Oxidation of Mercury in Products of Combustion

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Team Members

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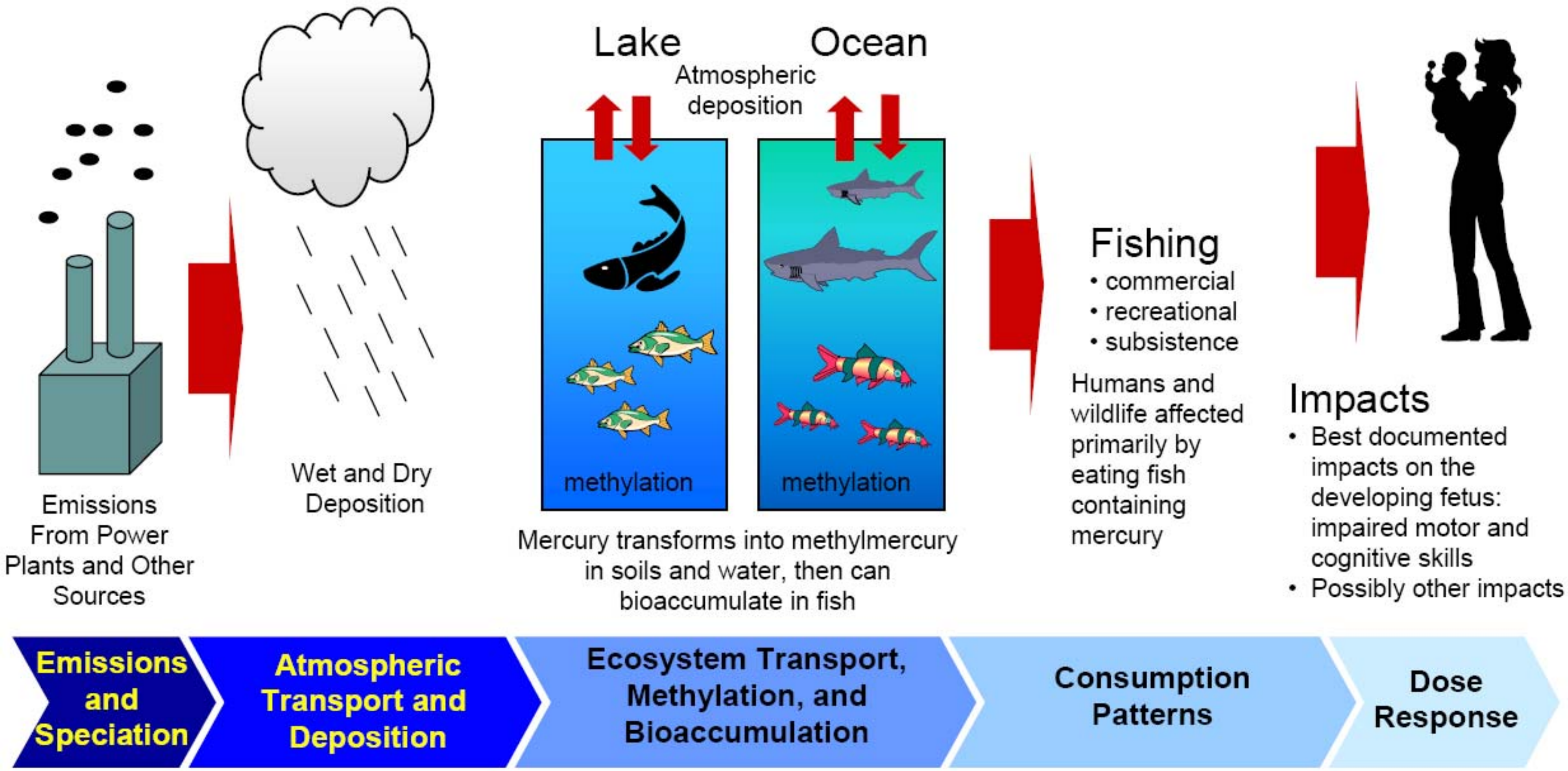
- Southern Research Institute
- Clark Atlanta University
- Gas Technology Institute
- Southern Company Services

Mercury: A Leading Air Toxic Metal



volatility, persistence, bio-accumulation & neurological health impacts

Coal-Fired Boilers: Largest Single Anthropogenic Source of Hg Emission

48 tons emitted to atmosphere in 1999 from coal-fired utility boilers

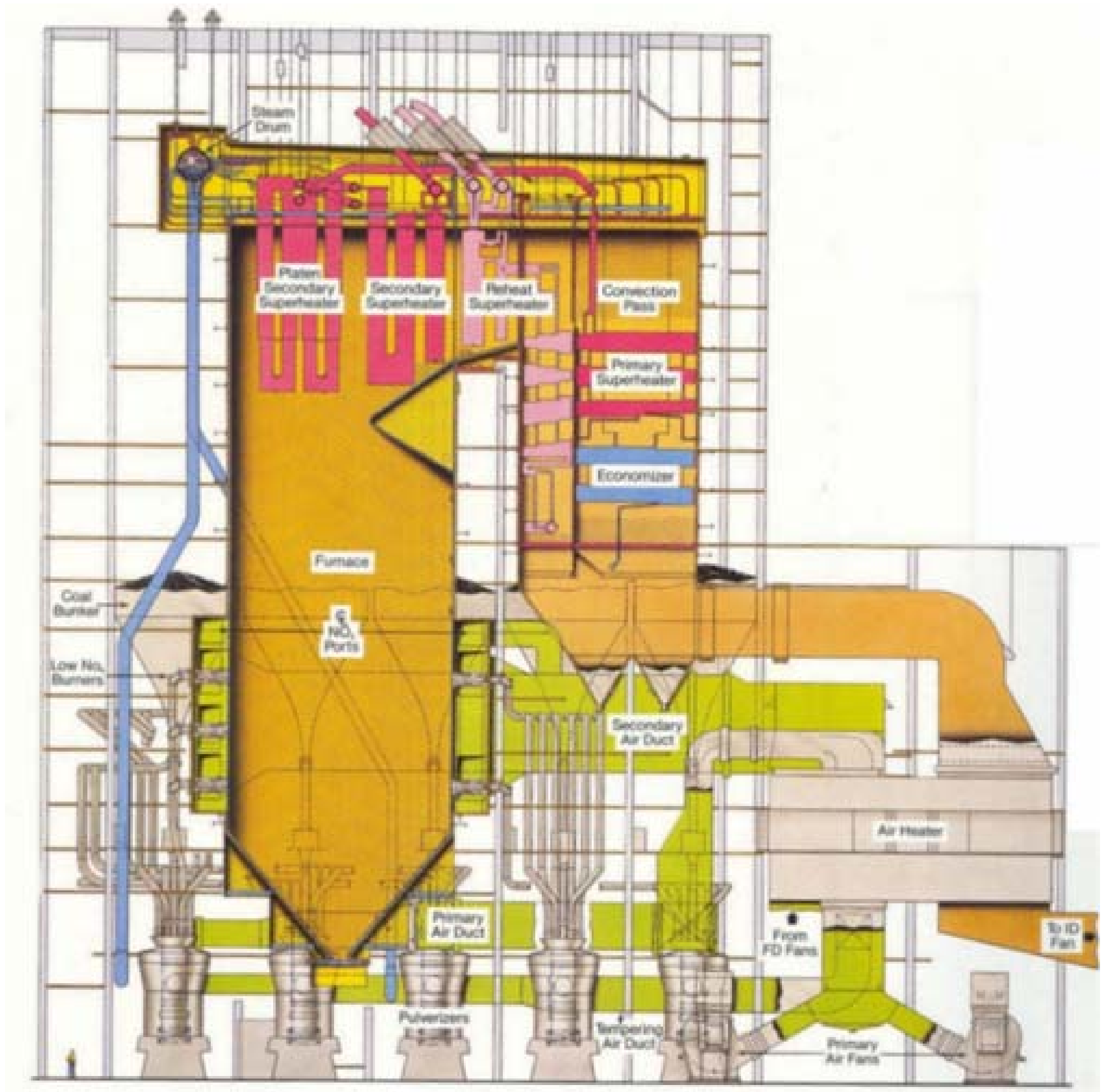
Legislative and Regulatory Background

- The 1990 CAAA required EPA to study health and environmental impact of HAPs from boilers.
- In 1997 & 1998, EPA published The Hg report and HAPs report to Congress.
- In Dec 2000, EPA decided to regulate HAPs from coal-fired utility units.
- In March 2005, EPA issued Clean Air Interstate Rule to regulate Hg emissions.
- The new rule created a market-based cap-and-trade program will reduce nationwide Hg emissions in two phases: 38 tons in 2010 and 15 tons in 2018.

