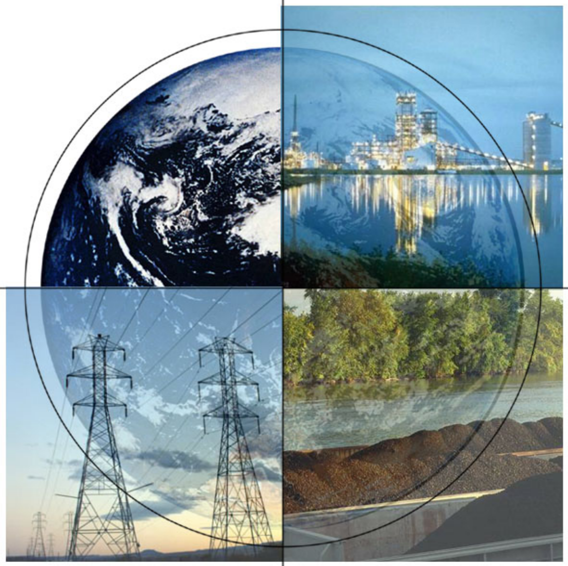
DOE's Perspective and Research on Mercury in Coal Utilization By-Products (CUBs)



American Coal Ash Association
2007 Winter Meeting

January 30, 2007
Jacksonville, FL

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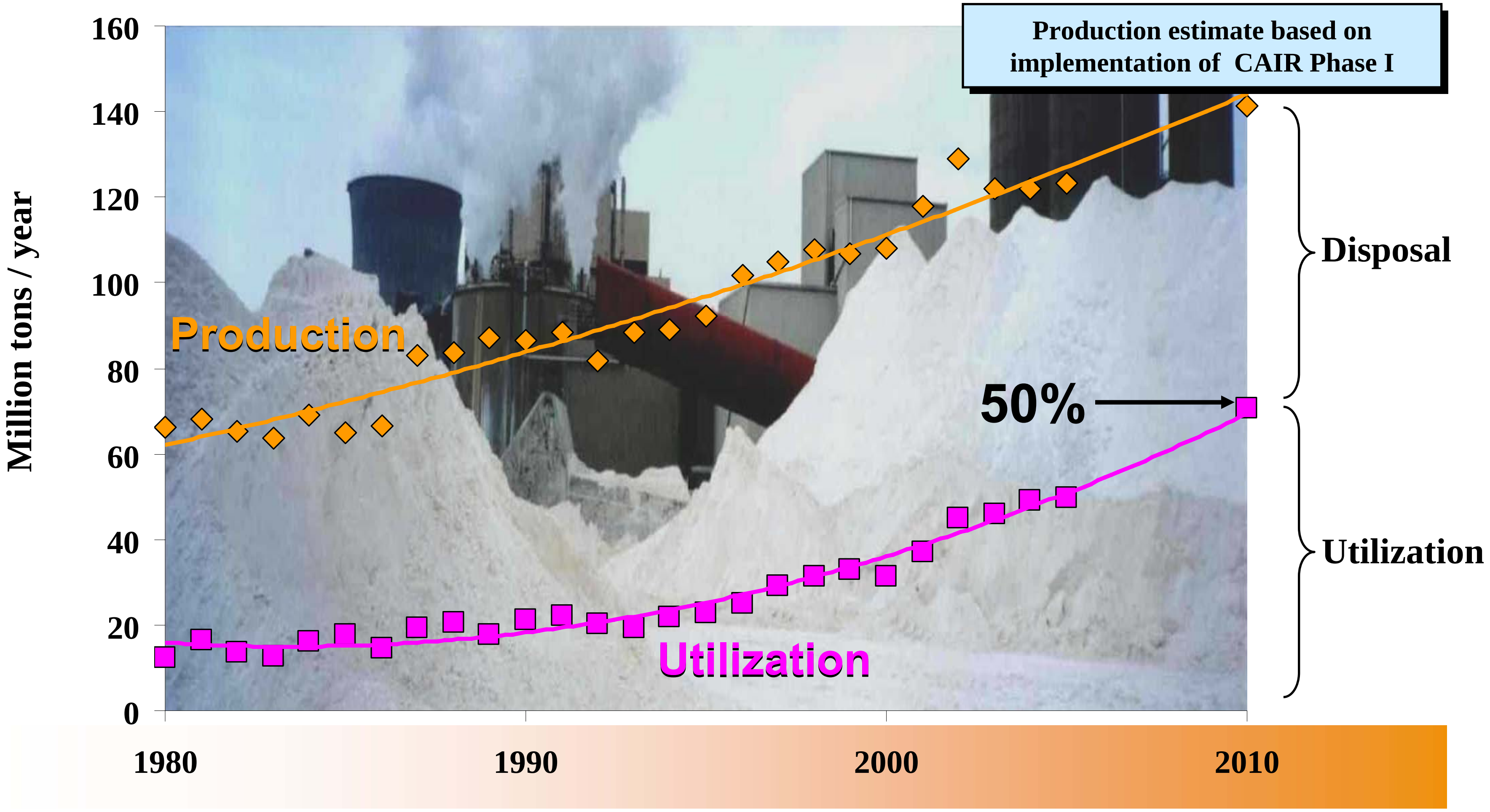
DOE Terminology: CUBs

- **<u>C</u>oal <u>U</u>tilization <u>B</u>y-products**
  - Includes Fly ash, Bottom ash, Boiler slag, FGD solids
  - Other acronyms: CCBs, CCPs, CCW, FFCW, CCR ...
- **<u>U</u>tilization includes:**
  - Combustion
  - Gasification & Hybrid systems
- **<u>B</u>y-products because:**
  - $ from electricity sales >> $ from CUB sales
  - Become “Products” when sold or beneficially used
  - Become “Wastes” when sent to a permanent disposal site
    - Can still become “products” after disposal

Outline

- **Potential effects of CAMR on Hg content of CUBs**
  - Hg control technology governs effect on CUBs
- **NETL-sponsored research on Hg release of "captured" Hg**
  - Leaching and volatilization
  - Disposal and re-use environments
- **Consider alternatives for:**
  - Minimizing Hg content of CUB solids
  - Minimizing Hg release from CUB during re-use

Realistic Near-term Goal:
50% Utilization by 2010



EPA Regulations Introduce Constant Challenges to CUB Utilization

- **CAIR SO_2 limits = More wet FGD byproducts in Eastern U.S.**
  - Will wallboard market continue to absorb excess?
  - Scrubbers vs. low-sulfur coals
    - South American imports; Western U.S coals

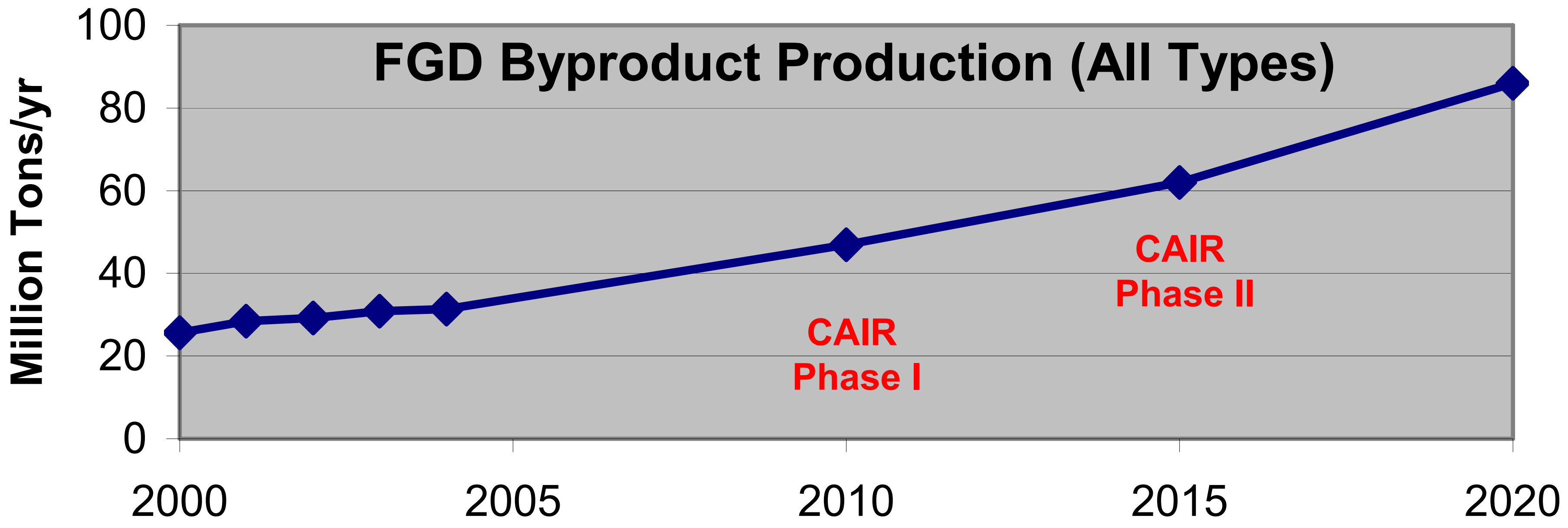
- **CAVR-BART rules = more dry FGD byproducts in Western U.S.**
  - Spray dryer ash unsuitable for wallboard

- **CAIR NOx limits = More Low-NOx burners, SCR, SNCR**
  - Will additional carbon/NH_3 in fly ash disrupt cement/concrete markets?

- **CAMR = Additional Hg in CUBs**
  - **How much more?**
  - **Which types of CUB will be affected most?**
  - **Impacts on disposal and re-use?**

