NOVEL TECHNIQUES FOR MERCURY CONTROL

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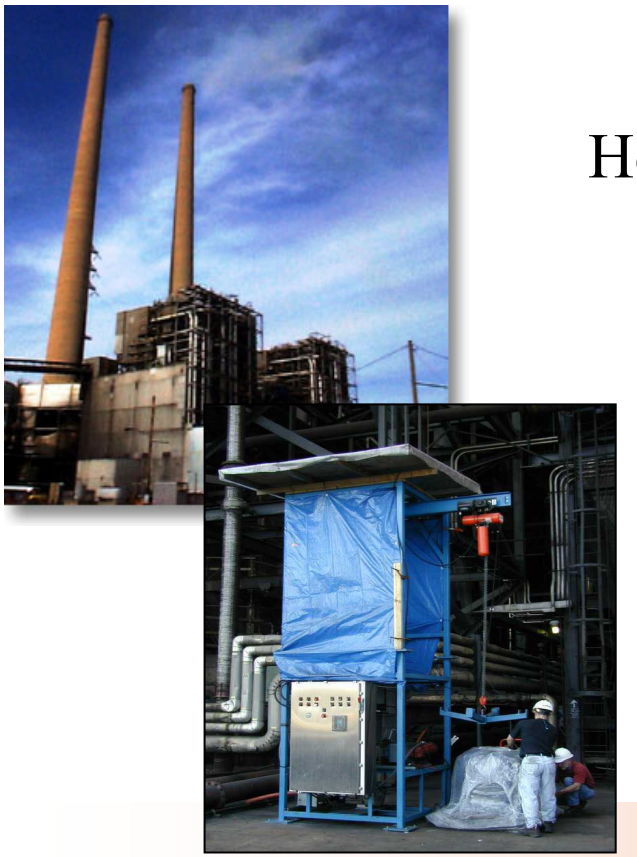
U.S. Department of Energy
National Energy Technology Laboratory

Mercury Control Technology
R&D Program Review Meeting
August 12-13, 2003

LAB-SCALE RESEARCH OBJECTIVES

- Develop cost-effective novel sorbents.
- Elucidate mercury-sorbent interactions.
- Explore innovative techniques for mercury removal, for example, photochemical oxidation.
- Develop high temperature mercury sorbents for gasification applications.

A Technique to Control Mercury From Flue Gas: The Thief Process



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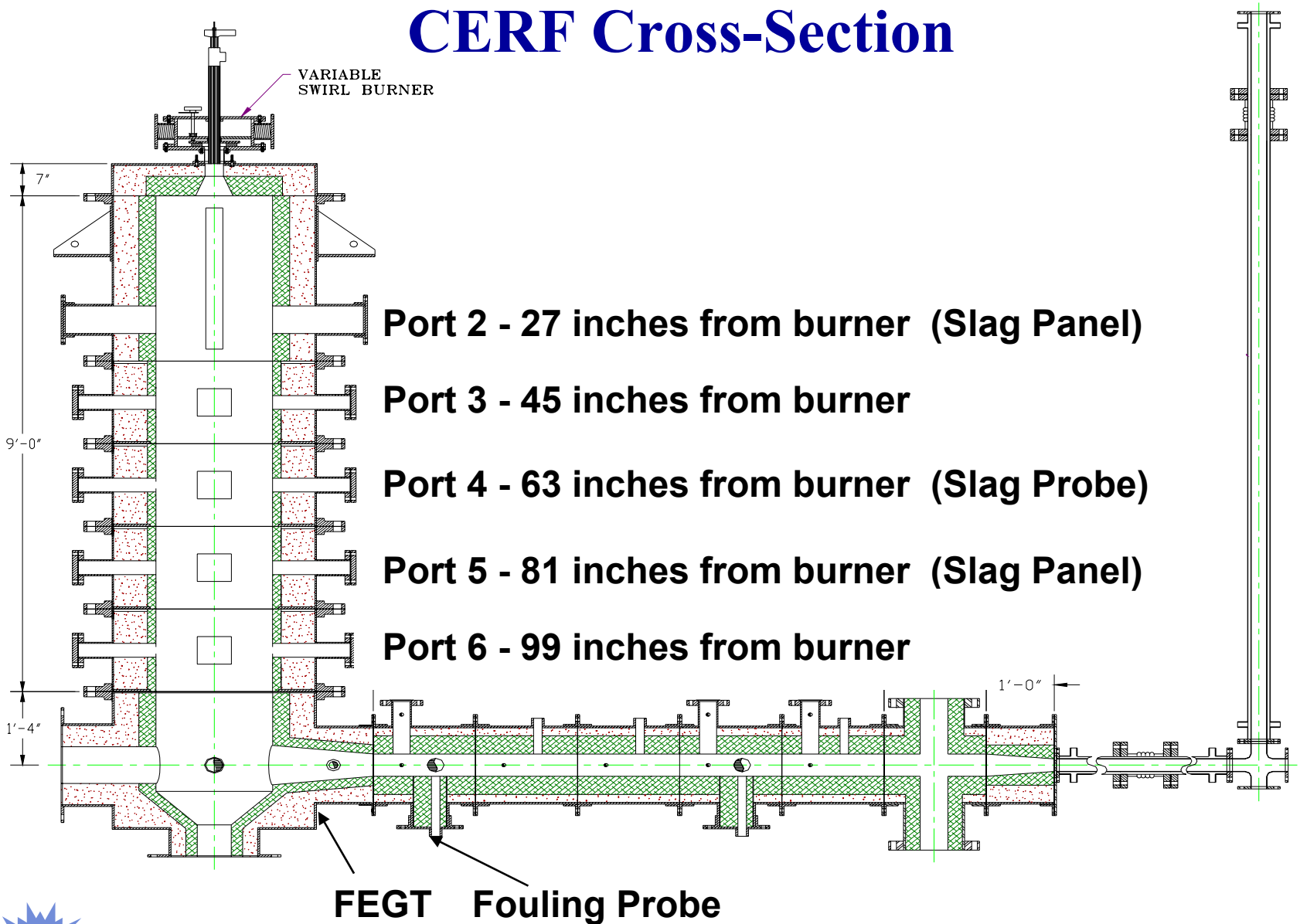
CERF Cross-Section



