NETL CUB Characterization

Ann Kim

Mercury Control Technology
R&D Program Review Meeting
August 13, 2003

Effect on CUB

- Control transfers Hg from gas phase to other phases

Hg →

Potentially increases cost of disposal and decreases utilization of CUB

Goals and Objectives

- Goal
  - To determine the stability of Hg in CUB
    - CUB properties
    - Receiving environment
- Objective
  - Determine rate of Hg release from CUB
    - What will happen (column leaching)
  - Determine mechanism of Hg retention
    - Why it will happen (isotherms)

Column Leaching Study

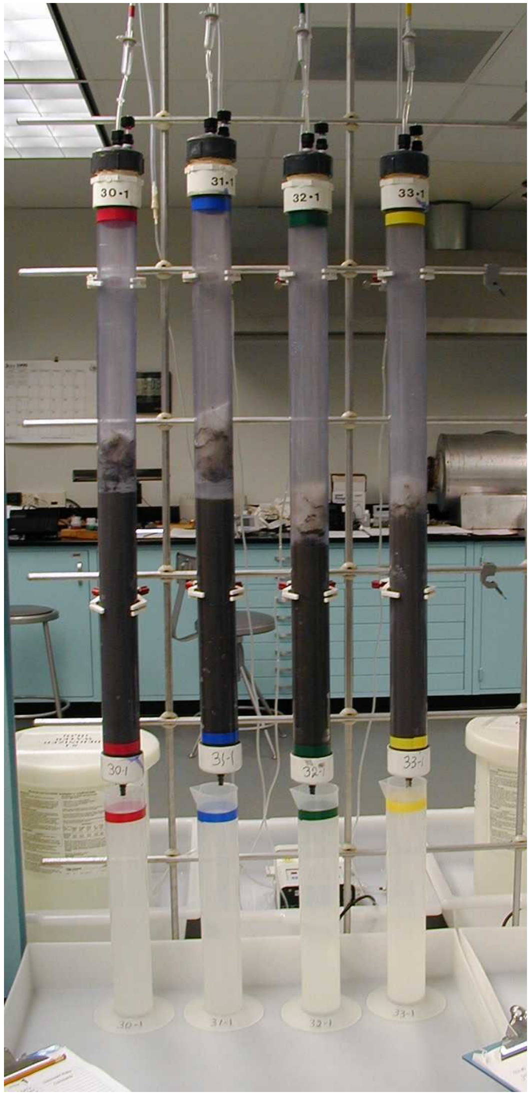
- **Stability of Captured Hg**
  - How much can be extracted from fly ash
  - Under what conditions – chemical environment

- **Materials -** high Hg fly ash
    - conventional PC
    - NETL Hg emission control test (MECT)
    - ADA PAC Injection Tests

- **Technical Challenges**
  - Inherent error in measuring very small numbers
  - Sample size
  - Effect of FA alkalinity
  - Porosity/permeability of high C FA

Technique - Column Leaching

- **20 columns - 5 cm id by 1 m acrylic**
- **5 leachant solutions**
  - Average flow rate 130 mL/d
- **CUB samples**
  - Sample size: 1 kg/column
- **Duration**
  - 30 to 180 days
- **Sampling frequency**
  - 2 to 3 days
- **Hg Analysis - CVAA**



Leachant Solutions

Leachant	ID	#	pH
Water	H_2O	1	6.0
Acetic Acid	HAc	2	2.9
Sodium Carbonate	Na_2CO_3	3	11.1
Synthetic Precipitation	SP	5	4.2
Sulfuric Acid	H_2SO_4	7	1.2

Hg Analysis

- **Solid**
  - DMA-80
  - Triple acid digestion + ICP
- **Leachate**
  - CVAA
    - DL = 1 ng/L

