Worldwide Pollution Control Association

WPCA/TVA

Coal & Gas Seminar

August 24, 2016

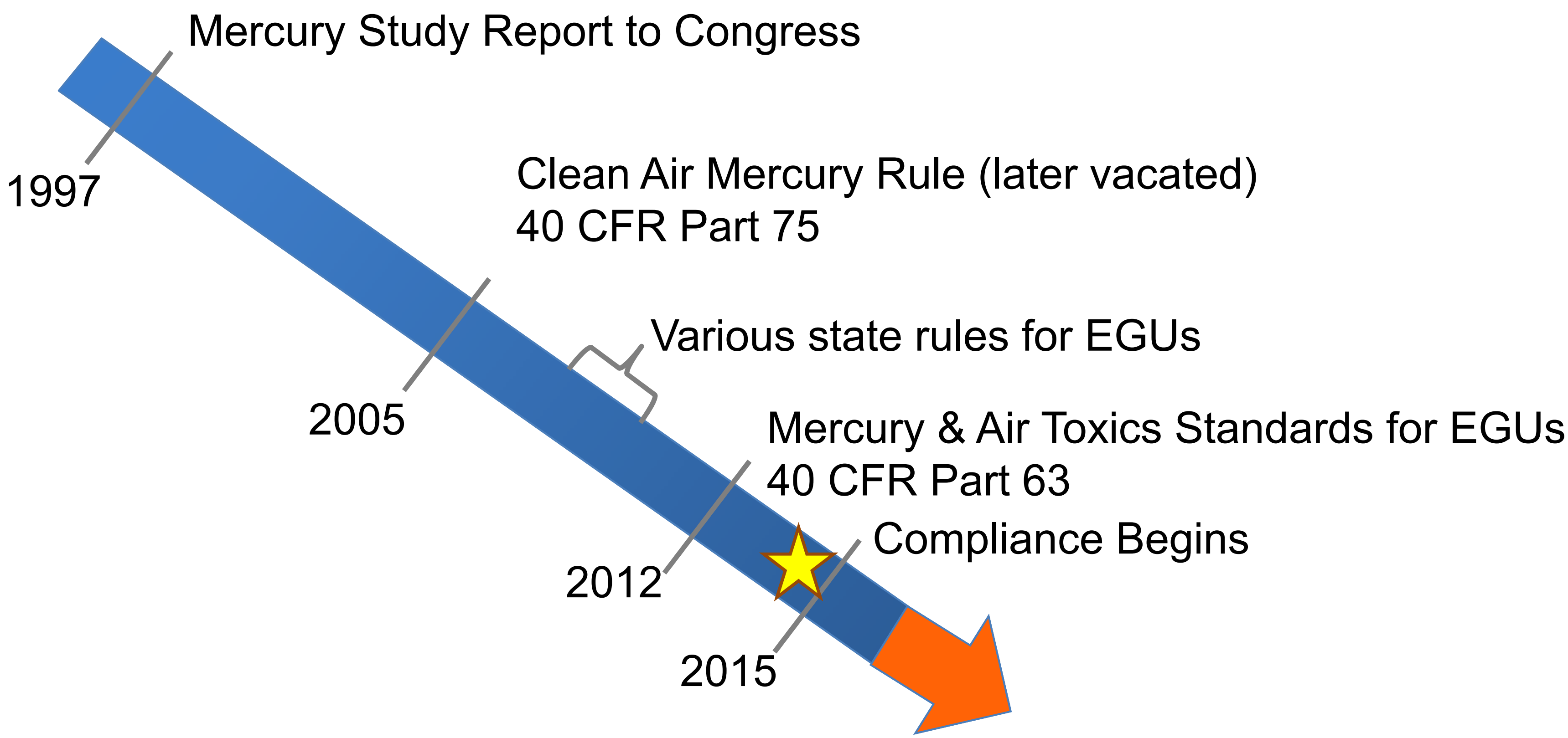
Visit our website at www.wpca.info

Mercury Testing

Sharon Sjostrom, ADA-ES, Inc.

WPCA: August 24, 2016

Mercury Control is Finally Here



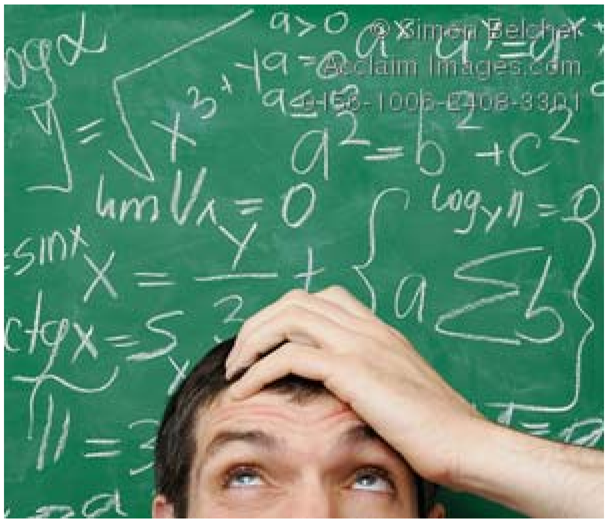
Mercury Testing: Agenda

- Evaluating new or optimized mercury control technologies while maintaining compliance
- Monitoring Techniques
  - Sorbent Trap Monitoring Systems (STMS)
  - Continuous Emissions Monitoring System (CEMS)
  - Achieving reliable mercury measurements
    - CEMS, Process Analyzers
    - STMS, EPA M30B

Mercury Testing in 2016 and Beyond

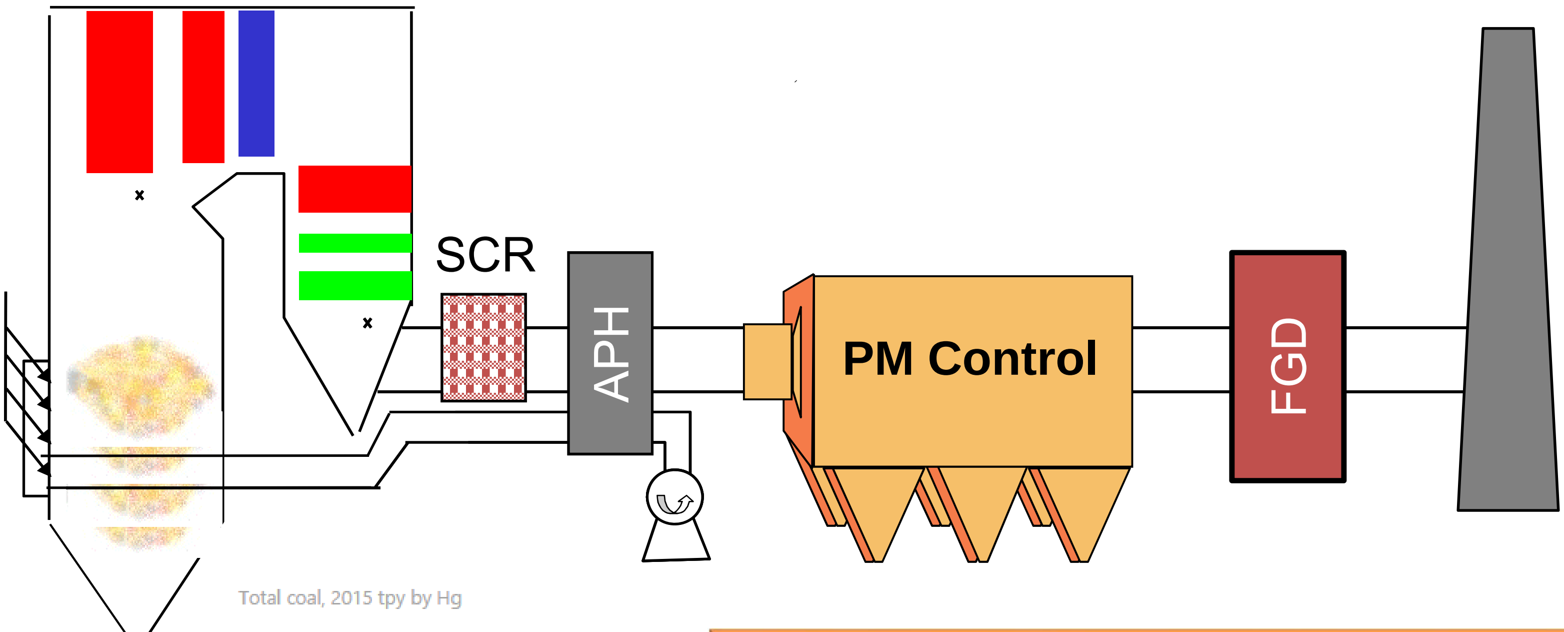
- What are you trying to achieve with testing?
  1. Improved reliability?
  2. Reduced operating costs?
  3. Reduced balance-of-plant impacts and related risks?
  4. Respond to changes in performance due to reduced capacity factor and/or load cycling?
  5. You're an engineer and can't help yourself?
  6. All of the above?

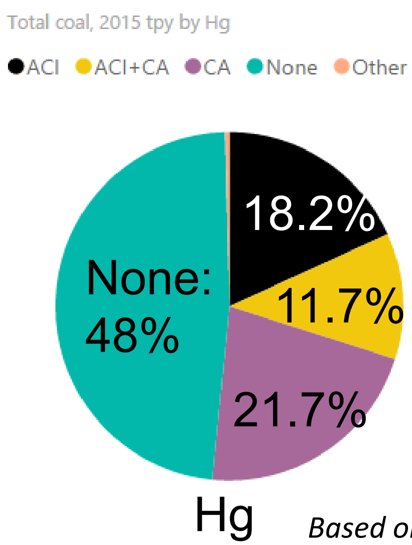
Now That You're in Compliance, How do you Evaluate New Advancements?



- "Baseline" tests will affect monthly average
- Short "parametric" tests don't always reflect changes in fuel or operations
- You'll probably overlook something if you **only** consider mercury emissions

Mercury Control: Bituminous Plants





"Testing" will often include trim technologies such as additives or ACI, scrubber additives, DSI to reduce SO_3, or impact of operational changes (temperatures, LOI, SCR, scrubber chemistry)

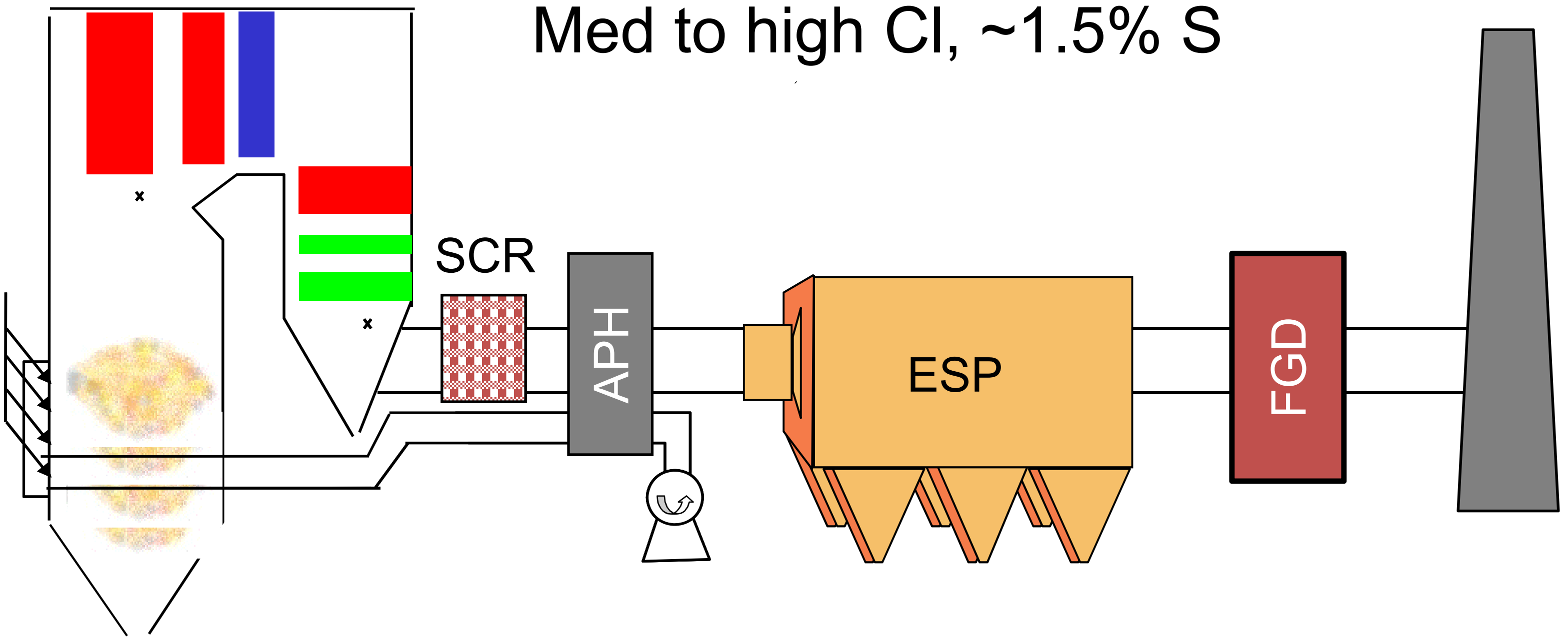
Based on Tons Coal Fired in 2015 (EIA data)

