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# A technique to control mercury from flue gas: The Thief Process

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#### Abstract

The Thief Process is a mercury removal process that may be applicable to a broad range of pulverized coal-fired combustion systems. This is one of several sorbent injection technologies under development by the U.S. Department of Energy for capturing mercury from coal-fired electric utility boilers. A unique feature of the Thief Process involves the production of a thermally activated sorbent in situ at the power plant. The sorbent is obtained by inserting a lance, or thief, into the combustor, in or near the flame, and extracting a mixture of partially combusted coal and gas. The partially combusted coal or sorbent has adsorptive properties suitable for the removal of vapor-phase mercury at flue gas temperatures that are typical downstream of a power plant preheater. One proposed scenario, similar to activated carbon injection (ACI), involves injecting the extracted sorbent into the downstream ductwork between the air preheater and the particulate collection device of the power plant. Initial laboratory-scale and pilot-scale testing, using an eastern bituminous coal, focused on the concept validation. Subsequent pilot-scale testing, using a Powder River Basin (PRB) coal, focused on the process development and optimization. The results of the experimental studies, as well as an independent experimental assessment, are detailed. In addition, the results of a preliminary economic analysis that documents the costs and the potential economic advantages of the Thief Process for mercury control are discussed.

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Keywords: Mercury; Flue gas; Sorbent; Activated carbon; Thief Process

#### 1. Introduction

The scrutiny of mercury emissions from coal-fired utilities that began with Title III in the Clean Air Act Amendments of 1990 has resulted (December 2000) in a determination by the U.S. EPA that such emissions should be regulated. In March 2005 the U.S. EPA issued the Clean Air Mercury Rule (CAMR) to significantly reduce mercury emissions from coal-fired power plants. The CAMR employs a phased approach, and when fully implemented, the utility mercury emissions will be capped at 15 ton, representing a 70% reduction from the current utility emissions. In the past decade, there have been numerous proposed techniques for control of mercury emissions from power plants [1,2]. The current suite of mercury control technologies under development employs sorbents, catalysts, scrubbing liquors, flue gas or coal

A considerable amount of research and development effort has focused on the evaluation of sorbent-based processes for the removal of mercury from flue gases, much of which has been supported under the Department of Energy's (DOE) Innovations for Existing Plants (IEP) Program. The common theme existing in these processes is that a sorbent is injected into the flue gas to remove the vapor-phase mercury, both elemental and oxidized forms, whose concentration is on the order of one part per billion by volume (ppbv). The majority of the research has focused upon the injection of activated carbon sorbents for the adsorption of mercury due to its relative simplicity, commercial availability, and successful application for the incinerator market.

Activated carbon can remove mercury from flue gas produced by the combustion of coal. Because activated carbons are general adsorbents, other flue gas components will also

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additives, combustion modifications, barrier discharges, and ultraviolet radiation [2–4]. One mercury control approach that has received a great deal of attention by the EPA, utilities, and technology developers is dry sorbent injection upstream of an existing particulate control device.

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adsorb on carbon with some species competing with mercury during the adsorption step. Carbon sorbents operate effectively over a limited temperature range, typically working best at temperatures below 300 °F (149 °C). The major drawback of using activated carbon is that the projected annual operating cost for an activated carbon cleanup process can be considerable, not only because of the cost of the sorbent, but also because of its poor utilization/selectivity for mercury. In addition, the commercial carbon-based sorbents require trucking from an off-site manufacturing facility and storage at the power plant.

The need for the development of cheaper, novel sorbents along with a less costly method to remove the mercury from flue gas has prompted an investigation in this area. A technique to produce an inexpensive activated solid from a pulverized coal-fired combustor for the removal of mercury from the flue gas could be a major technological breakthrough in the area of mercury control. A process has been identified that may be applicable to a broad range of pulverized coal-fired combustion systems [5]. The Thief Process involves extracting a mixture of partially combusted solids and gas from the combustor (in or near the flame region) and injecting either the extracted mixture or the separated partially combusted solids into the flue gas downstream of the air preheater. The injected thermally activated solid, or sorbent, captures the vapor-phase mercury

in the flue gas. Depending on the nature of the particulate control device, additional mercury capture may occur during the sorbent collection step; this additional mercury capture may be relatively modest for dry electrostatic precipitators, whereas fabric filters (i.e., baghouses) offer opportunities for higher levels of mercury removal. This is one of several sorbent injection technologies under development by the U.S. Department of Energy for capturing mercury from coal-fired electric utility boilers. The description of the experimental validation and economics of the Thief Process follows.

#### 2. Experimental

# 2.1. Preliminary studies

The NETL Combustion and Environmental Research Facility (CERF) was the unit initially used to obtain solid sorbent samples for evaluation. The initial hypothesis was the possibility that partially combusted coal might have characteristics that are more favorable for mercury removal relative to conventional fly ash, beneficiated fly ash concentrated with unburned carbon, or other thermally/chemically treated fly ash. The CERF unit [6,7] is a well-instrumented, dry bottom, pulverized-coal combustion system that simulates the firing found in a utility power plant. It has one down-fired burner where air and pulverized coal are mixed and combusted with a typical firing rate of 500,000 Btu/hr (147 kW<sub>t</sub>). The CERF is equipped with a conventional single-register burner with adjustable swirl, a dual-register low-NO<sub>x</sub> burner, and options for overfire air injection and cofiring of multiple fuels with an

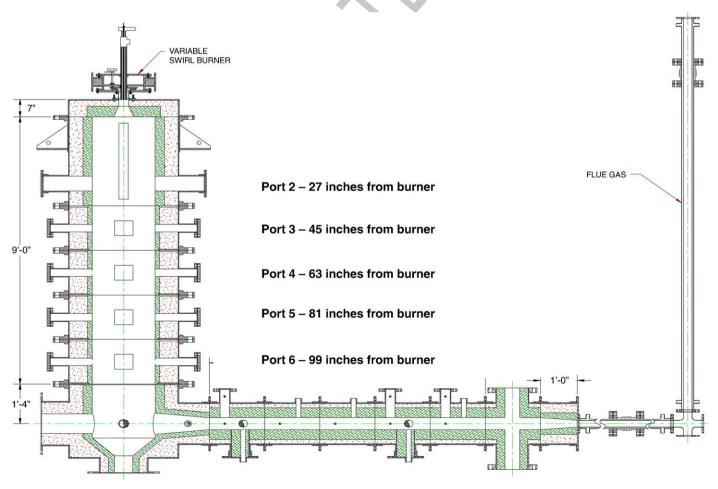


Fig. 1. CERF cross-section.

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106 automated process control system. There are numerous ports axially along the combustor radiant section available for the extraction of samples over a range of residence times (about 0.5 to 3 s) depending on the firing rate. The flue gas passes through a convective section, where ash-fouling behavior may be investigated, followed by multiple heat exchangers before entering a pulse-jet baghouse. In past combustion testing, solid samples were withdrawn at the various locations, axially and radially, along the radiant section of the combustor to characterize the carbon burnout behavior of coal and other fuels, and to map furnace profiles of gas temperature and gas composition while adjusting burner conditions

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In order to study the effect of the extent of combustion on the properties of partially combusted solids, it was necessary to map the radiant section of the CERF. Fig. 1 shows the cross-section of the CERF combustor and the axial location of the available sample ports. The sampling focused on the upper regions of the radiant section and included ports 2, 3, and 4, which correspond to 27 in. (0.69 m), 45 in. (1.14 m), and 63 in. (1.60 m) from the burner, respectively. The initial combustor sampling employed a high-volume sampling probe that had been previously designed to map the solids profile in the CERF combustor. The probe, which is water-cooled and utilizes a sintered thimble filter at the tip of the probe to remove the solids from the gas, collects a solid sample of several grams or less. Carbon burnout behavior, char composition and other properties can be subsequently determined with standard ASTM techniques. The probe's water-cooled design drops the temperature rapidly and passivates the sample by halting further combustion.

To overcome the limitations of the standard sample probe, which only collects a small batch sample, the initial testing phase utilized a modified probe design. This modified water-cooled probe utilizes a cyclone to separate and concentrate the extracted particles. The advantage of this modified design is that it allows for the continuous collection of increased quantities of sorbent. However, the main reason that the continuous probe was included in the initial testing was to determine whether the ultimate physical and chemical properties of the extracted partially combusted solids would be a function of both the combustor sampling location and the extraction technique (probe design).

