

Fate of Mercury in Wet FGD Wastes



■ Project Sponsors:

- ◆ U. S. Department of Energy's - National Energy Technology Laboratory
- ◆ Ohio Coal Development Office within the Ohio Department of Development
- ◆ Babcock & Wilcox

■ Host Utilities:

- ◆ Michigan South Central Power Agency
- ◆ Cinergy

by: **Gerald T. Amrhein**
McDermott Technology Inc.

Presentation Outline



■ Laboratory Studies

- ◆ Analyses of Wet FGD wastes by Standard Methods
- ◆ Fate of Mercury (FOM) - Thermal Dissociation Tests
 - Standard Prep and Testing
 - PSA Mercury CEM
 - Thermal Dissociation Tests
- ◆ Conclusions

■ Full-Scale Wet FGD Hg Removal Demonstration

- ◆ MTI Wet FGD Pilot
- ◆ Endicott
- ◆ Zimmer
- ◆ Conclusions

Phase 1 Pilot Waste Samples



Wet Scrubber Sludge Analysis				Hg in Solids, mg/kg dry				Filtrate
Test	MTI ID	Code	% solids	Std 1	Std 2	HNO ₃	HNO ₃ /HCl	mg/l
1	WS-1C	Baseline	38.9	#N/A	0.072	0.064	0.069	<0.00050
2	WS-2B	App1 0.1x	39.2	#N/A	0.074	0.074	0.064	
3	WS-3C	App1 0.01x	39.1	#N/A	0.069	0.072	0.079	
4	WS-4C	App1 1.0x	48.0	#N/A	0.075	0.081	0.081	
5	WS-5C	Alt App1	48.8	#N/A	0.160	0.160	0.160	
6	WS-6C	App2 0.25x	52.3	#N/A	0.130	0.130	0.140	<0.00050
7	WS-7B	Alt App1+App2	52.6	0.21	0.190	0.190	0.190	<0.00050
8	WS-8C	App1+App2	52.7	#N/A	0.150	0.150	0.160	<0.00050
9	WS-9C	App2 0.125x	54.8	#N/A	0.093	0.091	0.100	<0.00050
ESP Ash Analysis					TCLP			
SI-1	SI-1C	Sorb1 350F		#N/A	0.038	0.031	0.031	
SI-2	SI-2B	Sorb2 250F		0.22				<0.01
SI-3	SI-3C	Sorb3 750F		0.34				<0.01
= Tested by Thermal Decomposition								

Method Key

Std1=SW846-7471

Std2=SW846-7471 w/high mass sample

HNO₃=50% HNO₃ at room temp for 60 min

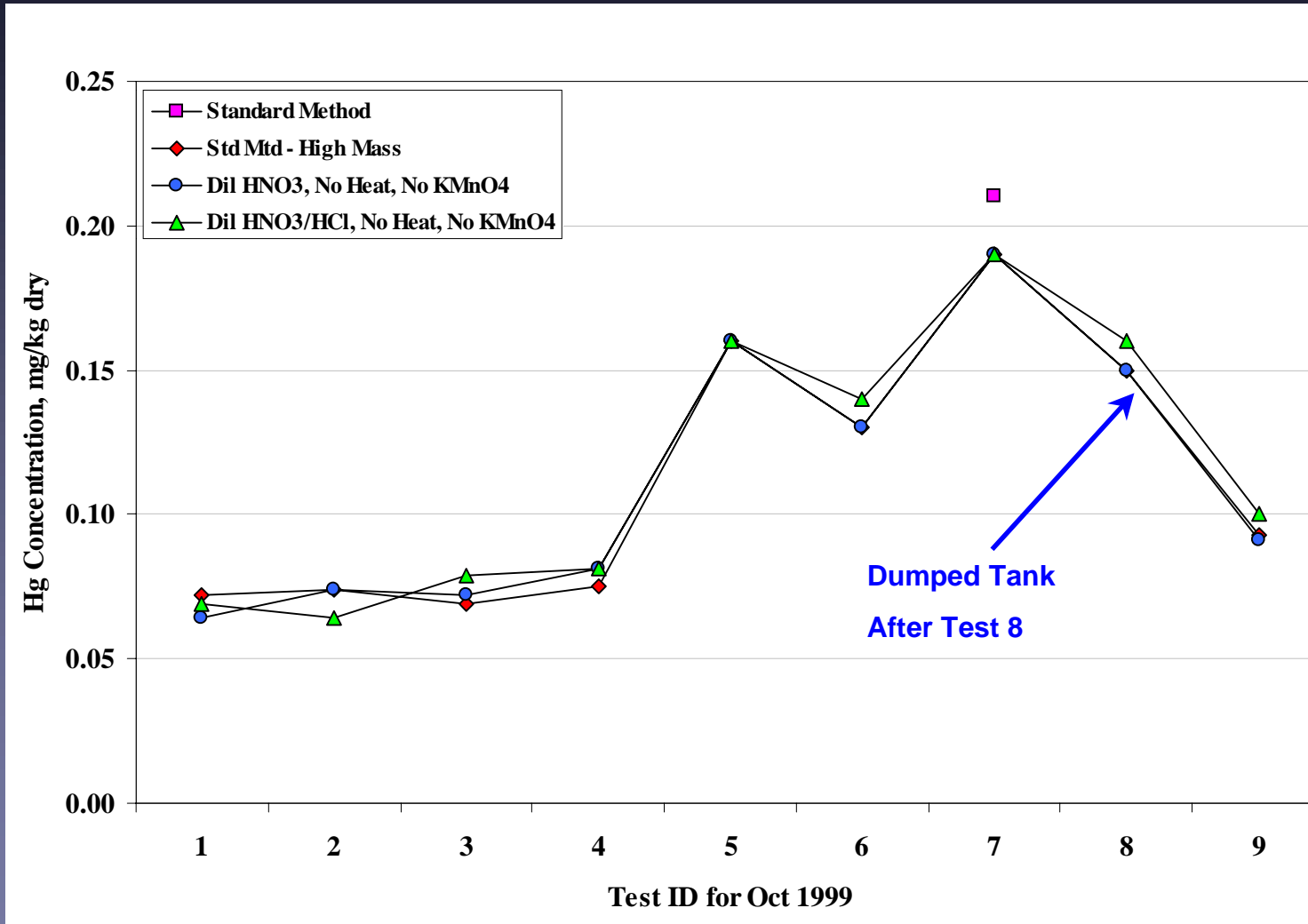
HNO₃/HCl=50% HNO₃/HCl at room temp for 60 min

Filtrate=SW846-7470A/EPA 245.2

TCLP=SW846-1311

- No Hg in Filtrates/TCLP
- Digestion Step can be much less aggressive.

Effect of Digestion Step



- Digestion Step can be less aggressive
- Hg is not strongly bound to gypsum crystals

Phase 2 Pilot Waste Samples



Wet Scrubber Sludge Analysis			Hg in Solids, mg/kg		Filtrate
Test	MTI ID	Code	% solids	Std 2	mg/l
1	WS2-2A	Base	45.0	0.130	<0.00050
2	WS2-2C	Alt App1A-1x	43.0	0.140	<0.00050
3	WS2-3C	Alt App1A-0.1x	44.0	0.180	<0.00050
4	WS2-4C	Base	47.0	0.150	<0.00050
5	WS2-5C	Alt App1A-0.02x	49.0	0.180	<0.00050
6	WS2-6C	Alt App1-1x	49.0	0.170	<0.00050
7	WS2-7B	Base	50.0	0.170	<0.00050
8	WS2-8B	Alt App1A-1x	50.0	0.200	<0.00050
9	WS2-9C	App2-Mix	53.0	0.140	<0.00050
ESP Ash Analysis					
9	WS2-9C	Base		<0.10	
= Tested with Hg CEM by Thermal Decomposition					