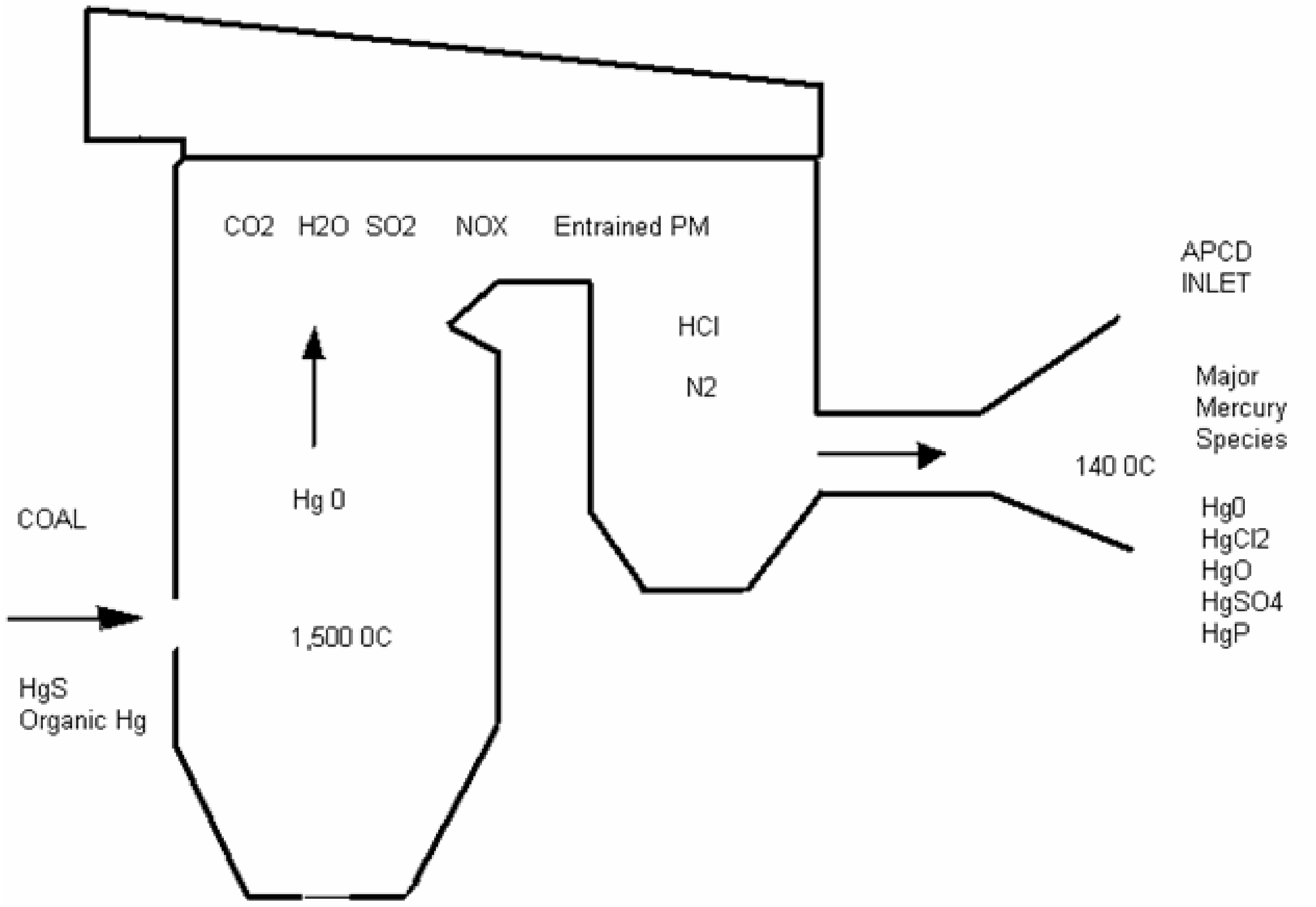
Mercury Speciation

- Hg naturally exists in coal as sulfur bound compounds & compounds associated with organic fraction.
- The high combustion temperature in boiler vaporizes Hg in coal to form Hg^0
- Subsequent cooling and interactions of Hg^0 with flue gas, results in Hg converted to other forms.
- Basic forms of Hg in flue gas includes
  - Elemental Hg
  - Compounds of oxidized Hg
  - Particle-bound Hg
- Elemental Hg can pass through current APCD, and oxidized Hg is easier to captured.

455 MW Radiant PC Boiler



Mercury Transformation in PC Boilers



Factors Affecting Hg Speciation

- Type and properties of coal burned.
- Combustion condition in furnace.
- Flue gas temperature profile.
- Flue gas composition.
- Fly ash properties.
- Post combustion emission control devices.
- Potential mechanisms for Hg oxidation are
  - Gas phase oxidation
  - Fly ash mediated oxidation
  - Oxidation by post combustion NO_x controls

EPA ICR Data for PC Boilers

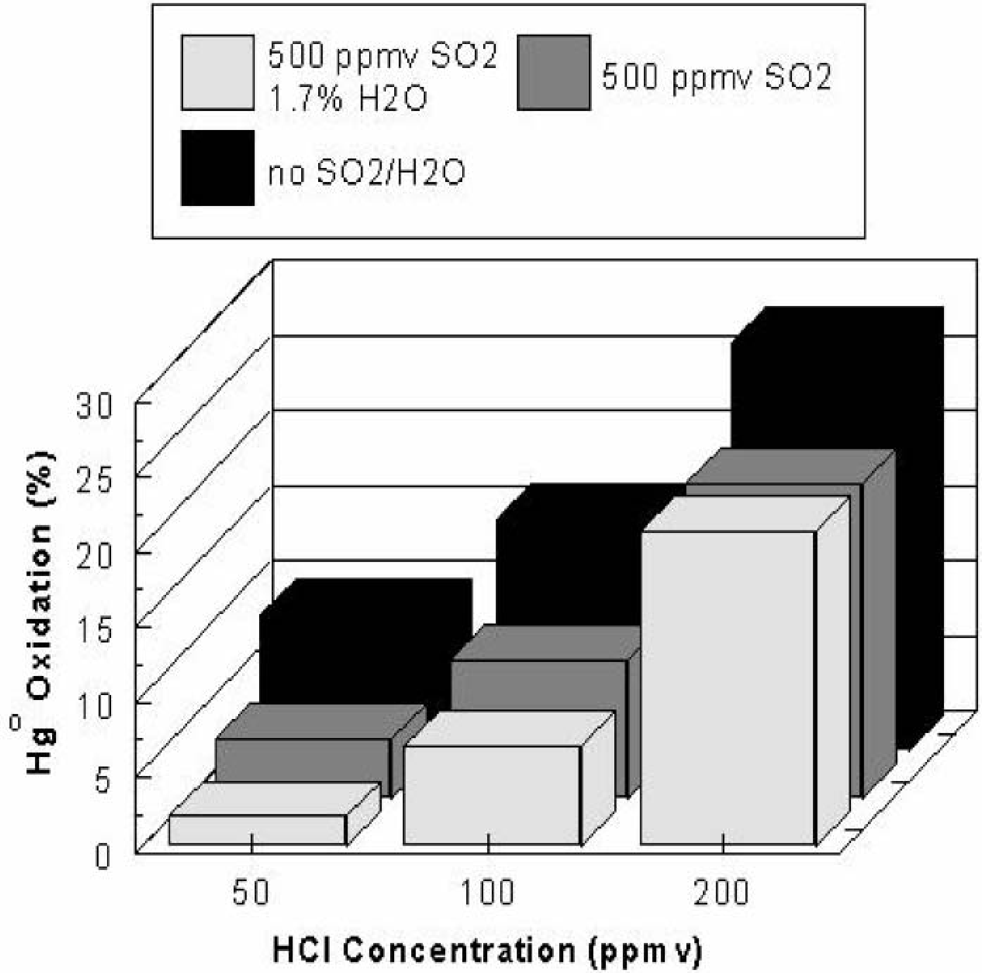
Post-combustion Emission Controls Used for PC Boiler		Average Mercury Emission Reduction (%) [a]		
		Bituminous-coal-fired	Subbituminous-coal-fired	Lignite-fired
PM Control Only	CS-ESP	36 %	3 %	-4 %
	HS-ESP	9 %	6 %	not tested
	FF	90 %	72 %	not tested
	PS	not tested	9 %	not tested
PM Control and Spray Dryer Adsorber	SDA + ESP	not tested	35 %	not tested
	SDA + FF	98 %	24 %	0 %
	SDA + FF + SCR	98 %	not tested	not tested
PM Control and Wet FGD System	PS + FGD	12 %	-8 %	33 %
	CS-ESP + FGD	75 %	29 %	44 %
	HS-ESP + FGD	49 %	29 %	not tested
	FF + FGD	98 %	not tested	not tested