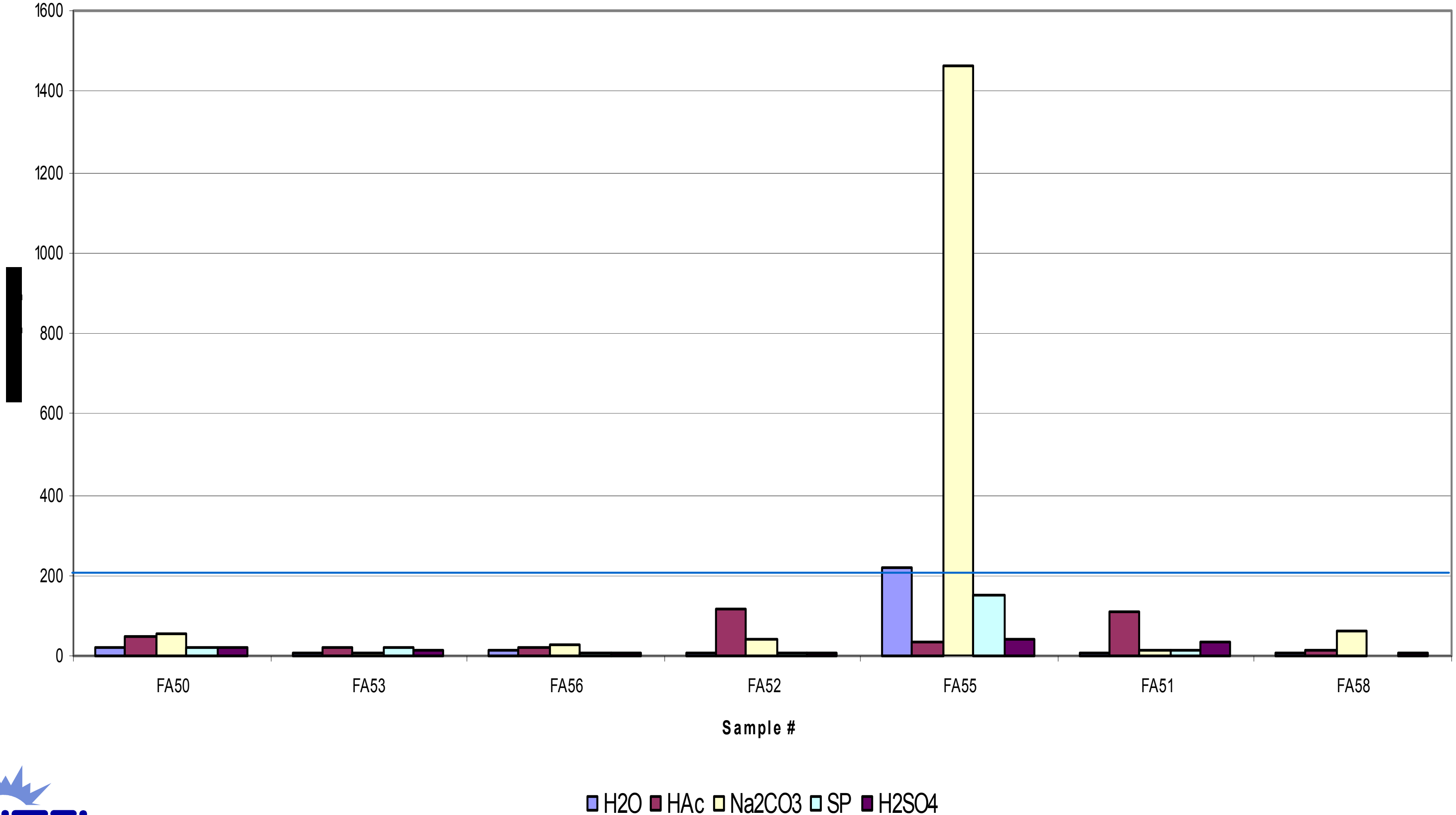
CUB Samples

Sample #	Type	Source	Hg conc., ug/kg	LOI, %
FA50	500#PAC	NETL	1156	1.31
FA53	500#PAC	NETL	1091	2.45
FA56	500#PAC	NETL	1209	1.89
FA52	ADA PAC	Gaston Station	88100	28.66
FA55	ADA PAC	Brayton Point	1527	16.08
FA51	PC		1587	6.46
FA58	500#	NETL	87	1.79