Method Key

Std1=SW846-7471

Std2=SW846-7471 w/high mass sample

Filtrate=SW846-7470A/EPA 245.2

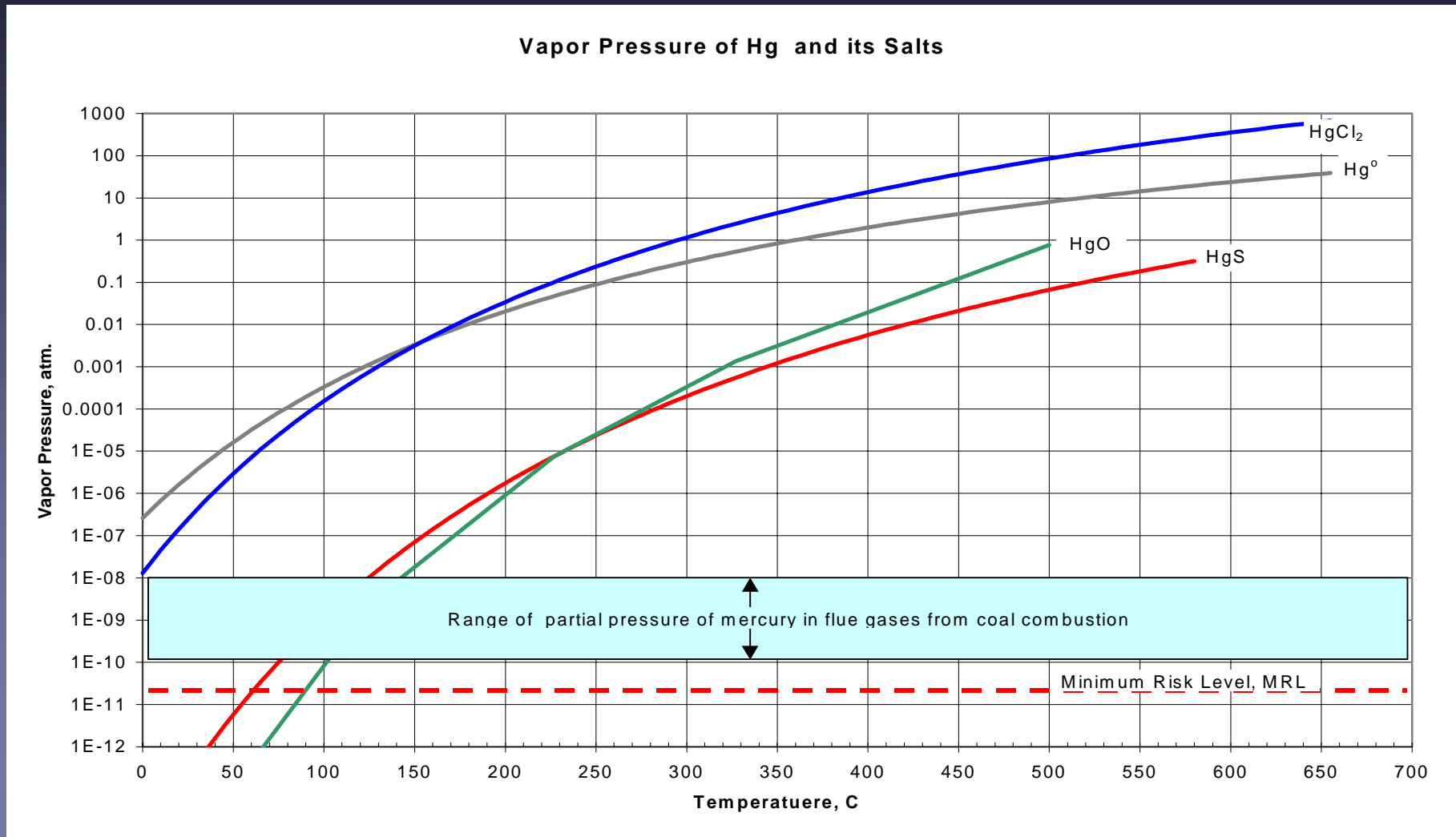
TCLP=SW846-1311

■ No Hg in Filtrates

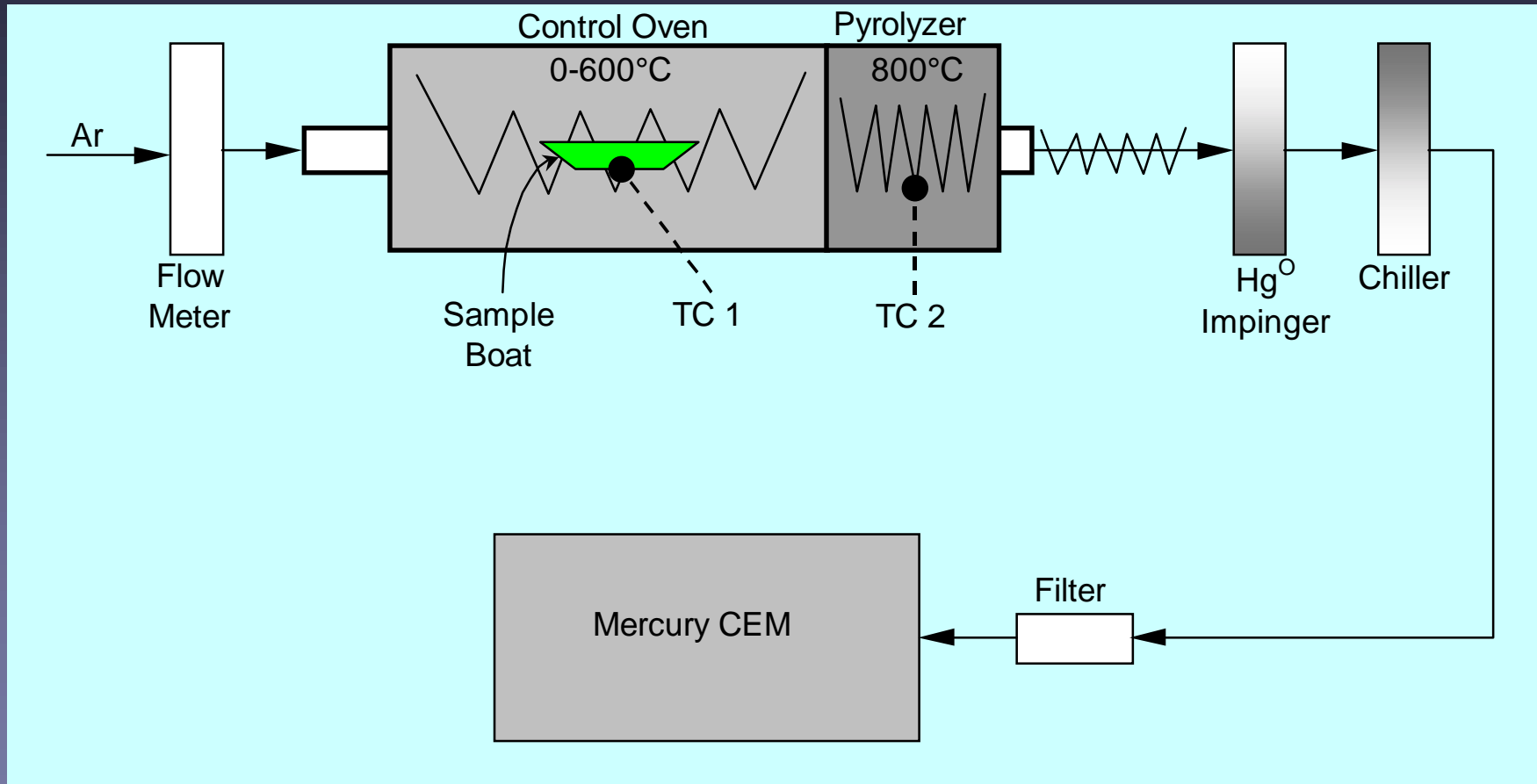
Thermal Dissociation Tests



■ Vapor Pressure of Select Pure Hg Compounds



Thermal Dissociation Test apparatus





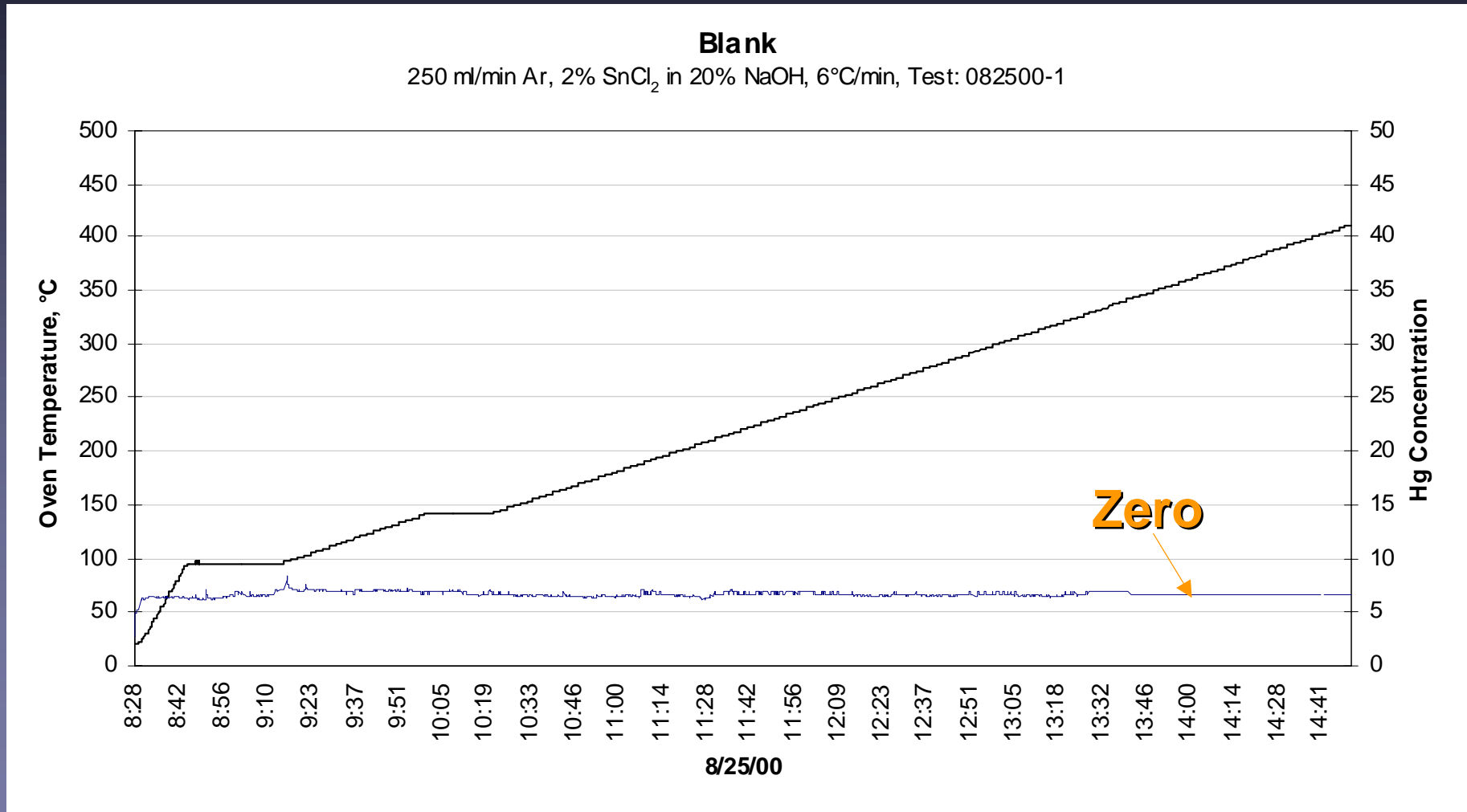
■ PS Analytical

- ◆ Sir Galahad AF Analyzer
- ◆ Preconditioner to convert all Hg to Hg⁰

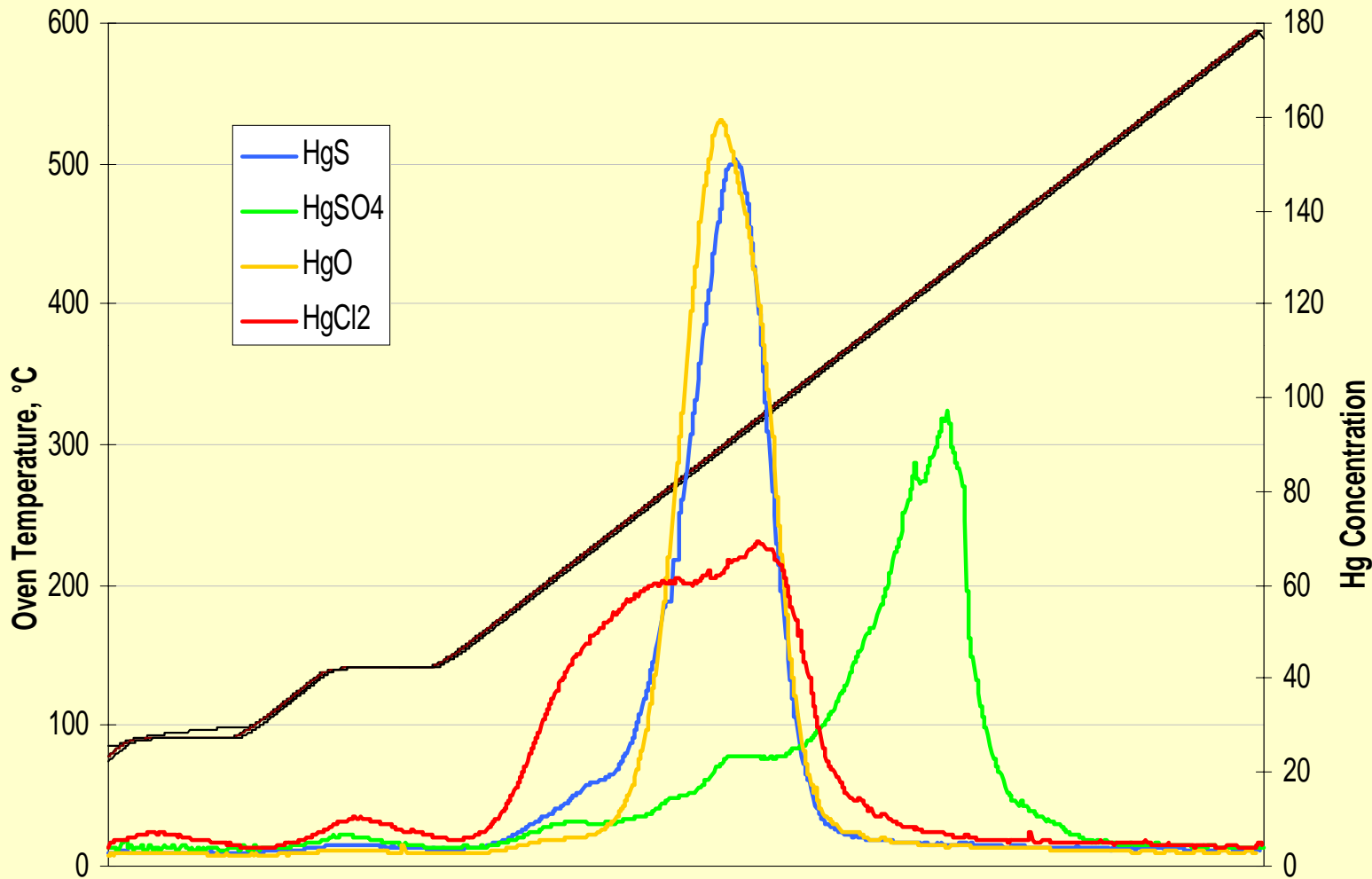
Blank Result



■ Good Blank Data



Mercury Standards

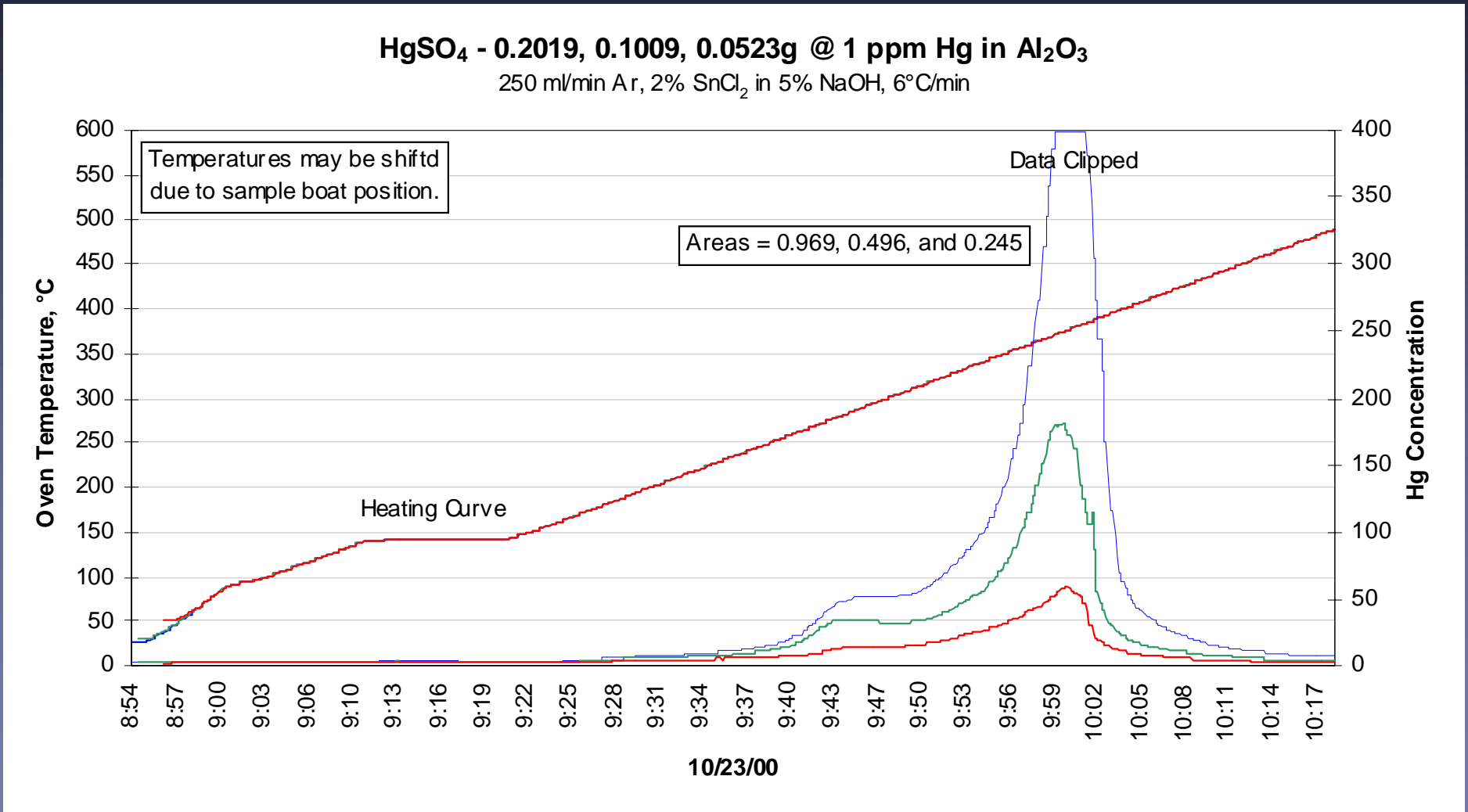


- Standards were prepared by diluting pure, dry samples in oven treated Al_2O_3 to about 1 ppm.
- Good agreement with Vapor Pressure Data

