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Short communication

The thief process for mercury removal from flue gas

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Abstract

The Thief Process is a cost-effective variation to activated carbon injection (ACI) for removal of mercury from flue gas. In this scheme, partially combusted coal from the furnace of a pulverized coal power generation plant is extracted by a lance and then re-injected into the ductwork downstream of the air preheater. Recent results on a 500-lb/h pilot-scale combustion facility show similar removals of mercury for both the Thief Process and ACI. The tests conducted to date at laboratory, bench, and pilot-scales demonstrate that the Thief sorbents exhibit capacities for mercury from flue gas streams that are comparable to those exhibited by commercially available activated carbons. A patent for the process was issued in February 2003. The Thief sorbents are cheaper than commercially-available activated carbons; exhibit excellent capacities for mercury; and the overall process holds great potential for reducing the cost of mercury removal from flue gas. The Thief Process was licensed to Mobotec USA, Inc. in May of 2005.

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1. Introduction

The United States Environmental Protection Agency has issued a regulation for the reduction of mercury emissions from coal-fired power plants (The Clean Air Mercury Rule). With EPA's Clean Air Mercury Rule, and several states promulgating their own regulations, the need exists for a low cost mercury removal process that can be applied to coal-burning power plants. Activated carbon injection (ACI) is projected to be the most commonly employed technique for the removal of mercury from flue gas. However, a notable drawback in the use of activated carbon for mercury capture in power plant flue gas is the annual operating cost. Activated carbons are expensive, ranging in price from \$500 to \$3,000 per ton. The resulting annual cost of activated carbon for mercury clean-up at a typical 500-MW_e coal-burning power plant is projected to be around one million dollars.

Many technologies are being developed for the control of mercury emissions from coal-fired power plants (Feeley

et al., 2003). These methods employ sorbents, catalysts, scrubbing liquors, flue gas or coal additives, combustion modification, barrier discharges, and ultraviolet radiation for the removal of mercury from flue gas streams (Benson et al., 2005; Diaz-Somoano et al., 2005; Eswaran and Stenger, 2005; Feeley et al., 2003; Granite and Pennline, 2002; Granite et al., 2000; Hargis et al., 2000; Hargis et al., 2001; Lee et al., 2004; Niksa and Fujiwara, 2005; O'Dowd et al., 2004). Because of its relative simplicity and proven successful application for the incinerator market, most of the research has focused upon the injection of activated carbon sorbents for the adsorption of mercury. However, it is noted that incinerator flue gases often contain much greater concentrations of both chlorine and mercury compared to coal-derived flue gases. These factors facilitate the removal of mercury by activated carbons introduced into incinerator flue gases.

The Thief Process forms carbon sorbents in-situ (Granite et al., 2004, 2005; Pennline et al., 2002, 2003; The license of the Thief Process). A partially-combusted coal is withdrawn from the furnace after a brief residence time (in or near the flame). The carbonaceous material can be continuously withdrawn from the furnace and then injected

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1 into the ductwork upstream of the existing particulate
 3 collection device. In another variation, the sorbent can be
 5 injected downstream of the plant particulate collection
 7 device but upstream of a particulate collection device
 9 dedicated solely to the sorbent. In other versions of the
 11 process, Thief sorbent can be withdrawn and stored for
 13 later use. The surface area of the Thief sorbents can be
 15 comparable to commercially available activated carbons.
 17 The surface area and reactivity towards mercury are
 19 dependent upon where the solid is withdrawn from the
 21 furnace, as well as the withdrawal method employed. A
 23 schematic of the Thief Process is shown in Fig. 1. The
 25 purpose of the experimentation presented here is to
 27 determine the important parameters in optimizing the
 29 Thief Process, and thereby further reduce the costs for
 31 removal of mercury from coal-derived flue gases.

