Kinetic Models for Predicting the Behavior of Mercury in Coal-Fired Power Plants

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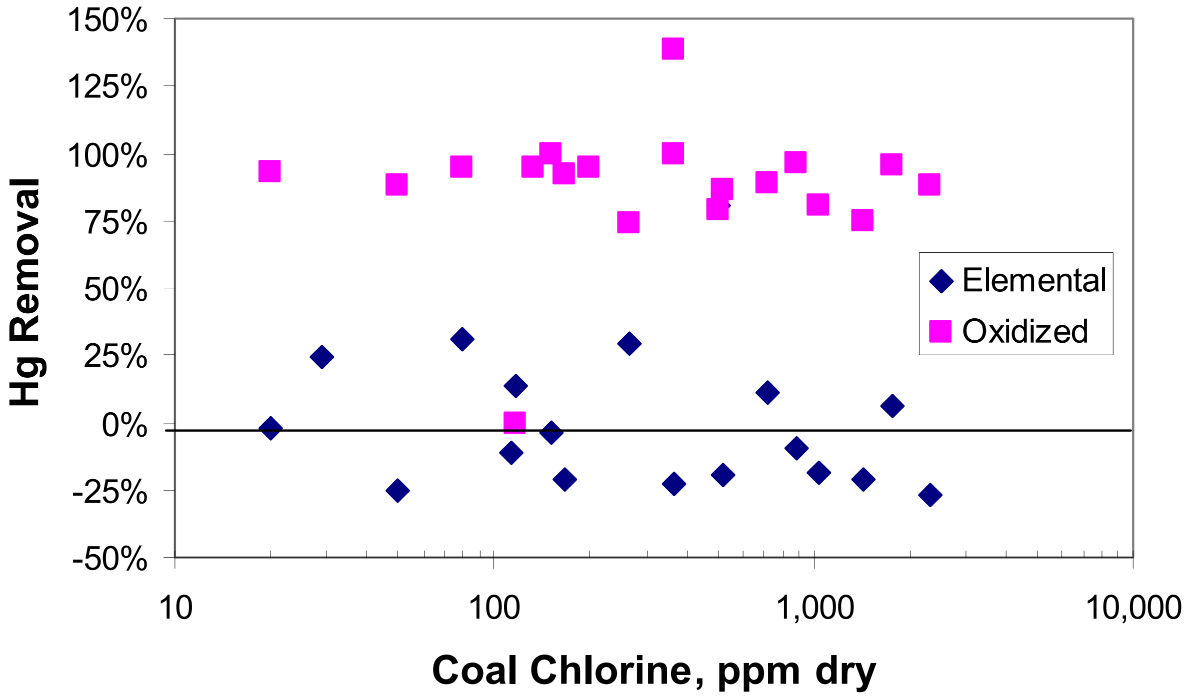
Motivation

- EPA to control emissions of mercury from power plants beginning in 2004
  - Approach and levels to be determined in 2003
- No commercially available control technologies for mercury from coal-fired power plants
- Existing control equipment for other pollutants (SO_2, NO_x, particulate) provides some level of mercury removal
- ***Cost-effective control of mercury emissions requires an understanding of mercury behavior within air pollution control devices***

Forms of Mercury in Flue Gas

- Hg found in vapor-phase and bound to particulate matter; partitioning depends on
  - carbon content
  - particulate control device (ESP vs. FF)
  - NO_x control (post-combustion)
  - coal type (bituminous vs. low rank)
- Vapor-phase species:
  - Elemental: difficult to remove from gas
  - Oxidized: soluble in wet scrubbers, adsorbed more readily by some sorbents

