
Investigation of Mercury Measurement and Control Technologies under Oxy-fired Conditions

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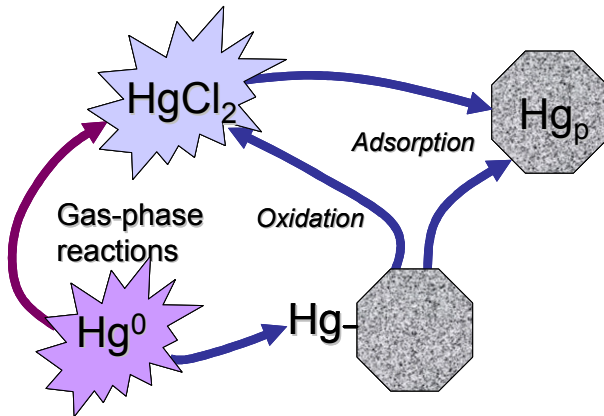
Presentation Outline

- Project objectives
- Definition of mercury terms
- Overview of experimental facilities and conditions
- Overview of measurement techniques
- Results
 - Mercury measurement comparison and mass balance
 - Mercury oxidation, emissions, and removal
- Conclusions

Project Objectives

- Characterize mercury behavior in a pilot-scale PC combustor under air- and oxy-firing conditions with sub-bituminous and bituminous coals
 - Compare mercury measurement methods
 - Evaluate mercury emissions and removal when injecting CaBr_2 and activated carbon (AC)

Mercury Material Balance



Hg^0 - Gas-phase elemental mercury (difficult to remove)

Hg^{2+} - Gas-phase oxidized mercury (easily removed)

Hg^P - Particulate-bound mercury (native removal)

Hg^{Coal} - Mercury input with coal

Total measured mercury : $Hg^T = Hg^0 + Hg^{2+} + Hg^P$

Total measured gas-phase mercury : $Hg^{TG} = Hg^0 + Hg^{2+}$

Mercury mass balance : $\frac{Hg^T}{Hg^{Coal}}$

Mercury removal : $1 - \frac{Hg^{TG}}{Hg^{Coal}}$

These equations highlight the need to separate particulate-bound mercury from gas-phase mercury

Coal Analysis

Black Thunder PRB			
Coal Analyses		Mineral Matter Analyses	
C	54.04	Al	14.19
H	3.74	Ca	16.13
N	0.82	Fe	5.99
S	0.38	Mg	3.33
O	13.69	Mn	0.04
Ash	5.66	P	0.71
Moisture	21.67	K	0.47
Volatile Matter	36.77	Si	36.76
Fixed Carbon	35.91	Na	0.93
HHV, Btu/lb	9320	S	10.11
Hg, µg/g	0.047±0.004	Ti	1.11

Produces gas-phase mercury concentrations of ~6 µg/dscm (~4 lb/TBtu)

Pratt Bituminous			
Coal Analyses		Mineral Matter Analyses	
C	69.23	Al	25.91
H	4.82	Ca	3.41
N	1.69	Fe	13.20
S	2.22	Mg	1.18
O	6.54	Mn	0.04
Ash	13.14	P	0.83
Moisture	2.38	K	2.33
Volatile Matter	35.64	Si	44.78
Fixed Carbon	48.85	Na	0.47
HHV, Btu/lb	12659	S	3.72
Hg, µg/g	0.21±0.01	Ti	1.25

Produces gas-phase mercury concentrations of ~26 µg/dscm (~17 lb/TBtu); ~70X CI

L1500 Furnace Operating Conditions

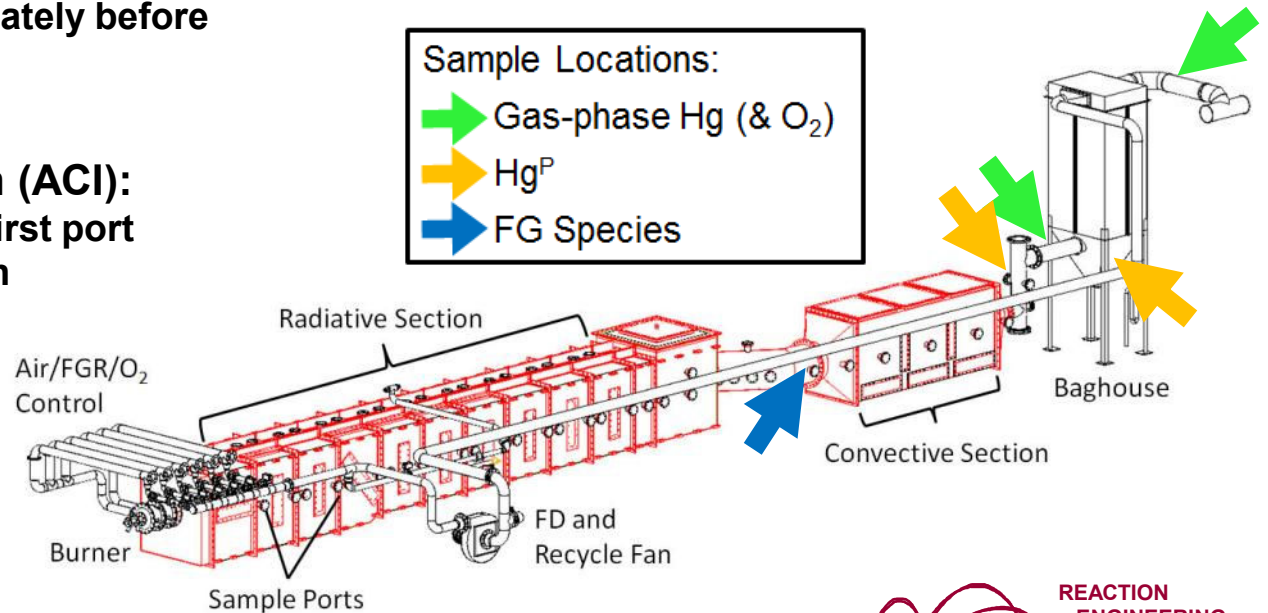
Coal	Condition	Firing Rate (kW)	O ₂ (% dry)	CO ₂ (% dry)	BH inlet (F)	BH outlet (F)
PRB	Air-Fired	780-860	4.0	14	380	250
PRB	Oxy-Fired	780	3.5	83	300	140
Bituminous	Air-Fired	775-1025	3.5	15	356	239
Bituminous	Oxy-Fired	775-880	3.4	87	341	146

Bromine addition:

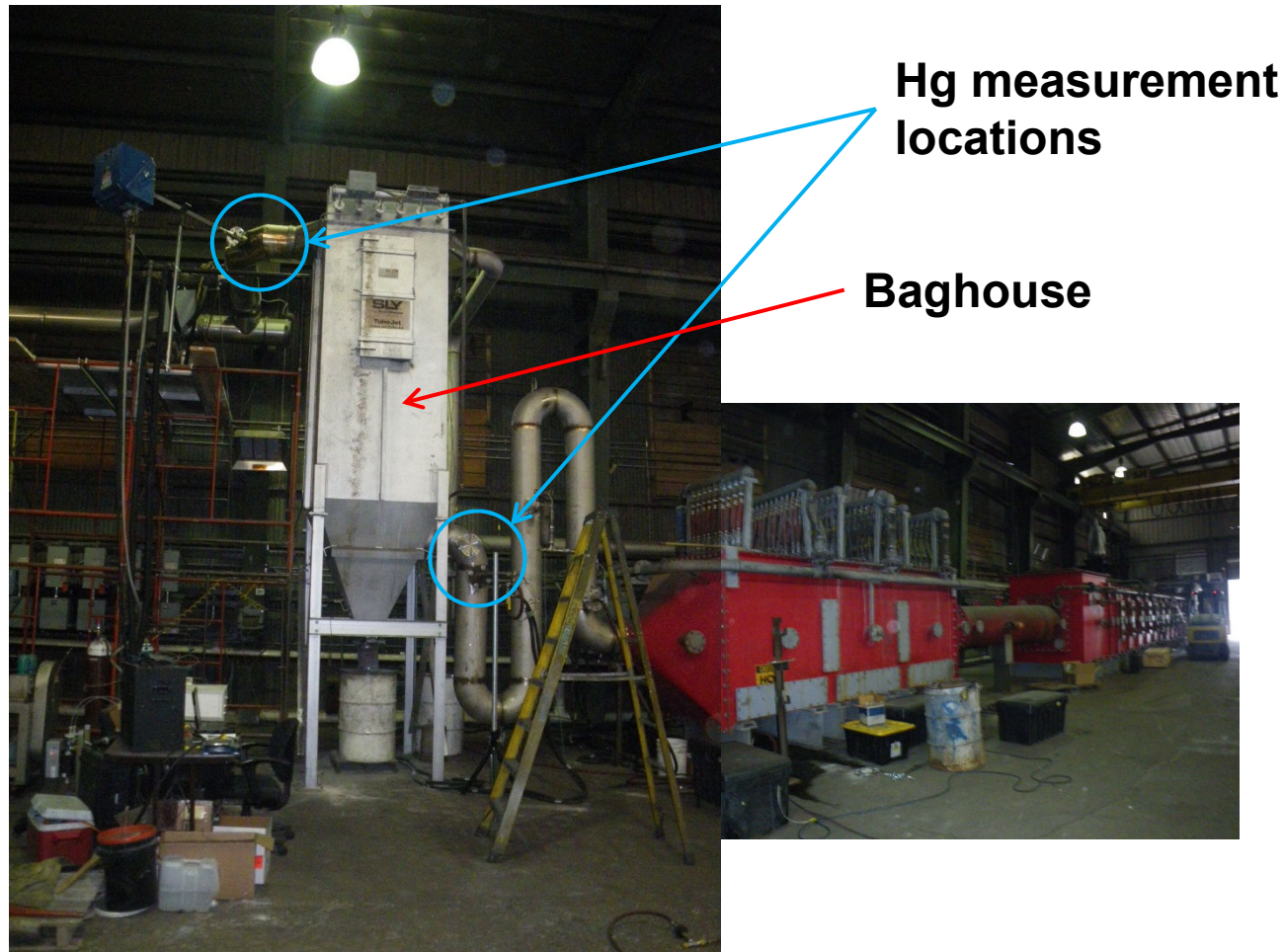
Solid CaBr₂ injected immediately before coal entered burner
(~8-75 ppm Br wet on coal)

Activated Carbon Injection (ACI):

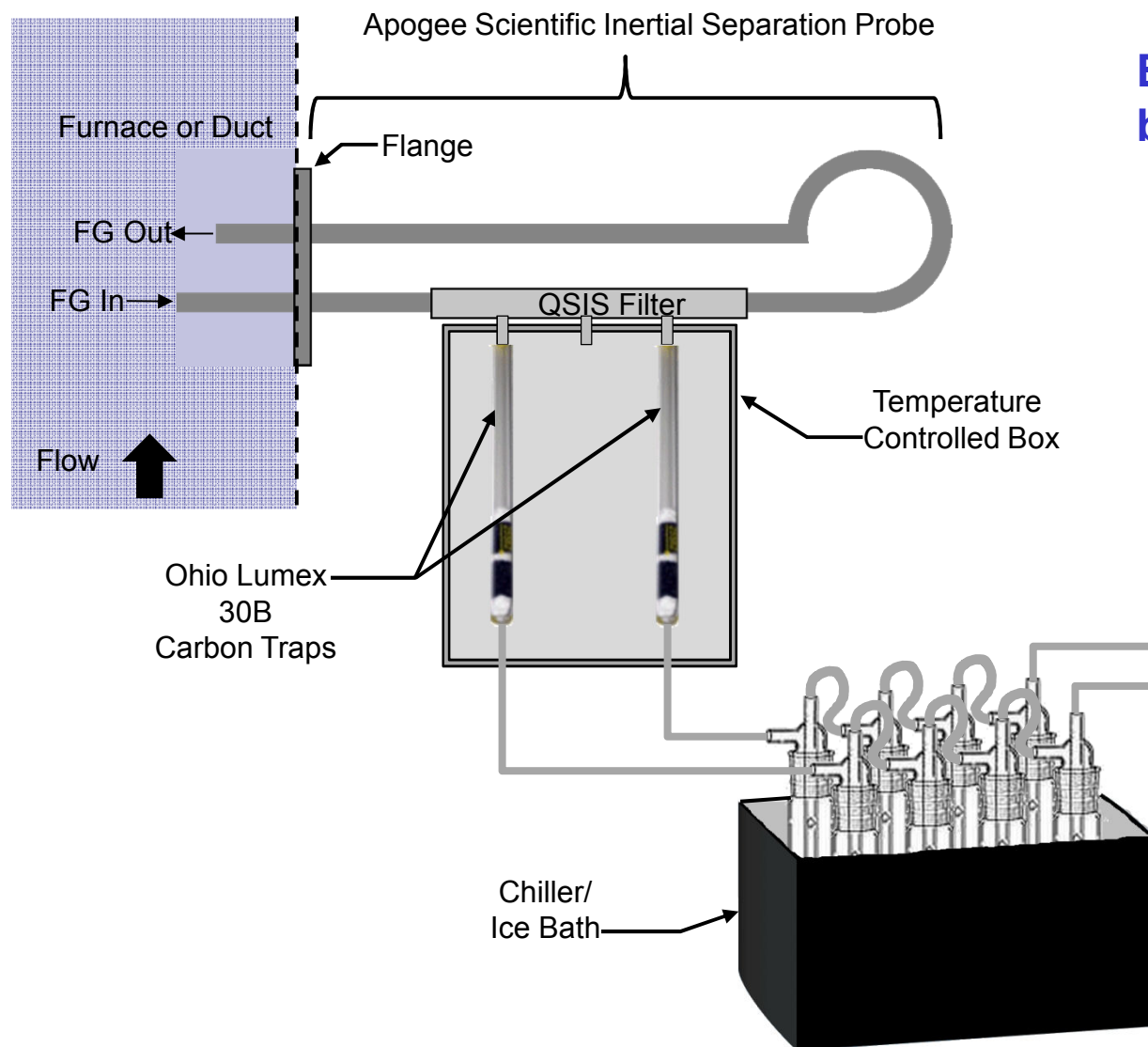
Darco Hg injected through first port following convective section
(~0.5-10 lb/MMacf)



