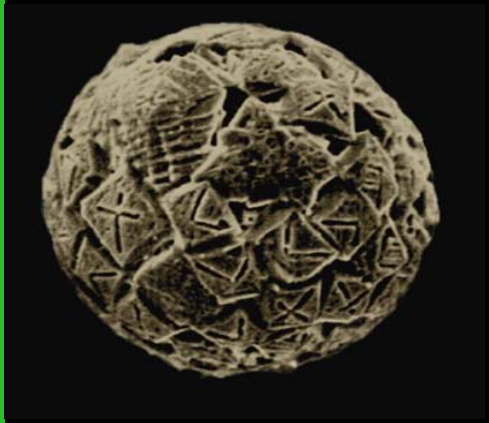
Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization

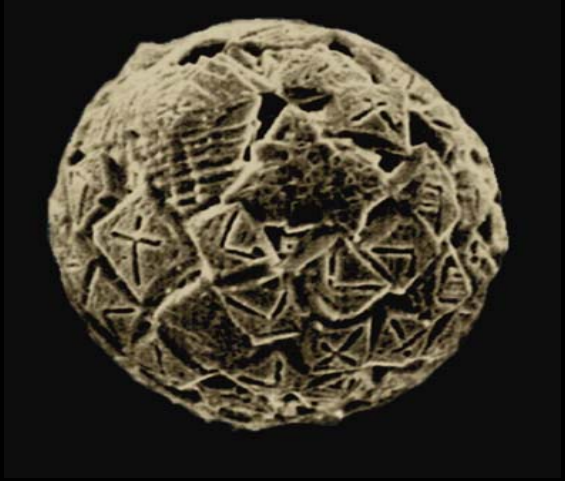


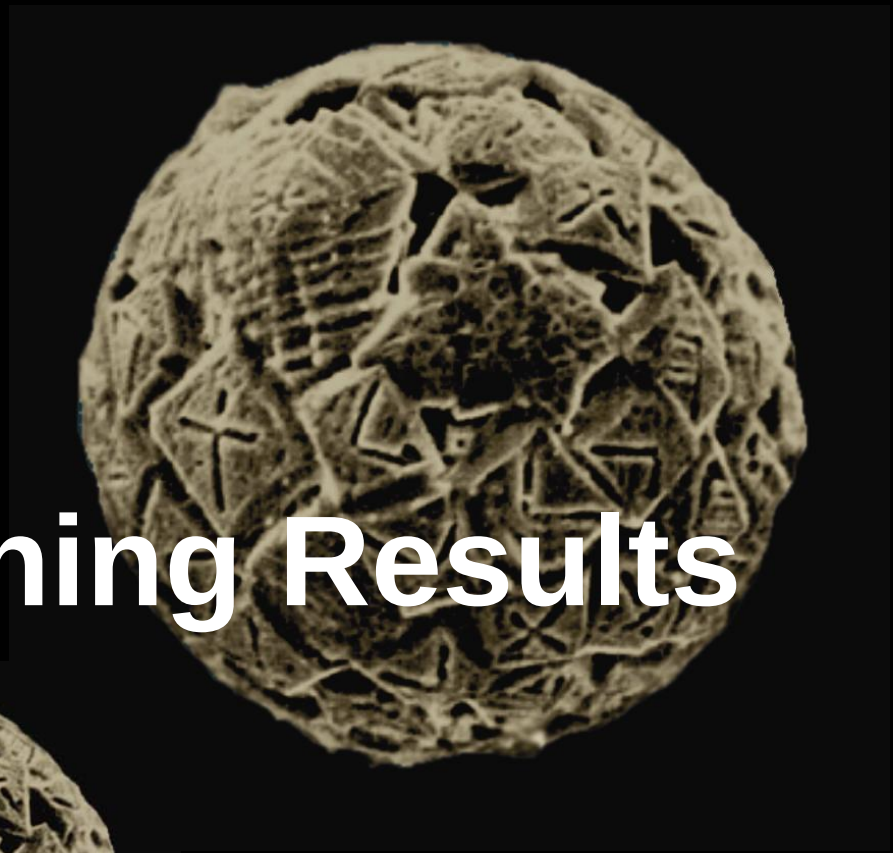
DOE NETL Mercury Control
Project Review Meeting
July 12–14, 2005

Debra F. Pflughoeft-Hassett
University of North Dakota
Energy & Environmental Research Center

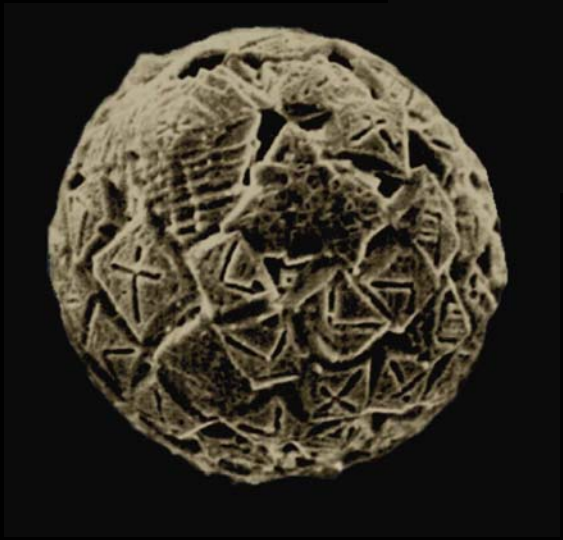
Project Tasks

1. Literature Search
2. Analytical Methods Selection
3. Sample Identification and Selection
4. Chemical and Physical Characterization
5. **Laboratory Evaluation of Air Toxic Element Releases**
   - **Leaching**
   - **Vapor Transport**
   - **Microbiological Release**
6. **Field Investigations**
7. Data Reduction and Interpretation



