Impacts of Sulfur Oxides on Mercury Capture by Activated Carbons

Albert A. Presto and Evan J. Granite
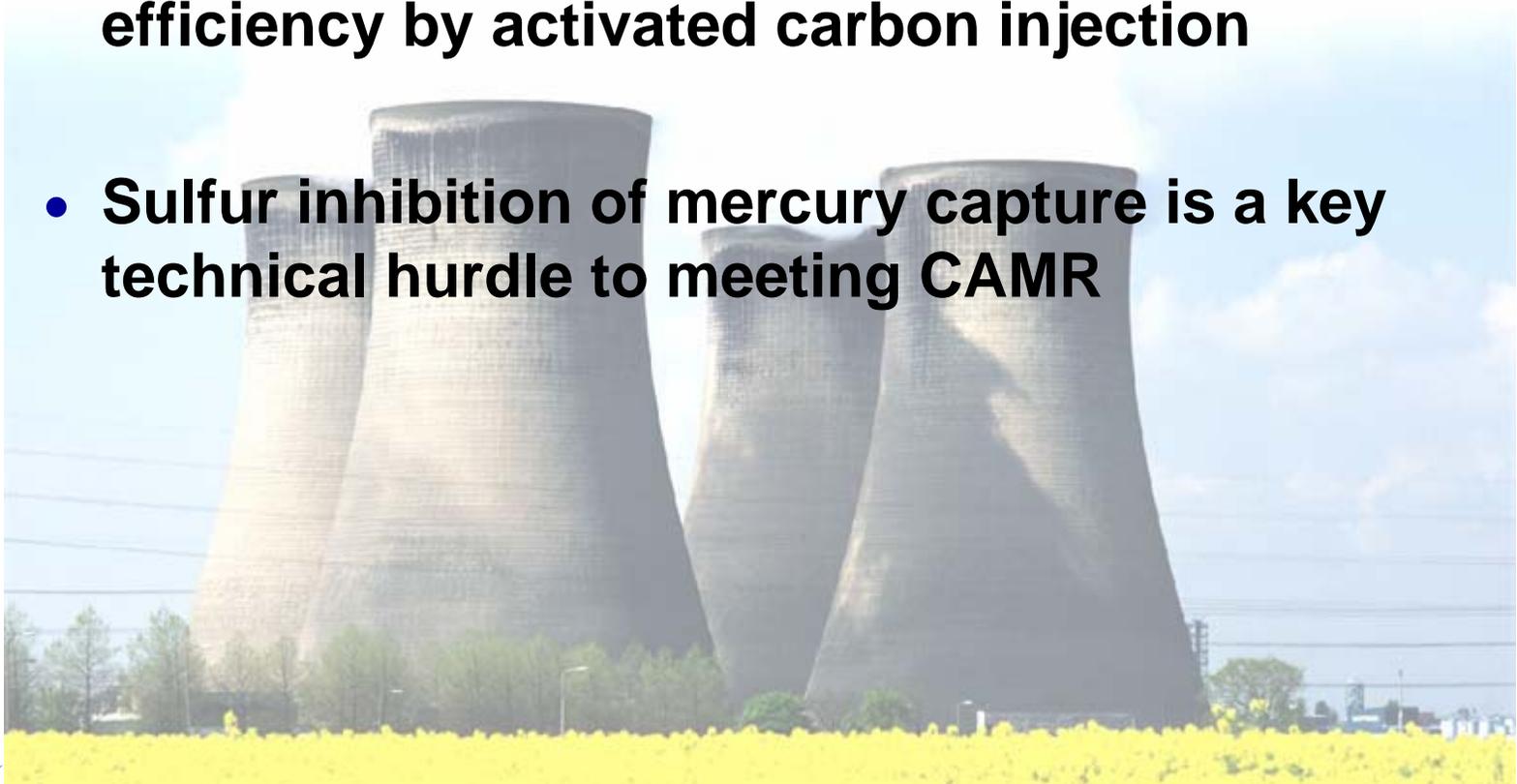*NETL*

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Challenge

- **Power plants with high concentrations of sulfur oxides show decreased mercury capture efficiency by activated carbon injection**

- **Sulfur inhibition of mercury capture is a key technical hurdle to meeting CAMR**

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Sulfur Oxides (SO$_X$) in Flue Gas

