

# NETL In-House Characterization of Mercury in Coal Combustion By-Products

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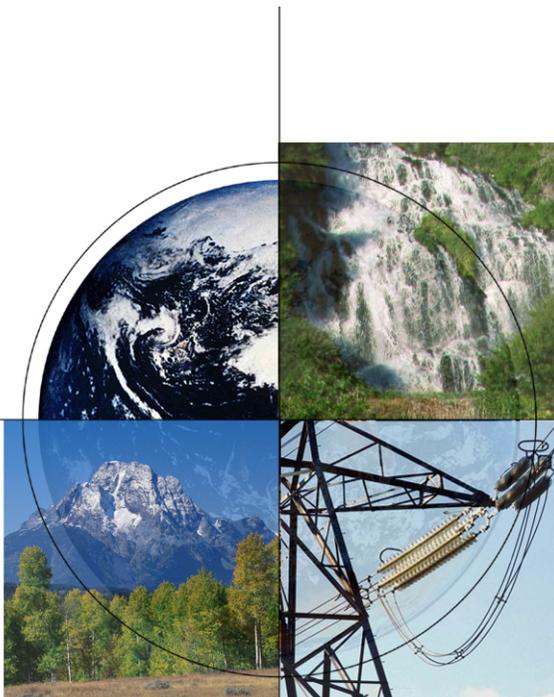
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**Session: Byproduct Characterization/  
Management**

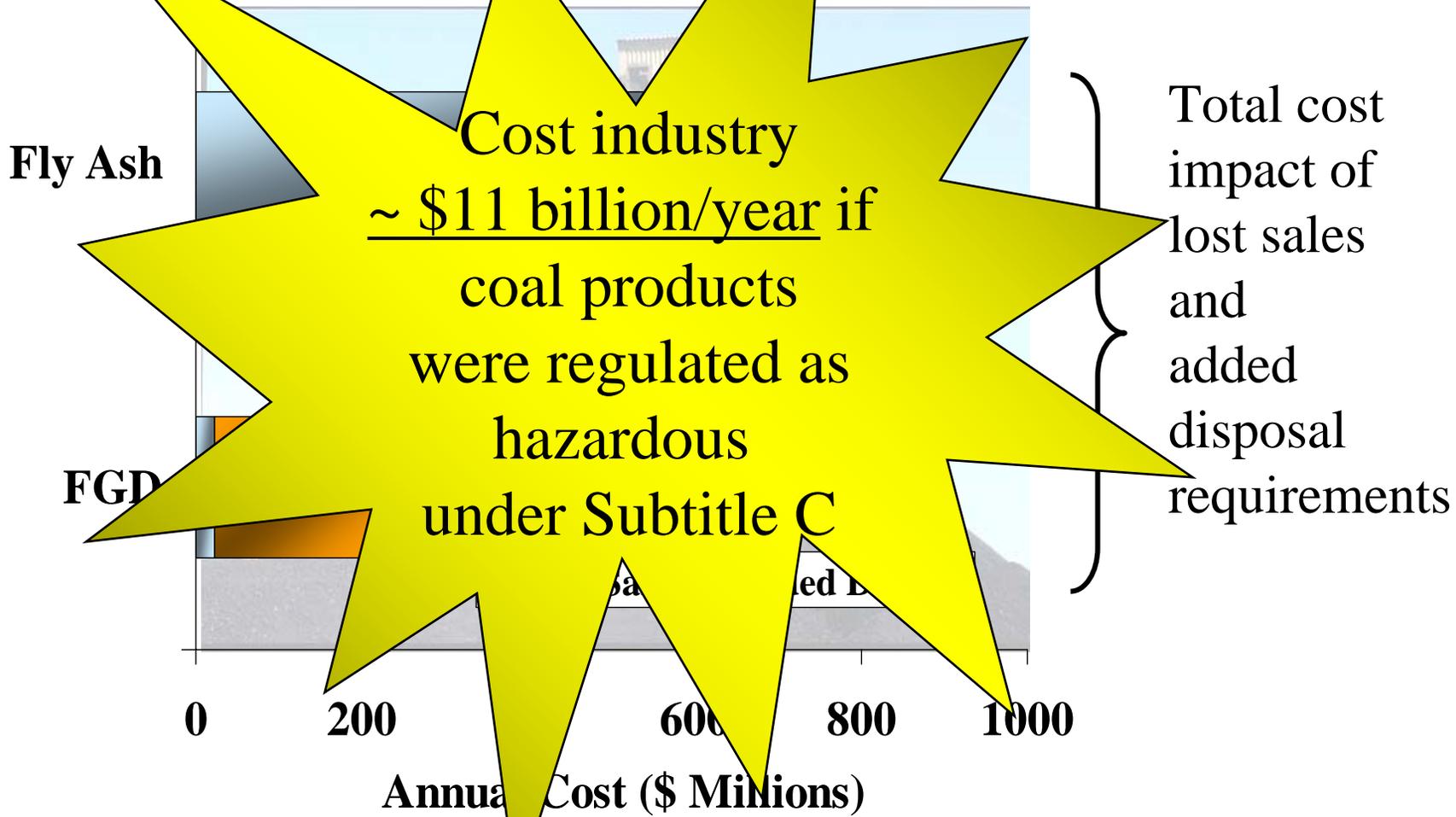
**Mercury Control Technology  
R&D Program Review**



**July 14, 2005**



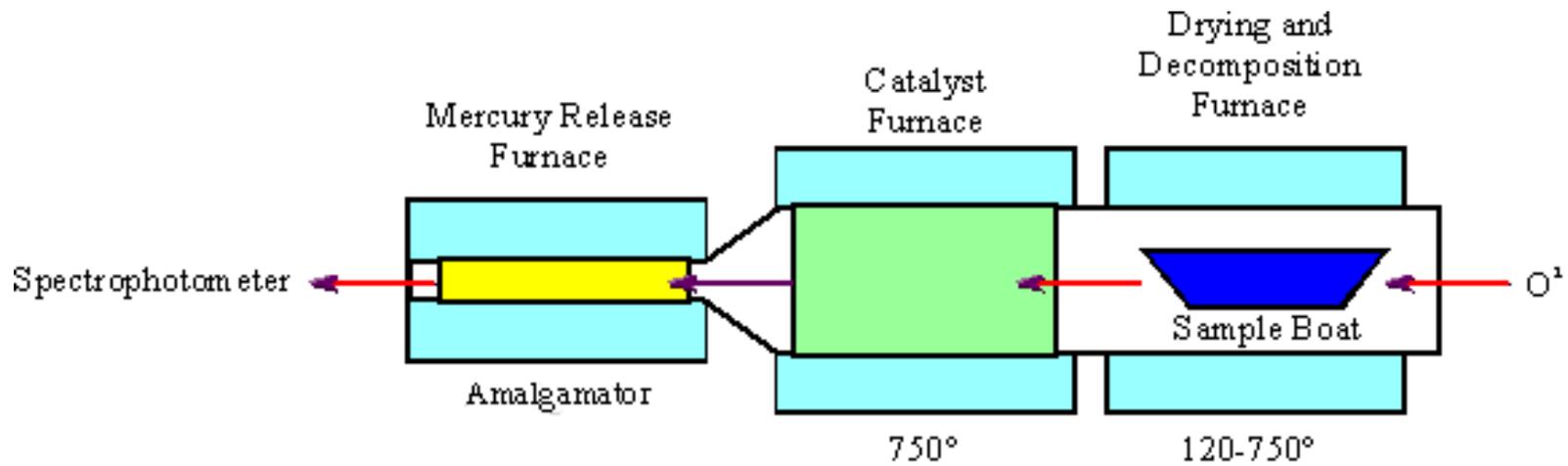
# Potential Impact of Regulations on Coal Product