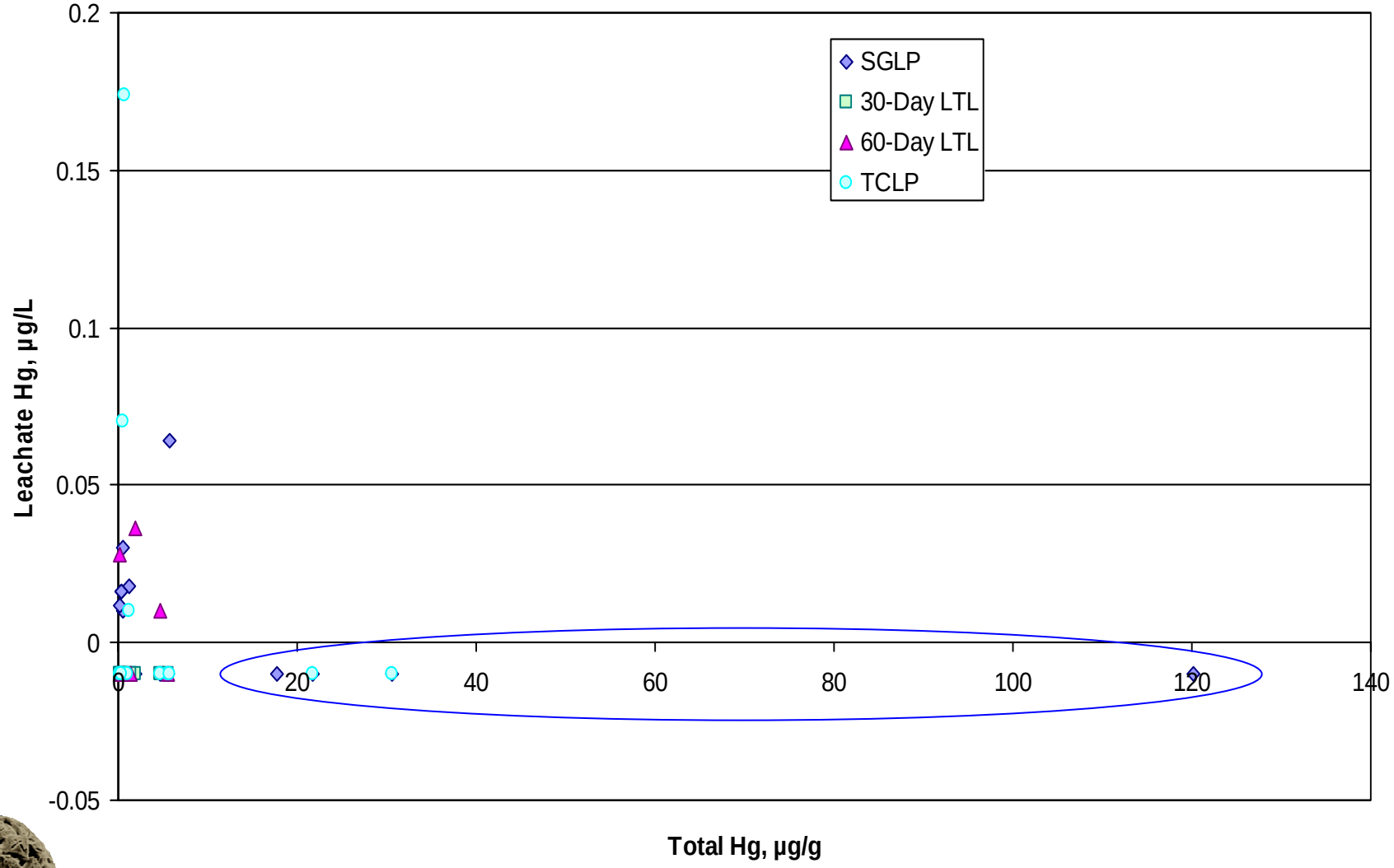


Direct Leaching Results



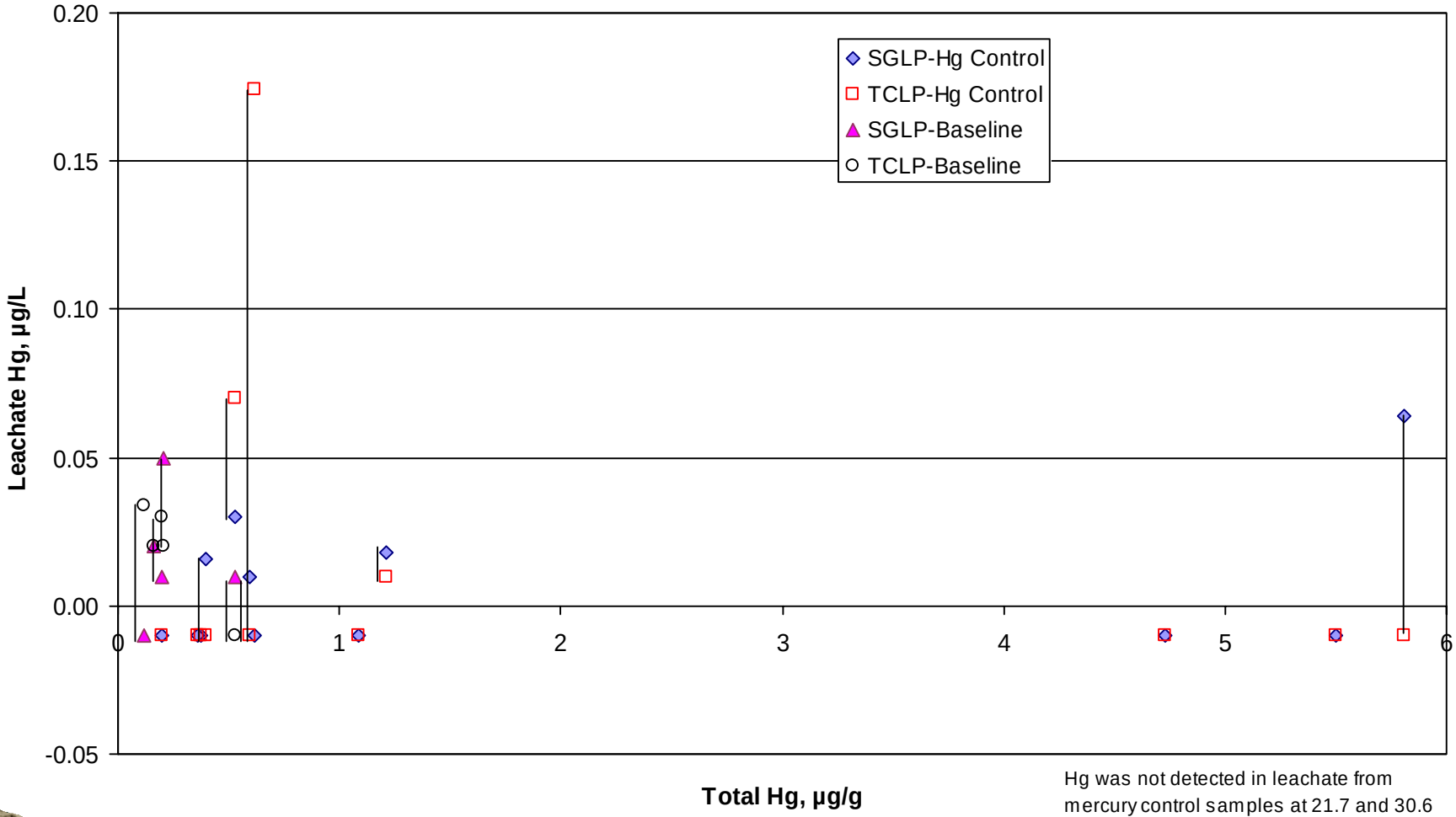
Leaching Results

Mercury – Fly Ash with Hg Control



Leaching Results

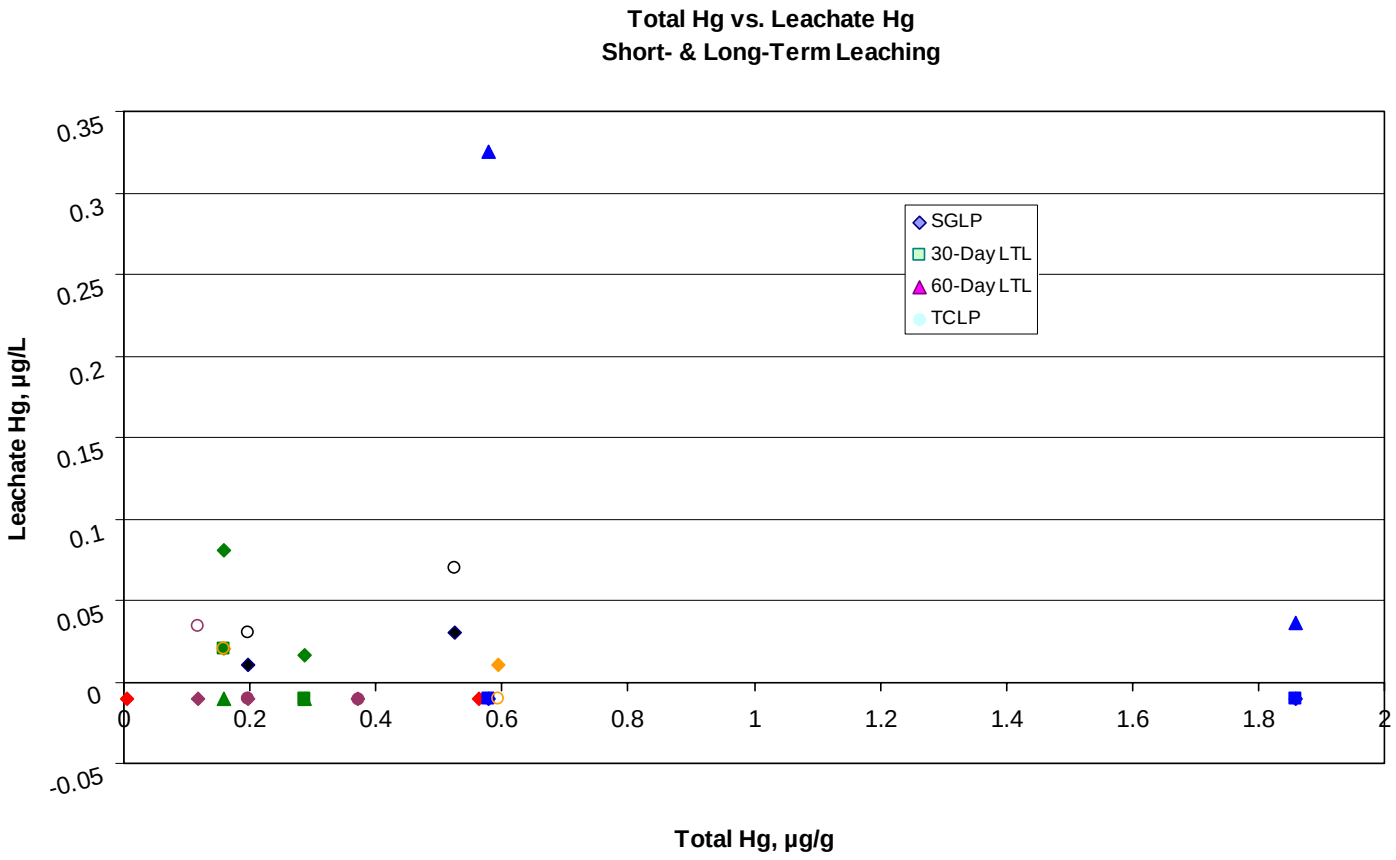
Mercury – Hg Control and No Hg Control *SGLP vs. TCLP*



Hg was not detected in leachate from mercury control samples at 21.7 and 30.6 µg/g