a) Mean reduction from test 3-run averages for each PC boiler unit in Phase III EPA ICR data base.

Gas Phase Oxidation

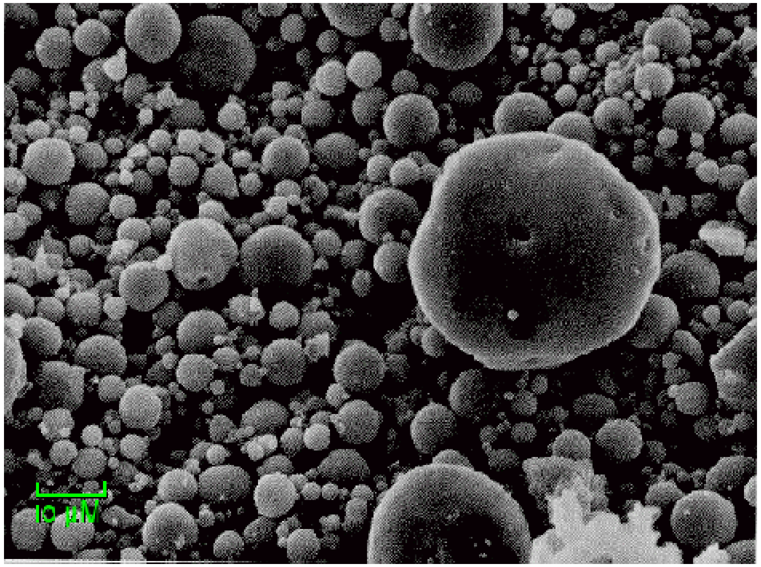
- Elemental Hg reacts with atomic chlorine (Cl) to form $HgCl_2$.
- The temperature at outlet of heat exchanger is 261 to 621^{0}F.
- Equilibrium calculation predicts that Hg oxidation starts at 1251^{0}F and completes at 801^{0}F.
- Hg oxidation does not complete due to kinetic limitations.

Effect of HCl, SO_2 & H_2O on Gas Phase Oxidation

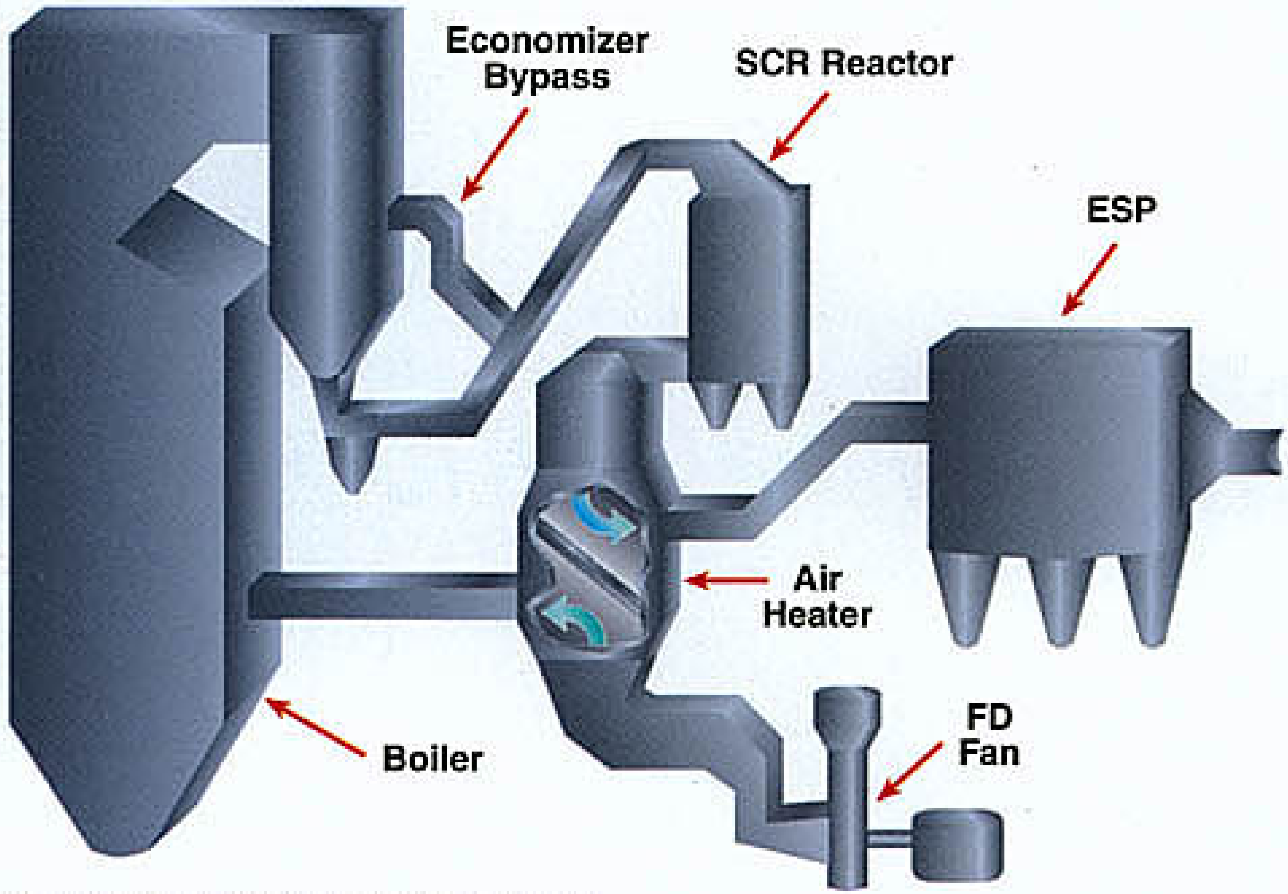


Fly Ash Mediated Oxidation

- Fly ash proved to promote mercury oxidation.
- In fabric filters, flue gas penetrates a layer of fly ash and Hg oxidation is the highest in EPA ICR data.
- Coal fly ash is a mixture of unburned carbon and metal oxides in both crystalline and amorphous forms.

