



*Christopher J. Zygarlicke  
Principal Investigator*

## MERCURY TRANSFORMATIONS IN COAL COMBUSTION FLUE GAS

**Key Personnel:** Chris Zygarlicke (EERC), Ye Zhuang, (EERC), Kevin Galbreath (EERC), Jeff Thompson (EERC), Ed Olson (EERC), Ramesh Sharma (EERC), Steve Benson (EERC), Richard Liggett (EERC), Ray DeWall (EERC), Richard Schulz (EERC), Dennis Laudal (EERC), Grant Dunham (EERC).

### ***Project Description***

The EERC is performing fundamental research to understand mechanisms responsible for conversion of mercury to other chemical species within combustion and gasification flue gas. This research is imperative for development and validation of improved mercury emission measurement, monitoring, and control. Several tasks are devoted to understanding mercury transformations.

Unburned carbon particles from two carbon-rich fly ashes derived from full-scale coal-fired utility boilers are being separated from inorganic ash fractions. The fly ash samples were selected based on a high propensity for effective capturing of mercury. Carbon concentrates are being characterized in detail to determine which physical and chemical properties may be important in capturing mercury.

A portable bench-scale entrained-flow reactor (EFR) is being used to determine mercury oxidation and particulate formation rates as a function of coal type (at least two highly differing in rank and composition), flue gas residence time, and flue gas temperature.

Sulfur species in unburned carbon from coal or tire rubber are being explored as possible reaction sites for oxidizing and stabilizing gaseous mercury.

Chemical additives are being investigated in combination with tetrasulfide flue gas injection to determine the impact on mercury oxidation and capture. Finally, the effects of SO<sub>2</sub>, SO<sub>3</sub>, and HCl on mercury speciation in the presence of selective catalytic reduction catalyst material and a coal flue gas environment will be tested in a bench-scale system.

### ***Goal***

The overall goal of this project is to develop a fundamental understanding of Hg transformations in flue gas for the purpose of developing more effective mercury control strategies. Specific objectives to accomplish this goal include:

- Obtain time–temperature-resolved measurements of mercury transformations (oxidation of  $\text{Hg}^0$  to both  $\text{Hg}^{2+}$  and particulate-bound forms) for up to three different coals (Powder River Basin [PRB], lignite, and bituminous) using an EFR attached to a pilot-scale or full-scale combustor.
- Determine the effect of injecting HCl or  $\text{Cl}_2$  on the kinetics of mercury transformations in combustion flue gas.
- Define optimum conditions for  $\text{Hg}^0$  conversion using injected reactants.
- Identify the physical and chemical properties of unburned carbon particles in coal fly ashes that promote mercury species adsorption and  $\text{Hg}^0$  oxidation using existing fly ash samples and innovative analytical techniques.
- Determine the kinetic mechanisms related to  $\text{Hg}^0$  oxidation.
- Identify the sulfur species in flue gas that derive from tetrasulfide injection that serve to promote oxidation and stabilization of mercury in low-chlorine flue gas.
- Develop sulfur compounds for flue gas injection for more effective mercury control.
- Investigate specific acid gas effects on mercury speciation in the presence of selective catalytic reduction (SCR).

### ***Rationale***

#### **Kinetics of Mercury Transformation**

Proposed mercury regulations for coal-fired utilities require that control strategies be planned immediately. The effectiveness of various control methods will depend on the species of mercury that are formed upstream of the control device. Mercury speciation depends on the coal's chemical and mineralogical composition, combustion conditions, and the time–temperature history of mercury and other gaseous components in the boiler from combustion zone to stack. Thus the concentrations of mercury species will vary from plant to plant.

Mercury species measurements and related chemical kinetic models suggest that the chlorine content of flue gas is the main contributor to mercury oxidation in flue gas leaving the boiler and entering air pollution control devices. These models (1–3) also suggest that the concentration of atomic chlorine (Cl), the predominant oxidizing reactant, is controlled by interactions and concentrations of other gases, including HCl, CO,  $\text{H}_2\text{O}$ , and NO. Increases in HCl and CO concentrations promote Cl and  $\text{HgCl}_2$  formation, while increases in  $\text{H}_2\text{O}$  concentration inhibit their formation. NO can either inhibit or promote Cl and  $\text{HgCl}_2$  formation, depending on its concentration.  $\text{SO}_2$  may inhibit formation of Cl relevant to gas-phase mercury oxidation (4, 5). However, the calculated mercury oxidation predicted by models based on homogeneous gas reaction does not accurately match the transformation observed in combustion systems. Other possible mechanisms for oxidation involve physical and chemical adsorption on fly ash or sorbent particles and related heterogeneous reaction. Certain metallic constituents of fly ash such as CuO and  $\text{Fe}_2\text{O}_3$  have been shown to catalytically oxidize mercury, especially in the presence of HCl and  $\text{NO}_x$ . Other results have demonstrated that unburnt carbon in fly ash can substantially enhance the sorption of mercury. Most of the studies on mercury gas–solid partitioning and speciation in coal combustion flue gas, however, have been performed in fixed packed-bed reactors instead of in entrained-flow reactors as

in coal combustion. Much research still remains to understand the complex thermodynamic and kinetic constraints on mercury species transformations.

To assess mercury transformations in more detail, engineers at the EERC designed and built a portable bench-scale EFR that could be attached to a 580-MJ/hr pilot-scale combustion system. This system was used to measure time- and temperature-resolved  $\text{Hg}^0$  transformations (6) during this reporting period.

