559 and 0.0256 μg/g for bottom ash and fly ash, respectively. The corresponding particulate-associated mercury in the flue gas was 0.41 μg/m³.

With 200 ppm HCl(g) injection into the combustion zone, the total mercury vapor concentration was substantially decreased to 2.46 μg/m³ with only 0.62 μg/m³ of Hg⁰, indicating significant scavenging of mercury vapor from the flue gas due to the HCl injection. Mercury concentration in the fly ash was measured at 0.0732 μg/g, which is not high enough to account for the observed mercury vapor depletion. The bottom ash deposited in the convective pass zone was also analyzed for mercury content, showing an extremely high concentration of 9.43 μg/g, compared with the mercury concentration of 0.0559 μg/g in the bottom ash collected in the baseline test. This finding indicated significant Hg_{gas}-to-Hg_p conversion in the convective

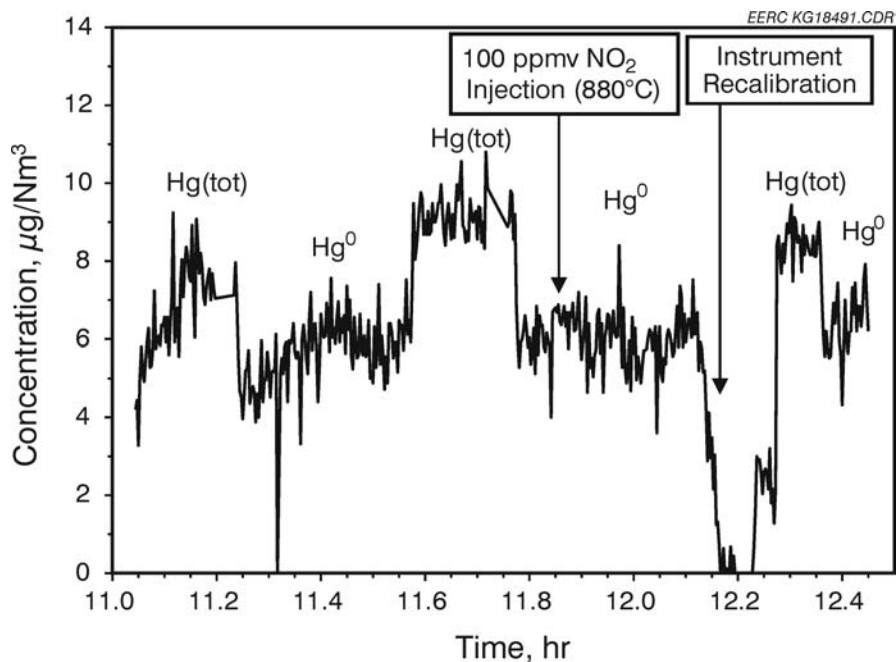


Figure 3. On-Line Hg^0 and $\text{Hg}(\text{tot})$ Measurements (baghouse inlet) of Baseline and 100 ppmv NO_2 -Spiked Falkirk Flue Gases

