



Mercury Control Technologies for Electric Utilities Burning Lignite Coals – Phase I - Bench-Scale Testing

Goal of Sorbent Screening

- Narrow to 3 to 5 sorbents
 - High capacity
 - High reactivity
 - Commercial promise
- Provide information for PTC testing – decreasing variables to test
- Narrow to one to two carbon types – if they have similar properties
- Options for additional sorbent options
 - Consideration of preparation procedures

Overview

- Background information on lignite variability and Hg sorbents
- Bench Scale Testing
 - Sorbent preparation
 - Sorbent characterization
 - Hg sorbent testing
 - Packed Bed – break through curves
 - Entrained Flow – mercury reduction curves
 - Exposed sorbent characterization
- Sorbent ranking for pilot scale testing
 - Criteria – capacity, reactivity, and cost

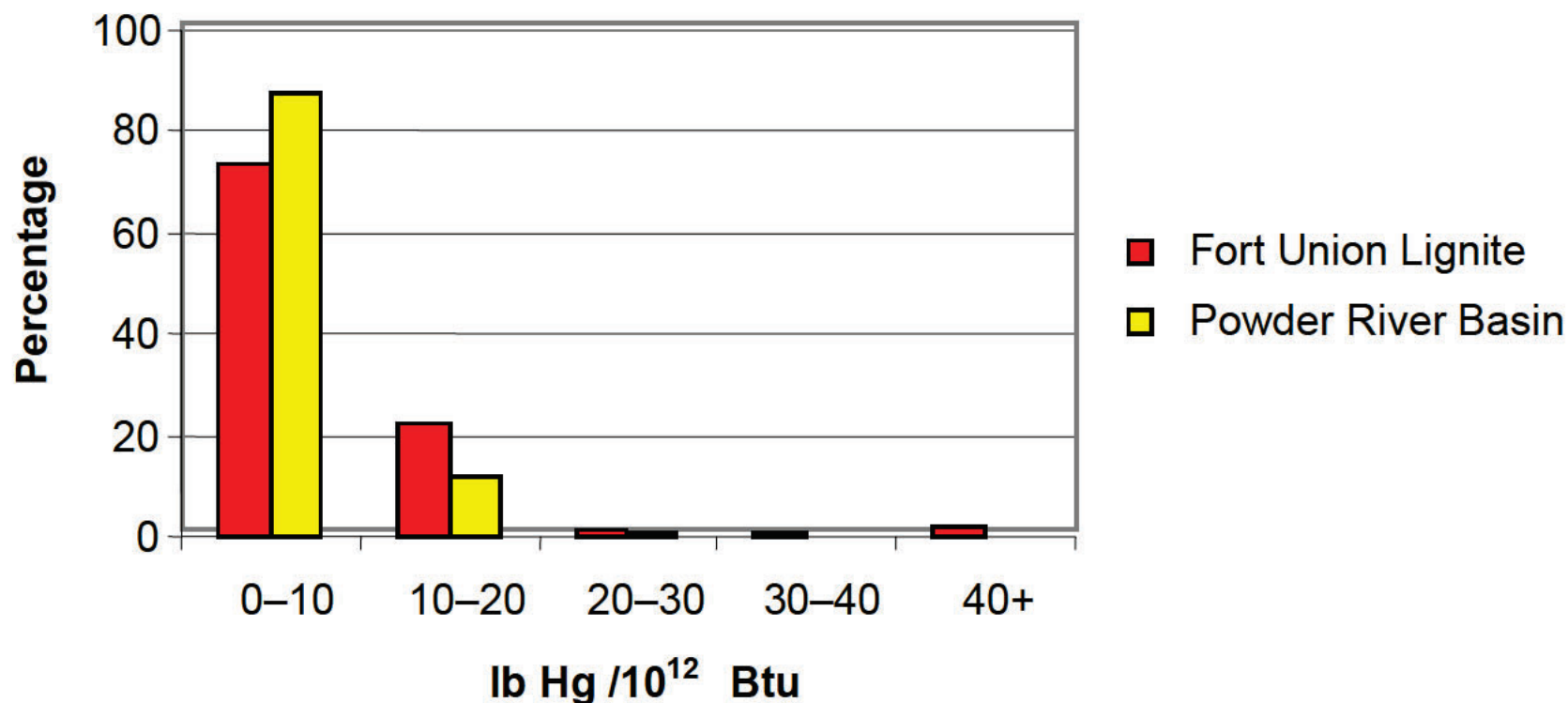
*Limits of Variation in Proximate Analysis
of Fort Union Region Lignite
(as-received basis)*

Sample Group	Number of Sample Locations	Proximate Analysis, Weight Percent			
		Moisture	Volatile Matter	Fixed Carbon	Ash
Fort Union Region—Average	212	37.2	26.3	30.3	6.2
Range: High		43.59	28.30	34.82	12.09
Low		32.47	23.40	24.10	3.16
2s limit ^a		2.16	1.46	1.91	1.70
Confidence range on average ^b		0.15	0.10	0.13	0.12
^a "2s limit" equals twice the standard deviation and represents the interval on either side of the average within which 95% of the individual values are expected to lie. ^b "Confidence range on average" represents the range around the average within which there is a 95% confidence that the true average lies.					

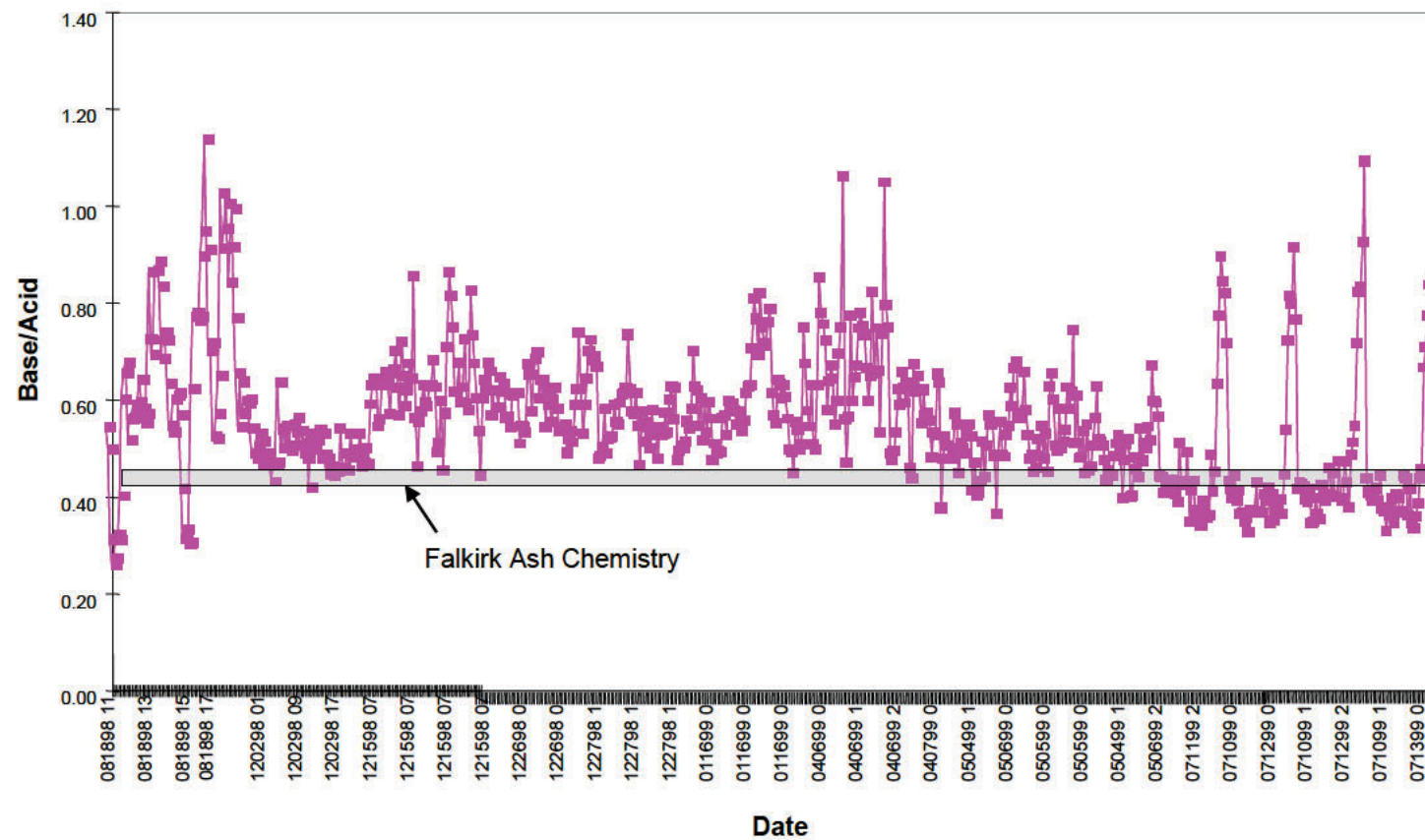
Limits of Variation in Ash Analyses of Fort Union Region Lignite