Previous testing to understand mercury kinetic transformations using the EFR were performed using Powder River Basin (PRB) coal (Belle Ayr) with the EFR being operated at 400°, 275°, and 150°C and a flow rate corresponding to residence times of 0–7 s. These temperatures were selected because extensive lab, pilot, and field research had shown that  $\text{Hg}^0$  oxidation occurs between 150°–400°C.  $\text{Hg}^0$  and  $\text{Hg}(\text{tot})$  concentrations in the EFR were measured using an online Hg analyzer. At both 400° and 275°C, approximately 30% of the mercury in the PRB (Belle Ayr) coal was in the oxidized form  $\text{Hg}^{2+}$  leaving the 580-MJ/hr combustion system and entering the EFR. Oxidation occurred rapidly  $\geq 275^\circ\text{C}$ , as evidenced by similar  $\text{Hg}^0$  concentrations at 275° and 400°C and the lack of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  conversion measured across the EFR for residence times of 0.5–7 s. However, conversions of  $\text{Hg}(\text{tot})$  to  $\text{Hg}(\text{p})$  and  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and/or  $\text{Hg}(\text{p})$  were measured across the reactor at 150°C. The reaction order and rate constants for  $\text{Hg}(\text{tot})$  and  $\text{Hg}^0$  conversions were calculated. Additional research was performed on the EFR firing a different PRB coal (Absaloka), with 200 ppm HCl injection in the combustion zone (7). Results at 150°C showed significant mercury enrichment on the combustion ash. Formation of  $\text{Hg}(\text{p})$  may have been promoted by the very high flue gas quenching rate in the combustor (4833°C/s). High cooling rates promote the generation of atomic chlorine and the transformation of  $\text{Hg}^0$  to  $\text{Hg}(\text{p})$  particulate.

Further investigations using the EFR will expand the knowledge base regarding kinetic mercury transformations in various coal combustion flue gases.

### **Mercury Adsorption on Unburned Carbon**

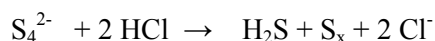
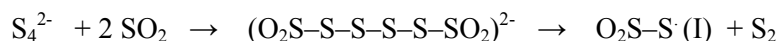
Another task of research in this program the past year has dealt with understanding the physical and chemical interactions between unburned carbon particles in coal fly ashes and mercury. It has long been known that carbon in fly ash will promote mercury species adsorption and even  $\text{Hg}^0$  oxidation; however, there is still a significant lack of empirical knowledge in this area. The biggest market for coal fly ash is in concrete applications as a cement additive. According to ASTM International (American Society for Testing and Materials) Standard 618, the fly ash loss-on-ignition (LOI) must be <6 wt% to be used as a cement additive. Historically, fly ash carbon contents have generally been in the range of 2–12 wt%. However, the promulgation of emission limits on nitrogen oxides ( $\text{NO}_x$ ) has caused most utilities to employ  $\text{NO}_x$  reduction strategies (e.g., install low- $\text{NO}_x$  burners, SCR, staged combustion) that have resulted in fly ash carbon increases to as high as 20 wt% in some cases because of oxygen-deficient and/or lower-temperature combustion conditions that are created as a result of these strategies. The EERC and other research organizations have observed these relatively carbon-rich fly ashes while evaluating mercury control technologies. In several cases, these carbon-bearing fly ashes were effective in capturing mercury, whereas in others they were not. Hassett and Eylands (8) demonstrated in a bench-scale system that increases in fly ash carbon content and decreasing temperature promoted mercury capture on fly ash. Hower et al. (9) and Sakulpitakphon et al. (10) noted similar relationships for fly ashes collected from utility-scale combustion systems. Hower et al. (11) also demonstrated, using density gradient centrifugation; Brunauer, Emmett, and Teller (BET) surface area calculations; and petrography measurements, that mercury capture is related to BET surface area and carbon form in the following order: inertinite < isotropic coke < mixed isotropic-anisotropic coke < anisotropic coke. The mercury

removal effectiveness of unburned carbon particles depends on their physical and chemical characteristics and, possibly, on the composition of the flue gas.

### **Sulfur Species Determination and Impact on Mercury Oxidation and Stabilization**

In a narrower focus that examines mercury kinetic reactions in flue gas or interaction with different carbon particles, some research this year is being done to determine the effect of specific sulfur species on mercury in flue gas. Sodium tetrasulfide solution has been added to flue gas for Hg control, but its effectiveness is questionable. Tests conducted at the EERC showed no improvement in capture across an electrostatic precipitator (ESP), but others reported success (12, 13). In German tests, waste was being burned, and the Hg species was mostly HgCl<sub>2</sub>, which would react readily with the tetrasulfide. Gale and Merritt's research (13) was conducted with low-Cl coals, which releases more of the Hg in elemental form, and chlorine addition reduced Hg capture. The molecular mechanism of capture is unknown, and the following questions need to be answered: 1) do reactions occur in the gas phase, droplet interphase, or solid phase and 2) what species or intermediates actually react with Hg? The intact tetrasulfide anion is not a good oxidizing agent, but upon decomposition to monoatomic or diatomic sulfur (radicals) in the hot flue gas, these intermediates may combine with elemental Hg. These forms certainly have potential for Hg<sup>0</sup> capture, but much more knowledge is required to use this technology effectively.

Tetrasulfide can be expected to react in the flue gas stream or on particulate surfaces in various ways. It could dissociate thermally to sulfide and sulfur atoms or diatomic molecules, either of which may react with Hg<sup>0</sup> and form thermally stable HgS. These would be much more reactive than the normal elemental form of sulfur, S<sub>8</sub>. Alternatively, it could react with SO<sub>2</sub> to form a polythionite ion(I). These would subsequently dissociate to various sulfur radical ions and sulfur atoms that could react with Hg in the gas or solid phase.



