



# Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants Burning Low Rank Fuels

DE- FC26-03NT41728

Final Briefing  
4 October 2004

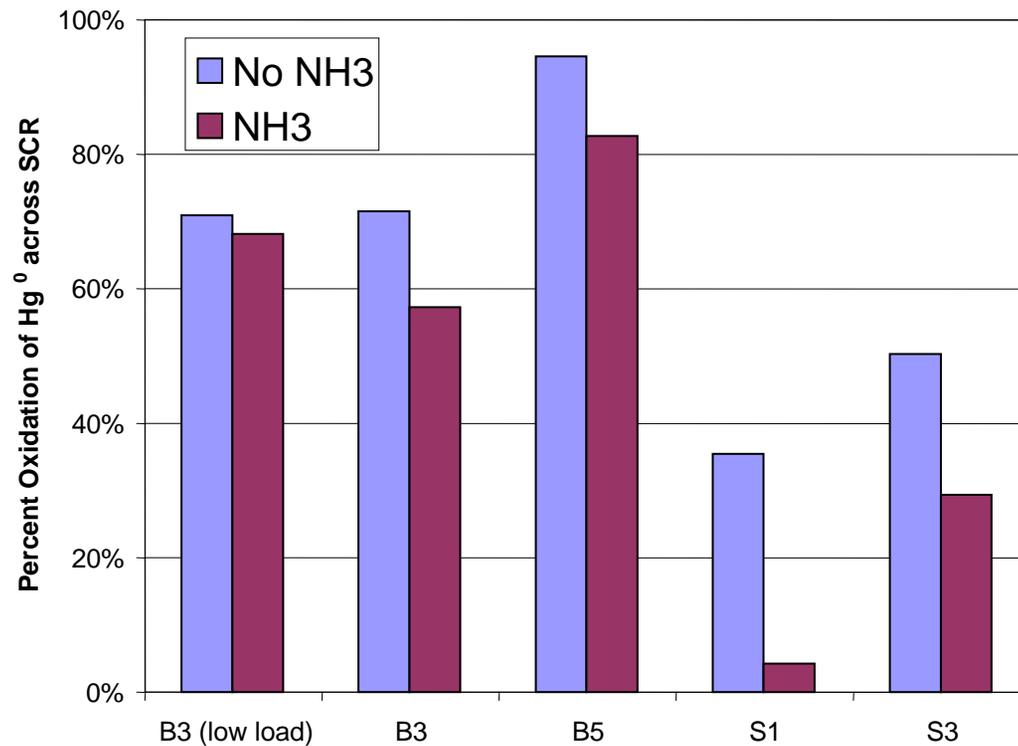


# Outline

- Problem Statement/Objectives
- Measurement Campaign
- Mechanisms
  - Review of lab, pilot and full-scale data
  - Suggested mechanisms and critical parameters
  - Preliminary model for oxidation
- Conclusions and Recommendations
  - Prediction of mercury speciation across SCRs
  - Recommendations for additional testing



# Oxidation Across Full-Scale SCRs



- Full-scale data
- Large variation in observed oxidation
- What is it about PRB coals that results in low oxidation?

➤ Subbituminous (S1) vs. bituminous



# Project Organization

- Slipstream reactor built under catalyst deactivation program (DOE- NETL)
- Mercury testing carried out under separate program (DOE – NETL)
- Additional support from EPRI and Argillon GmbH
- Field test support from AEP

# Project Team

REI: Planning/analysis, slipstream reactor operation

- Connie Senior, Temi Linjewile, Darren Shino, Dave Swensen

URS: Mercury measurement and analysis

- Carl Richardson, Mandi Richardson, Tom Mahalek

AEP: Field test support and program review

- Steve Pfeister, Steve Batie
- Gary Spitznogle, Aimee Toole

Program review

- José Figueroa, Bruce Lani, Lynn Brickett (DOE-NETL)
- Chuck Dene (EPRI)
- Jeanette Bock (Argillon GmbH)



# Project Objectives

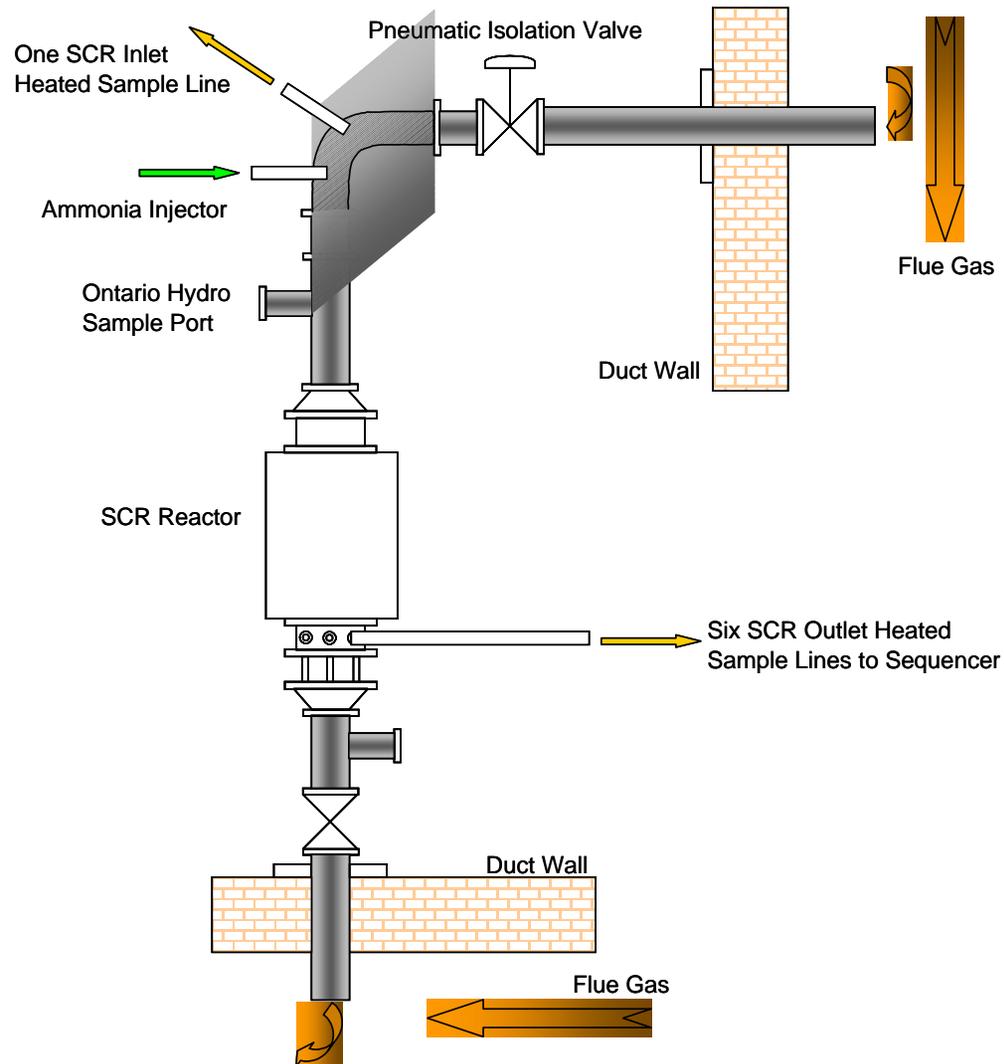
- Gather data on the behavior of mercury across SCR catalysts
  - Measurements at power plant burning blend of bituminous, subbituminous coals
  - Slipstream reactor with six catalysts
    - One blank honeycomb
    - Three commercial honeycomb catalysts
    - Two commercial plate catalysts
- Analysis of other data (lab, pilot, full-scale)
- Simple model for predicting Hg speciation leaving SCRs



# Slipstream Reactor

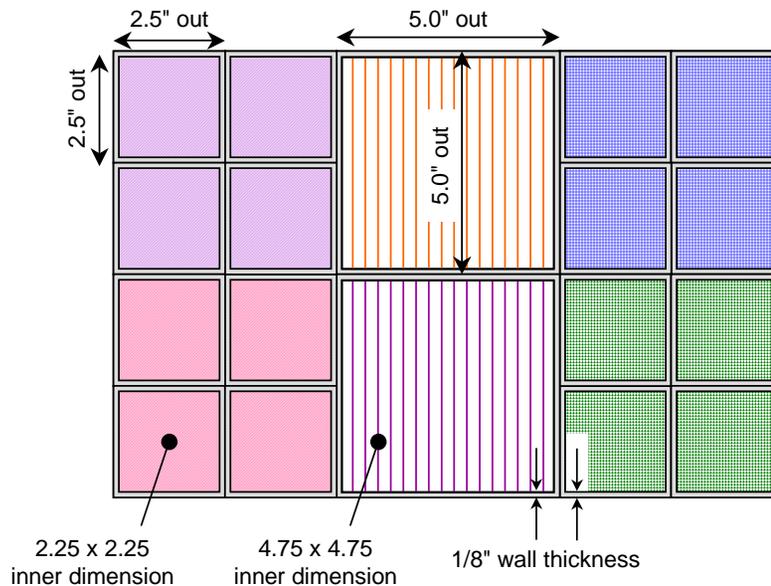
- Slipstream reactor built under catalyst deactivation program (DOE- NETL)
- Mercury testing carried out under separate program (DOE – NETL)
- Additional support from EPRI and Argillon GmbH
- Field test support from AEP

# Multi-catalyst Slipstream Reactor



# Catalyst Dimensions

Chamber:	1 (Blank)	2	3	4	6	5
Catalyst type:	Monolith	Monolith	Plate	Plate	Monolith	Monolith
Chamber porosity:	58.7%	70.0%	85.0%	86.9%	70.0%	68.3%
Length of catalyst in chamber (inch):	24.40	21.50	39.25	43.25	20.06	19.75



- Five commercial catalysts from four manufacturers
- One blank cordierite honeycomb

# Testing Summary

- AEP Rockport:
  - Two 1300 MW<sub>e</sub> B&W opposed-wall, supercritical boilers
  - Testing on Unit 1 across air preheater
  - Burn a subbituminous-bituminous blend
- Two test series (March and August, 2003)
- Measurements
  - Coal, economizer ash, ESP ash composition
  - Ontario Hydro measurements at inlet to slipstream
  - SCEM measurements at inlet/outlet of catalyst chambers
  - NO<sub>x</sub> and O<sub>2</sub> at inlet/outlet of catalyst chambers
  - Carbon trap and acid gas measurement at inlet of catalyst

# Coal Properties

Date	3/28/03	4/1/03	4/2/03
<b>(As Received):</b>			
Carbon	50.67	51.80	51.75
Hydrogen	3.51	3.64	3.46
Oxygen	10.89	11.04	11.18
Nitrogen	0.76	0.78	0.75
Sulfur	0.32	0.30	0.37
Ash	5.12	5.99	6.10
Moisture	28.74	26.45	26.39
HHV	8,723	8,989	8,989
<b>(Dry Basis):</b>			
Hg, ug/g	0.088	0.118	0.091
Cl, ug/g	120	160	200
SO <sub>2</sub> , lb/MBtu	0.74	0.67	0.82
Hg, lb/TBtu	10.10	13.13	10.13
Hg, ug/dnm <sup>3</sup> (5%O <sub>2</sub> )	8.02	10.82	8.46

- Coal blend – 87% subbituminous
  - Higher Cl than typical subbituminous
- 8-10 μg/dnm<sup>3</sup> Hg (gas-phase equivalent)
- Ash contains ~6 wt% Fe<sub>2</sub>O<sub>3</sub>, ~16 wt% CaO

# Flue Gas Composition

(Inlet to Slipstream Reactor)

## Calculated from coal:

HCl 6-12 ppm (5% O<sub>2</sub>)

SO<sub>2</sub> 275-325 ppm (5% O<sub>2</sub>)

