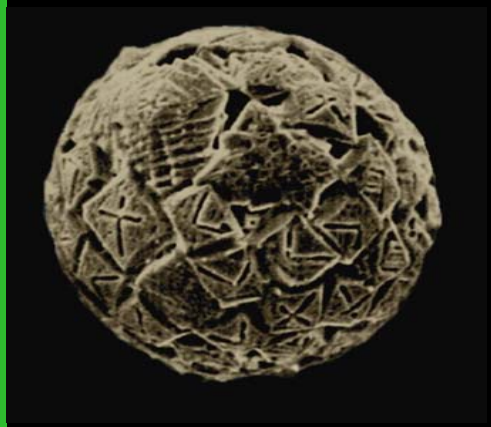
Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization



DOE NETL Mercury Control
Project Review Meeting
December 12–14, 2006

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

Project Sponsors

- Cinergy
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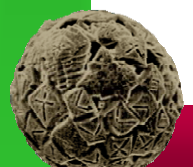
- Utility Solid Waste Activities Group



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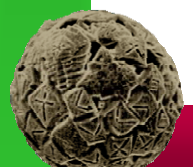
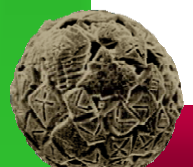


Project Tasks

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



Project Samples

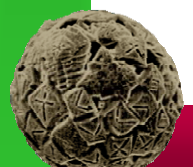
Sample Type	Coal Type	# Samples by Hg control	24-hour pH range	LOI range, %	Total Hg range, µg/g
Fly ash	E. Bit.	9 with ACI	3.99–9.20	12.6–24.4	0.742–120
		17 none	5.52–12.44	0.47–12.7	<0.01–0.685
Fly ash	Subbit.	5 with ACI	10.95–12.60	2.11–4.14	0.640–5.81
		2 none	12.27–12.56	0.48–1.08	0.261–0.578
Fly ash	Lignite	17 with ACI	10.52–12.77	0.59–13.2	0.147–64.5
		13 none	10.50–12.74	0.22–7.48	<0.01–0.878
Fly ash + FGD-SDA	Lignite	1 with ACI	12.50	1.12	0.332
		1 none	12.54	0.95	<0.01
FGD material	E. Bit.				
– wet Mg-enhanced lime		3 none	7.75–8.86	1.22–6.06	0.032–1.80
– wet limestone – nonoxidized		6 none	7.70–12.43	3.11–6.19	0.136–0.305
– wet limestone – forced oxidation		3 none	7.72–7.95	1.60–2.26	0.043–0.103