### **Acid Gas Effects on Mercury Species in the Presence of an SCR**

Finally, part of the program this year was to continue bench-scale testing of the factors that have the potential to alter mercury speciation when SCR technologies are used. Specifically, the effects of the different variables of flue gas chemistry, fly ash type, and residence time were evaluated. The acid gases NO and NO<sub>2</sub> were always present in the flue gas mix during testing. SO<sub>3</sub>, SO<sub>2</sub>, and HCl were introduced into the flue gas together as an individual test variable. The two fly ash types studied were bituminous and subbituminous coals. Initial results showed that the oxidation of mercury increased when the acid gases SO<sub>3</sub>, SO<sub>2</sub>, and HCl were introduced and increased even further in an SCR environment. These acid gases together had the greatest effect on mercury speciation, but their effects were not evaluated independently. Ash type and residence time had comparatively minor effects. More detailed testing is needed to determine the impacts of acid gases on mercury oxidation or particulate formation across an SCR system.

## ***Approach***

### **Task 1 – Kinetics of Heterogeneous and Homogeneous Mercury Conversion**

A portable bench-scale EFR was used to determine overall Hg<sup>0</sup> oxidation rates and particulate-bound Hg formation rates in coal combustion flue gases. Previous studies showed the utility of this

system to evaluate mercury transformations and their kinetics in the postcombustion zone. Coal combustion tests in a 580-MJ/hr particulate test combustor (PTC) provided a range of flue gases and associated mercury transformations for investigation using the EFR. A continuous mercury monitor (CMM) was positioned at the inlet (0 seconds residence time) to the EFR and at four succeeding residence times of 1, 3, 5, and 7 seconds using the different sampling ports in the EFR. Ontario Hydro samples for Hg analysis were collected at various points in the EFR to verify the CMM results.

Two sets of tests were conducted: one focused on heterogeneous reactions using PRB coal from the Caballo Mine and one focused on homogeneous reactions using a North Dakota lignite from the Freedom mine. For the homogeneous testing on the PRB, the EFR was set up and operated to generate kinetic data for mercury transformations under baseline conditions (flue gas only) for two temperatures (275° and 150°C). Following the baseline measurements, calcium chloride (CaCl<sub>2</sub>) was injected with the coal into the combustor and mercury speciation determined at the inlet and four succeeding residence times of the EFR for a temperature of 150°C. Data from these tests will be integrated with previous research on this same PRB coal/additive experiment. A bituminous coal will also be tested under these same conditions later in this program.

Under a second set of tests, a small ESP was used at the inlet to the EFR to collect or remove ash particulate for simulating homogeneous reactions. During these runs, the EFR was set up and operated to generate kinetic data for mercury transformations under baseline conditions (no additives) at two temperatures (275° and 150°C). Following the baseline measurements, halogens were injected with the coal into the combustor. Previous results had shown that 200 ppm HCl could significantly oxidize Hg<sup>0</sup> for PRB coal combustion. Modeling efforts were used to determine the amount of additive to inject. A CMM was used to monitor concentration variations in total gaseous mercury as well as elemental mercury as functions of residence time and temperature for each testing scenario.

Table 1 outlines the test matrix for the EFR kinetic runs. PRB and North Dakota lignite tests were performed in conjunction with other ongoing tests on the PTC. A bituminous coal may be tested in the future.

**Table 1. Test Matrix for Kinetic Testing of Mercury Transformations**

<b>Coal</b>	<b>Caballo Mine, PRB</b>	<b>Freedom Mine, lignite</b>
Temperature, °C	275 150	275 150
Residence Time, seconds	Inlet (0), 1, 3, 5, 7	Inlet (0), 1, 3, 5, 7
Combustor Additives	CaCl <sub>2</sub>	Halogen salts
ESP Setting	Off (heterogeneous)	On (homogeneous)

The data generated from these tests were shared with researchers developing control options for elemental mercury in projects related to Program Area 3 of CATM. The data were also used in the ongoing effort to model mercury transformations.

## **Task 2 – Mercury Adsorption on Fly Ash: Unburned Carbon Separation and Characterization**

### *Ash Selection*

Most of the research in this task is still ongoing. An in-house EERC fly ash repository supplied a sample containing significant amounts of carbon and mercury. An additional fly ash that also contains significant amounts of carbon but not mercury will be selected in the near future. Previously determined information and selection criteria for these two fly ashes includes mercury concentrations, volatile loss on ignition (LOI), limited oxide chemistry analysis, and associated flue gas compositions.

### *Unburned Carbon Separation and Characterization*

Unburned carbon from the two fly ashes will be concentrated using separation methods such as gravity separation and froth flotation processes developed by Michigan Technological University (14–16). These processes are expected to yield carbon concentrates with LOI values of >80 wt% and a fly ash residue containing <1 wt% carbon (16). Carbon and mercury analyses of the carbon and inorganic ash concentrates will be used to determine if carbon and mercury are preferentially enriched in either of the fractions. In addition, analyses of the corresponding bulk ash samples will be used in mass balance calculations to evaluate potential carbon and mercury losses or gains resulting from the separation procedure. Classification of carbon in the fly ash samples will be attempted using standard petrography methods developed by Hower et al. (11) for fly ash carbon. Carbon material will be classified into inertinite, isotropic coke, mixed isotropic–anisotropic coke, and anisotropic coke. This classification exercise will not be exhaustive; it will be attempted on a few samples to gauge effectiveness for future tests.