Method Validation



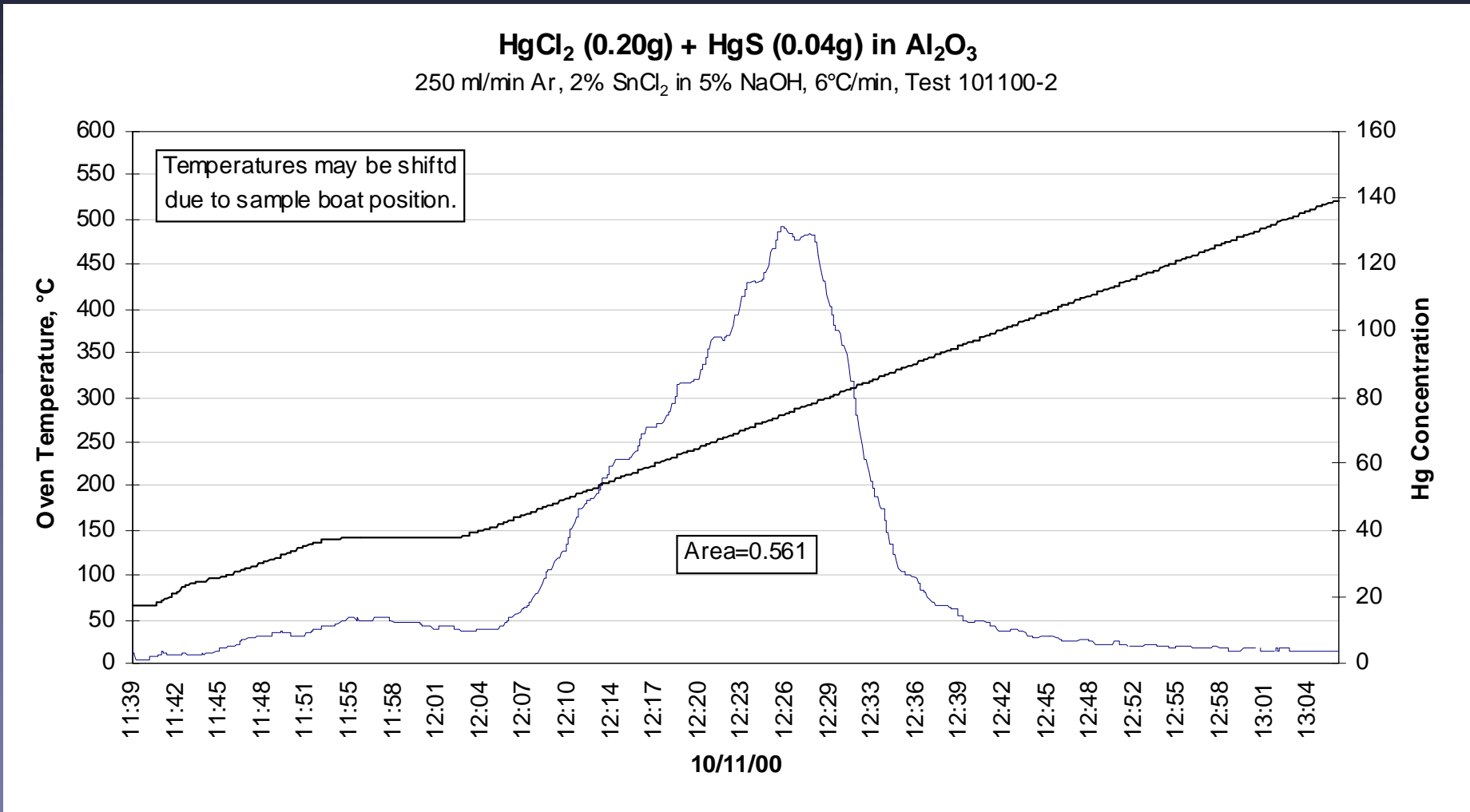
- Sample weight is directly proportional to the area under the curve.



Method Validation



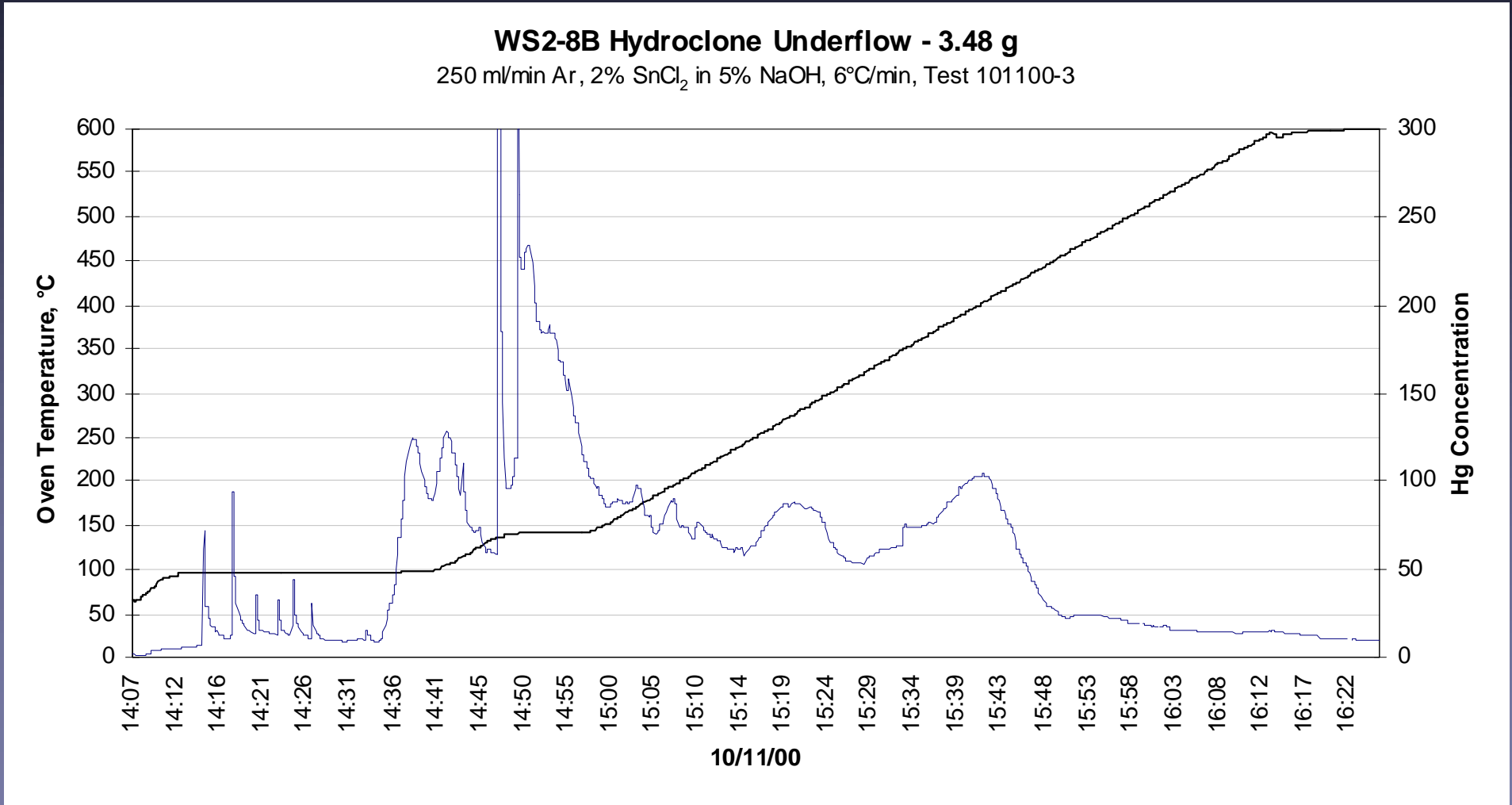
- The shape of the curve for two compounds are additive



Water Spikes



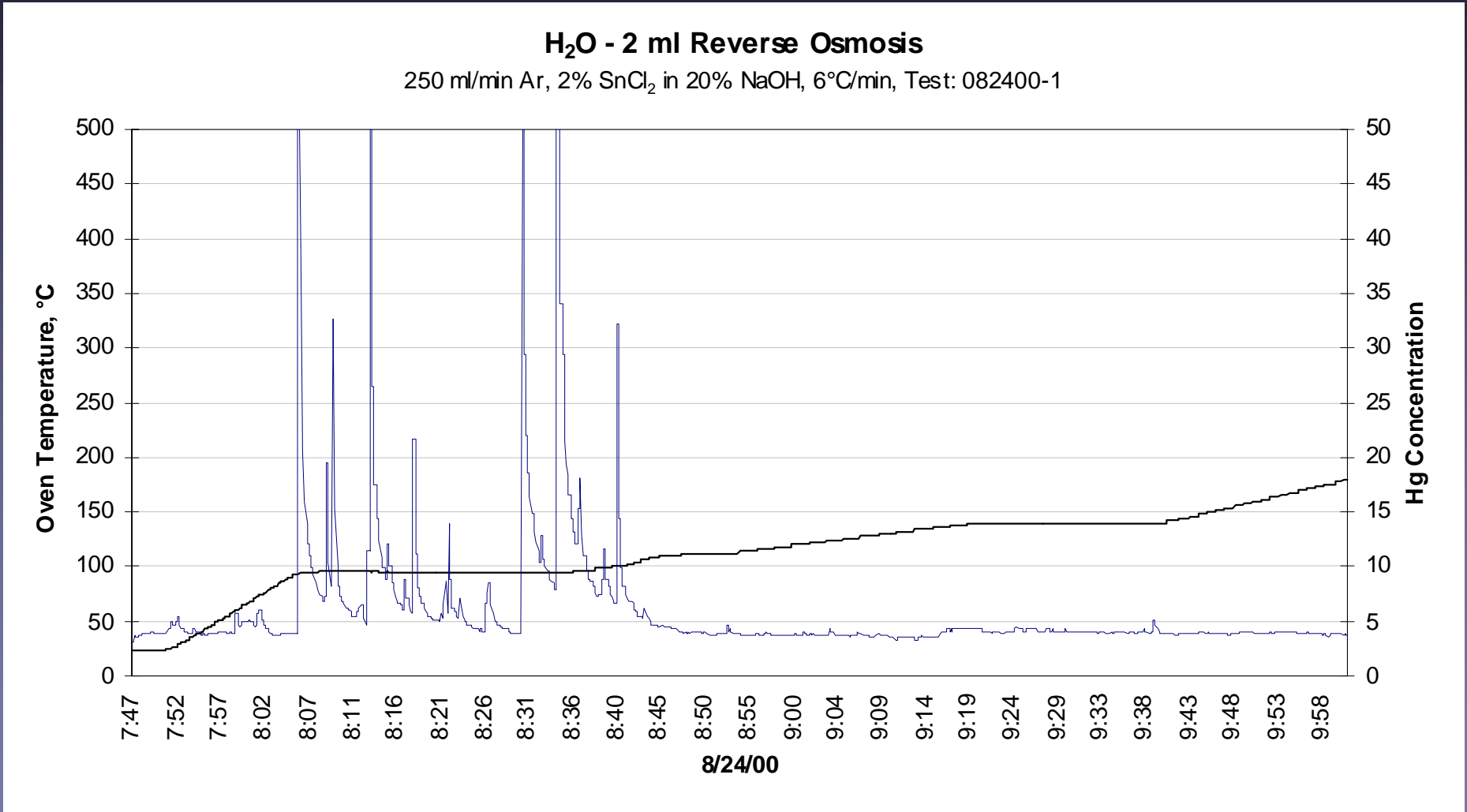
- Wet samples produced multiple low temp spikes



