



## FUNDAMENTAL MECHANISMS OF MERCURY SPECIES FORMATION IN COAL COMBUSTION FLUE GAS

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### ***Project Description***

The U.S. Environmental Protection Agency (EPA) has made a determination to control mercury emissions from coal-fired power plants. The exact ruling for mercury control, the allowed concentrations of gaseous and particulate emissions, and final compliance regulation will be determined in the next few years by EPA. This project is focused on providing crucial fundamental information on the species of mercury that form prior to emission from the power plant stack. Mercury is released in three fundamental forms: in particulate association, as an oxide ( $\text{Hg}^{2+}$ ) species, or as an elemental ( $\text{Hg}^0$ ) species. Knowing the proportions of these mercury species for specific power plants is essential for devising effective control strategies, building effective continuous emission monitors (CEMs), and constructing useful predictive models. Research was conducted to discern the mechanisms by which  $\text{Hg}^0$  in coal combustion flue gas transforms to gaseous inorganic mercuric compounds (e.g.,  $\text{Hg}[\text{NO}_3]_2 \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2$ ,  $\text{HgSO}_4$ , and  $\text{HgO}$ ) or particulate mercury ( $\text{Hg}[\text{p}]$ ). Recent efforts have focused on the effects of  $\text{NO}_2$  and fly ash crystalline iron oxide components (i.e., hematite [ $\alpha\text{-Fe}_2\text{O}_3$ ] and maghemite [ $\gamma\text{-Fe}_2\text{O}_3$ ]) on mercury speciation.

### ***Goal***

The goal of this work was to discern the mechanisms by which  $\text{Hg}^0$  transforms to  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$  because of interactions with coal combustion flue gas and fly ash components. The primary objectives were to assess the roles of  $\text{NO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\gamma\text{-Fe}_2\text{O}_3$  in promoting the conversion of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and/or  $\text{Hg}(\text{p})$ .

### ***Rationale***

According to the *Mercury Study Report to Congress*, coal combustion is the primary source of anthropogenic mercury emissions in the United States, accounting for 72 of the 158 tons/yr of total point-source mercury emissions [1]. More recently, EPRI estimated 1999 coal combustion mercury emissions at 45 tons/yr [2]. In December 2000, EPA made a formal determination that mercury emissions from coal-fired power plants should be regulated. Specific levels of mercury emissions that are allowed for fossil fuel-fired combustion systems will be established by 2003, and compliance will be mandatory by 2007. Knowledge of mercury's physical and chemical transformations in coal combustion flue gas is imperative for understanding the transport and fate of mercury released into air pollution control systems and the atmosphere. The current

knowledge of mercury transformation in coal combustion flue gas is based largely on thermodynamic and kinetic modeling and experimental investigations of mercury reactions in simulated flue gases and on the interpretations of field test data [3, 4]. Mercury exists primarily as  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  in coal combustion flue gas. Mercury emissions from coal-fired boilers can be empirically classified, based on the capabilities of currently available analytical methods for determining mercury speciation, into three main forms:  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}(\text{p})$ . Mercury concentrations in coal combustion flue gas generally range from 5 to 10  $\mu\text{g}/\text{m}^3$ , with a large range in the relative proportions of  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$ , and  $\text{Hg}(\text{p})$ . During combustion, mercury is liberated from coal as  $\text{Hg}^0$ ; however, a significant fraction of the  $\text{Hg}^0$  is generally transformed to  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$  in the postcombustion environment of a coal-fired boiler.  $\text{Hg}^0$  is the most abundant and persistent (residence time of 0.5 to 2 years) form of mercury in the atmosphere [5–8]. Relative to  $\text{Hg}^0$ ,  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$  are more effectively captured in conventional pollution control systems (wet scrubbers and fabric filters) and are more apt to deposit locally or regionally [3, 7, 9]. Mercury emission control efficiencies, transport/deposition models, and CEMs for coal-fired boilers can be improved by identifying the fundamental mechanisms involved in mercury–flue gas interactions that transform  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$ .

