

**Proceedings of the 22<sup>nd</sup> Annual International Pittsburgh Coal Conference**  
**Paper 5-2**  
**Pittsburgh, PA**  
**September 12-15, 2005**

## **The Thief Process for Mercury Removal from Flue Gas**

Evan J. Granite\*, Mark C. Freeman, Richard A. Hargis, William J. O'Dowd, and  
Henry W. Pennline

United States Department of Energy  
National Energy Technology Laboratory  
P.O. Box 10940 MS 58-106  
Pittsburgh, PA 15236-0940

Tel (412) 386-4607; fax (412) 386-6004; e-mail [evan.granite@netl.doe.gov](mailto:evan.granite@netl.doe.gov)

### **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/hr 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. Independent verification of the sorbent activity at a pilot-plant that uses a slipstream from a Wisconsin utility has been accomplished. A patent for the process was issued in February 2003 [1]. 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 [1-5]. The Thief Process was licensed to Mobotec USA, Inc. in May of 2005 [6].

*Keywords:* Mercury; flue gas; sorbent; activated carbon; Thief Process

### **1. Introduction**

The United States Environmental Protection Agency has issued a regulation for the reduction of mercury emissions from coal-fired power plants [7]. 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<sub>e</sub> coal-burning power plant is projected to be around five million dollars.

Many technologies are being developed for the control of mercury emissions from coal-fired power plants [8]. 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 [8-13]. 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. 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 into the ductwork upstream of the existing particulate collection device. In another variation, the sorbent can be injected downstream of the plant particulate collection device but upstream of a particulate collection device dedicated solely to the sorbent. In other versions of the process, Thief sorbent can be withdrawn and stored for later use. The surface area of the Thief sorbents can be comparable to commercially available activated carbons. The surface area and reactivity towards mercury are dependent upon where the solid is withdrawn from the furnace, as well as the withdrawal method employed. A schematic of the Thief Process is shown in Figure 1.

## 2. Experimental Apparatus

The lab-scale packed bed reactor is a ¼-inch outer diameter (1/6-inch inner diameter) by 20-inch long cylindrical quartz tube held in a vertical position. Typically, 10 milligram (mg) of 200/325-mesh (45-75- $\mu\text{m}$ ) sorbent is placed in the center of the tube and is supported by 50 mg of quartz wool. The carrier gas for the elemental mercury can be argon, nitrogen, air, or a simulated flue gas. When the carrier gas is argon, an on-line atomic fluorescence spectrophotometer monitors the elemental mercury concentration in the inlet and outlet streams of the reactor. Breakthrough curves and sorbent capacity are determined from these measurements. For more complex carrier gases, sorbent capacity is determined off-line by 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 [9-11].

The bench-scale packed bed reactor is a ½-inch outer diameter by 12-inch long quartz tube. 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/hr 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 liters/min. A PS Analytical Sir Galahad continuous emissions monitor was employed to measure the concentrations of mercury entering and exiting the packed bed. A schematic of the bench-scale packed bed reactor is shown in Figure 2.

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, 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 Figure 3. Additional information about the pilot unit is presented in several papers [11-13].

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

Tests were then conducted on the 500-lb/hr 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/hr 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/hr 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.

The results of measured removals across the ductwork and baghouse are shown in Figure 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, 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/hr combustion facility are shown in Figure 5. A low-chlorine, Powder River Basin subbituminous coal was burned in the pilot unit for the tests depicted in Figure 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 Figure 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. Additionally, independent verification of the Thief sorbent activity at a pilot-plant that uses a slipstream from a Wisconsin utility has been recently accomplished [3-5].

#### **4. Discussion**

The Thief sorbents have comparable capacities to commercially available activated carbons for mercury despite possessing modest BET surface areas in comparison. Coal contains an abundant number of moieties such as halogens, oxygen, sulfur, and metal oxides which can react with and capture mercury [9]. The concentrations of these species are enormous relative to the concentration of mercury present within the coal. Activated 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 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.

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 [9]. 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 [14]. Initial extractions during the combustion of Evergreen bituminous coal yielded sorbents having BET surface areas around 70 m<sup>2</sup>/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 subbituminous Powder River Basin coal yielded carbons having BET surface areas higher than 200 m<sup>2</sup>/g. The test results for the low-chlorine, Powder River Basin subbituminous coal are especially encouraging because of the known difficulties in capturing mercury from low-rank coal-derived flue gases.