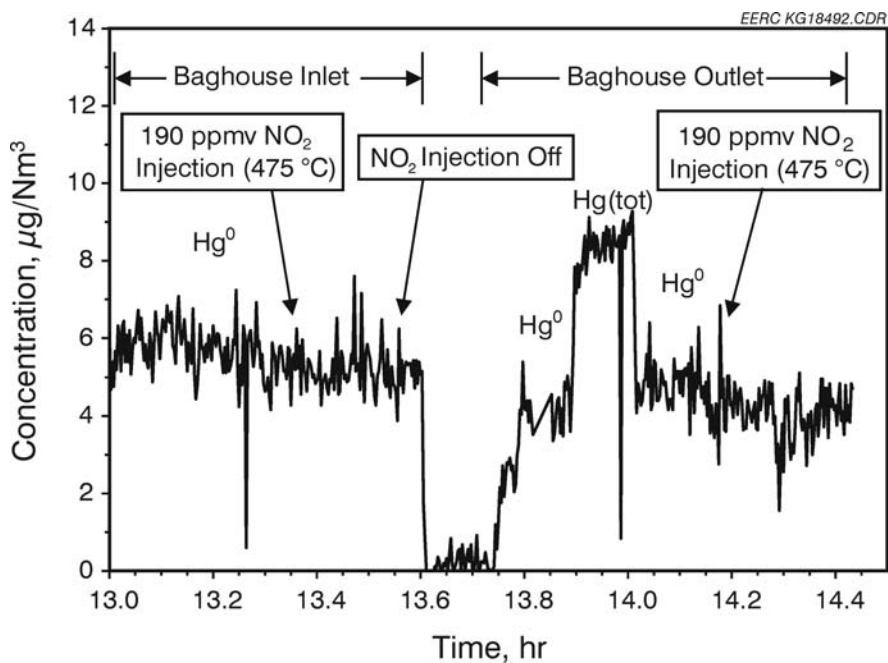


Figure 4. On-Line Hg^0 and $\text{Hg}(\text{tot})$ Measurements of Baseline and 190 ppmv NO_2 -Spiked Falkirk Flue Gases

Table 1. Flue Gas Compositions in Absaloka and Belle Ayr Coal Combustion

Compositions	Absaloka	Belle Ayr
O ₂ , %	4.7	4.5
CO ₂ , %	17.4	14.5
CO, ppmv	14	1-5
SO ₂ , ppmv	502	320
NO _x , ppmv	1508	510

Table 2. Elemental Analysis of Fly Ash from Belle Ayr and Absaloka Coal Combustion, wt%

Coal	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	SO ₃	LOI
Belle Ayr	20.9	16.1	7.3	34.8	5.93	3.14	0.8	2.87	1.58	6.4	0.15
Absaloka	29.1	20.8	4.48	33.8	4.28	2.43	0.64	0.49	1.04	2.98	0.08

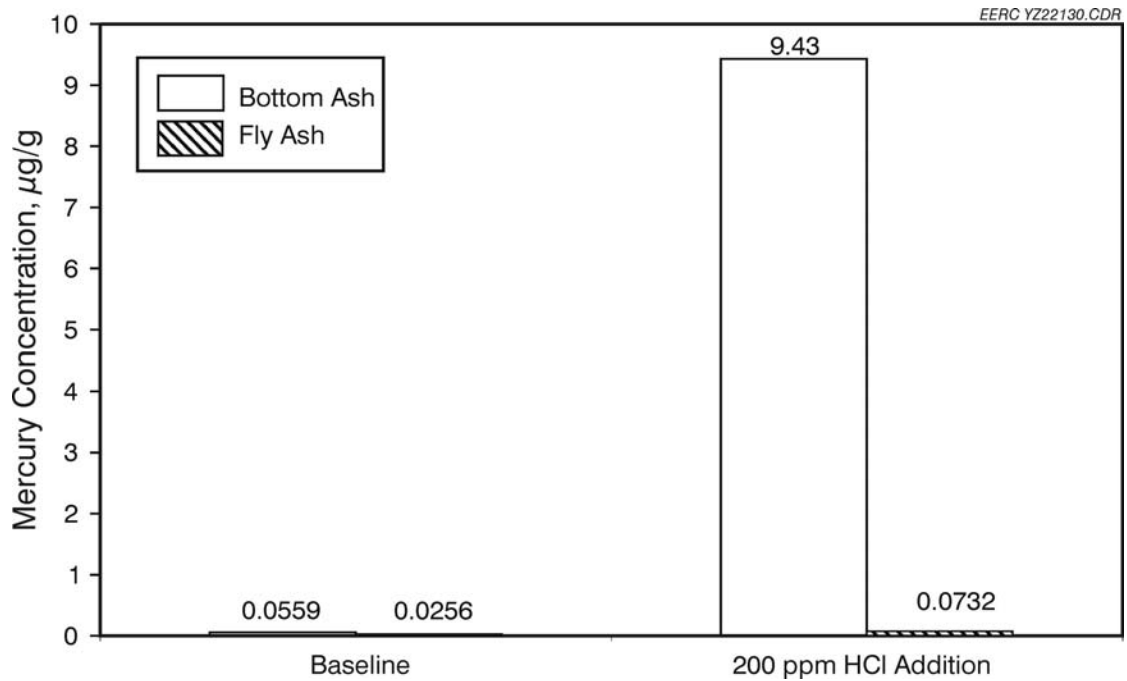


Figure 5. Mercury Concentration in Bottom Ash and Fly Ash from Absaloka Coal Combustion in the CEPS

pass zone where the temperature was 440°–878°C. The total Hg (p) was 8.14 $\mu\text{g}/\text{m}^3$, accounting for 76.8% of the total mercury.