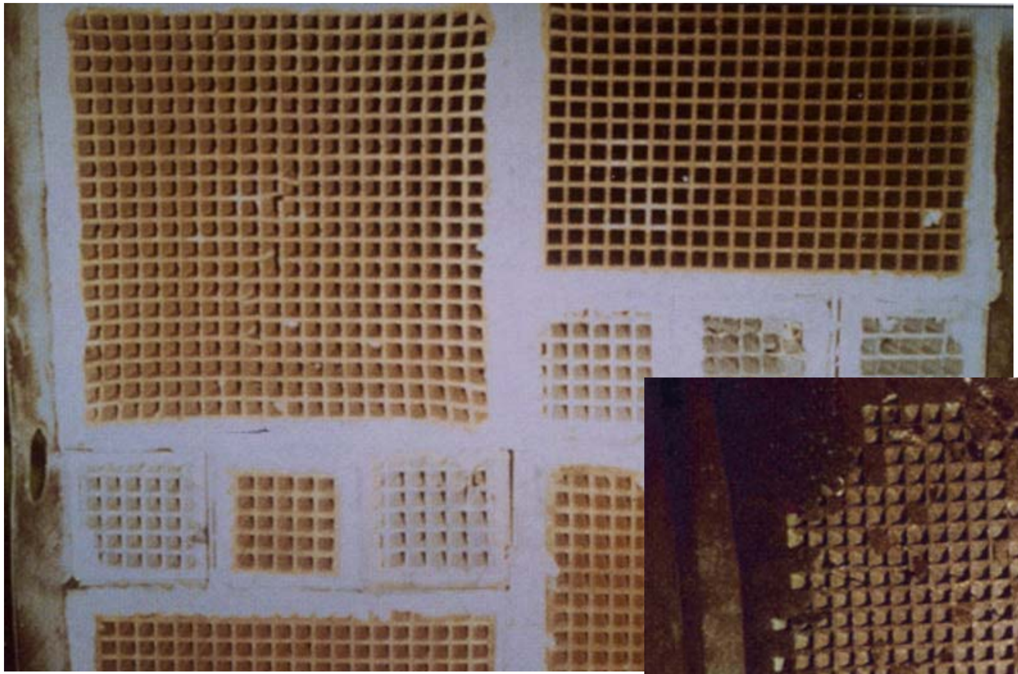


Schematic of SCR for NOx Control



Schematic flow diagram of SCR process

Honeycomb Catalyst In SCR Reactors



Research Challenges

- Develop a fundamental understanding and predictive model for mercury speciation.
- Optimize NOx controls for Hg control.
- Develop cost effective sorbents for Hg control for sub-bituminous coal & lignite.
- Determine effects of coal blending on Hg speciation and capture.
- Evaluate the enhancement of fly ash Hg capture by combustion modification.
- Minimize effects of Hg control on power plant operability.

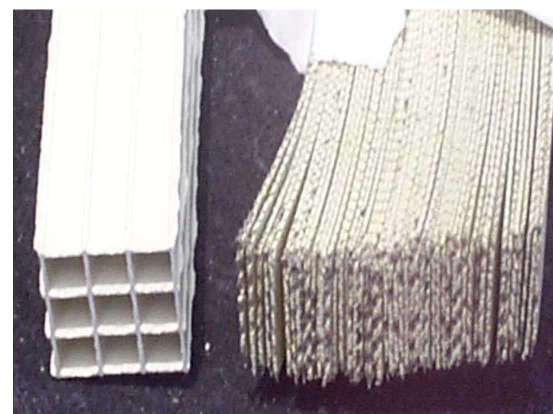
Overall Goal

- Develop and test SCR catalysts having high activity for both NOx reduction and mercury oxidation.
- Obtain fundamental understanding on mercury speciation and reaction kinetics in the flue gas.

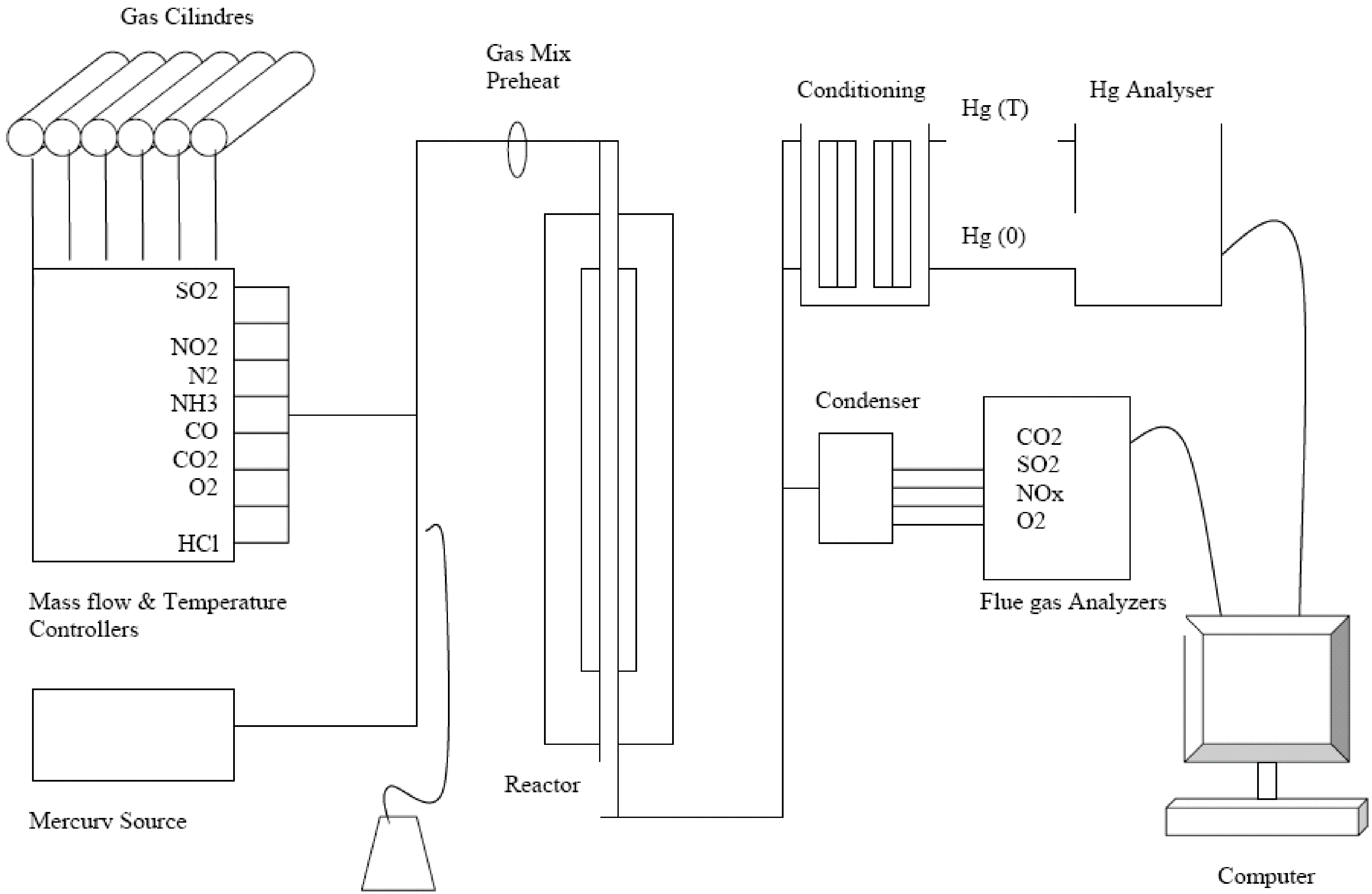
Work Plan

- Catalyst Formulation (GTI, CAU)
- Catalyst Test and Characterization (SRI, UAB, SCS)
- Model Development (UAB, SRI)

