

# The Thief Process for Mercury Removal from Flue Gas



Evan J. Granite, Mark C. Freeman,  
Richard A. Hargis, William J. O'Dowd,  
Henry W. Pennline NETL  
and Brian S. Higgins Mobotec USA

**United States Department of Energy  
National Energy Technology Laboratory  
Mercury Control Technology Conference  
Pittsburgh, PA  
December 2006**



---

# Thief Process

- **Alternative to activated carbon injection (ACI)**
- **Extraction of partially combusted coal from furnace & re-injection downstream of preheater**
- **Recent results show similar removals to ACI**
- **Licensed to Mobotec USA May 2005**
- **Further development through collaborative research efforts**
- **Utility pilot tests shortly**



# Regulatory Drivers

- **EPA Announcement March 15, 2005**
- **Clean Air Mercury Rule**
- **Several States Requiring Stricter Reductions**
- **70-90% Removal Requirement**
- **Phased in Over Several Years**



# Fossil Energy Program Goals

## Develop more effective mercury control options

- **Cost-effective and high level of mercury removal**
- **Meet long-term IEP program goal of 90% mercury reduction at cost reduction of 25-50%**



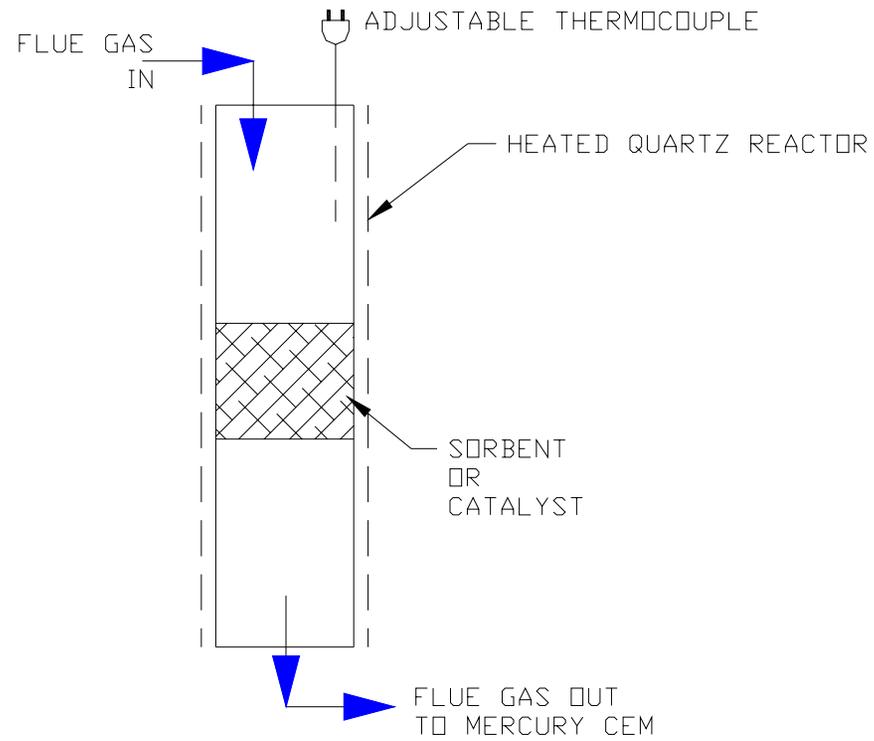
# Technical Challenges

## *Mercury is Difficult to Capture*

- Low concentration
- Can exist as  $\text{Hg}^0$
- Harsh conditions of coal-derived flue gas
- Competitive adsorption / poisoning
- Low sorbent reactivity
- Hg is semi-noble metal



