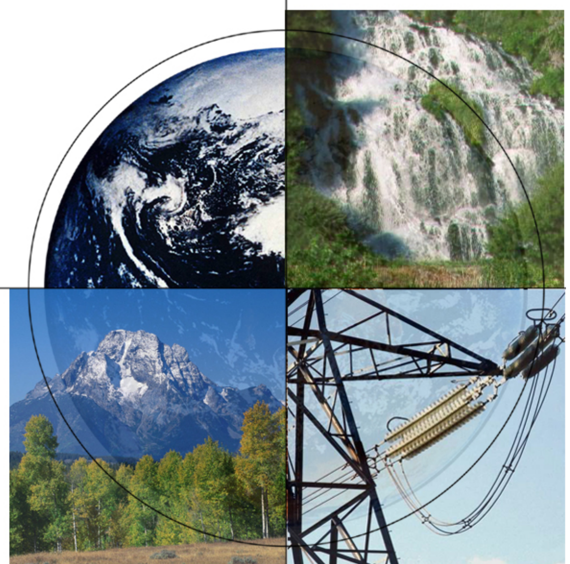
Fate of Mercury in Coal Utilization Byproducts



Coal Combustion Product Optimization Conference

August 31 – September 1, 2005
Denver, Colorado

Thomas J. Feeley, III
thomas.feeley@netl.doe.gov
National Energy Technology Laboratory

Outline

- DOE/NETL's Hg control technology program
- Characterization of fly ash
- Characterization of FGD solids
- Summary/conclusion

What are CUBs?

- **Coal Utilization Byproducts (a.k.a. CCBs, CCPs, CCW, FFCW, CCR ...)**

- **Utilization includes:**
  - Combustion
  - Gasification
  - Hybrid systems

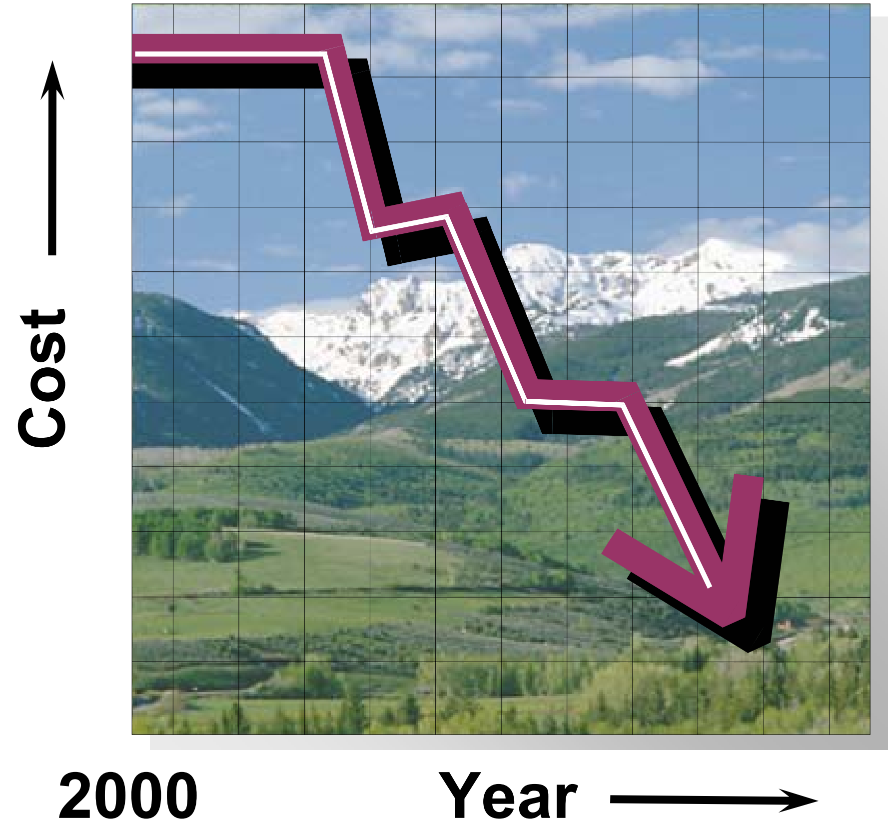
4 Key Regulatory Challenges to Increased CUB Use

- Installation of additional FGD to meet CSI or CAIR would increase volume of scrubber solids
- Installation of additional advanced combustion technology and SCR to meet CSI or CAIR could increase UBC and NH_3 in fly ash
- Use of AC injection for Hg control could negatively impact fly ash utilization due to increased carbon content
- Increased scrutiny of CUBs due to transfer of Hg from flue gas to fly ash and scrubber solids

