Mercury Emissions and Control on Coal-fired Units with ESP and Wet FGD

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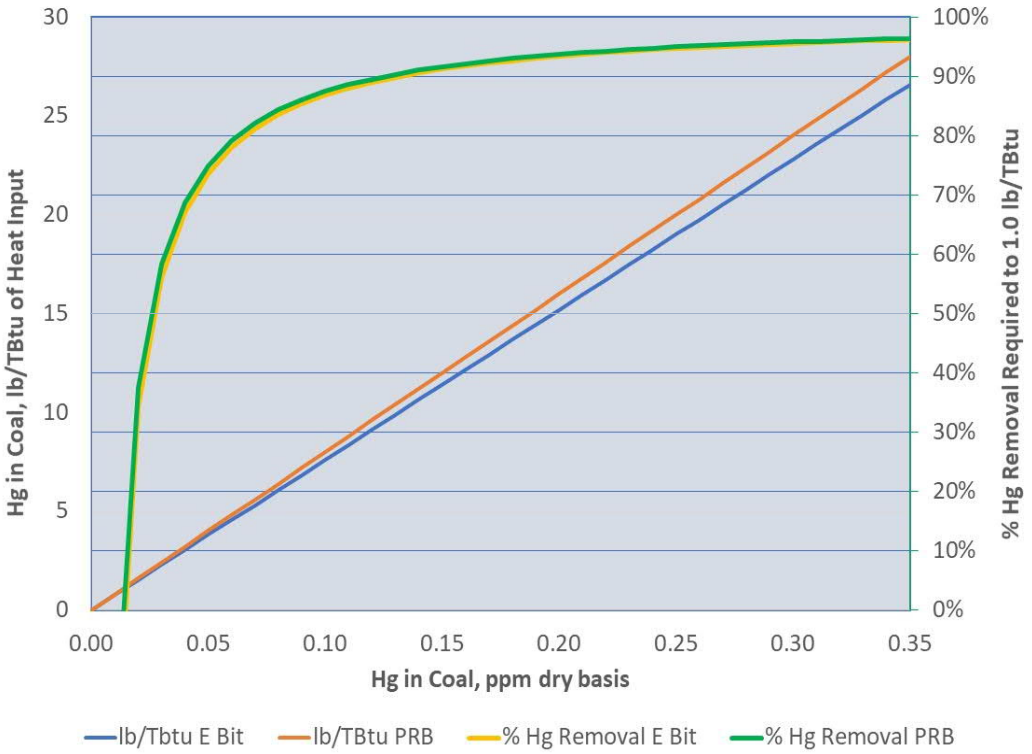
Introduction

- This presentation summarizes the general state of knowledge about mercury (Hg) emissions and control on coal units with ESPs for PM control and wet FGD
- Topics covered include effects of:
  - Fuel
  - Combustion
  - Selective catalytic reduction (SCR) for NO_X control
  - Air heaters
  - PM control devices
  - Powdered activated carbon (PAC) injection (briefly)
  - Wet flue gas desulfurization (FGD) systems

Fuel Effects on Hg Emissions

- Hg concentration in coal
  - Affects required Hg oxidation and/or capture efficiency
- Halogen in coal
  - Higher concentrations of Cl, Br, and/or I in coal enhance Hg oxidation, improve capture efficiency in ESP and wet FGD
  - $CaBr_2$ or KI may be added to coal to increase Hg oxidation
- Sulfur in coal – increased sulfur can lead to:
  - Higher SO_3 and reduced Hg capture by LOI in ash/PAC
  - Higher mass rate of gypsum and lower Hg conc. in solids
  - Higher limestone consumption can increase pyrite in FGD slurry and reduce tendencies for Hg re-emission
- Ash in coal – greater fly ash conc. can enhance heterogenous Hg oxidation
- Volatility/firing characteristics – impact LOI and native Hg capture by fly ash

