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

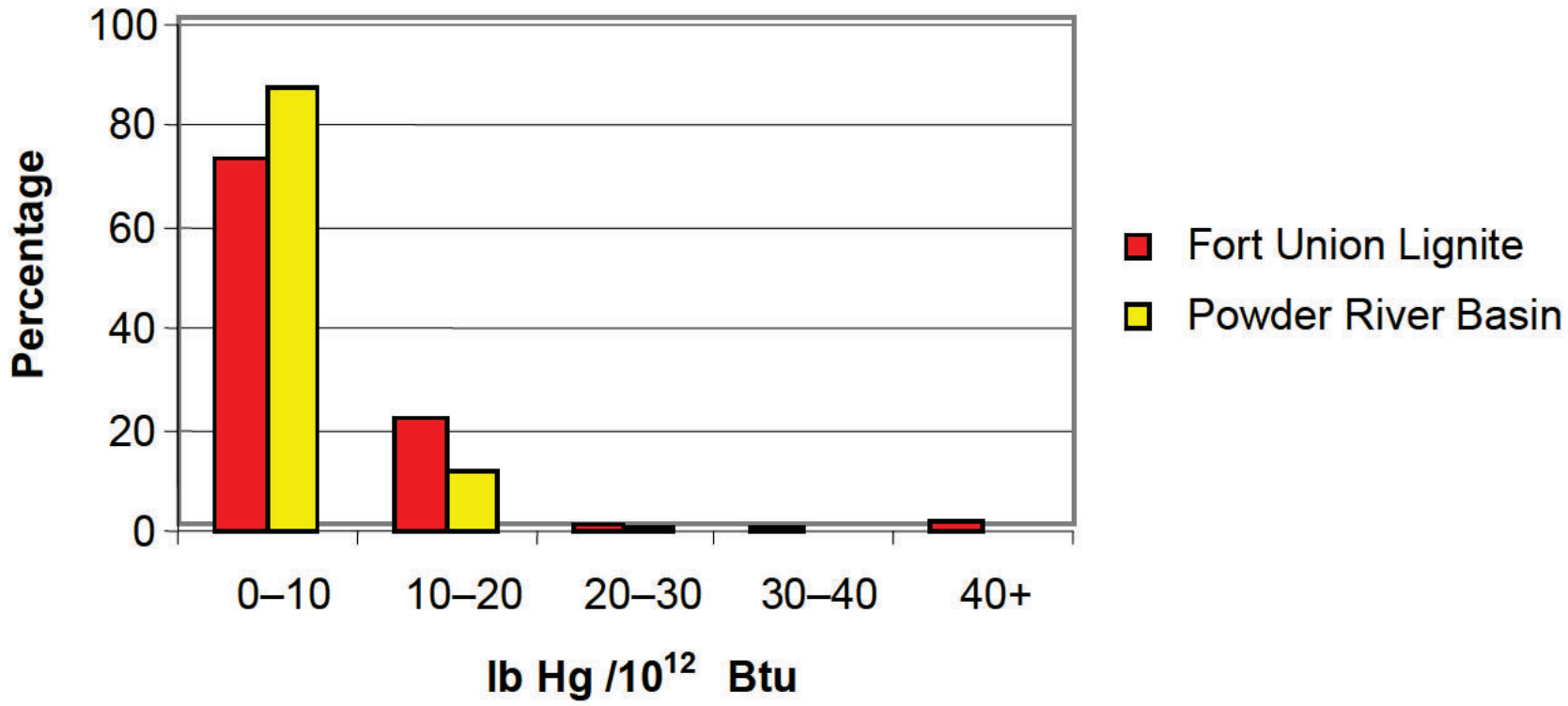
[a] "2s limit" equals twice the standard deviation and represents the interval on either side of the average within which 95% of the individual values are expected to lie.
[b] "Confidence range on average" represents the range around the average within which there is a 95% confidence that the true average 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_2O_3	Fe_2O_3	CaO	MgO	Na_2O	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



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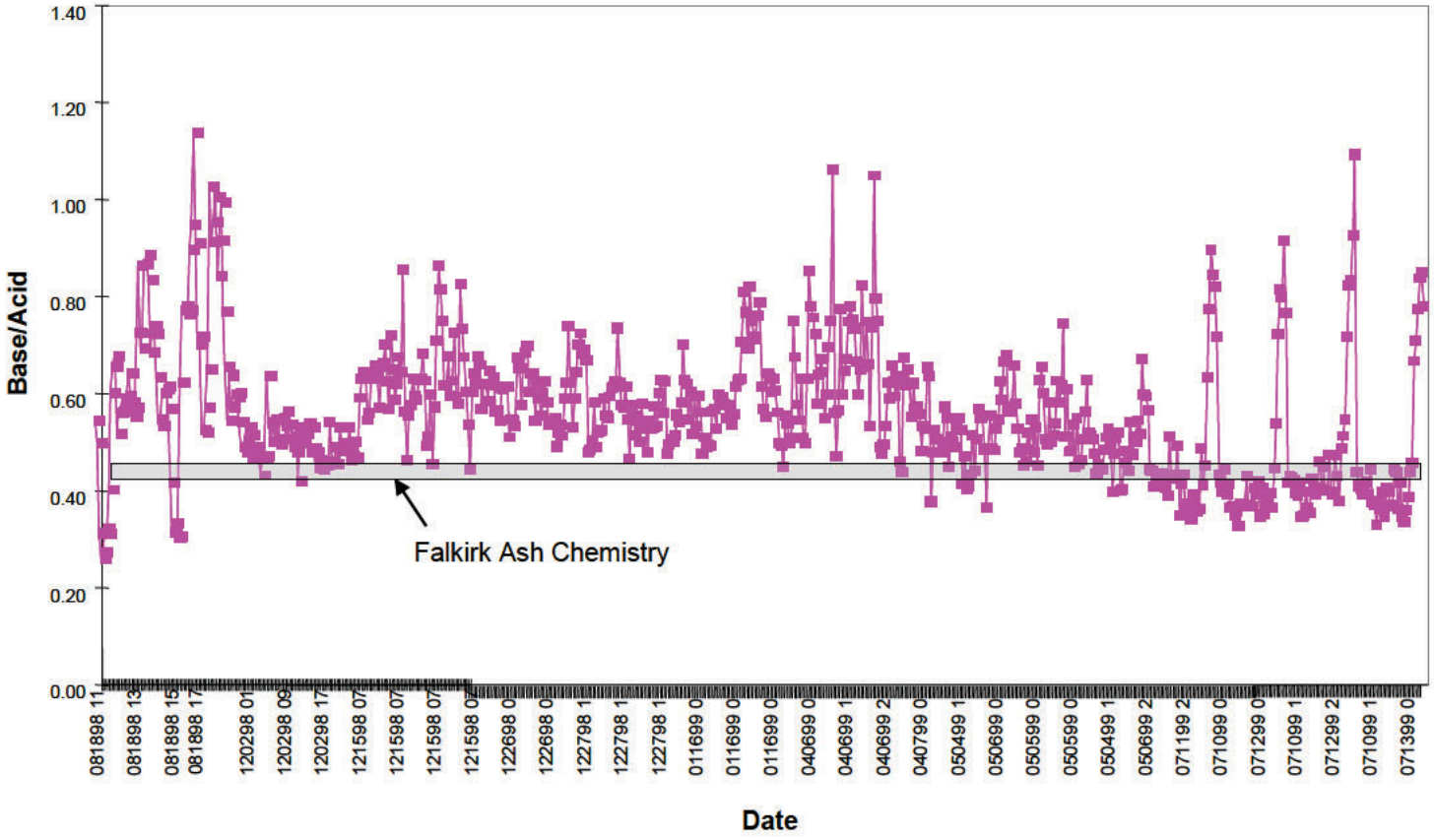
As-Fired Coal Variability – ND Lignite