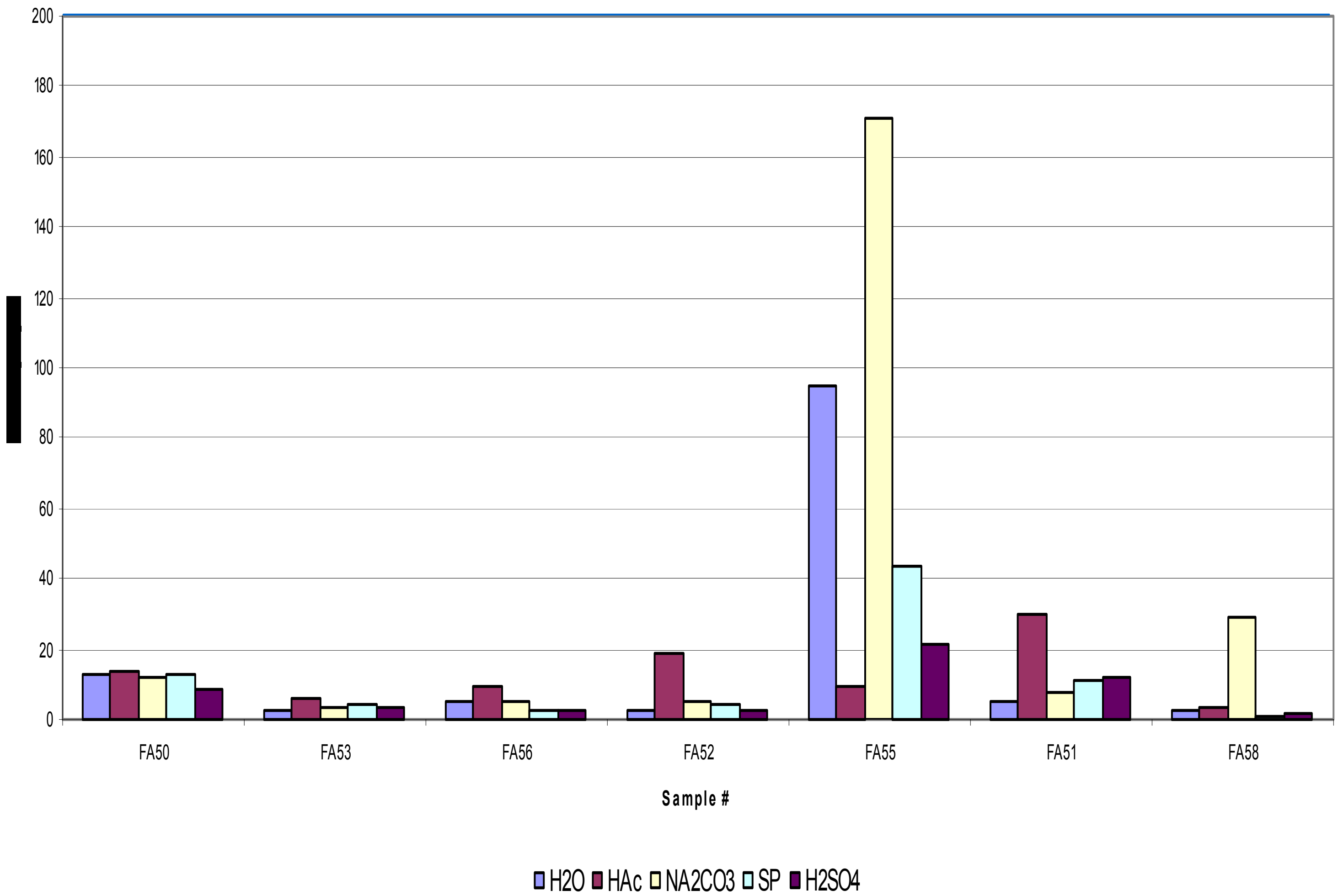
Cumulative Leached Hg, ng/kg

	H2O	HAc	Na2CO3	SP	H2SO4
FA50	259	410	130	94	148
FA53	10	112	8	15	25
FA56	5	146	58	23	42
FA52	3	47	26	3	4
FA55	846	43	1263	465	83
FA51	12	754	7	9	20
FA58	15	45	517	0.5	12

