

# The Fate of Mercury in Coal Utilization Byproducts - DOE/NETL's Research Program



## Combined Power Plant Air Pollutant Control Mega Symposium

September 1, 2004

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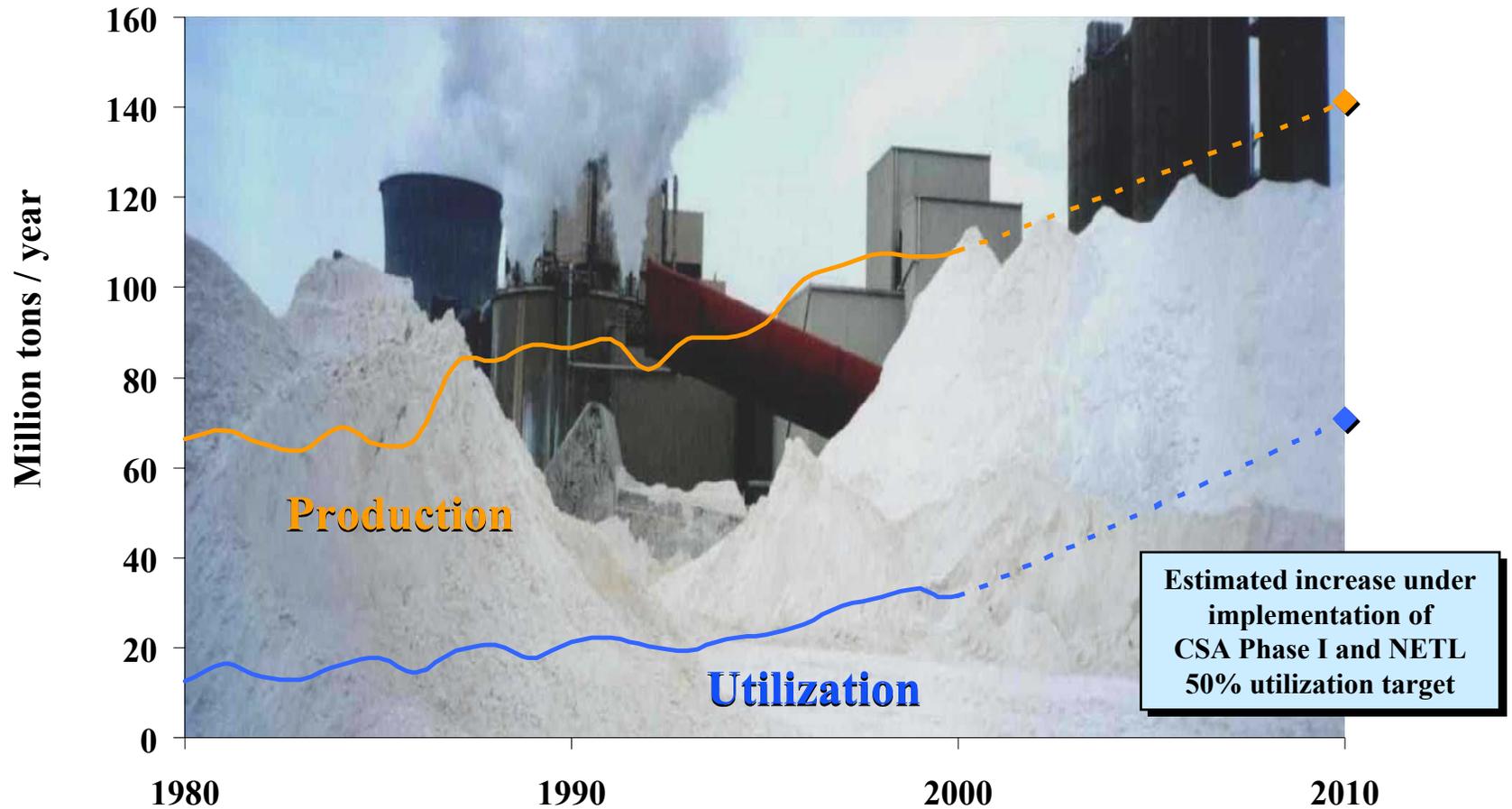


# What are CUBs?

- **Coal Utilization Byproducts (a.k.a. CCBs, CCPs, CCW, FFCW, CCR ...)**
- **Utilization includes:**
  - Combustion
  - Gasification
  - Hybrid systems
- **Byproducts because:**
  - \$ from electricity sales >> \$ from CUB sales
  - Aren't "wastes" or "residues" until sent to disposal site