Chlorine species ( $\text{Cl}$ ,  $\text{HCl}$ , and  $\text{Cl}_2$ ) are generally assumed to be the dominant  $\text{Hg}^0$  reactants in coal combustion flue gas [10, 11]. In addition to chlorine, nitrogen oxides ( $\text{NO}_x$ ) are potential  $\text{Hg}^0$  reactants in flue gas [12, 13].  $\text{NO}_2$  generally composes  $\leq 5\%$  and  $\text{NO}$  composes  $\geq 95\%$  of the total  $\text{NO}_x$  in flue gas. Kinetic limitations and the relatively short flue gas residence time in a duct or stack preclude the occurrence of homogeneous reactions involving  $\text{Hg}^0$  and  $\text{NO}$  or  $\text{NO}_2$  [14, 15]. Bench-scale test results indicate, however, that  $\text{NO}_2$  reacts heterogeneously with  $\text{Hg}^0$  on fly ash and sorbent surfaces to form  $\text{Hg}^{2+}$  in heated ( $< 200^\circ\text{C}$ ) simulated coal combustion flue gases [16, 17]. This effect was noted for  $\text{NO}_2$  concentrations as low as 20 ppmv [16]. Ghorishi et al. [18] have also demonstrated that  $\text{NO}$  is a potent  $\text{Hg}^0$  reactant in the presence of fly ash components. Olson et al. [19] identified a  $\text{Hg}^0\text{--NO}_2\text{--C--MnO}_2$  reaction product as gaseous mercuric nitrate monohydrate,  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , using gas chromatography–mass spectrometry. They hypothesized that  $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , in addition to  $\text{Hg}^0$  and mercuric chloride ( $\text{HgCl}_2$ ), is a major Hg species existing in coal combustion flue gas and the atmosphere.

Bench-scale investigations using heated ( $\leq 370^\circ\text{C}$ ) simulated flue gases have also demonstrated that specific metal oxide components of fly ash, including hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), promote the formation of  $\text{Hg}^{2+}$  in the presence of  $\text{HCl}$  and/or  $\text{NO}_x$ , possibly via surface redox reactions [18, 20–22]. Bench-scale experiments by Miller et al. [16] and Hitchcock [23] indicate that maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), a polymorph of  $\alpha\text{-Fe}_2\text{O}_3$  that also occurs in fly ash, does not catalyze the formation of  $\text{Hg}^{2+}$  but rather it readily reacts with  $\text{Hg}^0$  at  $155^\circ\text{C}$ , resulting in  $\text{Hg}^0$  removal from a simulated coal combustion flue gas. Maghemite is an oxidation product of magnetite ( $\text{Fe}_3\text{O}_4$ ), an inverse spinel structure mineral and the thermal decomposition product of pyrite in coal. The oxidation of  $\text{Fe}_3\text{O}_4$  to  $\gamma\text{-Fe}_2\text{O}_3$  involves the addition of free oxygen at the surface of the crystal and the diffusion of  $\text{Fe}^{3+}$  through an oxygen framework to the crystal surface, thus creating cation vacancies in the spinel structure [24]. Physical properties of the  $\text{Fe}_2\text{O}_3$  polymorphs are compared in Table 1.

The presence of nitrogenated and/or oxygenated species and metal oxides on fly ash surfaces may be an important factor controlling the transformation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  and  $\text{Hg}(\text{p})$  in chemically complex coal combustion flue gases. In this investigation, the potential effects of  $\text{NO}_2$ ,  $\alpha\text{-Fe}_2\text{O}_3$ , and  $\gamma\text{-Fe}_2\text{O}_3$  on Hg speciation were evaluated by spiking them into coal combustion flue gases produced from burning subbituminous and lignitic coals in a 7-kW combustion system. Hg transformation results from these tests are presented and compared to previously reported results obtained from using bench-scale flue gas simulators [16–18, 20–23]. Results from this investigation demonstrate the importance of evaluating potential  $\text{Hg}^0$  reactants and oxidation catalysts in actual coal combustion flue gases.

