Effects of SCR Catalyst and Sodium Hydrosulfide on the Speciation and Removal of Mercury within a Forced-Oxidized Limestone Scrubber

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Motivation and Objectives

➢ Hg^{2+} retention and control within a Wet FGD (WFGD)

- ➢ Effective in bituminous coals; verified in this program (Mt. Storm fires a medium sulfur bituminous coal)
- ➢ PRB coals: recent analysis of literature data and modeling have shown less effectiveness (Niksa, 2004); needs to be assessed (beyond this study)

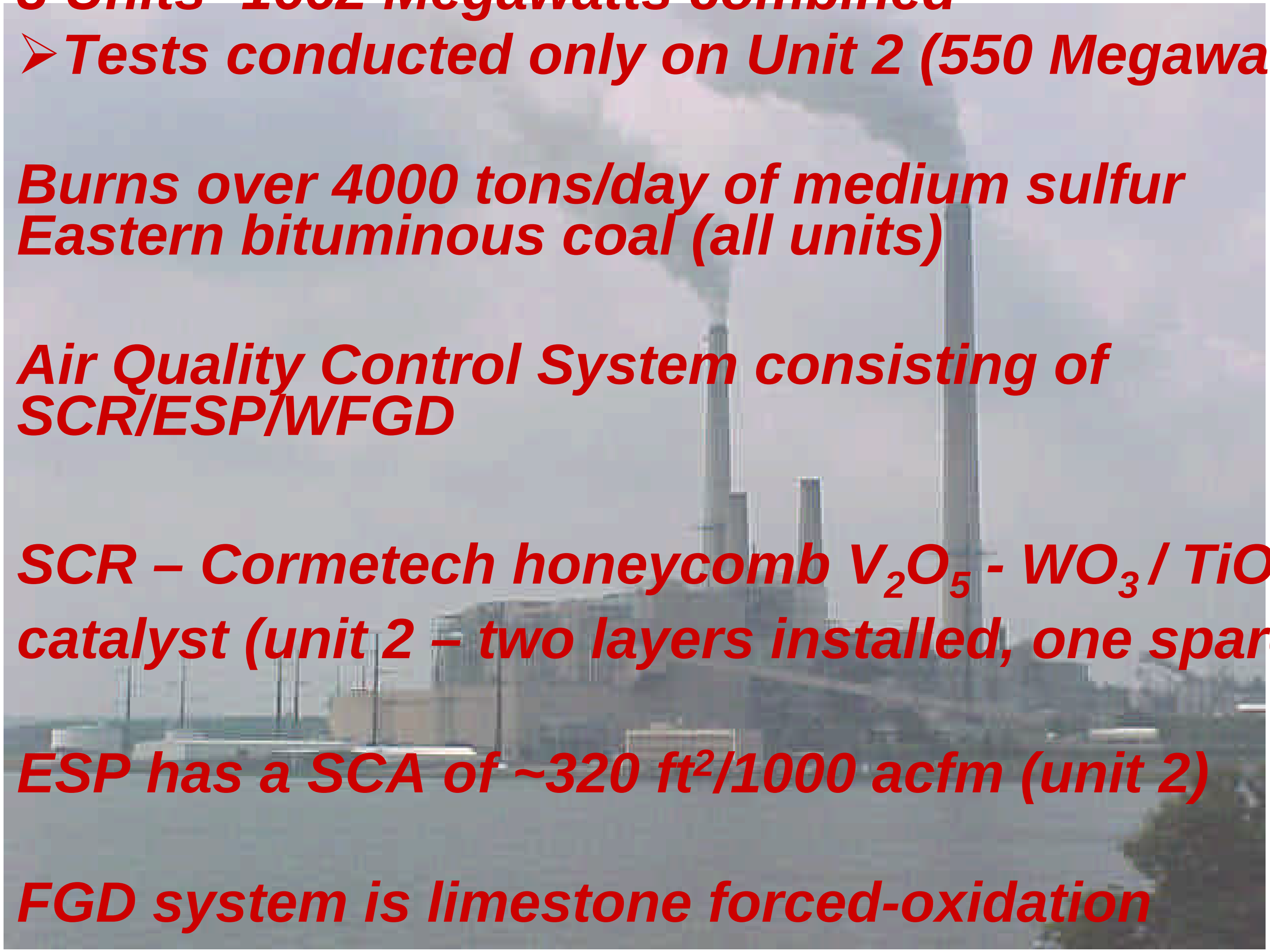
➢ The all important liquid-phase chemistry of Hg^{2+} and its reduction reaction to Hg^0 and re-emission of Hg^0 from WFGD

- ➢ Does it happen in this LSFO unit?
- ➢ Can it be prevented using B&W's technology (addition of NaHS)?