- **Coal-S is oxidized in the furnace primarily to sulfur dioxide (SO$_2$) with small amounts of sulfur trioxide (SO$_3$)**
  - SO$_2$ concentrations range from hundreds of ppm to over 1,000 ppm and SO$_3$ concentrations are generally 0 – 30 ppm
- **SO$_3$ (ppm levels) is injected into the flue gas as a conditioning agent to improve ESP performance**
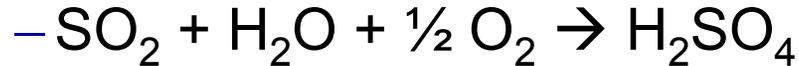- **SO$_3$ can form from the oxidation of SO$_2$ across SCR catalysts**

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High - SO$_X$ Mercury Capture Examples

- **AEP Conesville**
  - High-sulfur coal, ~30 ppm SO$_3$ in flue gas
  - Maximum mercury capture: 31% (Darco E-12 at 12 lb/MMacf)

- **Mississippi Power Plant Daniel**
  - 6 ppm SO$_3$ reduced native mercury capture by 40% and effectiveness of ACI (Darco Hg at 10 lb/MMacf) by 25 – 35%

- **Other power plants have seen the same inhibiting effect of SO$_3$**

- **Laboratory results at EERC**
  - Adding 1600 ppm SO$_2$ to a simulated flue gas caused previously captured Hg^{2+} to desorb from activated carbon

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Possible Mechanisms for SO_X Effect

- **Activated carbon catalyzes formation of S(VI)**
  - $SO_2 + H_2O + \frac{1}{2} O_2 \rightarrow H_2SO_4$
    - Oxygen source can either be flue gas ($O_{2(g)}$) or surface-bound oxygen
  - Activated carbon is used commercially to oxidize SO_2
  - SO_2 binds to the same basic sites as mercury, and has a strong binding energy (~ 80 kJ mol^{-1})
  - H_2SO_4 has low volatility ($P_{VAP} = 1$ torr at 300° F)
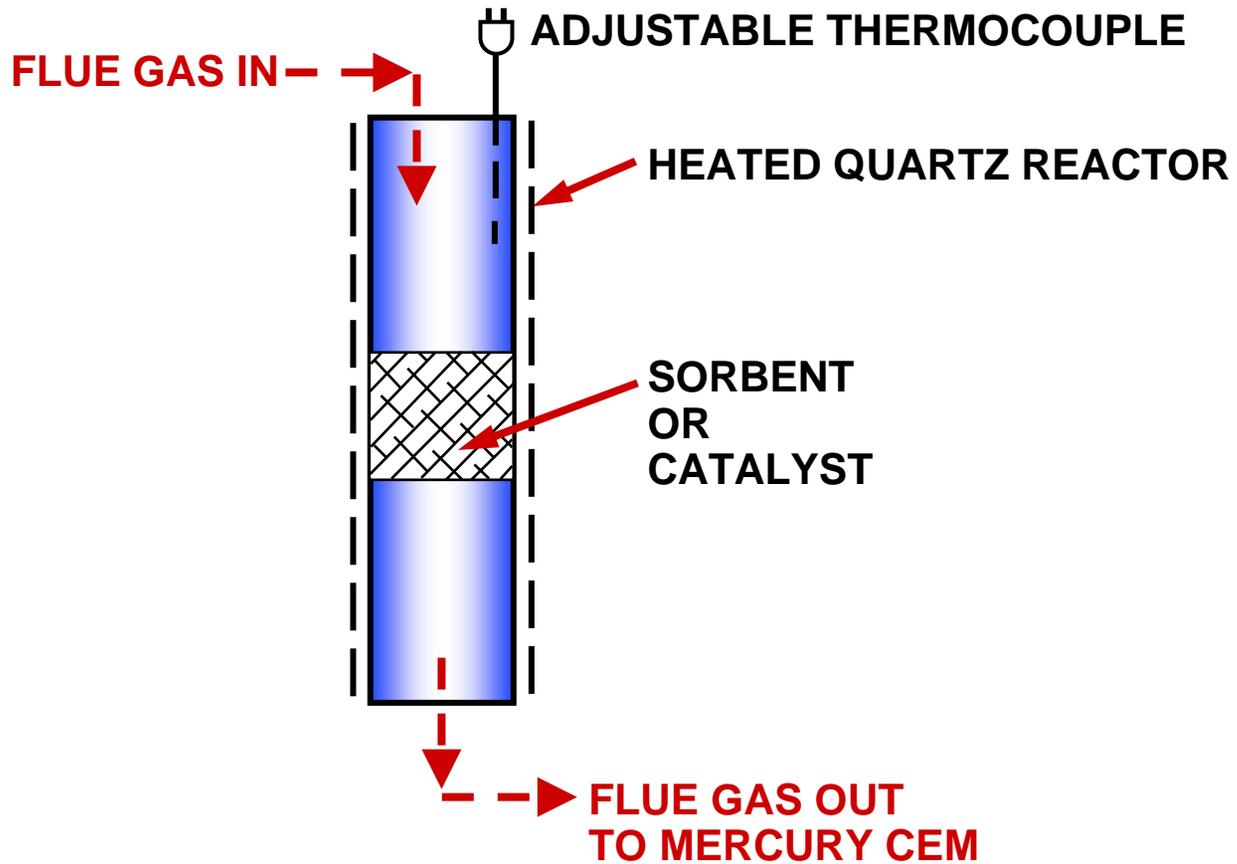 - NO_2 or another electron sink may be required to have a high conversion to sulfate