Mercury Field Testing Program

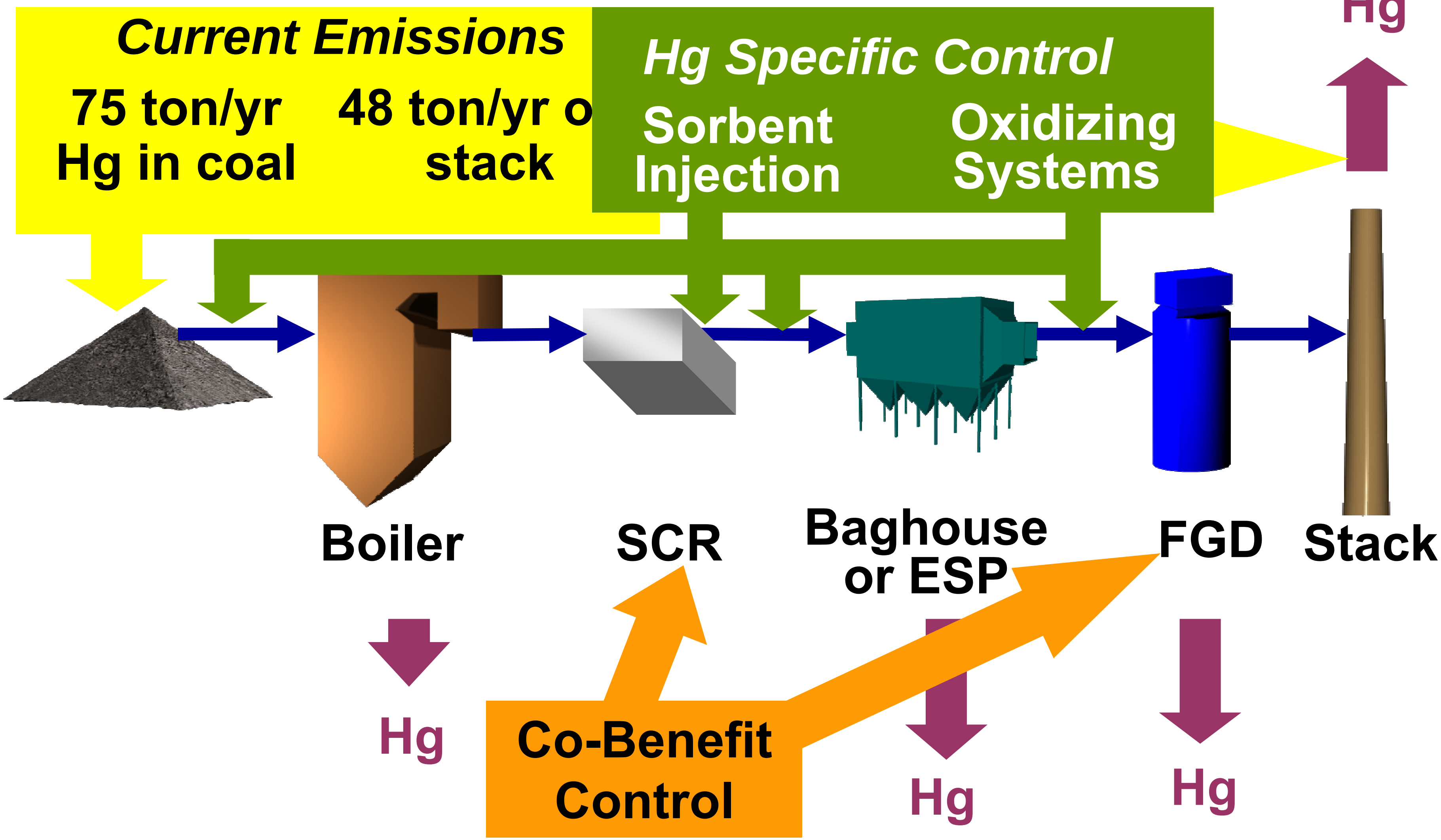
Objectives

- Have technologies ready for commercial demonstration by 2007 for all coals
- Reduce emissions 50-70%
- Reduce cost by 25-50% compared to baseline cost estimates



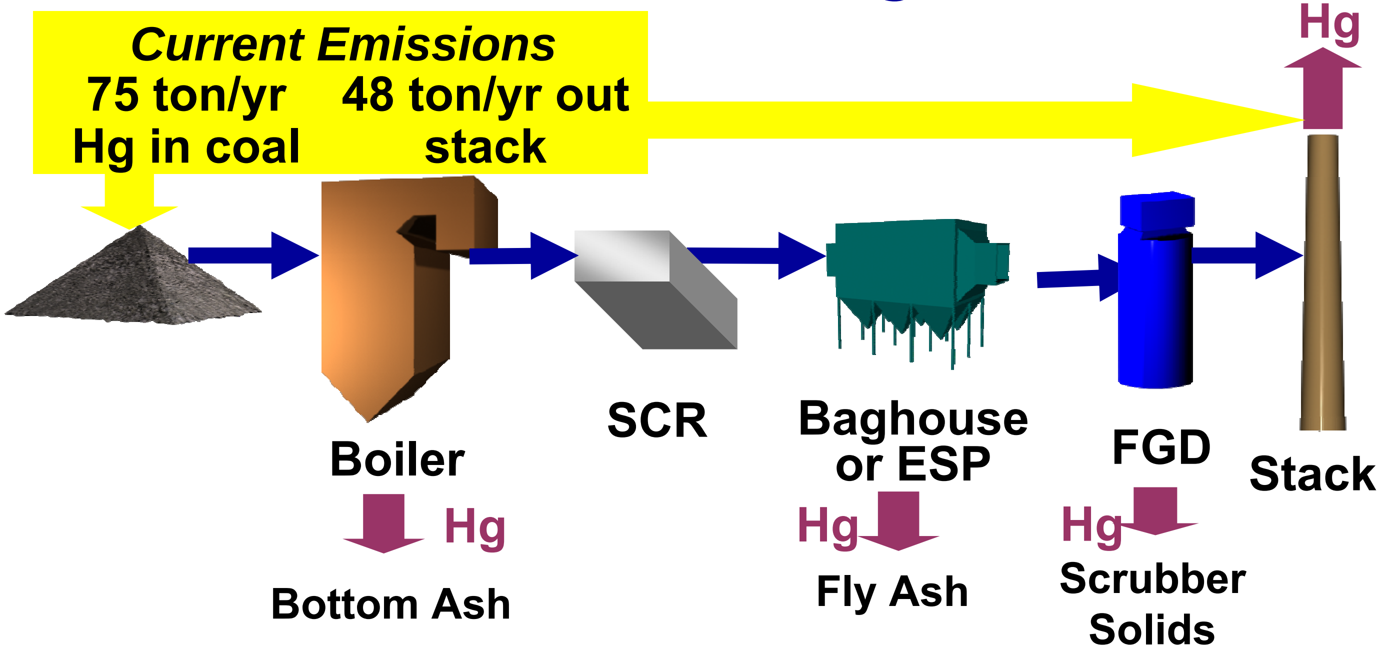
Baseline Costs: $50,000 - $70,000 / lb Hg Removed