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

The thermal heat rate penalties include: 1. combustible heat loss based upon the heating value of extracted Thief solids; 2. sensible heat loss when cooling extracted Thief solids and gas prior to reinjection upstream of the particulate collection device; and 3. incident heat transfer

from the furnace gas (boiler) to the small high temperature Thief probe. It should be noted that the latter two considerations can be minimized by using a heat exchanger. Parasitic power requirements are: 1. fan power for extraction of Thief sorbent and gas from the furnace and reinjection into the downstream location; 2. pneumatic injection if Thief sorbent is stored and handled in a manner similar to activated carbon; 3. pulverizer power required for make-up coal from the thermal heat penalty; 4. parasitic power associated with circulating any heat exchanger cooling media; and 5. incremental ID fan requirements from additional flue gas associated with make-up coal.

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

The mass of solids extracted from the furnace is exceedingly small in comparison to the mass of coal being burned. Therefore, the heat rate penalty is estimated at less than 0.3% for a 500 MW<sub>e</sub> power plant burning Powder River basin subbituminous coal. Parasitic power requirements are also estimated as less than 0.05%. These energy penalties are for a sorbent injection rate of 5 lb/MM acf, and are reduced to less than 0.2% at injection rates of 1-2 lb/MM acf. The cost for the Thief sorbents is estimated to be in the range of \$90 - \$200/ton. As in the case for injection of commercially available activated carbons, the impacts upon the fly ash, manifested as increases in unburned carbon, are calculated to be minimal. An advantage of the Thief Process is that no external sorbents or chemicals are introduced into the power plant.

## **5. Conclusions**

The tests conducted to date at laboratory, bench, and pilot-scales demonstrate that the Thief sorbents exhibit high capacities for mercury from flue gas streams. For the most part, the experimentally determined capacities for mercury are comparable to those exhibited by commercially available activated carbons. The process demonstrated high levels of mercury removal at pilot-scale for a subbituminous coal. The combined heat rate and parasitic power penalties associated with the process will be less than 0.4%, and impacts upon the resulting fly ash, manifested by increases in loss on ignition levels, will be minimal. The cost for the Thief sorbents is estimated to be in the range of \$90 - \$200/ton. The Thief sorbents are significantly lower in cost than commercially available activated carbons, and the process has excellent potential for commercial application in removing mercury from coal-derived flue gases.

## **Acknowledgements**

The authors thank their colleagues at the National Energy Technology Laboratory for helpful comments and suggestions. Robert Thompson, Deborah Hreha, Bill Garber, Chuck Perry, Jeffrey Palcic, William Brown of Parsons Project Services, Inc. were responsible for the operation of the pilot combustion unit, manual sampling, and analysis of samples. Clement Lacher of the Department of Energy did an outstanding job in the design and assembly of the various probes and lances. Andrew Karash of the Department of Energy did terrific work in managing the pilot unit and mercury analyzers.

## Disclaimer

Reference in this report to any specific commercial process, product or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