Comparison of the two tests demonstrated mercury enrichment in the bottom ash with HCl injection, which is somewhat surprising because mercury was expected to be in the gas phase in the convective pass zone where the temperature was 440°–878°C during these tests.

Mercury distributions between fly ash and bottom ash for the two tests are shown in Figure 6. For the baseline test, 10% of the total particulate mercury was associated with bottom ash. In the 200 ppm HCl injection test, 87% of the total particulate mercury was deposited in the bottom ash. The observed mercury enrichment in the bottom ash is speculated to be because of the increased level of Cl coupled with an excessive high quenching rate in the convective pass zone of the CEPS. More research is needed to understand the detailed mechanisms of the flue gas quench rate effect on Cl preservation and mercury transformations.

EFR testing was also performed to compare Absaloka flue gas mercury transformations to those of Belle Ayr flue gas. Mercury vapor concentrations, both Hg_{gas} and Hg^0 , were measured as a function of residence time at 150°C, which is believed the most reactive temperature for mercury vapor sorption on ash. Mercury vapor species concentrations in both Absaloka and Belle Ayr coal flue gases (as shown in Figures 7 and 8) decreased with increasing residence time in the reactor where temperature was isothermally 150°C. During the Belle Ayr coal test, Hg_{gas} was 8.3 $\mu\text{g}/\text{Nm}^3$ at the reactor inlet and reduced to 5.3 $\mu\text{g}/\text{Nm}^3$ after 5 seconds, showing an obvious Hg_{gas} -to- Hg_{p} conversion at 150°C. The measured Hg (gas) of 8.3 $\mu\text{g}/\text{m}^3$ at the reactor inlet was lower than the calculated total mercury concentration of 11.7 $\mu\text{g}/\text{m}^3$, indicating an additional Hg_{gas} -to- Hg_{p} conversion occurred in the connecting tube between the 580-MJ/hr combustion unit and the flow reactor.