Power Plant Mercury Control



Impact of Regulation on Coal Byproducts

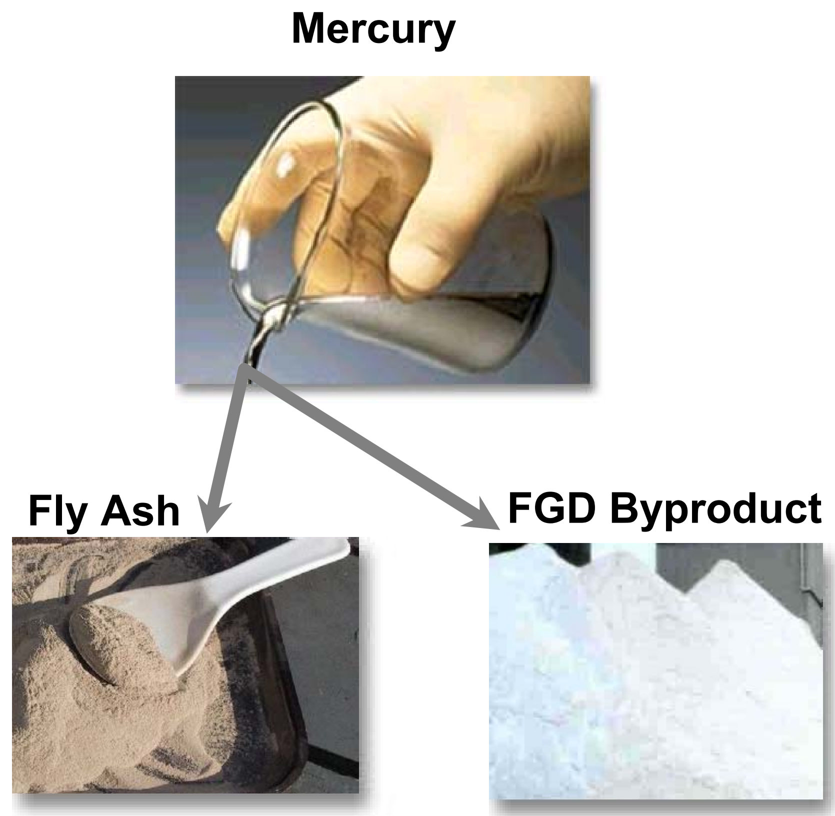
Where Does Hg Go?



% Hg Reduction	Tons/Yr Hg Reporting to Byproducts
BAU	27
70	61
80	65
90	70

Why are We Concerned About Fate of Hg?

- **Impact on environment?**
  - Does Hg removed from flue gas get back into environment?
- **Impact on disposal and reuse options?**
  - Will existing use markets be lost?
  - Will CUBs have to be disposed of as hazardous wastes?



What is DOE/NETL Doing?

Project Title	Lead Organization
CUB Analysis from ACI Mercury Control Field Testing	ADA-ES and Reaction Engineering
CUB Analysis from Wet FGD Reagent Hg Field Testing	Babcock & Wilcox
Characterization of Coal Combustion By-Products for the Re-Evolution of Hg into Ecosystems	CONSOL Energy
Hg and Air Toxics Element Impacts of Coal Combustion By-product Disposal and Utilization	UNDEERC
Effect of Hg Controls on Wallboard Manufacture	CBRC and TVA
Fate of Hg in Synthetic Gypsum Used for Wallboard Production	USGypsum
CUB Batch Characterization and Interlaboratory Comparison	NETL In-house
Hg and Metals Stability in CUBs	NETL In-house
Hg Capture and Potential Release from FGD Products	NETL In-house

Characterization of Hg in CUBs from Activated Carbon Injection Projects

- **E. C. Gaston (AL) - Bituminous**
  - ESP + COHPAC FF for particulate control
- **Brayton Point (MA) – Bituminous**
  - 2 ESPs in series
- **Salem Harbor (MA) – Bituminous**
  - ESP: 474 SCA
- **Pleasant Prairie (WI) – PRB**
  - ESP: 468 SCA