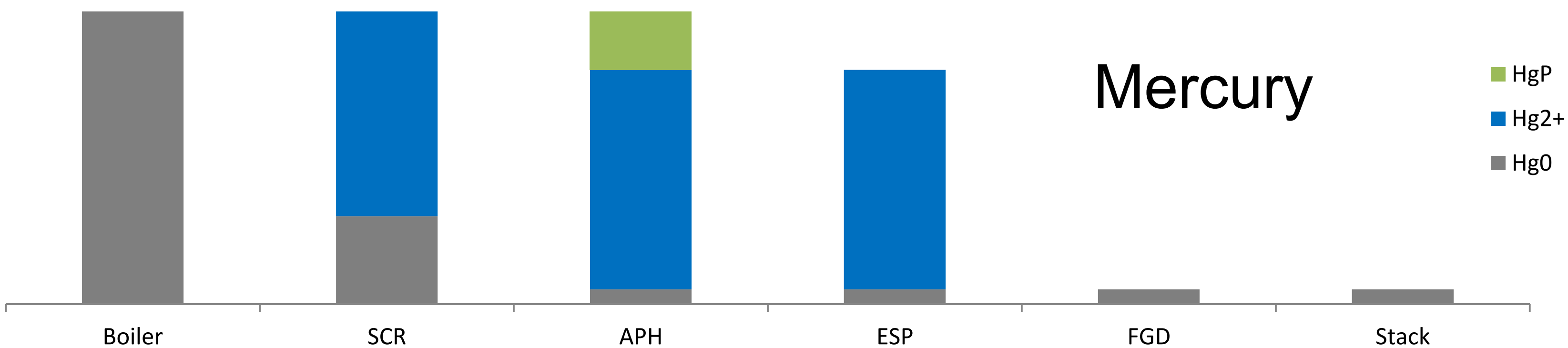
Key Factors Affecting Success with Co-Benefit Approach for Mercury Control

- Coal
  - Sulfur, mercury, halogen, LOI
- SCR
  - Lower = better: temperature, NH_3, age, gas flow rate, CO, H_2O, SO_2
  - Higher = better: halogen concentration, O_2
  - Other: SCR management scheme
- Particulate Controls
  - Hg removed before WFGD: fraction of particulate-phase Hg (LOI, temperature, SO_3, ESP SCA, FF cleaning)
- Scrubber
  - Fraction of oxidized Hg at inlet, ORP, halogens, temperature, pH

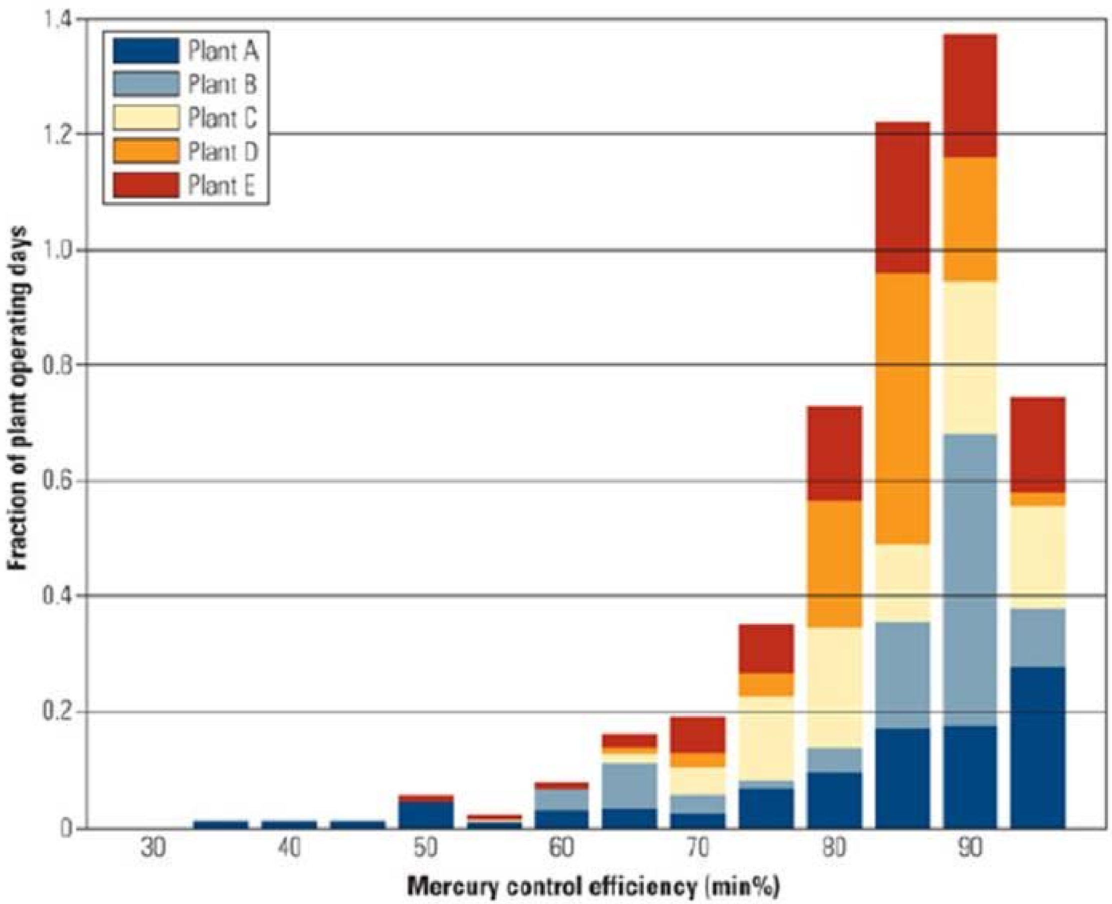
Example: CAPP Coal, Co-Benefit Hg Control

Med to high Cl, ~1.5% S





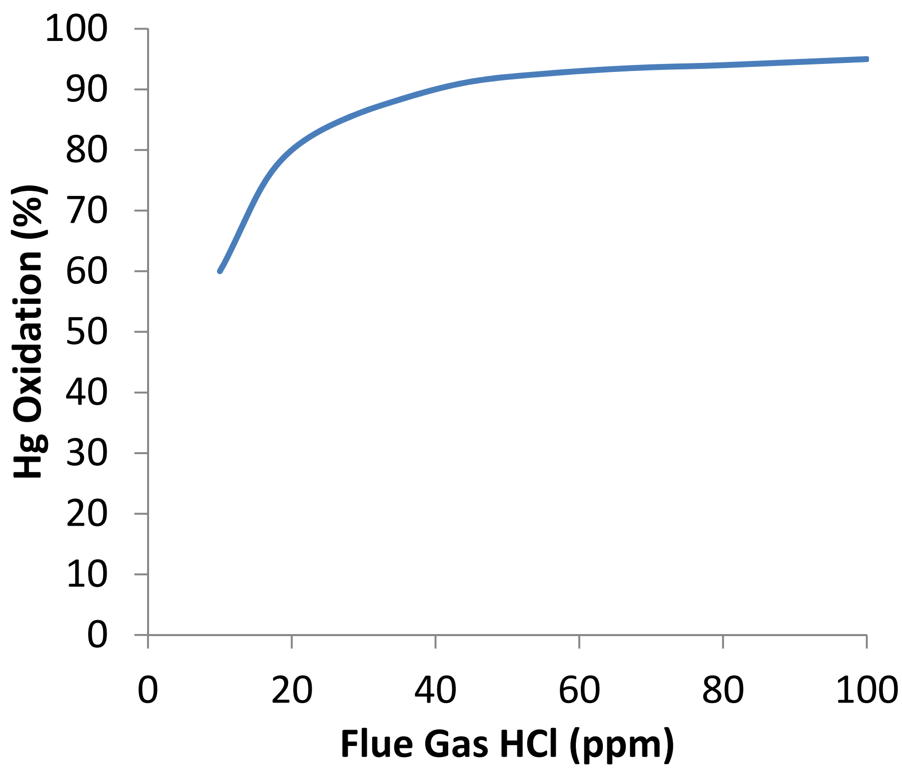
Can you Rely on Co-Benefits Alone?

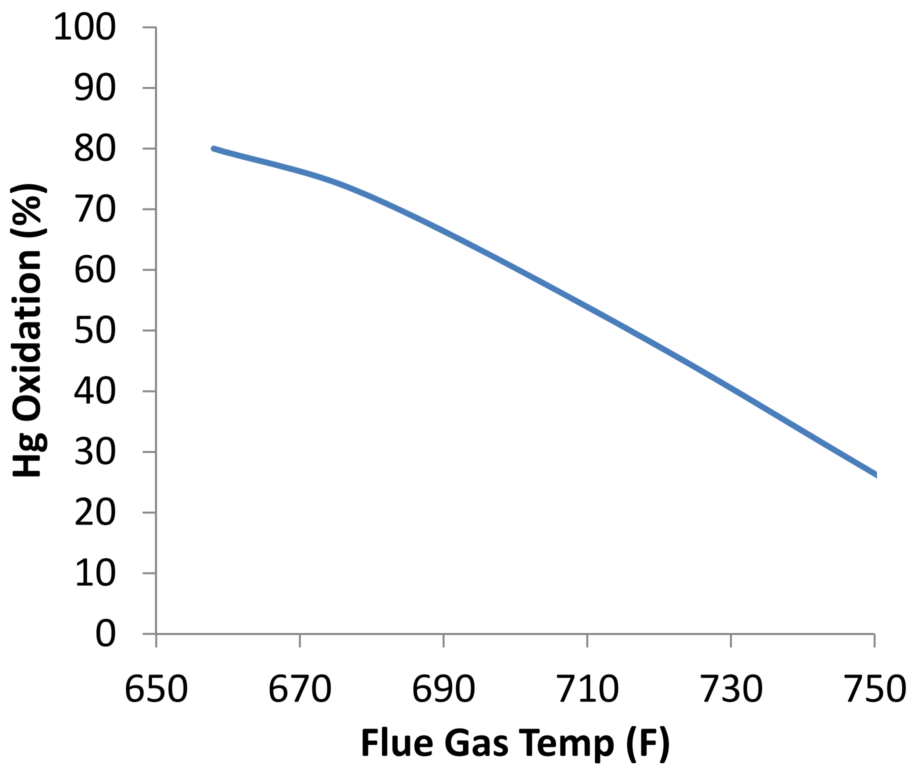


- Southern Company Plants with SCR, ESP, WFGD
- More than 40 months of WFGD operations
- Mercury control greater than 90% was achieved 47% of the time
- Important factors include SCR temperature, age, coal halogen