The investigation included the chemical and physical characterization of extracted solid samples, withdrawn at various locations along the length of the CERF combustor, for two different bituminous coals: Pittsburgh #8 and Evergreen. In addition, the solids characterization included two parent coals, two commercial activated carbons, and fly ash samples taken immediately before the baghouse. The two activated carbons (FluePac™ made by Calgon Carbon Corporation and Norit Darco FGDTM) are sorbents identified in previous sorbent injection research for mercury removal sponsored by the DOE's IEP Program. For the Evergreen coal, an additional sampling campaign was included to determine the reproducibility of the initial results as well as expand the characterization to include both sample extraction techniques.

The characterization of the extracted samples included BET surface area measurements and pore volume determinations; a Coulter Multisizer for particle size distribution; and bulk chemical analysis for determination of key components. In addition, the physical characterization included Raman microanalysis of select samples to determine the degree of graphitization.

Additional testing, utilizing a laboratory-scale packed bed reactor, focused on the ability of the extracted solids to adsorb mercury. For these tests, the laboratory packed-bed reactor system, described by Granite et al. [8], was used to determine mercury capacities of select solids. For this test, a 10-mg sample of 200/325 mesh (44-74 µm) size was placed in a small reactor and then heated to 160 280 °F (138 °C). The solid was then exposed to a simulated flue gas that contained 16% carbon dioxide, 5% oxygen, 2000-ppm sulfur dioxide, 500-ppm nitric oxide, 270 ppb elemental mercury, and the remainder nitrogen, for 350 min. The solid sample was then analyzed for total mercury using cold vapor atomic absorption (EPA Method 3052) on the digested sample.

#### 165 2.2. Pilot-scale studies

After the completion of the initial phase with the CERF, the Thief Process development transitioned to the 500-lb/h (227-kg/h) pulverized coal-fired combustion system (PCFC) that is nominally rated at 6 MMBtu/h (1.76 MWt). The PCFC was set up to provide a reasonable simulation of the proposed process. The simulation included extracting partially combusted coal (and gas) and injecting the material downstream after the preheater for mercury control.

#### 2.2.1. Description of pilot combustion unit

The PCFC, shown in Fig. 2, is an indirect-fired unit consisting of a 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). Coal is first pulverized off-line in a Williams roller mill and then transported through a series of hoppers to an Acrison weight-loss differential feeder which regulates the coal feed rate to the combustor. The wall-fired, dry bottom type combustor is capable of firing both coal and/or natural gas. The combustor has four burners equipped with adjustable secondary air registers. On-line temperature readings, flow measurements, and four separate banks of continuous gas analyzers (O2, NO2, CO, SO2 and CO<sub>2</sub>) characterize the system performance.

The flue gas flows from the combustor to a convective section, then to a secondary air preheater. The cooled flue gas then flows through a spray drying vessel (not in use for these tests), a sorbent injection duct (SID) test section, and then to a pulse-jet baghouse. The SID and baghouse are heat-traced to minimize heat losses downstream of the spray dryer. There are numerous ports located along the SID available for sorbent injection, allowing for a wide range of sorbent in-duct residence times. The sorbent injection system consists of a hopper, screw feeder, scale, an eductor and a compressed air line. The fly ash and the injected sorbent are collected in a cylindrical (6 ft (1.83 m) internal diameter), pulse-jet baghouse that contains 57 bags arranged in nine rows. The Goretex™ Nomex™ bags are 8 ft (2.4 m) long and 4.5 in. (0.11 m) in diameter. The baghouse bags are cleaned (pulsed) with 80 psi (0.55 MPa) air when either the preset pressure drop is exceeded (where the upper limit is typically set at 5.5 in. of water column, 1.4 kPa, with a deadband of 2 in., 0.5 kPa) or at regular time intervals. The dislodged fly ash and sorbent are collected in a lined, 55-gal (0.18 m<sup>3</sup>) drum. A more detailed description of the PCFC has been given previously [9,10].

# 2.2.2. Thief Process testing

The initial pilot-scale testing of the Thief Process focused on determining mercury removals and was based on the initial CERF sorbent characterization study. The focus of the investigation included the impact of the sorbent injection feed rate and to a lesser extent, the probe design on the system mercury removals. A single eastern bituminous coal (Evergreen mine) was fired and the PCFC operating conditions were held constant for the entire sorbent injection test matrix. The investigation included two Thief probes. The first probe was the same water-cooled probe used in the preliminary studies on the CERF, using the cyclone separator, and the second probe incorporated minor modification to increase sample collection and further quench the combustion.

The probe was inserted through a narrow pre-existing port on the PCFC side wall with an angular view of the bottom right burner. The location of the probe tip was maintained at about 9 in. from the wall-face of the burner in the combustor. The temperature was near 2380 °F (1304 °C) at this location, as determined by a water-cooled high-volume suction pyrometer. The batches of extracted partially combusted solids weighed between 50 and 100 g and were combined and homogenized to form a single batch. The collected sorbent was then injected into the SID upstream of the baghouse to remove the vapor-phase mercury.

The most recent phase of pilot-scale testing focused on the evaluation of the Thief Process while firing a subbituminous Powder River Basin (PRB) coal. The main objectives of this testing were to develop baseline data, while firing a low rank coal, and to initiate the optimization of the Thief Process. For consistency, similar to the initial testing described above, a single source of PRB coal, obtained from We Energies Pleasant Prairie Power Plant, was fired and the PCFC operating conditions were held relatively constant for the entire sorbent injection test matrix. In order to better characterize or optimize the process, two significant modifications to the Thief extraction system were necessary. First, to facilitate the mapping of the near burner region of the combustor, it was necessary to alter the orientation of the Thief probe, allowing the probe to enter from the back wall of the furnace directly across from a burner. Second, to allow for an increased rate of extraction from the flame area, it was necessary to increase the probe size. Using the new extraction system, batch samples of 100 to 300 g were extracted at various locations in the near burner region and analyzed for ash content (i.e. losson-ignition, LOI). The batch samples were combined for ranges of ash content, homogenized into a single batch, and then injected into the SID upstream of the baghouse to remove the vapor-phase mercury.

The sorbent injection testing for both the bituminous and subbituminous coals included testing with a commercial activated carbon, Norit Darco FGD, as W.J. O'Dowd et al. / Fuel Processing Technology xx (2006) xxx-xxx

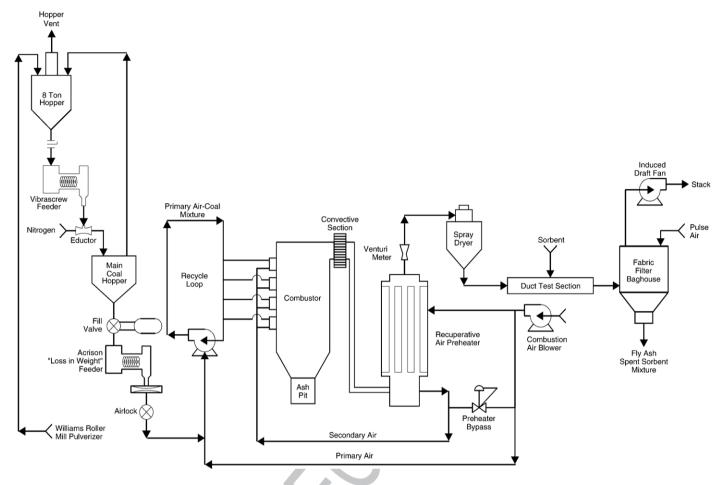


Fig. 2. Schematic of the 500-lb/h pulverized coal-fired combustion system.

well the extracted solids from the Thief Process. The sorbent, either the extracted sorbent or the Norit Darco FGD, was injected into the SID upstream of the baghouse to remove the vapor-phase mercury. For each test, the operating conditions, including the SID temperature, average baghouse temperature, and sorbent in-duct residence time were held constant. The effect of sorbent injection rates on the mercury removals was determined from the mercury measurements upstream, in the SID, and in the stack downstream of the baghouse.

In addition to the pilot work conducted at NETL, the evaluation of the Thief sorbent was included in an IEP sorbent screening project entitled an "Assessment of Low Cost Novel Sorbents for Coal-Fired Power Plant Mercury Control" directed at an evaluation of novel sorbents on a slipstream from a power plant burning a PRB coal [11]. Testing was performed on a slipstream of flue gas from We Energies, Pleasant Prairie Power Plant. The injection of all the sorbents was by a batch dump technique into EPRI's Pollution Control Test Device (PoCT) configured as a COHPAC Baghouse. The PoCT was maintained at 300 °F (149 °C), and tests with Norit Darco FGD activated carbon provided one-on-one comparison between the sorbents [11].