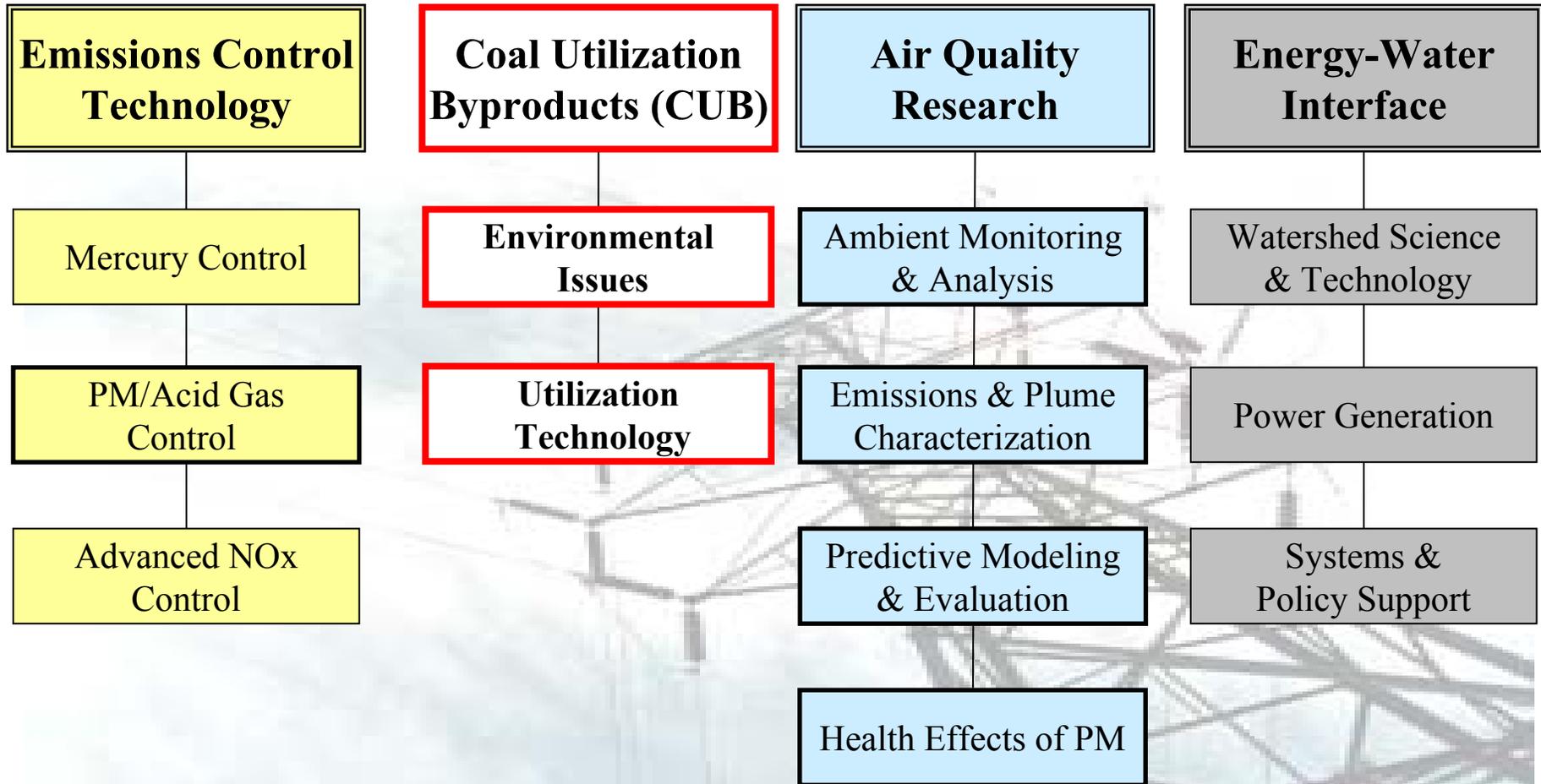
# DOE/NETL Goal: Increase CUB Utilization to 50% by 2010



Source: USGS, Historical Statistics for Mineral Commodities in the United States, May 2002

Mega Symposium, September 1, 2004

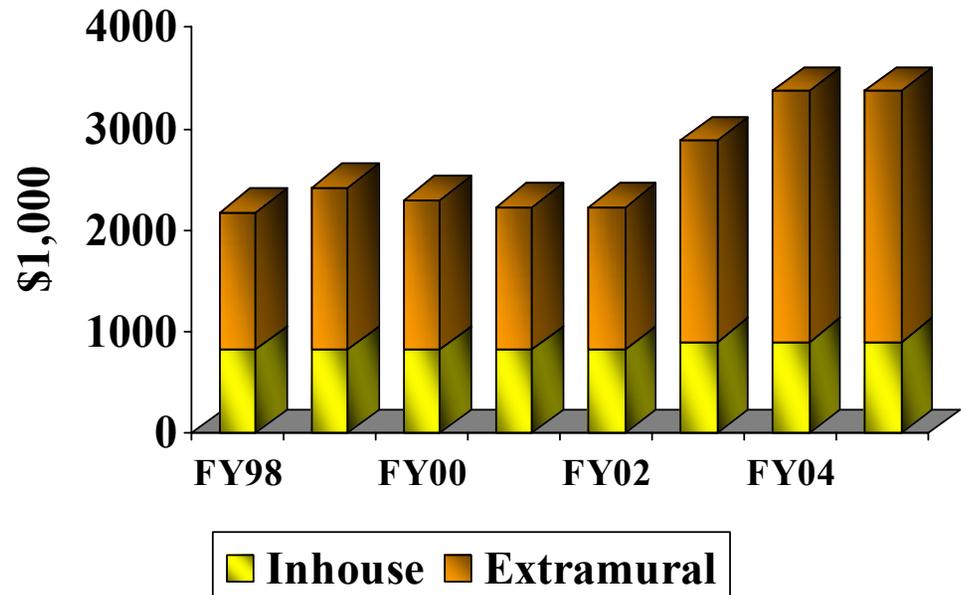
# Context: DOE-FE's "Innovations for Existing Plants" R&D Program