19 2. Experimental apparatus

21 The lab-scale packed bed reactor is a 1/4-inch outer
 23 diameter (1/6-inch inner diameter) by 20-inch long
 25 cylindrical quartz tube held in a vertical position.
 27 Typically, 10 milligram (mg) of 200/325-mesh (45–75- μ m)
 29 sorbent is placed in the center of the tube and is supported
 31 by 50 mg of quartz wool. The carrier gas for the elemental
 33 mercury can be argon, nitrogen, air, or a simulated flue gas.
 35 When the carrier gas is argon, an on-line atomic
 37 fluorescence spectrophotometer monitors the elemental
 39 mercury concentration in the inlet and outlet streams of
 41 the reactor. Breakthrough curves and sorbent capacity are
 43 determined from these measurements. For more complex
 45 carrier gases, sorbent capacity is determined off-line by
 47 analyzing the spent sorbent (after 350 min of exposure to

the simulated flue gas) with a cold vapor atomic absorption
 spectrophotometer.

The simulated flue gas used in these experiments
 contains carbon dioxide (16%), oxygen (5%), sulfur
 dioxide (2000 ppm), nitric oxide (500 ppm) and nitrogen
 (balance). The concentration of mercury was 270 ppb. The
 flow rate of simulated flue gas through the packed bed was
 60 ml/min. The operating temperature range for the lab-
 scale packed bed reactor is from ambient temperature to
 700 °F. During a test, the reactor temperature and the
 concentration of elemental mercury in the inlet gas are held
 constant. Additional information on the lab-scale facilities
 is detailed in other papers (Granite and Pennline, 2002;
 Granite et al., 2000; O'Dowd et al., 2004).

The bench-scale packed bed reactor is a 1/2-inch outer
 diameter by 12-inch long quartz tube. A schematic of the
 bench-scale packed bed reactor is shown in Fig. 2. The
 mass of sorbent is typically 100-mg supported on quartz
 wool. The quartz wool has been demonstrated to be inert
 towards mercury. The temperatures of the flue gas stream
 were between 280 and 320 °F. Gas compositions were
 slipstreams of flue gas supplied by the 500-lb/h pilot-scale
 combustion facility. Either Powder River Basin (PRB) or
 blends of PRB/bituminous coal were burned in the pilot
 unit. A particulate-free flue gas stream was supplied to the
 packed bed reactor at a flow rate of 8 L/min. A PS
 Analytical Sir Galahad continuous emissions monitor was
 employed to measure the concentrations of mercury
 entering and exiting the packed bed.

The 500-lb/h pilot-scale combustion facility consists of a
 pulverized coal wall-fired furnace equipped with a water
 cooled convection section, a recuperative air heater, spray
 dryer, baghouse, and associated ancillary equipment (fin-
 fan coolers, surge tanks, coal hoppers, blowers, pumps,

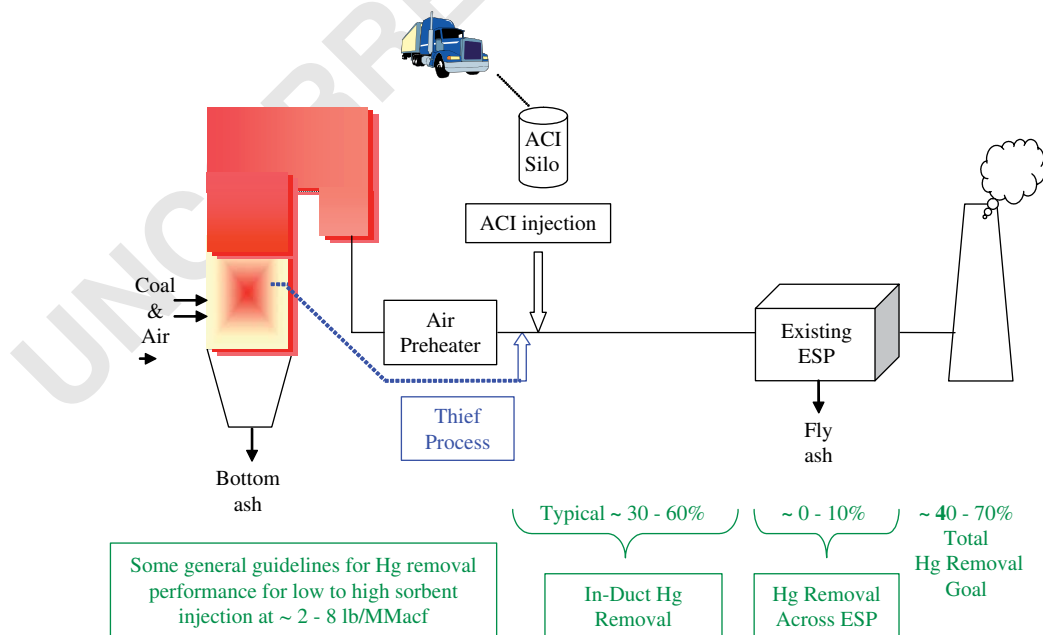


Fig. 1. Thief process vs. ACI.