# NETL BENCH-SCALE PACKED BED REACTOR

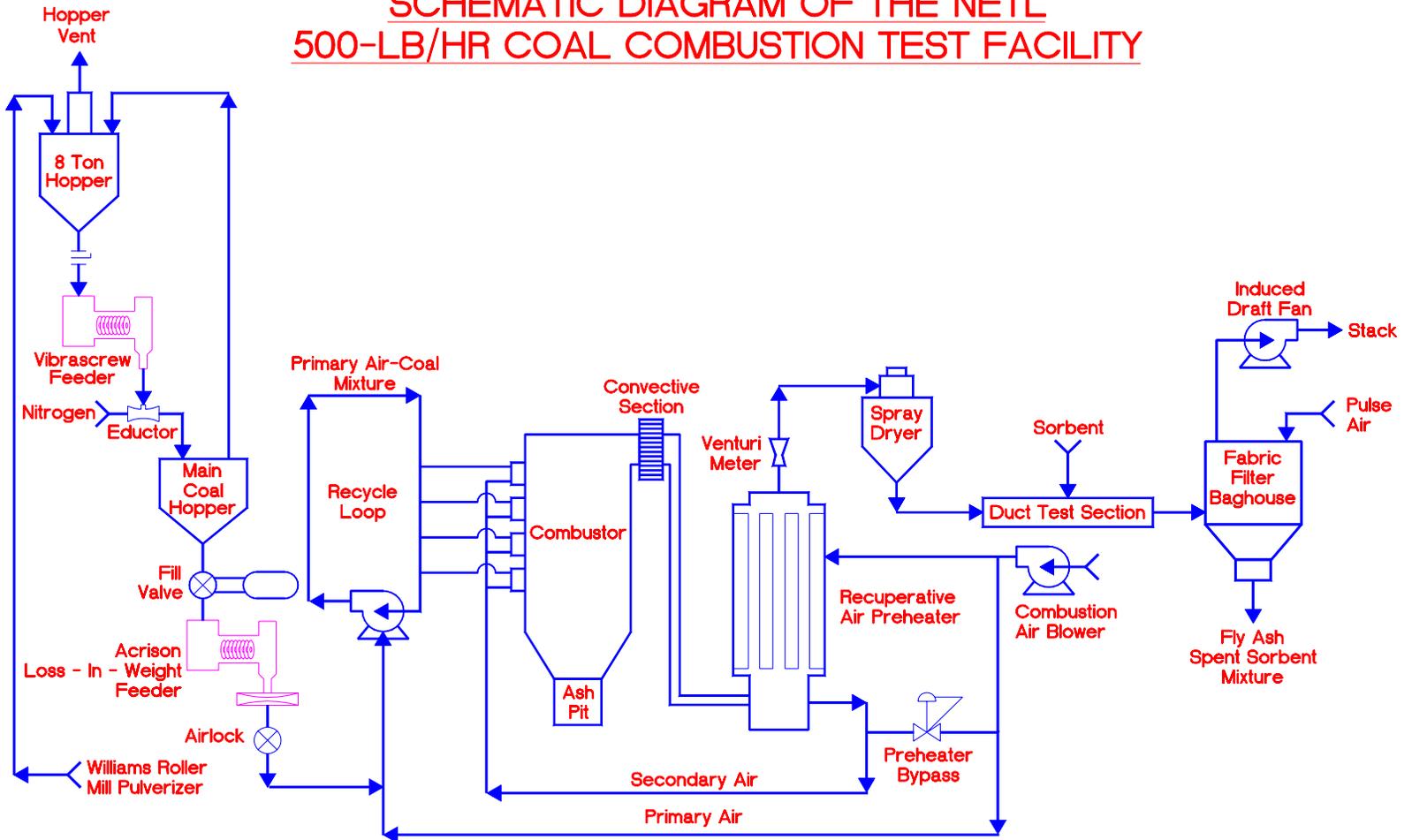


# Bench-Scale Packed Bed Reactor

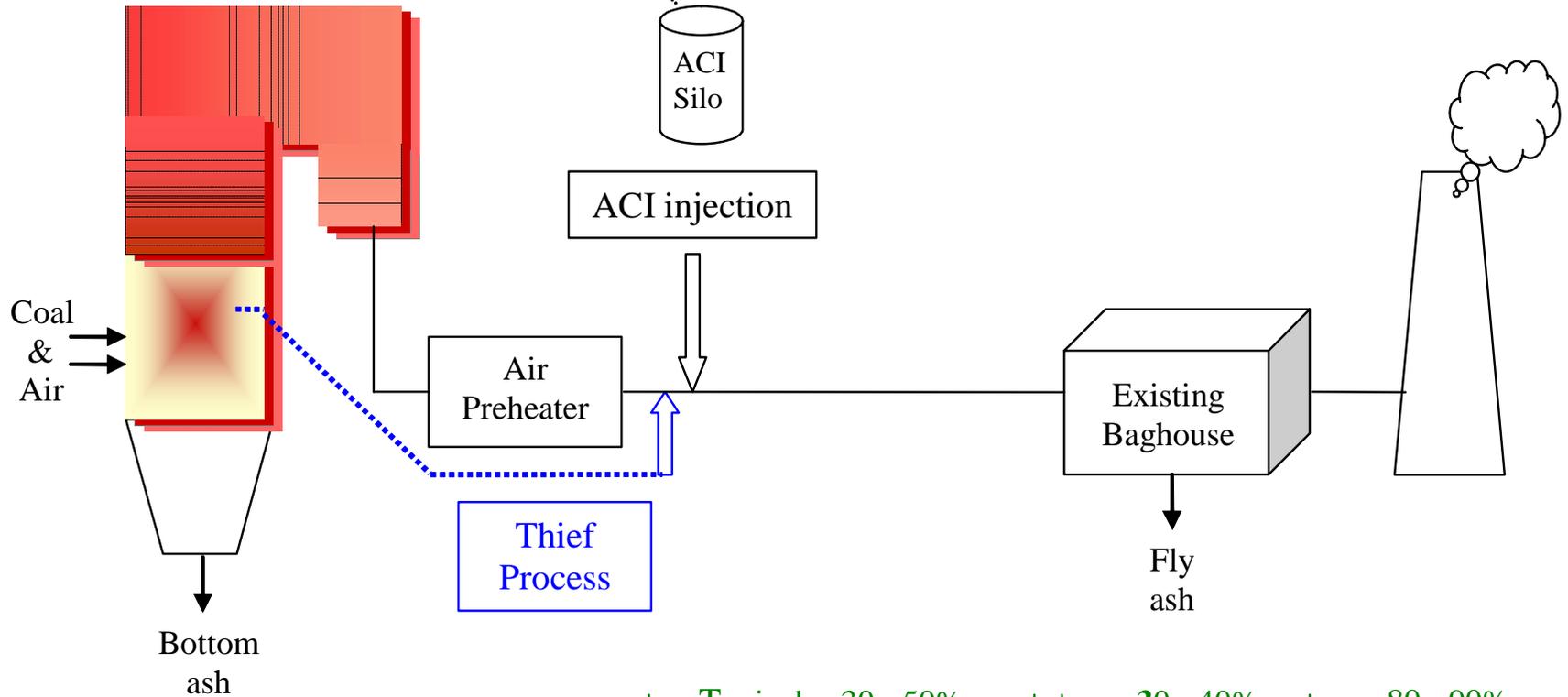
- **1/2-inch OD by 12-inch long quartz tube**
- **100 mg of sorbent**
- **Temperature: 280°F - 320°F**
- **Gas Composition: slipstream of PRB or PRB/Bituminous particulate-free flue gas**
- **Flow-rate: 8 liters/min**
- **Sir Galahad CEM: inlet/outlet mercury**



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



# Thief Process and ACI Technology



Thief Process

Some general guidelines for Hg removal performance for lower levels of sorbent injection at ~ 2 - 4 lb/MMacf

Typical ~ 30 - 50%

In-Duct Hg Removal

~ 30 - 40%

Hg Removal Across BH

~ 80 - 90%  
Total Hg Removal Goal

# Lab Results: Commercial Carbons

<u>Sorbent</u>	<u>Capacity (mg/g)</u>	<u>Temp (°F)</u>
FluePac AC	0.89	280
Darco AC	1.60	280
<b>Insul AC</b>	<b>1.96</b>	<b>280</b>
<b>Insul AC</b>	<b>0.19</b>	<b>400</b>
<b>S-AC-1</b>	<b>1.55</b>	<b>280</b>
<b>S-AC-2</b>	<b>1.39</b>	<b>280</b>

