A kinetic approach to catalytic oxidation of mercury in flue gas

Albert A. Presto and Evan J. Granite

National Energy Technology Laboratory

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Mercury in Flue Gas

- **Elemental mercury (Hg^0)**
  - Emitted from high-temperature coal combustion
  - Insoluble in water
  - Can be removed with activated carbon injection (ACI)
- **Oxidized mercury (Hg^{2+})**
  - Typically assume $HgCl_2$
  - Water soluble, sorbs to AC
- **Particle-bound mercury (Hg(p))**
  - Both Hg^0 and Hg^{2+}
  - Typically a small fraction of total mercury
- **Ratio of Hg^0/Hg^{2+} depends on a number of factors (coal-Cl, LOI, time-temperature history, etc.)**

Mercury Removal Technologies

- **Activated carbon injection (ACI)**
  - Inefficient mixing/contact: Requires C/Hg ratios >1000:1
  - AC is a general sorbent
  - Potentially makes fly ash unusable as cement additive
  - Current 'best bet'
- **Catalytic mercury oxidation**
  - Use catalyst to convert Hg^0 to Hg^{2+}
  - Removal of Hg^{2+} with wet FGD (>90% efficient)
    - Use of FGD is expected to increase because of CAIR

Mercury oxidation catalysts

- **SCR**
- **Carbon-based materials**
  - Fly ash, carbon catalysts
- **Metals and metal oxides**
  - Iron, iron oxides
  - Noble metals (i.e., gold)
- **Data are often reported as '% oxidation'**
  - '% oxidized' is not an inherent physical or chemical parameter
  - Difficult to interpret results and relate different experiments and conditions
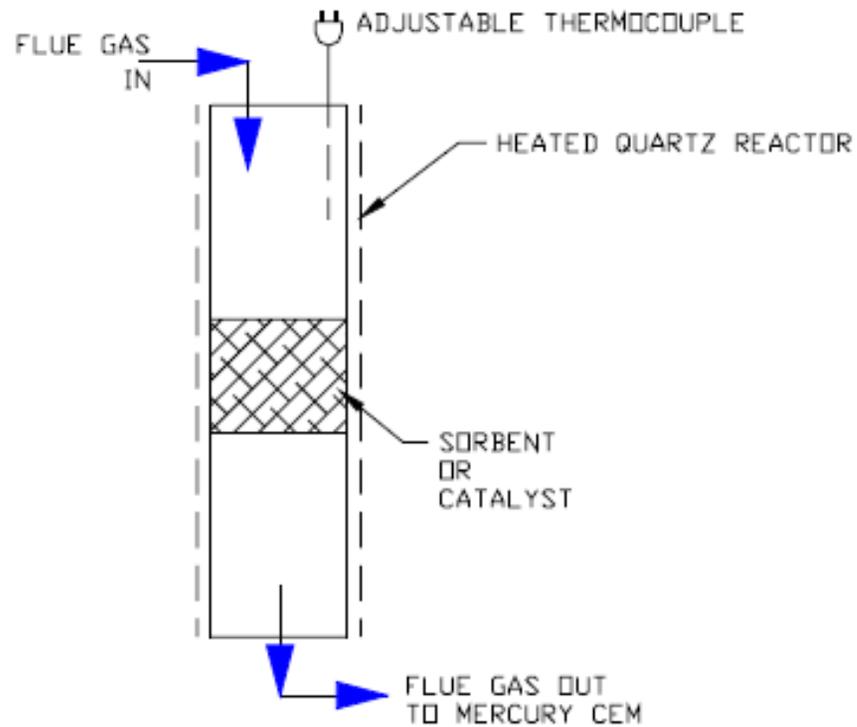
Mercury catalysts: What is needed?

- **Better understanding of different catalyst materials and supports**
  - Many materials have been tested, but certainly not comprehensive
  - What is the most cost-effective?
- **Reaction mechanism and kinetics**
  - Treat catalyst experiments as what they are – kinetics experiments
  - Develop consistent nomenclature
  - Consider relationships among broad groups of materials (i.e., noble metals)

Catalysts tested

- **Iridium (Ir)**
  - 1% Ir on 4 mm γ-Al$_2$O$_3$ beads
- **Ir/HCl**
  - Prepared by soaking Ir (on γ-Al$_2$O$_3$) in 37% trace metals grade HCl, air dry
- **Norit Darco FGD**
- **Thief/HCl**

NETL BENCH-SCALE PACKED BED REACTOR

FLUE GAS IN

ADJUSTABLE THERMOCOUPLE

HEATED QUARTZ REACTOR

SORBENT OR CATALYST

FLUE GAS OUT TO MERCURY CEM

Experimental conditions

- **Slip stream from pilot combustor**
  - Particle-free, dehumidified flue gas
  - Flow rate: 8 ± 1 lpm
  - T ~ 280° F (411 K)
  - Hg^0 concentration adjusted using mercury spiking system (5 – 50 μg Nm^{-3})