etc.). The 500-lb/h combustor is an indirect-fired unit. That is, coal is first pulverized off-line in a Williams roller mill, and then transported through a series of hoppers before it is fed by an Acrison weight-loss differential feeder to the combustor. The wall-fired, dry bottom type combustor is

capable of firing both coal and/or natural gas. The combustor's four wall-fired burners are equipped with secondary air registers that can be adjusted to improve combustion. On-line temperature readings, flow measurements and four separate banks of continuous gas analyzers (O_2 , NO_x , CO , SO_2 and CO_2) characterize the overall system operating performance.

A wide range of flue gas temperatures can be obtained at the duct test section, baghouse, and stack. The options for altering the flue gas temperature include indirect cooling by adjusting system operating conditions and/or direct cooling by humidification. Also, sorbent can be injected at one location selected from numerous ports along the duct test section, allowing for a wide range of sorbent in-duct residence times relative to the baghouse and gas sampling locations. A schematic of the 500-lb/h pilot-unit is shown in Fig. 3. Additional information about the pilot unit is presented in several papers (Hargis et al., 2000, 2001; O'Dowd et al., 2004).

3. Results

The capacities for some commercially available activated carbons determined in a lab-scale packed bed reactor are shown in Table 1. Capacities for some of the Thief sorbents are given in Table 2. The measured capacities for both the activated carbons and the Thief sorbents were near 1–2 mg

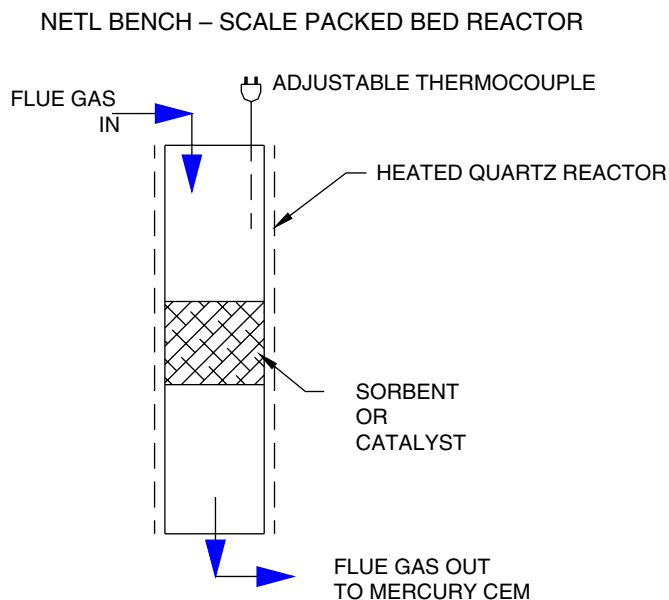


Fig. 2. NETL bench-scale packed bed reactor.