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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 %

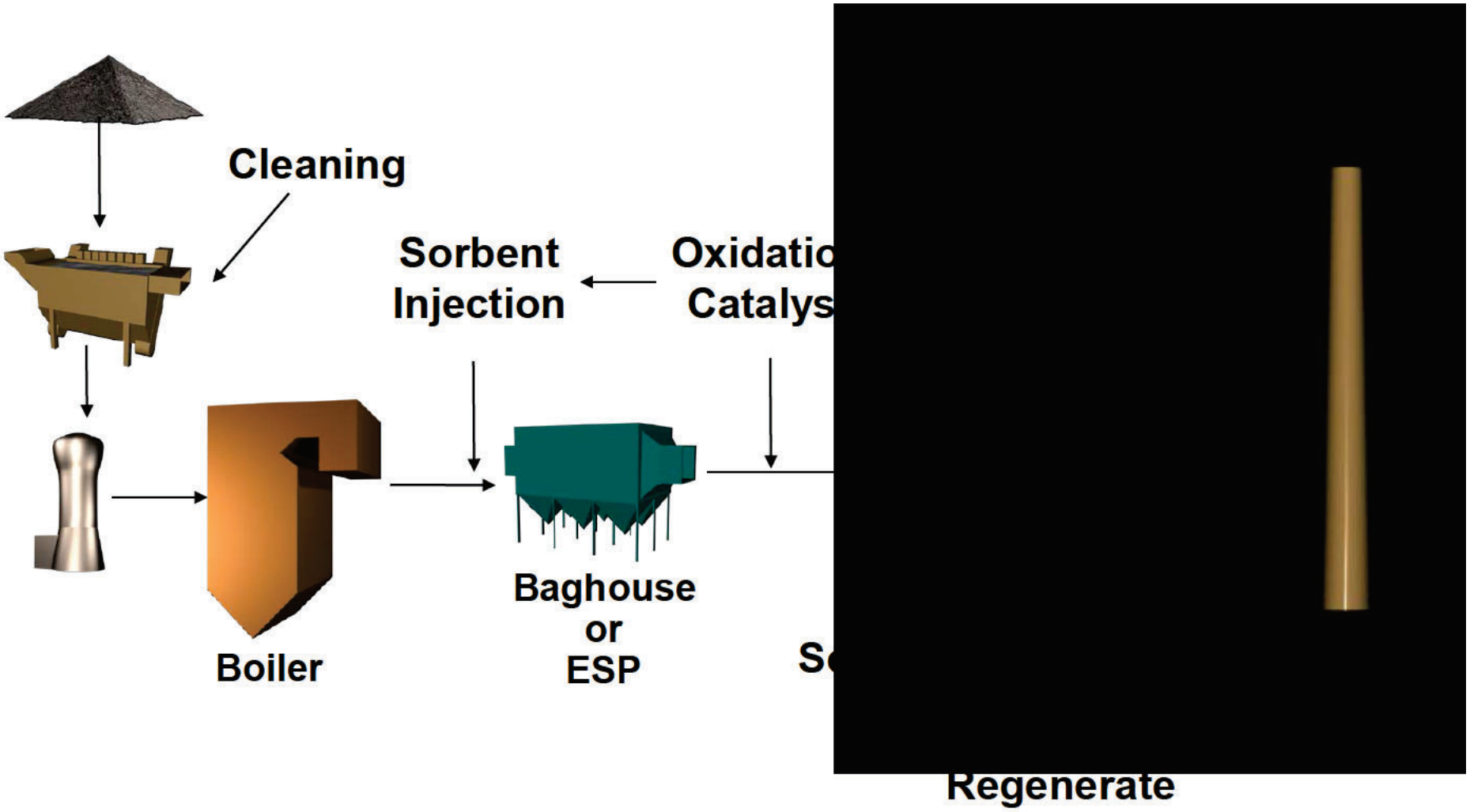
Correlation Coefficients for Ash Components and Hg Speciation

(>0.36 significant)

% Flue Gas	Coal Cl	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O
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



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
  - Na_2S_4-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?

