Oxidation of Mercury Across SCR Catalysts in Coal-Fired Power Plants

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Reaction Engineering International

DOE/NETL Mercury Control Technology R&D Program Review

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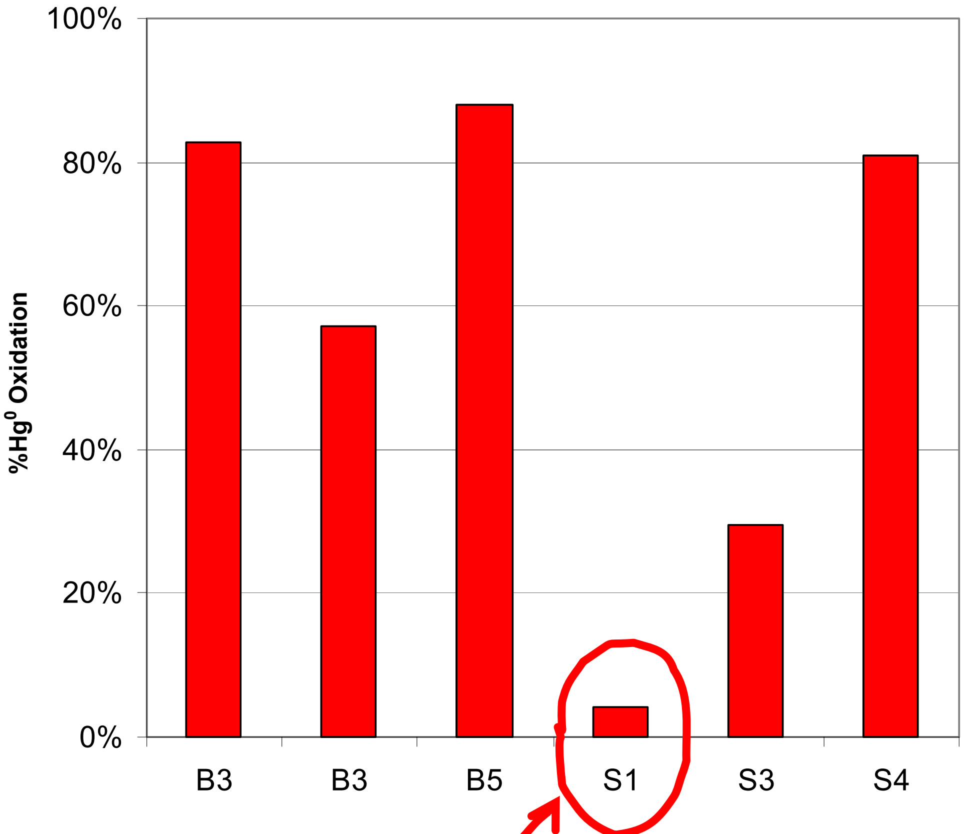
Oxidation Across Full-Scale SCRs



- Full-scale data
- Large variation in observed oxidation

- Subbituminous (S1) vs. bituminous

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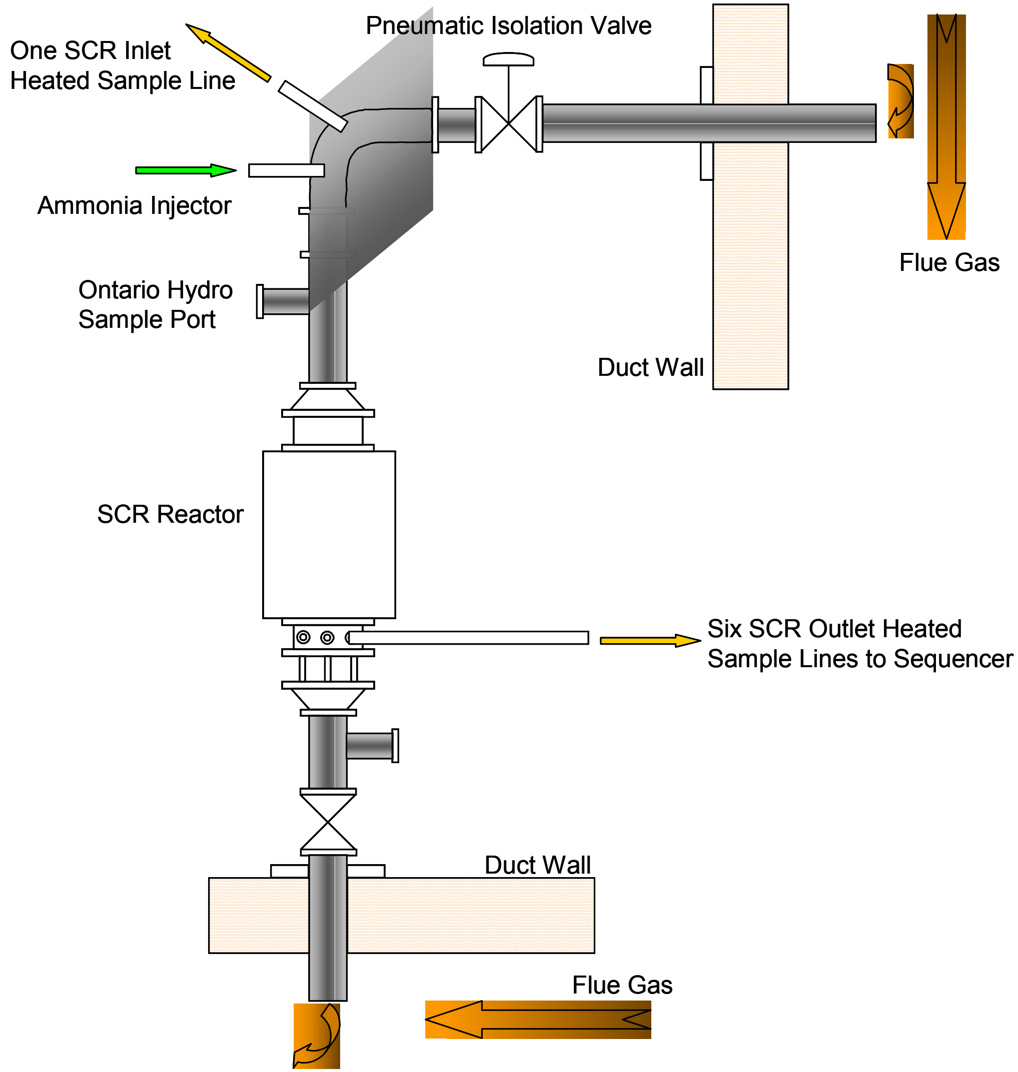
Project Objectives