Sample Group	Number of Sample Locations	Composition, Weight Percent of Ash						
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	SO ₃
Fort Union Region—Average	212	19.7	11.1	9.1	24.6	6.9	6.5	19.5
Range: High		39.4	26.1	34.3	52.0	13.6	27.8	32.0
Low		6.3	4.2	0.9	12.4	2.8	0.1	8.3
2s Limit ^a		8.39	3.06	7.25	6.57	2.13	5.14	7.27
Confidence range on average ^b		0.57	0.21	0.49	0.45	0.15	0.35	0.49
^a “2s limit” equals twice the standard deviation and represents the interval on either side of the average within which 95% of the individual values are expected to lie. ^b “Confidence range on average” represents the range around the average within which there is a 95% confidence that the true average lies.								

Fort Union Lignite Compared to Powder River Basin Coals



As-Fired Coal Variability – ND Lignite



Hg Speciation and Emissions for Fort Union Lignite

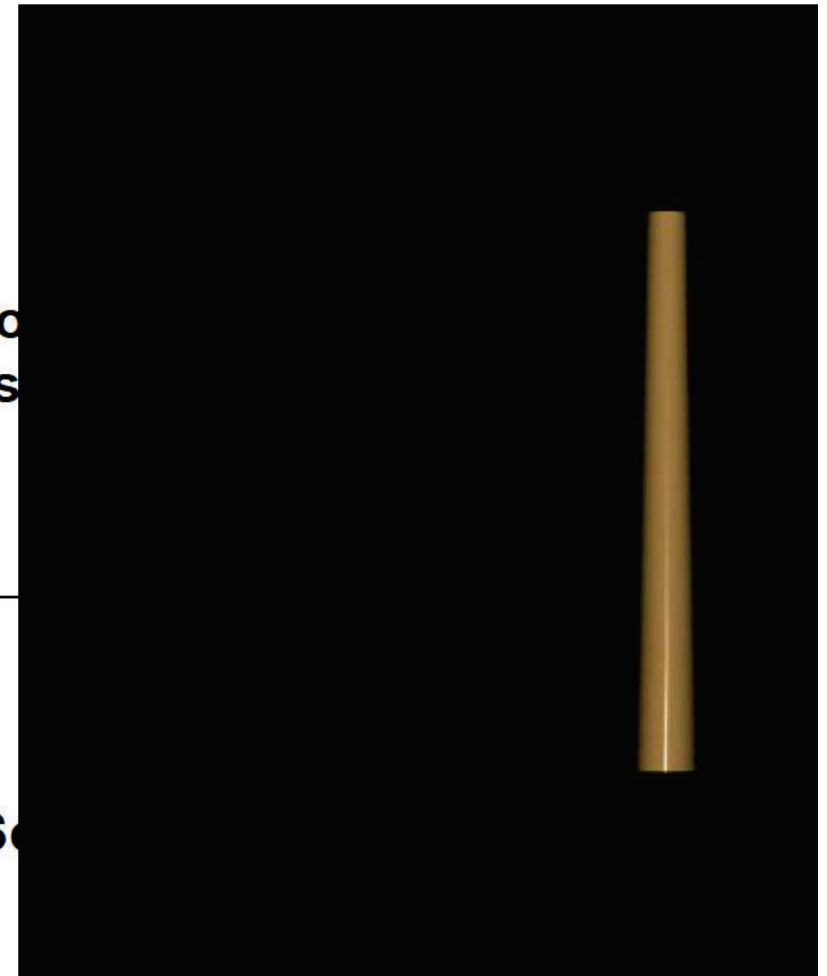
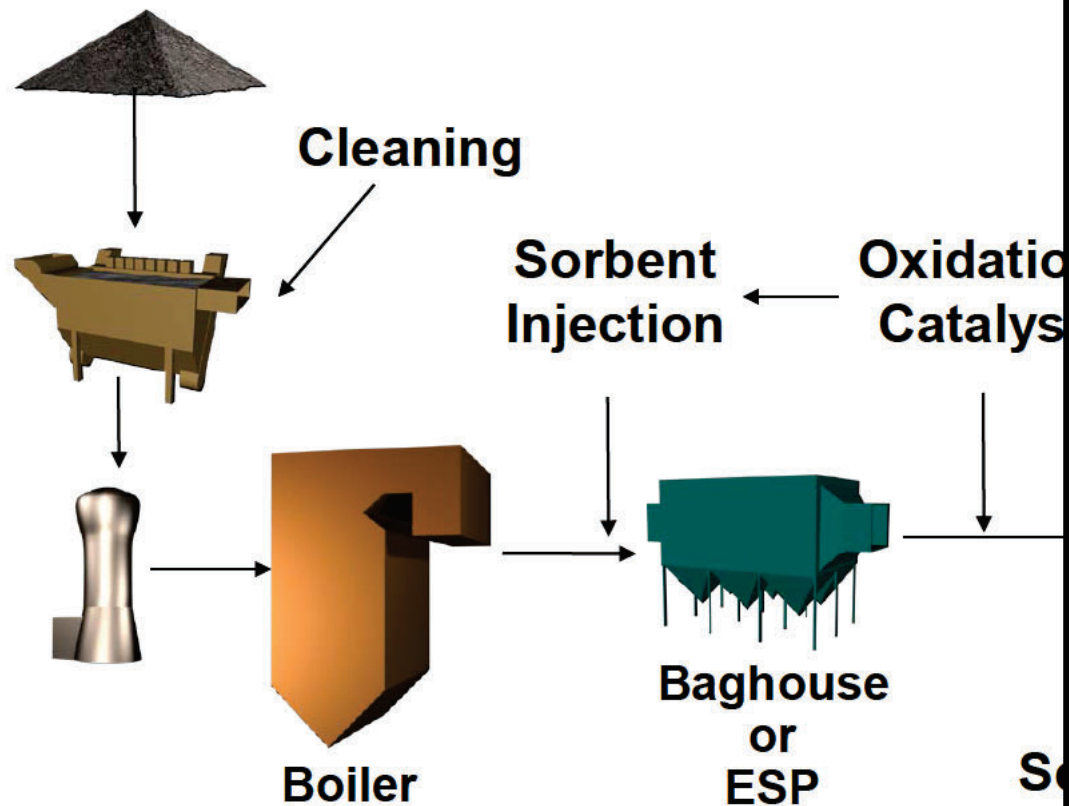
- Speciation of Hg in flue gas
 - Elemental Hg ranged from 63 to 96 %
 - Oxidized Hg ranged from 4 to 44 %
- Stack Hg ranged from 2.94 to 9.24 lb/Tbtu (avg =6.3 lb/Tbtu).
- Emitted mercury ranged from 45 to 91 %