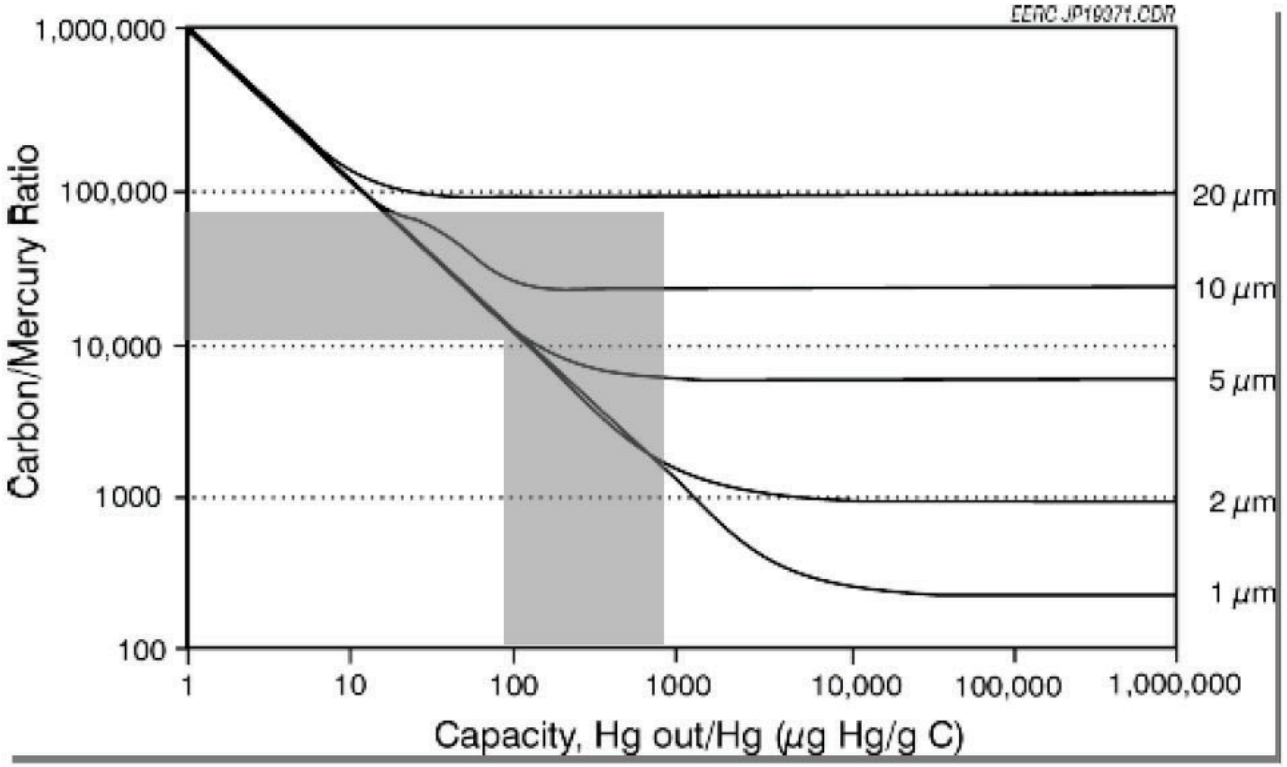
- Hg typically 5–10 µg/m^3 in flue gas.
- Assume 1000:1 sorbent to Hg.
- For 10 µg/m^3 Hg, required sorbent loading is 10 mg/m^3.
- Only 0.1% to 0.2% of fly ash.
- Should not affect control device, utilization, or disposal.

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)

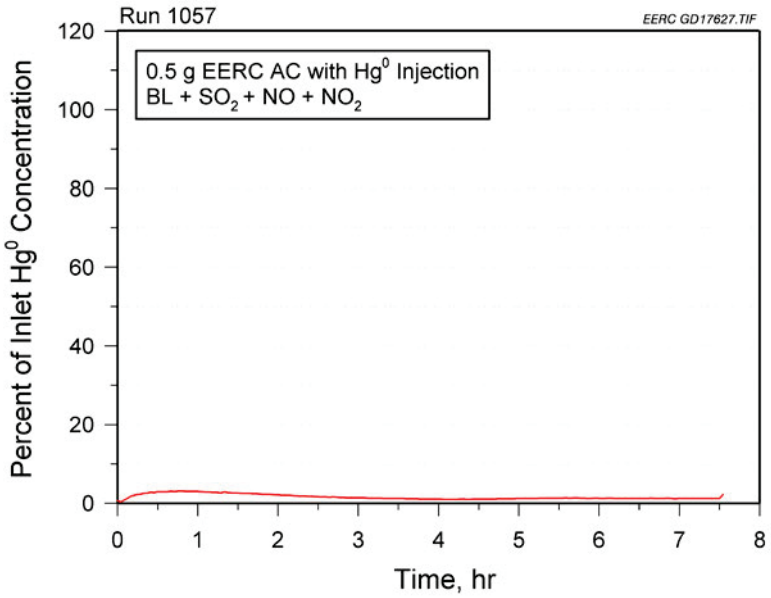
Dependence of Carbon/Mercury Ratio on Mercury Capacity

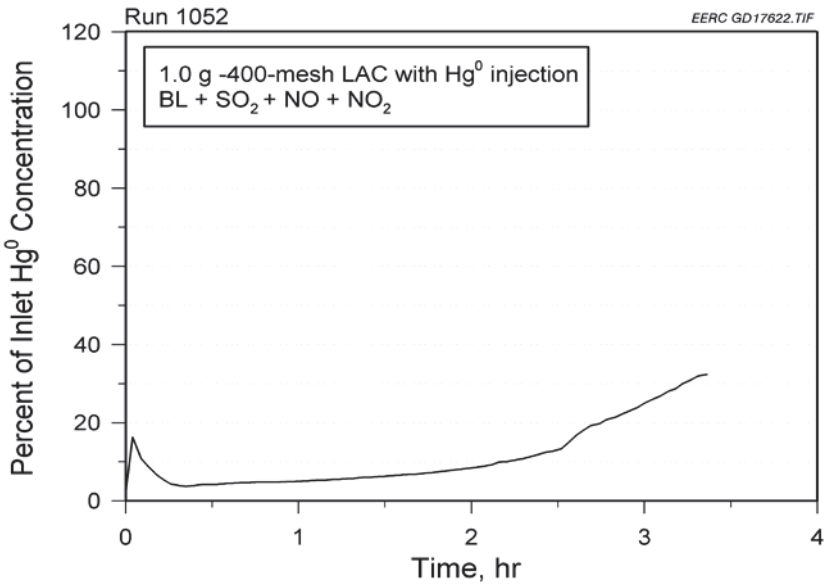
(90% removal of 10 µg/Nm³ Hg)