## Physical Adsorption Favored By Low Temperature

- Unpromoted carbons display good capacity
- Sulfur promotion does not increase capacity
- Cost of sulfur addition is not justified

# Lab Results: Thief Sorbents

<u>Sorbent</u>	<u>Capacity (mg/g)</u>	<u>Temp (°F)</u>
Thief-1	2.19	280
Thief-2	1.80	280
Thief-3	1.38	280

## Promising Carbon Sorbents

- Cheaper than activated carbons
- Large removals displayed in lab and pilot tests
- Partially combusted coal, produced in-situ
- Removal from furnace via lance (“Thief”)

# Initial Bench-Scale Results

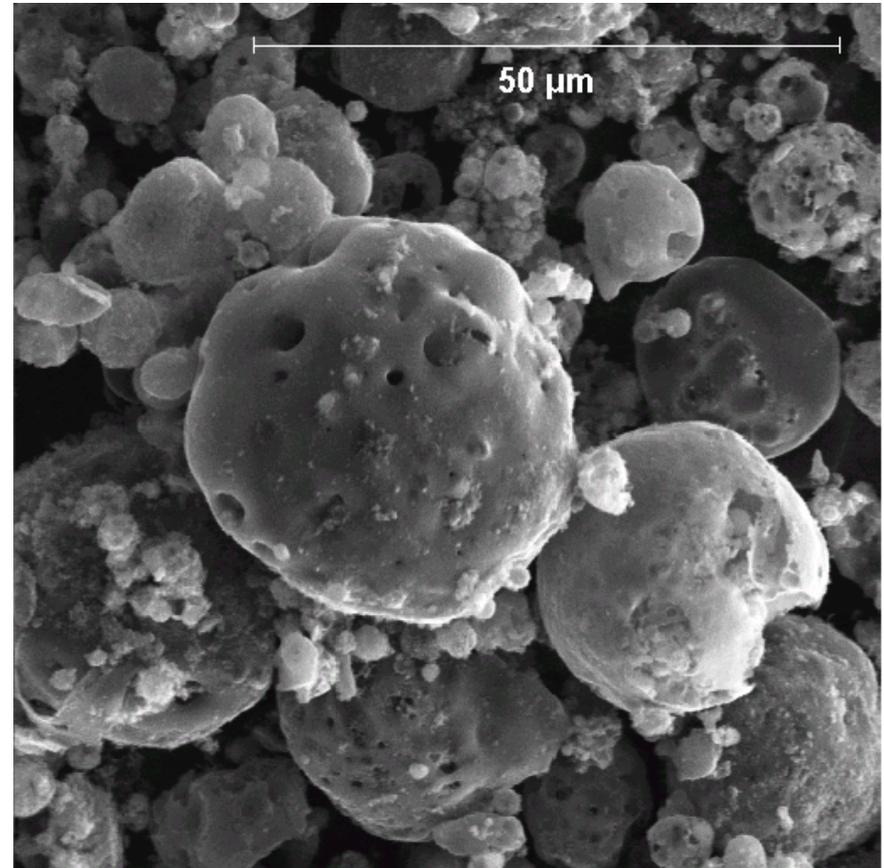
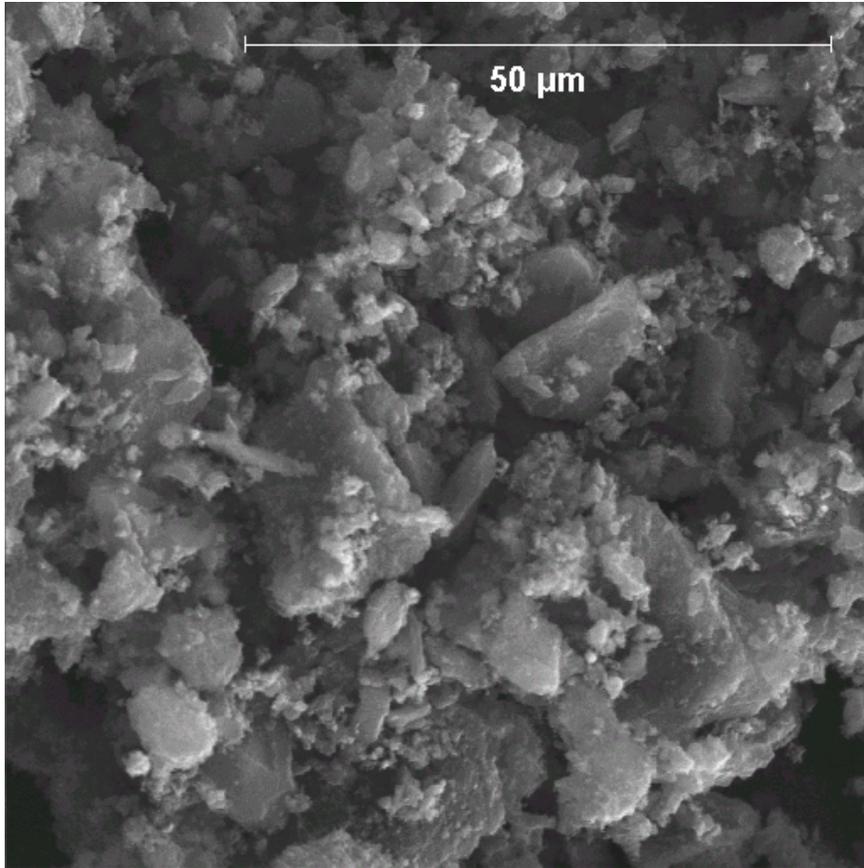
<u>Sorbent</u>	<u>5% Breakthrough (min)</u>
Darco AC	120
Thief	60
Thief-HCl	90
Fly Ash	$\leq 10$