# DOE/NETL CUB Research Funding

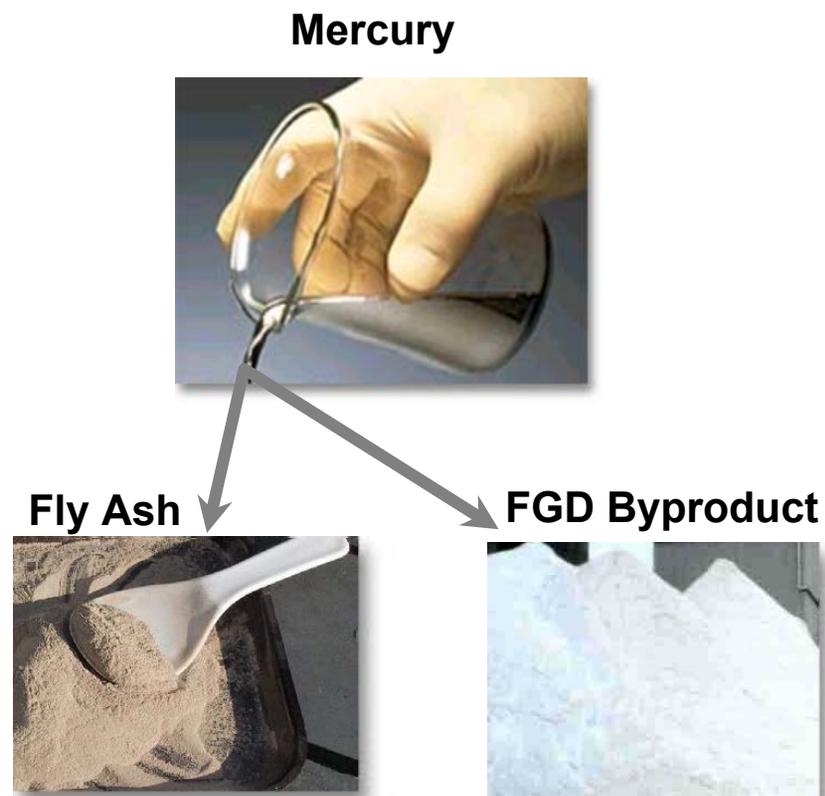
- Over \$22 million from FY98 – FY05 under IEP Program
- Additional \$22 million for CUB technology demonstration under DOE's clean coal program

