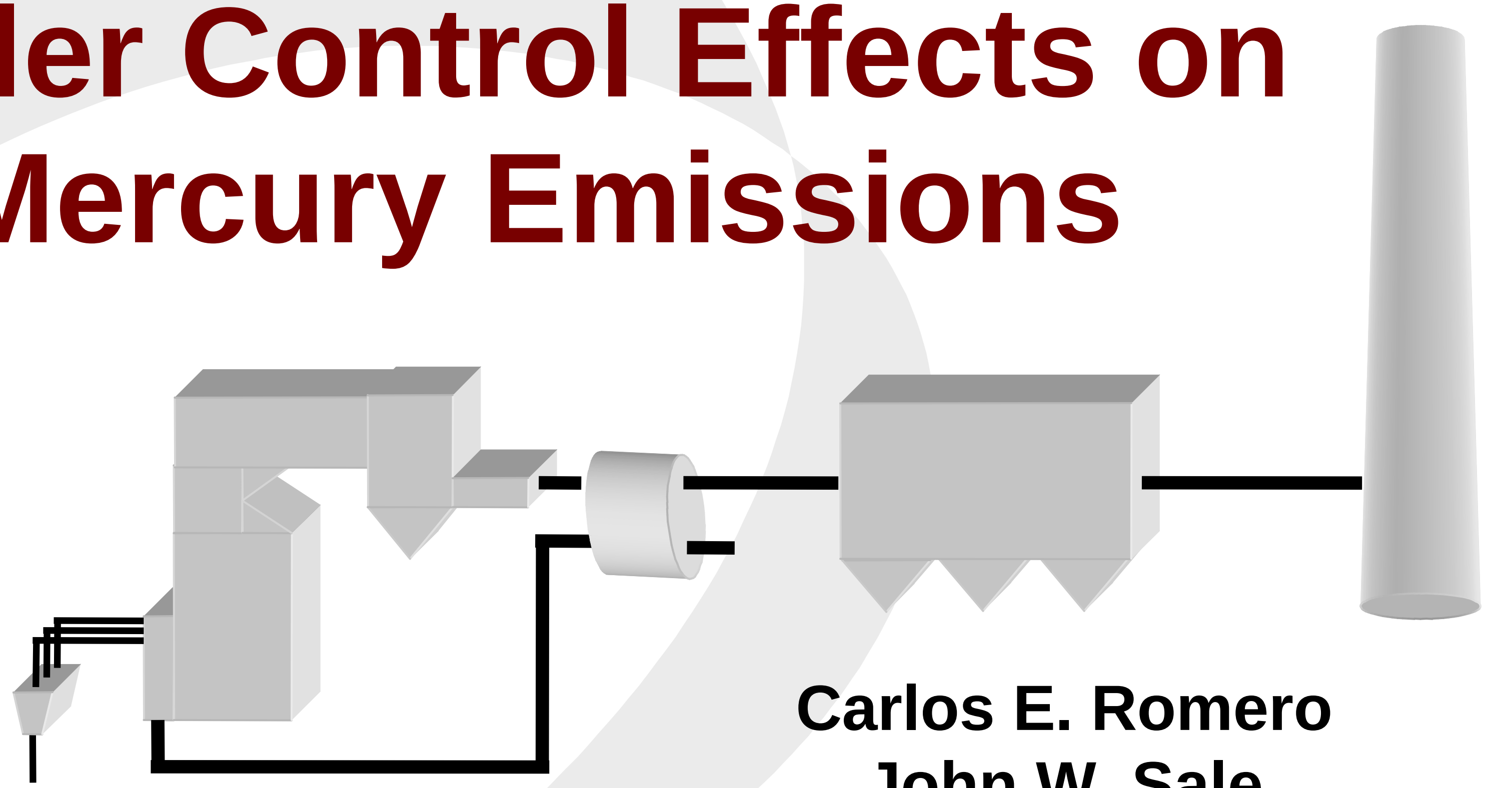
ENERGY RESEARCH CENTER

Boiler Control Effects on Mercury Emissions



Carlos E. Romero
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OUTLINE

- Background
- Current Federal and State Initiatives
- Industry Mercury Reduction Approach
- Boiler Optimization Overview

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BACKGROUND

Approximately 75 tons of mercury are found in the coal delivered to coal-fired power plants each year and about two thirds of this mercury is emitted to the air, resulting in about 50 tons being emitted annually. This 25-ton reduction is achieved in the power plant boilers and through existing pollution controls such as fabric filters (FF) for particulate matter, scrubbers for SO_2 and Selective Catalytic Reduction (SCR) systems for NO_x[1].

[1] Controlling Power Plant Emissions: Overview, USEPA Web Site.

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MERCURY REDUCTION RULES

Of the 189 substances designated as hazardous air pollutants by the EPA, Hg has attracted significant attention due to its increased levels in the environment and well-documented food chain transport and bio-accumulation.

The Bush administration is pushing Congress for passage of Clear Skies (multi-pollutant approach) and the related energy bill.

The EPA Mercury Reduction Rule proposes three mercury alternatives:

- Rule requiring utilities to install Maximum Achievable Control Technologies (MACT). (Section 112 of the Clear Air Act).
- Federally run Cap-and-Trade Program (Section 111 of the Clear Air Act).
- Proposed rule establishing “Standards of Performance.” State run program similar to the federally run program above.

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EPA PROPOSED MACT PROGRAM

- Would be administered by the EPA.
- Would reduce Hg emissions by 14 Tons (29%) by the end of 2007.
- Would provide the EPA with the flexibility to consider a more cost effective way to control mercury emissions.

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EPA PROPOSED MARKET-BASED "CAP-AND-TRADE" MERCURY PROGRAM

- Would be jointly administered by the states and the EPA.
- Would reduce Hg emissions in the first phase due by 2010 (co-benefits based cap level).
- Would reduce Hg emissions in the second phase by 33 tons (69%) when fully implemented in 2018.

The Clear Air Initiative is also a cap and trade program. The EPA is required to issue the rule by March 15, 2005.

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STATE INITIATIVES

- Four states have established mercury emissions limits that are more aggressive than the federal rules.
  - Connecticut
  - Massachusetts
  - New Jersey
  - Wisconsin
- Other states, such as Maryland, have bills in legislation.

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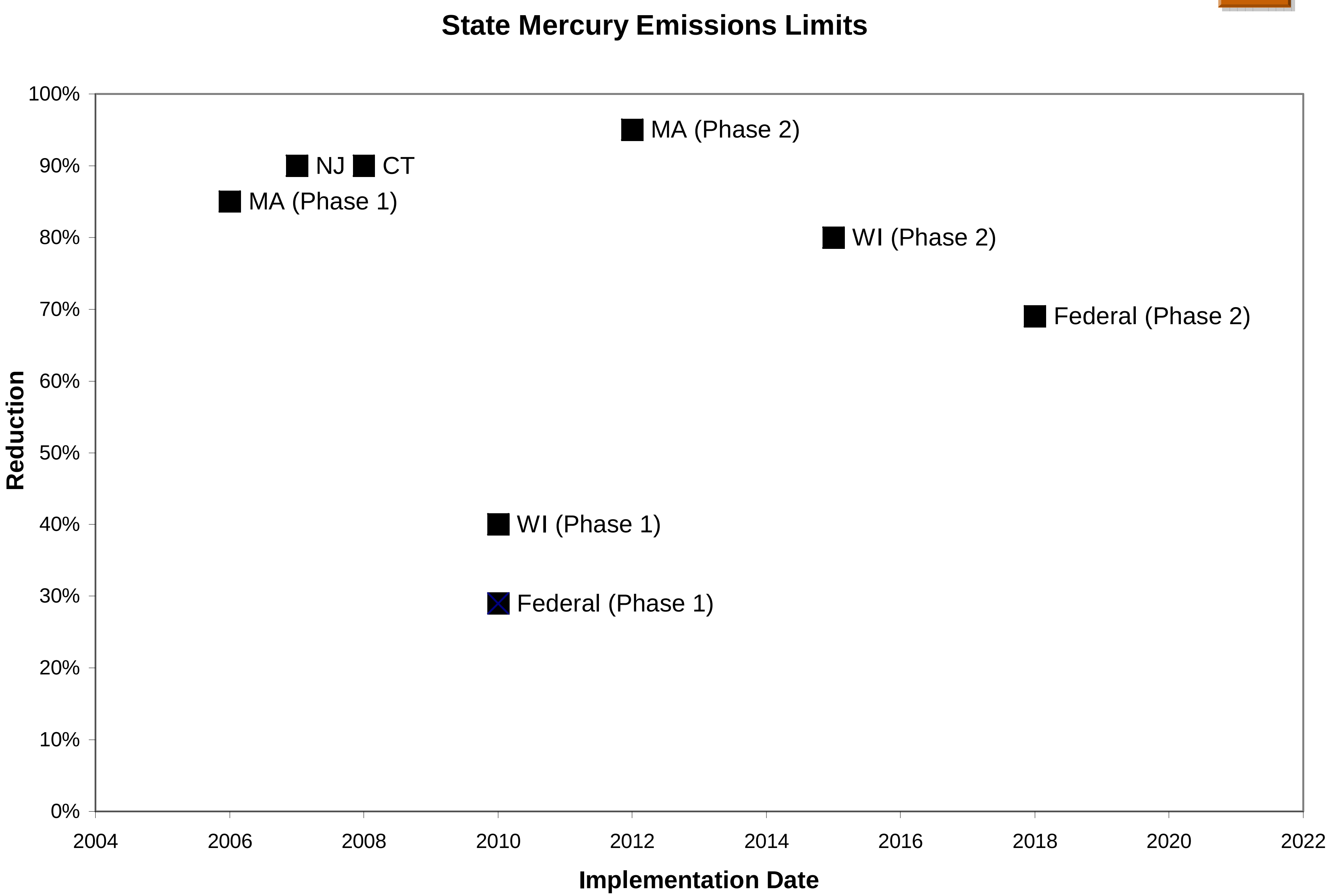

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CONNECTICUT MERCURY EMISSIONS PROGRAM

- An emissions rate equal to or less than 0.6 pound of mercury per trillion BTU of heat input or alternatively,
- An emissions rate comparable to a 90 percent reduction in mercury emissions.
- Compliance would be achieved through the installation of Best Available Control Technology (BACT).
- If a facility installs and properly maintains the best available control technology and still fails to meet the emissions rate, it can request an alternative emissions rate from the Department of Environmental Protection.

MASSACHUSETTS MERCURY EMISSIONS PROGRAM

- Issued draft mercury regulations for 4 of the state's power plants in October 2003 calling for two phases of mercury reductions.
- The first attainment level is a facility average total mercury removal efficiency of at least 85 percent, or a facility average total mercury emissions rate of 0.0075 lbs/GWh by October 1, 2006.
- The second attainment level is a facility average total mercury removal efficiency of at least 95 percent, or a facility average total mercury emissions rate of 0.0025 lbs/GWh by October 1, 2012.

NEW JERSEY MERCURY EMISSIONS PROGRAM

- Require the state's 10 coal-fired power plants to reduce mercury emissions by 90 percent by December 15, 2007, or to a level of 3 mg/MWh.
- The compliance date may be extended until December 15, 2012, for power plants that achieve significant additional reductions in sulfur dioxide, nitrogen oxides and fine particulate matter.

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WISCONSIN MERCURY EMISSIONS PROGRAM

- Approved a mercury rule in June 2004, that places a cap on mercury emissions from major electric utilities as of January 8, 2008.
- Requires major electric utilities to reduce mercury emissions by 40 percent beginning January 1, 2010.
- Requires major electric utilities to reduce mercury emissions by 80 percent beginning January 1, 2015.
- The Wisconsin Department of Natural Resources may enter into a multi-pollutant reduction agreement with a major electric utility as an alternative to compliance with the initial 40 percent reduction level.

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MERCURY CONTROL TECHNOLOGIES

Several mercury-specific control technologies are in various stages of development, testing, and demonstration. Currently none of these technologies are in commercial operation on power plants in the U.S.

Mercury control options include:

- Coal cleaning
- Sorbent injection
- Wet and dry scrubbers
- Adsorption structures, catalysts and fixed or fluid beds

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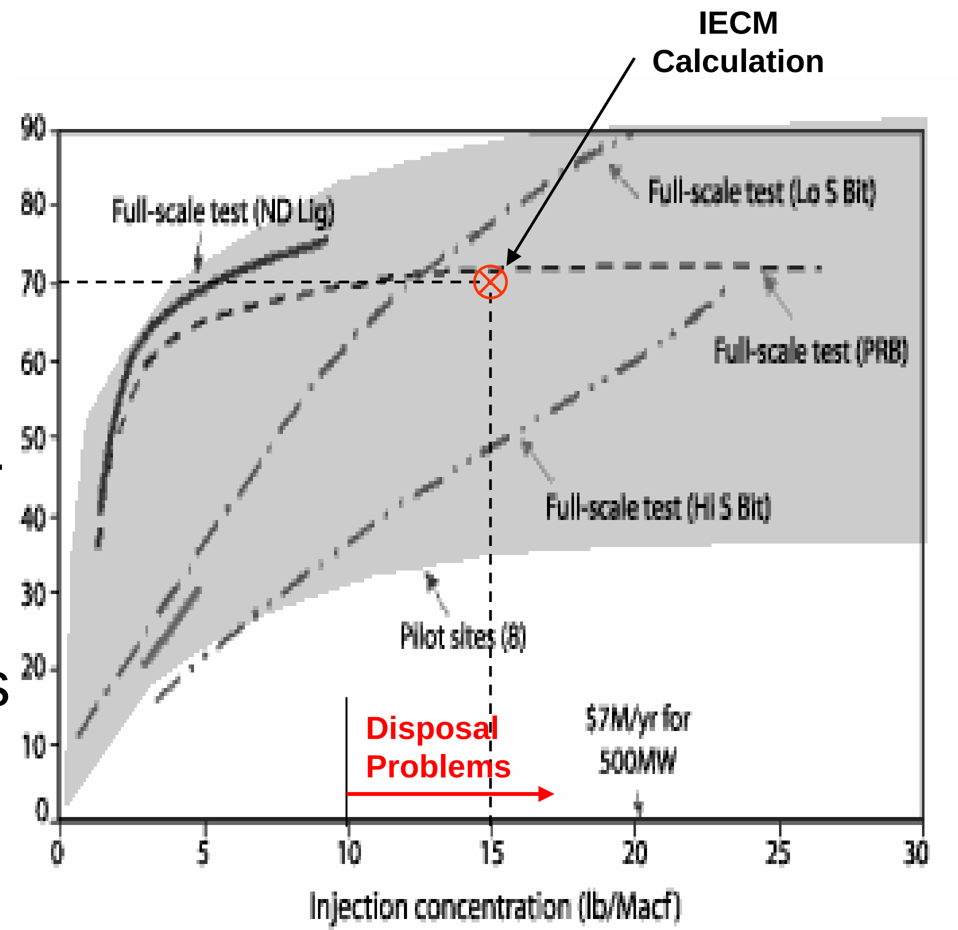
LEADING MERCURY CONTROL TECHNOLOGY

- Injection of AC upstream of Electrostatic Precipitators (ESP) or Fabric Filters (FF) is seen as the retrofit technology with the widest potential application for Hg control.
- From all Hg control technologies being pursued for 90 percent reduction, 60 percent include use of activated carbon injection.

Company	Technology	Status
ADA	**Activated Carbon**	Guarantee: 80% removal w/FF, 60% w/ESP.
Babcock Borsig	Various Reagents & **Activated Carbon**	>90% removal demonstrated on MSW units. No test data on pc units.
Lurgi	**Activated Carbon**	70-95% removal depending on Hg species and PCD.
Sorbent Tech. Corp.	**Activated Carbon** & powdered sorbents	Up to 85% removal demonstrated.
B&W	Reagent Injection in wet FGD	Up to 80% removal demonstrated.
Phalman	MnOx Injection	No full-scale test data reported.
Powerspan	Electro-catalytic oxidation (ECO)	No full-scale test data reported.
Apogee Sci. Inc.	Adsorption processes (MerCAP)	90% removal demonstrated at one site.

ACTIVATED CARBON FOR MERCURY CONTROL

- To achieve 90 percent Hg control by AC, approx. 18,000:1 C/Hg ratios are needed for 10 μm particles.
- AC is forecasted to incur an approximated cost factor of 0.4 mils/kWh (assumes injection ratios of C/Hg of 10,000:1, \$0.50/lb of AC).
- Anticipated level of AC injection represents 1 to 2 percent of ash loading.