**Table 1.** Physical Properties of Fe<sub>2</sub>O<sub>3</sub> Polymorphs

Parameter	Hematite ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> )	Maghemite ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> )
Crystal System	Hexagonal–rhombohedral	Cubic
Crystal Structure	Corundum ( $\alpha$ -Al <sub>2</sub> O <sub>3</sub> ) structure; isostructural with eskolaite (Cr <sub>2</sub> O <sub>3</sub> ) and karelianite (V <sub>2</sub> O <sub>3</sub> )	Cation-deficient ferric spinel with ideal formula [Fe] {Fe <sub>1.67</sub> □ <sub>0.33</sub> }O <sub>4</sub> where □ represents a vacancy
Density, g/cm <sup>3</sup>	5.27	4.88
Magnetization	Antiferromagnetic (no net magnetization)	Ferrimagnetic

### Approach

NO<sub>x</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were added into actual coal combustion flue gases produced from burning coals in a conversion and environmental process simulator (CEPS), an approximately 7-kW cylindrical downfired combustion system. A schematic of the CEPS is presented in Figure 1. Internal components of the system are composed primarily of Alumina 998 ceramic and Narcast 60 refractory materials to minimize contamination from metal surfaces. The system was cleaned and then maintained at high temperatures prior to each test to minimize contamination.

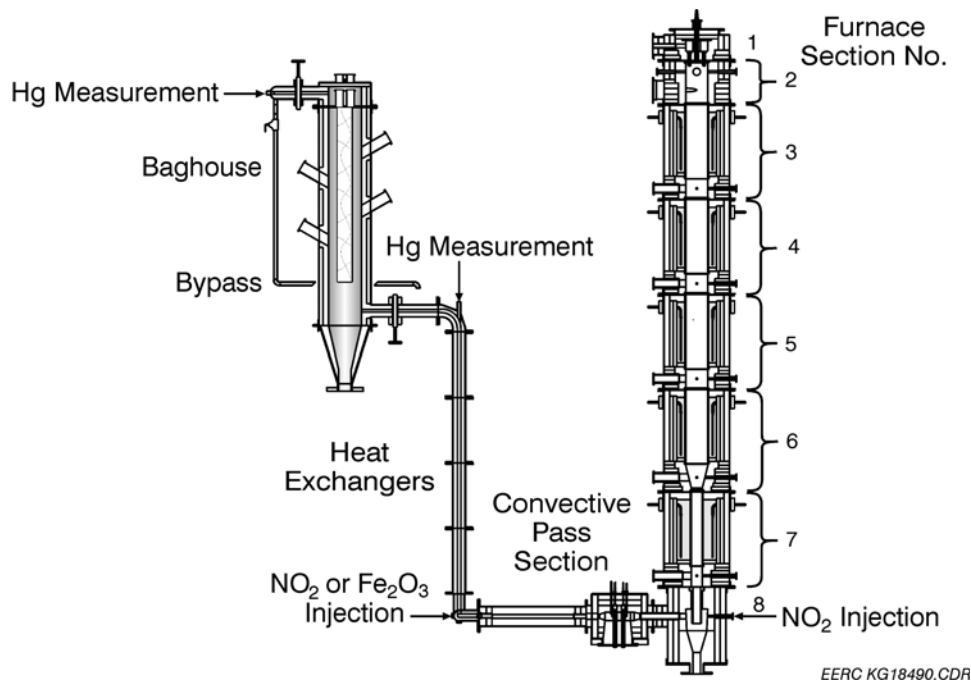


Figure 1. Schematic of the CEPS. Mercury Measurement and NO<sub>2</sub>,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and HCl Addition Locations Are Shown