Mercury Removal in Scrubbers



Wet scrubbers remove:
~90% of Hg^{+2}
<25% of Hg^0

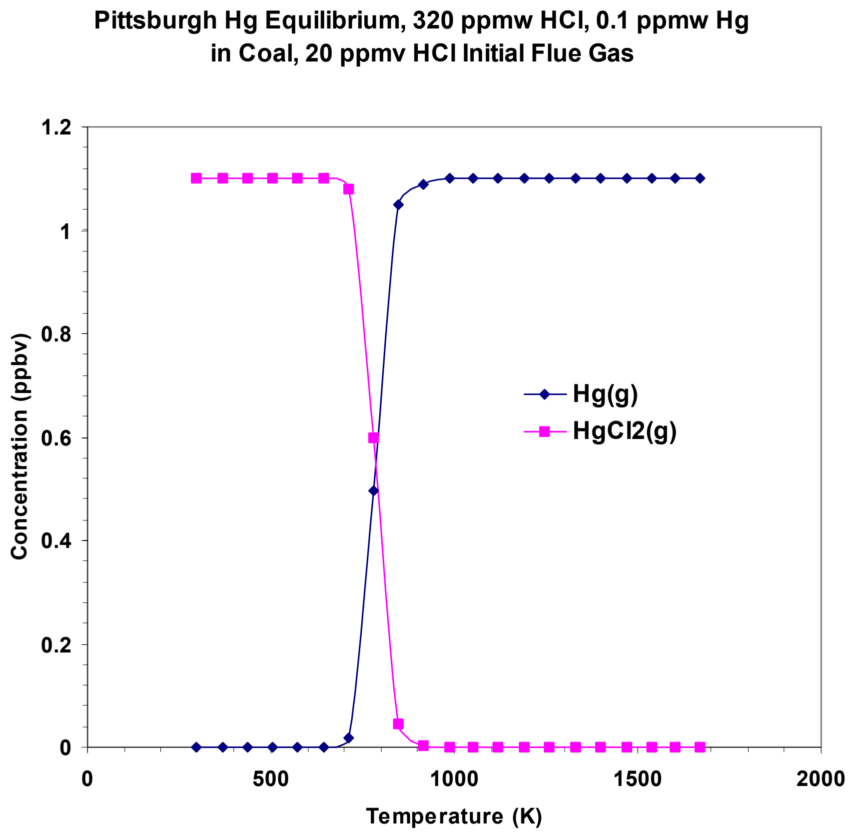
Source: ICR Data

Mercury Model Overview

- ***Objective***: Develop a model for mercury speciation in post-combustion flue gases.
- Model inputs:
  - Coal ultimate analysis, Hg, Cl
  - Fired stoichiometric ratio (S.R.)
  - Initial flue gas composition is computed assuming complete combustion.
  - Time-Temperature profile of the flue gases to the air heater exit
- Detailed chemical kinetics for gas-phase reactions
- Global reaction rate for heterogeneous reaction with fly ash

Equlibrium Calculations

- Compute Hg speciation versus temperature, composition.
- Initial flue gas composition from Pittsburgh coal with 20% excess air.
- Curves shift to higher temperatures with increasing chlorine in coal.
  - 200 K shift for HCl = 5-100 ppmw in flue gas.
- HgCl concentration is negligible.
- Transition temperature is around 800 K.



Homogeneous Hg Reactions

- General 2-Step Mechanism for Hg oxidation to $HgCl_2$

$$\mathbf{Hg} \xrightarrow{\textit{(Cl species)}} \mathbf{HgCl} \xrightarrow{\textit{(Cl species)}} \mathbf{HgCl_2}$$

Reaction	k_o	β	E_a
	(moles, cm^3, s)	---	(cal/mol)
$Hg + Cl + M = HgCl + M$	9.00E+15	0.5	0
$Hg + Cl_2 = HgCl + Cl$	1.39E+14	0	34000
$Hg + HCl = HgCl + H$	4.94E+14	0	79300
$Hg + HOCl = HgCl + OH$	4.27E+13	0	19000
$HgCl + Cl_2 = HgCl_2 + Cl$	1.39E+14	0	1000
$HgCl + Cl + M = HgCl_2 + M$	1.16E+15	0.5	0
$HgCl + HCl = HgCl_2 + H$	4.64E+03	2.5	19100
$HgCl + HOCl = HgCl_2 + OH$	4.27E+13	0	1000

$$k = k_o \cdot T^{\beta} \cdot e^{-E_a / RT}$$

Heterogeneous Kinetics

- Hg vapor reacts heterogeneously with fly ash.
- Two treatments.
  1. Detailed Langmuir-Hinshelwood type model developed for HgCl formation.
  2. Simplified global model.
- A global model is used due to lack of adequate data for the detailed scheme.

Langmuir-Hinshelwood Model

- HgCl formation by surface reaction of adsorbed Hg, Cl.
- Let θ_i be the number of surface sites occupied by species i, where θ = sum (θ_i).
- Balance the rate of adsorption and desorption of i:

$$k_{ai} \cdot (1-\theta_i) \cdot [i] = k_{d,i} \cdot \theta_i$$

- Solve for θ, and θ_i, where $K_i = k_{a,i}/k_{d,i}$:

$$\theta = \frac{\sum K_i \cdot [i]}{1+\sum K_i \cdot [i]}$$

$$\theta_i = K_i \cdot (1-\theta) \cdot [i] = \frac{K_i \cdot [i]}{1+\sum (K_i \cdot [i])}$$

- Compute rate of HgCl formation:

$$\frac{d[HgCl]}{dt} = k_s \cdot \theta_{Hg} \cdot \theta_{Cl} = \frac{k_s \cdot [Hg][Cl] \cdot K_{Cl} \cdot K_{Hg}}{\left(1+\sum K_i \cdot [i]\right)^2}$$

Global Model

- **Stoichiometric reaction:**

  Hg (g) + 2HCl (g) + 1/2 O_2 (g) == $HgCl_2$ (g) + H_2O (g)

- **This reaction is based on the sum of the following two reactions under fuel lean conditions.**

  Hg (g) + 2HCl (g) == $HgCl_2$ (g) + H_2 (g)

  H_2 (g) + 1/2 O_2 (g) == H_2O (g)

- **Rate of $HgCl_2$ formation:**

$$\frac{d[HgCl_2]}{dt} = k_f \cdot [Hg][HCl] - k_r \cdot \frac{[HgCl_2][H_2O]}{[HCl][O_2]^{1/2}}$$

- **k_f and k_r are related by gas-phase equilibrium.**

$$\frac{k_f}{k_r} = K_c = \frac{[HgCl_2][H_2O]}{[Hg][HCl]^2[O_2]^{1/2}} = K_p \cdot (R \cdot T)^{3/2}$$

Global Model Cont.