- 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

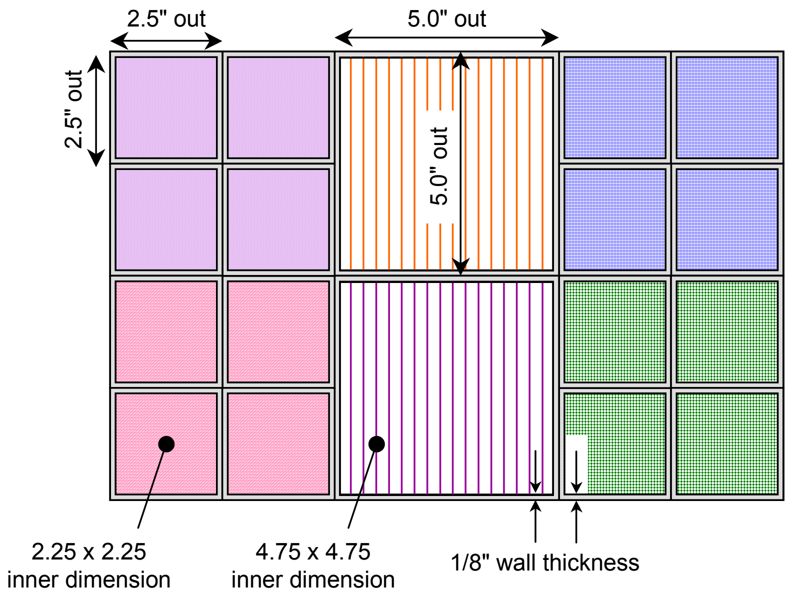
- Slipstream reactor built under catalyst deactivation program (DOE- NETL)
- Mercury testing carried out under separate program (DOE – NETL)
- Additional support from EPRI and Argillon GmbH
- Field test support from AEP

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

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Testing Summary

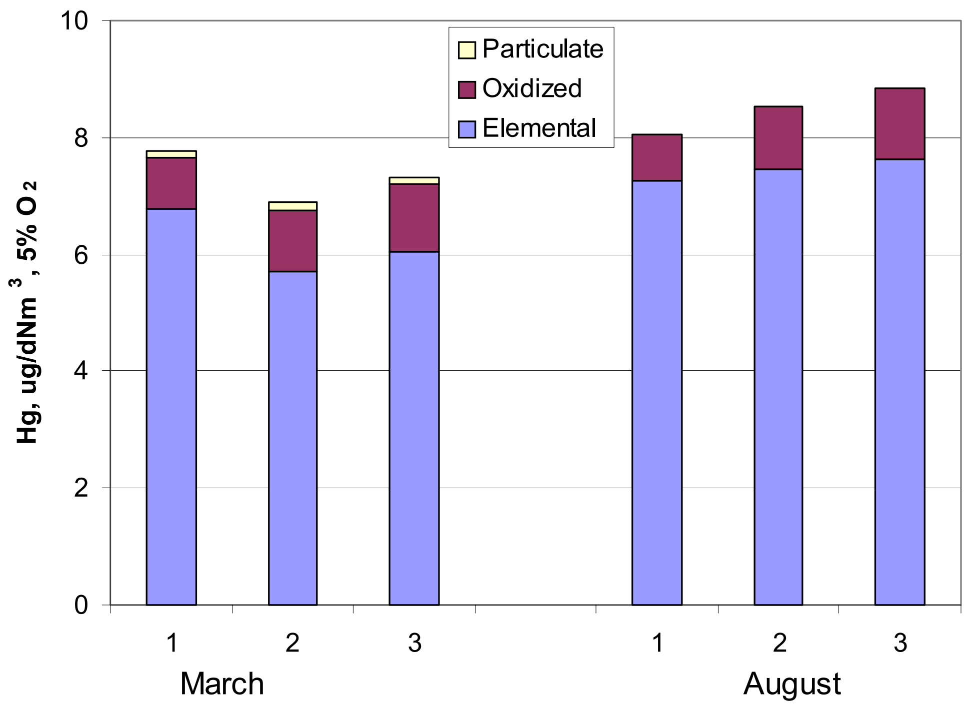
- AEP Rockport:
  - Two 1300 MW_e B&W opposed-wall, supercritical boilers
  - Testing on Unit 1 across air preheater
  - Burn a subbituminous-bituminous blend
- Two test series (March and August)
- Measurements
  - Coal, economizer ash, ESP ash composition
  - Ontario Hydro measurements at inlet to slipstream
  - SCEM measurements at inlet/outlet of catalyst chambers
  - NO_x and O_2 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
(As Received):			
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
(Dry Basis):			
Hg, ug/g	0.088	0.118	0.091
Cl, ug/g	120	160	200
SO_2, lb/MBtu	0.74	0.67	0.82
Hg, lb/TBtu	10.10	13.13	10.13
Hg, ug/dnm^3 (5%O_2)	8.02	10.82	8.46

- Coal blend – mostly subbituminous
- Higher Cl than typical subbituminous
- 8-10 μg/dnm^3 Hg (gas-phase equivalent)
- Ash contains ~6 wt% Fe_2O_3, ~16 wt% CaO