Corey A. Tyree, Southern Company, 2010

Hg Oxidation Across SCRs



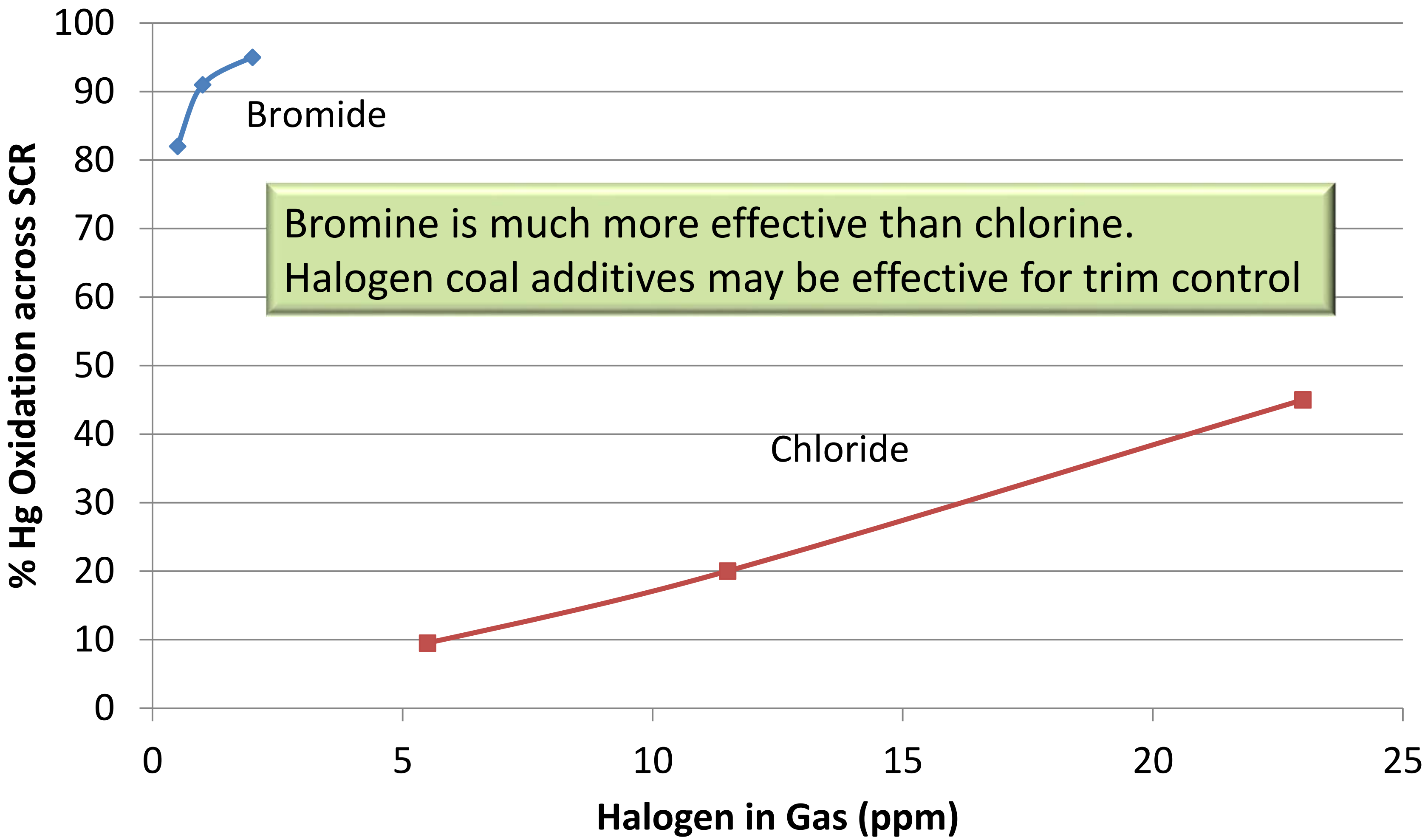


- Higher temperature → Lower oxidation
- Higher ammonia → Lower oxidation

Some plants may achieve good oxidation EXCEPT during summer months

Shintaro Honjo, Mitsubishi Heavy Industries America, Mega Symposium 2012

Improving Hg Oxidation Across SCR with Halogens



Adapted from Cormetech, 2015 Reinhold NOx conference

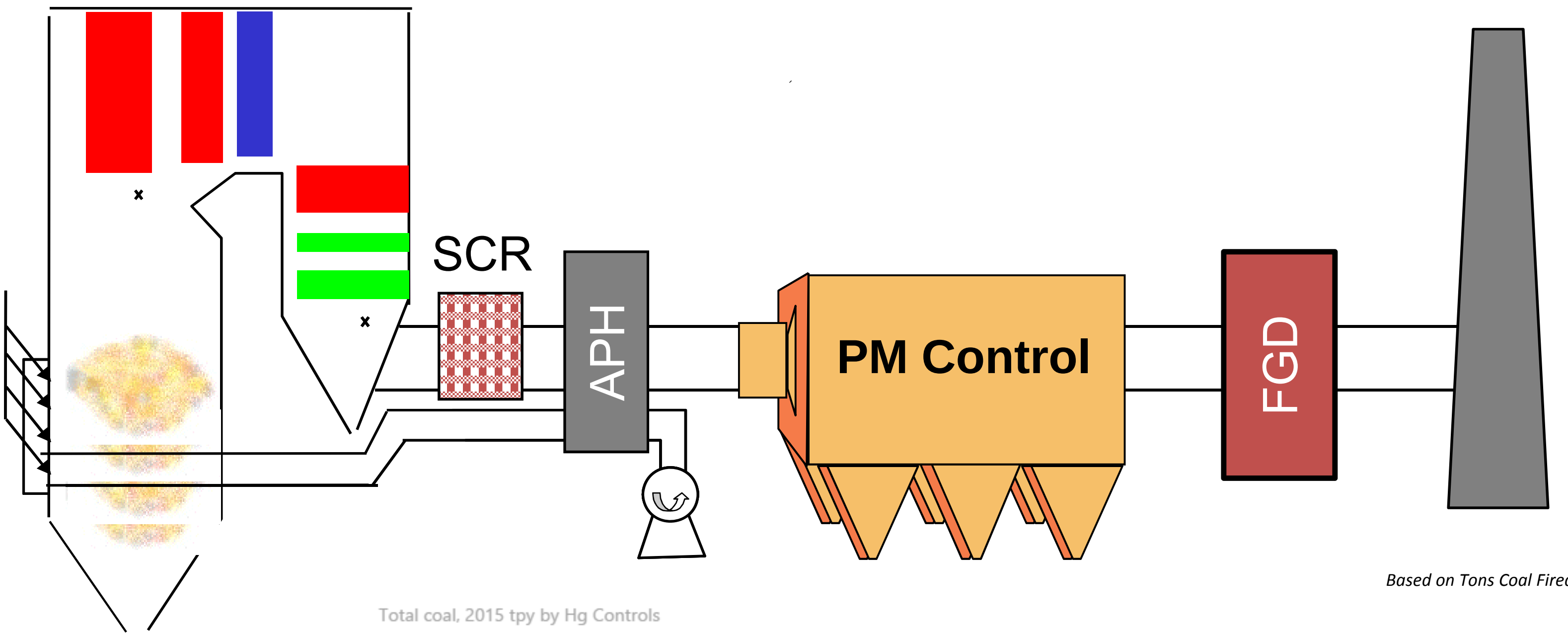
Measurement Techniques to Determine SCR Effectiveness

- Speciating sorbent traps (KCl on quartz + IAC)
  - Manage temperature: high enough to prevent moisture build-up, but cool enough to limit breakthrough

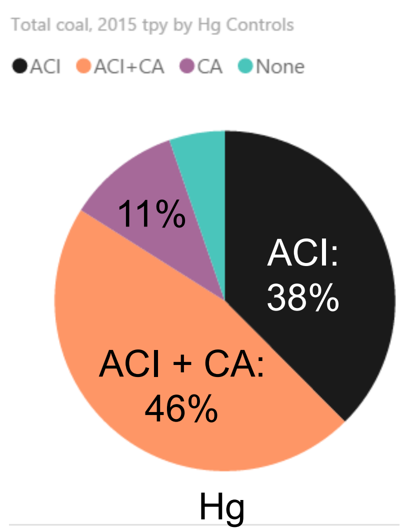
  - Some have experienced high breakthrough when testing halogen-based coal additives
  - Use probe shield and filter for particulate to minimize bias

- Process mercury analyzer
  - Preferred if operating conditions are varying

Mercury Control: Subbituminous Plants



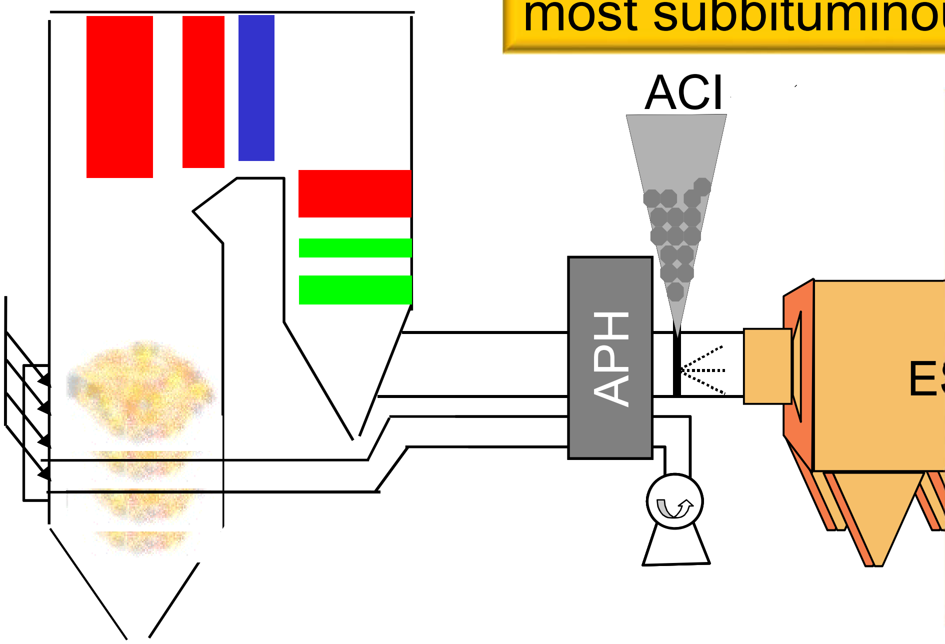
Based on Tons Coal Fired in 2015 (EIA data)



- Most subbituminous plants rely on activated carbon injection (ACI) or a combination of ACI and coal additives(CA)
- Testing will often include variations on CA or ACI

Mercury Control - Subbituminous Coal

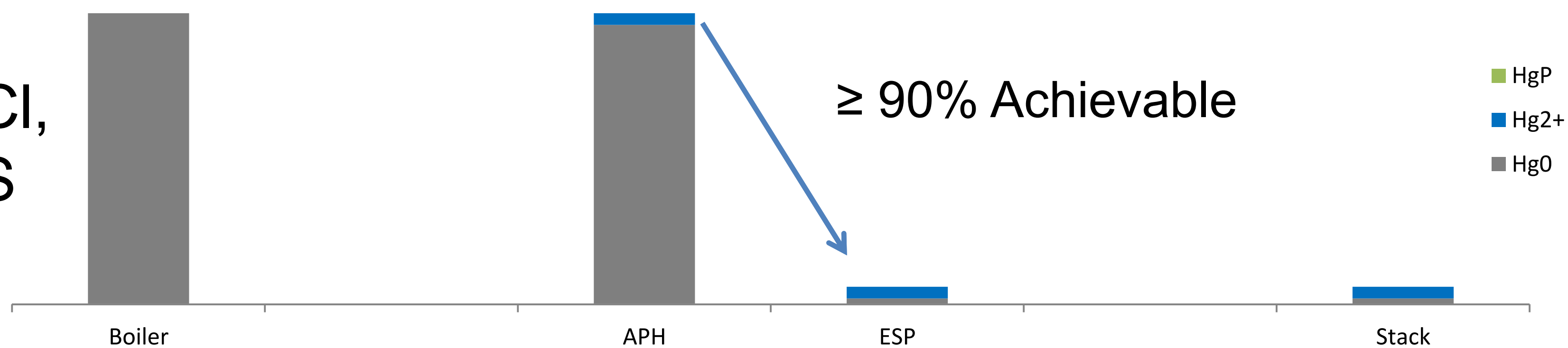
ACI effectively controls Hg for most subbituminous plants



Options to optimize include:

- Reduce Temperature
- Improve Mass Transfer
  - PAC size
  - Distribution
  - Residence Time
- Limit SO_3, NO_2, NH_3
- Add halogen

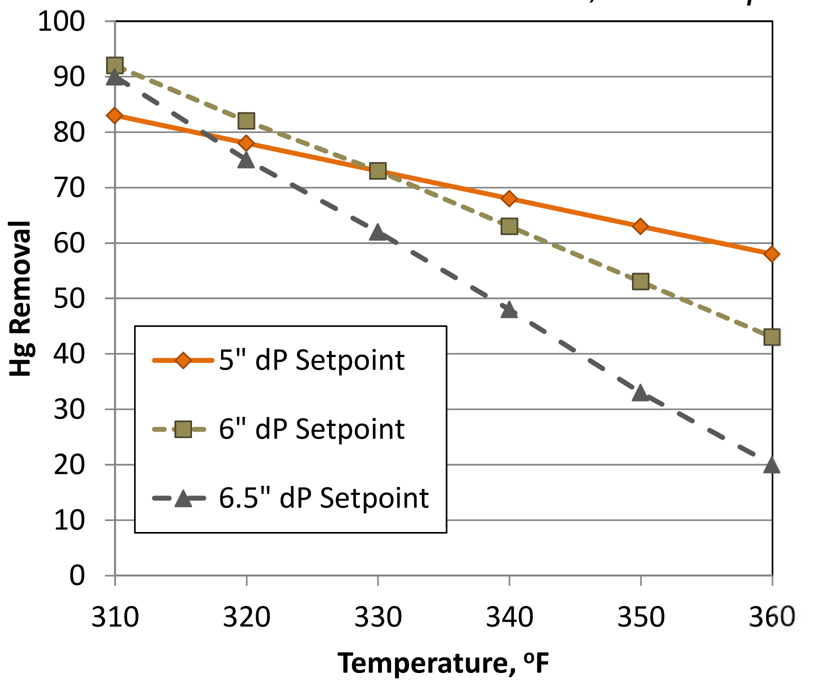
Low Cl,
Low S

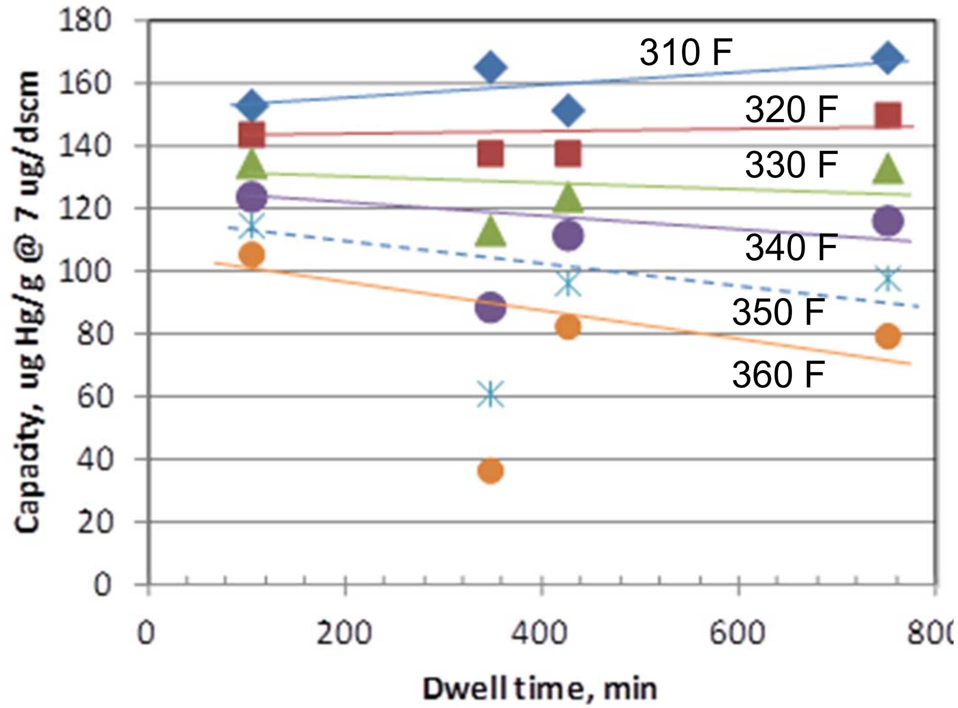


Getting the Most Out of ACI with Fabric Filters

- Lower temperature at the particulate control device
- Provide sufficient contact time
- Clean bags before increasing temperature