From EPRI Journal On-Line.
http://www.epri.com/journal/details.asp

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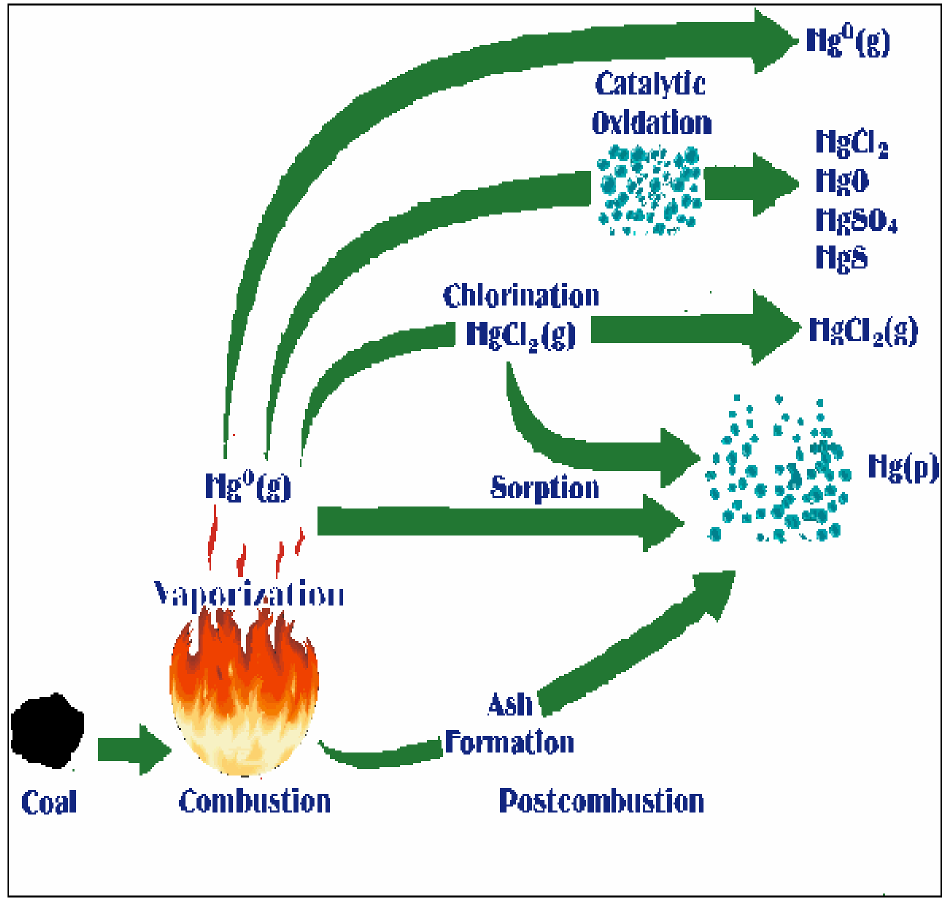
MERCURY FORMATION IN COAL-FIRED BOILERS

- Coal-fired power boilers contribute approximately one third of anthropogenic mercury emissions (~50 tons in 1999).
- Three forms of mercury emissions are produced:
  - Elemental mercury (Hg^0) – insoluble, volatile.
  - Oxidized mercury (Hg^{+2}) – water soluble, easy to absorb.
  - Particulate mercury (Hg_p) – associated with the fly ash.
- At combustion temperatures all mercury is present as Hg^0. Mercury speciation occurs as the combustion gases cool down in the convective pass.



After Zygarlicke, J., et.al. "Fundamental Mechanisms of Hg Species Formation in Coal Combustion Flue Gas."

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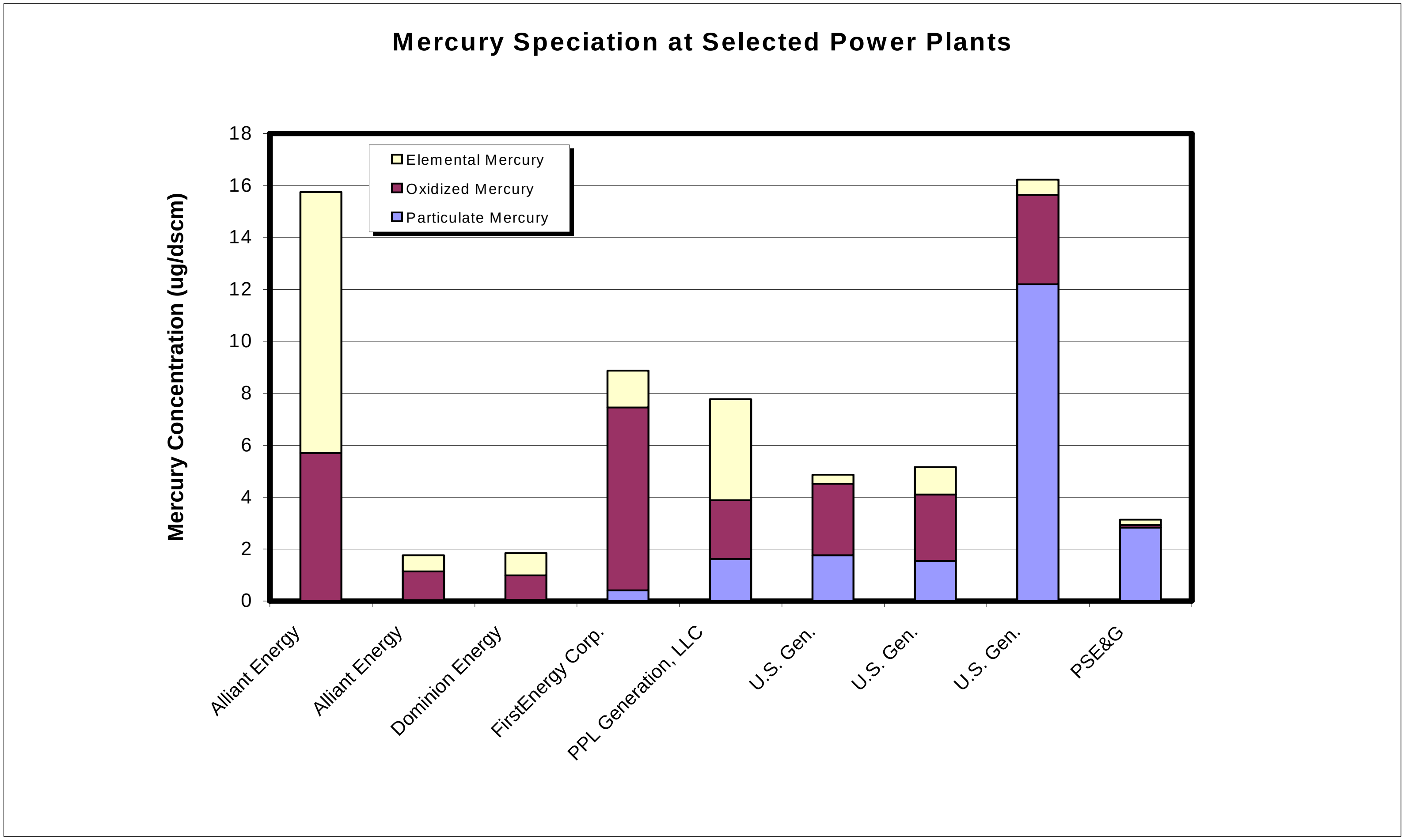
BASELINE MERCURY SPECIATION FROM SELECTED POWER PLANTS (ICR Database)



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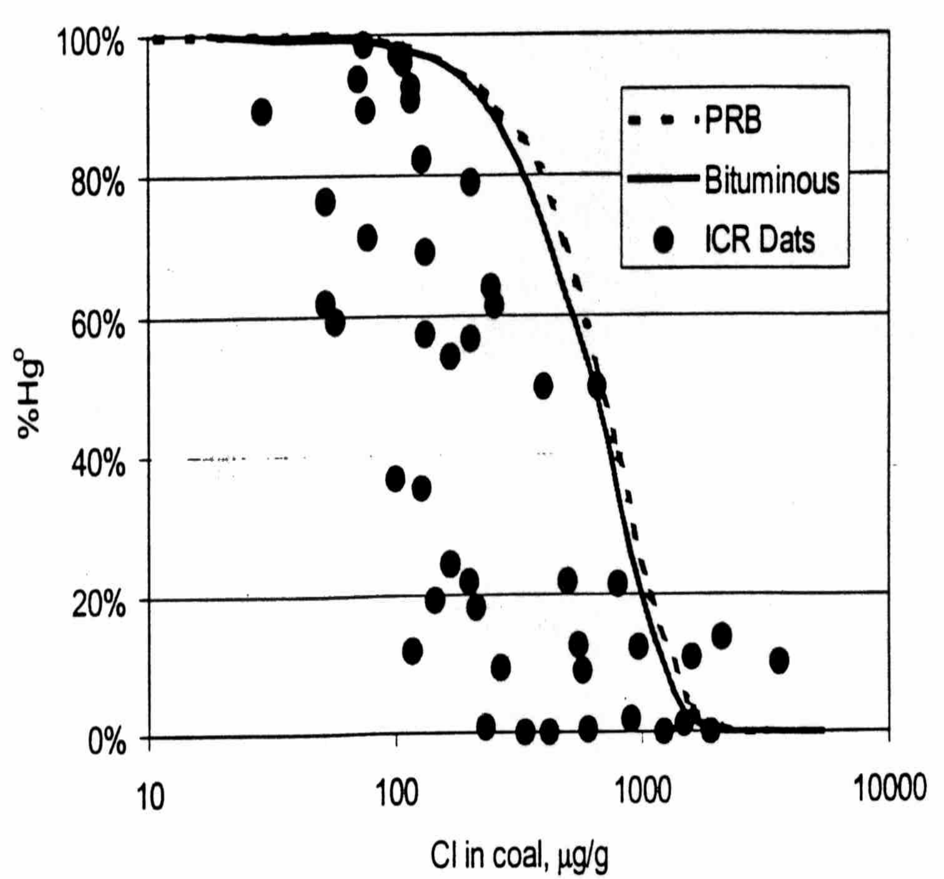
MERCURY EMISSIONS FROM COAL-FIRED BOILERS

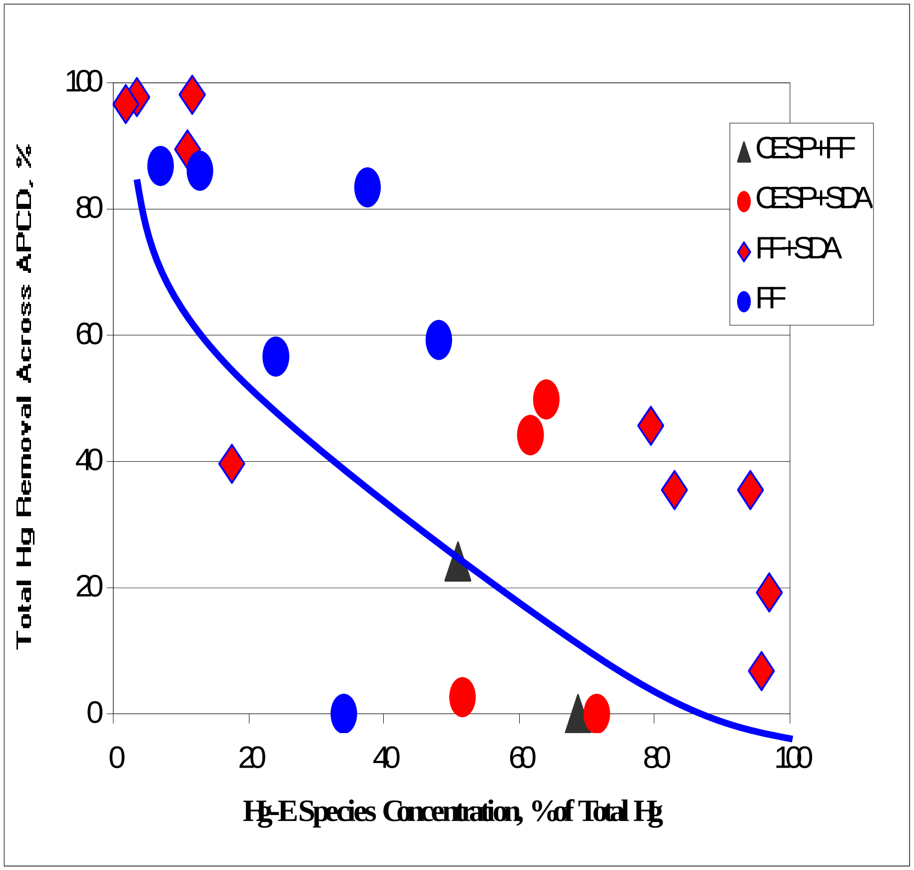
- Concentration of Hg^0 from coal-fired boilers varies from 10 to >90%. It depends on:
  - Coal Blend Characteristics
  - Boiler Design/Equipment
  - **Boiler Operating Conditions!!**
- Coal blend effect on Hg emissions is related to the Cl concentration in the coal and to some extent to other elements such as S, Fe and Ca.
- Emission factors: 7.6, 7.0, 4.5, 9.0 μg/MJ for anthracite, bituminous, subbituminous and lignite, respectively.



After Senior, C., et.al. "Modeling Gaseous Hg Behavior In Practical Combustion Systems."

BOILER EQUIPMENT IMPACT ON MERCURY EMISSIONS

- Mercury removal varies across air pollution control devices (APCD's):
  - Cold-side ESP's ⇗ 27 percent.
  - Hot-side ESP's ⇗ 4 percent.
  - Fabric Filters ⇗ 58 percent.
  - Wet/dry FGD and spray dryer absorbers ⇗ between 80 to 90 percent of bivalent Hg.
  - SCR ⇗ between 40 to 60 percent.



Higher fraction of Hg^0 is a problem irrespective of the APCD.

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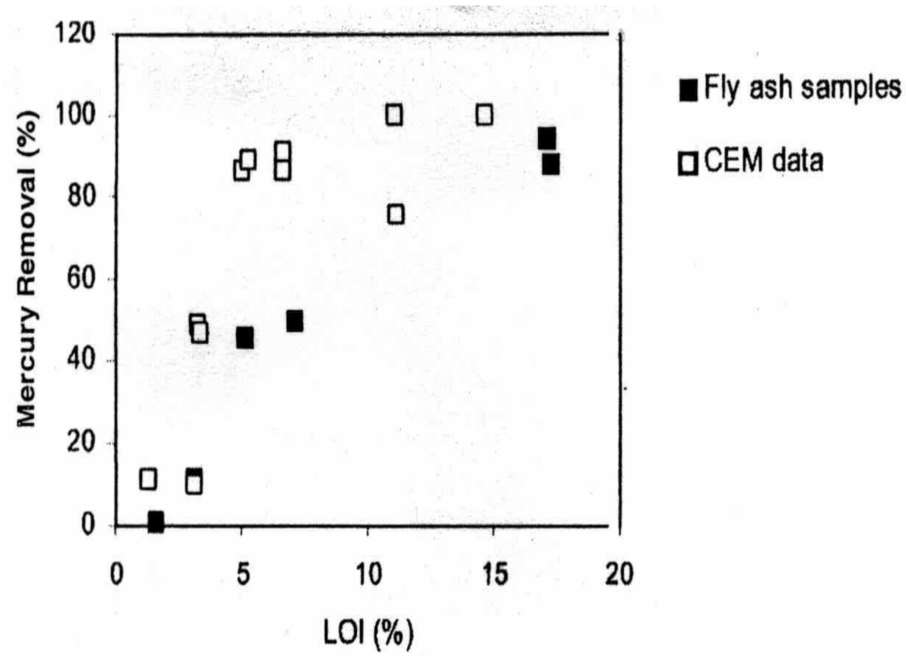
IMPACT OF BOILER OPERATING CONDITIONS ON MERCURY

- **The fate of Hg emissions is impacted by the chemical and physical processes occurring in the boiler convective pass.**
- **Boiler operating conditions affect Hg oxidation and capture:**
  - Homogeneous Hg oxidation is a kinetically controlled process occurring in the flue gas. It is affected by flue gas conditions and composition.
  - Heterogeneous oxidation and absorption is affected by the combined effect of surface chemical kinetics and mass diffusion. It is promoted by the nature of the fly ash and flue conditions and composition.
- **Link between boiler conditions and Hg emissions:**
  - Kinetic time-temperature history (flue gas temperature, residence time or stack flow).
  - Fly ash characteristics (mill operation)
  - Combustion environment (gas composition, reducing/oxidizing conditions).
  - Operating practices (boiler load profile, sootblowing, etc.).



After Lissianski, V., et.al. "Novel Technology for Multiple Pollutant Control."

These variables ensure that Hg speciation is site-specific.

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IMPORTANCE OF BOILER OPERATION ON MERCURY EMISSIONS

- Interpretation of Hg test data.
- Development of Hg emissions control options.
- Reduce the cost of compliance.
  - Average cost of removing Hg from stack gas is estimated by DOE at $25,000-70,000/lb Hg, with higher costs projected for plants <200 MW.
  - For a 250 MW unit (~150 lb Hg/year), average cost of Hg control to 50 % level is ~$2 million.
  - A modest improvement in Hg oxidation and capture by boiler operation optimization for Hg control (~15 %) = $546,000/year.

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BOILER OPTIMIZATION FOR MERCURY CONTROL PROJECTS AT THE ERC

- **Feasibility Study**
- **Boiler Optimization Project**
- **Activated Carbon Injection Project**
- **Objectives:**
  - Develop technical understanding and analytical models of Hg behavior in the flue gas in relation to appropriate boiler controllable parameters.
  - Investigate the extent of Hg reduction by optimization of boiler operation through field testing at full-scale boilers.
  - Investigate activated carbon injection requirements for Hg compliance.