Ontario Hydro Data



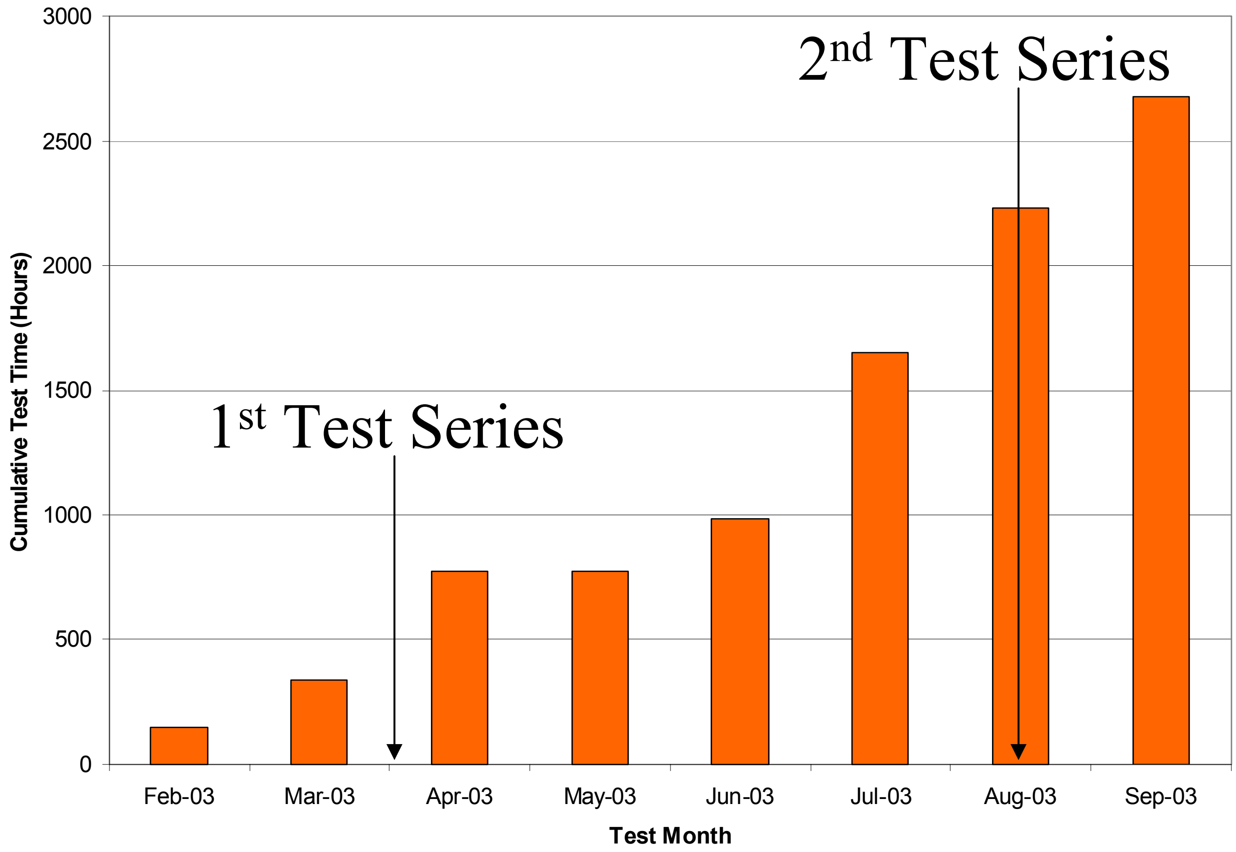
- Hg concentration in OH ash higher than in ESP fly ash BUT fraction of Hg in particulate very low
- 80-90% elemental Hg at inlet to catalysts

Hg and Cl in ash

Date	LOI, wt%	Hg, ug/g	Cl, ug/g	% Hg in Ash	% Cl in Ash
Economizer					
3/28/03	0.08%	0.005	29	0.03%	1.71%
8/11/03	0.00%	0.005	<5	0.04%	<0.3%
8/15/03	0.00%	0.000	<5	0.00%	<0.2%
ESP Hopper					
3/28/03	0.31%	0.081	20	0.41%	1.21%
3/31/03	0.37%	0.118	25	--	--
4/1/03	0.31%	0.127	24	0.44%	1.20%
4/2/03	0.34%	0.101	27	0.55%	1.11%
8/7/03	0.06%	0.034	21	0.23%	1.38%
8/11/03	0.30%	0.050	21	0.45%	0.67%
8/15/03	0.13%	0.055	23	0.47%	1.01%

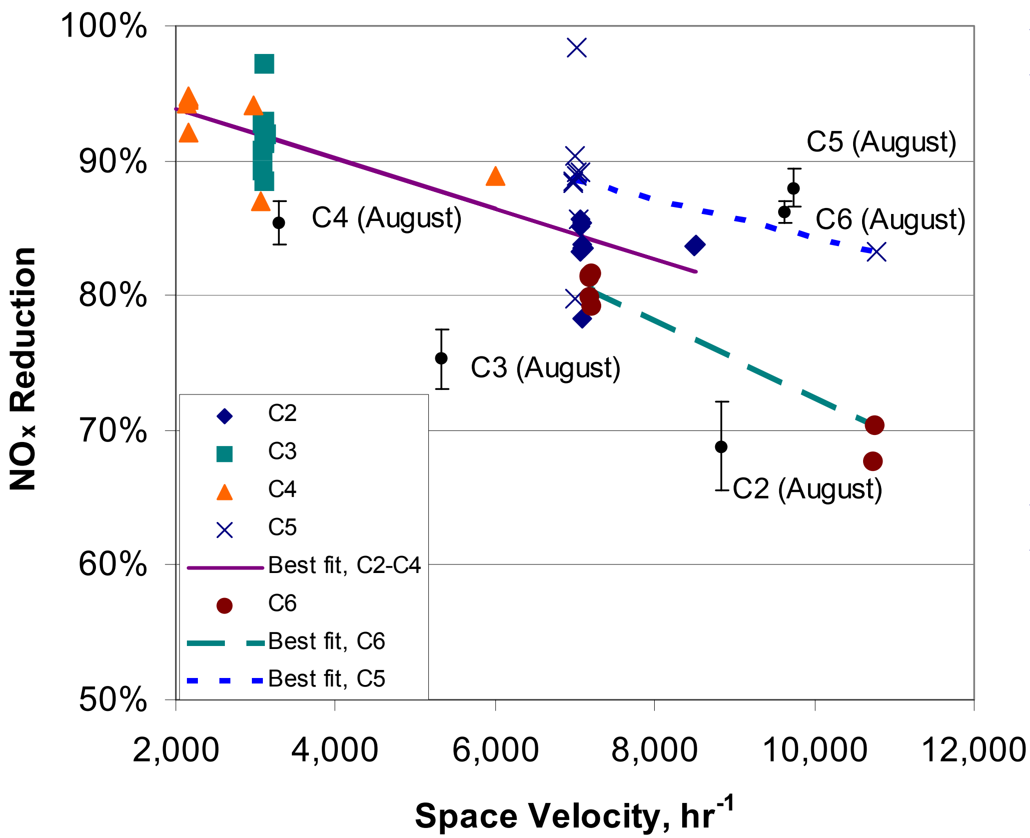
- Low LOI in ESP ash
- ESP ash has very little Hg, ~0.5% of coal Hg (consistent with OH data)
- Cl content of ESP ash low, ~1.5% of coal