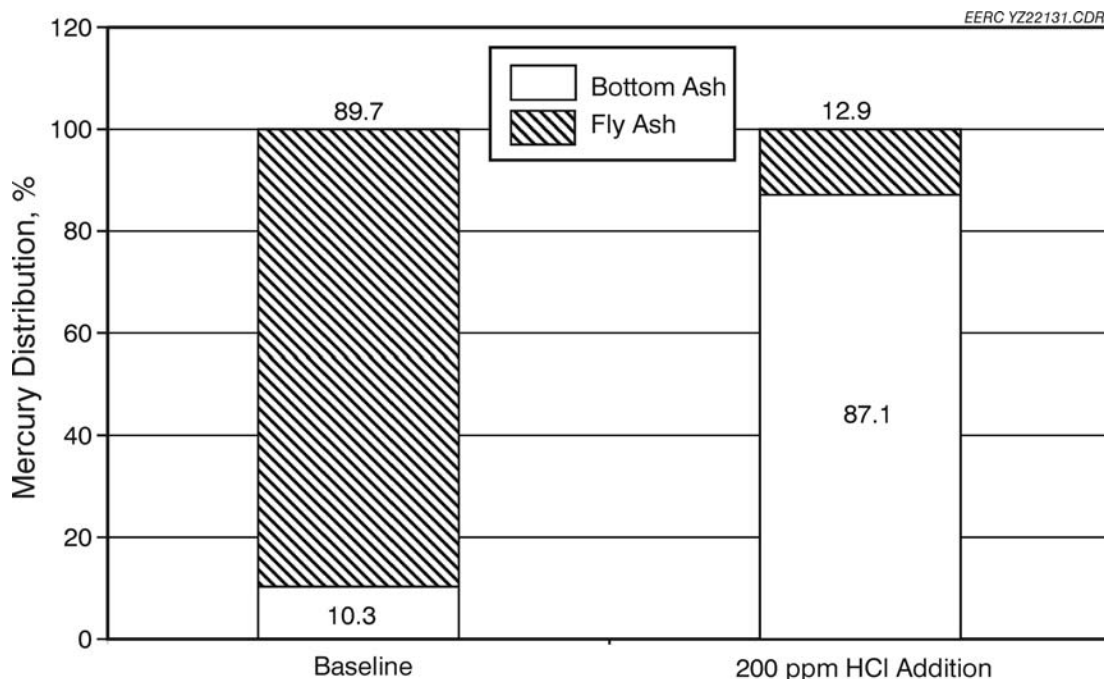


Figure 6. Mercury Distribution Between Bottom Ash and Fly Ash from Absaloka Coal

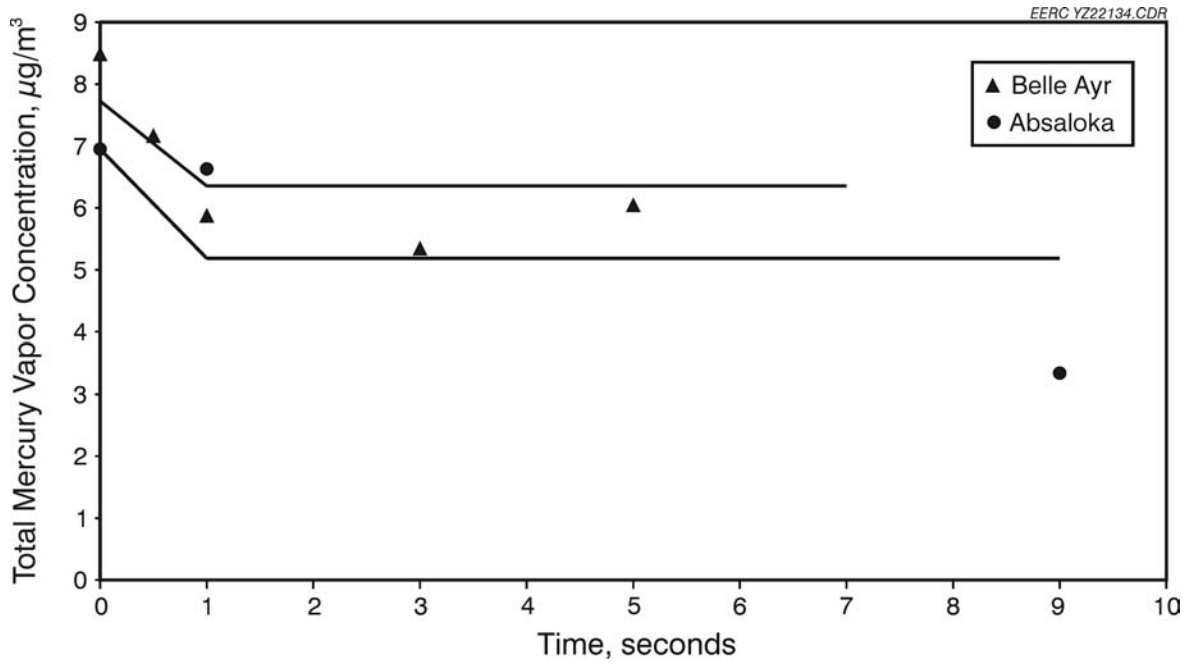


Figure 7. Total Mercury Vapor Transformation as a Function of Residence Time for Belle Ayr and Absaloka