Future Trends in FGD Byproduct Production

Response to CAIR and CAVR



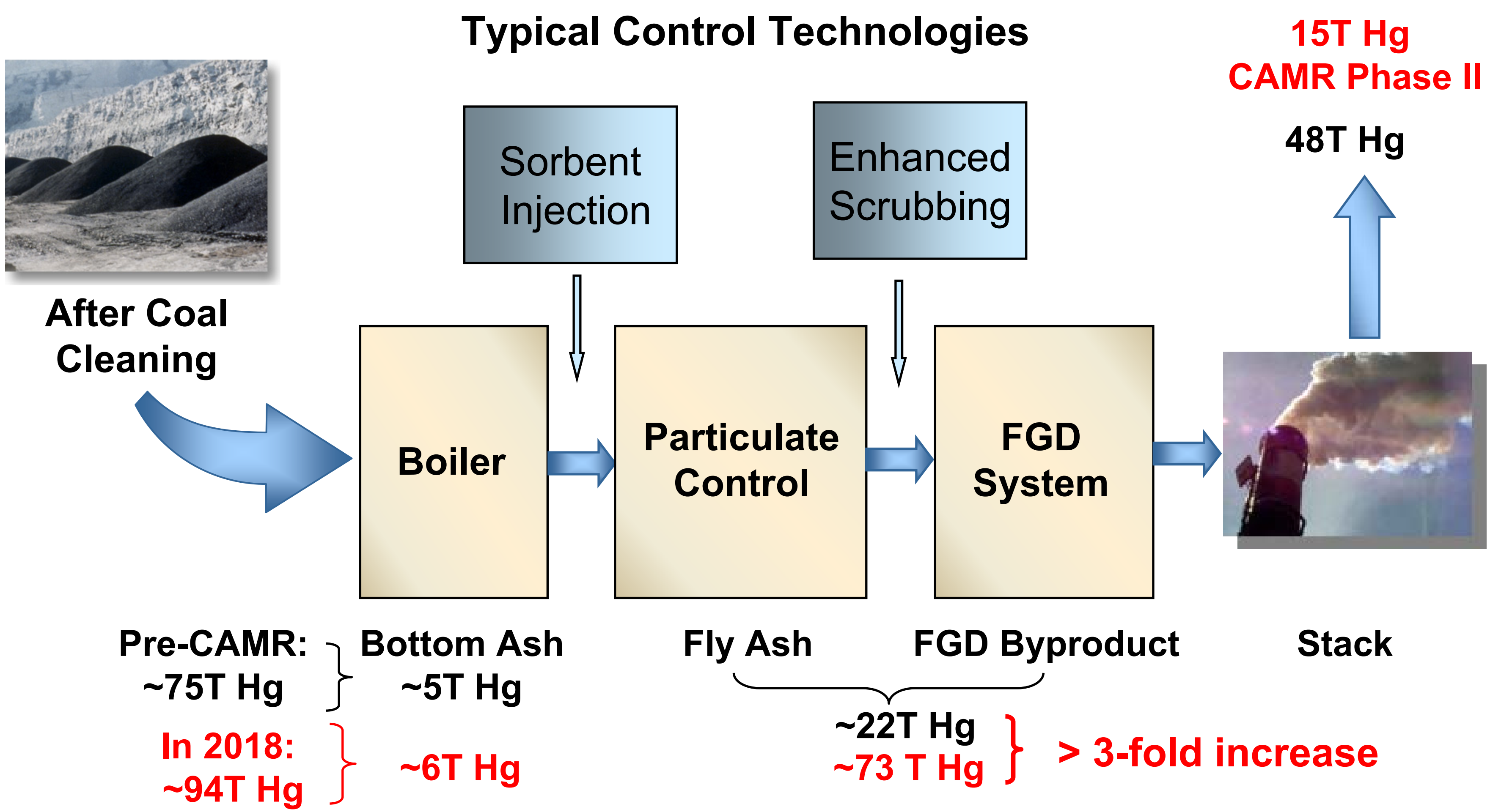
Effect of CAMR on CUBs

Mercury Content ⇧

Vs.

Mercury Release ?

Impact of CAMR on Mercury Partitioning



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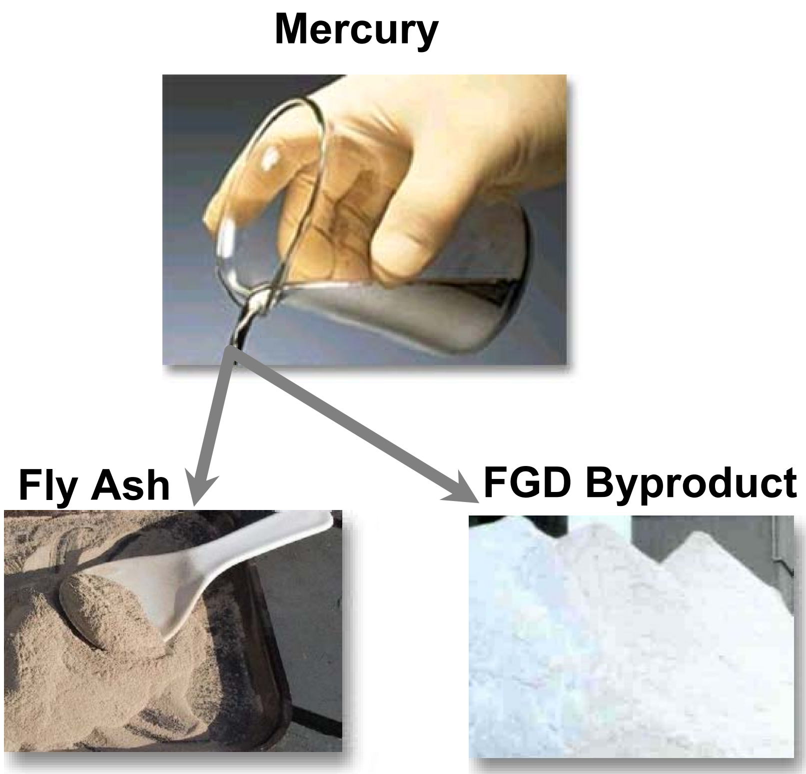
Potential Economic Impact of CAMR

Fly Ash

- **Loss of all reuse applications ~ $908 M/yr impact**

FGD Solids

- **Loss of all reuse applications ~ $213 M/yr impact**



“Hazardous” designation (RCRA Subtitle C disposal) could cost more than $11 billion/year

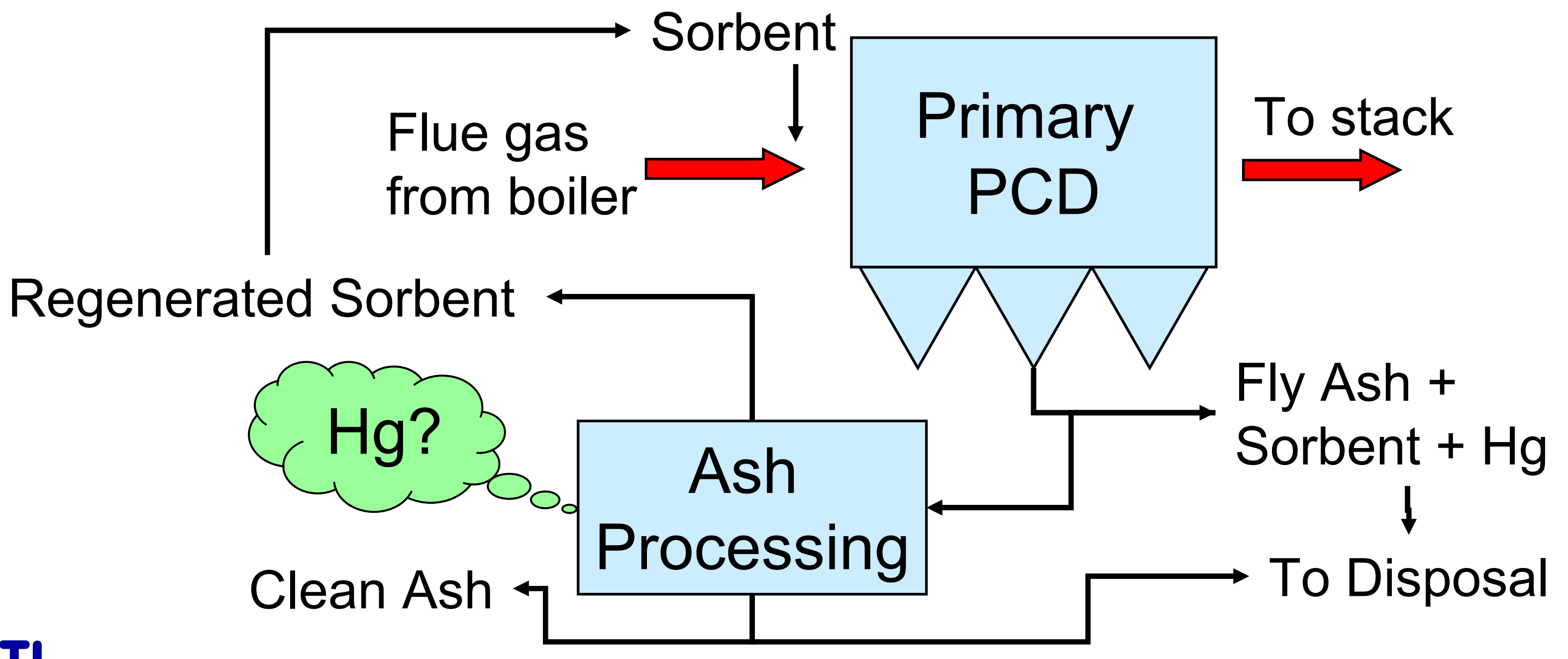
Mercury Partitioning Across CUB Types

- **First, the good news: CAMR will have almost no effect on bottom ash**
  - Possible exceptions:
    - Coal switching
    - Addition of halide salts to boiler to enhance Hg oxidation

- **Effects on fly ash and FGD byproducts will vary, depending on:**
  - Location of sorbent injection (if sorbent is used)
  - Type of FGD system (if present)

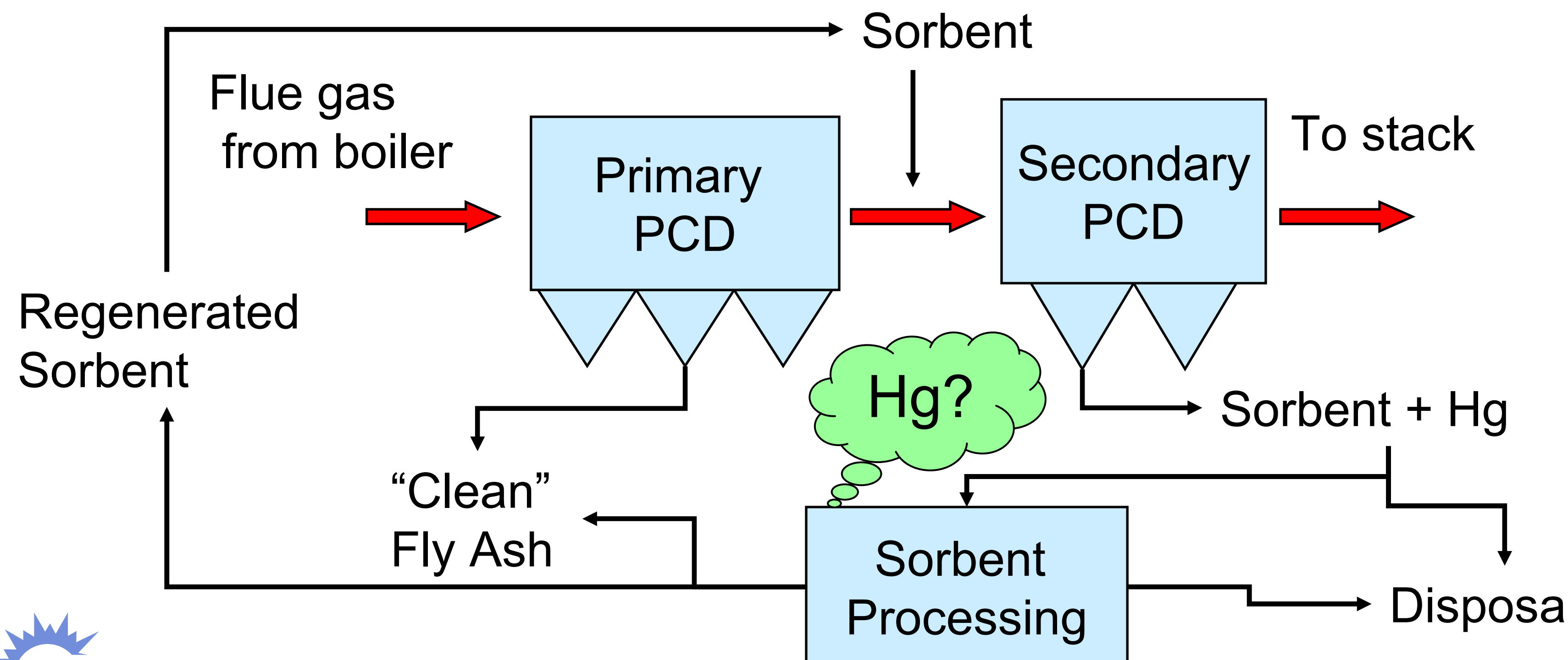
Effects of CAMR on Hg in Fly Ash

- **<u>Case 1:</u> No FGD; Sorbent injected upstream of primary particulate control device (PCD)**
  - **<u>Some</u>** additional Hg; **<u>much</u>** additional sorbent (carbon)
  - Additional Hg **<u>may possibly</u>** affect disposal
  - Sorbents **<u>will probably</u>** affect re-use