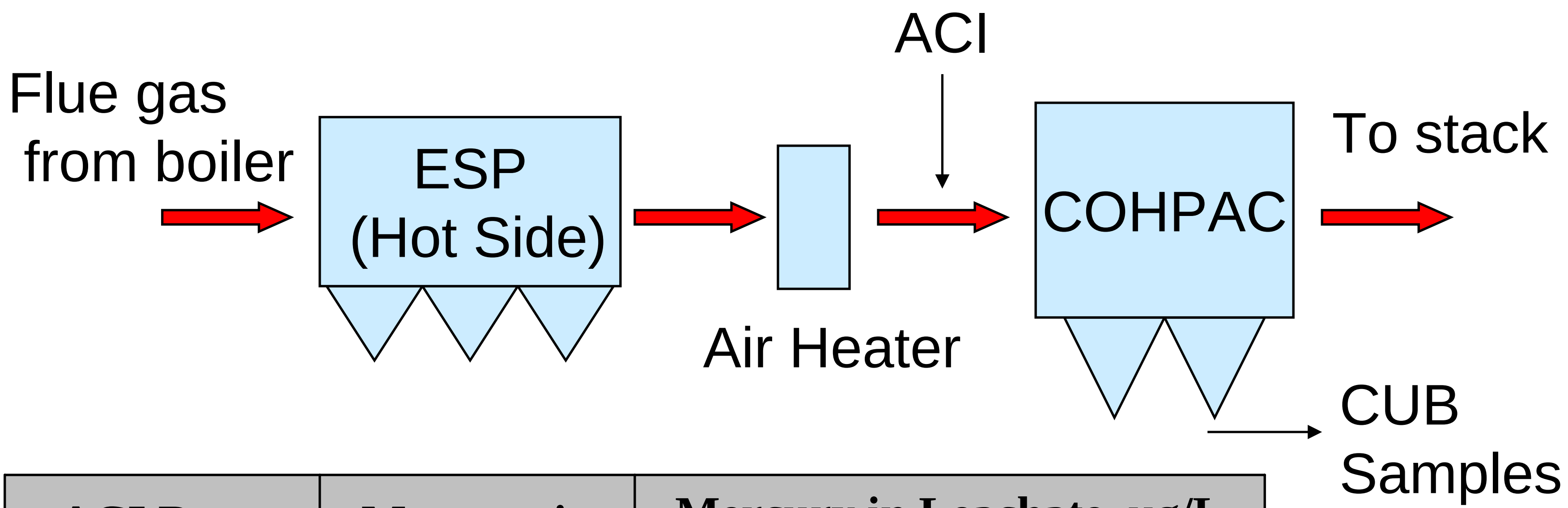
Activated Carbon Storage Silo

Impact of ACI on Fly Ash Mercury Concentration

	Alabama Power E.C. Gaston	WeEnergies Pleasant Prairie	PG&E Brayton Point	PG&E Salem Harbor
APCD Configuration	Hot-side ESP and COHPAC	Cold-side ESP	Cold-side ESP (two)	Cold-side ESP & SNCR
Coal Rank	Bituminous	Subbituminous	Bituminous	Bituminous
Coal Ash, %	14.78	5.25	10.76	4.15
Coal Hg, ppm	0.146	0.156	0.068	0.063
Baseline Ash Hg, ppm	0.2 – 2	< 0.5	<0.5	NA
ACI Ash Hg, ppm	10 – 50	0.5 – 5	0.2 – 1.4	0.1 – 0.7

Results from DOE/NETL 2001-02 activated carbon injection field tests

E.C. Gaston Plant
Leaching Results

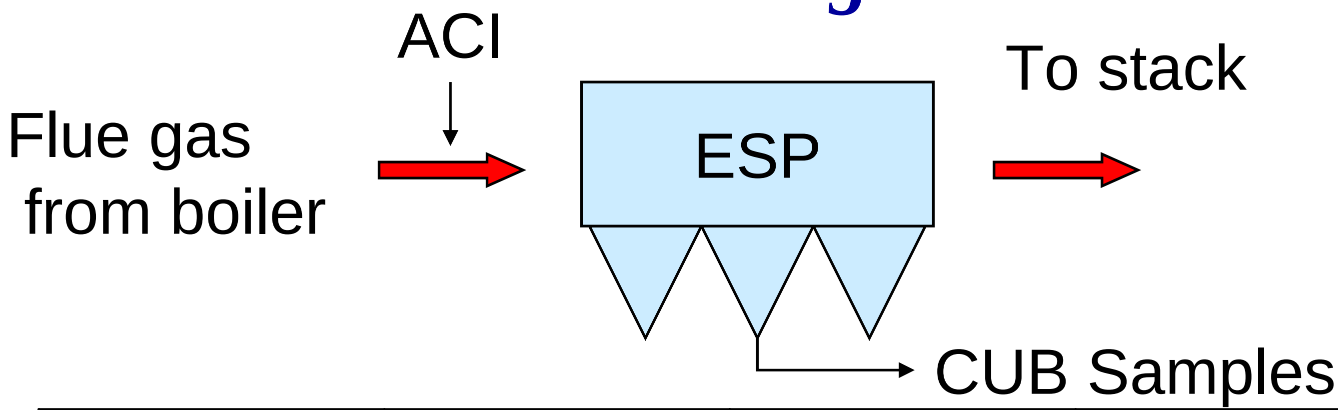


ACI Rate, lb/MMacf	Mercury in Solid, µg/g	Mercury in Leachate, µg/L	
		TCLP	SGLP
1.5	10 – 50	0.01	BDL*
1.5	10 – 50	N/A+	BDL
1.5	10 - 50	BDL	BDL

* µg/g = ppm

* Below Detection Limit of 0.01µg/L

Salem Harbor and Pleasant Prairie
Leaching Results



Plant	ACI Rate, lb/MMacf	Mercury in Solid, µg/g	Mercury in Leachate, µg/L	
			TCLP	SGLP
Pleasant Prairie	10	0.5 - 5	BDL	BDL
Pleasant Prairie	10	0.5 - 5	BDL	BDL
Pleasant Prairie	10	0.5 – 5	BDL	N/A
Salem Harbor	0	0.1 – 0.7	0.034	BDL
Salem Harbor	10	0.1 – 0.7	BDL	BDL
Salem Harbor	10	0.1 – 0.7	BDL	BDL

Summary of Hg Release from CUB after ACI
Phase I Field Testing Program

Activated carbon silo

- **Hg in solids increased after ACI**
- **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*

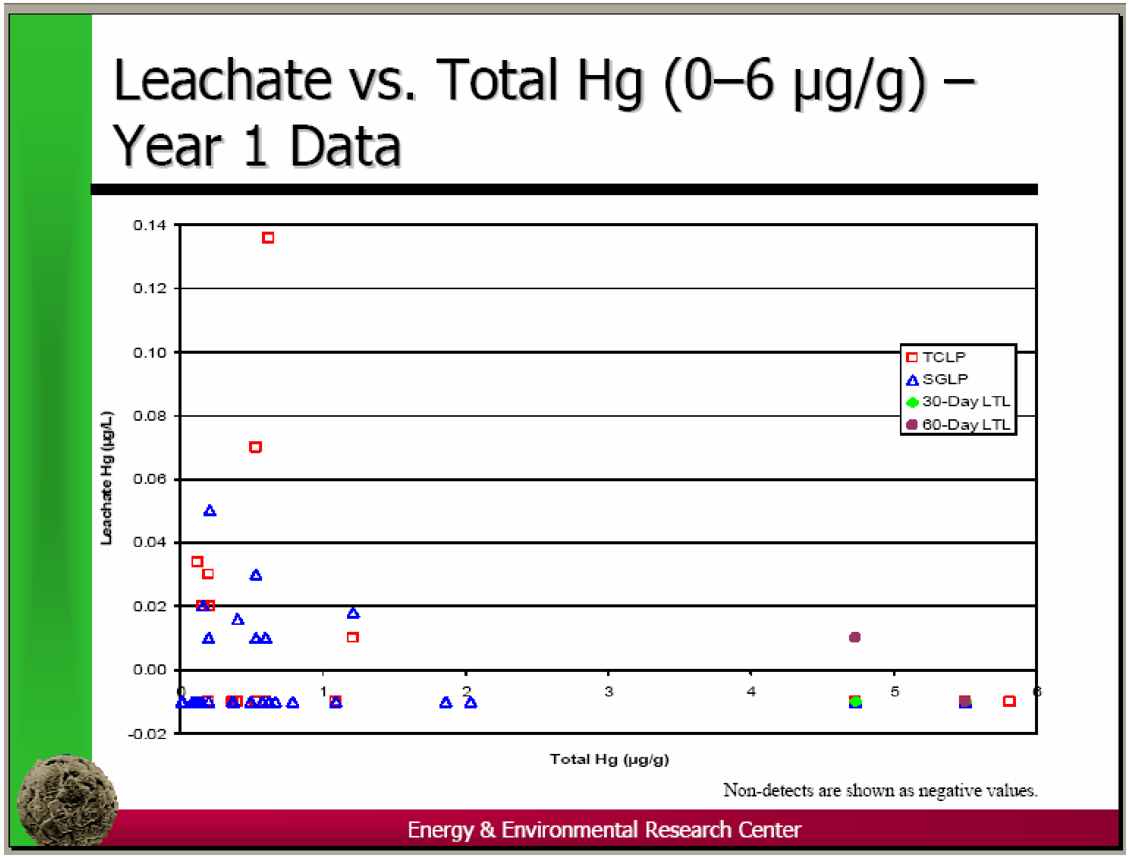
Hg Release from CUB Disposal and Beneficial Use Applications - CONSOL