Port 2 - 27 inches from burner (Slag Panel)

Port 3 - 45 inches from burner

Port 4 - 63 inches from burner (Slag Probe)

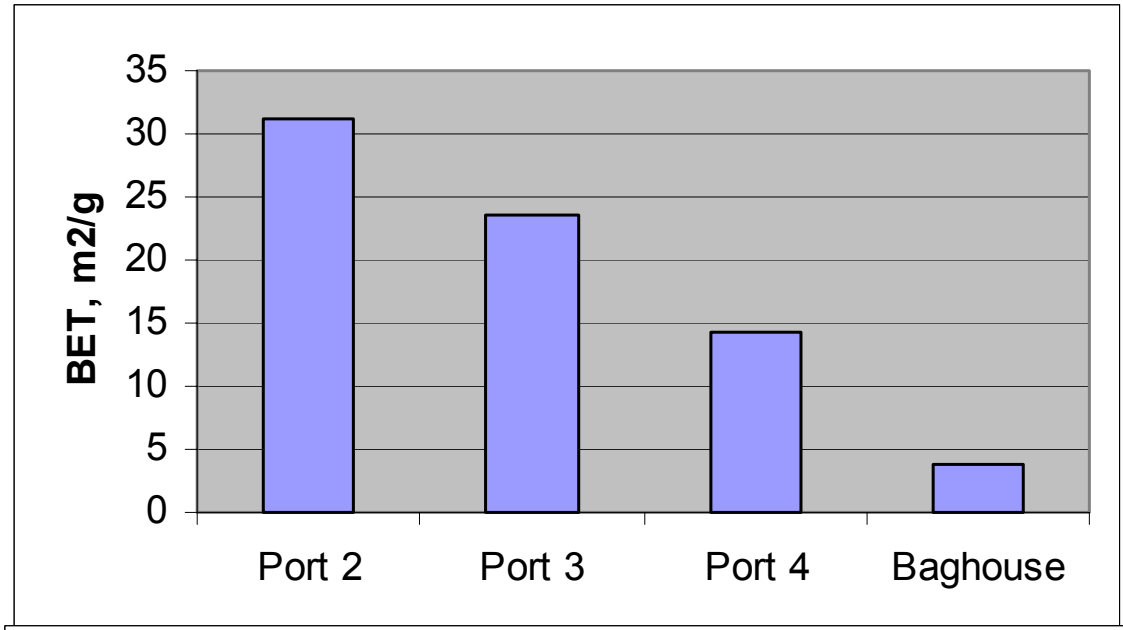
Port 5 - 81 inches from burner (Slag Panel)