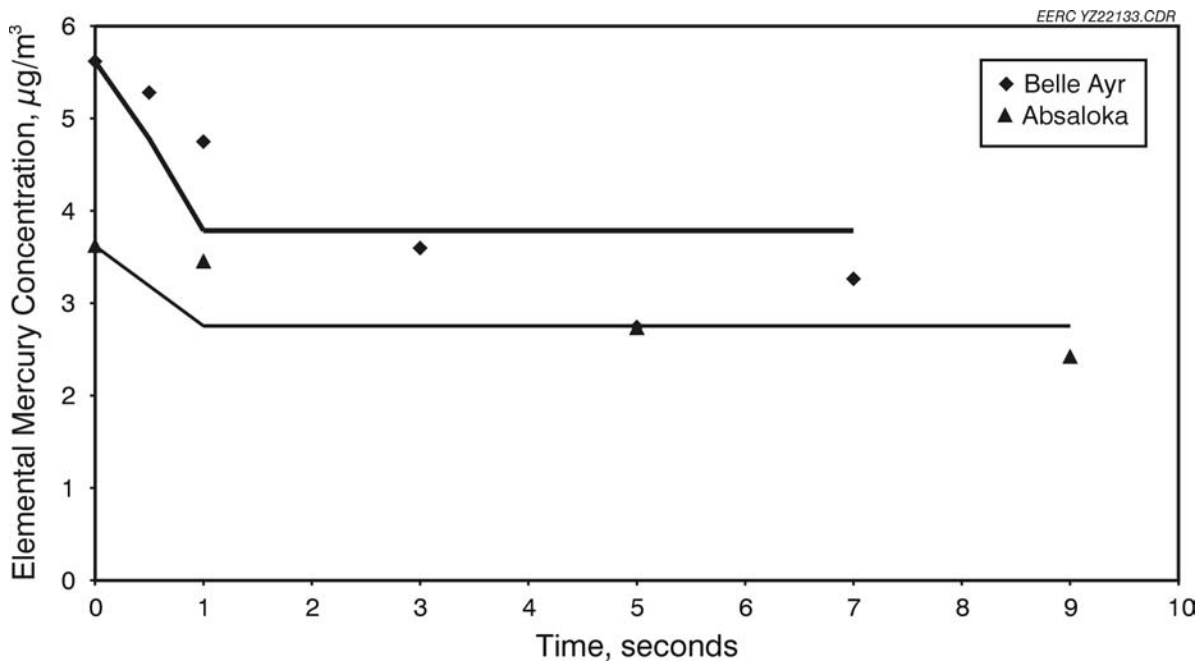


Figure 8. Elemental Mercury Vapor Transformation as a Function of Residence Time for Belle Ayr and Absaloka Coals

9 seconds' residence time. Compared with the calculated total mercury concentration of $10.1 \mu\text{g}/\text{m}^3$ in the flue gas, 31.8% of the total mercury was associated with particulate before it entered the reactor.

Hg^0 was also measured at different residence times during these tests to evaluate the Hg^0 transformation rate in the two different flue gases. For the Belle Ayr flue gas, Hg^0 was $5.62 \mu\text{g}/\text{m}^3$ at the reactor inlet and decreased to $2.75 \mu\text{g}/\text{m}^3$ at the 5-second residence time, indicating an effective Hg^0 conversion and/or oxidation with extended residence times at 150°C . Compared with the Hg_{gas} concentration of $8.3 \mu\text{g}/\text{m}^3$ at the reactor inlet, it is noted that 32.2% of the mercury had already been oxidized before it entered the reactor. The same decreasing trend of Hg^0 with residence time was also observed in Absaloka coal testing data.

Since the EFR tests for both coals were conducted at the same 150°C with varied residence times in the range of 0–9 seconds, the experimental data were, therefore, directly fit to the mass transfer–capacity limit model (Equation 1) to quantify and compare the reactivities of the different fly ashes with mercury in the flue gas:

$$\frac{C_g}{C_0} = \frac{\frac{H}{m}}{1 + \frac{H}{m}} + \frac{1}{1 + \frac{H}{m}} \exp\left[-k_g \frac{a}{V} \left(1 + \frac{H}{m}\right)t\right] \quad [\text{Eq. 1}]$$

where C_g is the mercury vapor concentration, C_0 is the initial mercury vapor concentration, m is the flash concentration, k_g is a mass transfer coefficient, a is the total external surface area of the fly ash, V is volume of the duct, and t is time. The Henry's Law constant H was then inferred by fitting the model directly to the experimental data from the EFR tests. Henry's Law isotherm is a simple description for mercury sorption on fly ash; all the factors are lumped into the parameter H .

The parameters used in the modeling calculation are listed in Table 3. The Levenberg–Marquardt iterative method was used to solve the nonlinear equation in order to determine H (Table 4), a parameter that reflects in-flight fly ash reactivity with mercury. A smaller value of H means that the fly ash has a higher reactivity for mercury sorption at the specific temperature.