The chemical composition, morphology, and microstructure of individual unburned carbon particles will be determined using scanning electron microscopy (SEM), electron probe microanalysis (EPMA), and field emission scanning electron microscopy (FE–SEM). Depending upon funding resources, the inorganic fraction of the fly ash may be examined using the same analyses to note any obvious correlations. X-ray photoelectron spectroscopy (XPS) will be used to characterize the surface chemical compositions of carbon particles which may indirectly reflect differences in mercury sorption on ash. XPS, also known as electron spectroscopy for chemical analysis (ESCA), involves irradiating a sample with a monoenergetic x-ray beam that causes photoelectrons to be emitted from the sample. The photoelectrons are emitted from the first 30–50 angstroms of the sample surface. An energy analyzer is used to determine the binding energy of the emitted electrons. From the binding energy and intensity of the photoelectron peak, the elemental identity, chemical state, and quantity of an element is determined. XPS analysis will be used to identify the species of S, N, Cl, and O on unburned carbon surfaces.

Using the chemical composition and morphological information derived from XPS, SEM, FE–SEM analyses, and petrographic data (if available), correlations will be attempted between this information and mercury content. Since the information will be derived directly from organic coal materials, correlations will be sought to link mercury content with carbon chemistry or morphology.

## **Task 3 – Sulfur Species Determination and Injection for Mercury Oxidation and Stabilization**

Most of the research in this task is still ongoing. Spectroscopic and chromatographic measurements of the sulfur species in coal fly ash, unburned carbon, and tetrasulfide pyrolysis-generated particulate will be conducted to characterize these samples and determine their potential for reaction with Hg. Results for

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Hg capture efficiencies in the initial sampling experiment as well as limited bench-scale retesting of separated products will be correlated with the sulfur species types and concentrations.

The proposed research will utilize ash samples collected during a PTC run using low-chlorine, low-sulfur fuel where tetrasulfide is injected and mercury capture efficiency is determined. Unburned carbon and ash will be separated from ash collected in a bag filter or ESP using flotation or density separations. Specifically, sulfur forms such as sulfide, disulfide, organosulfide, thiosulfate, sulfate, and carbon-attached sulfide will be determined after separation of unburned carbon and ash. Separated samples will be tested in the thin-bed bench-scale unit described in Miller et al. (14) to determine Hg capture efficiency. The test parameters will simulate low-chlorine (no additive), moderate temperature (150°C) conditions as previously described (14).

XPS will be used initially to identify sulfur forms in both carbon and ash. This will mainly determine the oxidation states of sulfur compounds and identify inorganic and organic sulfide. More specific characterization research will be done with extracts. Reagents (nitron spin trapping) will be added to the solids to trap any radical forms remaining, and alkylating reagents will be added to react with sulfide species. The resulting derivatives will be analyzed by gas chromatography–mass spectroscopy (GC–MS) if volatile or by Fourier transform infrared (FT-IR), Raman, and solid state nuclear magnetic resonance (NMR) and electron spin resonance (ESR) if nonvolatile or attached to the particulate.

A preliminary bench-scale pyrolysis experiment was performed that simulates the duct injection of tetrasulfide. The tetrasulfide solution was injected into a heated synthetic flue gas and passed through a thin bed of carbon and, separately, ash. A variety of temperatures were tested to determine the decomposition temperatures on the stainless steel surface. The beds were analyzed as described above.

#### **Task 4 – Acid Gas Effects on Mercury Species in the Presence of an SCR**

A bench-scale flue gas simulation was set up to test the effects of SO<sub>3</sub>, SO<sub>2</sub>, and HCl on mercury oxidation across an SCR catalyst. This system has been previously described in detail (18). The nominal gas flow rate was 14 L/min and the mercury concentration, 15 µg/m<sup>3</sup>. The baseline flue gas concentrations were approximately 12% CO<sub>2</sub>, 6% O<sub>2</sub>, 8% H<sub>2</sub>O, 400 ppm NH<sub>3</sub>, 400 ppm NO, and 18 ppm NO<sub>2</sub> with N<sub>2</sub> balance. These concentrations were held constant for all tests, and the independent variables were the HCl, SO<sub>2</sub>, and SO<sub>3</sub> concentrations. The SO<sub>3</sub> was generated using a vanadium/platinum catalyst bed to oxidize SO<sub>2</sub>.

The SCR catalyst reactor and ash in a stainless steel filter holder were both maintained at 343°C in a high-temperature oven. The flue gas was heated to 343°C before passing through the reactor. After passing through the high-temperature reactor, the flue gas was directed through an external fixed bed of ash maintained at 177°C in a stainless steel filter holder. A slipstream of the exiting flue gas was sampled for mercury concentration and speciation. An ECOM portable gas analyzer was used to verify the NO<sub>x</sub> reduction across the catalyst.

### ***Progress***

#### **Task 1 – Kinetics of Heterogeneous and Homogeneous Mercury Conversion**

During this period, two EFR slipstream tests were conducted in conjunction with pilot-scale coal combustion tests in the PTC facility at the EERC. The goal of the EFR testing was to obtain additional

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understanding of mercury kinetics for different coals and to note the impact of halogen species on mercury transformation in coal combustion flue gas.