# Hg Analysis

## Techniques

- Solids via Milestone DMA-80
- Leachate via CVAA (DL = 1 ng/L = 1 ppt)



DMA-80 Mercury Analyzer

# In a Nut Shell

## 1. FLY ASH - Comparison of leaching methods for a single bituminous ash

- complex leaching chemistry
- 5 batch leaching methods + long term column leaching

## 2. FGD GYPSUM - Continuous leaching of FGD-derived gypsum and wallboard

- no mercury in leachate
- retention due to unidentified iron-containing phase



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# 1

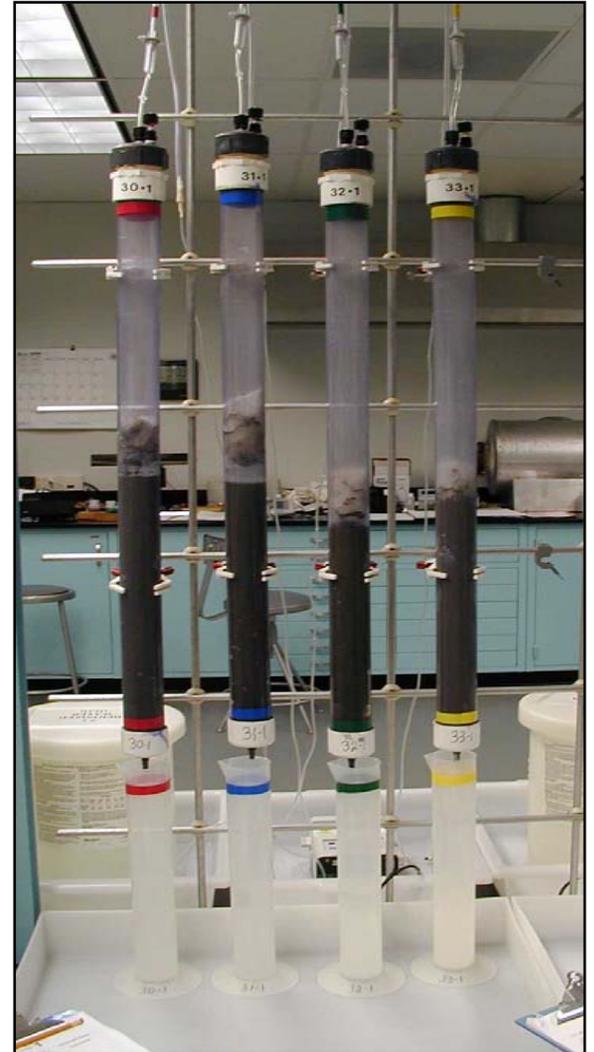
## Comparison of leaching methods for a single ash

**bituminous coal fly ash**

- a. Leaching chemistry**
- b. Multi-method comparison**

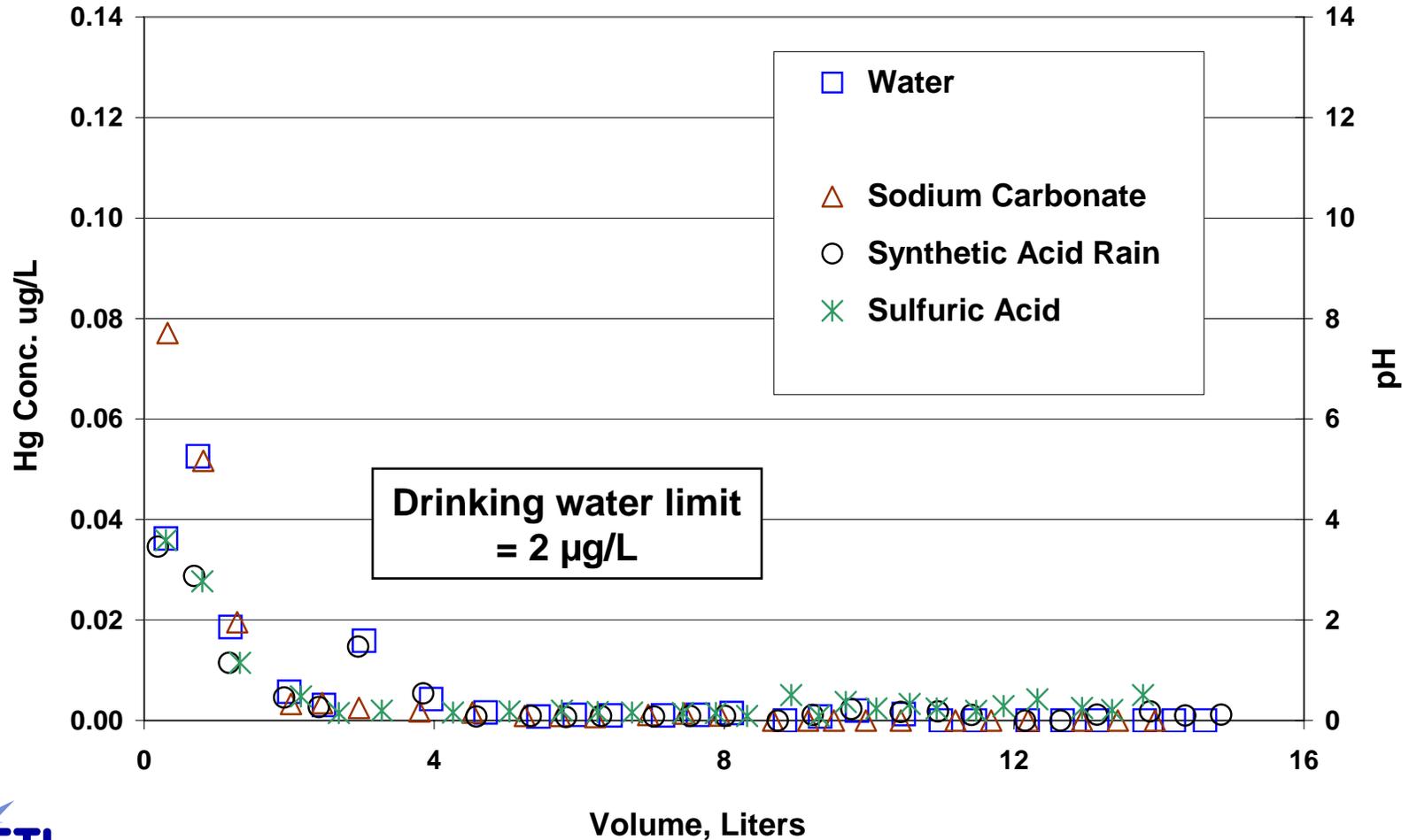
# Long-Term Column Leaching

Leachant	ID	Type	pH
Sulfuric Acid	H <sub>2</sub> SO <sub>4</sub>	acid mine drainage	1.2
Acetic Acid	HAc	MSW landfill	2.9
Synthetic Precipitation	SP	acid rain	4.2
Water	H <sub>2</sub> O	neutral	6.0
Sodium Carbonate	Na <sub>2</sub> CO <sub>3</sub>	high pH	11.1

