Pilot Testing of Mercury Oxidation Catalysts for Upstream of Wet FGD Systems

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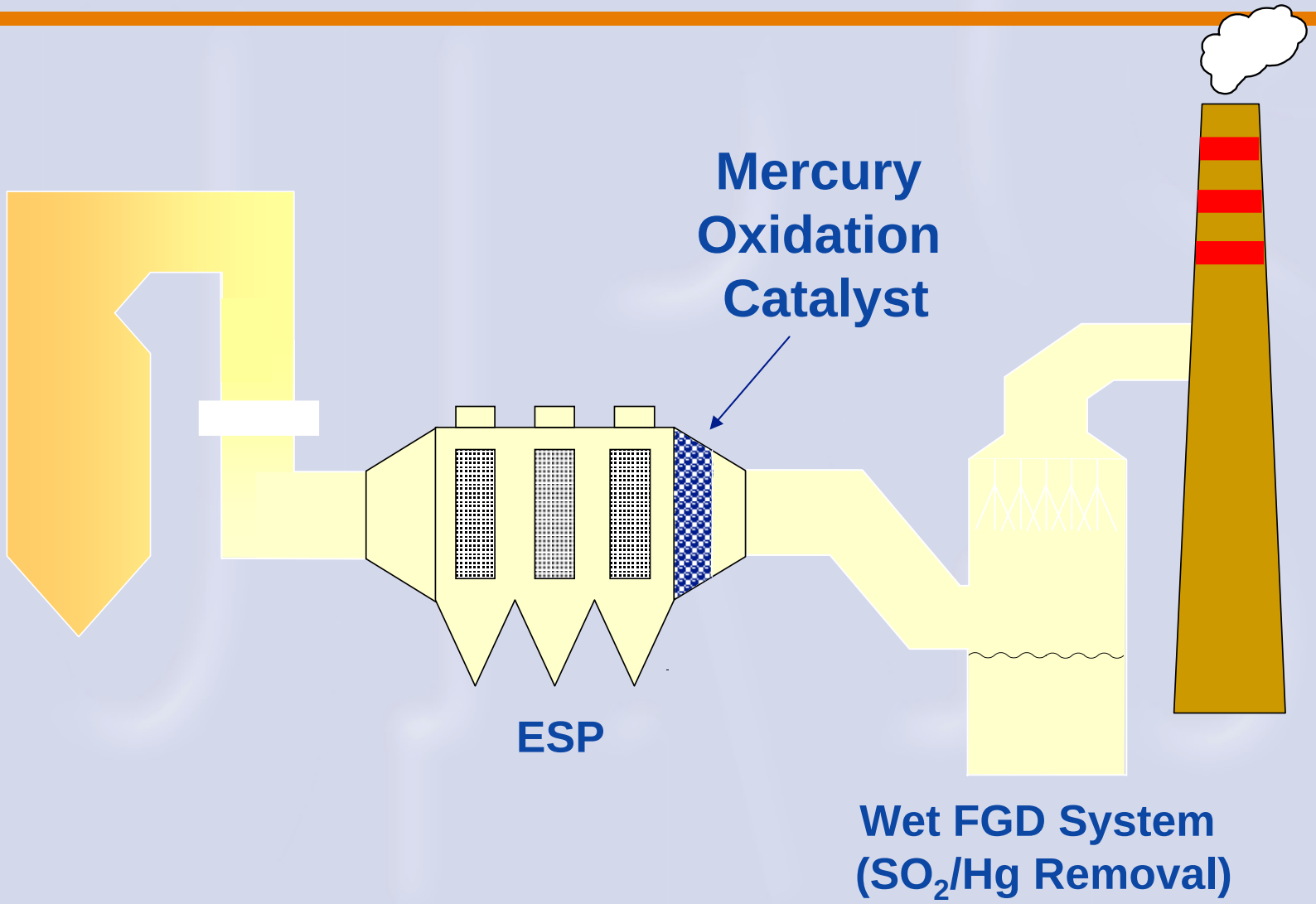
Hg Control Technology Concept

- Catalytic oxidation of Hg^0 in flue gas to increase Hg removal across wet FGD systems
- Development focused on fuel/plant configurations that produce higher Hg^0 percentages in flue gas
  - Initial pilot testing (Project 41185) on PRB and ND lignite
  - New project (41992) adds TX lignite and LSEB fuels
- In commercial concept, catalyst would be installed at ESP outlet

Illustration of Process Concept



Process Development Background

- Initial concept development funded by EPRI (early 1990s)
- Further development in NETL/EPRI co-funded MegaPRDA project (95260)
  - 6-month sand bed catalyst tests at 3 coal fired sites
- Follow-on pilot-scale project (41185) began late 2001(NETL, EPRI, utility co-funded)
- Second pilot-scale project (41992) began January 2004

41185 Project

- Conduct pilot-scale tests of honeycomb Hg^0 oxidation catalysts at two sites
  - 4 catalysts tested in parallel (~2000 acfm each)
  - 14-months automated operation at each site
  - Monthly catalyst activity measurements with Hg SCEM
- Host stations:
  - GRE's Coal Creek (ND lignite, ESP, Mg-lime wet FGD)
  - CPS's Spruce Plant (PRB, RGFF, LS wet FGD)

41992 Project

- Use existing pilot units (1 DOE, 1 EPRI) to test Hg oxidation catalysts at 2 new sites starting Summer 04
  - TXU's Monticello Station (TX lignite/PRB, ESP, LSFO wet FGD)
  - *Duke Energy's Marshall Station (low S Eastern bit., ESP)*
- Build and operate new wet FGD pilot unit downstream of oxidation catalysts
  - 2000 acfm inlet flow rate to match one catalyst
  - Conduct short-term wet FGD tests at all 4 sites (test at Coal Creek before pilot unit shuts down)
  - Test LSFO vs. Mg-lime chemistries