Operating Experience



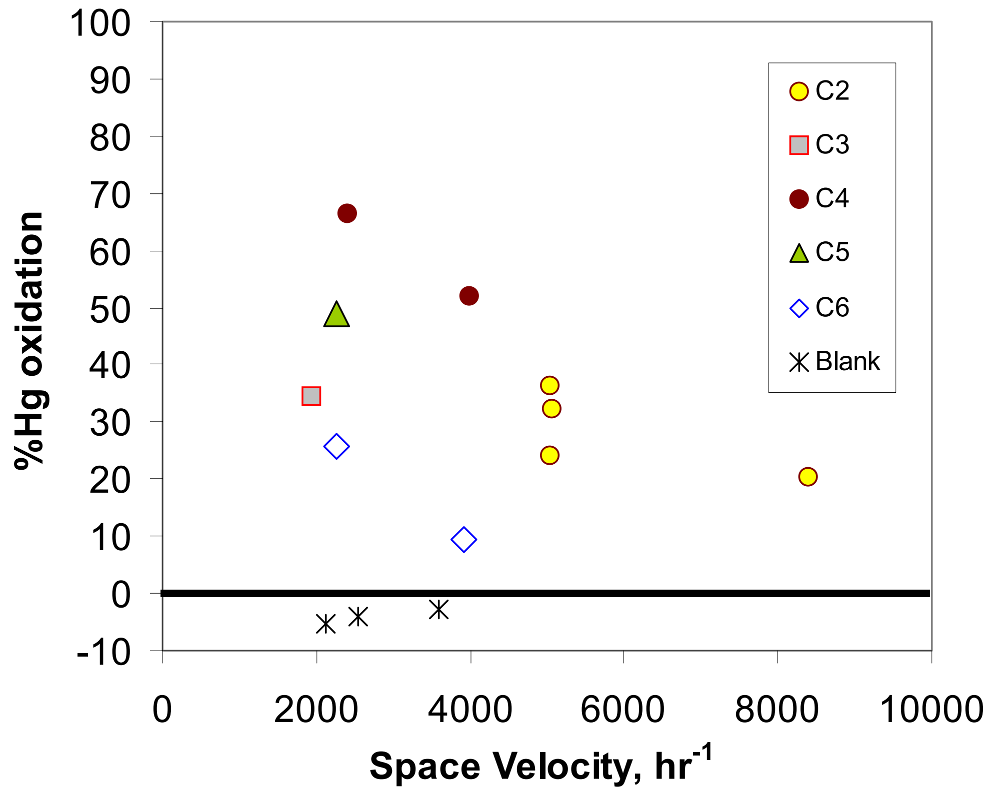
~2700 hours of cumulative flue gas exposure

Change in NO_x Activity



- Commercial catalysts: 85-90% NO_x reduction at full-scale space velocities
- Activity decreased for catalysts C2, C3, C4 (corrected for temperature)