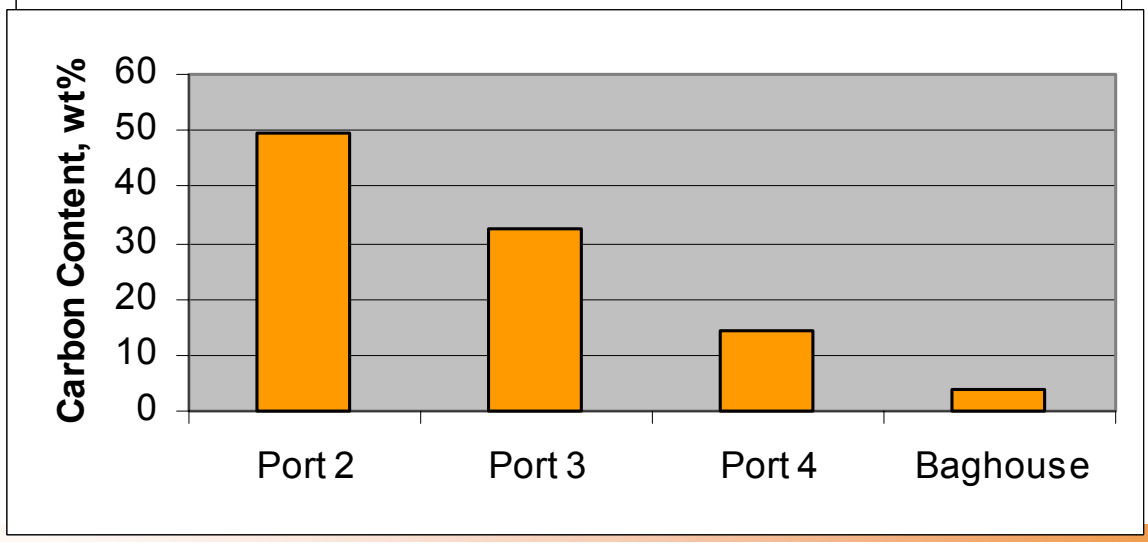
Port 6 - 99 inches from burner

Sorbent Characterization

- **Physical**
  - Surface area (BET) and pore volume
  - Bulk chemical analysis
  - Particle size
  - Raman microanalysis
- **Chemical**
  - Mercury capacity

Evergreen Bituminous Coal





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  - Surface area (BET) and pore volume
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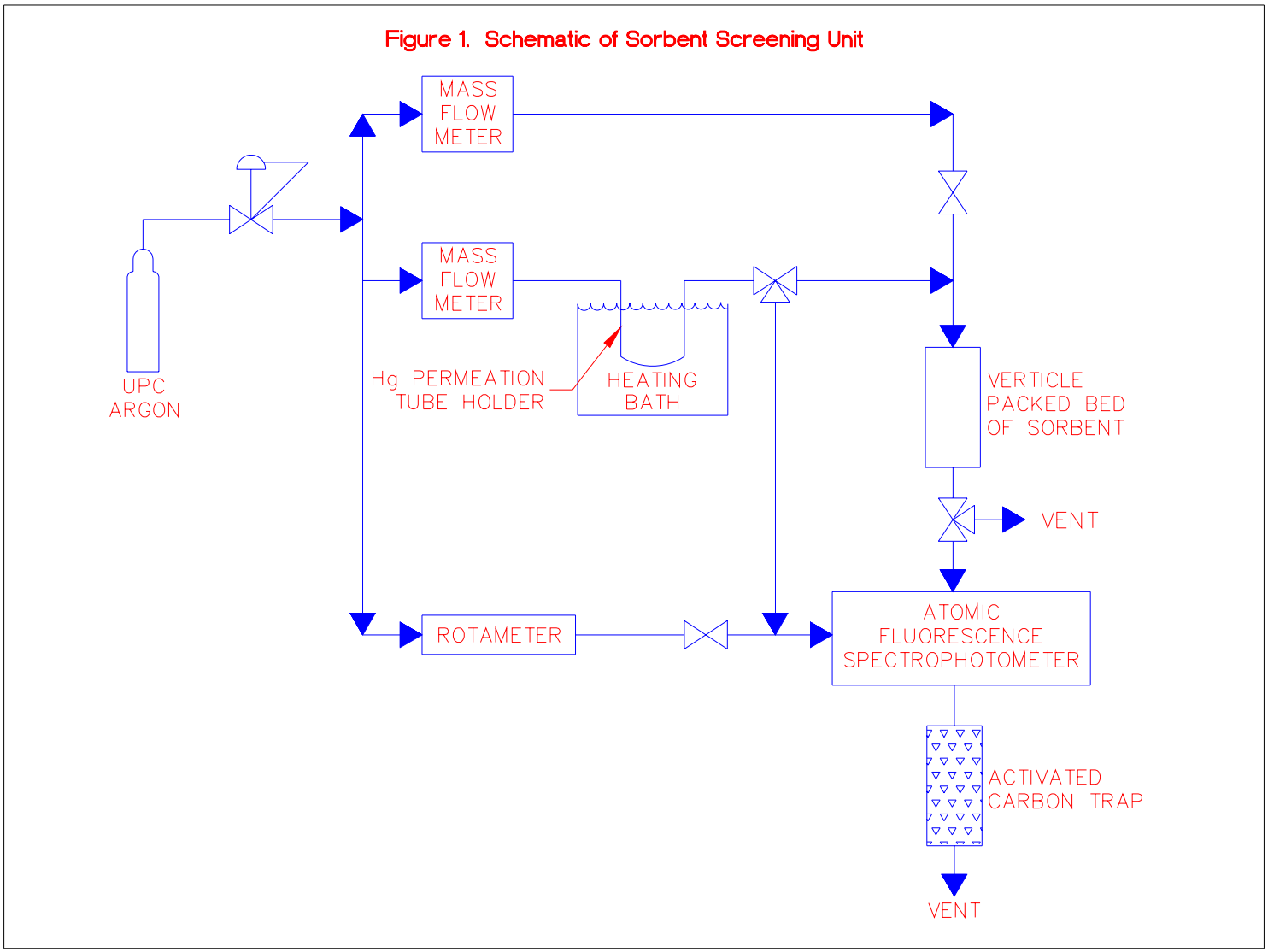
LAB-SCALE SORBENT SCREENING UNIT