In the first test, a subbituminous Wyoming coal from the Caballo Mine was combusted in the PTC facility at the EERC, and a slipstream flue gas was tapped for the EFR tests. During the tests, the EFR was isothermally heated at 150° and 275°C, respectively. The high-temperature slipstream flue gas (~400°C) was isokinetically extracted from the system, quenched to the same temperature as the EFR temperature, and then introduced into the EFR. A CMM Tekran 2537A was used to monitor Hg(g) variation with residence time at each temperature. Flue gas exiting the EFR was then conditioned to remove fly ash, acid gases, and moisture prior to a MISCO Control Box (Model 7200) to measure the flow rate. More detailed sampling information has been reported elsewhere (19).

Figure 1 shows Hg transformation for baseline Caballo flue gas at 150° and 275°C. Compared to the calculated Hg concentration of 12.34  $\mu\text{g}/\text{m}^3$  (based on Hg content in coal and ultimate and proximate analyses), Hg(g) concentration at the EFR inlet was 9.1 and 8.0  $\mu\text{g}/\text{m}^3$  for 150° and 275°C, respectively, with a variation in the range of 6.7–11.6  $\mu\text{g}/\text{m}^3$ . A lower measured Hg(g) concentration is caused by Hg deposition or loss in the connecting tube between the PTC and EFR because of a high quench rate. Hg(g) concentration at 1 s residence time reduced to 6.2 and 6.7  $\mu\text{g}/\text{m}^3$  for 150° and 275°C, respectively, and no further significant decreases of Hg(g) were observed at longer residence times. The above experimental data demonstrate somewhat moderate interactions between Caballo coal flue gas constituents and mercury species at flue gas temperatures of 275°C and less, which is consistent with data from other subbituminous coal data (19).

After the baseline test of Caballo coal flue gas, a 30-g/hr  $\text{CaCl}_2$  additive, corresponding to 590 ppm of Cl in the coal, was fed into the combustor with the coal. The added  $\text{CaCl}_2$  was decomposed in the combustion zone to form, most likely, atomic chlorine, which is very reactive with Hg in flue gas. Figure 2 shows Hg(g) variation with time at 150°C during the chlorine addition test. Also included are the baseline data for comparison. With the chlorine additive into during combustion, Hg(g) concentration was dramatically decreased from 7.4  $\mu\text{g}/\text{m}^3$  at the EFR inlet to 1.7  $\mu\text{g}/\text{m}^3$  at 1-s residence time and stabilized approximately at 2  $\mu\text{g}/\text{m}^3$ . In comparison with the baseline data, the  $\text{CaCl}_2$  additive apparently shifted Hg–flue gas chemistry equilibrium, resulting in more effective Hg(g)-to-Hg(p) transformation.

In a second set of tests, homogeneous Hg transformations and kinetic constraints were studied by pulling a slipstream of fly ash-free flue gas derived from North Dakota lignite (Freedom Mine) coal combustion in the PTC through the EFR unit at the EERC. Fly ash was removed from the high-temperature (400°C) flue gas, using a bench-scale ESP, heated to approximately 400°C. A fly ash-free flue gas exiting the ESP was then quenched to either 150° or 275°C and introduced into the EFR. The Freedom coal showed similar characteristics as the subbituminous Caballo coal used in Test 1, such as low sulfur and chlorine; however, the Freedom coal had higher ash content. With virtually no fly ash present in the flue gas entering the EFR, the observed Hg transformations were solely due to homogeneous gaseous reactions between mercury and other gaseous constituents.

Figure 3 presents Hg kinetic data in a fly ash-free environment under 150° and 275°C when approximately 300 ppm Cl in coal was fed into the combustor. Also plotted is the homogeneous baseline (no chlorine addition) Hg kinetic data obtained at 150°C. Both 150° and 275°C testing data show that, with chlorine addition into combustion,  $\text{Hg}^0$  and Hg(g) concentrations in the flue gas entering the EFR had already been at significantly reduced levels, and there were virtually no continuous homogeneous reactions occurring in the EFR. The experimental data indicate that the chlorine additive considerably