➢ Effect of SCR on Hg speciation

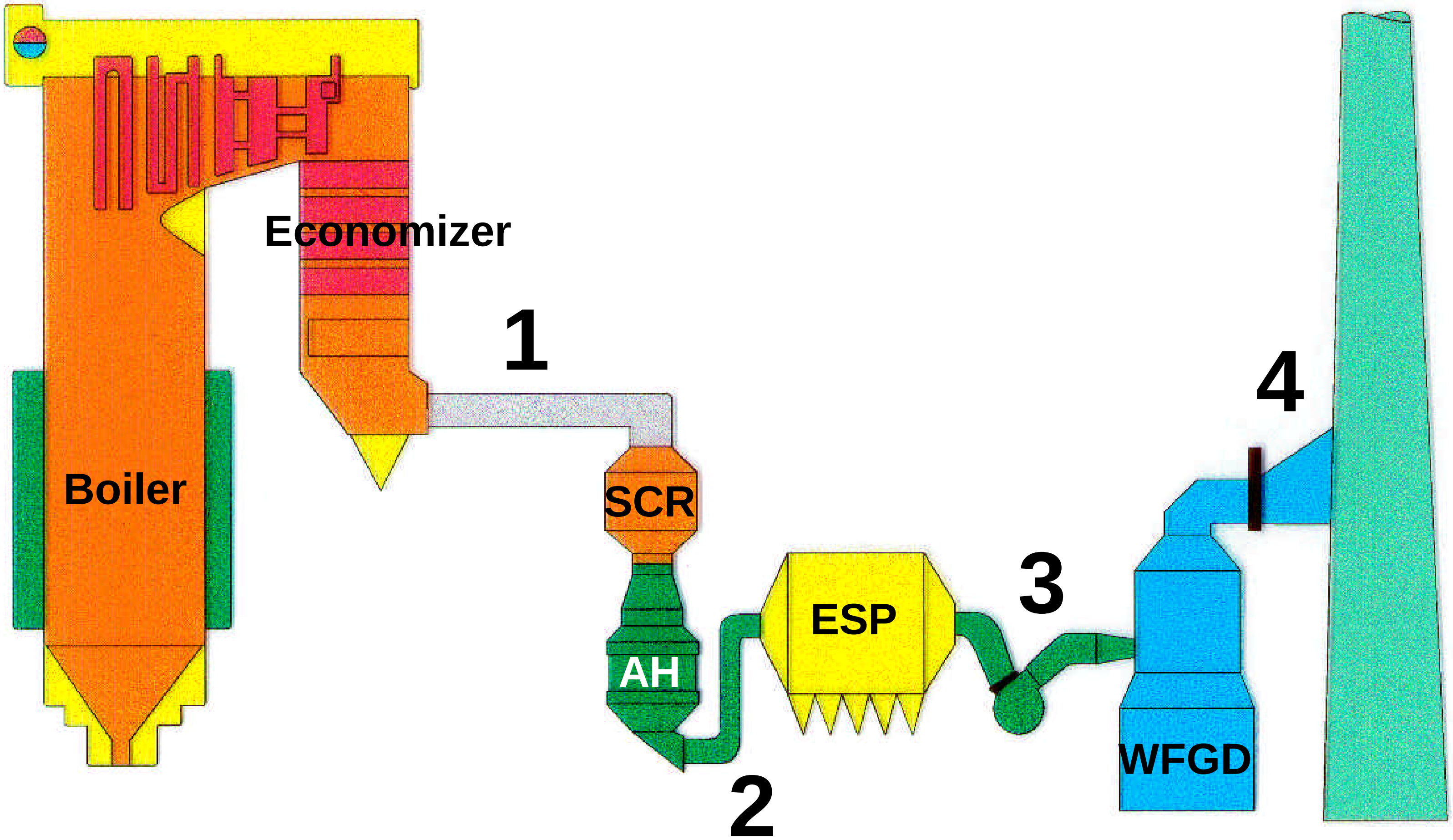
- ➢ Does it change at the inlet of the WFGD? Production of additional Hg^{2+}?
- ➢ If yes, is WFGD effective in the removal of the additional Hg^{2+}? Re-emission of Hg^0? Implementation of B&W's technology needed?
- ➢ Can SCR Hg oxidation be accurately modeled?
- ➢ What are the key field measurement and design parameters for SCR oxidation of Hg^0?