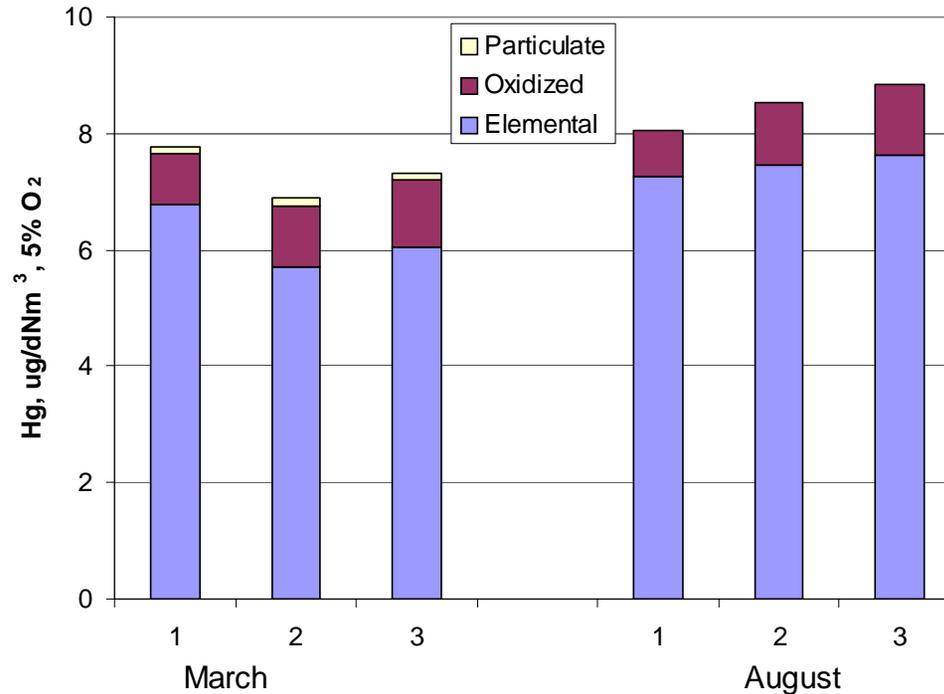
## Measured:

NO<sub>x</sub> 300-350 ppm (5% O<sub>2</sub>)

Total Hg 7-9 ug/dNm<sup>3</sup> (5% O<sub>2</sub>)



# Ontario Hydro Data



- Hg concentration in OH ash higher than in ESP fly ash BUT fraction of Hg in particulate very low
- 80-90% elemental Hg at inlet to catalysts

# Hg and Cl in ash

Date	LOI, wt%	Hg, ug/g	Cl, ug/g
<b>Economizer</b>			
3/28/03	0.08%	0.005	29
8/11/03	0.00%	0.005	<5
8/15/03	0.00%	0.000	<5
<b>ESP Hopper</b>			
3/28/03	0.31%	0.081	20
3/31/03	0.37%	0.118	25
4/1/03	0.31%	0.127	24
4/2/03	0.34%	0.101	27
8/7/03	0.06%	0.034	21
8/11/03	0.30%	0.050	21
8/15/03	0.13%	0.055	23

- Economizer ash has 10-20 times less Hg than ESP ash
- Little Cl on economizer ash
  - Expect most Cl in gas phase at inlet to slipstream
  - Not consistent with gas sampling

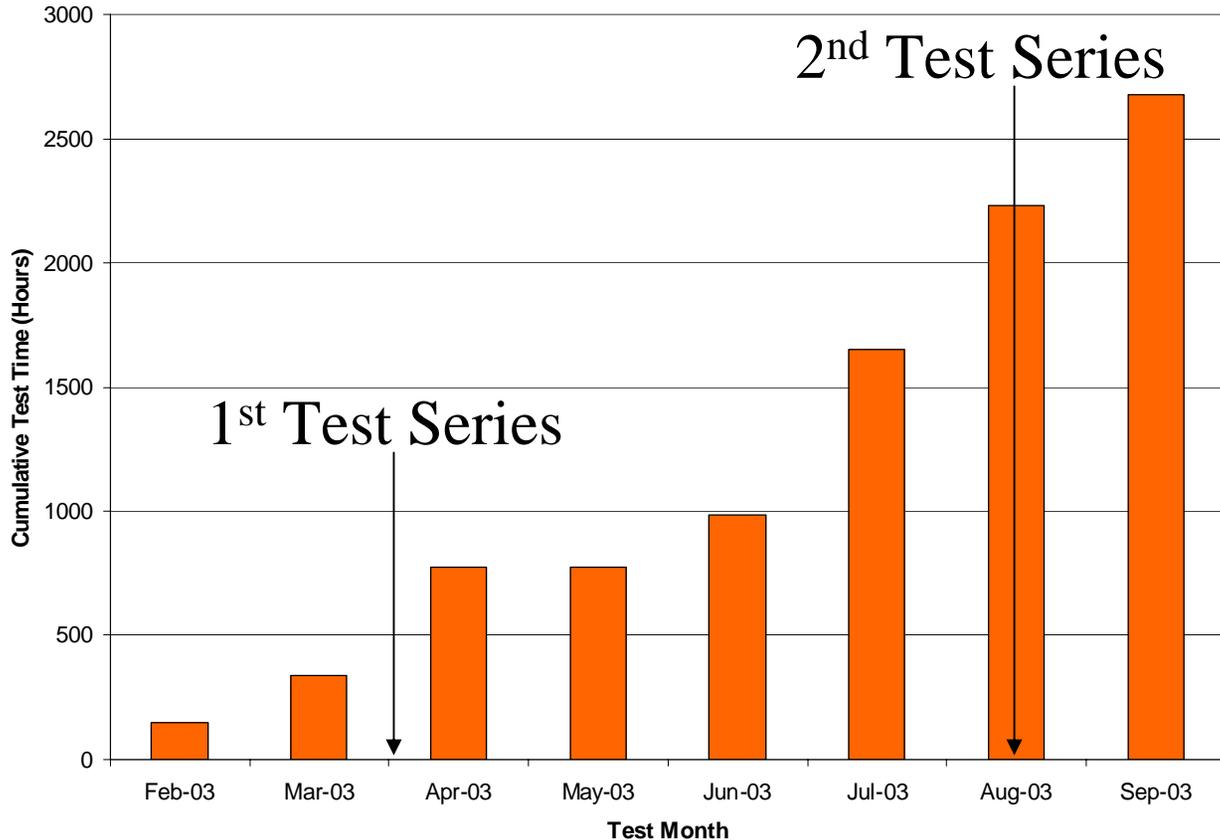
# Hg and Cl in ash

Date	LOI, wt%	Hg, ug/g	Cl, ug/g
<b>Economizer</b>			
3/28/03	0.08%	0.005	29
8/11/03	0.00%	0.005	<5
8/15/03	0.00%	0.000	<5
<b>ESP Hopper</b>			
3/28/03	0.31%	0.081	20
3/31/03	0.37%	0.118	25
4/1/03	0.31%	0.127	24
4/2/03	0.34%	0.101	27
8/7/03	0.06%	0.034	21
8/11/03	0.30%	0.050	21
8/15/03	0.13%	0.055	23

- Low LOI in ESP ash
  - Predominantly PRB
- ESP ash has very little Hg, ~0.5% of coal Hg (consistent with OH data)
- Cl content of ESP ash low ~1.5% of coal



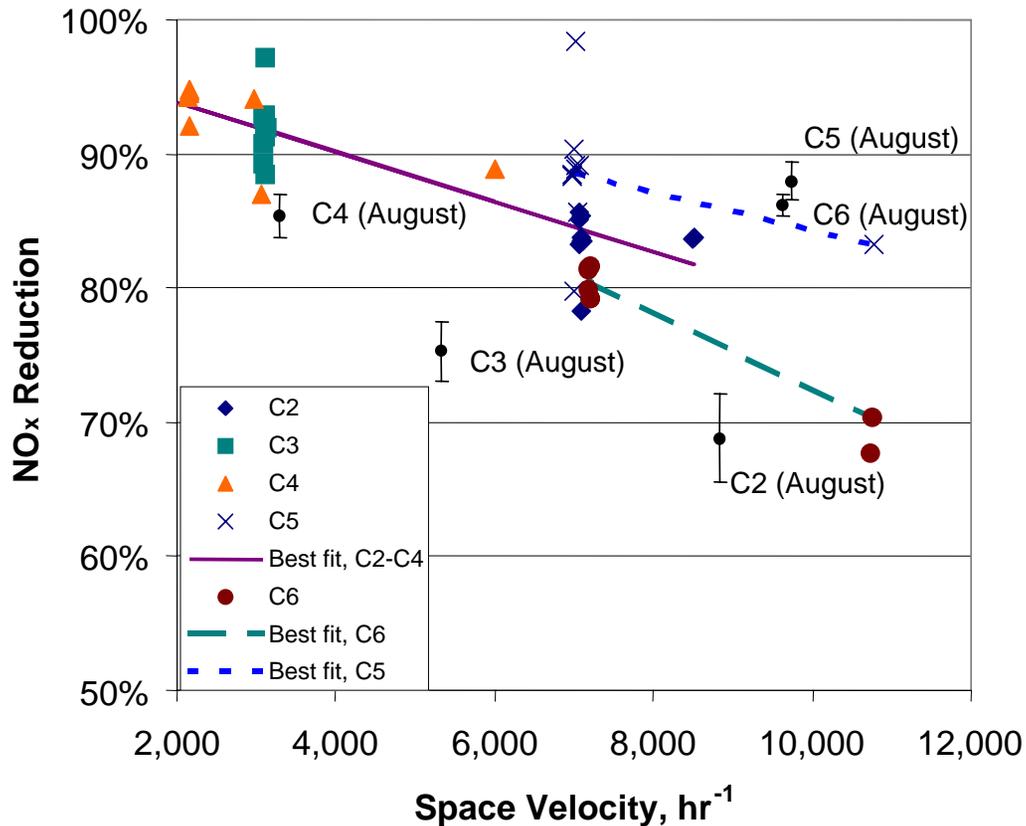
# Operating Experience



~2700 hours of cumulative flue gas exposure



# Change in $\text{NO}_x$ Activity

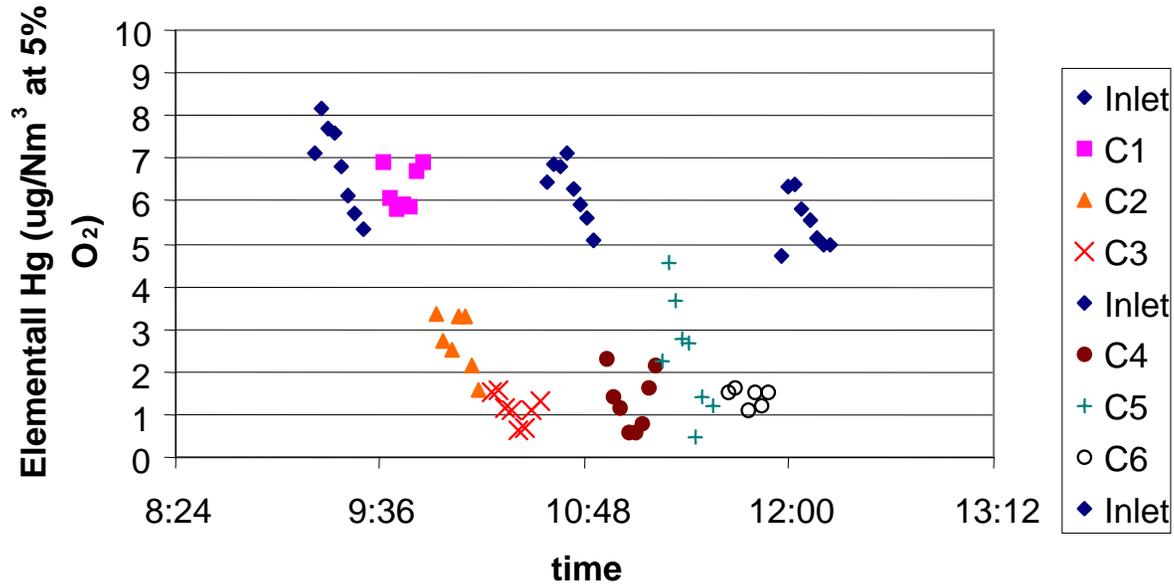


Commercial catalysts: 85-90%  $\text{NO}_x$  reduction at full-scale space velocities

Activity decreased for catalysts C2, C3, C4 (corrected for temperature)