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Possible Mechanisms for SO_X Effect

- **SO_3 adsorbs to activated carbon**
  - $SO_3 + H_2O \rightarrow H_2SO_4$
  - SO_3 can also react with surface-bound oxygen to form H_2SO_4
  - SO_3 binds to the same sites as mercury
  - AC catalysts for H_2SO_4 are self-poisoned by SO_3
- **Activated carbon catalyzes the formation of flue gas halides**
  - $SO_2 + Cl_2 \rightarrow SO_2Cl_2$
  - Reaction can remove surface-bound halogens
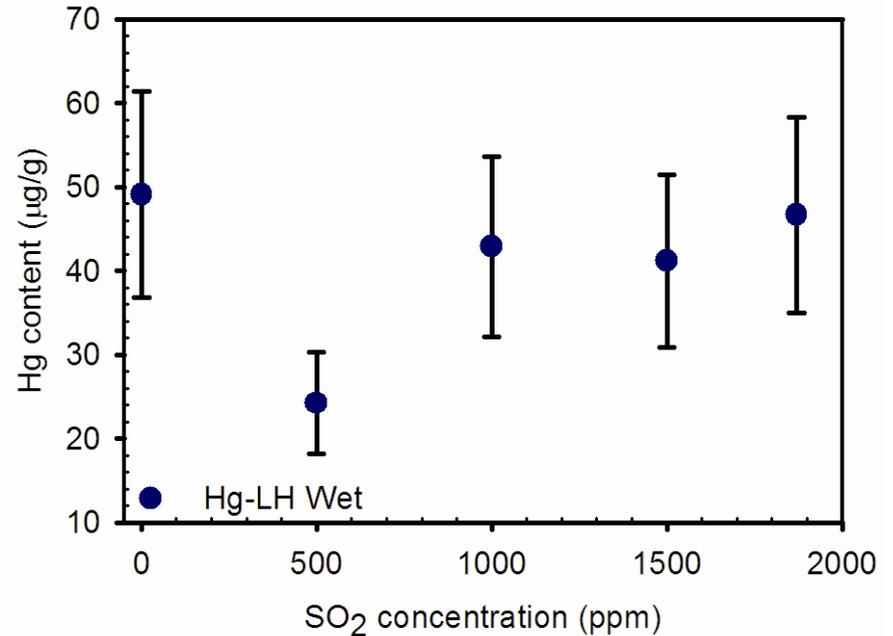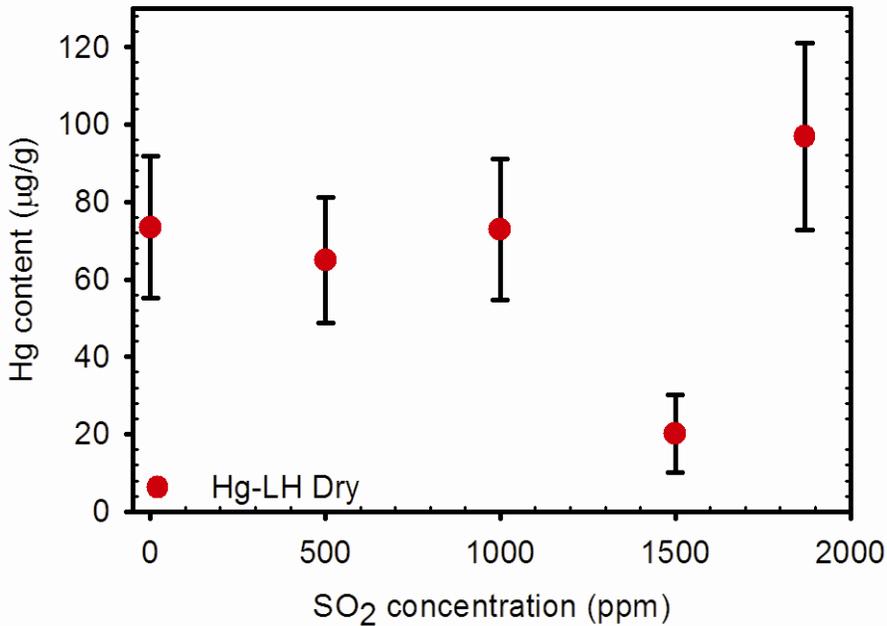 - Analogous reactions for NO and CO

