



Steven A. Benson
Principal Investigator

MODELING MERCURY SPECIATION IN COAL COMBUSTION SYSTEMS

Key Personnel: Steven A. Benson (EERC), Lingbu Kong (EERC), Li Yan (EERC), Donald P. McCollor (EERC), and Bruce C. Folkedahl (EERC)

Project Description

The aim of the research conducted in 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 combination of a homogeneous reaction model on gas-phase speciation and a heterogeneous adsorption (or reaction) model is beneficial in predicting mercury control in coal-fired combustion systems. Mercury control is dependent upon coal and combustion/environmental control system characteristics. Coal characteristics influence the form 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 inject. Combustion systems equipped with wet scrubbers will likely rely on mercury oxidation upstream of the scrubbers. Systems equipped with dry scrubbers, spray dryer FFs, or spray dryer ESPs will rely on mercury oxidation as well as on sorbent injection. This project is focused on predicting mercury oxidation and mercury interactions with entrained particulate matter either being sorbents or fly ash particles.

Goal

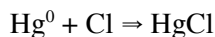
This proposed modeling effort is aimed at developing a mercury transformation model consisting of a gaseous homogeneous speciation model and a kinetic model for mercury interaction/adsorption by particulate material.

Rationale

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 (Hg^0). When the flue gas cools, passing the low-temperature heat-exchange zones in the boiler, it has been observed that a portion of Hg^0 can be oxidized to Hg^{2+} through reactions with other gaseous components (particularly, when HCl or molecular chlorine [Cl_2] 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 [7–12]. 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 [7–9]. 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 [8].

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 information 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 Hg⁰(g) transforms to Hg²⁺X(s,g) and Hg(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 the U.S. Environmental Protection Agency's (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 [1]. Thermodynamic models provide insight into the species of mercury likely to exist in flue gas at chemical equilibrium. Several models predict that Hg⁰(g) will react with other gaseous phases to form HgCl₂(g), HgO(s), or HgSO₄(s). Empirical evidence clearly indicates, however, that the assumption of gas-phase equilibrium for mercury species in coal combustion flue gas is invalid [1–4]. Work by Chen [5] and Senior [6] 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 air pollution control devices (APCD). Cooling rate also plays a significant role in mercury transformations. Senior [4] used an idealized cooling rate for a pulverized coal (pc)-fired utility boiler, while Chen [5] 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.

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. The overall modeling effort for mercury control is shown in Figure 1.

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 deciding 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 Energy & Environmental Research Center (EERC) experimental data are available for this subtask.

Progress

Homogeneous Hg Speciation Model

A gas-phase kinetic model of Hg speciation has been obtained and implemented. This model was obtained from results of a bench-scale test of Hg transformations in coal combustion flue gas at a temperature range from 400° to 275°C [1, 2]. A simple rate equation is used as the first step to express Hg transformation rate as a function of temperature, residence time, and Hg concentration in the flue gas:

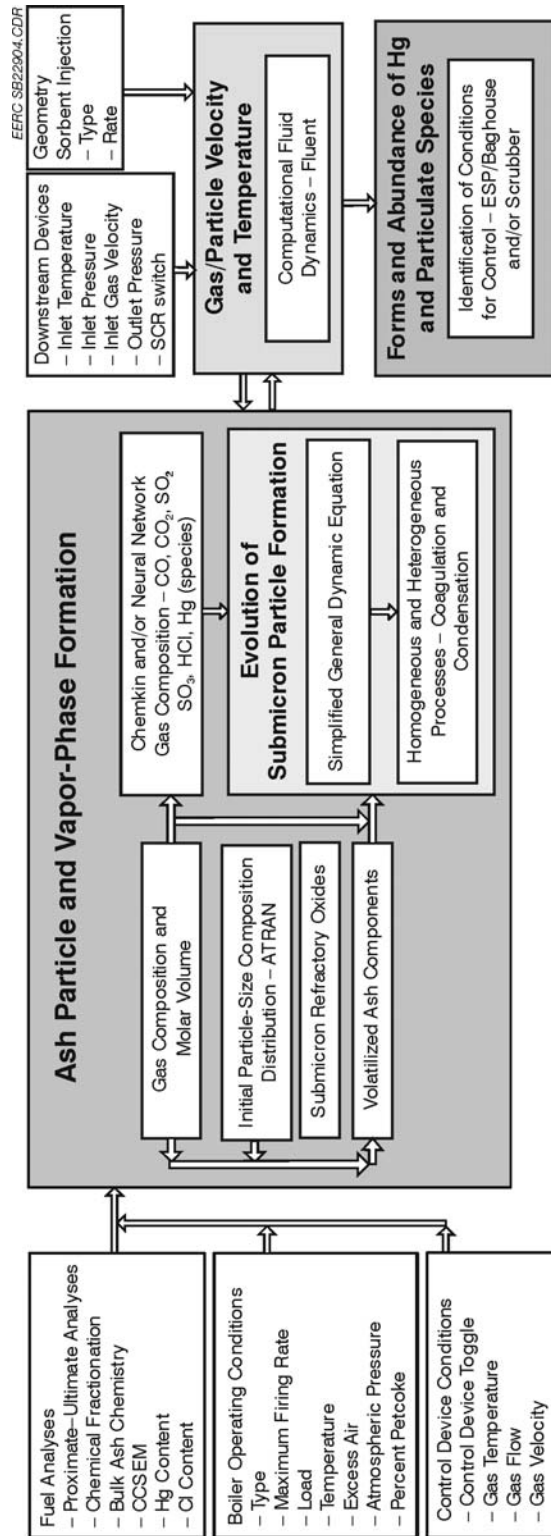


Figure 1. Overall Modeling Effort for Ash Formation, Mercury Speciation, and Reactions with Particulate Matter

$$\frac{dC_{\text{Hg}}}{dt} = -kC_{\text{Hg}}^a$$

This rate equation combines all Hg transformation mechanisms between vapor and particulate phases together. The reaction order and reaction rate constants for conversions of Hg(gas) to Hg(p) and Hg⁰ to Hg²⁺ and/or Hg(p) are listed in Table 1.

Table 1. Reaction Order and Reaction Rate Constant

	Reaction Order, <i>a</i>	Reaction Rate Constant, <i>k</i> , at 150°C	Reaction Rate Constant, <i>k</i> , at 275°C	Reaction Rate Constant, <i>k</i> , at 400°C
Hg(gas)	4.62	9.8 E-3	0.000003	0.000001
Hg ⁰	1.73	0.051	0.0027	0.0023

Heterogeneous Model for Hg Interaction with Particulates

A new heterogeneous model accounting for Hg interaction with particulates (including sorbent particles and/or ash particles) is being developed and refined, based on Serre and Silcox's work [7]. This model is different from Senior's model or Niksa's model on heterogeneous Hg interaction with particles [8, 9], which are the latest models on Hg heterogeneous transformation found in the open literature.

In general, our model will account for mass transfer of Hg⁰ from bulk gas phase onto particle surfaces by diffusion, expressed by:

$$\frac{dC_{\text{bg}}}{dt} = -\beta \cdot \alpha \cdot (C_{\text{bg}} - C^*)$$

Where C_{bg} is the Hg concentration in the bulk gas (kg/Nm³), t is time (sec.), β is the Hg mass-transfer coefficient in the flue gas (m/s); α is the specific surface area of particulates per unit gas volume (m²/Nm³); and C^* is the gas-phase Hg concentration on particle surface, (kg/Nm³).

The dynamic adsorption/desorption of Hg on particle surface is expressed:

$$r_{\text{ad}} = k_{\text{ad}} \cdot C^* (\omega_{\text{max}} - \omega) - k_{\text{de}} \cdot \omega$$

where k_{ad} is the adsorption rate constant, k_{de} is the desorption rate constant (m³/kg-s); ω_{max} is the maximum Hg adsorption per unit mass of the particle (kg Hg_(s)/kg); and ω is the adsorbed Hg(solid) concentration on particle surface (kg Hg_(s)/kg).

Note that here the maximum Hg adsorption ω_{max} is different from the concept of equilibrium adsorption capacity [10]. The ω_{max} is related to particle properties (e.g., chemical composition and micro-structure) and temperature but not a function of gas-phase Hg concentration. ω_{max} and the adsorption/desorption equilibrium constant can be obtained by regression of a number of Langmuir isotherm data pairs under equilibrium adsorption and desorption at a given temperature. The adsorption rate constant can be estimated from breakthrough curves of fixed-bed tests, according to Serre [7]. As a preliminary assumption, the desorbed Hg from the particle surface is in an oxidized form, according to Olson et al. [11]. The above two equations can be combined to solve by considering proper initial conditions and boundary conditions.

The distinct advantage of this model over other heterogeneous models in the literature is that the dynamic changes in Hg⁰, Hg²⁺, and Hg(p) due to heterogeneous interactions may be numerically computed as a function of temperature–time history and duct locations, as a general Hg heterogeneous model. The

difficulty is to accurately obtain corresponding parameters in the dynamic adsorption/desorption equation from bench-scale or pilot-scale experimental data.

Model Integration

Temperature and residence time of Hg in combustion flue gas in postcombustion systems are major factors affecting homogeneous Hg transformation, while fine fly ash and sorbent particle-size distribution play critical roles in heterogeneous condensation of vapor-phase Hg. Modeling of temperature profile, flue gas velocity, and fly ash size distribution is one of the major modeling efforts. Gas temperature and velocity in the air preheater (APH) and ductwork upstream of an APCD are functions of location and were modeled by a CFD model. An ash transformation model, ATRAN, can be used to model the fly ash particle-size distribution. However, ATRAN does not work well in predicting particles less than $1\ \mu\text{m}$ in diameter. A simple general dynamic equation (GDE) was introduced to model the fine particulates in flue gas.