Fly Ash Sample Subset

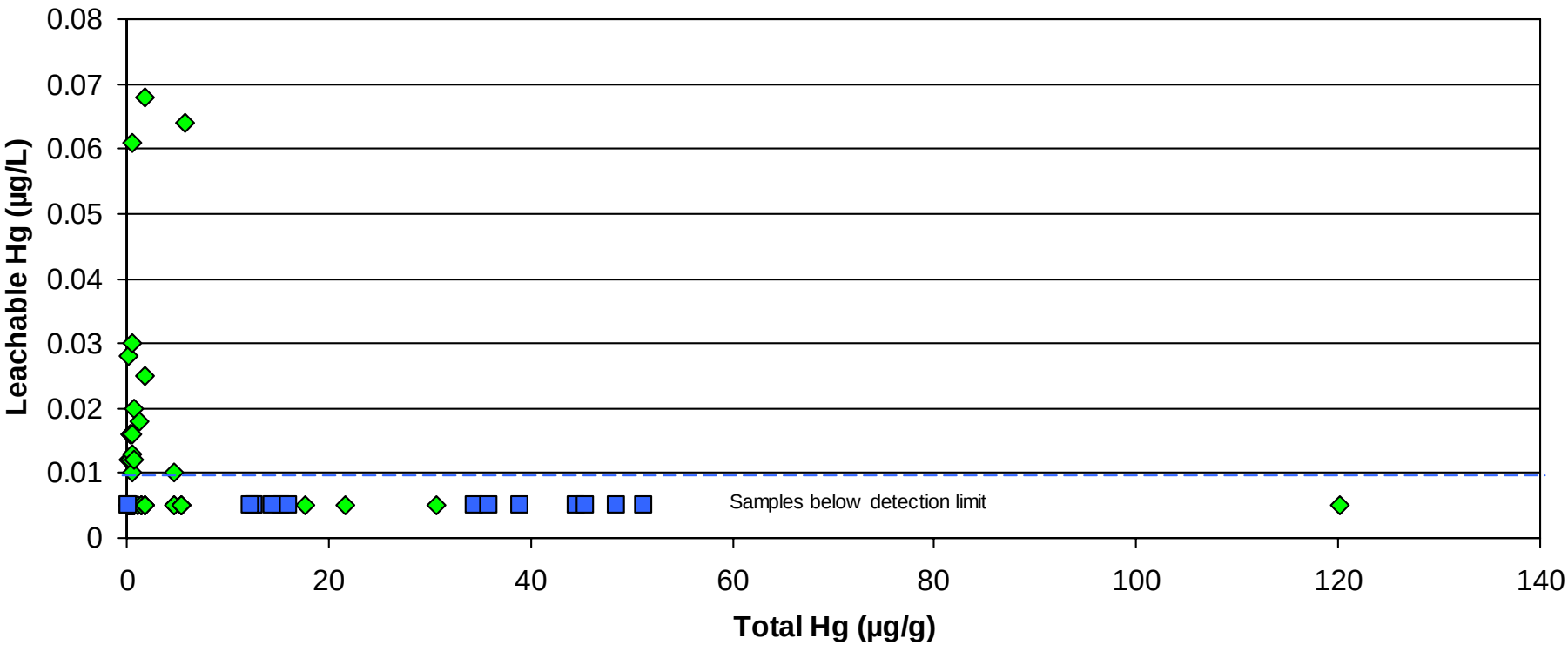
ID No.	Test Type	AC Type	AC Injection Rate, lb/Macf	Ash Loading, lb/Macf	LOI, %	24-hr pH	Total Hg, µg/g
Baseline	Baseline	N/A	N/A	4.7	0.22	11.73	0.104
Low Ash-1	Midterm	Luscar 4	2.5	4.7	13.2	11.33	39.0
High Ash-1	Midterm	Luscar 4	2.1	34	3.84	12.00	12.7
Low Ash-2	Midterm	DARCO®	2.0	4.7	9.45	11.41	35.9
High Ash-2	Long-term 1	DARCO®	1.8	34	3.18	11.99	12.6
Low Ash-3	Long-term 2	DARCO®	2.0	4.7	9.68	11.36	44.5
Low Ash-4	Long-term 2	DARCO®	2.0	4.7	11.7	11.37	64.5