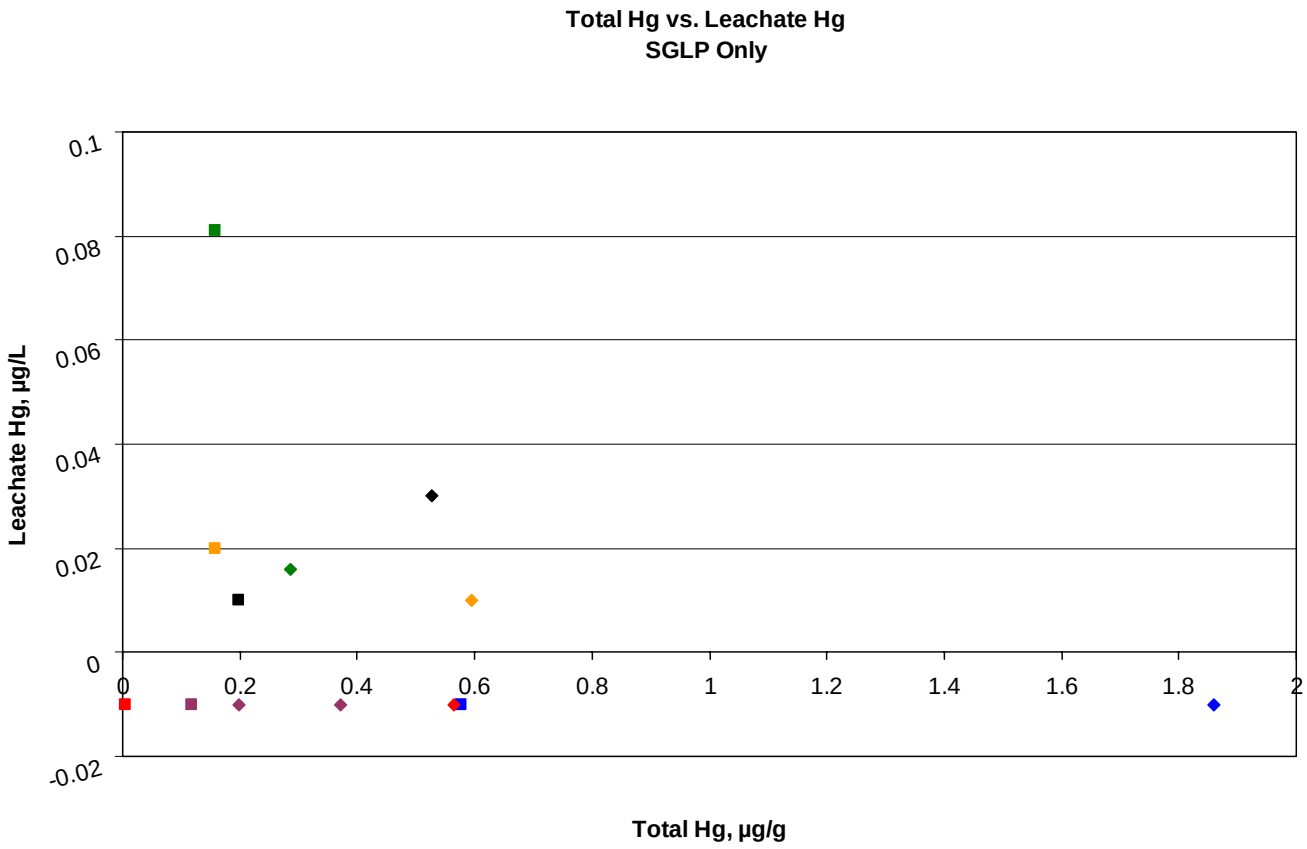
Total Hg vs. Leachate Hg

Paired Fly Ash with & without Hg Control



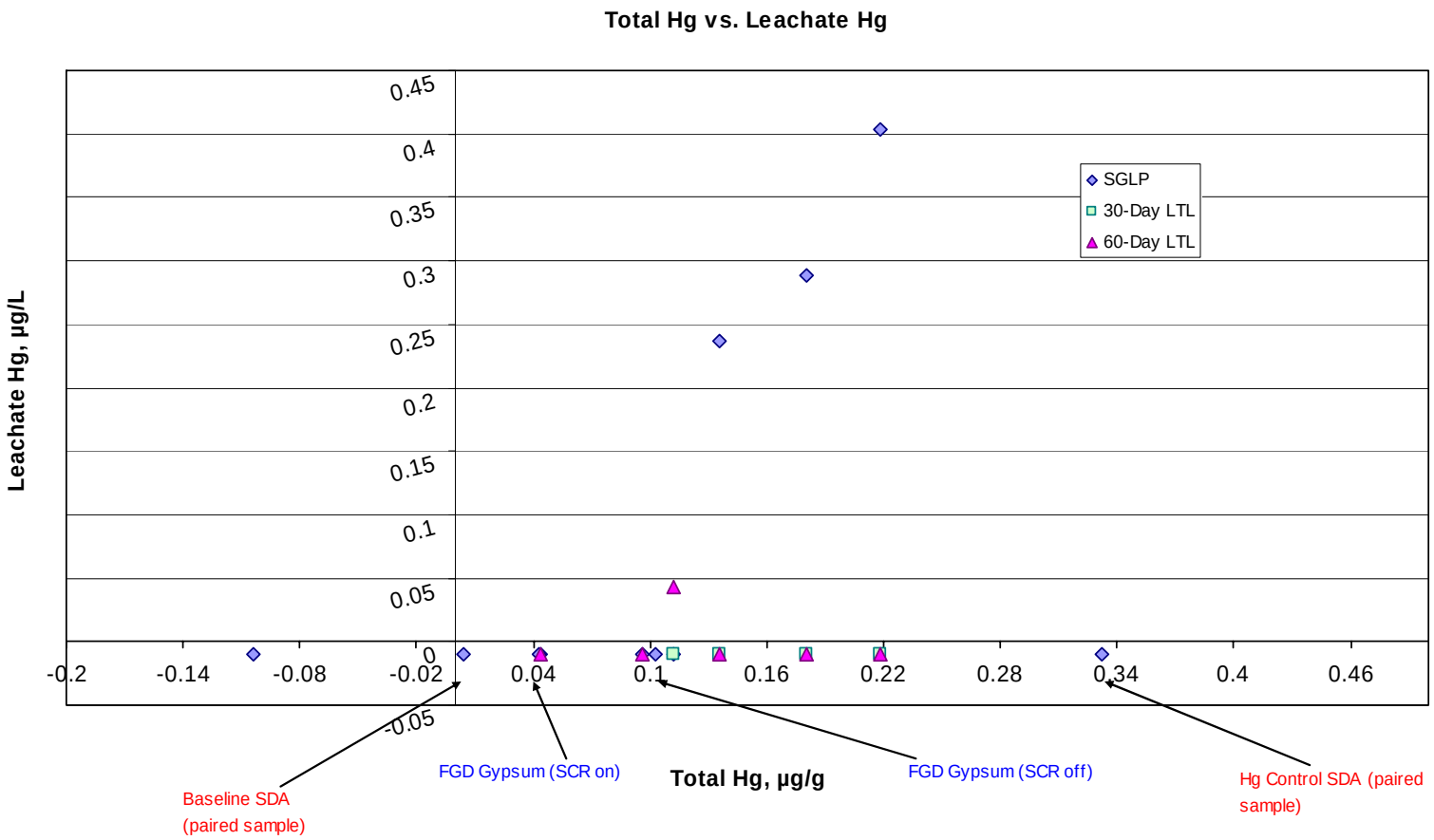
Total Hg vs. Leachate Hg

Paired Fly Ash without & with Hg Control



Leaching Results

Mercury – FGD Materials

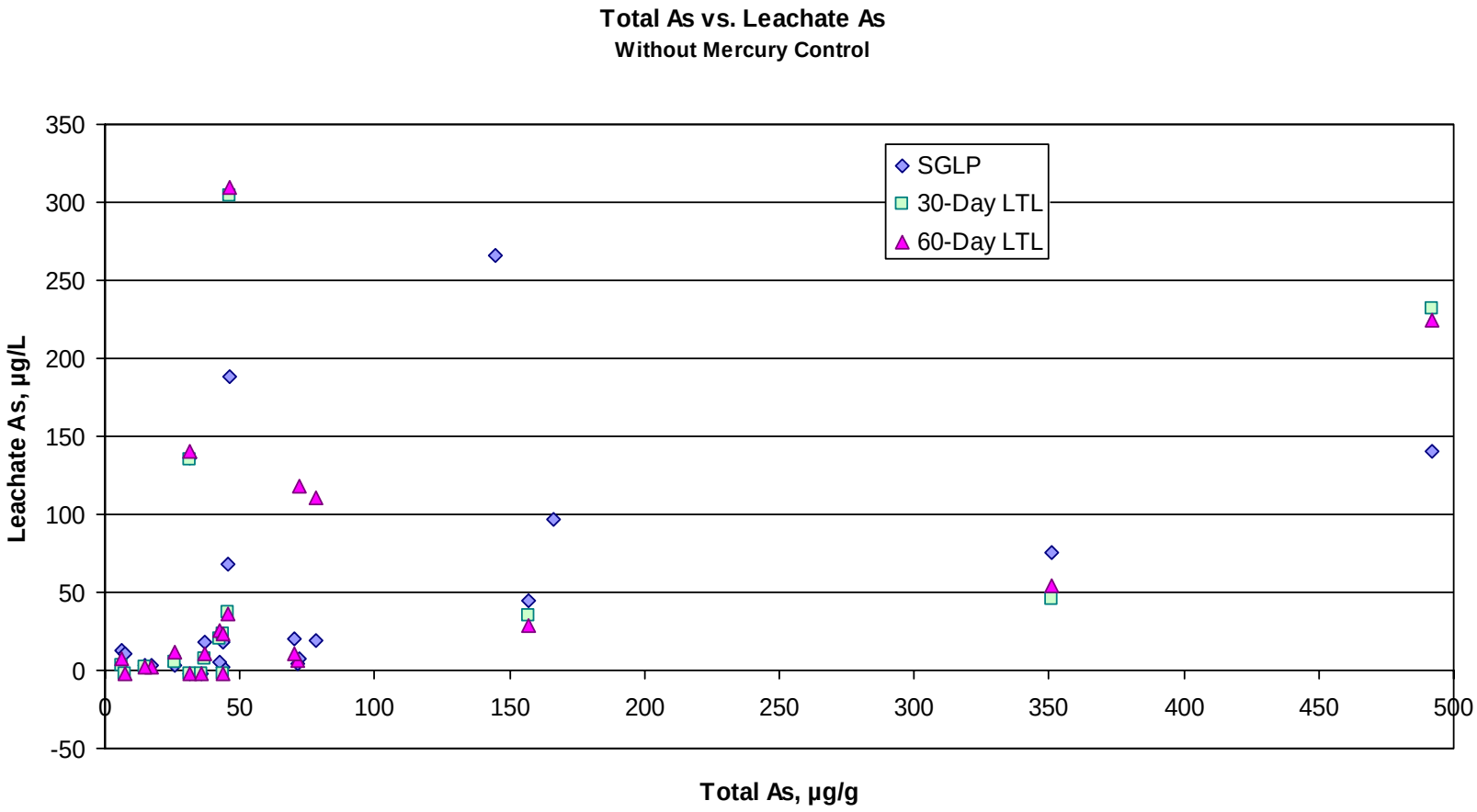


Mercury Leaching Conclusion