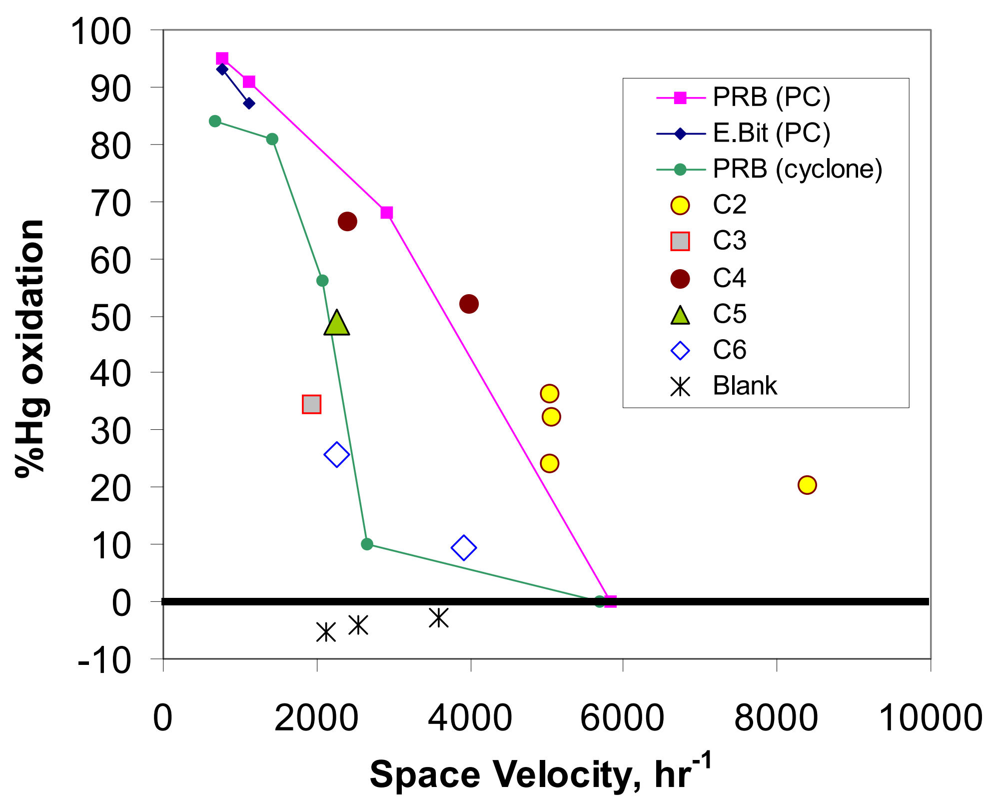
Oxidation of Hg^0 Across Catalyst



March data

- Blank (C1) does not show oxidation

Oxidation of Hg^0 Across Catalyst



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

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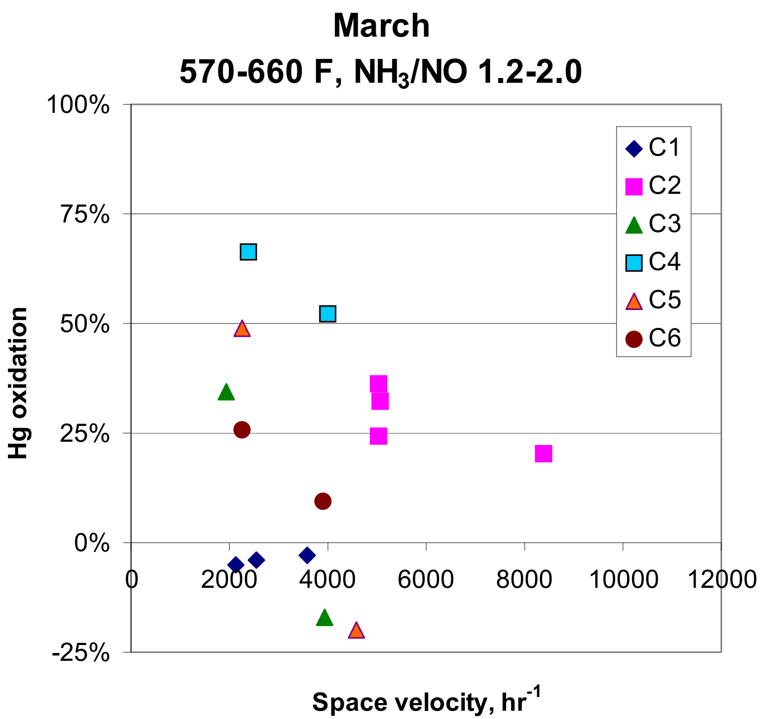
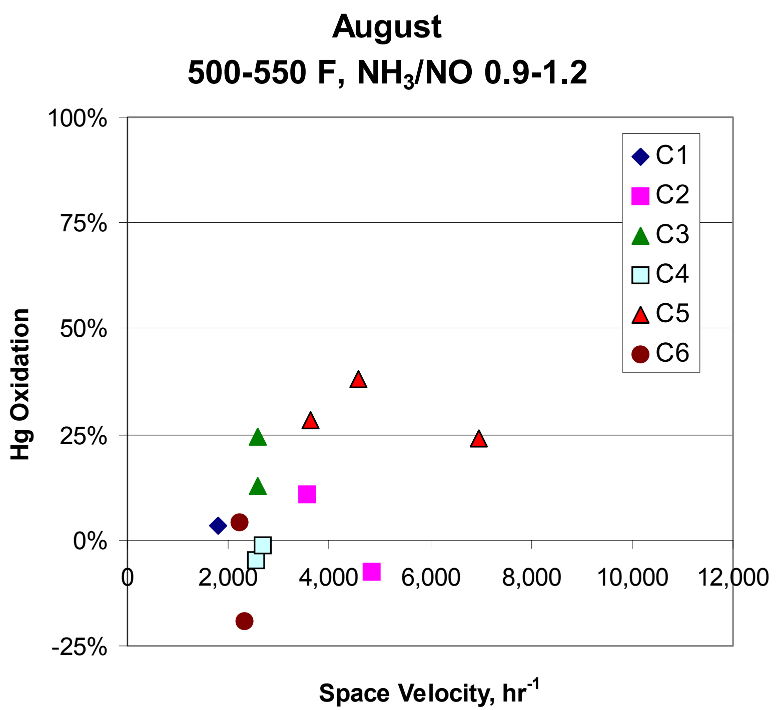
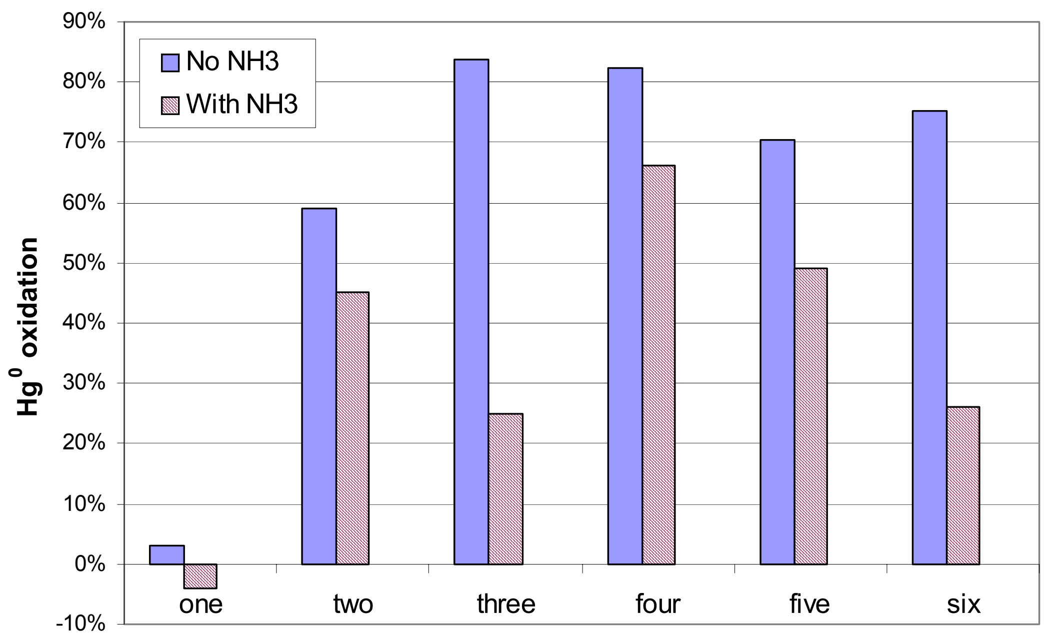
Oxidation of Hg^0 Across Catalyst