Water Spikes



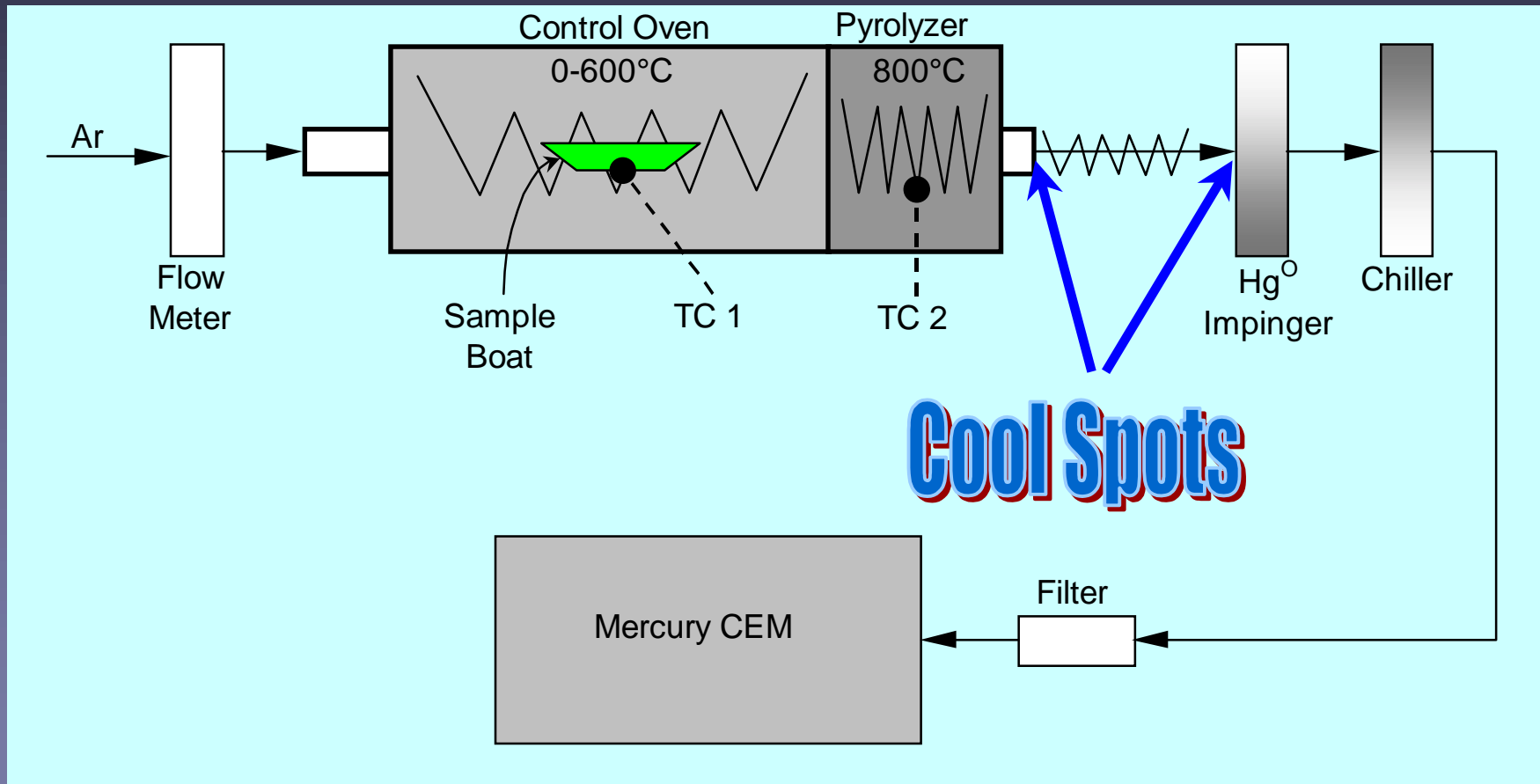
- Even water sometimes produced spikes



Water Spikes



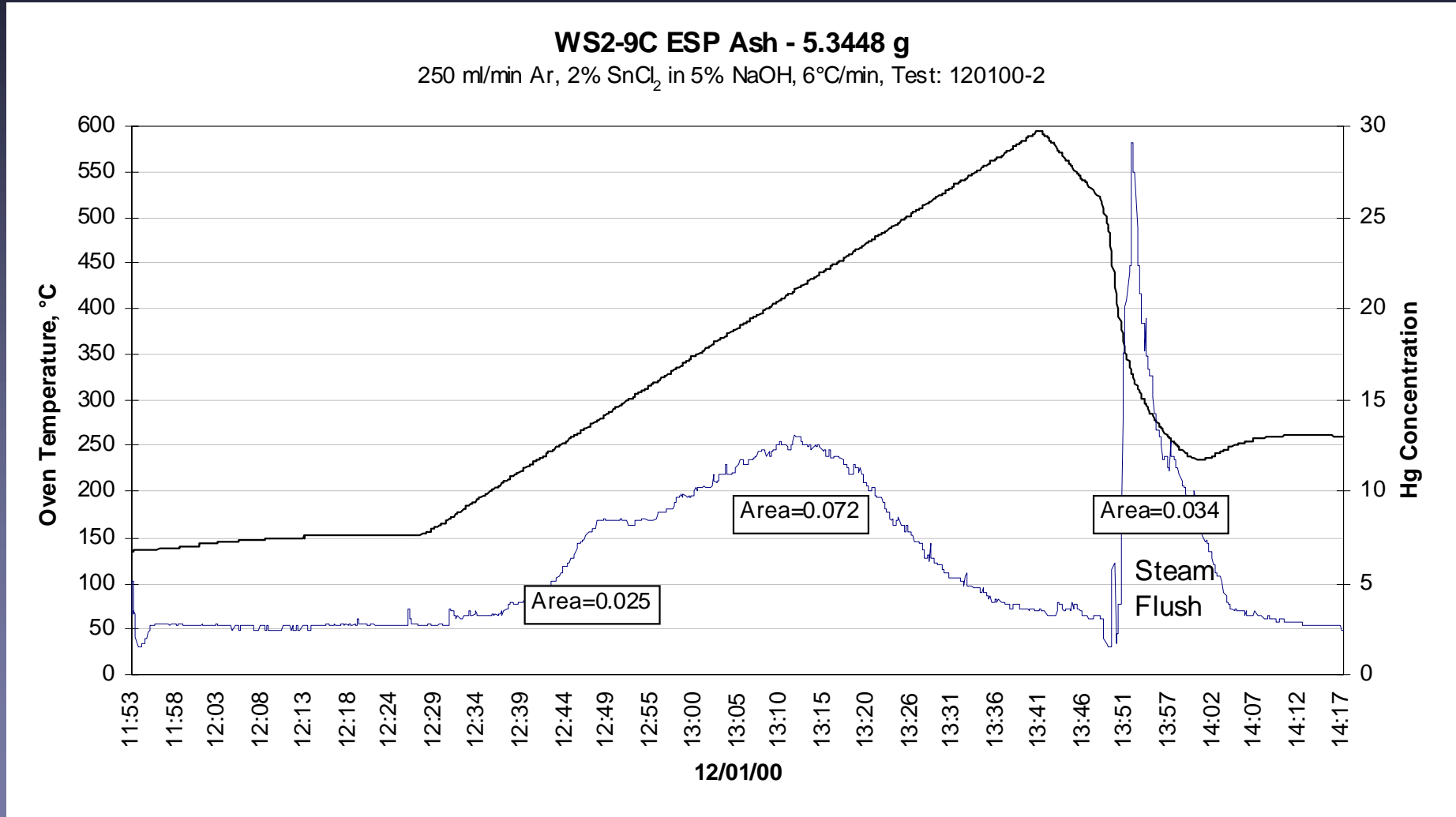
- To eliminate/reduce the effects of cool spots:
 - ◆ Modified apparatus and added insulation
 - ◆ Added “steam flushes” before and after each test



Results of a "Steam Flush"



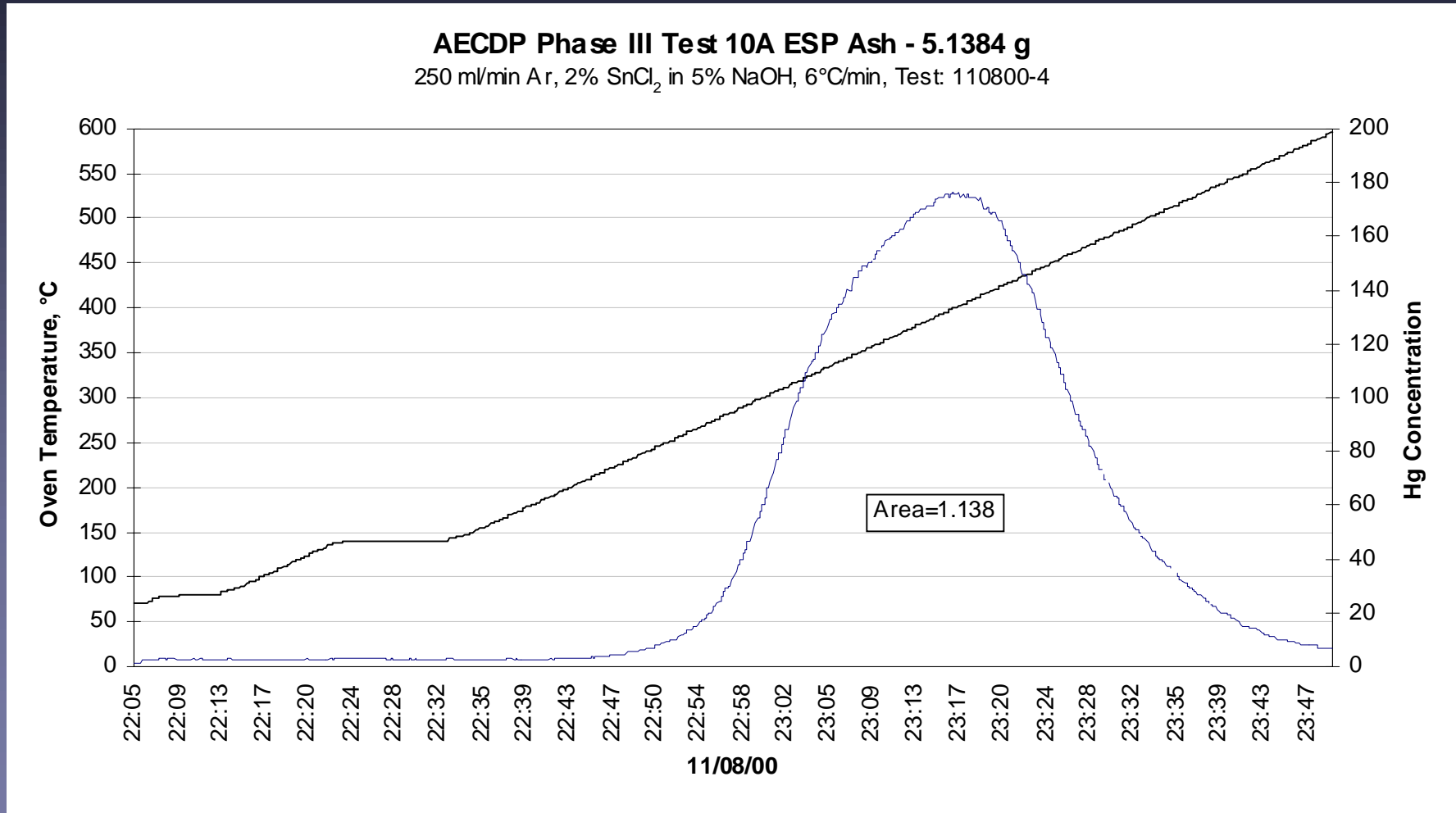
- Steam flush was 26% of the Hg for this ESP Ash