Correlation Coefficients for Ash Components and Hg Speciation (>0.36 significant)

<u>% Flue Gas</u>	<u>Coal Cl</u>	<u>SiO₂</u>	<u>Al₂O₃</u>	<u>Fe₂O₃</u>	<u>CaO</u>	<u>Na₂O</u>
Elemental Hg	0.02	-0.55	-0.34	0.81	0.78	0.38
Oxidized Hg	-0.05	-0.08	-0.14	-0.57	-0.22	-0.27
Particulate Hg	-0.25	0.18	0.07	-0.66	-0.41	-0.08

- Database of lignite and subbituminous coals from ICR data

Mercury Control Options



Regenerate

Sorbent Options

- Sorbents – injection and capture with particulate control
 - Carbons: activated carbons derived from coal, impregnated with iodine, sulfur, and other materials
 - Metal oxides: oxides of iron, manganese, and other metals
 - Calcium silicates – derived from fly ash or slag
 - Lime/activated carbon
 - Na₂S₄-impregnated activated carbon
 - Activated carbon derived from tires (Wojtowicz and Serio, Patent No. 6,322,613)
 - Iron chloride
 - Titania with added metals/oxides
 - Palladium chloride
 - Noble metals: gold, tin, zinc, copper, lead, cadmium, silver
 - Corn fibers
 - Fly ash reinjection (Knowles, Patent No. 5,787,823).

Oxidation Options

- Oxidizing agents: react with elemental mercury and oxidize for control in a scrubber; little distinction between sorbents and oxidizing agents
 - Transition metals: iron, chromium, nickel, and others
 - Selective catalytic reduction (SCR) catalysts have shown ability to oxidize elemental Hg.
 - Iron oxide: maghemite and HCl
 - Carbon beds
 - Noble metal – gold-coated silica bed and dilute HCl (Meishen and Van Pelt, Patent No. 6,136,281)
 - Permanganate
 - Iron chloride
 - UV radiation and titanium dioxide (Biswas and Wu, Patent No. 6,248,217)

Sorbent Injection Upstream of Particulate Control

- Sorbent captures both elemental and oxidized forms of mercury – sorbent must be able to oxidize and capture elemental mercury.
- Sorbent characteristics: particle size, reactivity, and capacity
- Residence time and temperature
- Stability

How Much Sorbent Is Needed?

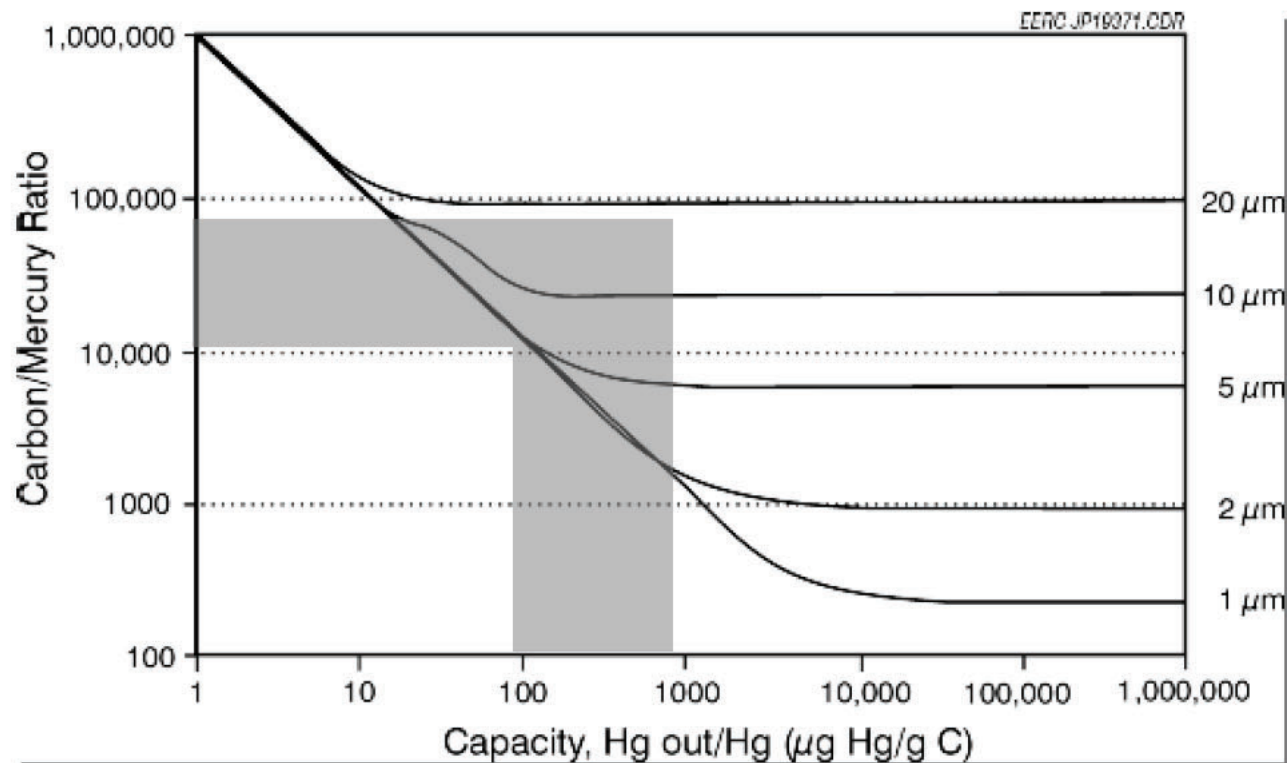
- Hg typically 5–10 $\mu\text{g}/\text{m}^3$ in flue gas.
- Assume 1000:1 sorbent to Hg.
- For 10 $\mu\text{g}/\text{m}^3$ Hg, required sorbent loading is 10 mg/m^3 .
- Only 0.1% to 0.2% of fly ash.
- Should not affect control device, utilization, or disposal.

