DOE/NETL Mercury Control Conference

The PCO Process for Photochemical Removal of Mercury from Flue Gas

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Office of Fossil Energy

GP-254 / PCO Process

- Irradiation of Flue Gas with 254-nm Light
- Oxidation of Mercury → Facilitate Removal
- Licensed for Application to Coal-Burning Power Plants (Powerspan Corp)
- Potential Applications for Incinerators

GP-254 / PCO Process

- 91% Oxidation/Removal Attained at Bench-Scale

Removal of Oxidized Mercury

- Wet-ESP, ESP, Baghouse, Scrubber, or AC
- Low Parasitic Power (less than 0.35%)
- Pilot-Scale Test Program in Place

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Technical Challenges
Mercury is Difficult to Capture

- Low concentration
- Exists as Hg^0
- Harsh conditions of coal-derived flue gas
- Competitive adsorption / poisoning
- Low sorbent reactivity
- Hg is semi-noble metal

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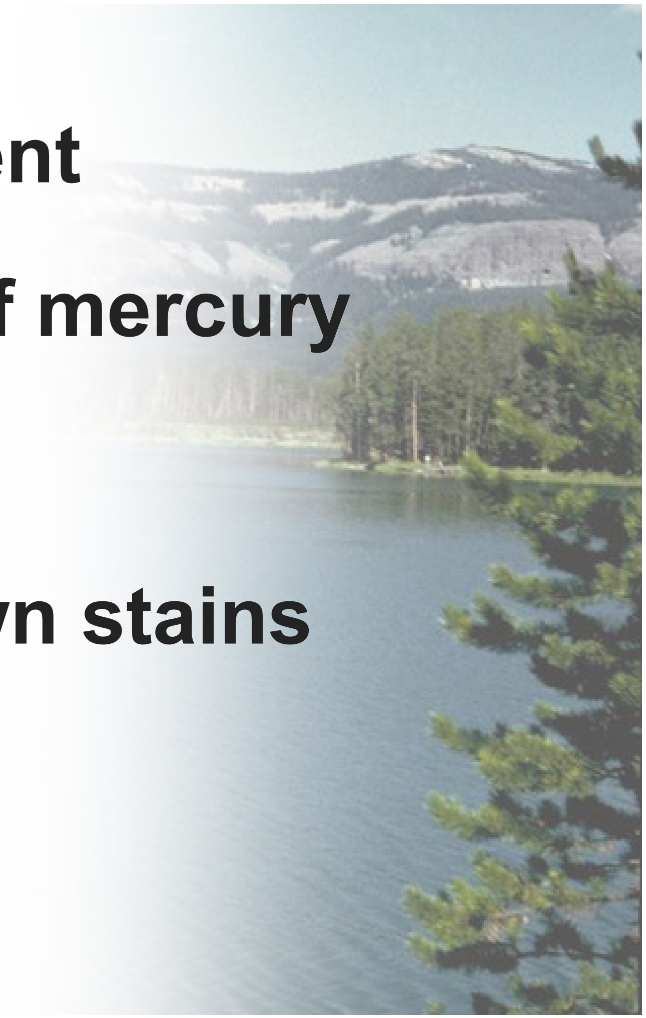
Background: GP-254 Process

Discovery

- Sorbent development
- UV measurement of mercury
- AFS
- Unwanted red-brown stains
- Mercuric oxide
- Serendipity



Technical Challenges
Mercury is Difficult to Measure

- Low concentration & harsh conditions
- Exists as Hg, $HgCl_2$, and $Hg_{(particulate)}$
- Continuous conversion among three
- Broad-band absorbers
- Quenching
- Photosensitized oxidation
- Competitive adsorption/ poisoning

Photochemical Oxidation of Mercury

- Mercury can absorb and emit 253.7 nm light
- Atomic Absorption (AAS)

  $Hg + 253.7\ nm\ radiation \rightarrow Hg^*$ Hg 6 ($^3P_1$) (I)

- Atomic Emission (AES)

  $Hg^* \rightarrow Hg + 253.7\ nm\ radiation$ (II)

- Atomic Fluorescence (AFS): steps (I) and (II)
- Basis for CEMs

What Is Quenching?