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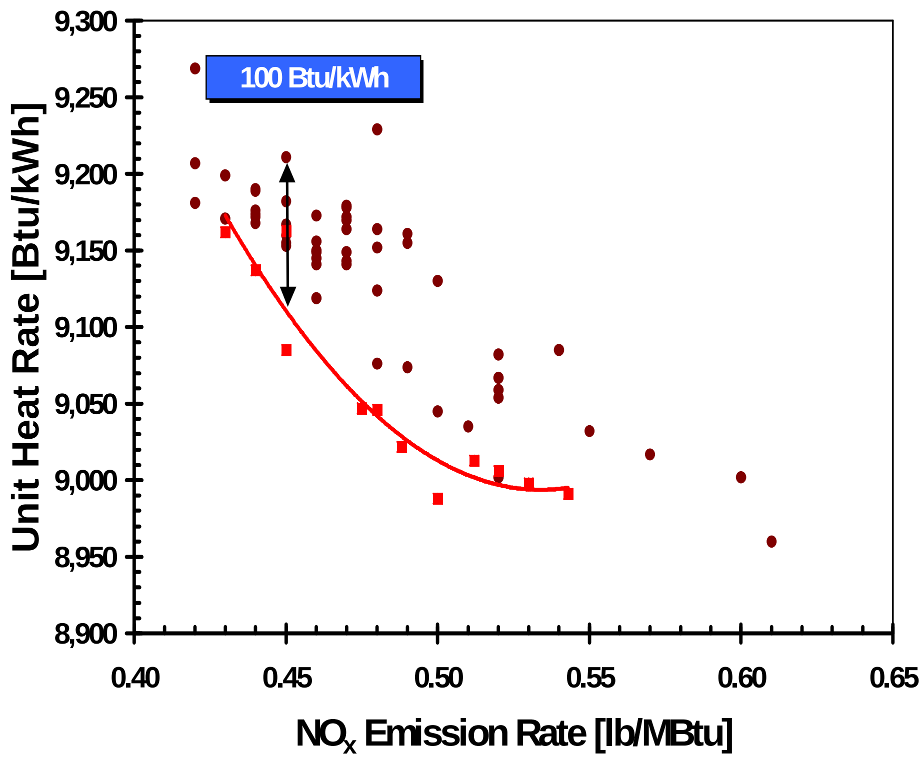
POWER PLANT OPTIMIZATION EXPERIENCE

- ERC experience with coal-fired plant optimization includes: combustion optimization, sootblowing optimization, and SRC and ESP tuning.
- There is a trade-off between:
  - Hg^0 oxidation and the production of other emissions such as CO and NO_x.
  - The level of unburned carbon in the fly ash.
  - Unit heat rate.
  - ESP collection efficiency.
  - Stack opacity



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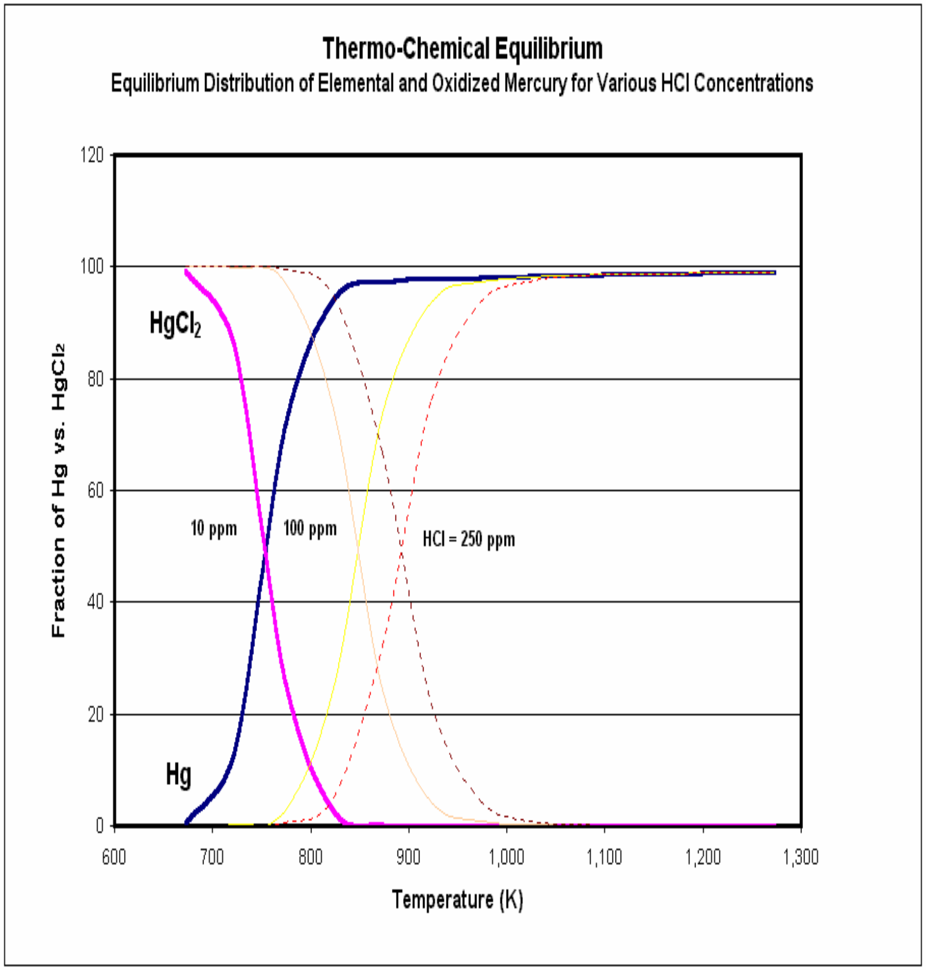
ROLE OF KINETICS ON MERCURY OXIDATION

- Equilibrium results indicate that at high temperatures, 99 percent of the Hg is elemental, at low temperatures is mercuric chloride.
- The reaction between Hg and HCl dominates the equilibrium chemistry.
- The assumption of gas-phase equilibrium for mercury-containing species in the coal-fired exhaust gas is not valid.
- Mercury speciation is controlled by finite rate chemistry (and also diffusion-limited). Minor species in the flue gas do not have time to equilibrate as the gas cools.
- Gas phase Hg speciation demonstrated to be affected by quenching and concentration of other species in the flue gas (i.e., O_2, SO_x, NO_x).



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SOME GAS PHASE MERCURY REACTIONS

$Hg^0 + Cl_2 (+M)$ ⇙ $HgCl_2 (+M)$	Fast Reaction
$Hg^0 + HCl$ ⇙ $HgCl + H$	Slow Reaction (no consequences)
$2\ HCl + ½\ O_2$ ⇘ $Cl_2 + H_2O$	Deacon Eq. (< 770K, 200-500 K/s, HCl Favored)
$Hg^0 + Cl\ (+M)$ ⇙ $HgCl\ (+M)$	HgCl Very Reactive
$HgCl + HCl$ ⇙ $HgCl_2 + H$	Fast Reaction
$HCl + OH$ ⇘ $Cl + H_2O$	Rate Limiting Reaction

- **Research has verified that the major kinetic pathway for the formation of $HgCl_2$ involves the reaction of Cl with Hg^0.**

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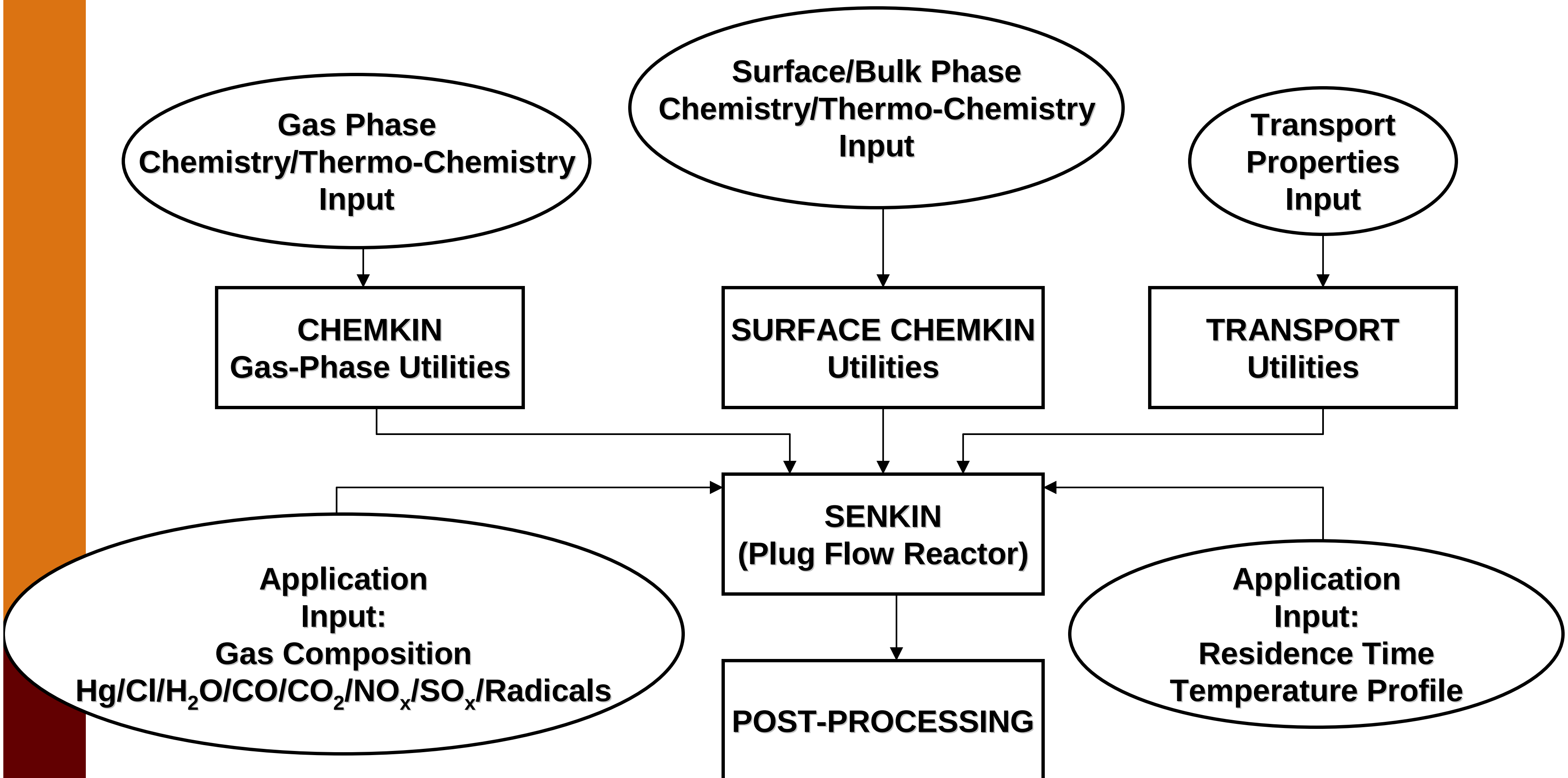
CHEMICAL KINETICS MODEL

- The Chemkin Software Architecture



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MERCURY MODELING RESULTS

- The model contains a reaction scheme with 35 species and 92 elementary reversible reactions (Hg/Cl/O_2/NO_x/SO_x/HC/NH_3/Radicals). Includes heterogeneous Hg oxidation by fly ash.
- Model validated against a range of laboratory datasets.
- Gas-phase Hg oxidation varies with the thermo-chemical conditions characteristic of the boiler convective pass.
  - Increased quenching rates result in accelerated rates of Hg oxidation in the convective pass.
  - To a large degree, the chemistry of Cl-species governs Hg speciation. The pool of Cl-species impacted by the chemistries of CO (increases Cl concentration), SO_x, NO_x and the Cl-species transformations.
  - O_2 weakly promotes homogenous Hg oxidation. Moisture is a strong inhibitor.
  - NO extends Hg oxidation for progressively faster quenching. NO_2 causes slight Hg oxidation.
  - SO_2 reduces Hg^{+2} to Hg^0.
  - There is an optimal level of NH_3 slip that results in maximum Cl radical residence time.

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MERCURY MODELING RESULTS (Cont.)

- Variations in Hg behavior on fly ash are due to coal origin and characteristics, acid gases in the flue gas and temperature.
  - Mercury capture on fly ash progressively increases as flue gas temperature is reduced below 750☜F. Reductions of ESP temperatures below 360☜F help Hg capture.
  - Mercury capture is enhanced by high levels of fly ash UBC!!
  - Mercury sorption on fly ash is enhanced by HCl and NO. However, Hg sorption capacity is inversely proportional to concentration of SO_2 and NO_2.
  - CuO and Fe_2O_3 are active promoters of Hg oxidation. CaO causes a reduction in the rate of Hg oxidation. Other compounds such as SiO_2, Al_2O_3 were found to be inactive.
  - Enhanced Hg oxidation occurs on finer fractions of fly ash.
  - Enhanced Hg absorption occurs on adequate fly ash particle size.

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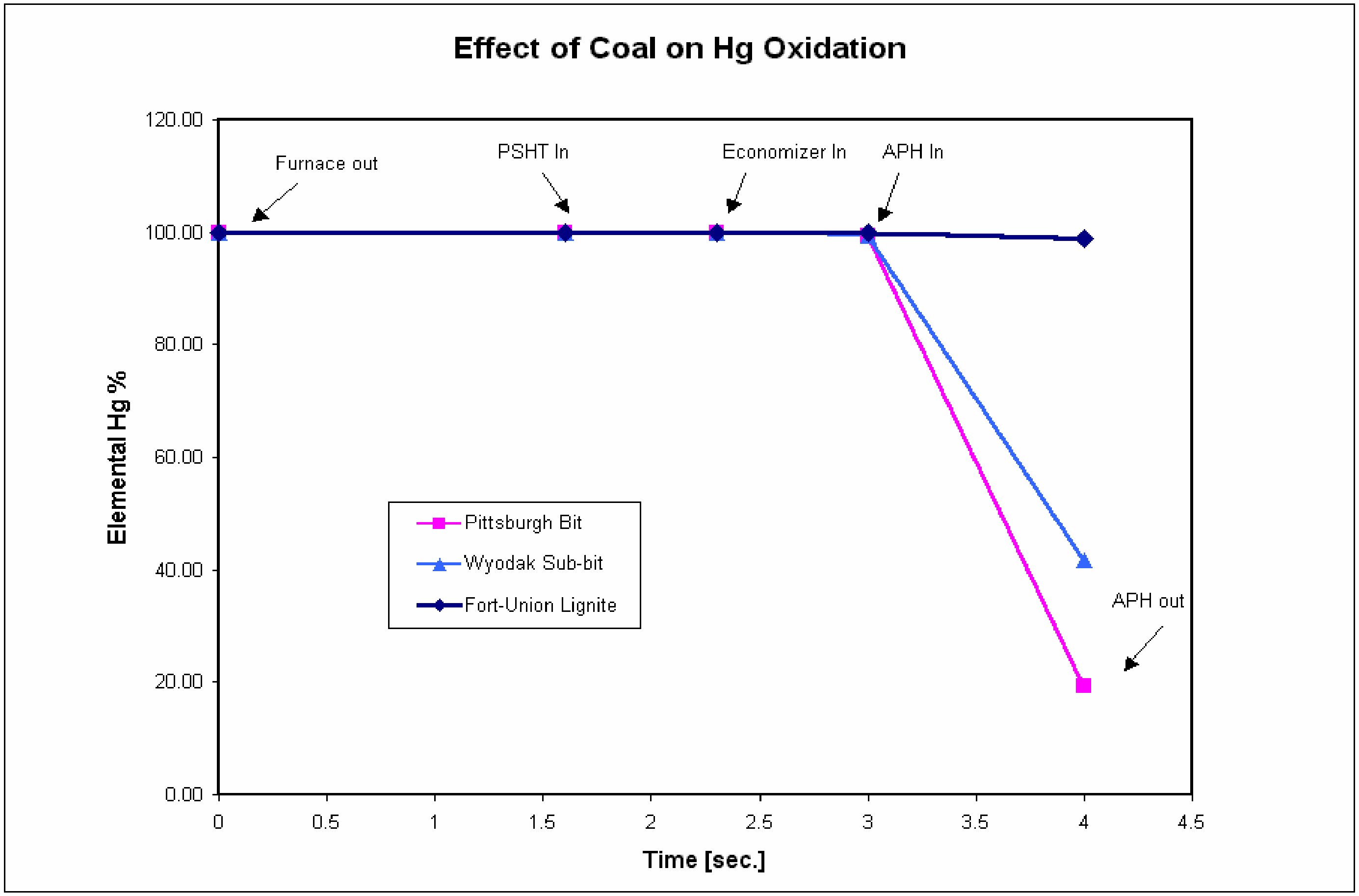
MODEL RESULTS –
Effect of Coal Rank on Mercury Oxidation

- Coal composition (Hg/Cl) impacts Hg transformation.