CUB Research Funding  
under IEP program

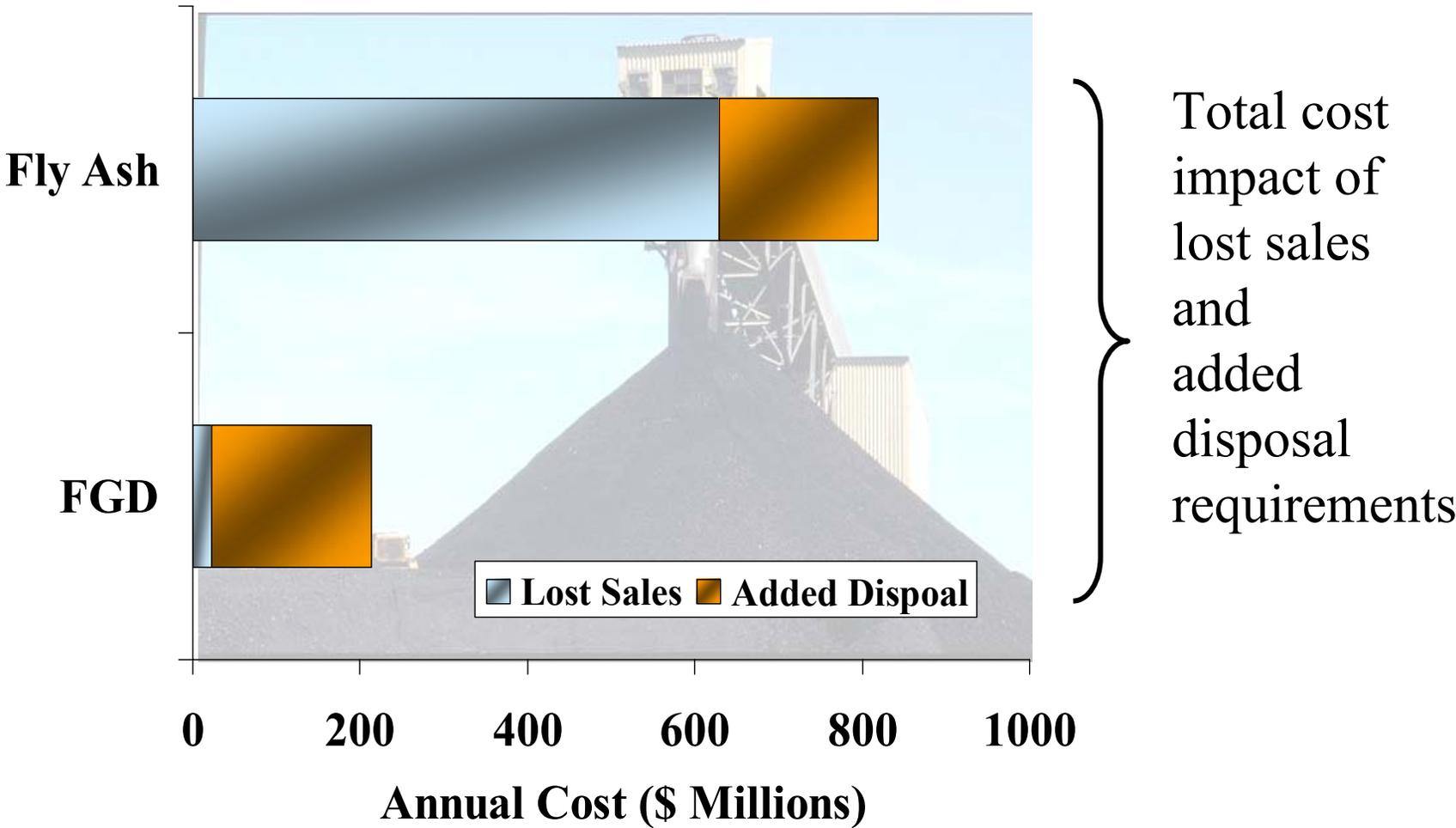


# Hg Control and CUBs

- Almost all “Hg Control Technology” projects increase Hg concentration in byproducts
- Ultimate fate?
- Perceptual Impacts?
- Regulatory Impacts?



# Cost Impact of “Hazardous” Designation



# Characterization and Fate of Hg in CUBs

## *NETL Project Initiation Mechanisms*

- **Subtasks under “Hg control technology” demonstrations**
  - Activated carbon injection
  - Enhanced oxidation & removal in wet FGD
- **Proposals submitted under NETL “Broad-based” Solicitations**
- **NETL-sponsored Consortia**
  - CBRC (West Virginia University)
  - CARRC (University of North Dakota EERC)
- **Unsolicited Proposals**
- **Targeted Solicitation (closed 8/24/04)**
- **NETL In-house (OSTA-Environmental Sciences Division)**