#### 2.2.3. Sampling and analysis

In order to characterize the PCFC unit and determine mercury removals across the system, mercury measurements were made in the SID upstream of the baghouse and at the stack using manual sampling, such as EPA Method 101A [12] for total mercury or the Ontario-Hydro method [13] for total and speciated mercury. In addition, a mercury semi-continuous emissions monitor (SCEM), developed by P.S. Analytical [14], was used to determine mercury concentrations at the stack. When the pilot unit testing transitioned from the eastern bituminous to the PRB coal, the additional capability to measure mercury concentrations in-duct at the baghouse inlet was available. The in-duct mercury measurement capabilities expanded the applicability of the pilot-scale testing at NETL to sorbent injection for mercury capture at full-scale utilities with an

electrostatic precipitator for particulate control. To determine in-duct mercury removals, the vapor-phase mercury concentrations immediately upstream of the baghouse were measured using an inertial separation device with the solid sampling method (FAMS<sup>TM</sup>) developed by Frontier Geosciences [15] and the on-line mercury SCEM. The inertial separation device used was the Apogee Quicksilver Inertial Separation (QSIS) probe that was found to be a reliable method for measuring vapor-phase mercury in flue gas in the presence of active mercury sorbent [16,17]. The in-duct mercury removals were determined from the difference between the total mercury measured with the manual sampling in the SID and the vapor-phase mercury measured immediately upstream of the baghouse using Frontier Geosciences FAMS<sup>TM</sup> method.

For each day of testing, coal was sampled at regular intervals, then combined, and riffled for a single representative sample for analysis. Similarly, the daily ash deposits, bottom ash and sootblow ash, from each day were collected, weighed, and analyzed. In addition, the baghouse ash for each test condition was collected, weighed, and analyzed. The results of these solids analysis combined with the mercury measurements were used to calculate mercury material balances around the entire system and around the baghouse. The material balances were one measure of data quality and were generally  $\pm 1/20\%$ .

#### 3. Results and discussion

#### 3.1. Preliminary studies

The chemical and physical characterization of the extracted CERF solids, summarized in Table 1, indicates several trends. Intuitively, the samples withdrawn along the length of the combustor reflect the progression of the combustion process. In

Table 1

Analytical characterization of two bituminous coals using standard laboratory analyses and mercury (Hg) capacity results with a laboratory-scale packed bed reactor

		BET surface area $(m^2/g)$	Pore volume (cc/g)	Mean diameter (pop.) (μm)	Sulfur (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Ash (%)	Hg capacity (mg/g)
1	Pitts. #8									
I	Port 2	26.7	0.053	37.0		61.4	0.5	0.6	35.3	1.38
I	Port 3	23.1	_	44.4	0.2	30.1	0.2	0.1	70.6	_
I	Port 4	17.3	_	_	_	_	_	-	80.2	_
I	Baghouse	3.1	_	28.4	0.6	6.2	0.1		93.0	_
I	Parent	1.8	_	37.4	2.3	75.6	5.5	6.0	9.4	_
	coal									
1	Evergreen									
I	Port 2	35.1	_	39.9	0.5	62.1	0.7	0.1	35.7	_
I	Port 3	20.9	_	37.7	_	_	-	-	73.6	_
I	Baghouse	3.5	_	26.8	0.6	3.0	0.1	1.2	95.0	_
1	Evergreen									
I	Port 2	31.2	0.042	34.4	0.6	49.8	0.5	2.6	46.6	2.03
I	Port 2	14.7	0.013	34.4	0.4	28.1	0.4	0.1	71.3	0.76
	(Cegrit)									
I	Port 3	23.6	0.041	32.7	0.6	32.5	0.3	_	67.9	_
I	Port 4	14.2	_	37.3	0.2	14.5	0.2	-	86.6	_
I	Baghouse	3.7	_	31.4	0.2	3.6	0.1	_	96.8	_
I	Parent	3.2	0.008	32.2	1.1	70.9	4.8	7.1	14.9	0.19
	coal									
1	Activated carb	oons								
	FluePac	606	0.285	32.0	0.7	83.3	1.7	5.8	5.8	0.89
1	Norit	481	0.535	36.9	1.0	66.5	1.3	2.6	28.2	1.61
	Darco					-				

the CERF, samples near the burner (port 2) have: 1) higher carbon content; 2) larger mean diameter; and 3) lower ash content as compared to samples collected at the baghouse. As combustion occurs along the path to the baghouse, the coal is pyrolyzed as well as oxidized. As compared to the parent coal, once the coal is injected into the combustor, the hydrogen content decreases indicating that hydrocarbons are immediately released. The rapid moisture release and devolatilization during the early stages of combustion are accompanied by the rapid evolution of gas that significantly alters the size and pore structural characteristics of the remaining char particles.

t1 1

t1.2

The decrease of the BET area along the particle flow path reflects the combustion process. It should be noted that samples extracted near the burner were an order of magnitude larger in BET area than the fly ash samples as well as the parent coals, but the BET surface areas of these samples were still at least an order of magnitude smaller than commercial activated carbon. Limited pore volume data indicate that the coal, extracted samples, and activated carbon have an order of magnitude difference between each, with the coal having the smallest volume. A trend in particle size, as related to the mean particle diameter, was not apparent.

A few selected samples, including a commercial activated carbon, were also subjected to Raman microanalysis [18]. Samples were prepared by pressing them into pellets under moderate pressure. Using a Renishaw Raman microprobe with an argon ion laser excitation source, the observed spectra were the result of 10 signal-averaged scans collected at 4 cm<sup>-1</sup> resolution, using an

integration time of 30 s per point. In general, the spectra recorded on each of the samples were nearly identical, each exhibiting the band associated with disorder in graphite (1350 cm<sup>-1</sup>) and the band associated with highly ordered graphite (1580 cm<sup>-1</sup>). However, line broadening indicates more ordered graphitization with the commercial activated carbon than the extracted samples. Raman results of these samples extracted from the combustion zone were different from Raman results found in the literature for samples of unburned carbon separated from fly ash [19].

Also shown in Table 1 are the mercury capacity test results for select samples. It must be emphasized that these tests reflect the overall mercury capacity of the sorbent and not the kinetics of the reaction. The choice of the extracted solid samples from port 2 was due to the more favorable physical and chemical properties, such as higher carbon content, and thus, the likelihood that these would be more reactive toward mercury removal. In addition, the mercury capacities of the Evergreen parent coal and two commercial activated carbons were included in the laboratory-scale reactor tests for direct comparison. Samples of extracted sorbent, before mercury capacity testing, had an average mercury concentration of 0.4 micrograms per gram ( $\mu g/g$ ) of sorbent. As can be seen, the samples from Port 2 have capacities (the standard deviation is 30%) comparable to the activated carbon. As would be expected, the parent coal is much lower in mercury capacity. Because the activities of these sorbents extracted near the burner showed promise, the research effort was expanded to include limited tests at the pilot scale.

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t3.10

t2.1 Table 2 t2.2 Characterization of Evergreen material extracted from 500-lb/h combustion unit

t2.3	Evergreen	Sorbent a	Sorbent analysis										
t2.4	Thief sorbent mixture	BET (m <sup>2</sup> /g)	Pore volume (cc/g)	Mean diameter (population) (μm)	Sulfur (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	Ash (%)	Hg capacity (mg/g)			
t2.5	Test week 1	63.2	0.087	34.6	0.6	60.1	1.3	3.5	33.8	_			
t2.6	Test week 2	74.9	0.080	41.5	0.5	66.3	0.57	2.9	28.7	1.80			

# 49 3.2. Pilot-scale studies: Evergreen bituminous coal

Upon completion of the preliminary studies, the Thief Process development transitioned to the PCFC unit, which was being used to evaluate mercury sampling methods, as well as sorbent injection for mercury removal. A single bituminous coal (from the Evergreen mine) was fired for consistency. As discussed previously, the testing dedicated to the Thief Process included extracting sorbent material from the combustor and injecting the sorbent upstream of the baghouse to remove mercury. Mercury measurements before and after the baghouse were made to quantify the mercury removal across the system and when combined with solids analyses (baghouse ash, etc.) were used to calculate the mercury material balances. The mercury material balances were used as the primary measure of data quality.