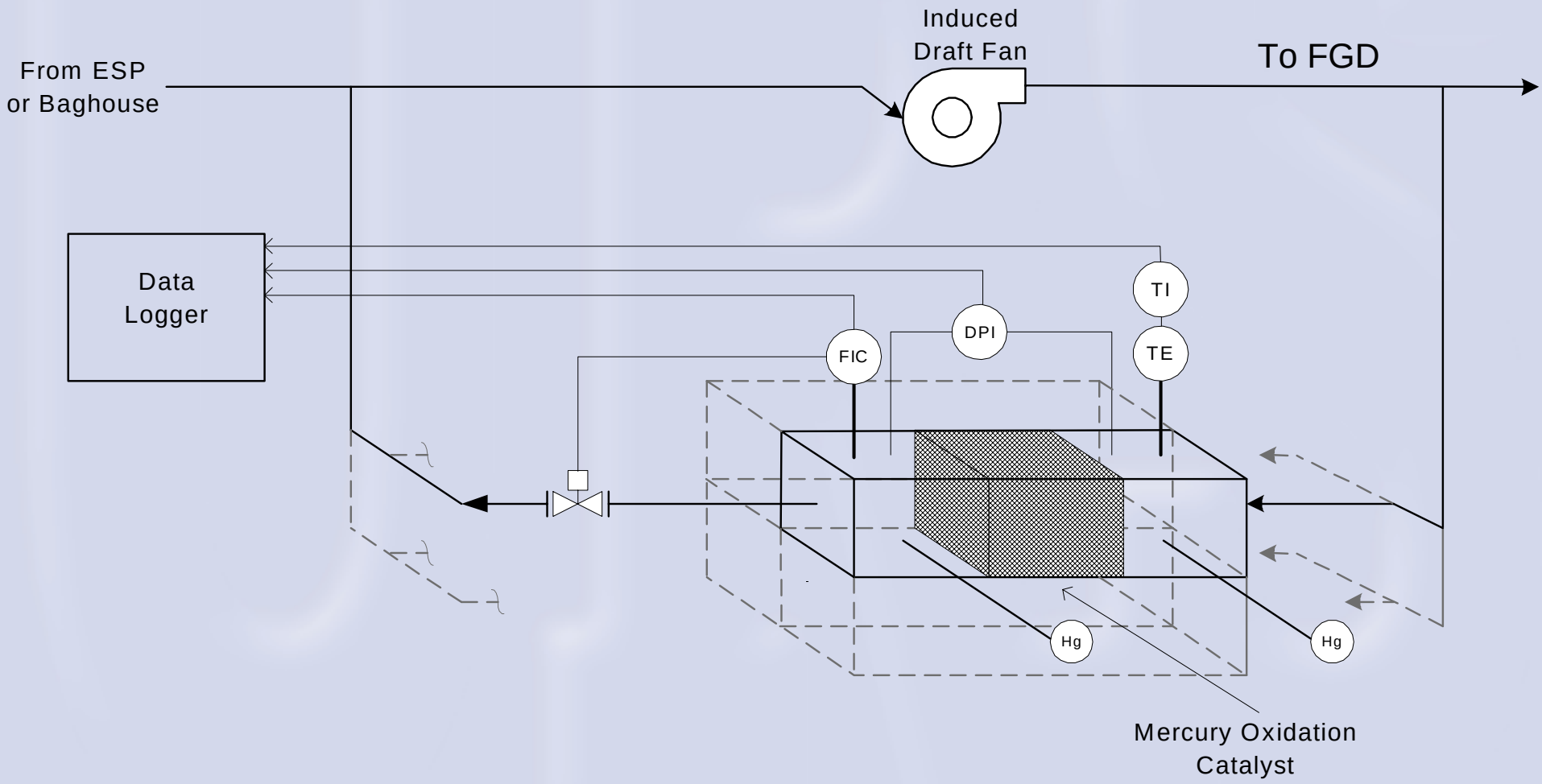
Flue Gas Characterization

- Ontario Hydro relative accuracy tests for EPRI Hg SCEM – three times each site
- Measure HCl, Cl_2, HF, F_2, and metals (Method 29) at catalyst pilot inlet – once each site
- Measure effects of catalysts on other flue gas species – once each site
  - Controlled Condensation for oxidation of SO_2
  - NO_X CEM to measure oxidation of NO

Catalyst Types Tested

- Metal-based
  - Palladium (Pd #1) – All sites
  - Ti/V (SCR) – All sites
  - Gold (Au) – Spruce and 41992 sites
- Carbon-based
  - Experimental activated carbon (C #6) – All sites
- Fly-ash-based – Coal Creek only

Catalyst Pilot Unit P&ID



Hg Oxidation Catalyst Pilot Unit at Coal Creek Station (CCS)

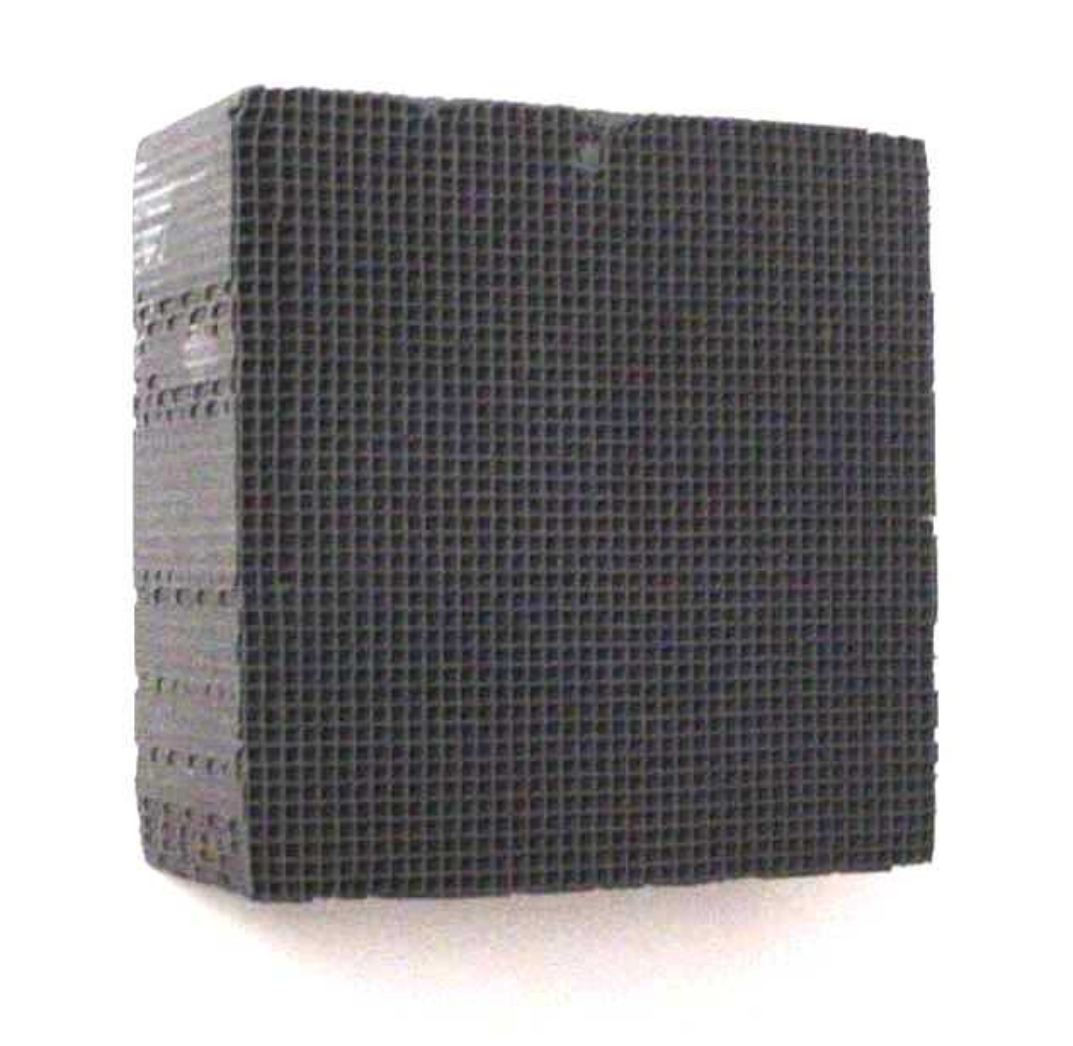
Catalyst Dimensions for CCS Pilot

Catalyst	Cells per in.^{2} (cpsi)	Cross Section (in. x in.)	Length (in.)	Area Velocity (sft/hr)
Pd #1	64	30 x 30	9	49
C #6	80*	36 x 36	9	27
SBA #5	80*	36 x 36	9	27
SCR	46	35.4 x 35.4	19.7	14**