## References

1. Pennline, H.W.; Granite, E.J.; Freeman, M.C.; Hargis, R.A.; O'Dowd, W.J. Thief process for the removal of mercury from flue gas, U.S. Patent 6,521,021, Feb. 18, 2003.
2. Pennline, H.W.; Granite, E.J.; Freeman, M.C.; Hargis, R.A.; O'Dowd, W.J. A Technique to Control Mercury from Flue Gas, AIChE National Meeting, Indianapolis, IN, November 2002.
3. Granite, E.J.; Freeman, M.C.; Pennline, H.W.; Hargis, R.A.; O'Dowd, W.J. The Thief Process for Mercury Removal from Flue Gas, Proceedings of AWMA Mega Symposium, Washington, DC, August 2004.
4. Granite, E.J.; Freeman, M.C.; Hargis, R.A.; O'Dowd, W.J.; Pennline, H.W. The Thief Process for Mercury Removal from Flue Gas, Proceedings of the 30<sup>th</sup> International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, April 2005.
5. O'Dowd, W.J.; Freeman, M.C.; Pennline, H.W.; Granite, E.J.; Hargis, R.A.; Karash, A.; Lacher, C. A Technique to Control Mercury from Flue Gas: The Thief Process, Fuel Processing Technology, in preparation.
6. The license of the Thief Process was announced on the USDOE website: [www.fe.doe.gov/news/techlines/2005/tl\\_thief\\_process.html](http://www.fe.doe.gov/news/techlines/2005/tl_thief_process.html)
7. The Clean Air Mercury Rule is available on the USEPA website: [www.epa.gov/air/mercuryrule](http://www.epa.gov/air/mercuryrule)
8. Feeley, T.J.; Murphy, J.T.; Hoffmann, J.W.; Granite, E.J.; Renninger, S.A. DOE/NETL's Mercury Control Technology Research Program for Coal-Fired Power Plants, EM, 2003.
9. Granite, E.J.; Pennline, H.W.; Hargis, R.A. Novel Sorbents for Mercury Removal from Flue Gas, Industrial & Engineering Chemistry Research, 39, 1020-1029, 2000.
10. Granite, E.J.; Pennline, H.W. Photochemical Removal of Mercury from Flue Gas, Industrial & Engineering Chemistry Research, 41, 5470-5476, 2002.
11. O'Dowd, W.J.; Hargis, R.A.; Granite, E.J.; Pennline, H.W. Recent advances in mercury removal technology at the National Energy Technology Laboratory, Fuel Processing Technology, 85, 533-548, 2004.
12. Hargis, R.A.; O'Dowd, W.J.; Pennline, H.W. Pilot-scale research at NETL on sorbent injection for mercury control, Proceedings of 26<sup>th</sup> International Technical Conference on Coal Utilization and Fuel Systems, Clearwater, Florida, March 2001.
13. Hargis, R.A.; O'Dowd, W.J.; Pennline, H.W. Mercury control by injection of activated carbon, Proceedings of 17<sup>th</sup> International Pittsburgh Coal Conference, Pittsburgh, PA, September 2000.
14. Maroto-Valer, M.M.; Zhang, Y.; Granite, E.J.; Tang, Z.; Pennline, H.W. Effect of porous structure and surface functionality on mercury capacity of a fly ash carbon and its activated sample, Fuel, 84, 105-108, 2005.

**Table 1: Laboratory Packed Bed Capacities of Commercial Carbons**

<u>Sorbent</u>	<u>Capacity (mg/g)</u>	<u>Temperature (°F)</u>
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

Flue Gas Composition: 16% CO<sub>2</sub>, 5% O<sub>2</sub>, 2000 ppm SO<sub>2</sub>, 500 ppm NO, 270 ppb Hg, balance N<sub>2</sub>  
Flow-Rate: 60 ml/min

**Table 2: Laboratory Packed Bed Capacities of Thief Sorbents**

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

Flue Gas Composition: 16% CO<sub>2</sub>, 5% O<sub>2</sub>, 2000 ppm SO<sub>2</sub>, 500 ppm NO, 270 ppb Hg, balance N<sub>2</sub>  
Flow-Rate: 60 ml/min