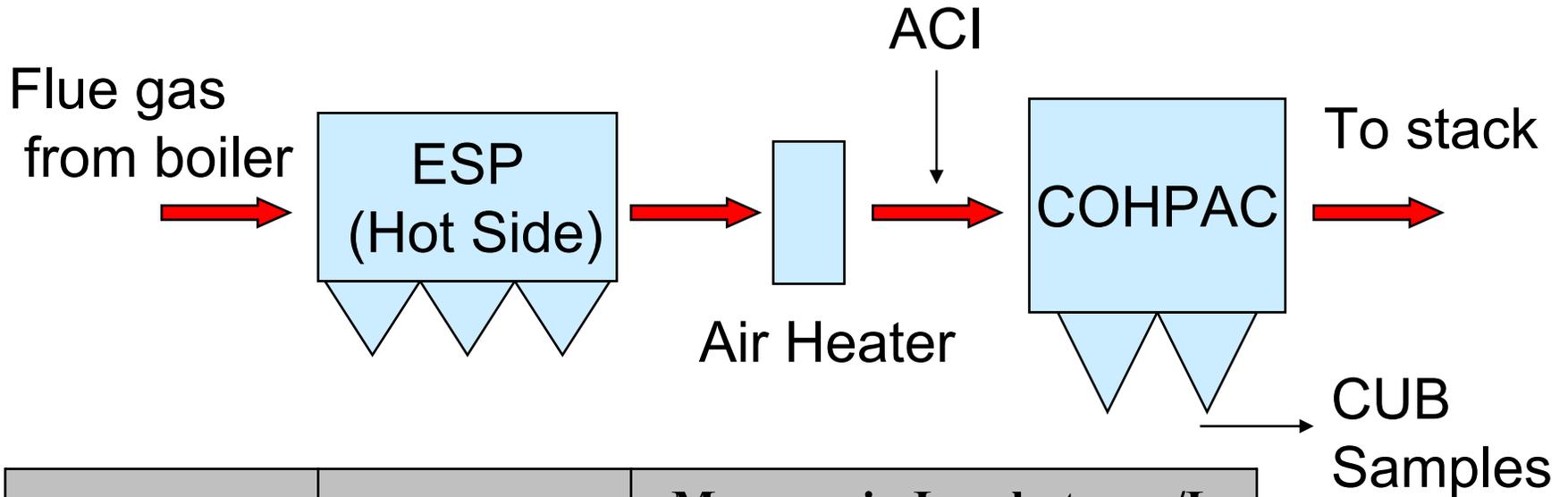


# Characterization of Hg in CUBs from Activated Carbon Injection Projects

- **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



# Results: E.C. Gaston Plant

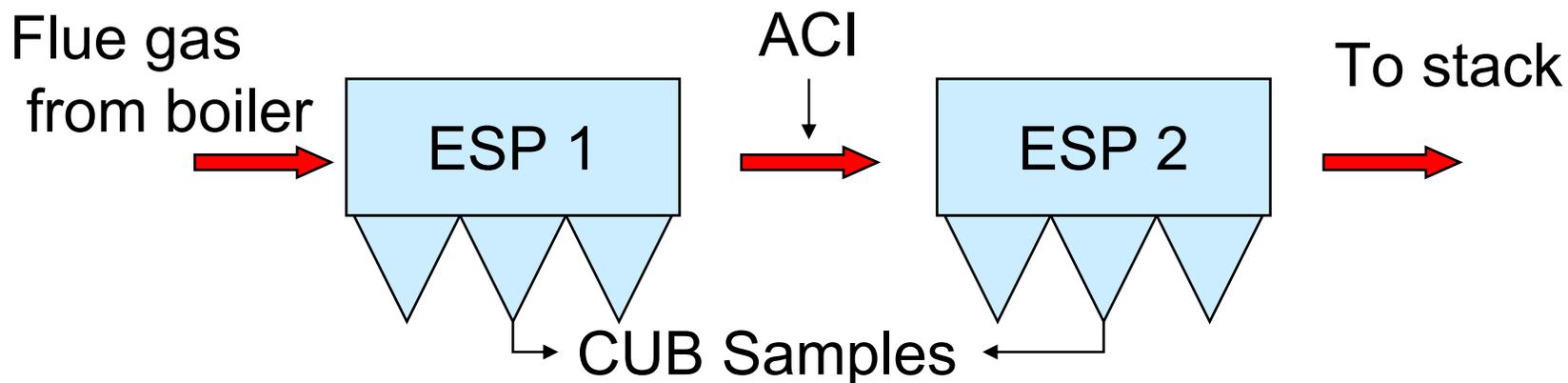


ACI Rate, lb/MMacf	Mercury in Solid, $\mu\text{g/g}$	Mercury in Leachate, $\mu\text{g/L}$	
		TCLP	SGLP
1.5	10 – 50	0.01	BDL*
1.5	10 – 50	N/A <sup>+</sup>	BDL
1.5	10 - 50	BDL	BDL

\* Below Detection Limit of  $0.01\mu\text{g/L}$

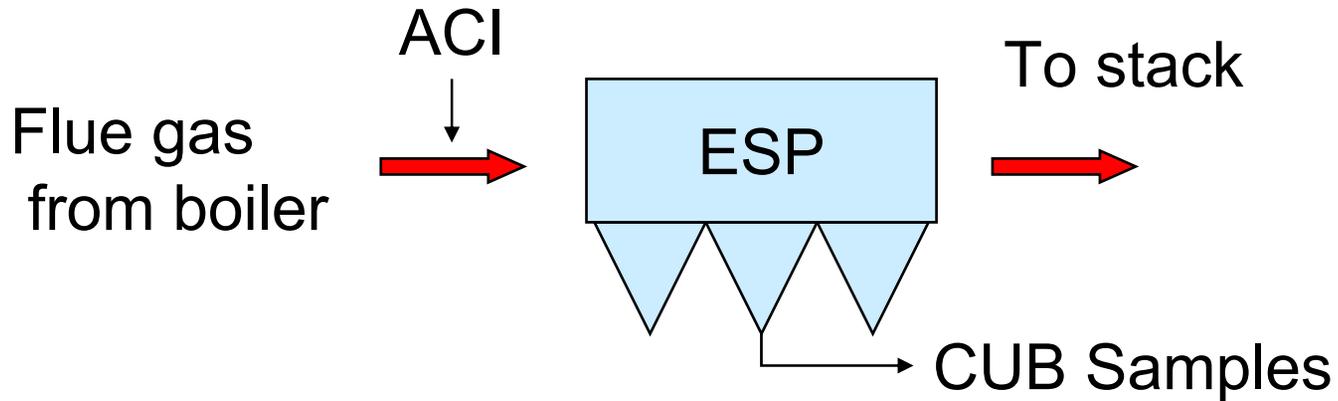


## Results: Brayton Point



Sample Location	ACI Rate, lb/MMacf	Mercury in Solid, $\mu\text{g/g}$	Mercury in Leachate, $\mu\text{g/L}$	
			TCLP	SGLP
ESP 1	0	0.2 – 0.32	0.02	0.05
ESP 2	0	0.2 – 0.53	BDL	0.01
ESP 1	10	N/A	0.03	0.01
ESP 2	10	0.4 – 1.4	0.07	0.03
ESP 1	20	N/A	0.02	0.02
ESP 2	20	0.4 – 1.4	BDL	0.01

# Results: Salem Harbor and Pleasant Prairie



Plant	ACI Rate, lb/MMacf	Mercury in Solid, $\mu\text{g/g}$	Mercury in Leachate, $\mu\text{g/L}$	
			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: Hg Release from CUB after ACI



- Hg in solids increased slightly after ACI
- Most leachates below 0.01  $\mu\text{g/L}$
- Max. leachate 0.07  $\mu\text{g/L}$  (Brayton Point)
- *EPA Freshwater continuous criterion concentration = 0.77  $\mu\text{g/L}$*

# Characterization of Hg in CUBs from Enhanced Oxidation & Wet FGD Removal



- 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

# Results: Hg from wet FGD byproducts

- **Standard leaching tests (TCLP, SGLP) not conducted**
- **Hg concentrations in liquid process streams (in-plant)**
  - $<0.5 - 3.0 \mu\text{g/L}$
- **Minimal volatilization below  $140^{\circ}\text{C}$  ( $284^{\circ}\text{F}$ )**
- **Mercury in FGD solids**
  - Concentrations higher in fine particle fractions
  - Separation techniques may be of interest



# Hg Release from CUB Disposal and Beneficial Use Applications

- **CONSOL Energy – laboratory and field studies**
- **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  $<1.0 \mu\text{g/L}$
  - Detailed analysis (6 samples):  $0.0075 - 0.084 \mu\text{g/L}$
- **Volatilization tests (140°F)**
  - CUBs acted as mercury “sinks”
- **Field leachates from disposal sites still being analyzed**
  - Screening: All leachates  $<1.0 \mu\text{g/L}$