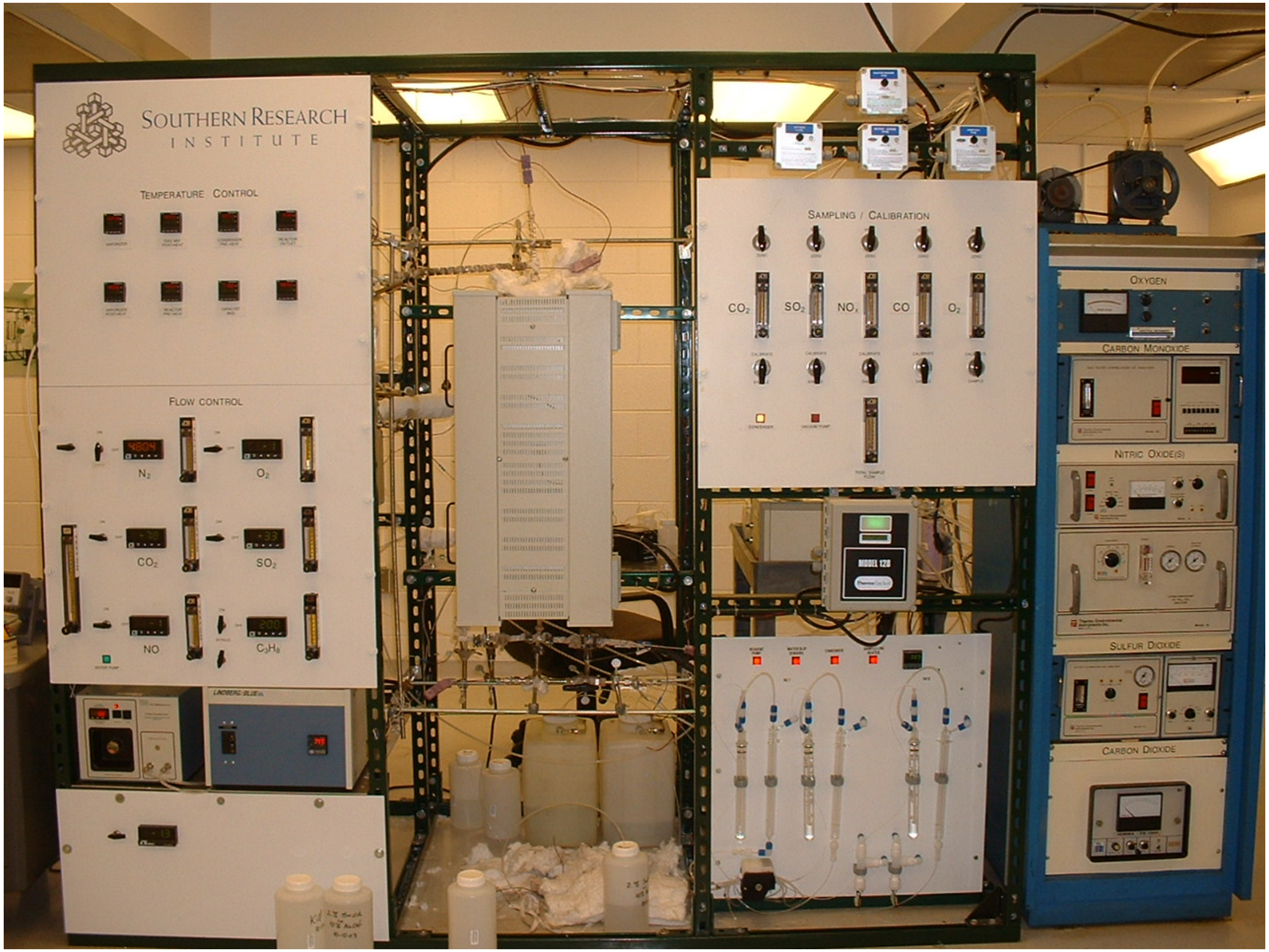
Catalyst Samples



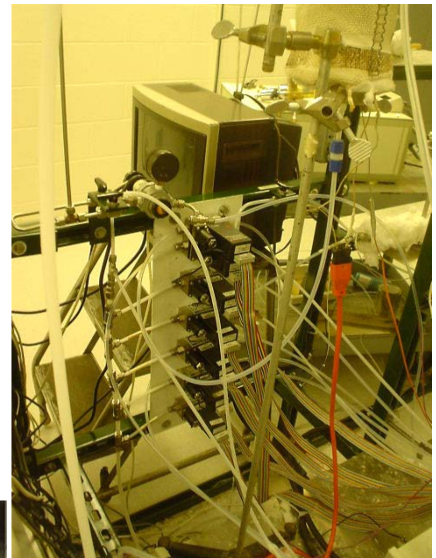
Schematic of Experimental System

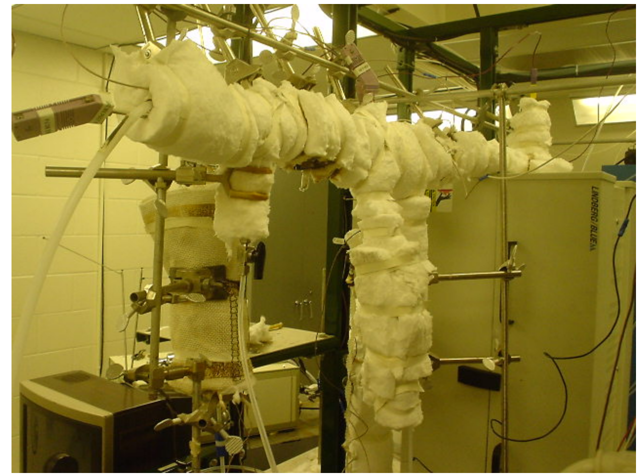


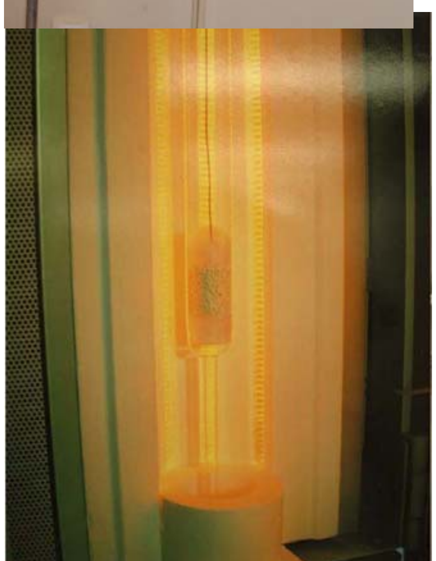
Picture of Catalyst Test Facility

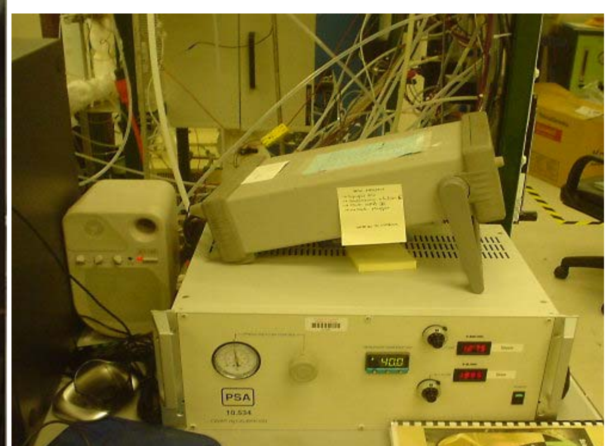


Pictures of Components





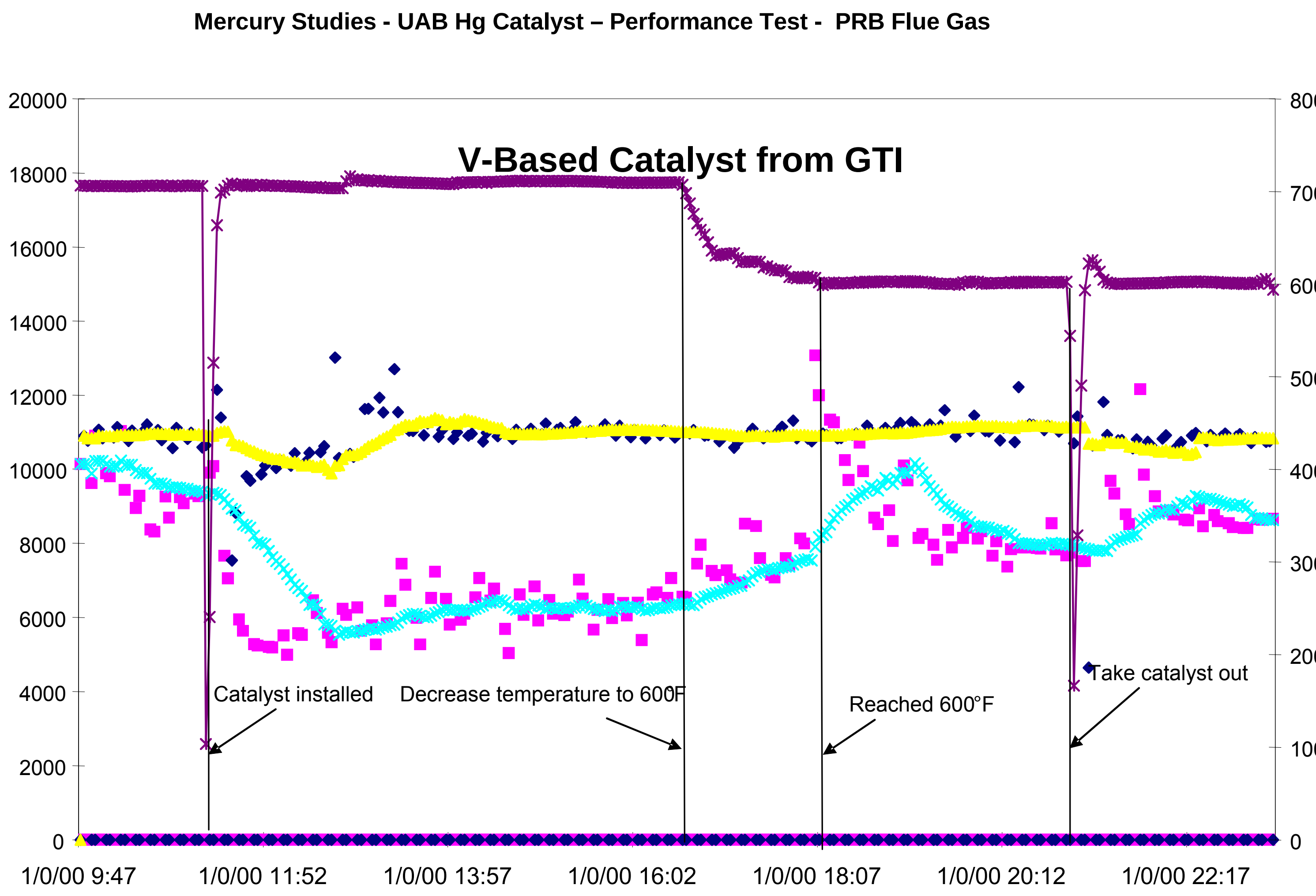




Simulated PRB Flue Gas Composition

Gas Concentrations	**Value**	**Unit**
Water Vapor	10	%
Oxygen	5	% (dry, by volume)
Carbon Dioxide	15	% (dry, by volume)
Nitric Oxide	300	ppm (dry, by volume)
Ammonia	0 or 300	ppm (dry, by volume)
Sulfur Dioxide	500	ppm (dry, by volume)
Hydrogen Chloride	2	ppm (dry, by volume)
Mercury	10	mg/Nm^3 (dry)
Nitrogen	Balance	

Data Plot for Vanadium-Based Catalyst



Vanadium-Based Catalyst in Simulated PRB Flue Gas

Catalyst	Hg0	STD	%STD	HgT	STD	%STD	Hg2	Hg2/HgT	Net