- **Evaluating CUBs from 14 plants & end products made from CUBs (wallboard, fly ash concrete, etc.)**
  - Wide range of coal types, CUB types, and pollution control configurations
- **Laboratory leaching tests**
  - Screening: All leachates <1.0 µg/L
  - Detailed analysis (6 samples): 0.0075 – 0.084 µg/L
- **Volatilization tests (140^{o}F)**
  - **CUBs acted as mercury "sinks"**
- **Field leachates from disposal sites still being analyzed**
  - Screening: All leachates <1.0 µg/L

Hg Release Studies - UNDEERC

- **Comprehensive investigation of Hg and other air toxics in CUBs including:**
  - Chemical & physical characterization of CUBs
  - Laboratory methods development & Hg release studies
    - Leaching (TCLP, SGLP, short and long term)
    - Volatilization (short and long term)
    - Microbiologically-mediated release
  - Field investigations

UNDEERC Leaching Test Results



Below all EPA water quality/drinking water criterion:

CCC = 0.77 µg/L
CMC = 1.4 µg/L
MCL = 2.0 µg/L

Source: D. P. Hassett at DOE/NETL's Mercury Control Technology R&D Program Review, July 14-15, 2004

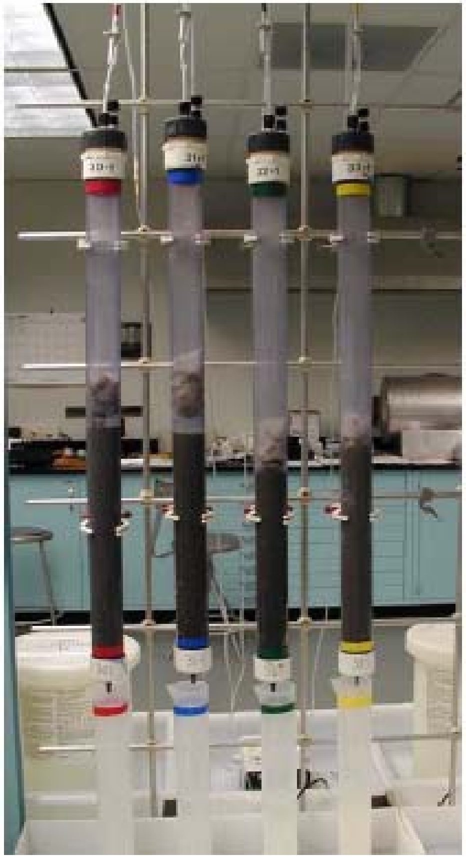
Characterization of CUB from Mercury Control Field Testing

- **Examine Hg in CUBs from NETL-sponsored Hg control projects**
  - 14 projects awarded in 2003-04
- **Use uniform testing procedures and inter-laboratory comparison**
- **Examine leaching, volatilization, and microbial mobilization**
- **Single award ~ August 2005**

NETL In-house Research - Hg Release from CUB

- **Long-term column leaching tests**
  - 30 to 180 days
  - Leaching liquids
    - Water
    - Acetic acid (TCLP)
    - Synthetic precipitation
    - Sodium carbonate
    - Sulfuric acid

