Study of Speciation of Mercury under Simulated SCR NO_x Emissions Control Conditions

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Background

- Speciation influences emissions control
  - Ionic Hg^{2+} is removed easily by wet scrubbers
  - Volatile elemental Hg^0 is difficult to capture
- Many Selective Catalytic Reduction (SCR) units are meeting stringent NO_x regulations
  - Vanadia/titania (V_2O_5/TiO_2) catalyst
  - Ammonia (NH_3) or Urea (CH_4ON_2) reductant
- SCR has an impact on mercury speciation
  - Limited field data in Europe and U.S.
  - Increase in Hg^{2+} across SCR reactor

Factors Affecting Hg Chemistry

- Apparent dependence on coal type
  - Higher Hg^{2+} across SCR for bituminous coal-fired boilers
  - Little change in Hg speciation across SCR for boilers burning sub-bituminous (Powder River Basin) coal
- Possible effects of SCR system
  - Changes in flue gas chemistry (NO_x, NH_3, Cl_2, SO_3)
  - Catalytic oxidation by vanadium based catalysts
- Important reactions transforming Hg^0 to Hg^{2+} in SCR systems are not well understood

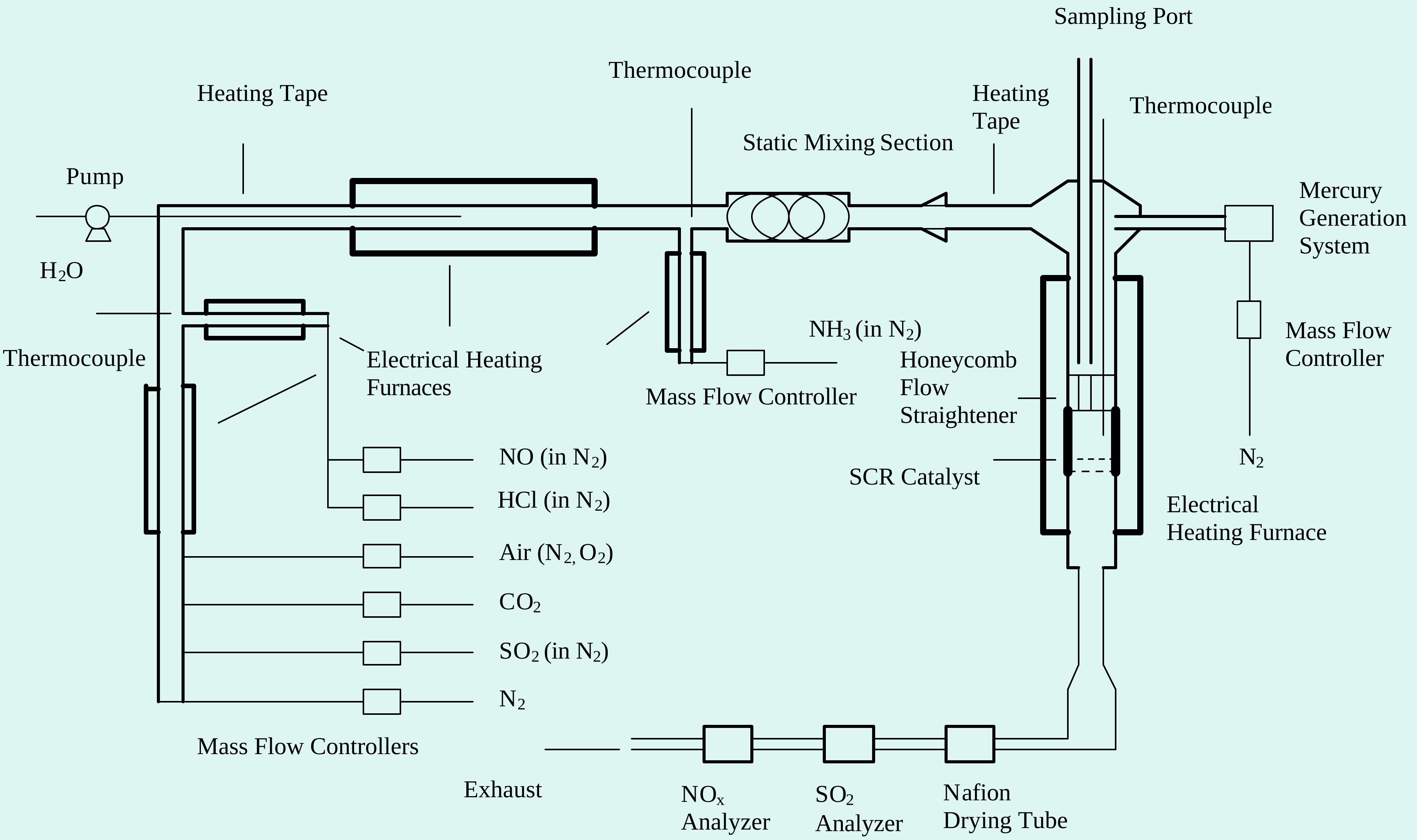
Objectives

- Identify important parameters for enhancing Hg^0 oxidation in SCR systems
- Provide scientific base for apparent coal-type dependence on SCR effect on Hg^0 oxidation
- Better understanding of the fundamentals of SCR enhanced mercury oxidation for developing multi-pollutant control strategies

Approach

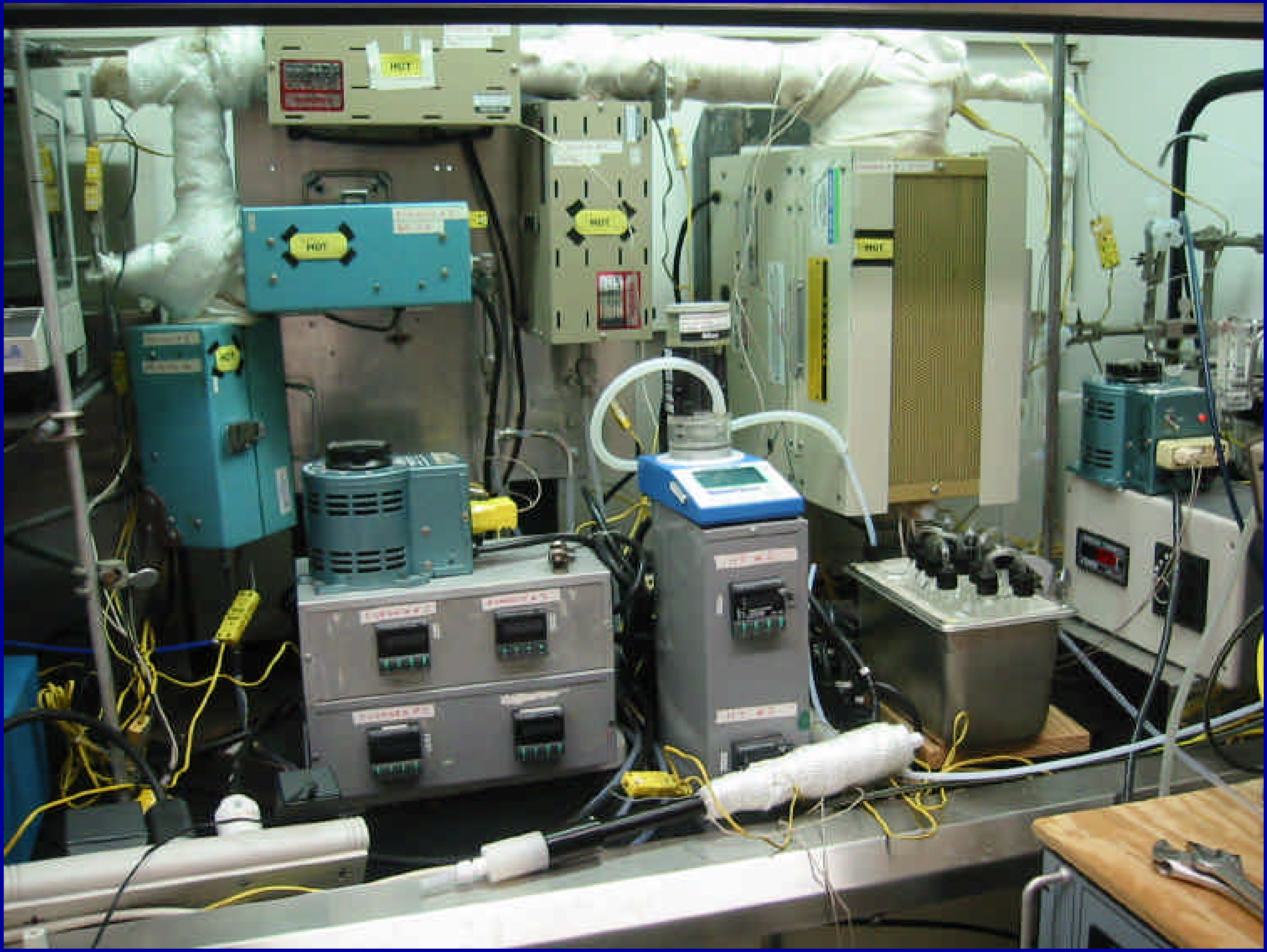
- Good control on experimental variables
  - Bench-scale SCR reactor
  - Simulated combustion flue gases for bituminous and sub-bituminous coals
- Modified Ontario Hydro (OH) method for speciation sampling/analysis
  - Lower sampling volume
  - Mini-impingers