Table 3. Parameters Used in Model Calculation

Parameter	Value	Unit
Fly Ash Diameter	8	μm
Dust Loading in Flue Gas	3.28	g/cm^3
Fly Ash Density	2.4	g/cm^3
Pressure	1	atm
Molecular Weight of Flue Gas	28.97	g/mole
Molecular Weight of Mercury	200.59	g/mole
Collision Diameter of Flue Gas	3.617	Å
Collision Diameter of Mercury	2.969	Å
Temperature	150–400	$^\circ\text{C}$
Residence Time	0–7	second

Table 4. Calculated H for Hg_{gas} and Hg⁰ for Belle Ayr and Absaloka Fly Ash – Henry’s Law Isotherm

	Belle Ayr	Absaloka
Hg _{gas}	15.2	9.64
Hg ⁰	6.78	10.4

The mercury vapor sorption (C*) on fly ash was more precisely defined assuming a reaction order (n) determined by experiments of mercury vapor in equilibrium (C_sⁿ) and the parameter H as in Equation 2:

$$C^* = H \cdot C_s^n \quad [\text{Eq. 2}]$$

Since mercury vapor sorption also depends on the availability of activated sites on fly ash, a more sophisticated model is proposed to describe heterogenous mercury transformation (Equation 3):

$$-\frac{dC_g}{dt} = k_g \cdot \frac{a}{V} \cdot A \cdot \left[C_g - H \left(\frac{C_0 - C_g}{m} \right)^n \right] \quad [\text{Eq. 3}]$$

where A stands for the fraction of surface area on fly ash that is reactive, n is the reaction order, and H is the flight mercury adsorption reactivity of fly ash.

The calculated H showed that the Belle Ayr coal fly ash was more effective for Hg⁰ capture at 150°C than the Absaloka coal fly ash. For total mercury vapor, however, the Absaloka coal fly ash had a better capability for mercury sorption than the Belle Ayr coal fly ash because of the higher percentage of Hg²⁺ vapor in the Absaloka flue gas.

Conclusions

In summary, NO₂ injections into Absaloka and Falkirk coal combustion flue gases did not significantly affect Hg speciation, even though NO_x has been shown to be an important heterogeneous Hg⁰ reactant in bench-scale simulated flue gases. The lack of heterogeneous Hg⁰–NO_x reactions in the 42-MJ combustion system suggests that components of Absaloka and Falkirk combustion flue gases and/or fly ashes inhibit heterogeneous Hg⁰–NO_x reactions or the residence time–temperature conditions in the combustion system are much different relative to bench-scale flue gas simulators.

Kinetic experiments designed to obtain quantitative data on the time–temperature oxidation of Hg⁰ to Hg²⁺ were performed in an EFR using the subbituminous Absaloka and Belle Ayr coals. Hg transformations were not detected in the reactor at 400° and 275°C. At 150°C, however, Hg(gas) and Hg⁰ were transformed primarily into Hg(p) with increasing residence time. The reaction order and rate constant for both Hg(gas) and Hg⁰ to convert were 4.62 and 1.73 and $9.8 \times 10^{-5} \mu\text{g}^{-3.62}/(\text{m}^{-10.86} \cdot \text{s})$ and $5.1 \times 10^{-2} \mu\text{g}^{-0.73}/(\text{m}^{-2.19} \cdot \text{s})$, respectively.

Significant mercury transformation from the bulk gas phase to the particulate phase was observed at high temperatures of 440°–878°C when 200 ppmv HCl was injected into the combustion zone, which might be the result of an increase in Cl followed by a rapid flue gas quenching rate of 4833°C/s.

For both Belle Ayr and Absaloka coals, entrained-flow tests demonstrated mercury oxidation and conversion with increasing residence time at 150°C. The entrained-flow testing data also provide intrinsic information on in-flight fly ash reactivity with mercury species by best-fitting with a mass transfer–capacity limit model. The modeling results showed the Belle Ayr coal fly ash was more effective for capturing Hg⁰ than the Absaloka coal fly ash. For the total mercury vapor, however, the Absaloka coal fly ash had a better capability for mercury sorption than the Belle Ayr coal fly ash because of the higher percentage of Hg²⁺ vapor in the Absaloka flue gas.

