



Steven A. Benson
Principal Investigator

MODELING MERCURY SPECIATION IN COAL COMBUSTION SYSTEMS AND INTERACTIONS ON ACTIVATED CARBON

Key Personnel: Steven Benson (EERC), Lingbu Kong (EERC), Li Yan (EERC), Don McCollor (EERC), Ye Zhuang (EERC), Bruce Folkedahl (EERC), Ed Olson (EERC), Jason Laumb (EERC), Nathan Kadrmas (EERC), Robert Jensen (EERC)

Project Description

This project is focused on modeling mercury transformations utilizing a gaseous homogeneous speciation model and a kinetic model for mercury interaction/adsorption by particulate material. The first part of the project developed a combined homogeneous reaction model for gas-phase speciation, and a heterogeneous adsorption (or reaction) model is needed in order to predict mercury control in coal-fired combustion systems and associated air pollution control devices (APCD). The second component of the project is aimed at developing better thermodynamic and kinetic data for the mercury interactions with activated carbon using a quantum mechanical model.

Mercury control is dependent upon coal composition and the configuration and operating conditions of the combustion system and APCD. Coal characteristics influence the form or speciation of mercury in the flue gas stream, composition of flue gas, and the size distribution and composition of the entrained ash particles. Combustion and air pollution control systems influence the approach to mercury control. For example, unscrubbed systems equipped with electrostatic precipitators (ESPs) and or fabric filters (FFs) will likely rely upon sorbent injection. Combustion systems equipped with wet scrubbers will likely rely on mercury oxidation upstream of the scrubbers. Systems equipped with dry scrubbers followed by an ESP or FF will rely on mercury oxidation as well as on sorbent injection. The modeling effort is focused on predicting mercury oxidation and mercury interactions with entrained particulate matter either being sorbents or fly ash particles.

The EERC had developed a model that describes the reaction of elemental mercury with activated carbon. The model involves a zigzag carbene site on the carbon edge that can function as a Lewis acid oxidation site activated by acidic gas components as well as a site that performs as a Lewis base in reacting with both the oxidized mercury formed at the oxidation site and with the acidic flue gas components in competing reactions to form organochlorine, sulfinate, and sulfate ester moieties on the carbon edge. Owing to the difficulty of measurements on carbon and the complexity of the reactions, details of reaction rates and thermodynamic stabilities have yet to be determined. In fact, this is the first specific structure/mechanism model of any kind on a carbon surface. However, the model's specificity offers the platform for performing calculations of energy stationary points that would contribute greatly to the understanding of mercury interactions on carbon through the use of the quantum mechanical model.

Goals

There are two primary goals of the modeling efforts. The first is to develop a mercury transformation model consisting of a gaseous homogeneous speciation model and a kinetic model for mercury interaction/adsorption by particulate material to predict the partitioning of mercury between particulate, oxidized, and elemental forms as a function of system conditions and coal/additive composition.

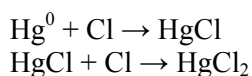
The second goal is to establish validity and usefulness of the quantum mechanical model to provide thermodynamic and kinetic data for the reactions of mercury and halogens with the carbon surface. Specifically, the efforts will focus on determining the energy minima and provide thermodynamic and kinetic constants for zigzag carbene and armchair benzyne structures with Hg(II) and HCl and for the corresponding carbenium ions with Hg⁰ and halide ions.

Rationale

Modeling Mercury Speciation in Coal Combustion Systems

The knowledge of mercury speciation in the coal-combusted flue gas is important for the control of mercury emission from coal-fired power plants. During high-temperature combustion of coal, Hg is vaporized into the gaseous phase as elemental mercury (Hg⁰). When the flue gas cools, passing the low-temperature heat-exchange zones in the boiler, it has been observed that a portion of Hg⁰ can be oxidized to Hg²⁺ through reactions with other gaseous components (particularly, when HCl or molecular chlorine [Cl₂] is present). In the same pathway, Hg can also interact with particulates (such as entrained ash particles and/or injected sorbent particles) to be converted or removed from the gas phase. In the literature, most modeling efforts have studied homogeneous gas-phase Hg speciation. Limited modeling efforts have been done for Hg removal by heterogeneous interaction with particulates. Furthermore, there is a lack of a combination of these two modeling approaches. Since the homogeneous gas reactions and the heterogeneous interaction are dynamically competing processes, it is believed that the combination of these two models will be superior in predicting Hg evolution in the postcombustion environment.