# Hg Release Studies - UNDEERC

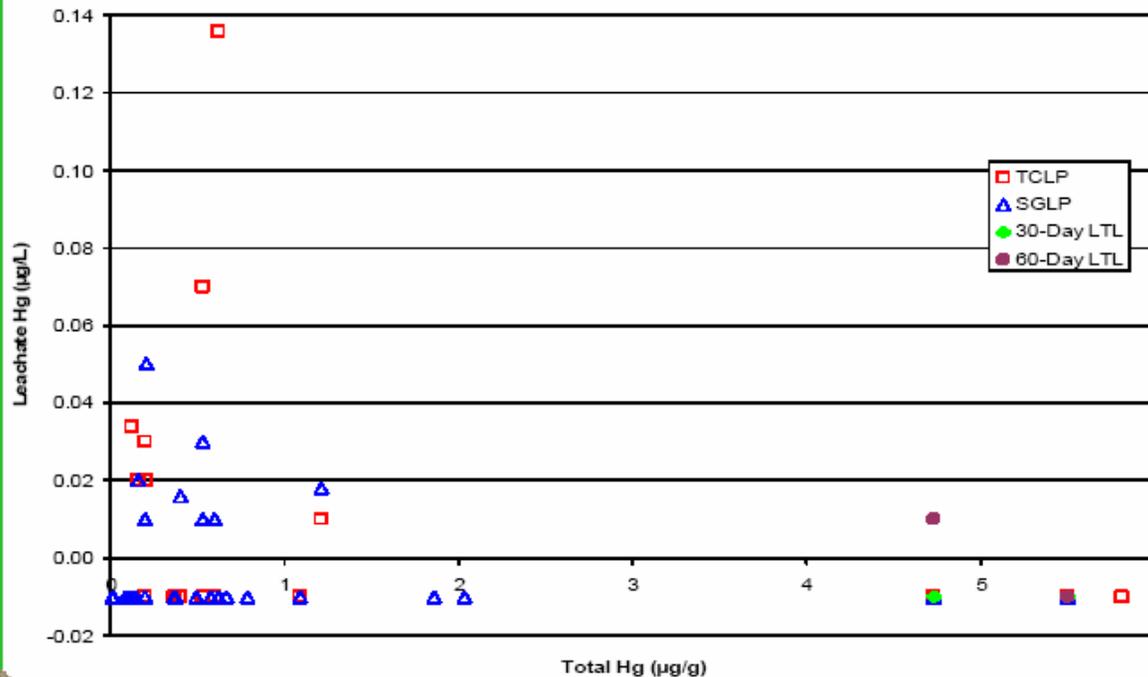
- **Comprehensive investigation of Hg and other air toxics in CUBs including:**
  - Chemical & physical characterization of CUBs
  - Laboratory methods development & Hg release studies
    - Leaching (TCLP, SGLP, short and long term)
    - Volatilization (short and long term)
    - Microbiologically-mediated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



# UNDEERC Leaching Test Results

## Leachate vs. Total Hg (0–6 $\mu\text{g/g}$ ) – Year 1 Data

(Presented by D. P. Hassett at DOE/NETL's Mercury Control  
Technology R&D Program Review, July 14-15, 2004)



Non-detects are shown as negative values.

Energy & Environmental Research Center



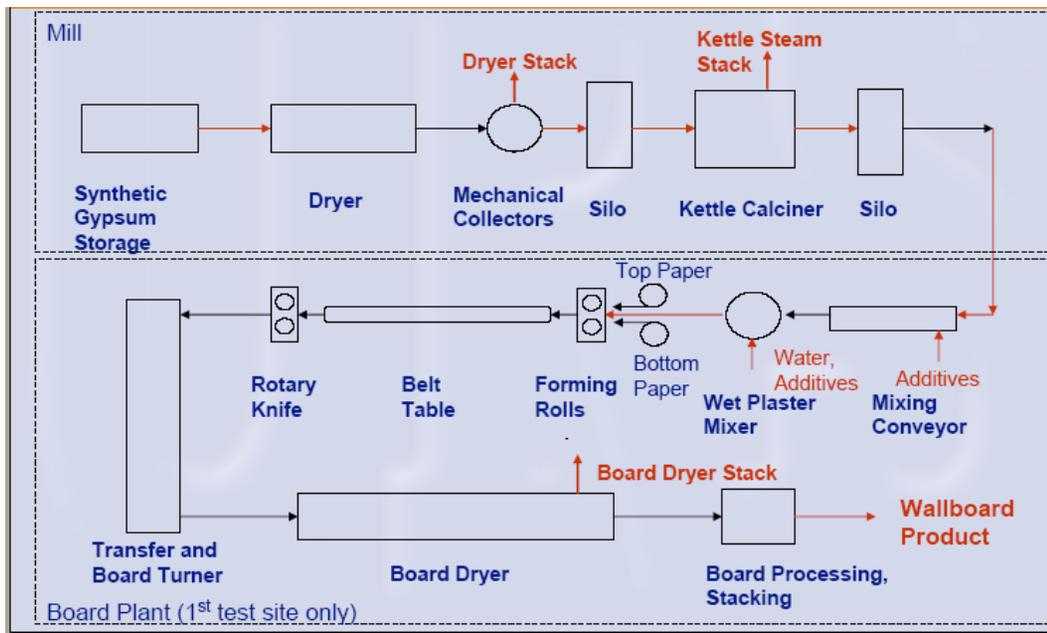
# Preliminary UNDEERC Test Results

- **Ambient Temperature Volatilization**
  - Samples acted as mercury “sinks”
- **Thermal Volatilization**
  - Mercury generally released at temperatures greater than 200°C
- **Microbiologically-mediated release (1 sample)**
  - Greater than non-microbiologically mediated releases but still low
  - Evidence of methylation & organomercury compounds
- **Paper #111, 9:15 a.m., this session**
  - Lab study to determine organomercury compounds