Pilot ESP Ash - Baseline



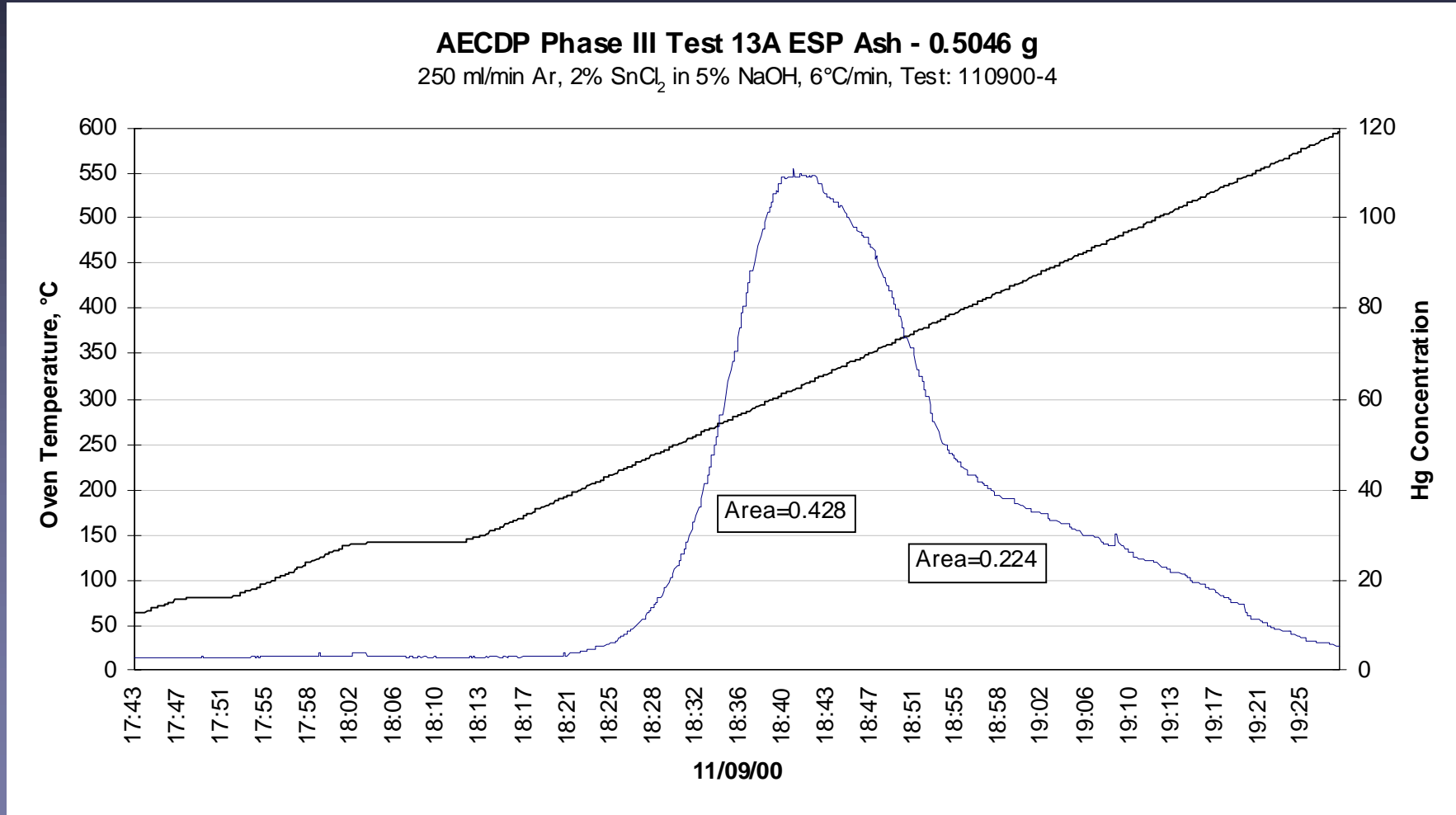
- Peak at 400°C with 5 grams



Pilot ESP Ash w/Sorbent Injection



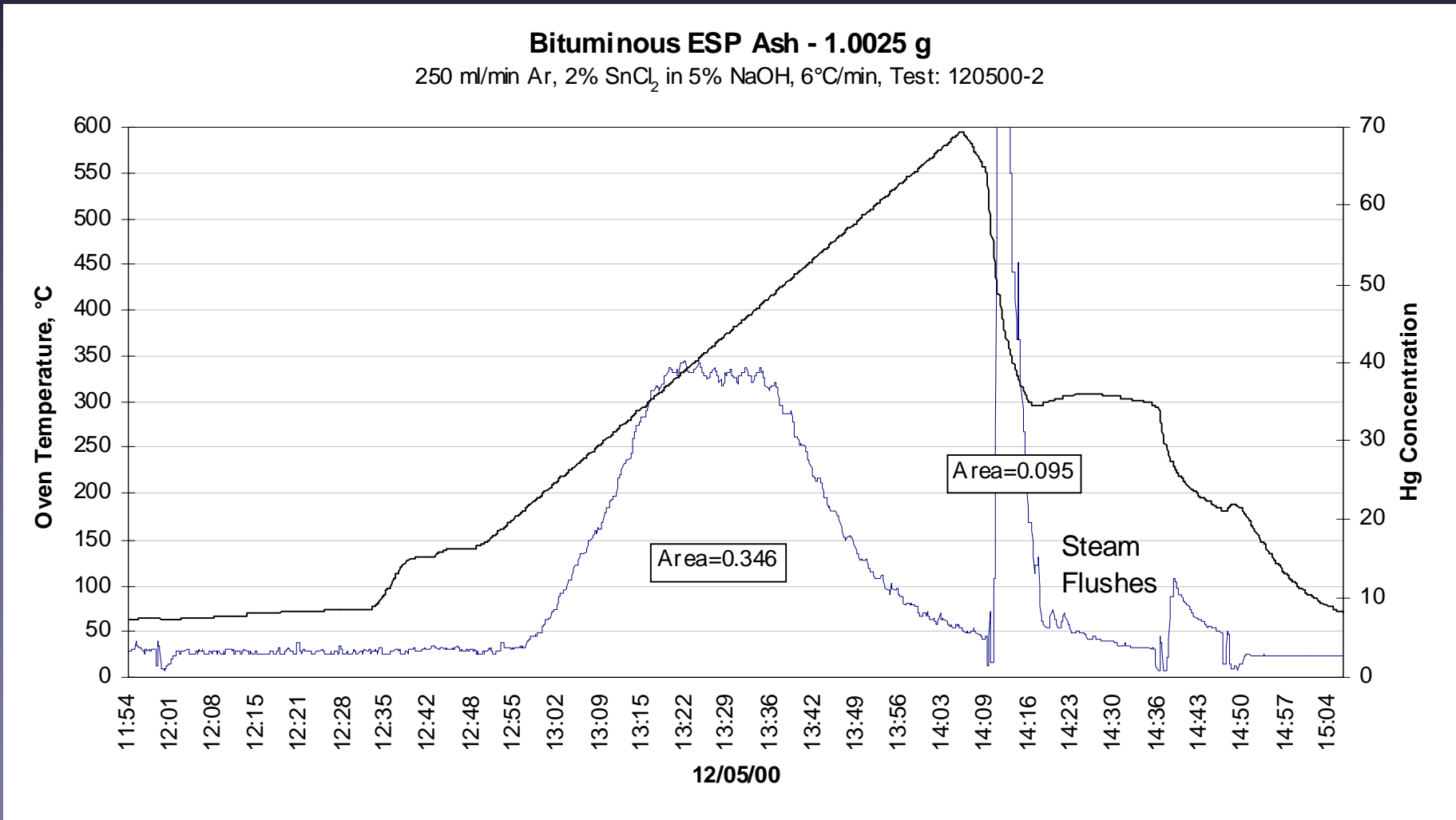
- Peak at 320°C with 0.5 grams
- Large shoulder likely represents baseline Hg



Eastern Utility ESP Ash



- Eastern Utility Ash is similar to MTI Pilot



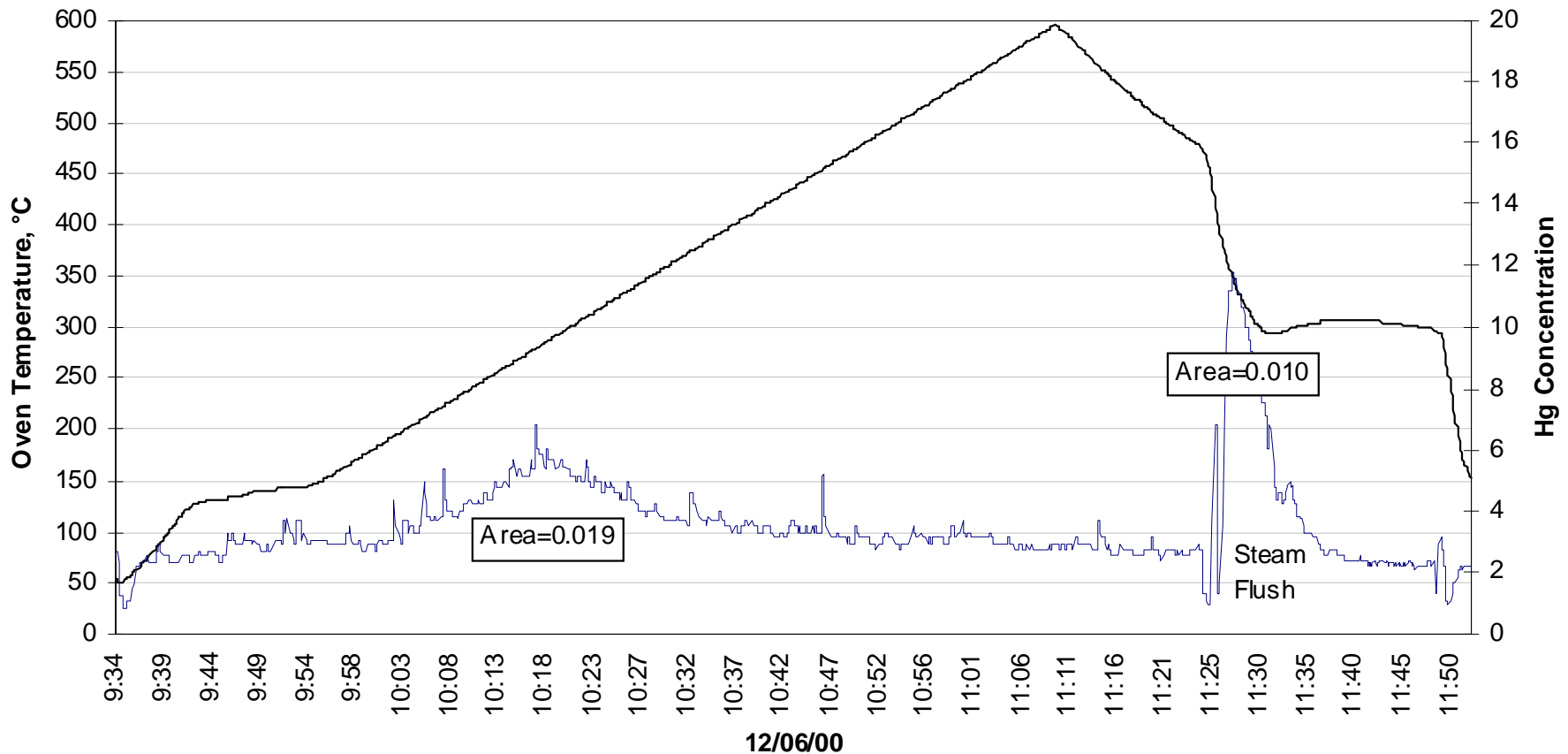
Western Utility ESP Ash



■ Virtually no Hg in ESP Ash

Western Subbituminous Coal - ESP Ash - 20.7178 g

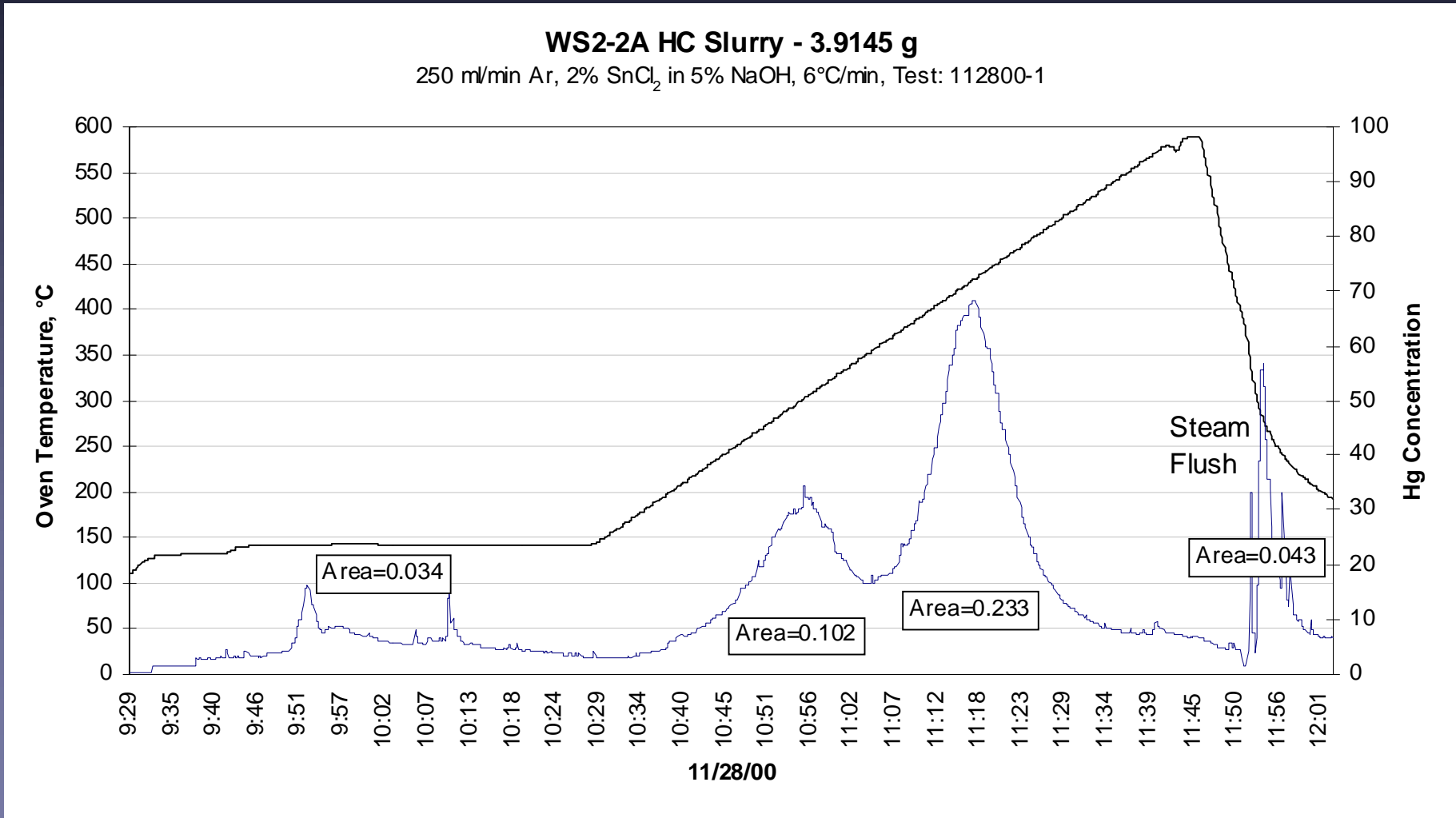
250 ml/min Ar, 2% SnCl₂ in 5% NaOH, 6°C/min, Test: 120600-1