Mount Storm Site Description



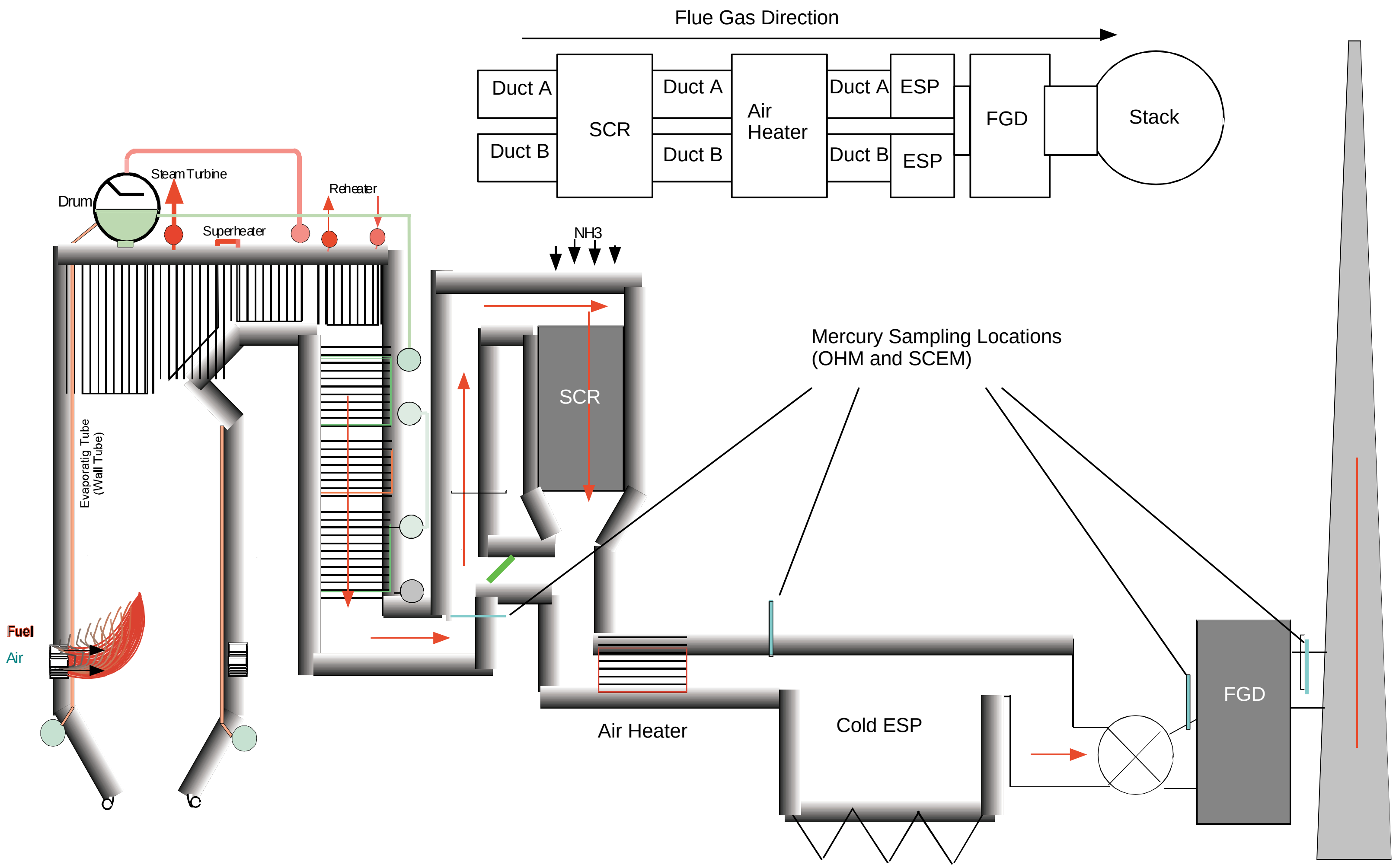
- ***3 Units -1662 Megawatts combined***
  - ***Tests conducted only on Unit 2 (550 Megawatts)***
- ***Burns over 4000 tons/day of medium sulfur Eastern bituminous coal (all units)***
- ***Air Quality Control System consisting of SCR/ESP/WFGD***
- ***SCR – Cormetech honeycomb V_2O_5 - WO_3 / TiO_2 catalyst (unit 2 – two layers installed, one spare)***
- ***ESP has a SCA of ~320 ft^2/1000 acfm (unit 2)***
- ***FGD system is limestone forced-oxidation***

Mt. Storm Unit 2 Schematic



1-4: Locations of Hg measurements: OHM and Hg CEM (PSA analyzer)
SCR was by-passed during the initial testing (non-ozone season)

Detailed Duct/Sampling Locations



FGD Scrubber Attributes

Dominion Power – Mt. Storm Station Unit 2	
Number of FGD modules	1
FGD inlet SO_2 concentration, ppmdv	1400
FGD reagent	Limestone
Recycle slurry pH	5.60
Recycle slurry total suspended solids, %	14 – 16
Recycle slurry operating level, ft	29.1
FGD liquid to gas ratio, gal/1000 acf	70
FGD forced-oxidation method	In-situ – lance method
DBA concentration, ppm	294 – 557
Chloride concentration, ppm	35,000
Slurry dewatering – Primary	Hydroclone
Slurry dewatering – Secondary	Rotary drum vacuum filters
FGD purge	None, closed system
Gypsum use	Mine reclamation
De-foaming agent use	Yes, sporadically

Economizer Outlet (Duct A and Duct B)