Bituminous, subbituminous, and lignitic coals from the Blacksville, Absaloka, and Falkirk Mines, respectively, were burned in the CEPS primarily because they range widely in their chemical and mineralogical properties and are commonly utilized to generate steam and electricity for utilities. Mercury speciation measurements were conducted at the baghouse inlet (160°–195°C) and outlet (110°–140°C) locations of the system using the Ontario Hydro (OH) method or an on-line Hg analyzer, Semtech Mercury 2000 or Tekran 2537A, equipped to measure Hg<sup>0</sup> and total gaseous mercury (Hg[tot]). Even though Hg(p) concentrations were not determined on-line, the nearly continuous monitoring of Hg<sup>0</sup> and Hg(tot) concentrations was sufficient to evaluate whether NO<sub>2</sub>, α-Fe<sub>2</sub>O<sub>3</sub>, or γ-Fe<sub>2</sub>O<sub>3</sub> additions into the coal combustion flue gases effectively promoted the conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> or Hg(p).

NO<sub>2</sub>, α-Fe<sub>2</sub>O<sub>3</sub>, γ-Fe<sub>2</sub>O<sub>3</sub>, and HCl spiking locations are indicated in Figure 1. A cylinder of certified-working-class-grade NO<sub>2</sub> (5045 ppmv NO<sub>2</sub> in N<sub>2</sub>) was used as an NO<sub>2</sub> injection source. NO<sub>2</sub> injection concentrations, ranging from about 80 to 200 ppmv, were controlled using a calibrated flowmeter. Dried reagent-grade (<1 wt% impurities) α-Fe<sub>2</sub>O<sub>3</sub> powder was injected into the combustion flue gases using a Model 3410 dry powder disperser manufactured by TSI, Inc. α-Fe<sub>2</sub>O<sub>3</sub> and γ-Fe<sub>2</sub>O<sub>3</sub> were also simply brushed onto the baghouse fabric filters to evaluate their effects on Hg speciation. During the γ-Fe<sub>2</sub>O<sub>3</sub> addition tests, a cylinder of certified-working-standard-grade HCl (10,290 ± 510 ppmv HCl in N<sub>2</sub>) and a calibrated flowmeter were used to inject 100 ppmv HCl into the main furnace section of the combustor as indicated in Figure 1.

### *Progress*

The baseline Blacksville flue gas was composed predominantly of Hg<sup>2+</sup> (Hg<sup>2+</sup>/Hg[tot] = 0.77), whereas Absaloka and Falkirk flue gases contained primarily Hg<sup>0</sup> (Hg<sup>0</sup>/Hg[tot] = 0.84 and 0.78, respectively). The low Hg<sup>0</sup> concentration, ≈ 2 μg/Nm<sup>3</sup>, of Blacksville flue gas did not allow for a thorough assessment of the effects of NO<sub>x</sub>, α-Fe<sub>2</sub>O<sub>3</sub>, and γ-Fe<sub>2</sub>O<sub>3</sub> on the Hg<sup>0</sup> to Hg<sup>2+</sup> or Hg(p) transformation.

Injections of 80–190 ppmv NO<sub>2</sub> at 440°–880°C into subbituminous Absaloka and lignitic Falkirk coal combustion flue gases did not significantly affect Hg speciation. Similarly, α-Fe<sub>2</sub>O<sub>3</sub> injections (15 and 6 wt%) at 450°C did not catalyze heterogeneous Hg<sup>0</sup> oxidation reactions. Results from this investigation indicate that although NO<sub>x</sub> and α-Fe<sub>2</sub>O<sub>3</sub> promote the conversion of Hg<sup>0</sup> to Hg<sup>2+</sup> in simulated flue gases, these flue gas components are chemically inert with respect to Hg transformations in actual coal combustion flue gases. The lack of conversion in the 7-kW combustion system suggests that components of Absaloka and Falkirk combustion flue gases and/or fly ashes inhibit heterogeneous Hg<sup>0</sup>-NO<sub>x</sub>-α-Fe<sub>2</sub>O<sub>3</sub> reactions or that the flue gas quench rate in the 7-kW system is much different relative to those in bench-scale flue gas simulators.