---

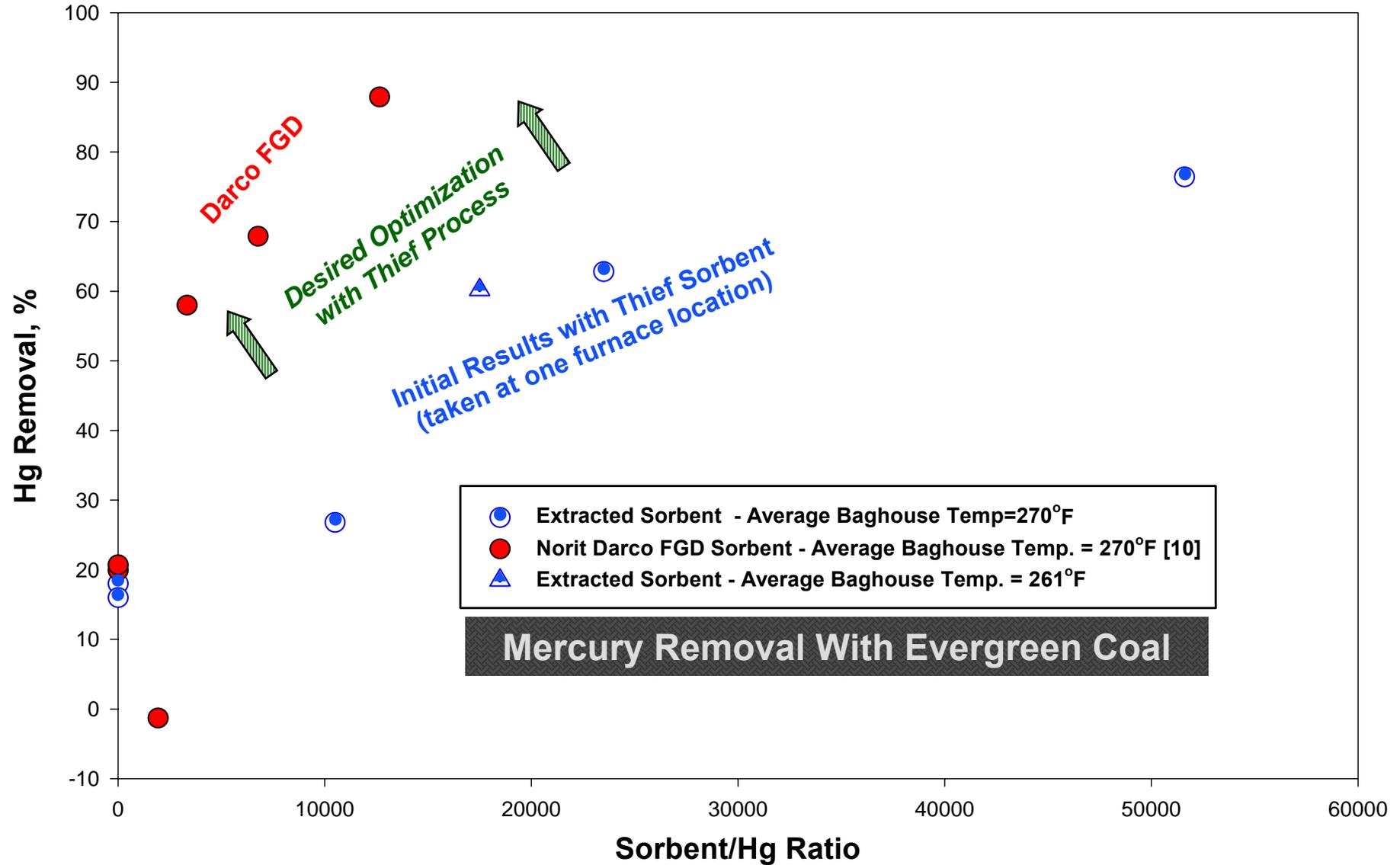
# **Coal: Activated Carbon Precursor**

- **Contains Numerous Reactive Moieties**
- **Enormous Concentration Relative to Hg**
- **Conventional AC Manufacture Harsh**
- **High Temperature and Long Residence Time**