Status

Within CATM, research continues in the area of fundamental mercury transformations during coal combustion. The effects of various flue gas constituents on the oxidation of Hg^0 , in combination with low-acid gas concentrations, will continue to be investigated. There will also be additional testing of oxidizing agents like sodium chloride which optimize Hg^0 conversion or capture.

With respect to kinetic studies of mercury transformation, research will continue to develop an understanding of the temperature, residence time, and kinetic constraints on Cl oxidation of Hg^0 with continued publication of results to add to this series of investigations [18–21]. Low-sulfur (<1 wt% sulfur) coals, such as Powder River Basin subbituminous coal, will continue to be a focus. Flue gas that is spiked or doped with various oxidizing agents will be introduced into the EFR, where temperature is isothermally controlled, and experiments will focus on kinetic transformations of mercury.

The experimental data derived from the EFR tests will be used to evaluate the homogeneous chlorination rate of Hg^0 in an essentially fly ash-free, chlorine-spiked, flue gas environment. In some tests, an electrostatic precipitator will be turned on or off to evaluate the potential effects of fly ash particles on Hg^0 chlorination. Test results will be used to calculate an overall Hg^0 transformation rate as a function of temperature, residence time, and Hg^0 concentration for various coal types.

Researchers on this project will continue to collaborate closely with modelers who have developed a mechanistic model for coal combustion ash transformations and chemical partitioning and will be incorporating mercury speciation into their model. Collaboration will essentially involve supplying mechanistic information on mercury species formation to the modelers. The Energy & Environmental Research Center (EERC) hopes to make mercury prediction models available for use by other researchers and utilities to help determine appropriate control approaches in accordance with the EPA ruling on allowable mercury emission levels.

Quality Assurance/Quality Control

The primary quality objectives for this project included the following:

- 1) Combustion conditions, as set forth by the project managers and engineers, for the scope of work were followed correctly and implemented precisely by combustion technicians. Specified combustion conditions (excess air, feed rates, gas cooling rates, and other conditions), concentrations of spiking components, and residual carbon in the fly ash (influenced by combustion conditions) were monitored so that the test plan put forth by the project manager was followed.
- 2) Sampling and procurement of all physical states of fuels and combustion by-products were adhered to, according to accepted published standards and American Society for Testing and Materials (ASTM) methods. Chain-of-command procedures were followed to allow for quality control (QC) when gathering samples and submitting for analysis.
- 3) Measurement techniques for mercury and other critical combustion flue gas components were monitored for quality and precision. Concentrations of oxidized, elemental, and particulate forms of mercury were compared between on-line analyzer and wet-chemical OH mercury speciation methods. Quality assurance/QC standards for specific instrument calibrations were followed and checks and balances employed to account for particular mercury concentrations as determined by specific instruments (i.e., an inductively coupled argon plasma mass spectrometer).

- 4) The objectives and hypotheses of the project, as specified in the proposed research plan, were checked against real and projected results and conclusions at the midway mark of the project. This ensured that the research was proceeding as planned and with quality and that reasonable answers or explanations to the hypotheses were being attempted.

Coals, combustion flue gases, and fly ashes were sampled, prepared, and chemically analyzed using EPA and ASTM approved methods. A variety of QC activities were used to assess and control precision, accuracy, representativeness, completeness, and comparability of the sampling and analytical measurement processes. QC objectives were established to support decisions concerning test validity and adequacy with respect to the project objectives.

Potential Users/Technology Transfer

The U.S. Department of Energy, utilities, state agencies, control technology vendors, other industries, and other government agencies will benefit from the information generated in this project with respect to mercury transformation and speciation. Several ongoing research consortia composed of these groups have ongoing projects with the EERC and are dedicated to mercury emission characterization and control. Workers in this CATM project meet regularly with other researchers within the EERC performing work in these consortia; therefore, information dissemination is efficacious.

Other users of the project results are special interest and environmental groups seeking a scientific assessment of the transformations and potential fate of air toxic metals and the general public by having access to unbiased information related to sources and potential emissions of air toxics. The pending establishment of a final mercury emission limit and possible credits trading system require that more work be done to unravel the fundamental mechanisms that govern which species form and how best to control them.

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