*Die sized for 64 cpsi, cores shrank during drying
**1500 acfm, other catalysts operate at 2000 acfm

Example Catalyst Module (1 of 3)

Close-up of One Catalyst Block

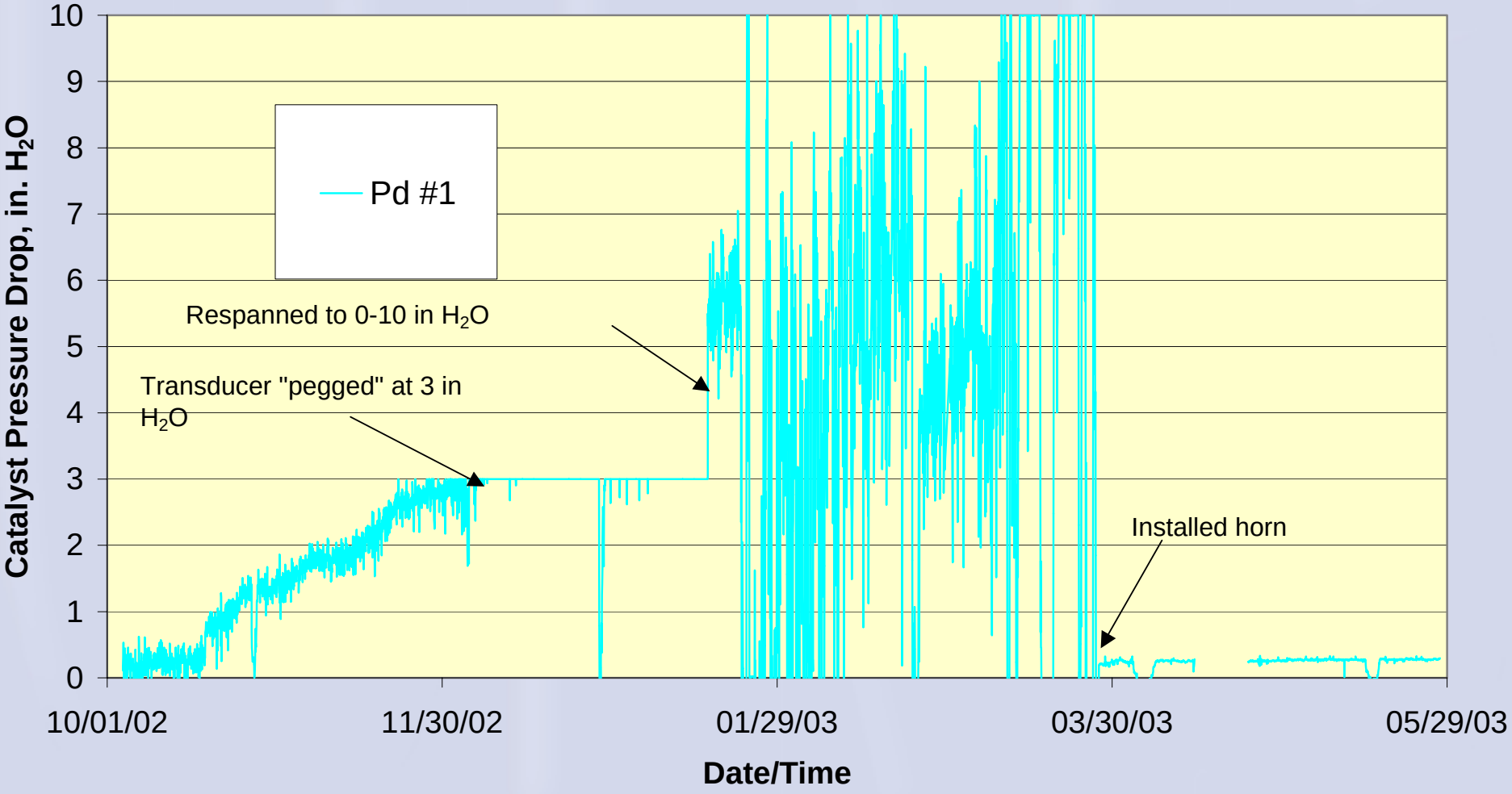


Example Catalyst Installation

41185 Project Pilot Testing Status

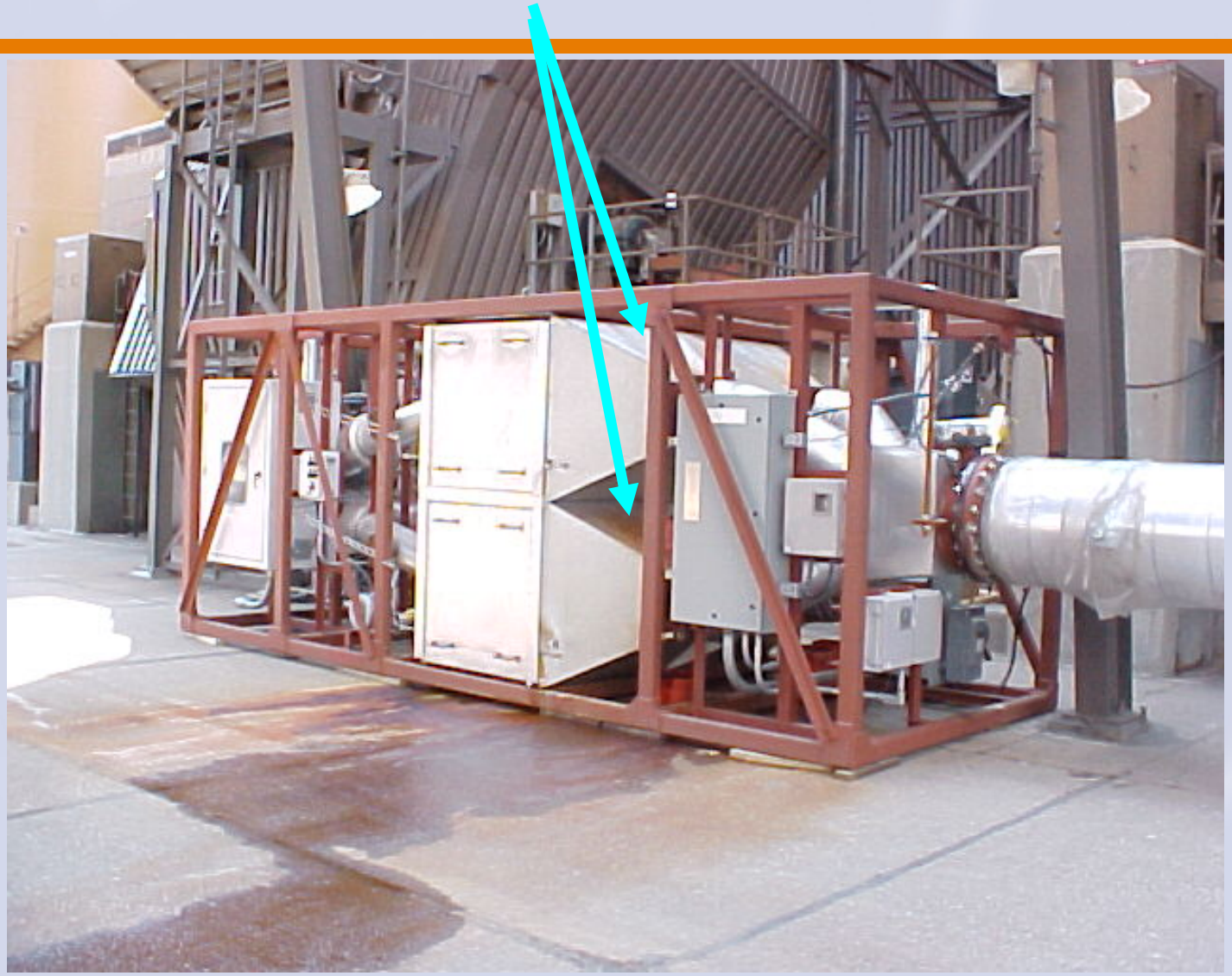
- First pilot unit:
  - First 2 catalysts installed October 02
  - 3rd catalyst installed December 02
  - 4th catalyst installed June 03
  - FGD pilot & catalyst regeneration tests July 04
- Second pilot unit:
  - First 2 catalysts started up August 03
  - Restarted with 4 catalysts after station outage (November 03)
  - Scheduled to operate through December 04

Pd #1 Catalyst ΔP through 5/27/03 (shows effect of sonic horn)