Chemical kinetic modeling of bench-scale testing data suggests that the dominant Hg⁰ reactant in coal combustion flue gas is atomic chlorine (Cl) and to a lesser extent Cl₂ (1–5). The most likely reaction pathway for Hg⁰ oxidation is:



Chemical kinetic models also suggest that the Cl concentration of a coal combustion flue gas is controlled by interactions with and by the concentrations of other gases, including HCl, CO, H₂O, and NO (1–3). Increases in HCl and CO concentrations promote, whereas increases in H₂O concentration inhibit, Cl and mercuric chloride (HgCl₂) formation. NO can either inhibit or promote Cl and HgCl₂ formation, depending on its concentration (2).

A question that remains to be answered is whether the oxidation of Hg⁰ by chlorine is only a homogeneous gas-phase reaction or if fly ash plays a critical role in Hg⁰ oxidation (heterogeneous gas–solid reactions), such as catalyzing the formation of Hg⁰ reactants (e.g., Cl₂) or serving as activated sites where Hg⁰ reacts with other flue gas constituents, or both processes occur simultaneously. This project

will provide insight for mercury control strategies if we can differentiate the two processes. Also, the information will benefit further development of mercury speciation models.

In order to properly model mercury gas–solid partitioning and speciation, the mechanisms by which $\text{Hg}^0(\text{g})$ transforms to $\text{Hg}^{2+}\text{X}(\text{s,g})$ and $\text{Hg}(\text{p})$ in the postcombustion environment of a boiler must be known. Under the CATM Program, a kinetic model of mercury oxidation based on homogeneous gaseous reactions is being developed. To date, the model contains several hundred reactions and has been validated by comparing the model's predicted values with values obtained from EPA's information collection request (ICR) data. The conditions listed for the collection of the ICR data were used as input to the model, and the predicted values compared very favorably with the experimentally measured values. This suggests that homogeneous gas-phase reactions may play a significant role in the oxidation of mercury in coal combustion systems.

Several researchers have predicted mercury gas–solid partitioning and speciation in coal combustion flue gas using thermodynamic models (6). Thermodynamic models provide insight into the species of mercury likely to exist in flue gas at chemical equilibrium. Several models predict that $\text{Hg}^0(\text{g})$ will react with other gaseous phases to form $\text{HgCl}_2(\text{g})$, $\text{HgO}(\text{s})$, or $\text{HgSO}_4(\text{s})$. Empirical evidence clearly indicates, however, that the assumption of gas-phase equilibrium for mercury species in coal combustion flue gas is invalid (6–9). Research by Chen (10) and Senior (11) has been directed at developing kinetic models to account for the limitations of the thermodynamic equilibrium models. In these modeling efforts, it has been found that the Cl content of the flue gas is the main contributor to mercury oxidation prior to the APCDs. Cooling rate also plays a significant role in mercury transformations. Senior (9) used an idealized cooling rate for a pulverized coal (pc)-fired utility boiler, while Chen (10) used the results of a computational fluid dynamic (CFD) model of the backpass regions of a utility boiler to model the time–temperature speciation history of mercury in a combustion system. In both studies, the models were compared to data from the EPA ICR data. The studies found that kinetic gas-phase speciation could not solely account for the transformations that occur in combustion systems. Existing mercury speciation models are attempting to account for any kinetic or mixing limitations that may control species formation; however, most of these models do not adequately account for the effects of variable fly ash compositions that may catalyze mercury reactions and provide surfaces for physical and chemical adsorption.

Modeling Mercury Interactions on Activated Carbon

One of the major technological solutions to the control of mercury emissions in power plants is the injection of powdered activated carbon into the flue gas stream. To minimize the carbon-to-mercury ratio, both kinetics and capacity need to be considered. Extensive parametric experimentation has elucidated the interaction of mercury with flue gas components on activated carbon, and spectroscopic examination of the sulfur and chlorine forms present before and after breakthrough (12) has led to an improved model to explain the kinetic and capacity results. The model describes a zigzag carbene site on the carbon edge that can function as a Lewis acid oxidation site activated by acidic gas components as well as a site that performs as a Lewis base in reacting with both the oxidized mercury formed at the oxidation site and with the acidic flue gas components in competing reactions to form organochlorine, sulfinate, and sulfate ester moieties on the carbon edge. Owing to the difficulty of measurements on carbon and the complexity of the reactions, details of reaction rates and thermodynamic stabilities have yet to be determined. In fact, this is the first specific structure/mechanism model of any kind on a carbon surface. However, the model's specificity offers the platform for performing calculations of energy stationary points that would contribute greatly to the understanding of mercury interactions on carbon.