- **High Surface Area**
- **Lose or Passivate Reactive Species**
- **O, S, Se, Te, Cl, Br, I, and Metal Oxides**
- **Likely Retained on Surface for Thief Carbons**

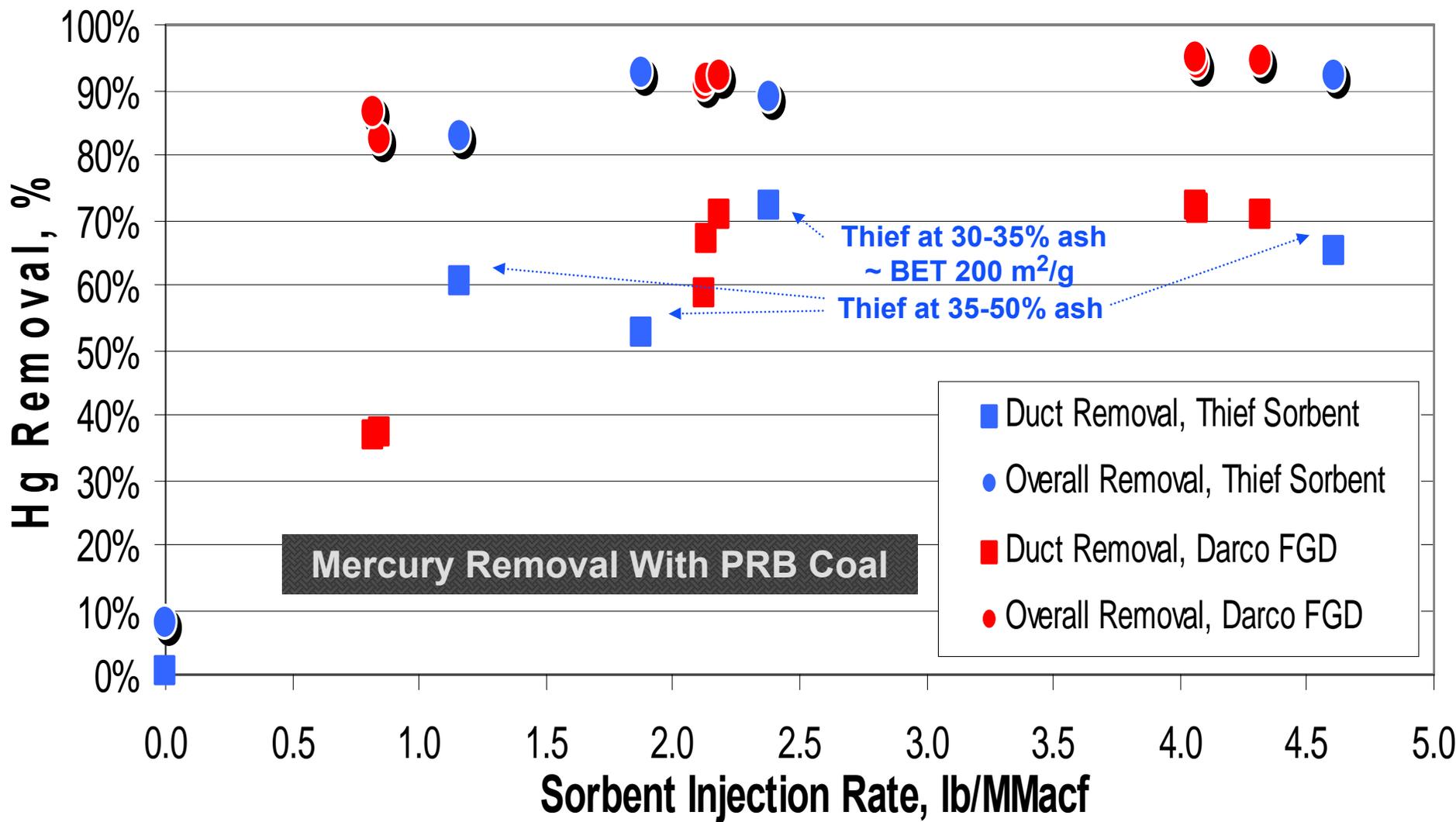
# Norit Darco Versus Thief Sample (50 micron)