- k_f is tuned to experimental data assuming E_a = -19 kJ/mol, and adjusting k_{fo}, with an average coal ash content of 8.3% assumed.

$$k_f = k_{fo} \cdot \frac{\%Ash\_in\_coal}{8.3} \cdot \exp\left(\frac{-E_a}{R \cdot T} \right)$$

- The following relation for K_p is computed:

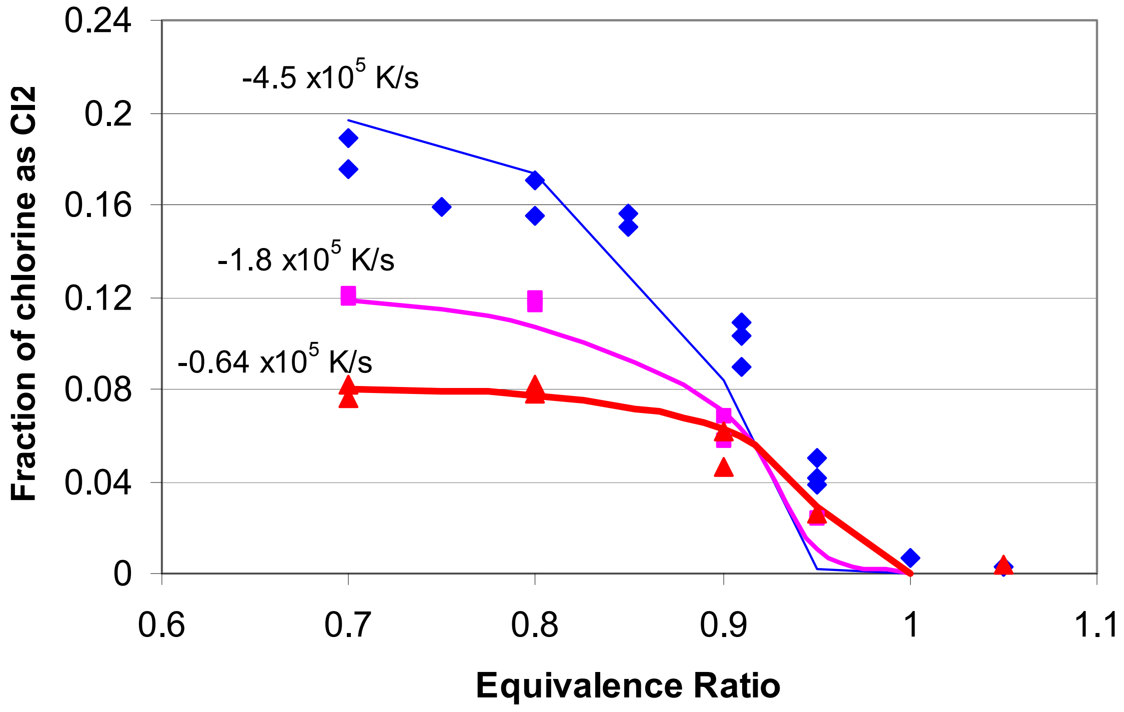
$$\log_{10} K_p = \frac{13820}{T} - 8.7235$$

- Homogeneous rates for species $HgCl_2$, Hg, HCl, O_2, and H_2O, are augmented by the heterogeneous rate for $HgCl_2$, and the stoichimetric relationship between species.

Model Evaluation

- Test chlorine kinetics
- Evaluate the homogeneous model and tune the heterogeneous model
- Compare Hg oxidation versus coal Cl content to experimental data
- Use a Pittsburgh bituminous coal as a basis for calculation. Vary Cl in coal

