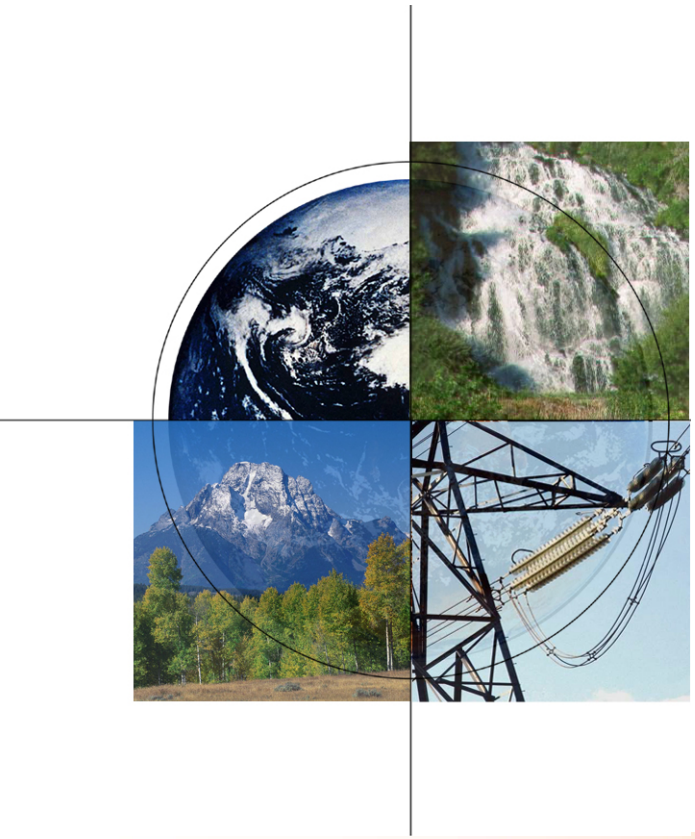
Fixation and Mobilization of Mercury in FGD Gypsum



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DOE / NETL
Mercury Control Technology Conference

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Mercury in FGD gypsum

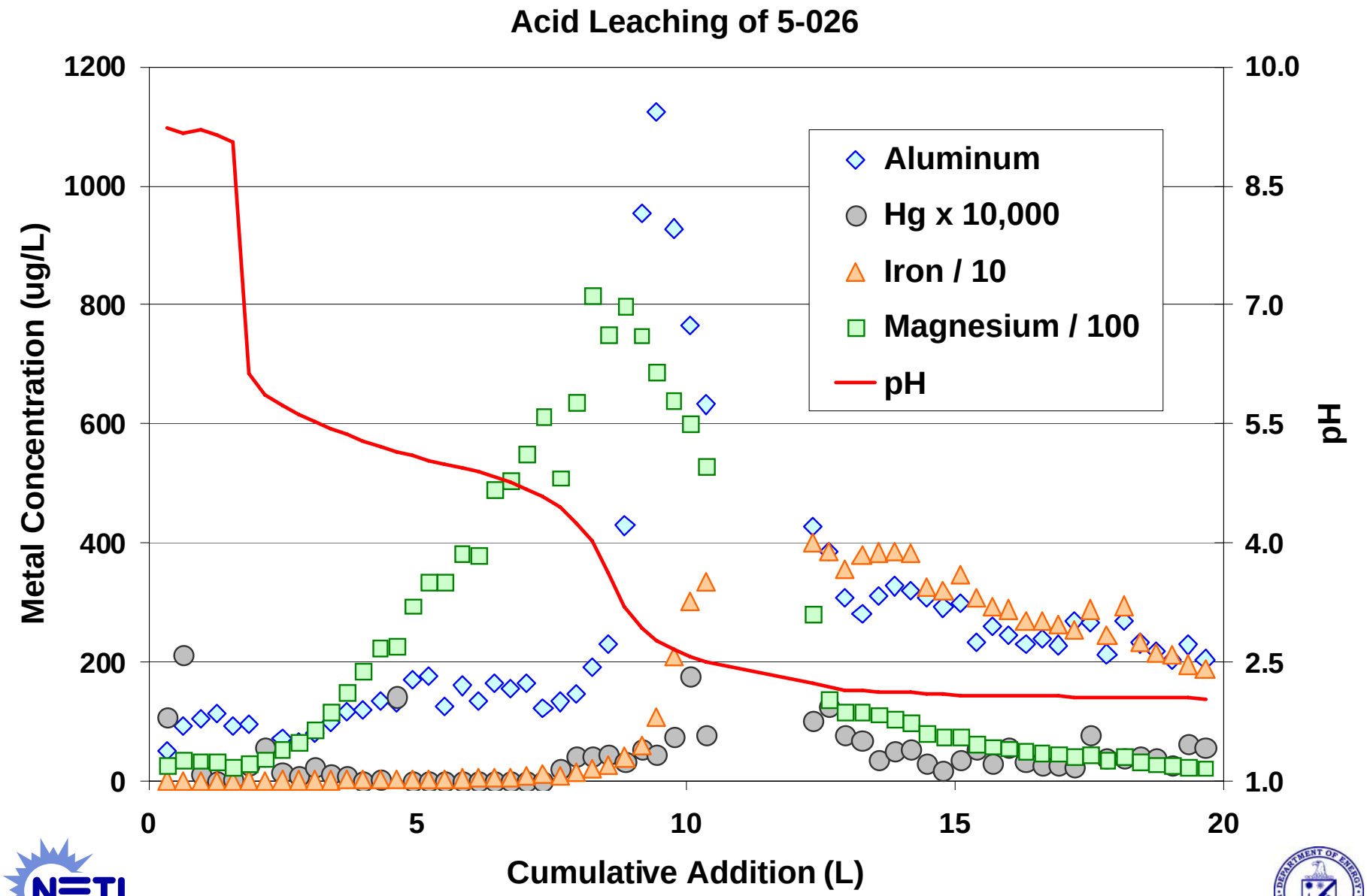
- A leachable fraction
- A residue bound fraction
  - Bound to a phase containing Al, Fe or both
  - Present as H_2O_2 oxidizable phase such as a sulfide
- Gas phase elemental mercury
  - Absorbed elemental mercury
  - Generated by aqueous processes

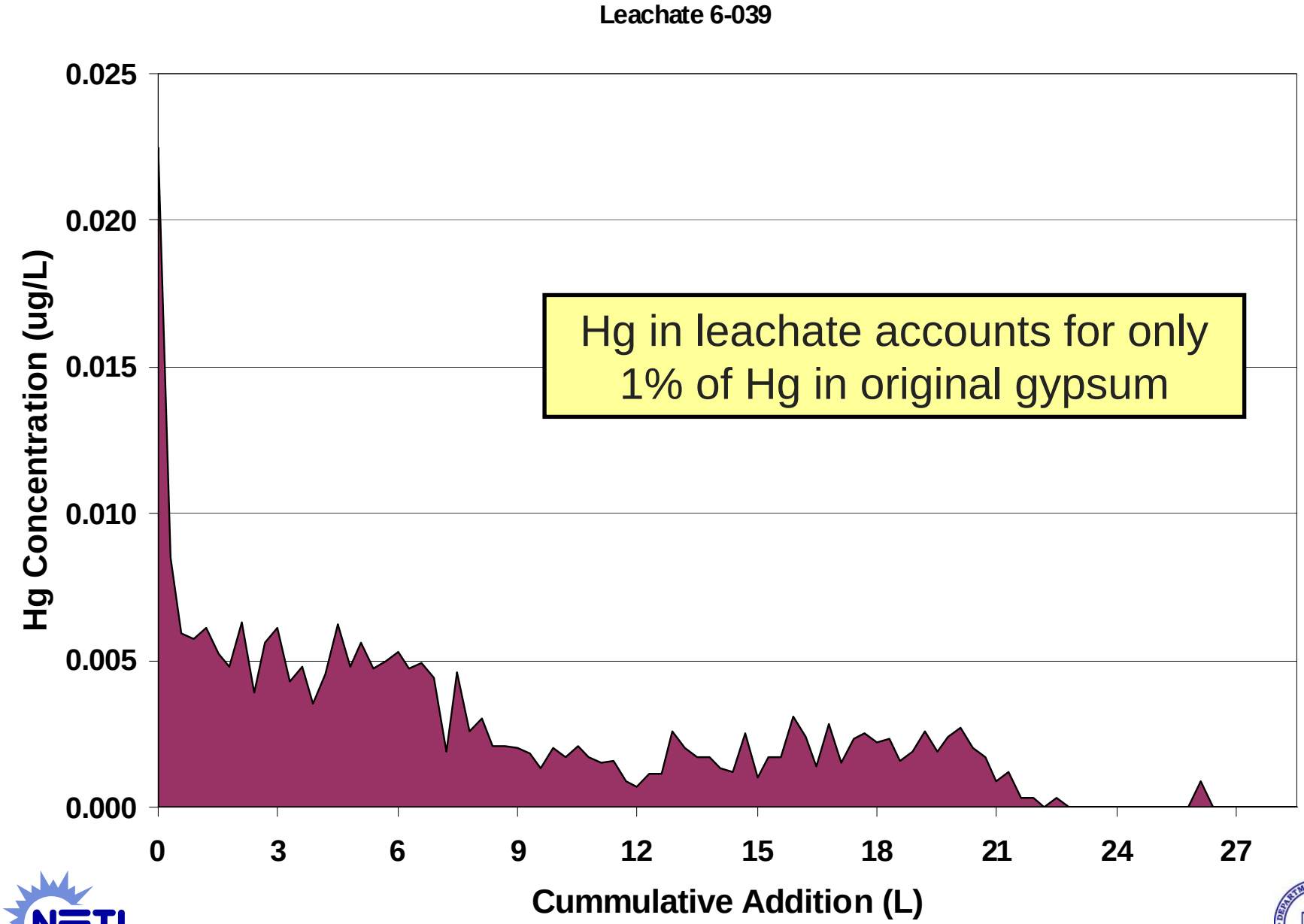
Fixation and Mobilization of Mercury in FGD Gypsum