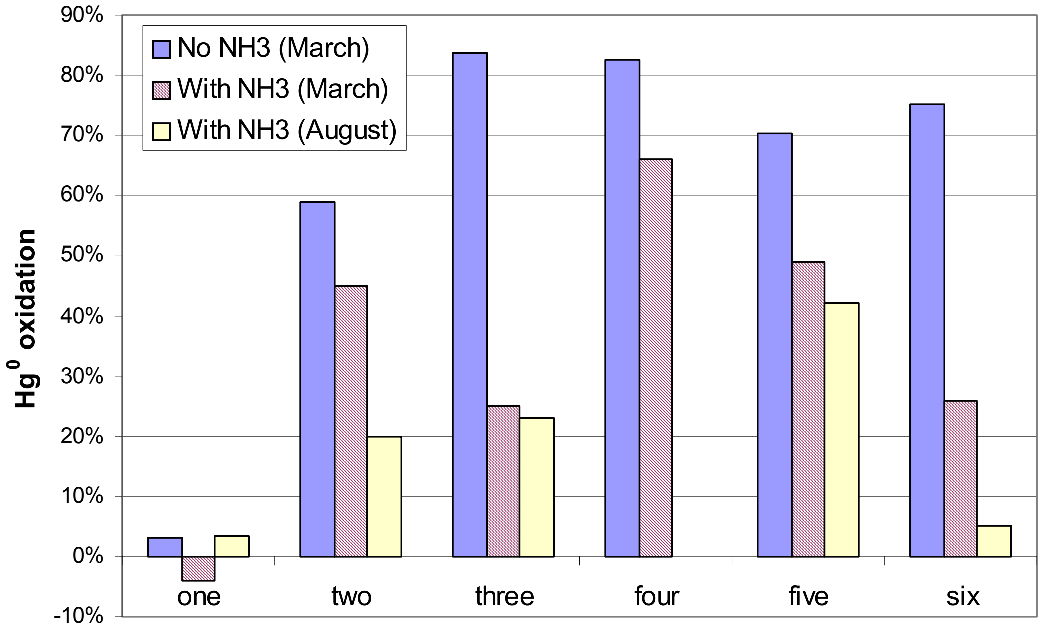
- Blank (C1) does not show oxidation
- August data (lower temperature) show some decrease in oxidation

Effect of Ammonia



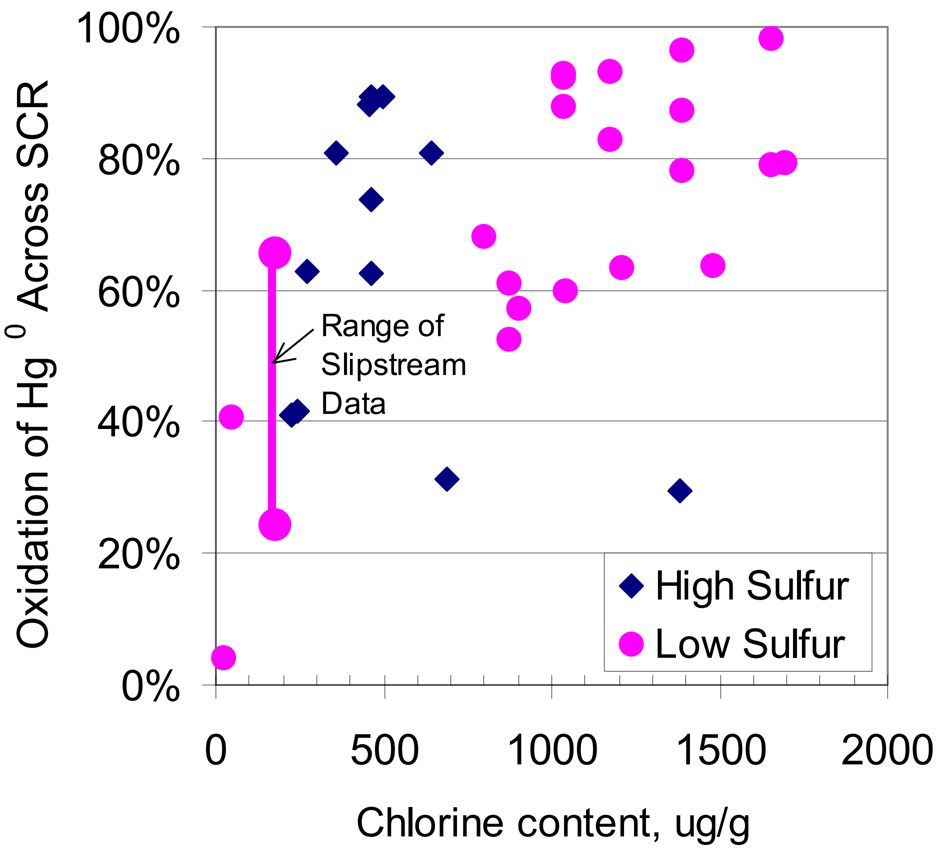
- No ammonia vs. excess ammonia (NH_3/NO ~ 2)
- March:
  - SV interpolated to ~ 2,500 hr^{-1}
  - T ~ 610-630 F
- Oxidation decreased in presence of ammonia
- No effect of blank monolith (C1)

Comparison of March and August



- August:
  - SV interpolated to ~ 2,500 hr^{-1}
  - T ~ 500-550 F
  - NH_3/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

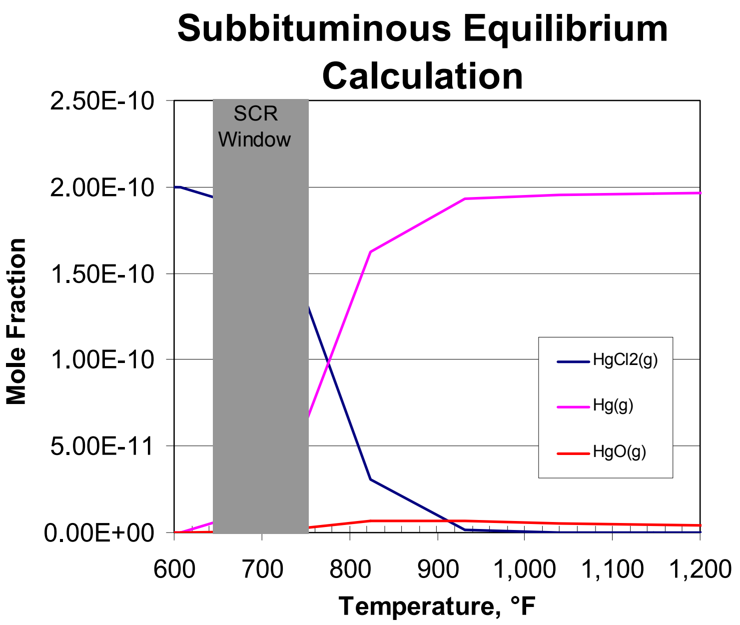


- Slipstream data for blend show oxidation in range of low-chlorine coals (full-scale data)
- Lack of data for < 500 ug/g Cl
- Full-scale data: 10 boilers
- Scatter in full-scale data

Equilibrium & SCR Catalyst

- What does a catalyst do?

