The Thief Process for Mercury Removal from Flue Gas

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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

- Patent issued February 2003

- Licensed to Mobotec USA May 2005
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%
- Must be better than ACI
Technical Challenges

*Mercury is Difficult to Capture*

- Low concentration
- Can exist as Hg$^0$
- Harsh conditions of coal-derived flue gas
- Competitive adsorption / poisoning
- Low sorbent reactivity
- Hg is semi-noble metal
ACI for Mercury Removal

- Benchmark technology but has drawbacks for flue gas application
- General adsorbent
- Limited temperature range
- Sequestration
- High sorbent to Hg ratio (3,000:1 to 100,000:1)
- Contacting methods
- Expensive: $1,000 - 3,000/ton
- 500 MW_e power plant: $0.5-10 MM/yr
- Potential market of $10 billion/year
Project Objectives

**Develop Cost Effective Sorbents**

- Alternatives to activated carbon
- Identify novel sorbent candidates
- Commercialization of Thief Process
NETL BENCH-SCALE PACKED BED REACTOR

FLUE GAS IN

ADJUSTABLE THERMOCOUPLE

HEATED QUARTZ REACTOR

SORBENT OR CATALYST

FLUE GAS OUT TO MERCURY CEM
Bench-Scale Packed Bed Reactor

- ½-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
Some general guidelines for Hg removal performance for lower levels of sorbent injection at ~ 2 - 4 lb/MMacf

- Typical ~ 30 - 50%
- ~ 30 - 40%
- ~ 80 - 90% Total Hg Removal Goal

Thief Process and ACI Technology
500 LB/HR PILOT COMBUSTOR AND PULSE JET FABRIC FILTER
# Lab Results: Commercial Carbons

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Capacity (mg/g)</th>
<th>Temp (ºF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FluePac AC</td>
<td>0.89</td>
<td>280</td>
</tr>
<tr>
<td>Darco AC</td>
<td>1.60</td>
<td>280</td>
</tr>
<tr>
<td>Insul AC</td>
<td>1.96</td>
<td>280</td>
</tr>
<tr>
<td>Insul AC</td>
<td>0.19</td>
<td>400</td>
</tr>
<tr>
<td>S-AC-1</td>
<td>1.55</td>
<td>280</td>
</tr>
<tr>
<td>S-AC-2</td>
<td>1.39</td>
<td>280</td>
</tr>
</tbody>
</table>

**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

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<tr>
<th>Sorbent</th>
<th>Capacity (mg/g)</th>
<th>Temp (°F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thief-1</td>
<td>2.19</td>
<td>280</td>
</tr>
<tr>
<td>Thief-2</td>
<td>1.80</td>
<td>280</td>
</tr>
<tr>
<td>Thief-3</td>
<td>1.38</td>
<td>280</td>
</tr>
</tbody>
</table>

Extraordinary Carbon Sorbents

- Dramatically 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

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>5% Breakthrough (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Darco AC</td>
<td>120</td>
</tr>
<tr>
<td>Thief</td>
<td>60</td>
</tr>
<tr>
<td>Thief-HCl</td>
<td>90</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>≤ 10</td>
</tr>
</tbody>
</table>
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

- Darco FGD
- Desired Optimization with Thief Process
- Initial Results with Thief Sorbent (taken at one furnace location)

- Extracted Sorbent - Average Baghouse Temp=270°F
- Norit Darco FGD Sorbent - Average Baghouse Temp. = 270°F [10]
- Extracted Sorbent - Average Baghouse Temp. = 261°F

Mercury Removal With Evergreen Coal
Mercury Removal Results - Darco FGD versus Thief Sorbent

Mercury Removal With PRB Coal

Thief at 30-35% ash ~ BET 200 m²/g
Thief at 35-50% ash

Duct Injection Rate, lb/MMacf

Sorbent Injection Rate, lb/MMacf

Duct Removal, Thief Sorbent
Overall Removal, Thief Sorbent
Duct Removal, Darco FGD
Overall Removal, Darco FGD
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$^2$/g
- Approaching SA of Commercial AC
- Far Cheaper than Commercial AC

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 than AC
- Small parasitic power requirements
- Minor heat rate penalties
- Excellent commercial potential
- Further development by Mobotec USA
Acknowledgements

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• Tom Feeley
• Dave Wildman
• Bob Kleinmann