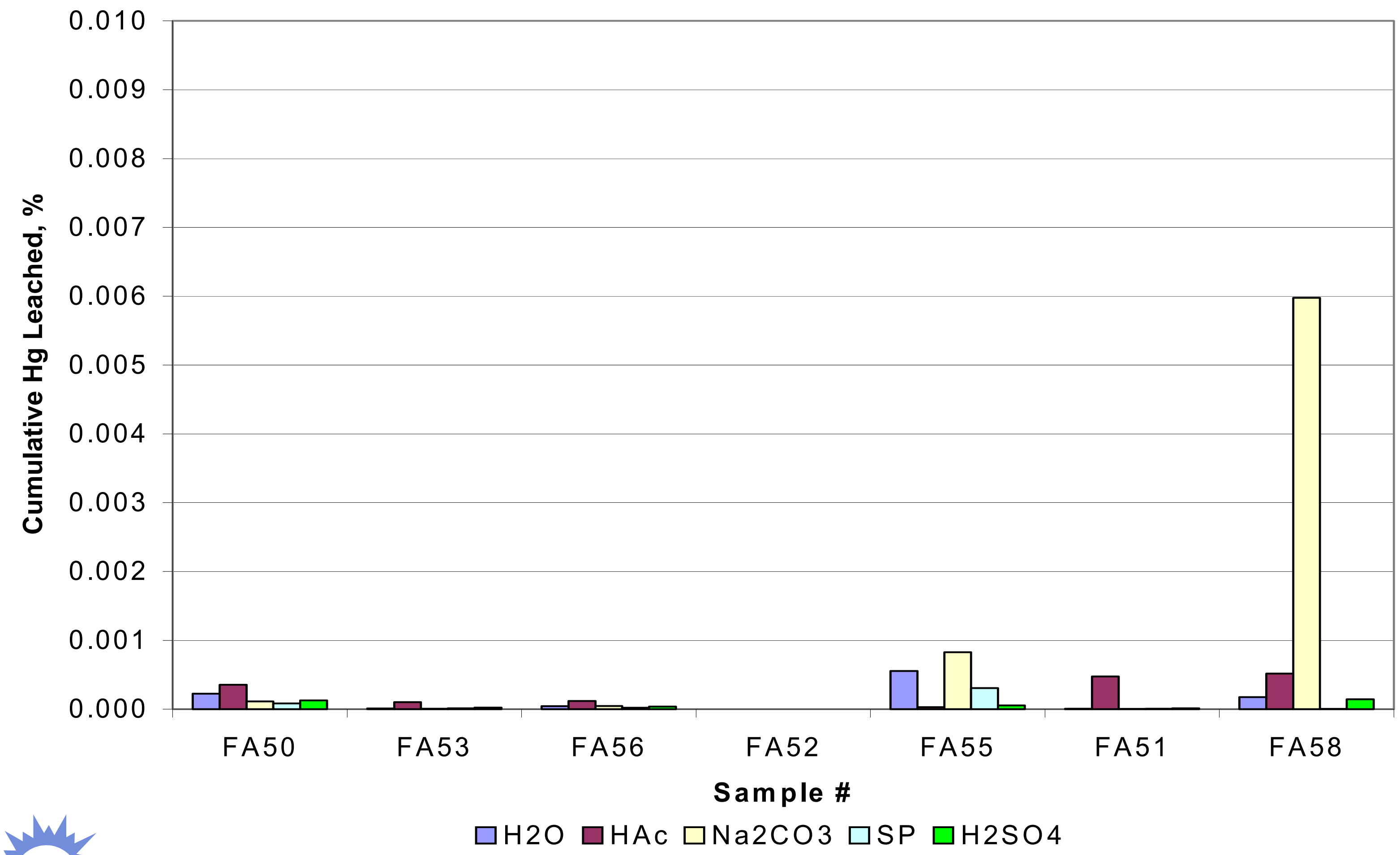
Maximum concentration, ng/L



Average concentration, ng/L



Cumulative Hg Relative to Solid



Adsorption Isotherms

- **Stability of Captured Hg**
  - At equilibrium, how much Hg can fly ash hold
- **Materials**
  - 2 Class F PC fly ash samples
    - FA17 - high C
    - FA24 - low C
- **Technical Challenges**
  - pH control
  - Analytical accuracy/reproducibility