L1500 Mercury Testing Setup



Mercury Measurement Method (Modified 30b)



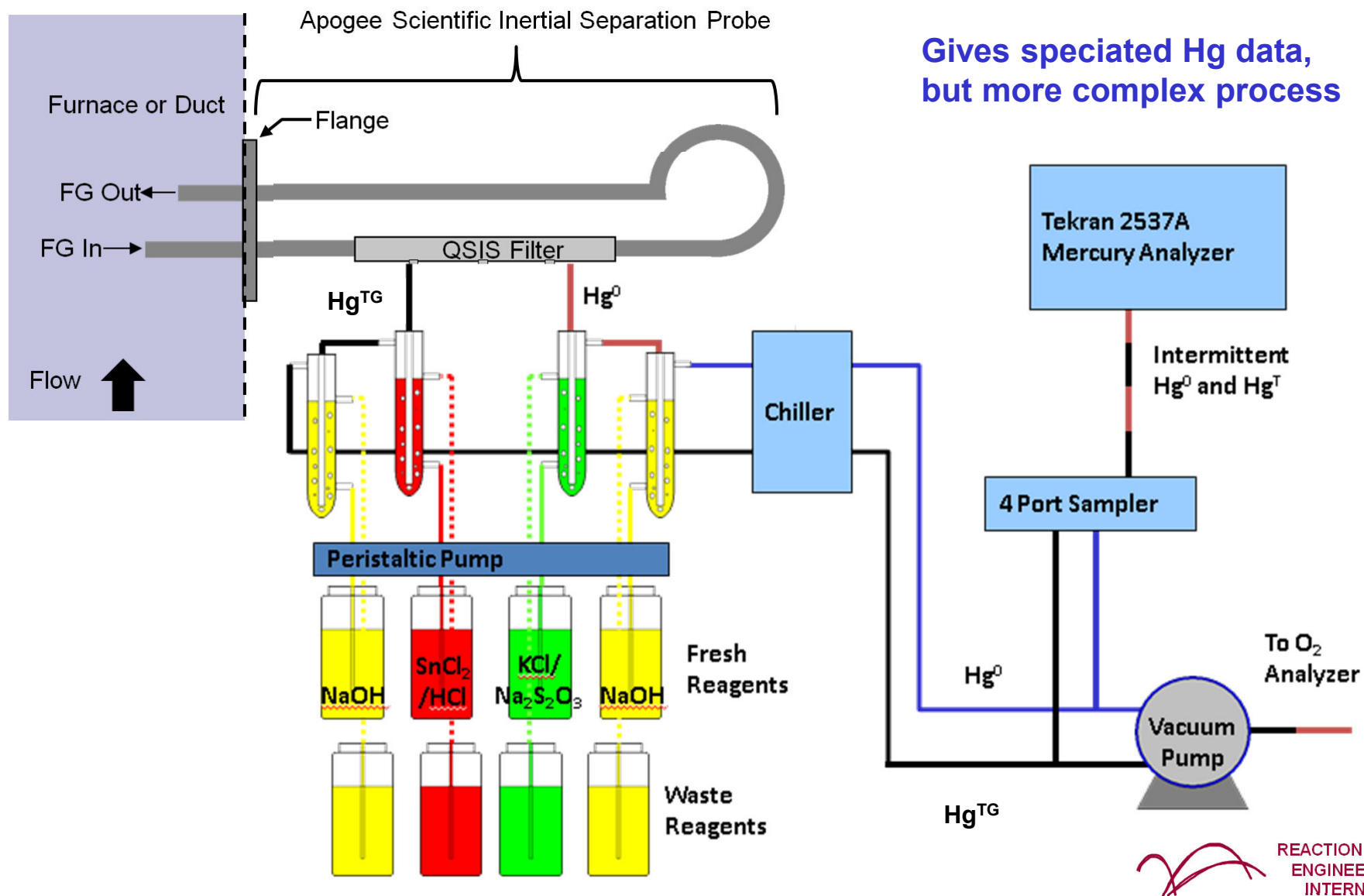
**Established technique,
but no speciation**



Apex Instruments
Dry Gas
Meter/Monitor
(Method 30b)

Mercury Measurement Method

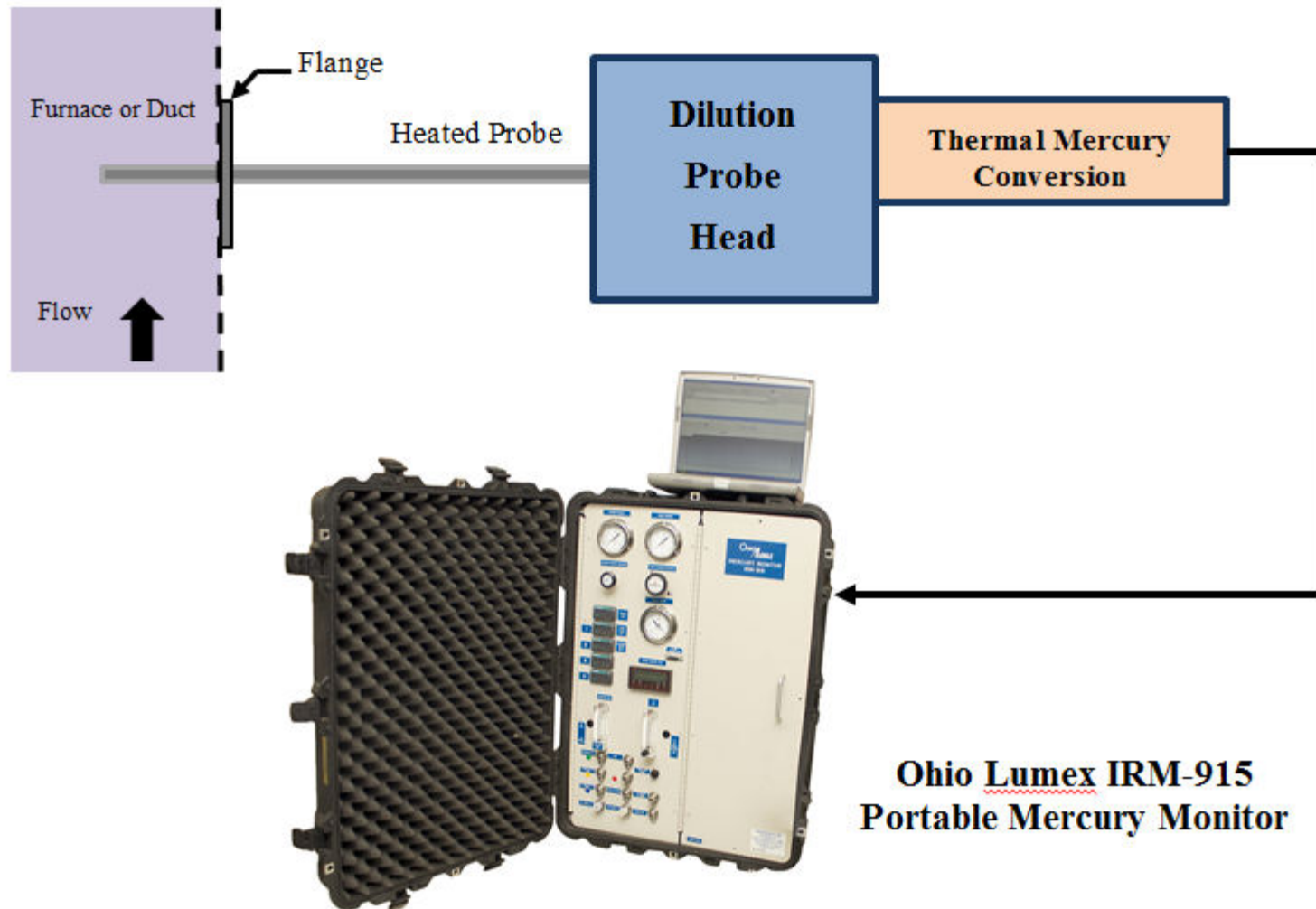
(Tekran CEM w/ wet conditioning)