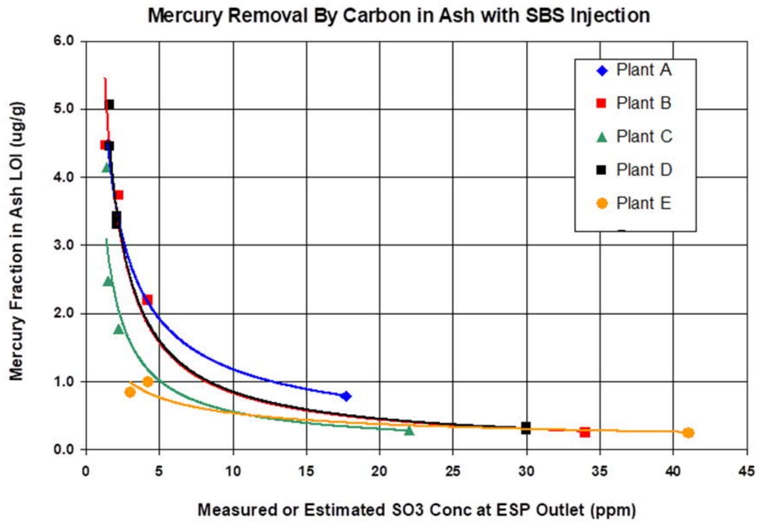
Fuel Effects – Hg in Coal vs. Required Hg Removal

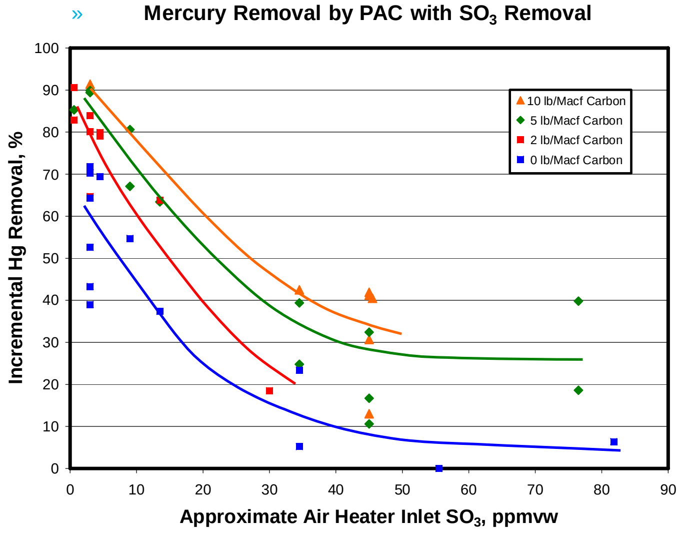


- Not much difference between PRB and E. Bit when compared on a dry ppm Hg basis
- For either, Hg > ~0.12- 0.13 ppm requires 90+% coal-to-stack removal

Effects of SO_3 from S in Coal on Hg Capture

- Plots illustrate downward trend for Hg capture at increasing SO_3 in flue gas
- Removal across ESP by both LOI and PAC affected