Mercury Sorbent Capacity

- Sorbent chemical and physical properties
- Temperature
- Mercury species
- Mercury levels
- Flue gas composition (SO_2 , NO_x , HCl , O_2 , CO , Cl_2 , and HF)

Dependence of Carbon/Mercury Ratio on Mercury Capacity

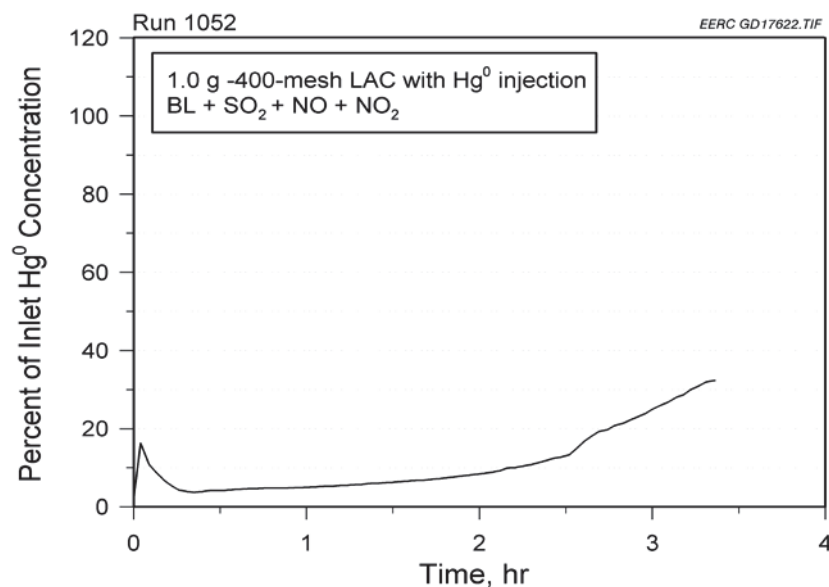
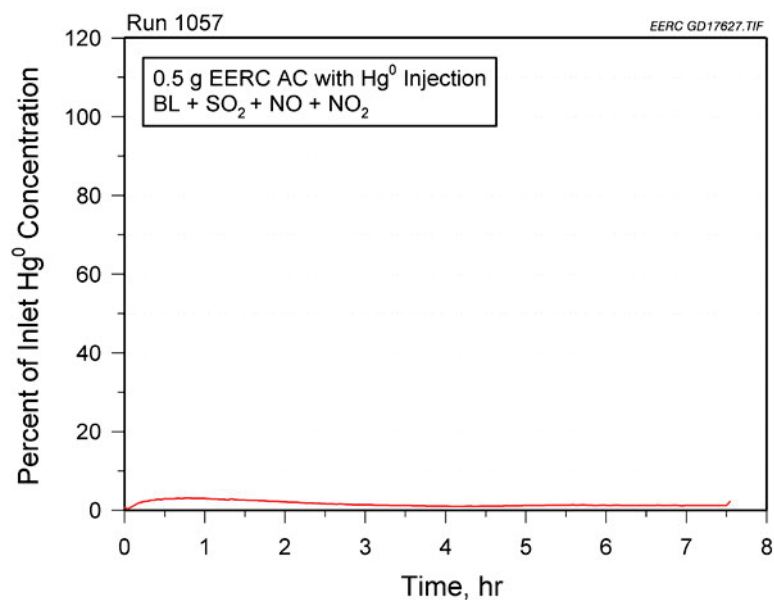
(90% removal of $10 \mu\text{g}/\text{Nm}^3 \text{ Hg}$)



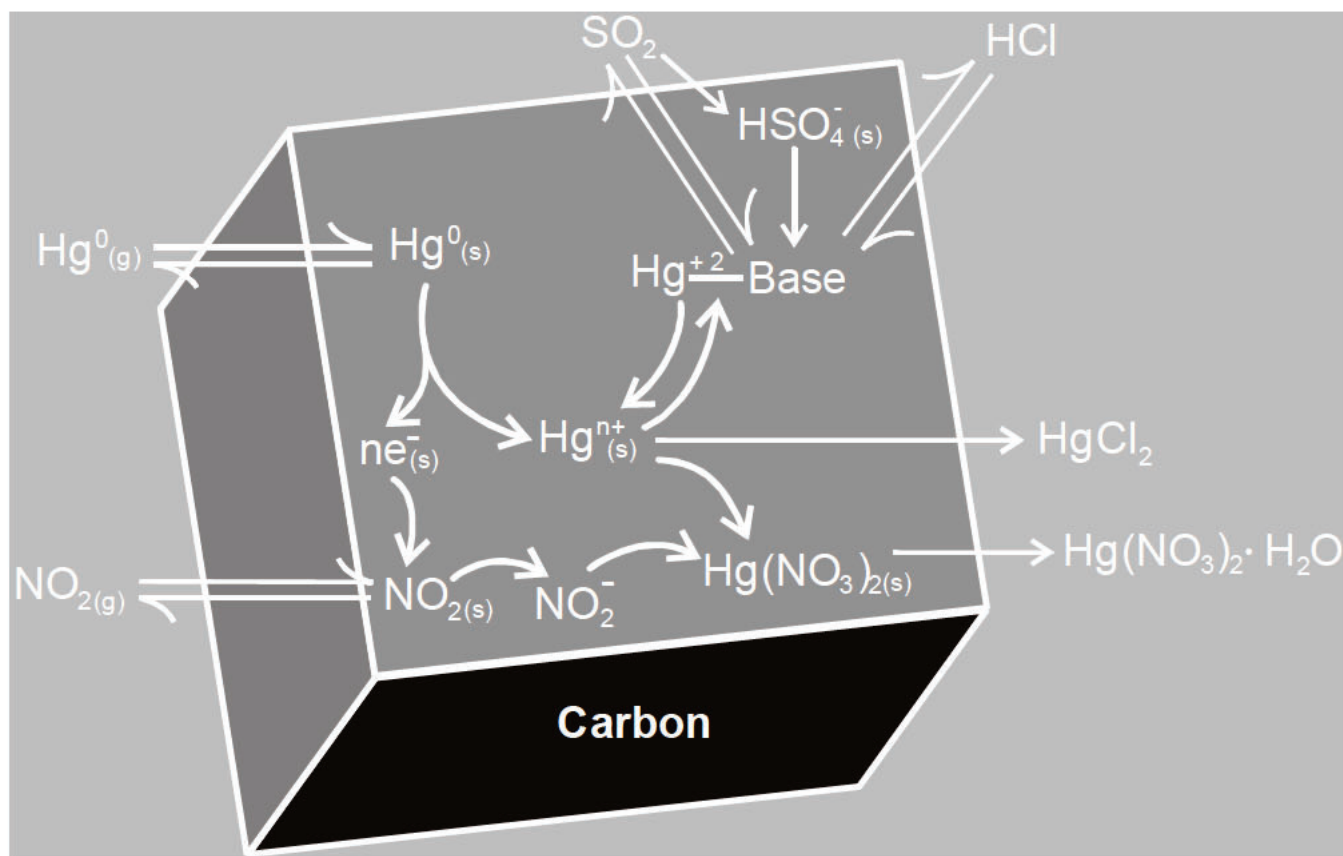
Source: Chen, Rostam-Abadi, and Chang, 2001
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Exhibit 2032
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Breakthrough Curves for Norit FGD and High-Sodium North Dakota Lignite AC



Mechanism of Mercury Capture with Carbon Sorbents



Bench Scale Testing

Bench-scale screening

- Evaluate a number of different sorbents, sorbent enhancements/modifications, gas species interactions, oxidation potential, sorbent size, temperature, etc
- Fixed bed and entrained flow using simulated gas similar to that produced from burning lignite coal
- Initial screening of sorbents to evaluate capture effectiveness, oxidation potential, and capacity
- Provide relative ranking to determine most promising sorbent for pilot and full scale testing based on capacity and cost