A recent attempt to theoretically model the interaction of Hg^0 with carbon was overly simplistic in terms of the species whose interaction was to be studied (13).

The EERC has developed a capture mechanism, based on experimental findings, that has evolved in the last few years. The next logical step is to apply quantum mechanical calculations to this capture mechanism to determine its validity. It is unclear what the appropriate levels of ab initio quantum mechanical calculations are for answering questions involving Hg interactions with coal mimetic organic molecules. Ab initio methods include all terms in Schrodinger's equation, making them more accurate yet time-consuming. At present, there is only one English language-published article on the results of ab initio calculations of Hg interacting with coal mimetic organic molecules (14) (there are a few additional articles in Chinese language journals that do not have widespread distribution [15, 16]). However, there have been a few recent presentations on the topic (17, 18). In contrast, there have been significant publications on ab initio results for the interactions of Hg with atmospheric molecules (19) and with small, electronically simple, organic molecules. One should expect some similarities between these calculations and the proposed Hg-coal mimetic molecule studies. Keep in mind that there are many methods for performing ab initio calculations. We briefly review the accuracy of several methods in the following.

In recent research, Khalizov et al. (19) considered the reaction of elemental Hg with the halogen atoms F, Cl, and Br and with their monoxides, XO. Specifically, they evaluated the accuracy of results as measured by geometrical parameters and thermochemistry vs. the level of calculation as a function of method of inclusion of electron correlation and of bases set. It was found that a surprisingly high level of theory was required to produce results in good agreement with the experiment. If we focus on the Cl results, since F presents well-documented unique difficulties for electronic structure theory and Br exhibits relativistic effects that are not germane to the organic systems of present interest, it was found that the often reliable B3LYP variant (20) of density functional (DFT) methods was in rather unacceptable agreement with the experiment in both HgCl and HgCl₂, unless inconveniently large one electron-basis sets were used. For HgCl₂, B3LYP with the double quality LANL2DZ basis (21–23) (abbreviated L2 for short), which has a relativistic effective core, gives a bond length that is an unacceptable 0.112 Å longer than the longest experimental prediction. Likewise, the predicted vibrational frequency is 8% less than the smallest experimental value and 14.5% less than the mean experimental value. To contrast, QCISD (24), with the same basis on Hg and a 6 311G(2df) basis (25, 26) (denoted G6 for short) on Cl, predicted a bond length only 0.02 Å from the experimental mean.

The deviations from the experiment in the low-level-predicted thermochemistry of Hg and Cl reactions are even more disconcerting (19). For the HgCl + Cl → HgCl₂ reaction, B3LYP/L2 is in error by 85.4 kJ/mol (i.e., almost 25%). In comparison, a coupled cluster singles and doubles (CCSD) approach (27), with perturbative inclusion of triples (24), single-point calculation at QCISD geometries, CCSD(T)/L2&G6//QCISD/L2&G6, is in error by only 15.3 kJ/mol.

Khalizov et al. (19) show that high-level calculations (i.e., CCSD[T]) with large basis sets on the stationary points of Hg + Cl → HgCl, when used with the Canonical Variational Transition State Theory (28), gave kinetic results in rather good agreement with the experiment (i.e., easily within a factor of 10 for kinetic rates).

Approach

The speciation of mercury in postcombustion flue gas is kinetically controlled. Meanwhile, gaseous Hg species can interact with ash particles carried by the flue gas or with injected sorbent particles (e.g., activated carbon [AC]) along the pathway. Therefore, the combination of a homogeneous reaction model on gas-phase speciation and a heterogeneous adsorption (or reaction) model will be beneficial for understanding the effects of a number of factors controlling mercury evolution.

Gas-Phase (homogeneous) Hg Speciation Model

It has been recognized that the thermochemical equilibrium approach does not work well in predicting gas Hg speciation in the flue gas. The better approach is to consider reaction kinetics in the gas phase. Some gas-phase reaction kinetics data relevant to mercury speciation are available from the literature. With this approach, main efforts will include identifying the significant gaseous species, Hg species, and their concentrations in a post-coal combustion environment similar to that in the coal-fired furnace exit; identifying a series of reaction circumstances, including time-temperature histories similar to those in boiler convective pass; and retrieving, comparing, and determining gas-phase reaction mechanisms and relevant reaction kinetic data published in the literature. The solution of chemical reaction mechanisms can be obtained by using SENKIN (the most useful component in CHEMKIN 3.6).