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

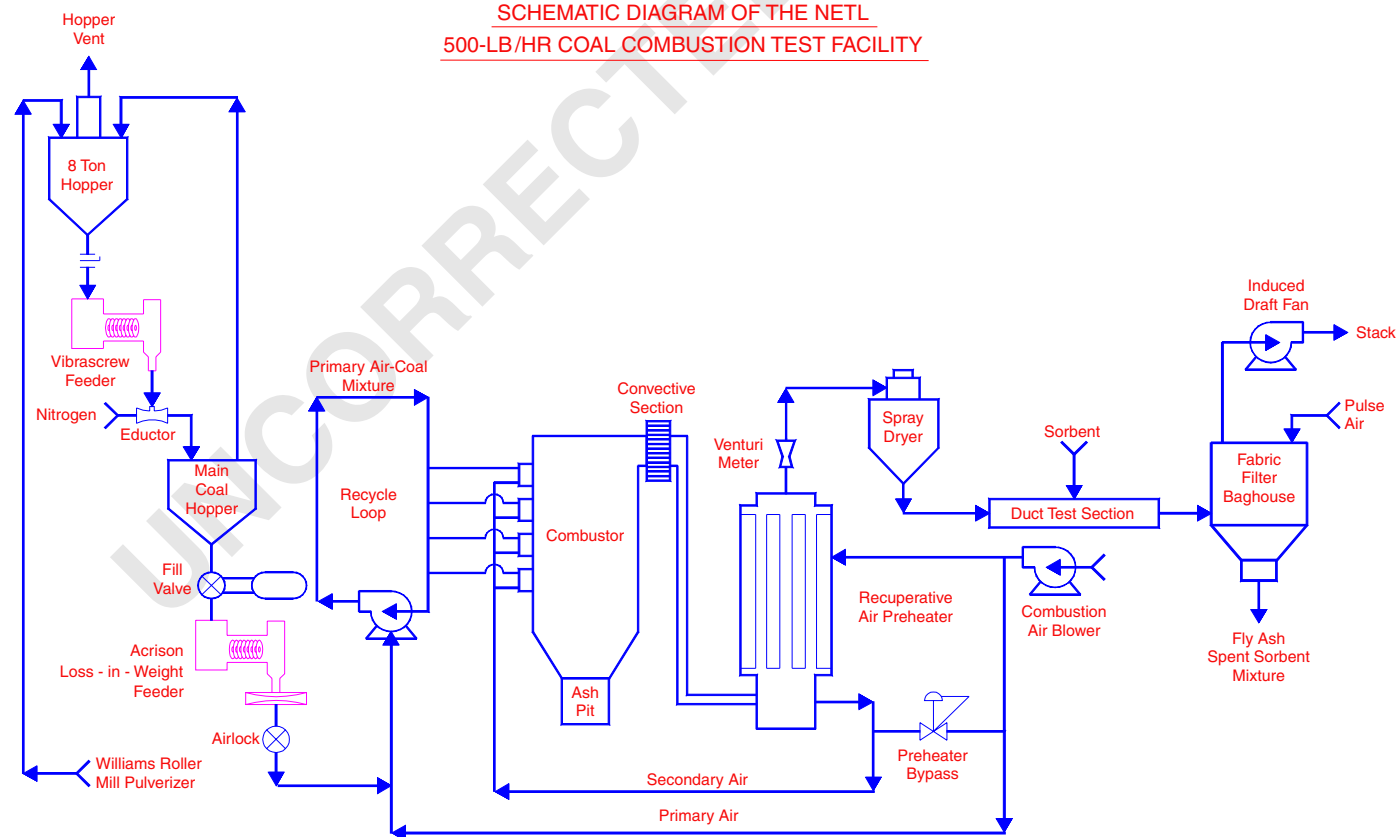


Fig. 3. Schematic diagram of the NETL 500-lb/h coal combustion test facility.

1 Table 1
Laboratory packed bed capacities of commercial carbons

| 3 Sorbent | Capacity (mg/g) | Temperature (°F) |
|--------------|-----------------|------------------|
| 5 FluePac AC | 0.89 | 280 |
| Darco AC | 1.60 | 280 |
| 7 Insul AC | 1.96 | 280 |
| Insul AC | 0.19 | 400 |
| S-AC-1 | 1.55 | 280 |
| 9 S-AC-2 | 1.39 | 280 |

11 Flue gas composition: 16% CO₂, 5% O₂, 2000 ppm SO₂, 500 ppm NO,
270 ppb Hg, balance N₂.
Flow-rate: 60 ml/min.

13 Length of experiment: 350 min exposure of sorbent to simulated flue gas.

15 Table 2
Laboratory packed bed capacities of thief sorbents

| 19 Sorbent | Capacity (mg/g) | Temperature (°F) |
|------------|-----------------|------------------|
| 21 Thief-1 | 2.19 | 280 |
| Thief-2 | 1.80 | 280 |
| Thief-3 | 1.38 | 280 |

23 Flue gas composition: 16% CO₂, 5% O₂, 2000 ppm SO₂, 500 ppm NO,
270 ppb Hg, balance N₂.

25 Flow-rate: 60 ml/min.

Length of experiment: 350 min exposure of sorbent to simulated flue gas.