Mercury Measurement Method

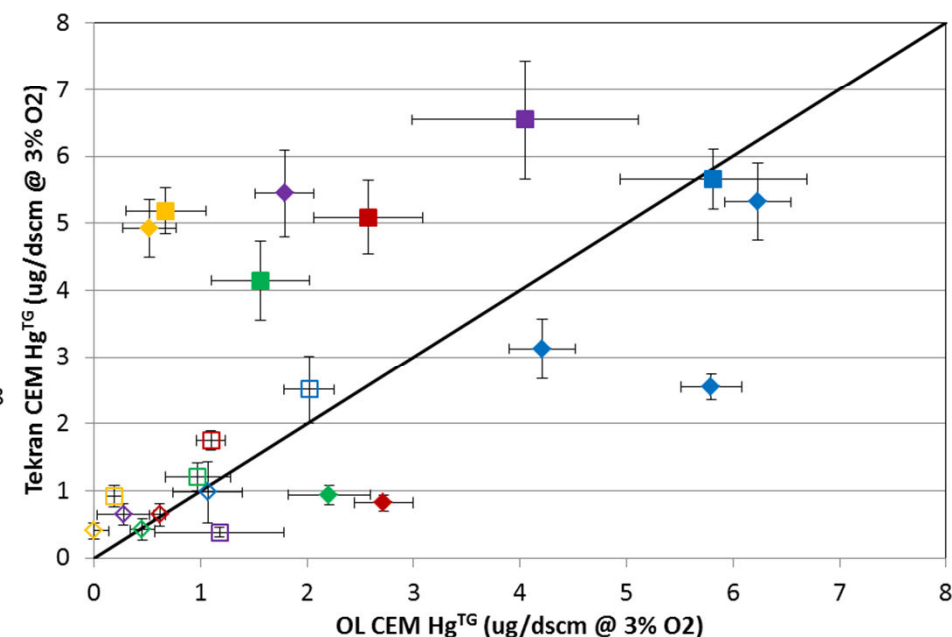
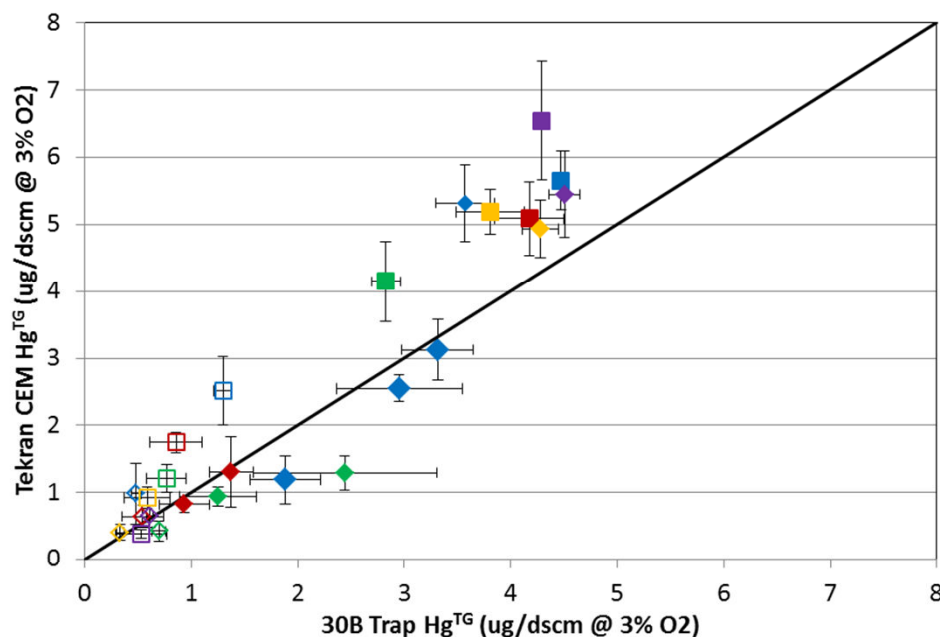
(Ohio Lumex IRM-915 CEM)