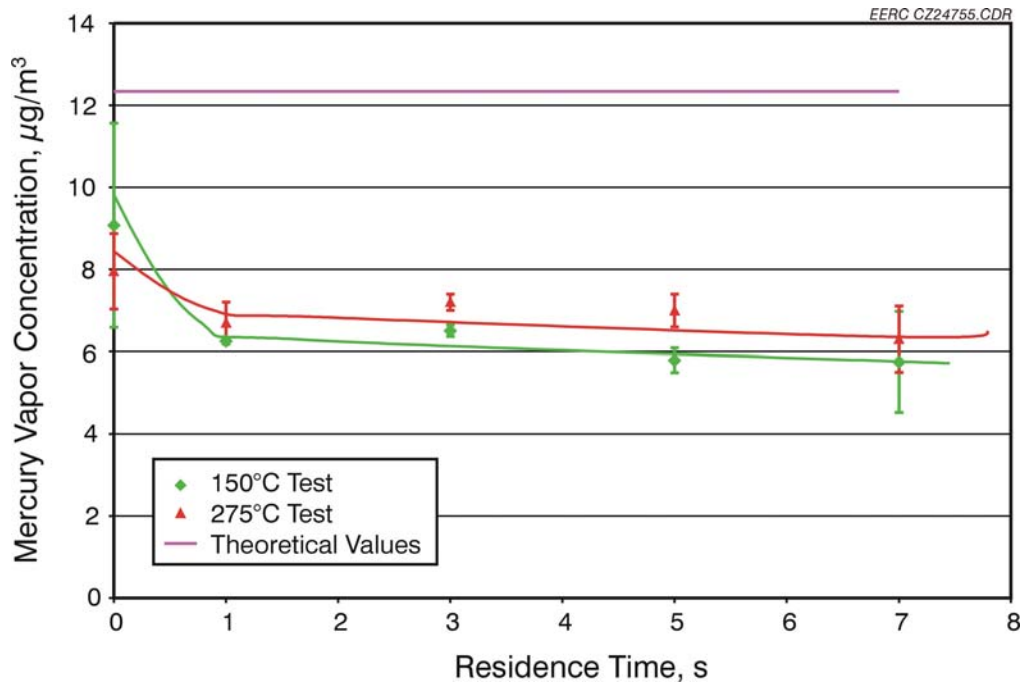


Figure 1. Baseline heterogeneous Hg[g] transformation for subbituminous coal (Caballo) flue gas at different temperatures as a function of time.

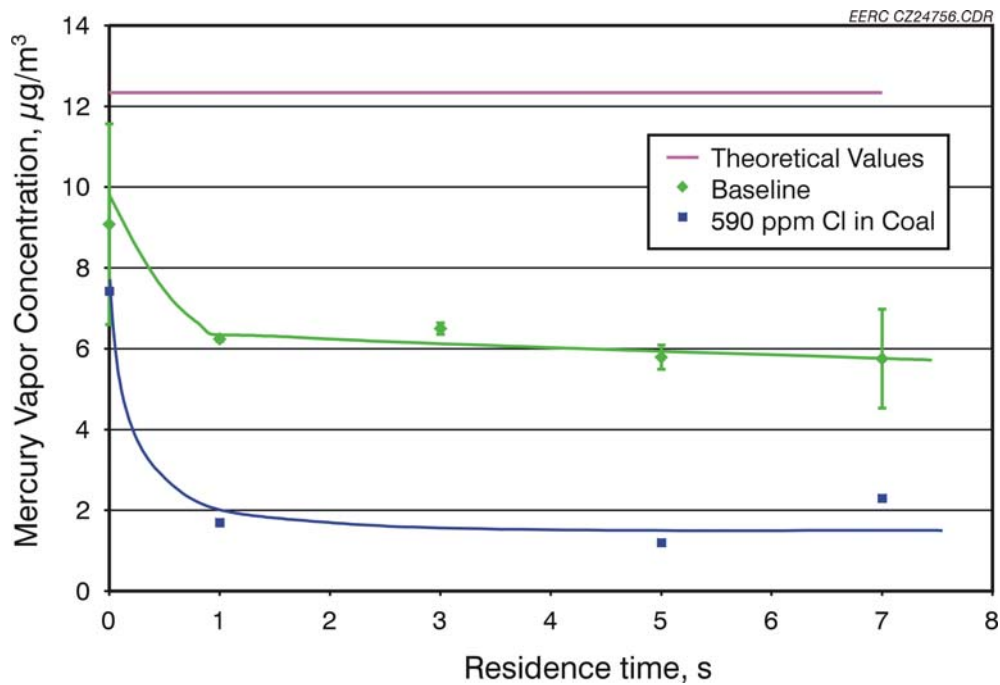


Figure 2. Heterogeneous Hg[g] transformation for subbituminous coal (Caballo) with CaCl<sub>2</sub> addition to the coal with EFR temperature of 150°C.

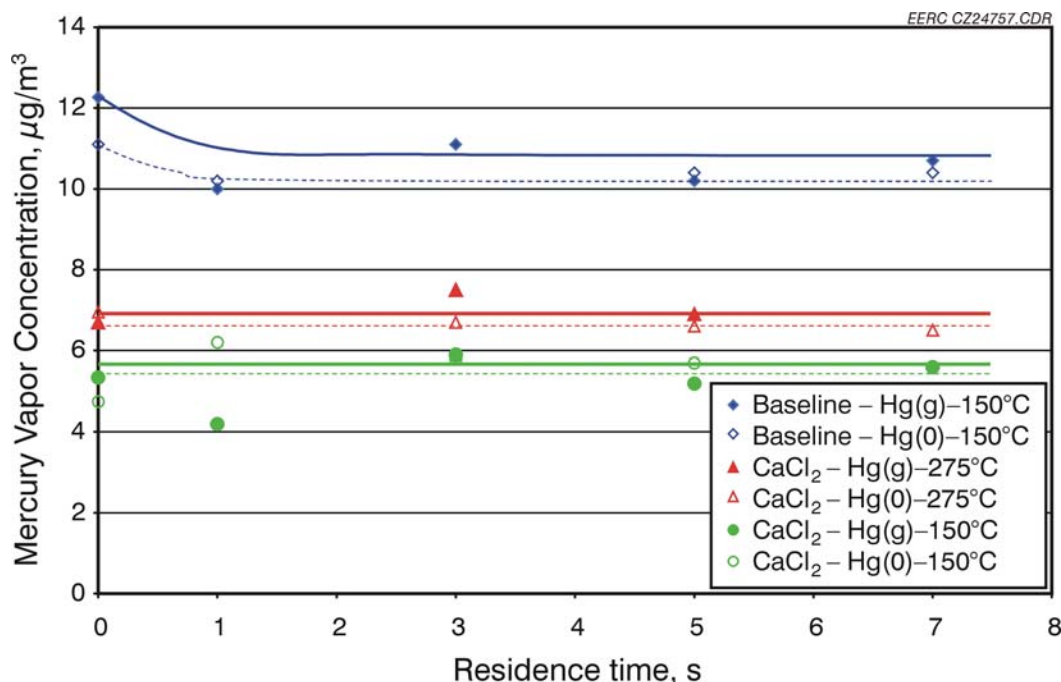


Figure 3. Homogeneous Hg[g] species transformation with CaCl<sub>2</sub> addition to the coal.