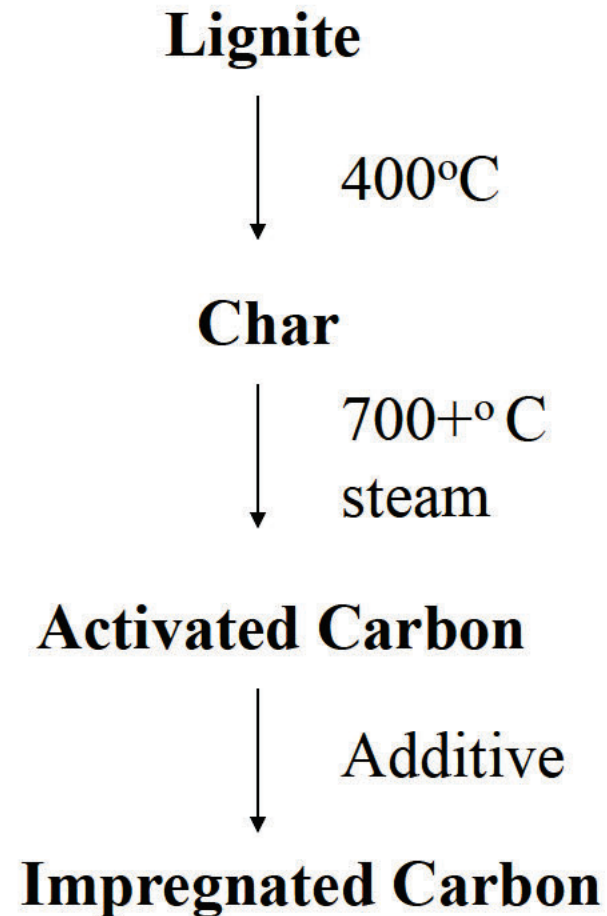
Screening Criteria

- Reactivity – Comparison to baseline Norit FGD
- Capacity – Bench-scale break through curves
- Physical properties – particle size, surface area, functionality
- Residence time – Entrained flow reactor studies
- Cost – relative to FGD carbon (50 cents/lb)

Potential Sorbents— for testing

- Carbon-based Sorbent selection – 6 sorbents
 - Baseline – Norit FGD
 - Luscar – coal, char, fines
 - Minnkota – high sodium Center lignite
 - Basin/ Otter Tail – high sodium Beulah-Zap lignite
 - Others – Falkirk – high calcium
 - Calcium silicate – derived from slag
 - Lime/Carbon mixture
 - Impregnated carbons – I, S, Cl
- Char preparation - pyrolysis/steam activation
 - Tube reactor -- Bench scale
 - 4lb/hr unit – Pilot scale studies (0.03 to 0.04 lb/hr injection rates)