Source: Derenne and Stewart, Final Report





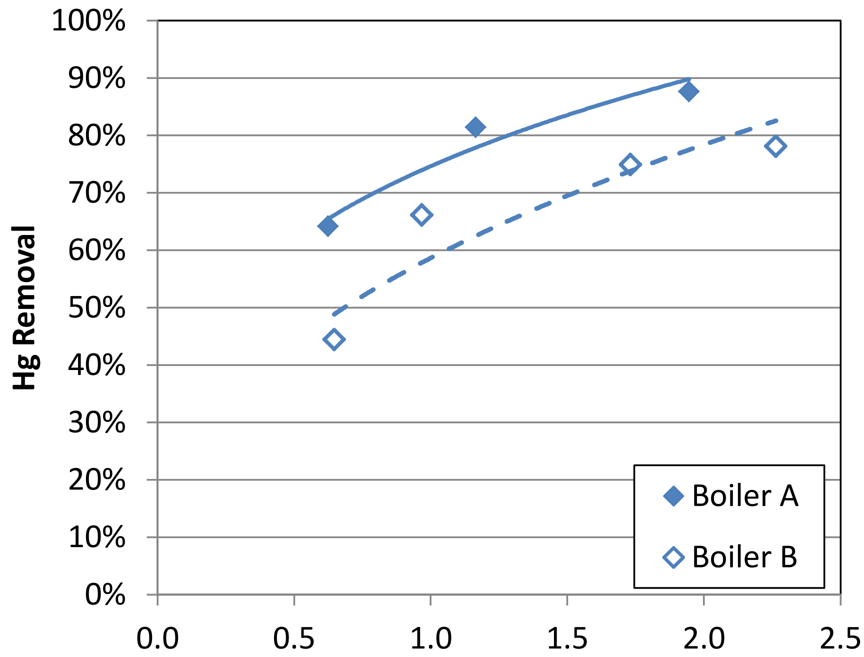
Presque Isle TOXECON fabric filter, 1 lb/MMacf non-brominated PAC

ESPs: Mass Transfer Important

PAC usage with an ESP can be reduced by improving mass transfer to the PAC

Options

- Use a PAC with faster reaction kinetics
- Reduce PAC particle size
- Use mixing devices to improve distribution



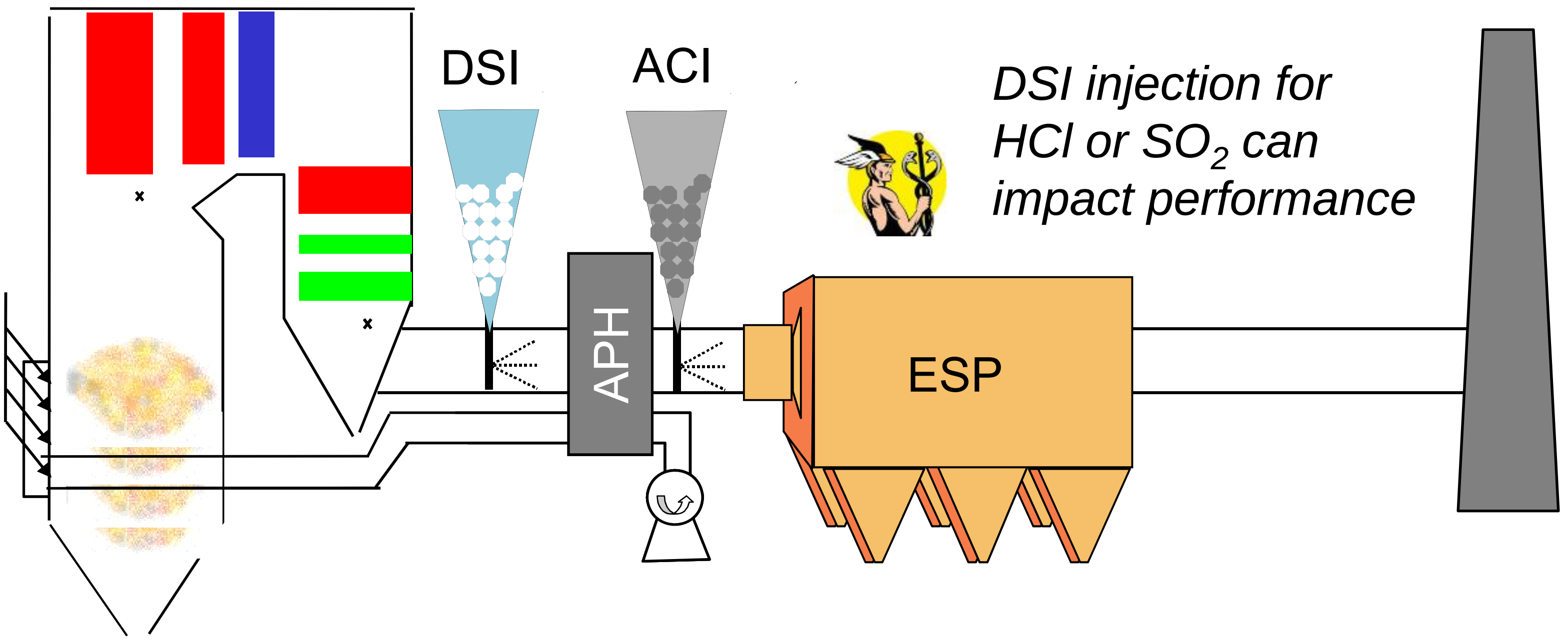
ADAir™ Mixer

Example: Two boilers burning similar PRB coal
Testing of brominated PAC on both units at 315-320°F

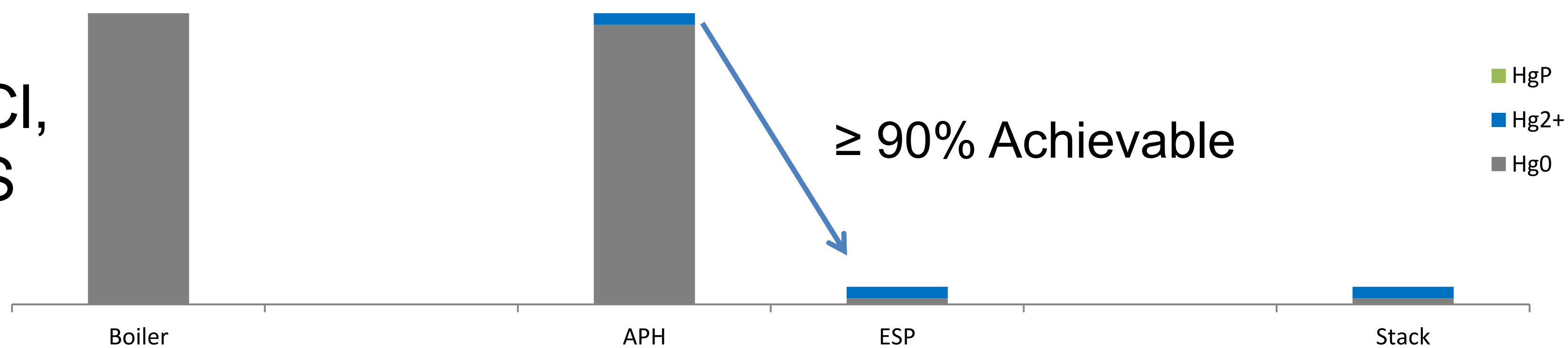
Boiler B has short residence time between APH and ESP inlet AND Chevron-style inlets

Boiler A has longer duct residence time

Mercury and HCl Control: Subbituminous Coals

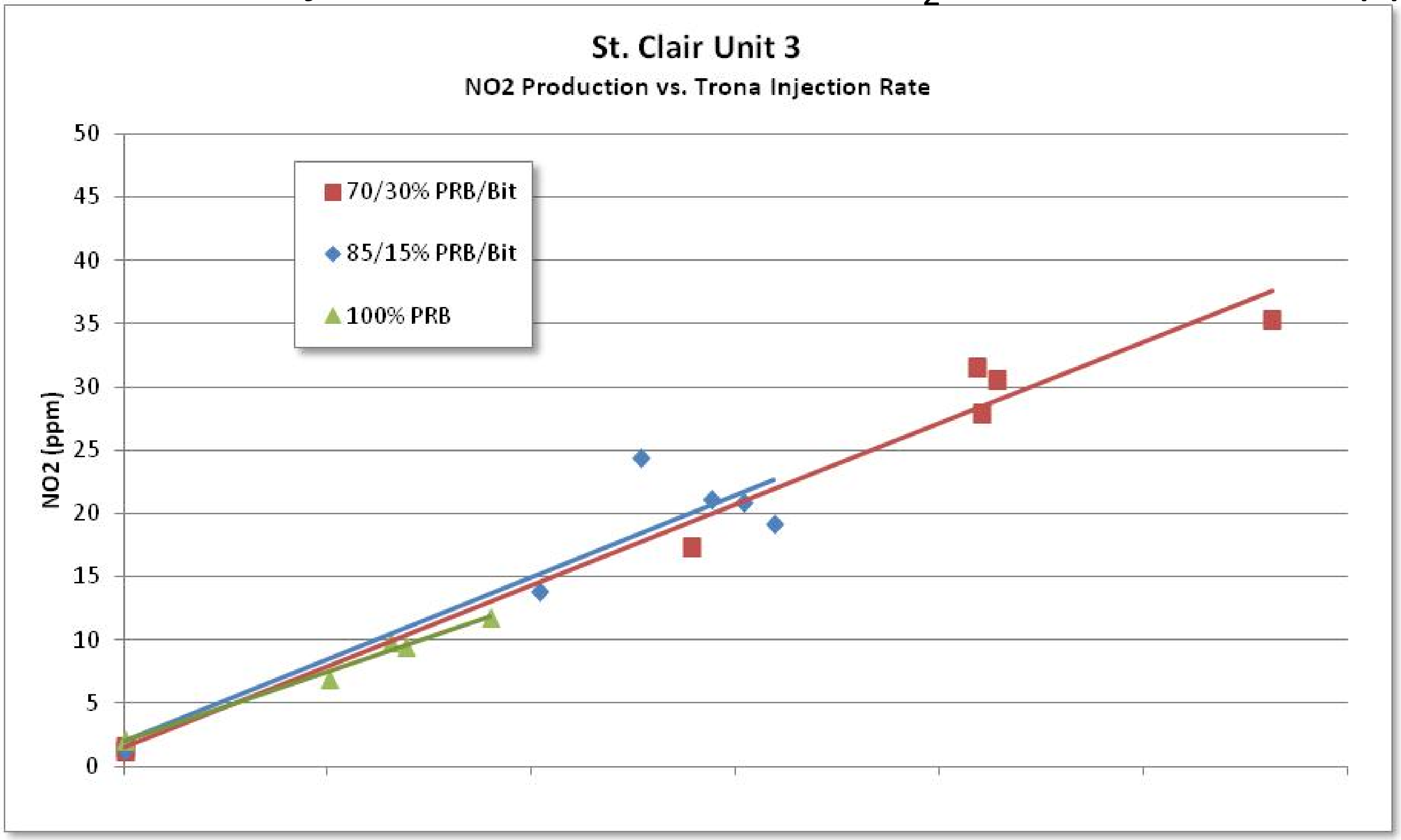


Low Cl,
Low S



DSI Challenge: NO_2 Production with Trona Injection

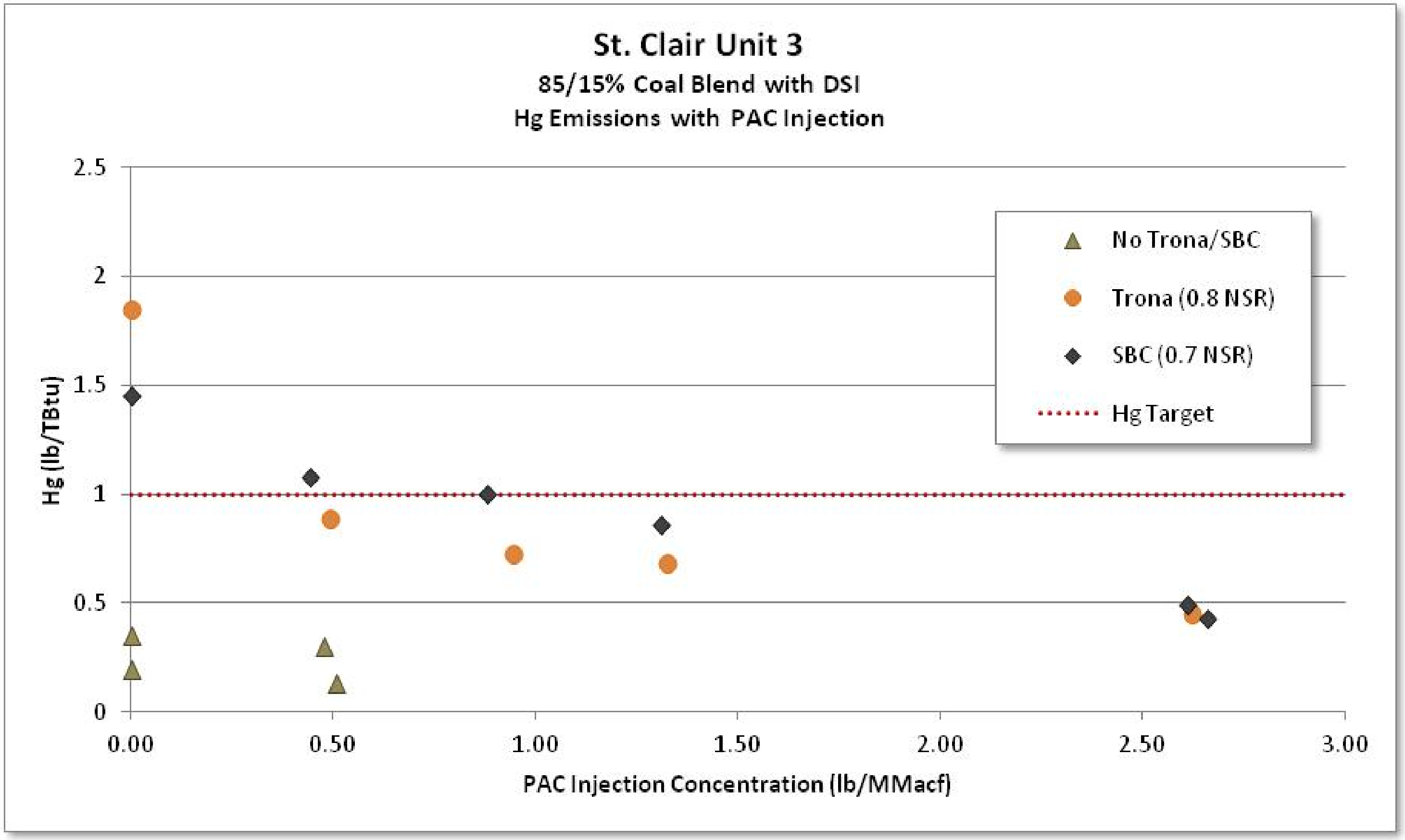
- Sodium-based DSI can increase flue gas NO_2
- Trona or SBC injection increased stack NO_2 to as much as 35 ppmv



Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

Impacts of NO_2 on PAC

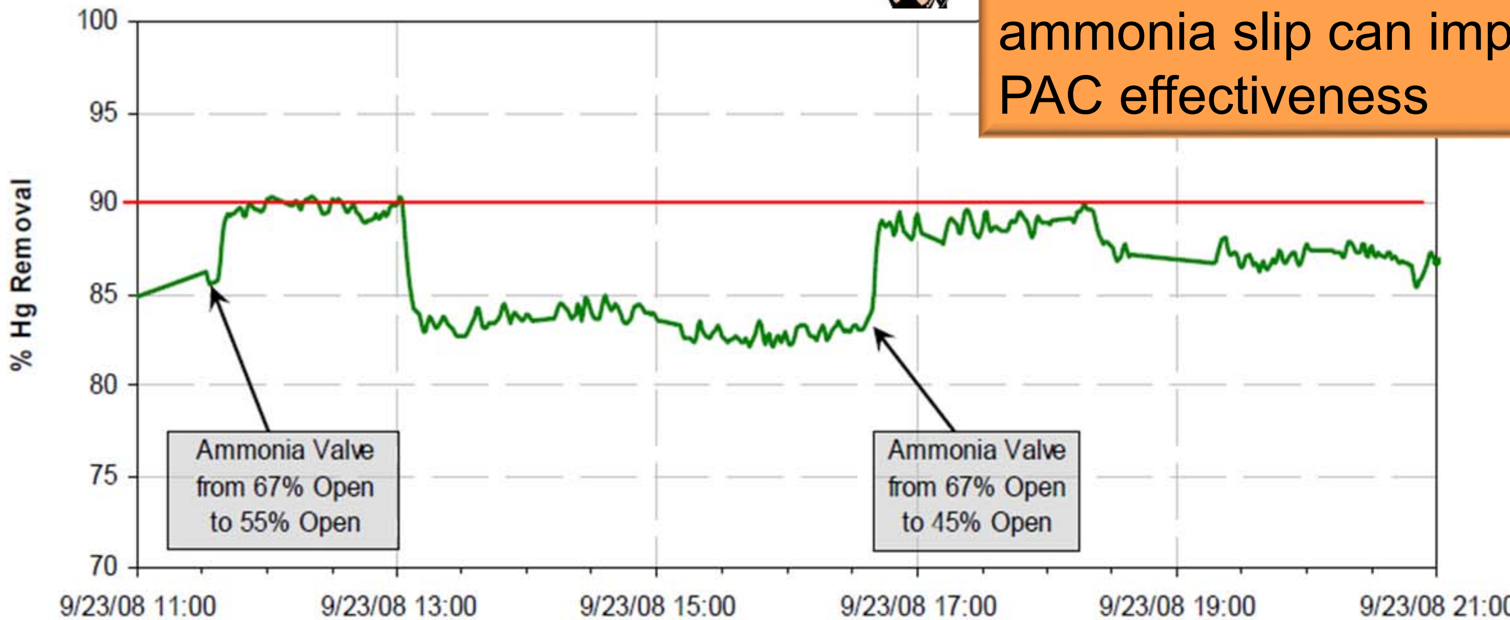
- NO_2 will interfere with Hg removal by PAC



Non-brominated PAC injected downstream of air preheater and trona or sodium bicarbonate injected upstream of air preheater for HCl control

Results from Testing at DTE St. Clair Unit 3, W. Rogers, EUEC 2013

Impacts of NH_3 on PAC Performance Clues from 2008 DOE Testing



Hardin Station: Spray Dryer + Fabric Filter, Subbituminous Coal

Data suggests that high ammonia slip can impact PAC effectiveness

- Many plants use feedback control on NO_X to control NH_3 injection
- Cycling operation can increase risk due to SCR degradation and reduced SCR efficiency
- Monitor NH_3 feed rate to manage risk

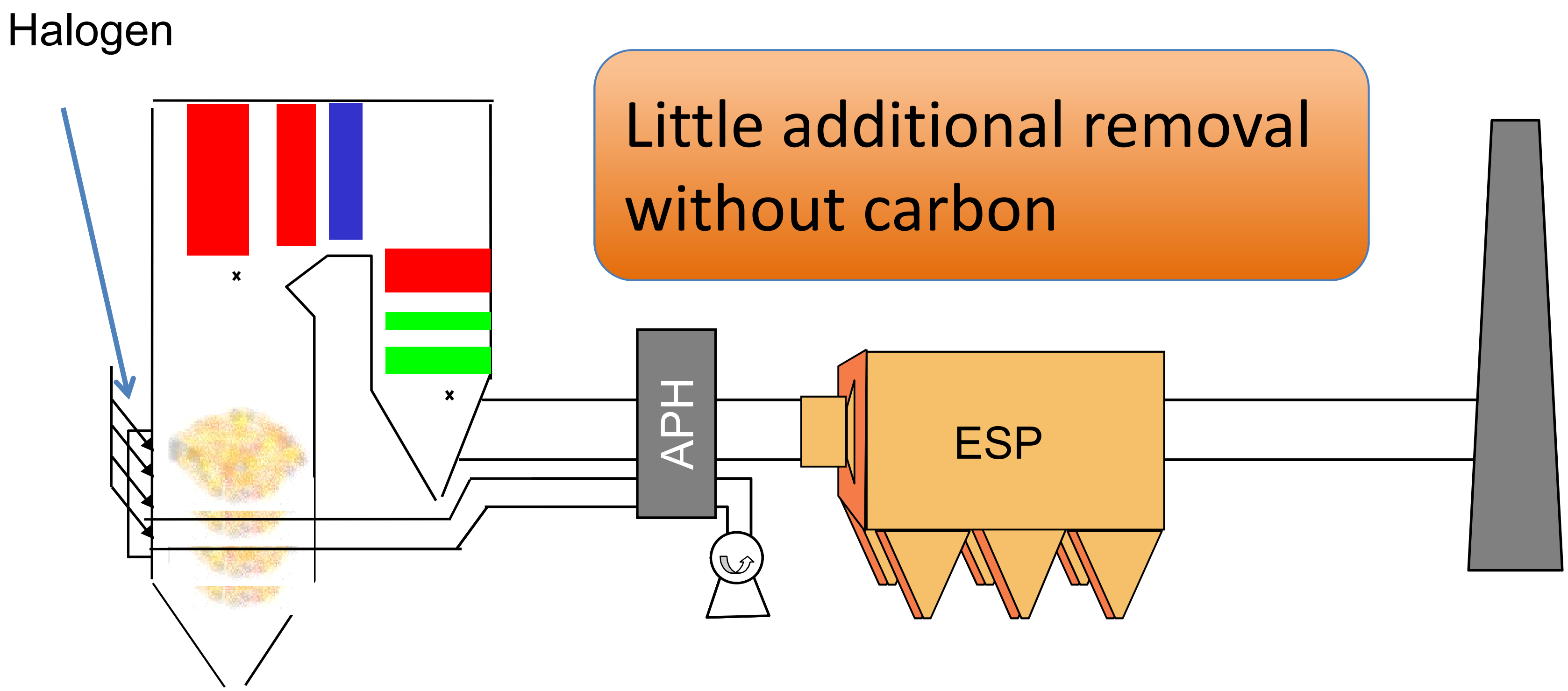
Option to Reduce PAC: Halogen Addition

- Adding halogens increases oxidized Hg:
  - Increased effectiveness of non-Br activated carbon for Hg capture
  - Increase capture of Hg in SO_2 scrubber
  - Adding some forms of iron can reduce halogen requirements*
- Potential balance-of-plant impacts:
  - Possible increased corrosion in flue gas
  - Halogens build up in wet scrubber liquor
    → Corrosion and potential permit issues

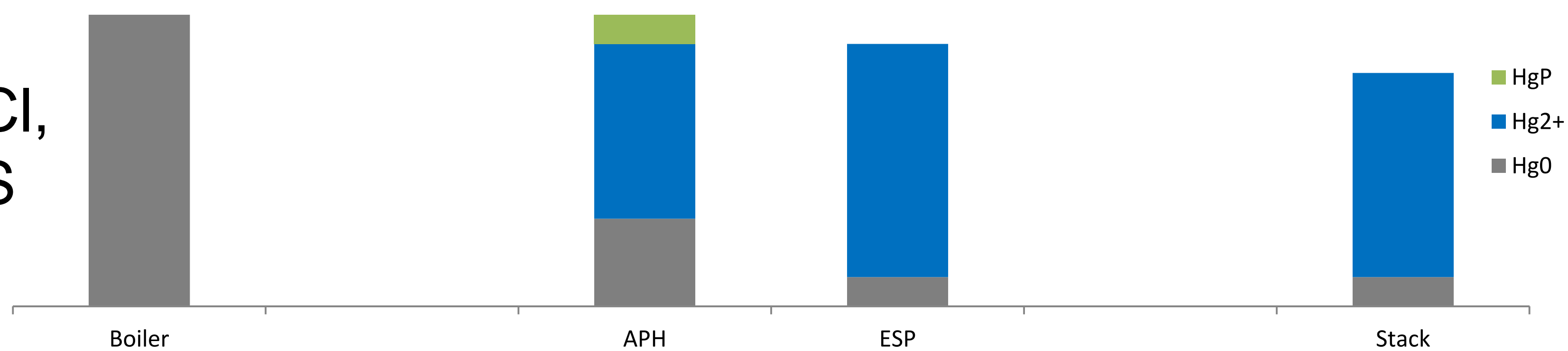
Subbituminous Coal
- Over 80% of units with ESPs have an additive system
- Less than 40% of units with FF's have an additive system

*ADA-ES, Inc. patented technology

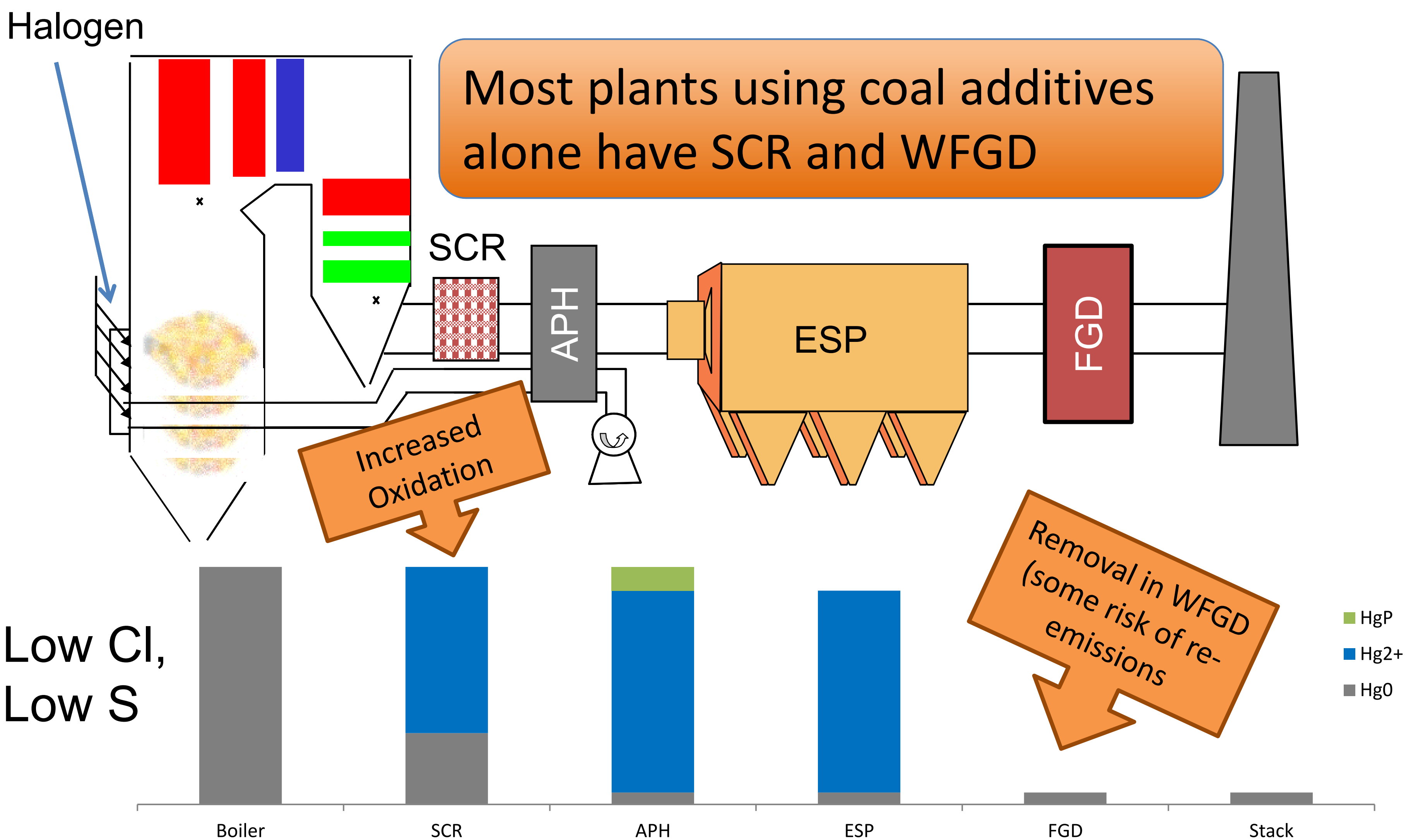
Can Halogen Eliminate the Need for PAC?