Heterogeneous Model for Hg Interaction with Particulates

The Langmuir-Hinshelwood Isotherm Equation is the most commonly used method to consider the kinetic adsorption process between Hg species and fly ash or AC and will be selected initially as the starting point. However, it is realized that the Langmuir-Hinshelwood Isotherm was established based on a single-layer molecular adsorption assumption and ignored competing effects among other species. Other models such as Temkin, Mars, or Freundlich might be better in elucidating the relationship between gaseous Hg concentration on the particle surface and the solid (adsorbed) Hg concentration. The most important mechanism responsible for vapor-phase reduction in the low-temperature zones is the reaction/condensation on existing ash particles, when the local temperature is less than the dew point corresponding to the vapor pressure in the gas-phase species. Efforts will be made to develop a better model for Hg adsorption on fly ash. Existing EERC experimental data are available for this subtask.

Mercury Interaction Model on Activated Carbons

The study will be completed using the EERC's Sun Fire V1280 server with Gaussian, GAMESS, or MolPro software. We expect that either CCSD(T) will prove to be adequate (perhaps with an empirical correction added) or a multiconfiguration self-consistent field (MCSCF)-based method, such as multireference perturbation theory or its University of North Dakota (UND)-developed variant, Generalized Van Vleck Perturbation Theory (GVVPT), will provide the best agreement with multireference configuration interaction, including single and double excitation (MRCISD) results. In either case, it will be possible to study larger model problems such as Hg + benzene-sized radicals to determine the energy minima of the complexes. The researchers have extensive experience researching with the required software (i.e., Gaussian for CCSD[T], GAMESS for MRPT, and MolPro for MRCISD, in addition to the UND-developed software). The new 8 processor Sun workstation that the EERC has in place will be adequate for the proposed studies. Within the 1-year performance period, several energy minima of Hg with the larger model compounds will be obtained, and a few transition states between the most promising energy minima will be located. These results will enable estimation of the reaction rates between the minima.

Progress

Hg Speciation Model

A CHEMKIN-based homogeneous mercury reaction model was improved with the latest information about the reaction mechanisms relevant to mercury species. This model was connected to the previously developed heterogeneous mercury speciation model. In the CHEMKIN model, Cl (in the form

of HCl) is computationally identified as one of the most important oxidation agents regarding mercury gaseous species reaction. However, the split between solid Cl and gaseous Cl cannot reasonably be predicted for the time being. It is assumed that a fraction of total Cl in coal is released into the flue gas and is, therefore, available for participating homogeneous reactions. Chlorine-containing additives are often used to enhance oxidation of mercury. The EERC has conducted many pilot-scale tests with the particulate test combustor (PTC) in the past regarding mercury speciation. Caballo is one subbituminous coal tested at the PTC with various sorbent enhancement agents, including chlorine-containing additives. As the first-of-its-kind effort, the integrated model was employed to simulate mercury transformation for the coal.

Figures 1 and 2 show the model-predicted vs. measured mercury species in flue gas of Caballo coal as a function of time. For convenience, the temperature is also shown on the top of the figures. Without any additives with the coal, it is experimentally observed that the flue gas at the ESP inlet contains mostly elemental mercury (about 90%~95% of total gaseous Hg species), and oxidized mercury species only account for 5%~10% of total gaseous Hg species. The model predicts this speciation trend, indicating the oxidization occurs in a narrow time span.

Figures 3 and 4 are the model-predicted vs. measured mercury species in flue gas of Caballo coal fired with 2.0 lb/Macf CaCl_2 together with the coal. With the additive cofiring in the furnace, measured gaseous elemental Hg at the ESP inlet drops to around $8 \mu\text{g}/\text{Nm}^3$ (accounting for 80% of total gaseous Hg species). The model predictions match the measured results reasonably well.

Mercury Interaction Model

The Gaussian03 modeling software has been installed on the Sun Fire server. The test runs have been performed, and we are in the process of evaluating the output from these runs. Once we verify that the software is running correctly, we will begin modeling the specific reactions.