# Online Hg Measurement

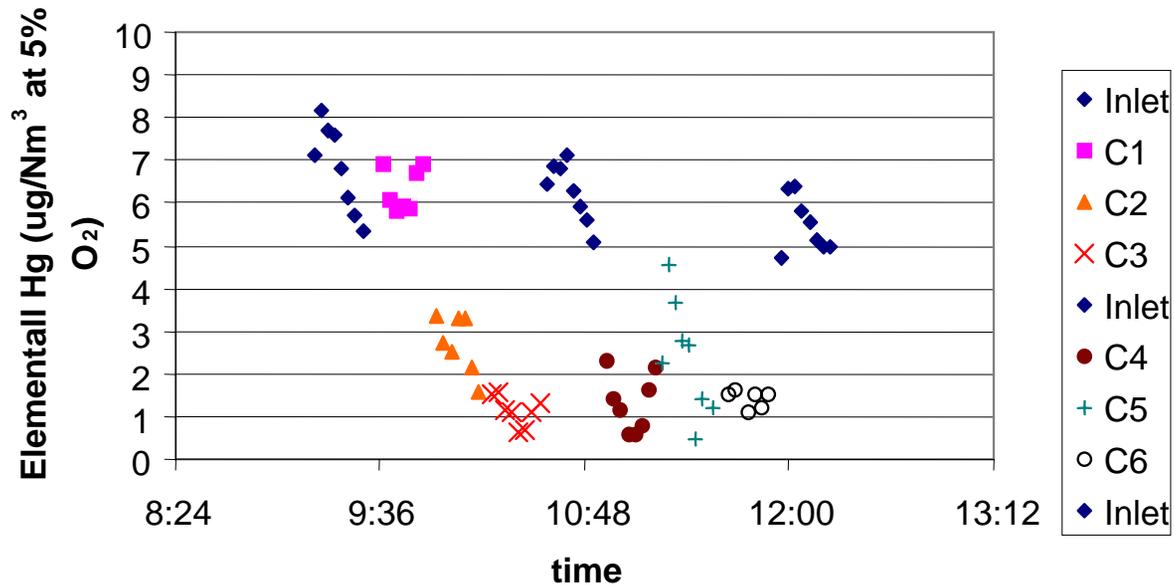
02-April-2003: without ammonia



- Example of Hg measurement vs. time
- Switch between inlet and outlet of catalysts

# Online Hg Measurement

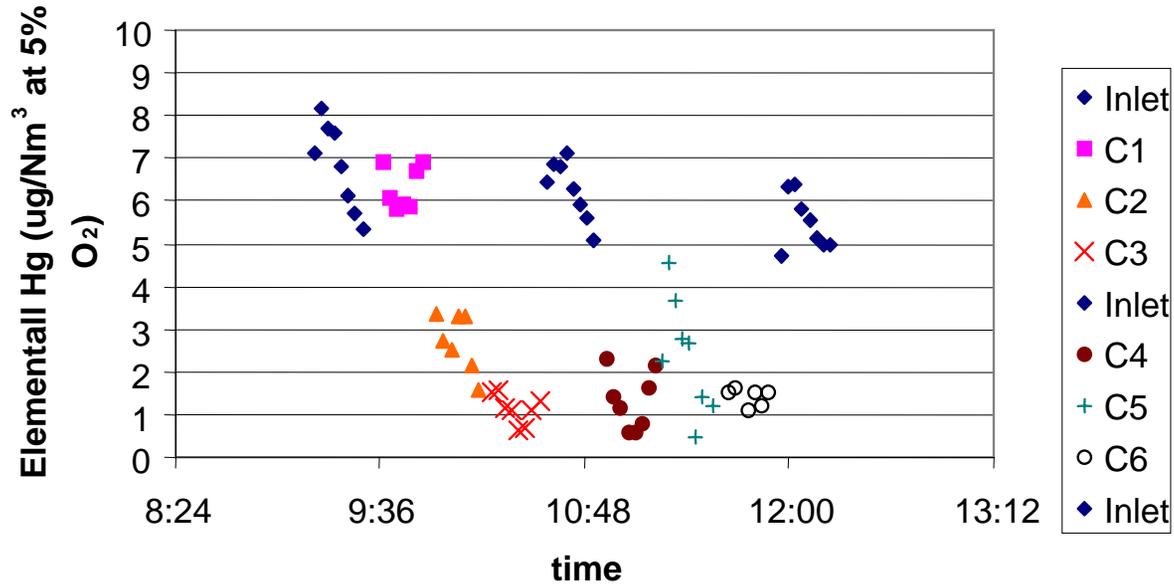
02-April-2003: without ammonia



➤ Switching channels: transients

# Online Hg Measurement

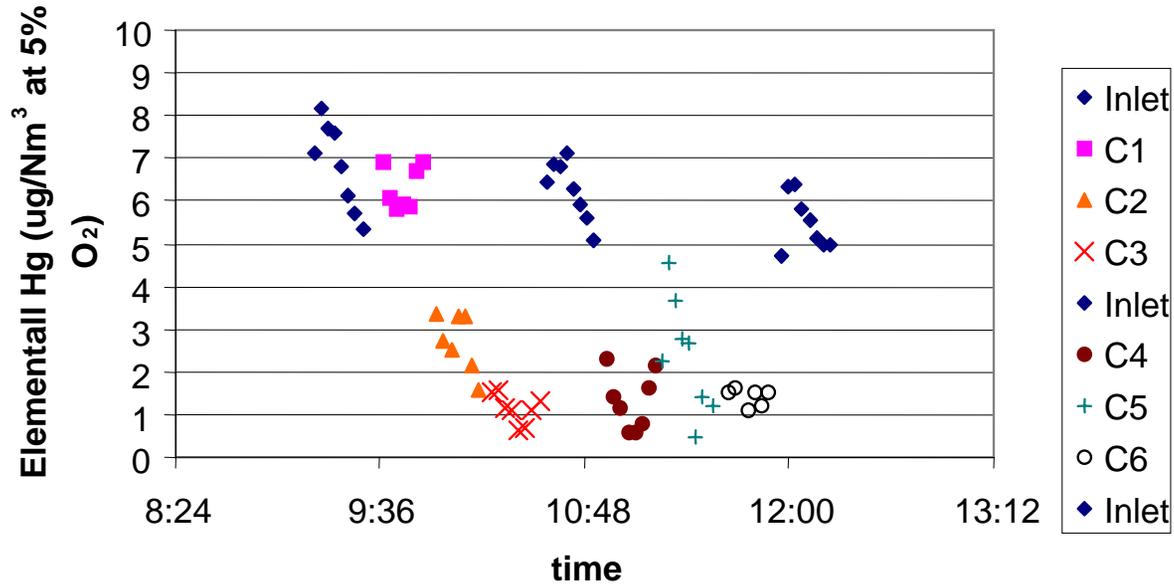
02-April-2003: without ammonia



- Inlet and blank monolith showed same level of oxidation

# Online Hg Measurement

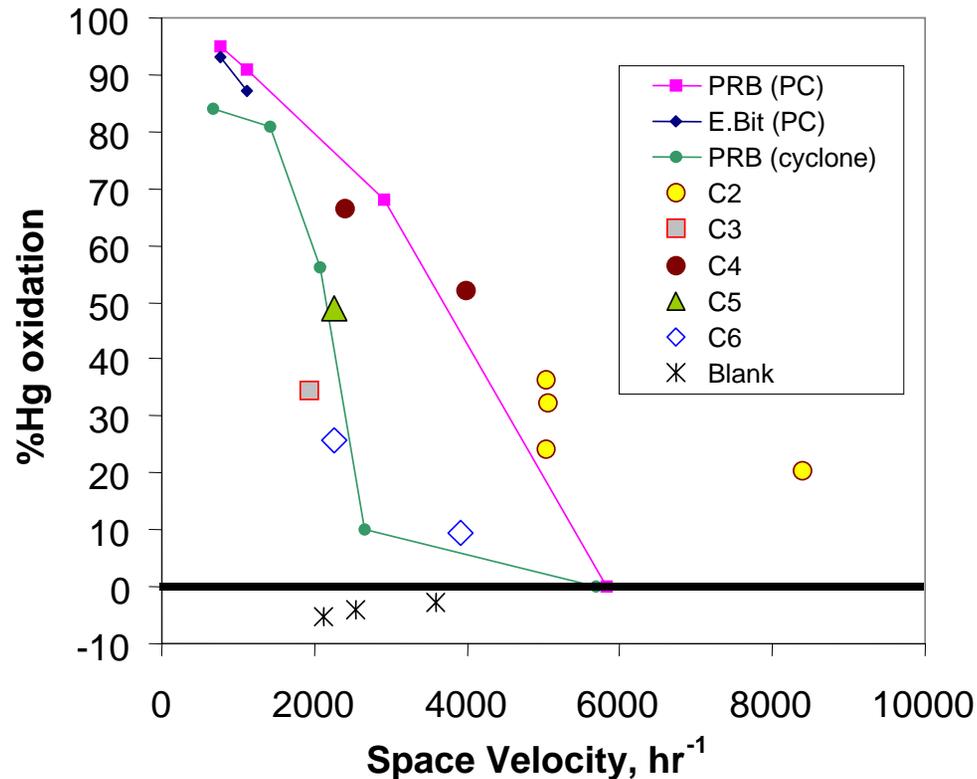
02-April-2003: without ammonia



➤ Catalysts showed oxidation relative to inlet/blank

# Oxidation of $\text{Hg}^0$ Across Catalyst

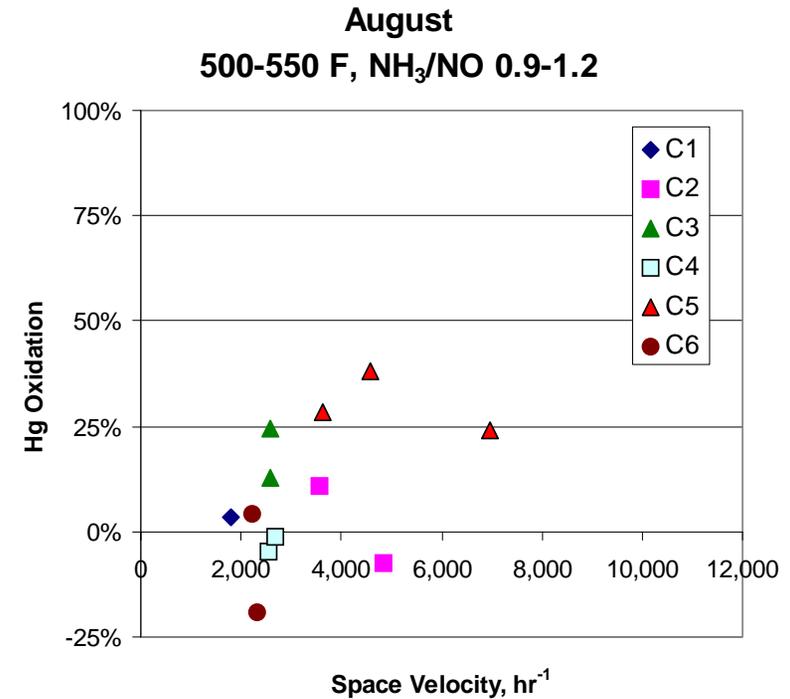
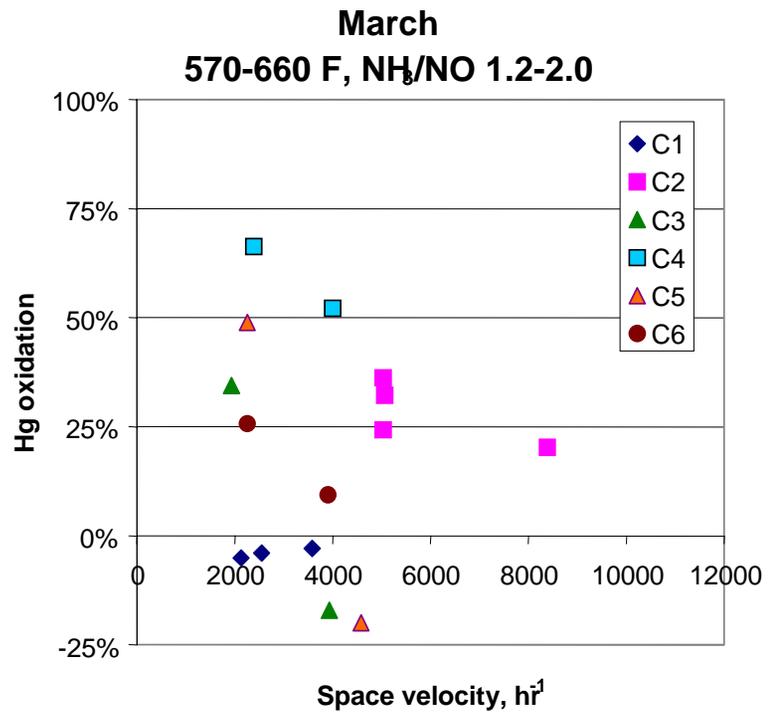
## Comparison with Other Pilot-Scale Data