accelerated Hg<sup>0</sup> oxidation and Hg(g)-to-Hg(p) conversions in flue gas, and Hg-flue gas chemistry reached equilibrium before the flue gas entered the EFR. The slight differences between 150° and 275°C testing data might be caused by Hg loss in the quenching tube. Hg concentrations in the flue gas entering the high-temperature ESP were also measured to further clarify the experimental results, and the measurements showed approximately 8.1 µg/m<sup>3</sup> of Hg(g) with 6.8 µg/m<sup>3</sup> of Hg<sup>0</sup>. By comparing the ESP inlet data with the EFR inlet data, it indicates that although there were some limited Hg reactions across the 400°C ESP, most Hg transformations had taken place upstream of the 400°C flue gas.

Testing involving 38 ppm NaBr addition to the coal produced concentrations at the EFR inlet of 3.4/3.9 µg/m<sup>3</sup> and 3.8/4.2 µg/m<sup>3</sup> of Hg<sup>0</sup>/Hg(g) for the 150° and 275°C tests, respectively, which are much lower than the 11.1/12.0 µg/m<sup>3</sup> of Hg<sup>0</sup>/Hg(g) in the baseline test. In comparison, the baseline tests showed virtually no homogeneous Hg reactions with extended residence time, but for the bromine additions, slight continuous Hg<sup>0</sup> oxidation and/or Hg(g) condensation occurred along the EFR. The measured 4.3/5.1 µg/m<sup>3</sup> of Hg<sup>0</sup>/Hg(g) at the 400°C ESP inlet indicated that most of the observed Hg transformations occurred upstream of the 400°C flue gas as a result of bromine-promoted Hg oxidation.

### Task 2 – Mercury Adsorption on Fly Ash: Unburned Carbon Separation and Characterization

Most of the research in this task is still ongoing, and results at this time are limited. An in-house EERC fly ash repository supplied an ash from a coal-fired utility containing significant amounts of carbon and mercury. An additional fly ash that also contains significant amounts of carbon, but not mercury, will be selected in the near future for carbon separation and analysis. Research on separating carbon from fly ashes and characterizing the carbon concentrates is anticipated to begin early in 2005.

**Task 3 – Sulfur Species Determination and Injection for Mercury Oxidation and Stabilization**

Most of this research is just beginning, and there are few results to report at this time. Organohalogens were evaluated in the literature and will undergo cursory laboratory screening to see if they hold promise for improved oxidation and capture of mercury in combination with or without tetrasulfide injection.

**Task 4 – Acid Gas Effects on Mercury Species in the Presence of an SCR**

Bench-scale flue gas simulation was used to study the effects of SO<sub>3</sub>, SO<sub>2</sub>, and HCl on mercury oxidation across an SCR catalyst. This was a continuation of testing performed in 2003.

A nominal gas flow rate of 14 L/min and a mercury concentration of 42 µg/m<sup>3</sup> were used in the bench-scale setup. A high concentration was chosen to be able to identify more sensitive changes in mercury speciation. The baseline flue gas concentrations were as follows: 12% CO<sub>2</sub>, 6% O<sub>2</sub>, 8% H<sub>2</sub>O, 483 ppm NH<sub>3</sub>, 600 ppm NO, and 18 ppm NO<sub>2</sub> with N<sub>2</sub> balance. These concentrations were held constant for all tests, and the independent variables HCl, SO<sub>2</sub>, and SO<sub>3</sub> were turned on and off to produce a test matrix as shown in Table 2. A CMM was used to measure mercury concentrations and speciation in a simulated SCR environment that included Cormetech SCR catalysts and fly ash conditioning using bituminous and subbituminous ash. The primary CMM used was the NIC DM-6B, but both a PSA Sir Galahad and a Semtech were used to verify the numbers. The SCR catalyst reactor and fly ash were housed in a stainless steel filter holder maintained at 343°C in a high-temperature oven. Flue gas passed through the high-temperature reactor and high-temperature ash bed and then passed through an external fixed bed of ash maintained at 177°C in a stainless steel filter holder. A slipstream of the exiting flue gas was sampled for mercury concentration and speciation. An ECOM portable gas analyzer was used to verify the NO<sub>x</sub> reduction across the catalyst, and EPA Method 26 analyses were performed to determine ammonia slip.

Preliminary data sets from research performed this year are shown in Table 2 and organized by parameters tested. For both sets of tests using subbituminous and bituminous ash, the baseline test with no HCl or SO<sub>x</sub> added shows no conversion of elemental mercury (Hg<sup>0</sup>) to an oxidized form. However, for HCl addition, major mercury oxidation occurs as observed by depletion of Hg<sup>0</sup> in the flue gas. SO<sub>2</sub> and SO<sub>3</sub> alone had little to no effect. However, in the presence of HCl, SO<sub>3</sub> helped the SCR further oxidize the mercury, thus making HCl and SO<sub>3</sub> in combination the best seen oxidizer during testing. SO<sub>2</sub> was seen to hinder the reaction, thus reducing a small percentage of mercury. There seemed to be little effect of the different coal ashes. Finally, the SCR catalyst only required acid gases to oxidize mercury; NH<sub>3</sub> was not required for oxidation of mercury, only NO<sub>x</sub> reduction.