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Experimental Method

- **Test activated carbons (Darco FGD and Hg-LH) in a packed-bed reactor**
  - Realistic Hg concentration: 9.3 μg Nm^{-3}
  - Temperature: 300° F
  - 200 mg activated carbon
- **Expose carbons to simulated flue gas (SFG)**
  - 5.3% O_2, 12.5% CO_2, 0 – 1.5% H_2O, 500 ppm NO, 50 ppm HCl, variable SO_2
  - Vary SO_2 concentration from 0 – 1870 ppm
  - 6 hour exposure time
- **Analyze exposed carbons for mercury content (μg/g) and sulfur content via ICP-AES**
  - Monitor gas-phase species with mass spectrometer (MS)

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Experimental Method

FLUE GAS IN →

ADJUSTABLE THERMOCOUPLE

HEATED QUARTZ REACTOR

SORBENT
OR
CATALYST

FLUE GAS OUT
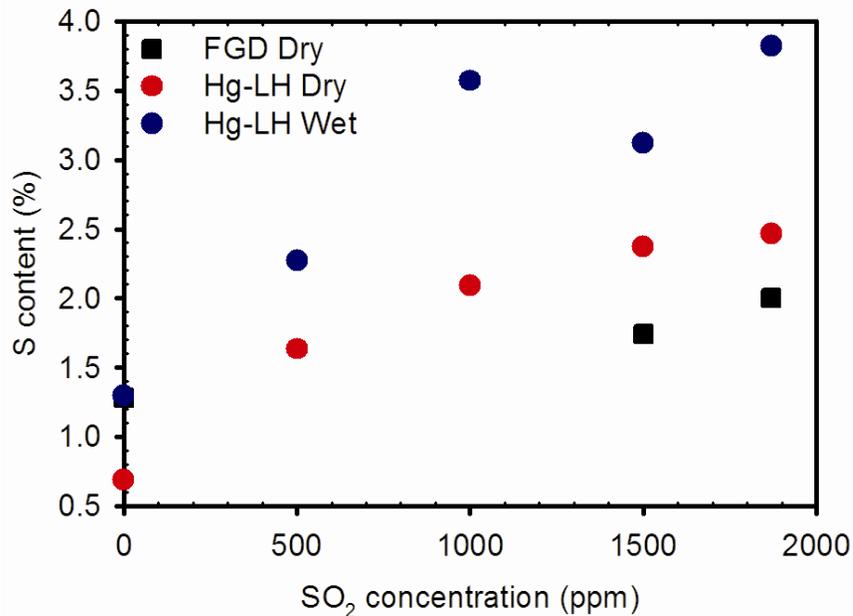TO MERCURY CEM

Results: Hg Capture

Hg capture is independent of SO$_2$ concentration

Results: S Content

- **Initial S content of AC**
  - 0.7 – 1.5%
- **Hg-LH picks up more sulfur than FGD**
  - Hg-LH is superior for Hg capture, and SO_2 adsorbs to the same sites as Hg
- **More sulfur is captured (and converted to sulfate) when water is present in the SFG**
- **XPS data show that sulfur exists as sulfate on the AC surface**

Results: SO$_2$ and Hg Capture

- **Exposure to simulated flue gas increases S content from ~1% to 1.5 – 4%**
  - This increase in S content results from the capture of ~1 – 2 mg of SO$_2$
  - A very small fraction (<0.1% at 1870 ppm SO$_2$) of the SO$_2$ that contacts the bed is captured
- **Hg capture is essentially constant for SO$_2$ concentrations ranging from 0 – 1870 ppm**
  - Increasing the S content of the AC (up to 4%) has no discernable effect on Hg capture from the SFG
  - Hg capture is higher in the dry SFG (~75 μg/g) than the wet SFG (~45 μg/g)