Low Cl,
Low S



Subbituminous Coal with SCR and WFGD



Removal of Hg in Wet FGDs

- Maximize gaseous oxidized Hg at scrubber inlet
- Stabilize Hg^{2+} in the liquid
  - Control redox potential (e.g., Mitsubishi Heavy Industries has a patent covering ORP control to optimize net mercury capture)
  - Halogens in the scrubbing solution can complex with Hg^{2+} and reduce Hg re-emission (sometimes)
- Increase amount of Hg removed in solid phase
  - Amount of suspended solids in the absorber slurry (impacts fines concentrations and surface area available for mercury adsorption)
  - Iron in fine particles (fines) in the scrubber (from limestone and/or fly ash) that react with Hg
  - Use an additive to the scrubbing solution to tie up Hg or precipitate to solid phase

Potential Balance-of-Plant Impacts with Halogen Addition

- APH cold-end corrosion
- Higher halogen levels in FGD (corrosion) and waste water (TDS and treatment)
- Formation of additional trihalomethanes (THM) in downstream water
- Increased gas-phase Se at scrubber inlet

Interaction of Bromine and Se

- Adding bromine to the fuel can shift Se from fly ash to wet FGD
- EPRI study* noted data from three test sites showing an increase in Se concentration in FGD liquor during bromine addition to fuel
- For example, at one bituminous-fired boiler bromine was added for 10 days:

Condition	Se in Fly Ash, µg/g	%Se Capture by Fly Ash	Se in FGD Liquor, µ/L
Baseline	24	70%	300
Br Addition	10	20%	4,900

- Test at a subbituminous-fired boiler** with SCR, ESP and wet FGD showed 110% increase in gas-phase Se at wet FGD inlet: 30 ppmw Br addition compared to baseline

**Dombrowski et al., Air Quality VIII Conference, 2011*
***Gadgil et al., APC Roundtable, 2013*

Emissions Testing: Typical Performance Test Criteria

Steady operation

- Load (MW, million Btu heat input/hr) as close to but not greater than design maximum
- Load stabilized at least two hours before the start of the performance test and held constant (±2% - 3%) during all runs of the performance test
- Fuel being fired should be as close to process design as practical and should not change over the course of the performance tests
- Performance test run not overlapping the scheduled daily calibration of installed CEMS
- Air Preheater outlet temperature "typical"
- Flue gas flow rate (acfm) at injection point "typical"
- SO_3 concentration at the ACI injection location "typical"

Emissions Testing: Minimum "Test" Time Under Ideal Conditions

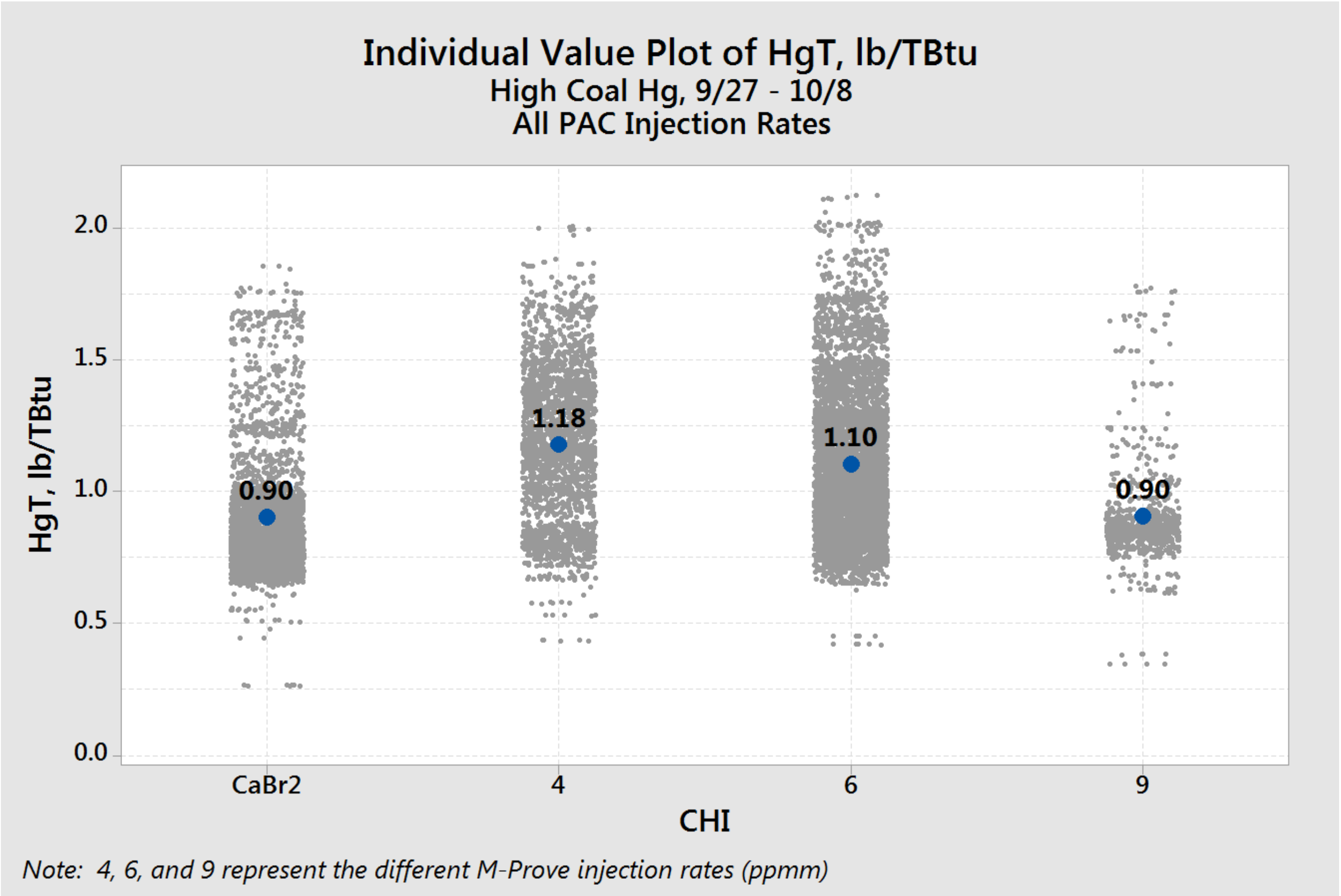
- Downstream equipment operating at "steady state", or at least a steady level of sorbent, mercury re-emission additive, or FGD process chemistry, some suggestions are:

ESP, 1 day	PAC buildup on the collecting electrodes/plates could affect the electrical operation of the ESP, with a minor effect on Hg removal.
Baghouse, 3-5 days	PAC starts to accumulate on the bags, through multiple cleaning cycles. This can affect both Hg removal and pressure drop. The baghouse should be allowed to come to steady state.
Dry FGD/FF, 5-7 days	Recycle of the FF ash back into the dry FGD will take a few days to come to steady state. Hg sorbent will be recycled along with the lime from the dry FGD.
Wet FGD, 1 week minimum	Either with additives or sorbent injection, it may take a considerable time for the chemistry in the FGD slurry to stabilize, depending on the blowdown rate and volume of absorber tank.

Testing During MATS Compliance

- Obtaining a new “baseline” not practical.
- “Steady” operation may not be practical.
- Statistical analysis of historical performance with existing compliance approach is recommended to establish benchmark.
- Extended test period (days to weeks) with new approach is recommended. Duration will be determined by APCD and operating variability.
- Information from Plant Information system or Historian should be archived (load, temperatures, flow rates) for the test periods
- Recommend collecting additional data that can affect performance, especially if test is short or coal has changed. Suggestions include:
  - Inlet mercury concentration (flue gas and/or coal sampling)
  - SO_3 and/or NH_3 concentration (typically at air preheater outlet)
  - Scrubber testing and grab samples
- “Tests” are often 30-days or longer to verify economic benefit and assess potential impacts.

Example: Statistical Review Testing of Coal Additives



- PAC injected with coal halogen (either $CaBr_2$ or M-Prove Additive)
- Data filtered for full load conditions only

Mercury Monitoring Techniques

Compliance

- Hg continuous emissions monitoring system (CEMS) or sorbent trap monitoring system (STMS) used for both initial compliance and continuous compliance, except where the low emitting EGU (LEE) requirements apply
- About 500 Hg CEMS were purchased and installed*

Reference Methods

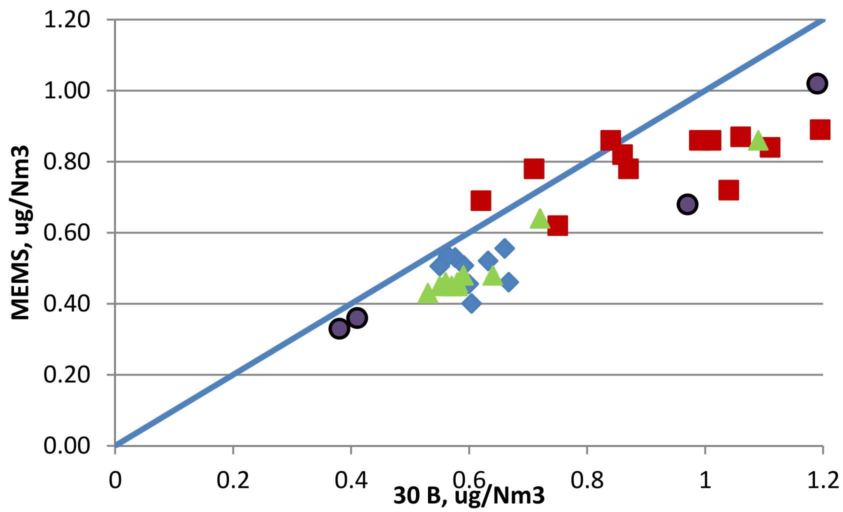
- M30A Instrumental Reference Method
- M30B Sorbent Traps (**primary method for EGUs**)
- ASTM D6784-02 “Ontario Hydro Method” and M29

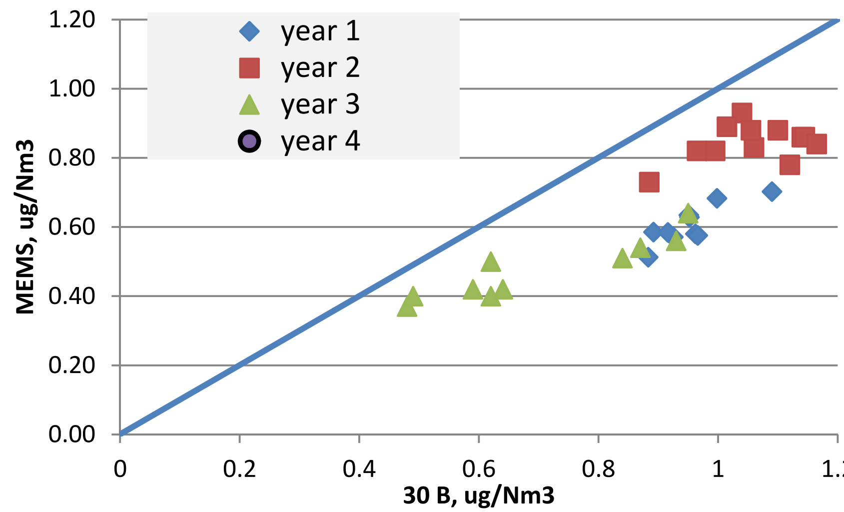
**Andover Technology Partners, 2014*

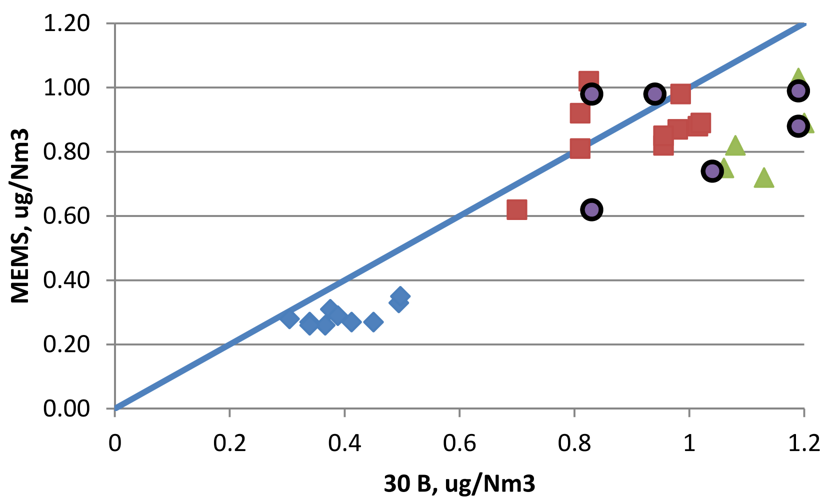
RATA Results: 4 Units, 4 Years

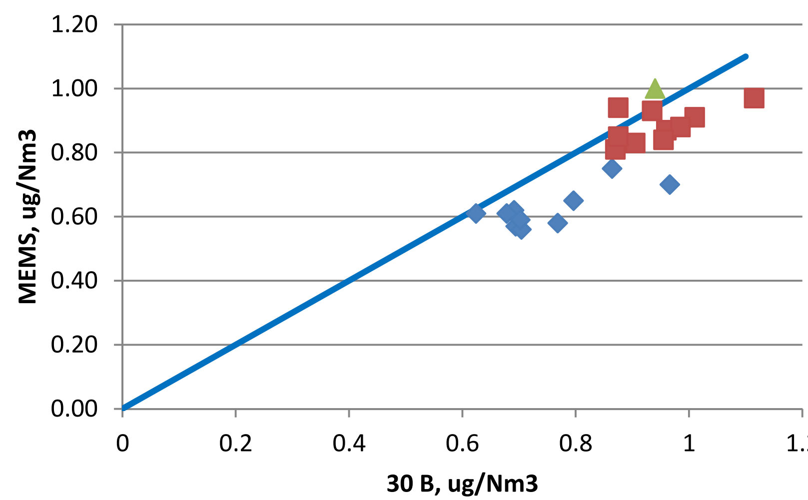
Comparison of CEMS to 30B

M30B often reports higher Hg than CEMS









Br addition varied each year

Andover Technology Partners

STMS "Bias" from Hg on PM

Mercury tends to be on fly ash that is most difficult to capture – more concentrated in small size fraction that escapes PM control device