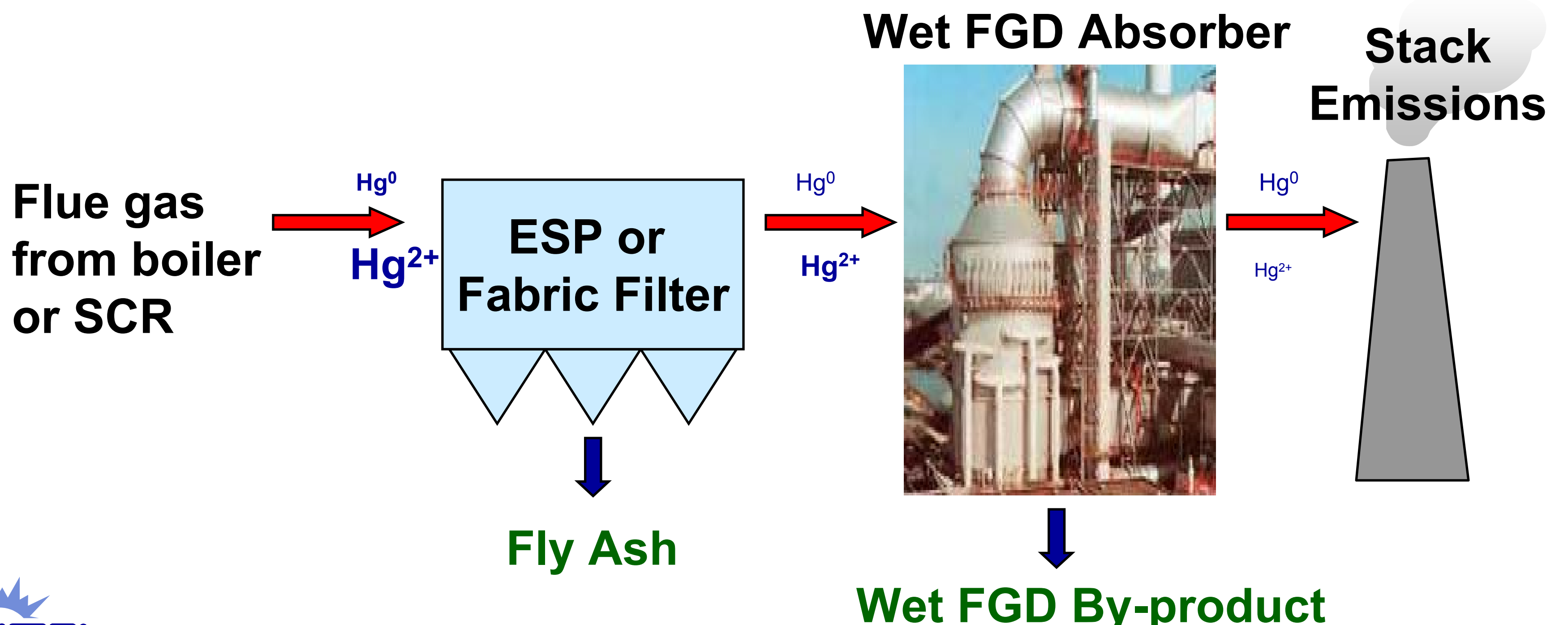
Effects of CAMR on Hg in Fly Ash (cont'd)

- <u>Case 2:</u> **No FGD; sorbent injected <u>downstream</u> of primary particulate collection device (e.g., TOXECON)**
  - Fly ash: little change from pre-CAMR byproduct
  - Spent sorbent: completely new byproduct



Effects of CAMR on Hg in Wet FGD Byproducts

- **Case 1: No sorbent injection; flue gas is mostly Hg^{2+}**
  - Fly ash and FGD byproducts already capture 70-90% of Hg^{2+}
  - Hg in all CUBs same as pre-CAMR

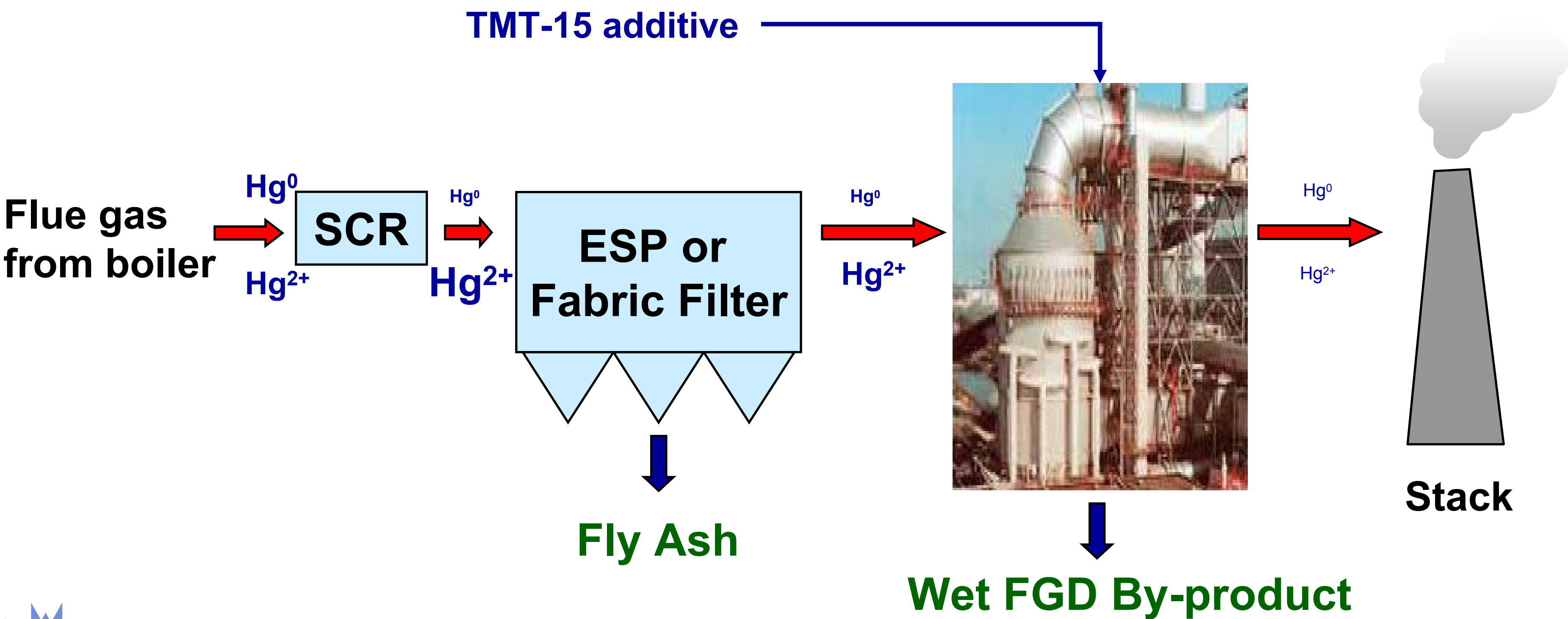


Effects of CAMR on Hg in Wet FGD Byproducts (cont'd)

- **Case 2: Oxidation "enhancements" added, but no sorbents; Hg removal achieved via FGD**
  - Used mostly at plants where incoming $Hg^{2+} \geq Hg^0$
  - Hg in wet FGD byproducts: slightly higher than pre-CAMR

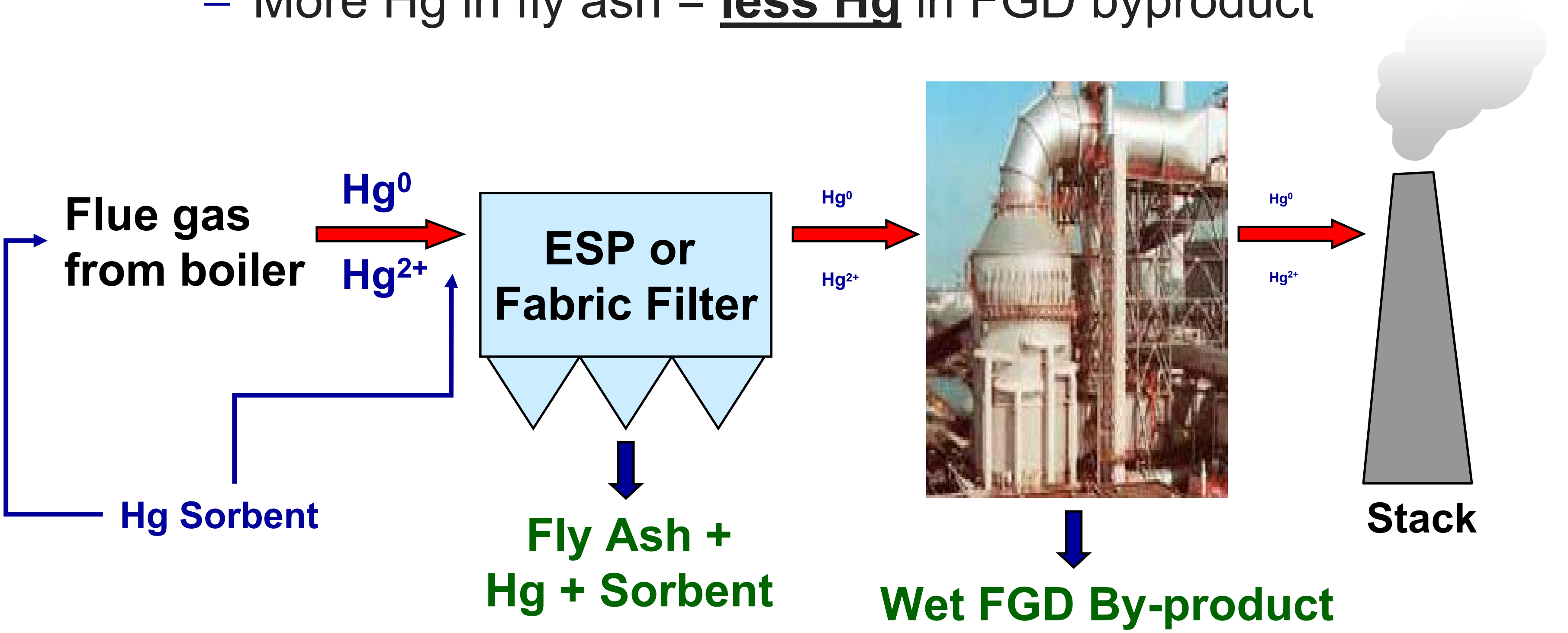
Effects of CAMR on Hg in Wet FGD Byproducts (cont'd)