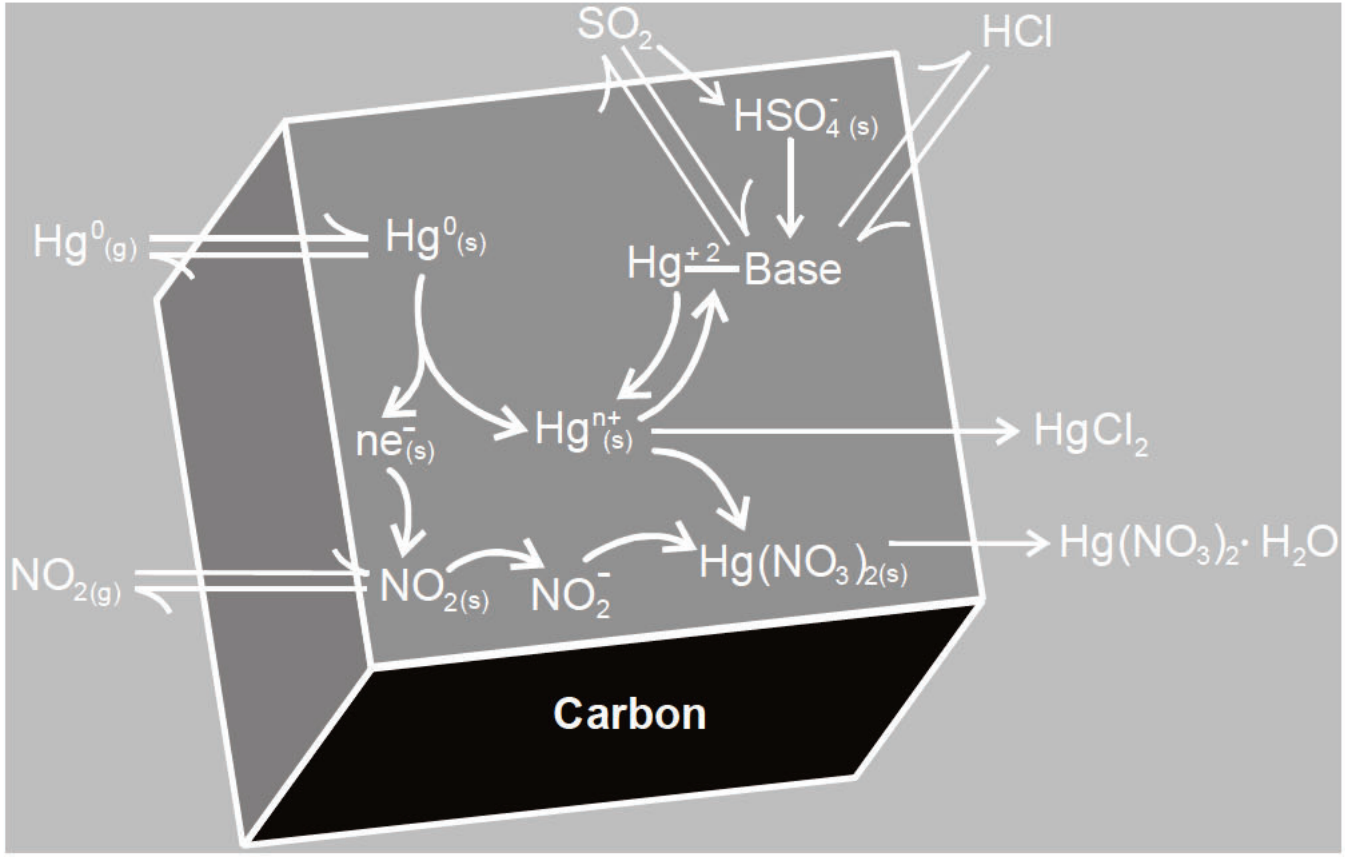
Source: Chen, Rostam-Abadi, and Chang, 2001