SCR Reactor System

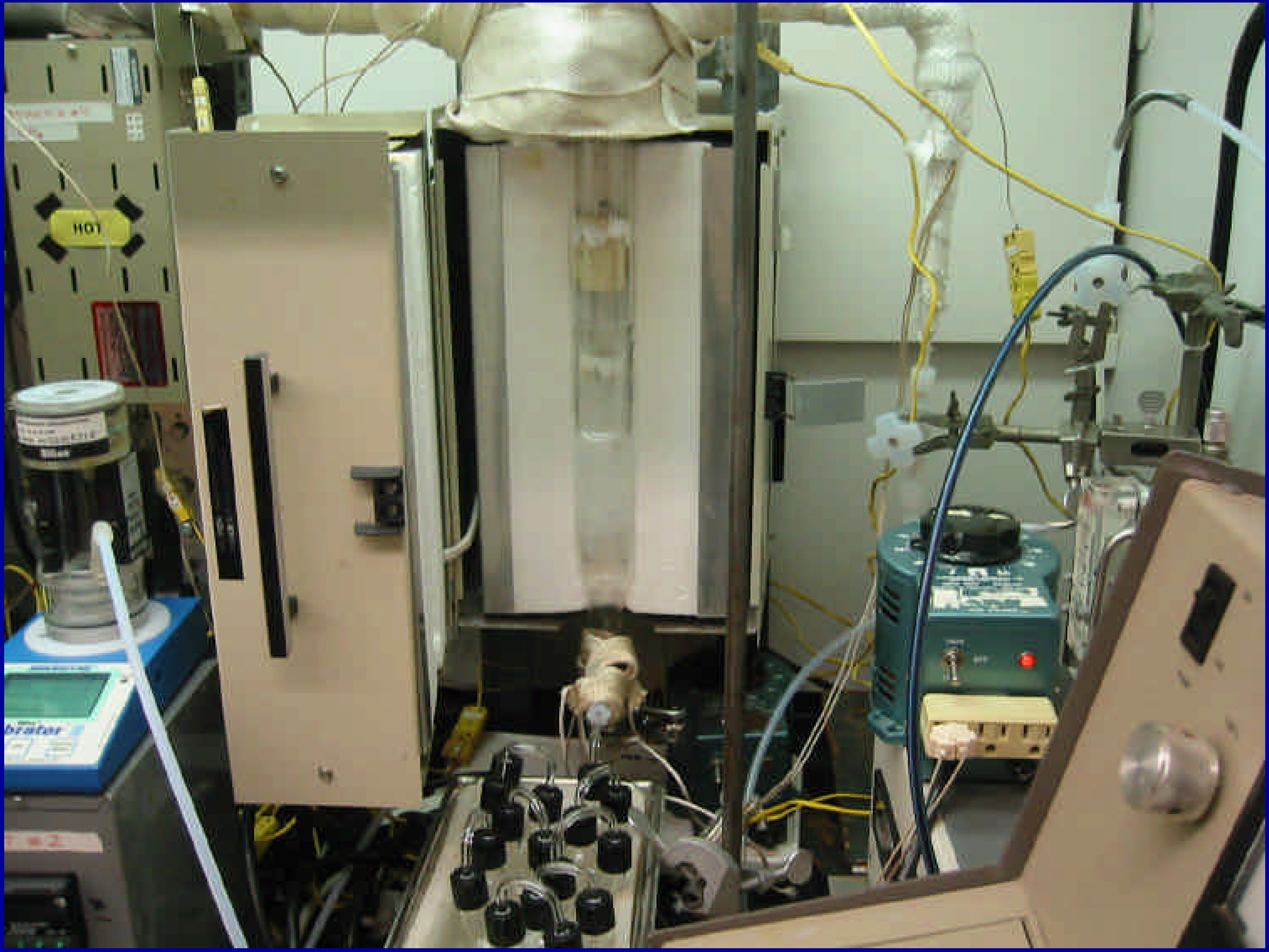


Bench-Scale SCR Reactor System