- Intensity of fluorescent emission diminished
- Energy transfer due to collisions
- Function of size, shape, and reactivity
- **Primed for chemical reaction (activation)**
- **Interferes with ultraviolet spectroscopy**

$Hg + 253.7\ nm\ light \rightarrow Hg^*$	$Hg\ 6\ (^3P_1)$
$Hg^* \rightarrow Hg + 253.7\ nm\ light$	Fluorescence
$Hg^* + M \rightarrow Hg + M^*$	Quenching

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Quenching Cross Sections

$$Hg\ 6(^3P_1) + M \rightarrow Hg\ 6(^1S_0) + M^*$$

Function Of Size, Shape And Reactivity

Species	Cross Section (cm^2)
HCl	37.0×10^{-16}
NO	24.7×10^{-16}
O_2	13.9×10^{-16}
CO	4.1×10^{-16}
CO_2	2.5×10^{-16}
H_2O	1.0×10^{-16}
N_2	0.4×10^{-16}

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Photochemical Oxidations

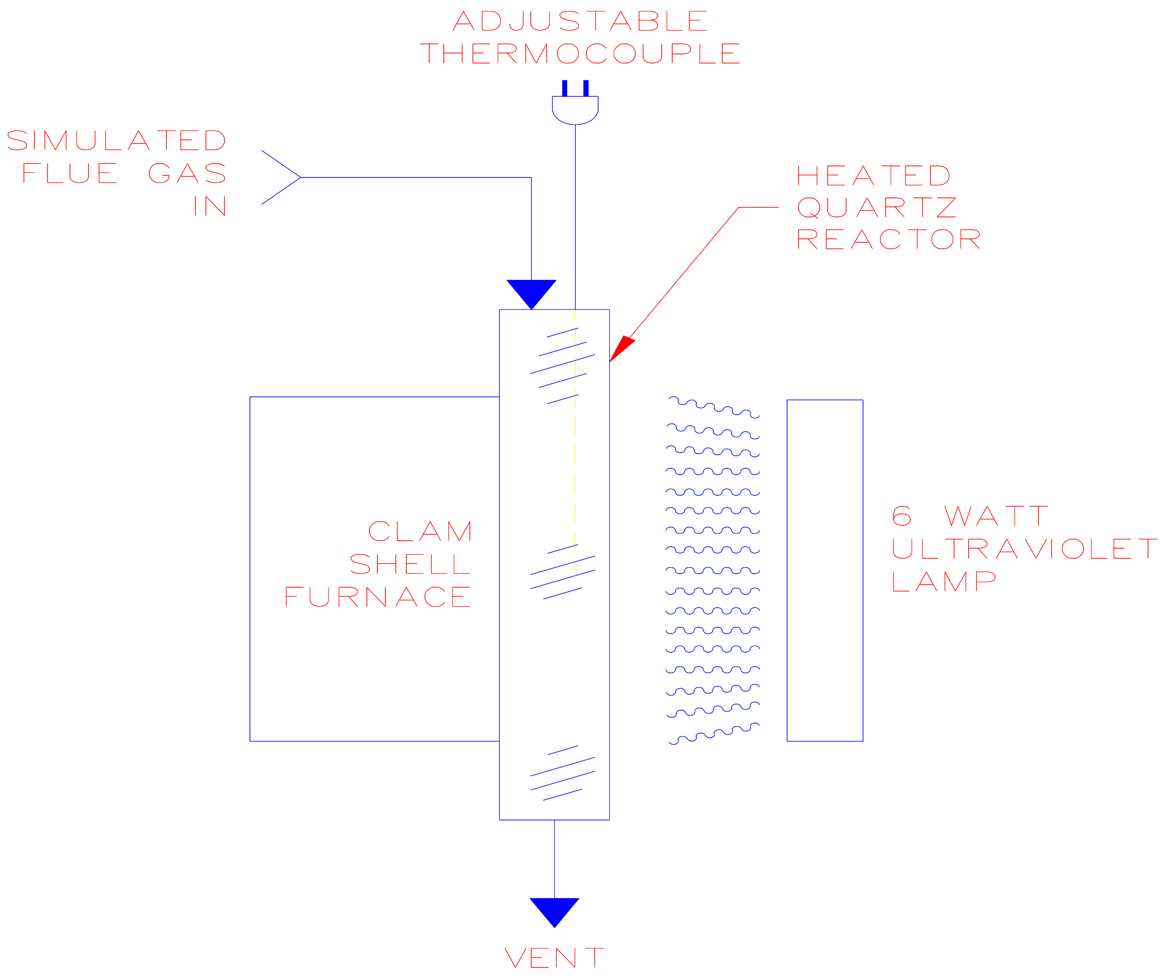
- First described in 1926 by Dickinson & Sherrill (O_2)
- Gunning discovered others in 1950s (HCl, H_2O, CO_2)