- **Methods of Investigation**
  - Leaching
    - Continuous, Batch, Natural pH, Acidified
  - Mineral Extractions
  - Vaporization
    - Environmental Chamber
    - Continuous Leaching Effluent Gas

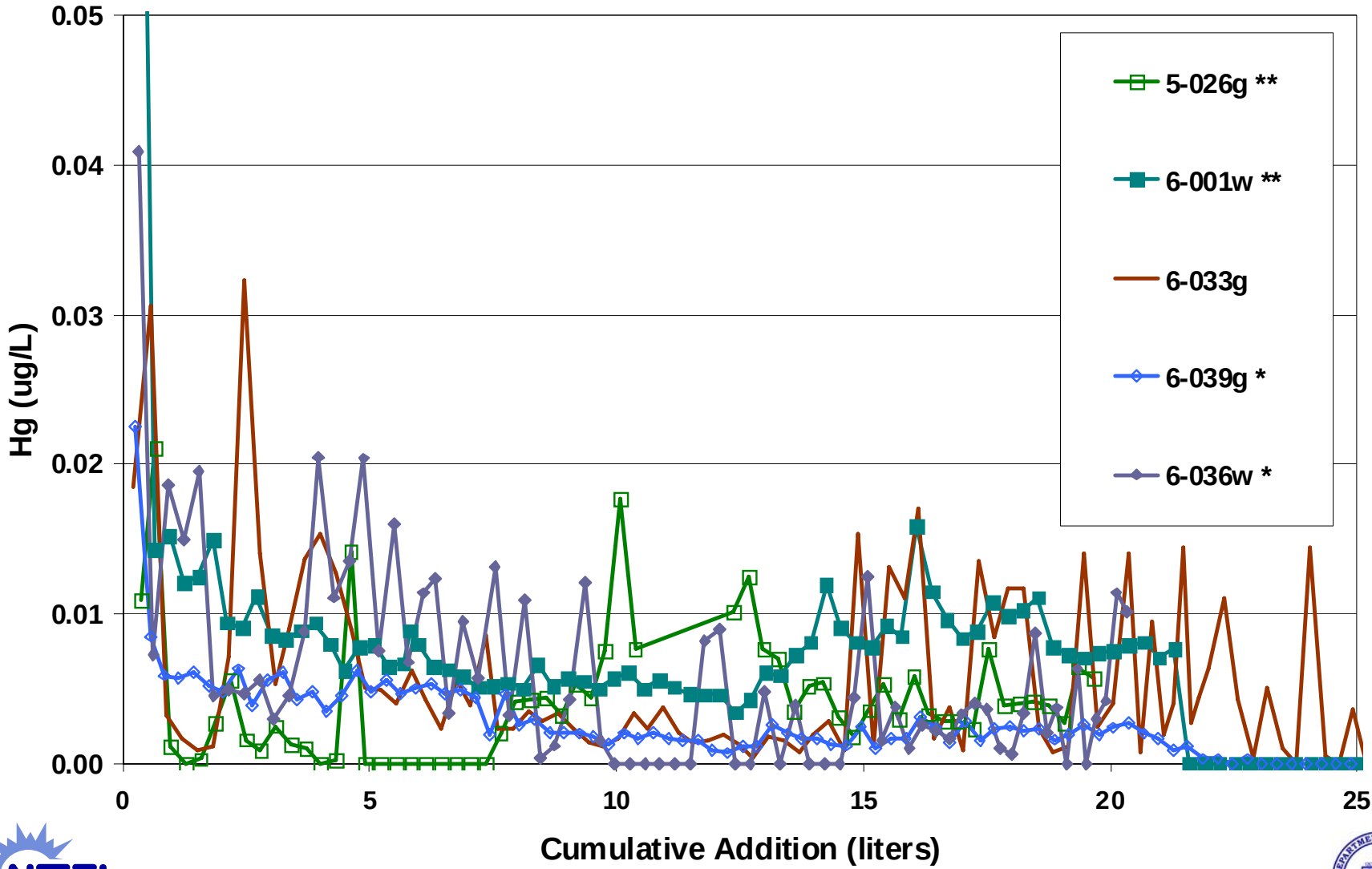
Continuous Leaching Experimental

- **Sample suspended in MQW under N_2 purge**
- **Leachants**
  - MQW leach for 6 samples
  - Followed by 0.01-0.02N HCl leach
- **pH, ORP continuously monitored**
- **300 mL samples collected**
- **Leachate analysis**
  - ICP-OES
  - ICP-MS
  - CVAA or **CVAF**
  - QA/QC
- **Remaining material removed, filtered**
  - Solids analysis of separate splits
    - Digestion EPA 3051, EPA 3052, ASTM D6349
    - ICP-OES, ICP-MS
    - DMA-80


Acid Leaching of 5-026
Metal Concentration (ug/L)
pH
Cumulative Addition (L)
Aluminum
Hg x 10,000
Iron / 10
Magnesium / 100
pH
1200
1000
800
600
400
200
0
10.0
8.5
7.0
5.5
4.0
2.5
1.0
0
5
10
15
20


Leachate 6-039
0.025
0.020
0.015
0.010
0.005
0.000
Hg Concentration (ug/L)
0
3
6
9
12
15
18
21
24
27
Cummulative Addition (L)
Hg in leachate accounts for only
1% of Hg in original gypsum

Mercury in Leachate



Leaching of Mercury from FGD Gypsum (G) and Wallboard (W)

RUN	Mercury Charged		Mercury Leached	
	ug/kg	ug	ug	%
G7	1517	91.0	0.10	**0.1%**
G6	143	28.4	0.05	**0.2%**
G5	490	36.8	0.07	**0.2%**
G3	1162	87.2	0.56	**0.6%**
G4	550	33.0	0.24	**0.7%**
G2	118	7.1	0.20	**2.8%**
W6	147	29.5	0.19	**0.6%**
W7	1306	94.4	1.31	**1.4%**
W5	84	6.3	0.14	**2.2%**
W2	110	6.6	0.29	**4.4%**
W4	343	25.7		
W3	1141	84.9	NA	

Mercury in Leaching Residues

RUN	Mercury Charged		Mercury Leached		Residue Mercury	
	ug/kg	ug	ug	%	ug	%
G7	1517	91.0	0.10	**0.1%**	38.0	**42%**
G6	143	28.4	0.05	**0.2%**	23.7	**83%**
G5	490	36.8	0.07	**0.2%**	26.3	**72%**
G3	1162	87.2	0.56	**0.6%**	84.2	**97%**
G4	550	33.0	0.24	**0.7%**	37.8	**115%**
G2	118	7.1	0.20	**2.8%**	1.8	**26%**
W6	147	29.5	0.19	**0.6%**	53.7	**182%**
W7	1306	94.4	1.31	**1.4%**	93.1	**99%**
W5	84	6.3	0.14	**2.2%**	11.4	**181%**
W2	110	6.6	0.29	**4.4%**	2.4	**36%**
W4	343	25.7			23.2	**90%**
W3	1141	84.9	NA		90.4	**106%**

Post-leaching Residue

Table 3. Amount in residue (ug/g)

	Plant A	Plant B	Plant D	Plant E
Al	30900	40100	75400	88900
As	16.5	19.0	173	18.5
Ca	3080	1820	1900	6760
Cd	5.40	< 2	< 2	<2
Cr	222	257	287	145
Fe	28500	23800	102000	89200
Hg	33.1	6.53	57.0	54.2
Mg	7080	14100	7990	7410
Mn	118	80.0	394	171
Ni	33.2	171	134	115
Pb	29.6	25.0	39.6	40.6
S	10400	350	8710	7010
Se	54.6	< 9	< 9	276
Zn	592	285	340	139