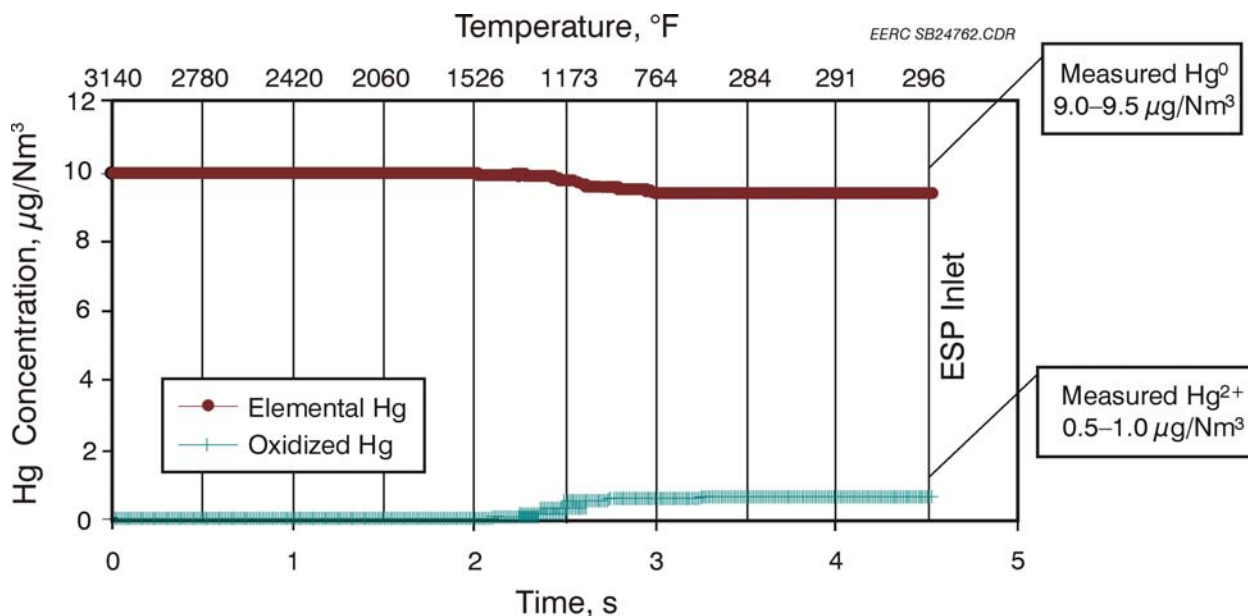


Figure 1. Model-predicted gas-phase mercury speciation (Caballo coal fired in the PTC).

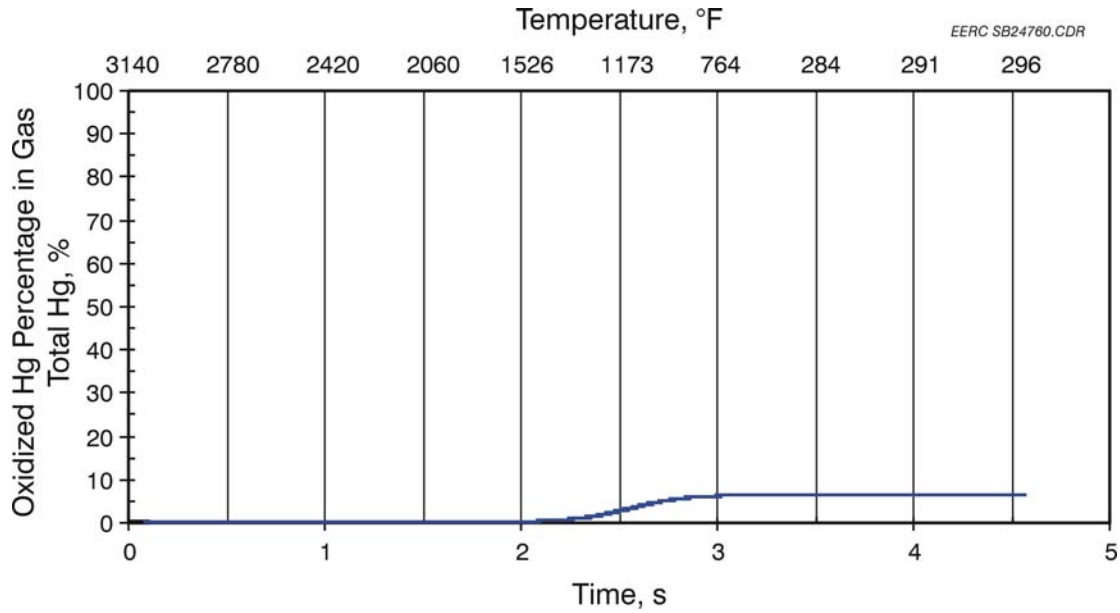


Figure 2. Model-predicted oxidized Hg fraction in the total gas mercury (Caballo coal fired in the PTC). Ontario Hydro measured ESP inlet Hg^{2+} is around 5% in total gaseous Hg.