ESP Inlet

FGD Outlet

Ontario Hydro and Hg CEM (PSA analyzers)

WFGD Reagent Feed System (B&W's technology)

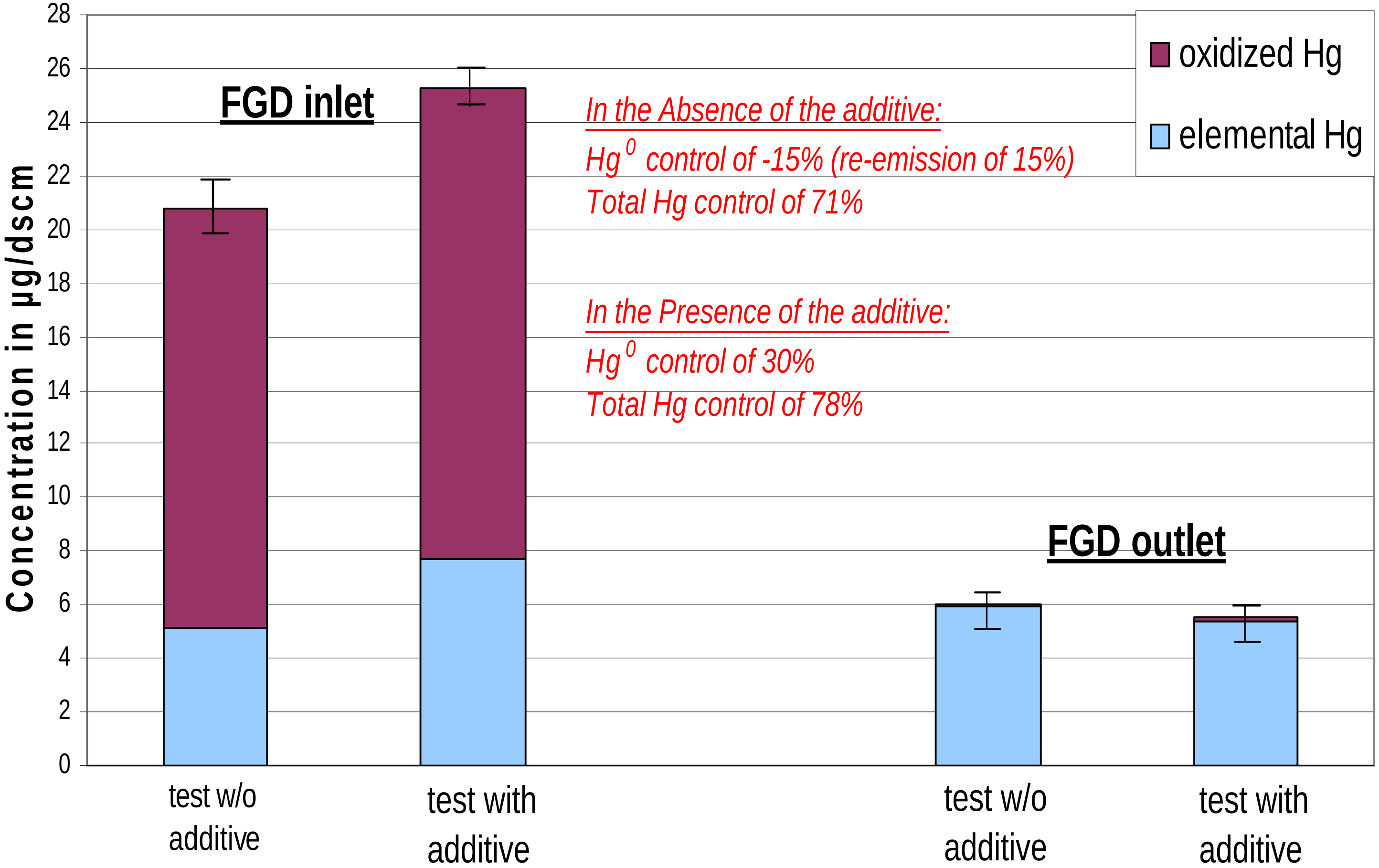
Results

Mt. Storm Coal Analysis Results

	Average*	RSD**, (%)	Minimum	Maximum
Moisture, %	7.46	24	5.20	13.09
Ash, %	14.62	11	12.21	19.10
Volatile Matter, %	16.67	10	14.87	20.86
Sulfur, %	1.82	9	1.39	2.16
Heating value, Btu/lb	12026	3	11219	12676
Carbon, %	69.51	3	64.79	72.81
Hydrogen, %	3.86	5	3.54	4.34
Nitrogen, %	1.17	11	0.89	1.28
Oxygen, %	8.97	21	6.48	14.66
Chloride, ppm	555	12	423	678
Mercury, ppm	0.20	16	0.16	0.30

* Result of 23 different catches during the test program
** RSD: Relative Standard Deviation [(standard deviation/average)*100]