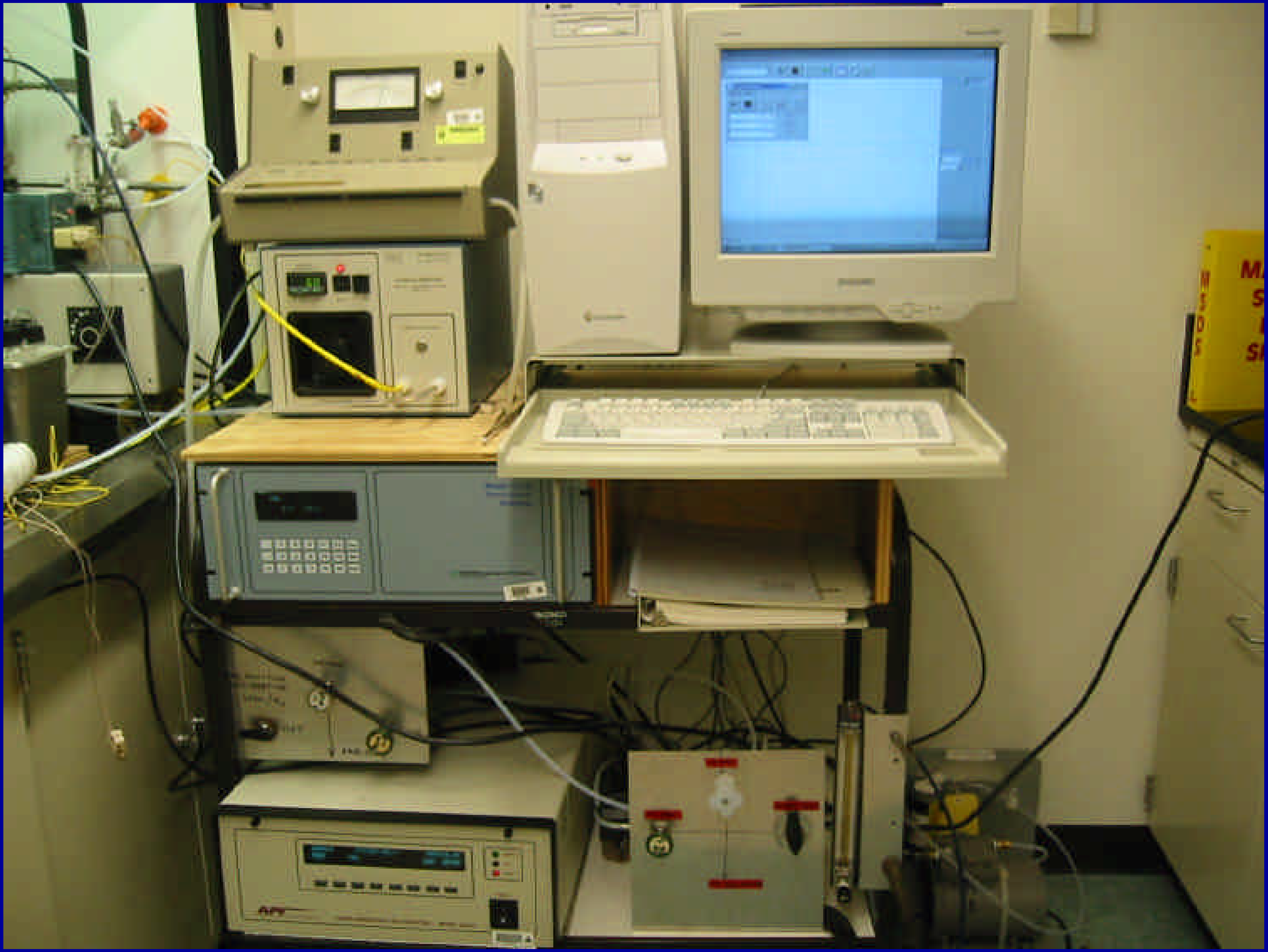
Simulated Flue Gas Preheating and Mixing