Speciated, time-resolved data



Results

Measurement Technique Comparison - PRB



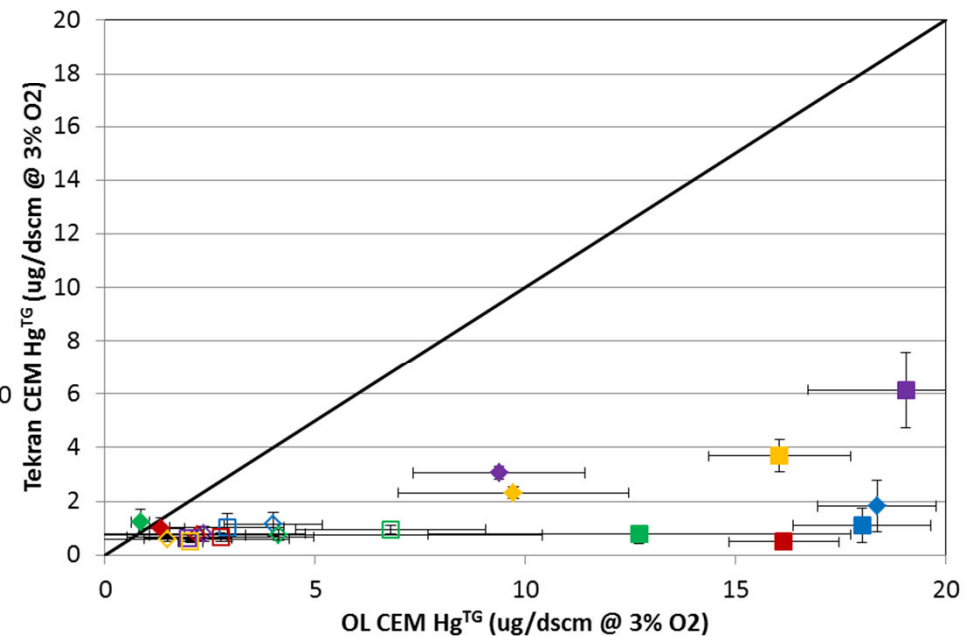
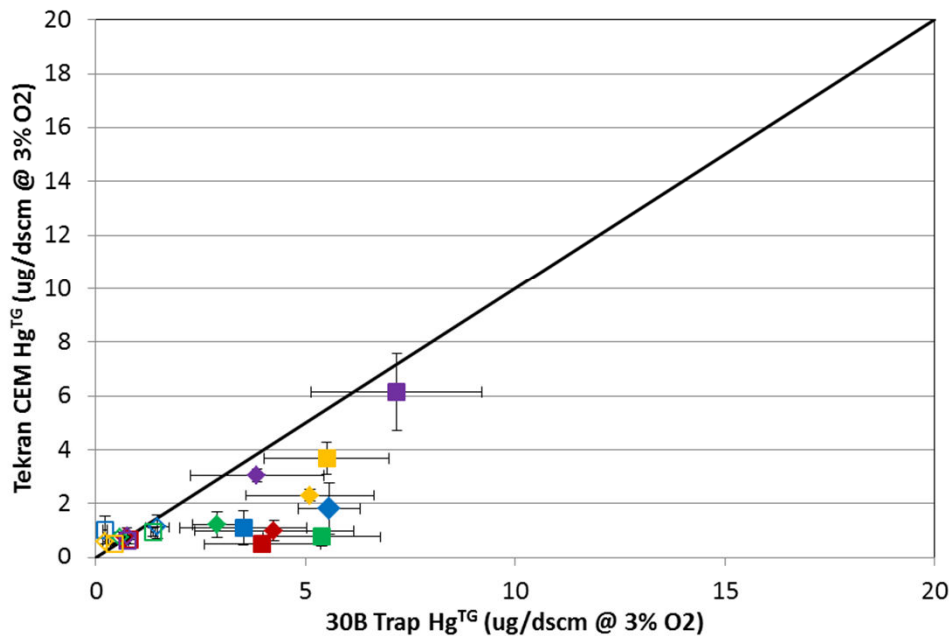
- | | |
|----------------------------|---------------------------|
| ◆ before BH, air | ◇ after BH, air |
| ◆ before BH, air, low Br | ◇ after BH, air, low Br |
| ◆ before BH, air, high Br | ◇ after BH, air, high Br |
| ◆ before BH, air, low ACI | ◇ after BH, air, low ACI |
| ◆ before BH, air, high ACI | ◇ after BH, air, high ACI |

- | | |
|----------------------------|---------------------------|
| ■ before BH, oxy | □ after BH, oxy |
| ■ before BH, oxy, low Br | □ after BH, oxy, low Br |
| ■ before BH, oxy, high Br | □ after BH, oxy, high Br |
| ■ before BH, oxy, low ACI | □ after BH, oxy, low ACI |
| ■ before BH, oxy, high ACI | □ after BH, oxy, high ACI |

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Measurement Comparison - Bituminous



- | | |
|----------------------------|---------------------------|
| ◆ before BH, air | ◇ after BH, air |
| ◆ before BH, air, low Br | ◇ after BH, air, low Br |
| ◆ before BH, air, high Br | ◇ after BH, air, high Br |
| ◆ before BH, air, low ACI | ◇ after BH, air, low ACI |
| ◆ before BH, air, high ACI | ◇ after BH, air, high ACI |

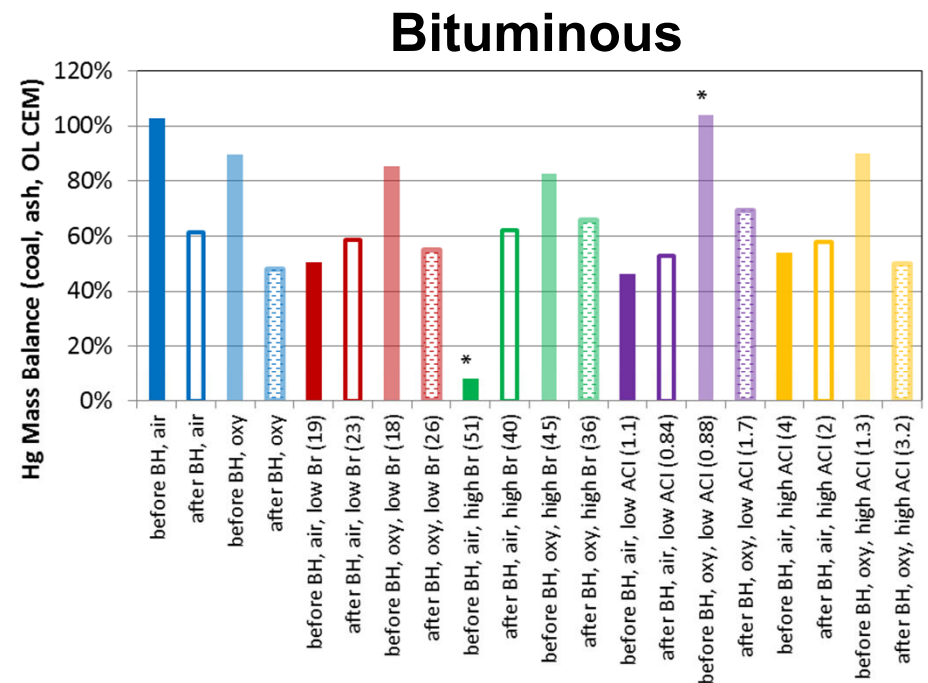
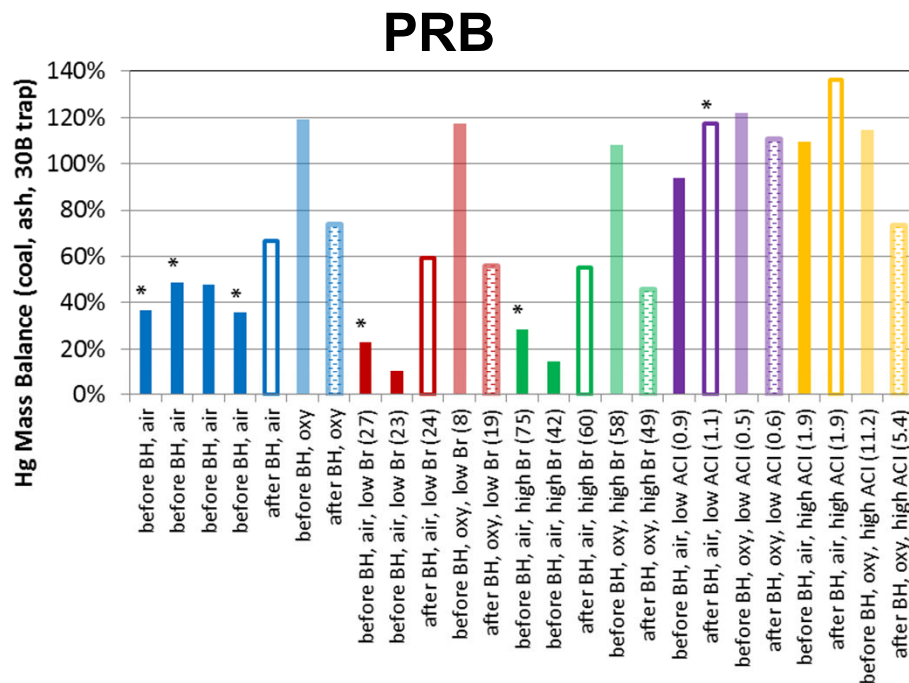
- | | |
|----------------------------|---------------------------|
| ■ before BH, oxy | □ after BH, oxy |
| ■ before BH, oxy, low Br | □ after BH, oxy, low Br |
| ■ before BH, oxy, high Br | □ after BH, oxy, high Br |
| ■ before BH, oxy, low ACI | □ after BH, oxy, low ACI |
| ■ before BH, oxy, high ACI | □ after BH, oxy, high ACI |