The integrated model is shown in Figure 2. The model consists of several components that include combustion calculations to predict flue gas composition; an ash transformation model (ATRAN) to predict the particle-size composition distribution of the supermicron particles; a kinetic model to predict mercury speciation; a CFD (FLUENT) model to predict gas and particle velocities, temperatures, and trajectories; and GDE to predict particle condensation, diffusion, and coagulation.

With the integrated model, calculations can be applied to a flue gas stream as it passes through an APH and the ductwork upstream of an APCD. Two examples of the predictions from the entrance to the APH to the entrance of the APCD are shown in Figures 3 and 4. Figure 3 shows a case that has high levels of Hg^0 typical of a subbituminous coal flue gas. Figure 4 shows a case where Hg^{2+} dominates. These results are, at

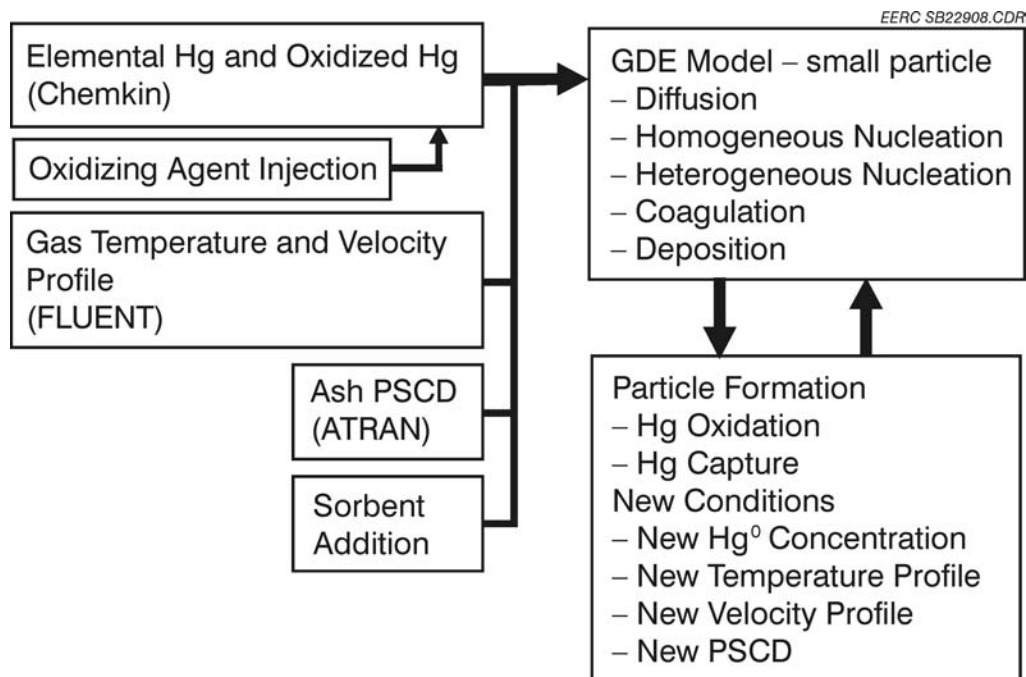


Figure 2. Overview of the Integrated Model

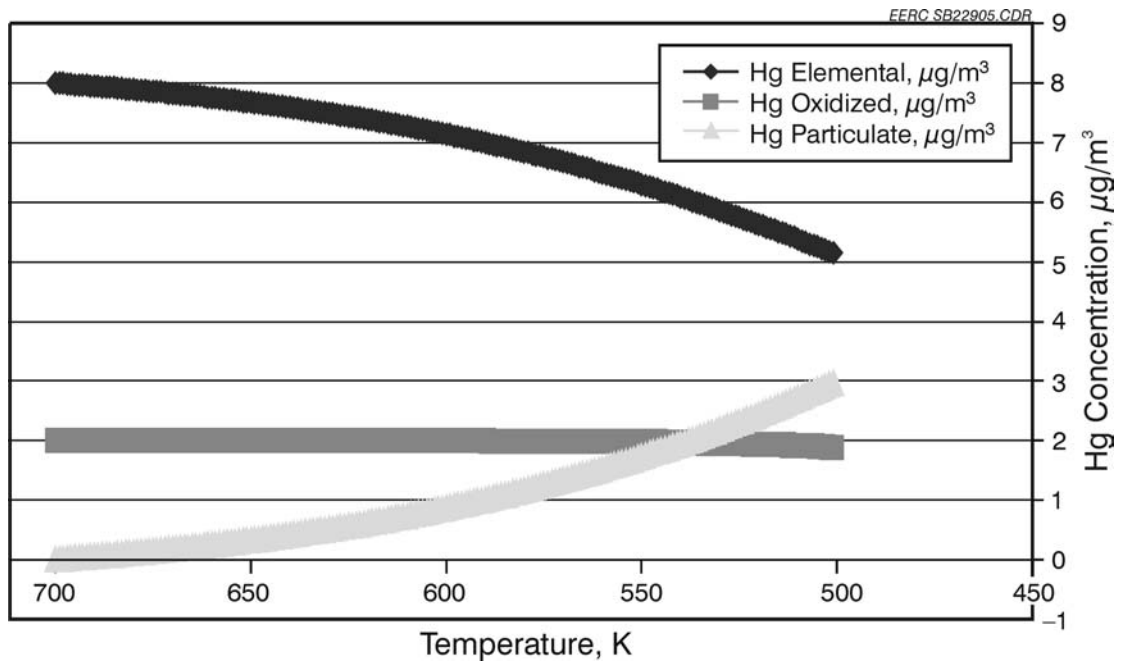


Figure 3. Integrated Model Predictions from APH to Entrance of Air Pollution Control Device for a Flue Gas Stream Dominated by Elemental Mercury ($\text{Hg}^0 = 8 \mu\text{g}/\text{m}^3$, $\text{Hg}^{2+} = 2 \mu\text{g}/\text{m}^3$)

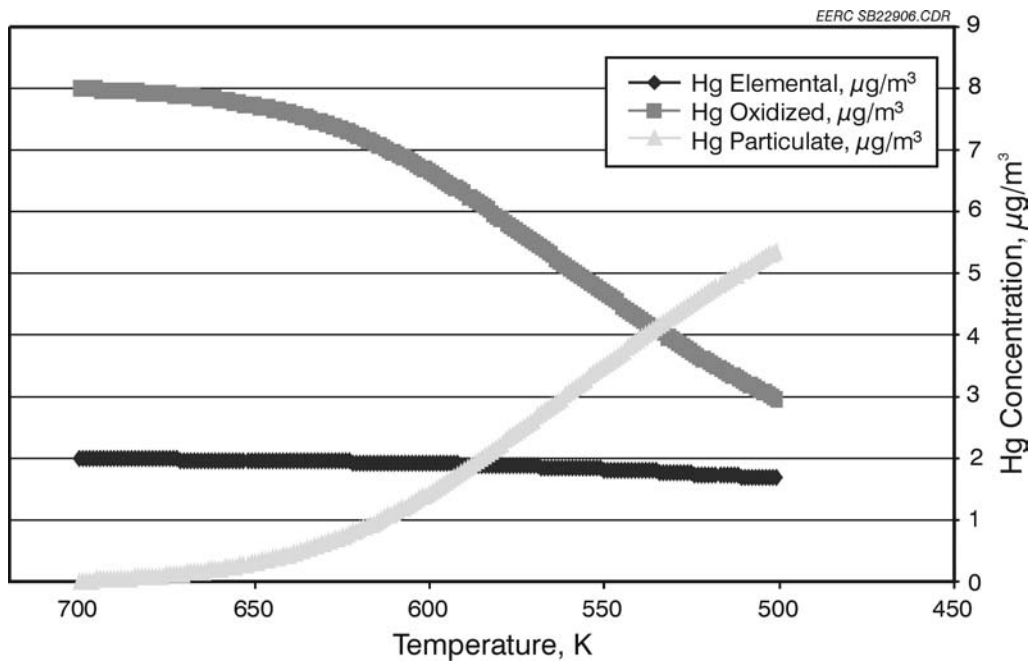


Figure 4. Integrated Model Predictions from APH to Entrance of Air Pollution Control Device for a Flue Gas Stream Dominated by Oxidized Mercury ($\text{Hg}^0 = 2 \mu\text{g}/\text{m}^3$, $\text{Hg}^{2+} = 8 \mu\text{g}/\text{m}^3$)

this time, preliminary and are being validated using experimental data. Reactions of Hg^0 to oxidized forms as well as the interaction with particulate materials are still under development. However, the overall integrated model has been developed and is in the process of being refined.

Status

A preliminary mercury transformation model has been developed. This model integrates a GDE model with a kinetic Hg interaction model. The CHEMKIN-based mercury speciation model has not been integrated to the model yet since it has not been made available. Both the GDE model and kinetic model need to be further refined and validated. Both models need to incorporate test results that account for the Hg oxidation resulting from additives and sorbent injection. The GDE model also needs to take into account particle nucleation and coagulation in the postcombustion environment.

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 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 Hg^0 to Hg^{2+} and $\text{Hg}(p)$ 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 test are needed for overall model validation.

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.

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