- from ESP inlet: 1.0925 mg/kg (ppm)
- inside ESP: 0.6615 mg/kg (ppm)
- from ESP outlet: 7.5303 mg/kg (ppm)

Mercury concentration (mg/kg or ppm) in fly ash particles at ESP outlet

- Higher concentration on smaller particles
- Would expect concentration of Hg in activated carbon to be significantly higher

Dust diameter (µm)				
0-3	3-10	10-24	24-45	Diam, µm
9.0827	6.2917	3.6420	1.0657	Hg, ppm

Jedrusik, M., and Swierczok, A., "The influence of unburned carbon particle on electrostatic precipitator collection efficiency", 13th International Conference on Electrostatics, Journal of Physics: Conference Series 301 (2011) 012009

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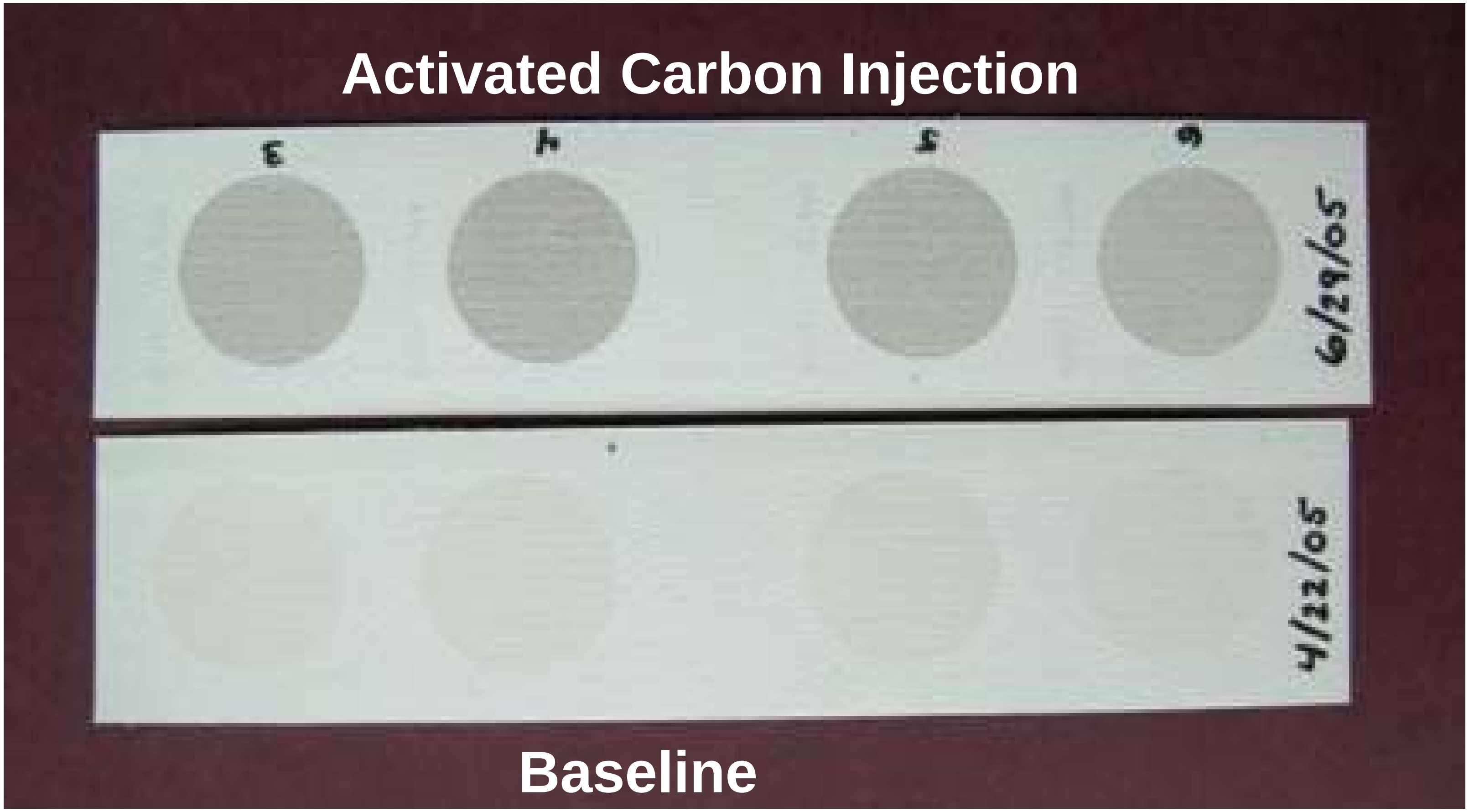
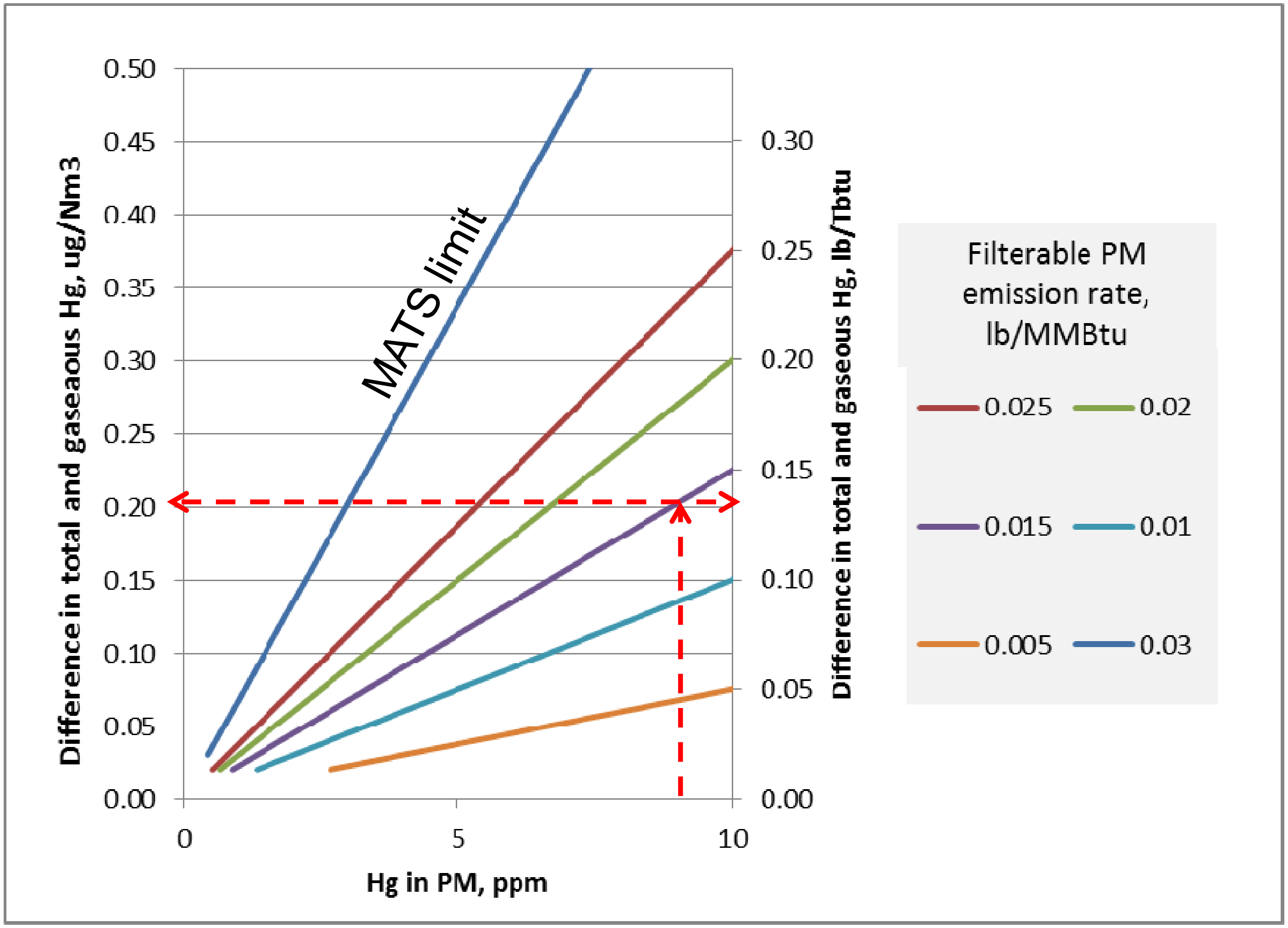
Activated Carbon at Outlet of ESP



No measurable differences in particulate emissions for two periods shown
Capacity of activated carbon is typically >100 ppm Hg at APH outlet temps

Hg in PM, PM emission rate and difference in gaseous and total Hg – how they relate



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Keys to Maintaining Reliable CEMS Operation

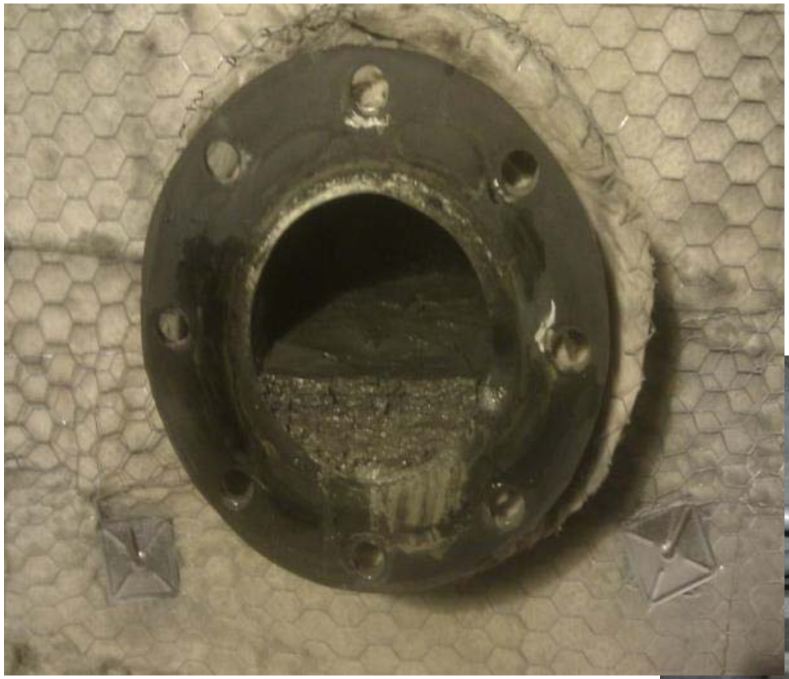
- Assure CEMS are Optimized
  - Assess current CEMS operations
    - Calibration records
    - Maintenance records
    - Visual inspection
  - Upgrades as required to improve performance
- Provide Targeted Operator Training
- Support Operations
  - Regular review of system operations
  - Expert troubleshooting assistance and coaching
  - Routine maintenance

CEMS Remote Monitoring can Help

- Continuous Remote Monitoring and Diagnostics
  - Monitor operational parameters and continuously analyze performance trends
  - Proactively identify emerging problem areas and provide corrective maintenance actions for resolution to prevent "failure" events

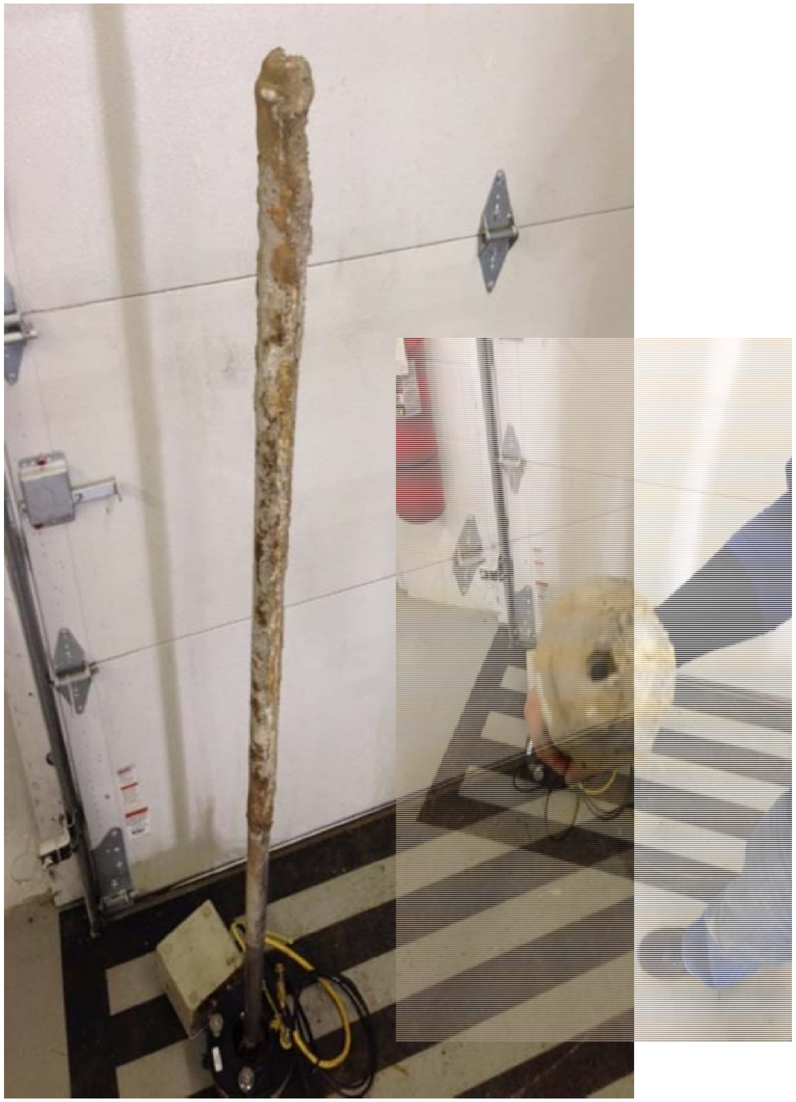
Goal: Ensure accurate, reliable, and "hassle-free" equipment operation