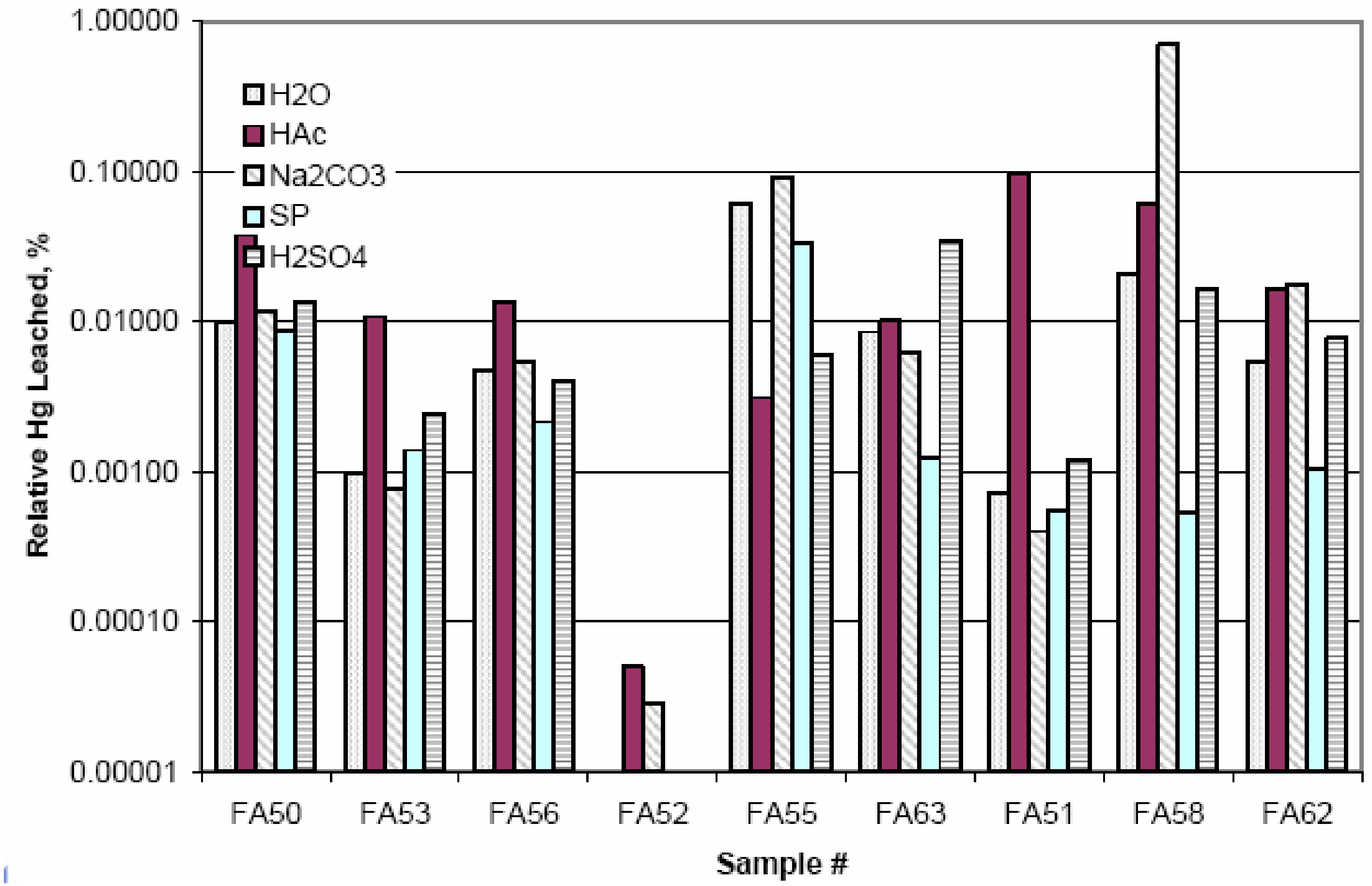
- **Development of rapid leaching protocol**
  - Alternative to TCLP, SGLP; simulates column leaching



Laboratory leaching columns

Cumulative Hg Release – NETL In-House Column Leaching Tests

Maximum amount of Hg leached from fly ash less than EPA Hg drinking water standard of 2 ppb



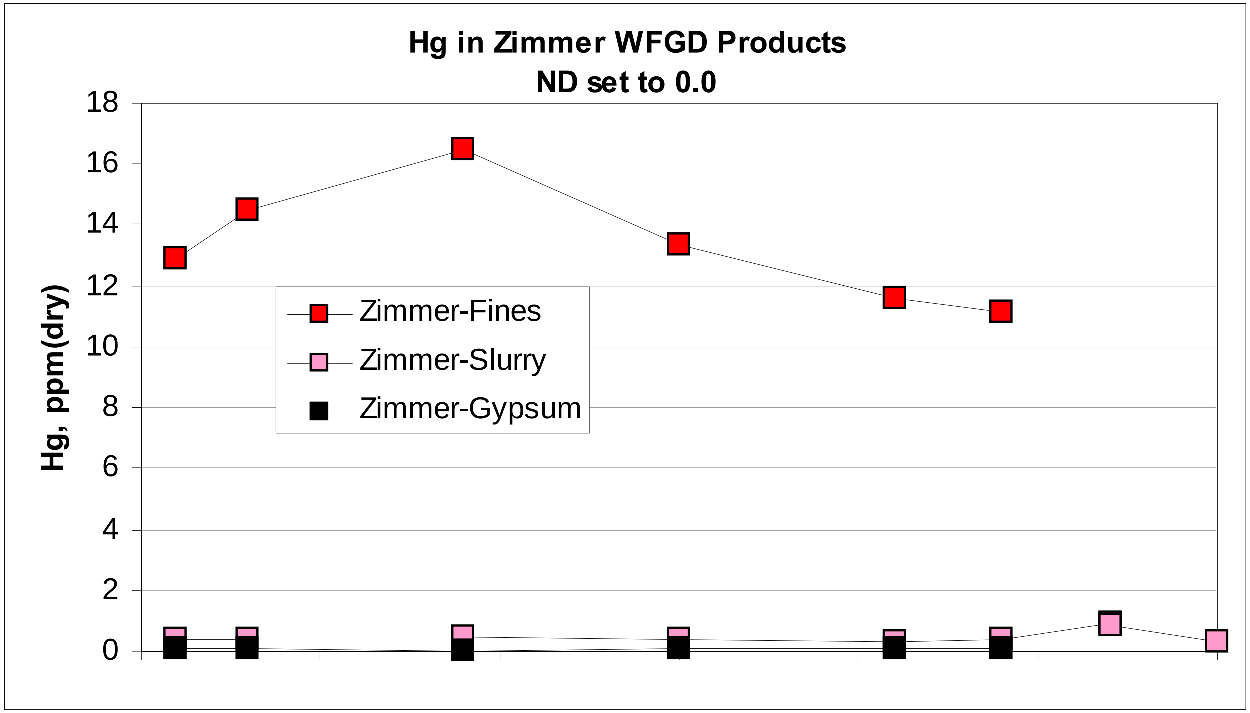
Ref. A. G. Kim at DOE/NETL's Mercury Control Technology R&D Program Review, July 14-15, 2004

Hg Release from Enhanced Oxidation & Wet FGD Removal – B&W

Wet FGD Scrubber

- **Endicott Station (MI) and Zimmer Station (OH)**
- **Both used high-S OH bituminous coal and cold-side ESPs**
- **Endicott FGD: Limestone in-situ forced oxidation**
- **Zimmer FGD: Mg-lime external forced oxidation**