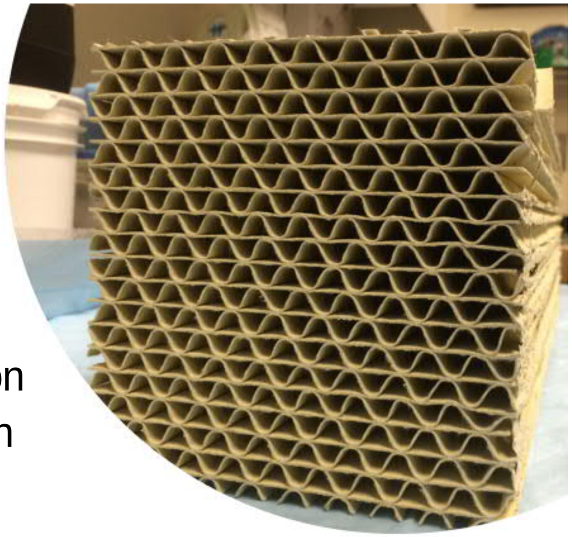

Mercury Removal By Carbon in Ash with SBS Injection


Mercury Removal by PAC with SO_3 Removal

Combustion Effects

- Time-temperature relationship in furnace and back pass
  - Elemental Hg^0 is favored over oxidized $HgCl_2$ at temperatures over ~950°F
  - Increased residence time at lower temps increases conversion to oxidized form, which is more readily removed
- SO_3 formation in the back pass
  - Adversely affects Hg adsorption by LOI and PAC
- Combustion efficiency
  - Higher LOI in fly ash promotes Hg adsorption, particularly at low SO_3

SCR Effects



- Halogen Concentration in Flue Gas
  - Higher halogen conc. promotes Hg oxidation across SCR
  - Lower halogen conc. (e.g., PRB) typically achieves lower Hg oxidation across SCR unless halide is added to coal
- Flue Gas Temperature
  - Higher temps promote SO_3 formation and reduce Hg oxidation
  - Lower temps reduce SO_3 formation and promote Hg oxidation
- NH_3 to NO_X Ratio
  - Higher ratios mean more catalyst surface area has NH_3 adsorbed and less surface area available for Hg oxidation
  - Aged catalysts that require higher ratios to meet deNOX requirements will adversely affect Hg oxidation
  - “Hg optimized” catalysts are available to promote Hg oxidation at good $deNO_X$ performance

Air Heater Effects

- Drop in flue gas temperature across air heater - favorable to Hg removal
  - Lower flue gas temps increase equilibrium percentage of $HgCl_2$ in flue gas
  - SO_3 concentrations generally drop due to adsorption/condensation on ash
  - Lower temp, lower SO_3, increased Hg oxidation favor Hg capture by LOI and PAC
  - Increased percentage of oxidized Hg in flue gas promotes Hg capture by FGD
- Heterogenous oxidation of Hg across air heater
  - Anecdotal observation: the presence of fly ash in the flue gas is an important contributor to Hg oxidation across AH
    - Limited data from units with hot-side ESPs (fly ash removed upstream of AH) show less Hg oxidation across AH compared to cold-side ESP units

Caution: Very low AH exit flue gas temps at low load on PRB-fired units using bromine addition to coal may cause AH cold-end corrosion. Some brominated PACs injected upstream of AH may have similar impact.

“Native” Hg Removal across PM Control Devices

- Native removal is primarily due to LOI (unburned carbon) in fly ash
- Typical order of effectiveness:
  - Reverse-gas FF > Pulse-jet FF > Cold-side ESP >> Hot-side ESP
- Hg capture generally increases with higher LOI
- Lower flue gas temperature and increased halogens in flue gas enhance Hg capture
- SO_3 in flue gas adversely affects Hg capture by LOI
  - For plants not using SO_3 for ash conditioning, SO_3 control upstream of ESP can reduce the negative effects of SO_3
- Potential range of Hg capture by LOI in ESP is very large (~0% to 90%)