SCR Reactor



NO_x and SO_2 Monitors



Experimental Procedures

- Catalyst
  - Cormetech commercial honeycomb catalyst (2.2 x 2.2 x 1.9 cm, 9 channels)
  - Space velocity 2609 hr^{-1} at 400 cm^3/min gas flow rate
- Thermal pre-treatment of catalyst
  - Heating of catalyst overnight at 425 °C under N_2 flow
  - Minimize residual effect from previous experiment
- Catalyst pre-conditioning
  - Passing SO_2 and HCl through catalyst overnight at levels for next day's experiment
- Add remaining flue gas components (O_2, CO_2, H_2O, NO, NH_3, Hg^0) before experiment

Mercury Sampling and Analysis

- OH sampling
  - Sampling started after NO_x reached steady state level
  - Two hour sampling time (0.05 m^3 total sampling volume)
  - Measure sampling flow (400 cm^3/min) every 10 min
- Sampling impingers
  - Hg^{2+} collected by first three impingers containing KCl (1N) solution
  - Hg^0 collected by one impinger containing HNO_3 (5%) and H_2O_2 (10%) solution and three impingers containing H_2SO_4 (10%) and $KMnO_4$ (4%) solution
- Each fraction prepared/analyzed for mercury by cold vapor atomic absorption (CVAA)

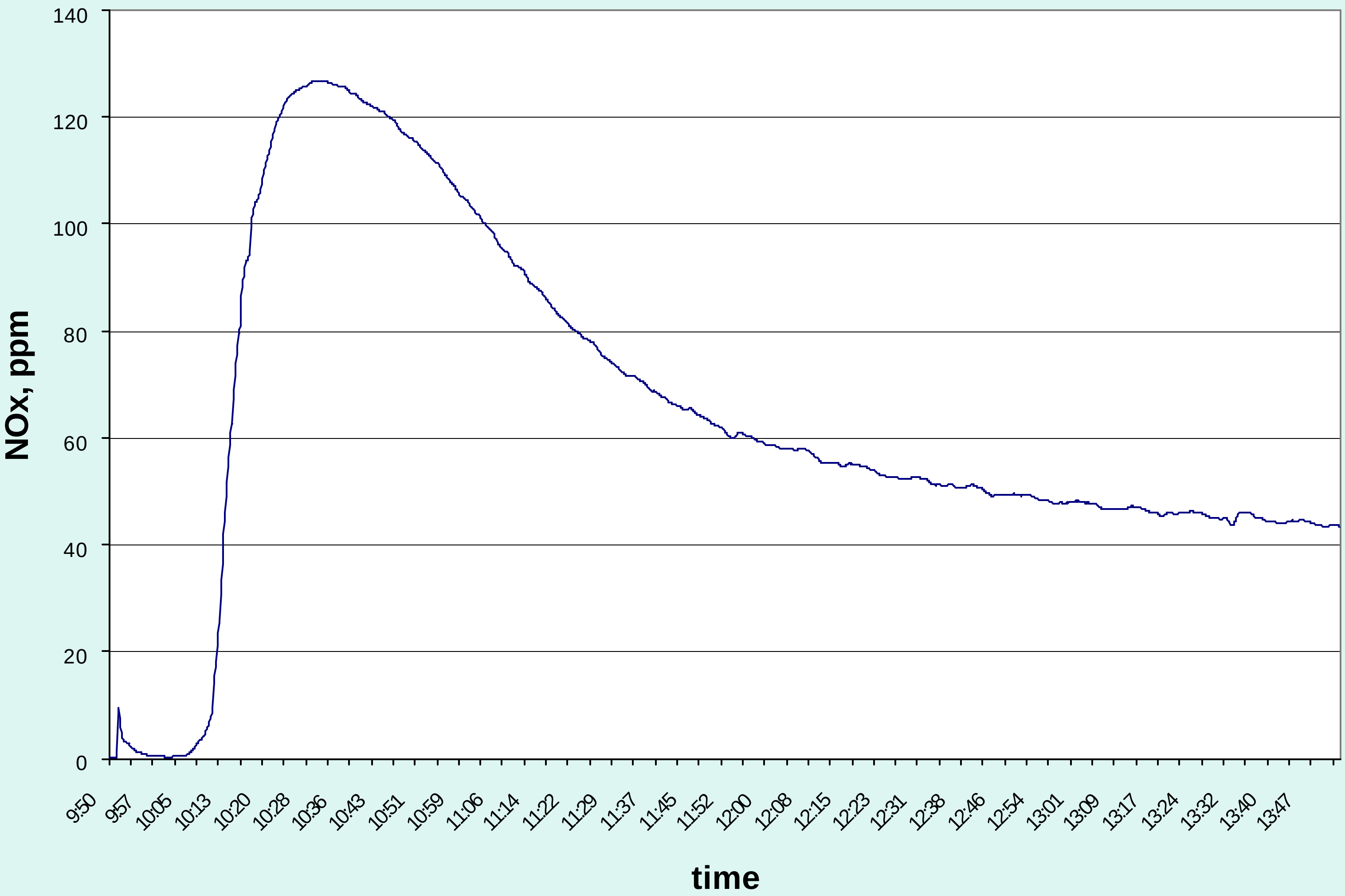
Simulated Powder River Basin Coal Combustion Flue Gas Mixtures