- **<u>Case 3:</u> Hg removal achieved via FGD; additive (TMT-15) to remove Hg from FGD liquor and reduce Hg^0 "re-emissions"**
  - Hg in wet FGD byproducts: higher than pre-CAMR

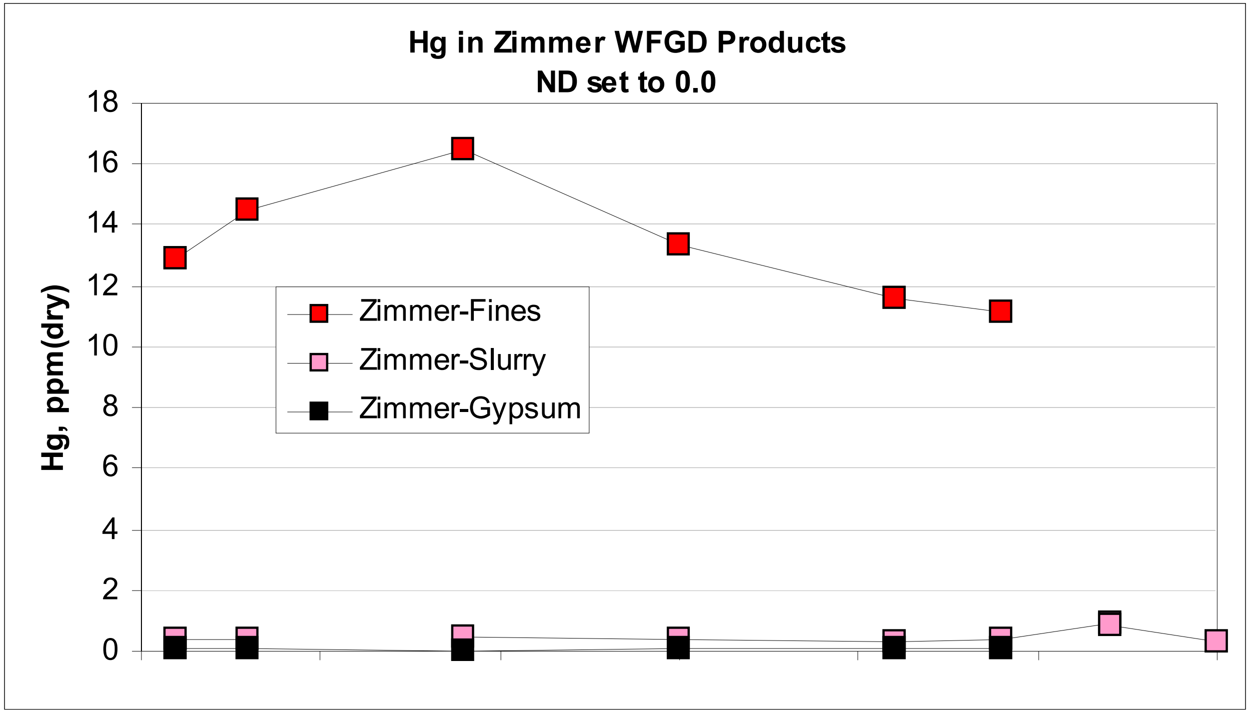


Effects of CAMR on Hg in Wet FGD Byproducts (cont'd)

- **Case 4:** **Sorbents used for Hg capture on fly ash**
  - More Hg in fly ash = **less Hg** in FGD byproduct



Where Does the Hg Go upon Capture ?

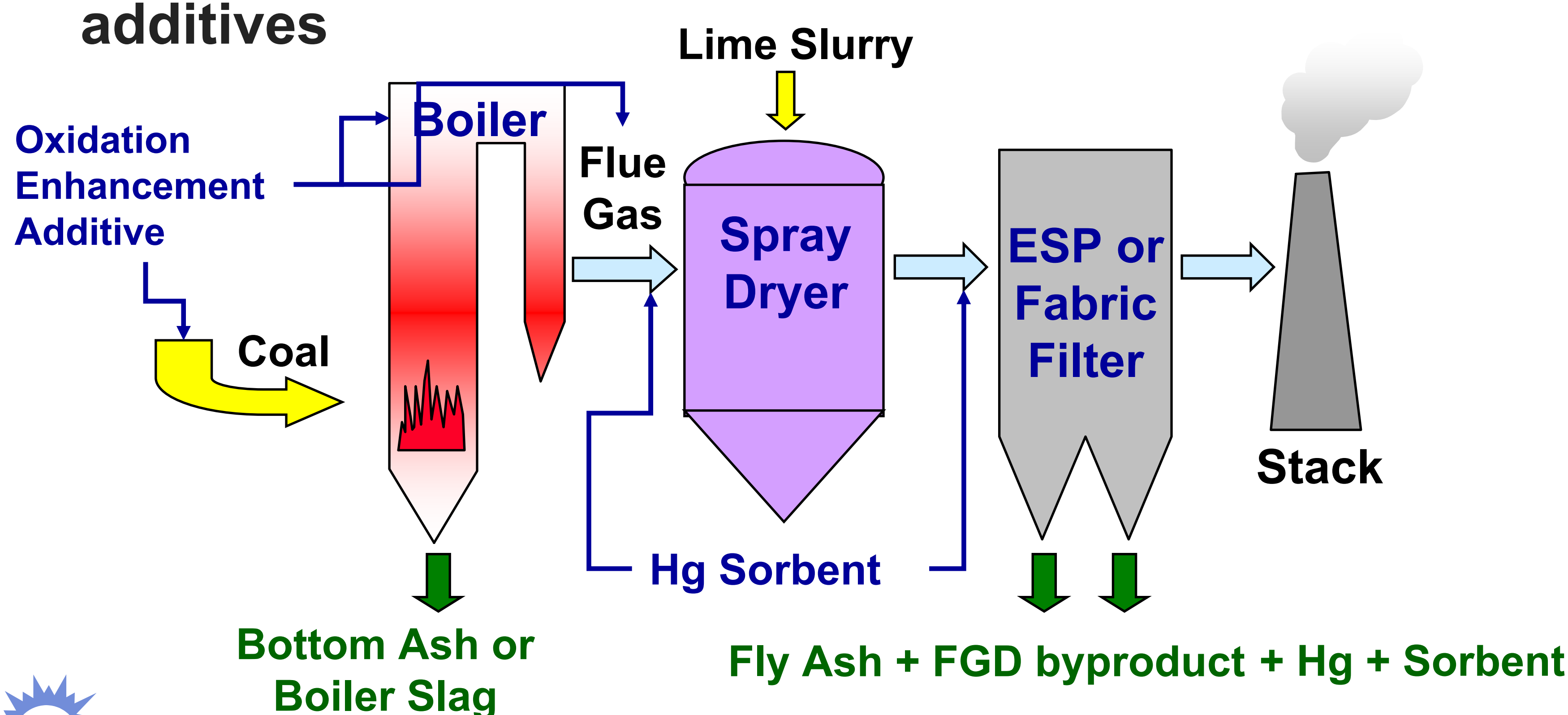


"… the mercury compound formed in the wet scrubber is associated with the fines and is not tied to the larger gypsum crystals."

Source: "FULL-SCALE TESTING OF ENHANCED MERCURY CONTROL TECHNOLOGIES FOR WET FGD SYSTEMS" Final Report, DE-FC26-00NT41006, BABCOCK & WILCOX CO. and McDERMOTT TECHNOLOGY, INC. May 7, 2003

Effects of CAMR on Hg in Dry FGD By-products

- Probable Hg control method: Powdered sorbents
- May or may not use oxidation additives
- Some additional Hg; much additional sorbent & additives



Hg Release from CUB : Fundamental Questions

- **Is Hg release from <u>existing</u> CUBs a "problem?"**
  - How do we measure Hg release in a realistic manner?
  - What release rates/forms constitute a "problem?"
  - If it is a "problem," what can we do about it?
    - "Problem solving" vs. "problem shifting"
- **If Hg release from existing CUBs is "not a problem," will it become a "problem" after CAMR?**
  - Will overall perception of CUBs worsen, even if they remain unchanged from pre-CAMR condition?
- **R&D can answer some, <u>but not all</u> of these questions**

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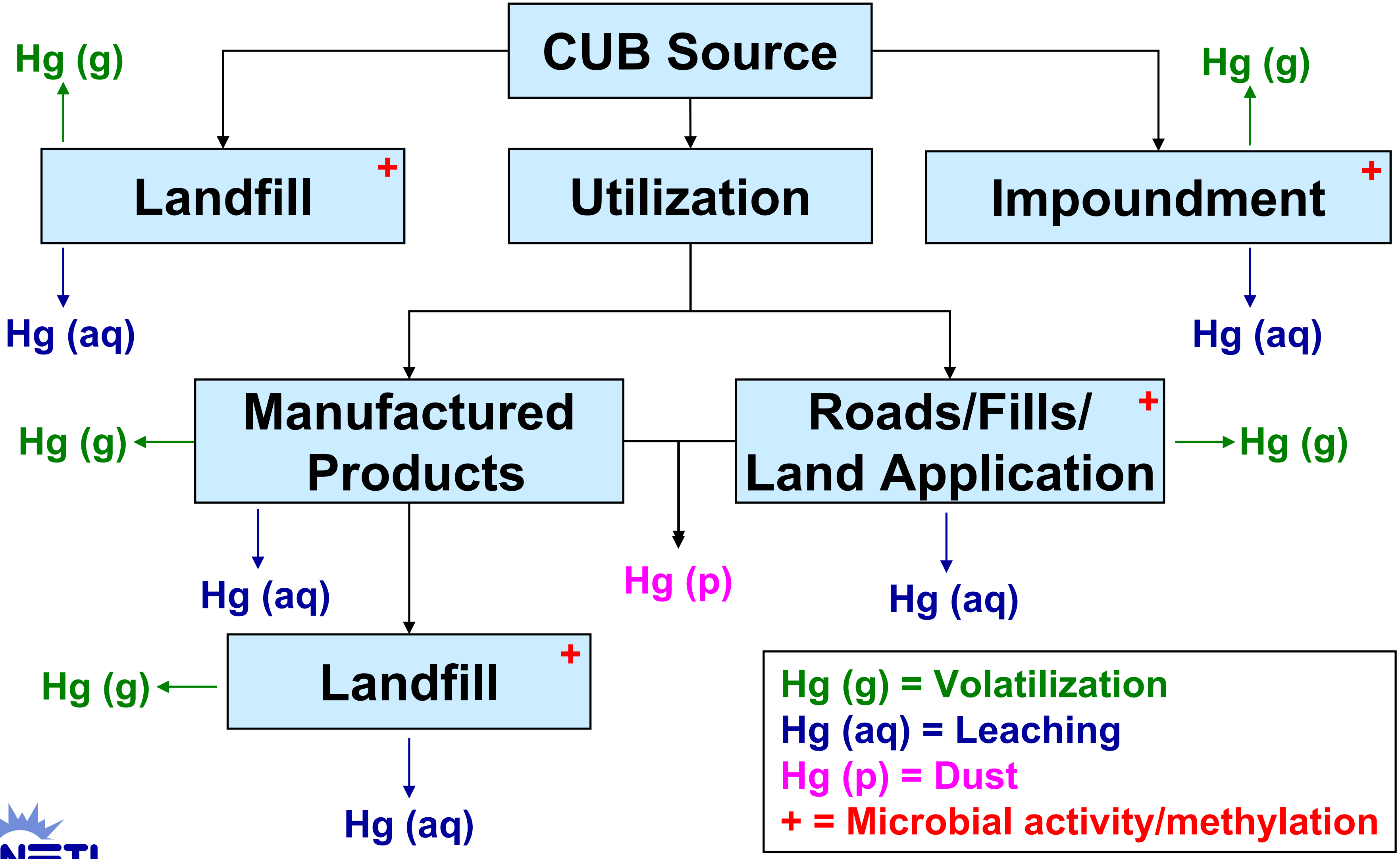
Environmental Release of Hg from CUBs