- Blank (C1) does not show oxidation
- March data in same range as previous pilot-scale data on flue gas (slipstream)
  - Richardson, et al. 2002

# Oxidation of $\text{Hg}^0$ Across Catalyst

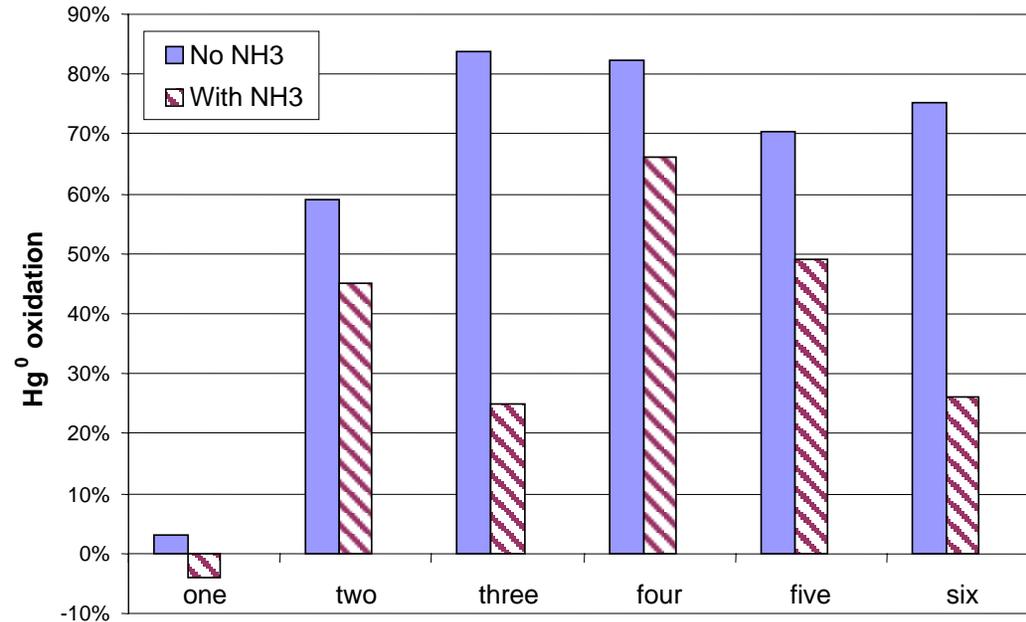
## Comparison of March and August



- Blank (C1) does not show oxidation
- August data (lower temperature) show some decrease in oxidation

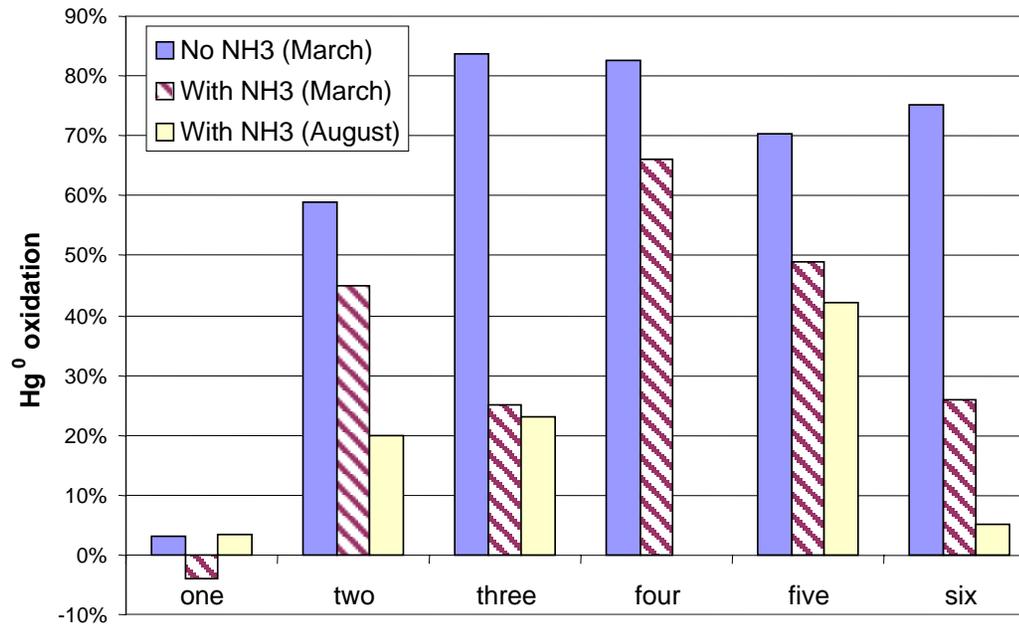


# Effect of Ammonia



- No ammonia vs. excess ammonia ( $\text{NH}_3/\text{NO} \sim 2$ )
- March:
  - SV interpolated to  $\sim 2,500 \text{ hr}^{-1}$
  - $T \sim 610\text{-}630 \text{ F}$
- Oxidation decreased in presence of ammonia
- No effect of blank monolith (C1)

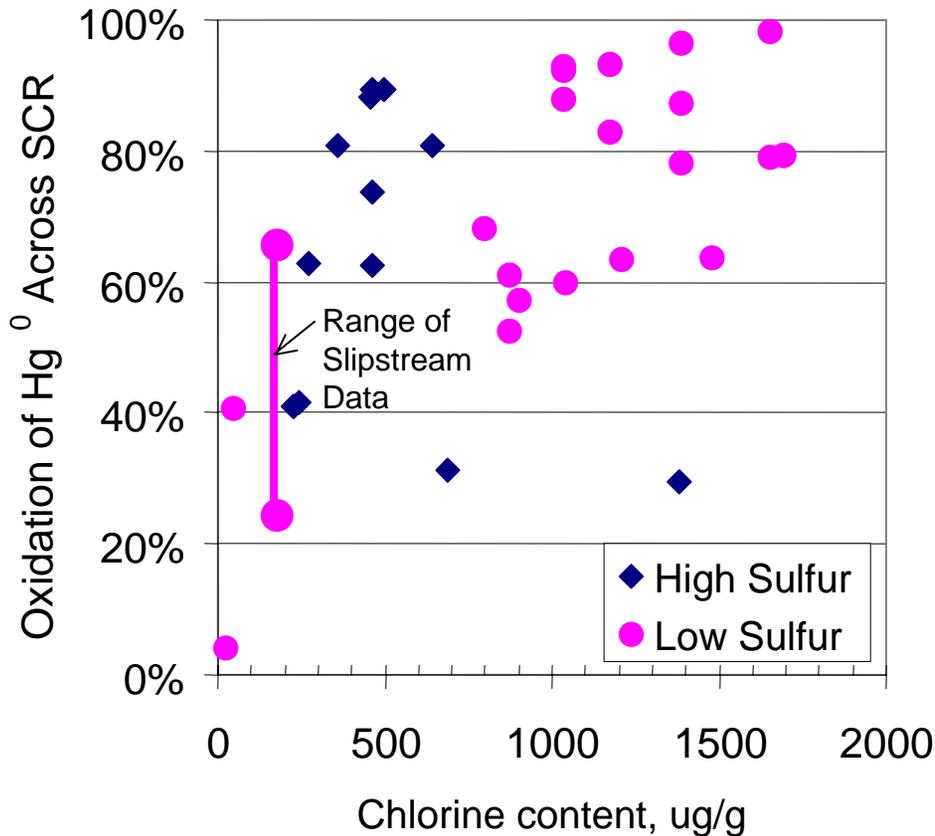
# Comparison of March and August



- August:
  - SV interpolated to ~ 2,500 hr<sup>-1</sup>
  - T ~ 500-550 F
  - NH<sub>3</sub>/NO ~ 0.9-1.2
- Two catalysts (C3 and C5 ) show little change March -> August
- Other catalysts had decrease in oxidation
- No effect of blank monolith (C1)



# Comparison with Full-Scale Data



- Slipstream data for blend show oxidation in range of low-chlorine coals (full-scale data)
- Lack of full-scale data for < 500 ug/g Cl
- Full-scale data: 10 boilers
- Scatter in full-scale data



# Conclusions: Multicatalyst Slipstream Reactor

- Blank monolith showed no oxidation
- Differences in oxidation among catalysts
- Slipstream data for PRB-bituminous blend show oxidation in range of low-chlorine coals (from full-scale data)
  - Coal chlorine content important for  $\text{Hg}^0$  oxidation
- Oxidation of mercury increased without ammonia present
  - Observed in other pilot-scale studies

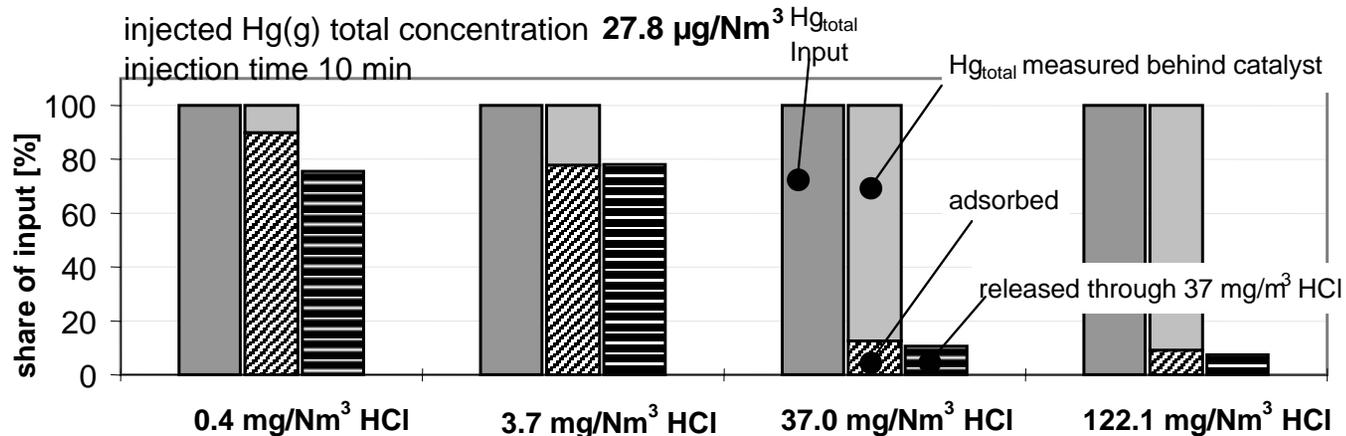


# Review of Lab, Pilot and Full-Scale Data

- Laboratory data
  - Effects of temperature, ammonia, HCl, space velocity
  - Adsorption of  $\text{Hg}^0$
- Pilot data
  - Effects of temperature, ammonia, space velocity, flue gas
  - Transients

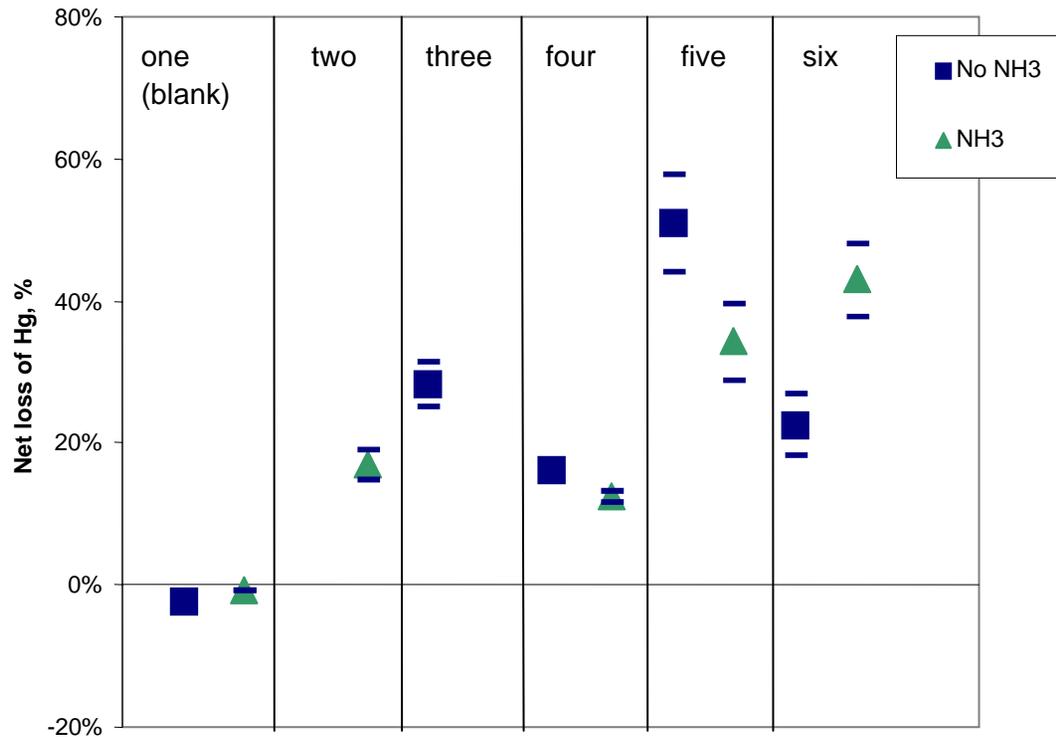
# SCR Catalysts Adsorb $\text{Hg}^0$

- Lab data from Hocquel et al.