Effect of Quench Rate on Chlorine

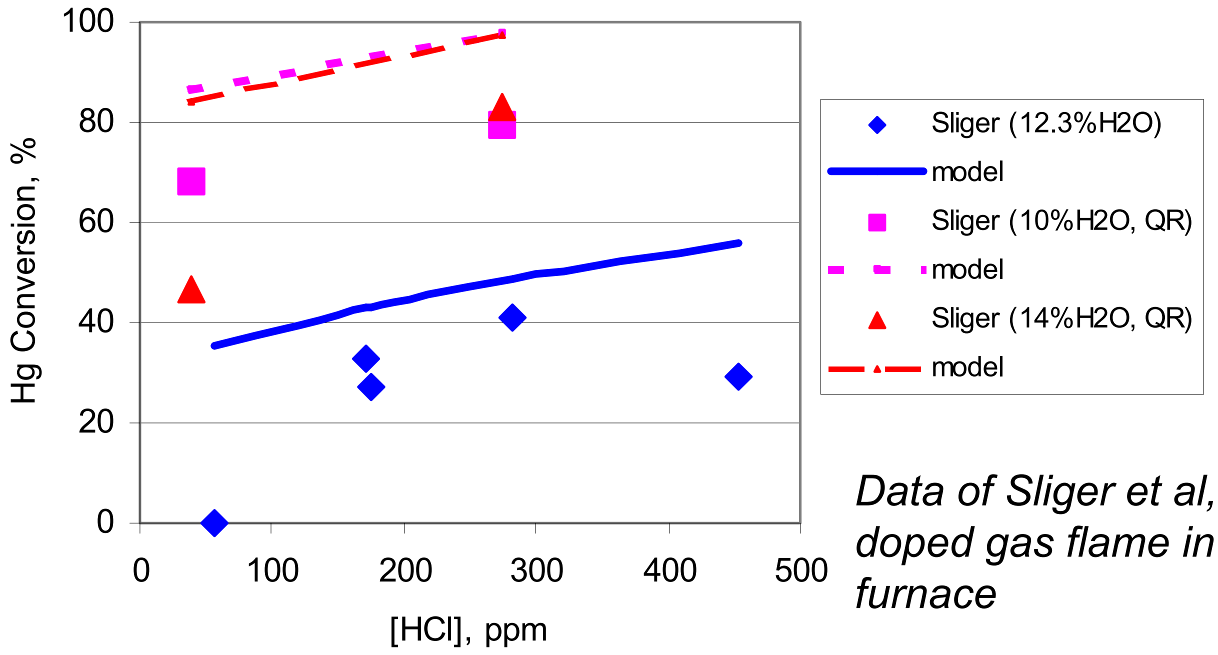


Conclusion:

- Quench rate affects production of Cl and Cl_2
- Cl is critical for Hg oxidation

Comparison of model and data for Cl-doped gas flame. Data of Procaccini et al

Validation: Lab Data



Data of Sliger et al, doped gas flame in furnace