Challenging Source Conditions



Problems with Instrumental CEMs…scrubbing

- Scrubbing in the sampling system
  - Particulate on probe filter
  - Dirty probes lines
  - Umbilical lines
- Review calibration data
- Periodically inspect probe



Photos provided by

Problems with Traps

- Particulate Entrainment
  - Could bias the number high if the particulate is reactive
  - Mitigated with particulate shields
- Moisture Entrainment
  - Could bias the number or create problems with breakthrough and spike loss
  - Mitigated with shields and moisture resistant traps

Sorbent Trap Probe Shields







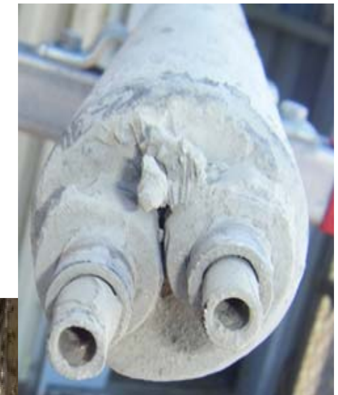


Photos provided by

OhioLumex
Simplifying Hg

Shield Contamination

- BUT…Shields may become a source
  - What to do
    - Swap out your shields
    - Clean up your shields

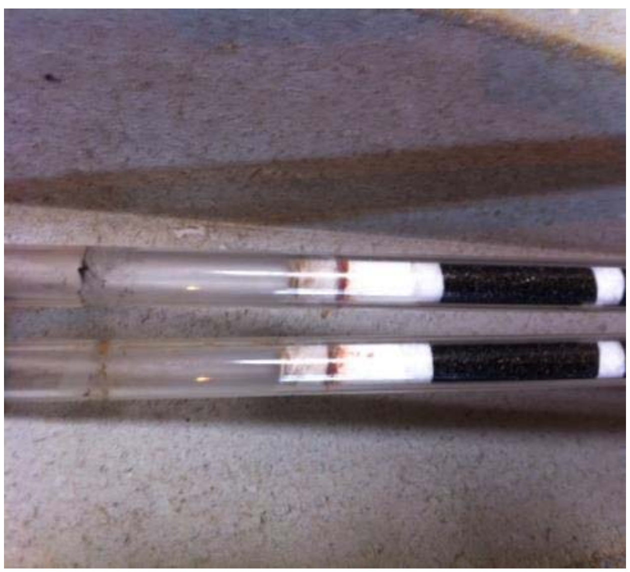


Photos provided by

Ohio Lumex Simplifying Hg

Sorbent Trap Moisture Entrainment

- Prevent Moisture Accumulation
  - Verify your probe temp 300-350F
  - Shields
  - Moisture resistant longer traps



Photos provided by Ohio Lumex Simplifying Hg

Mercury Testing in 2016 and Beyond

- Clearly define drivers for testing (economic, reliability, BOP risk, etc.)
- Design test to assure goals are met and unanswered questions are minimized
- Test durations will often be longer than pre-compliance experience to minimize impacts to plant operations and to account for resulting variability
- Maintain monitoring equipment, monitor performance
- Data analytics are recommended
  - Improved test quality
  - Improved ongoing CEMS operation

Discussion and Questions

Appendix

MATS Hg Measurement: CEMS

- Representative samples of flue gas are continuously extracted from the stack or duct
- Particulate matter is removed (i.e., filtered) from the gas samples
- Hg analyzer measures vapor phase Hg^0 and total Hg (only total Hg needed for MATS compliance)
- Calibrated using NIST traceable Hg gas generators

- Typical Hg CEMS Components:
  - Probe
  - PM filter
  - Sample conditioning
  - Sample transport (sample line and pump)
  - Gas analyzer (with or without converters)
  - Calibration gas system

MATS Hg Measurement: STMS

- Representative sample of flue gas are continuously extracted from the stack or duct
  - Mercury captured on "Trap", typically iodated activated carbon
  - Total volume of sample gas used to calculate average concentration
- Particulate matter is <u>not</u> removed from the gas samples
- Paired traps, in-stack with 3 sections
- Sample rate proportional to gas flowrate
- Sample for 5-10 days continuously

- Typical Sorbent Trap Components:
  - Sampling probes and paired sorbent traps. The sorbent traps have three sections: (1) main sample collection section; (2) breakthrough section; and (3) section spiked with a known mass of Hg^0, for QA/QC .
  - Moisture removal system
  - Vacuum pump
  - Sample gas flow meter

Mercury Monitoring Certification Requirements

Performance Test	Test Specifications	Criteria	MATS Reference
Seven-Day Calibration Error Test	Zero and upscale check for seven consecutive days.	≤ 5.0% of span value *or* ≤ 1.0 μg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 4.1.1.1
Linearity Check	Challenge monitor with low, mid, and high reference gases.	≤ 10% of ref. value *or* ≤ 0.8 μg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 4.1.1.2
3-Level System Integrity Check	Three-point converter efficiency test.	≤ 10% of ref. value *or* ≤ 0.8 μg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 4.1.1.3
Cycle Time Test	Zero and upscale.	< 15 minutes to 95%	40 CFR Part 63 Subpart UUUUU Appendix A Section 4.1.1.4
Relative Accuracy Test Audit (RATA)*	One set of 12 test runs.	< 20% rel. accuracy *or* ≤ 0.5 μg/m³ absolute if RM < 2.5 μg/m³	40 CFR Part 63 Subpart UUUUU Appendix A Section 4.1.1.5**

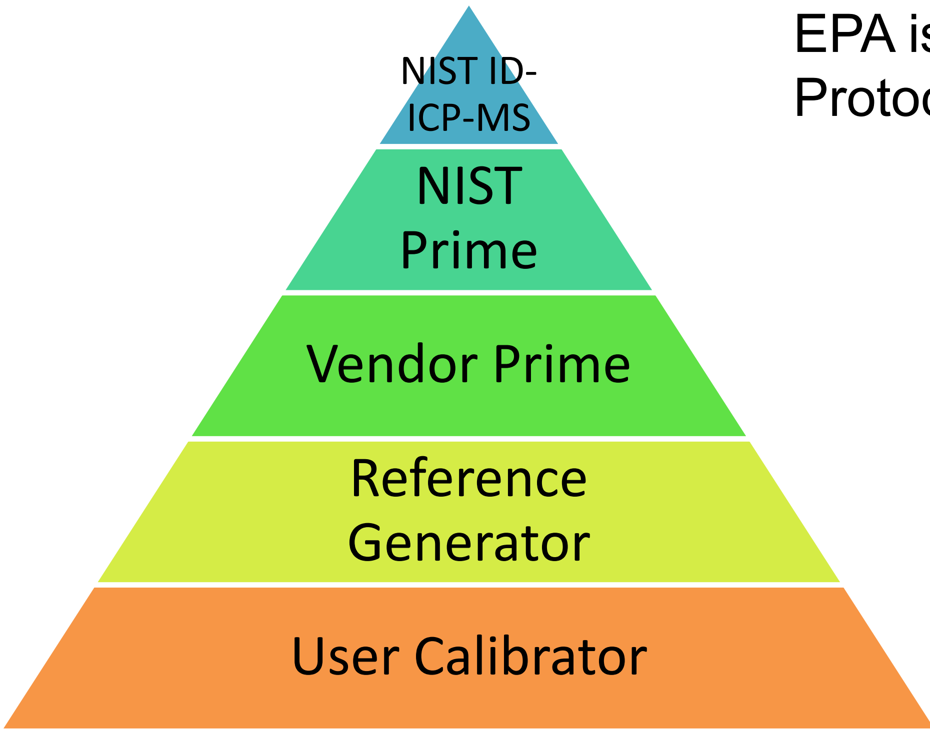
**For sorbent trap monitoring systems, only a RATA is required*
***Updated in revised Final Rule*

Mercury Monitoring On-going Requirements

Performance Test	Test Specifications	Criteria	MATS Reference
Daily Calibration Error Test	Two-point calibration check (zero and upscale).	≤ 5.0% of span value *or* ≤ 1.0 µg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 5.1.2.1
Quarterly Linearity Check	Challenge monitor with low, mid, and high reference gas.	≤ 10% of ref. value *or* ≤ 0.8 µg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 5.1.2.2
Weekly System Integrity Check	Single-point converter efficiency test.	≤ 10% of ref. value *or* ≤ 0.8 µg/m³ absolute	40 CFR Part 63 Subpart UUUUU Appendix A Section 5.1.2.3
Relative Accuracy Test Audit (RATA) and Bias Test*	One set of 12 test runs.	< 20% rel. accuracy *or* ≤ 0.5 µg/m³ absolute if RM < 2.5 µg/m³	40 CFR Part 63 Subpart UUUUU Appendix A Section 5.1.2.4**

**For sorbent trap monitoring systems, only a RATA is required*
***Updated in revised Final Rule*

Certified Reference Gas: Calibrators



EPA issued “Final” Interim Calibrator Protocols in July 2009

Thermo calibrators being tested

QC Requirements for CEMS Calibrators

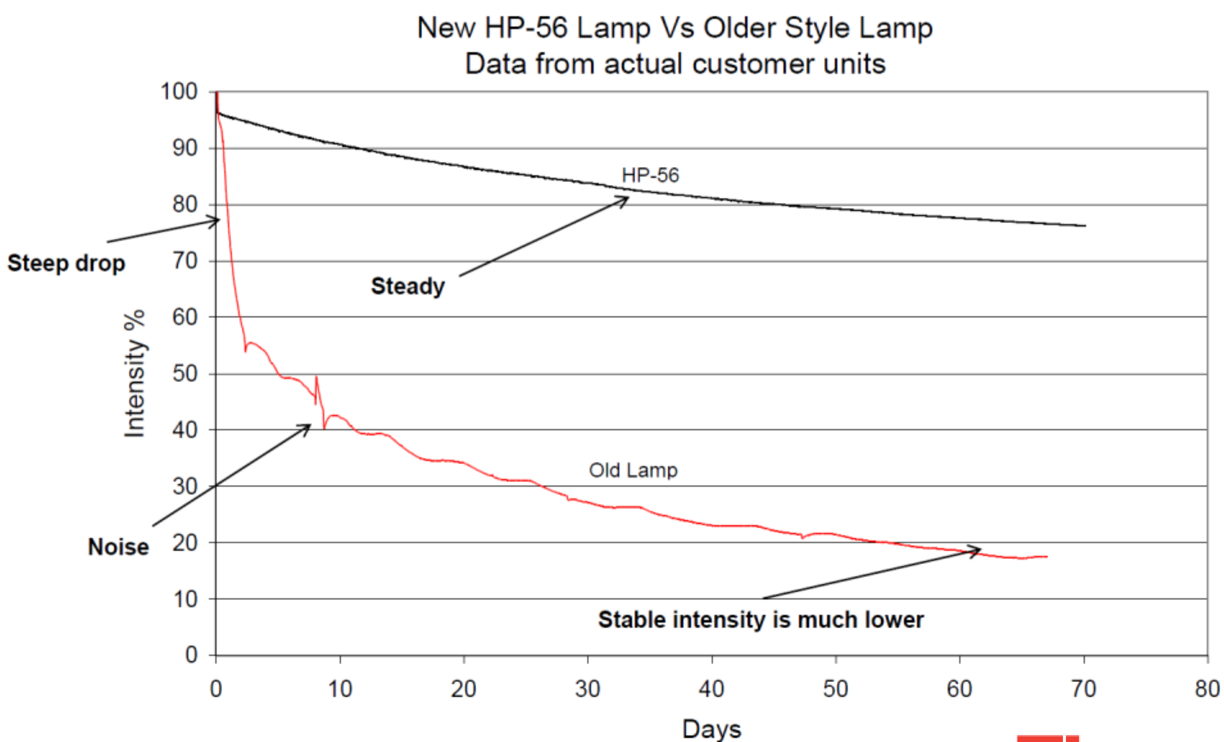
Option	Approach	Frequency	Criteria
A	Field Reference Generator	Quarterly	Avg. of 3 replicates (bracketing) within ± 5% or ± 0.5 μ/m^3
B	Permeation Tube*	Monthly or Weekly	Avg. of 1 to 3 pairs must be within ± 5% of the base ratio (perm/gen)
C	Sorbent Tubes	Quarterly	Avg. of 3 replicates within ± 5% of the certified concentration, or difference no greater than 0.5 μ/m^3
D	Cylinder Gas	Quarterly	Avg. output concentration is within ± 5% or ± 0.5 μ/m^3 of the certified Hg concentration

*If a permeation source is used, a quarterly audit is required using one of the options listed above. The major CEMS suppliers offer a permeation source that can conduct automatic calibrator QC checks through the data acquisition system

Keep Equipment Updated

Example 1: Thermo changed lamp vendors to improve performance

New lamp drift is < 0.5% per day



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Keep Equipment Updated

- Example 2: Thermo offers probe replacement to address reliability issues

Trade in your existing model 83i-GC probe, get a credit towards a new Mercury probe.

- Contact your local representative for more details.

Model 83i Mercury Probe Advantages:

- Dilution system for wet basis measurement
- High flow inertial filter to reduce particulate matter contamination
- Glass coated components to prevent reactions with mercury
- Conversion at the stack to prevent loss of elemental mercury
- Proprietary dry converter/scrubber requires no wet chemistry or water supply

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