Physical and chemical properties of the sorbents that were extracted and used during the two test weeks are listed in Table 2. An average analysis from various batches of sample is reported for the second test week. Slight differences were obtained with these samples as compared to the CERF samples. In general, the surface areas, pore volumes, and carbon contents were higher for the PCFC samples as compared to the CERF samples. The mercury capacities, as determined by laboratory packed-bed tests, were similar to those of commercially activated carbons (Norit Darco and FluePac). It should be noted that there is a geometrical difference between the PCFC combustor and CERF combustor. Additionally the PCFC combustor extraction location was fixed at 9 in. (0.23 m) from the burner tip versus 27 in. (0.69 m) for the CERF, allowing for less particle residence time, which is also reflected in the higher unburned carbon levels. In addition, the probe design was modified between the test weeks on PCFC unit

so that quenching of the sample would occur more readily. The higher carbon content of this sample (Test 2), and the corresponding decrease in the ash fraction, would indicate some limited success of the modified probe design.

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The initial Thief testing focused on the effect of sorbent feed rate on the mercury removal. The Thief sorbent was injected into the ductwork upstream of the baghouse, which was held at a constant temperature of approximately 270 °F (132 °C). Throughout the sorbent injection testing, the PCFC combustor was intentionally operated to achieve high combustion efficiency with very low unburned carbon levels (less than 1 wt.%) in the fly ash. The PCFC combustor typically operates in the range of 3 to 4% O<sub>2</sub> with a primary air/total air greater than 20%. The purpose of maintaining low unburned carbon levels in fly ash is to minimize the confounding effect of unburned carbon acting as a mercury sorbent and obscuring the interpretation of the effect of sorbent injection. For the PCFC unit, minimal effects from the fly ash would be expected at unburned carbon levels near 1% [20,21]. However, a thorough evaluation of the sorbent injection results should include a comparison to the baseline mercury removals, without sorbent injection, since there is an indication of some baseline mercury removal that could be attributable to the presence of unburned carbon in the fly ash and/or to the difficulty in the mercury sampling and analysis. Therefore, in addition to the sorbent injection tests, two baseline tests (without sorbent injection) were included to quantify baseline mercury removals. Testing included triplicate sets of mercury measurements for each test condition (with one exception) and the averages are shown in Table 3.

Prior to the Thief sorbent injection tests, parametric tests were conducted with a commercial activated carbon (Norit Darco FGD) [9,21]. The commercial activated carbon, Norit Darco

t3.1 Table 3
 t3.2 Results of Thief sorbent injection testing (Evergreen coal) on the 500-lb/h pilot unit

	3( 3										
t3.3	Thief sample	Sorbent injection rate (g/h)	Sorbent injection rate (lb/MMacf)	Average baghouse temperature (°F)	Mercury removal (%)	System mercury balance (%)					
t3.4	Test 1 — baseline	0	0	270	1	109					
t3.5	Test 1 — sorbent	308	6.2	261	57.0	110					
t3.6	Test 2 — baseline	0	0	269	17.4	108					
t3.7	Test 2 — sorbent	141	2.7	270	20.7	122					
t3.8	Test 2 — sorbent a	334	6.4	270	59.6	_					
t3.9	Test 2 — sorbent	558	10.5	270	73.5	105					

<sup>&</sup>lt;sup>a</sup> Single test (one set of Hg measurements).

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FGD, has become a benchmark sorbent for comparing mercury removal results with other sorbents. Shown in Fig. 3 are the results of the activated carbon and Thief sorbent injection tests at similar operating conditions. As can be seen, a significantly lower Darco FGD feed rate is required to achieve the same mercury removal with the Thief sorbent. Even though the mercury removals were significantly lower than obtained with this commercial activated carbon, these initial pilot-scale tests demonstrated that extracted Thief sorbent could remove significant levels of mercury in actual flue gas, demonstrated the process concept, and provided the required data needed to continue the development of the technology.

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While these preliminary Thief Process results were encouraging, it should be emphasized that results were obtained from partially combusted coal that had been obtained from only one furnace location. Because Evergreen coal testing in the PCFC unit had concluded shortly after the initial Thief tests, there was essentially no opportunity to begin optimization on the Evergreen coal. Thus, it was decided that further testing and optimization – including a more extensive mapping of the furnace conditions in the selection of the extraction location – would be resumed while burning a different coal.

After conducting Evergreen coal operations, PCFC unit testing was initiated using a Wyoming Powder River Basin (PRB) subbituminous coal similar to that burned at the Wisconsin Energy (We) Pleasant Prairie Station. These pilot tests were undertaken in order to complement utility mercury field studies funded by DOE as well as the growing interest in evaluating activated carbon injection with PRB coals where higher levels of elemental mercury and lower concentrations of chlorine in the flue gas prevail, as compared to eastern bituminous coals where speciation favors oxidized mercury species. Thus, PRB coals are thought to represent a more challenging situation given that elemental mercury is less reactive and somewhat more difficult to remove as compared to the more reactive oxidized mercury species.

#### 3.3. Pilot-scale study: Powder River Basin subbituminous coal

As the pilot unit transitioned from testing with a bituminous coal to a subbituminous coal (PRB), modifications to the sorbent

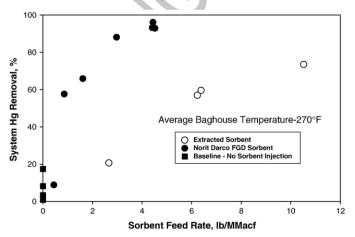


Fig. 3. Comparison of the effectiveness of Norit Darco FGD and extracted sorbent (bituminous coal).

extraction system were implemented. The choice of the initial sorbent extraction location, implemented during the bituminous coal testing, was the simplest and quickest option, requiring minimum combustor modifications for the initial probe design. However, this initial assembly had limited flexibility that inhibited the ability to extract the partially combusted solids at different locations in the near burner region. In addition, the flame from a PRB coal has a longer flame root position (in part due to the higher coal moisture content) relative to the bituminous coal, potentially rendering the initial extraction location inadequate. With the initial extraction set up, an angular approach from the side wall to the burner, probe movement is accompanied by changes in the both the axial and radial distance at the extraction location relative to the burner/flame position, while the probe orientation and sample collection alter particle trajectories. Therefore, it was necessary to modify both the orientation in the combustor and probe design to allow for a more thorough mapping of the furnace in conjunction with sorbent collection. First, altering the orientation allowed the Thief probe to enter from the back wall of the furnace directly across from a burner, which facilitated the mapping of the near burner region with a clearer view of the flame. Second, increasing the probe size allows for an increased rate of extraction from the flame area. As the extraction location moves away from the burner, the solids concentration (in the gas extracted from the combustor) decreases from the initial concentration in the coal/primary air mixture that results from the mixing of secondary air in conjunction with the moisture release, devolatilization, and char burnout behavior during combustion.

The initial phase of testing with PRB coal involved extracting the partially combusted coal from various locations in the near burner region and determining the physical properties. Numerous samples, typically 100 to 200 g, were extracted from various locations in the combustor near the burner and analyzed. Those samples with similar ash content were composited and homogenized into a single sample before being evaluated in subsequent sorbent injection testing on the pilot unit. Table 4 lists the physical properties of four Thief sorbent mixtures. The changes in the physical properties, such as an increase in ash content and decrease in the volatile fraction followed by a decrease in the carbon fraction, are consistent with an increase in combustion efficiency. In addition, as the combustion efficiency increases, there is a significant increase in the BET surface area and pore volume of the extracted solids. The measured particle size of the collected sorbent typically ranged from 30 to 45 µm, with no noticeable trend with extraction location, although it should be noted that the smallest particles might escape cyclone collection. Because the cyclone separator is more efficient in removing the larger particle sizes, this may have contributed to the lack of a trend in the measured particle

While the physical properties of the extracted sorbent changed substantially with the extraction location, the ultimate objective was to determine the reactivity or the effectiveness of the extracted sorbent mixtures for removing the vapor-phase mercury. In order to determine the effectiveness of the various sorbent mixtures, the material was included in the sorbent injection test matrix on the PCFC unit. As with the Evergreen

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t5.1 t5.2

t5.3

t5.4t5.5t5.6 t5.7 t5.8t5.9

Table 4 Characterization of Thief sorbent (subbituminous coal)

t4.3	Extracted	Sorbent analysis									
t4.4	sorbent mixture (% ash)	BET (m <sup>2</sup> /g)	Pore volume (cc/g)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Sulfur (%)	Carbon (%)	Hydrogen (%)	Oxygen (%)	
t4.5	9 to 15 <sup>a</sup>	77.5	0.131	32.3	47.6	13.1	0.36	67.1	2.1	9.4	
t4.6	17 to 21	133	0.192	12.2	61.4	20.0	0.58	67.2	1.0	3.8	
t4.7	30 to 35	227	0.250	14.3	49.8	31.8	0.84	57.8	0.6	3.9	
t4.8	35 to 50 <sup>a</sup>	226	0.205	11.8	46.9	37.4	0.76	55.1	0.5	1.5	

t4.9 <sup>a</sup> Average value.

coal, the testing involved injecting the sorbent into the SID upstream of the baghouse and measuring the mercury removals. Since the effectiveness of the various sorbent mixtures was the main variable of interest, the pilot unit was operated to maintain constant SID and baghouse temperatures. In addition, the sorbent injection location was the same for all tests, resulting in an in-duct residence time of 2.4 s. Table 5 summarizes the relevant operating conditions, both in-duct and system mercury removals, and system mercury mass balances.