Total Elemental Concentrations, µg/g

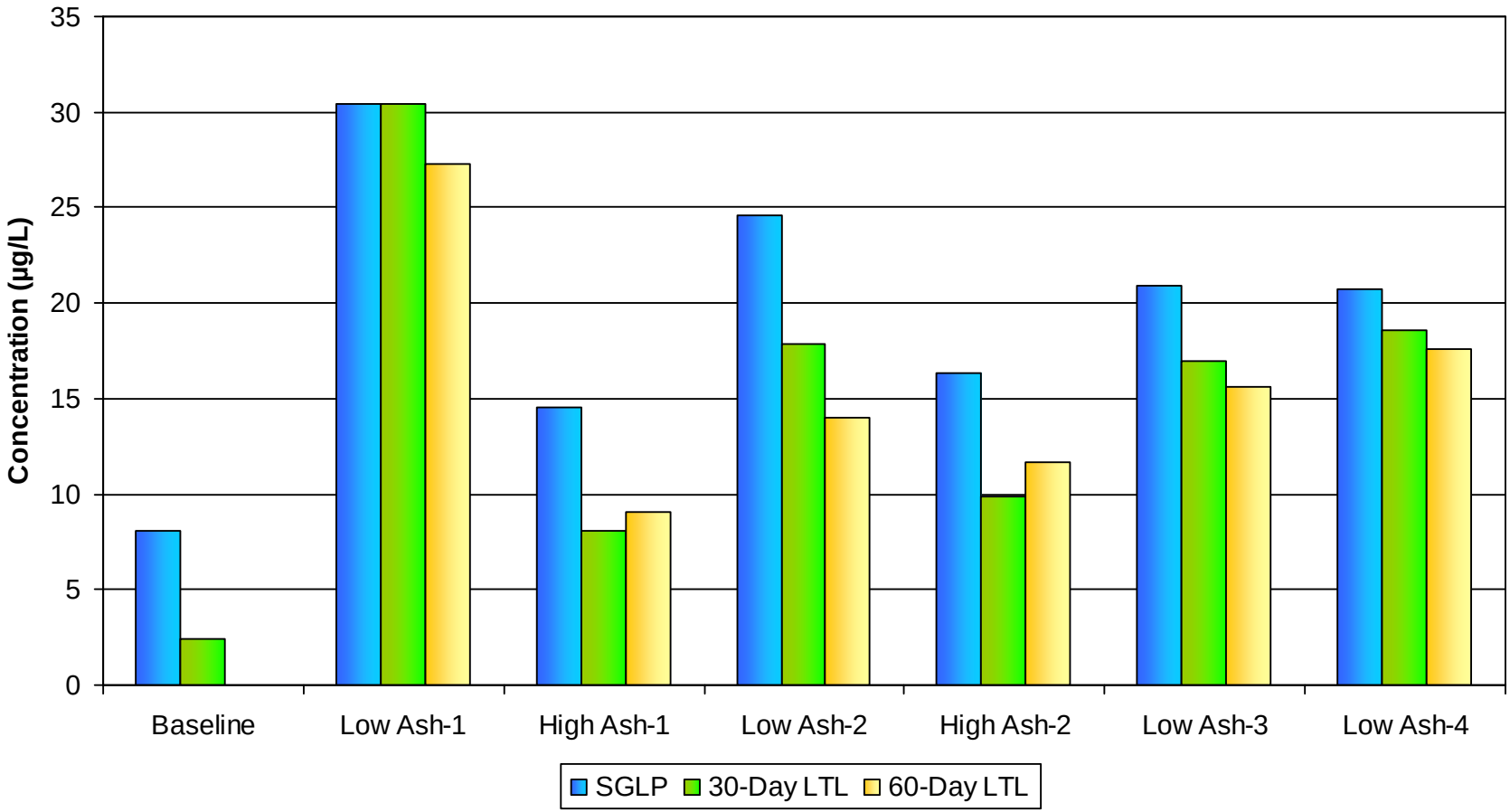
ID No.	As	Cd	Cr	Pb	Hg	Ni	Se
Baseline	43.4	0.864	43.4	90.1	0.104	21.1	23.4
ML-low	38.6	0.682	36.5	73.2	39.0	15.4	60.3
ML-high	48.3	0.865	42.6	87.1	12.7	18.6	22.5
MD-low	42.5	0.848	35.5	82.2	35.9	17.6	87.3
L1D-high	46.8	0.971	39.1	84.7	12.6	20.4	30.1
L2D-low	38.4	0.776	42.2	74.5	44.5	22.0	42.2
L2D-low2	35.5	0.708	39.8	72.0	64.5	20.6	38.9