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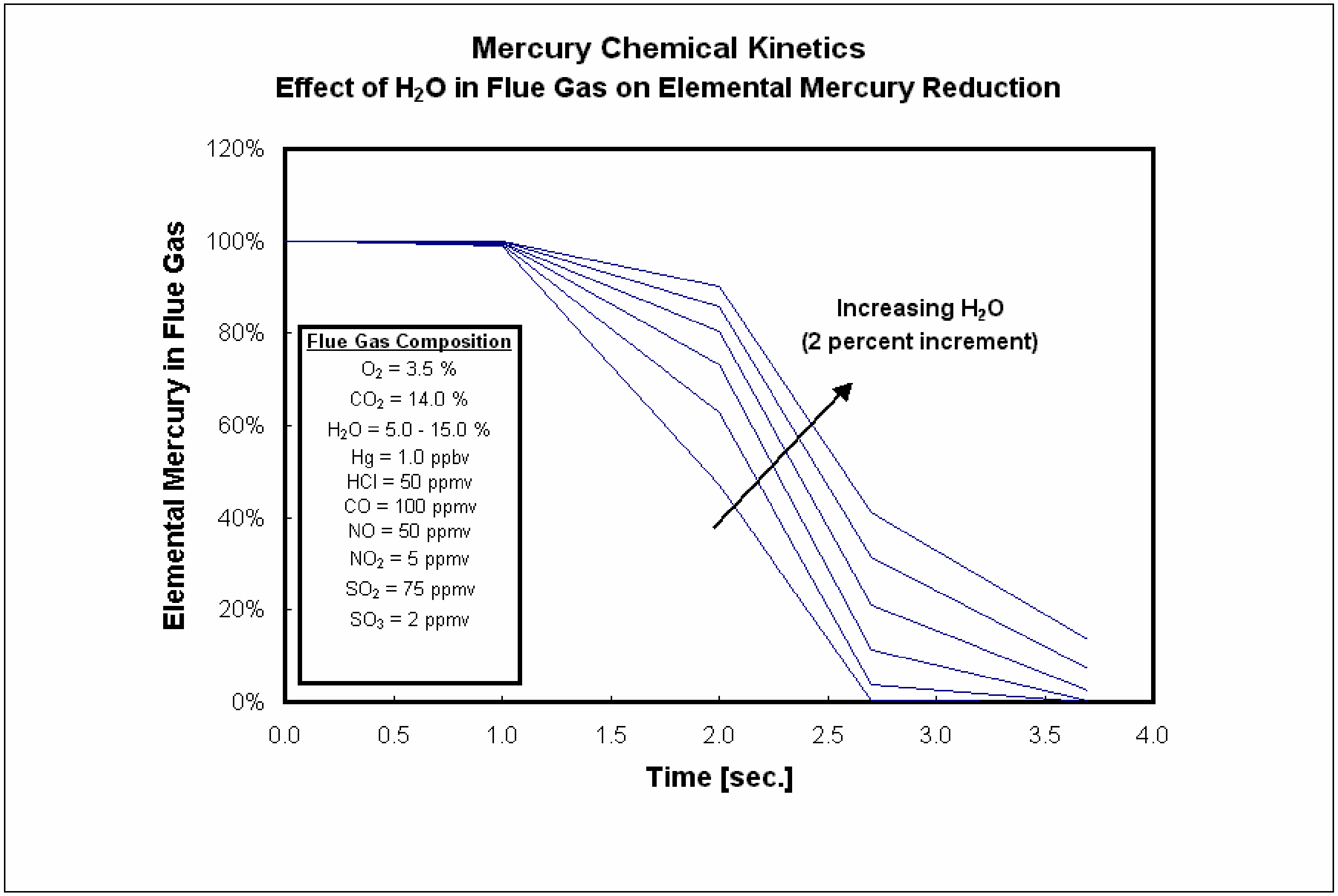
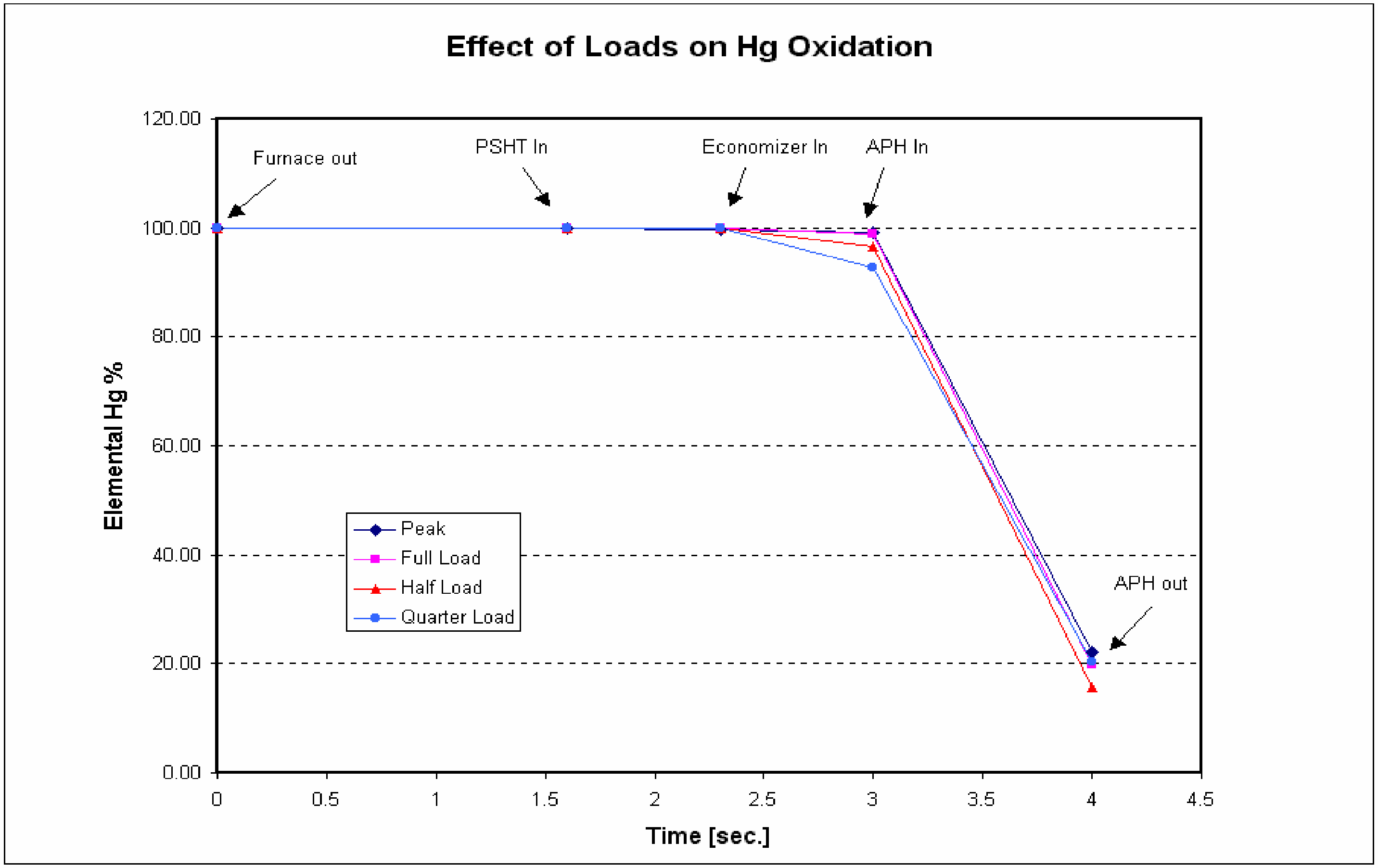
MODEL RESULTS –
Effect of Flue Gas Moisture on Mercury Oxidation

- Coal and flue gas moisture has a first order effect on the resulting $HgCl_2$ at the exhaust.



MODEL RESULTS –
Effect of Load on Mercury Oxidation

- Unit electrical generation has an impact on Hg oxidation.



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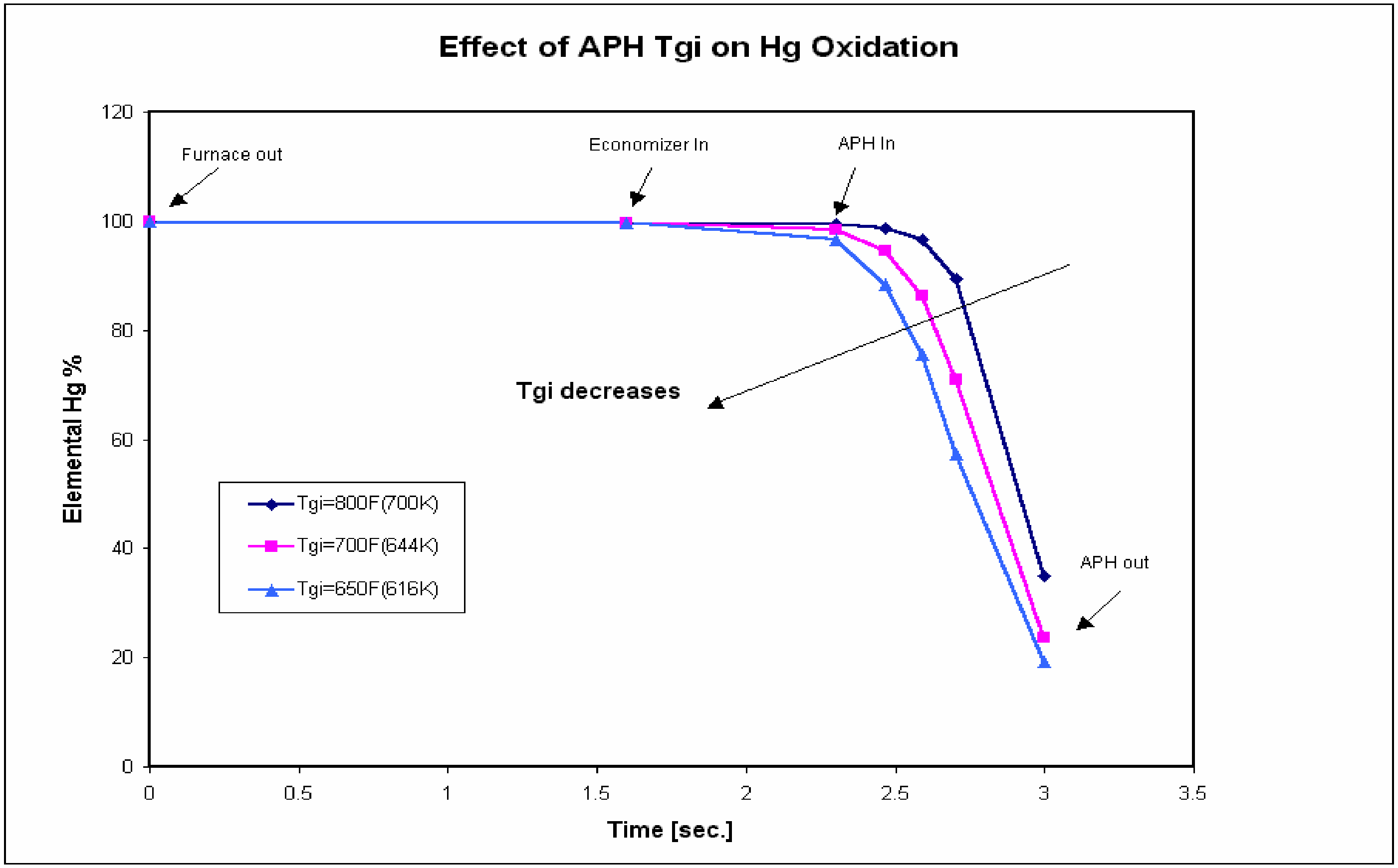
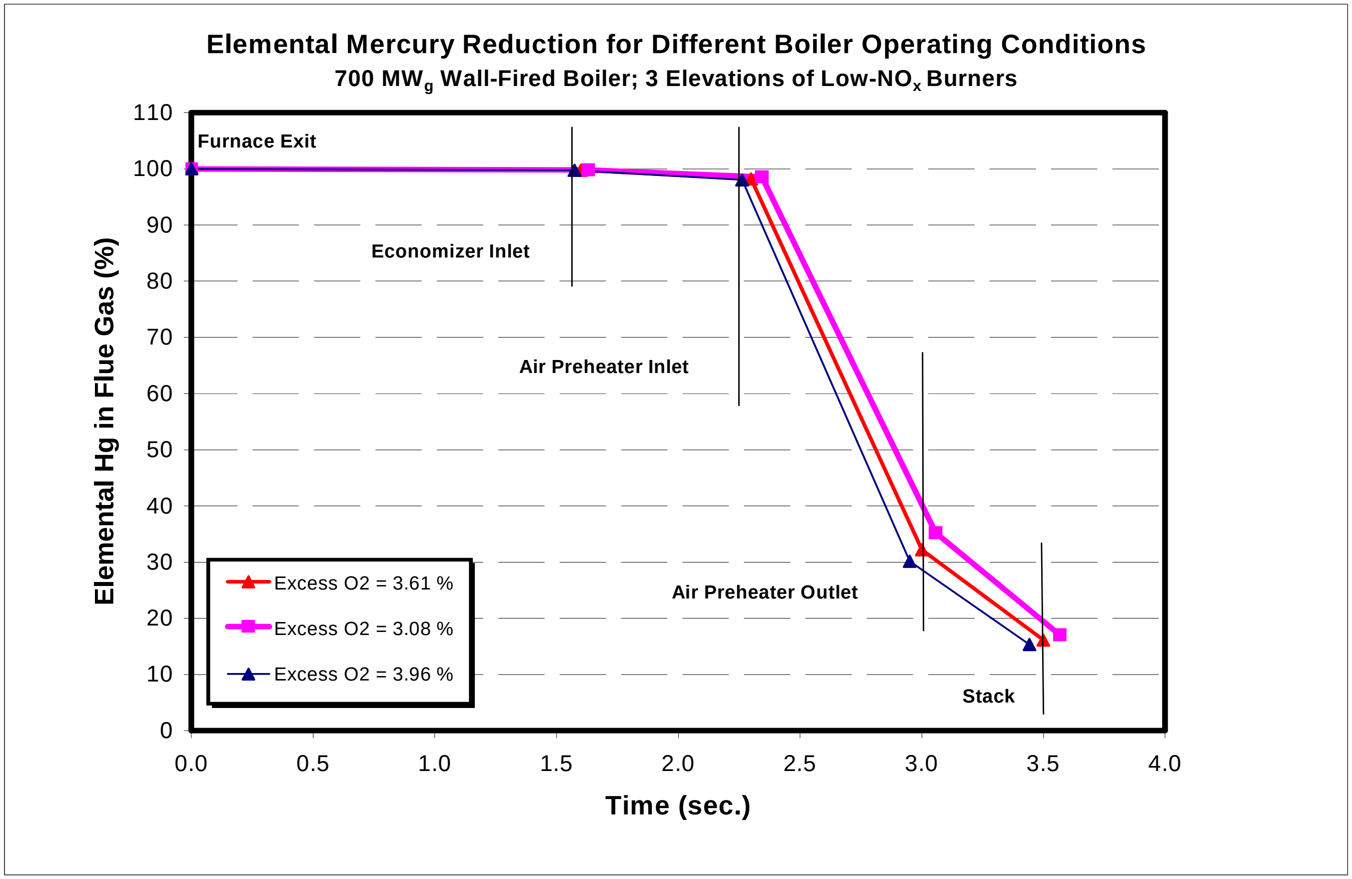
MODEL RESULTS –
Effect of APH Gas Inlet Temp. on Hg Oxidation

- Operation of the air preheater impacts the $Hg^0/HgCl_2$ ratio at the air preheater outlet.



MODEL RESULTS –
Effect of Boiler Excess Air on Hg Oxidation

- The amount of excess O_2 in the boiler directly impacts the amount of $HgCl_2$ at the boiler outlet.



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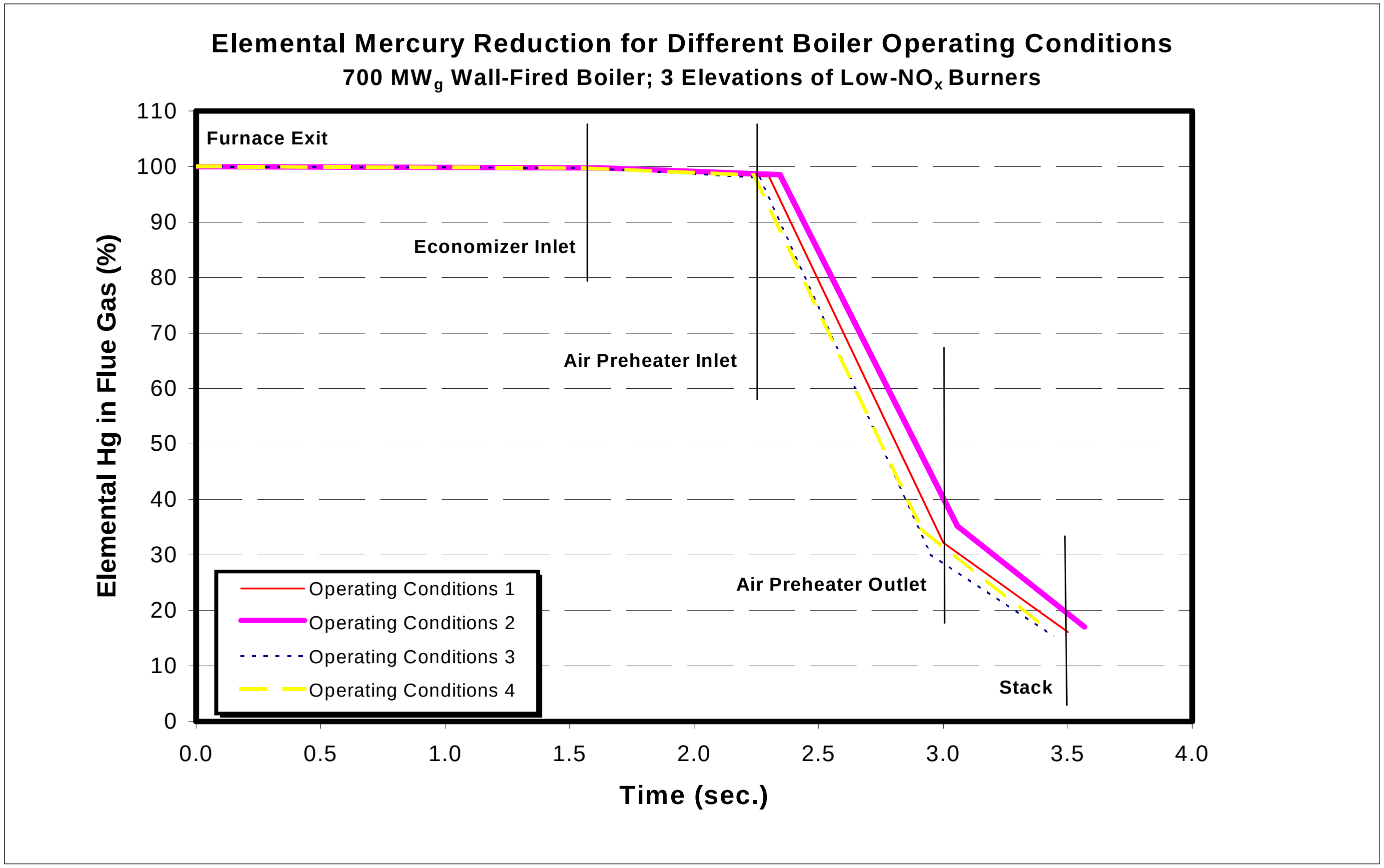
MODEL RESULTS – Example of Boiler Operation vs. Hg Oxidation

- Each trend corresponds to a combination of boiler control settings that result in changes to flue gas conditions and, consequently, the $Hg^0/HgCl_2$ ratio.