# Fate of Mercury in Synthetic Gypsum Used for Wallboard Production

- Paper # 156, 10:10 a.m., this session
- Measure mercury concentrations in solid, liquid, and gaseous streams at 3 operating wallboard manufacturing plants



# Characterization of Coal Utilization By-Products from Mercury Control Field Testing

*Solicitation DE-RP26-04NT42110*



- **Examine Hg in CUBs from NETL-sponsored Hg control projects**
  - 10-15 projects awarded in 2003-04
- **Use uniform testing procedures and inter-laboratory comparison**
- **Examine leaching, volatilization, and microbial mobilization**
- **Solicitation closed: 08/24/2004**
  - Expect 1 award ~ Fall 2004



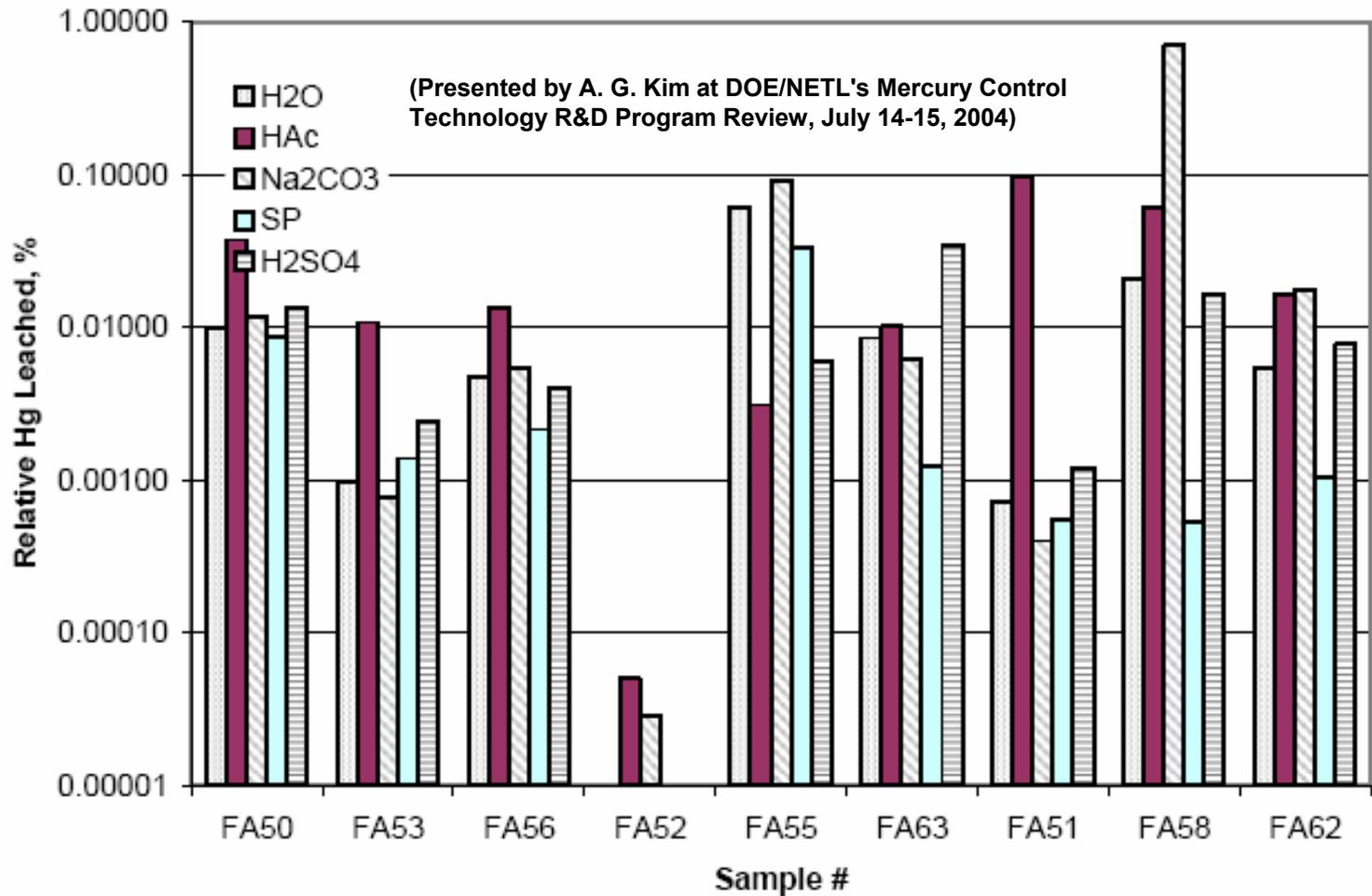
# NETL In-house Research - Hg Release from CUBs

*Office of Science, Technology, & Analysis (OSTA)*  
*Environmental Sciences Division*