Blank @ 700 F	9457	48	1%	10923	34	0%	1466	13%	base
V-GTI 700	6282	86	1%	11111	151	1%	4829	43%	30%
Blank @ 600 F	8984	220	2%	10777	139	1%	1793	17%	base
V-GTI 600	8040	119	1%	11158	22	0%	3118	28%	11%

Hg Adsorption Experiment

- Quartz reaction chamber diameter: 1.5”
- Carbon Sample: 3 g
- Residence Time: 0.12 sec
- Volumetric Flow Rate: 83.3 cm^3/sec
- Temperature: 421 K, 477 K, 533 K
- HCl concentration: 2 ppmv, 50 ppmv, 100 ppmv, 250 ppmv
- Pressure: 1 atm
- Carbon type: Activated carbon, Unburned carbon

Adsorption by Unburned Carbon

Temp (K) / HCl	2 ppmv	50 ppmv	100 ppmv	250 ppmv
421.9	53.0	81.2	94.5	97
477.4	0	18.5	33.8	39.0
533.2	0	0	0	0

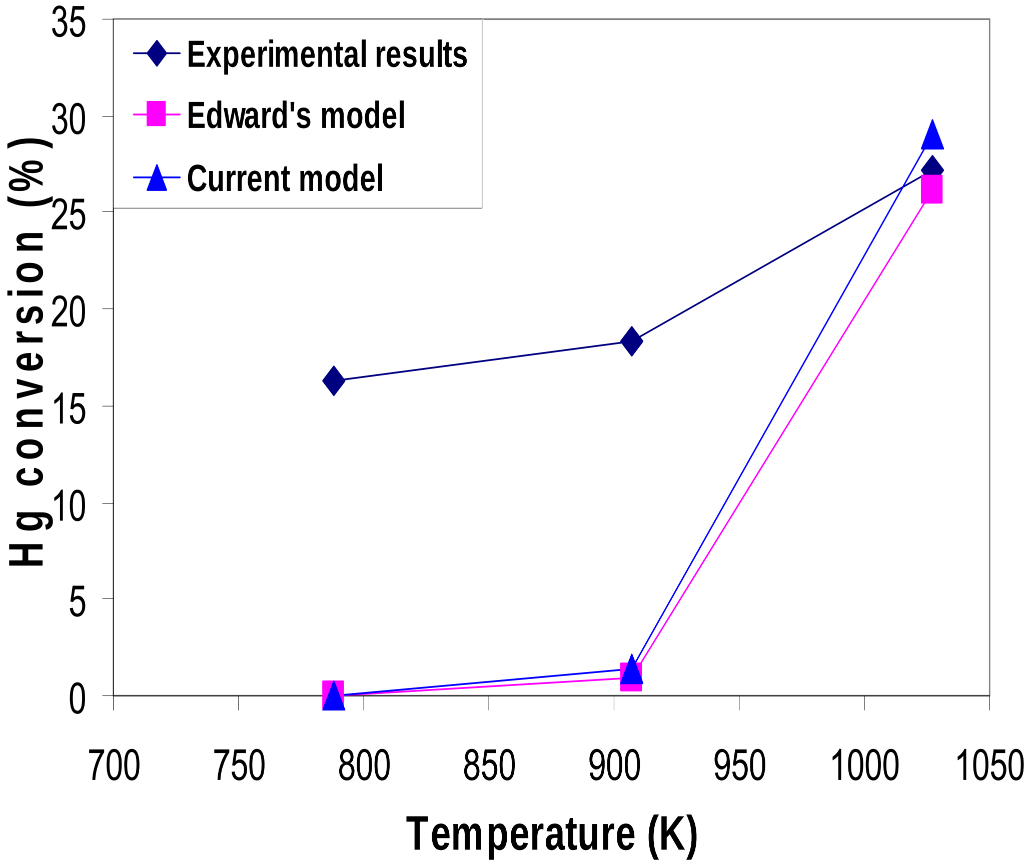
Adsorption by Activated Carbon

Temp (K) / HCl	2 ppmv	50 ppmv	100 ppmv	250 ppmv
421.9	87.0	93.7	92.4	91
477.4	9.0	50.2	61.3	68.0
533.2	0	9.3	9.3	25.3