Activated Carbon Production

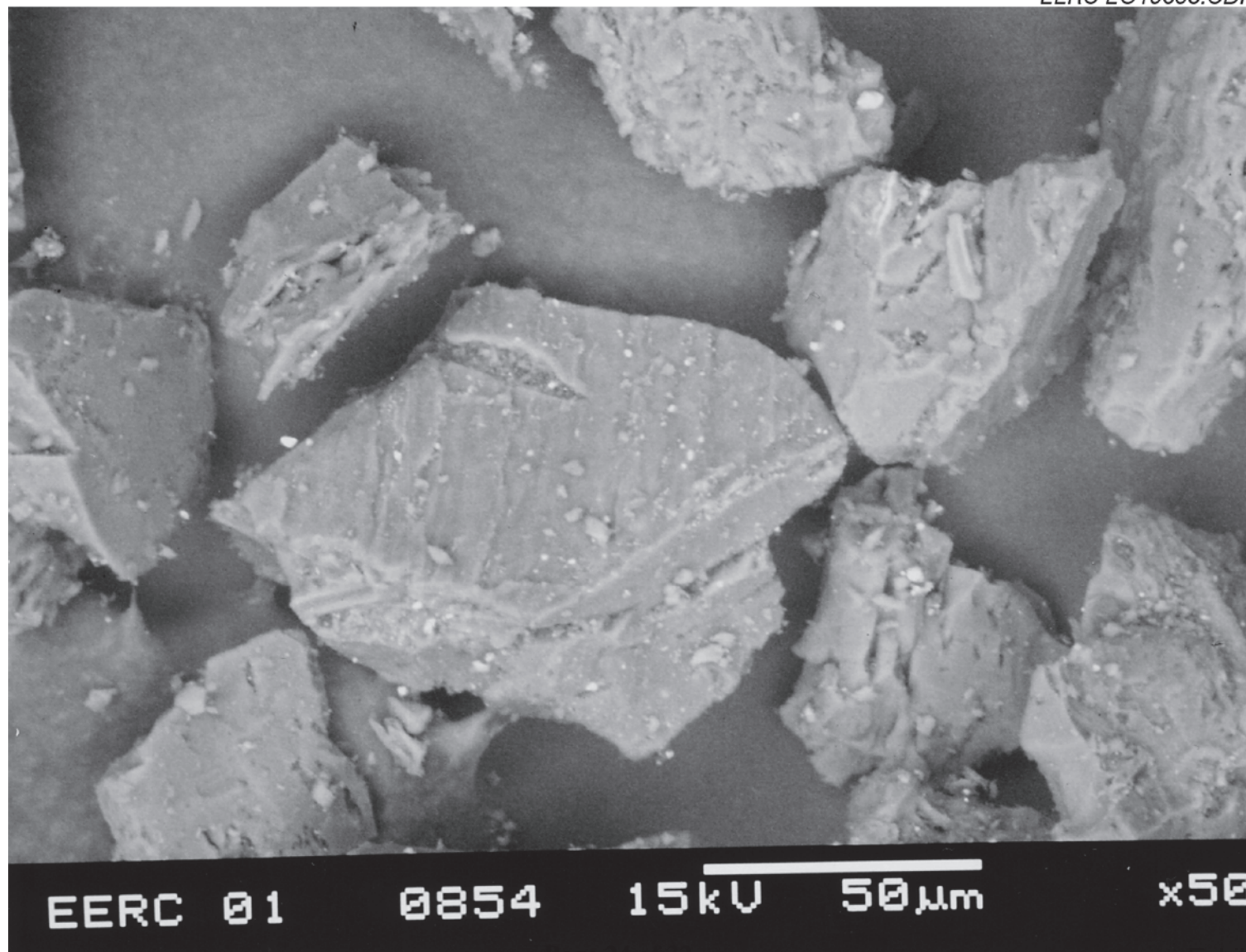


Activated Carbon Properties

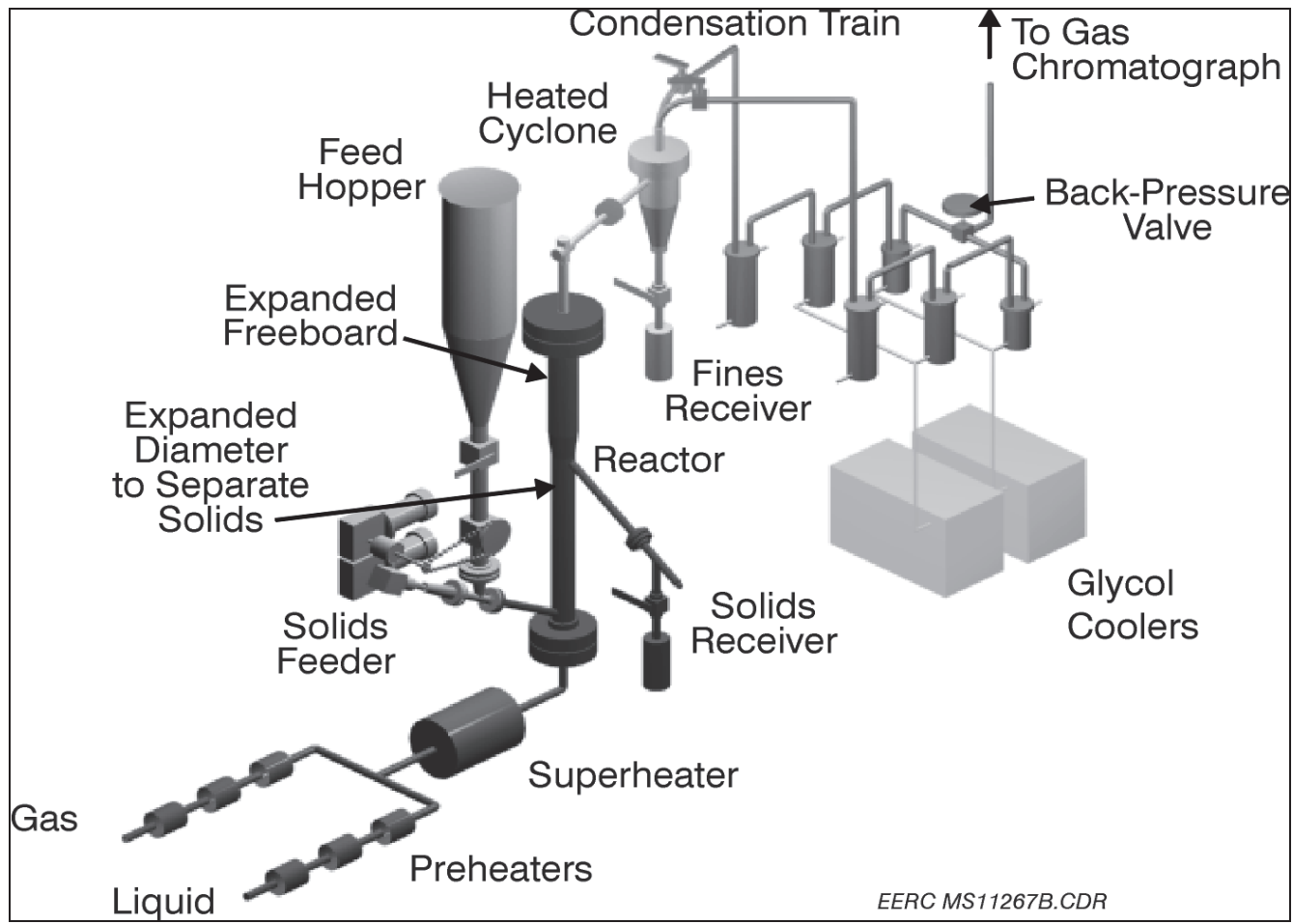
Metal Content	BET Surface Area (m ² /g)	Pore Volume (cc/g)	Avg. Pore Width (nm)
High Na	245	0.14	1.2
High Na (washed)	250	0.15	1.2
High Ca	370	0.20	1.1
Low Na, Low Ca	349	0.17	1.0

SEM Microphotograph of High-Sodium Carbon

EERC EO19658.CDR



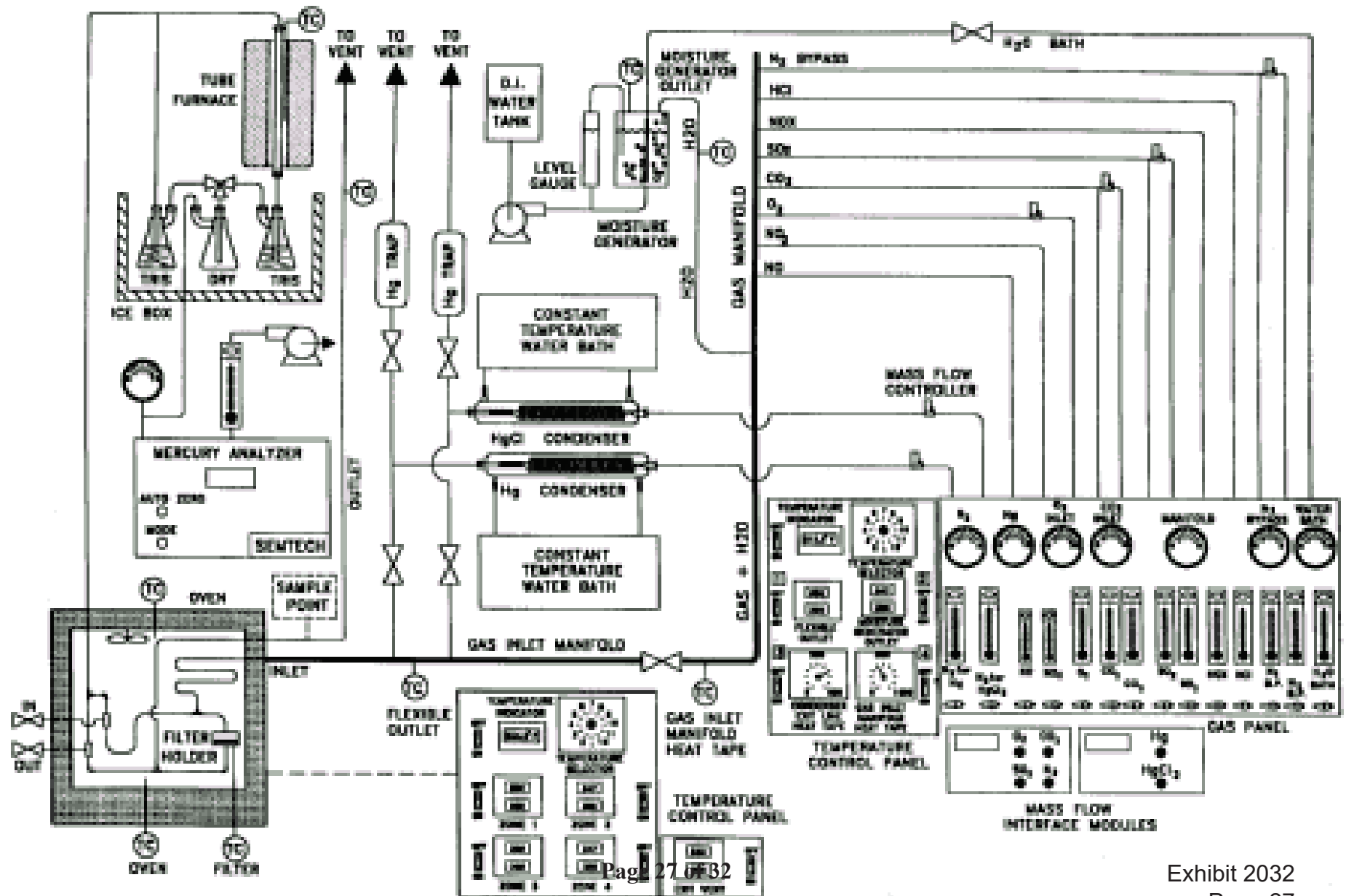
Small Reactor to Produce Char (4lb/hr)