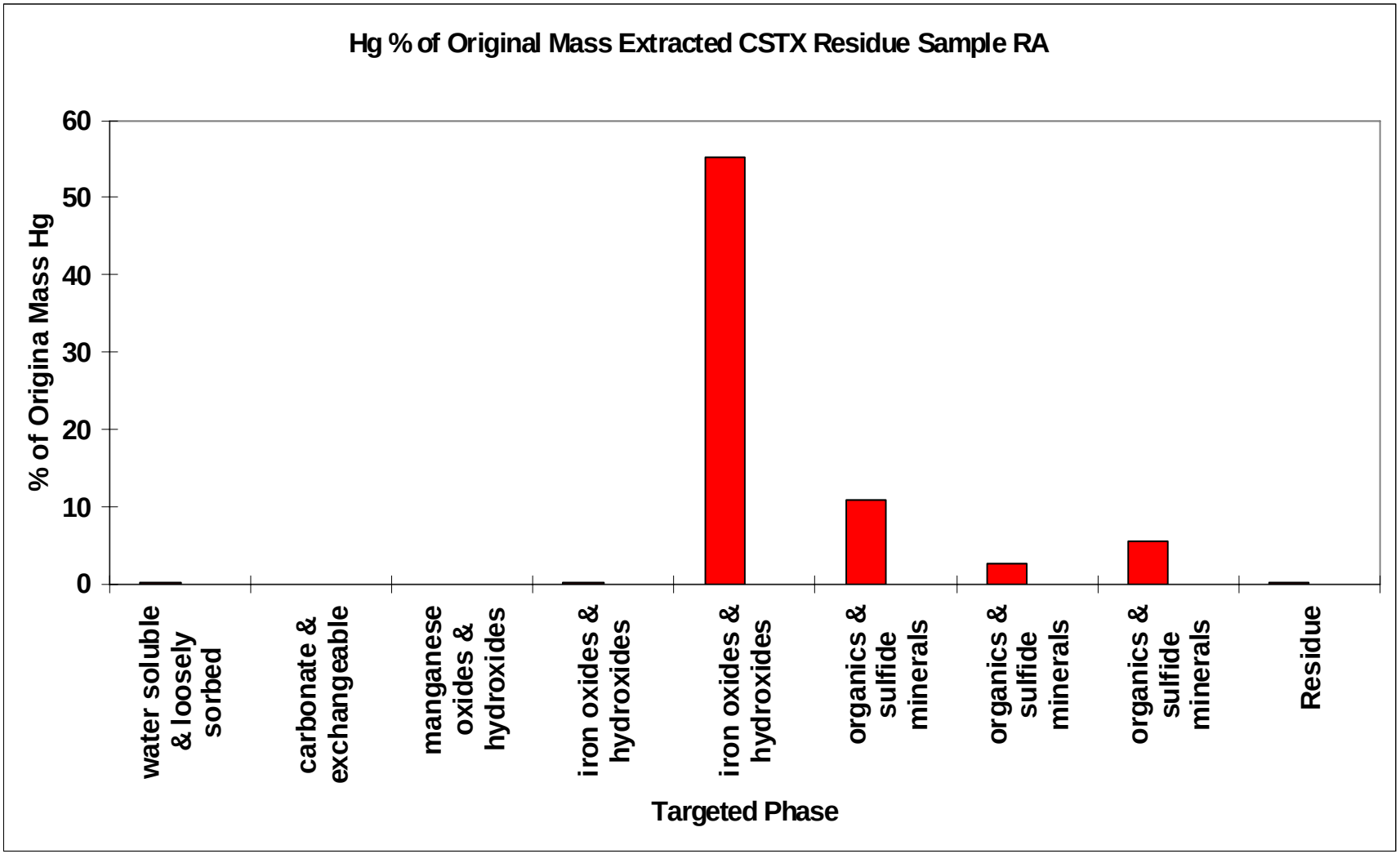
- **Accounts for < 2% of the original material**
  - **Phase responsible for retention is <u>not</u> gypsum**
  - **Fe or mixed Fe-Al phase**

Mineral Extractions

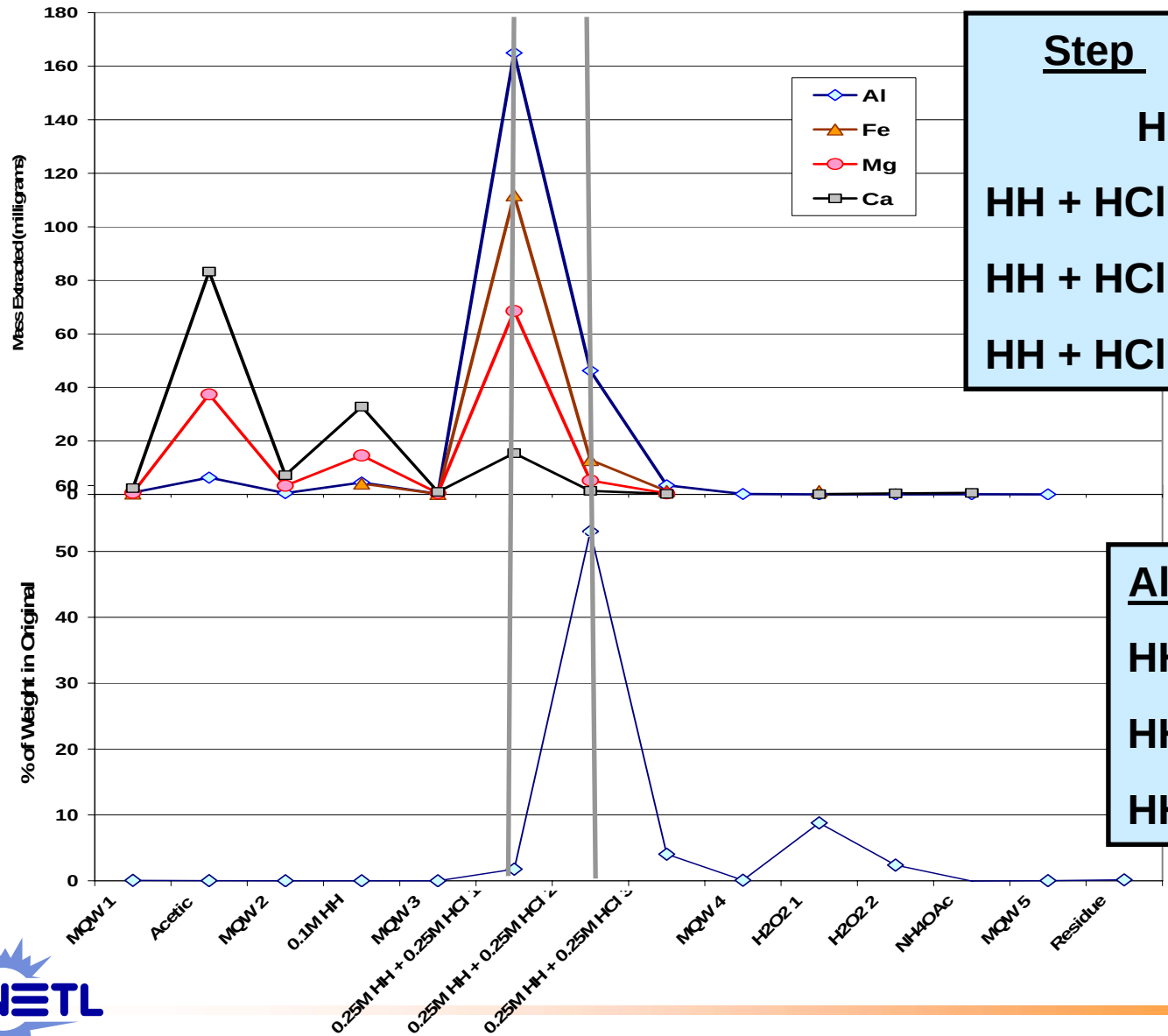
Sequential Extraction Procedure

Step	Target
• MQW Rinse	Water soluble/loosely sorbed fraction
• 0.11 M Acetic Acid	Carbonate and exchangeable fraction
• 0.1 M Hydroxylamine Hydrochloride Extraction	Manganese oxides and hydroxides
• Hot 0.25 M Hydroxylamine Hydrochloride in 0.25 M HCl	Iron oxides and hydroxides
• Hot Hydrogen Peroxide, Ammonium Acetate	Organic matter and sulfide mineral fraction

Example Mineral Extraction



Mineral Extractions of FGD Material

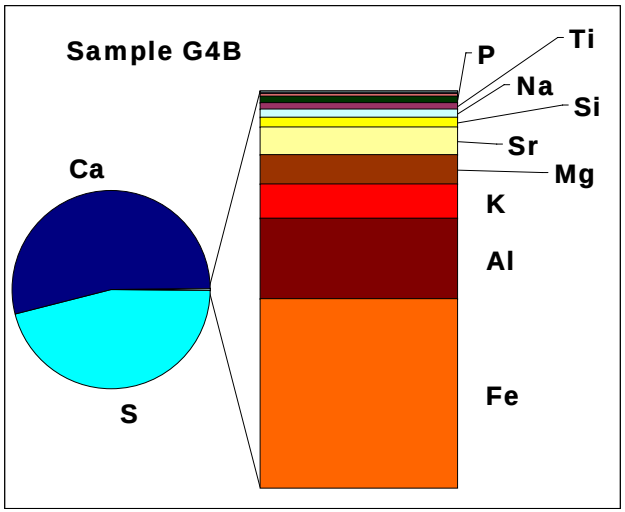


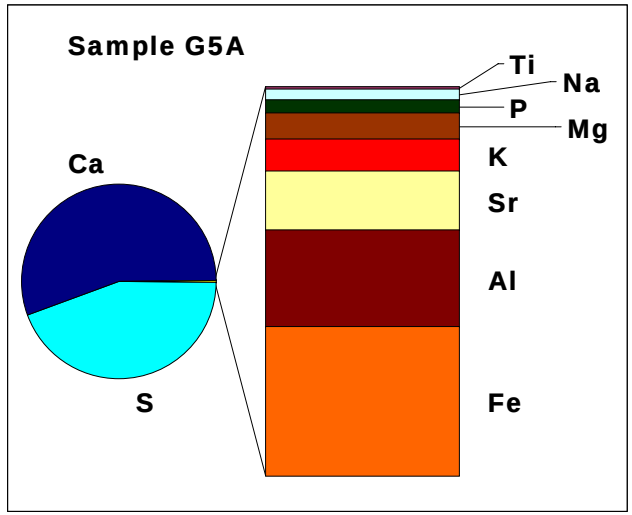
Step	pH	ORP
HH	4.29	100
HH + HCl 1	1.96	260
HH + HCl 2	0.85	330
HH + HCl 3	0.89	345