- Five different laboratory studies
- Flow tubes and flames
- Trends reproduced

Boiler Modeling Inputs

Pittsburgh Coal

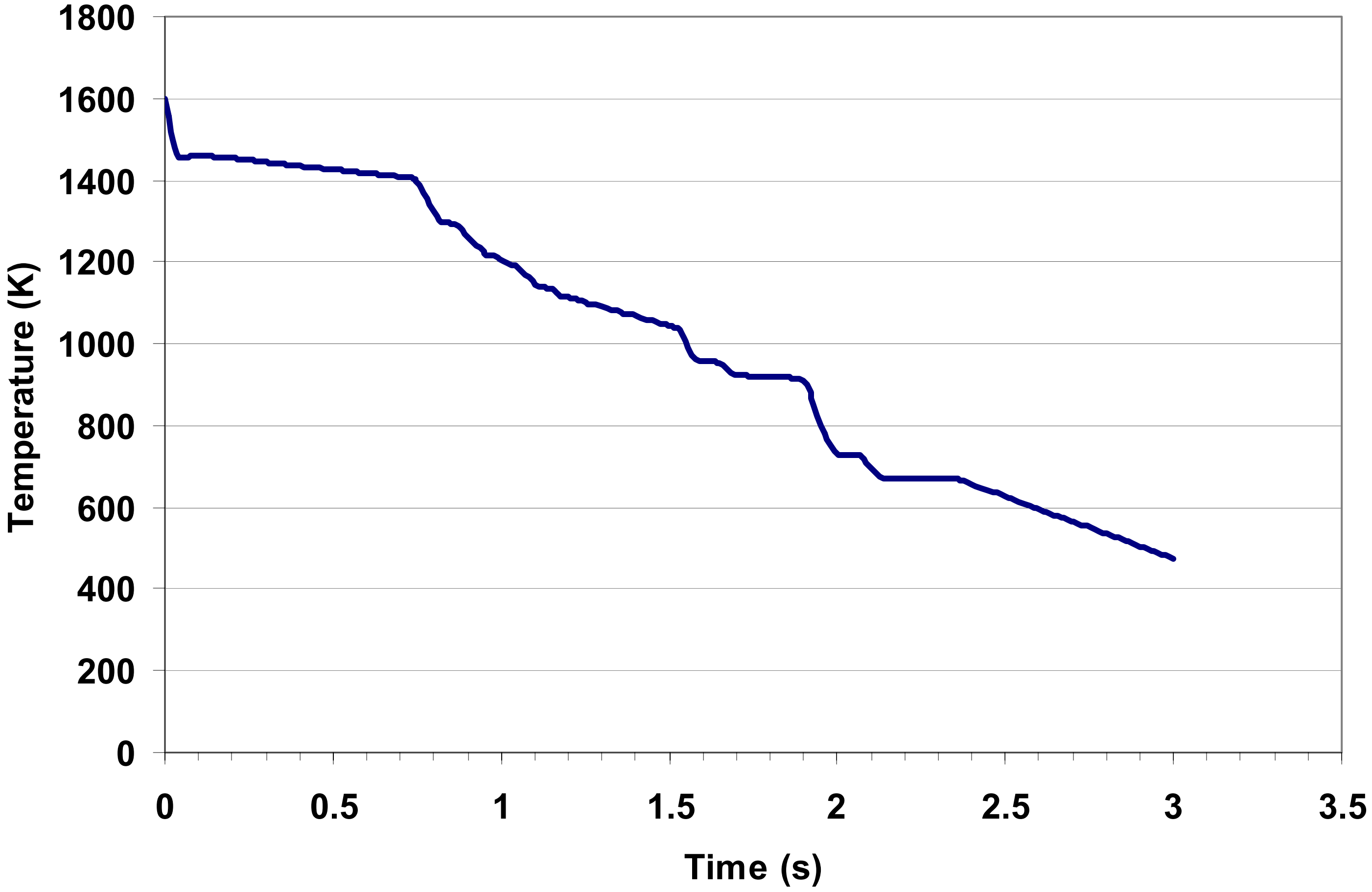
Coal Ultimate Analysis **(As Received)**	
Carbon	76.72%
Hydrogen	4.80%
Oxygen	6.91%
Nitrogen	1.48%
Sulfur	1.64%
Ash	7.01%
Moisture	1.44%
Coal Chlorine (ppmw)	2235
Coal Mercury (ppmw)	0.1