Model Development

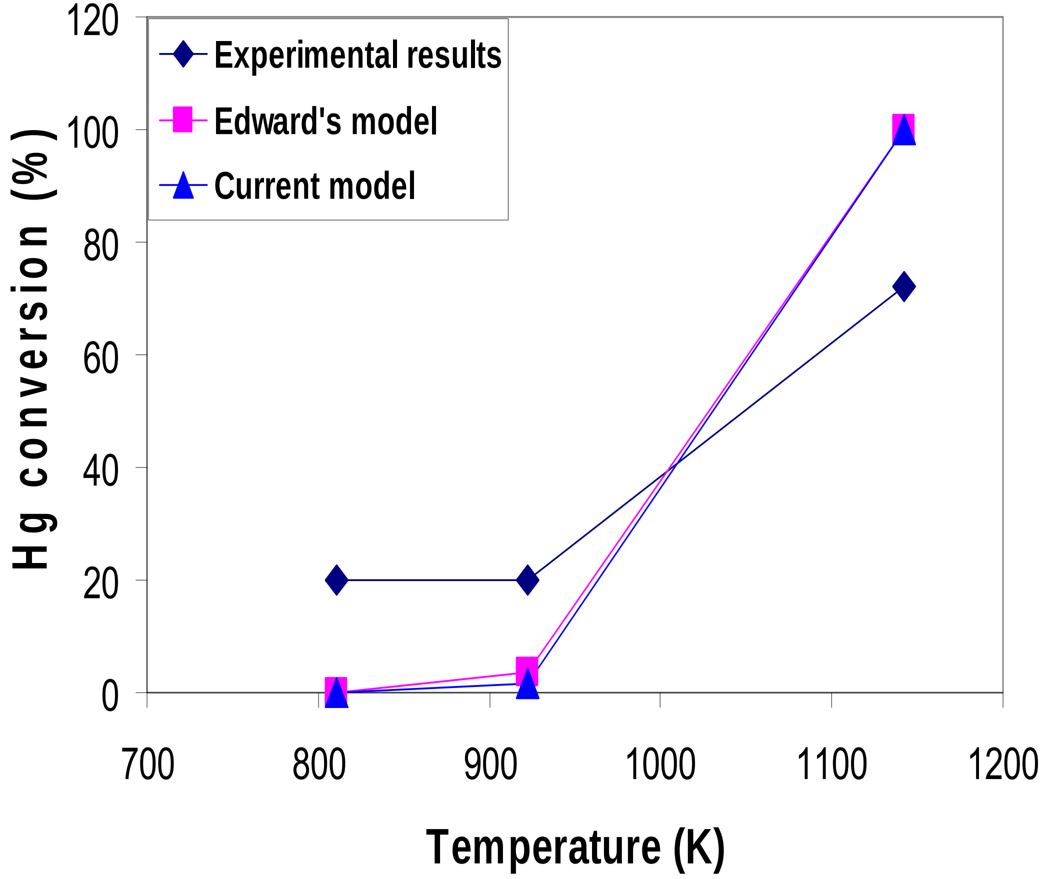
- Investigate mechanisms driving mercury oxidation and removal in coal-fired flue gas
- Develop surface reaction mechanisms that governs adsorption, desorption and oxidation of mercury
- Develop chemical kinetic model (Arrhenius form, $k = A * T^{\beta} * \exp(-Ea/RT)$) and establish reaction-rate constants
  - Homogeneous model using rates from NIST and literature data
  - Heterogeneous model using rates extracted from experiments

Homogeneous Model



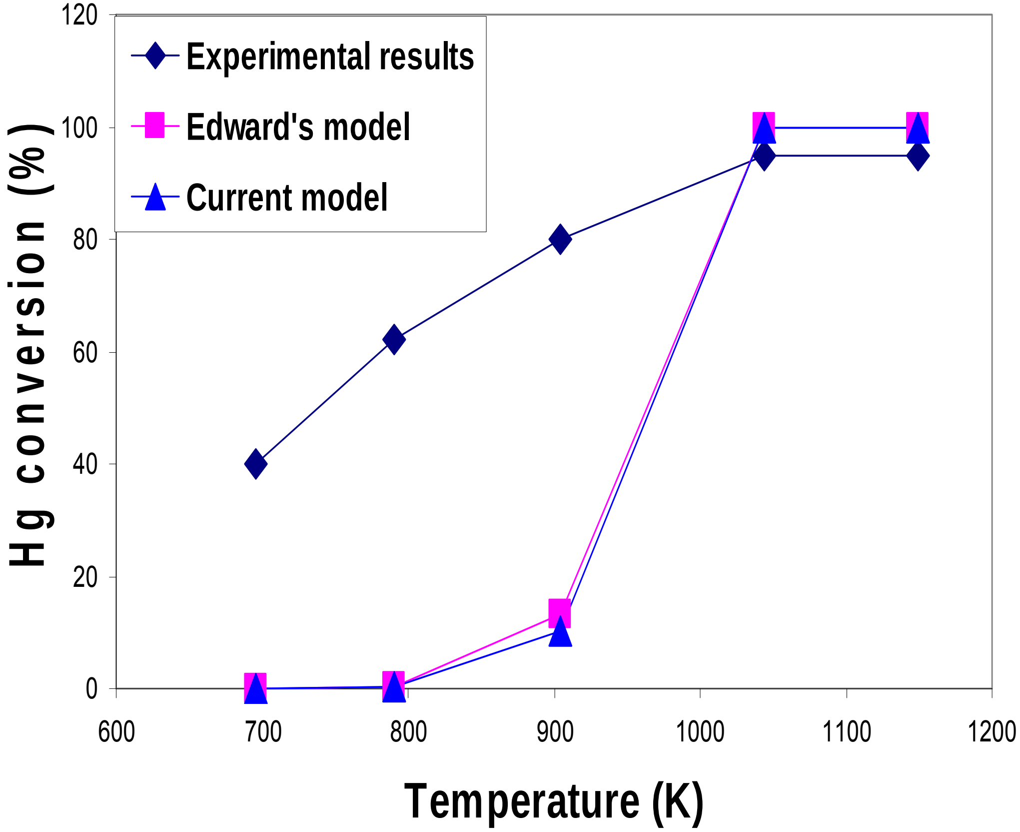
Experimental vs simulation results for HCl 200 ppmv for Ghorishi data

Homogeneous Model



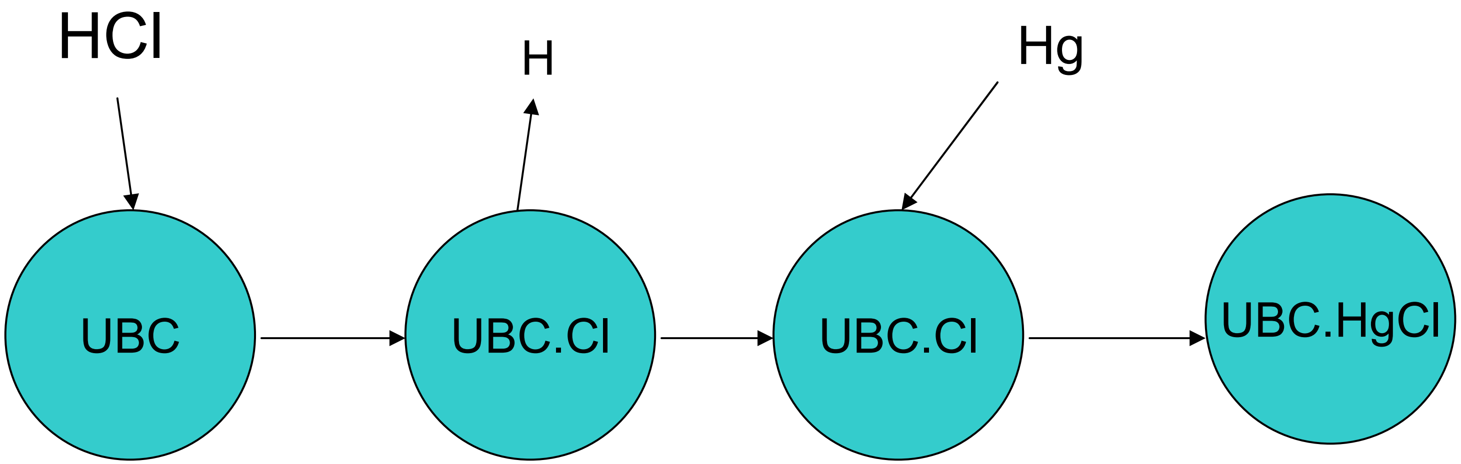
Experimental vs simulation results for HCl 300 ppmv for Widmer data