SCR bypassed: Effect of B&W additive (NaHS); OHM results



- Total Hg at Economizer Outlet: 22-27 µg/dscm

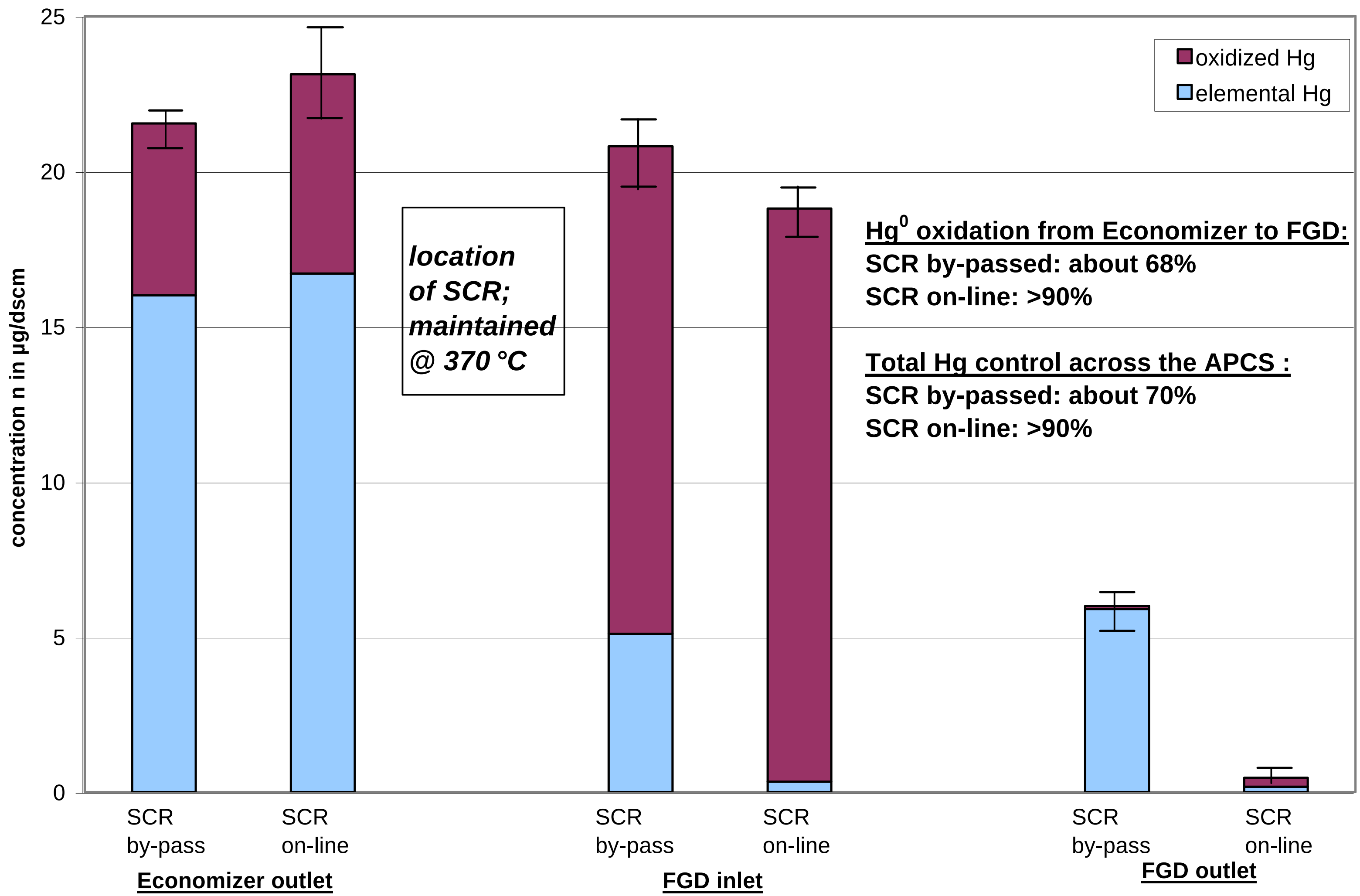
- No control of Hg with AH/ESP; very little Hg_P

Ash Sample Analysis from Mt. Storm

Date	LOI, %	Inorganic carbon, %	Mercury, ppm
5/21/04	6.5	0	0.15
5/24/04	9.0	0	0.25
6/02/04	6.3	0	0.17
6/09/04	8.7	0	0.24
Average	8.1	0	0.21 (very low Hg_P)