Pilot Wet FGD Waste - Baseline



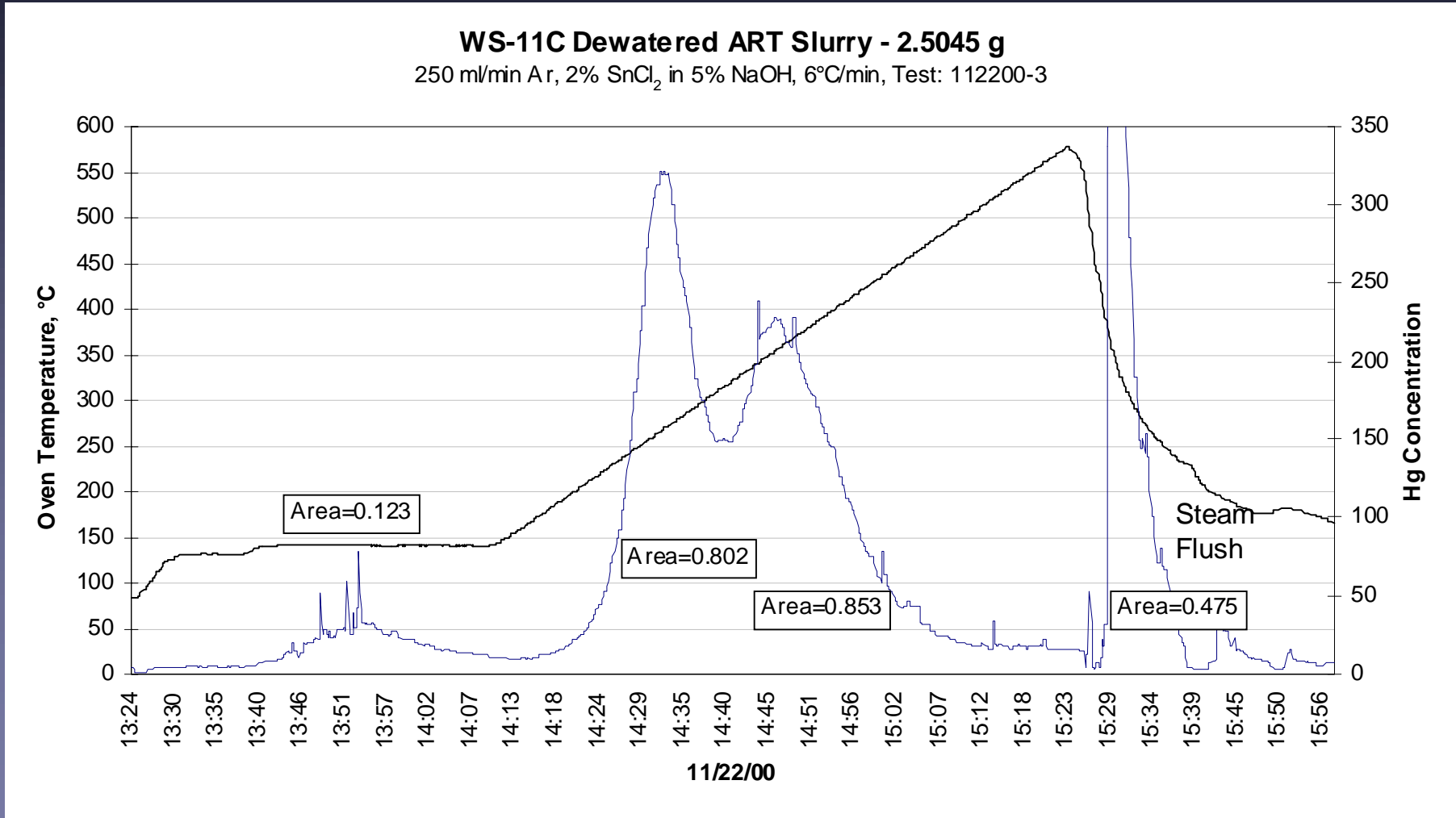
■ Two Peaks - Second is Larger



Pilot Wet FGD Waste - App2



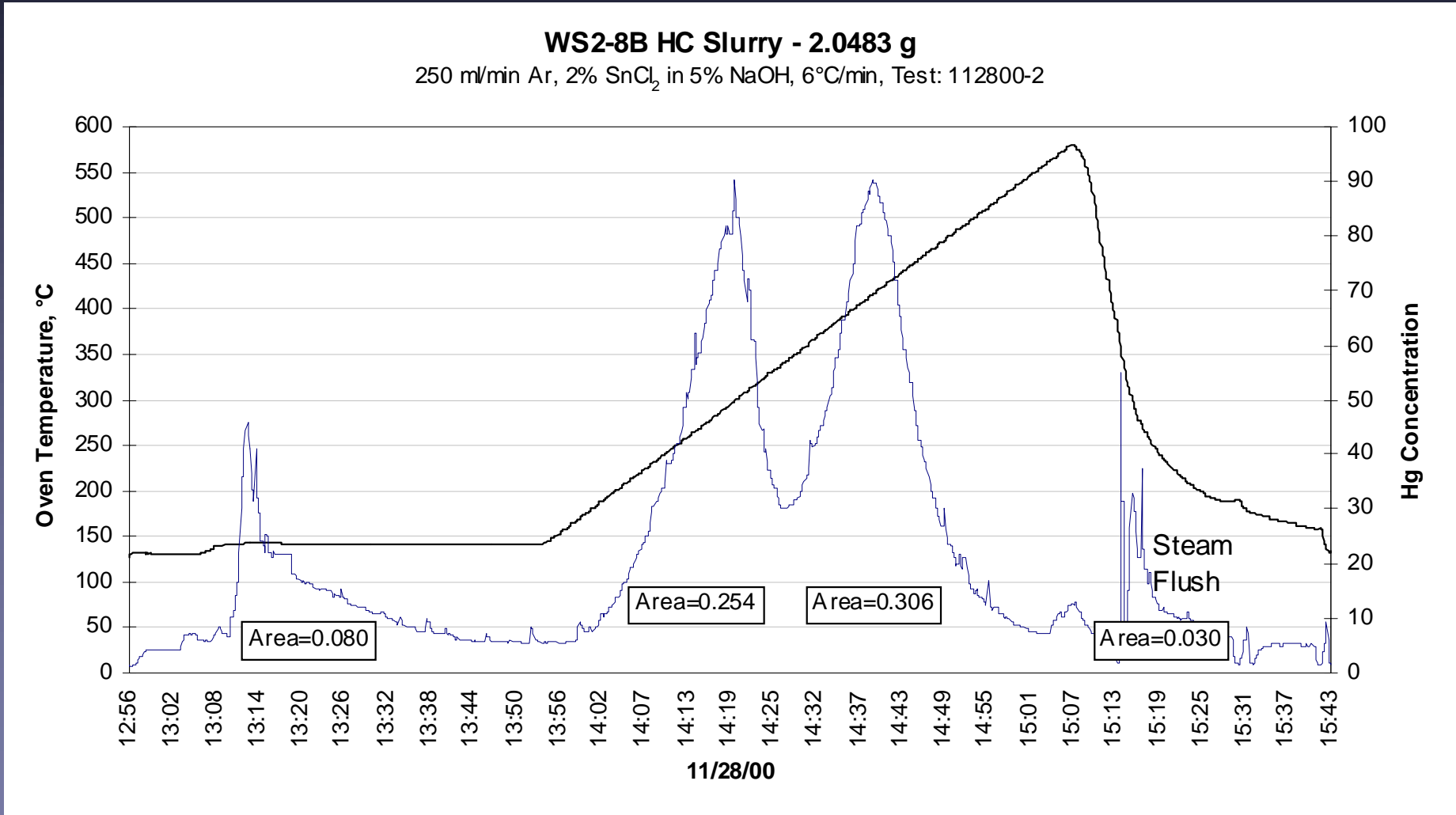
■ First Peak is Larger w/Reagent Injection



Pilot Wet FGD Waste - AltApp1A



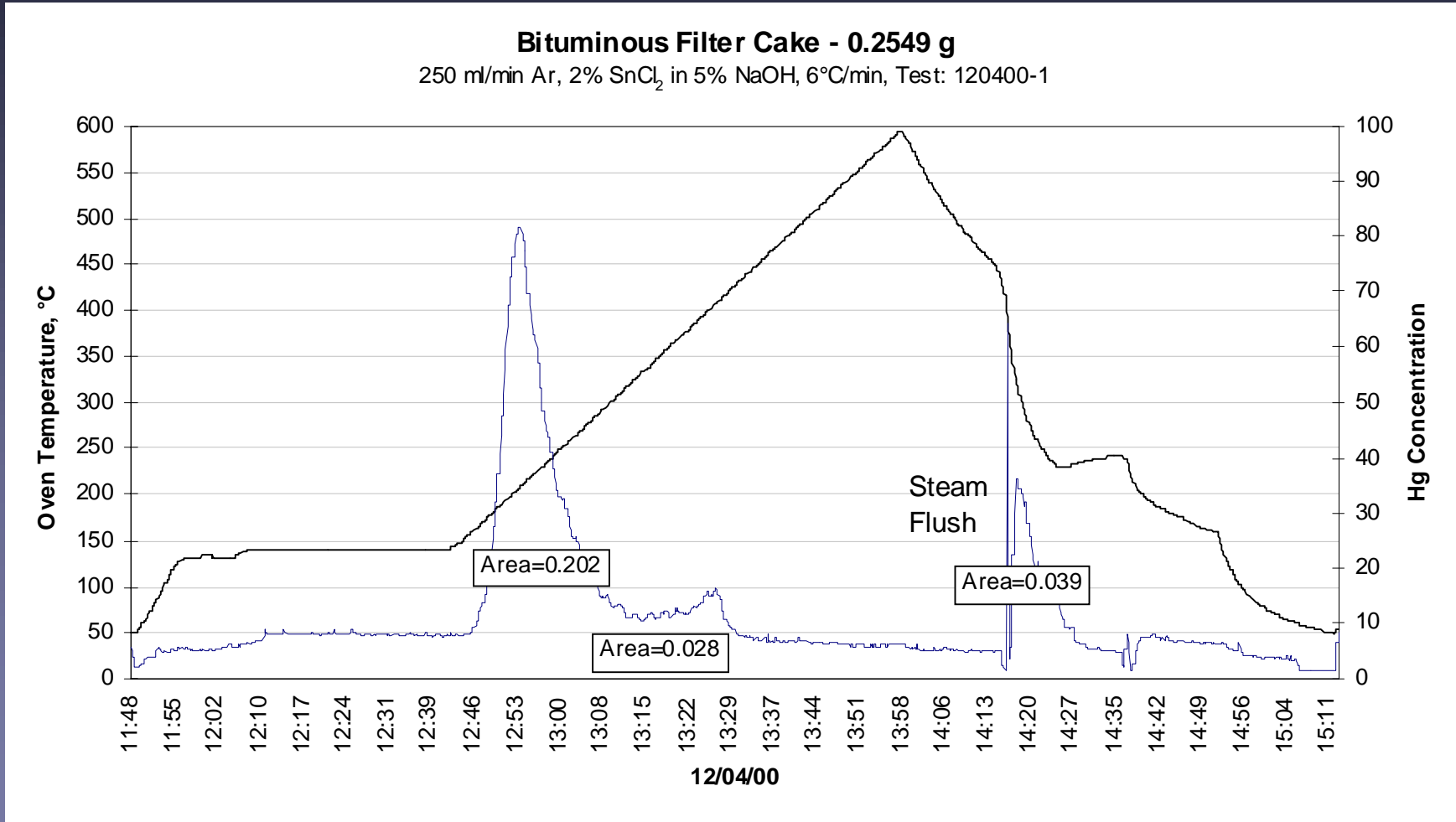
■ First Peak is Larger than Baseline



Eastern Utility Wet FGD Waste



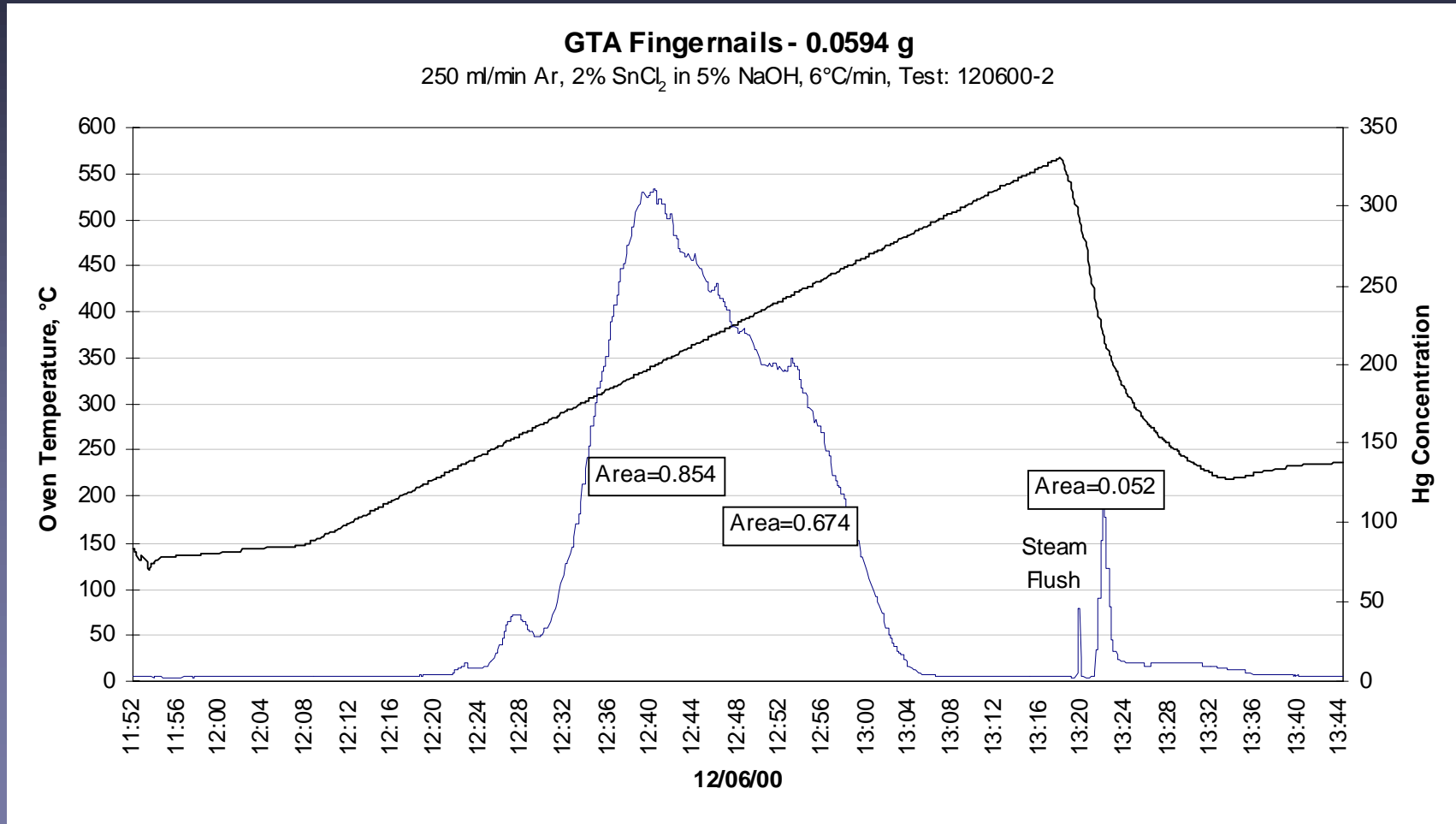
- This Unit uses maglime in the Wet FGD
- Note the low peak temperature of 220°C



Fingernails



- Note the high Hg concentration for just 0.06 g of fingernails
- Hg conc. is **83 times** higher than the highest Wet FGD waste tested



Fate of Mercury Conclusions



- All samples contained **too little mercury** to fail the TCLP test, even if it was all soluble. Therefore, using enhanced mercury control technologies should not affect CCP post use.
- HgCl_2 is not present CCP wastes tested since no mercury was detected in the liquid fractions.
- MTI dry sorbent injection forms a different mercury compound than normally found in the ESP ash.
- Thermal dissociation appears to be a viable way of detecting mercury in CCP wastes. With further development, it may be possible to measure mercury quantities and distinguish between mercury compounds at a fraction of the cost of conventional chemistry methods.
- Wet FGD sludge produced at MTI contained **two** distinct mercury compounds. Only one of these compounds was affected increased by reagent use. Wet FGD sludge from an eastern utility, using maglime, contained a different mercury compound than anything tested to date.
- ESP ash from an eastern utility had a mercury concentration similar to the MTI pilot. A western ESP ash contained almost no mercury.
- All samples were stable up to 140°C , the temp at which wallboard plant rotary kilns operate.
- Normal fingernail clippings contained **83 times more mercury** than a typical wet FGD sludge.