Figure 1. Schematic of Sorbent Screening Unit



Parametric Scan In Packed-Bed Reactor

Sorbents/Promoters: Carbons/Sulfur

Temperatures: 140, 280, 350^{o}F

Gases: Simulated Flue Gases

Elemental Mercury Concentration: 270 ppb

Mass of Sorbent: 10 mg

Time: 350 minutes

Mercury Measurement: CVAAS

Coals: Evergreen and Pittsburgh #8

Results: Commercial Carbons

Sorbent	Capacity (mg/g)	Temp (ºF)
FluePac AC	0.89	280
Darco AC	1.60	280
Insul AC	1.96	280
Insul AC	0.19	400
S-AC-1	1.55	280
S-AC-2	1.39	280

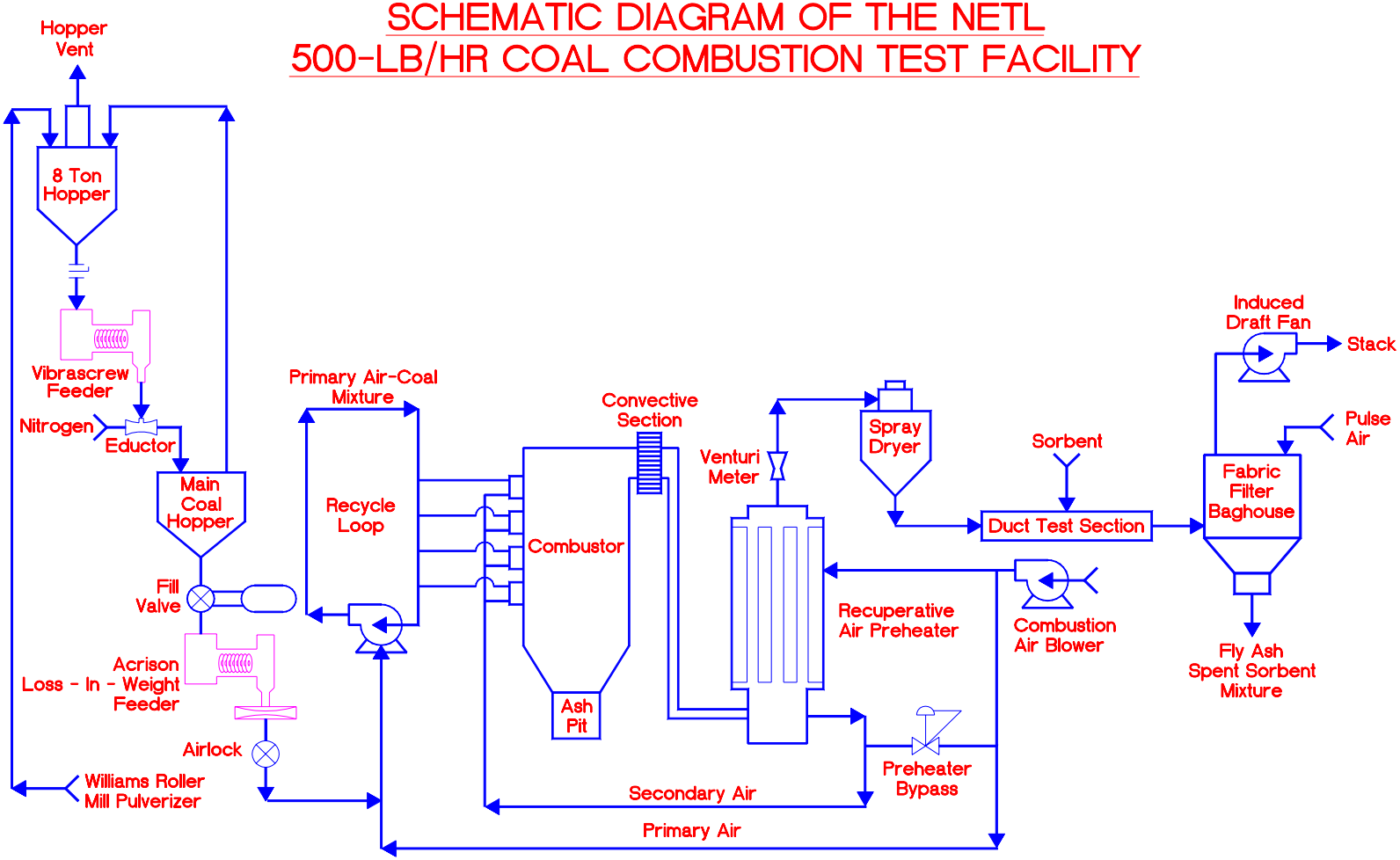
- Unpromoted carbons display good capacity
- Adsorption favored by low temperature
- Sulfur promotion does not increase capacity