Al / Fe Molar Ratio	
HH + HCl 1	3.1
HH + HCl 2	7.4
HH + HCl 3	5.6

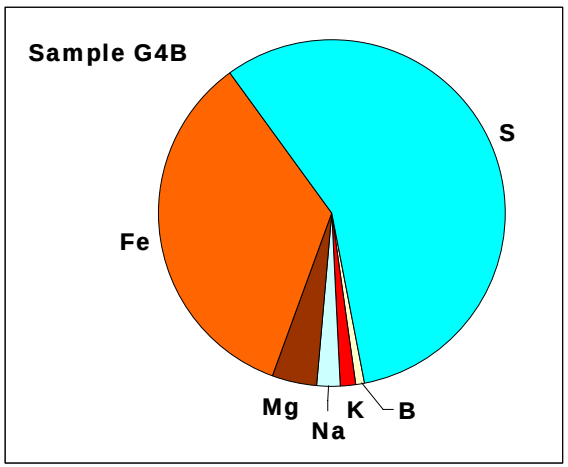
FGD Gypsum

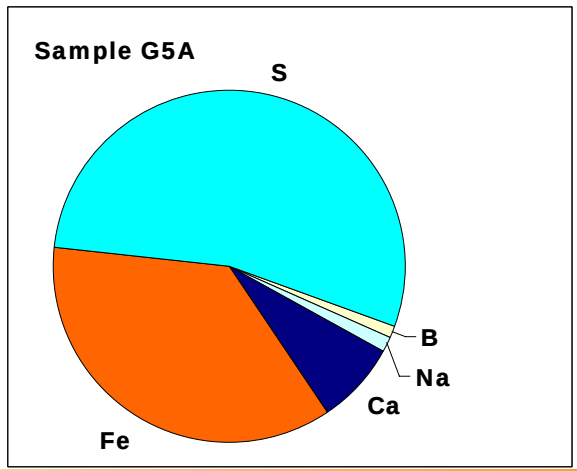
The major Hg-associated phase is dominated by Fe and Al. The presence of significant amounts of Mg, Si, and K is also typical.





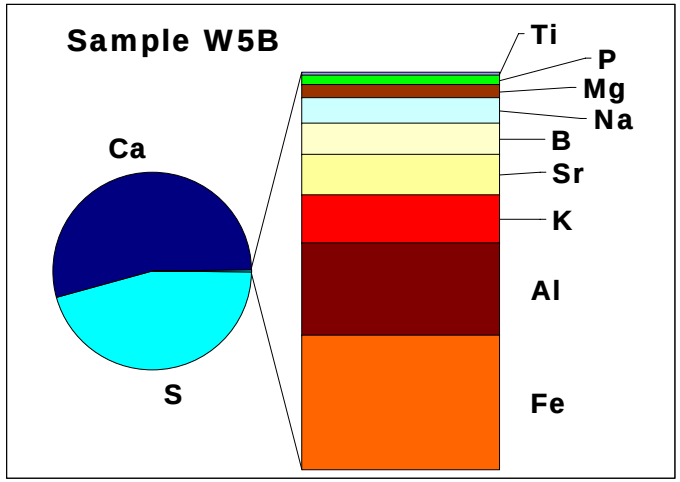
The minor Hg-associated phase of FGD gypsum contained significant amounts of S and Fe.

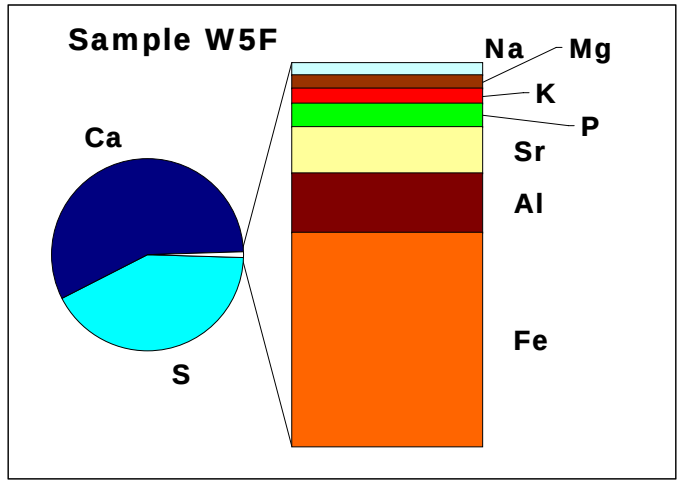


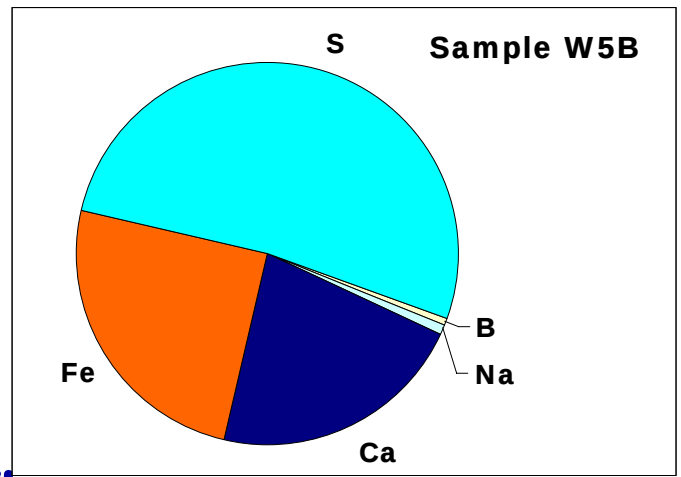


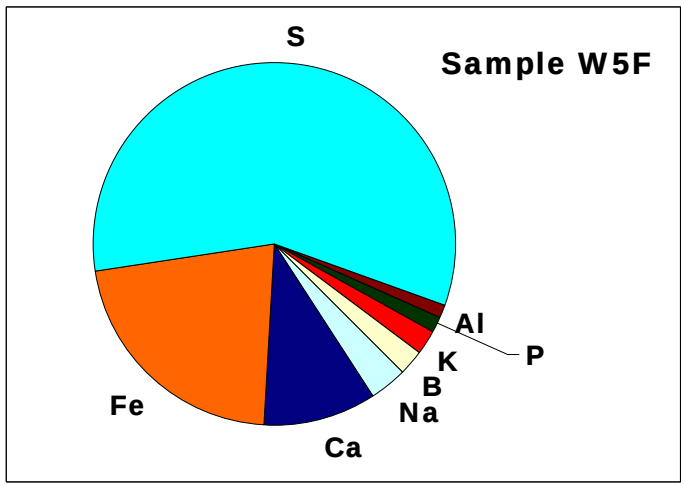
FGD Wallboard

The major and minor Hg-associated phases of FGD wallboard were similar to those of their source gypsum.