Air Composition	
Nitrogen	77.33%
Oxygen	20.75%
Argon	0.93%
Moisture	1.00%

Flue Gas Composition (by volume)	
CO_2	14.04%
H_2O	6.38%
O_2	3.75%
N_2	74.83%
SO_2	0.11%
Ar	0.89%
HCl (ppmv)	12.4

Combustion S.R. = 1.23

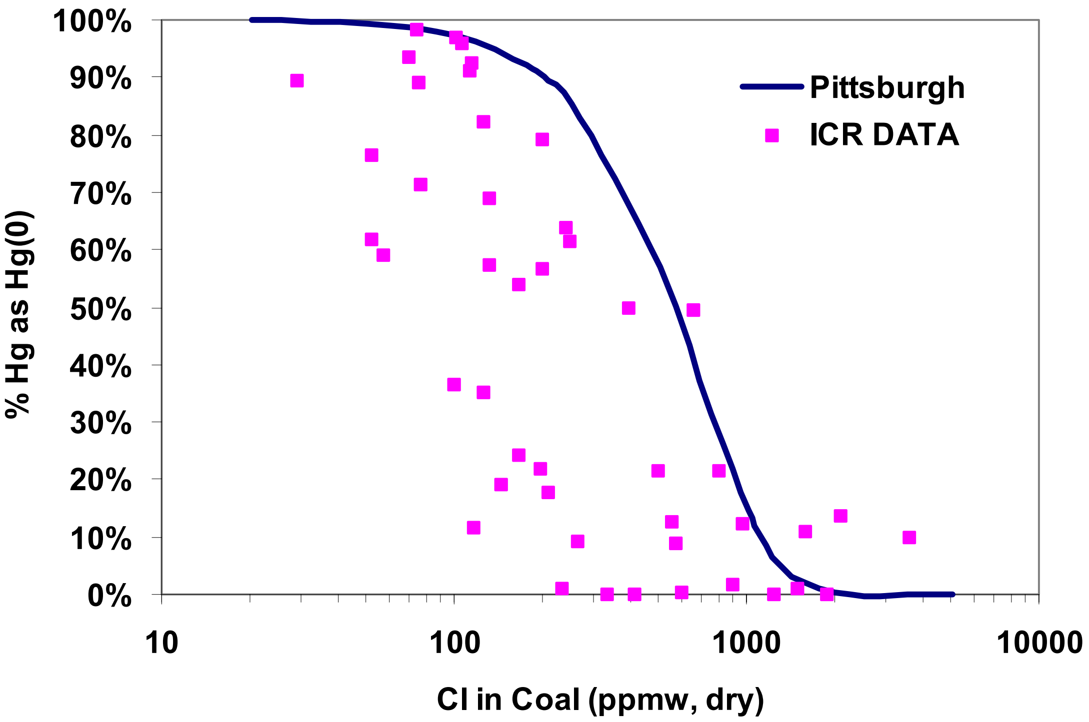
Typical Boiler Temperature Profile Used



Final temperature corresponds to the air preheater exit

Homogeneous Results

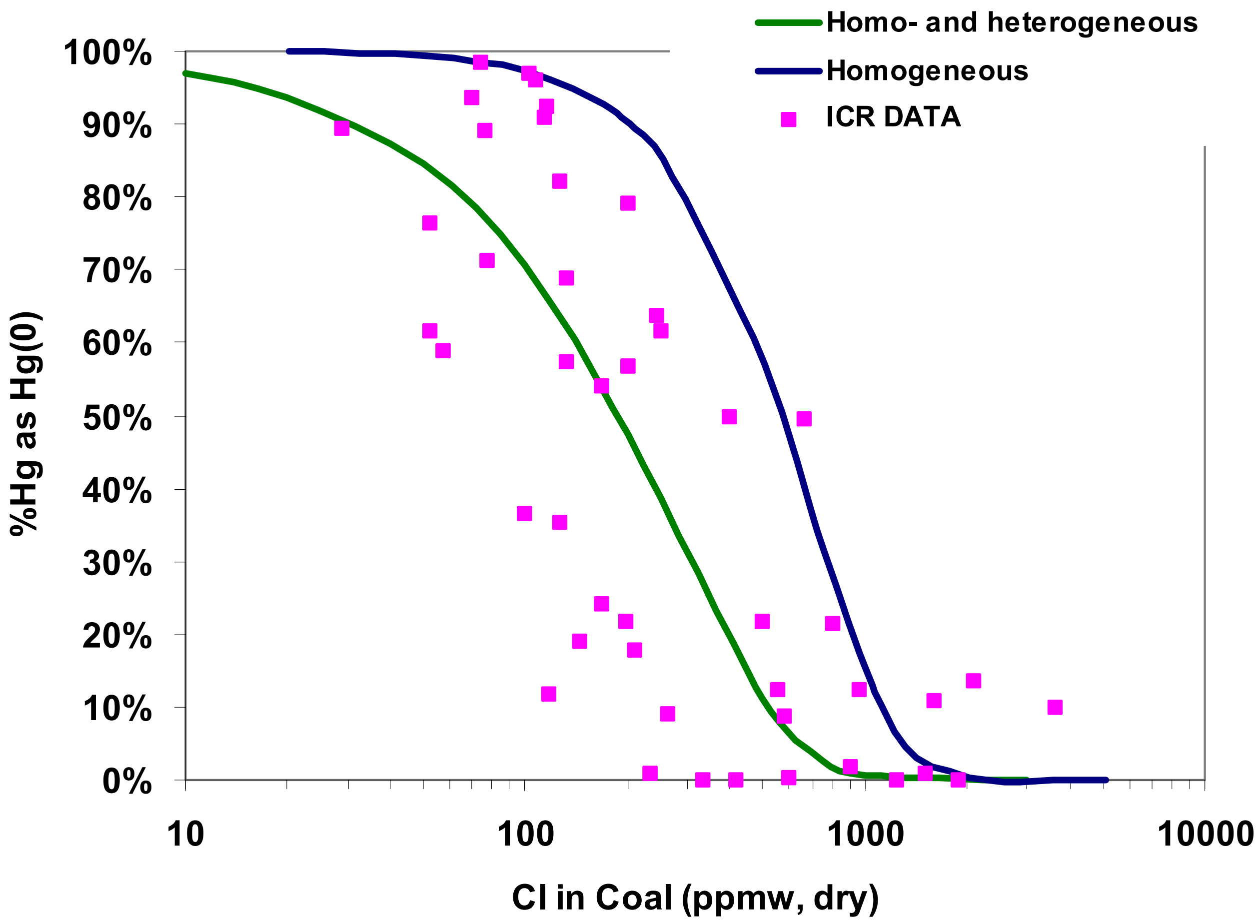
The homogeneous model tends to underpredict the degree of mercury oxidation and overpredicts the amount of elemental mercury.