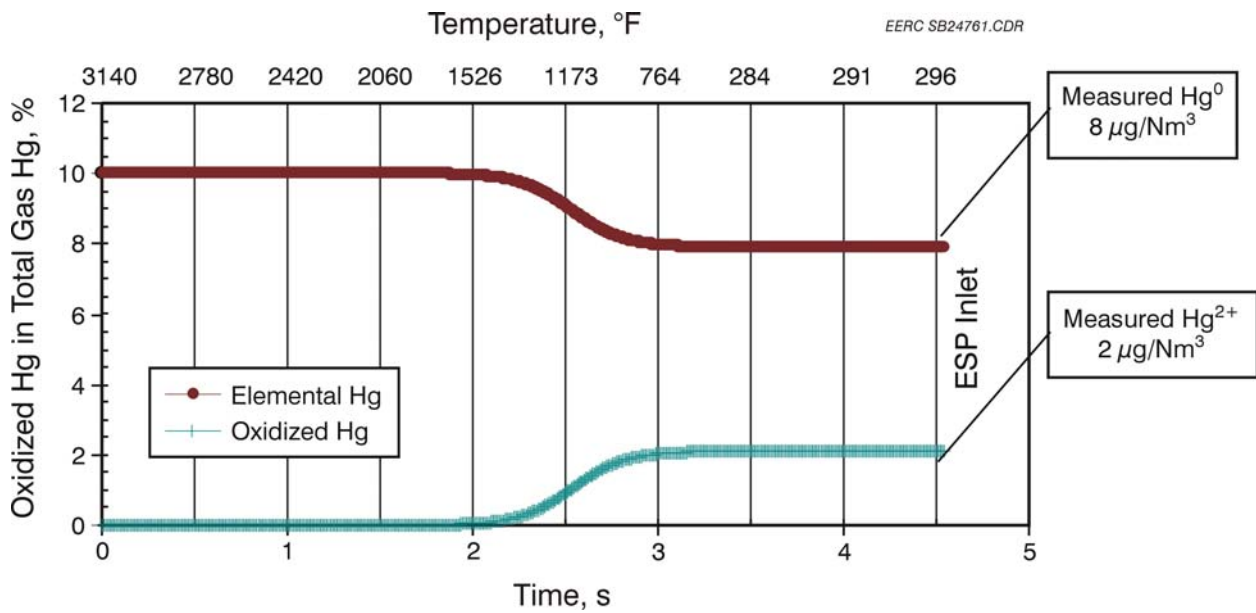


Figure 3. Model-predicted gas Hg speciation, Caballo coal fired with 2.0 lb/Macf $CaCl_2$ addition to the PTC furnace.