“Native” Hg Removal by Fly Ash Varies

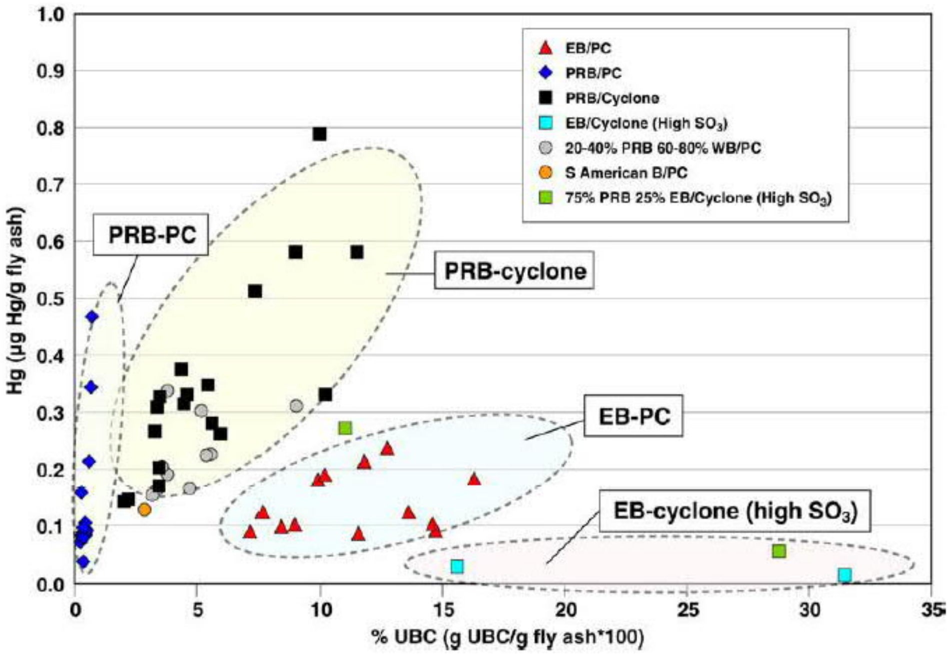
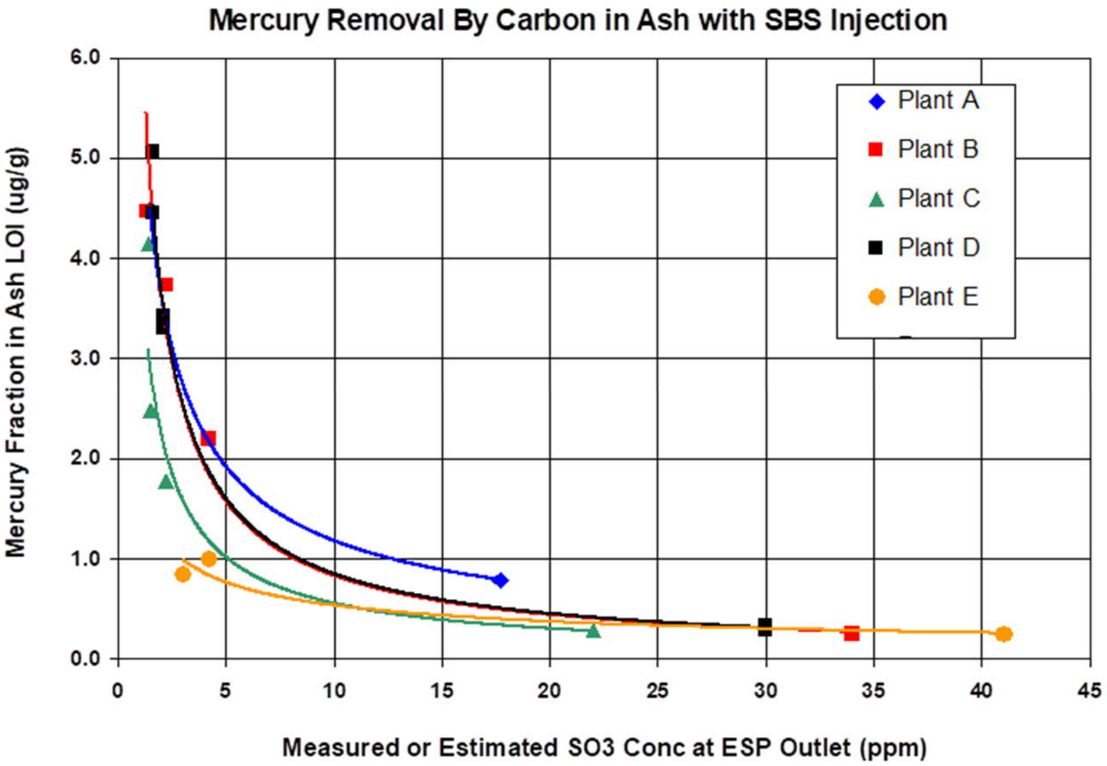