- Total mercury content of samples generated both with and without mercury emission controls present and leachate concentrations did not correlate and were independent of short-term leaching procedures used.

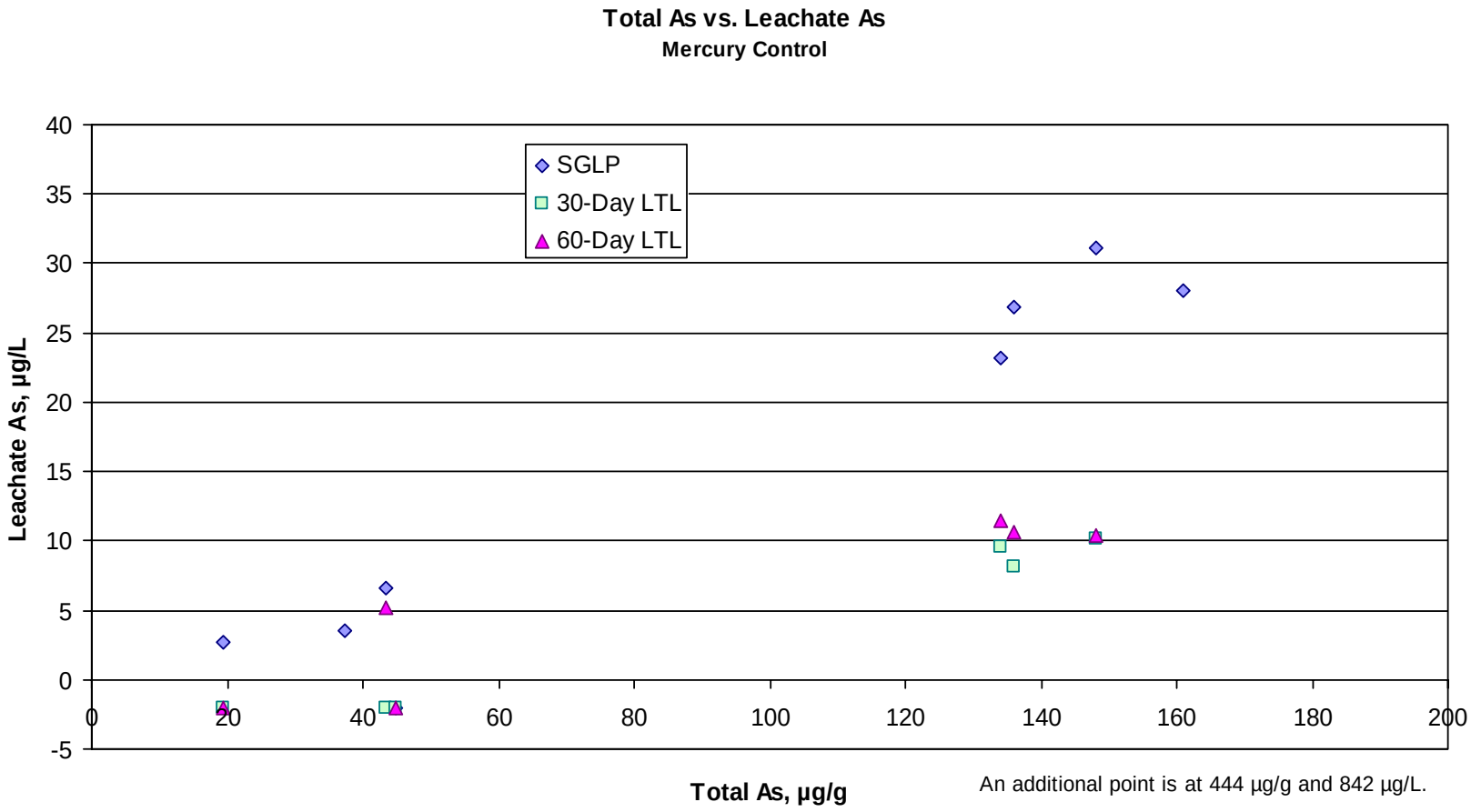
Leaching Results

Arsenic – Fly Ash Without Hg Control



Leaching Results

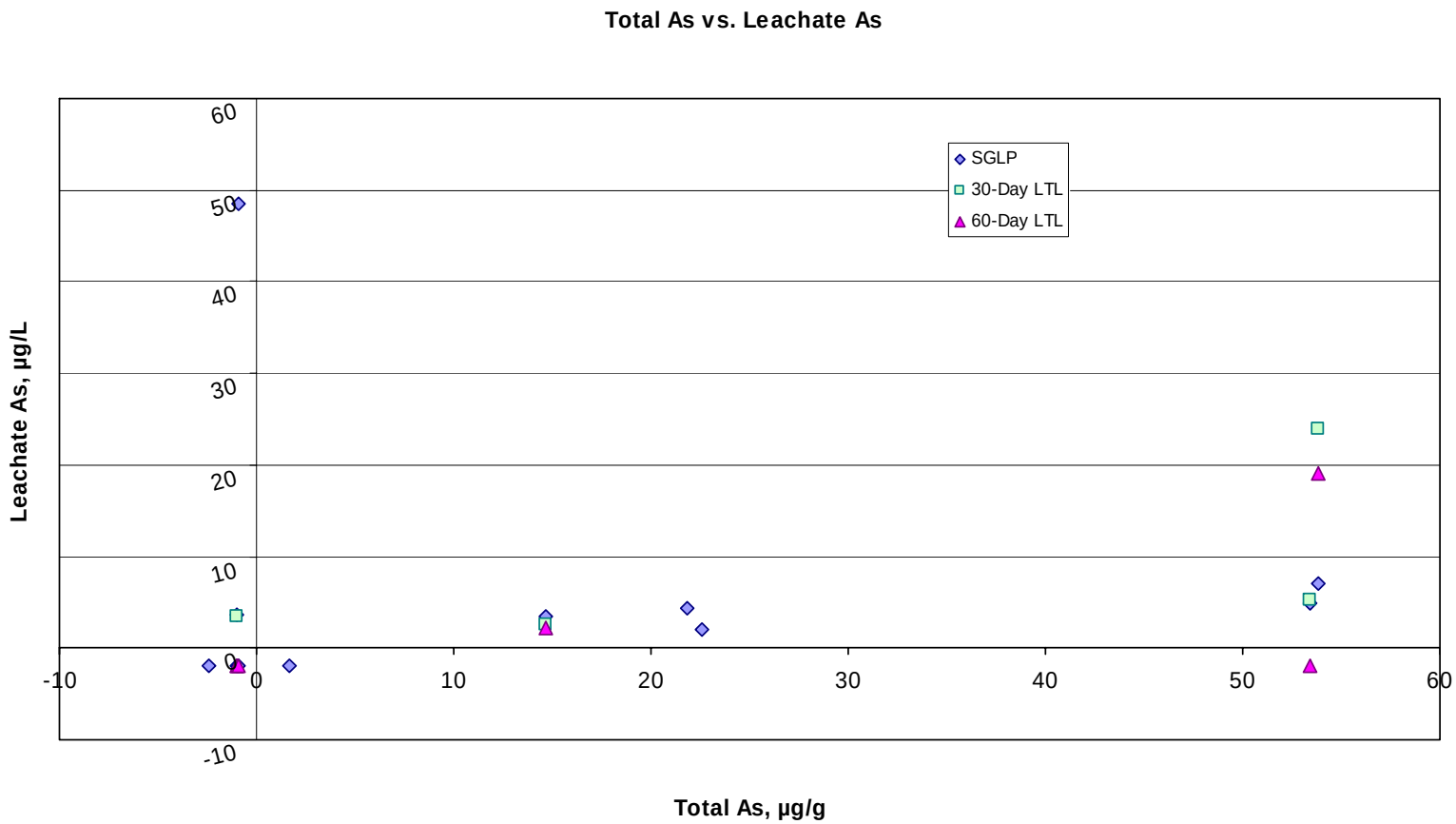
Arsenic – Fly Ash with Hg Control



An additional point is at 444 µg/g and 842 µg/L.