An abundance of Hg<sup>2+</sup>, HCl, and γ-Fe<sub>2</sub>O<sub>3</sub> in Blacksville coal combustion flue gas and fly ash and the inertness of injected α-Fe<sub>2</sub>O<sub>3</sub> with respect to heterogeneous Hg<sup>0</sup> oxidation in Absaloka and Falkirk flue gases suggest that γ-Fe<sub>2</sub>O<sub>3</sub> rather than α-Fe<sub>2</sub>O<sub>3</sub> catalyzes Hg<sup>2+</sup> formation and that HCl may be an important Hg<sup>0</sup> reactant. These hypotheses were tested by injecting γ-Fe<sub>2</sub>O<sub>3</sub> and HCl and applying γ-Fe<sub>2</sub>O<sub>3</sub> to the baghouse fabric filter. As shown in Figures 2 and 3, about 30% of the Hg<sup>0</sup> was converted to Hg<sup>2+</sup> and/or Hg(p) as a result of the filtration of Absaloka and Falkirk combustion flue gases through 150°C fixed γ-Fe<sub>2</sub>O<sub>3</sub> beds. 100 ppmv HCl injection into the Absaloka combustion flue gas converted most of the Hg<sup>0</sup> to Hg<sup>2+</sup>, whereas HCl injection into the Falkirk flue gas converted most of the Hg<sup>0</sup> and Hg<sup>2+</sup> to Hg(p). γ-Fe<sub>2</sub>O<sub>3</sub> and HCl did not have a synergistic effect on Hg<sup>0</sup> oxidation.

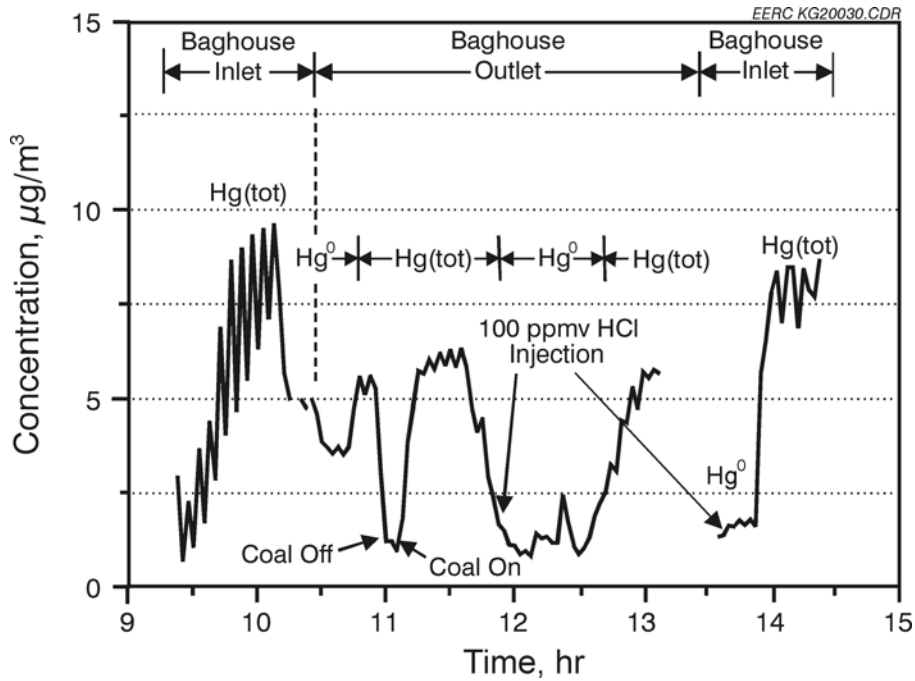


Figure 2. On-Line  $Hg^0$  and  $Hg(tot)$  Measurements of Baseline and  $\gamma-Fe_2O_3$ - and HCl-Spiked Absaloka Flue Gases