Figure 1-9
Amount of Mercury Adsorbed on Fly Ash Depends on Coal Type, Level of Unburned Carbon in Fly Ash, and Boiler Type
(PC = pulverized coal, EB = eastern bituminous coal)

Mercury Control Update 2009. EPRI, Palo Alto, CA: 2009. 1017564

Effects of SO_3 on Hg Removal by Unburned Carbon (LOI) across ESPs

- Effectiveness of Hg capture is limited above 10-15 ppm SO_3
- Effectiveness increases rapidly as SO_3 is lowered from ~5 ppm to 2 ppm



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Hg Removal by Wet FGD Systems

- Hg^0 is essentially insoluble in aqueous solutions, is very minimally removed by wet FGD
- Oxidized Hg (Hg^{2+}) is scrubbed at high efficiency (≥ 95%) in modern, high-performance wet FGD systems
  - ➢ Net removal may be limited by re-emission (reaction with sulfite to reduce Hg^{2+} to the insoluble Hg^0 form)
  - ➢ In some cases “negative Hg removal” can be seen across FGD during re-emission episodes

Hg Re-emission from Wet FGD Systems

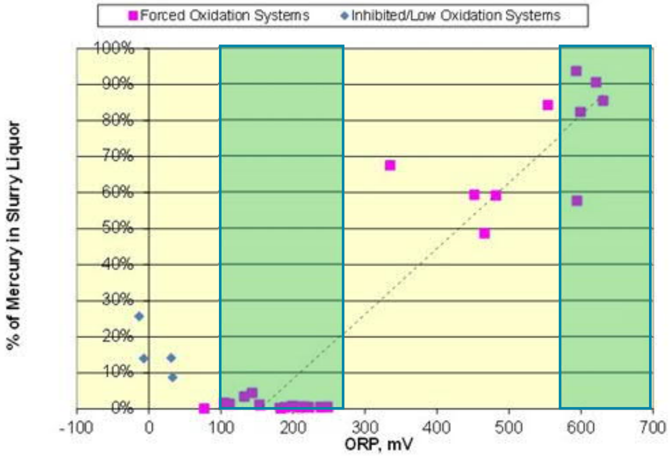
- Best evidence of Hg^0 re-emission: when the Hg^0 concentration in the stack flue gas is greater than the Hg^0 concentration in the FGD inlet flue gas
  - Hg re-emission is difficult to confirm without inlet Hg speciation measurements
  - Stack speciation data not critical to have, as there should be near 100% Hg^0 downstream of wet FGD systems with high SO_2 removal and no bypass reheat
- Plant owners/operators generally see only stack Hg CEM results, often assume increases in stack Hg represent re-emissions, but also could be a result of:
  - Increased coal Hg content
  - Decreased Hg oxidation upstream of FGD (e.g., loss of SCR catalyst activity)
  - Decreased Hg capture upstream with fly ash or PAC (e.g., due to higher SO_3 in flue gas)

Hg Re-emission Control

- Limestone reagent, forced oxidation (LSFO), gypsum-producing FGD systems often benefit from transfer of Hg^{2+} from the liquor to the solid phase
    - Hg in solids less available for aqueous re-emission reactions with sulfite
    - Effect is believed to be from pyrite (FeS_2), a common LS impurity, forming highly insoluble HgS precipitate
    - Effectiveness of pyrite requires that FGD conditions not be "over-oxidizing," which converts S^{2-} to oxidized forms that do not precipitate Hg
        - Desired ORP is ~100 to 250-300 mV
    - Many U.S. LSFO wet FGD systems gas rely solely on FGD capture of Hg^{2+} and native re-emission control to meet Hg emission limits
    - FGD re-emission additives are available to supplement the pyrite as needed
        - Include "organo-sulfides", inorganic sulfides (e.g., NaHS), and PAC added to FGD slurry to adsorb (rather than precipitate) Hg