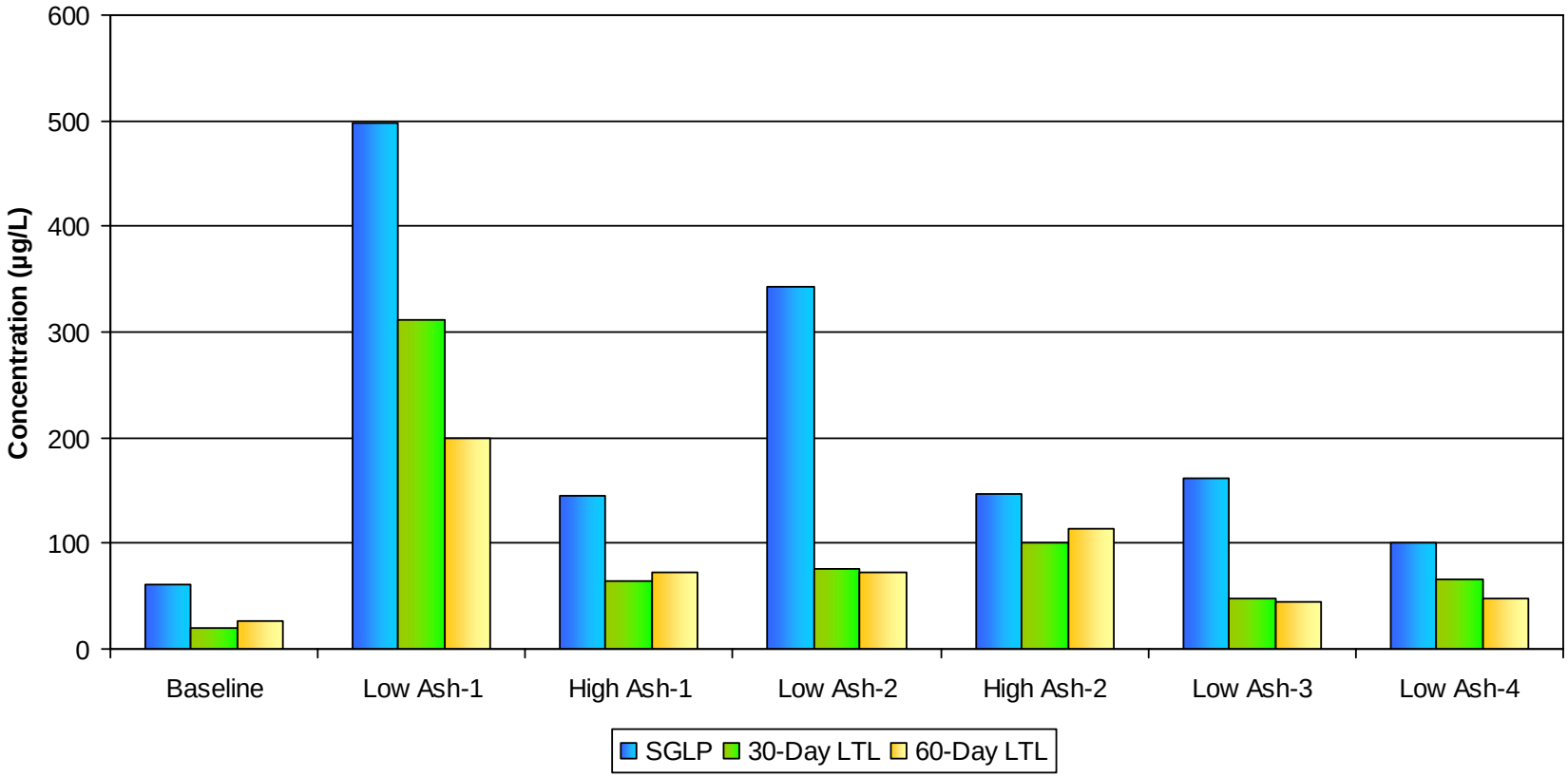
Total Hg vs. Leachable Hg