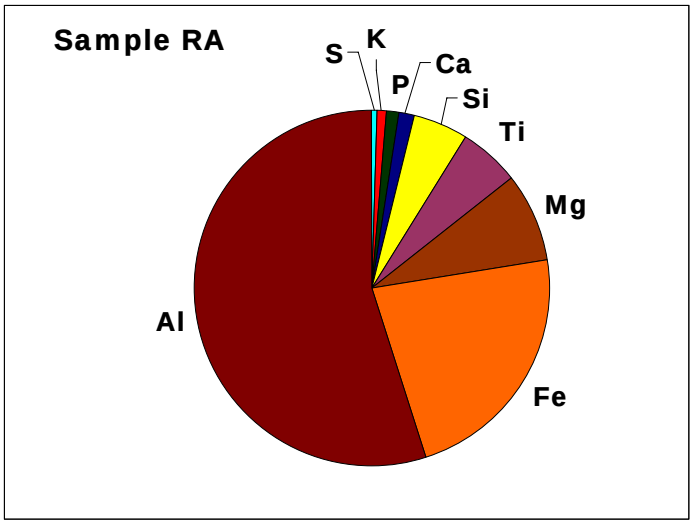


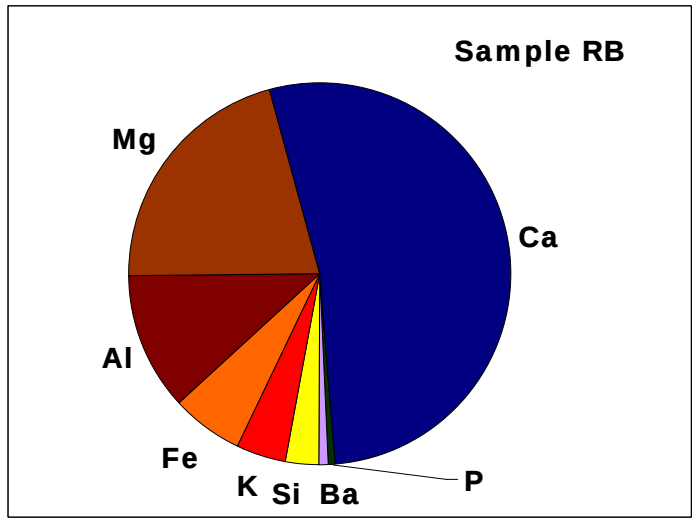




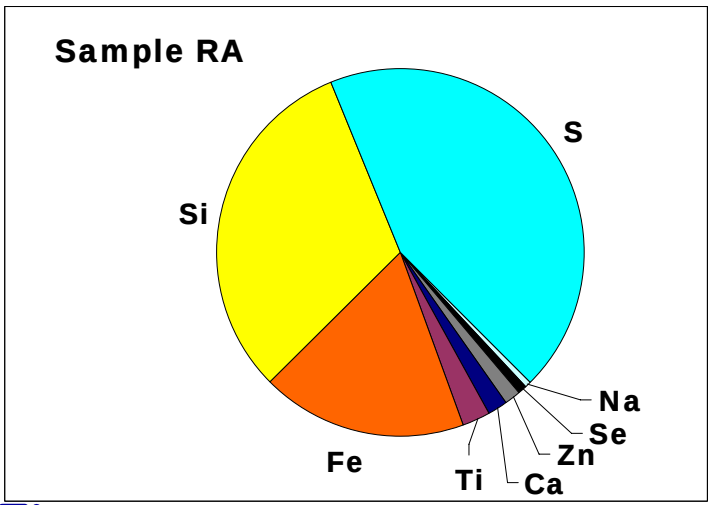
CSTX Residues

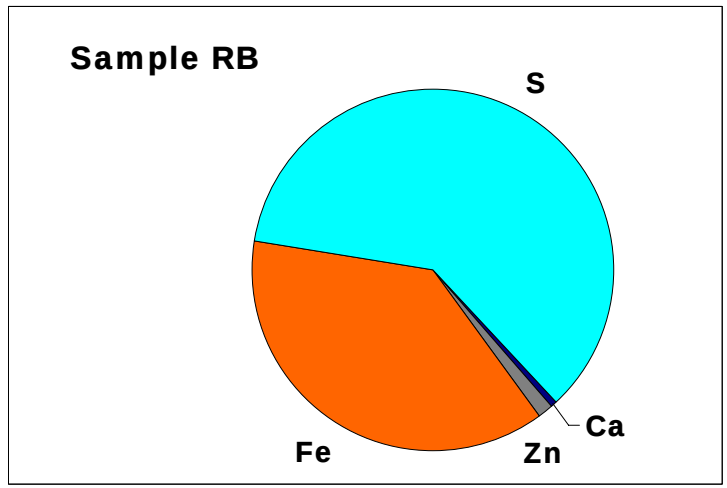
The major Hg-associated phase characterized by Ca, Al, Mg, Fe, K, Ti and Si





The minor Hg-associated phase contained major amounts of S, Fe and Si





% of Mercury Recovered in Mineral Phases

Target	soluble and loosely sorbed	carbonate and exchange-able	manganese oxides and hydroxides	iron oxides and hydroxides	organic matter and sulfide minerals	unreactive residue	Hg Balance
Reagent	MQW	0.1 M HOAc	0.1 M NH_2OH-HCl	0.25 M NH_2OH-HCl in 0.25 M HCl	H_2O_2 followed by 0.1 M NH_4OAc	none	Sum of Fractions
Sample							
OFS a	0.1	0.0	0.0	55.5	19.0	0.1	74.7
OFS b	0.1	0.0	0.0	58.8	11.1	0.1	70.1
RB a	0.1	0.0	0.0	37.0	17.9	7.0	62.1
RB b	0.3	0.0	0.0	45.8	34.0	1.3	81.4
G4A	0.1	0.1	0.0	56.1	5.0	0.1	61.4
G4B	0.2	0.8	0.2	38.4	4.7	2.1	46.3
G5A	*17.6*	0.3	0.6	85.0	15.6	1.9	120.9
W5B	0.5	0.3	0.3	52.0	11.8	0.5	65.4
G5E	*11.2*	0.8	-0.7	87.6	18.8	0.1	117.7
W5F	0.9	0.5	-1.1	40.3	23.8	0.2	64.7
G6A	0.3	0.2	0.0	358.1	NA	NA	358.6
W6B	0.1	0.1	0.0	33.4	0.1	NA	33.7
G6E	0.3	0.2	0.0	49.7	NA	NA	50.2
W6F	0.7	0.5	0.0	38.8	0.3	NA	40.3

OFS = Orange Fluffy Stuff

R prefix = gypsum leaching RESIDUE

G prefix = GYPSUM

W prefix = WALLBOARD

NA = Data Not Available Yet

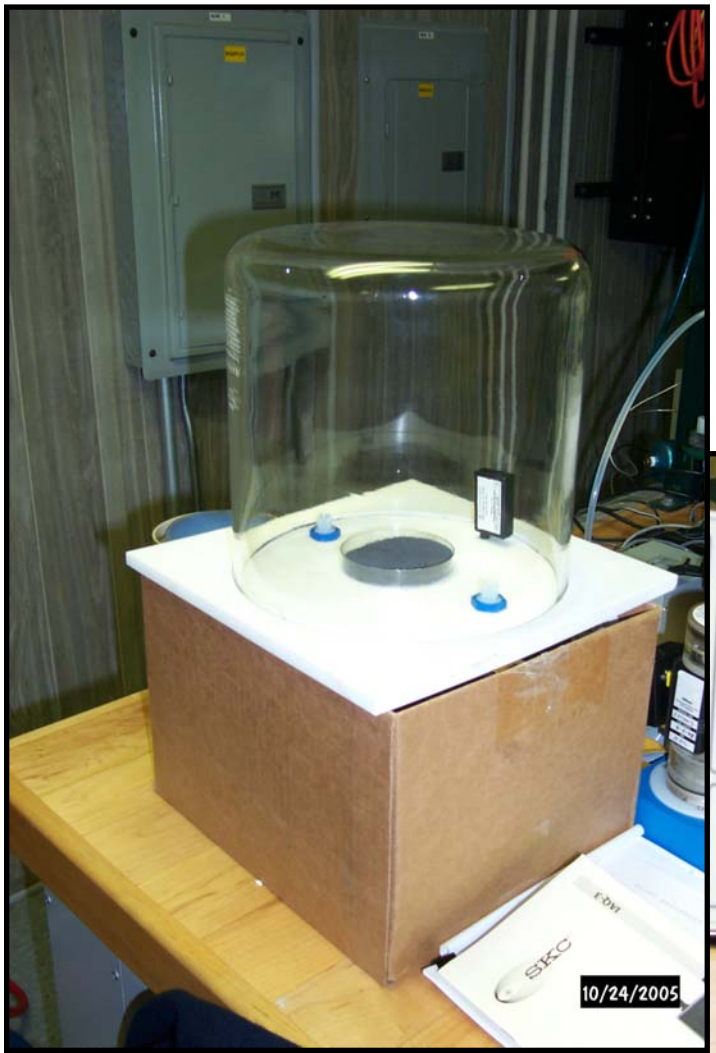
Summary – Mineral Extractions

- **No major differences between parent gypsum and wallboard products, both gave the same:**
  - pattern of Hg release
  - elemental constituents
  - However, for gypsum/wallboard pairs, the wallboard was depleted in the iron oxide associated Hg

- **Hg release from the iron oxide fraction occurred in a narrow range of pH (pH < 1) and reducing conditions at high temperature**
  - pH < 1
  - ORP < 350
  - low pH or high temperature alone not sufficient

- **Hg material balances were usually less than 100%**
  - does Hg volatilization occur