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

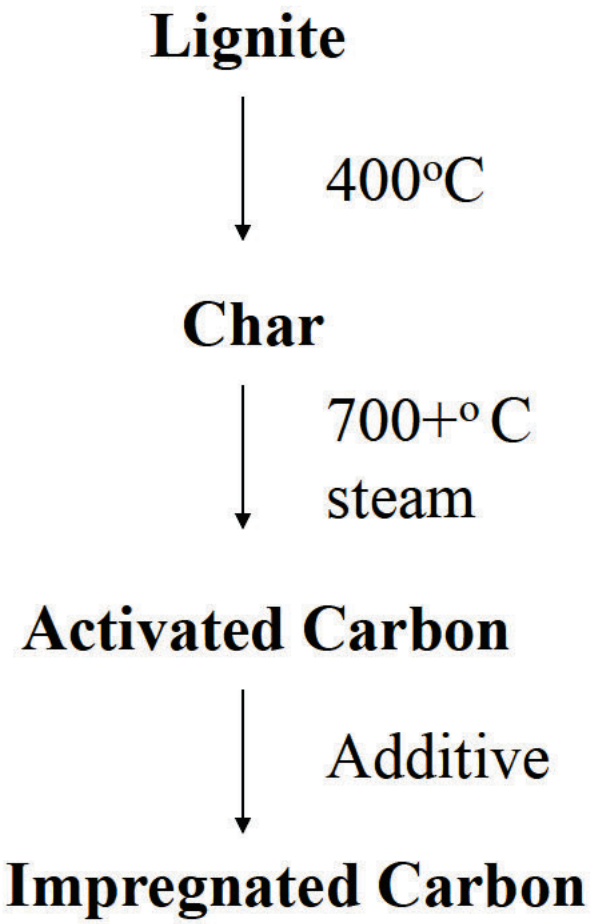
Screening Criteria

- 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

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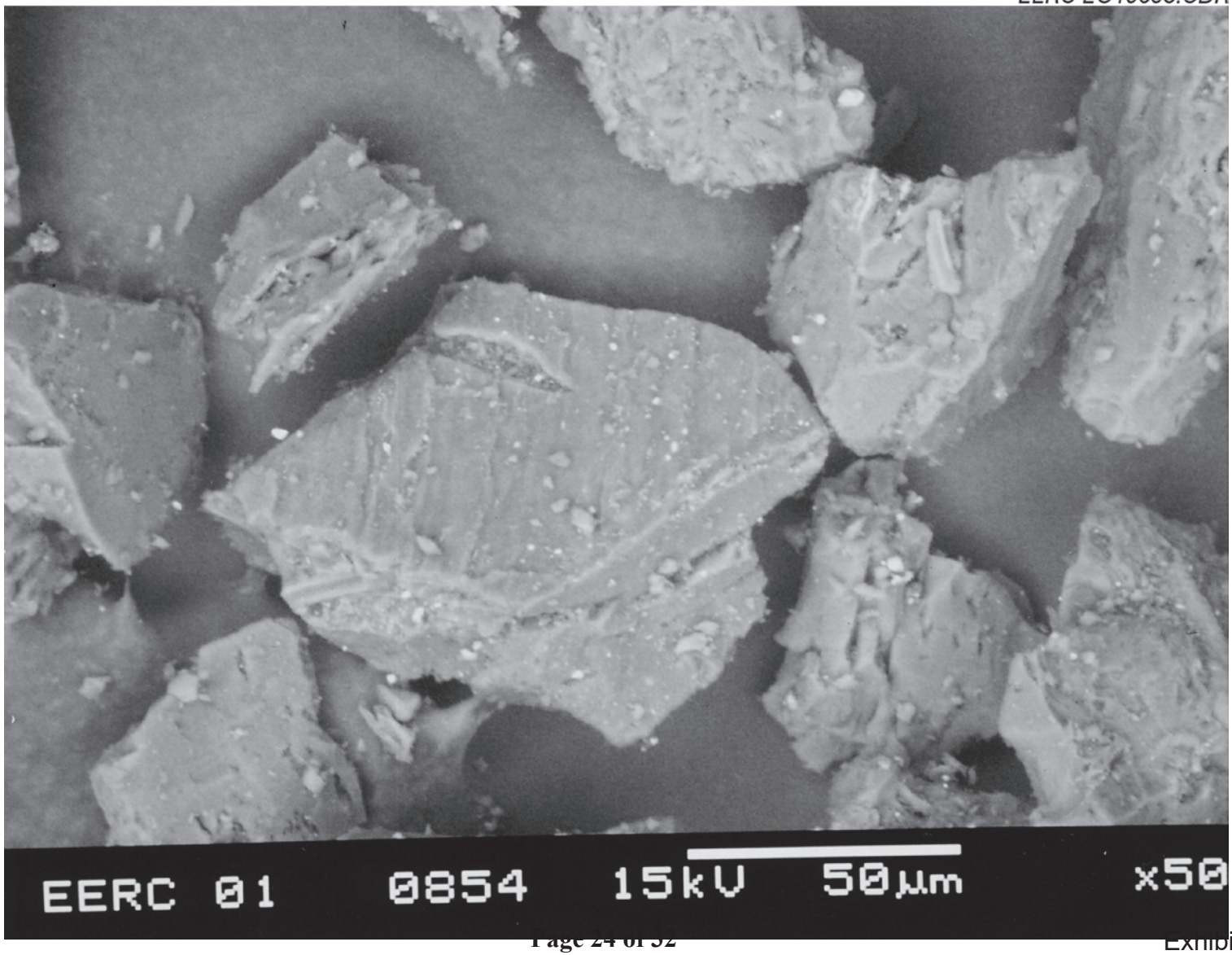
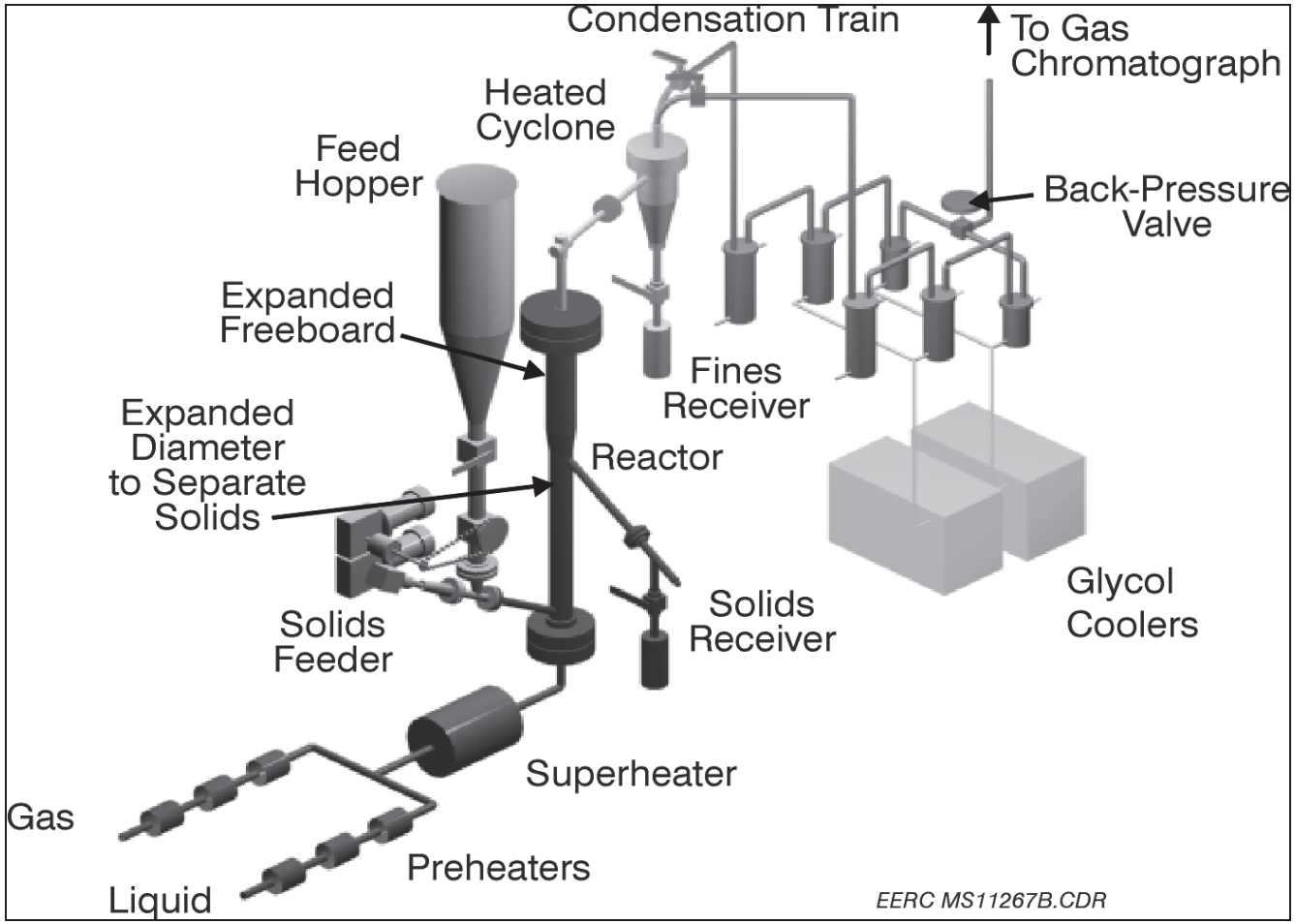