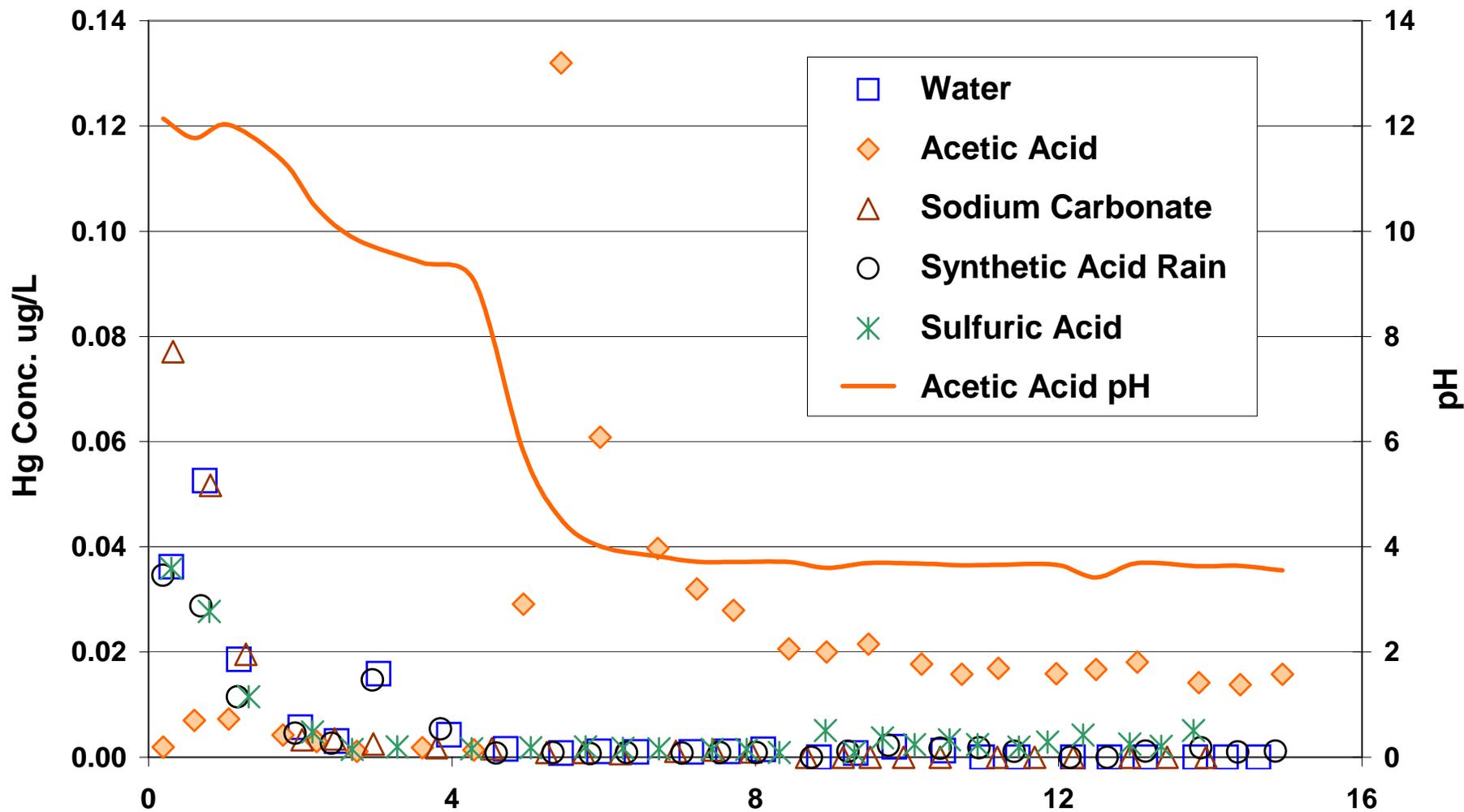


# Leaching Chemistry

## Mercury in FA77 (Bituminous, Interlab sample) Leachates



# Mercury in FA77 (Bituminous, Interlab sample) Leachates

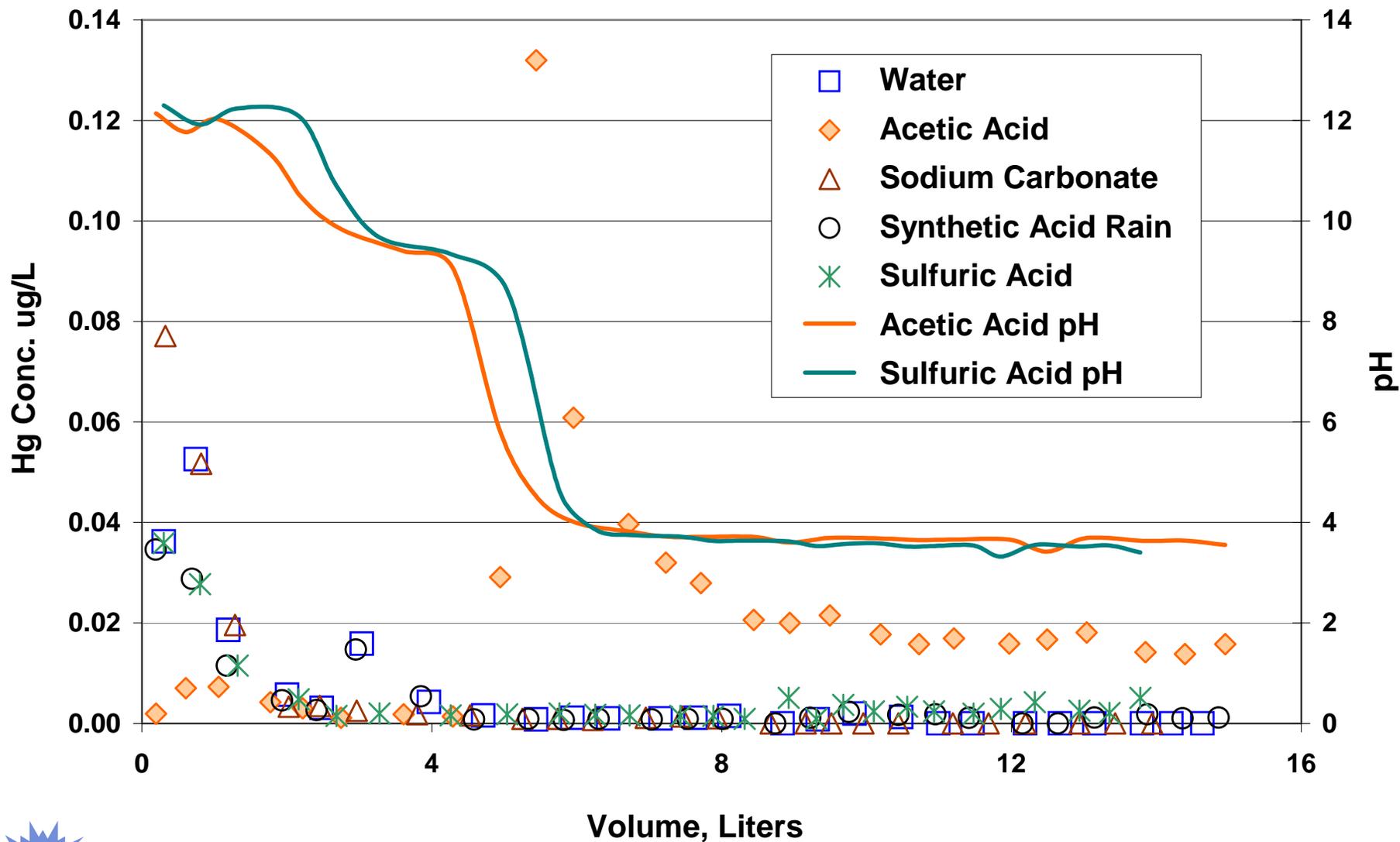


**Drinking water limit  
= 2  $\mu\text{g/L}$**

**Volume, Liters**



# Mercury in FA77 (Bituminous, Interlab sample) Leachates



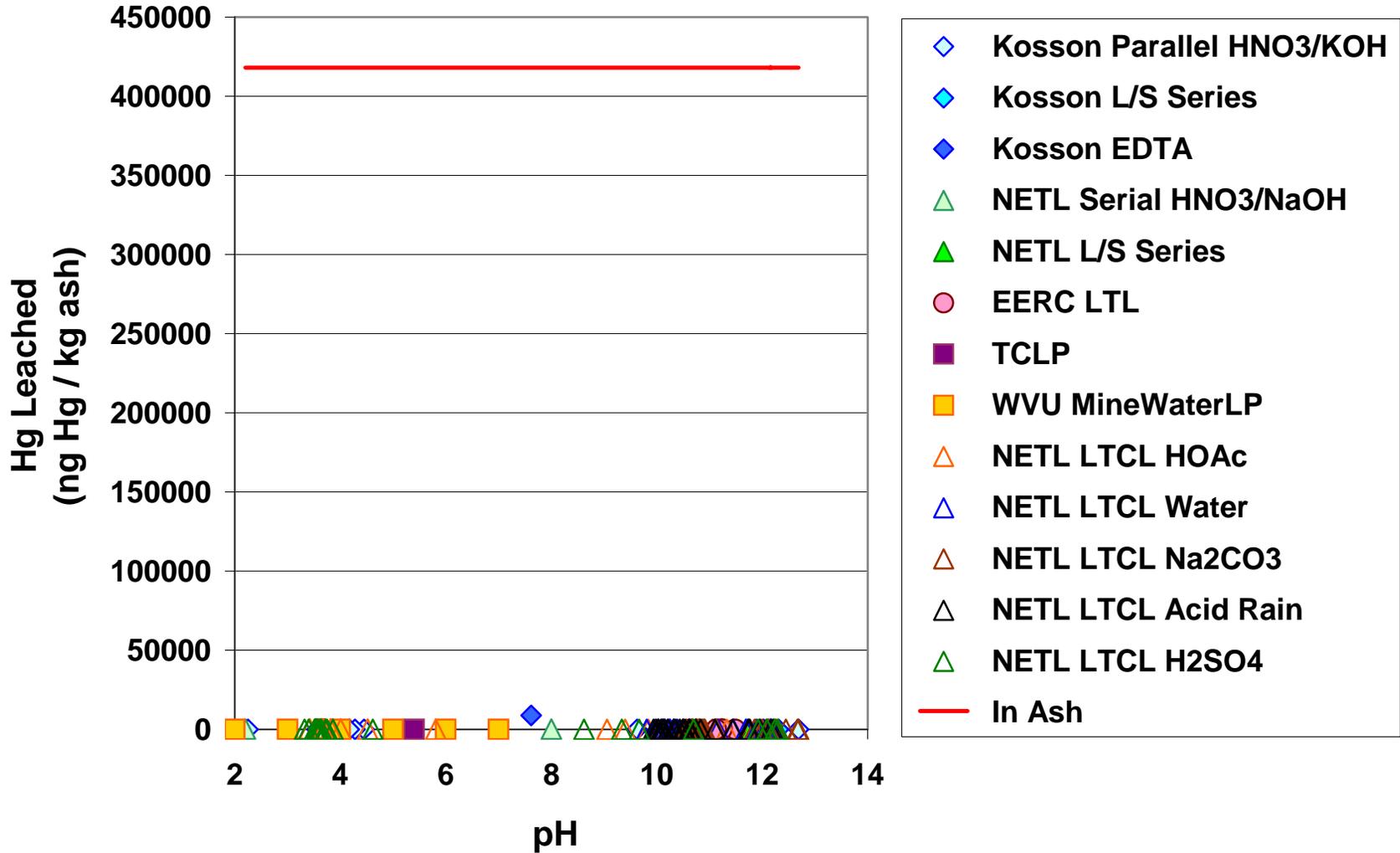
# Batch Leaching Procedures

## Method Comparison Summary

Method (Source)	Leaching Type	Total Steps	Minimum Time	Sample Per Rep	Leachants
SBLP (NETL)	Serial batch	8	2 d	50 g	H <sub>2</sub> O HNO <sub>3</sub>
SGLP (EERC)	Batch	3	60 d	300 g	H <sub>2</sub> O
MWLP (NMLRC)	Serial batch	Varies	Varies 1 d / cyc.	100 g	H <sub>2</sub> O H <sub>2</sub> SO <sub>4</sub>
3-Tier (Kosson)	Titrations + Batch	2 19	2 d / run 14 ?	900 g	H <sub>2</sub> O EDTA HNO <sub>3</sub> KOH