Results: Thief Sorbents

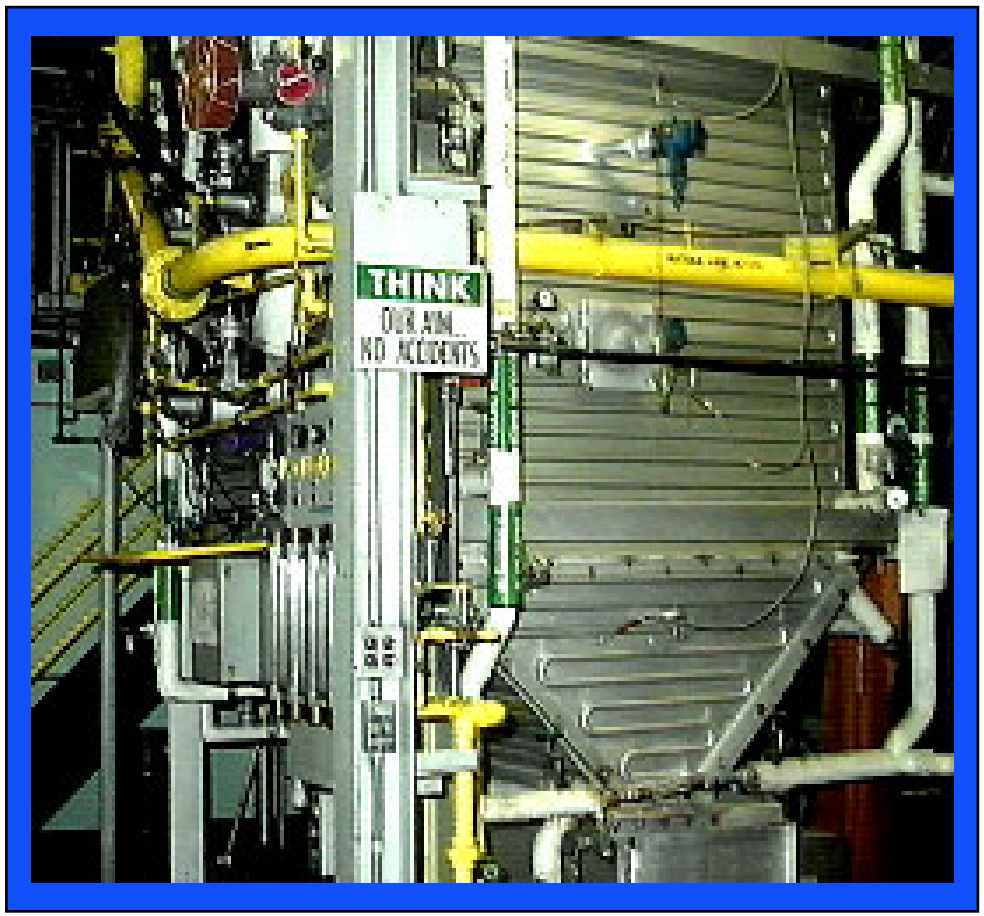
Sorbent	Capacity (mg/g)	Temp (ºF)
Evergreen-Port 2	2.03	280
Pittsburgh #8-Port 2	1.38	280

- Partially combusted coal, produced in-situ and removed from furnace by lance (“thief”)
- Similar capacity to activated carbon
- Cheaper than activated carbons