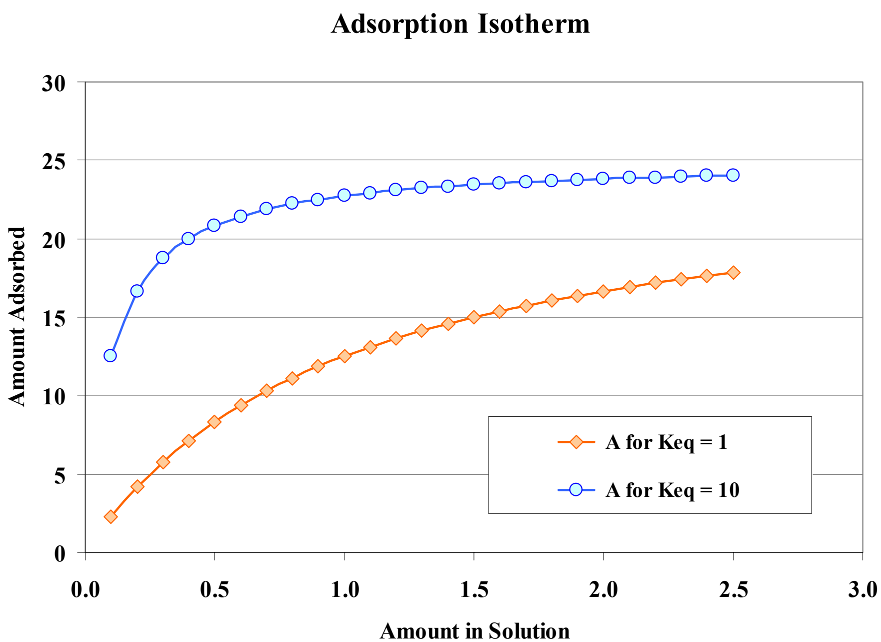
Technique - Adsorption Isotherms

Provide information about extent of adsorption

$A_{max} = 25$

Provide information about strength of adsorption

$K_{EQ}=1$ vs $K_{EQ}= 10$



Relevant Literature

- **Isotherms Hg adsorption onto other materials: Soils and Minerals**
  - Coals, Activated Carbons, Soot
  - Ion Exchange Resins
- **Langmuir Equation**

$$[A] = A_{\max} \frac{Keq[S]}{1+Keq[S]}$$

- **Freundlich Equation**

$$[A] = m[S]^{n}$$

- **Fly ash properties related to Hg adsorption: LOI**

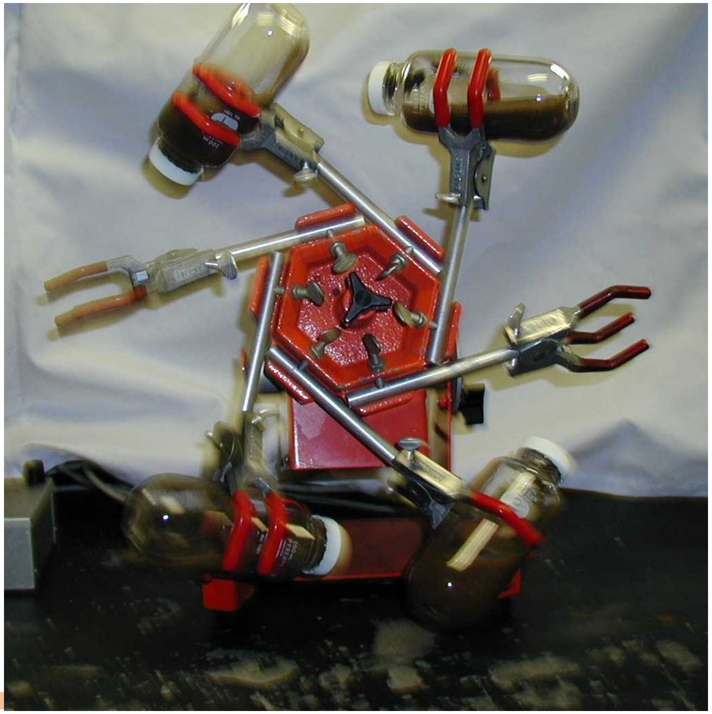
Experimental Procedure

1. Mix fly ash with known volume of H_2O
2. Measure [Hg] in solution at equilibrium

   (will be zero if no desorbable Hg in CUB)
3. Add known amount of Hg(II) to solution [$HgCl_2$ $Hg(OAc)_2$]
4. Allow to equilibrate (with agitation)
5. Measure Hg in solution (CVAA)
6. Calculate Hg adsorbed by difference
7. Measure total Hg in CUB

   digest + CVAA

   solid Hg analyzer



Desorption: done in a similar fashion starting with high [Hg] and diluting.