- **Packed bed**
  - D = 1.07 cm
  - τ = < 0.1 s

Flue gas composition

	90/10 PRB/Bituminous	PRB
O_2 (%)	8.3-9.6	8.7-9.4
SO_2 (ppm)	225-260	210-230
NO_x (ppm)	320-430	330-340
CO_2 (%)	10-11	10-11
HCl (ppm)	6.5	1.6

Hg concentration ($\sim$80-90% Hg^0) varied from 5 – 50 μg Nm^{-3} depending on extent of Hg^0 spiking

Typical Experiment
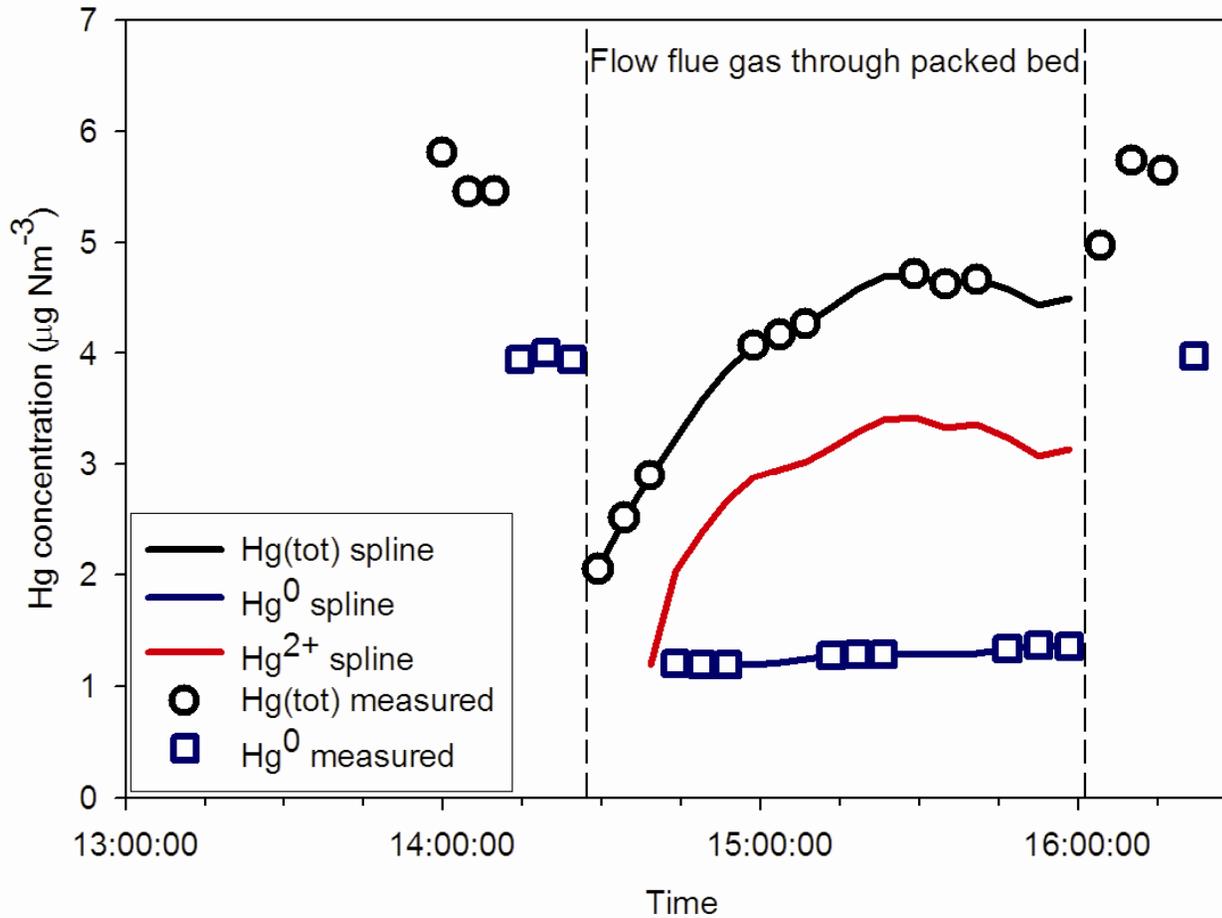
Sorbent activity

- **All of the tested materials initially act as sorbents**
  - Total mercury leaving the bed rises from an initial low level to an "equilibrium" value
  - Catalyst data is collected during equilibrium
- **Sorbent characteristics and time to equilibrium are material dependent**
  - Ir and Ir/HCl
    - Initial sorption: ~60%
    - Equilibrium sorption: ~10 – 20%
    - Time to equilibrium: ~1 hr
  - Darco FGD
    - Initial sorption: >90%
    - Equilibrium sorption: ~50%
    - Time to equilibrium: ~2.5 hr
    - "Used" Darco had smaller equilibrium sorption and time to equilibrium than new sorbent.

Catalyst Results

Catalyst	% oxidation	Catalyst mass (mg)
Ir	40	20
Ir/HCl	30	20 - 30
Darco	50	100
Thief/HCl	60 - 70	100

Thief/HCl gives the highest fractional conversion, but it is actually the worst catalyst!