- Net adsorption of  $\text{Hg}^0$  by catalyst in ten-minute experiments
- Amount of  $\text{Hg}^0$  adsorbed decreased with increasing HCl concentration
- *HCl interferes with  $\text{Hg}^0$  adsorption?*

# Adsorption of Hg Pilot-Scale Data

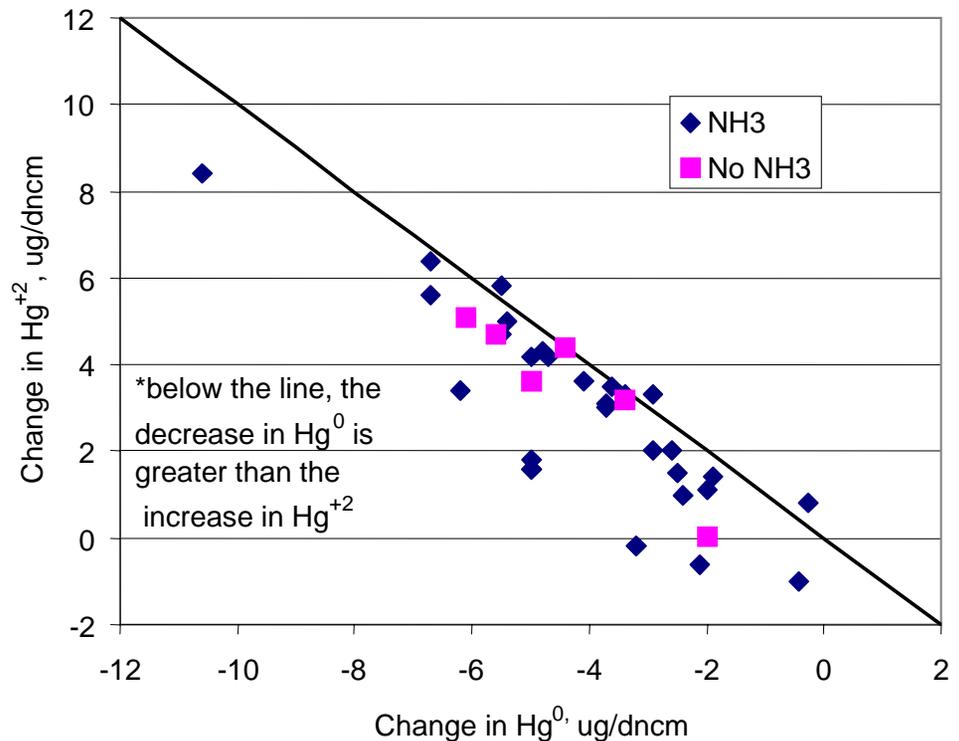


- Rockport data: loss of total Hg across catalysts observed in April, not in August
- No apparent loss across blank monolith

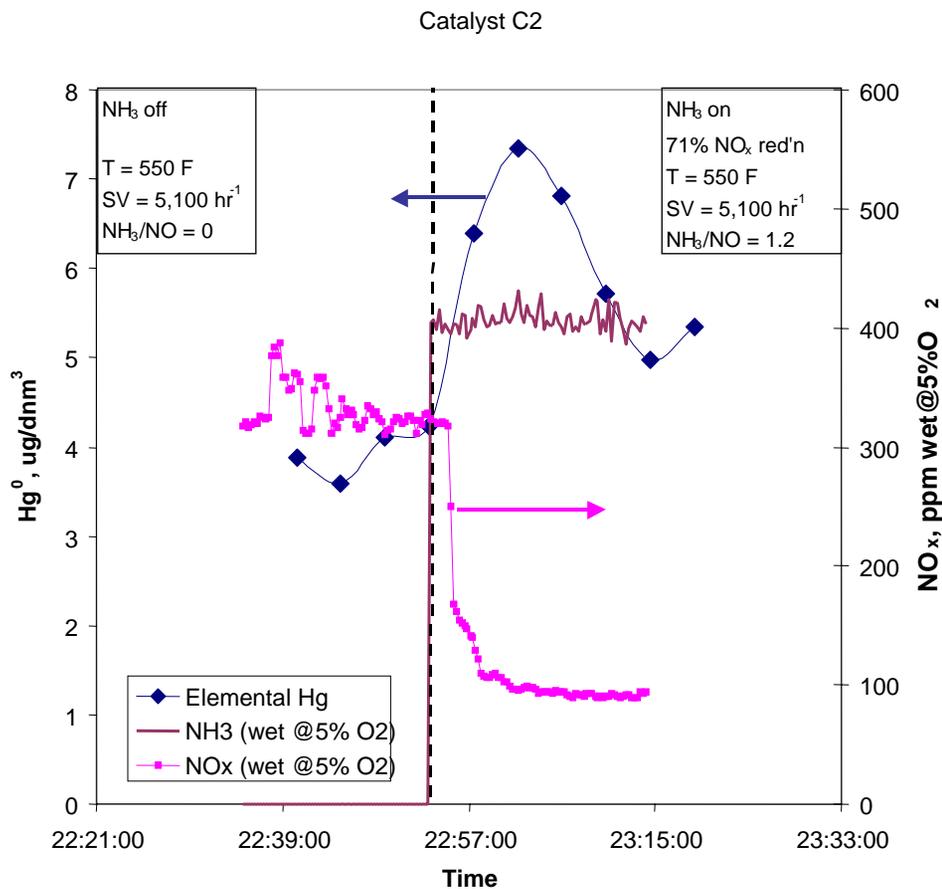
# Adsorption of Hg

## Full-Scale Data

- Adsorption of Hg observed in full-scale measurements?
- Yes, in some cases loss of  $\text{Hg}^0$  higher than gain of  $\text{Hg}^{+2}$  across SCR

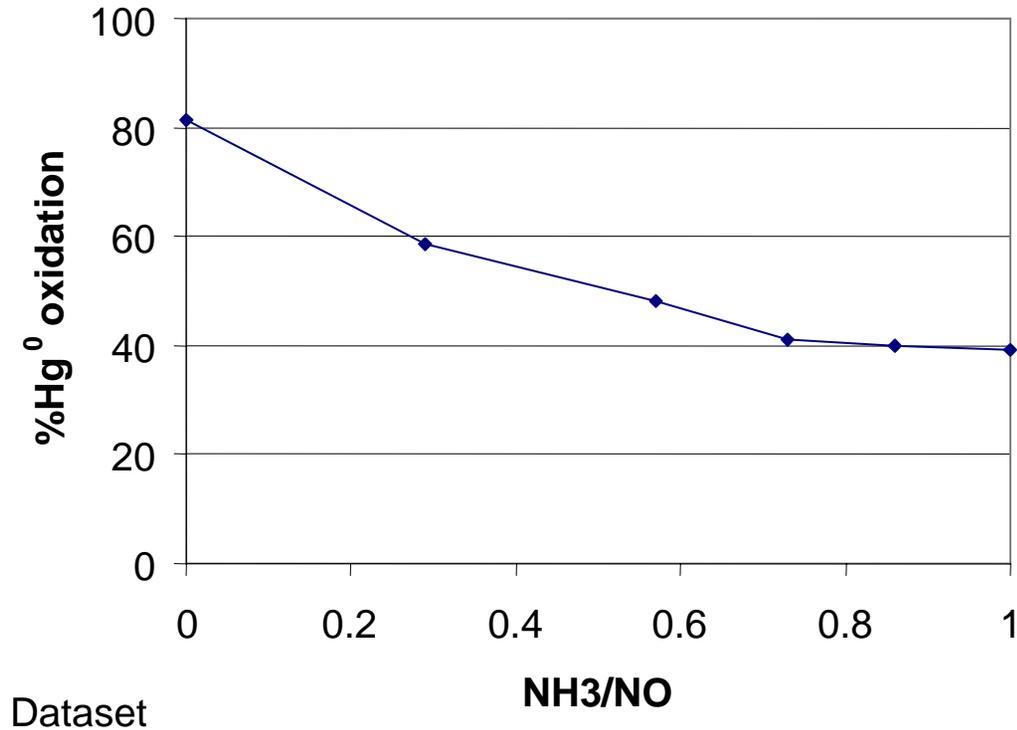


# Ammonia Affects $\text{Hg}^0$ Adsorption



- Transient from Rockport
- Turning ammonia on causes spike in  $\text{Hg}^0$
- *NH<sub>3</sub> interferes with  $\text{Hg}^0$  adsorption?*

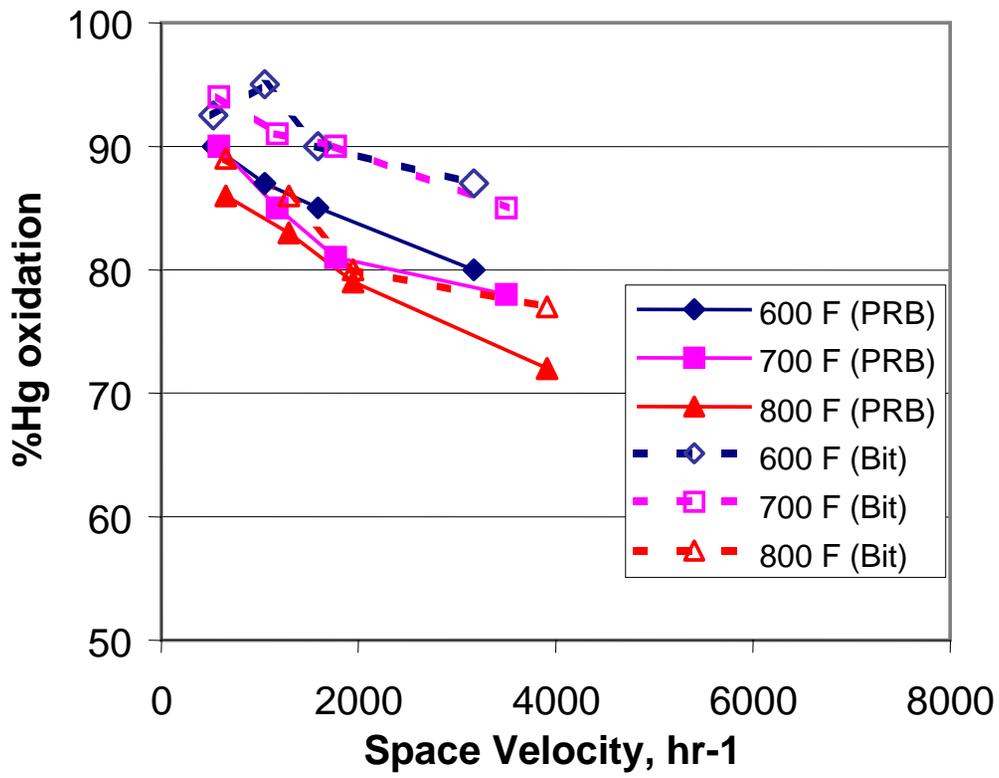
# Ammonia Affects Oxidation



- Slipstream data (Richardson et al.)
- Pilot-scale SCR with PRB flue gas
- Ammonia decreases Hg<sup>0</sup> oxidation