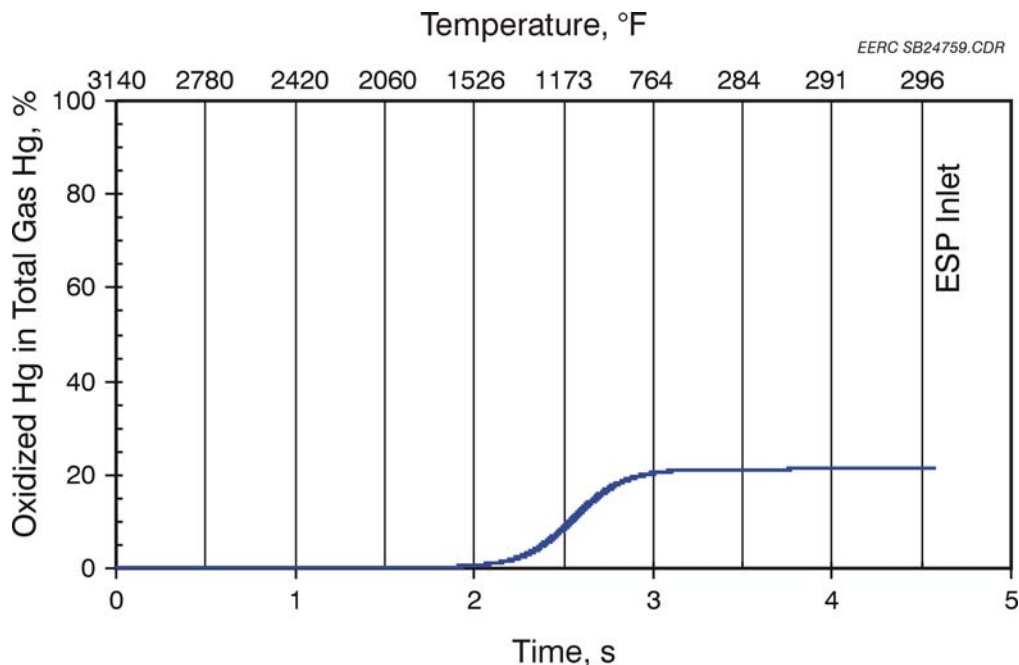


Figure 4. Model-predicted oxidized Hg fraction in total gas Hg, Caballo coal fired with 2.9 lb/Macf CaCl₂ addition to the PTC furnace. CEM measured Hg²⁺ in the gas phase at the ESP inlet is about 20%.

Quality Assurance/Quality Control

Quality Objective

The quality objective is to develop a model that predicts mercury speciation and transformation that can be validated by full-scale tests at power plants.

Measurement/Data Acquisition

The components of this model are either from known scientific theories (the GDE and CHEMKIN models) or from results of experiments (the kinetic model). The fly ash particle-size and composition distribution model (ATRAN) used by the GDE was developed at the EERC based on research of pc combustion over the past two decades. The flue gas properties, temperature, and velocity profiles in the postcombustion environment were simulated by FLUENT software. The reaction constants of Hg⁰ to Hg²⁺ and Hg(p) at different temperature were calculated from pilot-scale test data.

Assessment and Validation

ICR data and EERC test data were used for validation of some components during model development. More pilot- and full-scale tests are needed for overall model validation.

Status

The mercury speciation modeling effort for CATM Year 11 is finished, but the mercury interaction on activated carbon modeling study (CATM Year 12) is ongoing.

In Year 11 research, a fundamental model framework was established, which incorporated homogeneous gaseous reaction mechanisms relevant to mercury species and a heterogeneous mercury–particulate interaction mechanism. This model has shown promising predictions of mercury capture by particulates as well as gaseous split between elemental mercury and oxidized mercury.

However, some critical kinetic data are still lacking (such as elemental mercury adsorption rate constant, desorption rate constant). The ongoing computational chemistry modeling effort (quantum study in Year 12) could provide such fundamental information. On the other hand, the effects of various gaseous components (e.g., SO₂, NO_x) have been experimentally shown to affect the activated carbon sorption capacity significantly. These important effects should be addressed in the modeling effort in the future under the context of real coal-fired flue gases. Eventually, the modeling should be improved to a level that it not only mimics the known phenomena but also discovers the underpinning mechanisms so that methods can be computationally identified to maximize mercury control.

Potential Users/Technology Transfer

Power industry and coal companies can use this model to evaluate their fuel performance and mercury emission control options. The baseline case of this model should provide power plants with information related to levels of Hg emissions, which will help them in fuel selection. Alternate cases can be run with different Hg control technology options, which should allow for optimum selection of Hg control technologies to meet state and federal emission standards.

References

1. Galbreath, K.C.; Zygarićke, C.J. Mercury Speciation in Coal Combustion and Gasification Flue Gases. *Environ. Sci. & Technol.* **1996**, *30*, 2421–2426.
 2. Galbreath, K.C.; Zygarićke, C.J. Mercury Transformations in Coal Combustion Flue Gas. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; McClean, VA, Dec 1–4, 1998; Special Issue of *Fuel Processing Technology* **2000**, *65–66*, 289–310.
 3. Laudal, D.L.; Galbreath, K.C.; Heidt, M.K. *A State-of-the-Art Review of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-107080, Nov 1996.
 4. Senior, S.L.; Sarofim, A.F.; Zeng, T.; Helble, J.H.; Mamani-Paco, R. Gas-Phase Transformations of Mercury in Coal-Fired Power Plants. *Fuel Processing Technology* **2000**, *63*, 197–213.
 5. Chen, Z.; Senior, C.L.; Sarofim, A.F. Modeling of Mercury States in Coal-Fired Utility Boilers. In *Proceedings of the 27th International Technical Conference on Coal Utilization & Fuel Systems*; Clearwater, FL, March 4–7, 2002.
 6. Senior, C.L.; Chen, Z.; Sarofim, A.F. Mercury Oxidation in Coal-Fired Utility Boilers. Presented at the Air & Waste Management Association 94th Annual Conference and Exhibition, Baltimore, MD, June 2001.
 7. Serre, D.S.; Silcox, G.D. Adsorption of Elemental Mercury on the Residual Carbon in Coal Fly Ash. *Ind. Eng. Chem. Res.* **2000**, *39*, 1723–1730.
-