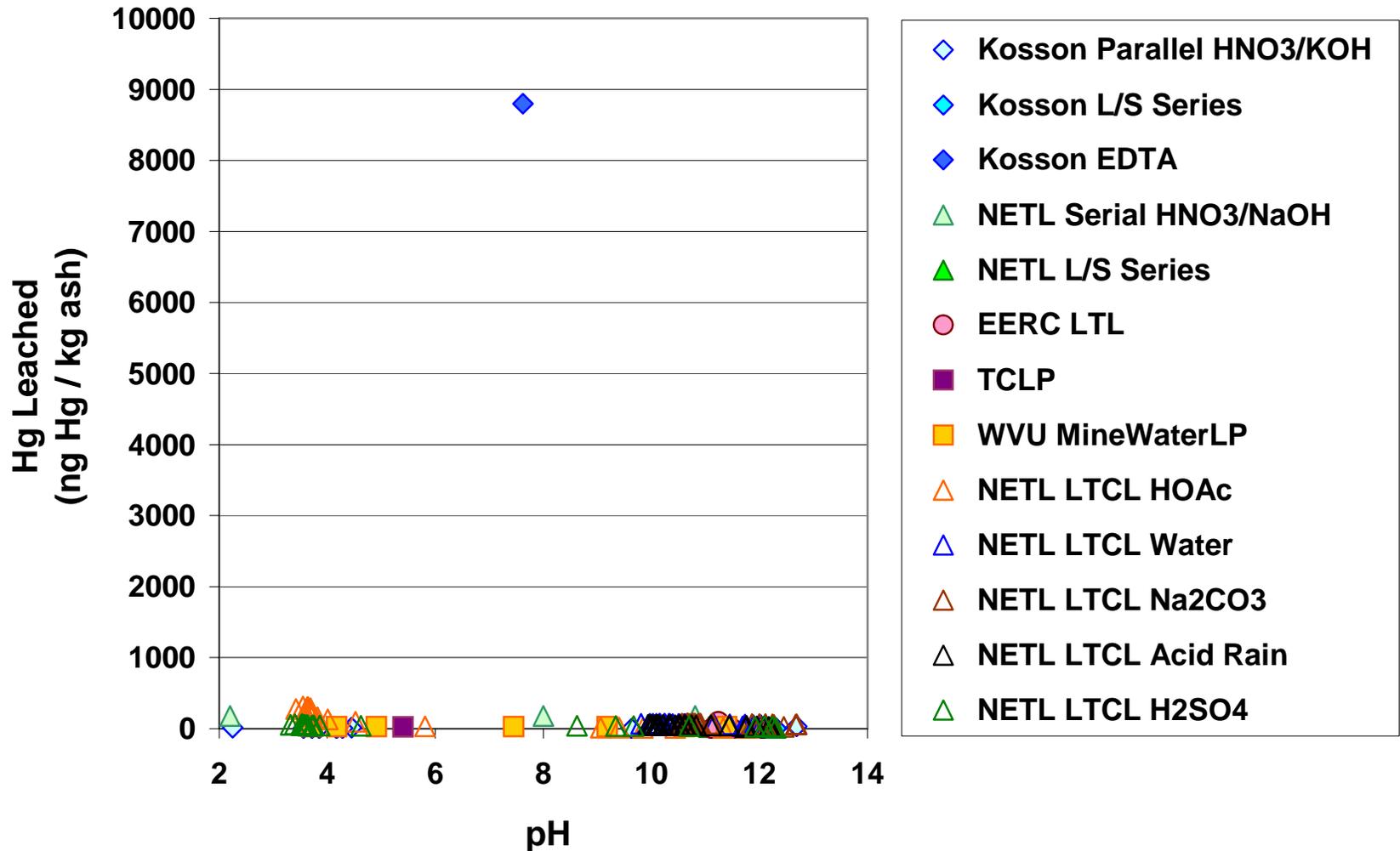
# Hg Leach



**Very little Hg is leached (Maximum = 2.1%)**



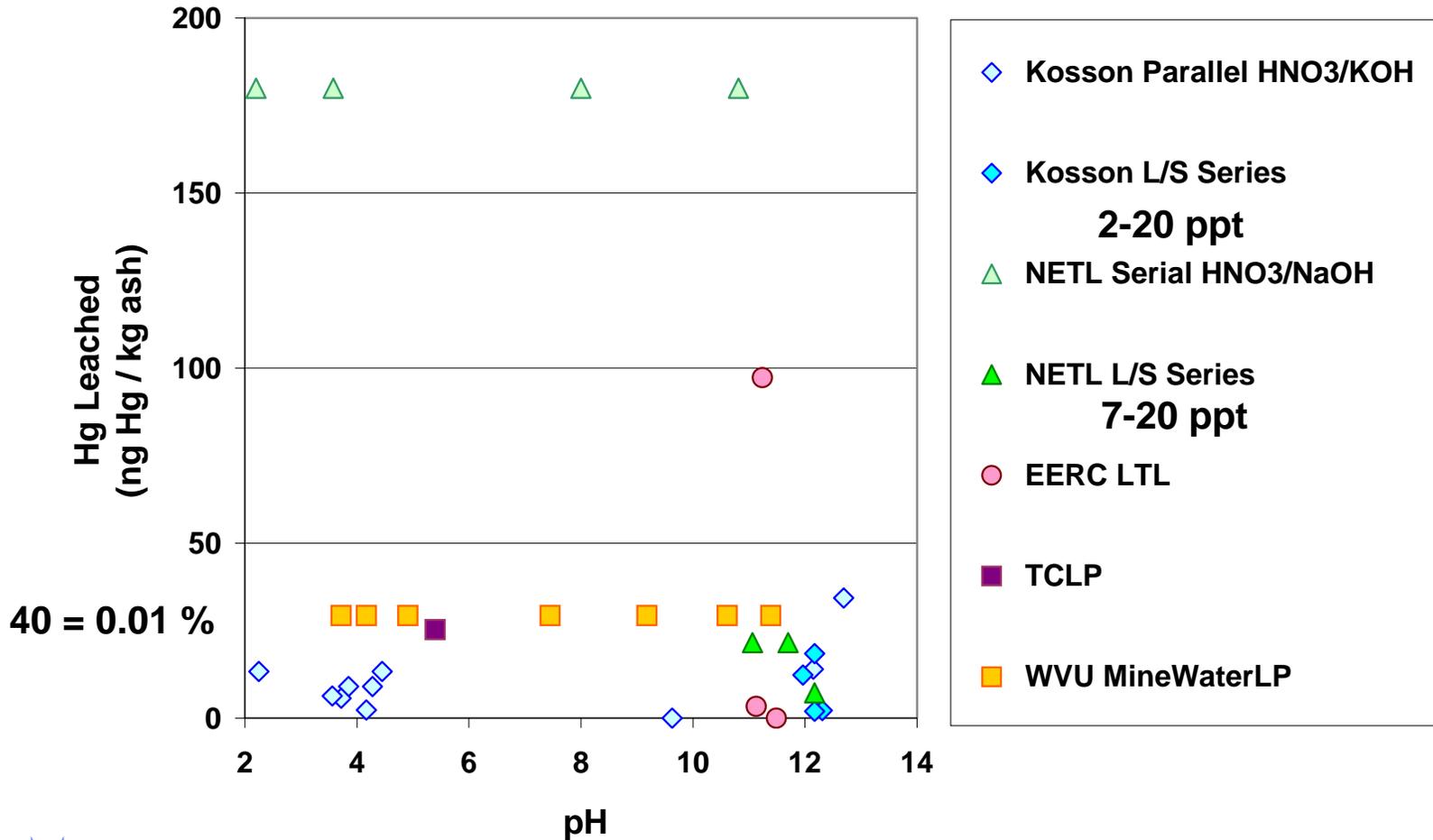