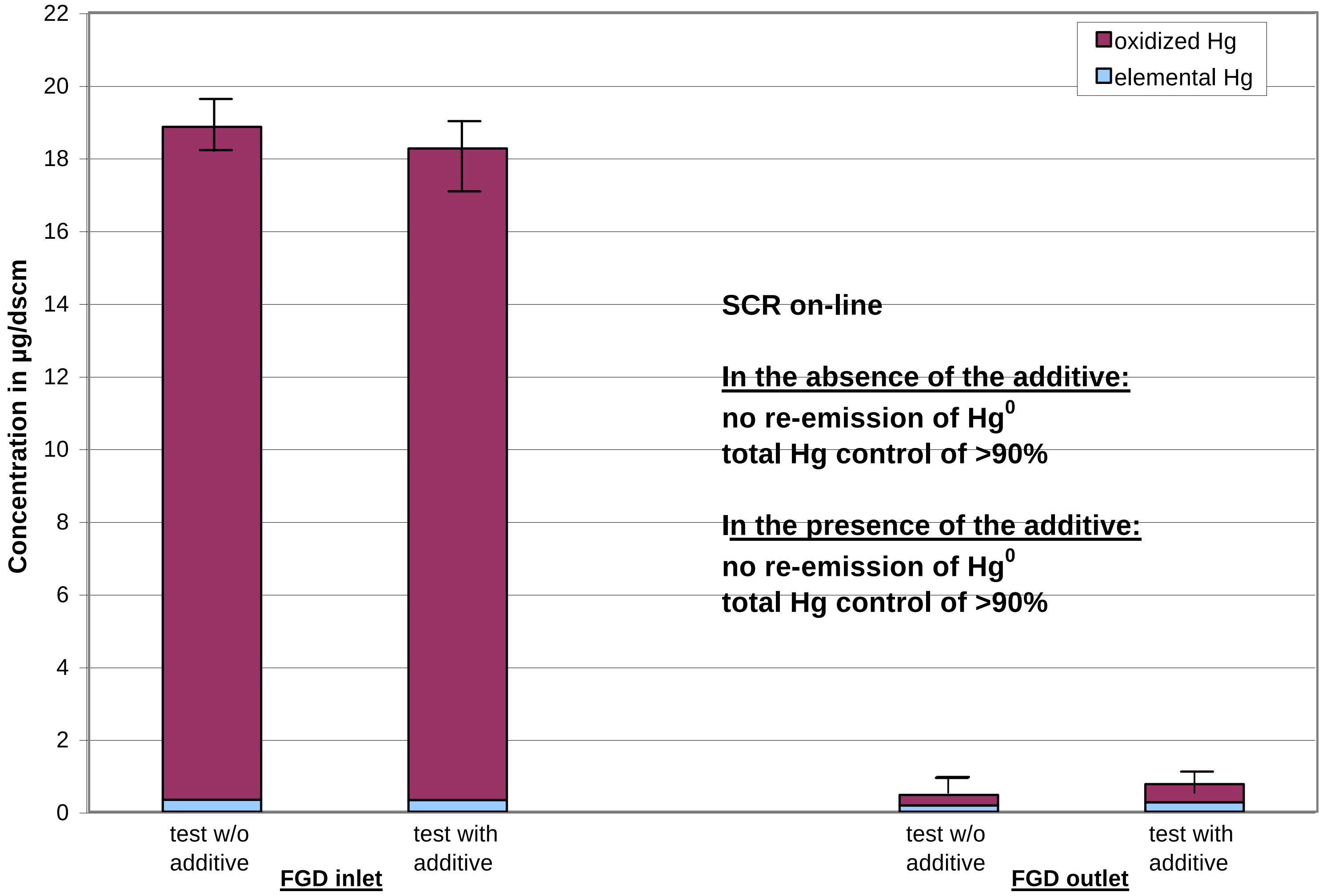
Despite rather high UBC (LOI) and high HCl in flue gas (about 35 ppm), very little Hg_P was observed; LOI not very active (in ESP contact mode) in the adsorption of Hg by this fly ash

Effect of SCR; no additive (NaHS); OHM results



Dual benefit of SCR:
1- increased net Hg^0 oxidation (economizer out to FGD inlet) from 64% Hg^{+2} to over 95% Hg^{+2}
2- Prevented re-emission of Hg^0

Effect of SCR and additive (NaHS); OHM results



SCR suppressed the re-emission of Hg^0; injection of the additive not needed

Mount Storm Project Summary

- **<u>Without SCR in service:</u>**
  - ***Total Hg removal across the FGD of ~70% w/o NaHS injection***
  - ***There was some re-emission of Hg^0 (outlet > inlet)***
  - ***With NaHS injection, total Hg removal across FGD of ~80%***
    - ***The additive prevented re-emission of Hg^0***

- **<u>With SCR in service:</u>**
  - ***SCR increased the extent of oxidation of Hg^0 (in a bituminous coal) from 64% to >95% from economizer outlet to FGD inlet***
  - ***Total Hg removal (across the FGD) averaged >90% with and without additive injection***
  - ***With the SCR in service, there was no re-emission to control.***