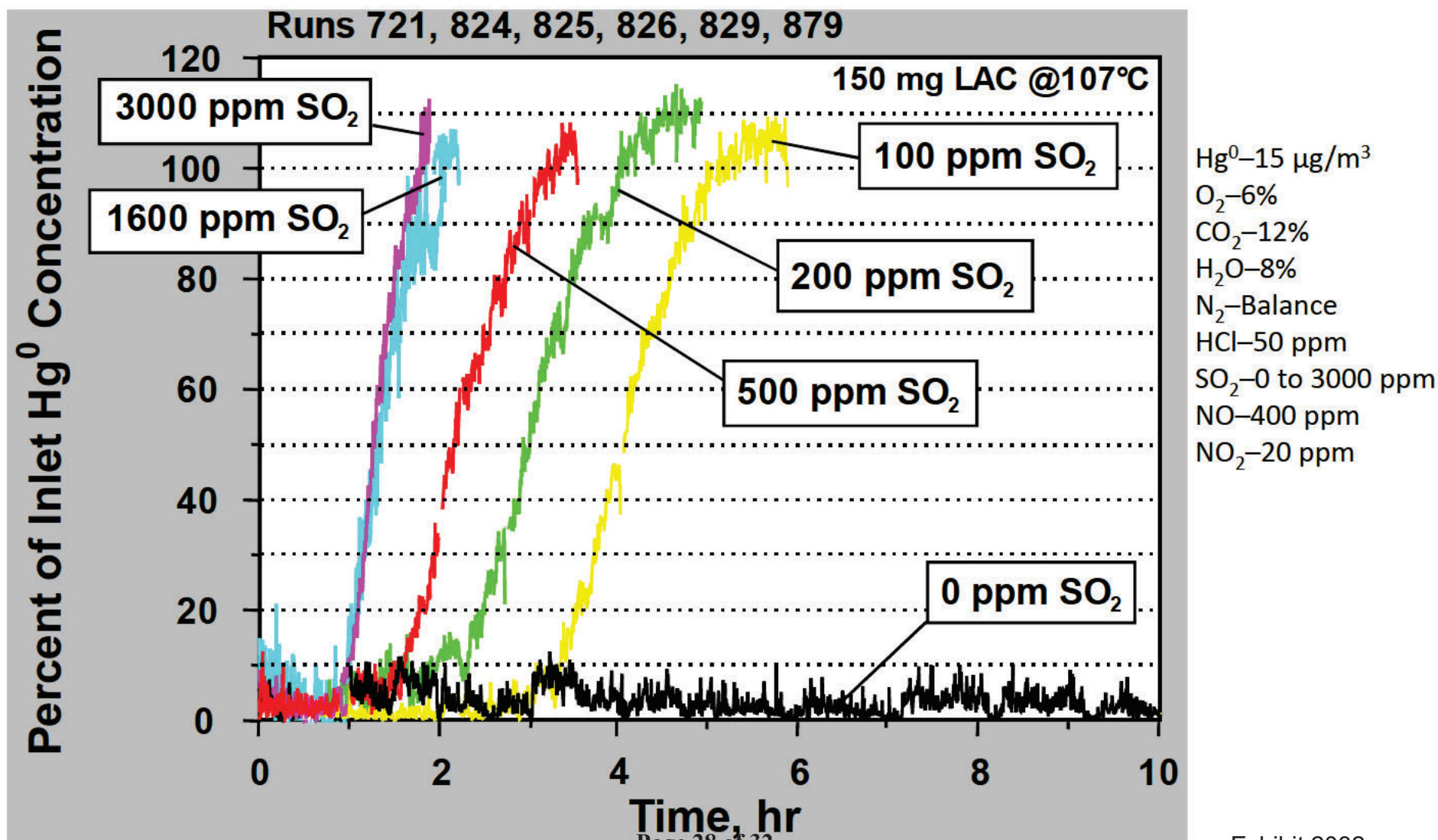
Characterization -- AC

- Carbon characterization
 - Chemical – C, H, N, S, and ash and ash composition
 - Physical – surface area (iodine #, one point nitrogen BET) – consider 10 point BET to calculate porosity (\$600 to 800), particle size distribution.
 - X-ray photoelectron spectroscopy (XPS) on selected starting and spent carbons to determine functionality