# Hg Leach



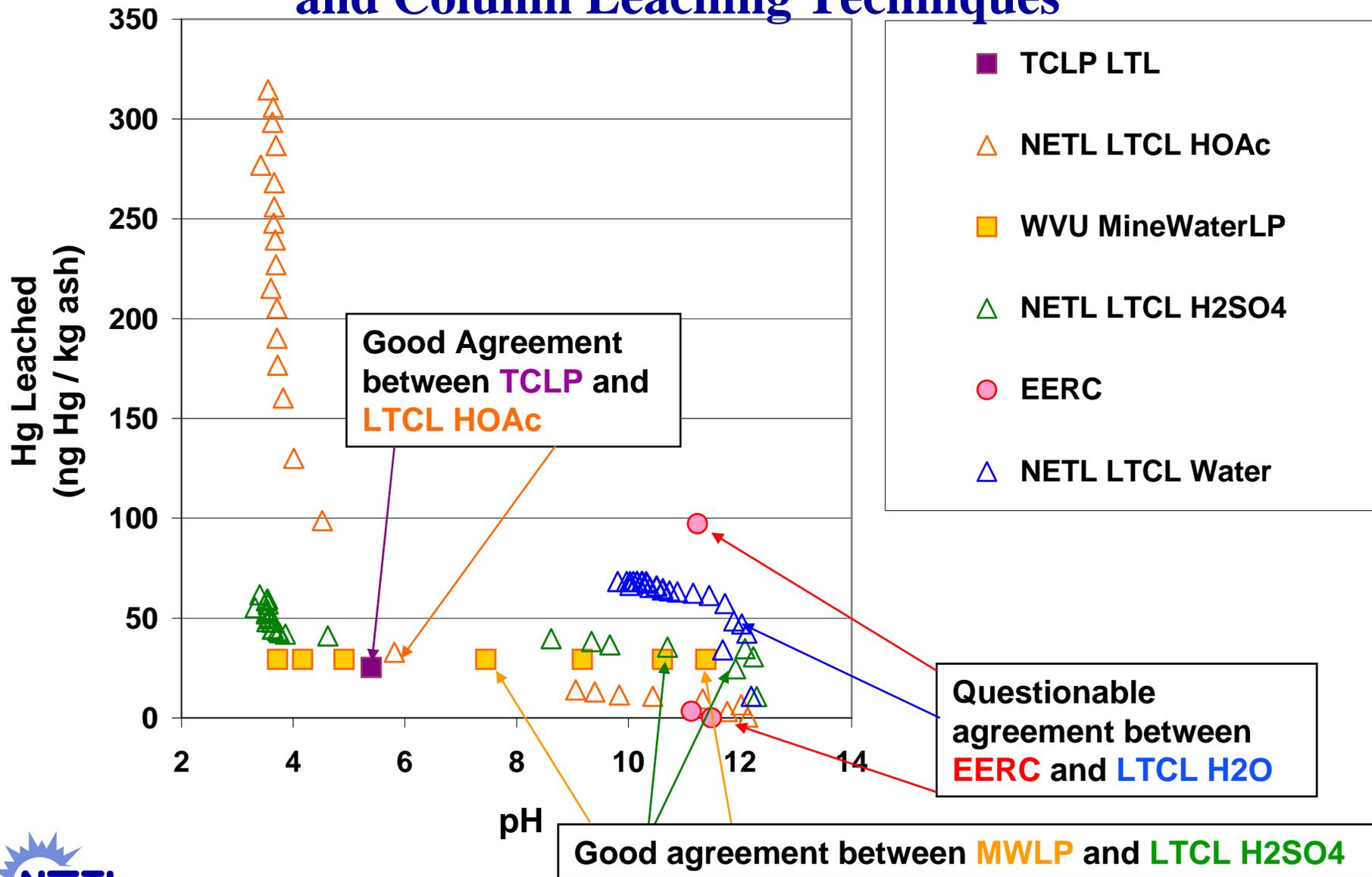
**Very little Hg is leached**  
**EDTA = 2.1%, HOAc 0.08%**