8. Senior, C. et al. Modeling Gaseous Mercury Behavior in Practical Combustion Systems. In *Proceedings of the Air Quality III: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 10–12, 2002.
 9. Niksa, S.; Fujiwara, N. Predicting Mercury Speciation in Coal-Derived Flue Gas. In *Proceedings of the Mega Symposium*; Washington, DC, May 2003.
 10. Pavlish, J.H. et al. Status Review of Mercury Control Options for Coal-Fired Power Plants. *Fuel Processing Technology* **2003**, *82*.
 11. Olson, E.S. et al. An Improved Model for Flue Gas–Mercury Interactions on Activated Carbons. In *Proceedings of the Mega Symposium*; Washington, DC, May 2003.
 12. Miller, S.J.; Dunham, G.E.; Olson, E.S.; Brown, T.D. Flue Gas Effects on a Carbon-Based Mercury Sorbent. In *Proceedings of the Air Quality II: Mercury, Trace Elements, and Particulate Matter Conference*; Special Issue of *Fuel Process. Technol.* **2000**, *65–66*, 343–363.
 13. Olson, E.S.; Laumb, J.D.; Benson, S.A.; Dunham, G.E.; Sharma, R.K.; Mibeck, B.A.; Crocker, C.R.; Miller, S.J.; Holmes, M.J.; Pavlish, J.H. The Mechanistic Model for Flue Gas–Mercury Interactions on Activated Carbons. In *Proceedings of Air Quality IV: Mercury, Trace Elements, and Particulate Matter Conference*; Arlington, VA, Sept 22–24, 2003; Paper A5 2.
 14. Li, L.C. et al. A Study on the Reaction Mechanism and Kinetic of Mercury Oxidation by Chlorine Species. *THEOCHEM* **2003**, *625* (1–3), 277–281.
 15. Li, L.C.; Deng, P. Study on the Reaction Mechanism and Kinetics of Mercury Chloride Series in Coal Combustion. *Sichuan Shifan Daxue Xuebao, Ziran Kexueban* **2002**, *25* (6), 637–640.
 16. Liu, J. et al. Reaction Mechanism of Mercury and Gases During Coal Combustion. *Gongcheng Rewuli Xuebao* **2003**, *24* (1), 161–164.
 17. Steckel, J.A.; Cugini, A.V. Computational Approaches to Modeling Interactions of Hg with Organic Compounds. In *Proceedings of the 225th ACS National Meeting*; New Orleans, LA; American Chemical Society, 2003
 18. Madsen, J.; Steckel, J.; Rogers, W.; Cugini, A. Computational Approaches to the Development of Advanced Mercury Control Technologies. Presented at the Mercury Control Technology R&D Program Review Meeting, Pittsburgh, PA, Aug 12–13, 2003.
 19. Khalizov, A.F. et al. A Theoretical Study on the Reactions of Hg with Halogens: Atmospheric Implications. *J. Phys. Chem. A* **2003**, *107*, 6360–6365.
 20. Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648.
 21. Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 270.
 22. Wadt, W.R.; Hay, P.J. *J. Chem. Phys.* **1985**, *82*, 284.
 23. Hay, P.J.; Wadt, W.R. *J. Chem. Phys.* **1985**, *82*, 299.
-

24. Pople, J.A.; Head, G.M.; Ragavachari, K. *J. Chem. Phys.* **1987**, 87, 5968.
 25. McLean, A.D.; Chandler, G.S. *J. Chem. Phys.* **1980**, 72, 5639.
 26. Krishnan, R. et al. *J. Chem. Phys.* **1980**, 72, 650.
 27. Purvis, G.D.; Bartlett, R.J. *J. Chem. Phys.* **1982**, 76, 1910.
 28. Kreevoy, M.M.; Truhlar, D.G. Transition State Theory. In *Investigation of Rates and Mechanisms of Reactions*; Bernasconi, C.F., Ed.; Wiley: New York, 1986; p 14.
-