The results of the Thief sorbent injection testing indicate that the mercury removal increased for Test 1 through Test 3 as the average sorbent ash content increased from 13.1% to 37.4%. This is especially noticeable when comparing Tests 2 and 3, where system mercury removals increased even though the sorbent injection rate was over 50% lower. In addition, Test 4 showed similar mercury removals to Test 6 (at a slightly lower ash concentration) at similar sorbent injection rates, which correlates to the similar physical properties (i.e. BET surface areas and pore volumes) of the mixtures. At a common sorbent composition (Tests 3–5), both the in-duct and system mercury removals increase as the sorbent injection rate increases. While the number of tests is few, it appears that no significant increase in system mercury removal occurs beyond about 2.2 pounds per million actual cubic feet (lb/MMacf, 35 g/km<sup>3</sup>), indicating that mass transfer effects may limit further removal efficiency, particularly as high mercury removals in the 90% range are achieved. Although there is scatter in the measured in-duct removals, it was clear that the in-duct removals were still significant at low sorbent injection rates (61% removal at 1.1 lb/ MMacf, 18 g/km<sup>3</sup>) and reached 65% for a sorbent injection rate of 5.3 lb/MMacf (85 g/km<sup>3</sup>).

A series of sorbent injection tests on the pilot unit using a commercial activated carbon, Norit Darco FGD, were also conducted while firing the PRB coal at various duct and

baghouse temperatures, sorbent residence times, and sorbent injection rates [22,23]. The pilot-scale results for both the mercury speciation and the in-duct mercury removals were similar to those obtained at the full-scale utility burning the same PRB coal. There is no direct comparison of the overall system mercury removals from the pilot unit to those of the fullscale utility due to the use of a baghouse versus an ESP. Fig. 4 shows the resulting mercury removals for Norit Darco FGD and the high ash Thief sorbents at similar operating conditions. Both in-duct and overall system removals using Thief sorbent compared favorably to the removals with Darco FGD sorbent over the range of sorbent feed rates. The in-duct mercury removals for the Thief sorbent showed similar behavior to the commercial activated carbon that had about twice the surface area and pore volume. This is particularly encouraging because it is the most relevant factor when translating the behavior to full-scale utilities. Therefore, the Thief sorbent should be competitive with activated carbon injection for removing mercury from flue gas at utilities burning PRB coal.

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As previously described in the Experimental section, the Thief sorbent was included in a sorbent screening project utilizing a flue gas slipstream from a power plant burning a PRB coal. The slipstream is rated for 30–50 acfm (0.014–0.024 m<sup>3</sup>/ s) and was equipped with EPRI's Pollution Control Test Device (PoCT) configured as a Compact Hybrid Particulate Collector (COHPAC) Baghouse [11]. These preliminary screening tests were of one-hour duration and utilized a semi-continuous mercury emissions monitor. Rather than continuous sorbent injection, the injection of sorbent was by a batch dump technique, where 0.55 g of sorbent was injected at two 4-minute intervals to achieve an overall 1-lb/MMacf (16 g/km<sup>3</sup>) injection equivalent level. The semi-continuous monitor determined mercury removals over time in a manner somewhat similar to "breakthrough curve" type analysis common with laboratory

Table 5 Results of pilot unit sorbent injection tests (subbituminous coal)

3	Extracted sorbent mixture	Average baghouse temperature (°F)	Sorbent injection rate (lb/MMacf)	In-duct mercury removal (%)	System mercury removal (%)	System mercury balance (%)
1	Test 1: (13.1% ash)	273	14.1	54.7	57.0	86
5	Test 2: (18.9% ash)	270	11.5	56.1	82.3	104
3	Test 3: (36.6% ash)	272	5.3	65.3	92.2	119
7	Test 4: (38.2% ash)	271	2.2	53.9	92.6	126
3	Test 5: (38.2% ash)	272	1.1	60.6	82.6	110
9	Test 6: (31.8% Ash)	269	2.3	72.7	88.7	102

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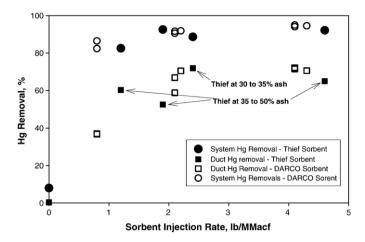


Fig. 4. Comparison of the effectiveness of Norit Darco FGD and extracted sorbent (subbituminous coal).

sorbent screening studies. The resulting mercury removals indicate that the Thief sorbent (35–50 wt.% ash fraction obtained from the PRB coal) for this test was not as active as Norit Darco FGD activated carbon [11,24]. The mercury removals for the Thief sorbent were 62% at an equivalent sorbent injection rate of 1-lb/MMacf (16 g/km³) and 81% at 2-lb/MMacf (32 g/km³) compared with a Darco FGD removal of 88% at 1 lb/MMacf (16 g/km³) and 94% at 2-lb/MMacf (32 g/km³) injection at 300 °F (149 °C).

There are several possible reasons to explain why the Thief sorbent comparisons with Darco FGD in the batch injection/ COHPAC screening tests differed from that observed in the PCFC unit where standardized mercury sampling was conducted under steady state conditions in obtaining good material balance closures. The batch injection screening tests were conducted on a slipstream scale (about 40 acfm, 0.019 m<sup>3</sup>/s) that is considerably smaller than the 2000 acfm (0.94 m<sup>3</sup>/s) pilot-scale PCFC; and because the screening test only lasted for one hour, the quantity of Thief sorbent was nearly 500-times less than that injected in the pilot-scale PCFC. Since Thief sorbent (particularly over a composite range of 35-50 wt.% ash) is not nearly as homogenous as Norit Darco FGD activated carbon, obtaining representative samples in such small quantities may have been an issue. Particle size is also an important consideration, and it should be noted that the Darco FGD had a mean particle size of 18 µm as reported in the batch injection slipstream study [11], which is considerably finer than the Thief sorbent. Given that the Thief sorbent particle size was larger than NORIT Darco FGD, variations in the number of particles for a given sorbent injection rate along with external surface area may have also played a role in the observed slipstream results. In using a batch type injection coupled with short residence times, this may make it somewhat more difficult to achieve a rapid and thorough gas/solid mixing inside the ductwork and the subsequent evenness of the entire filter cake cross-section that is critical with a "breakthrough-type" analysis. Because larger particles carry more momentum, this influences particle trajectories relative to the gas flow (i.e., particle slip) while dispersion will generally be superior with a much larger number of smaller particles for a constant total mass flow. For example, it is possible that the sorbent dispersion was not as thorough with the somewhat larger Thief particles and a batch dump injection within the limited residence time. It is noteworthy that some differences in mercury removals have been reported among various tests in comparing short 1-hour duration tests with longer-term test results in the slipstream study [11]. Nevertheless, this outside demonstration was useful to show that Thief sorbent is reactive and helped validate the technology.

#### 4. Thief Process economics

The Thief Process economics is based on managing a series of small heat rate penalties (that are intrinsically associated with the extraction/handling of sorbent inside the boiler) in order to avoid the purchase of commercially available activated carbons. Therefore, NETL has developed detailed spreadsheets based on material and energy balances to assist with the evaluation of boiler scale-up considerations, along with site-specific design and operational issues with the Thief Process relative to optimization and assessing inter-dependent tradeoffs associated with a small series of heat rate penalties. Ultimately, the operating costs for generating sorbent using the Thief Process will depend on a number of variables in concert with the energy management strategy.