Relevant Overall Reactions

$$Hg + 2\,O_2 + 253.7\text{ nm light} \rightarrow HgO + O_3$$
$$Hg + HCl + 253.7\text{ nm light} \rightarrow HgCl + 1/2\,H_2$$
$$Hg + H_2O + 253.7\text{ nm light} \rightarrow HgO + H_2$$
$$Hg + NO_2 + 253.7\text{ nm light} \rightarrow HgO + NO$$
$$Hg + CO_2 + 253.7\text{ nm light} \rightarrow HgO + CO$$

- Interferes with UV-based CEMs
- Potential removal method

Lab-Scale Photoreactor



Photoreactor for Removal of Mercury

Experimental Parameters

- **Quartz Photoreactor, 6-watt UV lamp**
- **Temperatures: 80^{o}F, 280^{o}F, 350^{o}F**
- **Flow-rate: 60 ml/min Reaction time: 350 min**
- **Intensity: 1.4 mW/cm^2**

Gas Compositions

A: 16% CO_2, 5% O_2, 2000 ppm SO_2,
300 ppb Hg, balance N_2

B: 16% CO_2, 5% O_2, 2000 ppm SO_2,
500 ppm NO, 300 ppb Hg, balance N_2

Results: Photochemical Removal

Gas	Temp (°F)	Mean Hg Capture (%)
A	350	2.3 ± 2.0
A	280	71.6 ± 30.1
A	80	67.8 ± 28.8
B	280	26.8 ± 11.7

- Removal as mercuric oxide/mercurous sulfate stain
- Higher removals below 300ºF
- Limited by thermal decomposition of O_3 (300-350ºF)
- NO reduces removal, possibly by consuming ozone
- Low energy consumption
- Potentially low operating costs

Conclusions: Photochemical Oxidation

Method For Mercury Removal

- Obvious interference For CEMs
- High levels of mercury removal from SFG
- Capture as HgO and Hg_2SO_4
- Enhanced removal below 300ºF

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Conclusions: Photochemical Oxidation

Potential For Better Performance

- Other oxidants (HCl, H_2O, NO_2) in flue gas
- Promising process economics
- Potential for multi-pollutant control
- Pilot-scale data needed
- Low rank coals are of particular interest