R&D Must "Check all the Boxes"



Environmental Release of Hg from CUBs

Selected NETL Cost-shared R&D Projects

Project Title	Lead Organization
CUB Analysis from Activated Carbon Injection (ACI) Mercury Control Field Testing – Phase I	ADA-ES and Reaction Engineering
Hg and Air Toxics Element Impacts of Coal Combustion By-product Disposal and Utilization	University of North Dakota - EERC
Characterization of Coal Utilization By-Products From Mercury Control Field Testing - Phase II	Frontier Geosciences, Inc.
Fate of Hg in Synthetic Gypsum Used for Wallboard Production	USG Corporation
Field Testing of a Wet FGD Additive for Enhanced Mercury Control	URS Group

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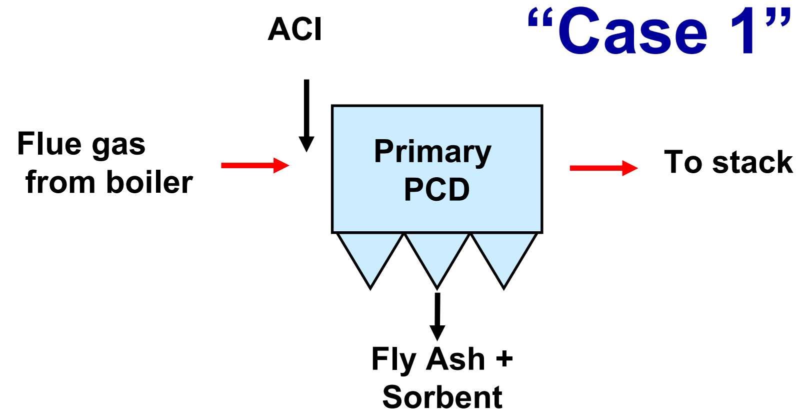
Characterization of Hg in CUBs from Phase I Hg Control Field Testing Program

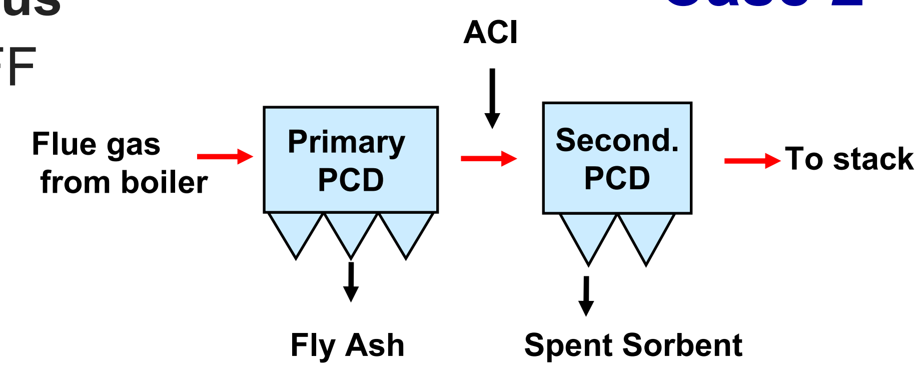
- **Salem Harbor (MA) – Bituminous**
  - ESP: 474 SCA
- **Pleasant Prairie (WI) – PRB**
  - ESP: 468 SCA

"Case 1"



- **E. C. Gaston (AL) - Bituminous**
  - Hot-side ESP + COHPAC FF for particulate control
- **Brayton Point (MA) – Bituminous**
  - 2 ESPs in series

"Case 2"



Summary: Effect of ACI on Hg in CUBs

Phase I Hg Control Field Testing Program

Activated carbon silo

- **Hg in solids increased slightly after ACI**
  - Significant Hg increase in COHPAC ash
- **Most leachates below 0.01 µg/L**
- **Max. leachate 0.07 µg/L (Brayton Point)**
- ***Below all EPA water quality/drinking water criterion:***
  - *CCC = 0.77 µg/L*
  - *CMC = 1.4 µg/L*
  - *MCL = 2.0 µg/L*

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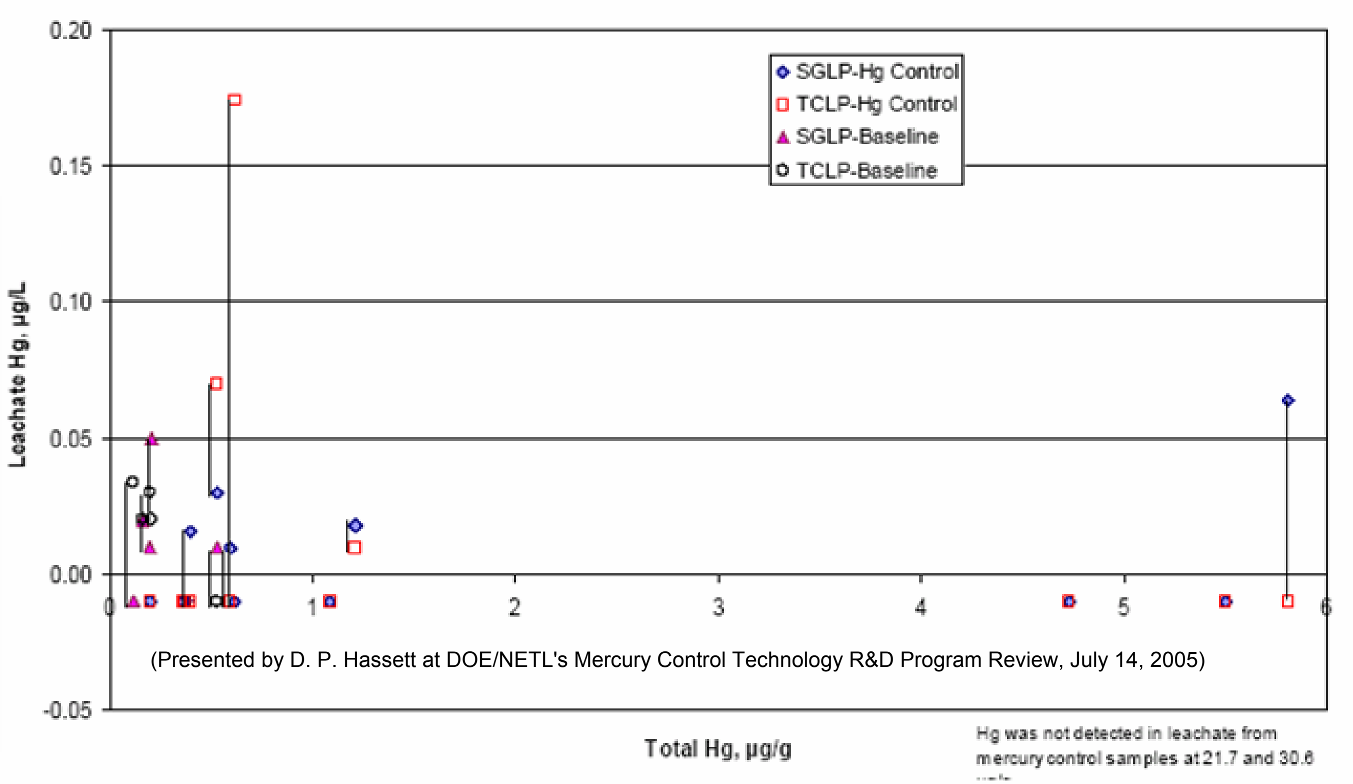
Hg Release Studies - UNDEERC

- **Potential release of Hg and other air toxics from CUBs**

- **Laboratory methods development & Hg release studies**
  - Leaching (TCLP, SGLP, short and long term)
  - Volatilization (short and long term)
  - Microbiologically-mediated release

UNDEERC Hg Leaching Test Results

Fly Ash with Hg Control vs. No Hg Control; SGLP vs. TCLP



- **Leachate Hg concentrations appear to be <u>independent</u> of:**
  - Total Hg content in solid
  - Leach test method (SGLP, TCLP)

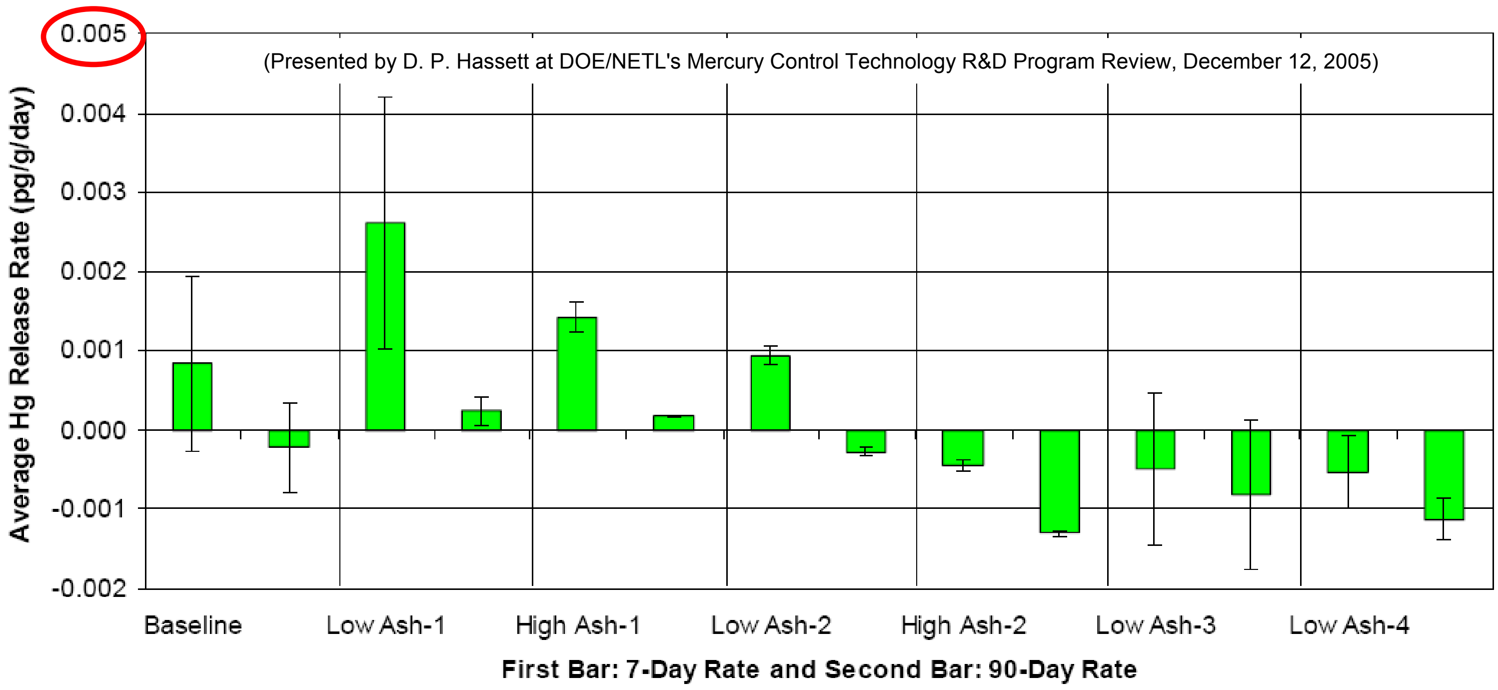
UNDEERC CUB Leaching Test Results
Other Observations