In the Thief Process economics methodology, the Thief sorbent effective cost (as extracted/used on a \$/ton (\$/kg) basis to compare with activated carbon) is calculated based on the annualized operating costs associated with the thermal heat rate penalties and parasitic power requirements.

In addition, the Thief capital costs are estimated based upon the energy and mass balances developed for the specific design. The total costs for the specific application of the Thief Process include the total capital requirement (TCR), fixed O&M costs, and variable O&M costs.

The following economic evaluation of the Thief Process and ACI is for a hypothetical, generic 500 MWe base-loaded pulverized coal-fired plant burning Wyoming PRB subbituminous coal with an 80% capacity factor. Much of the information is similar to other process economics studies in terms of the heat rate and other characteristics [27,28]. Of significance is that the We Energies Pleasant Prairie station field test results showed that 50% Hg removal was achieved at 3.3 lb/MMacf (53 g/km³) for activated carbon injection (ACI) upstream from a cold-side ESP [25]. Thus, sorbent requirements for the hypothetical 500 MWe reference plant are calculated based on 3.3 lb/MMacf (wet flue gas basis) after the preheater, at conditions of 290 °F (143 °C) and draft of 12 in.-H<sub>2</sub>O (3.0 kPa), and would amount to about 1365 ton/yr (1,238,000 kg/yr) sorbent.

# 4.1. Thief sorbent effective cost

The Thief sorbent cost is determined from the heat rate penalties and the parasitic power requirements associated with the extraction of sorbent/gas from the boiler and the subsequent re-injection into the ductwork upstream of the particulate control device. Depending on the extraction location, along with the desired sorbent injection rate to achieve a given mercury removal, the Thief Process generally involves the extraction of

t6.27

t6.28

t6.29

Base case - no heat recovery

With energy management case

Incremental coal (base case), ton/yr

very small quantities of partially combusted coal and furnace gas relative to the total boiler flows. Once the mass flows and temperature of extracted furnace gas and partially combusted coal are known at the extraction location, the thermal heat rate penalty can be calculated based on the combustible heat loss, sensible heat loss, and the incident heat loss. The parasitic power requirements for the base case Thief sorbent process include the suction requirements for the extraction of the Thief sorbent/gas and re-injection into the downstream location. In addition, parasitic power requirements include pulverizer power required for make-up coal to replace lost heat and incremental ID fan power requirements for the additional flue gas associated with the combustion of the make-up coal.

One of the most important design and operational considerations in the Thief Process is the amount of furnace gas extracted along with the partially combusted coal. During the early stages of combustion, the mass ratio of furnace gas to partially combusted coal is generally in the range of 15–60 depending on the extraction location, local air/fuel stoichiometry and mixing, along with the coal characteristics which influence particle drying, devolatilization, and char burnout during combustion. Table 6 illustrates the very low requirements for Thief gas extraction as compared to the total boiler flue gas flow along with some estimates of the ratio of furnace gas to partially combusted coal at the extraction location inside the boiler. In addition, the heat rate penalties are determined for each extraction location and summarized in Table 6. The combustible

heat loss is an estimate of the gross combustible higher heating value of the extracted char solids and the heating value of the Thief furnace gas (i.e. appreciable amounts of CO) at the boiler extraction location. The sensible heat loss is an estimate of the amount of heat lost due to the cooling of the extracted solids and furnace gas (extraction location temperature of 2600 °F (1427 °C)) through the high-temperature Thief/lance and system with continuous sorbent re-injection. The sensible heat loss calculation assumes a re-injection temperature of 270 °F (132 °C), which is slightly lower than the 290 °F (143 °C) duct location to provide a conservative estimate of potential thermal losses. The incident heat loss is an estimate of the amount of heat transferred to the Thief probe from the boiler/ furnace (assumed probe incident heat flux of 50,000 Btu/h-ft<sup>2</sup> (158 kW<sub>t</sub>/m<sup>2</sup>)). To convert the thermal losses into a gross thermal heat rate penalty cost, an as-delivered coal cost of \$1.25/ MMBtu (\$1.32/kJ) was used.

The parasitic power requirements associated with the base case Thief Process are shown in Table 6. The Thief suction power requirements (e.g., fan power) account for the extraction of the Thief sorbent/gas from the furnace and re-injection into the downstream location. The calculation of Thief suction power requirements is based on the Thief gas flow requirements and pressure drop through the various probe(s) and piping. The pulverizer parasitic power is required for make-up coal that is derived from the above thermal heat losses and a value of 22 kW-h/ton coal [26]. Incremental ID fan requirements are for

Table 6
Thief sorbent cost based on thermal heat rate penalties and parasitic power for a 500 MW reference plant burning PRB coal and a 3.3 lb/MMacf sorbent injection rate (1365 ton/yr sorbent)