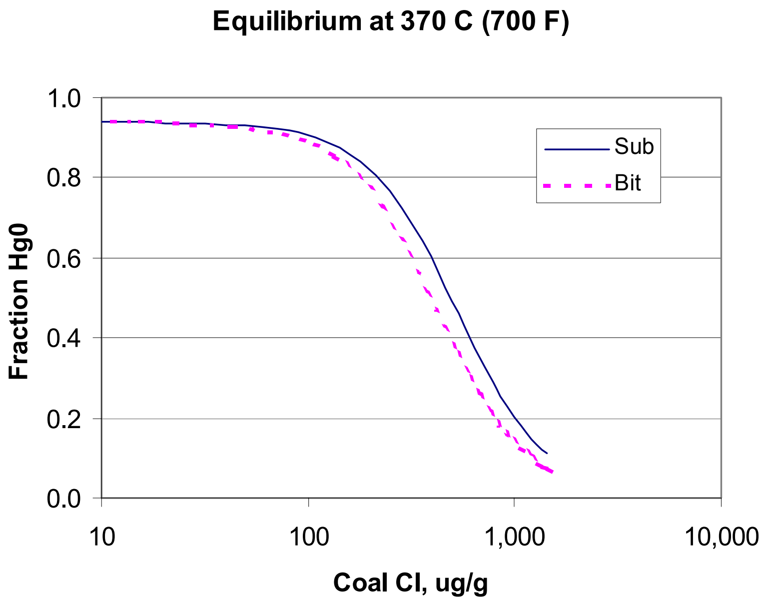
  Moves a chemical reaction toward equilibrium



- Hypothesis:

  SCR catalyst performing at design NO_x reduction will oxidize elemental mercury such that equilibrium between Hg^0 and $HgCl_2$ is achieved at the exit

Equilibrium Calculations



Major Species Composition:

	Subbit.	Bit.
N_2 [vol%]	70.6	75.4
CO_2 [vol%]	13.9	14.6
H_2O [vol%]	12.3	6.8
O_2 [vol%]	3.0	3.0
SO_2 [ppm]	350	1000
HCl [ppm]	1.75	31
Hg [ppb]	0.2	0.2

- HSC software used to calculate equilibrium for typical coal combustion compositions
- Little difference at equilibrium between bituminous and subbituminous coals

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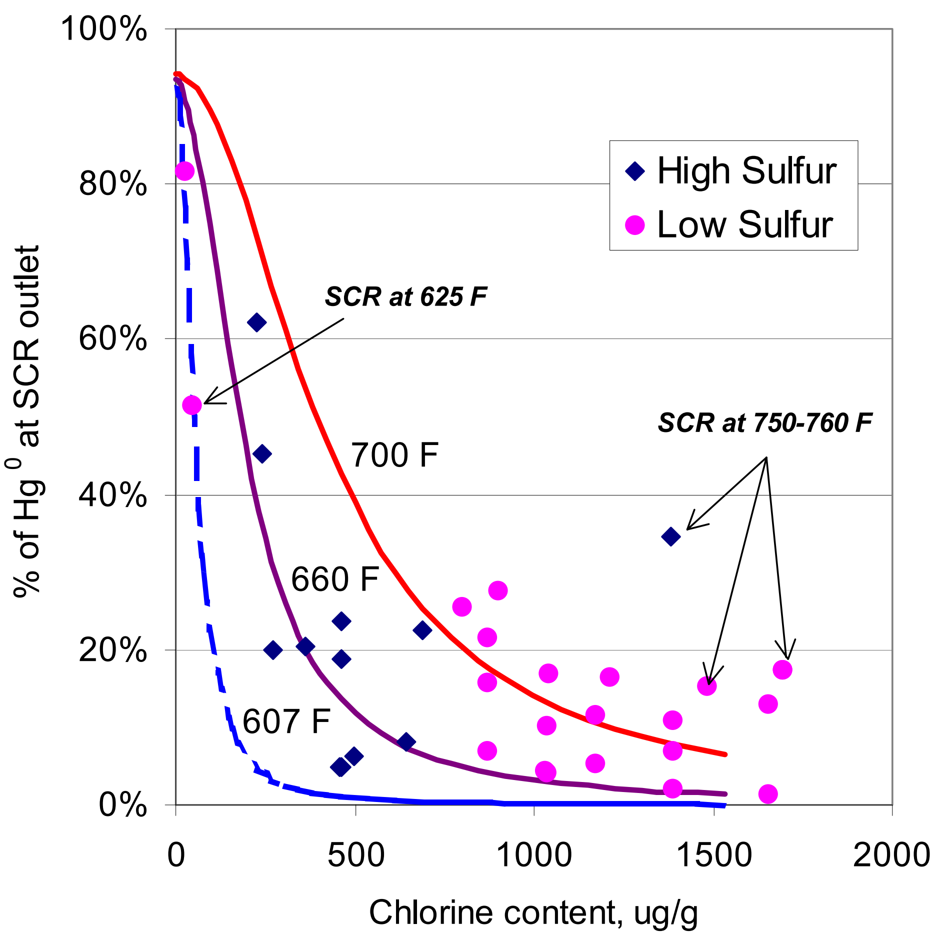
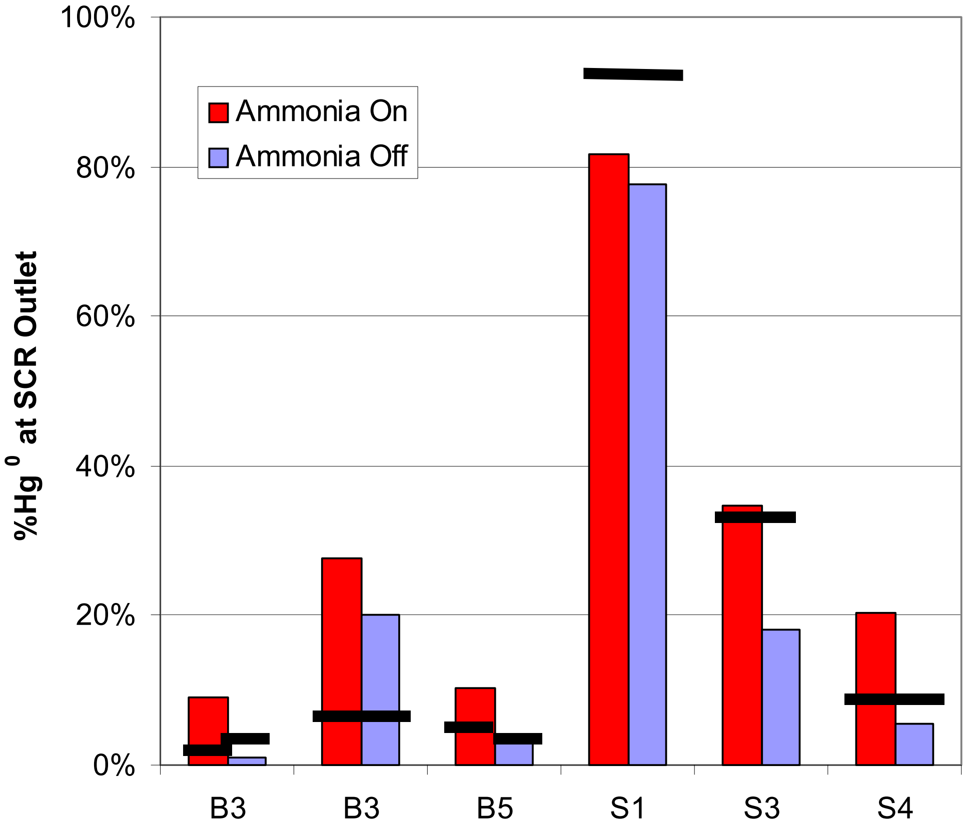
Hg Speciation at SCR Temperatures