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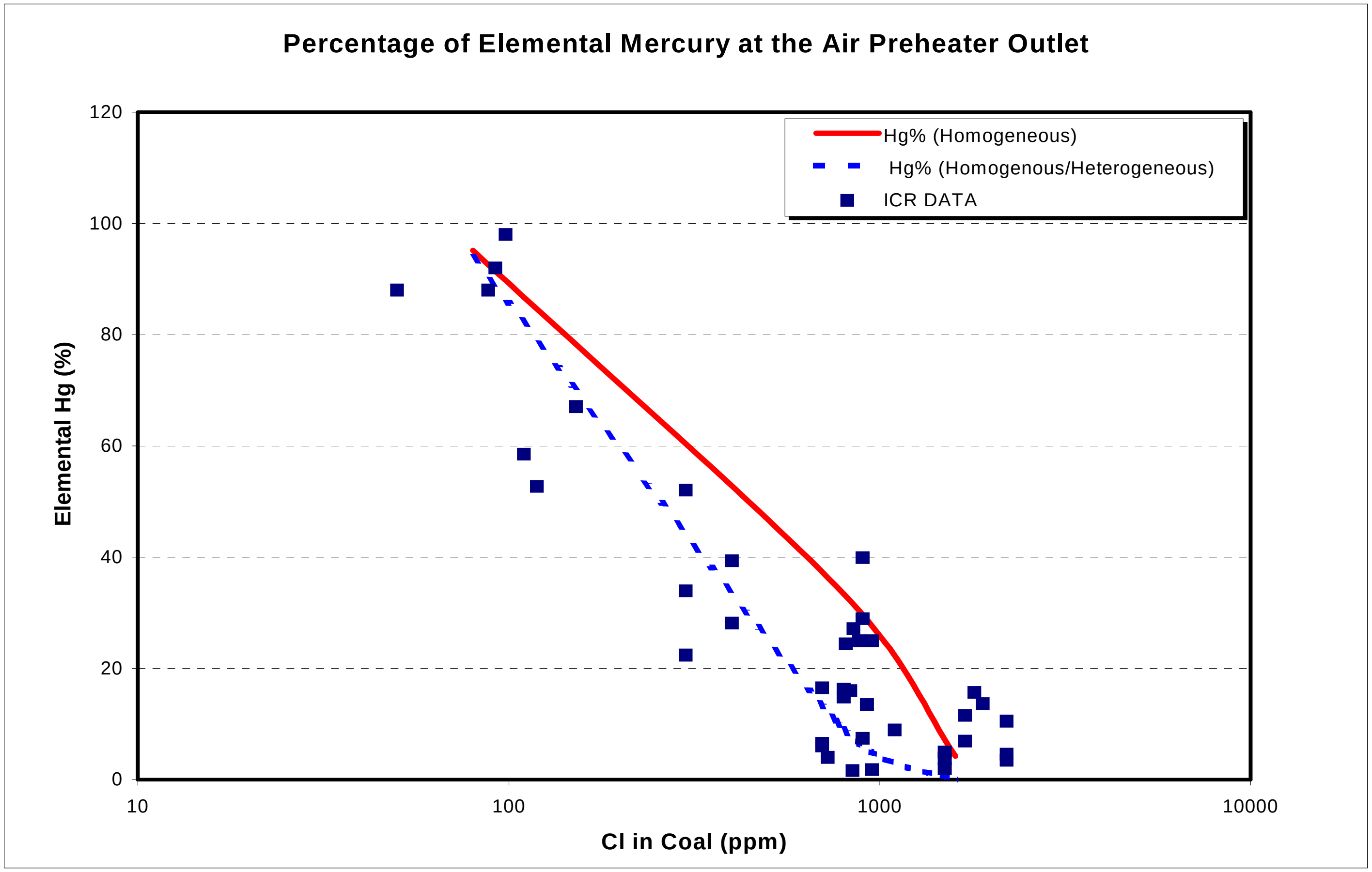
MODEL RESULTS – Fly Ash LOI Effect on Hg Emissions

- Fly ash UBC has a direct impact on Hg reduction by fly ash.



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FIELD TESTING

- Testing at three coal-fired units that fire bituminous coals was performed:
  - Site #1 is a 108 MW, T-fired boiler. Cold- and hot-ESP, and tubular APH. Conventional burners. Unit burns low-Sulfur Eastern U.S. bituminous coal.
  - Site #2 is a 250 MW, T-fired boiler. Rotating APH with two cold ESP's in series. LNCFS-III low-NO_x firing system. Unit burns U.S. bituminous and imported coals.
  - Site #3 is a 650 MW, opposed wall-fired boiler. Rotating APH with two cold ESP's in series. DRB-XCL low-NO_x burners with OFA. Unit burns U.S. bituminous and imported coals.

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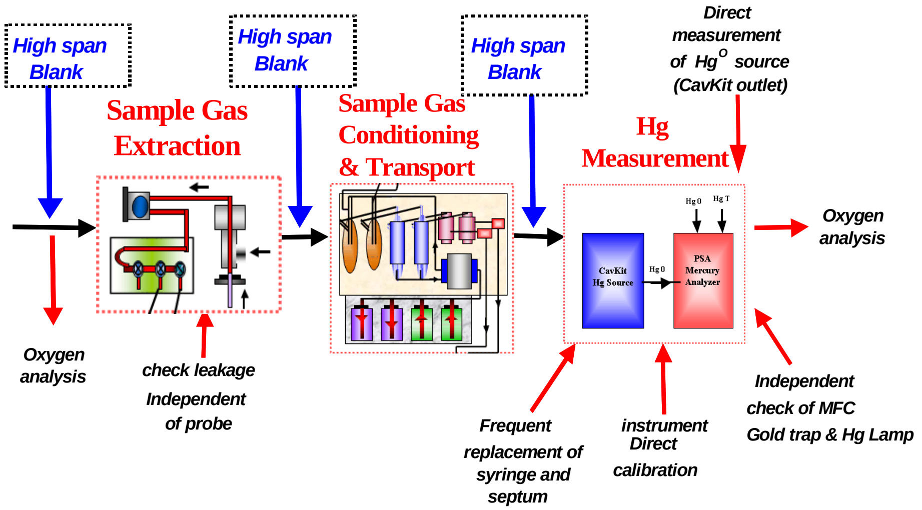
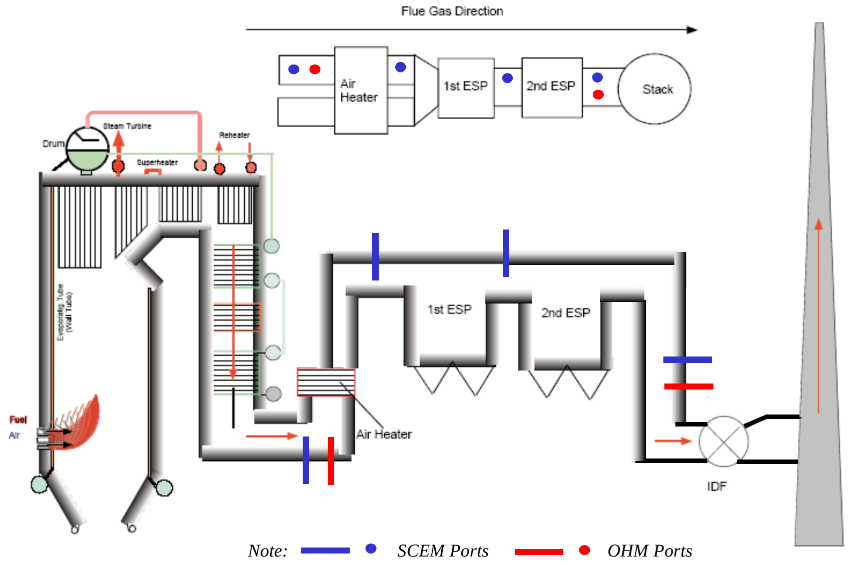
FIELD TESTING

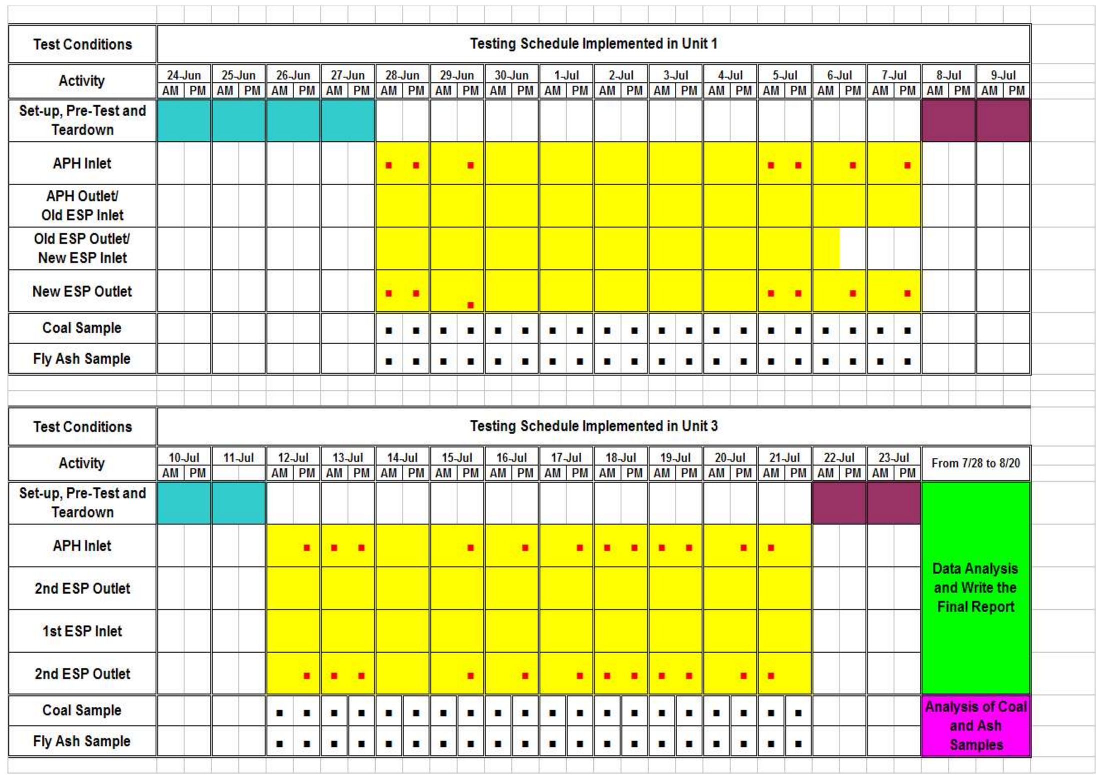
- Analytical capabilities:
  - Baldwin and Apogee inertial filtration probes.
  - Pretreatment/conditioning units.
  - PSA SCEM's for Hg speciation.
  - OHM with EPA Method 1¯ (performed on-site).
  - Coal, pyrite and fly ash analyses (ultimate and proximate analyses, Hg, S, LOI).





FIELD TESTING

- Feasibility phase involved five days of boiler manipulation.
- Boiler optimization project involved a ten-day test schedule that included setup, baselining, parametric testing, optimal condition tests, dismantling.
- Parameters investigated: unit load, excess air, OFA settings, mill bias and O/S configuration and classification, APH back-end temperature, ESP energization and rapping.
- AC injection project involved testing at different AC conditioning rates under normal and optimal operating conditions.



Sample Boiler Optimization Schedule

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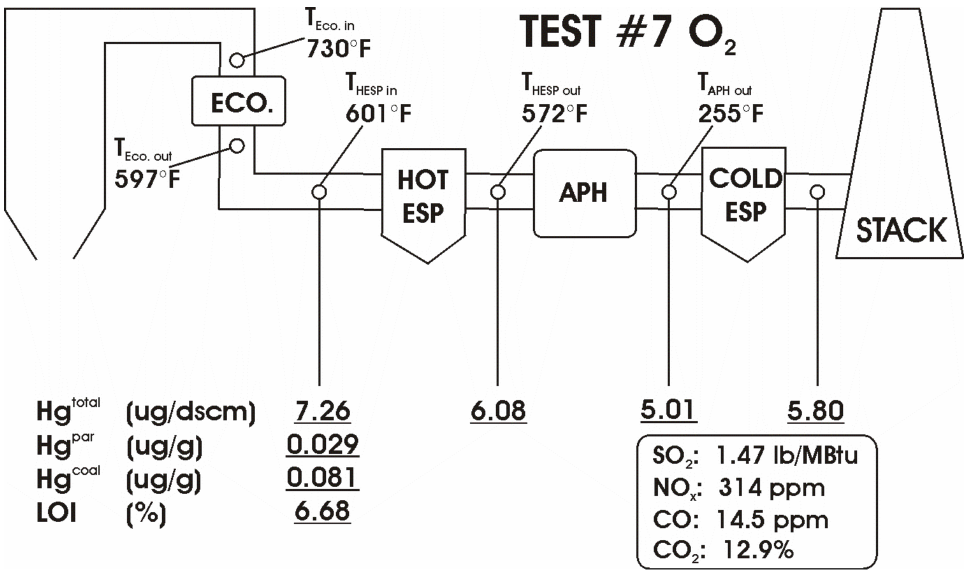
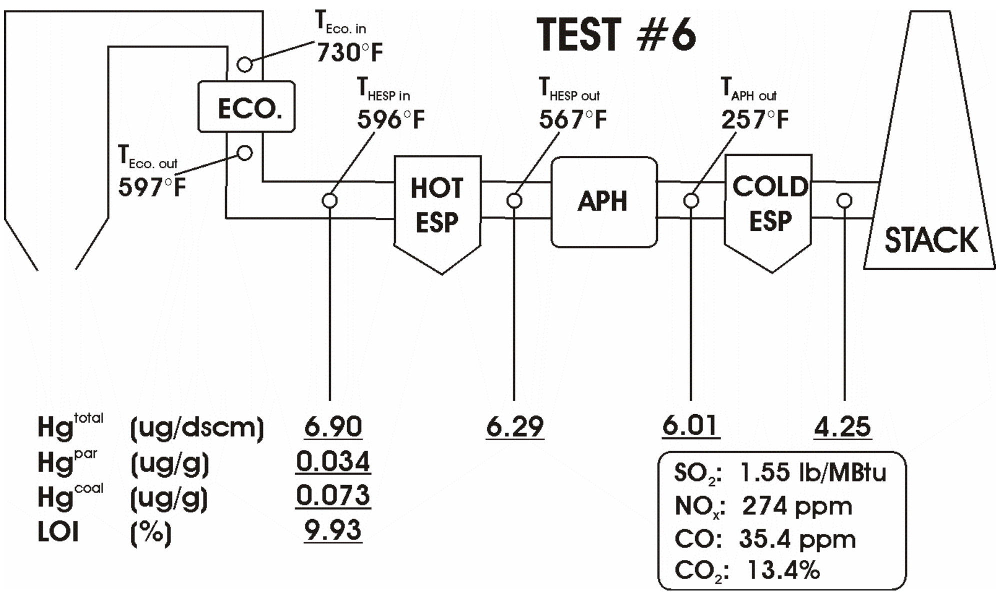
Field Test Results – Site #1



Overall Removal Efficiency = 20.0%
Average Excess O_2 = 2.69%
Fly Ash LOI = 6.68%



Overall Removal Efficiency = 38.4%
Average Excess O_2 = 2.13%
Fly Ash LOI = 9.93%