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Results: Hg Capture

- **High S content inhibits Hg capture**
  - One experiment was conducted with H_2SO_4 - impregnated FGD
    - S content: 10.6%
    - Hg capture from dry SFG with no SO_2: 4.13 $\mu g/g$
  - H_2SO_4 could be occupying binding sites or blocking pores
  - H_2SO_4 - FGD represents an extreme case of AC exposure to SO_2/SO_3
    - It is unlikely that AC injected into the ductwork would be able to pick up such large amounts of sulfur

Results: Mass Spectrometer Scans
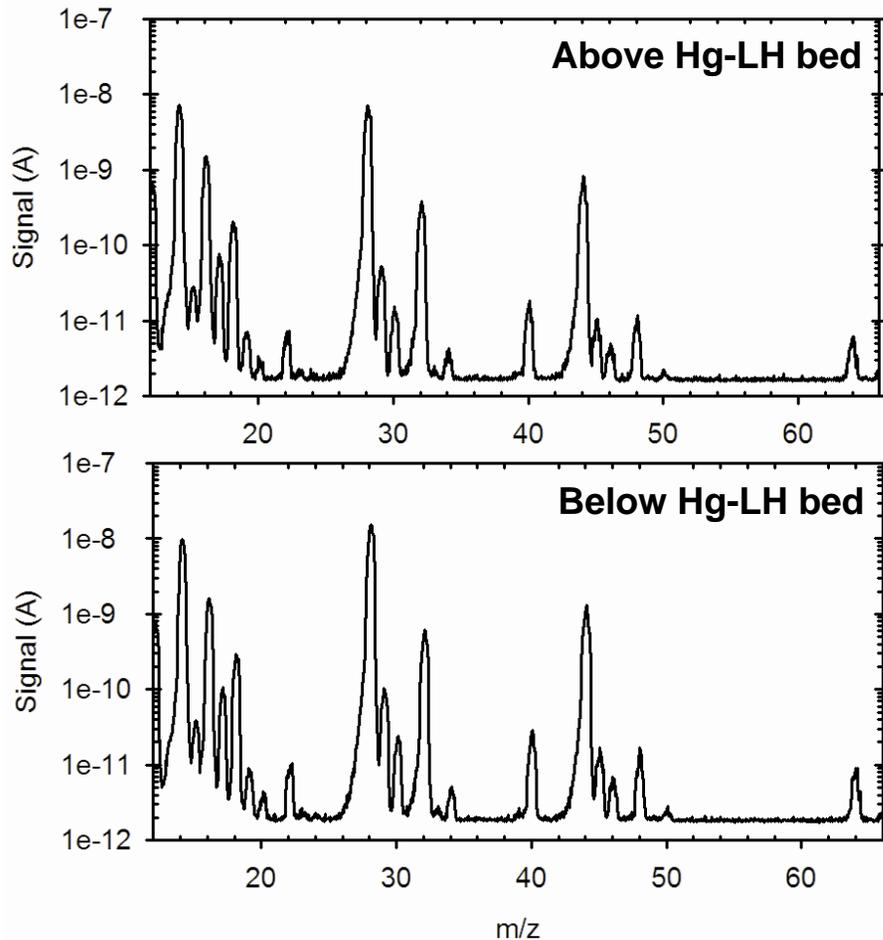
- **SO_2 = 1870 ppm**
- **MS data show no evidence of flue gas halides**
  - Does not rule out formation of halides
  - Perhaps below detection limit?
- **Concentrations above and below bed are generally constant**
  - Small ($\leq$ 2%) capture of SO_2 across the bed

Conclusions

- **Hg capture is independent of SO$_2$ concentration (0 – 1870 ppm) and S content (1 – 4%)**

  – The amount of sulfur captured by the AC represents a very small fraction (<0.1%) of the sulfur that contacts the packed bed

- **High S content (~10%) in the AC inhibits Hg capture**

  – Inhibition may result from pore blocking or H$_2$SO$_4$ occupying sites for Hg adsorption

- **There is no evidence of persistent flue gas halide formation**

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Implications for Future Work

- **SO_2 appears to have no effect on Hg capture, but SO_3 may be more important in power plants**
  - Small concentrations of SO_3 can cause large reductions in Hg capture by AC
- **The mechanism of SO_x inhibition is still unknown**
  - The lack of an SO_2 effect may indicate that SO_2 oxidation to H_2SO_4 is too slow to be important
    - SO_3 conversion to H_2SO_4 should be much faster
  - Experiments with H_2SO_4-FGD show that large amounts of H_2SO_4 can inhibit Hg capture
  - Flue gas halide formation appears to be of minor importance

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Future Work

- **Include SO$_3$ in the simulated flue gas**
  - A system for SO$_3$ introduction is currently being installed and tested

Acknowledgments

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