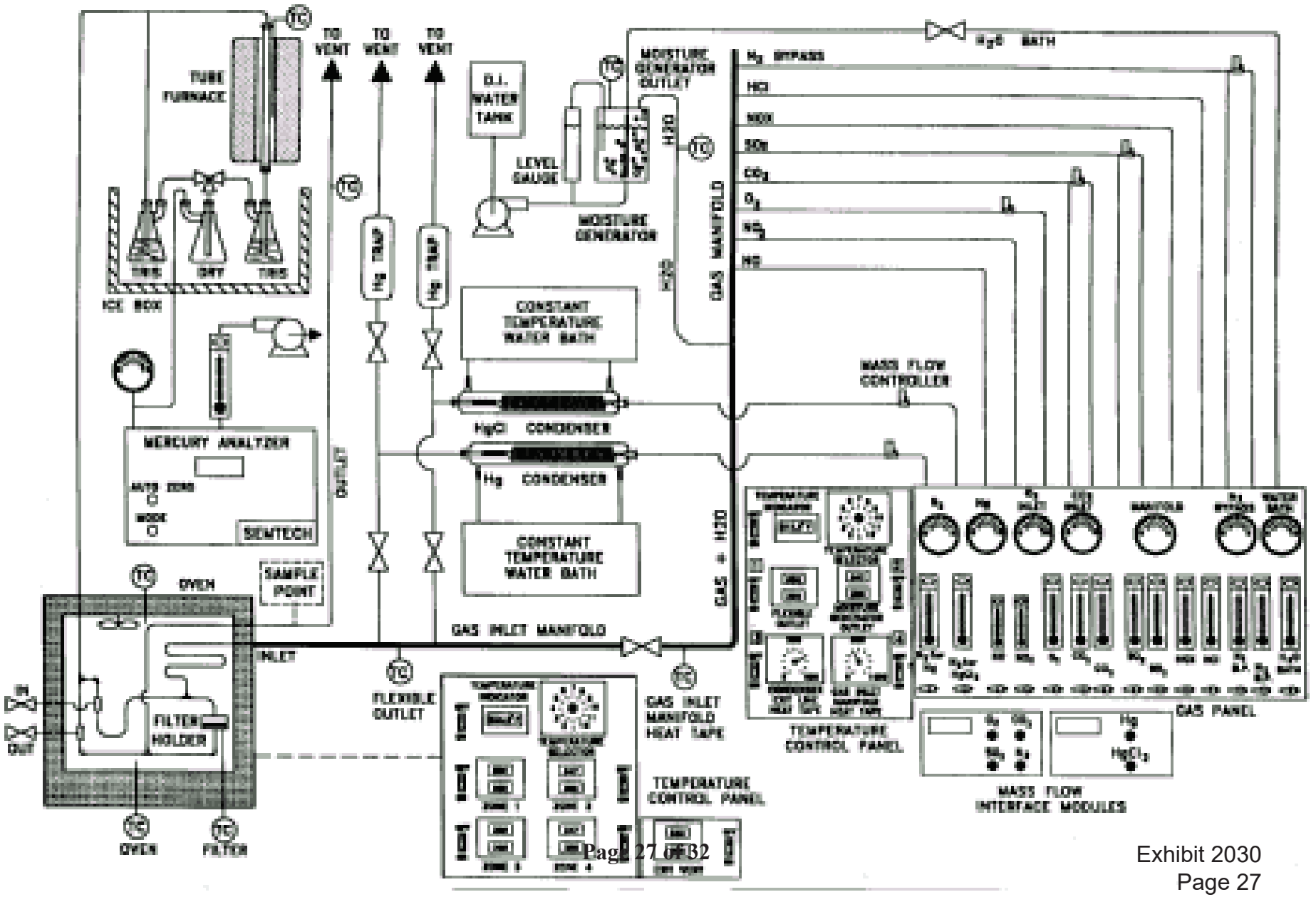
Small Reactor to Produce Char (4lb/hr)