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



500 LB/HR PILOT COMBUSTOR AND PULSE JET FABRIC FILTER



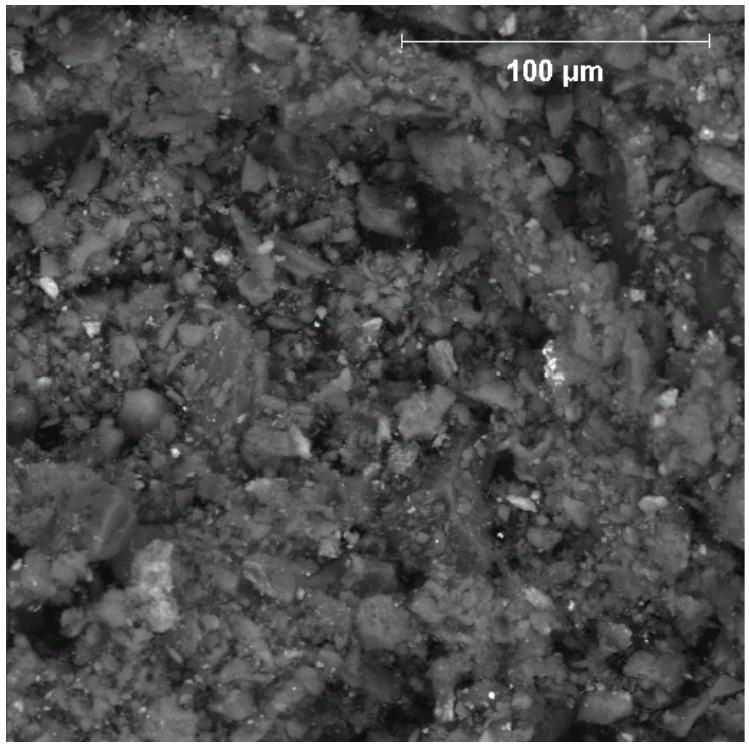

RETURN

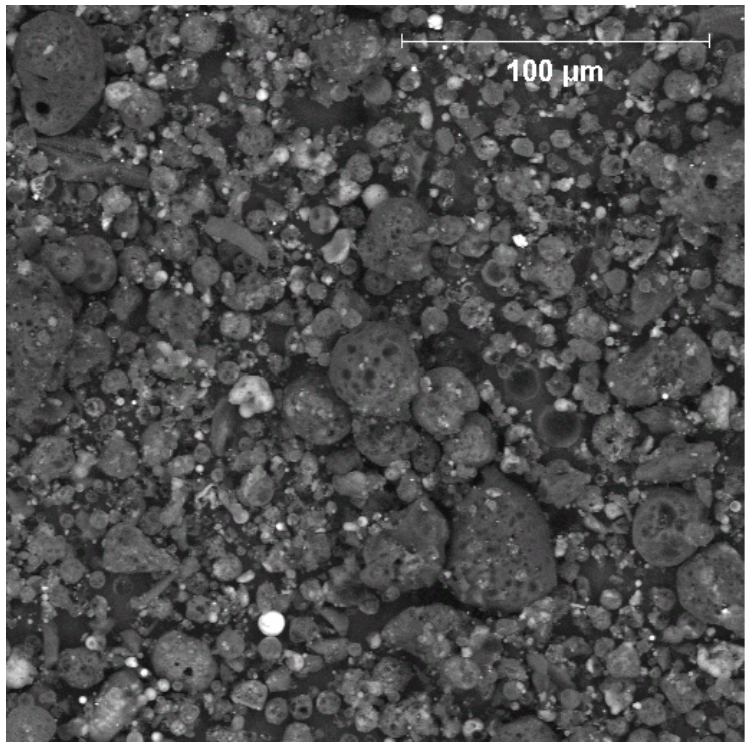

RECYCLE

Comparison of Sorbent (Evergreen)

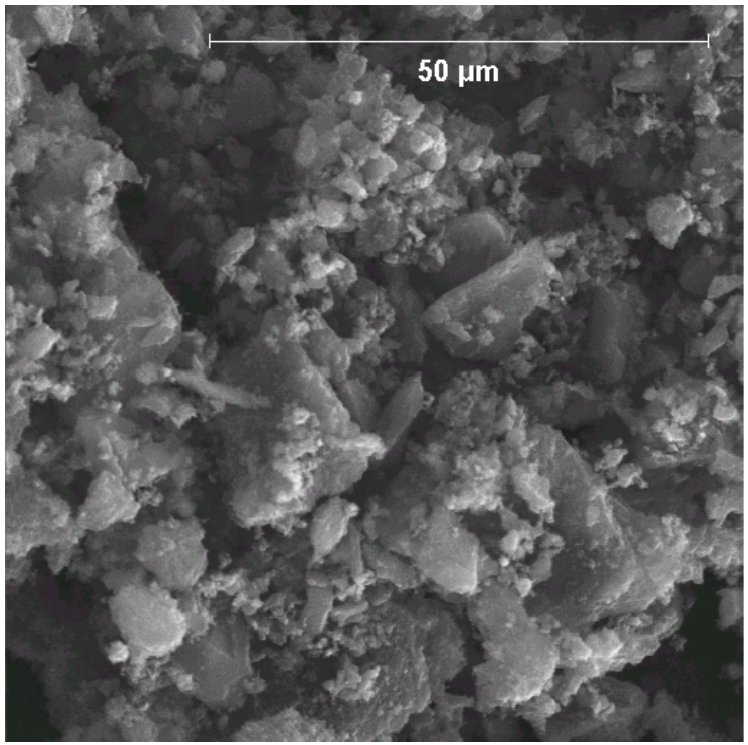
Parameter	*CERF Sample*	*500-lb/hr Sample*	*Activated Carbon*
BET, m^2/g	31.2	69.1	481
Carbon Content, wt%	49.8	63.2	66.5
Hg Capacity, mg/g	2.03	1.80	1.61

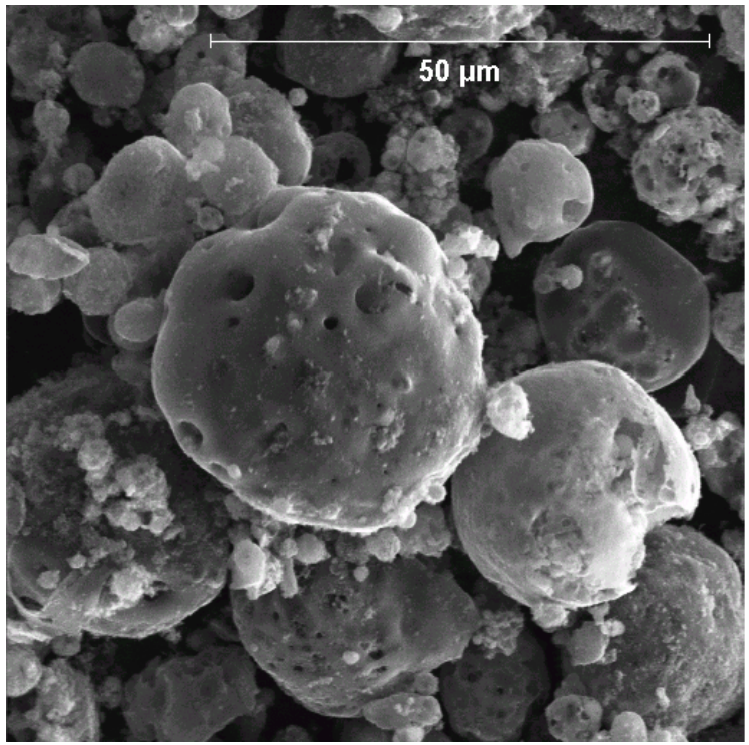
Norit Darco versus Thief Sample (100micron)