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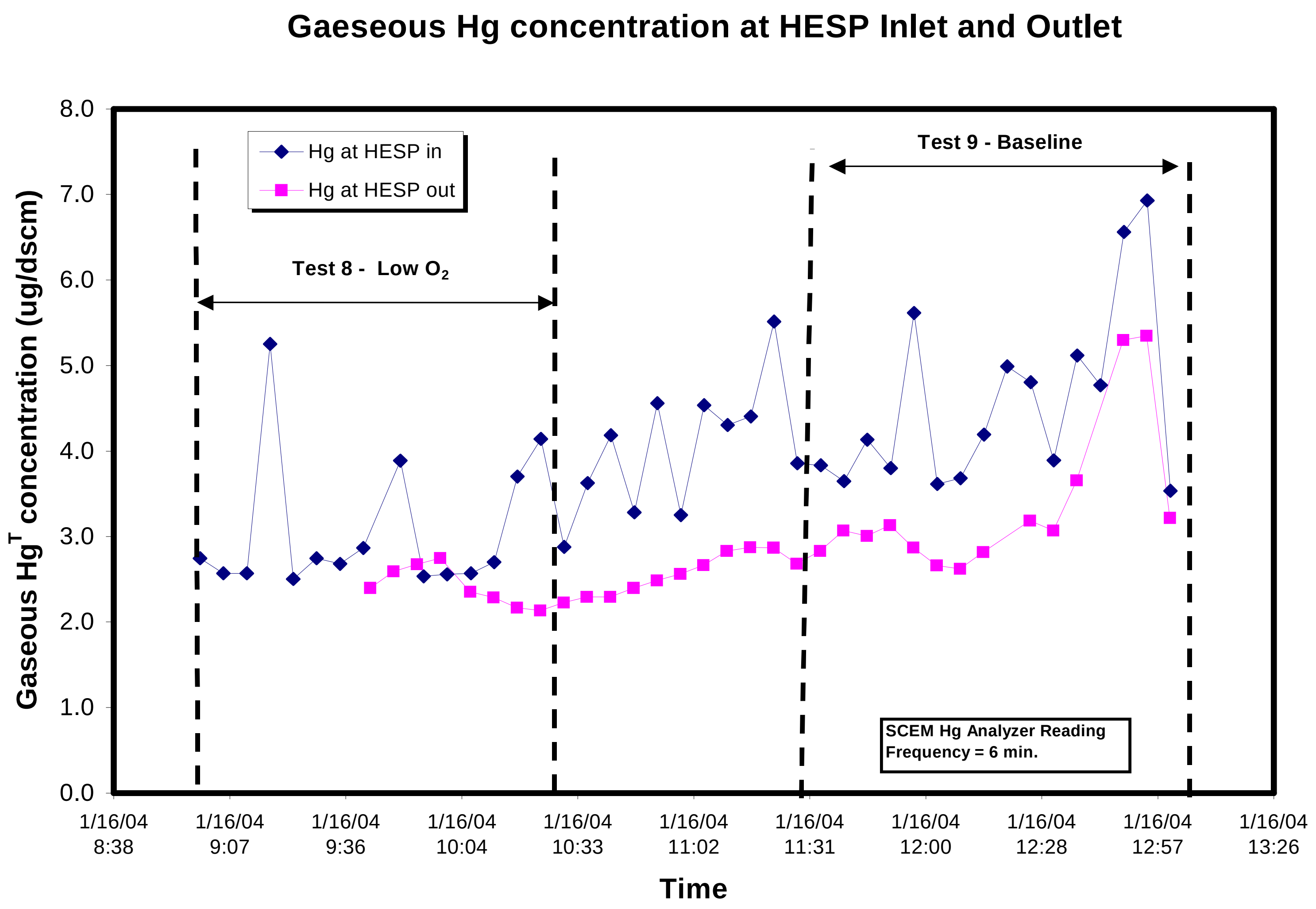
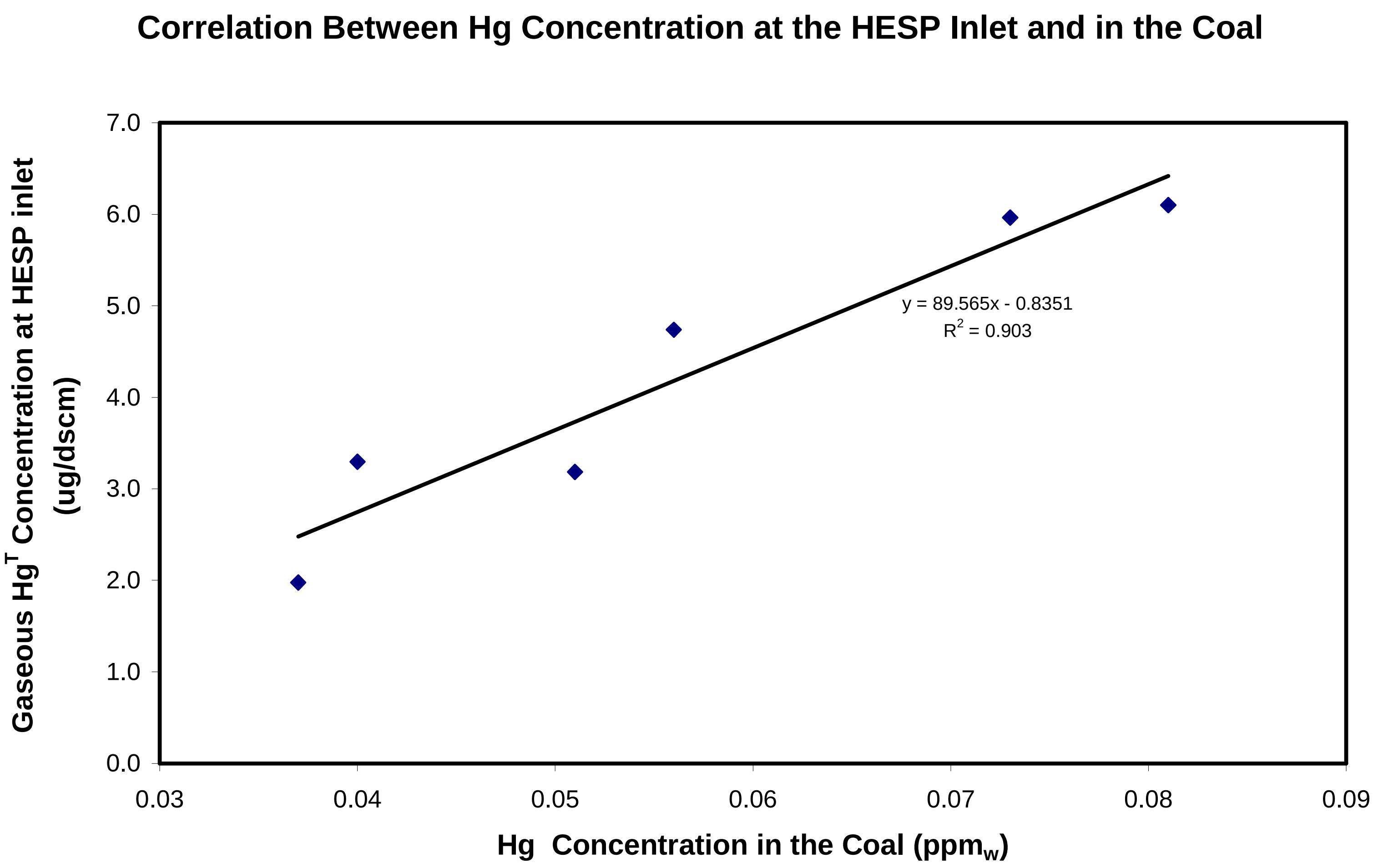
Field Test Results – Site #1



Field Test Results – Site #1



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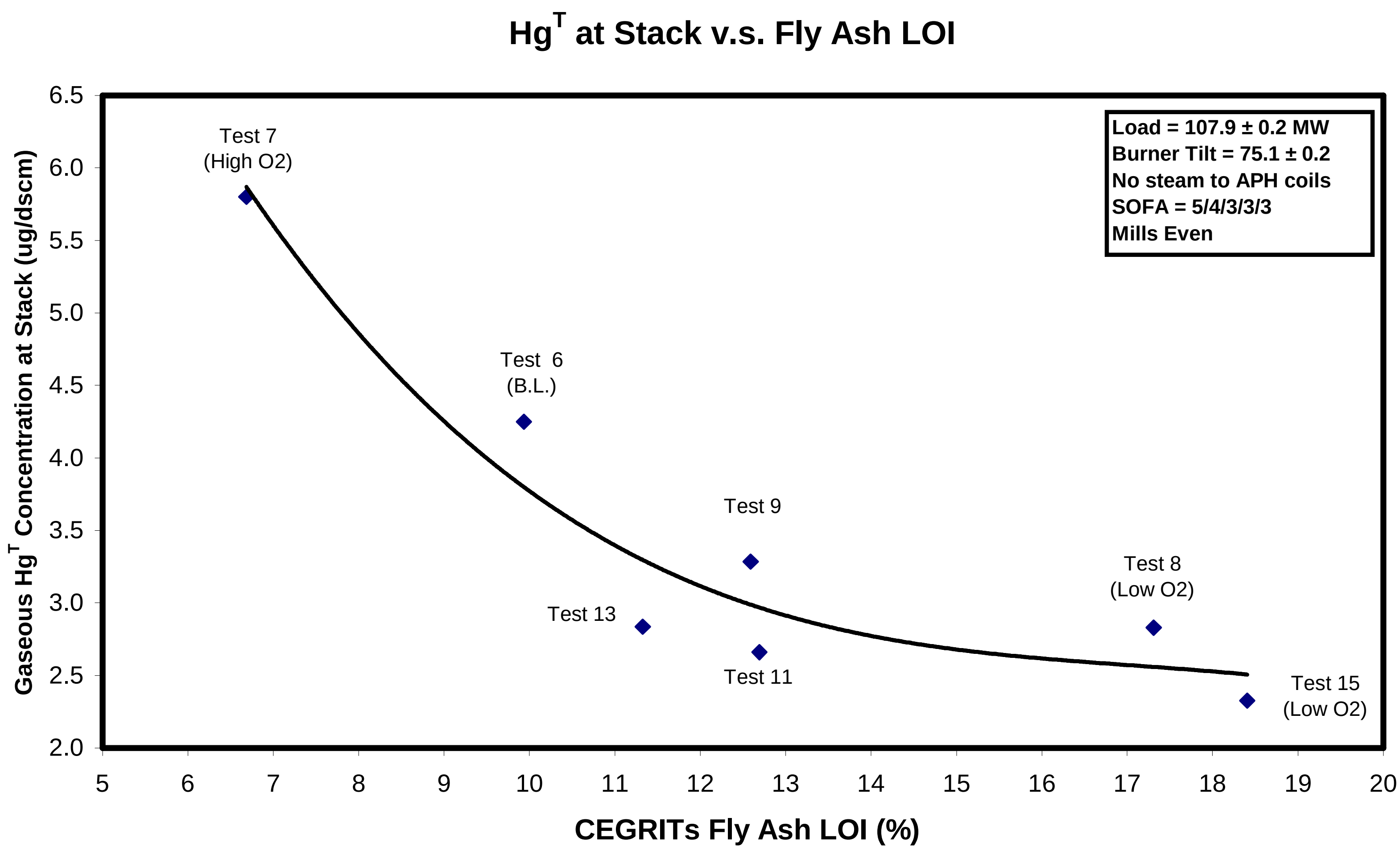
Field Test Results – Site #1



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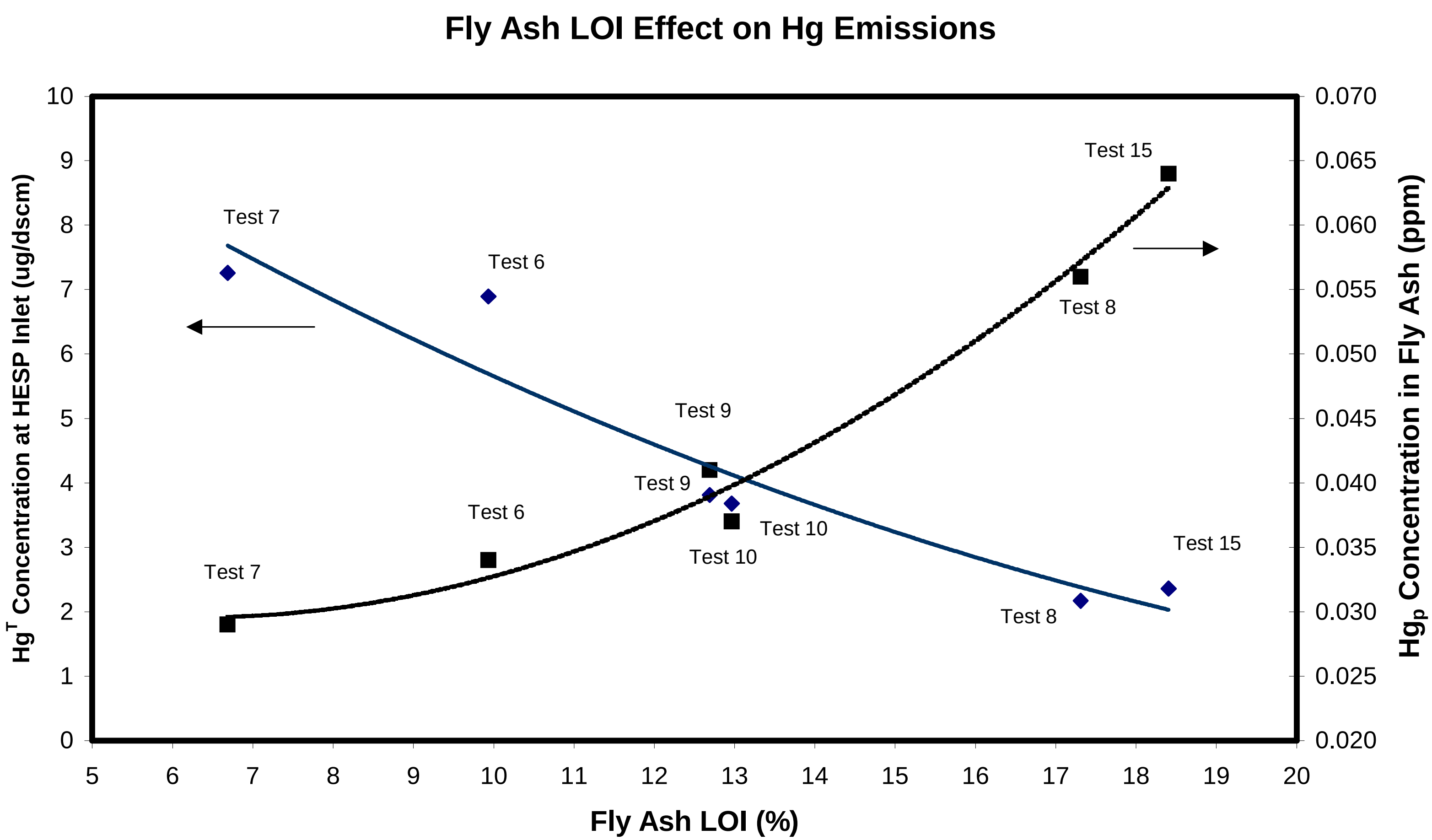
Field Test Results – Site #1



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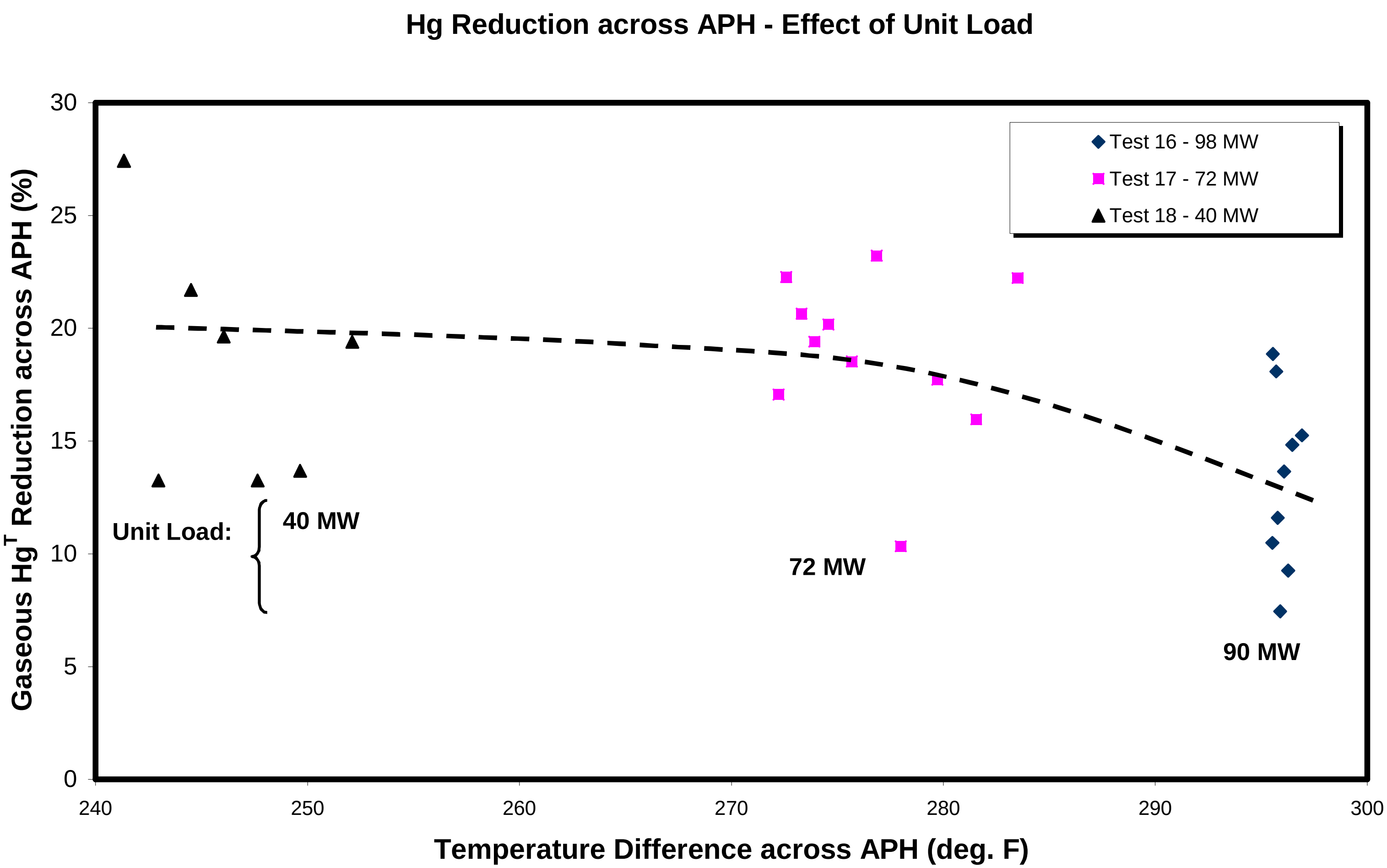