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Fly Ash Samples

	FA17	FA24
LOI (500°C)	5.2%	1.3%
FeO	9.0%	3.0%
CaO	1.8%	0.6%
Sand	9%	7%
Silt	86%	86%
Clay	5%	7%

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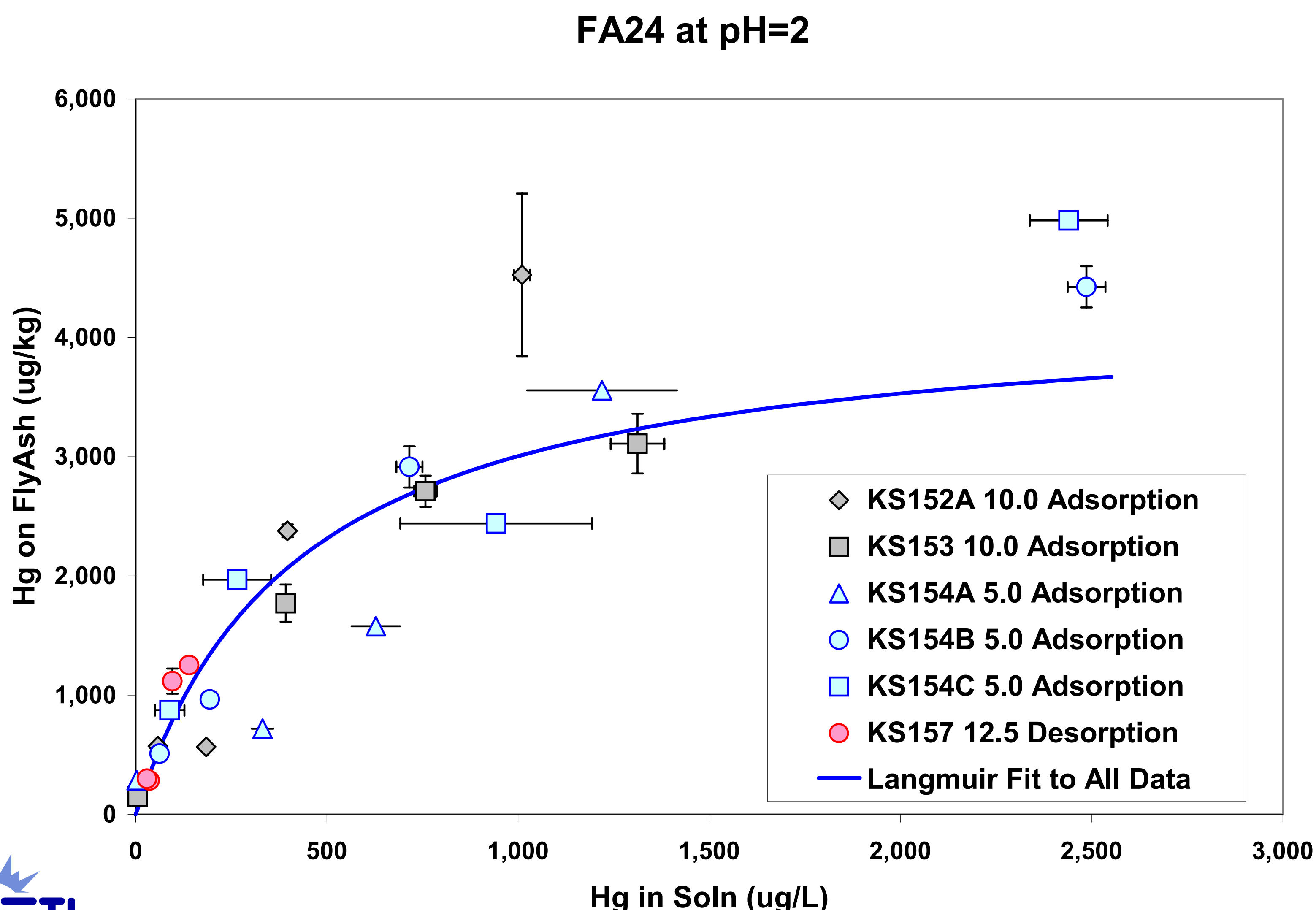
Productivity and Results