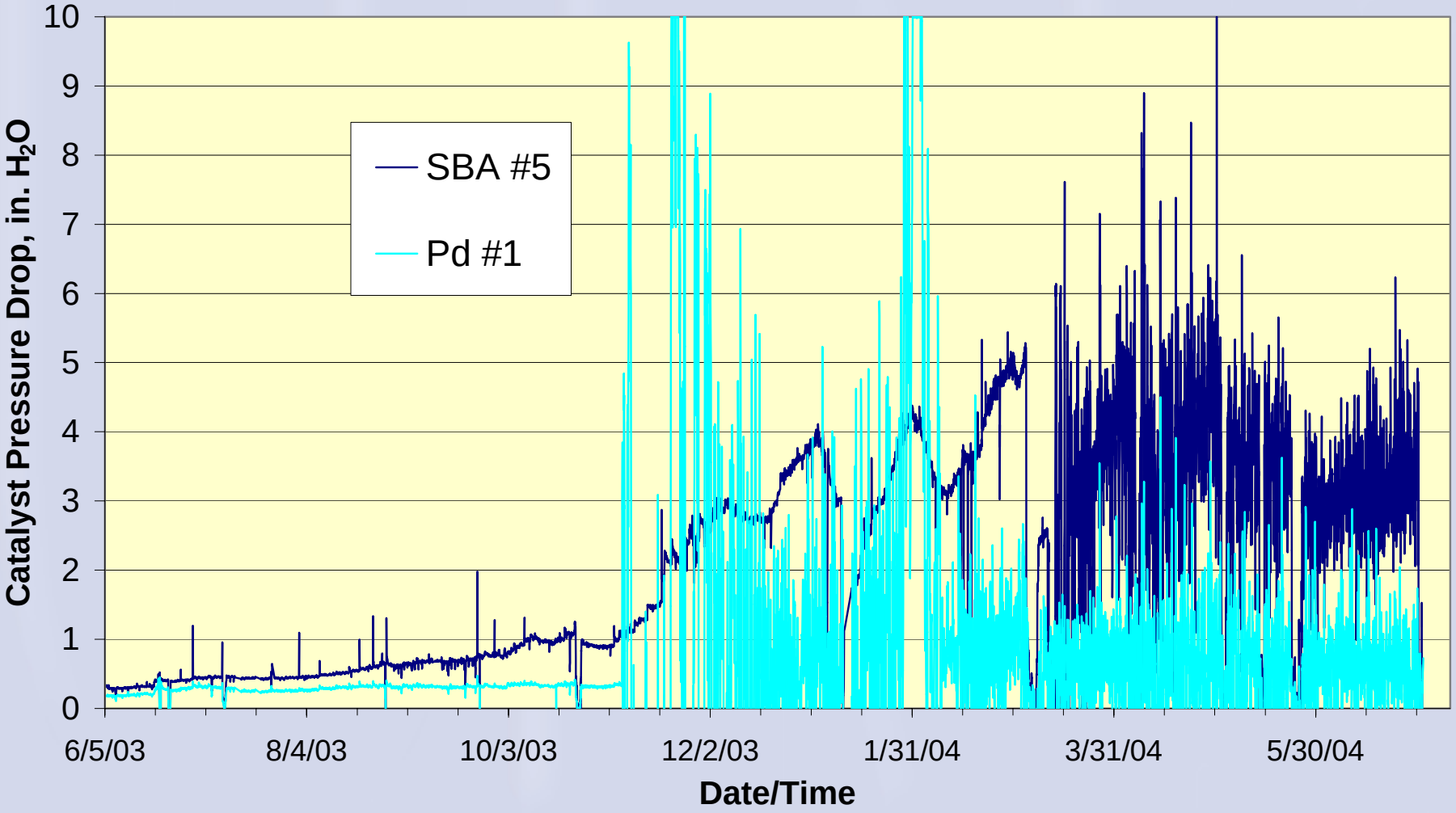


Sonic Horn Installation on Pilot Unit

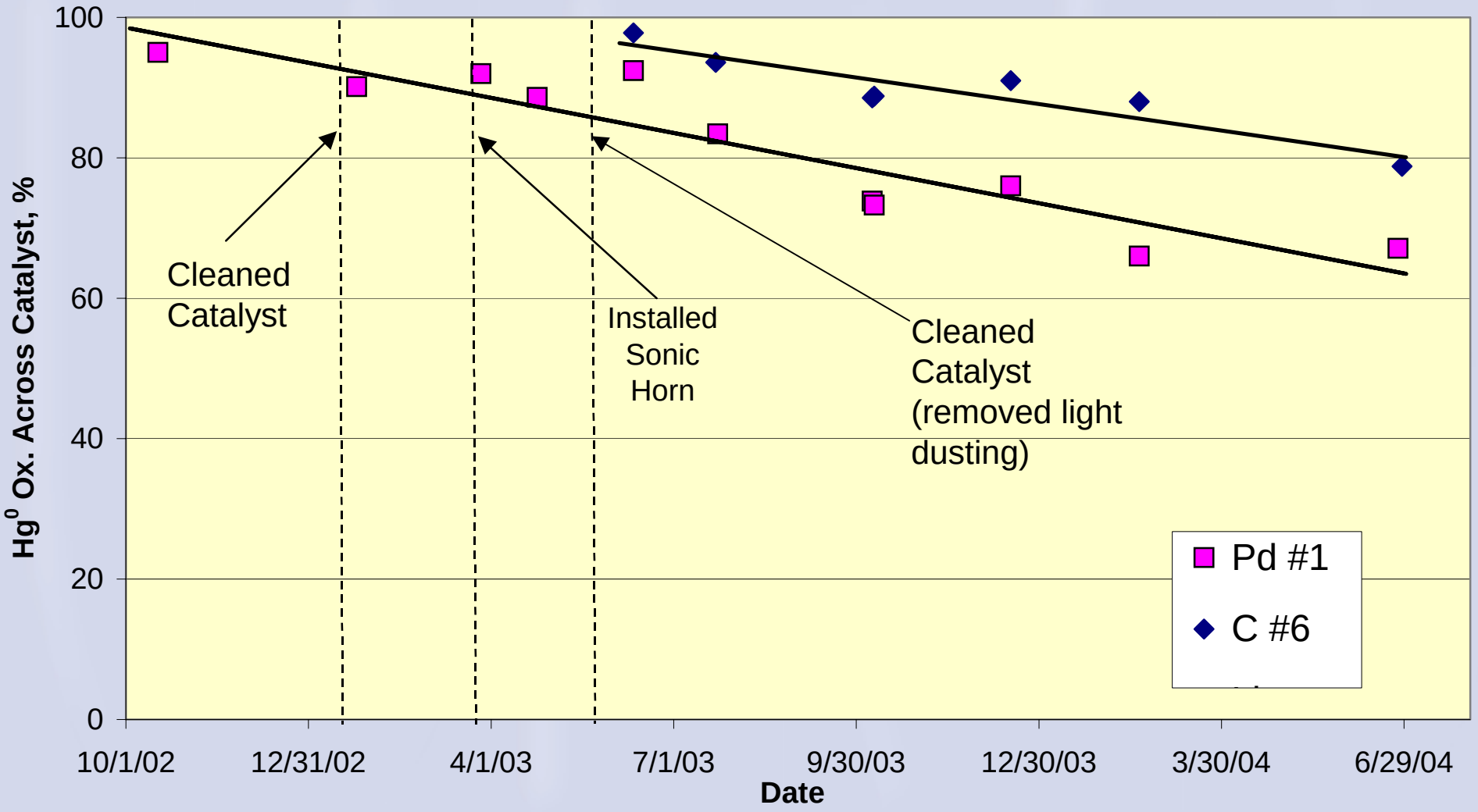
Sonic Horn Locations



Catalyst ΔP since 6/5/03 (sonic horns in all 4 compartments)



Catalyst Activity Trends over 20 Months at Coal Creek



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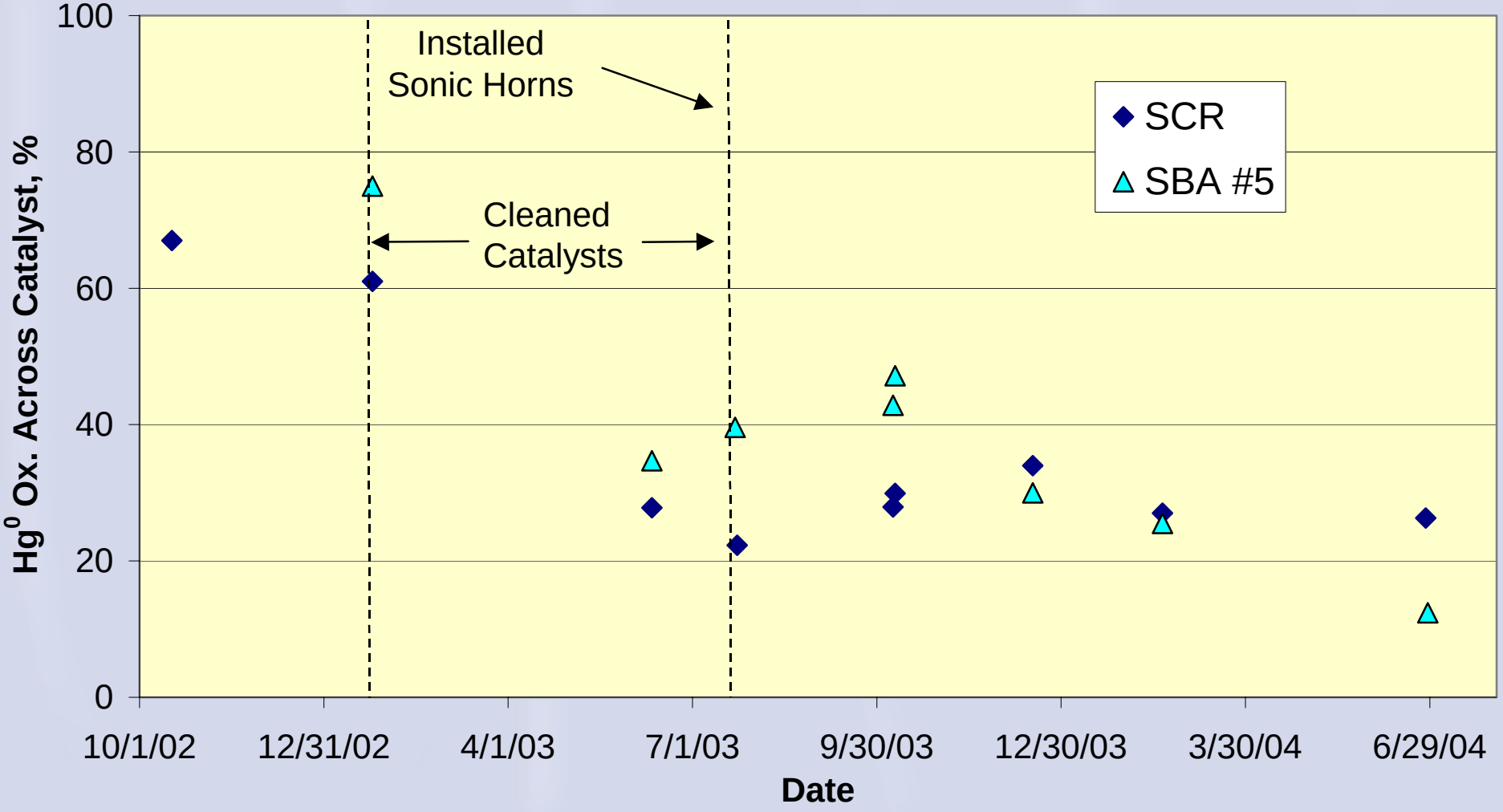


Flue Gas Characterization Results

- No effects seen on other flue gas species across catalysts
  - 0.1% or less oxidation of SO_2
  - No oxidation of NO
    - Inlet and outlet NO, total NO_X values agree within <1 ppm
  - No change in HCl (~1 ppm) or HF (~6 ppm) across catalysts

Flue Gas Characterization Results

- Ontario Hydro results do not always agree with Hg SCEM results
  - Inlet values agree reasonably well
  - OH often shows lower Hg^0 concentrations at catalyst outlets than Hg SCEM
  - Reason for bias remains unclear
    - Relative accuracy of OH unknown at <1 $\mu g/Nm^3$
    - Possible formation of alternate oxidized Hg form across catalysts?