Thief sorbent, wt.% ash (@ extraction point)	25.0	30.0	35.0	40.0	45.0
Thief Gas, lb gas/lb particle	26	34	42	51	59
Ratio — lb Thief gas/lb flue gas	0.00174	0.00226	0.00281	0.00338	0.00395
Thermal heat rate penalty — MMBtu/yr					
Combustible heat loss	32,826	31,494	29,971	28,335	26,623
Sensible heat loss	57,237	74,006	91,209	109,035	126,998
Incident heat loss	18,529	21,111	23,467	25,680	27,732
Total	108,593	126,611	144,645	163,049	181,354
Heat rate penalty, %	0.33	0.38	0.43	0.48	0.54
Gross thermal heat rate penalty cost, \$/yr	154,252	179,846	205,462	231,603	257,605
Energy management potential heat recovery or avoided heat at 70% of incident & sensible heat loss					
Heat rate penalty, % (adjusted)	0.17	0.18	0.20	0.21	0.23
Adjusted thermal heat rate savings, \$/yr	-75,336	-94,577	-114,023	-133,948	-153,852
Base case annual parasitic power					
Thief suction power, kW-h	393,315	510,578	630,834	755,435	880,982
Incremental pulverizer, kW-h	161,040	187,762	214,506	241,796	268,943
Thief gas incremental ID fan, kW-h	86,466	100,814	115,174	129,827	144,403
Parasitic power — Thief total kW-h	640,823	799,154	960,514	1,127,059	1,294,327
Parasitic power — Thief total, %	0.018	0.023	0.027	0.033	0.037
Parasitic power — Thief total, \$/yr	32,041	39,957	48,025	56,352	64,716
With energy management savings, \$/yr	-6044	-7588	-9148	-10,746	-12,343
Combined heat rate penalty & parasitic power summary					
Combined heat rate penalty & parastic power summary					
	Thief Gas, lb gas/lb particle Ratio — lb Thief gas/lb flue gas Thermal heat rate penalty — MMBtu/yr Combustible heat loss Sensible heat loss Incident heat loss Incident heat loss Total Heat rate penalty, % Gross thermal heat rate penalty cost, \$/yr Energy management potential heat recovery or avoided heat at 70% of incident & sensible heat loss Heat rate penalty, % (adjusted) Adjusted thermal heat rate savings, \$/yr Base case annual parasitic power Thief suction power, kW-h Incremental pulverizer, kW-h Thief gas incremental ID fan, kW-h Parasitic power — Thief total kW-h Parasitic power — Thief total, % Parasitic power — Thief total, \$/yr With energy management savings, \$/yr	Thief Gas, lb gas/lb particle Ratio — lb Thief gas/lb flue gas  Combustible heat loss Sensible heat loss Sensible heat loss Incident heat loss Incident heat rate penalty, %  Gorbustible heat loss Incident heat rate penalty, %  Incident heat loss  Incident heat rate penalty, %  Incident heat loss  Incident heat loss  Incident heat rate penalty, %  Incident heat loss  Incident h	Thief Gas, lb gas/lb particle       26       34         Ratio — lb Thief gas/lb flue gas       0.00174       0.00226         Thermal heat rate penalty — MMBtu/yr       32,826       31,494         Combustible heat loss       57,237       74,006         Incident heat loss       18,529       21,111         Total       108,593       126,611         Heat rate penalty, %       0.33       0.38         Gross thermal heat rate penalty cost, \$/yr       154,252       179,846         Energy management potential heat recovery or avoided heat at 70% of incident & sensible heat loss       164,252       179,846         Heat rate penalty, % (adjusted)       0.17       0.18         Adjusted thermal heat rate savings, \$/yr       -75,336       -94,577         Base case annual parasitic power       393,315       510,578         Incremental pulverizer, kW-h       393,315       510,578         Incremental pulverizer, kW-h       161,040       187,762         Thief gas incremental ID fan, kW-h       640,823       799,154         Parasitic power — Thief total, %       0.018       0.023         Parasitic power — Thief total, \$/yr       32,041       39,957         With energy management savings, \$/yr       -6044       -7588 <td>Thief Gas, lb gas/lb particle       26       34       42         Ratio — lb Thief gas/lb flue gas       0.00174       0.00226       0.00281         Thermal heat rate penalty — MMBtu/yr       32,826       31,494       29,971         Combustible heat loss       57,237       74,006       91,209         Incident heat loss       18,529       21,111       23,467         Total       108,593       126,611       144,645         Heat rate penalty, %       0.33       0.38       0.43         Gross thermal heat rate penalty cost, \$/yr       154,252       179,846       205,462         Energy management potential heat recovery or avoided heat at 70% of incident &amp; sensible heat loss       0.17       0.18       0.20         Heat rate penalty, % (adjusted)       0.17       0.18       0.20         Adjusted thermal heat rate savings, \$/yr       393,315       510,578       630,834         Incremental pulverizer, kW-h       161,040       187,762       214,506         Thief suction power, kW-h       161,040       187,762       214,506         Thief gas incremental ID fan, kW-h       86,466       100,814       115,174         Parasitic power — Thief total, \$W-h       640,823       799,154       960,514         Parasitic powe</td> <td>Thief Gas, lb gas/lb particle Ratio — lb Thief gas/lb flue gas Thermal heat rate penalty — MMBtu/yr Combustible heat loss Sensible heat loss Sensible heat loss Incident heat rate penalty, % Incident heat loss Incident heat rate penalty cost, \$/yr Incident heat loss Incident heat</td>	Thief Gas, lb gas/lb particle       26       34       42         Ratio — lb Thief gas/lb flue gas       0.00174       0.00226       0.00281         Thermal heat rate penalty — MMBtu/yr       32,826       31,494       29,971         Combustible heat loss       57,237       74,006       91,209         Incident heat loss       18,529       21,111       23,467         Total       108,593       126,611       144,645         Heat rate penalty, %       0.33       0.38       0.43         Gross thermal heat rate penalty cost, \$/yr       154,252       179,846       205,462         Energy management potential heat recovery or avoided heat at 70% of incident & sensible heat loss       0.17       0.18       0.20         Heat rate penalty, % (adjusted)       0.17       0.18       0.20         Adjusted thermal heat rate savings, \$/yr       393,315       510,578       630,834         Incremental pulverizer, kW-h       161,040       187,762       214,506         Thief suction power, kW-h       161,040       187,762       214,506         Thief gas incremental ID fan, kW-h       86,466       100,814       115,174         Parasitic power — Thief total, \$W-h       640,823       799,154       960,514         Parasitic powe	Thief Gas, lb gas/lb particle Ratio — lb Thief gas/lb flue gas Thermal heat rate penalty — MMBtu/yr Combustible heat loss Sensible heat loss Sensible heat loss Incident heat rate penalty, % Incident heat loss Incident heat rate penalty cost, \$/yr Incident heat loss Incident heat

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additional flue gas associated with the combustion of make-up coal. This incremental ID parasitic power requirement is determined from the ID fan characteristics (e.g., draft at ID fan inlet) and specification of the incremental flue gas flow rate associated with the make-up coal requirement taking into account the furnace stoichiometry and air in-leakage through the system prior to the ID fan. The cost of the parasitic power was assumed to be \$0.05/kW-h.

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Table 6 reveals that with the combination of the heat rate penalties and parasitic power costs, Thief sorbents would be expected to fall in the range of \$135-235/ton (\$0.149-0.259/kg) for the baseline cases – with no heat recovery or avoided heat concepts – over a wide range of Thief sorbent characteristics. Energy management concepts could drive these costs much lower and with less variability in the \$80-115/ton (\$0.088-0.127/kg) range as shown in Table 6. Table 6 is based on conservative estimates — for example, where all the sensible heat is lost as Thief gas is cooled from the furnace location (2600 °F, 1427 °C) to the injection (270 °F, 132 °C) location. Obviously, heat recovery could be included in the design/ operation — for example, by using the power plant boiler water system to cool the Thief probe. Other energy management strategies include injection at higher duct temperatures (i.e., upstream of the secondary air preheater) to reduce sensible heat loss, designing more compact Thief probes with less incident heat losses, and extraction concepts that further reduce the initial ratio of mass of furnace gas to partially combusted coal. Extraction at earlier stages of combustion and allowing for subsequent oxidation inside the probe would result in decreased thermal losses for sorbent particles, particularly those in the upper ranges of weight percent ash composition. This beneficial reduction in thermal losses could be further enhanced with the slight addition of external air as part of the Thief probe design, so that external air helps cool the furnace gas as it enters the probe while providing additional oxygen to assist with the desired particle oxidation/transformations [27]. Thus, a general case is included in Table 6 to illustrate the impact of recovering and/or avoiding 70% of the combined sensible or incident heat loss through a sound energy management strategy. This 70% energy management case would reduce the total thermal heat losses to only 0.17-0.23% with the lower values prevailing in cases where extraction occurs at the earlier stages of combustion.

# 3 4.2. ACI and Thief Process cost comparison

In order to compare the cost effectiveness of the Thief Process with ACI the total capital requirement, fixed O&M costs, and variable O&M costs for both technologies are required. The ACI control technology is a more mature technology and the literature contains documentation of the capital cost estimates [25,28]. The literature ACI capital cost estimates were for a system similar to the one required for the hypothetical 500 MW plant burning a PRB coal and were used directly in the cost analysis shown in Table 7. Table 7 compares the costs associated with the Thief Process and ACI using the EPRI TAG methodology to determine indirect costs. In addition, a pre-production cost (associated with the process shakedown) is included and

consists of one month of O&M costs along with 2% of the total control capital cost (TCCC). The total capital requirement (TCR) for ACI is estimated at \$1,047,673 (\$2.10/kW) for the hypothetical 500 MW power plant.

The Thief Process equipment consists of probe(s), duct work, heat exchanger, instrumentation, controls, and ID fan in addition to routine field and structural materials common with power plant modifications. In addition, the Thief Process may include an optional baghouse/cyclone device, small storage hopper, and pneumatic sorbent feeding system if it is desired to include an intermediate Thief sorbent collection/storage option. NETL has developed spreadsheets for estimating the TCCC for the Thief Process [27]. Table 7 includes the detailed capital costs for the base case Thief Process. Because the Thief Process is not as mature of a technology as ACI, where some utility field test experience has already been obtained, there is greater uncertainty associated with the Thief Process. Therefore, a retrofit factor of 1.2 is used along with generally higher indirect costs to account for this uncertainty. The estimated TCR of the base case Thief Process for the 500 MW hypothetical plant is \$1,444,972 (\$2.89/kW) which is (\$0.79/kW) higher than ACI. The impact of including an intermediate Thief collection/ storage option would increase the estimated TCR by about \$850,000 (\$1.70/kW) over the base case Thief Process (continuous extraction and re-injection).

The O&M costs for both the Thief Process and ACI are documented in Table 7. The notable difference in the fixed O&M costs between ACI and the Thief Process is the operating labor. Because the Thief Process is somewhat more complex than and not as mature as ACI, operating and maintenance labor may be somewhat higher for the Thief Process. The difference in variable O&M costs between ACI and the Thief Process is dominated by the difference in sorbent costs. The Thief sorbent cost is conservatively estimated at \$186/ton (\$0.205/kg) while the activated carbon is assumed to cost \$1000/ton (\$1.102/kg). The waste disposal costs assume that the additional sorbent, commingled with fly ash, is disposed of at a rate of \$17/ton (\$0.019/kg). While the assumptions used in estimating the fly ash disposal cost are identical for both technologies, the actual costs for a given power plant may be substantially higher. The levelized cost analyses under fly ash sales, reduced fly ash revenue, and lost fly ash revenue scenarios are discussed elsewhere, and reveal that potential fly ash impacts may influence overall economics much more strongly on a relative basis than sorbent cost or capital cost sensitivities [25,27,28].