Full-Scale Hg Removal Demonstration



■ Host Site Comparison

	MSCPA Endicott Station	Cinergy Zimmer Station
Electricity Generation	55 MW _e	1300 MW _e
Number of Wet Scrubber Modules	1	6
Wet Scrubber Reagent	Limestone	Thiosorbic [®] Lime
Wet Scrubber Oxidation Method	<i>In situ</i> Forced Oxidation	Natural Oxidation
Wet Scrubber Liquid-to-gas Ratio	78 gal/1000 acf	21 gal/1000 acf
Slurry pH	5.4 – 5.6	5.8 – 6.0
Inlet SO₂ Concentration	3600 ppm	3300 ppm
Gypsum Use	Cement	Wallboard



■ Endicott

- ◆ Baseline Tests and Five Reagent Flows
- ◆ 14 Day Verification - Baseline and One O-H per day
- ◆ 4 Month Long-Term (OCDO) - O-H every 2 wk., Hg CEM

■ Zimmer

- ◆ 14 Day Verification - Baseline and One O-H per day

■ Samples - Coal, ESP Ash, Slurry, Waste Water, Waste

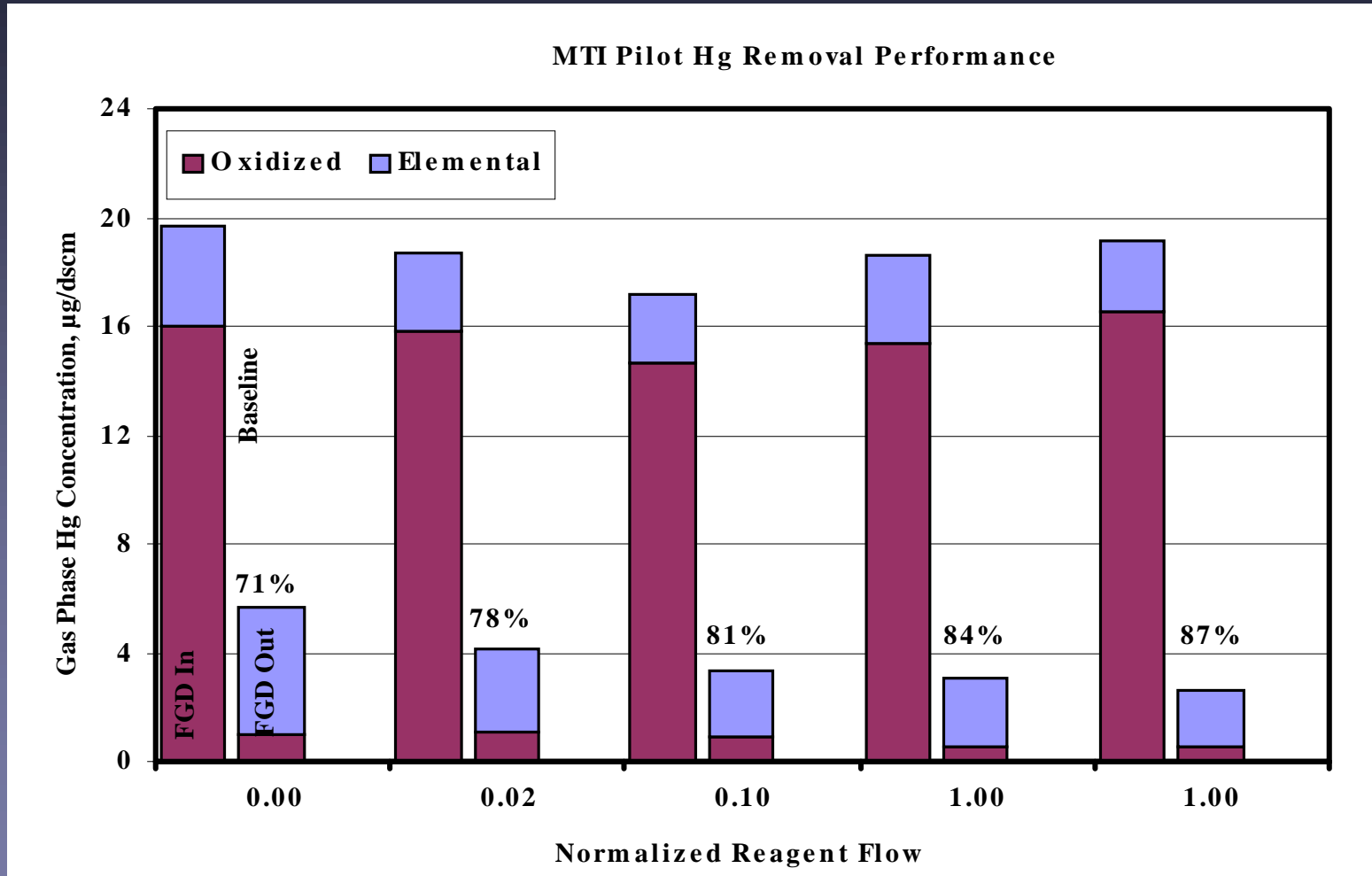
■ Mercury CEM - Continuous at wet FGD Inlet and Outlet

■ Data Acquisition - Select Boiler, wet FGD and Hg CEM Data

MTI Pilot O-H Data



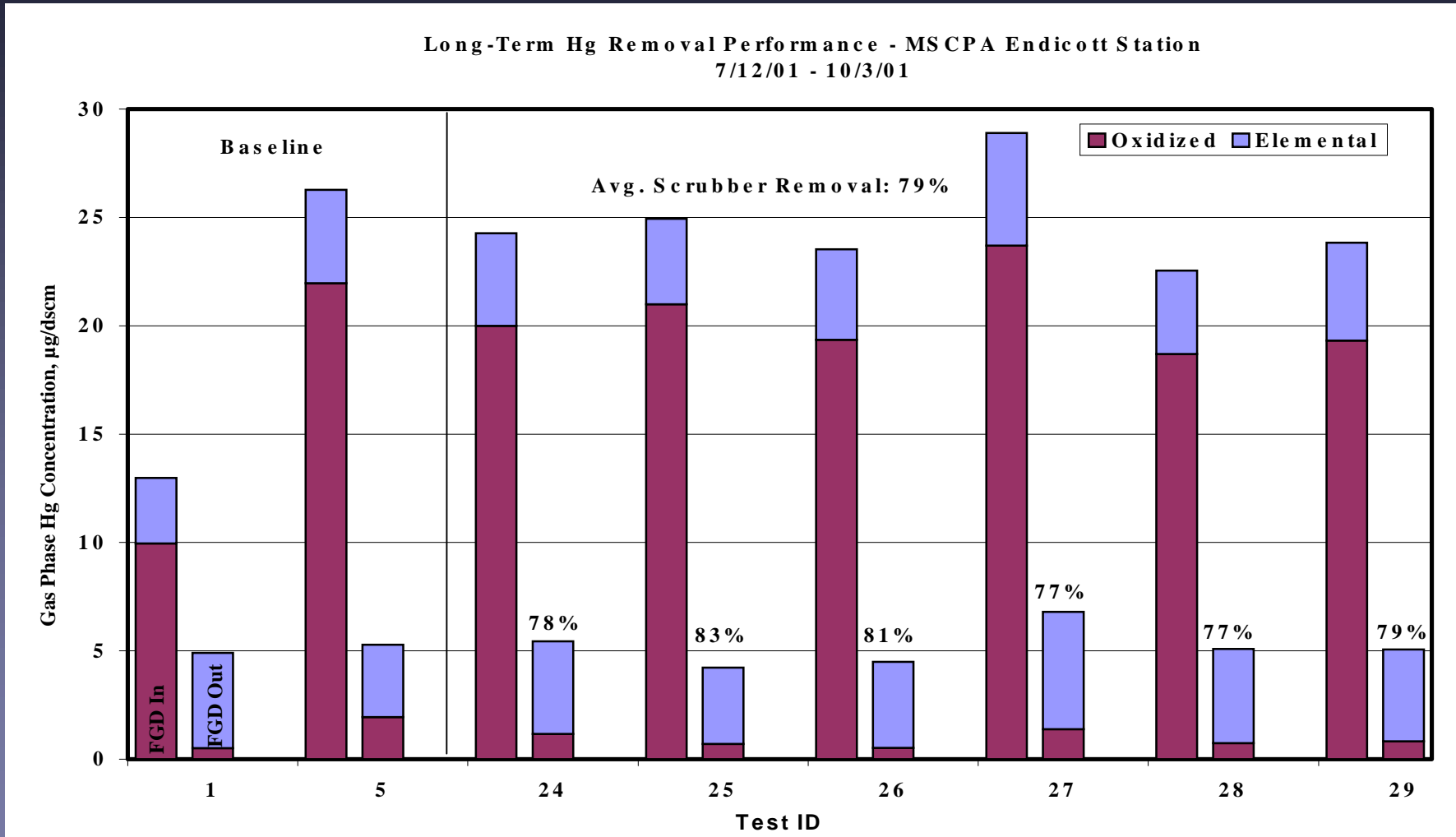
- Reagent use prevents reduction of Hg^{++} in scrubber



Endicott O-H Data



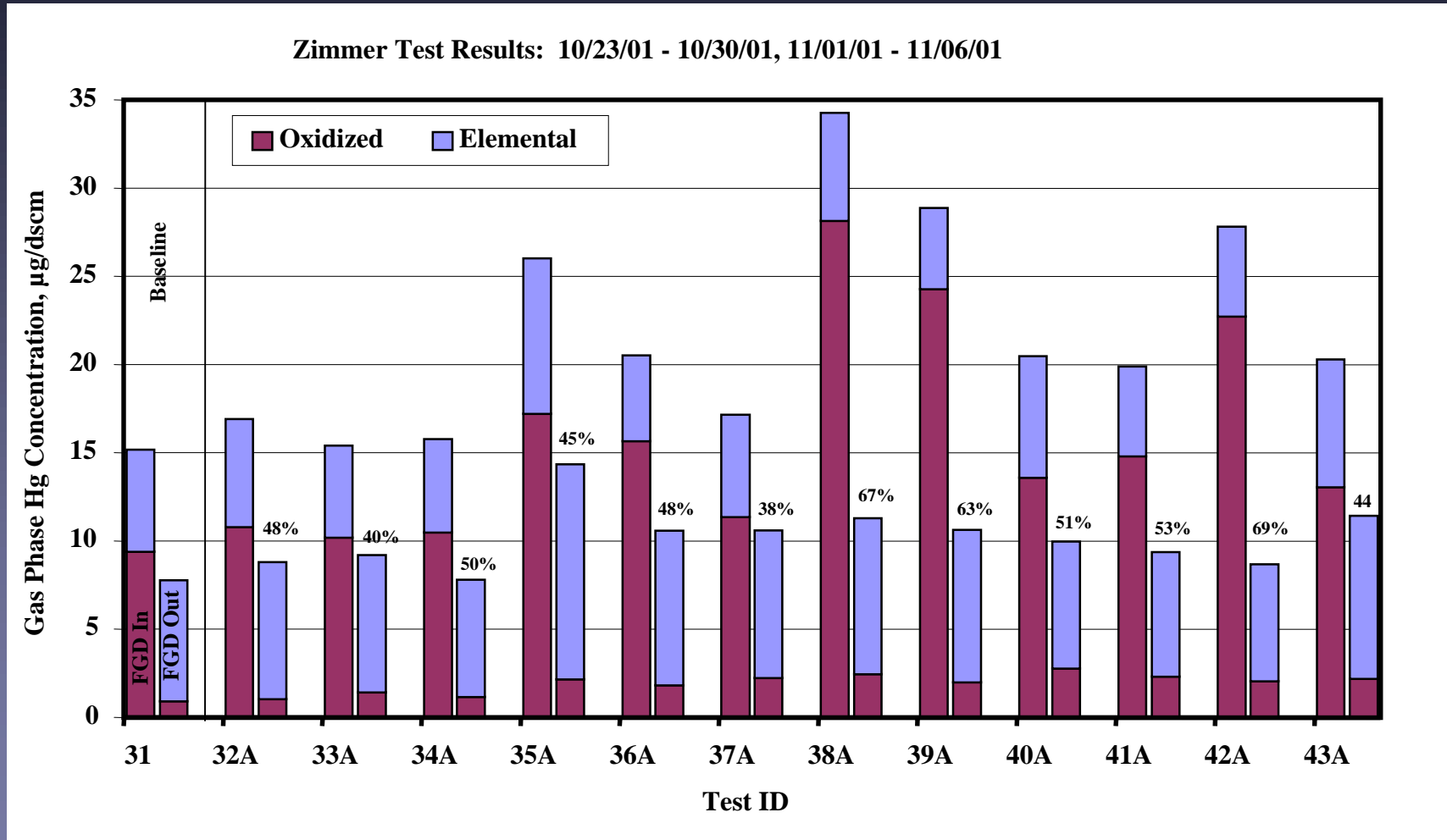
- Reagent use prevents reduction of Hg^{++} in scrubber