- **Presence of activated carbon appears to <u>inhibit</u> Hg leaching via standard test methods**
- **Presence of activated carbon may also have inhibited leaching of Nickel**
- **Long-term leaching is needed to evaluate alkaline fly ash for release of Arsenic and Selenium**

UNDEERC Hg Volatilization Test Results

Ambient Temperatures

- **Many samples acted as mercury “sinks”**
  - Especially fly ash with Activated Carbon
- **Time to release 100% of Hg in sample >100 Million Years**

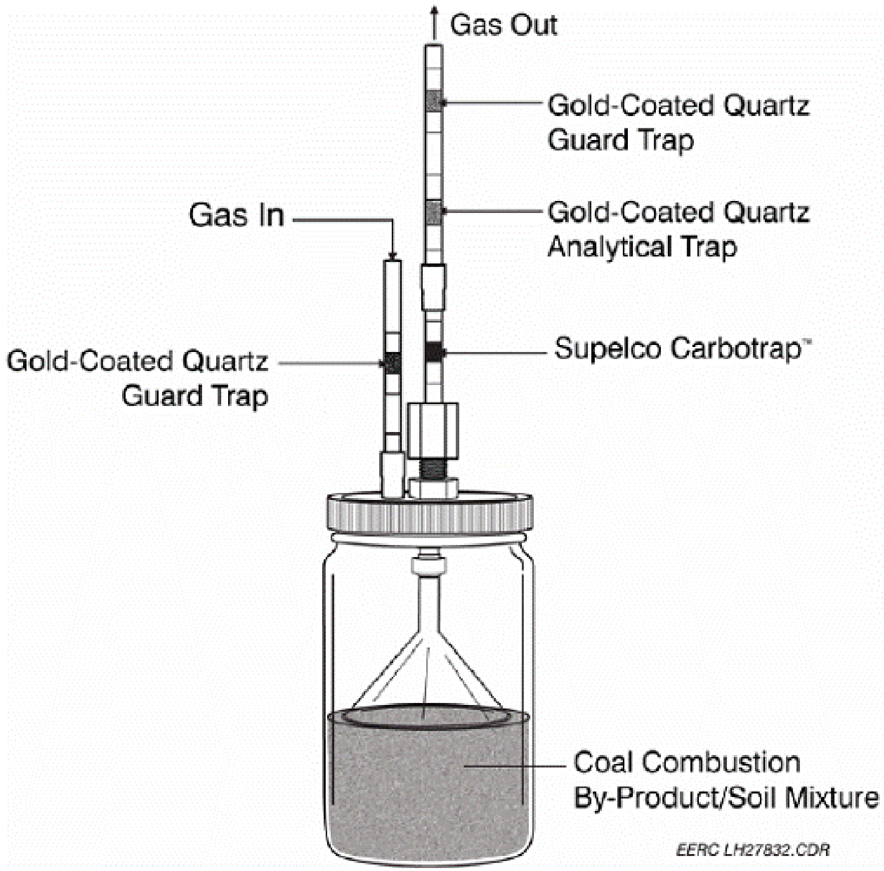


Positive values indicate release and negative values indicate sorption.

UNDEERC Hg Volatilization Test Results

- **Thermal Volatilization**
  - Mercury generally released at temperatures greater than 200°C
- **Volatilization at CUB field disposal sites**
  - Low emission, similar to background (~ 1ng/m^3)

UNDEERC Microbiological Hg Release Methods

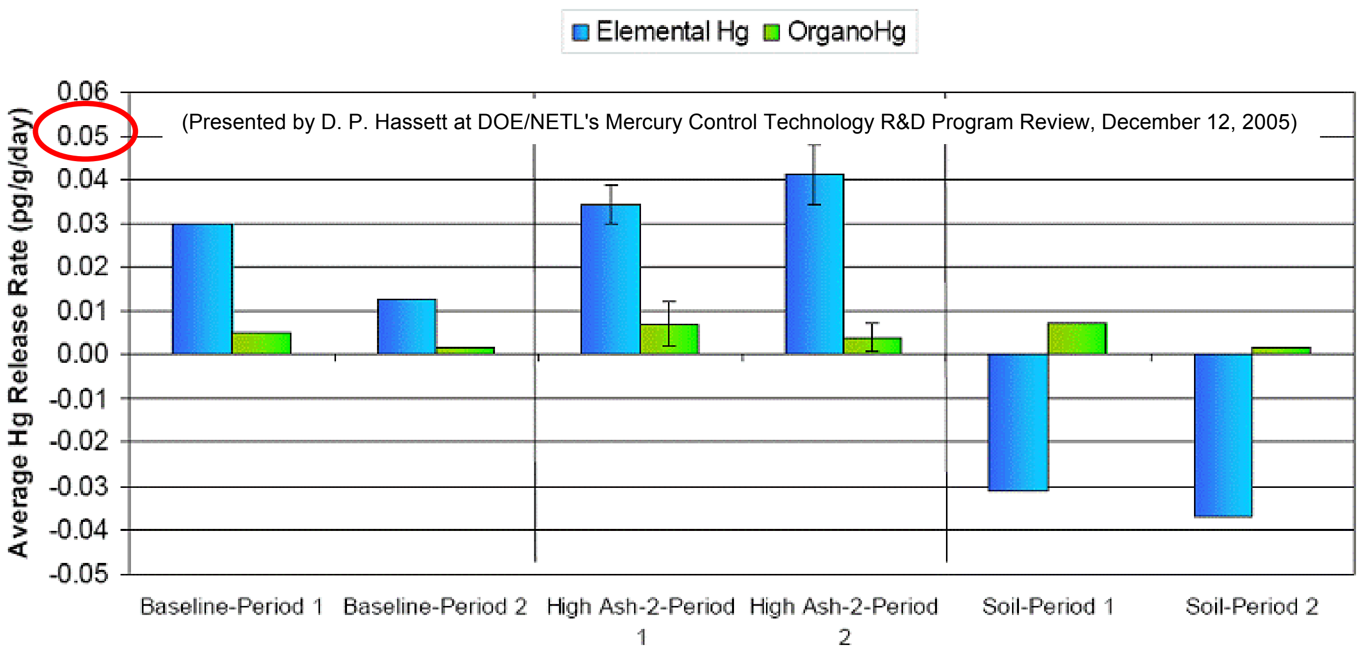


- Similar to long-term ambient-temperature setup
- 20% addition of CCB to soil
- Moisture added to soil to increase microbial activity
- Elemental and organomercury capture

Microbiologically Mediated Mercury Release

General Observations

- **Organomercury vapor-phase releases were similar in fly ash, fly ash-AC, and soil**
- **Elemental mercury vapor-phase releases were higher for fly ash and fly ash-AC than for soil**
  - Rates ~10x higher than for “sterile” samples
  - Still need >10 Million years to release 100% of Hg content



Positive values indicate release and negative values indicate sorption.

Characterization of CUBs From Mercury Control Field Testing - Phase II

- **Primary Performer: Frontier Geosciences, Inc.**
- **CUBs generated from mercury control projects awarded in 2003 and 2004 by NETL**
  - Ongoing analysis through 2007
- **Potential release of Hg, Ni, As, Se, Cd, Pb**
  - Leaching, Thermal release, Microbial mobility
- **Halides**

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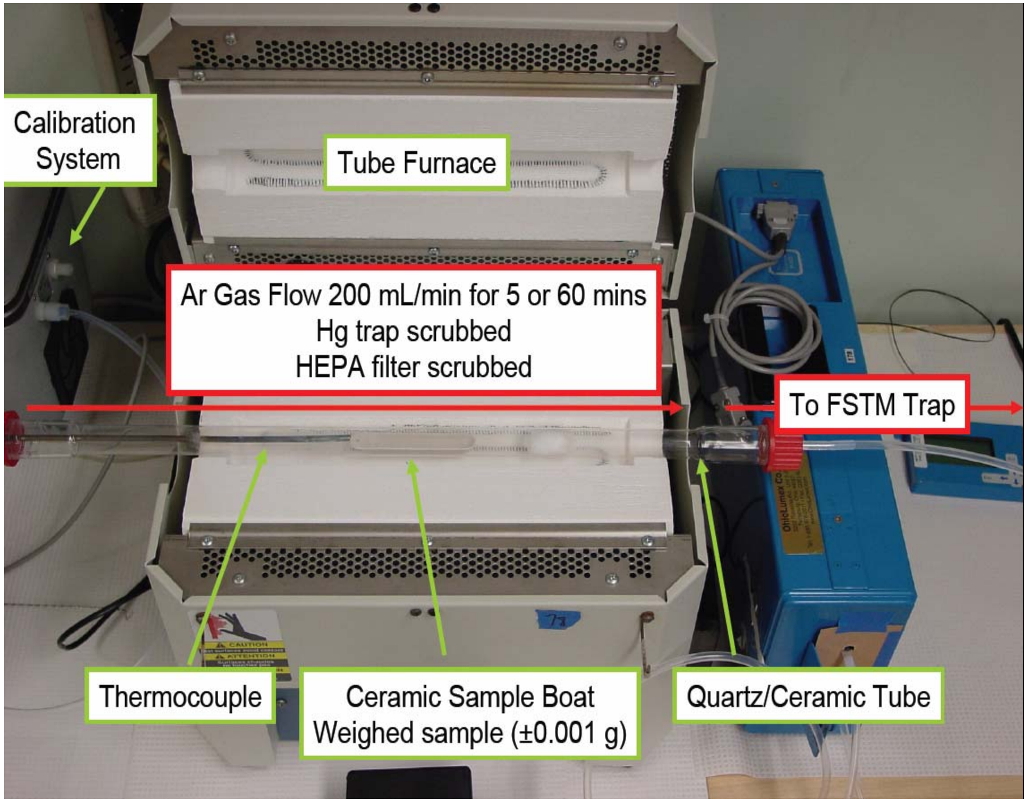
Frontier Leaching Test Protocol