Norit Darco versus Thief Sample (50 micron)

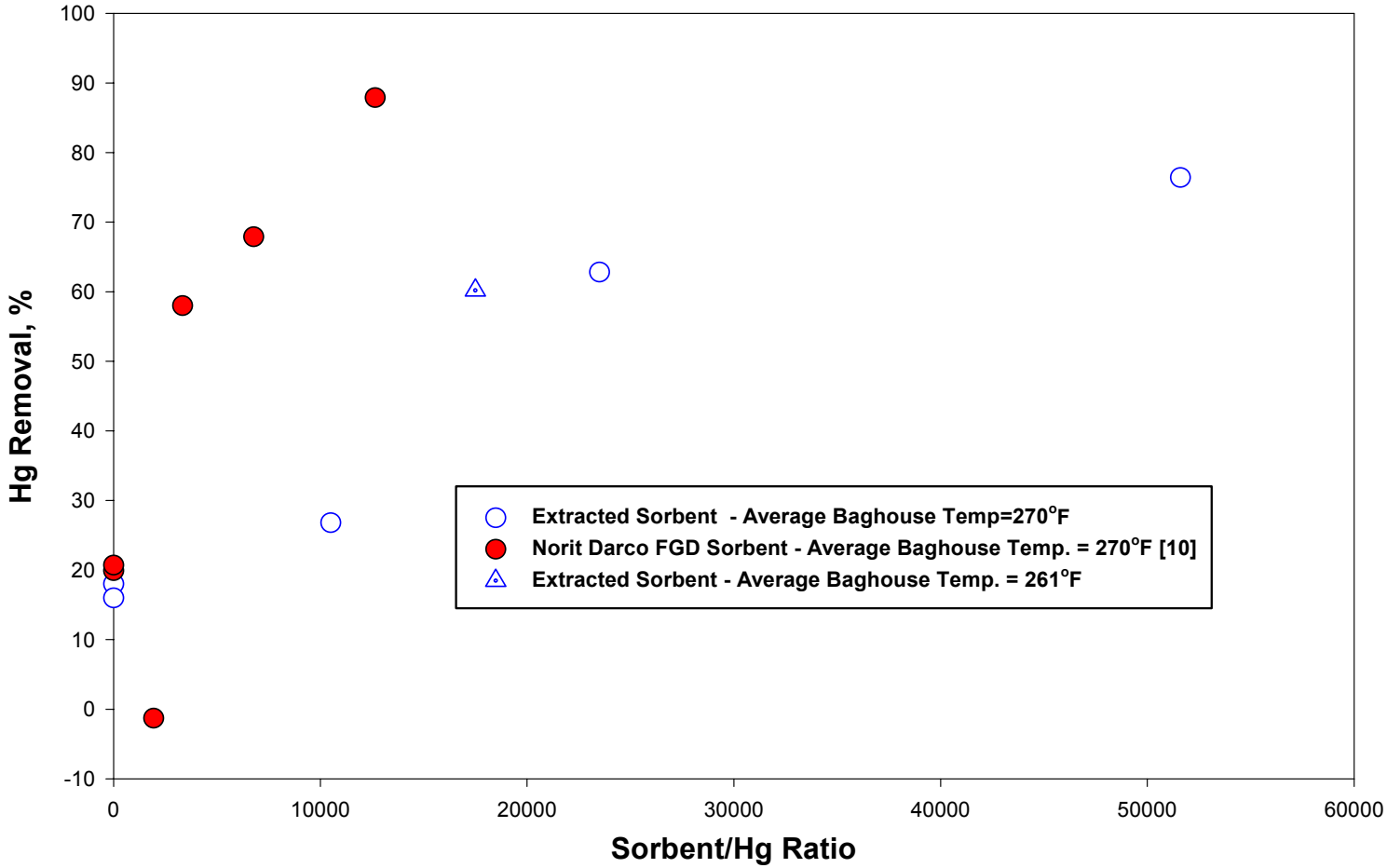




Typical 500-lb/hr Combustor Operating Conditions With Evergreen Coal

- **Coal flow: 360-lb/hr**
- **Duct gas composition:**
  - 7.2% O_2
  - 12.1% CO_2
  - 4.9% H_2O
  - 528ppm SO_2
  - 400ppm NO_x
  - Hg-oxidized 161-µg/min
  - Hg-elemental 23-µg/min
- **Inlet duct temperature: 300°F**
- **Outlet duct temperature: 280°F**
- **Average baghouse temperature: 270°F**
- **Ash loading: 23.8-lb/hr**

Comparison of the Effectiveness of Darco FGD and Thief Sorbent (Evergreen)