- **<u>B&W's additive did not affect SO_2 removal efficiency of Wet FGD</u>**

SCR Hg Oxidation Modeling

- **Cormetech Proprietary Model - Description**
  - ***Simultaneous NO_x Reduction and Hg^0 Oxidation to Hg^{+2}***
  - ***Numerical Integration of Differential Equations for Rx. Kinetics***
    - ***Allows for DeNOx, NH_3 Inhibition, Cl & Hg Thermodynamics, Catalyst Age, Coal(s) being Fired, and Field Operating Conditions***
  - ***Regression Constants Based on Extensive Parametric Pilot Studies***

- **Modeling Study - Components**
  - ***Determine Average Field Measurement Values & Uncertainties***
  - ***Pilot-Measured Catalyst DeNOx Activity (could also predict)***
  - ***Estimate non-SCR Contribution to Observed Hg Conversion***
  - ***Compare Field Data to Model Prediction***
  - ***Determine Key Operating & Design Parameters (Sensitivity Analysis)***

SCR Modeling – Input Parameters

- **Standard Inputs From Available Field Data**
  - *Unit Operating Conditions, Coal Properties, Catalyst Properties*
  - *DeNOx Performance – Inlet NO_x and NH_3 Slip (or Equivalent)*
  - *Flue Gas Concentrations – Especially Hg, Hg^{+2}, H_2O and HCl*

- **Estimate of Non-SCR Hg^0 Conversion**
  - *SCR Outlet Hg Speciation was not Measured at Mt. Storm Unit 2*
  - *Bias Seen in ESP Inlet Hg Data → Rely on FGD Inlet Data*
  - *SCR-Bypassed Hg Data (Economizer Outlet to FGD Inlet)*
    - *Baseline, w/o FGD Additive: 68% Conversion*
    - *Baseline, with FGD Additive: 59% Conversion*
    - *Average: 64% non-SCR Hg Conversion (8% Pooled Uncertainty)*

- **Estimate of HCl Concentration at SCR**
  - *33 ppmvd HCl Measurement (Corrected from FGD Inlet)*
  - *41 ppmvd HCl from Combustion Calculations – Utilized in Model*
  - *Statistically Different – Perhaps due to HCl Sorption after SCR*

SCR Modeling – SCR On-Line w/NH_3

- **Normal Operation: 93% NOx Reduction**

- **Field Estimate for SCR Hg Conversion to Hg^{+2}**
  - ***Theory:*** $?_{NET} = 1 – [(1 - ?_{SCR})(1 - ?_{NON\text{-}SCR})]$
  - ***Assumption:*** $?_{NON\text{-}SCR}$ ***= 64% Based upon SCR-Bypassed Data***
    (Additional Conversion After SCR of Remaining Hg^0)
  - ***Field Data:*** $?_{NET}$ ***= 98.3% with 0.5% Std. Uncertainty***
  - ***Field Estimate:*** $?_{SCR}$ ***= 95.9% with 1.7% Std. Uncertainty***

- **Predicted SCR Hg Conversion to Hg^{+2}**
  - ***Model Prediction:*** $?_{SCR}$ ***= 92.6% with 2.9% Std. Uncertainty***

- **Comparison of Field Estimate with Model Prediction**
  - ***Not Statistically Different at 80% Confidence Level***
  - ***Prediction is Consistent with Field Data***

SCR Modeling – SCR On-Line, NH_3 Off

- **Ontario Hydro Field Data Not Available**

- **Predicted Net Conversion (SCR + non-SCR)**
  - *SCR: Model Prediction – 97.9 % Conversion*
  - *Non-SCR: Assume SCR-Bypassed Value (64%)*
  - *Net Predicted Conversion – 99.3% Conversion*

- **Comparison to Ammonia Injection Case**
  - *Net Hg Conversion 98.5 % w/NH_3 vs. 99.3% w/o NH_3*
  - *Cannot Draw Conclusion r.e. Statistical Difference*
  - *But NH_3 Believed to Play Strong Role in SCR Hg Oxidation*
  - *Adequate SCR Catalyst Capability (volume & activity) at Mt. Storm 2 for High Hg^0 Conversion for Either Case*
    - *Predicted Difference in SCR Hg^0 Conversion: 5%*