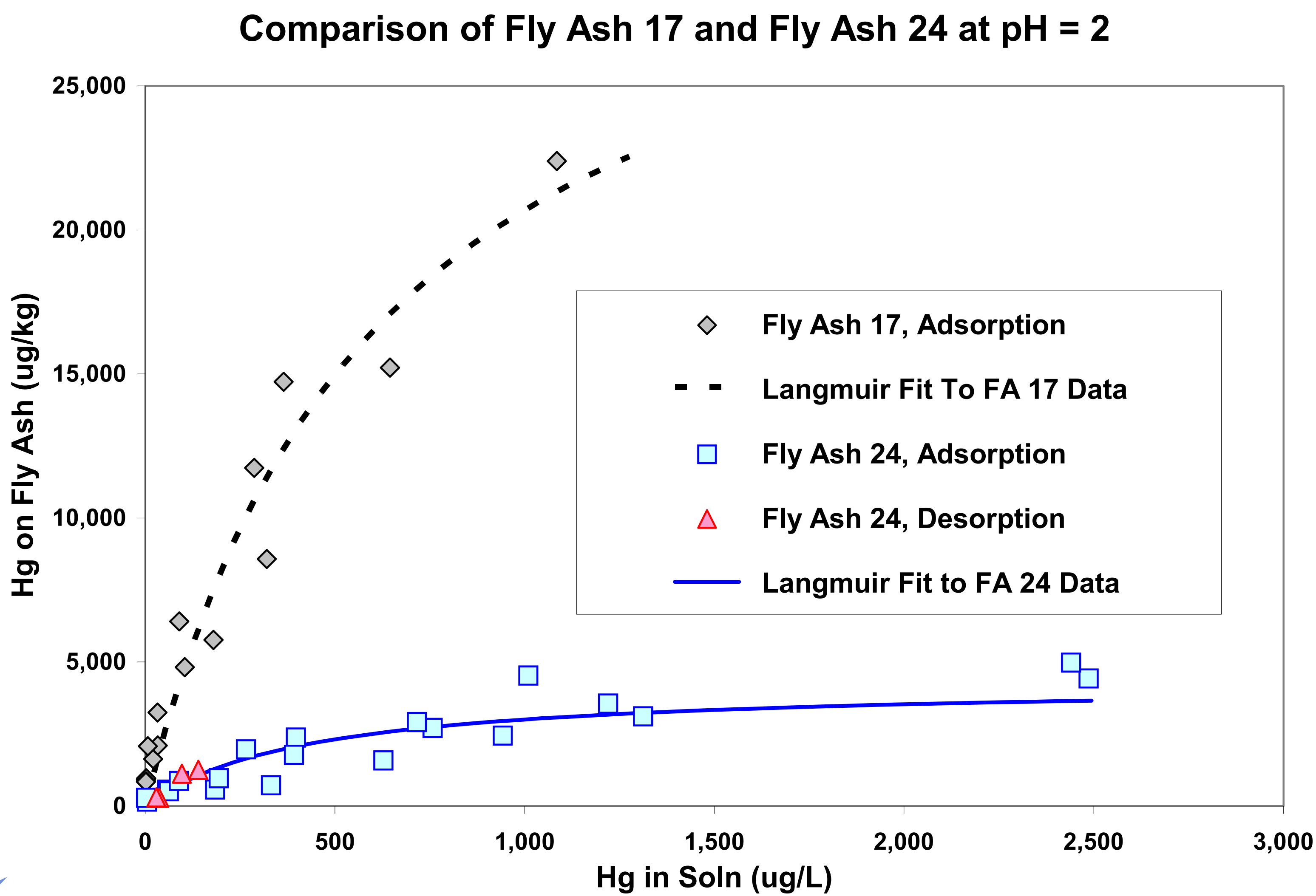
Minumum Duration of 4 Weeks for All Experiments
All Adsorptions Performed at 8 Hg/FA Ratios

Fly Ash		17	24
Adsorption at pH = 2	Liq/Solid = 5	✓	✓
	Liq/Solid = 10	✓	✓
Adsorption at pH = 7	Liq/Solid = 5	✓	✓
	Liq/Solid = 10	✓	✓
Desorption at pH = 2	Liq/Solid = 12		✓
Desorption at pH = 7	Liq/Solid = 12	✓	