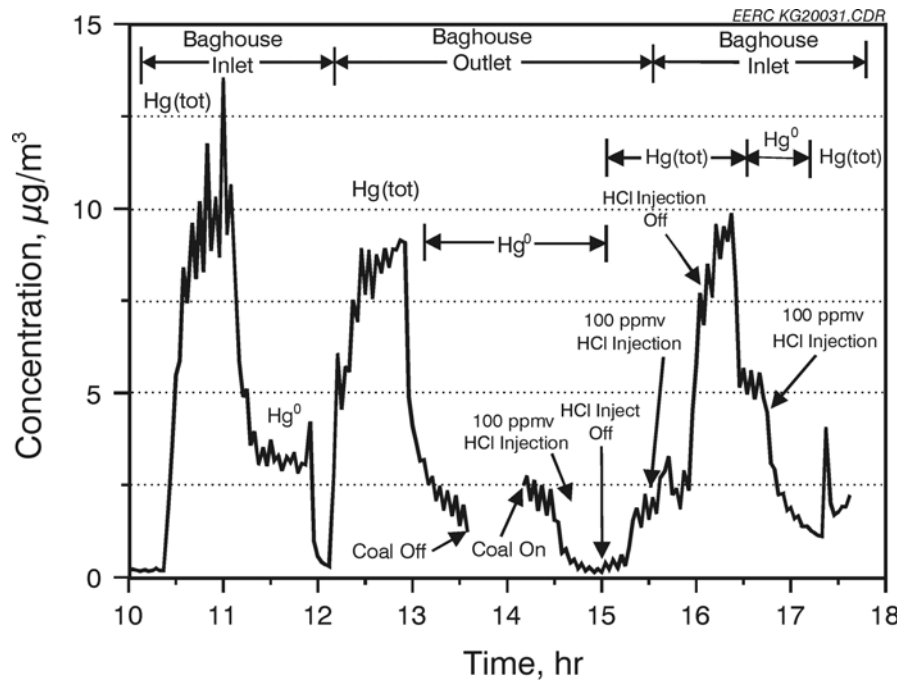


Figure 3. On-Line  $Hg^0$  and  $Hg(tot)$  Measurements of Baseline and  $\gamma-Fe_2O_3$ - and HCl-Spiked Falkirk Flue Gases

### Status

Recent CEPS testing indicates that additions of NO<sub>2</sub> and α-Fe<sub>2</sub>O<sub>3</sub> did not significantly affect Hg<sup>0</sup> oxidation in Absaloka and Falkirk coal combustion flue gases. However, γ-Fe<sub>2</sub>O<sub>3</sub> and HCl additions promoted the formation of Hg<sup>2+</sup> and Hg(p). Additional CEPS tests involving Hg speciation measurements using the OH method are being performed to quantify and optimize the apparent catalytic effect of γ-Fe<sub>2</sub>O<sub>3</sub> on Hg<sup>0</sup> oxidation. In addition, flue gas and fly ash components (SO<sub>x</sub>, NH<sub>3</sub>, H<sub>2</sub>O, CaO, Na<sub>2</sub>O, and CuO) suspected of influencing Hg transformations based on bench-scale testing results will be spiked into the CEPS to verify their role in controlling Hg<sup>0</sup> oxidation and/or mercury sorption on fly ash.

### Potential Users/Technology Transfer

Project results are of interest to developers and commercial vendors of pollution control devices and CEMs and to coal-fired utilities seeking ways to develop and implement Hg emission control strategies. Especially significant is the mercury oxidation that was evidenced with the addition of maghemite (γ-Fe<sub>2</sub>O<sub>3</sub>). If costs for production and injection of maghemite are reasonable, this may be one means of catalytically converting Hg<sup>0</sup> to Hg<sup>2+</sup>, which is more easily removed by conventional particulate removal and scrubbing devices.

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