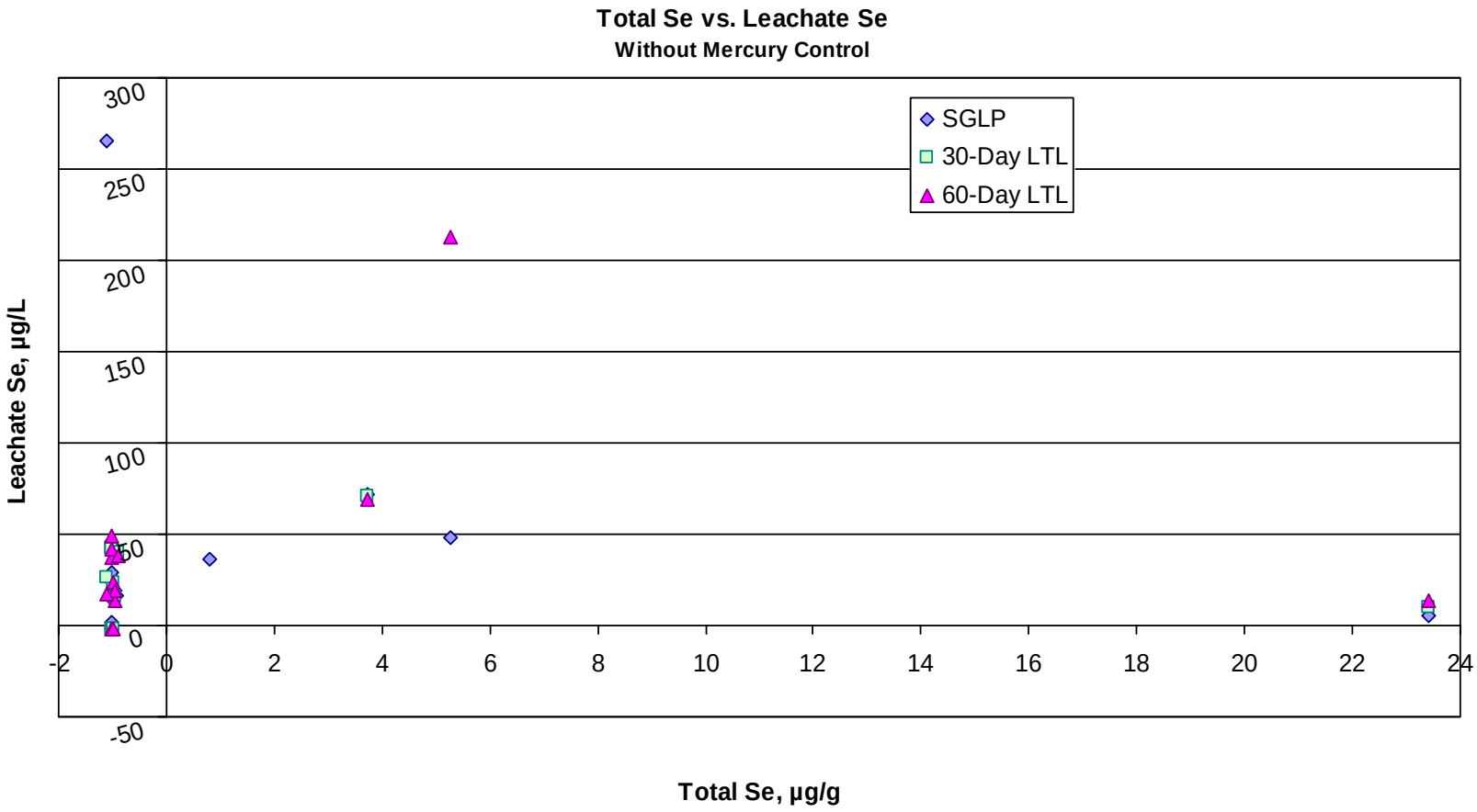
Leaching Results

Arsenic – FGD Materials



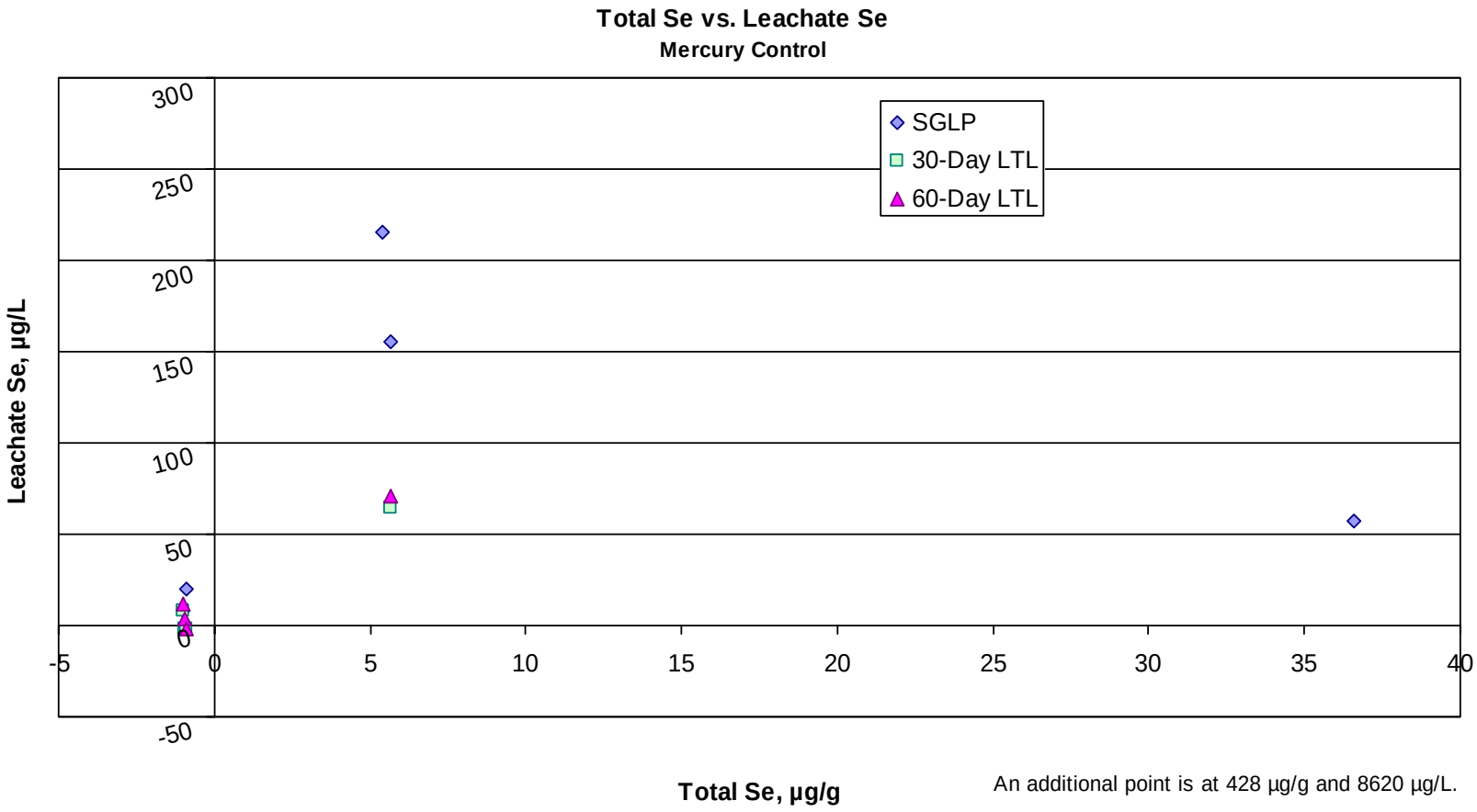
Leaching Results

Selenium – Fly Ash Without Hg Control



Leaching Results

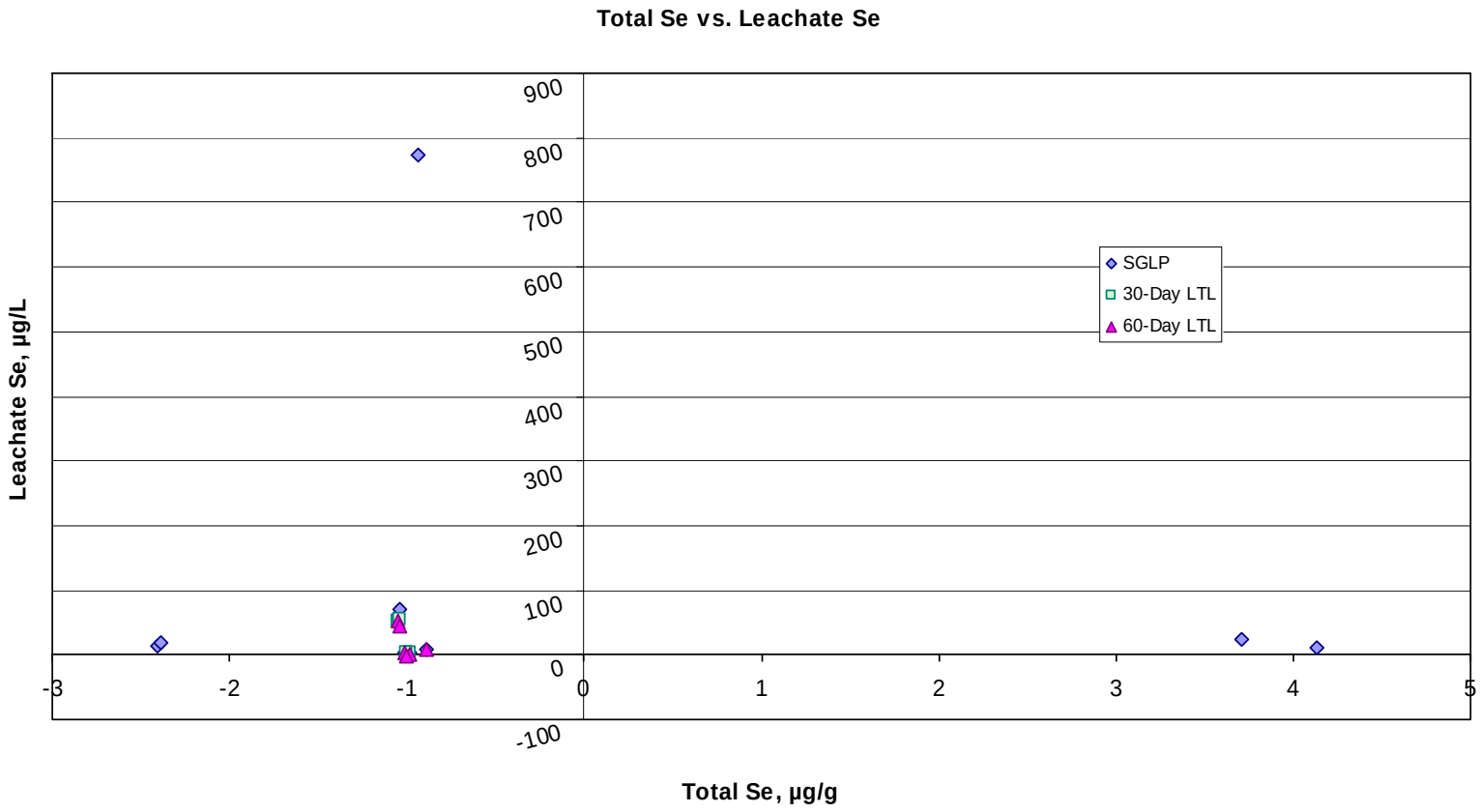
Selenium – Fly Ash with Hg Control



An additional point is at 428 µg/g and 8620 µg/L.

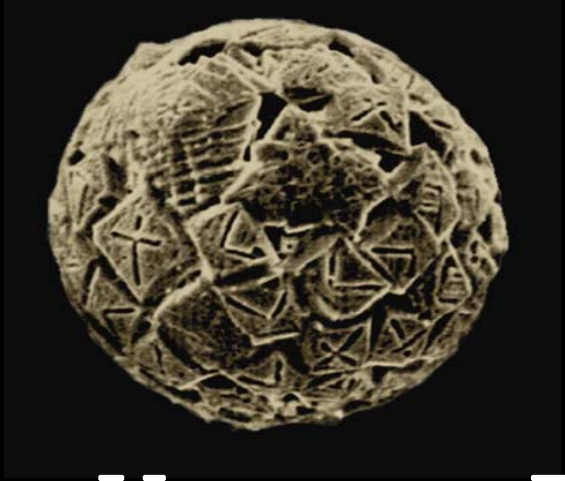