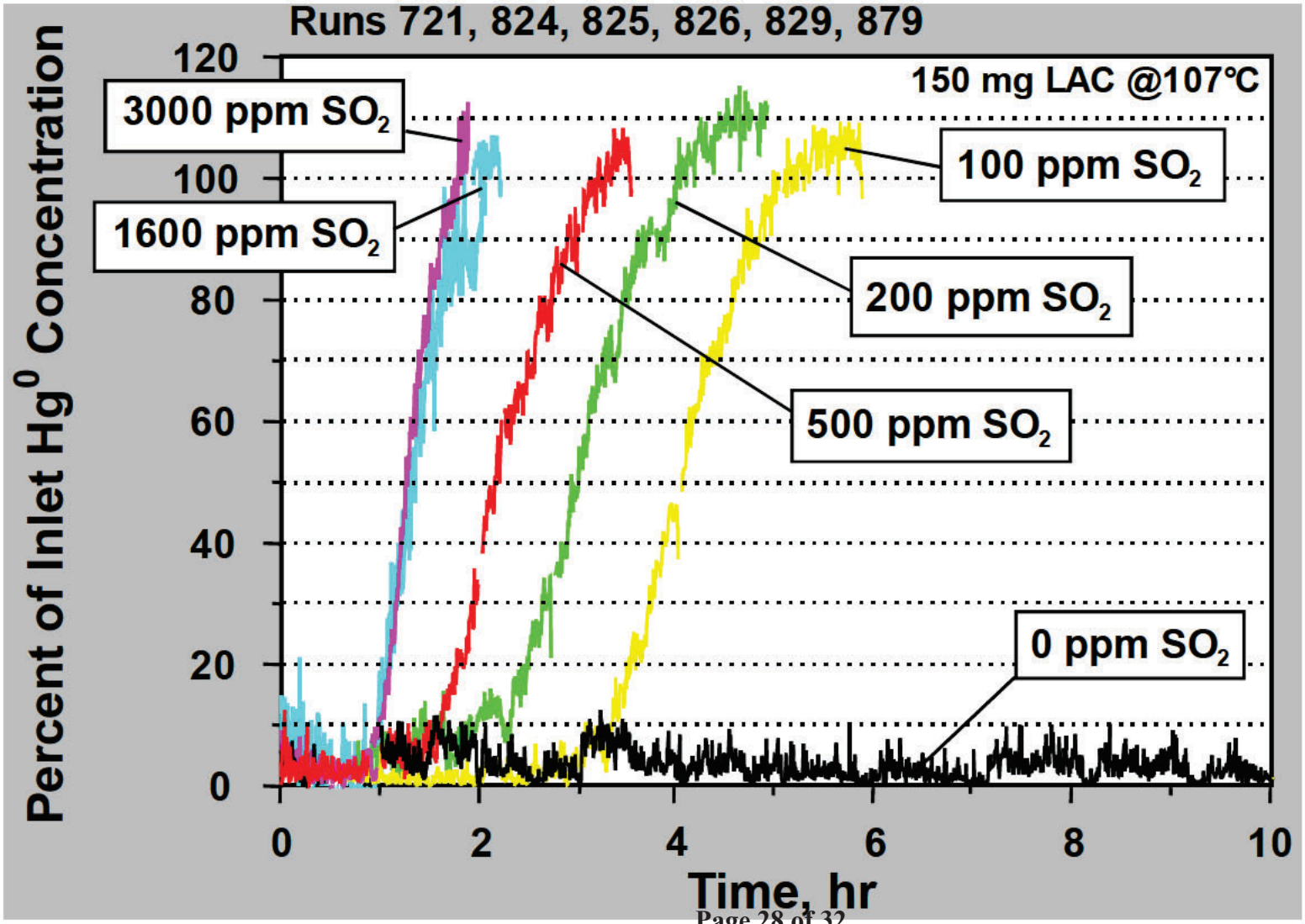
Characterization -- AC

- 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

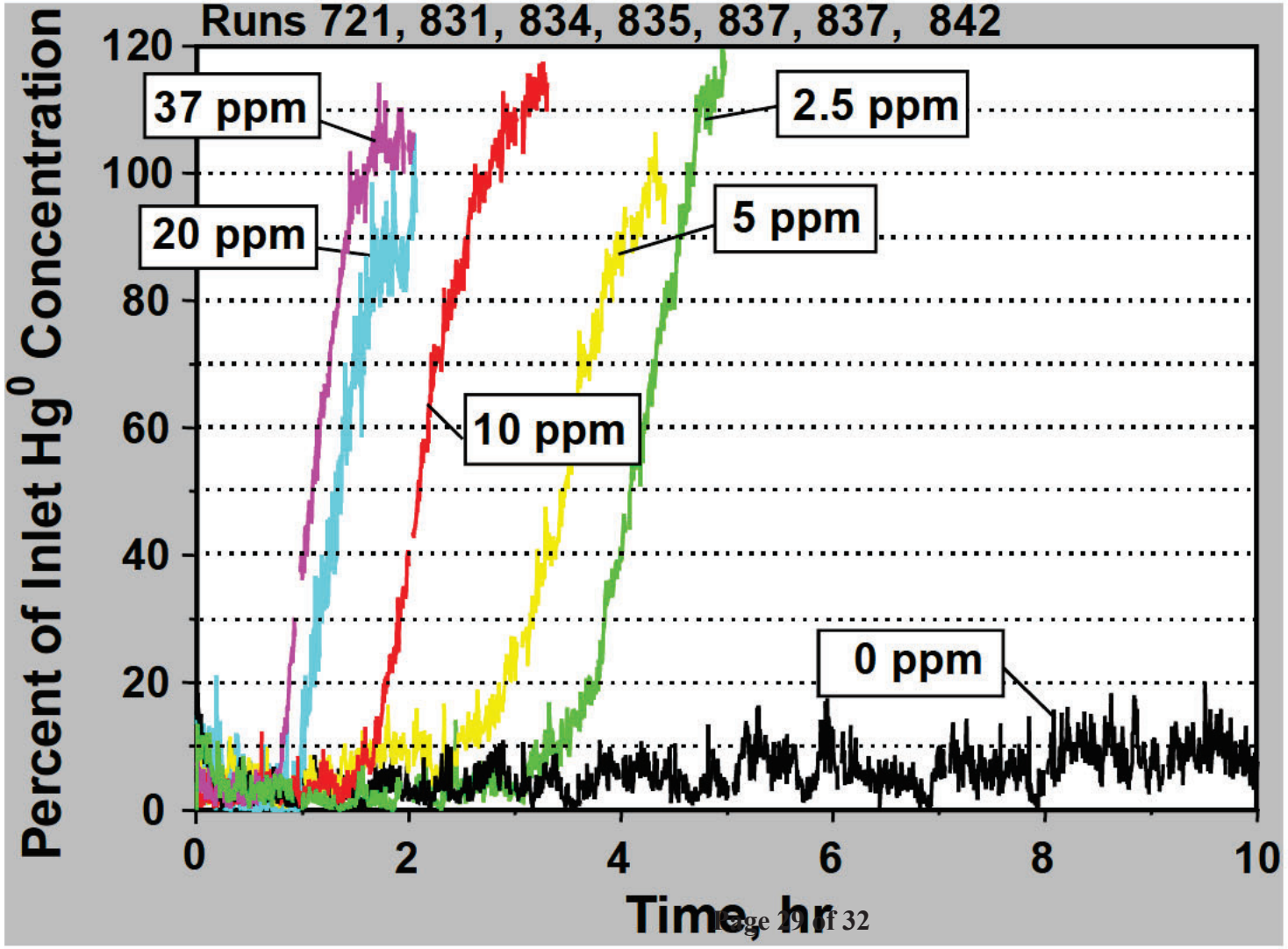


Effect of SO_2 Concentration on Hg^0 Capture with Activated Carbon



Hg^0–15 µg/m^3
O_2–6%
CO_2–12%
H_2O–8%
N_2–Balance
HCl–50 ppm
SO_2–0 to 3000 ppm
NO–400 ppm
NO_2–20 ppm