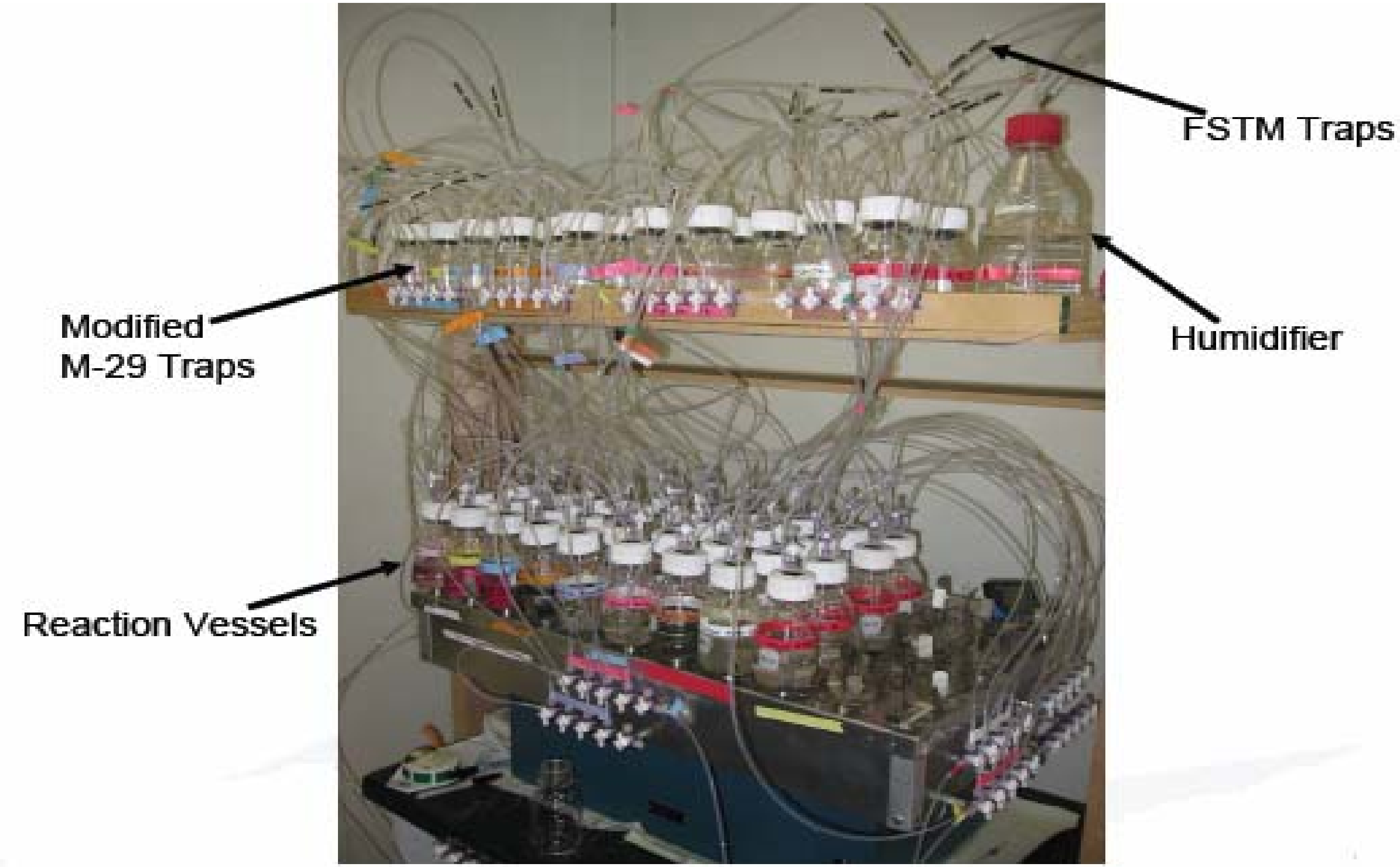
- **Synthetic Precipitation Leaching Procedure (SPLP)**
- **Sampling at 18 hours, 14 days, and 28 days**
  - Accounts for secondary mineral formation of ettringite (known to immobilize arsenic and selenium)
- **Solid at 28 days is sub-sampled for mass balance**

Frontier Volatilization Test Protocol

- **Low-Temperature Solids**
  - Landfills, etc: 21-45°C
- **Mid-Temperature FGD solids**
  - Wallboard production (calcining): 128-163°C
    - Promote release of water
    - Prevent anhydrous calcium sulfate formation
- **Mid-Temperature Fly ash**
  - Asphalt production: 125-190°C
- **High-Temperature Fly ash**
  - Cement production: 1400°C



Frontier Microbial Release Test Setup



Frontier Project Status

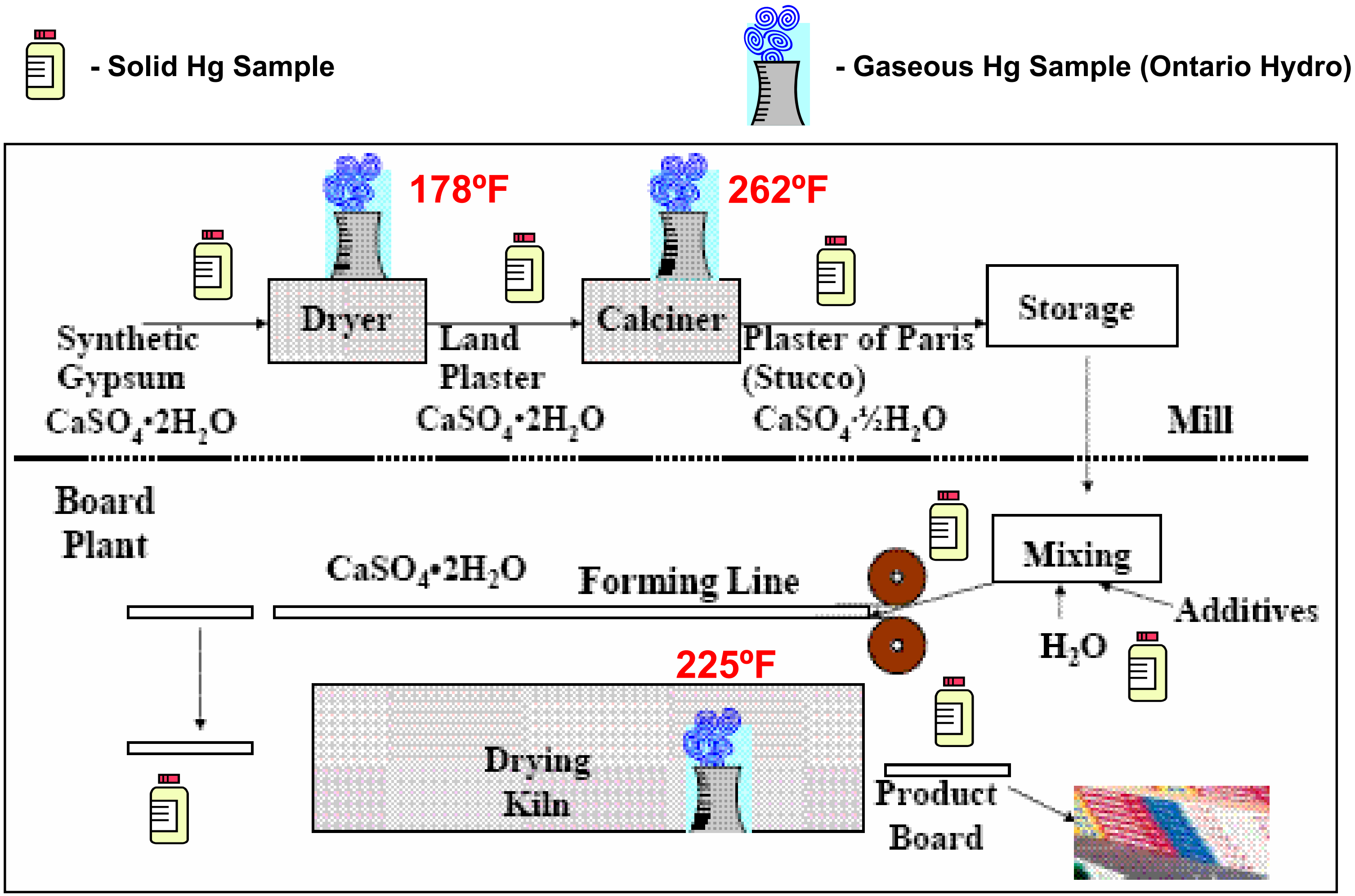
Location	Total Metals	Volatility	Microbial	Leaching	Halides
Leland Old Station	Completed	Completed	In process, report Apr 07	Completed	Completed
Holcomb	Completed	Completed	In process, report Apr 07	Completed	Completed
Meramec	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Monroe	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Buck, Unit 6	Completed	Completed	In process, report Jan 07	Completed	Completed
St. Clair, Unit 1	Completed	Test not authorized	Test not authorized	Test not authorized	Test not authorized
Antelope Valley Station, SDA	Completed	Completed	In process, report Apr 07	Completed	Completed
Antelope Valley Station, FF	Completed	Completed	In process, report Apr 07	Completed	Completed
Monticello	Completed	Completed	Test not authorized	Completed	Completed
Monticello (FGD Solids)	In process, report Jan 07	In process, report Jan 07	In process, report Apr 07	Completed	Completed
Monticello (FGD Liquids)	In process, report Jan 07	In process, report Jan 07	Test not authorized	Test not authorized	In process, report Jan 07
Yates	Completed	Completed	Completed	Completed	Test not authorized
Stanton	Completed	In process, report Jan 07	In process, report Apr 07	In process, report Jan 07	In process, report Jan 07

- (black) Test not authorized
- (blue) Completed
- (green) In process, report Jan 07
- (red) In process, report Apr 07

Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

Wallboard Manufacture from FGD Gypsum

Simplified Flow Diagram



Source: J. Sanderson, DOE-NETL Mercury Control Techology R&D Program Review, 12/12/06

Expected Effects of Power Plant Variables on Hg Content of FGD Gypsum

- **SCR Effect**
  - More Hg^{2+} in flue gas → more Hg capture in wet FGD → more Hg in FGD gypsum product with SCR

- **Fines Blowdown Effect**
  - Blowdown removes fines from FGD gypsum product → less Hg in FGD gypsum product with blowdown

- **Coal Type Effect**
  - Less Hg^{2+} in lignite flue gas → less Hg capture in wet FGD → less Hg in FGD gypsum product with lignite

- **TMT-15 Effect**
  - More Hg removal in wet FGD → more Hg in FGD solids
  - BUT, fines removed via blowdown → no effect on Hg in FGD gypsum product with TMT-15

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Hg Release from Wallboard Plants

USG Testing Scenarios

Test #	1	2	3	4	5	6
Power Plant	A	A	B	C	D	D
USG Plant	1	1	2	3	4	4
Coal Type	HS Bit	HS Bit	HS Bit	Lignite (TX)	HS Bit	HS Bit
Fines Blowdown	No	No	Yes	No	Yes	Yes
SCR Status	On Line	Bypassed	On Line	No SCR	Bypassed	Bypassed
TMT-15 Additive	No	No	No	No	No	Yes