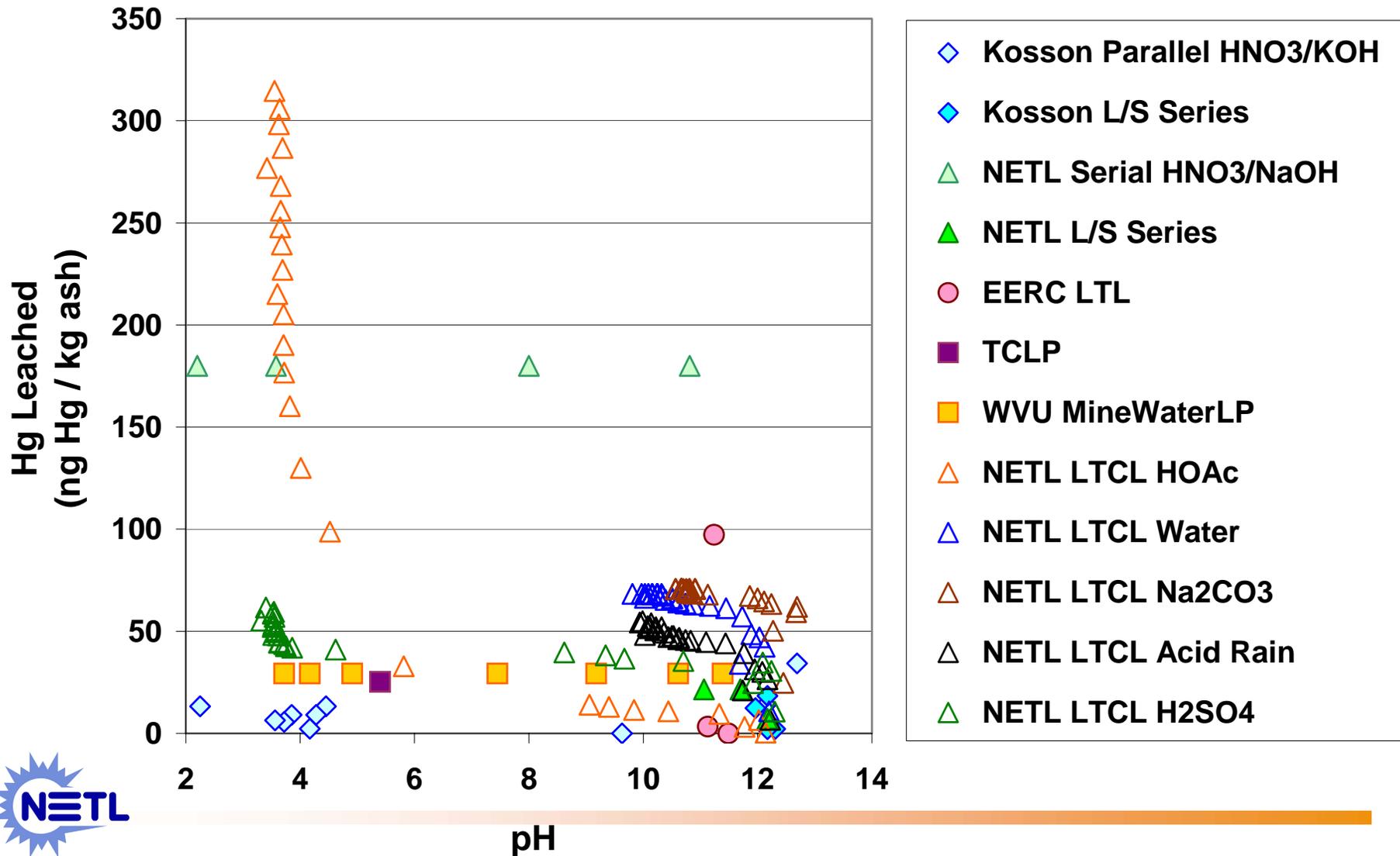
# Batch Leaching Techniques



# Comparison of Selected Batch and Column Leaching Techniques



# Comparison of Batch and Column Leaching Results for a Single Flyash



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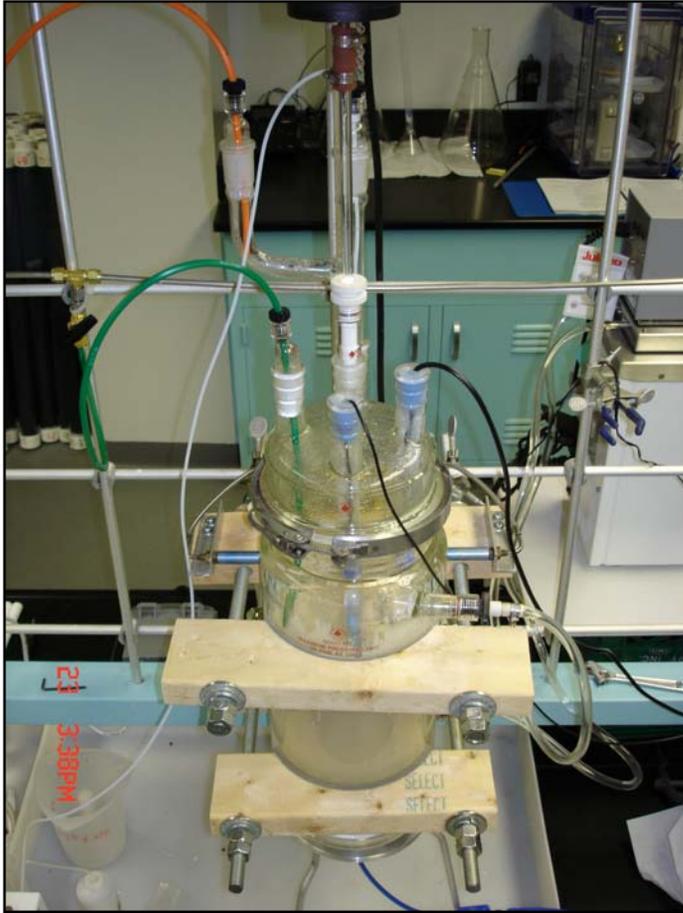
# Continuous leaching of FGD-derived gypsum and wallboard

# Hg Capture and Release in FGD Solids

- How mobile is the Hg in FGD gypsum and wallboard?
- What are the mechanisms of Hg retention in FGD products?



# Leaching of FGD-gypsum



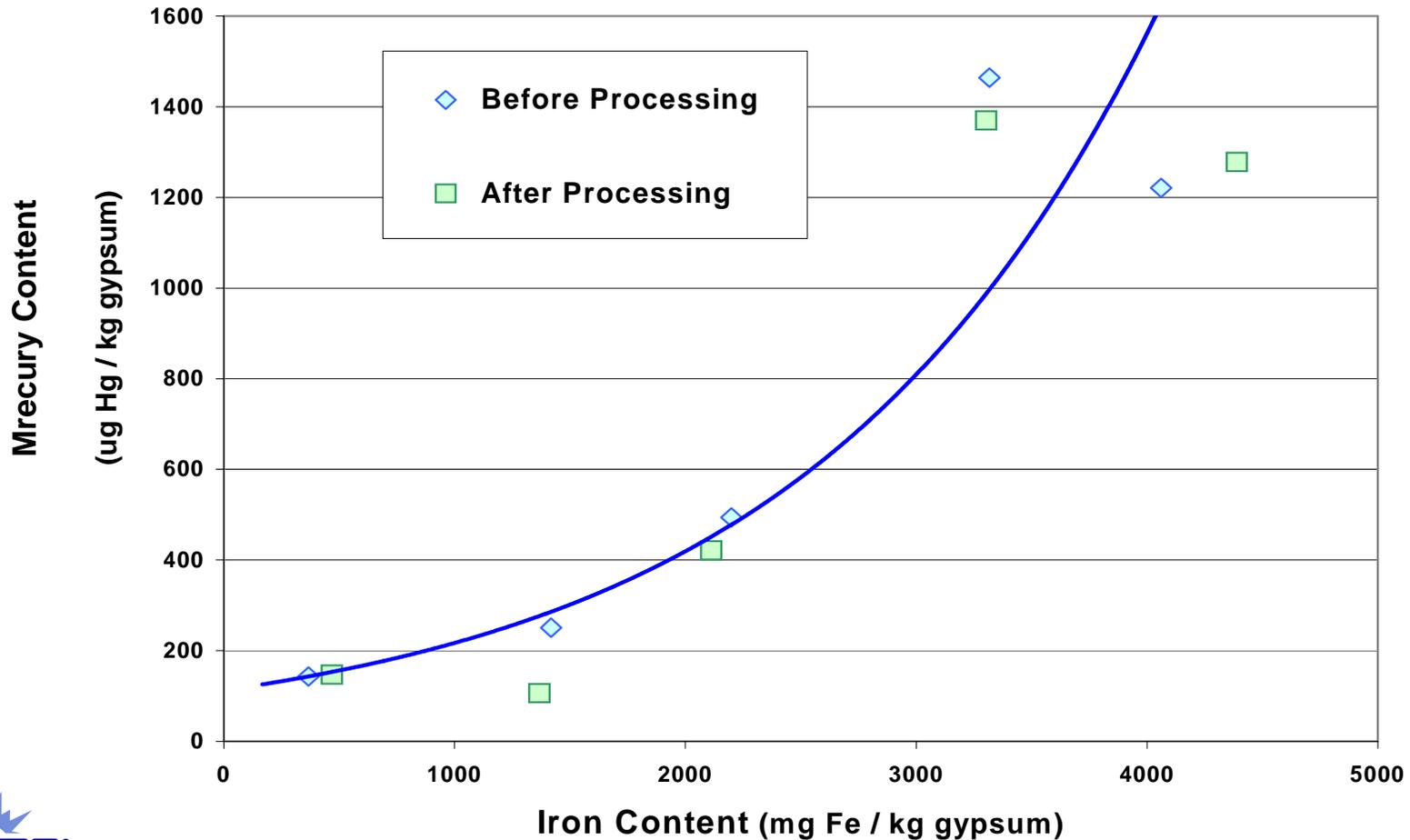
- **Gypsum leaching**
  - Gypsum totally dissolved
  - Leachate: No mercury
  - Residue
    - < 1% of original material
    - Fe, Al
    - Contains most of / all Hg
- **Wallboard post-leaching residue**
  - Gypsum totally dissolved
  - Leachate: About 1% of Hg leached
  - Residue
    - about 2% of original material
    - Fe, Al
    - Contains most of / all Hg
- **Conclusion: Phase responsible for strong Hg retention is not gypsum**
  - Fe or mixed Fe-Al phase
  - Mineralogy not determined