Environmental Chamber

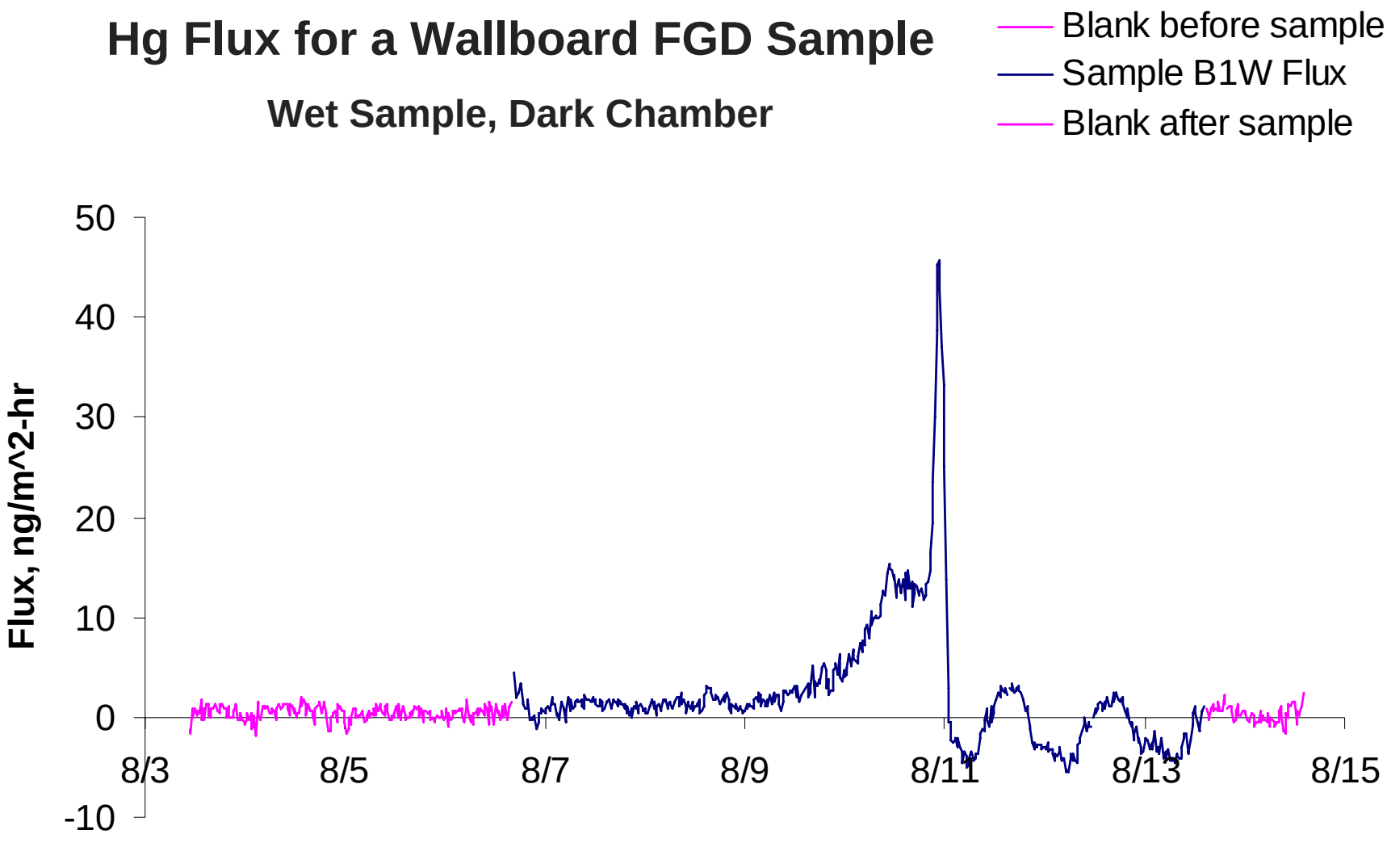


In addition to Mercury
- Temperature
- Relative Humidity
- Incident light

are monitored.