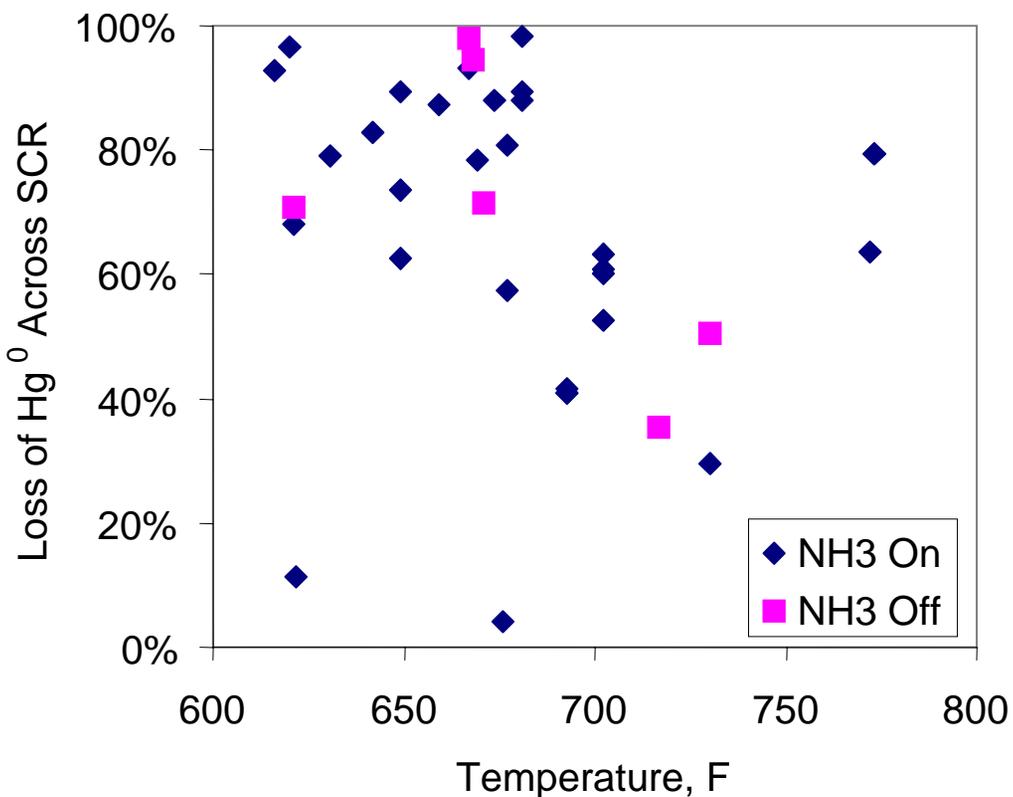
# Temperature Affects Oxidation Pilot-Scale



- › Pilot-scale SCR (Richardson et al.)
- › Oxidation decreases when temperature increases



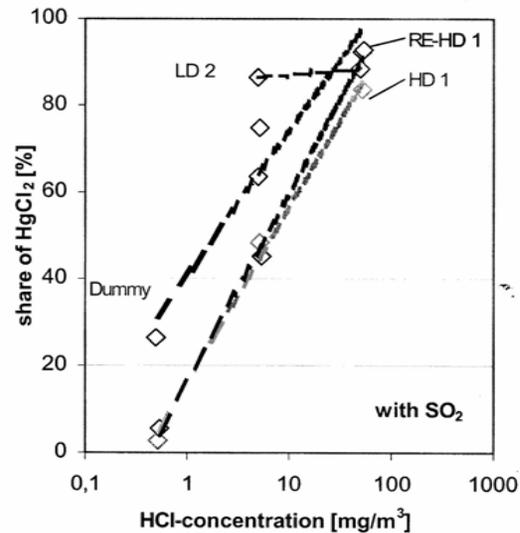
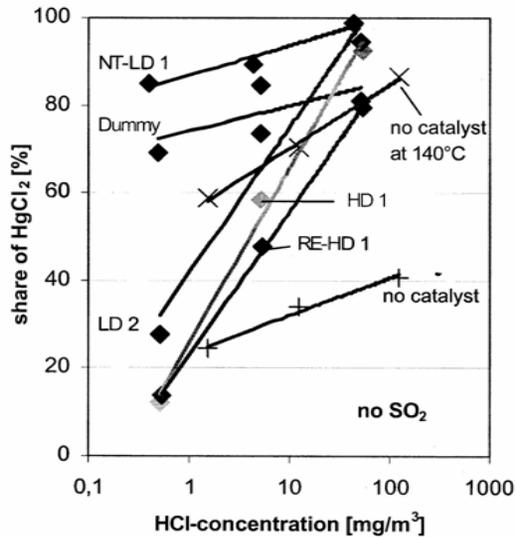
# Temperature Affects Oxidation Full-Scale



- Full-scale data (10 boilers)
- Oxidation decreases when temperature increases
- Confirms pilot-scale data
- Much scatter

# HCl Promotes Hg<sup>0</sup> Oxidation

- Lab data from Hocquel et al.

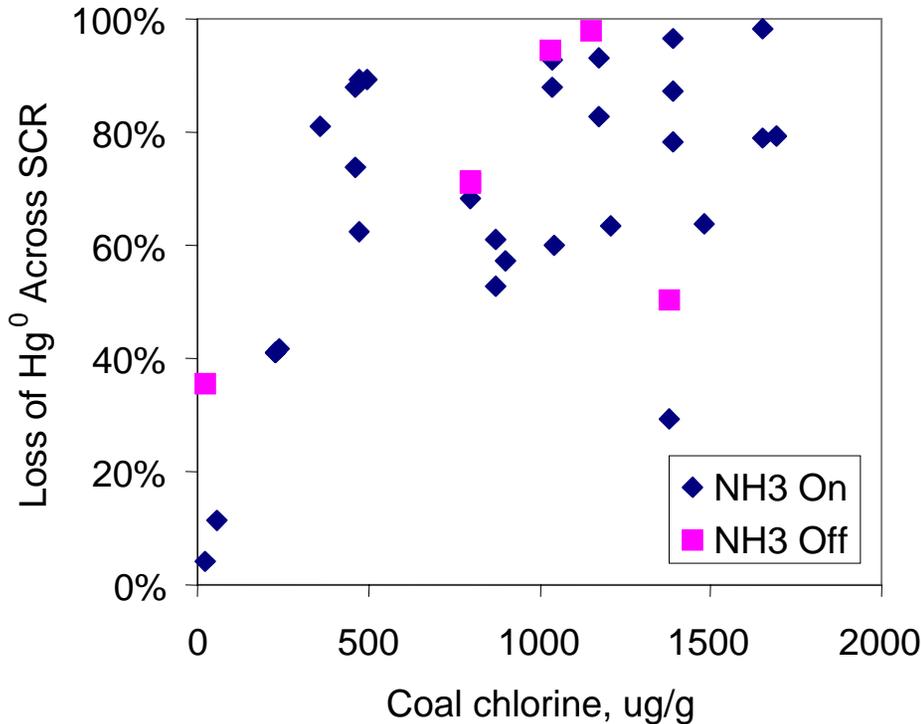


- Increasing HCl content of simulated flue gas increases oxidation
- Little effect of SO<sub>2</sub>
- *HCl reacts with adsorbed Hg<sup>0</sup> or is itself adsorbed?*



# HCl Promotes Hg<sup>0</sup> Oxidation

## ➤ Full-scale data



➤ Influence of coal chlorine (HCl)

➤ Other factors:  
– *Space velocity*  
– *Temperature*  
– *Ammonia*



# Suggested Mechanisms and Critical Parameters

➤ What does a catalyst do?

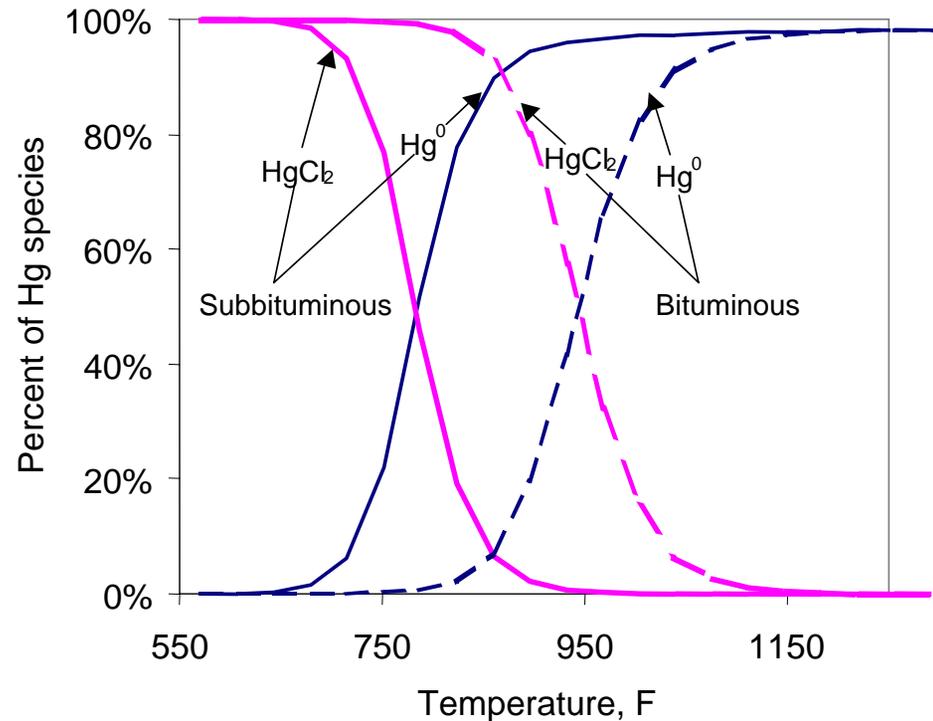
*Moves a chemical reaction toward equilibrium*

➤ Hypothesis:

*SCR catalysts drive  $Hg^0$  and  $HgCl_2$  to equilibrium values at outlet*

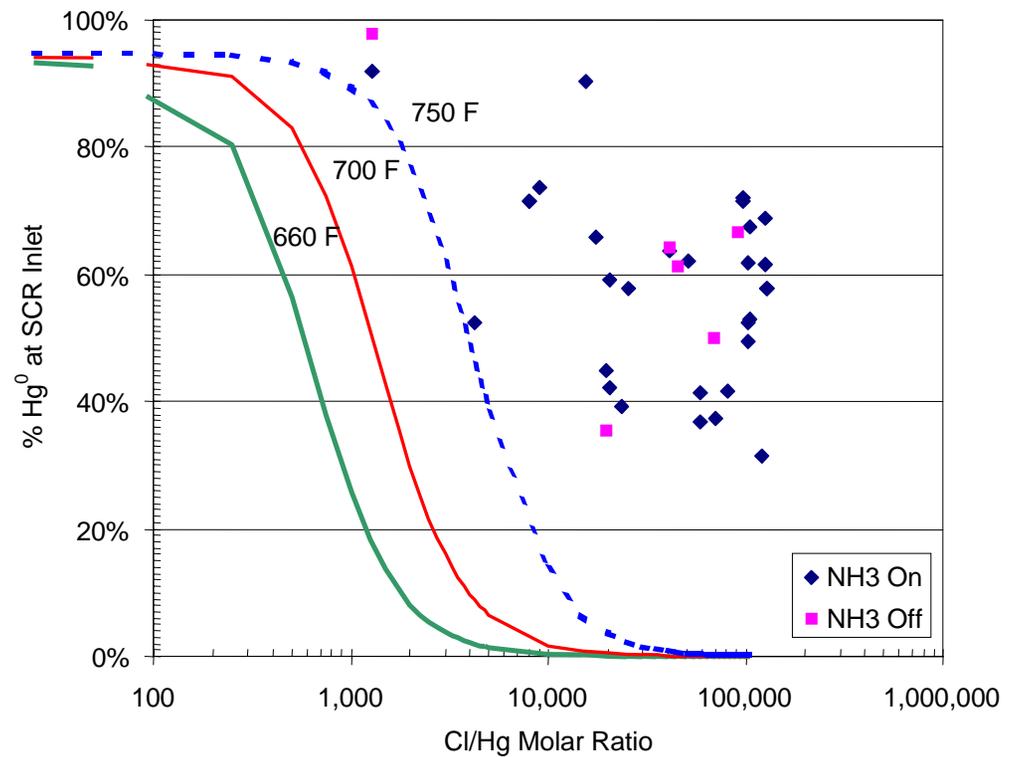
# Equilibrium Calculations

- HSC software used to calculate flue gas equilibrium for typical coal compositions:
  - Bituminous (higher chlorine) all oxidized at SCR temperatures
  - Subbituminous (low chlorine)