- **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

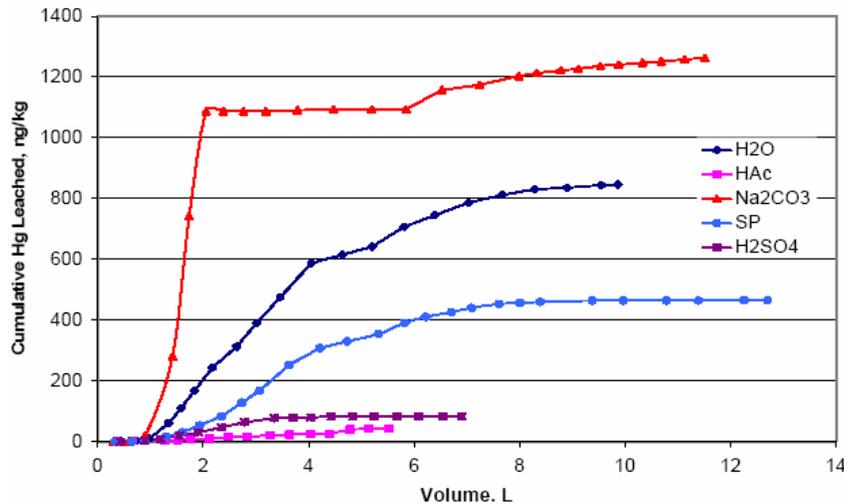


# Cumulative Hg Release - Column Leaching Tests

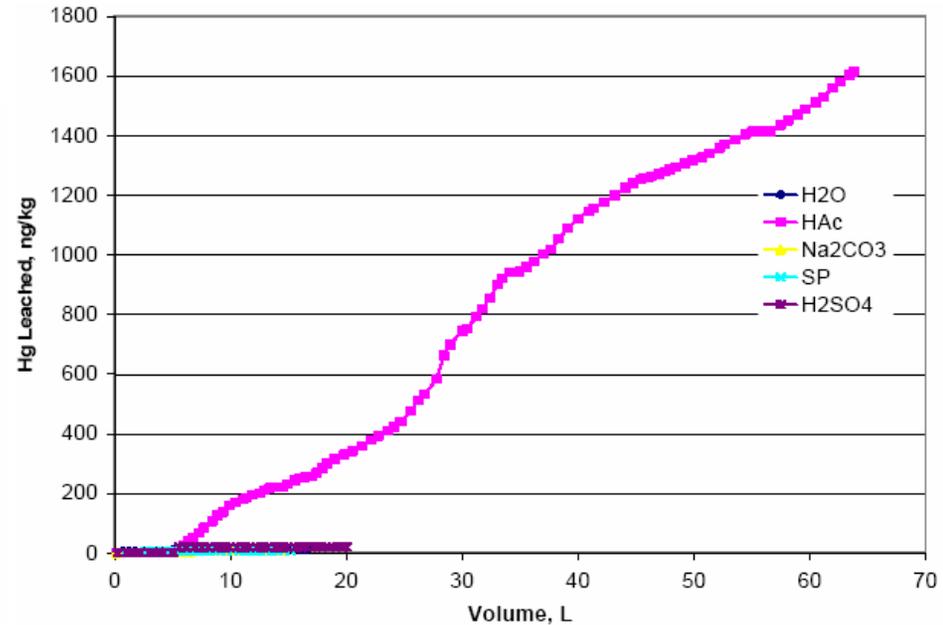


# Effect of Leaching Solution pH on Hg Release

- FA55 – Release increases with increasing pH



- FA51 – Significant release only with acetic acid



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



# Summary: NETL In-house CUB Leaching

- **Very little (<1% of total) Hg can be extracted from fly ash via leaching**
- **Release of Hg not related to total Hg in CUB**
- **Release of Hg may 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)



# Summary: NETL Research on Hg in CUBs

- **Minimal mercury release in typical disposal or utilization applications**
  - Leachate Hg concentrations were significantly lower than EPA drinking water standards (2.0  $\mu\text{g/L}$ ) and water quality criteria for protection of aquatic life (0.77  $\mu\text{g/L}$ )
- **Release of Hg from wallboard manufacture is currently being investigated**
- **Pressures to further regulate/restrict the use and disposal of CUBs because of Hg will likely continue (evidence notwithstanding?)**
- **DOE/NETL will need to continue to aggressively support research on environmental effects of CUBs**



# For additional information:

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

Address  <http://www.netl.doe.gov/coal/E&WR/ccb/index.html>

**NETL** NATIONAL ENERGY TECHNOLOGY LABORATORY  
COAL UTILIZATION BY-PRODUCTS (CUB)

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August 27, 2004

**Coal Utilization By-Products (CUB)**

*Characterizing the environmental performance and utilization of coal utilization by-products*

**The Coal Utilization By-Products (CUB) program** is sponsoring research to support the environmentally safe, technically sound handling of CUB material. The program sponsors numerous projects from bench to demonstration scale. The research area includes: 1) Evaluation of potential environmental impacts of CUB disposal or utilization, for example, the photo shows a flowable fill application, 2) Optimization of accepted and novel utilization methods, and 3) Collection and dissemination of data to assist in regulatory decisions related to CUB.

Utilization Research  
Environmental Research  
Consortium Projects  
Regulatory Drivers

**NETL**

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Utilization  
Environmental Consortium  
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