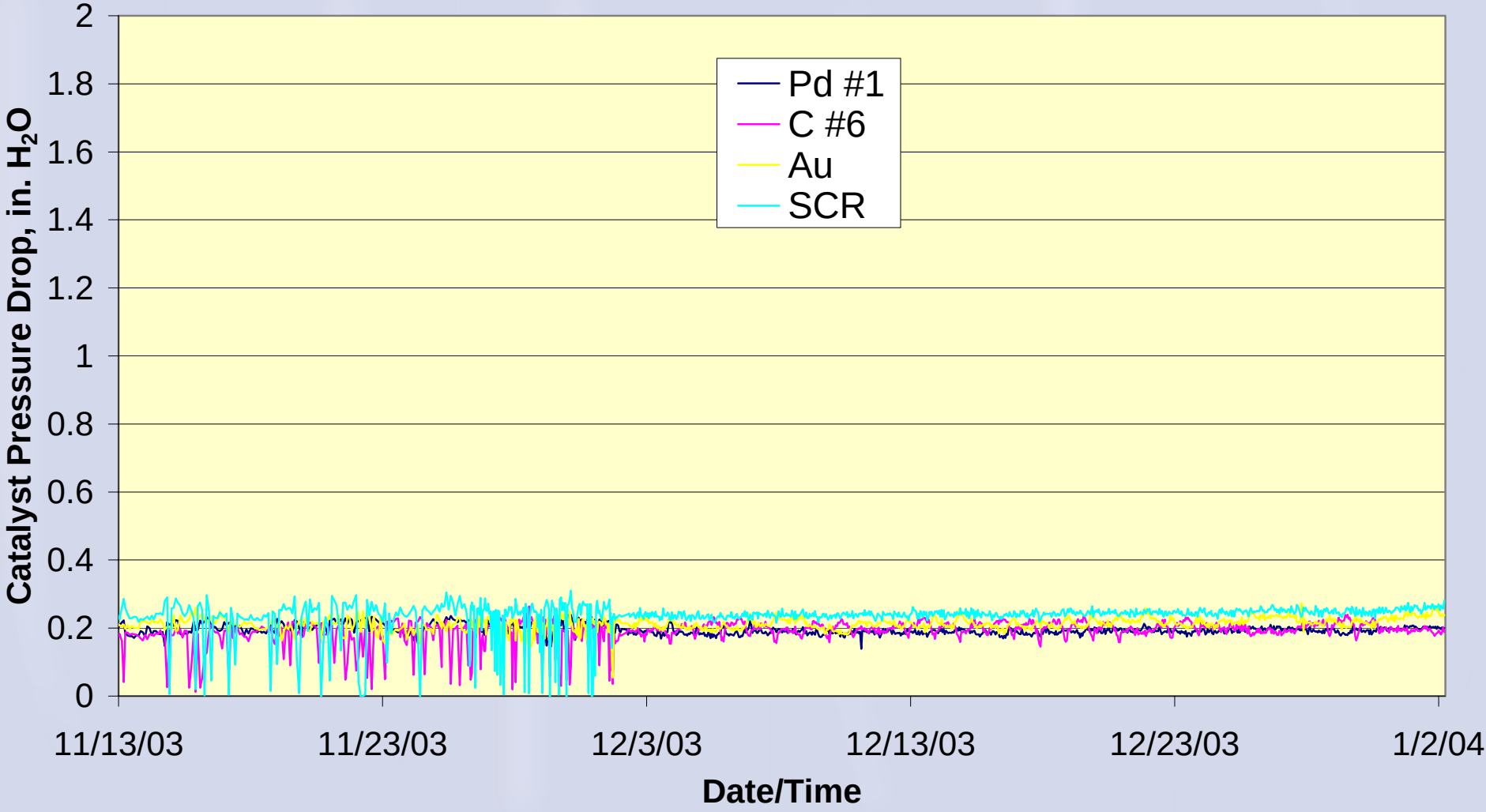
Second Pilot Unit at Spruce Plant

Catalyst Dimensions for Spruce Pilot

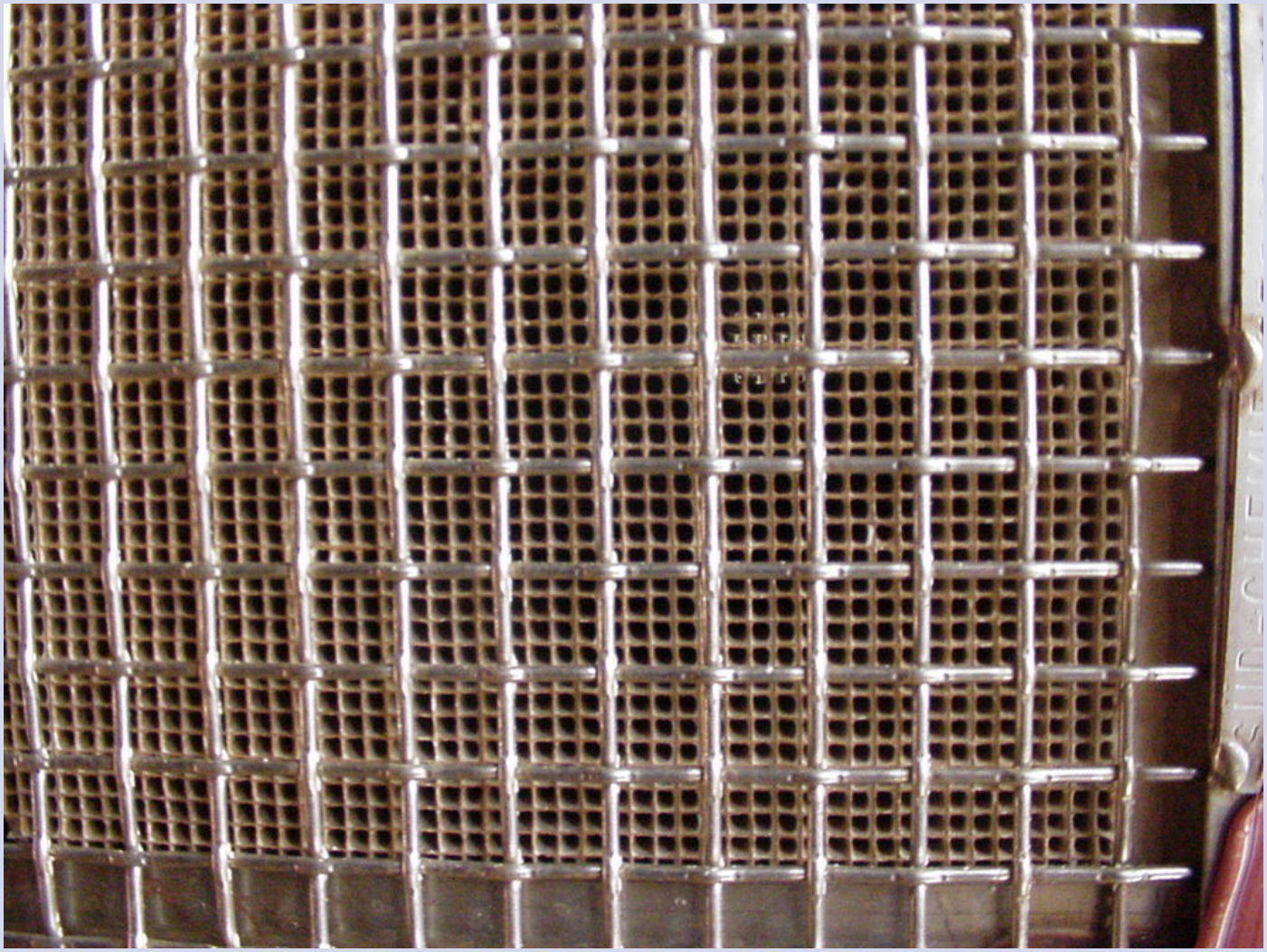
Catalyst	Cells per in.^{2} (cpsi)	Cross Section (in. x in.)	Length (in.)	Area Velocity (sft/hr)
Pd #1	64	30 x 30	9	49
Au	64	30 x 30	9	49
C #6	80*	36 x 36	9	27
SCR	46	35.4 x 35.4	29.5	13

*Die sized for 64 cpsi, cores shrink during drying

Catalyst Pressure Drop since 11/13 (no sonic horns in compartments)



Pd #1 Catalyst Module after 1 Month of Operation