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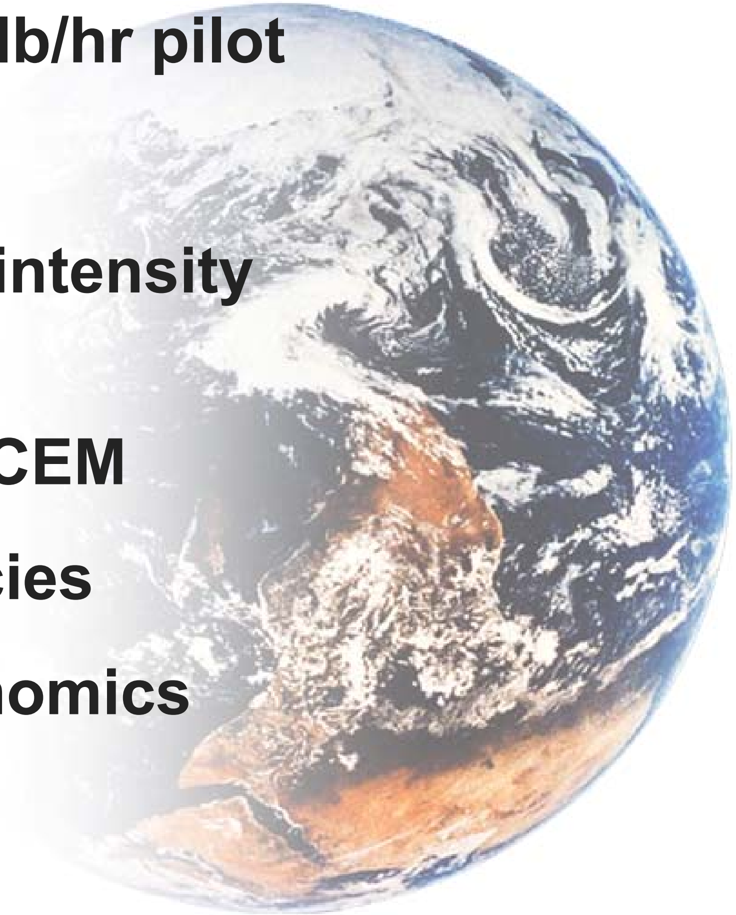
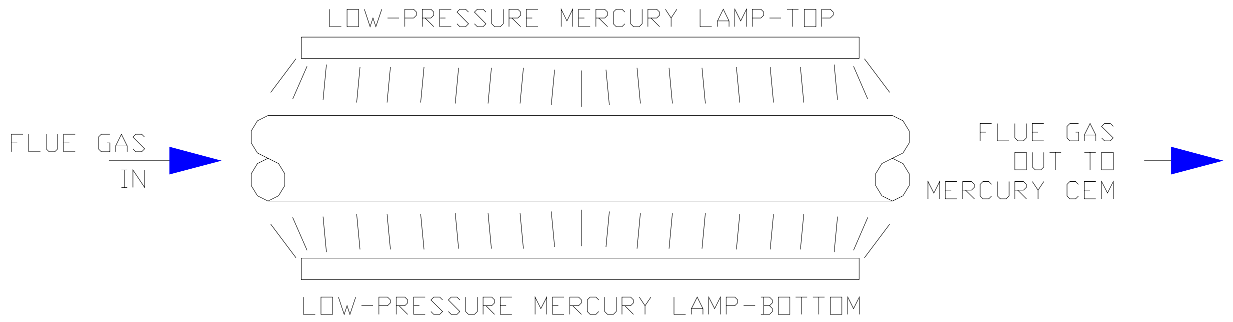
Larger Scale Testing

NETL Bench-Scale Photoreactor

- Slipstream of flue gas from 500-lb/hr pilot
- Temperature: 120ºF - 280ºF
- Effect of temperature, radiation intensity residence time & composition
- Removals measured on-line by CEM
- Impact upon other flue gas species
- Determine GP-254 process economics