Zimmer O-H Data



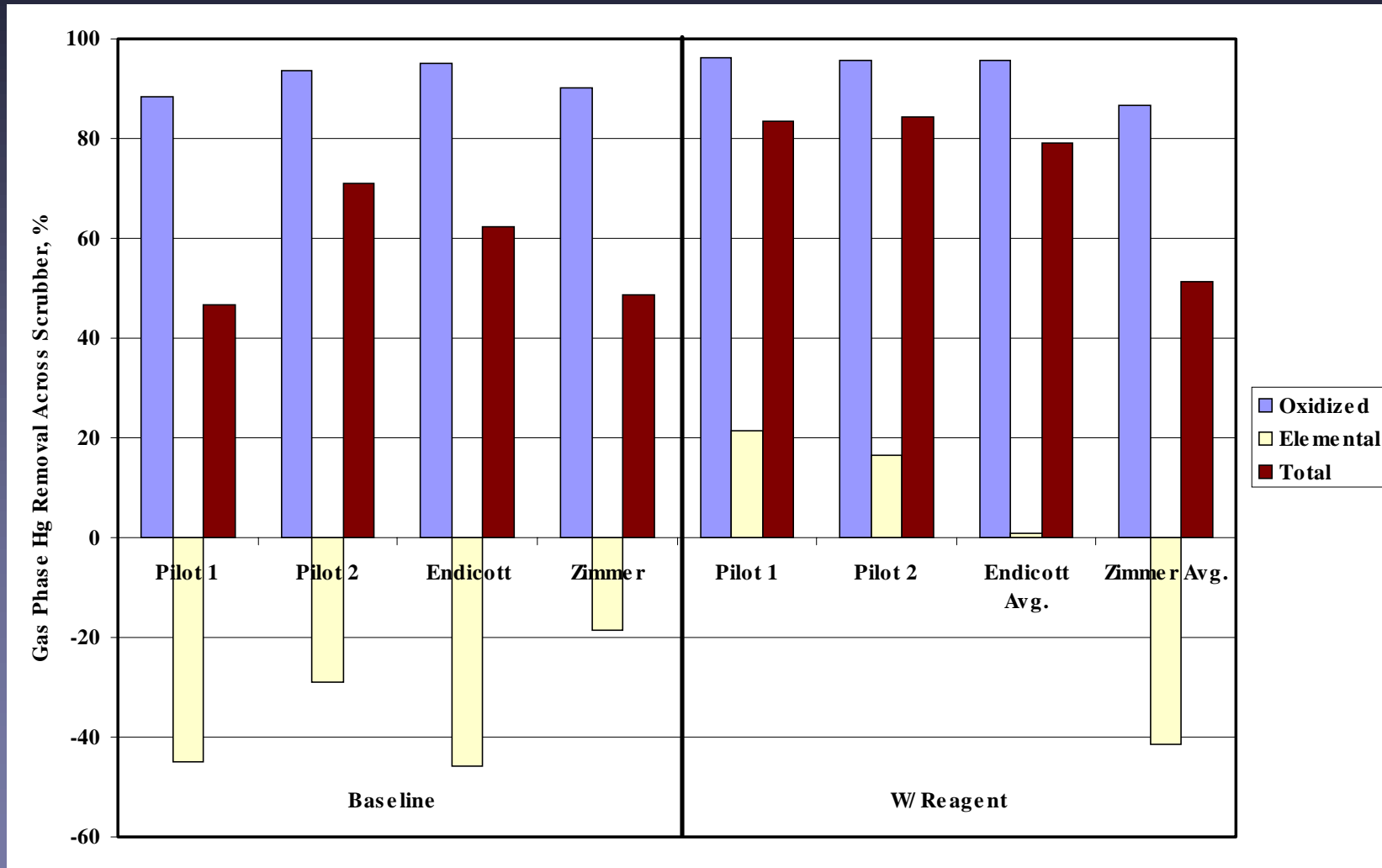
- Reagent use **did not** prevent reduction of Hg⁺⁺ in scrubber



Effect of Reagent and Hg Conversion



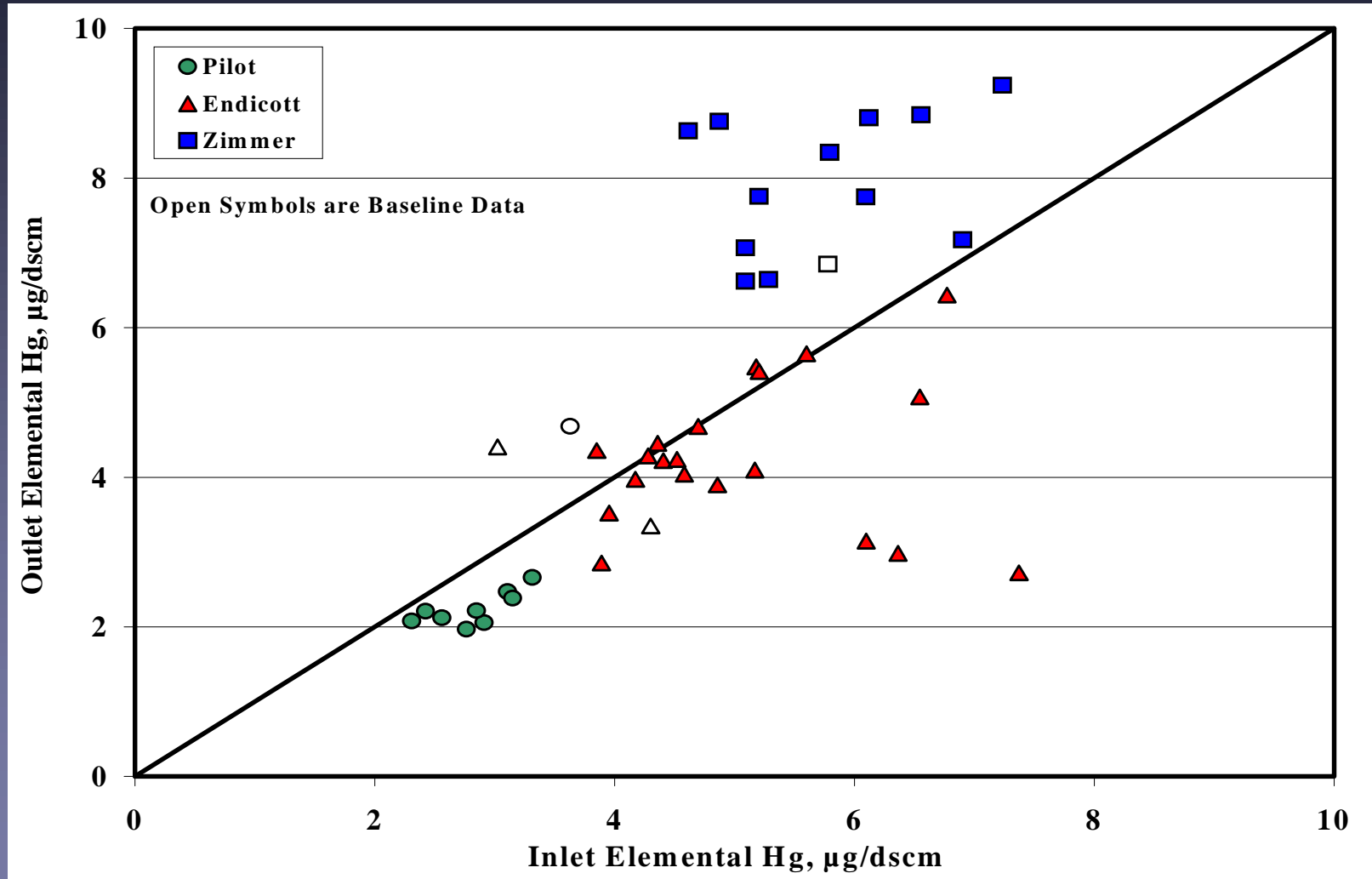
- B&W/MTI reagent prevent conversion, except at Zimmer.



Hg⁰ at the Scrubber Inlet and Outlet



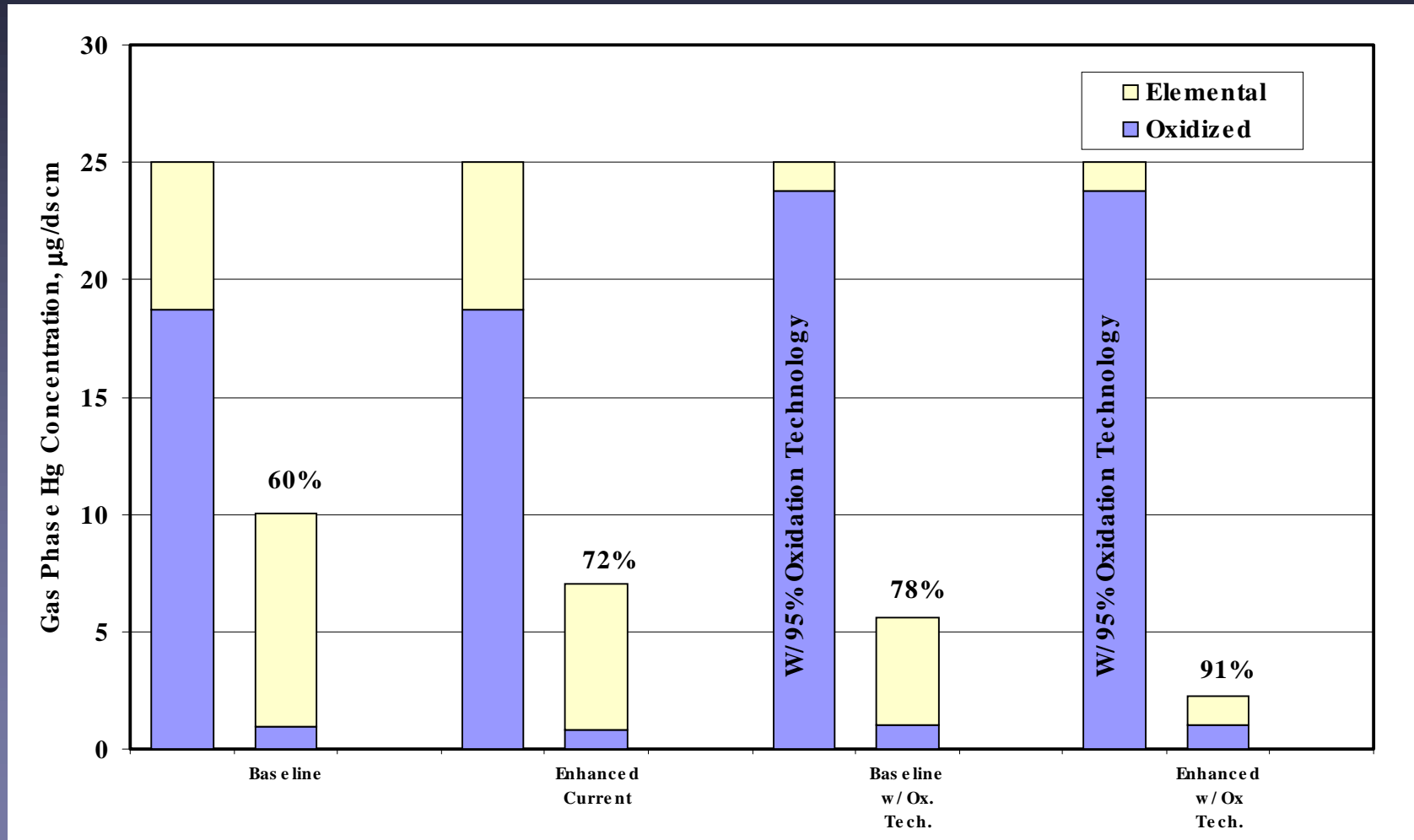
- Points above the 45° line mean Hg⁰ is created in the scrubber



The Future of Hg Removal in Wet FGD



- A combination of the B&W/MTI Reagent with an Oxidation Technology will yield high Hg removal across a wet FGD.



Field Demo Conclusions



- Overall mercury removal will be greater once particulate mercury is factored in.
- The B&W technology has no effect on scrubber operation.
- The B&W/MTI proprietary reagent is effective in preventing Hg⁺⁺ conversion across the scrubber in LSFO systems.
- Addition research is needed to explore the effect seen at Zimmer.
 - ◆ Higher SO₃⁻ in Thiosorbic system
 - ◆ Natural Oxidation in scrubber
- Scrubbers are very effective at removing oxidized mercury, but conversion must be prevented.