Hg Release from Enhanced Oxidation & Wet FGD Removal – B&W



"… 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

NETL In-House Research
Hg Release from CUB

- **Evaluate potential environmental impacts of CUB disposal or utilization**
- **Determine the stability of Hg and other metals in CUB under simulated end-use environments**
- **Explain the chemistry underlying metal stability**

Drywall ready for landfill

Synthetic Gypsum-Hg Issues

Wallboard manufacturing line

- Release to atmosphere, groundwater during manufacturing
- Release from manufactured products
- Post disposal mobilization

Mercury Retention During FGD-gypsum to Wallboard Production

Mercury in FGD Products (µg/kg = ppb)					
	Plant A	Plant B	Plant C	Plant D	Plant E
Feed FGD-Derived Gypsum	143 ± 4	251 ± 7	1221 ± 51	1464 ± 50	494 ± 16
Product FGD-Derived Wallboard	147 ± 2	106 ± 5	1278 ± 63	1370 ± 59	421 ± 3
% Hg Retained During Processing	103 ± 3%	42 ± 2%	104 ± 7%	94 ± 5%	85 ± 3%

Mercury Retention During FGD-gypsum Moisture Reduction

Mercury and Moisture Analysis	Before Drier		After Drier	
	Sample 1	Sample 2	Sample 1	Sample 2
As-Received Mercury (μg/kg)	140 ± 6	142 ± 6	151 ± 2	158 ± 9
As-Received Moisture (%)	29.9	30.3	24.6	24.9
Mercury, Dry Basis (μg/kg)	200 ± 8	204 ± 8	200 ± 3	211 ± 11
Hg, 2-Sample Average (μg/kg)	202 ± 8		205 ± 10	

Hg Partitioning During Laboratory FGD-Slurry Settling Studies

Mercury in FGD settled-slurry layers (µg/kg = ppb)	Top Layer	Bottom Layer	Ratio of Hg in Top to Hg in Bottom Layer
Slurry 1, Aliquot 1	3,560 ± 170	72 ± 6	49 ± 6
Slurry 1, Aliquot 2	2,900 ± 80	108 ± 10	26 ± 3
Slurry 2	13,000 ± 800	700 ± 27	19 ± 2

- **Mercury in the FGD-slurry reports preferentially to the less-easily settled material**
  – **Top layers enriched in Fe by an order of magnitude**

Leaching of FGD Products Using Continuous Stirred Tank Reactor (CSTX)

Continuous stirred tank reactor

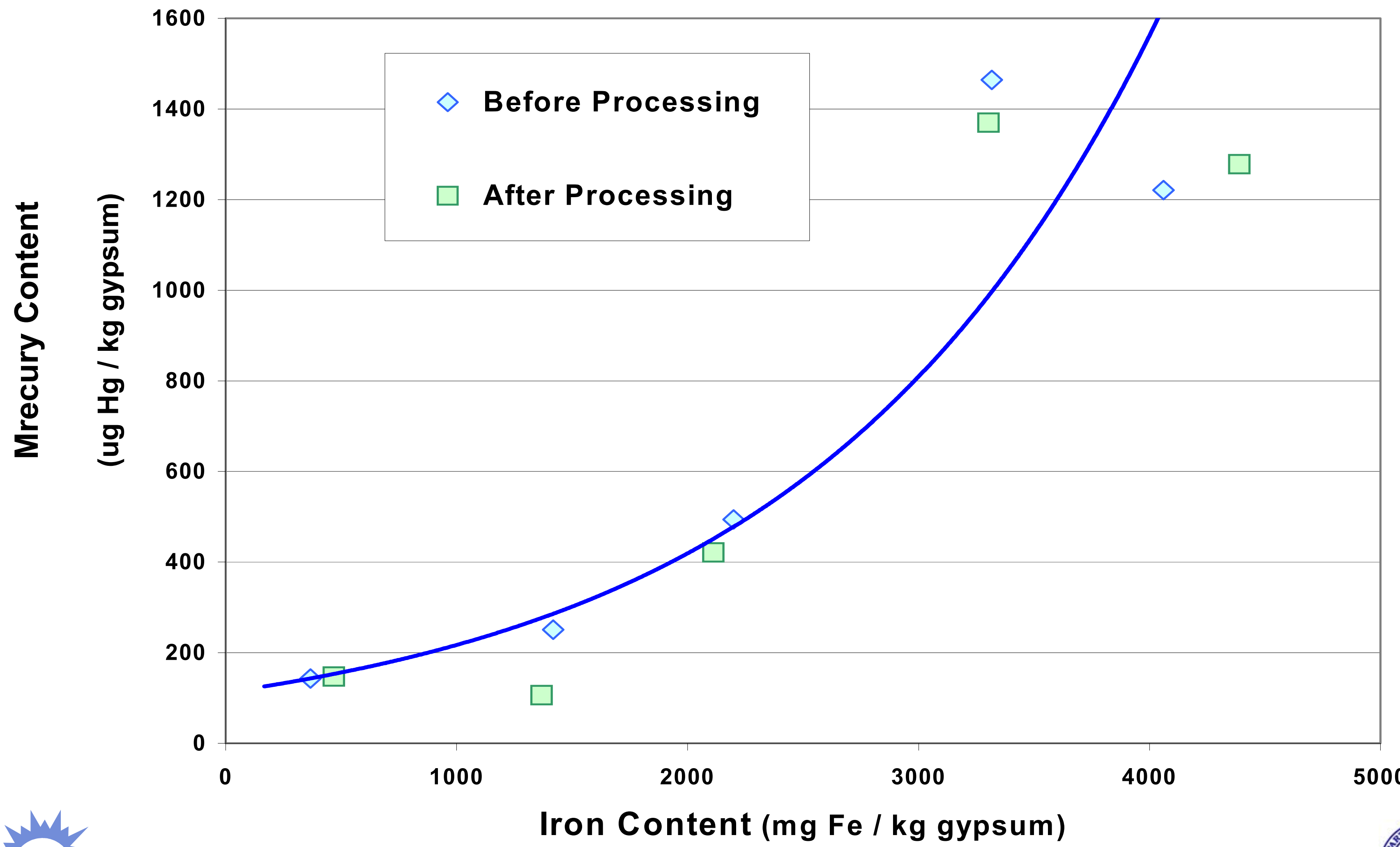
Gypsum

- Gypsum totally dissolved
  - Leachate: No Hg
  - Residue
    - < 1% of original material
    - Fe, Al, and all Hg