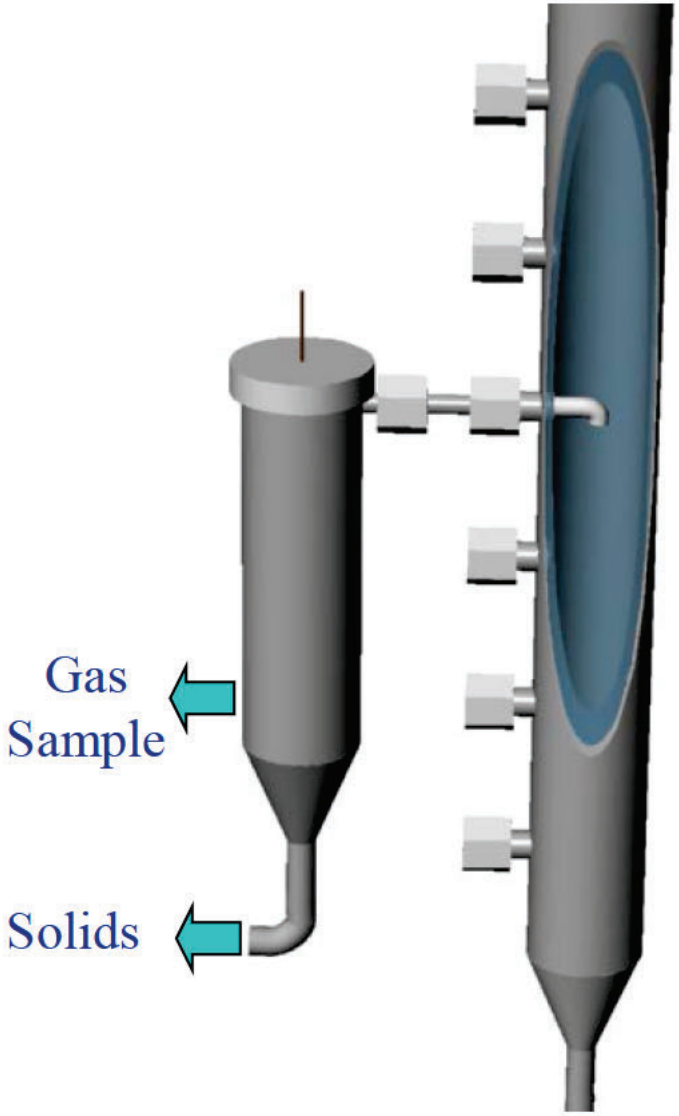
Effect of NO_2 Concentration on Hg^0 Capture with Activated Carbon



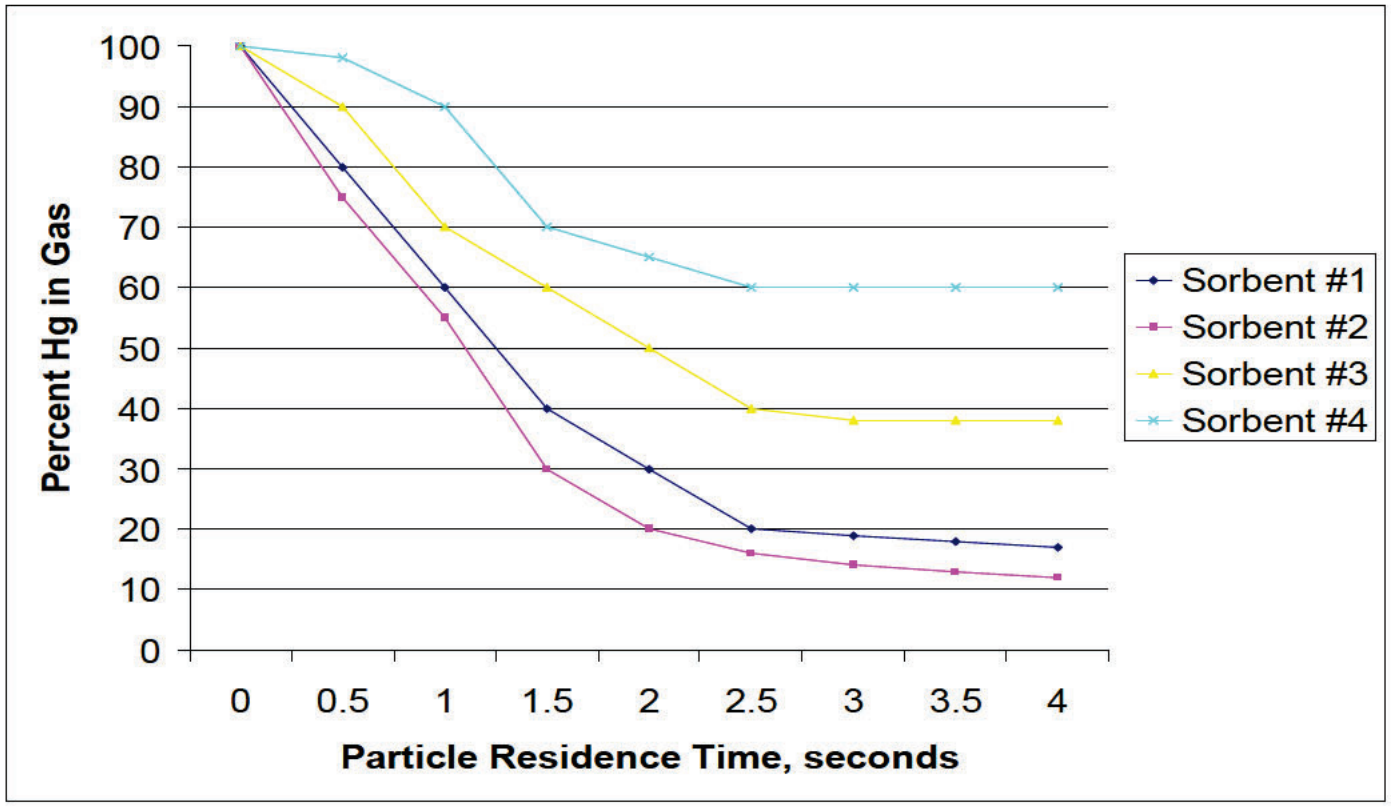
Hg^0–15 µg/m³
O_2–6%
CO_2–12%
H_2O–8%
N_2–Balance
HCl–50 ppm
SO_2–1600 ppm
NO–400 ppm
NO_2–0 to 37 ppm

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



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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