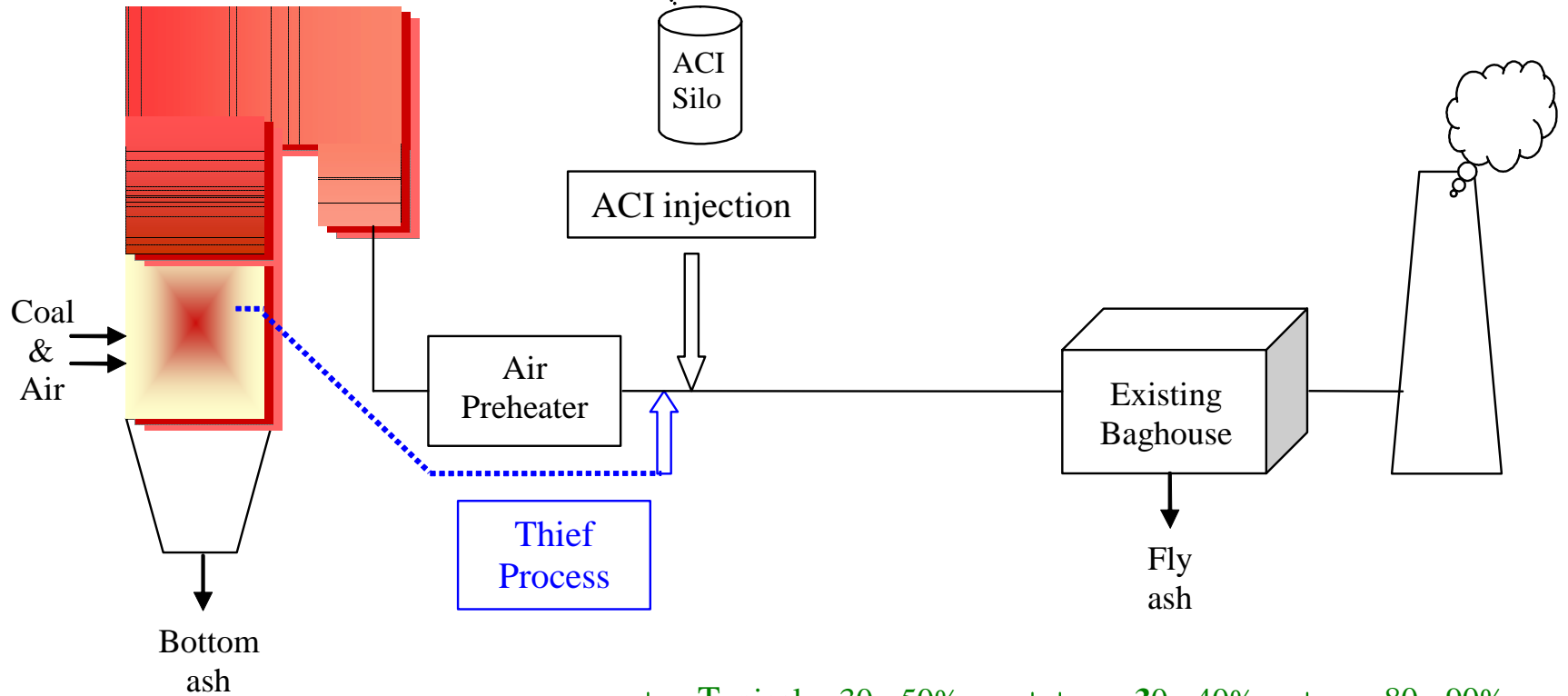
**Table 3: Initial Bench-Scale Packed Bed Results**

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

Flue Gas Supplied from 500-lb/hr Combustion Facility  
Flow-Rate: 8 liters/min  
Temperature: 280°F