Test No.	**P1**	**P2**	**P3**	**P4**
Simulation	PRB coal	PRB coal without HCl	PRB coal without NH_3	PRB coal without NH_3 and NO_x
HCl Concentration (ppm)	8	0	8	8
SO_2 Concentration (ppm)	280	280	280	280
NO_x Concentration (ppm)	350	350	350	0
NH_3 Concentration (ppm)	315	315	0	0
CO_2 Concentration (%)	15	15	15	15
O_2 Concentration (%)	3.5	3.5	3.5	3.5
H_2O Concentration (%)	5.3	5.3	5.3	5.3
Hg^0 concentration (ppb)	19	19	19	19

Simulated Bituminous Coal Combustion Flue Gas Mixtures

Test No.	B1	B2	B3	B4
Simulation	High Cl, low S	Medium Cl and S	B2 without SO_2	Low Cl, high S
HCl Concentration (ppm)	204	134	134	98
SO_2 Concentration (ppm)	934	2891	0	3116
NO_x Concentration (ppm)	350	350	350	350
NH_3 Concentration (ppm)	315	315	315	315
CO_2 Concentration (%)	15	15	15	15
O_2 Concentration (%)	3.5	3.5	3.5	3.5
H_2O Concentration (%)	5.3	5.3	5.3	5.3
Hg^0 concentration (ppb)	19	19	19	19