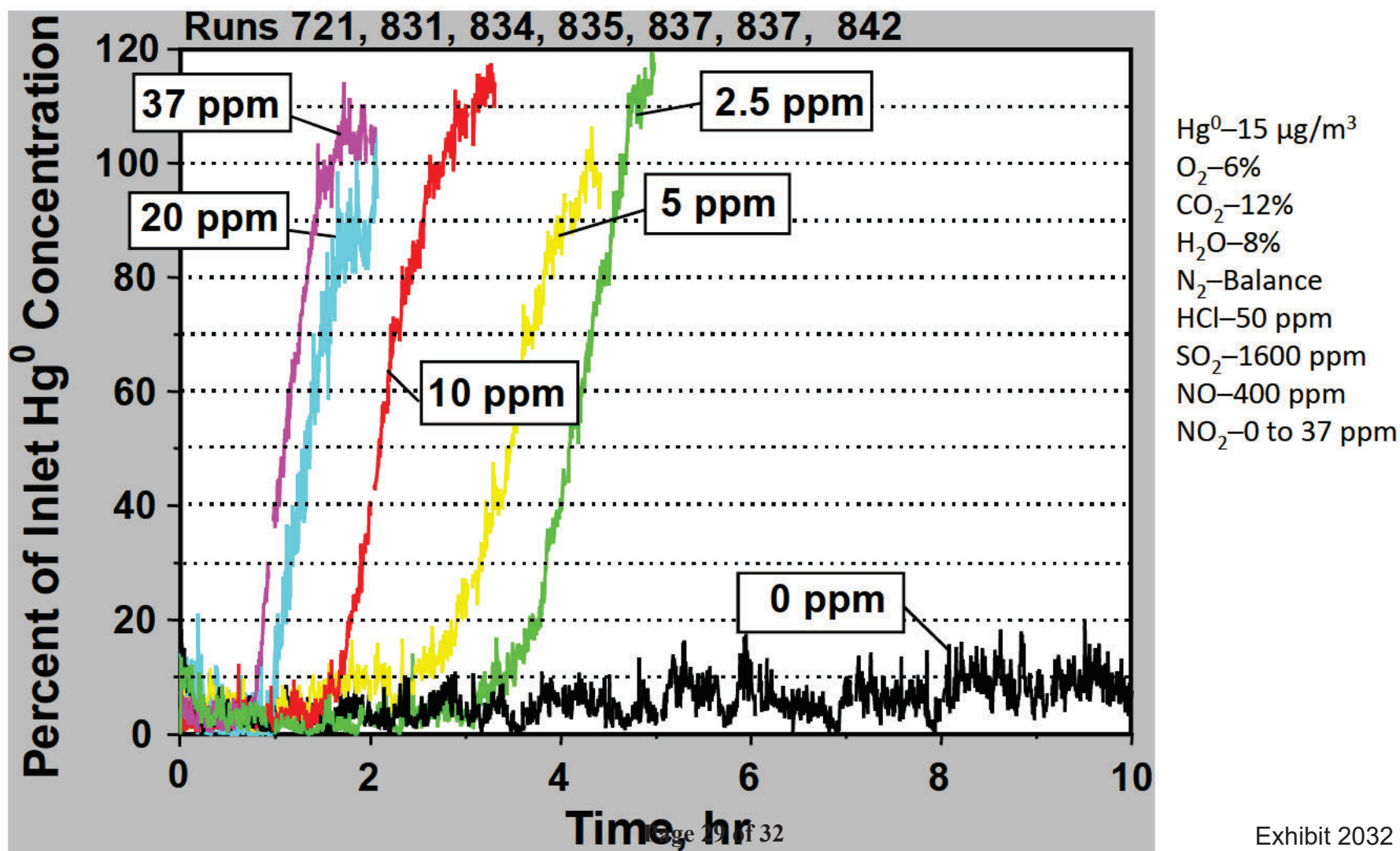
Packed Bed Testing



Effect of SO_2 Concentration on Hg^0 Capture with Activated Carbon



Effect of NO_2 Concentration on Hg^0 Capture with Activated Carbon



Entrained Flow Reactor

- Dimensions

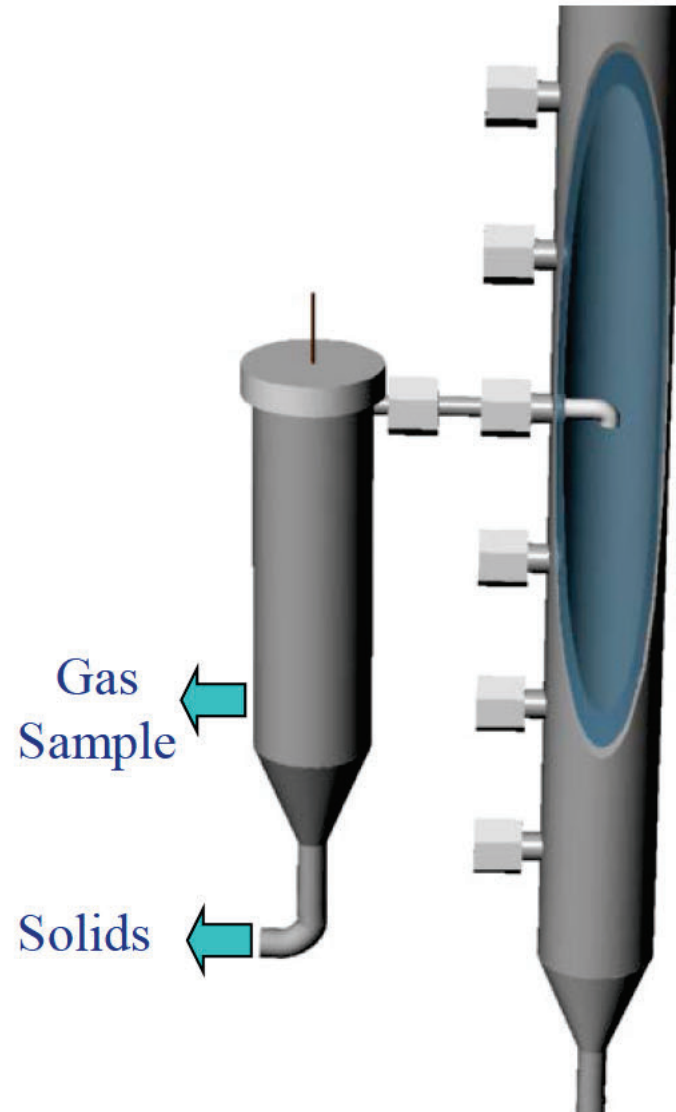
- Diameter ~ 2.5 to 3 inch
- Height ~ 6 ft
- Port size ~ ½ inch (qty 20)

- Flows

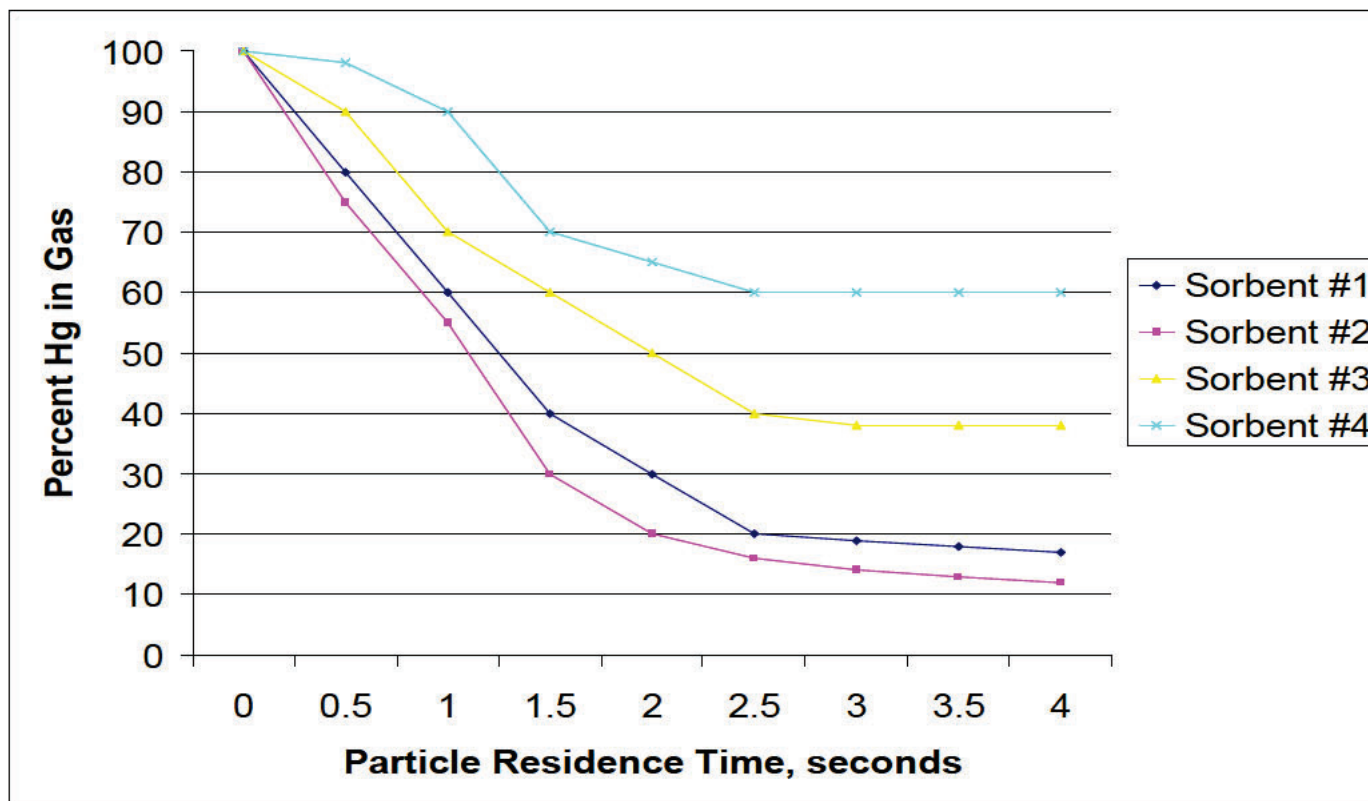
- Lab 30 scfh
- Res. Time testing 50 lpm
- Field tbd
- Residence time = 0 to 10 secs

- Sorbent injection rate

- 0 to 20 g/hr (lab)



Entrained Flow Reactor Results



Results of Bench Scale Testing – Identify the best sorbent for Larger scale testing

- Initial screening of sorbents to evaluate capture effectiveness, oxidation potential, and capacity
- Provide relative ranking to determine most promising sorbent for pilot and full scale testing
 - Criteria – reactivity, capacity, physical properties (size/surface area), residence time, and cost
- Prepare sorbents for pilot scale testing