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Mercury Mass Balance

- Poor mass balance closure was seen for many conditions
 - Likely due to unrepresentative ash samples
 - Some confidence in gas-phase measurements due to agreement between measurement techniques during PRB testing



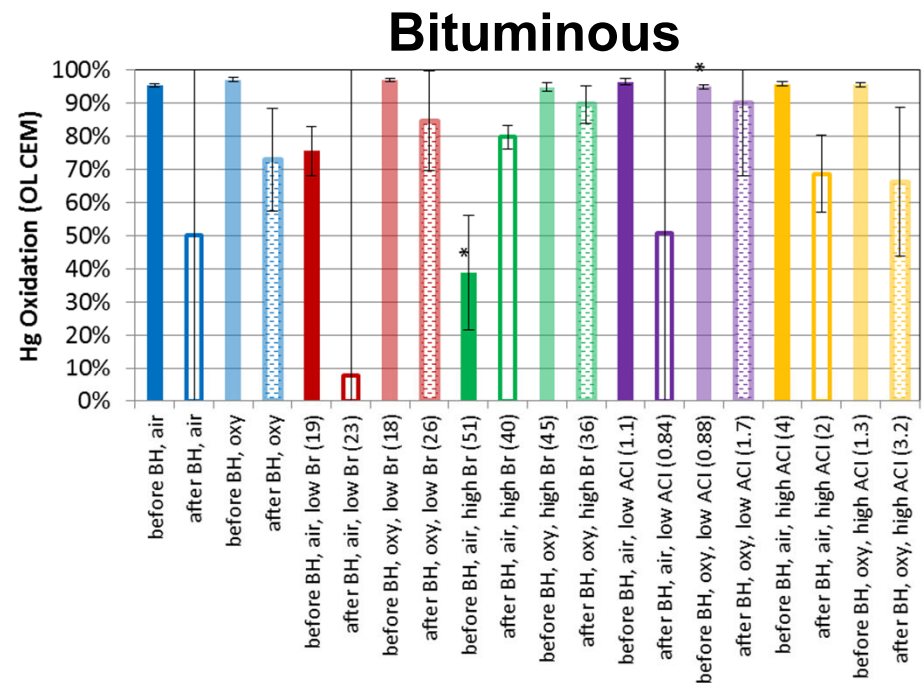
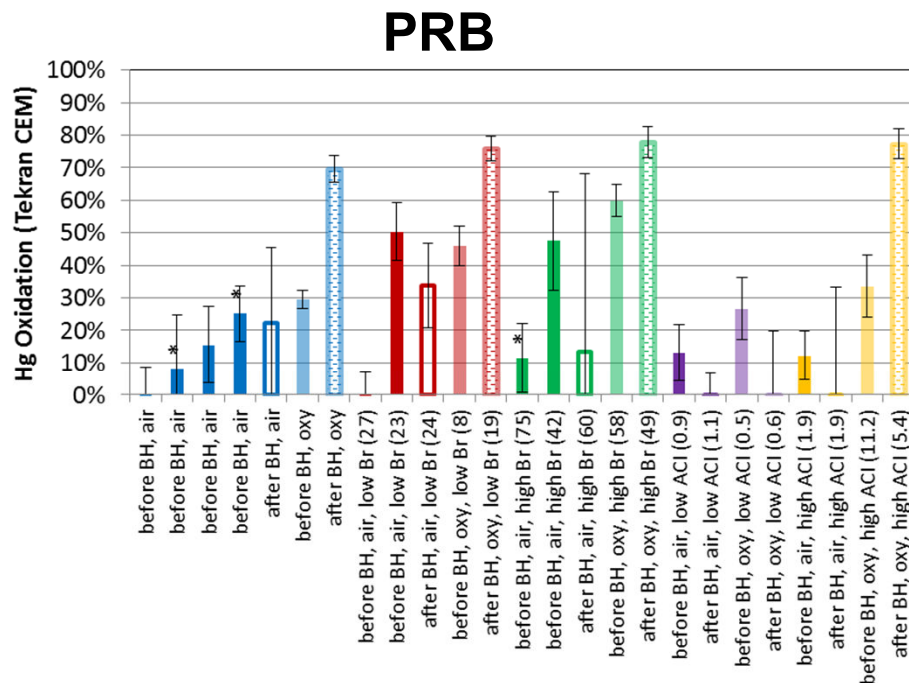
Numbers in parentheses indicate additive rate (ppmw Br on coal or lb/MMacf ACI),
 * LOI > 2 (PRB) or > 13 (bituminous)