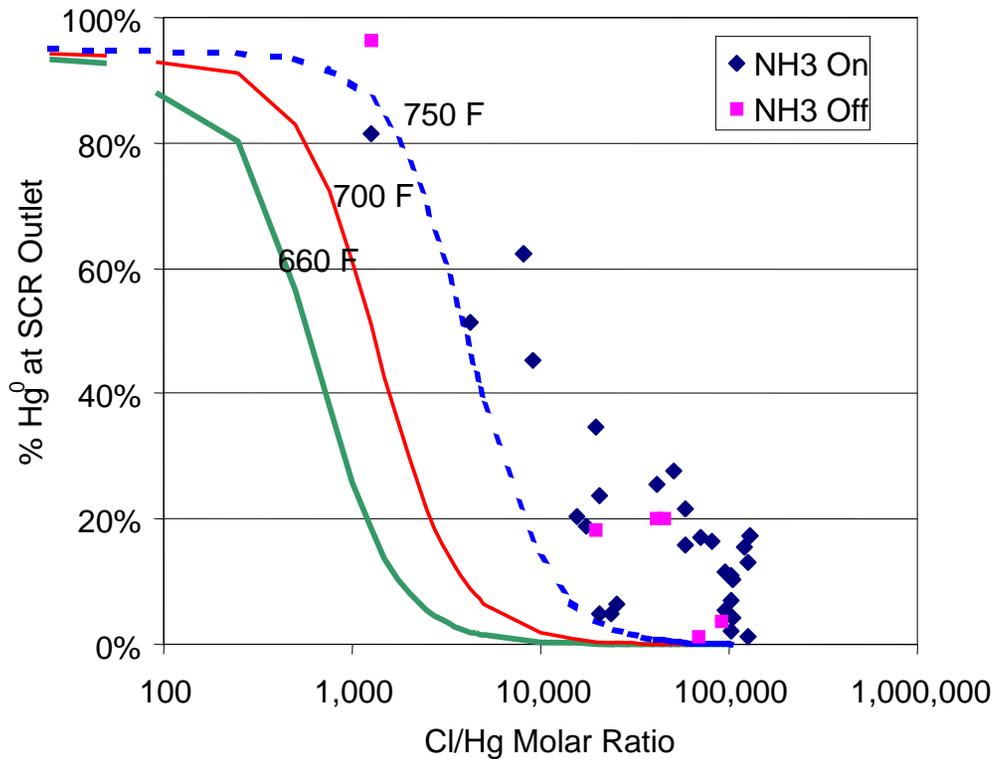
	Subbit.	Bit.
N <sub>2</sub> [vol%]	70.6	75.4
CO <sub>2</sub> [vol%]	13.9	14.6
H <sub>2</sub> O [vol%]	12.3	6.8
O <sub>2</sub> [vol%]	3.0	3.0
SO <sub>2</sub> [ppm]	350	1000
HCl [ppm]	1.75	31
Hg [ppb]	0.2	0.2

# Hg Speciation at SCR Temperatures



Inlet speciation  
far from  
equilibrium  
Expected from  
gas-phase  
kinetic  
calculations

# Hg Speciation at SCR Temperatures



- › Outlet speciation approaches equilibrium
- › Other effects:
  - Ammonia
  - Space velocity
  - Temperature
  - ??

# Conclusions: Mechanisms

- Predicting Hg ***oxidation*** across SCRs requires greater understanding of inlet  $\text{Hg}^0$
- BUT predicting outlet ***speciation*** appears straightforward
- Equilibrium (T, Cl) primary factor for outlet speciation
- Why don't we get to equilibrium?
  - Ammonia, sulfur?, other factors?
- More high-quality lab and pilot-scale data needed

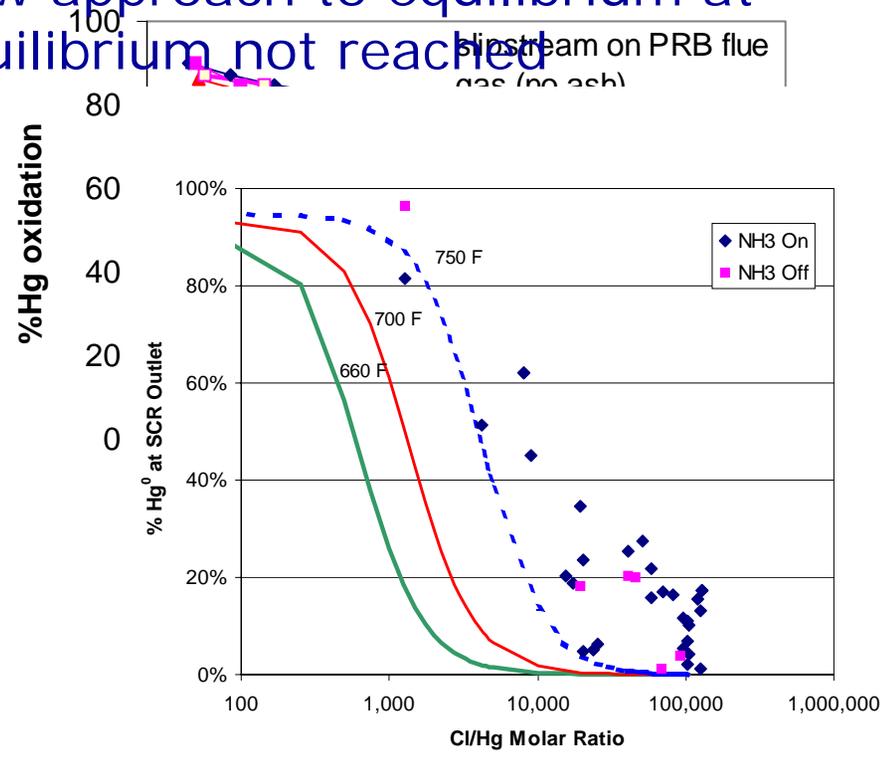
# Kinetic Analysis of Full-Scale Data

## ➤ Why kinetic analysis?

- Full-scale data show less oxidation than pilot-scale data (at similar space velocities)
- Full-scale data show approach to equilibrium at SCR outlet, but equilibrium not reached

## ➤ Approach

- Determine appropriate kinetic model
- Determine kinetic parameters





# Determine Rate Equation

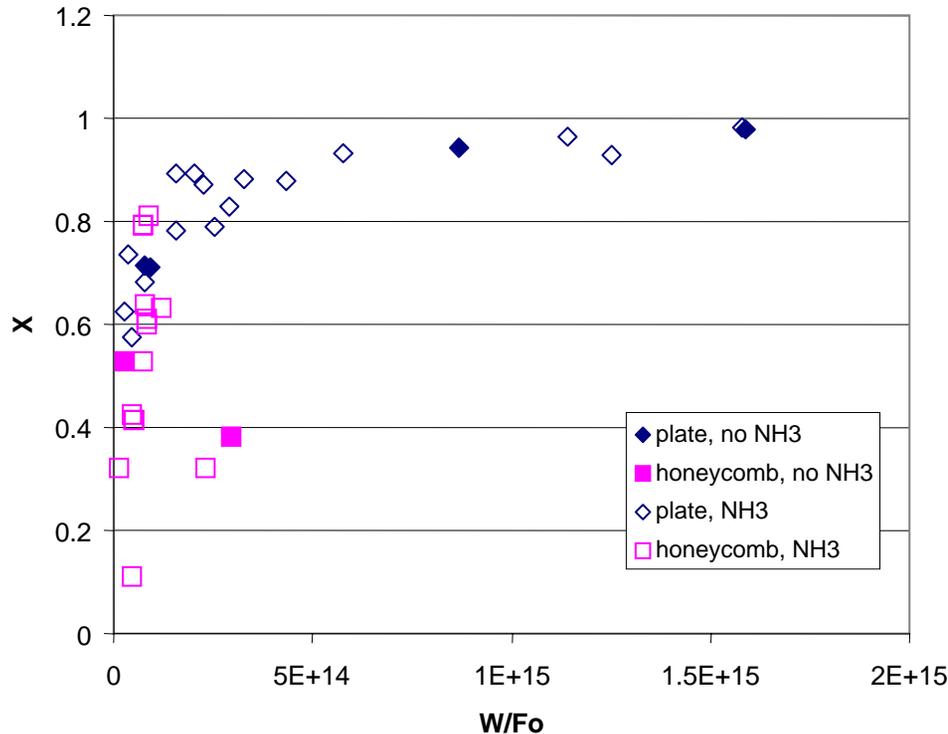
- Full-scale data provide “plug flow” experiments with variation in catalyst volume (space velocity) and inlet Hg concentration
- Integral analysis of rate of Hg oxidation,  $R_{Hg}$

$$\frac{W}{F_0} = \int_0^X \frac{dX}{-R_{Hg}} \quad \left\{ \begin{array}{l} W = \text{weight of catalyst} \\ F_0 = \text{input Hg flow, mol/s} \\ X = \text{conversion of Hg}^0 \\ R_{Hg} = \text{rate of conversion per g of catalyst} \end{array} \right.$$

- Plot  $W/F_0$  versus  $X \Rightarrow \text{slope} = R_{Hg}$

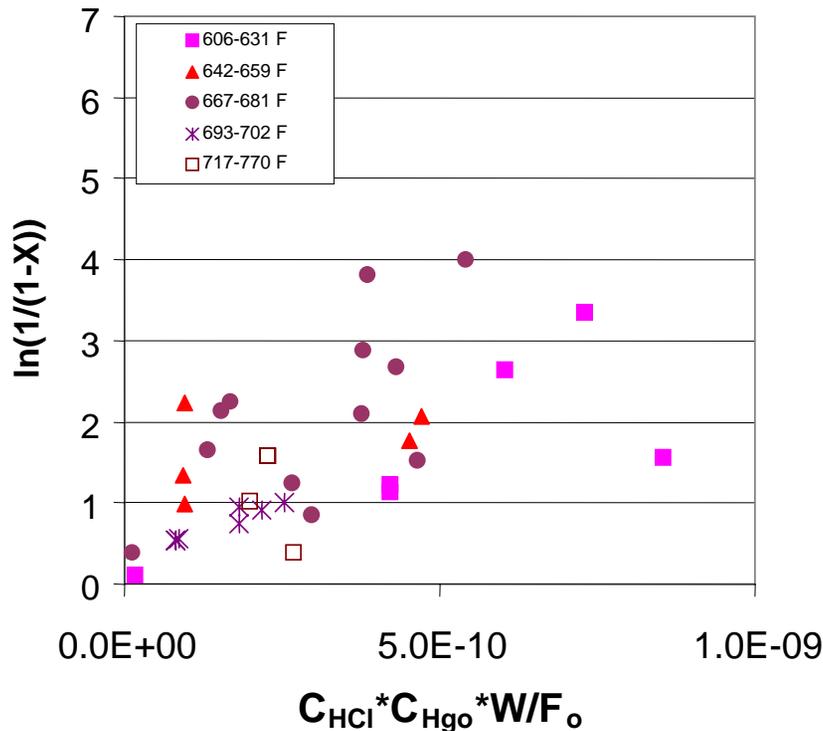


# Approach to Equilibrium



- Concentration expressed as  $(C - C^{eq})$ , where  $C^{eq}$  is the equilibrium concentration of elemental Hg
- HCl concentration may be important:
  - Very low chlorine coals (<100 ug/g) appear to be different
- No differences among catalyst types or ammonia