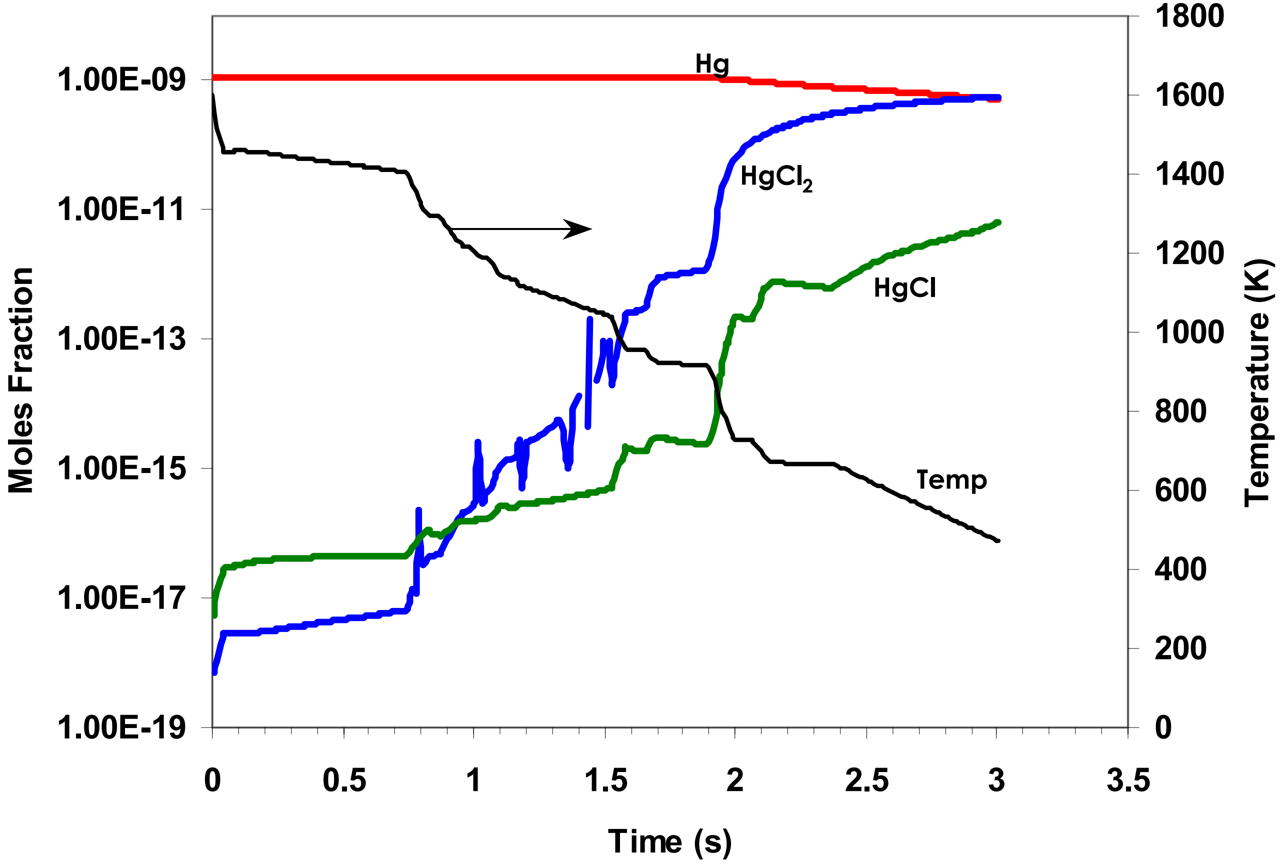
Data points are experimental values for boilers firing a range of coal ranks.

Data are at the inlet to the cold-side particle collection device.

