Fate of Mercury in Coal Byproducts from DOE's Mercury Control Technology Field Testing and Related Projects



China Workshop on Mercury Control from Coal Combustion

October 31 – November 2, 2005 Beijing, China

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Outline

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



DOE-NETL CUB Program Goal: 50% Utilization by 2010







EPA Regulations Introduce Additional Challenges to CUB Utilization

• CAIR = More FGD Byproducts

- Will wallboard market continue to absorb excess?
- Can new large-volume markets be developed?
 - PRB coal = dry FGD (unsuitable for wallboard)
- CAIR = More Low-NOx burners, SCR, SNCR
 - Will additional carbon/NH₃ in fly ash disrupt or prevent expansion of current cement/concrete markets?

• CAMR: Additional Hg in CUBs





Mercury Partitioning – Impact of CAIR & CAMR



Effects of CAMR on Hg in Fly Ash

If sorbent injected <u>upstream</u> of primary PCD

- -Some additional Hg; much additional carbon
- -Re-use issues will be affected by carbon more than Hg



• If FGD is sole means of Hg removal

- -Fly ash: unchanged from pre-CAMR byproduct
- Exception: "oxidation enhancement additives"



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

- If sorbent injected <u>downstream</u> of primary particulate collection device (e.g., hot-side ESPs, TOXECON)
 - -Spent sorbent: completely new byproduct
 - -Fly ash: little change from pre-CAMR byproduct
 - Depends on how spent sorbent is processed



Effects of CAMR on Hg in FGD Byproducts

• Wet FGD (new or existing)

- -Mostly unchanged from pre-CAMR byproducts
- -Exception: "oxidation enhancement additives"





Effects of CAMR on Hg in FGD Byproducts

• Dry FGD (spray dryers)

 If sorbent injection is used, most byproducts will contain significantly more Hg and spent sorbent





Fundamental Questions

(R&D must provide supporting data to answer these)

• Is Hg release from existing 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?

-Same 3 Questions as above!!

-Will overall perception of CUBs worsen, even if they remain unchanged from pre-CAMR condition?



Environmental Release of Hg from CUBs NETL Extramural R&D Projects

• Complete list of projects and relevant reports can be found on the NETL CUB Web site:

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

Project Title	Lead Organization
CUB Analysis from ACI Mercury Control Field Testing	ADA-ES and Reaction Engineering
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
Fate of Hg in Synthetic Gypsum Used for Wallboard Production	USGypsum



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

- E. C. Gaston (AL) Bituminous
 - Hot-side 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







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



Activated carbon silo

- Hg in solids increased slightly 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 μ g/L
 - $-CMC = 1.4 \ \mu g/L$
 - $-MCL = 2.0 \ \mu g/L$



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°F)
 - CUBs acted as mercury "sinks"
- Field leachates from disposal sites
 - All leachates <1.0 µg/L



Hg Release Studies - UNDEERC

- Comprehensive investigation of Hg and other air toxics in 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 Fly Ash with Hg Control vs. No Hg Control; SGLP vs. TCLP



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UNDEERC Volatilization Test Results

• Ambient Temperature Volatilization (Lab Tests)

-Samples acted as mercury "sinks"

• Thermal Volatilization

 Mercury generally released at temperatures greater than 200°C

• Volatilization at field sites

-Low emission, similar to background (~ 1ng/m³)



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 insitu 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 enduse environments
- Explain the chemistry underlying metal stability



Drywall ready for landfill



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</p>
 - ➢ Fe, AI, and all Hg

Wallboard

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



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

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









Preliminary Mercury Emission Results – Task 1

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

Source: USG



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 μ g/L) and water quality criteria for protection of aquatic life (0.77 μ g/L)
- 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)
- 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/