27 mercury/g sorbent and ranged from 0.19 mg/g for Insul at
29 400 °F to 2.19 mg/g for Thief-1 at 280 °F. The results of the
31 tests outlined in Table 2 showed that the Thief sorbent had
33 mercury sorption capacities of 1.4–2.2 mg/g at 280 °F,
35 which is similar to that found for the Darco FGD-activated
37 carbon. These results suggest that, with excellent gas-solid
39 contact provided by a packed-bed unit, unpromoted
41 carbons display good capacity and sulfur promotion does
43 not significantly increase capacity. Further, it appears that
45 physical adsorption may be involved in the adsorption
47 mechanism, as evidenced by the small capacity displayed
49 by the Insul carbon at 400 °F.

Tests were then conducted on the 500-lb/h unit using the
Thief Process for mercury removal. Sample (sorbent) was
extracted from the combustion chamber and then injected
into the ductwork before the baghouse to remove mercury.
A water-cooled probe was inserted into the 500-lb/h
combustion furnace to collect sorbent, while low-sulfur,
bituminous Evergreen coal was burned. The samples were
then combined, homogenized into a single batch, and then
used as sorbent in subsequent testing with the 500-lb/h
combustion system.

Table 3 presents some of the initial bench-scale packed
bed results. The times for 5% breakthrough are compared
for several sorbents exposed to a slipstream of flue gas
from the pilot-scale unit. The breakthrough tests suggest
initial reactivity towards mercury. The Thief sorbents,
untreated and treated with hydrochloric acid, showed
smaller but comparable breakthrough times as the Darco-
FGD activated carbon.

Table 3
Initial bench-scale packed bed results

| Sorbent | 5% Breakthrough (min) |
|-----------|-----------------------|
| Darco AC | 120 |
| Thief | 60 |
| Thief-HCl | 90 |
| Fly Ash | ≤10 |

Flue gas supplied from 500-lb/h combustion facility.

Flow-rate: 8 L/min.

Temperature: 280 °F.

The results of measured removals across the ductwork
and baghouse are shown in Fig. 4, as well as removals
obtained with Darco FGD activated carbon at similar
conditions. It is noted that there is no significant difference
in the mercury removals shown at 261 and 270 °F. The
process yielded removals as high as 76% when injecting the
Thief sorbent upstream of the baghouse. Although it is
apparent that the removals observed during these first
pilot-scale tests are lower for a given sorbent-to-mercury
mass ratio relative to the Darco FGD, the process had not
been optimized yet in terms of sorbent extraction location.

More recent pilot-scale tests of the Thief Process
conducted with the 500-lb/h combustion facility are shown
in Fig. 5. A low-chlorine, Powder River Basin subbitumi-
nous coal was burned in the pilot unit for the tests depicted
in Fig. 5. The average baghouse temperature for these tests
was approximately 270 °F. High levels of mercury removal
were obtained in-flight by both the commercially available
activated carbon and the Thief sorbent. The results of
measured removals across the baghouse are shown in Fig.
5, as well as removals obtained with Darco FGD activated
carbon at similar conditions. The process yielded removals
as high as 93% when injecting Thief sorbent upstream of
the baghouse. The levels of mercury capture were similar
for both the Thief and Darco carbons for the same sorbent
injection rate. For these more recent tests with PRB coal,
the process had been improved in terms of determining the
best location to extract Thief solids from the furnace.

4. Discussion

The Thief sorbents have comparable capacities to
commercially available activated carbons for mercury
despite possessing modest BET surface areas in compar-
ison. Coal contains an abundant number of moieties such
as halogens, oxygen, sulfur, and metal oxides which can
react with and capture mercury (Granite et al., 2000). The
concentrations of these species are enormous relative to the
concentration of mercury present within the coal. Acti-
vated carbons are often manufactured from coal. The
production of activated carbons from coal can entail
extensive, long residence time heat treatments. The coal is
reacted with oxygen, carbon dioxide, or steam in order to
generate porosity and large internal surface areas. The long
residence times used in the manufacture of activated