Fines Blowdown Effect (Test 2 ↔ Test 5)

Coal Type Effect (Test 2 ↔ Test 4)

Fines Blowdown Effect (Test 2 ↔ Test 3)

SCR Effect (Test 1 ↔ Test 2)

SCR Effect (Test 3 ↔ Test 5)

TMT-15 Effect (Test 5 ↔ Test 6)

Effect on Hg Content

$Hg_{SCR} > Hg_{Bypassed}$ $Hg_{Bit} > Hg_{Lignite}$

$Hg_{w/o} > Hg_{Blowdown}$

$Hg_{w/oTMT} \approx Hg_{w/TMT}$

Hg Release from Wallboard Plants

SCR Effect

Test #	1	2	3	4	5	6
	SCR Effect (1 → 2)		SCR Effect (3 → 5)			
Hg content of FGD gypsum (ppm)	0.96	1.10	0.21	0.21	0.20	0.15
Hg air emissions (g/h)	4.1	7.8*	8.2 *	0.32	2.0	1.0
Hg air emissions (% of input Hg)	5%	~8% *	~46-63% *	<3%	~50%	55%
Hg emitted from dryer (% of input Hg)	1%	<1%	1%	<1%	<2%	4%
Hg emitted from calciner (% of input Hg)	2%	3%	41%	<1%	50%	45%
Hg emitted from board kiln (% of input Hg)	2%	5% *	4-21%*	<1%	<2%	6%
	On Line	Bypassed	On Line		Bypassed	

* Based on solids analysis

Hg Release from Wallboard Plants

Fines Blowdown Effect

Test #	1	2	3	4	5	6
Hg content of FGD gypsum (ppm)	0.96	1.10	0.21	0.21	0.20	0.15
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Hg emitted from board kiln (% of input Hg)	2%	5% *	4-21%*	<1%	<2%	6%
	No	No	Yes		Yes	

Fines Blowdown Effect (Test 1 → Test 3)

Fines Blowdown Effect (Test 2 → Test 5)

* Based on solids analysis

Hg Release from Wallboard Plants

Coal Type and TMT-15 Effects

Test #	1	2	3	4	5	6
Hg content of FGD gypsum (ppm)	0.96	1.10	0.21	0.21	0.20	0.15
Hg air emissions (g/h)	4.1	7.8*	8.2 *	0.32	2.0	1.0
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Hg emitted from board kiln (% of input Hg)	2%	5% *	4-21%*	<1%	<2%	6%
		HS Bit		TX Lignite	No TMT	w/ TMT

Coal Type Effect (Test 2 vs. Test 4); TMT-15 Effect (Test 5 vs. Test 6)

* Based on solids analysis

Hg Release from Wallboard Plants

Total U.S. Wallboard Industry Estimates

Test #	1	2	3	4	5	6
Hg emitted per ton of FGD gypsum feedstock (grams)	0.045	0.08	0.09	0.01	0.09	0.06
FGD Gypsum used in wallboard (tons)*	← 8,178,079 →					
Estimated industry-wide Hg Emissions (lb/year)	800	1500	1600	200	1600	1100

* 2005 ACAA Estimate for U.S. CCP Industry

- **"Worst Case": Wallboard industry emitted <1 ton Hg in 2005**
  - Total depends on how much additional FGD gypsum is used in wallboard
  - Coal Plants will emit 15 tons/yr after CAMR

Observed Effects of Power Plant Variables on Hg Content of FGD Gypsum & Release from Wallboard Plants

- **SCR Effect**
  - Hg content w/SCR < Hg content w/o SCR (opposite of expected)
- **Fines Blowdown Effect**
  - Hg content w/Blowdown < Hg content w/o Blowdown (consistent w/expected)
  - Higher % of input Hg emitted from wallboard plants when blowdown used
    - Plant-specific variables may govern Hg emissions
- **Coal Type Effect**
  - Hg content & emissions w/Lignite < Hg content & emissions w/Bituminous (consistent w/expected)
- **TMT-15 Effect: Little to none (expected - fines removed)**
- **Hg emissions greatest across calciner and board kiln**

Field Testing of a Wet FGD Additive (TMT-15) for Enhanced Mercury Control

- **TMT-15: precipitates divalent heavy metals from wastewaters**
  - $3\ Hg^{2+} + 2\ TMTNa_3 \rightarrow Hg_3TMT_2 + 6\ Na^+$
- **Removal of Hg^{2+} from aqueous phase prevents Hg^0 formation in scrubber**
- **Currently used in 100's of incineration plants 10's of wet scrubbers worldwide**
- **Test sites:**
  - TXU Monticello 3 (Texas Lignite/PRB)
    - Pilot wet FGD
  - Southern Co. Plant Yates 1 (LS Bituminous)
    - Pilot and full-scale Jet Bubbling Reactor tests
  - IPL Petersburg 2 (HS Bituminous)
    - Full-scale spray tower

TMT-15 Field Tests – Results to Date

- **Pilot-scale test results:**
  - Inconclusive about effectiveness in controlling Hg^0 re-emissions
  - Greatly reduced Hg in FGD liquor
  - Most of the Hg reports to fines in FGD solids

- **Full-scale results:**
  - Modest decrease in Hg^0 re-emissions across absorber
  - Do not show expected effects of TMT addition in byproducts
    - No reduction in Hg in FGD liquor
    - No evidence of Hg concentration in fines in FGD solids

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NETL In-House Research
Hg Release from CUB

- Determine the stability of Hg and other metals in CUB under simulated end-use environments
- Explain the chemistry underlying metal stability
- Recent Focus: FGD by-products and wallboard

FGD solids ready for disposal

Drywall ready for landfill

Continuous Stirred Tank Extractor (CSTX)

Summary of Results for FGD Gypsum and Wallboard Samples

Continuous Stirred Tank Extractor

- **Prior to extraction, "orange fluffy stuff" at top of settling vessel had high concentrations of Fe and Hg**
- **<2% of original samples remained at end of extraction**
- **~99% of original Hg remained in final residue (i.e., leachates contained ~1% of original Hg)**
- **Residue composed of mostly Fe & Al compounds**

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Conclusions from CSTX Experiments

- An iron-containing phase, probably introduced with limestone, is responsible for sorption and "sequestration" of mercury

- Rapid Hg leaching is unlikely in typical disposal and land-application (agricultural) environments

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Release of Hg from CUBs

Summary of R&D Results to Date

- **Minimal mercury release via leaching in typical disposal or land-use applications**
  - Leachate Hg concentrations << water quality criteria for protection of aquatic life (0.77 µg/L)
- **Microbially-mediated Hg releases higher than "sterile" releases but still very low**
- **Release of Hg <u>not</u> related to total Hg in CUB**
  - Carbon content may inhibit Hg release from fly ash
- **Potential for significant Hg release in high-temperature applications**
- **Emissions of Hg from wallboard manufacture are site-specific**
  - Unclear how to reduce Hg emissions via "controlling" Hg content of FGD gypsum via SCR, Fines blowdown, or TMT-15
- **An iron-containing phase is responsible for sorption and "sequestration" of mercury in FGD byproducts**

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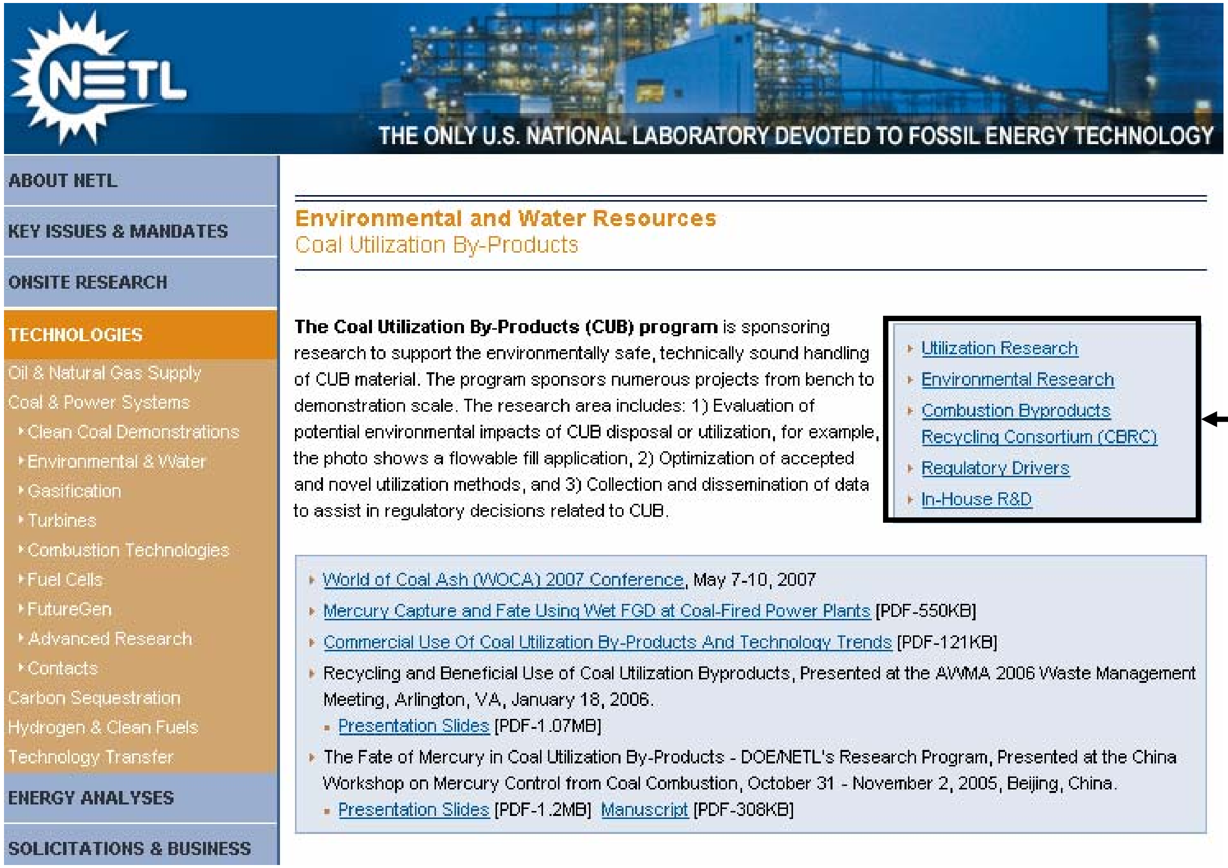
For More Information

- **DOE-NETL CUB Website**
  - http://www.netl.doe.gov/technologies/coalpower/ewr/coal_utilization_byproducts/



Click one of these links for detailed project information

DOE-EPA Report on Recent CUB Disposal Practices

- **Available at DOE Office of Fossil Energy website:**
  - http://www.fossil.energy.gov/programs/powersystems/pollutioncontrols/coal_waste_report.pdf

Coal Combustion Waste Management at Landfills and Surface Impoundments, 1994–2004

U.S. Department of Energy

Office of Fossil Energy
and the
Office of Policy and International Affairs

U.S. Environmental Protection Agency

Office of Solid Waste

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