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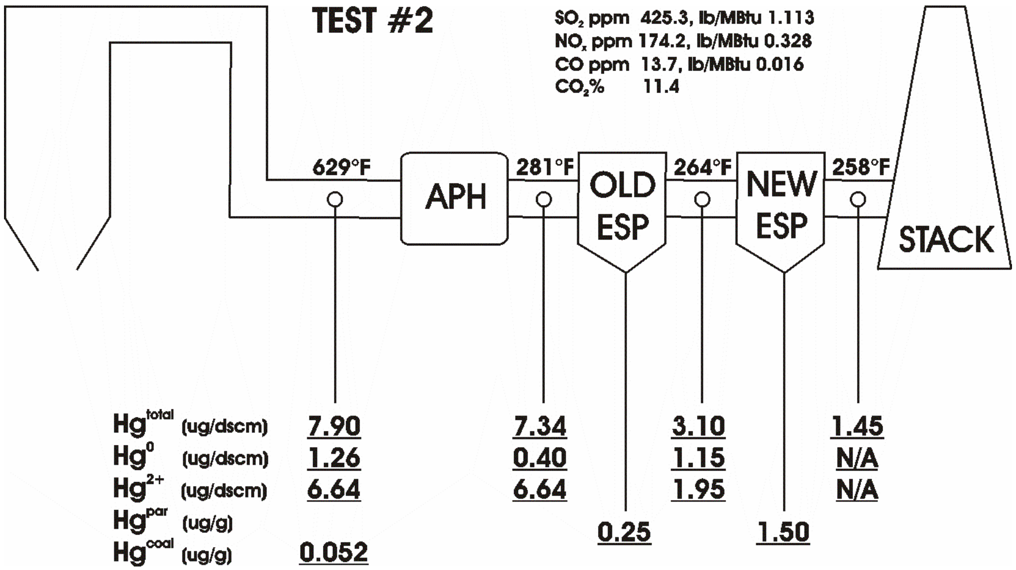
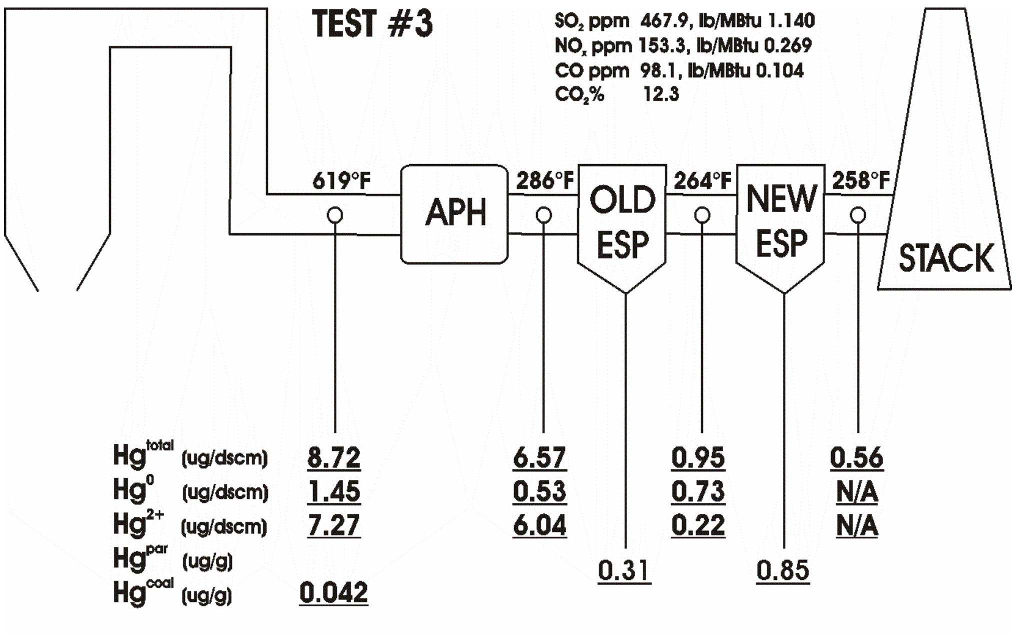
Field Test Results – Site #2



Overall Removal Efficiency = 81.6%
Average Excess O_2 = 3.5%
Fly Ash LOI = 17.4%



Overall Removal Efficiency = 93.6%
Average Excess O_2 = 1.8%
Fly Ash LOI = 22.3%

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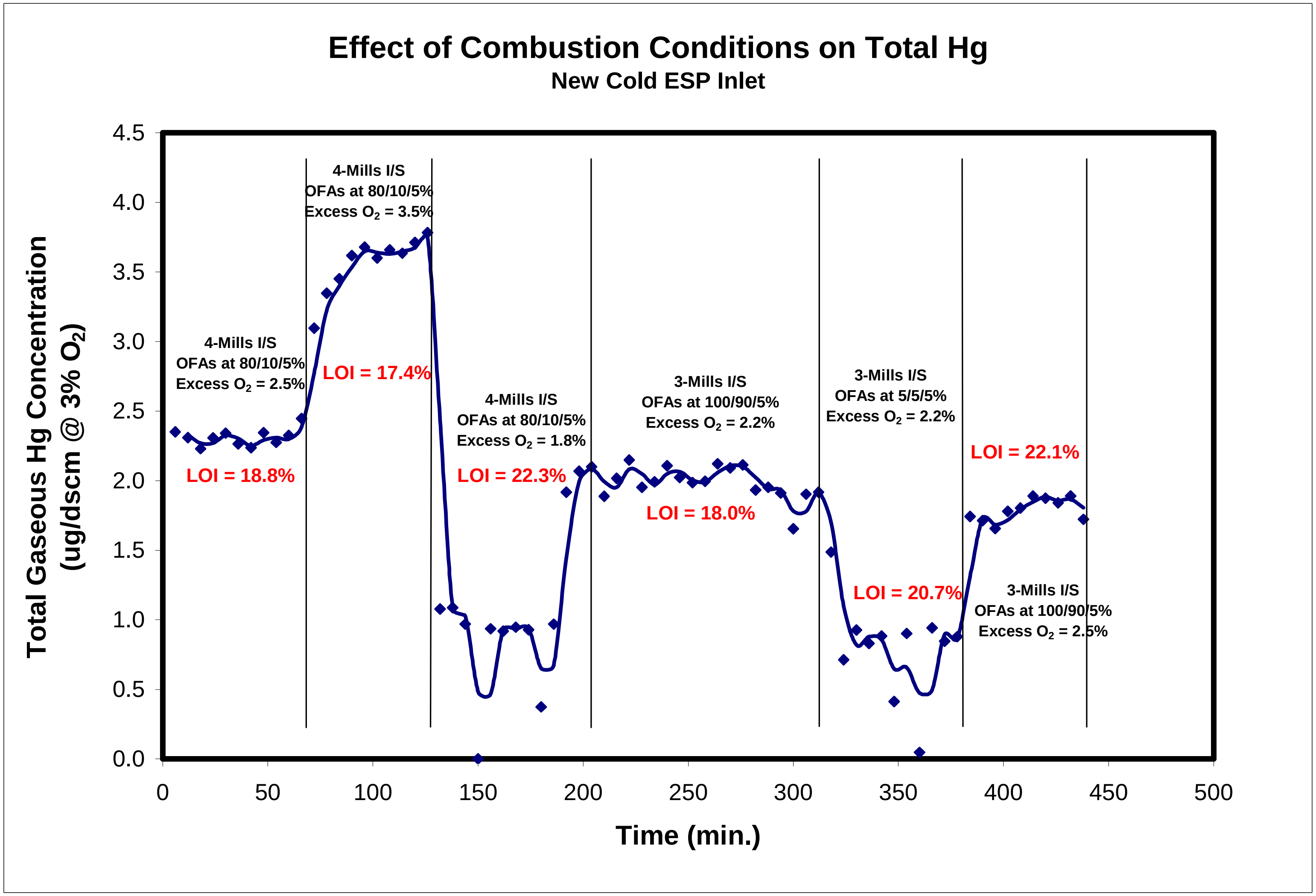
Field Test Results – Site #2



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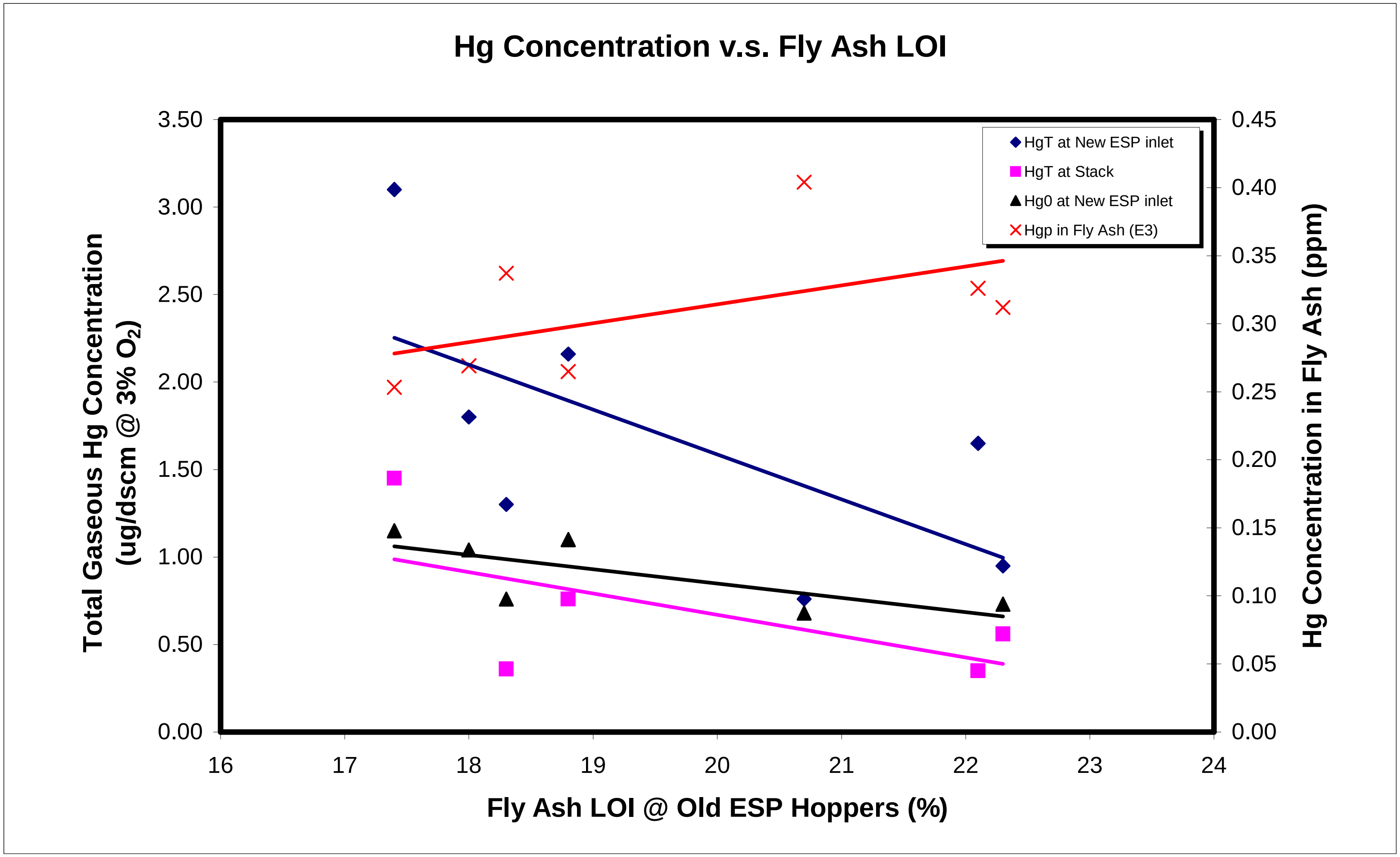
Field Test Results – Site #2



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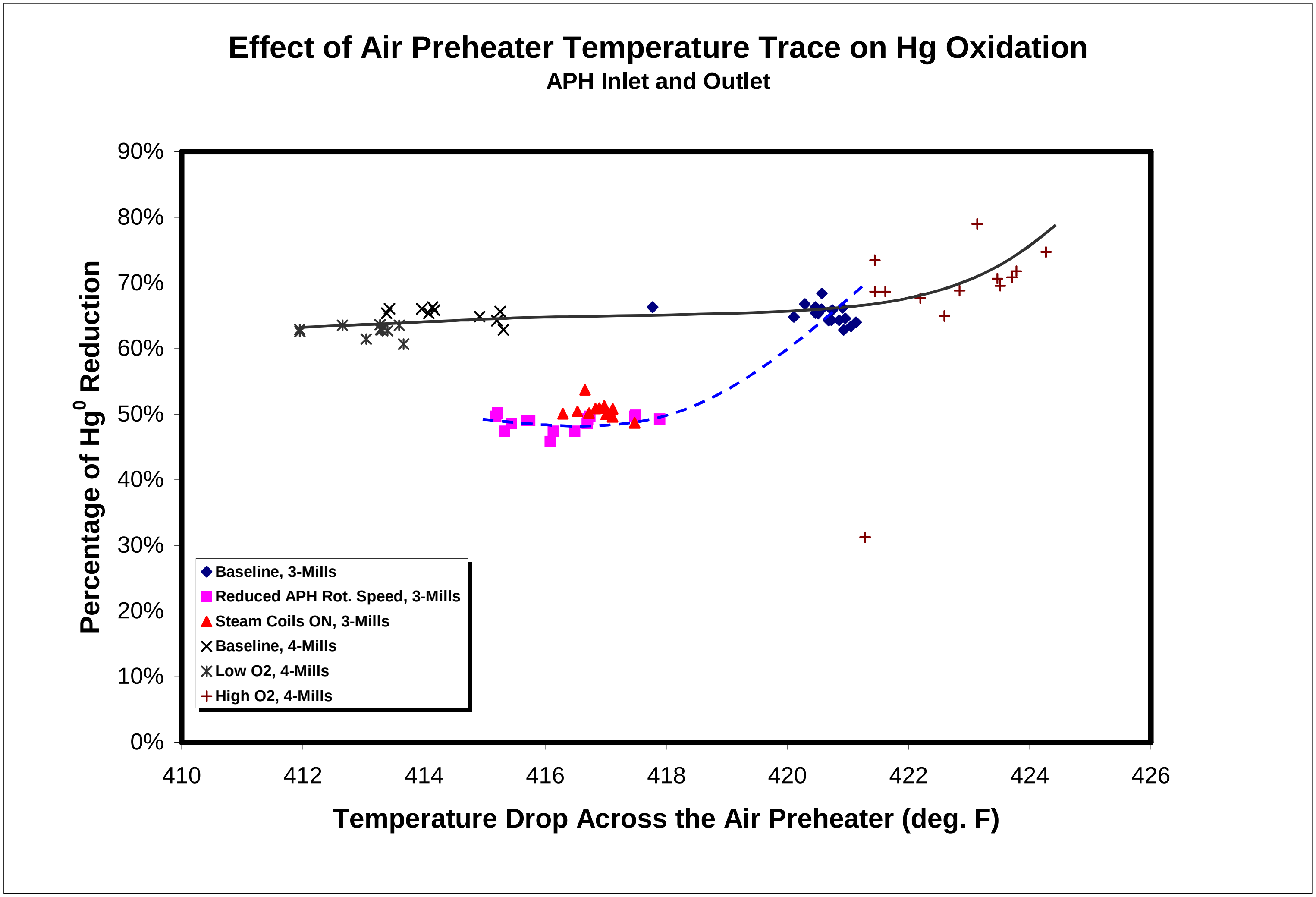
Field Test Results – Site #2



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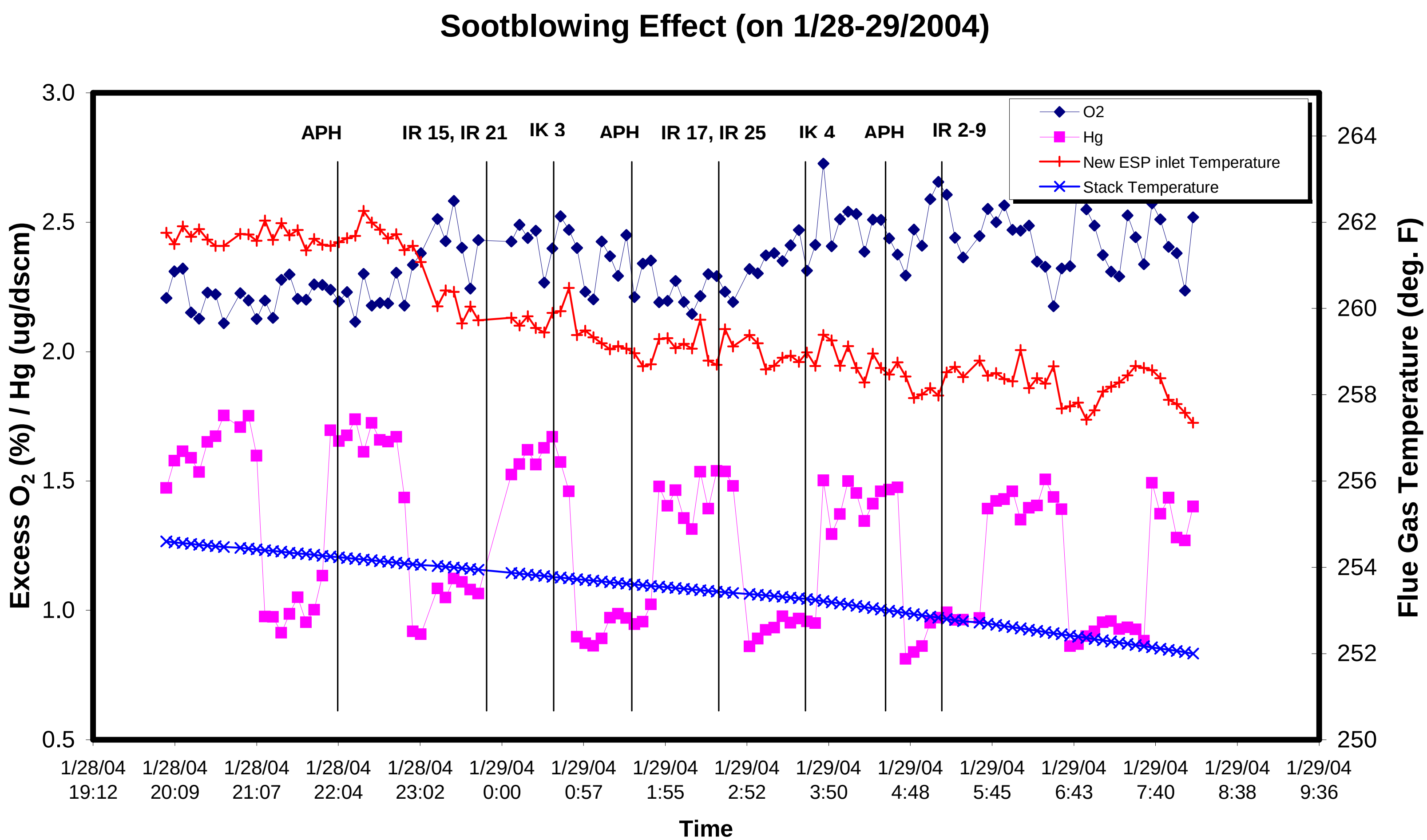
Field Test Results – Site #2