Pd #1 Catalyst Compartment after 1 Month of Operation

Flue Gas Speciation Results from Spruce (Jan 04, by Hg SCEM)

Location	Hg Conc. (ug/Nm^3)			Overall Hg Ox. (%)	Hg Removal Relative to Inlet (%)	Hg Removal Across Scrubber (%)		
	Hg Total	Hg^0	Hg^{+2}			Hg Total	Hg^{+2}	Hg^0
BH Inlet (7-Jan)	13.5	11.3	2.2	16	-	-	-	-
BH Outlet (6-Jan)	12.7	0.7	11.9	94	6	-	-	-
FGD Outlet (7-Jan)	3.2	1.4	1.8	-	76	75	85	-88

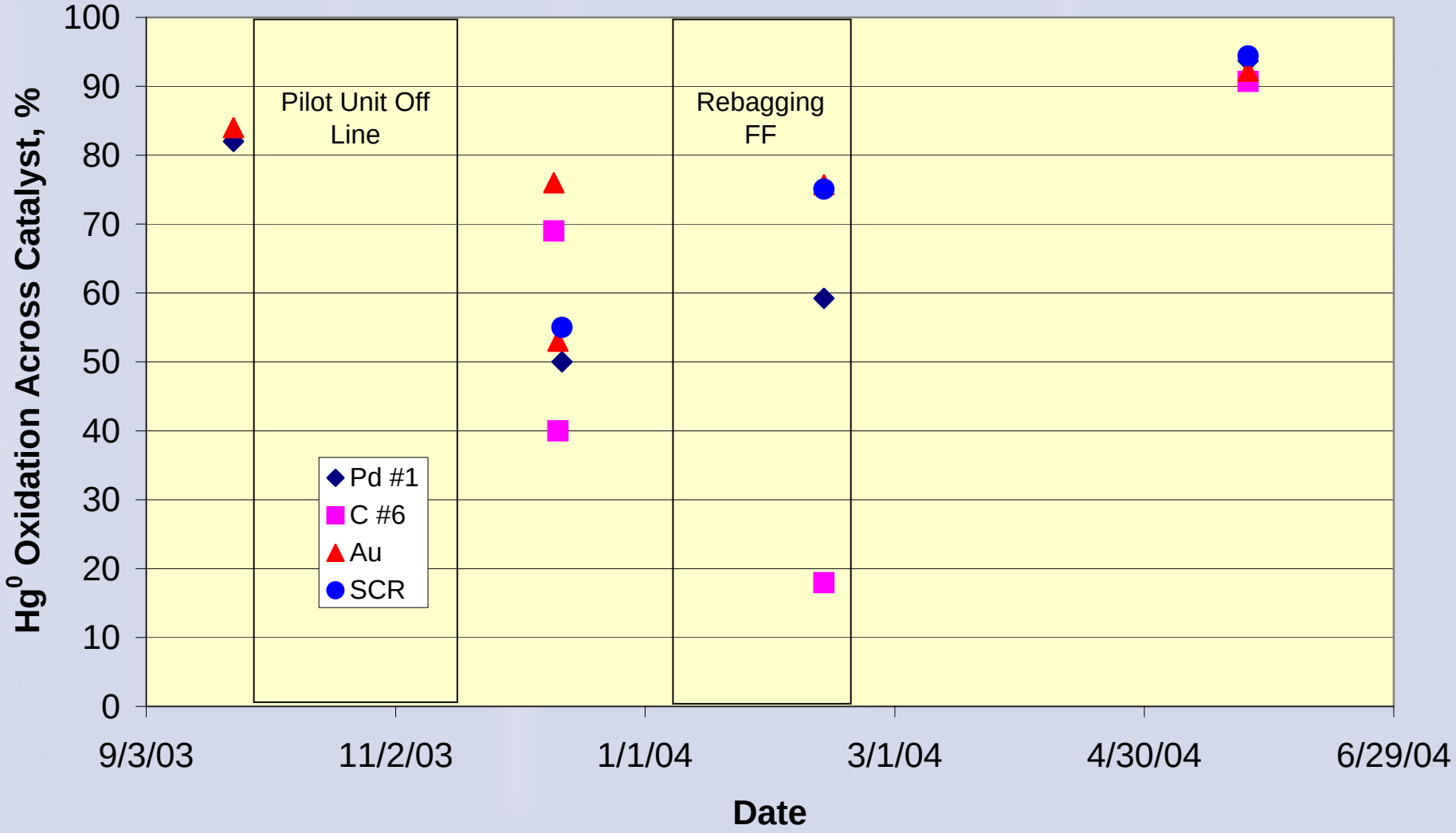
Possible Reasons for High Hg Oxidation at Catalyst Pilot Inlet