Hg Flux for a Wallboard FGD Sample

Wet Sample, Dark Chamber



Environmental Chamber

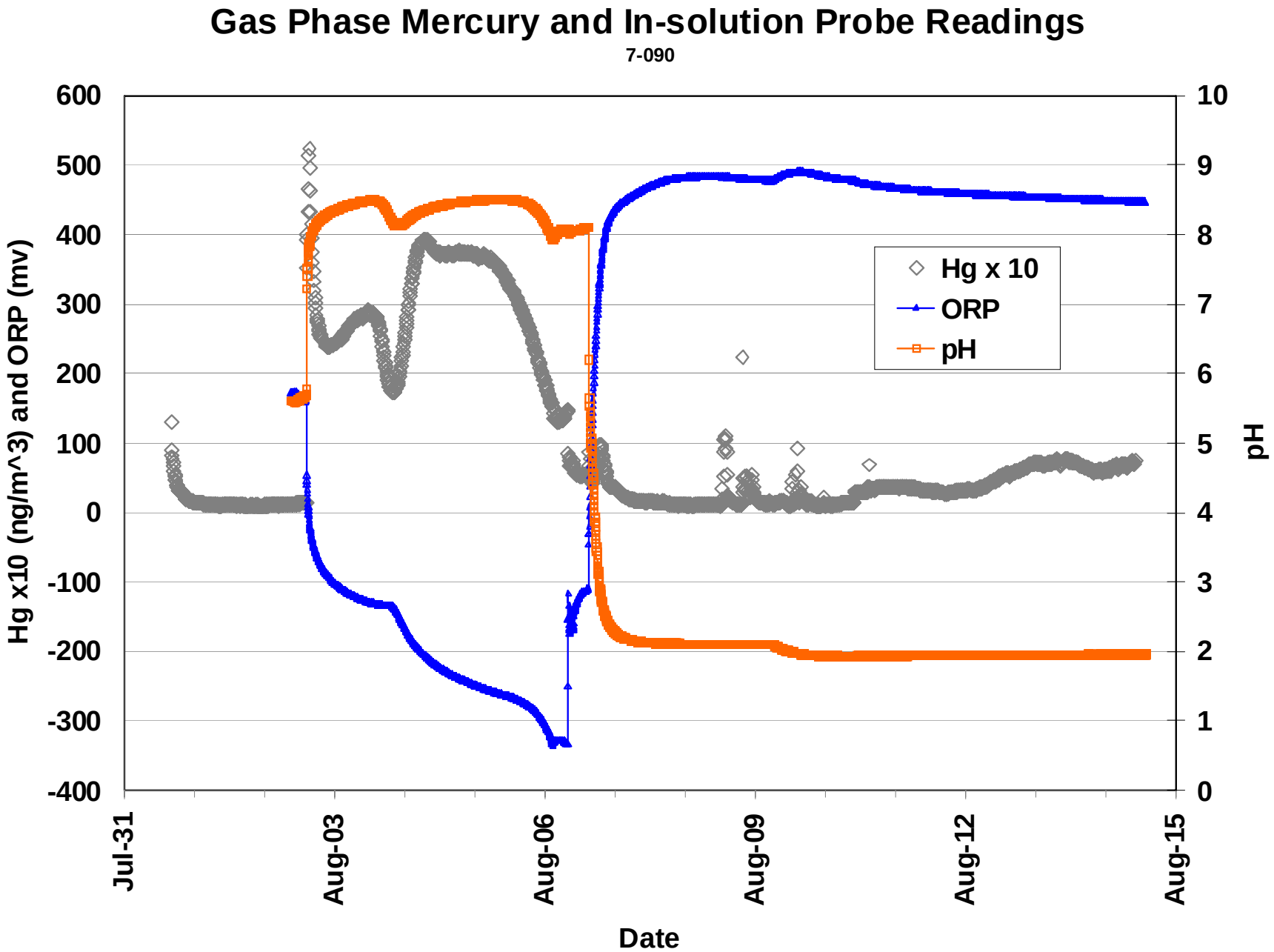
Average Flux

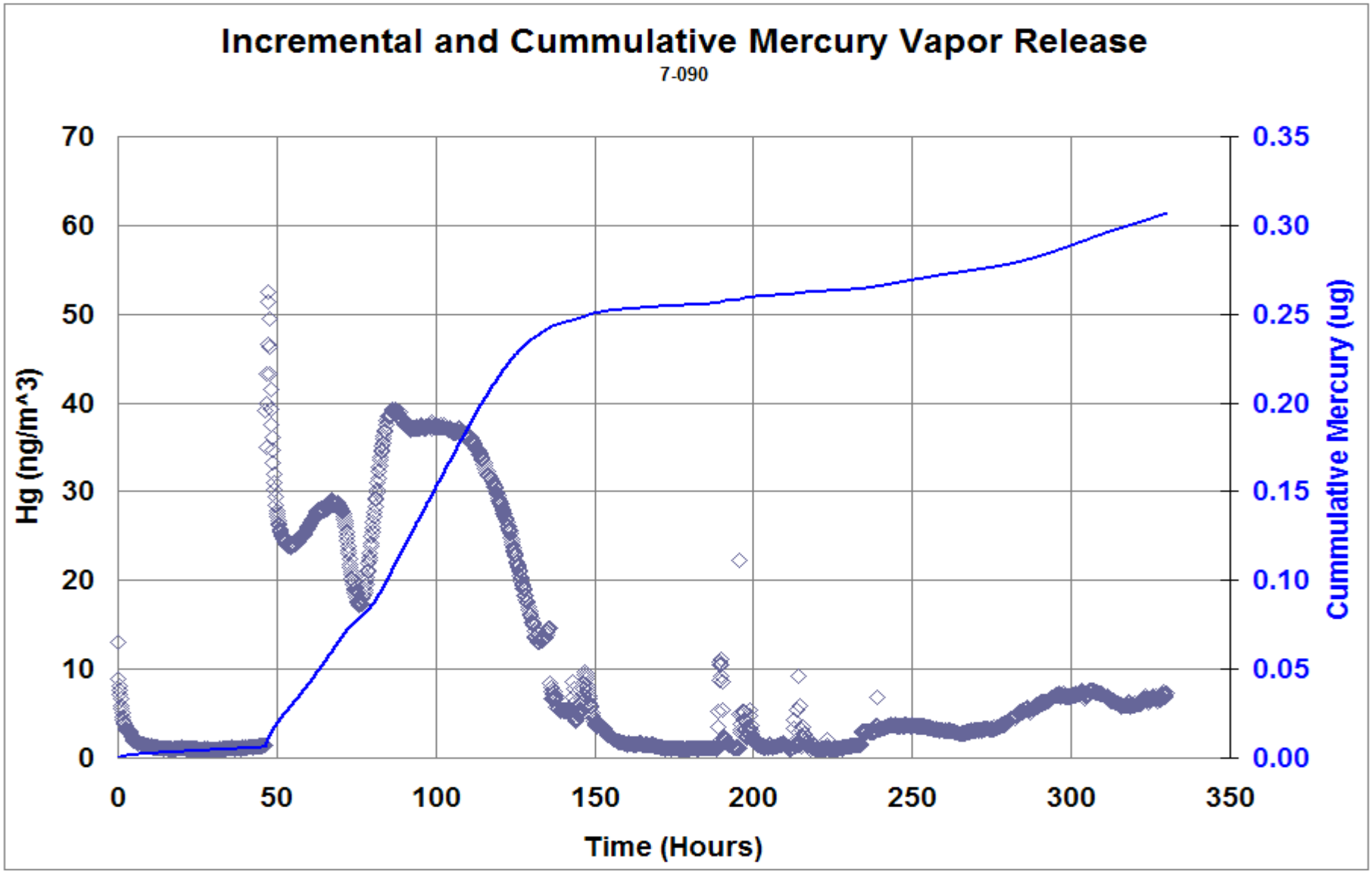
Average Sample Mercury Flux (ng/ m^2 /hr) for Dark/Light and Dry/Wet Chamber Conditions						
Sample Pair	***Description***	***Mercury Content (–g/kg)***	***Dry, Dark***	***Dry, Light***	***Wet, Dark***	***Wet, Light***
1	**Gypsum**	**150**	**10**	**13**	**30**	**20**
	Wallboard	**100**	**-1.8**	**-1.8**	**1.6**	**4.0**
2	**Gypsum**	**110**	**4.8**	**7.0**	**105**	**136**
	Wallboard	**140**	**-0.3**	**5.7**	**2.4**	**2.4**
3	**Gypsum**	***NA****	**-1.6**	**-1.4**	**1.1**	**0.2**
	Wallboard	**430**	**-2.5**	**-5.2**	**-0.5**	**0.3**
**NA* : Not yet analyzed.*						

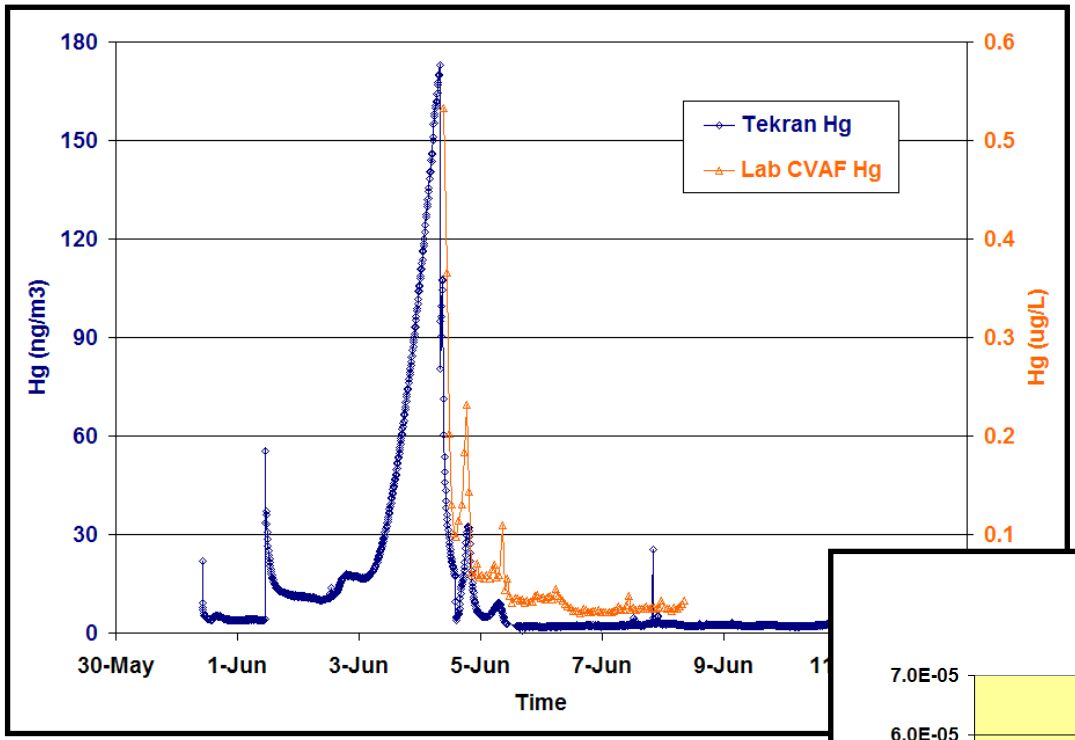
Environmental Chamber

Maximum Flux

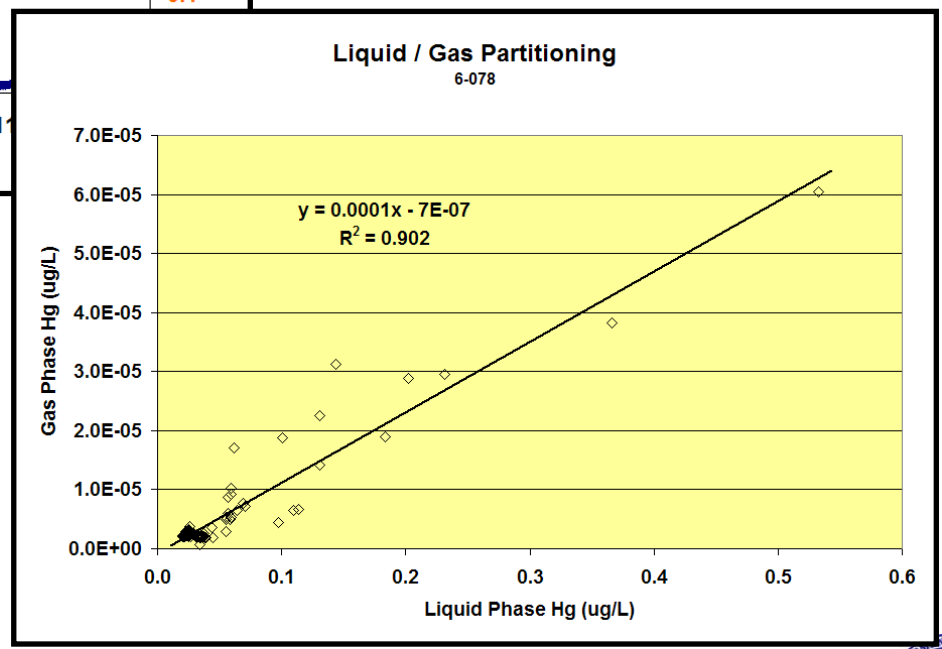
Maximum Mercury Flux (ng/ m^2 /hr) for Dark/Light and Dry/Wet Chamber Conditions						
Sample Pair	***Description***	***Mercury Content (μg/kg)***	***Dry, Dark***	***Dry, Light***	***Wet, Dark***	***Wet, Light***
1	**Gypsum**	**150**	**48**	**47**	**238**	**141**
	Wallboard	**100**	**3.9**	**4.0**	**46**	**40**
2	**Gypsum**	**110**	**79**	**50**	**450**	**630**
	Wallboard	**140**	**5.3**	**25**	**22**	**19**
3	**Gypsum**	***NA****	**1.7**	**2.4**	**5.1**	**3.6**
	Wallboard	**430**	**2.3**	**3.2**	**6.7**	**38**
**NA* : Not yet analyzed.						