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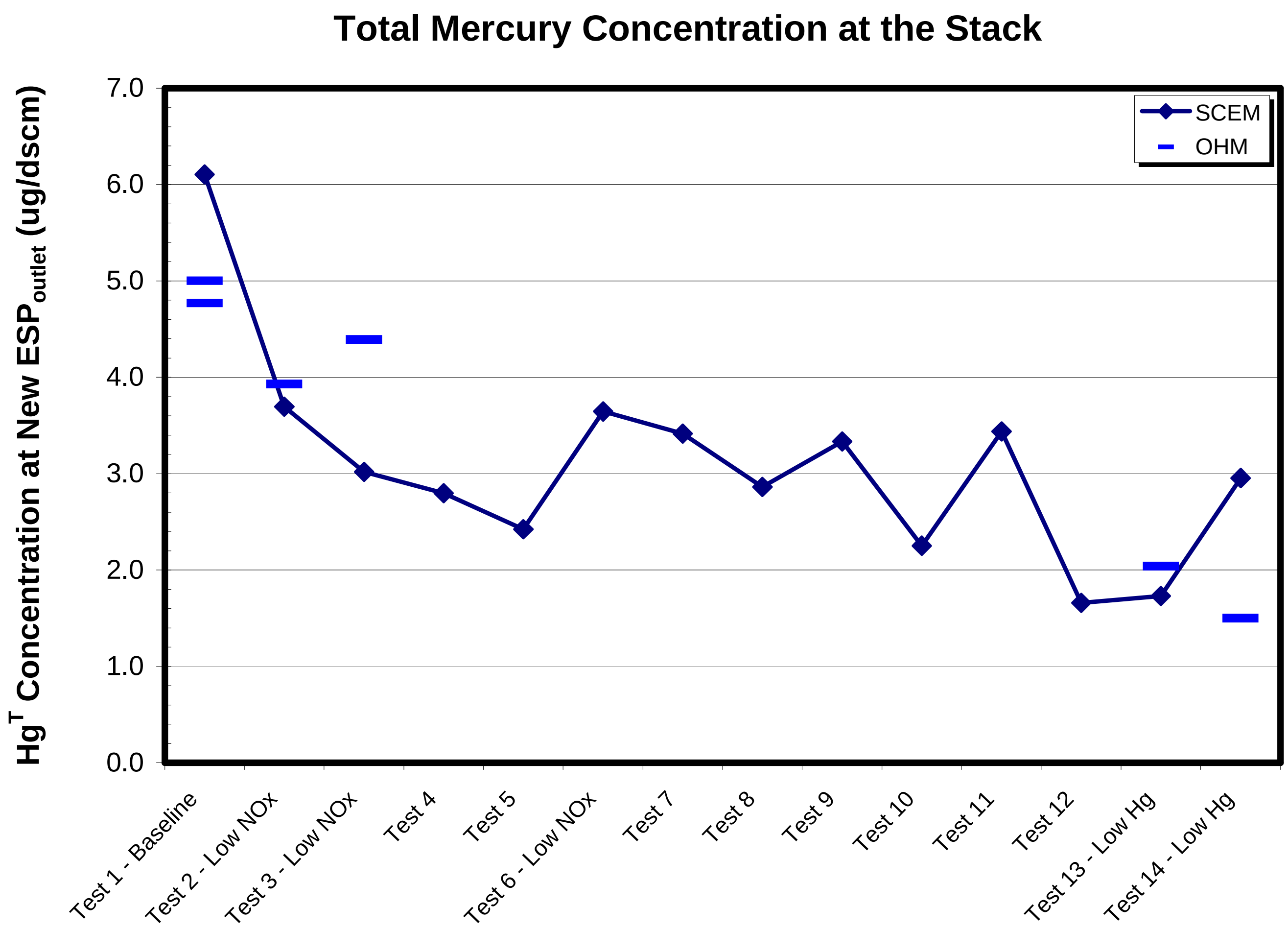
Field Test Results – Site #2



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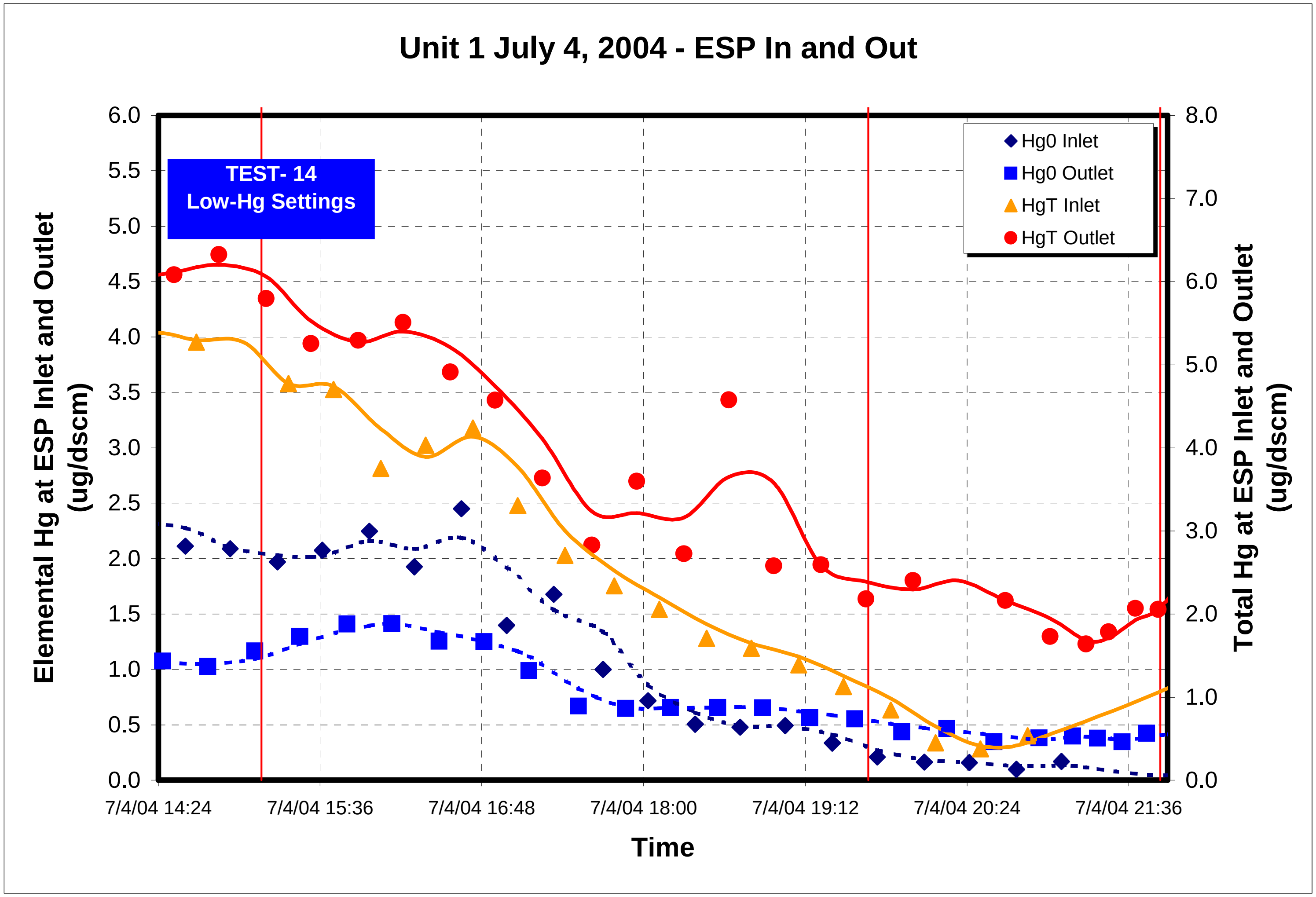
Field Test Results – Site #2



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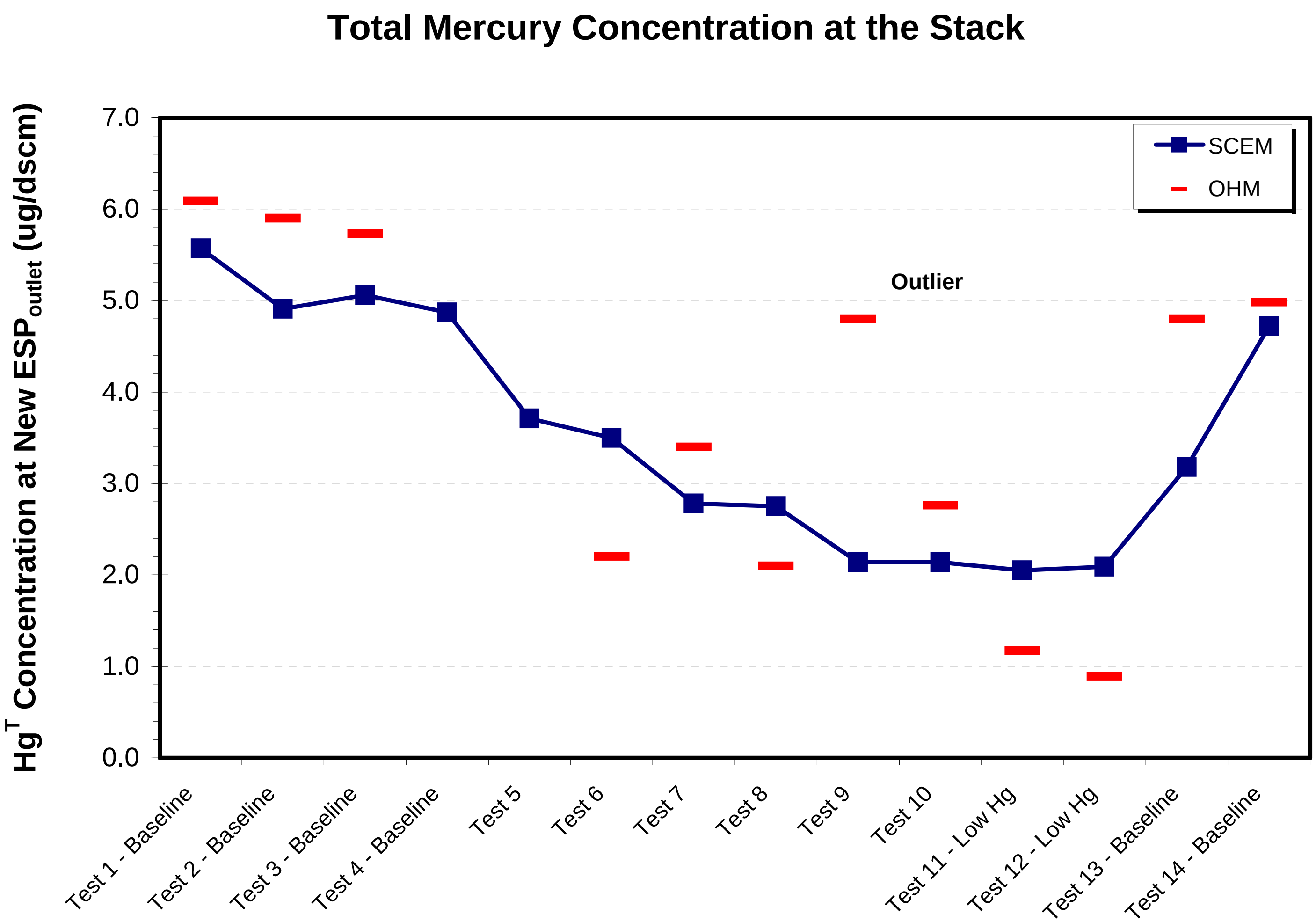
Field Test Results – Site #3



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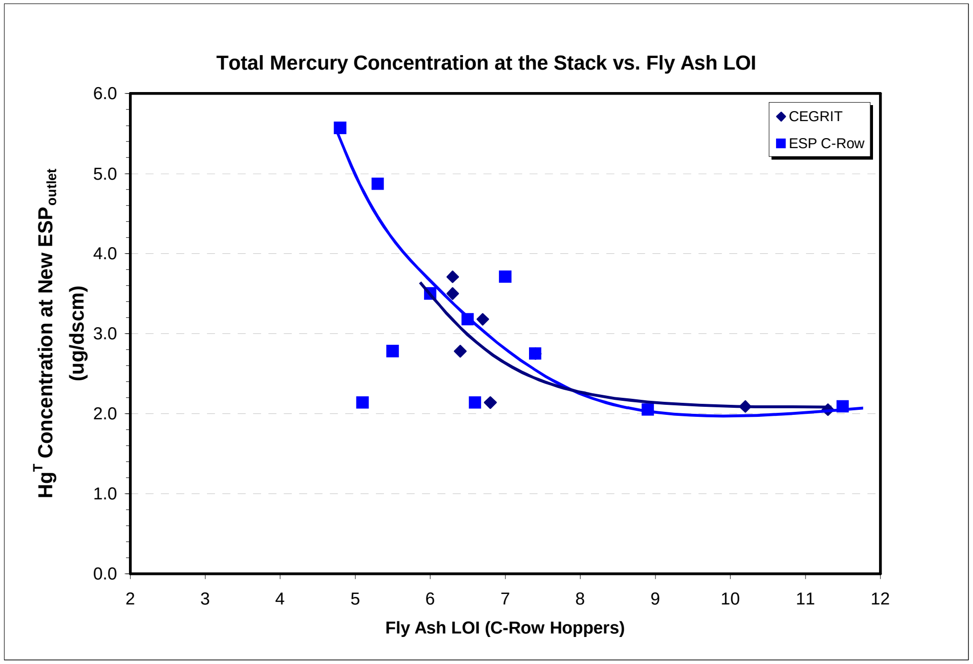
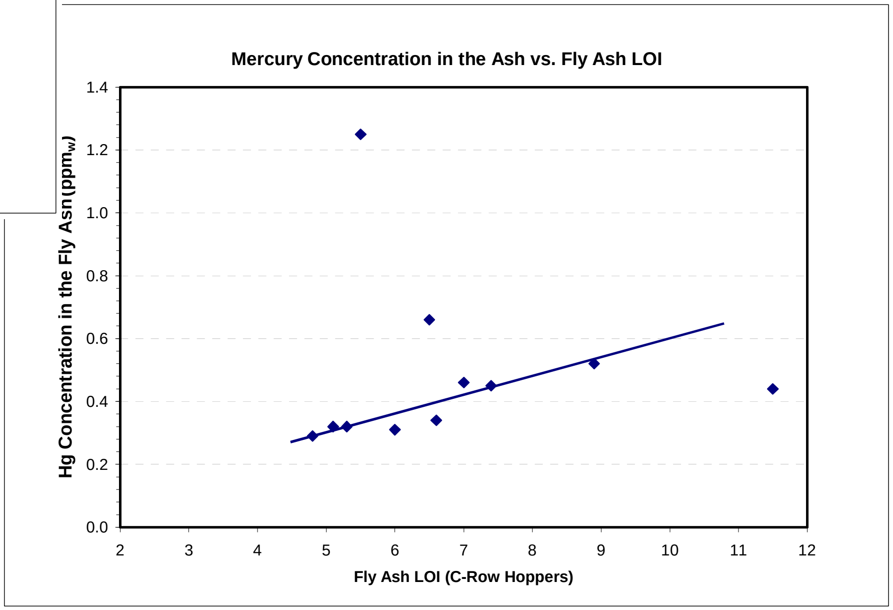
Field Test Results – Site #3





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CONCLUSIONS

- Mercury regulations are an urgent issue for the power industry.
- Analytical and experimental studies have suggested that boiler operating conditions can influence mercury oxidation and emissions from coal-fired boilers.
- Testing performed at three units, rated at 108, 250 and 650 MW, burning bituminous coals confirms the merit of optimizing boiler operation through changes to the control settings to reduce mercury emissions.
- Boiler optimization in combination with activated carbon can help to reduce the cost of mercury emissions compliance.
- The optimization test strategy involves unit baselining, parametric testing, extended test at optimal conditions and testing to determine AC requirement for trim control.

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Questions …

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