Although testing is complete, there is some research left to be done. Ammonia slip content will be analyzed, NO<sub>x</sub> numbers will be calculated from the ECOM, data points will be further verified from the logs, and statistical analysis will be performed. Final conclusions and ideas for future expansion of the test matrix in later projects will be addressed in a final report.

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**Table 2. Test Matrix for the Bench-Scale Combustion Flue Gas and SCR Reactor Simulation**

Test	Ash	HCl	SO <sub>2</sub>	SO <sub>3</sub>	NH <sub>3</sub>	NO <sub>x</sub>	Set 1	Set 2	Set 3	Set 4
		ppm	ppm	ppm	ppm	ppm	% Hg <sup>0</sup>	% Hg <sup>0</sup>	% Hg <sup>0</sup>	% Hg <sup>0</sup>
1	Sub.	50	2000	50	483		38.8%	31.5%	17.0%	
2	Sub.	50	2000		483		38.4%	31.0%	19.4%	39.5%
3	Sub.	50			483		30.8%	27.1%	27.7%	
4	Sub.	50		50	483			20.9%	12.0%	
5	Sub.		2000		483			69.0%	87.9%	
6	Sub.		2000	50	483			87.6%	93.0%	
7	Sub.			50	483			<b>73.2%</b>	<b>95.8%</b>	
8	Sub.				483		100.0%	92.7%	98.7%	
9	Bit.	50	2000	50	483		10.2%	44.1%	43.7%	
10	Bit.	50	2000		483		11.9%	43.0%	40.3%	
11	Bit.	50			483		<b>10.7%</b>	49.4%	44.7%	
12	Bit.	50		50	483		10.1%	43.3%	42.1%	
13	Bit.		2000		483		98.8%	99.8%		
14	Bit.		2000	50	483		97.1%	99.8%		
15	Bit.			50	483		94.8%	100.6%		
16	Bit.				483		99.6%	99.7%		
17	Bit.	1	2000	50	483		94.7%			
18	Bit.	5	2000	50	483		86.1%			
19	Bit.	5	2000	50	966		87.0%			
20	Bit.	5	0	0	966		90.5%			
21	Bit.	5	0	50	966		90.6%			
22	Bit.	50	2000	50	0	619	43.0%			

***Quality Assurance/Quality Control***

Quality assurance and quality control (QA/QC) objectives for this project were established to ensure that combustion conditions were properly implemented, sampling and procurement of all physical states of fuels and combustion by-products were adhered to according to accepted published standards, chain-of-command protocols were followed, and measurement techniques for mercury and other critical combustion flue gas components were properly monitored for quality and precision.

The EERC is committed to delivering consistent and high-quality research that meets client needs and expectations. A quality management system is in place for all laboratories, combustion and other demonstration facilities, and research groups at the EERC. This system governs all programs within the

organization. For this project in mercury transformation studies, compliance with the EERC Quality Manual and other project-specific QA procedures was mandatory. A fully dedicated EERC Quality Assurance Manager exercised oversight of this project.

The most critical aspect of QA/QC involved running the combustion equipment and sampling flue gas using precise and consistent combustion conditions and temperature control. The project manager and principal investigators maintained the use of nationally recognized or approved standards and methods put forth by EPA, ASTM, NIST, and other agencies for monitoring and measuring coal feed, chlorine and bromine spiking components, flue gas composition, gas temperatures, and mercury speciation. Particular attention was paid toward mass balancing mercury across the EFR and ESP devices and toward measuring concentrations of oxidized, elemental, and particulate forms of mercury using online analyzers and wet chemical Ontario Hydro mercury speciation methods. As mentioned in the Quality Manual, QA/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).

Regular meetings between engineers and principal investigators before and after combustion testing and during data reduction ensured reliability of all QA/QC results. A series of checks and balances, especially for mercury, revealed that results were of high quality. Measured quantities of mercury in the coal matched calculated and measured quantities in fly ash and flue gas over at least three runs for each parameter being measured.

### *Status*

Within the CATM Program, research continues in the area of fundamental mercury transformations during coal combustion. The effects of various flue gas constituents on the oxidation of  $\text{Hg}^0$ , in combination with low-acid gas concentrations (i.e., low-sulfur Wyoming coals), will continue to be investigated. There will also be additional testing of oxidizing agents.

In addition to continuing research on mercury kinetics in different coal combustion flue gases under temperatures ranging from 150° to 400°C, additional study should include kinetic experiments at a higher temperature regime, such as between 400° and 800°C.

Most of the research in mercury adsorption on unburned carbon in fly ash is still ongoing, and results as this time are limited. The chemistry and morphology of carbon from real-world utility boilers will be compared for fly ash that contains significant amounts of mercury and fly ash that shows little mercury.

Researchers from this Program Area 1 project will collaborate closely with modelers researching in CATM Program Area 4 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 in Program Area 4. The EERC hopes to make mercury prediction models available for use by other researchers and utilities to help devise control technologies in accordance with the EPA ruling on allowable mercury emission levels.

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### *Potential Users/Technology Transfer*

Potential users of the technologies and research results being generated by this project include other EPA-funded researchers at various universities, EPA, and the U.S. Department of Energy (DOE), labs, utilities, state agencies, control technology vendors, and other private industries. Information related to mercury transformation and speciation is especially relevant to researchers and regulators. Several ongoing research consortia composed of these groups have ongoing projects with the EERC and are dedicated to mercury emission characterization and control. Researchers in this CATM project meet regularly with other researchers within EERC performing research 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 requires that more research be done to unravel the fundamental mechanisms that govern which species form and how best to control them.

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