While a detailed treatment of cost levelization methodology is provided elsewhere [25], it is useful to illustrate key findings in several examples. Table 7 compares the levelized constant 2003 dollar cost structure for an example case Thief Process, using a Thief sorbent cost value of \$186/ton (\$0.205/kg), relative to ACI for 3.3 lb/MMacf (53 g/km³) injection to achieve 50% Hg removal upstream of an existing ESP in the 500 MWe reference plant. From Table 7, the Thief Process has a total levelized 0.21 mills/kW-h cost, which represents nearly a 57% reduction as compared to the 0.48 mills/kW-h levelized cost for ACI. Whereas the Thief Process fixed O&M and fixed

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t7.1	Table 7
t7.2	Economic evaluation of ACI and the Thief Process

t7.3				ACI		Thief Process —	- base case
1	Total control capital cost						
t7.5	Equipment cost			\$462,80	$0^{a}$	\$200,000	
t7.6	Freight			incl		\$10,000	
t7.7	Taxes			\$34,968	a	\$21,600	
t7.8	Field materials			\$120,00	$0_{\rm p}$	\$160,000	
t7.9	Field labor			\$85,000	b	\$300,000	
t7.10	Indirect field costs					\$21,000	
t7.11	Subtotal			\$702,76	8	\$712,600	
t7.12	Retrofit factor— Thief 1.20					\$142,520	
t7.13	Bare Installed Retrofit Cost (BIRC)			\$702,76	8 <sup>a</sup>	\$855,120	
t7.14	Engineering and home office fees (ACI — 1	0% and Thief — 20%	of BIRC)	\$70,277		\$171,024	
t7.15	Process contingency (ACI — 5%, Thief —	15% of BIRC)	\$35,138		\$128,268		
t7.16	General facilities cost (5% of BIRC)			\$35,138		\$42,756	
t7.17	Project contingency (15% of BIRC & indirect	et costs)		\$126,49	8	\$179,575	
t7.18	Total, \$			\$969,82	0	\$1,376,743	
t7.19	Total, \$/kW			1.94		2.75	
t7.20							
1	Pre-production/shakedown costs — shakedow	vn ACI 2 weeks, Thief	1 month				
t7.22	Fixed operating cost			\$4591		\$17,603	
t7.23	Variable operating cost			\$53,866		\$23,091	
t7.24	2% total capital cost			\$19,396		\$27,535	
t7.25	Total capital requirement (TCR),\$			\$1,047,0	573	\$1,444,972	
t7.26	Total capital requirement (TCR),\$/kW			2.10		2.89	
t7.27							
1	Fixed O&M						
t7.29	Operating labor (\$45/h)			\$70,200		\$140,400	
t7.30	Maintenance and materials (5% of BIRC)			\$35,138		\$42,756	
t7.31	Admin. and support labor (20% of operating	labor)		\$14,040		\$28,080	
t7.32	Total			\$119,37	8	\$211,236	
t7.33							
	Variable O&M costs						
t7.35	Sorbent (ACI — \$1000/ton Thief — \$186/to	on)		\$1,365,0		\$253,890	
t7.36	Incremental power (\$0.05/kW)		<b>X</b> /	\$12,300		N/A	
t7.37	Waste disposal (\$17/ton)			\$23,206		\$23,206	
t7.38	Total			\$1,400,	506	\$277,096	
t7.39	Levelized cost summary — constant \$	ACI	•		Thief Process	s — base case	
t7.40	20 years	\$	mills/kW-h	\$/lb Hg	\$	mills/kW-h	\$/lb Hg
t7.41	Fixed charges	174,123	0.050	1038	240,154	0.069	1432
t7.42	Fixed O&M	119,378	0.034	712	211,236	0.060	1260
t7.43	Variable O&M	1,400,506	0.400	8351	277,096	0.079	1652
t7.44		1,694,008	0.483	10,101	728,487	0.208	4344

t7.45<sup>a</sup> Cost reported in Ref. [28]. <sup>b</sup> Estimated from Ref. [28]. t7.46

charges are slightly higher than ACI, the levelized variable 833

O&M costs on a mills/kW-h basis are nearly an order of magnitude lower for the Thief Process as compared to ACI. The variable O&M costs dominate the ACI levelized cost structure, which is chiefly driven by the cost of activated carbon.

In comparing technology costs, levelized mills/kW-h is a very convenient and useful indication since it directly relates to the net cost of electricity. Annualized total dollars are readily determined from plant output and capacity. For example, the Thief Process 0.21 mills/kW-h estimate translates into an annual savings of \$965,500 in levelized constant dollars (2003) as compared to the 0.48 mills/kW-h ACI estimate for the 500 MW reference plant with an 80% capacity factor. While the costs of mercury control are often reported on a \$/lb (\$/kg) mercury

removed basis, it is important to note that this directly follows from the levelized mills/kW-h but is obviously very dependent on the initial Hg baseline level. Thus, for a plant with an initial baseline mercury level of 9 lb/trillion Btu (3.9 g/J), the ACI value of 0.48 mills/kW-h would translate into an incremental cost of over \$10,101/lb (\$4582/kg) Hg removed while the Thief Process translates into only about \$4344/lb (\$1970/kg) Hg removed.

# 5. Conclusion

The NETL patented Thief Process is a developing technology that offers an attractive approach for mercury control by allowing the possibility for strategically extracting low amounts of

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partially combusted coal for use as an effective mercury sorbent. The initial development that validated the Thief technology included both lab-scale and pilot-scale testing. The experimental studies focused on bituminous coal and the test results indicate that a sorbent could be produced that could remove the vaporphase mercury from flue gas. The extracted sorbent obtained from the pilot units while firing bituminous coal had surface areas of 75 m<sup>2</sup>/g which were an order of magnitude greater than the parent coal and fly ash. The effectiveness of the extracted sorbents was significantly less than Norit Darco FGD that has a surface area of approximately 500 m<sup>2</sup>/g, requiring approximately four times the amount of Thief sorbent to obtain similar mercury removals. Clearly, the bituminous coal test results indicated that it was necessary to optimize the Thief Process to maximize the extracted sorbent effectiveness.

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The pilot unit testing while firing a subbituminous coal focused on the optimization of the Thief Process. To assist the optimization, modifications to the probe and extraction system were initiated allowing for a more complete mapping in the targeted near burner region. The extracted solids physical properties for different regions in the near burner region showed that significant increases in BET surface area and pore volume were obtainable. The extracted solids effectiveness in removing the vapor-phase mercury in sorbent injection testing improved as the surface area and pore volumes increased. The extracted solids with surface areas greater than 200 m<sup>2</sup>/g showed similar mercury removals to activated carbon with mercury removals over 60% in-duct and over 90% across the system. The testing with the subbituminous coal did not fully define the limits of the Thief Process since this initial optimization did not include the full characterization of the near burner region and did not include a portion of the small size particles that escaped collection in the cyclone. In addition, future development focusing on the integration of an advanced probe/extraction system could potentially lead to significant improvements in the ultimate cost of the Thief sorbent.

The economic evaluation of the Thief Process was based on the pilot unit experimental results that showed the Thief sorbent (>30 wt.% ash) effectiveness for the subbituminous coal was similar to activated carbon. The Thief sorbent cost is based on the heat rate penalties and parasitic power requirements associated with the extraction of solids and gas from the combustor and re-injection upstream of the particulate control device. The Thief sorbent cost used in this analysis is conservatively estimated to be \$186/ton (\$0.205/kg) (35-wt.% ash) which is over 80% lower than the cost of activated carbon. In addition, the use of an energy management system could potentially decrease the cost of the Thief sorbent by an additional 50%. The Thief Process capital and fixed O&M costs are estimated to be greater than ACI and reflect the increased complexity of the Thief Process as well as the relative maturity of the technologies. The Thief Process capital and fixed O&M costs may decrease as the optimization and scale-up of the Thief Process continue. For a generic 500 MWe reference plant, the levelized cost savings of the Thief Process is \$0.27/kW-h, which 914 represents \$965,500 annually. While the Thief Process has been successfully tested at a pilot scale up to 0.5 MWe, these favorable results underscore the importance of further optimization testing and scale-up to be undertaken for the technology to become commercialized so that utilities may consider the Thief Process as a viable option for meeting the new EPA mercury regulations within the 2010–2020 time frame.

#### 6. 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.

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