Reporting catalytic activity

- **Is there another way to judge catalysts?**
- **Reaction: Hg^0 + Oxidant → Hg^{2+}**
  - Define bulk reaction rate

$$R = \frac{\Delta\left[Hg^{2+}\right]}{\Delta t}$$

  - $\Delta[Hg^{2+}]$ = concentration change in Hg^{2+} across the catalyst bed
  - Δt = residence time (based on bulk flow rate)
  - Reduces to derivative for small $\Delta[Hg^{2+}]$ and Δt

Using the bulk reaction rate

$$R_{gas} = \frac{\Delta[Hg^{2+}]}{\Delta t} = k_{gas}[Hg^0]^\alpha[Ox]^\beta = \frac{moles}{m^3 \cdot \sec}$$

- **R_{gas} (apparent gas-phase reaction rate) still hides experimental factors**
  - Catalyst mass/surface area

$$R_{cat} = R_{gas}\left(\frac{V_{cat}}{m_{cat}}\right) = \frac{moles}{g \cdot \sec}$$

- **In catalysis literature, results are typically reported as moles/(m^3 sec) or moles/(g sec)**

Where are the results now?

Catalyst	R_{cat} (x10^{11} mole Hg^{2+}/ g catalyst/sec)
Ir	3.8
Ir/HCl	2.3
Darco	2.2
Thief/HCl	2.1

Experimental conditions:
  $[Hg^0]_0 \sim 10 \ \mu g \ Nm^{-3}$
  $T \sim 280^o \ F$ (411 K)
  90/10 PRB/Bituminous mix

Rate constants

- **k$_{gas}$ (apparent gas-phase rate constant) hides experimental parameters (like R$_{gas}$)**

$$k_{cat} = k_{gas}\left(\frac{V_{cat}}{m_{cat}}\right)$$

$$R_{gas} = \frac{\Delta[Hg^{2+}]}{\Delta t} = k_{cat}\left(\frac{m_{cat}}{V_{cat}}\right)[Hg^0]^{\alpha}[Ox]^{\beta}$$

$$R_{cat} = k_{cat}[Hg^0]^{\alpha}[Ox]^{\beta}$$

First estimate for k_{cat}

- **Assumptions**
  - $\alpha, \beta = 1$
  - HCl is the oxidant

$$R_{cat} = k_{cat}\left[Hg^0\right]\left[HCl\right]$$

Catalyst	k_{cat}(411 K) $(m^3\ mole^{-1}\ sec^{-1})(m^3\ cat)(g\ cat)^{-1}$
Ir	25.4 ± 6
Ir/HCl	11.8 ± 3
Darco	3.6 ± 0.9
Thief/HCl	3.3 ± 0.8

Implications of measuring R and k

- **First step towards developing a predictive model for catalytic mercury oxidation**

- **Data reported as '% oxidation' are limited to the specific experiment, and are difficult to apply to different conditions**

  – Normalizing by catalyst mass (or surface area) helps remove this limitation

- **A reasonable goal: Predict extent (or rate) of mercury oxidation as process scale increases from lab → pilot → full-scale application**

Activation energy

$$k = A \exp\left(\frac{-E_a}{RT} \right)$$

- **For the catalytic reaction, E_a is the apparent activation energy**
  - Assuming no mass transfer limitations
- **For Ir/HCl, E_a ~ 20 kJ mole^{-1}**
  - Similar to 30 kJ mole^{-1} for gold catalyst reported by Zhao et al (*ES&T*, 2006, **40**, 1603-1608)

Reaction order

- **[Hg^0]$_{inlet}$**
  - Ir, Thief/HCl ~ 1
  - Ir/HCl: possibly negative
- **[HCl]**
  - Thief/HCl: positive
- **Mechanistic insight**
  - Langmuir-Hinshelwood mechanisms can be either +1 or -1 order in individual reactants
    - -1 order is a result of surface saturation
  - Eley-Rideal mechanisms can be first order in individual reactants

Conclusions

- **Ir, Ir/HCl, Darco, and Thief/HCl all catalyze Hg^0 oxidation**
  - Ir > Ir/HCl > Darco > Thief/HCl
  - Treating Ir with HCl (and supposedly binding Cl to the surface) reduces effectiveness as a catalyst. Why?
  - If oxidation occurs at carbon sites in Darco and Thief, we would expect Darco to be a better catalyst.
    - Thief may be a more economical choice because of low cost
- **Data presented as '% oxidation' can be very misleading**
  - Thief/HCl had the highest % oxidation, but the poorest kinetics
- **Considering Hg oxidation as a kinetic problem can lead to predictability**
  - Potential source of error: Bulk rate approximation

Future work

- **The data presented here are preliminary and encouraging; these catalysts require further study**
  - Temperature
  - HCl, Hg^0 concentrations
- **What is the role of SO_2, NO_x, etc?**
  - Bind/deactivate catalyst
  - Parallel reactions (i.e., Hg^0+HCl competing with Hg^0+SO_2)
    - NO_x, SO_2 reacting with surface Cl?

Acknowledgments