Leaching Results

Selenium – FGD Materials

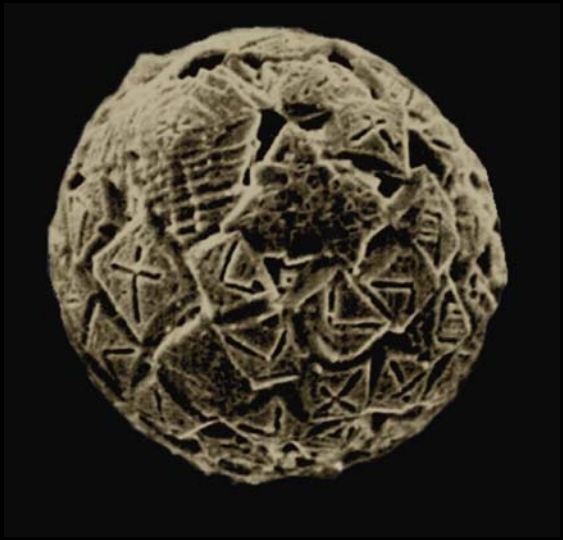


Some Leaching Observations

- Carbon sorbents present in leachates from fly ash samples WITH Hg control may sorb mobilized elements during the leaching tests.
- Leachate concentrations of some elements were lower in long-term leachates than in short-term leachates.