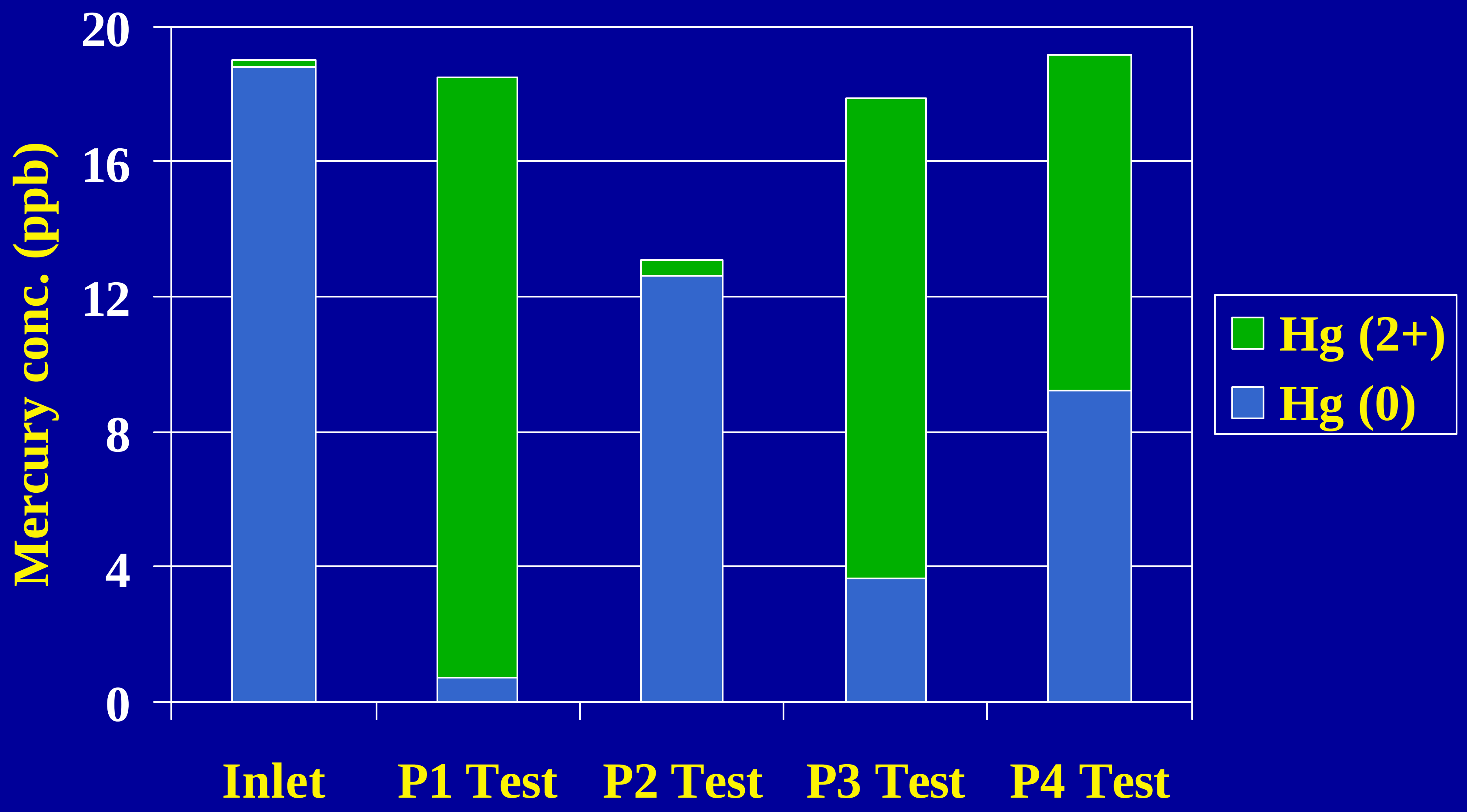
SCR Outlet NO_x Concentration Profile



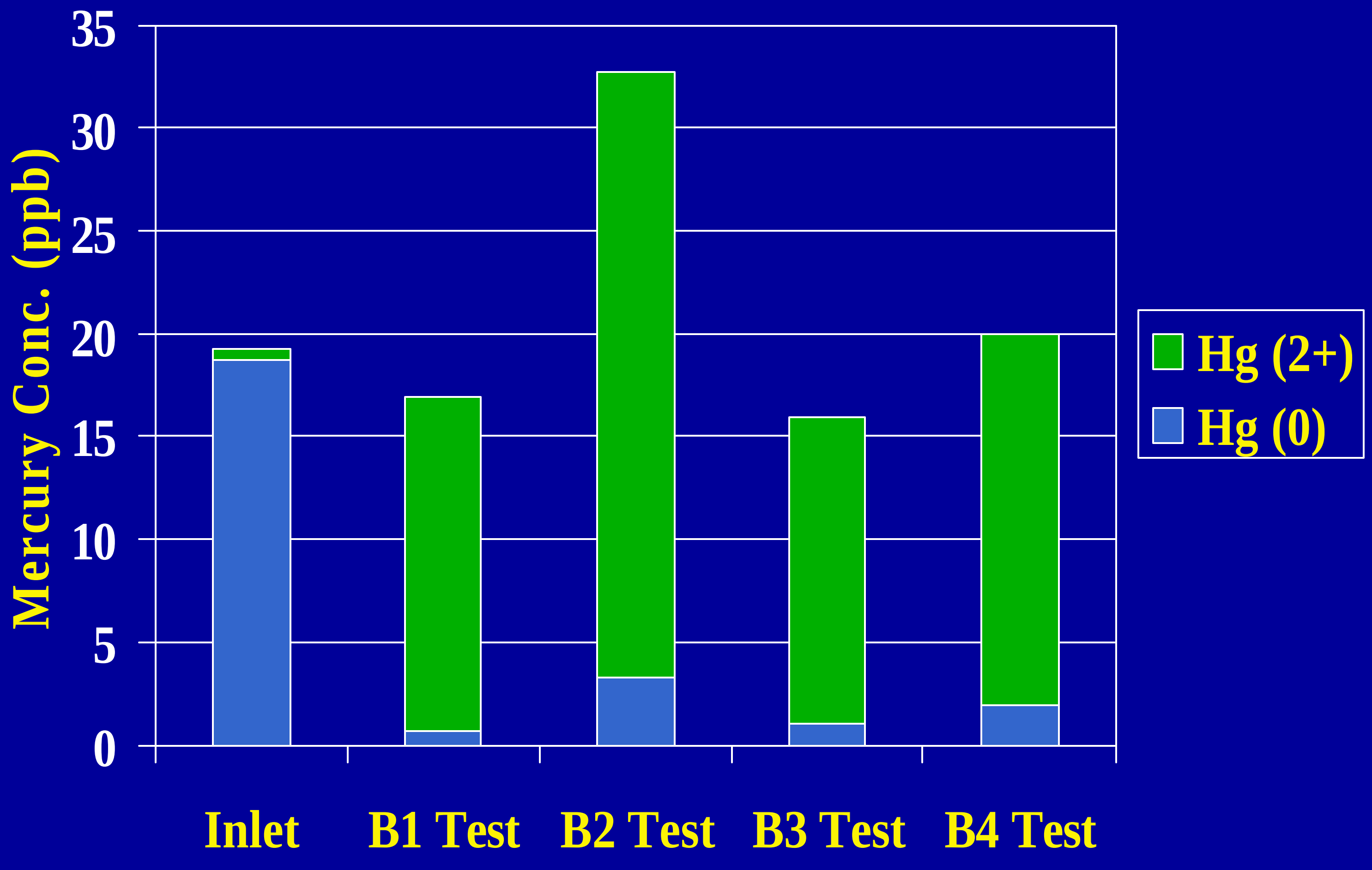
NO_x Reduction Results

Test No.	P1	P2	P3	P4	B1	B2	B3	B4
SCR Outlet NO_x Concentration (ppm)	44	52	350	0	44	43	47	46
NO_x Reduction (%)	87	85	0	0	87	88	87	87

SCR Outlet Mercury Speciation Results for PRB Coal Simulation Experiments



SCR Outlet Mercury Speciation Results for Bituminous Coal Simulation Experiments



Discussion

- Chlorine is critical for Hg^0 oxidation in SCR
  - Low Cl and high Ca in PRB coals cause little SCR impact
  - Cl in bituminous coals sufficient to cause significant impact
- Possible mechanisms involved over SCR catalyst
  - SCR catalyzed Deacon reaction: $2HCl + 1/2\ O_2 = Cl_2 + H_2O$
  - Chlorination reaction: $V_2O_5 + 2HCl = 2VO_2Cl(s) + H_2O$
- NO_x promotes Hg^0 oxidation in SCR
  - NO_x seems to play a significant role for Hg^0 oxidation in SCR
  - Chemisorption of NO_x creates active sites for Hg^0 adsorption
  - Reactions of NH_3 with NO_x inhibit Hg^0 adsorption
- SO_x does not seem to play a significant role in SCR Hg^0 oxidation under conditions tested to date
  - Suggests that Hg^0 is unlikely to be oxidized by SO_3

Summary and Conclusions

- Bench-scale system simulated field units closely
  - Achieved NO_x reduction levels similar to those in field units
- Different effects of flue gases on SCR Hg^0 oxidation
  - HCl provides critical chlorine source for Hg^0 oxidation
  - NO_x has a significant promotional effect
  - SO_x has little effect under the conditions of this study
- Complex interactions between Hg^0, flue gases, and SCR catalyst result in Hg^0 oxidation
- Results provide scientific evidence for apparent coal-type effect on Hg^0 oxidation in SCR systems

Future Work

- Effect of catalyst age
  - Aged samples collected in the field
- Effect of catalyst formulation
  - Catalysts for PRB coal application
- Effect of residence time
- Effect of NH_3/NO_x molar ratio
- Mechanistic and modeling studies

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