- Outlet speciation correlated with equilibrium
- Temperature, chlorine effects
- Other effects:
  - Ammonia
  - ??

Effect of Ammonia



- More Hg^0 at SCR exit with ammonia
- Closer to equilibrium value without ammonia for most points

Conclusions: Multicatalyst Slipstream Reactor

- Slipstream data for blend show oxidation in range of low-chlorine coals (from full-scale data)
- Oxidation of mercury increased without ammonia present
- Differences among catalysts
- Blank monolith showed no oxidation
- Hg oxidation not always correlated with NO_x reduction

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Conclusions: Mechanisms

- Predicting Hg ***oxidation*** across SCRs requires greater understanding of inlet Hg^0
- BUT predicting outlet ***speciation*** apears straightforward
- Equilibrium (T, Cl) primary factor for outlet speciation
- Why don't we get to equilibrium?
  - Ammonia, sulfur?, other factors?

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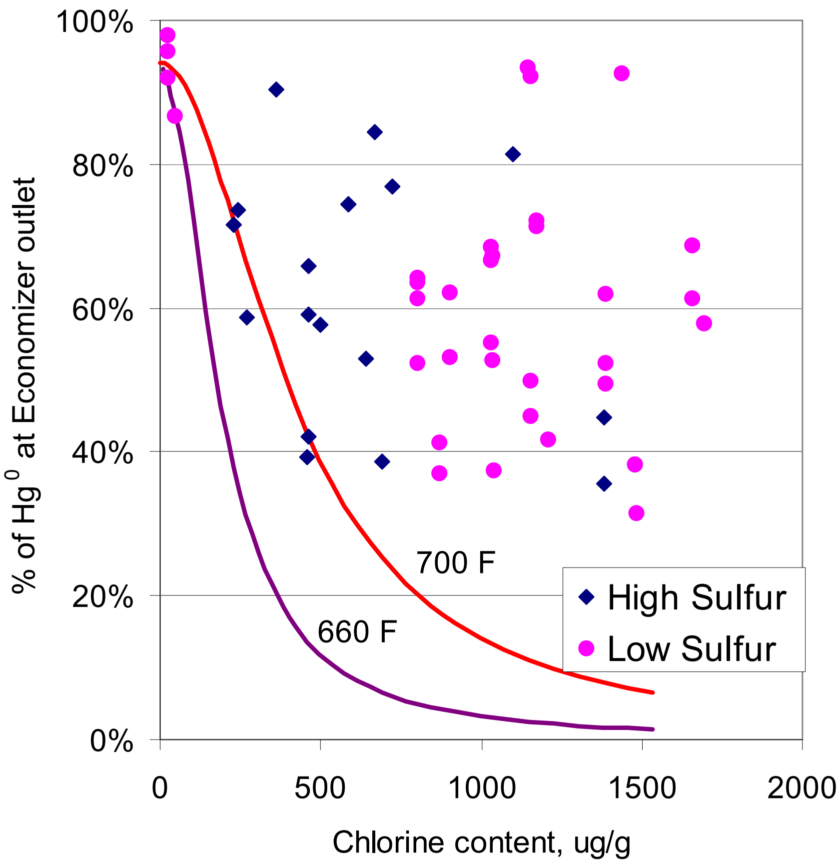
Conclusions: Strategies for SCRs

How to maximize Hg^{2+} at SCR exit?

- Sufficient residence time
- Increase chlorine content of flue gas
  - Less than ~500 µg/g coal equivalent Cl cannot achieve high levels of oxidation at SCR exit
- Lower temperature in SCR, if possible

Remember that SCR is a NO_x reduction process!

Predicting Hg Oxidation is Complex



- Predicting Hg ***oxidation*** requires understanding of inlet Hg^0
- Method for predicting inlet Hg^0 needs further work
- Predicting outlet ***speciation*** seems straightforward