Wallboard

- Gypsum totally dissolved
  - Leachate: ~1% of Hg
  - Residue
    - ~ 2% of original material
    - Fe, Al, and majority Hg

Mercury Content of Gypsum Tends to Correlate with Iron Content



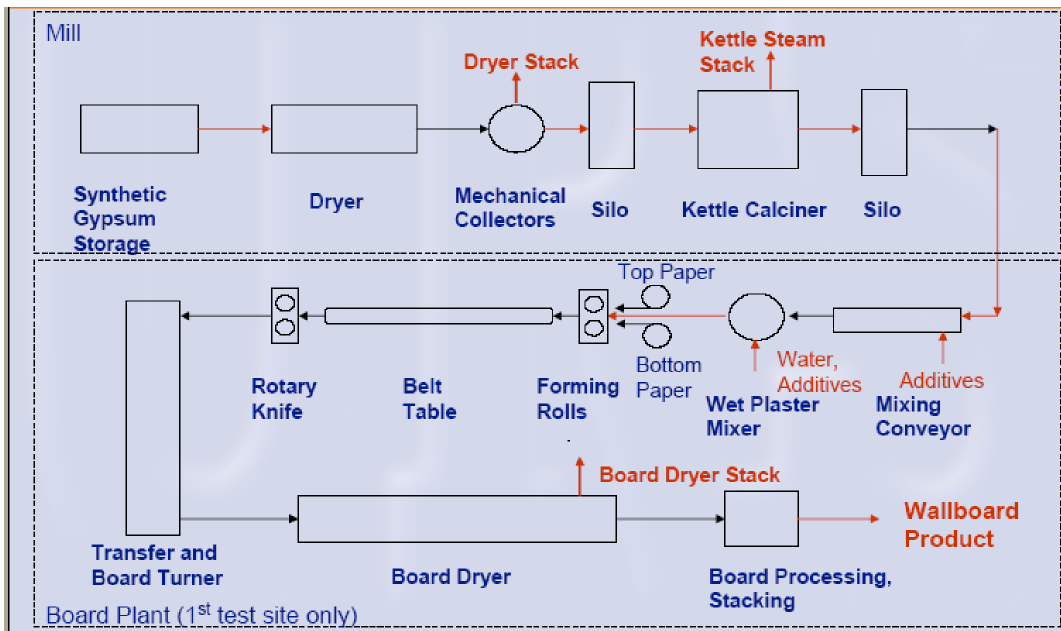
CSTX Results Summary

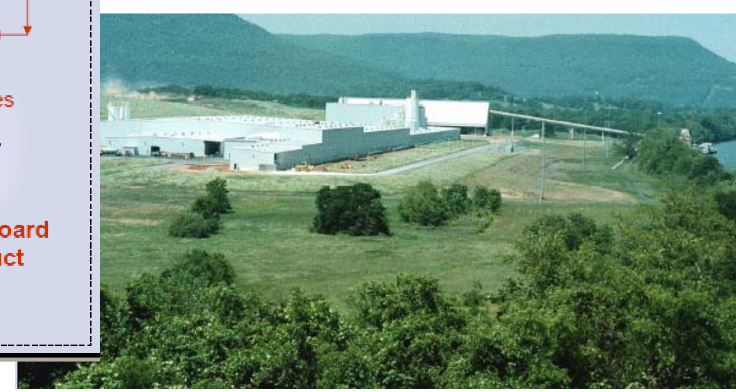
An iron-containing phase, probably introduced with limestone, is responsible for sorption of mercury

- All Hg remains in iron-rich residues after leaching experiments
- Both Hg and Fe preferentially report to top layers during settling experiments
- Hg content of FGD gypsum appears to correlate with Fe content

Fate of Mercury in Synthetic Gypsum Used for Wallboard Production - USG

- **Measure mercury concentrations in solid, liquid, and gaseous streams at 3 operating wallboard manufacturing plants**





USG Project Test Matrix

Synthetic Gypsum Source:					
Task	1	2	3	4	5
Power Plant	A	A	B	C	D
Coal Type	HS Bit	HS Bit	HS Bit	TX lignite	HS Bit
FGD Reagent	Limestone	Limestone	Limestone	Limestone	Lime
Forced Oxidation Mode	In Situ	In Situ	In Situ	In Situ	External
Gypsum Fines Blow Down?	No	No	Yes	No	Yes
SCR Status	On Line	Bypassed	On Line	No SCR	TBD*
USG Wallboard Plant Tested	1	1	2	3	1

*HS Bit – High Sulfur Bituminous; TX Lignite – Texas Lignite; TBD – To be determined

Preliminary Mercury Emission Results – Task 1

Mercury Emissions During Wallboard Production	Approximate Industry Production Rates (2004)
Less than 0.1 lb of mercury emitted per million square feet of wallboard produced	9,000 million square feet of wallboard using synthetic gypsum
0.045 grams of mercury per ton of dry gypsum processed	7.5 – 9 million ton of dry synthetic gypsum processed

Source: USG

NETL

Summary of Results to Date

- **Minimal mercury release in typical disposal or utilization applications**
  - Leachate Hg concentrations were significantly lower than EPA drinking water standards (2.0 µg/L) and water quality criteria for protection of aquatic life (0.77 µg/L)
- **Very little (<1% of total) Hg can be extracted from fly ash via leaching**
- **Release of Hg <u>not</u> related to total Hg in CUB**
- **Release of Hg <u>may</u> relate to carbon content**
  - Higher LOI ~ less Hg release
- **Capture via ACI may "retain" Hg better than capture via carbon in fly ash**
  - May relate to number & location of adsorption sites (more research needed)
- **Release of Hg from wallboard manufacture is currently being investigated**
- **DOE/NETL will need to continue to support research on environmental effects of CUB**

For additional information:

http://www.netl.doe.gov/coal/E&WR/ccb/