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Mercury Oxidation

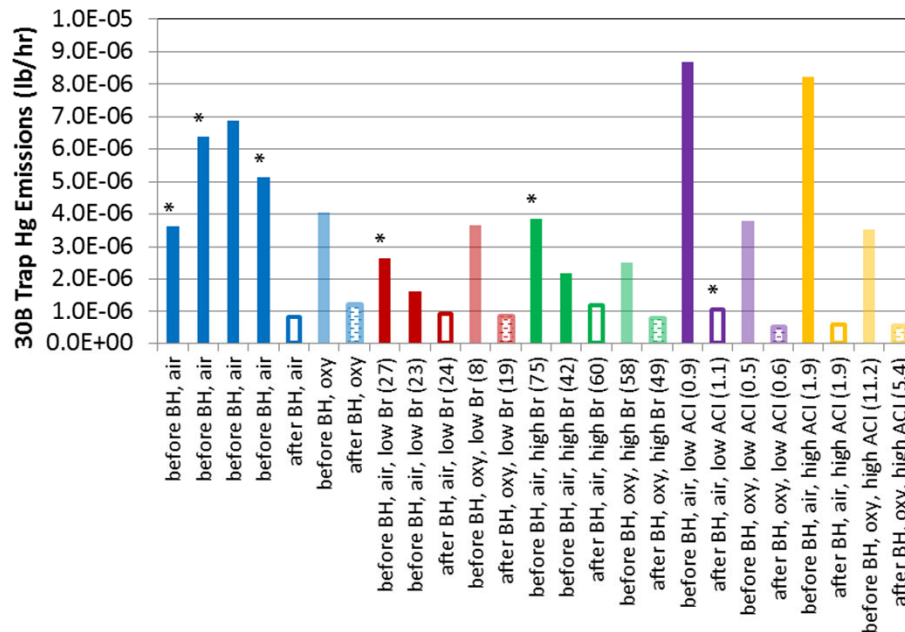
- Oxidation data show significant scatter
- Oxidation levels higher for bituminous coal (CI ~ 70x PRB)
- Addition of CaBr_2 increased oxidation for PRB, little impact on bituminous
- Oxy-firing had similar or higher levels of oxidation than air



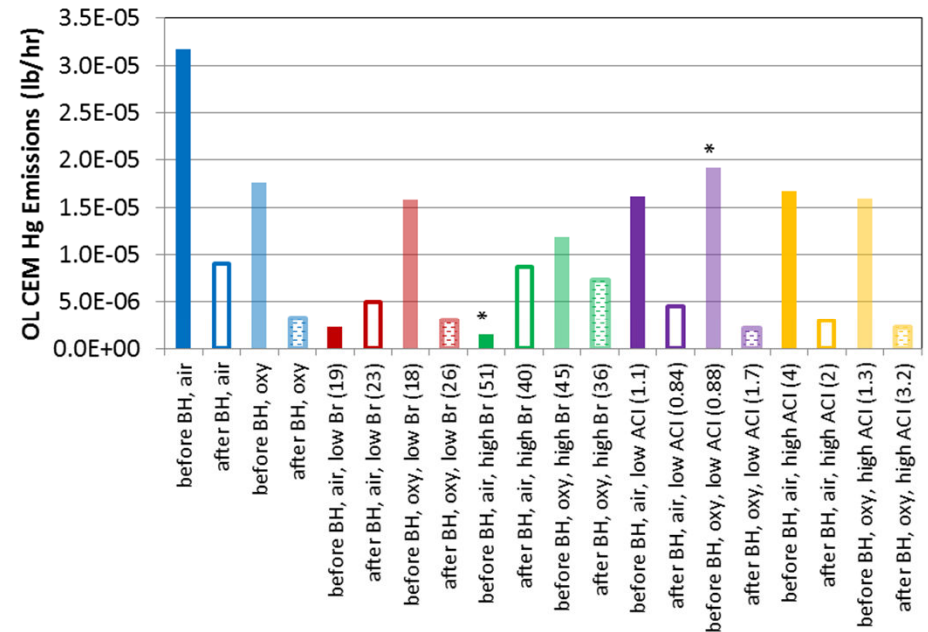
Mercury Emissions

- Post-bag house emissions lower for nearly all tests
- Pre-bag house emissions showed:
 - Generally higher emissions for bituminous coal
 - CaBr_2 addition more effective for air-firing than oxy-firing
 - ACI increased emissions for PRB with air-firing (native LOI?)

PRB

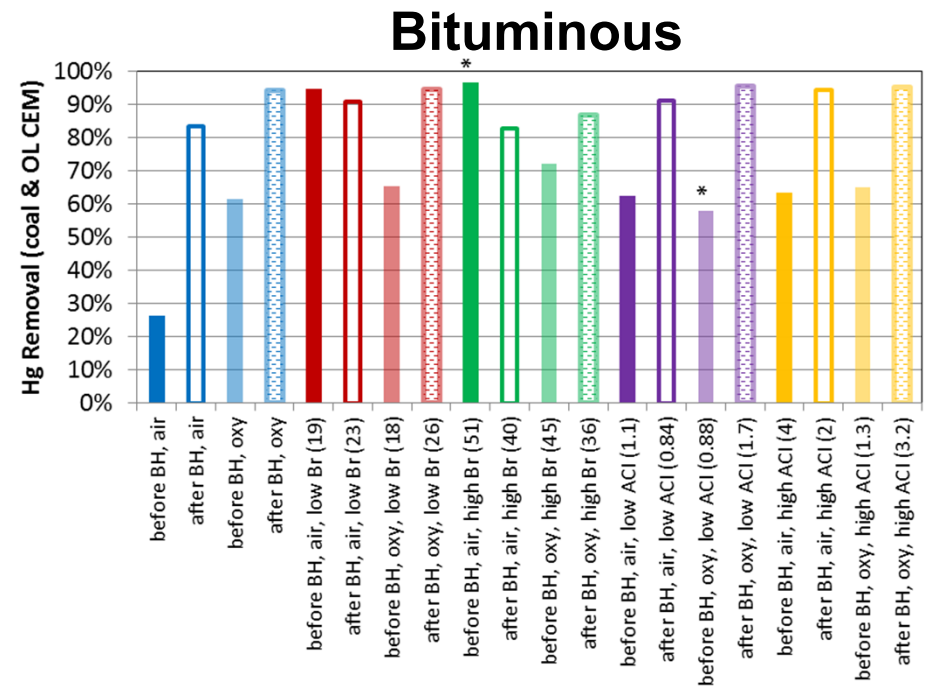
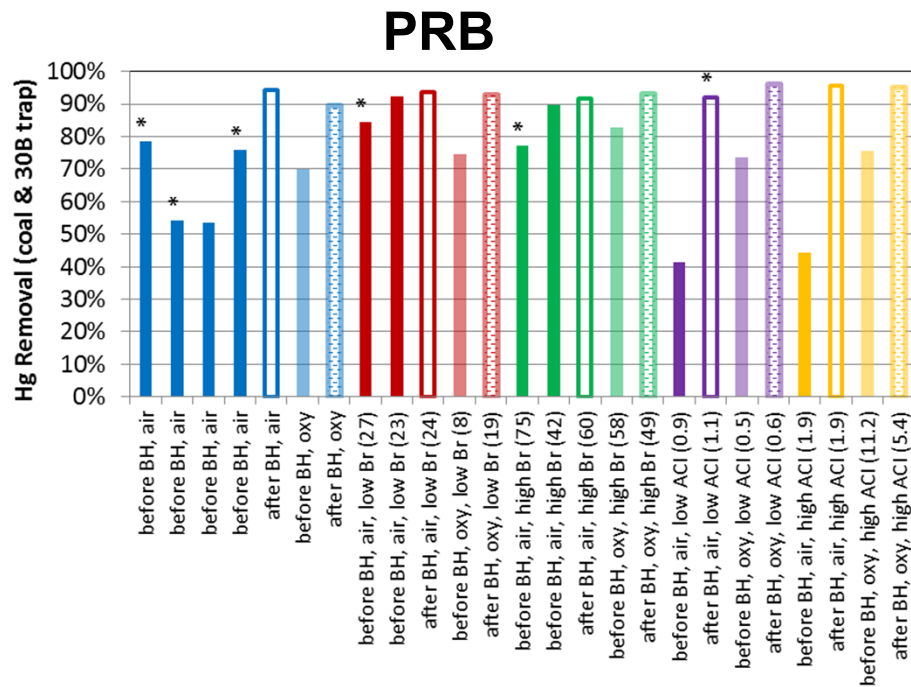