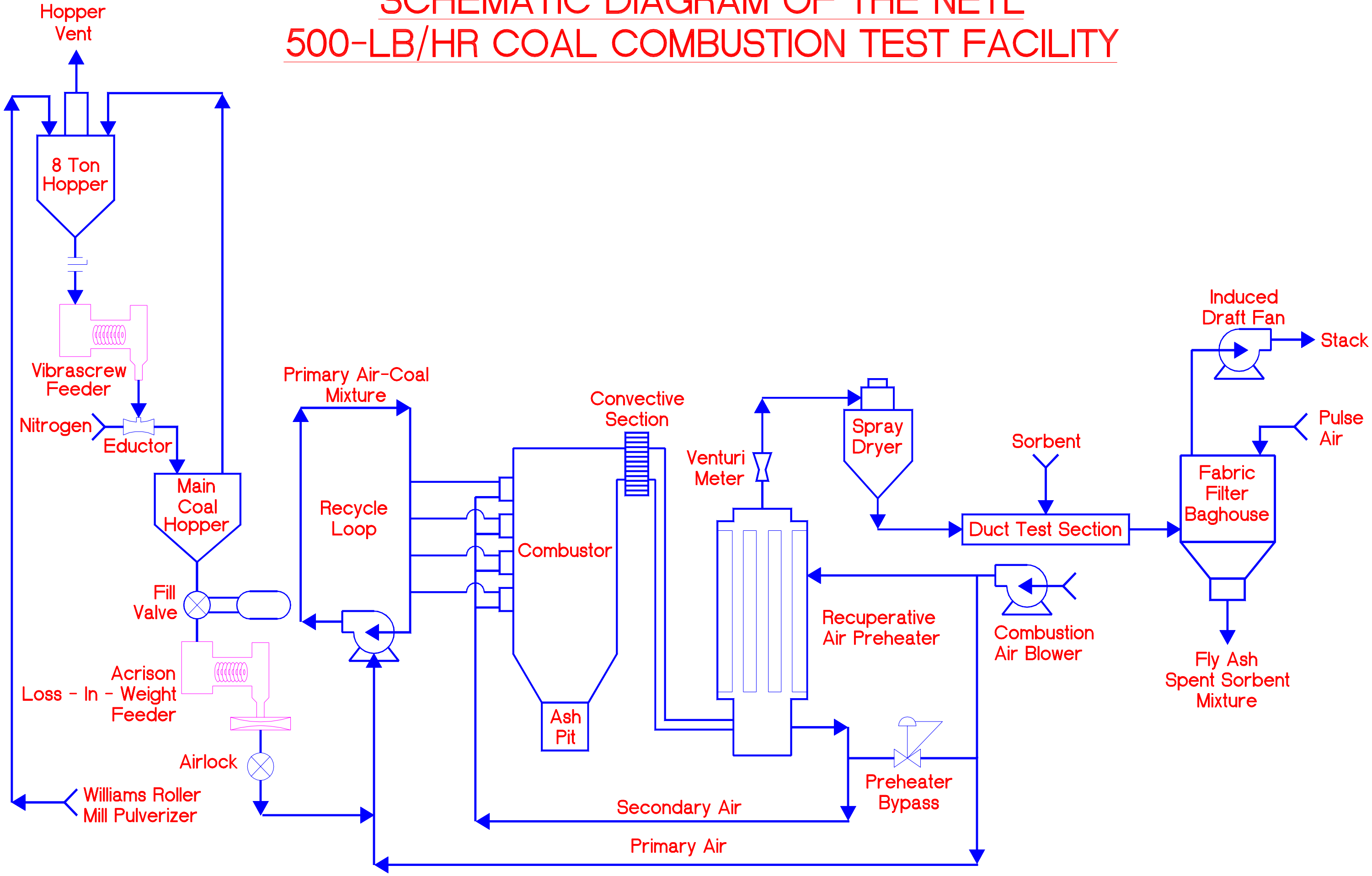
NETL BENCH-SCALE PHOTOREACTOR



NETL Bench-Scale Photoreactor

- ½-inch by 33-inch Quartz Tube
- Two 30-W Low Pressure Mercury Lamps
- 254-nm Intensity: 20 mW/cm^2
- Gas Composition: PRB Flue Gas
- Temperature: 120°F - 280°F
- Flow-Rate: 8 liters/min
- Sir Galahad CEM Monitor Inlet/Outlet Mercury

SCHEMATIC DIAGRAM OF THE NETL 500-LB/HR COAL COMBUSTION TEST FACILITY



NETL Bench-Scale Results

Significant Level of Mercury Oxidation

- Crude Bench-Scale Apparatus: Lamp
- Slipstream of Particulate-Free PRB Flue Gas
- 6 – 50 µg/Nm^3 Elemental Mercury (Spiking)
- Low Power Consumption
- Extremely Low UV Intensity Applied
- Typically 30-70% Removal of Mercury

Powerspan Lab-Scale Results

Commercial Lamp System

- Flow-rates: 24 – 100 scfm
- Temperature: 120 - 190°F
- Intensity: 13.8 W/cm^2 -- Low Parasitic Power
- Mercury Concentration: 9 - 40 $\mu g/Nm^3$
- 5.6% O_2, 13% CO_2, 8% H_2O, 1300 ppm SO_2, 220 ppm NO, 20 ppm CO, and balance N_2
- 91% Removal

Economics of PCO Process

Parasitic Power Major Operating Cost

- Parasitic Power < 0.35% for Removal > 90%
- Further Reductions in Parasitic Power Likely
- Improved Lamp Design
- Larger-Scale
- Operating Experience

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Future Work

Powerspan

- 2-MW Mobile Slipstream Test Unit
- Installation at Ameren Rush Island
- Tests in January 2007
- Pilot-Scale Tests at other Plants in 2008

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