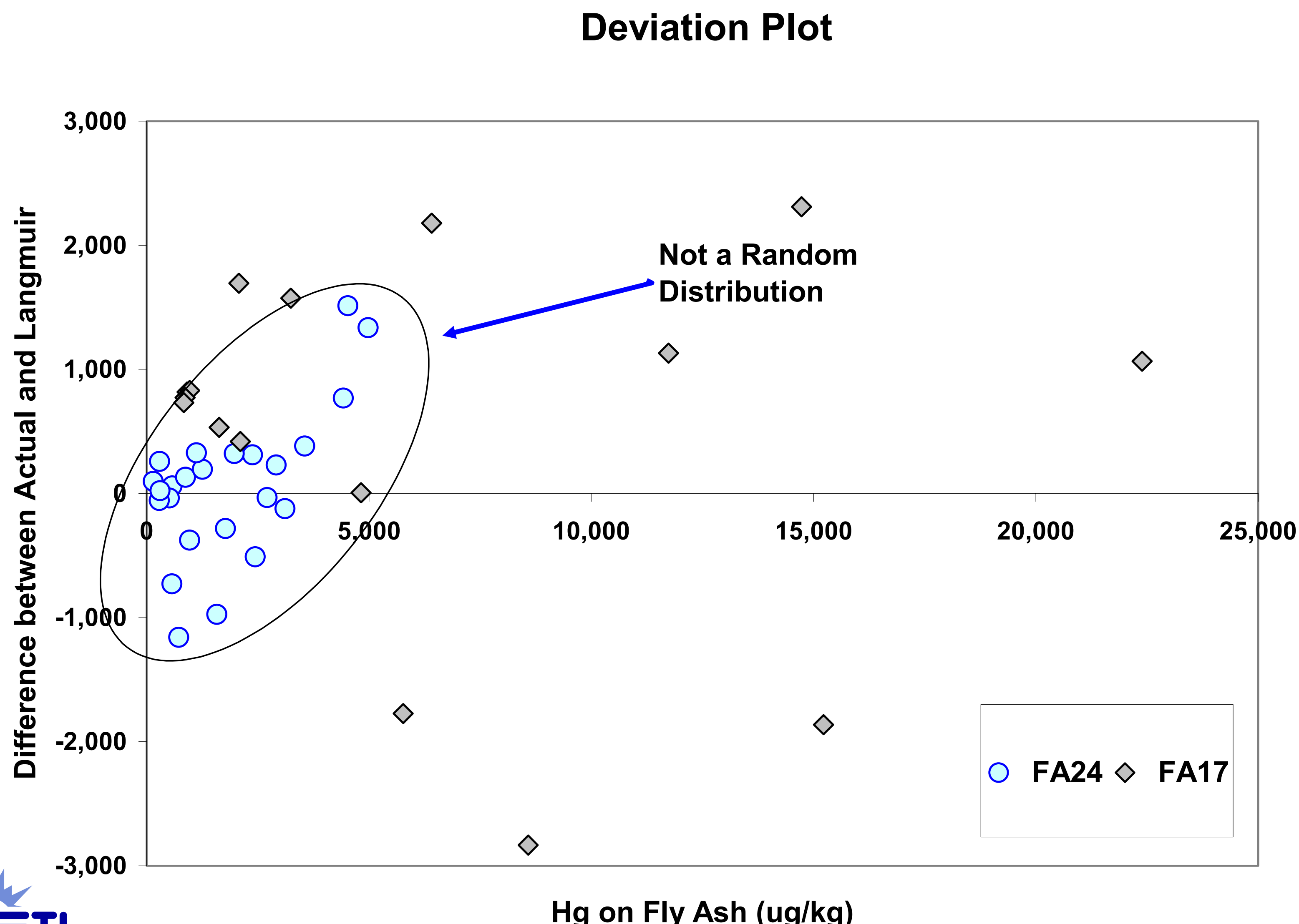
Productivity and Results



Productivity and Results



Productivity and Results



Productivity and Results

- **Although reproducibility continues to be a problem:**
  - The Langmuir adsorption model appears to be a reasonable, but not perfect, approximation for Hg adsorption onto fly ash.
  - No hysteresis upon desorption indicates that the adsorption is reversible at pH=2 for a pre-leached ash.
  - Because column leaching experiments indicate much of the Hg is immobilized, the mechanism for capture during fly ash formation may not be a simple adsorptive process.
  - The high-carbon fly ash (FA 17) has a much higher Hg adsorption capacity than the low-carbon fly ash.
  - The non-random deviation plot (for FA 24) indicates that a better adsorption model may be needed.
- **Analysis of data obtained at pH = 7 is underway.**

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Mercury in CUB

– Questions ????