Bituminous



Mercury Removal

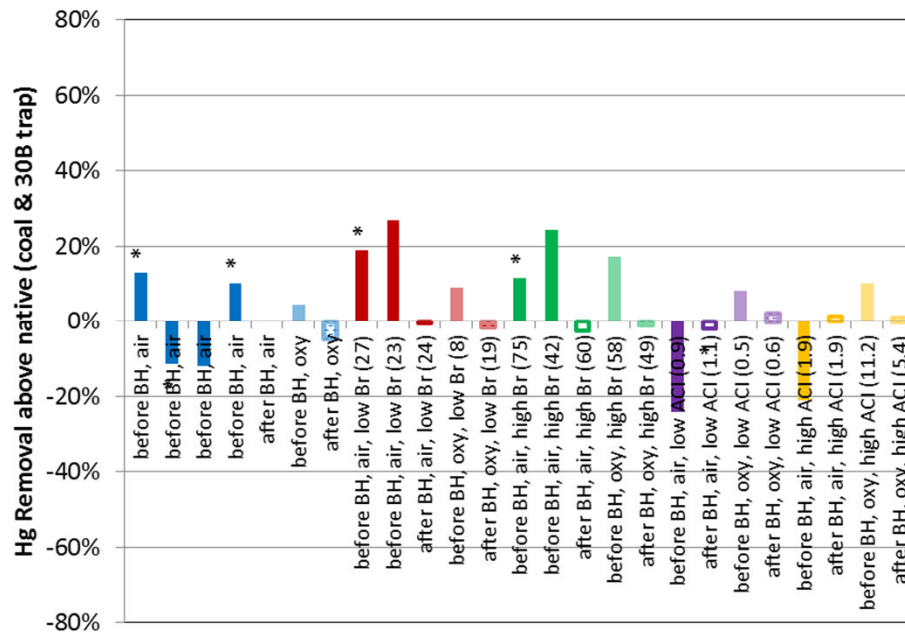
- Post-bag house removal high (~90%) for both coals with air and oxy-firing, with and without additives
- Pre-bag house removal high with CaBr_2 for air-firing, lower removal with oxy-firing; ACI limited



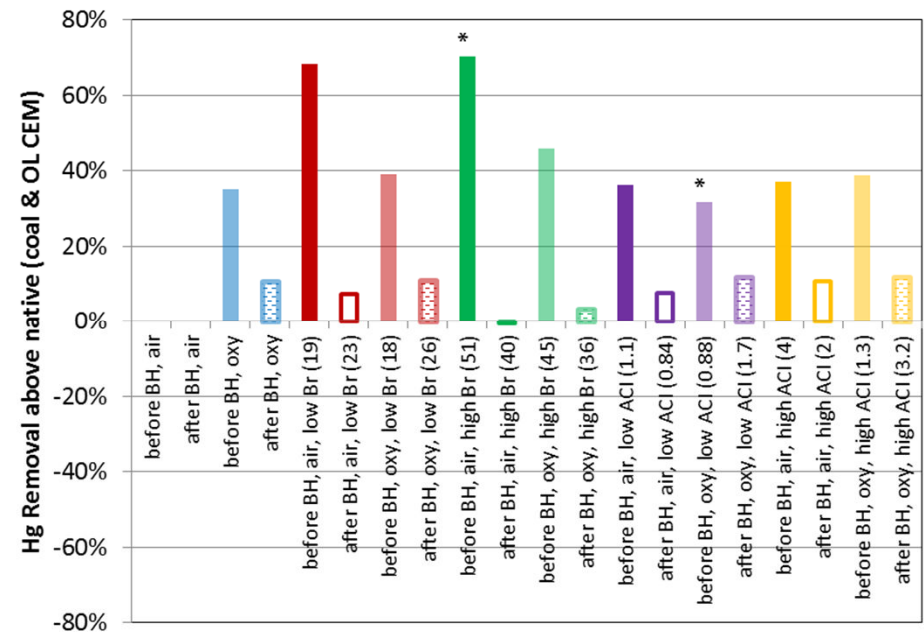
Mercury Removal (above native air firing)

- Low PRB removal beyond native, some CaBr_2 impact
- For bituminous coal before bag house:
 - Addition of CaBr_2 or AC increased removal for air-firing
 - Oxy-firing had higher removal than air, but minimal impacts from additives

PRB



Bituminous



Conclusions (1/2)

- A modified method 30B as well as two speciating CEM systems were used to distinguish gas-phase and particle bound mercury
 - For PRB testing, the measurement methods generally agreed with the exception of the OL CEM system before the baghouse
 - For bituminous testing, none of the three methods agreed well
- Mercury mass balance was poor for many conditions, most likely due to unrepresentative ash samples
- Oxidation data showed significant scatter
 - CaBr_2 addition increased oxidation
 - Oxidation higher for oxy-firing

Conclusions (2/2)

- Post-bag house emissions lower for nearly all conditions
 - 90%+ removal for nearly all cases (air and oxy-firing)
 - Filter very effective capturing Hg
- For pre-bag house with PRB sub-bituminous coal:
 - Low removal beyond native, some improvement with CaBr_2
- For pre-bag house with bituminous coal:
 - Addition of CaBr_2 or AC increased removal for air-firing
 - Oxy-firing had higher removal than air, but minimal impacts from additives
- Suspect that untreated FGR with oxy-firing biased the expected Hg capture behavior with additives

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Questions?

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