Gas Phase Mercury and In-solution Probe Readings
7-090
Hg x10 (ng/m^3) and ORP (mv)
pH
Date
Hg x 10
ORP
pH
600
500
400
300
200
100
0
-100
-200
-300
-400
10
9
8
7
6
5
4
3
2
1
0
Jul-31
Aug-03
Aug-06
Aug-09
Aug-12
Aug-15

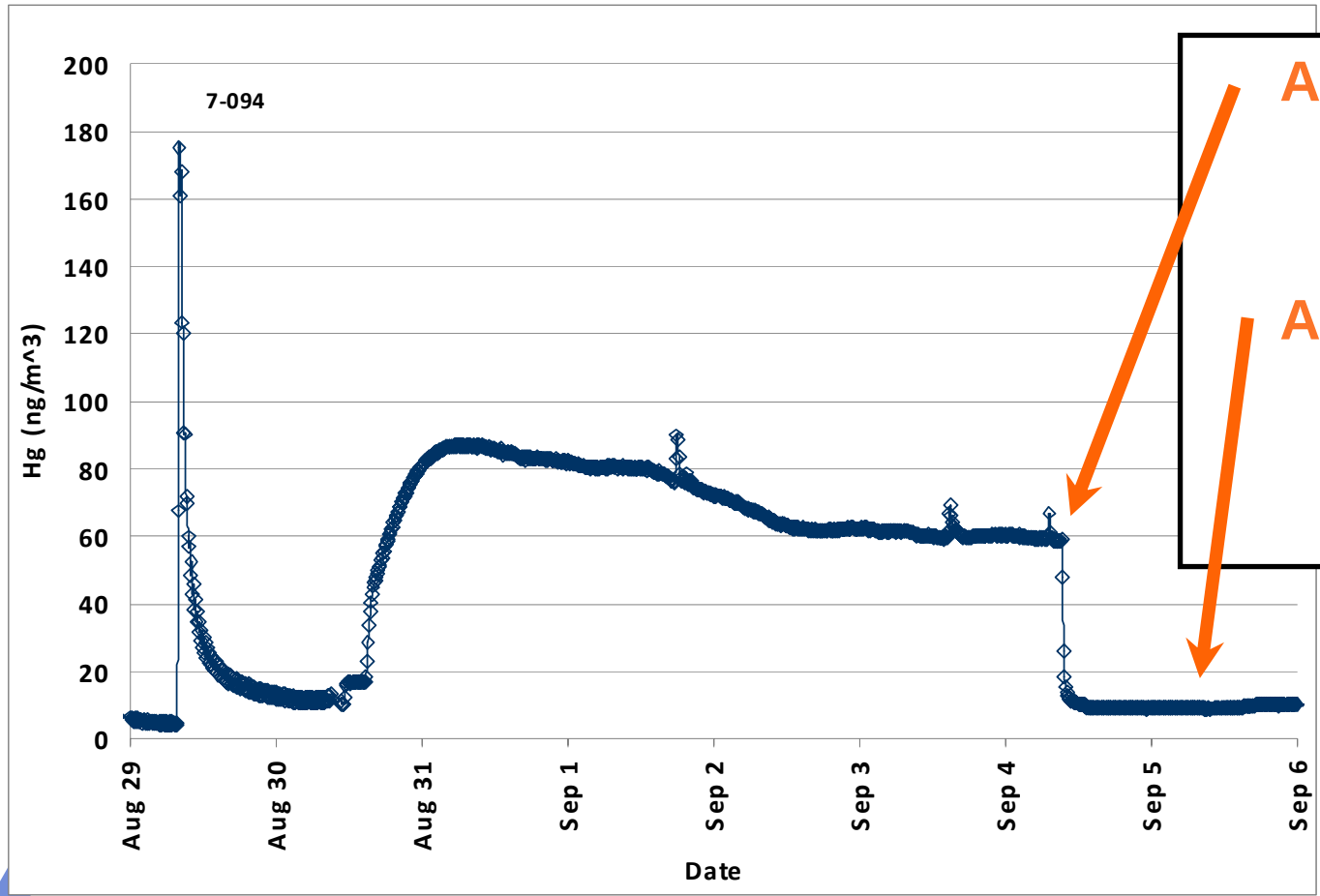

Incremental and Cummulative Mercury Vapor Release
7-090
Hg (ng/m^3)
Cummulative Mercury (ug)
Time (Hours)
0
10
20
30
40
50
60
70
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.35
0
50
100
150
200
250
300
350



Occasionally the liquid phase and gas phase mercury concentrations parallel each other



Effect of adding 10% air



Added 10% air to gas stream

Additional Increases had no effect

Elemental Mercury Mobilization from FGD Gypsums

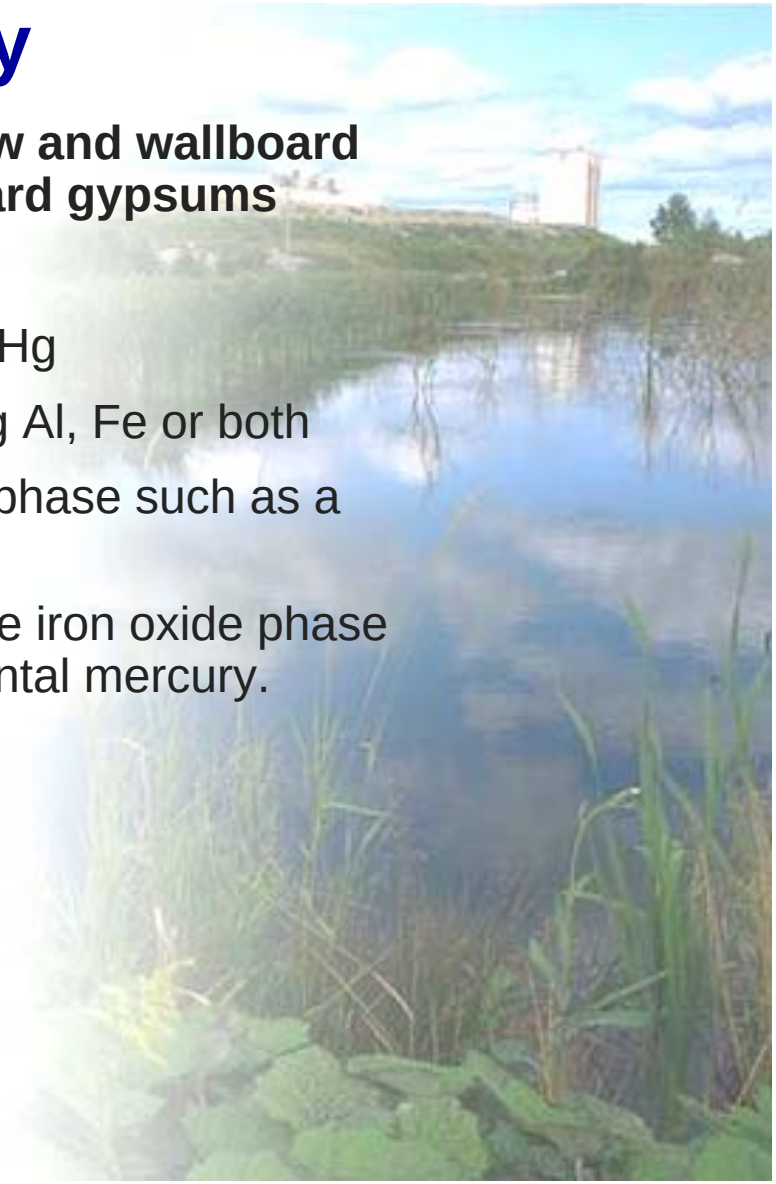
RUN	Mercury Charged		Mercury in Off Gas	
	ug/kg	ug	ug	%
G2	118	7.1		
W2	110	6.6		
G3	1162	87.2	14.6	**16.7%**
W3	1141	84.9	0.31	**0.4%**
G4	550	33.0	0.04	**0.1%**
W4	343	25.7	0.06	**0.2%**
G5	490	36.8	2.45	**6.7%**
W5	84	6.3		
G6	143	28.4		
W6	147	29.5		
G7	1517	91.0		
W7	1306	94.4	0.33	**0.3%**

Comparison of Feed Gypsum to Wallboard Gypsum

RUN	Mercury Charged		Mercury Leached		Residue Mercury		Mercury in Off Gas		Mercury Balance
	ug/kg	ug	ug	%	ug	%	ug	%	%
G2	118	7.1	0.20	**2.8%**	1.8	**26%**			29%
W2	110	6.6	0.29	**4.4%**	2.4	**36%**			41%
G3	1162	87.2	0.56	**0.6%**	84.2	**97%**	14.6	**16.7%**	114%
W3	1141	84.9	NA		90.4	**106%**	0.31	**0.4%**	107%
G4	550	33.0	0.24	**0.7%**	37.8	**115%**	0.04	**0.1%**	115%
W4	343	25.7			23.2	**90%**	0.06	**0.2%**	90%
G5	490	36.8	0.07	**0.2%**	26.3	**72%**	2.45	**6.7%**	79%
W5	84	6.3	0.14	**2.2%**	11.4	**181%**			183%
G6	143	28.4	0.05	**0.2%**	23.7	**83%**			84%
W6	147	29.5	0.19	**0.6%**	53.7	**182%**			183%
G7	1517	91.0	0.10	**0.1%**	38.0	**42%**			42%
W7	1306	94.4	1.31	**1.4%**	93.1	**99%**	0.33	**0.3%**	100%

Summary

- **The leachable fraction is small for both raw and wallboard gypsum but tends to be higher for wallboard gypsums**
- **A residue bound fraction**
  - Contains the largest amount of recovered Hg
  - Major fraction bound to a phase containing Al, Fe or both
  - Minor fraction present as H_2O_2 oxidizable phase such as a sulfide
  - Wallboards tend to be depleted in Hg in the iron oxide phase and wallboards emit less vaporized elemental mercury.
- **Gas phase elemental mercury**
  - Absorbed elemental mercury
  - Generated by aqueous processes
  - Minor for wallboard gypsums
  - Can be large for raw gypsums
  - Requires moisture to be present
  - Drastically reduced in the presence of air




"That's all Folks!"