SCR Modeling – Sensitivity Analysis

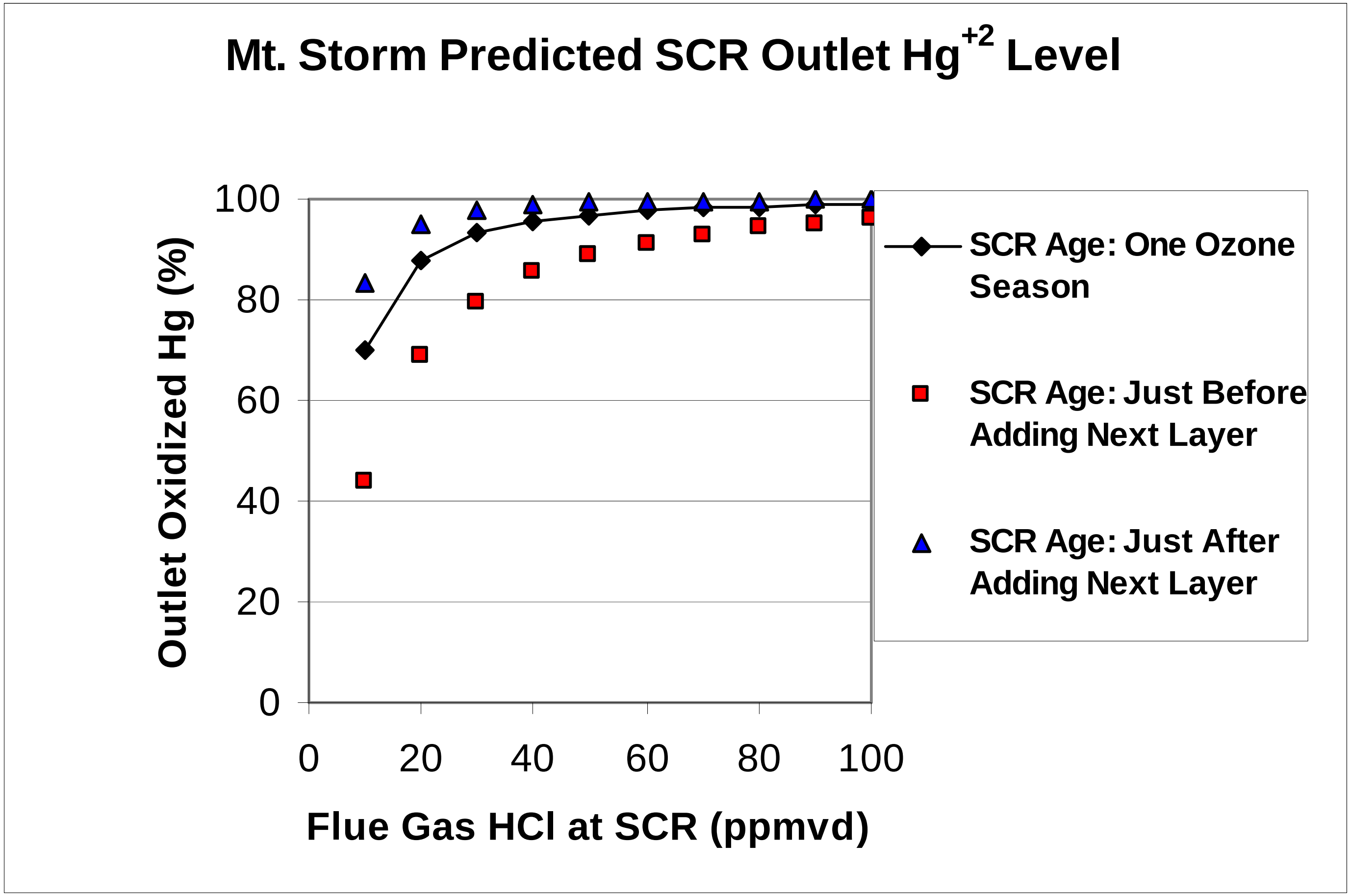
- **Parameter Uncertainties with Major Impact on Hg Prediction**
  - ***SCR Inlet HCl Concentration (or its Surrogate, coal Cl content)***
  - ***SCR Inlet H_2O Concentration***
  - ***Flue Gas Flowrate***

- **Estimated Parameters with Uncertainties of Major Impact**
  - ***SCR Outlet Hg Speciation (not measured directly)***
  - ***SCR Inlet NH_3/NO_x Molar Ratio – adjusted to match field DeNOx***

- **Parameter Uncertainties with Minor Impact on Hg Prediction**
  - ***SCR Temperature***
  - ***Inlet Concentrations - O_2, NO_x, Hg and Hg^{+2}***

- **Other General Considerations**
  - ***Availability of (as well as Design for) Spare Layer(s)***
  - ***Lifetime Performance of SCR for DeNOx and Hg Oxidation***

SCR Modeling – Catalyst Management



- Timing of Additions or Replacements – Consider Both $DeNO_x$ and Hg
- Performance Decline Rates – Accurate Predictions will be Helpful

Summary – SCR Hg Oxidation Modeling

- **Cormetech's SCR Hg^0 Oxidation Model Predictions were Consistent with the Field Data**
- **Key Field Measurement Parameters for Accurate SCR Hg Modeling and Prediction were Identified:**
  - ***NOx Conversion and NH_3/NO_x Molar Ratio***
  - ***Inlet Flue Gas Composition (Including HCl)***
  - ***Inlet and Outlet Hg^0 and Hg^{+2} Concentrations***
  - ***Flue Gas Temperature and Flowrate***
- **SCR Catalyst Management and Design Strategies Should Consider Both NO_x Reduction and Hg Oxidation Requirements**