- Spruce Plant has a reverse-gas baghouse for particulate control
  - Original bags were still in service (fiberglass) since 1992
  - Baghouse was operating at high ΔP (7-8 in. H_2O)
  - Low A/C ratio (less than 1.5 acfm/ft^2)
  - Plant intermittently fires pet coke (may add carbon, vanadium to permanent dust cake on bags)
  - FF rebag in early 2004 showed only a minor aged bag effect, though

Example Effects of Low Ratio FF for Plants Firing Western Coals

Plant	Configuration	Hg Removal Across FF (%)	Hg Oxidation at FF Outlet (%)
Comanche 2 (ICR)	PC boiler, FF	66	87
Boswell 2 (ICR)	PC boiler, FF	83	80
Intermountain (ICR)	PC boiler, FF, WFGD	34	83
Spruce	PC boiler, FF, WFGD	6-59	75-94

Catalyst Activity Trends at Spruce



Most Recent Spruce Catalyst Activity Data
(Simultaneous inlet/outlet SCEMs, Hg concentrations in μg/Nm³)

Catalyst	Inlet Hg_{Total}	Inlet Hg^0	Outlet Hg_{Total}	Outlet Hg^0	% Break-through	% Hg^0 Oxidation
Pd #1	10.7	1.89	9.91	0.12	93	94
C #6	10.3	2.01	10.2	0.19	99	91
Au	11.1	2.75	10.5	0.21	95	92
SCR	10.8	2.30	11.2	0.13	105	94

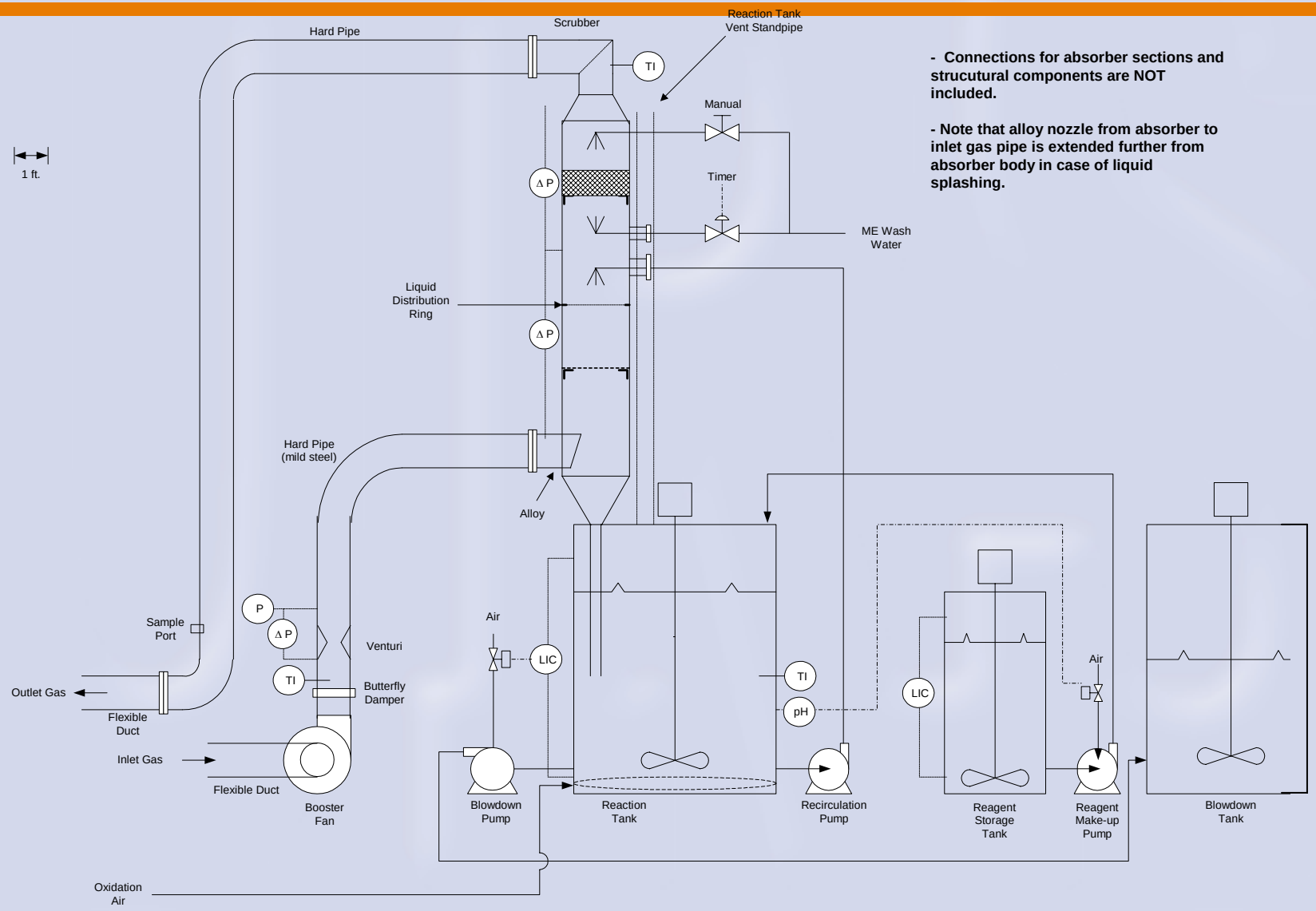
Schedule for 41992 Project

Design and build pilot wet scrubber	Jan 04 – June 04
Conduct wet scrubber tests at Coal Creek	July 04
Conduct wet scrubber tests at Spruce	October 04
Conduct oxidation catalyst pilot tests at Monticello	Sept 04 – Oct 05
Conduct oxidation catalyst pilot tests at *Marshall*	Feb 05 – March 06

Pilot Wet FGD Design

- Alloy absorber, 24-in. diameter, tray contactor
- Adjust L/G to get desired mass transfer
- No dewatering – will operate “open loop”
  - Use host site FGD liquor as makeup to get steady-state levels of soluble salts and trace metals
  - At Marshall will spike fresh water with salts & last-field fly ash to simulate steady-state liquor
- Tests will be short term (1 to 3 reaction tank residence times)
  - Solids should approach steady state, liquor will not
  - Compromise between cost of testing and information derived

Pilot Wet Scrubber P&ID



- Connections for absorber sections and strucutural components are NOT included.

- Note that alloy nozzle from absorber to inlet gas pipe is extended further from absorber body in case of liquid splashing.

Pilot Wet FGD Skid

Conclusions

- Sonic horns effective to prevent fly ash buildup
- Pd and C#6 catalysts are most active for Coal Creek ND lignite flue gas
  - Both continually lose activity vs. time
  - Regeneration tests in progress this month
- All four catalysts appear active in Spruce PRB flue gas
  - High Hg^0 oxidation across FF makes activity measurements difficult