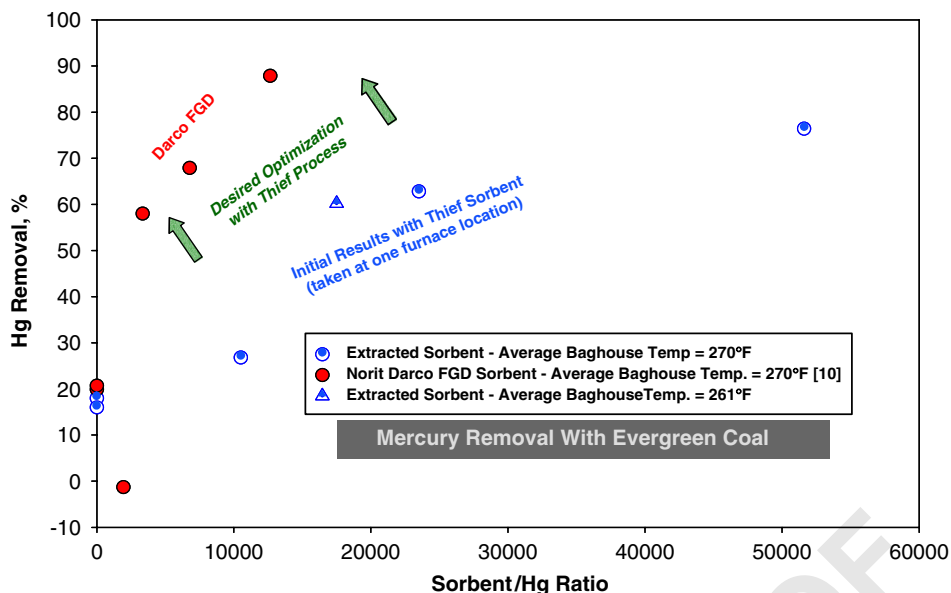


Fig. 4. Initial Mercury Removal Results: Darco FGD vs. Thief Sorbent.

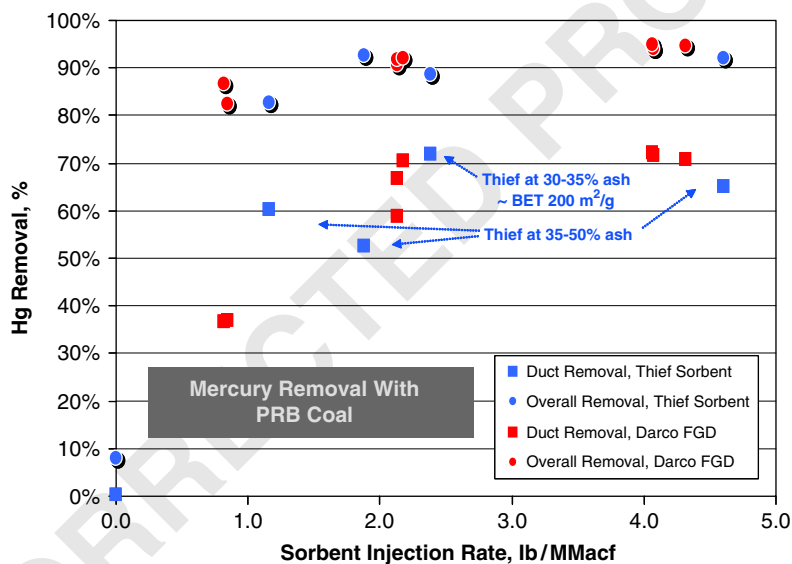


Fig. 5. Mercury Removal Results: Darco FGD vs. Thief Sorbent.

carbons will result in the loss of halogens, sulfur, oxygen, and metal oxides from the carbon. It is speculated that the Thief carbons, formed using a much shorter heat treatment, allows for the formation and retention of reactive surface entities containing oxygen, halogen, and sulfur functional groups, as well as metal oxides for the capture of mercury. In addition, the temperature treatment protocol may be as important as the residence time for the production of carbon sorbents.

It is also speculated that the Thief carbons are promoted in-situ by flue gas constituents during the withdrawal procedure from the furnace. The Thief carbons displayed excellent capacities for the removal of elemental mercury from argon, in stark contrast to the poor capacities

displayed by commercially available unpromoted activated carbons under these conditions (Granite et al., 2000). This suggests the presence of reactive surface functional groups on Thief carbons.