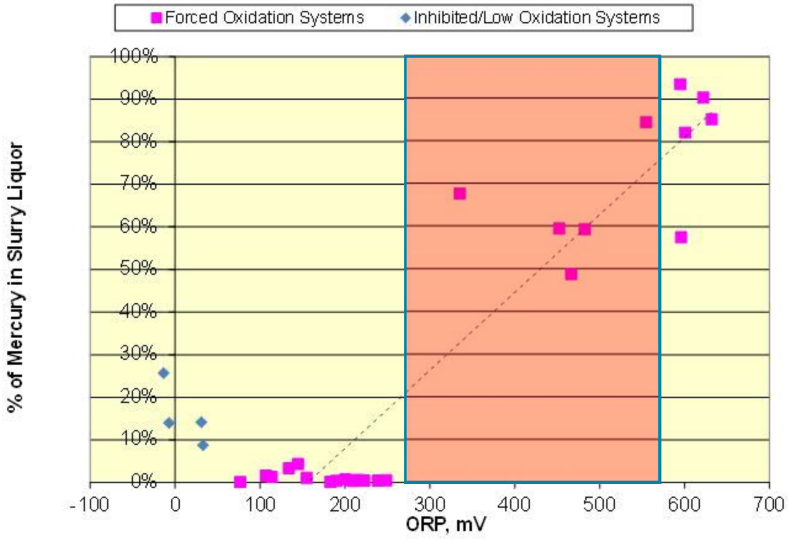
Hg Re-emission Control (continued)

- Two regimes of oxidation where Hg re-emission is minimal in LSFO systems
  1. Oxidation rate adequate to produce <1% $CaSO_3 \cdot ½H_2O$ in gypsum, but not over-oxidizing
     - Typical ORP ~100 to ~300 mV
     - Very little dissolved Hg to be reduced by sulfite
  2. Oxidation rate is so great there is no dissolved sulfite in slurry (ORP >~550mV) to reduce Hg^{2+}
     - High ORP regime is less advantageous due to Mn scaling, selenite to selenate oxidation, more aggressive to alloys, etc.
- ORP meters can scale up and become unresponsive – keep meters cleaned and calibrated with standards
  - Dissolved sulfite monitor or feed-forward ox air rate control are alternatives to ORP to avoid over-oxidation



Hg Re-emission Control (continued)

- Worst regime for Hg re-emissions: ORP greater than 250-300 mV but less than 550-600 mV
  - ➢ Pyrite gets oxidized, HgS particles dissolve
  - ➢ High dissolved Hg^{2+} concentrations
  - ➢ Minute amounts of sulfite available in slurry droplets to reduce Hg^{2+}
- When absorber slurry goes from “ideal” range to ~300 to 600 mV, re-emission can cause stack Hg to exceed FGD inlet Hg!
  - ➢ Hg-rich fine particles continually recycle to absorber in HC overflow reclaim
  - ➢ Hg buildup in fines at “ideal” conditions can represent days of inlet Hg



Additional Notes on Hg Removal by Wet FGD Systems

- Mg-lime or limestone inhibited oxidation FGD systems are not known to benefit from native pyrite in the reagent, generally use re-emission additives
- Hg captured by wet FGD and not emitted with the stack flue gas leaves the system in the solid byproduct and with the FGD wastewater
  - ➢ Hg could be present in byproduct solids or included moisture, in wastewater as dissolved or present in fine solids
  - ➢ Gypsum sold for beneficial reuse may have Hg concentration limits set by end user
    - o For a given Hg concentration in coal, higher S lowers Hg concentration in the gypsum by “dilution”
    - o Hydrocyclone tuning can vary the percentage of Hg that leaves in gypsum vs. wastewater to meet limits

Questions or Comments?