Heterogeneous Results

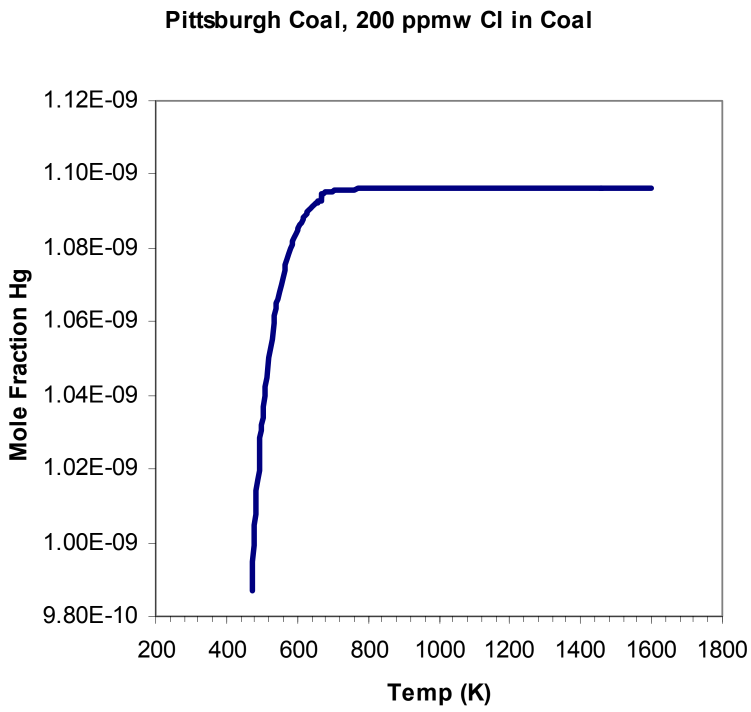


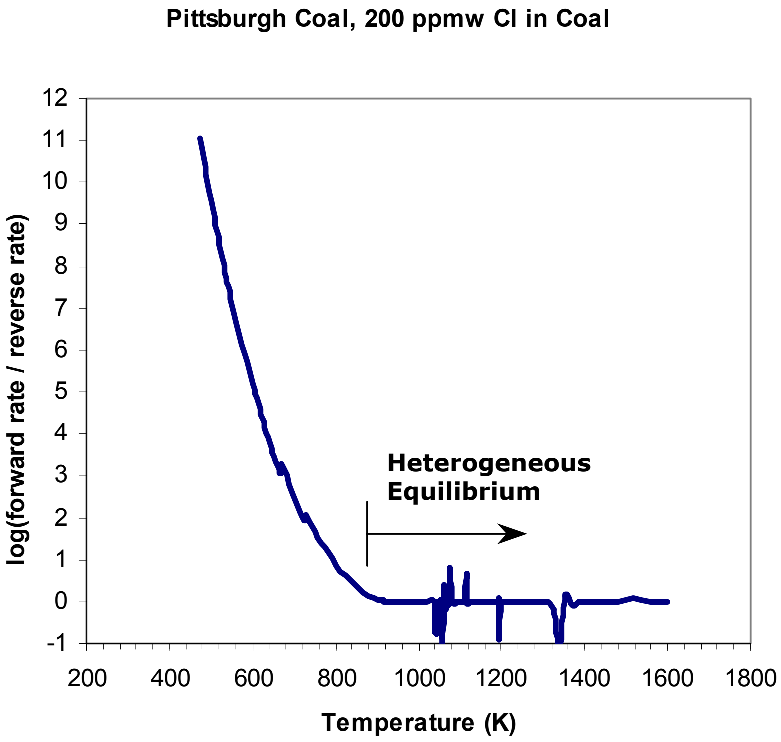
Concentration Profiles



Chemistry takes off at around 800 K, as predicted by equilibrium

Reaction Temperature





Homogeneous reactions only, for given time-temperature profile.

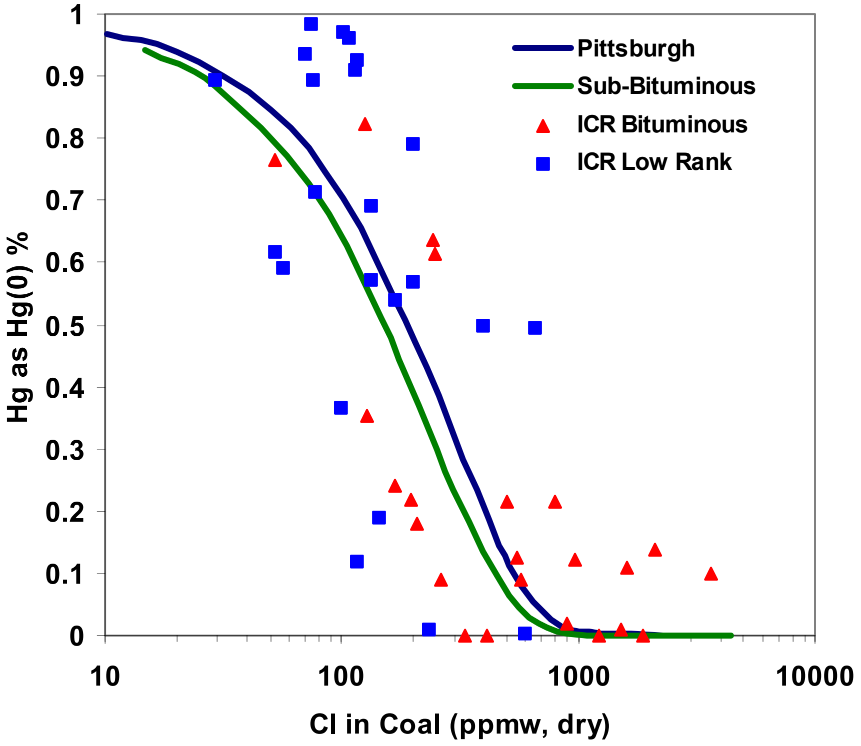
Mercury oxidation reactions begin around 800 K.

Heterogeneous reaction, for given time-temperature profile, with homogeneous reactions.

Hg oxidation occurs for large positive values

Effect of Coal Rank

- ICR data show no clear trend due solely to coal rank.
- Initial Hg concentration has a minimal effect.
- While the PRB has more ash, the HCl conc. is higher for the same ppmw Cl in coal, than the Pittsburgh, resulting in higher conversion for the PRB.
- Model does not account for ash composition: LOI, Ca (low rank)



Sub-bituminous: Jacob's Ranch PRB, 5% ash, 30% moisture, 3 ppmw Cl, 0.1 ppmw Hg

Conclusions

- The scatter in the experimental data points is significant, and could be due to
  - Ash composition, carbon in ash variations
  - Time-temperature profile variations
  - Measurement uncertainty: Cl and Hg in coal
  - Experimental uncertainty: Ontario Hydro measurement errors
- The global heterogeneous model agrees with experimental data, and with equilibrium predictions.
- The Langmuir-Hinshelwood model could be used if adsorption data were known.
- Scatter in experimental Hg oxidation versus coal Cl data cannot be explained on the basis of coal rank.
- NO and SO_2 interaction with Hg are not accounted for in the gas phase, and not explicitly accounted for in the heterogeneous model.