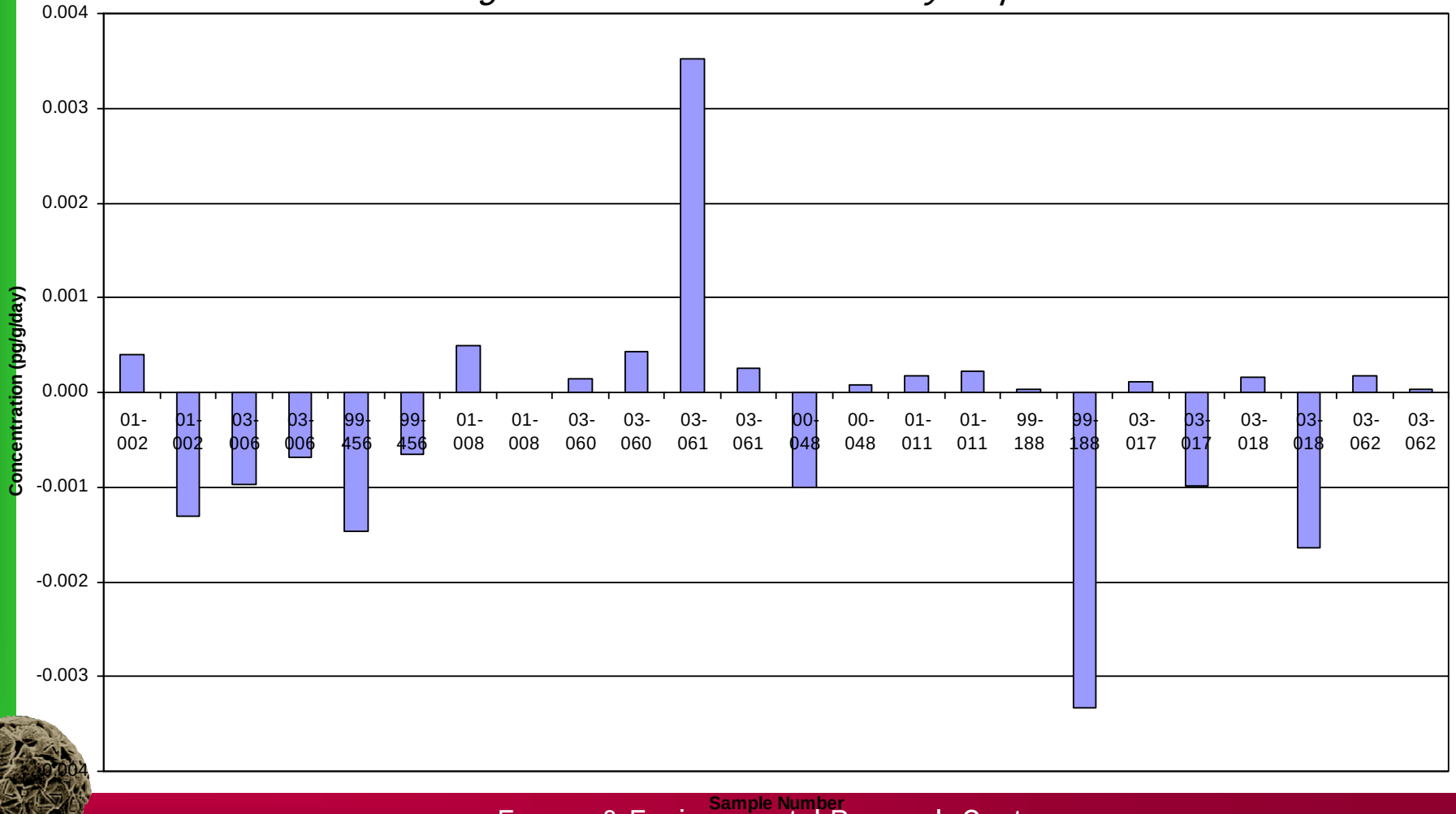


Vapor-Phase Transport Results



Vapor-Phase Transport
187-Day Release – *Sample Set 1*

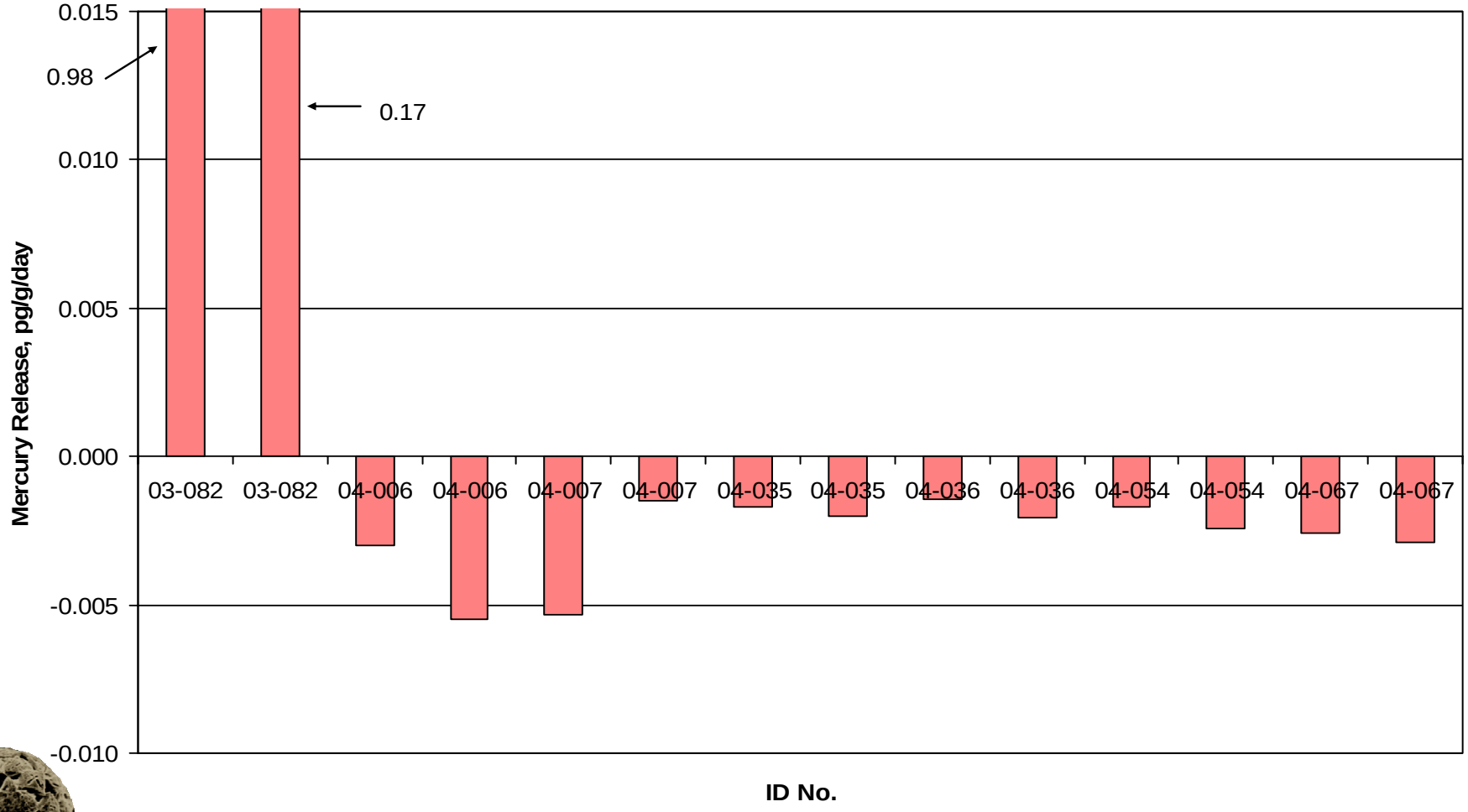
Positive values indicate mercury release,
and negative values indicate mercury sorption.



Vapor-Phase Transport

97-Day Release – *Sample Set 2*

Positive values indicate mercury release,
and negative values indicate mercury sorption.



Ambient Temperature Vapor-Phase Transport Conclusions

- Long-term ambient-temperature release of mercury from CCBs ranged from a net release to a net sorption of mercury at extremely low levels so this release mechanism has low potential to impact atmospheric mercury loading.

Field Sampling

Site Description

Substrate Type	Site Location	Site Description
Fly Ash	Section 26	Uncovered, fly ash landfill
FGD + Pyrite	Section 32 – 10 acres	Uncovered disposal of material from Ash Pond 91 during 2003
Fly Ash + Vegetated Soil	Section 32 – original 14 acres	Closed, reclaimed (vegetated) fly ash landfill with 2 ft clay cap and 3 ft soil cover
FGD Scrubber Material (wet disposal)	Ash Pond 91	Wet disposal in the middle of the pond (unstabilized)
FGD Scrubber Material + Bottom Ash/Pyrites (wet disposal)	Ash Pond 92	Wet disposal in the middle of the pond (unstabilized) surrounded by a bottom ash embankment
FGD + Fly Ash (stabilized)	SE Section 16	Uncovered HDPE-lined facility (stabilized)
Background Soil	5 miles NW of generation facility	Natural grassland

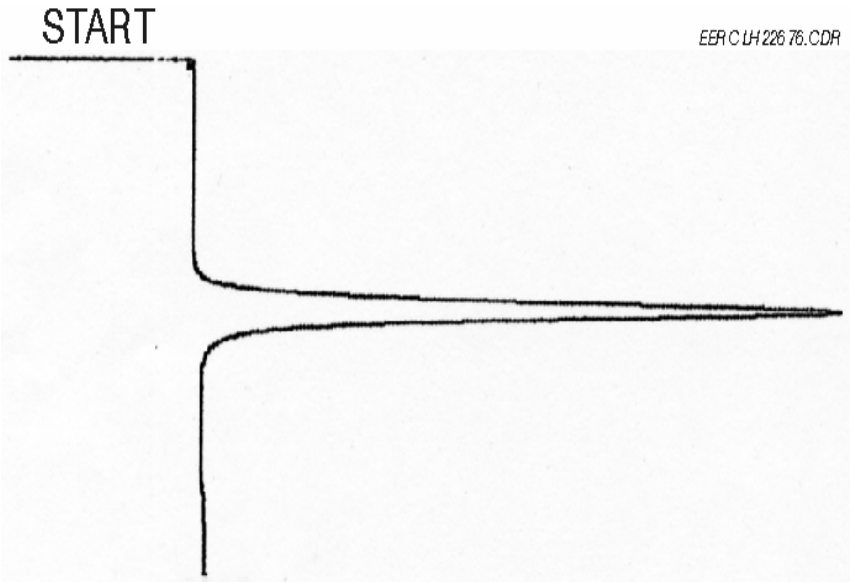
Field Sampling – Results

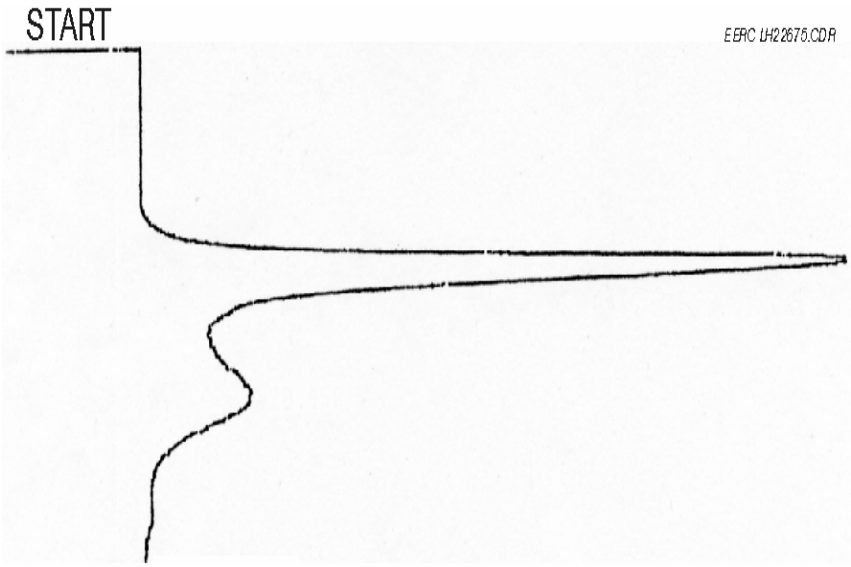
Substrate Type	Sample Location	Elemental Hg (ng/m³)	n	Organo-Hg (ng/m³)	n
Fly Ash	Section 26	1.021 (+/-) 0.238	4	0.052 (+/-) 0.038	2
FGD + Pyrite	Section 32 – 10 acres	1.459 (+/-) 0.995	4	0.006 (+/-) 0.002	2
Reclaimed Fly Ash (vegetated)	Section 32 – original 14 acres	0.616 (+/-) 0.277	4	0.019 (+/-) 0.026	2
FGD Scrubber Material (wet disposal)	Ash Pond 91	0.954 (+/-) 0.413	4	0.045 (+/-) 0.042	2
FGD + Bottom Ash/ Pyrites (wet disposal)	Ash Pond 92	0.541 (+/-) 0.193	4	0.023 (+/-) 0.011	2
FGD + Fly Ash (stabilized)	SE Section 16	0.849 (+/-) 0.378	4	0.354 (+/-) 0.476	2
Natural Grassland	5 miles NW of generation facility	0.640 (+/-) 0.270	4	0.017 (+/-) 0.004	2

Field Sampling – Vapor-Phase Transport Conclusions

- Most sites emitted mercury to the atmosphere at low rates, but measured mercury values were very low and comparable to background.
- The highest elemental mercury concentrations were measured at a disposal site with an FGD scrubber material and pyrite mill rejects landfill.
- No strong correlation was found between mercury flux and total mercury content in each substrate.
- The measured organomercury concentrations were all exceptionally low.