# Figure 1. Thief Process vs. ACI



Thief Process

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

Typical ~ 30 - 50%

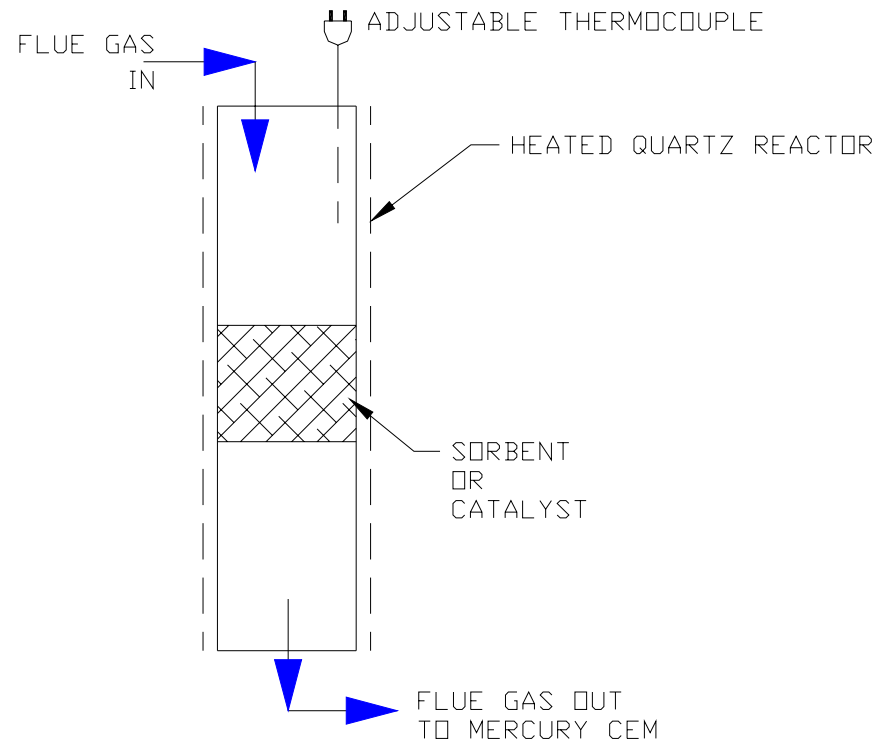
In-Duct Hg Removal

~ 30 - 40%

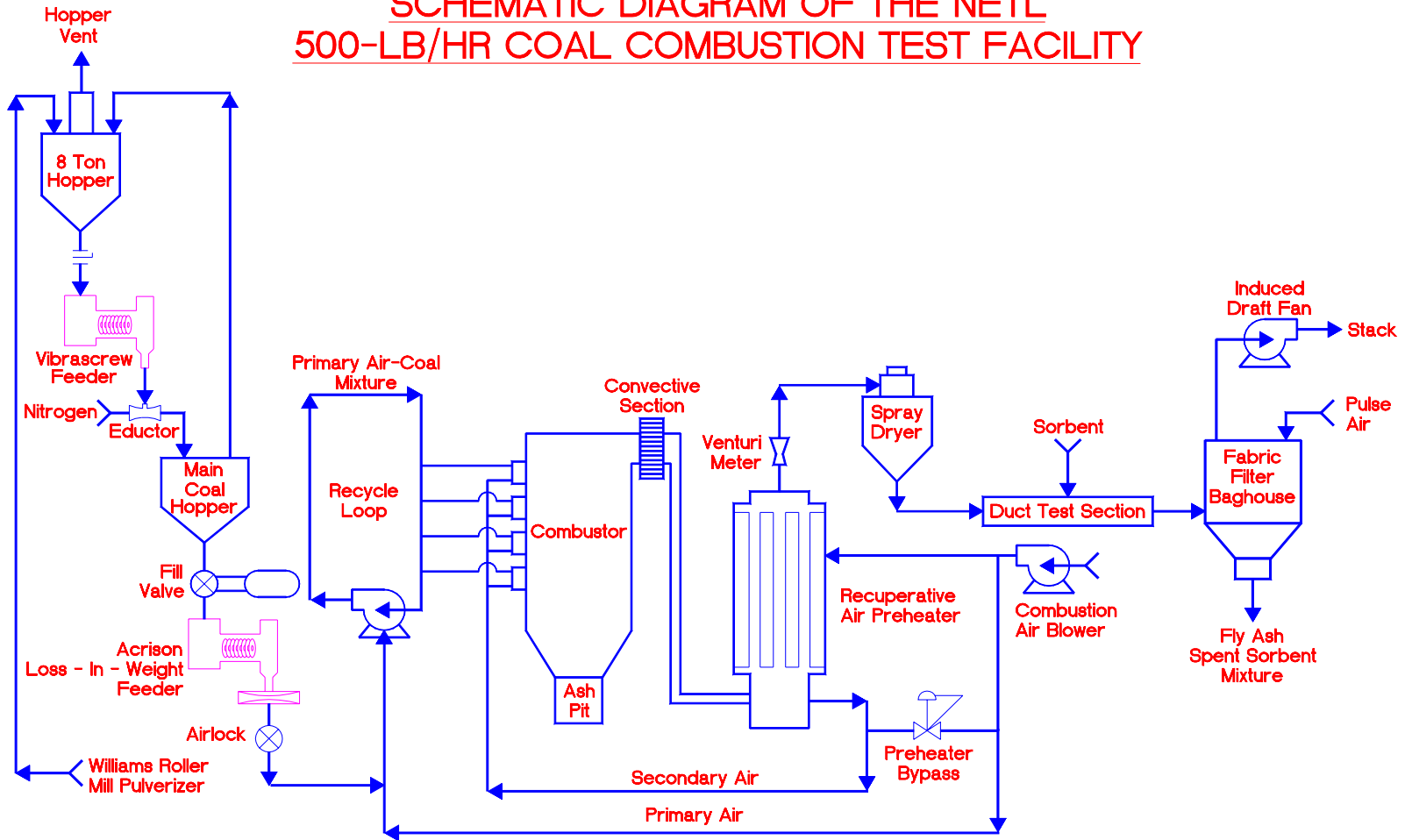
Hg Removal Across BH

~ 80 - 90%  