# Rate Equation



- Proposed rate equation:

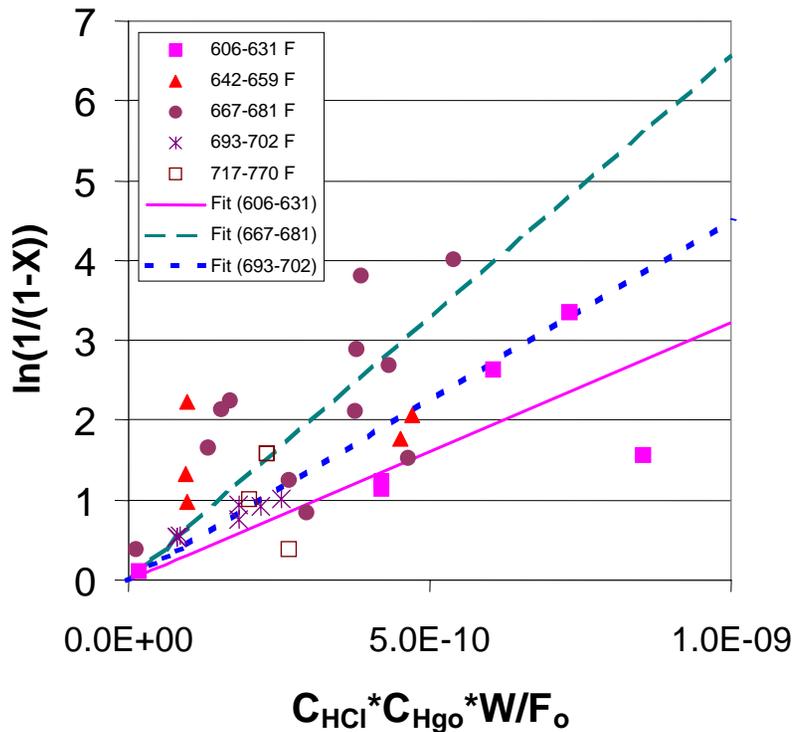
$$-R_{Hg} = k C_{HCl} (C_{Hg} - C_{Hg}^{eq})$$

- Integral form:

$$\frac{W}{F_0} = \frac{1}{k C_{HCl} (C_{Hg} - C_{Hg}^{eq})_0} \ln\left(\frac{1}{1-X}\right)$$

- Rate equation appears to fit full-scale data
- Temperature effects

# Effect of Temperature



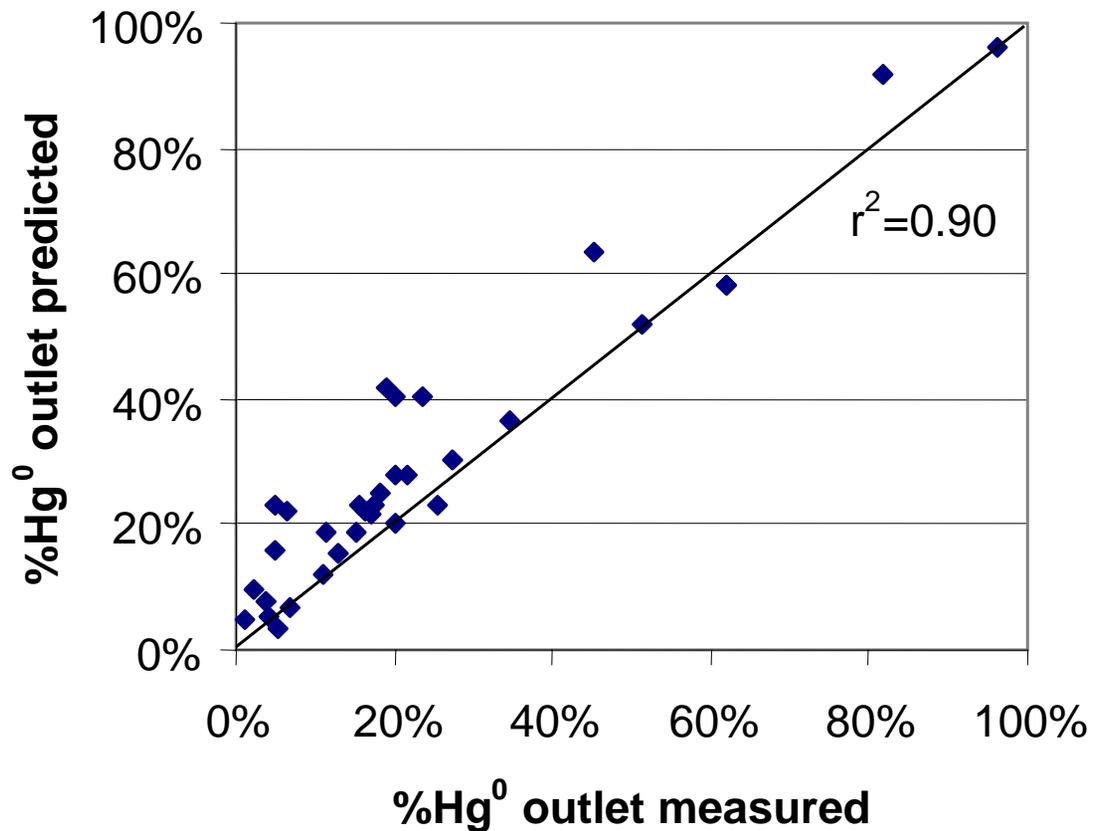
- Temperature affects rate of reaction rate (slope of line)
- More data needed to derive  $k(T)$
- Fit to specific temperature ranges for now

## Rate Constants:

T, °F	606-631	642-659	667-681	693-702	717-770
k	3.22E+09	4.86E+09	6.58E+09	4.50E+09	4.30E+09
$r^2$	0.56	-3.10	0.31	0.51	-0.21

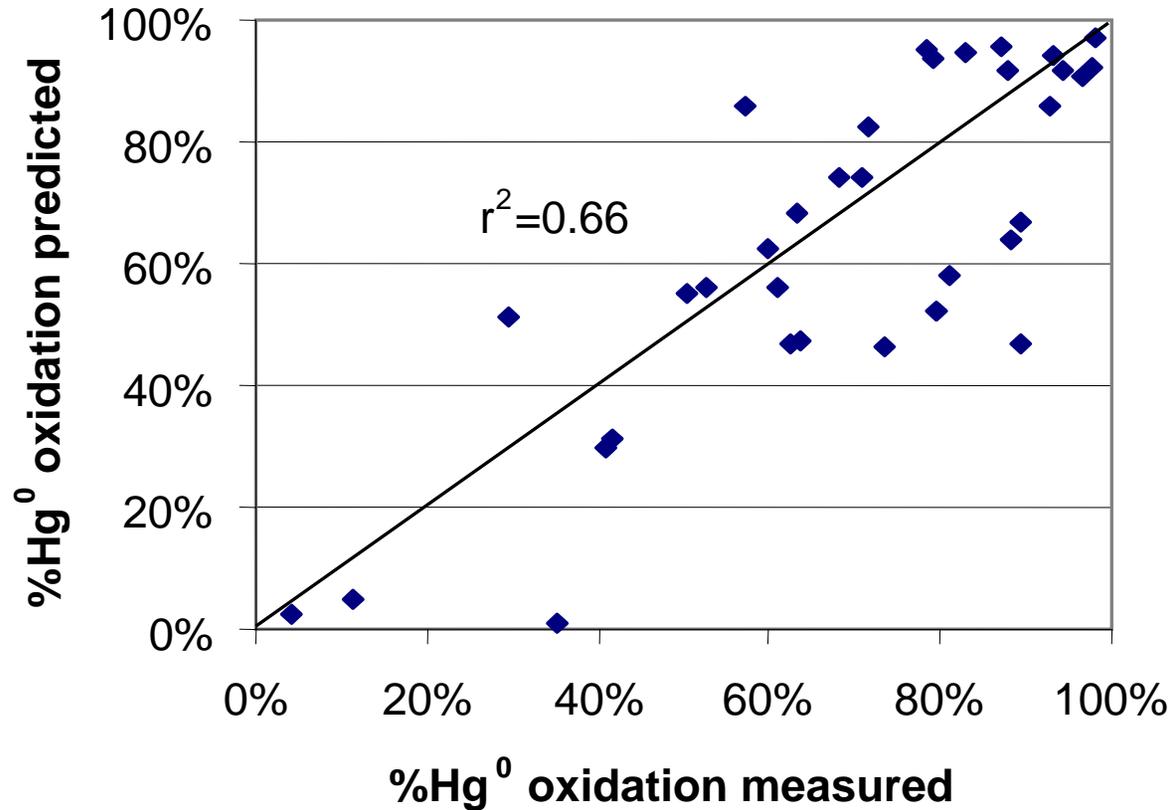


# Fitting Full-Scale Data: Outlet $\text{Hg}^0$ Speciation





# Fitting Full-Scale Data: $\text{Hg}^0$ Oxidation

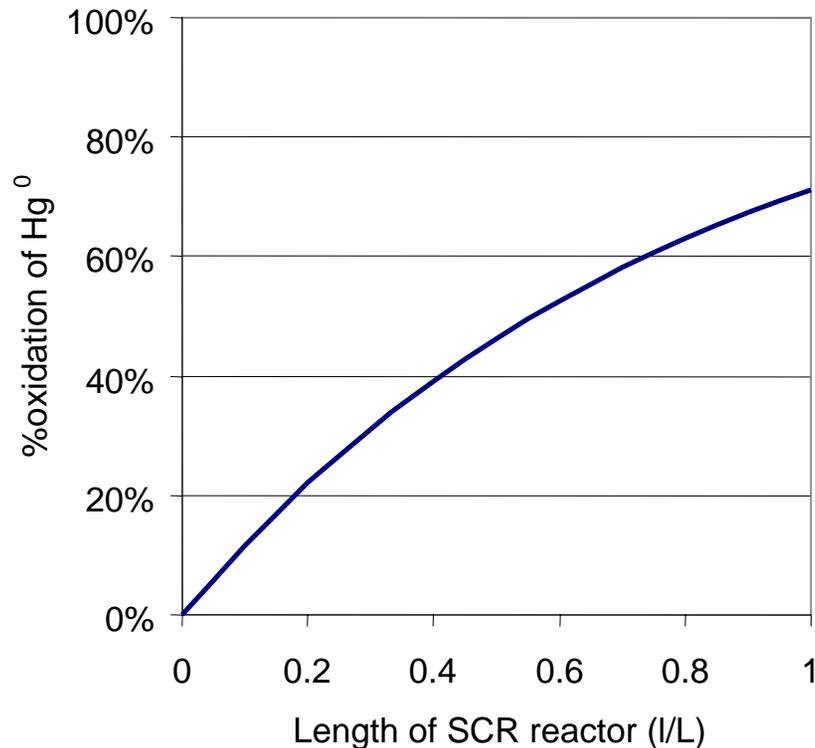




# Summary of Modeling Activity

- Rate equation fits full-scale data, showing dependence of Hg oxidation on
  - Concentration of  $\text{Hg}^0$
  - Approach to equilibrium
  - Concentration of HCl
  - Temperature
- No dependence on  $\text{NH}_3$  observed
  - Little full-scale data without  $\text{NH}_3$
  - Laboratory/pilot-scale data needed

# Use of Oxidation Model



- Example of oxidation as a function of length in SCR
  - Plate catalyst
  - $SV = 2000 \text{ hr}^{-1}$
  - $T = 700^\circ\text{F}$
  - Bituminous coal
    - $0.11 \text{ ug/g Hg}$
    - $800 \text{ ug/g Cl}$



# Conclusions: Strategies for SCRs

- Full-scale SCRs do not reach maximum  $\text{Hg}^0$  oxidation at outlet
- High levels of oxidation may be possible, even with low chlorine coals

*How to maximize  $\text{Hg}^{2+}$  at SCR exit?*

- Sufficient residence time
- Increase chlorine content of flue gas
- Lower temperature in SCR, if possible
- New catalyst formulations?