## Partitioning of Hg during laboratory FGD-slurry settling studies

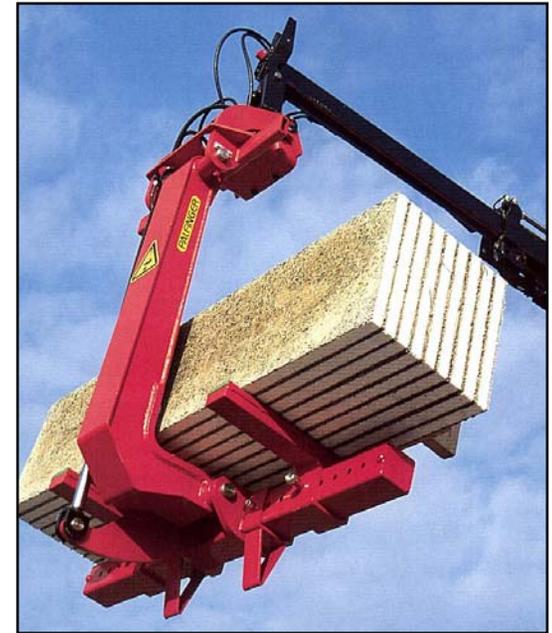
Mercury in FGD settled-slurry layers ( $\mu\text{g}/\text{kg} = \text{ppb}$ )	Top Layer	Bottom Layer	Ratio of Hg in Top to Hg in Bottom Layer
Slurry 1, Aliquot 1	$3,560 \pm 170$	$72 \pm 6$	$49 \pm 6$
Slurry 1, Aliquot 2	$2,900 \pm 80$	$108 \pm 10$	$26 \pm 3$
Slurry 2	$13,000 \pm 800$	$700 \pm 27$	$19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

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

# Mercury Content of Gypsum Tends to Correlate with Iron Content



**Current Hypothesis** – 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



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# Summary

- 1. Comparison of leaching methods for a single ash**
  - Complex leaching chemistry
  - General agreement on the magnitude of leaching
  - Much difference in the details
  
- 2. Leaching of FGD-derived gypsum and wallboard**
  - No mercury in leachate
  - Retention due to unidentified iron-containing phase

# NETL In-House Research

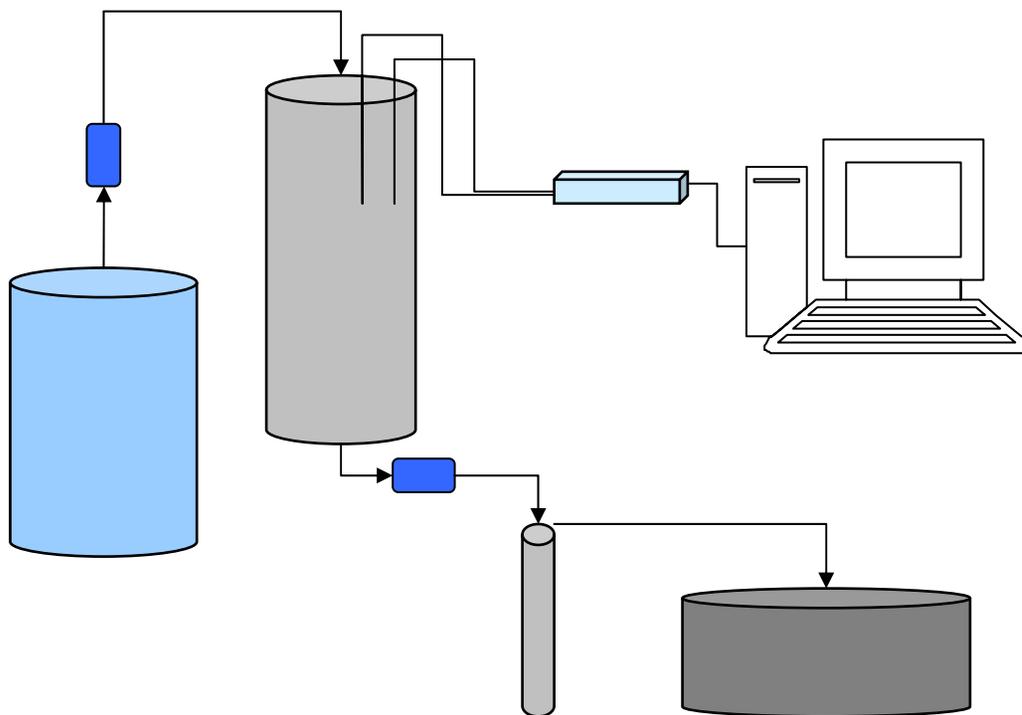
## Hg Release from CUB

- 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



# Leaching of FGD products using a CSTX

- Measure Hg and metals release
- Leachant
  - Ultra pure water
  - Dilute HCl



# Mercury retention during wallboard production from FGD-gypsum

<b>Mercury in FGD Products (<math>\mu\text{g}/\text{kg} = \text{ppb}</math>)</b>					
	<b>Plant A</b>	<b>Plant B</b>	<b>Plant C</b>	<b>Plant D</b>	<b>Plant E</b>
<b>Feed FGD-Derived Gypsum</b>	<b>143 <math>\pm</math> 4</b>	<b>251 <math>\pm</math> 7</b>	<b>1221 <math>\pm</math> 51</b>	<b>1464 <math>\pm</math> 50</b>	<b>494 <math>\pm</math> 16</b>
<b>Product FGD-Derived Wallboard</b>	<b>147 <math>\pm</math> 2</b>	<b>106 <math>\pm</math> 5</b>	<b>1278 <math>\pm</math> 63</b>	<b>1370 <math>\pm</math> 59</b>	<b>421 <math>\pm</math> 3</b>
<b>% Hg Retained During Processing</b>	<b>103 <math>\pm</math> 3%</b>	<b>42 <math>\pm</math> 2%</b>	<b>104 <math>\pm</math> 7%</b>	<b>94 <math>\pm</math> 5%</b>	<b>88 <math>\pm</math> 3%</b>

# Current Work

## Iron retention during FGD-gypsum to wallboard production

### Fe in FGD Products (mg/kg)

	Plant A	Plant B	Plant C	Plant D	Plant E
Feed FGD-Derived Gypsum	367	1418	4061	3317	2199
Product FGD-Derived Wallboard	468	1368	4389	3303	2112
% Fe Retained During Processing	128%	97%	108%	100%	96%