Total Hg Removal Goal

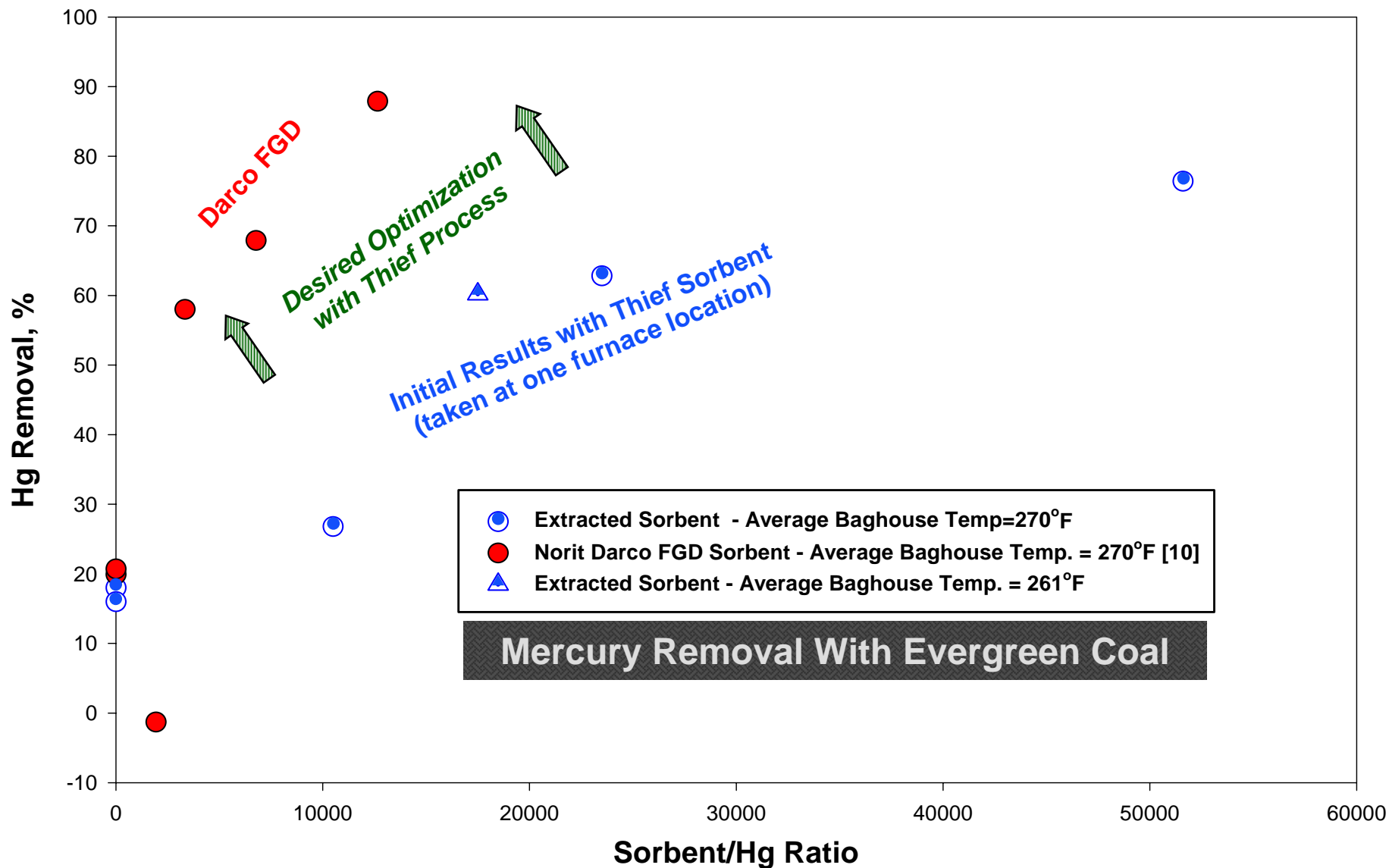
# NETL BENCH-SCALE PACKED BED REACTOR



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



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



# Figure 5. Mercury Removal Results: Darco FGD vs. Thief Sorbent