It is likely that the Thief carbons possess a good pore structure distribution between mesopores and micropores, as well as halogen and oxygen surface functional groups which enhance capacity for mercury (Maroto-Valer et al., 2005). Initial extractions during the combustion of Evergreen bituminous coal yielded sorbents having BET surface areas around $70 \text{ m}^2/\text{g}$. The optimization of the lance (Thief) probe location also significantly increases the BET surface area of the extracted Thief sorbents. Extractions at different locations during the combustion of the subbitu-

1 minous Powder River Basin coal yielded carbons having
 2 BET surface areas higher than 200 m²/g. The test results for
 3 the low-chlorine, Powder River Basin subbituminous coal
 4 are especially encouraging because of the known difficulties
 5 in capturing mercury from low-rank coal-derived flue
 6 gases.

7 The process equipment for the Thief Process is an
 8 assembly of small components for a furnace slipstream. A
 9 small high temperature probe (lance or Thief) is used to
 10 extract solids and associated gases from the furnace.

11 The thermal heat rate penalties include: 1. combustible
 12 heat loss based upon the heating value of extracted Thief
 13 solids; 2. sensible heat loss when cooling extracted Thief
 14 solids and gas prior to reinjection upstream of the
 15 particulate collection device; and 3. incident heat transfer
 16 from the furnace gas (boiler) to the small high temperature
 17 Thief probe. It should be noted that the latter two
 18 considerations can be minimized by using a heat exchan-
 19 ger. Parasitic power requirements are: 1. fan power for
 20 extraction of Thief sorbent and gas from the furnace and
 21 reinjection into the downstream location; 2. pneumatic
 22 injection if Thief sorbent is stored and handled in a manner
 23 similar to activated carbon; 3. pulverizer power required
 24 for make-up coal from the thermal heat penalty; 4.
 25 parasitic power associated with circulating any heat
 26 exchanger cooling media; and 5. incremental ID fan
 27 requirements from additional flue gas associated with
 28 make-up coal.

29 A key driver in the process is the engineering strategy for
 30 managing a small series of heat rate penalties in lieu of
 31 making sorbent purchases. The Thief Process entails the
 32 extraction of between 0.1–0.5% of the furnace gas inside
 33 the boiler, depending upon the desired sorbent injection
 34 rate and mercury removal level.

35 The mass of solids extracted from the furnace is
 36 exceedingly small in comparison to the mass of coal being
 37 burned. Therefore, the heat rate penalty is estimated at less
 38 than 0.3% for a 500 MW_e power plant burning Powder
 39 River basin subbituminous coal. Parasitic power require-
 40 ments are also estimated as less than 0.05%. These energy
 41 penalties are for a sorbent injection rate of 5 lb/MM acf,
 42 and are reduced to less than 0.2% at injection rates of
 43 1–2 lb/MM acf. The cost for the Thief sorbents is estimated
 44 to be in the range of \$90–\$200/ton. As in the case for
 45 injection of commercially available activated carbons, the
 46 impacts upon the fly ash, manifested as increases in
 47 unburned carbon, are calculated to be minimal. An
 48 advantage of the Thief Process is that no external sorbents
 49 or chemicals are introduced into the power plant.

51 5. Conclusions

52 The tests conducted to date at laboratory, bench, and
 53 pilot-scales demonstrate that the Thief sorbents exhibit
 54 high capacities for mercury from flue gas streams. For the
 55 most part, the experimentally determined capacities for
 56 mercury are comparable to those exhibited by commer-

57 cially available activated carbons. The process demon-
 58 strated high levels of mercury removal at pilot-scale for a
 59 subbituminous coal. The combined heat rate and parasitic
 60 power penalties associated with the process will be less than
 61 0.4%, and impacts upon the resulting fly ash, manifested
 62 by increases in loss on ignition levels, will be minimal. The
 63 cost for the Thief sorbents is estimated to be in the range of
 64 \$90–\$200/ton. The Thief sorbents are significantly lower in
 65 cost than commercially available activated carbons, and
 66 the process has excellent potential for commercial applica-
 67 tion in removing mercury from coal-derived flue gases.