# Initial Mercury Removal Results - Darco FGD versus Thief Sorbent



# Mercury Removal Results - Darco FGD versus Thief Sorbent



---

# Heat Rate Penalties

- **Heating Value Extracted Solids & Gas**
- **Sensible Heat Loss When Cooling Solids & Gas**
- **Heat Transfer from Furnace Gas to Small High Temperature Thief Probe**
- **Can Be Minimized by Use of Heat Exchanger**



# Parasitic Power Requirements

- **Fan Power for Extraction of Sorbent & Gas**
- **Fan Power for Reinjection of Sorbent**
- **Pneumatic Injection if Thief Sorbent Stored**
- **Pulverizer Power for Make-up Coal**
- **Circulation of Any Heat Exchanger Fluids**
- **Incremental ID Fan Requirements for Additional Flue Gas Associated With Make-up Coal**

---

# Thief Carbons

- High BET Surface Areas
- Large Iodine Numbers
- Between 80-250 m<sup>2</sup>/g
- Approaching SA of Commercial AC
- Cheaper than Commercial AC
- Comparable Mercury Capacity/Reactivity

## Cost Estimate for Thief Carbons

- \$90-\$200/ton
- \$500-\$3000/ton for AC



---

# Conclusions: Thief Process

## Thief sorbents exhibit high capacity

- Lab, bench, & pilot-scale tests
- Capacities comparable to AC
- Lower cost carbon
- Small parasitic power requirements
- Minor heat rate penalties
- Commercial potential
- Further development by Mobotec USA



---

# Application 2: Thief Carbon Catalysts

- **Simple Strategy → Oxidation of Hg**
- **Enhance Capture in Scrubbers**
- **Improve Capture in Particulate Control Device**
- **ESP or Baghouse**



---

# Thief Carbon Catalysts

## Advantages

- **Cheaper than Precious Metals or Activated Carbons**
- **Easy to Impregnate**
- **Cheap Enough to Be Throw-Away Catalyst**
- **Bench-Scale Results**



# Results: Thief Catalyst

## NETL 500-lb/hr Pilot Combustion Facility

- Catalyst: HCl-Treated Thief Carbon
- Mass: 100 mg
- Mercury Concentration: 10  $\mu\text{g}/\text{Nm}^3$  Total
- Mercury Concentration: 8  $\mu\text{g}/\text{Nm}^3$  Elemental
- 6 hrs On-Line
- 75% Oxidation of Mercury
- Level of Oxidation Increases With Time
- High Level of Oxidation Demonstrated