Homogeneous Model



Experimental vs simulation results for HCl 3000 ppmv for Widmer data

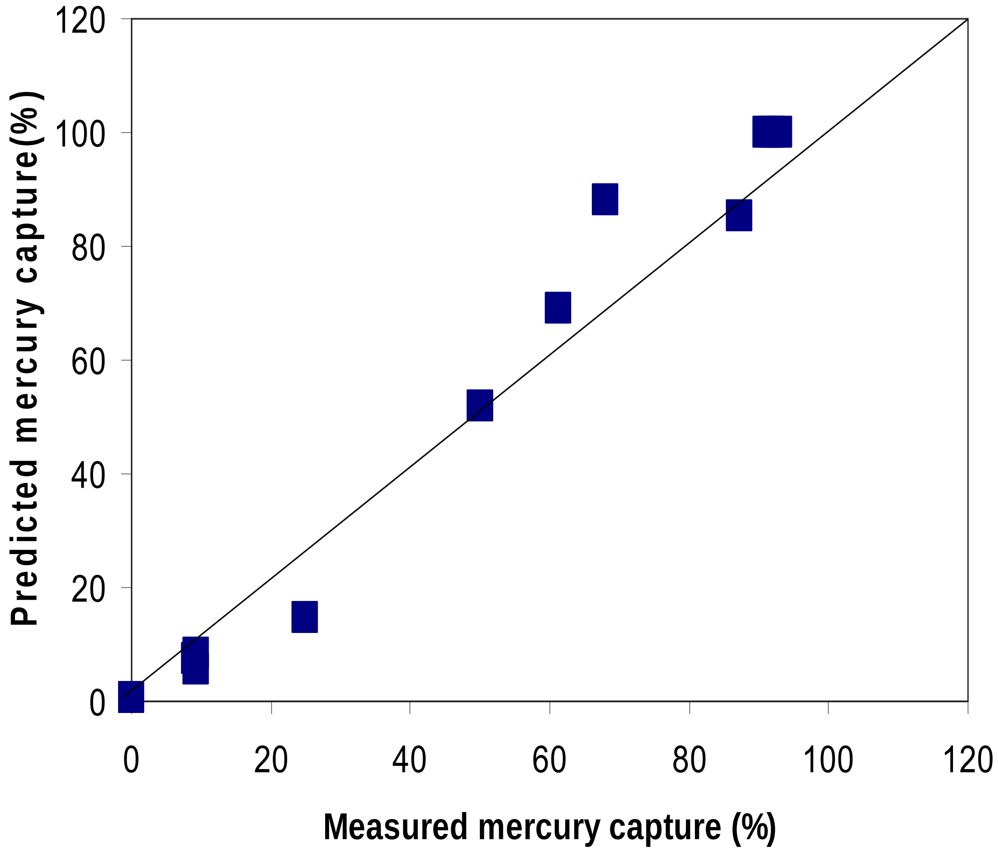
Proposed Surface Adsorption Mechanism



Kinetic Model of Hg Adsorption

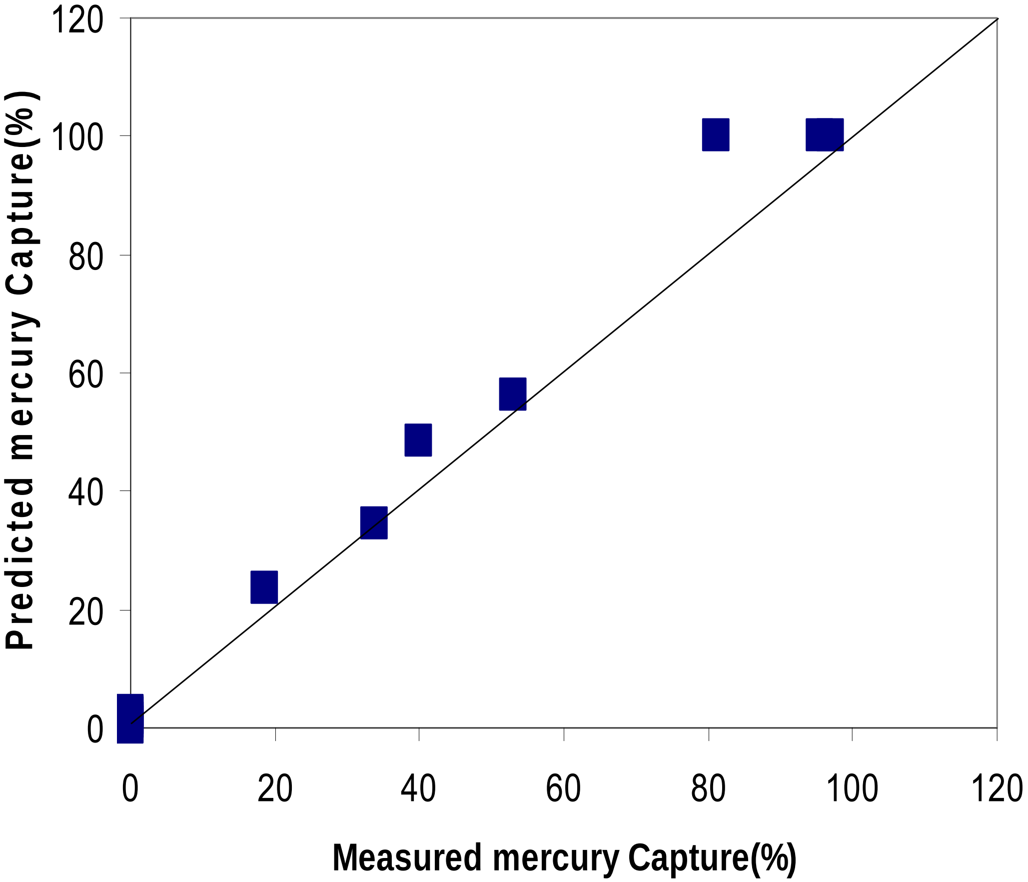
- Adsorption of Hg on carbon surface as a function of temperature and chlorine concentration
  - HCl + UBC = UBC.Cl + H
  - UBC.Cl + UBC.Cl = Cl_2 + 2 UBC
  - Hg + UBC.Cl = UBC.HgCl
    - UBC = unburned carbon sites
    - UBC.Cl = chlorinated carbon sites
    - UBC.HgCl = partial oxidized mercury adsorbed on carbon sites
- The unknown reaction rate constants were obtained by interfacing Simplex Centroid FORTRAN code with CHEMKIN software

Heterogeneous Model



Experimental vs simulation results for Hg capture on activated Carbon

Heterogeneous Model



Experimental vs simulation results for Hg capture on unburned Carbon

Summary

- Three catalysts are being tested for Hg oxidation.
- More catalysts are being developed.
- Established a homogeneous Hg oxidation model
- Developed a surface adsorption model that matched well with experimental data

Future Work

- Continue the catalyst development effort to provide new catalysts for the laboratory evaluation of Hg oxidation.
- Continue the experimental study at the Catalyst Reactivity Test Facility to determine the effect of various factors on Hg oxidation.
- Continue the development of the chemical kinetic model that includes surface catalyzed Hg oxidation, and produce results that are consistent with the data obtained in laboratory, data available in the literature, and data from field tests.

Question?