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93 Disclaimer

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99 References

- 100 Benson, S.A., Laumb, J.D., Crocker, C.R., Pavlish, J.H., 2005.
 101 SCR catalyst performance in flue gases derived from
 102 subbituminous and lignite coals. *Fuel Processing Technology* 86 (5),
 103 577–613.
- 104 Diaz-Somoano, M., Unterberger, S., Hein, K.R.G., 2005. Using Wet-
 105 FGD systems for mercury removal. *J. of Environmental Monitoring* 7
 106 (9), 906–909.
- 107 Eswaran, S., Stenger, H.G., 2005. Understanding mercury conversion in
 108 selective catalytic reduction (SCR) catalysts. *Energy & Fuels* 19 (6),
 109 2328–2334.
- 110 Feeley, T.J., Murphy, J.T., Hoffmann, J.W., Granite, E.J., Renninger,
 111 S.A., 2003. DOE/NETL's Mercury Control Technology Research
 112 Program for Coal-Fired Power Plants, EM.
- 113 Granite, E.J., Pennline, H.W., 2002. Photochemical removal of mercury
 114 from flue gas. *Industrial & Engineering Chemistry Research* 41,
 115 5470–5476.

- 1 Granite, E.J., Pennline, H.W., Hargis, R.A., 2000. Novel sorbents for
mercury removal from flue gas. *Industrial & Engineering Chemistry*
3 Research 39, 1020–1029.
- 3 Granite, E.J., Freeman, M.C., Pennline, H.W., Hargis, R.A., O'Dowd,
W.J., August 2004. The Thief Process for Mercury Removal from Flue
5 Gas. Proceedings of AWMA Mega Symposium, Washington, DC.
- 7 Granite, E.J., Freeman, M.C., Hargis, R.A., O'Dowd, W.J., Pennline,
H.W., April 2005. The Thief Process for Mercury Removal from Flue
Gas. Proceedings of the 30th International Technical Conference on
9 Coal Utilization & Fuel Systems, Clearwater, FL.
- Hargis, R.A., O'Dowd, W.J., Pennline, H.W., September 2000. Mercury
control by injection of activated carbon. Proceedings of 17th
11 International Pittsburgh Coal Conference, Pittsburgh, PA.
- Hargis, R.A., O'Dowd, W.J., Pennline, H.W., March 2001. Pilot-scale
13 research at NETL on sorbent injection for mercury control. Proceedings
of 26th International Technical Conference on Coal Utilization
and Fuel Systems, Clearwater, Florida.
- 15 Lee, C.W., Srivasta, R.K., Ghorishi, S.B., Karwowski, J., Hastings, T.W.,
Hirschi, J., 2004. Investigation of selective catalytic reduction impact
17 on mercury speciation under simulated NO_x emission control
conditions. *J. A&WMA* 54 (12), 1560–1566.
- Maroto-Valer, M.M., Zhang, Y., Granite, E.J., Tang, Z., Pennline, H.W.,
21 2005. Effect of porous structure and surface functionality on mercury
capacity of a fly ash carbon and its activated sample. *Fuel* 84,
105–108.
- 23 Niksa, S., Fujiwara, N., 2005. A predictive mechanism for mercury
oxidation on selective catalytic reduction catalysts under coal-derived
25 flue gas. *J. A&WMA* 55 (12), 1866–1875.
- O'Dowd, W.J., Hargis, R.A., Granite, E.J., Pennline, H.W., 2004. Recent
27 advances in mercury removal technology at the national
energy technology laboratory. *Fuel Processing Technology* 85,
533–548.
- 29 Pennline, H.W., Granite, E.J., Freeman, M.C., Hargis, R.A., O'Dowd,
W.J., November 2002. A technique to control mercury from flue gas.
AICHE National Meeting, Indianapolis, IN.
- 31 Pennline, H.W., Granite, E.J., Freeman, M.C., Hargis, R.A., O'Dowd,
W.J., 2003. Thief process for the removal of mercury from flue gas. US
33 Patent 6,521,021, February 18, 2003.
- The Clean Air Mercury Rule is available on the USEPA website:
35 www.epa.gov/air/mercuryrule
- The license of the Thief Process was announced on the USDOE website:
37 www.fe.doe.gov/news/techlines/2005/tl_thief_process.html

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