Preliminary Data for PRB Coal

Sample	Carbon Content, wt %	Sorbent Injection, lb/mmacf	System Mercury Removal, %
Thief	87-91	14.1	57
Thief	75-84	11.5	82
Thief	50-65	2.3	92
Darco	66.5	2.1	91

CONCLUSIONS

- **An alternate technique to activated carbon injection for Hg removal has been proposed.**
- **Process involves extracting partially combusted coal from the combustor and re-injecting downstream of the air preheater.**
- **As compared to activated carbon, partially combusted coal extracted near burner has:**
  - similar carbon content
  - lower surface area
  - similar elemental mercury capacity

CONCLUSIONS (cont'd)

- Test results indicate that the technique is promising on the pilot scale.
- Optimization in actual combustor requires best extraction location (modeling with coal particle mapping for validation) and good probe design.
- Economics appears favorable for near term goal.
- Technique patented.

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The GP-254 Process For Photochemical Removal of Mercury From Flue Gas

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August 12, 2003

Background: GP-254 Process

Discovery

- Sorbent Development
- UV Measurement of Mercury
- AFS
- Unwanted Red-Brown Stains
- Mercuric Oxide
- Serendipity

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)
- Analytical 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

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}

Photochemical Oxidations

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

Relevant Overall Reactions

$$Hg + 2\ O_2 + 253.7\ nm\ light \rightarrow HgO + O_3$$

$$Hg + HCl + 253.7\ nm\ light \rightarrow HgCl + 1/2\ H_2$$

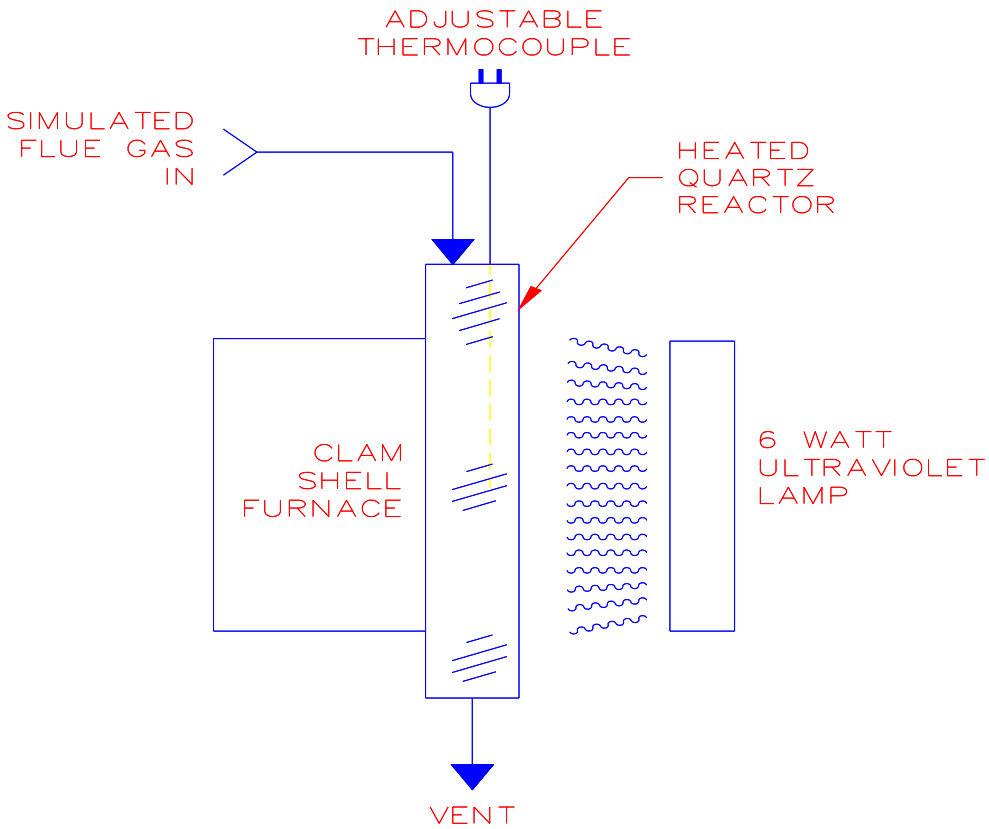
$$Hg + H_2O + 253.7\ nm\ light \rightarrow HgO + H_2$$

$$Hg + CO_2 + 253.7\ nm\ light \rightarrow HgO + CO$$

- Interferes with UV-Based CEMs
- Potential Removal Method

NETL

LAB-SCALE PHOTOREACTOR



Experimental Parameters

- Quartz Photoreactor, 6 Watt UV Lamp
- **Temperatures:** 80°F, 280°F, 350°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	T (°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 Ozone (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

Conclusions: Photochemical Oxidation

Potential For Better Performance

- Other Oxidants (HCl, H_2O) in Flue Gas
- Promising Process Economics
- Potential For Multi-Pollutant Control
- Pilot-Scale Data Needed
- Low Rank Coals Are of Particular Interest

Plans For FY04

Bench-Scale Photoreactor

- Slipstream of Flue Gas From 500-lb/hr Pilot
- Temperature: 280ºF - 350ºF
- 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