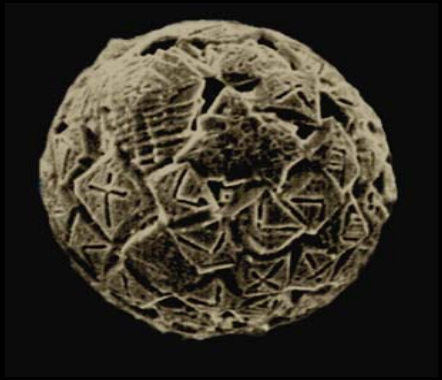
Elevated-Temperature Vapor-Phase Release – Typical Results



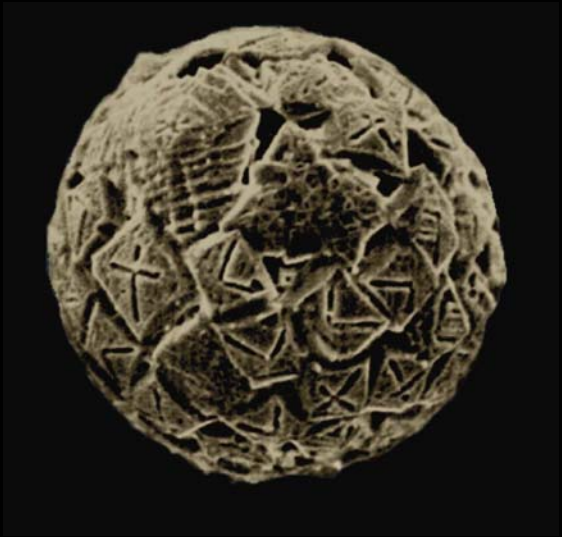


Observations on Hg & CCBs at Elevated Temperatures

- There may be multiple mechanisms affecting release of mercury at elevated temperatures.
- One- or two-peak desorption peaks were typical.
- Mercury generally released at temperatures greater than 200°C.
- For many samples, all mercury present was devolatilized between 200° and 750°C.
- Speciation is under continued evaluation.



Microbiologically Mediated Release Results



Microbiological Release

Vapor-Phase Release, pg/g

ID No.	Condition	Hg^0	OrganoHg	ID No.	Condition	Hg^0	OrganoHg
03-079	Anaerobic	4.1	5.7	03-079	Aerobic	14.7	9.1
03-079	Anaerobic	2.8	5.0	03-079	Aerobic	11.3	30.8
03-079	Anaerobic	5.3	6.7	03-079	Aerobic	19.8	2.5
03-082	Anaerobic	12.7	41.3	03-082*			
03-082	Anaerobic	0.7	2.6	03-082	Aerobic	486	90.0
03-082	Anaerobic	1.5	102	03-082	Aerobic	648	110
04-043	Anaerobic	1.3	1.1	04-043	Aerobic	46.5	4.5
04-043	Anaerobic	2.2	0.6	04-043	Aerobic	4.0	1.4
04-043	Anaerobic	1.9	1.0	04-043	Aerobic	9.1	1.3

**Flask broke near beginning of experiment*

Microbiological Release

Solution Methylmercury Release

ID No.	Condition	Measured, pg/mL	Released, pg/g	ID No.	Condition	Measured, pg/mL	Released, pg/g
03-079	Anaerobic	13	98	03-079	Aerobic	32	240
03-079	Anaerobic	15	113	03-079	Aerobic	7	53
03-079	Anaerobic	<5	<38	03-079	Aerobic	12	90
03-082	Anaerobic	**	**	03-082*			
03-082	Anaerobic	250	1875	03-082	Aerobic	18	135
03-082	Anaerobic	**	**	03-082	Aerobic	99	743
04-043	Anaerobic	31	233	04-043	Aerobic	<5	<38
04-043	Anaerobic	19	143	04-043	Aerobic	65	488
04-043	Anaerobic	18	135	04-043	Aerobic	13	98

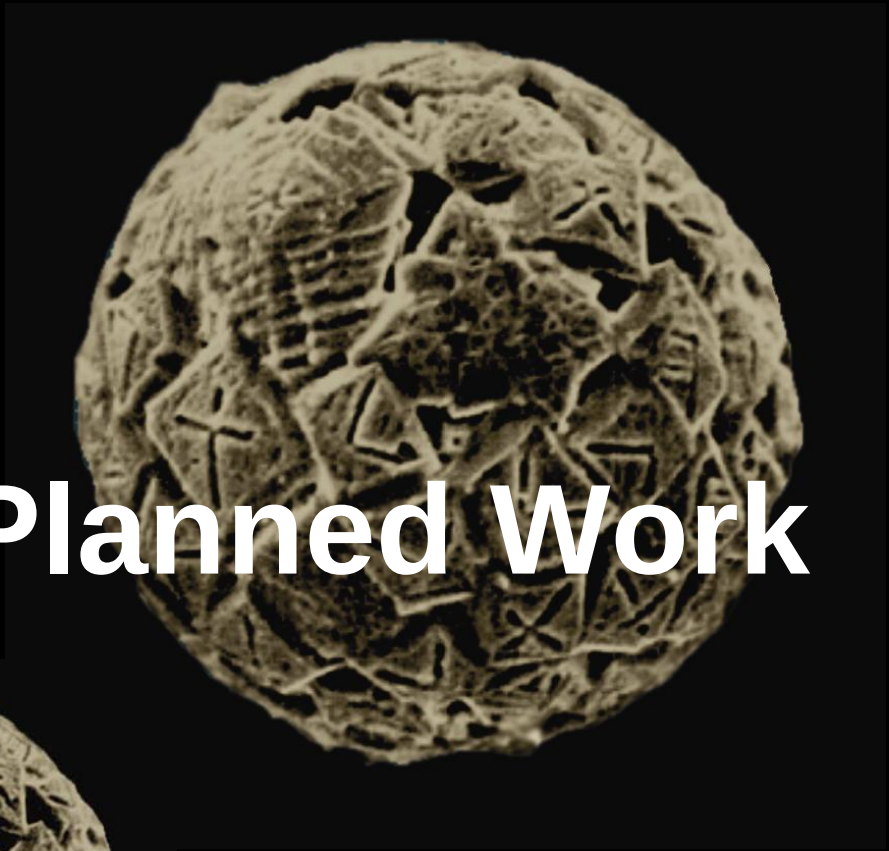
*Flask broke near beginning of experiment

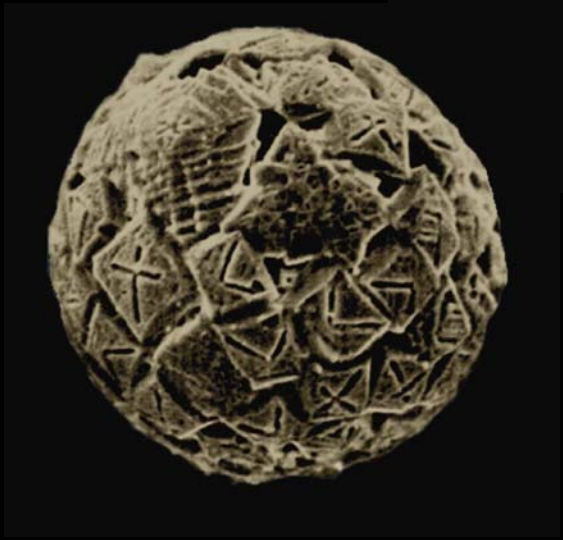
**Samples precipitated colloidal sulfur on standing and were not analyzed.

Observations on Microbiologically-Mediated Hg Release

- Results indicate methylation and release of organomercury in both vapor and leachate.
- Releases, were greater than direct leaching and ambient temperature vapor-phase releases, but were low.
- FGD materials provide needed conditions to promote microbiologically mediated releases.

Ongoing & Planned Work





Focus Areas for Year 3 Work

- Continue evaluation of “paired” samples to evaluate changes in release profiles for comparative samples without and with mercury controls present.
- Continue ambient-temperature vapor-phase release experiments including FGD materials.
- Continue microbiologically mediated release experiments including FGD materials and CCB–soil mixtures.
- Perform field testing at one additional site.

Acknowledgements

Sponsors

- Cinergy
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