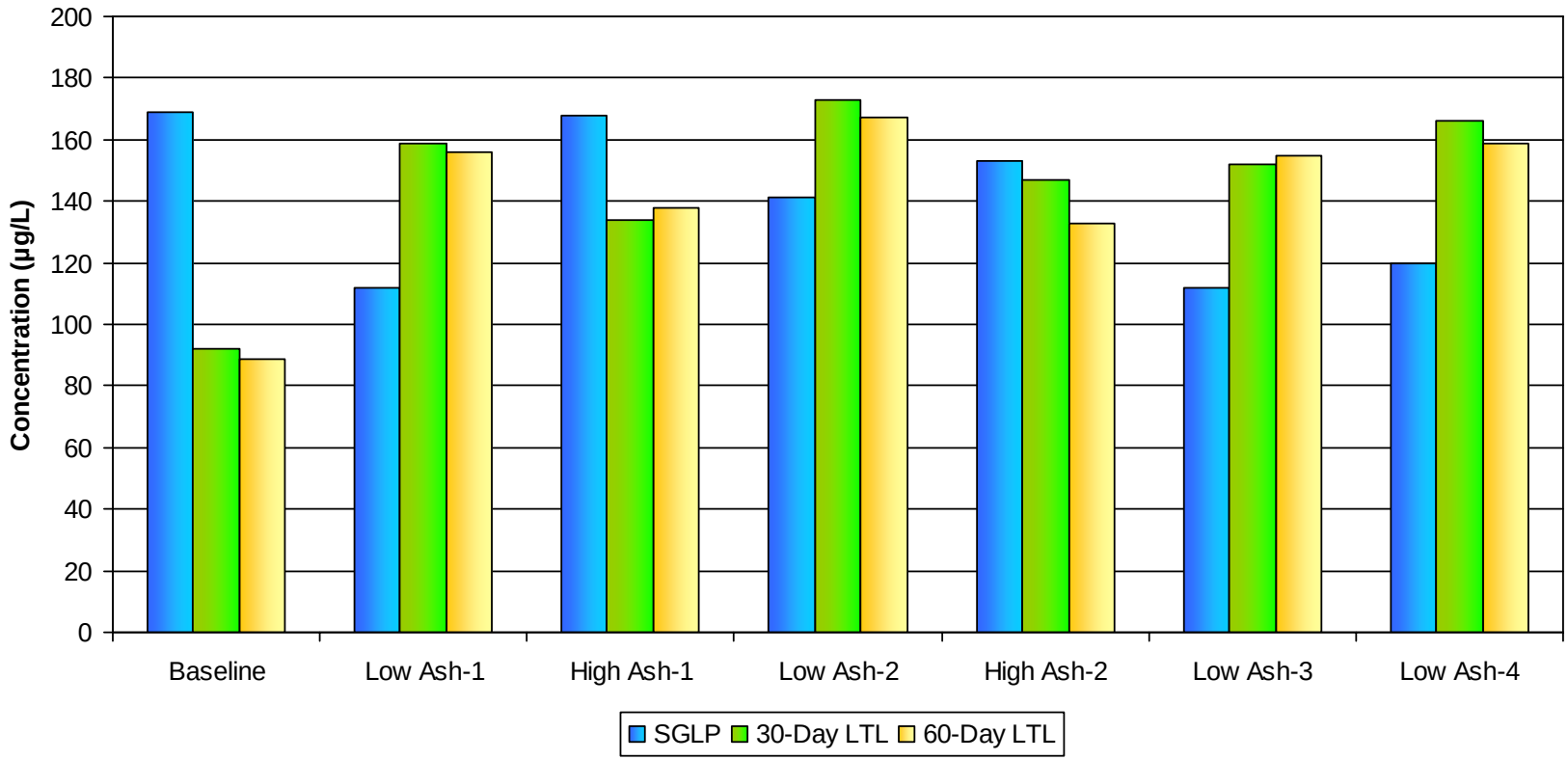
Leaching Results – Arsenic



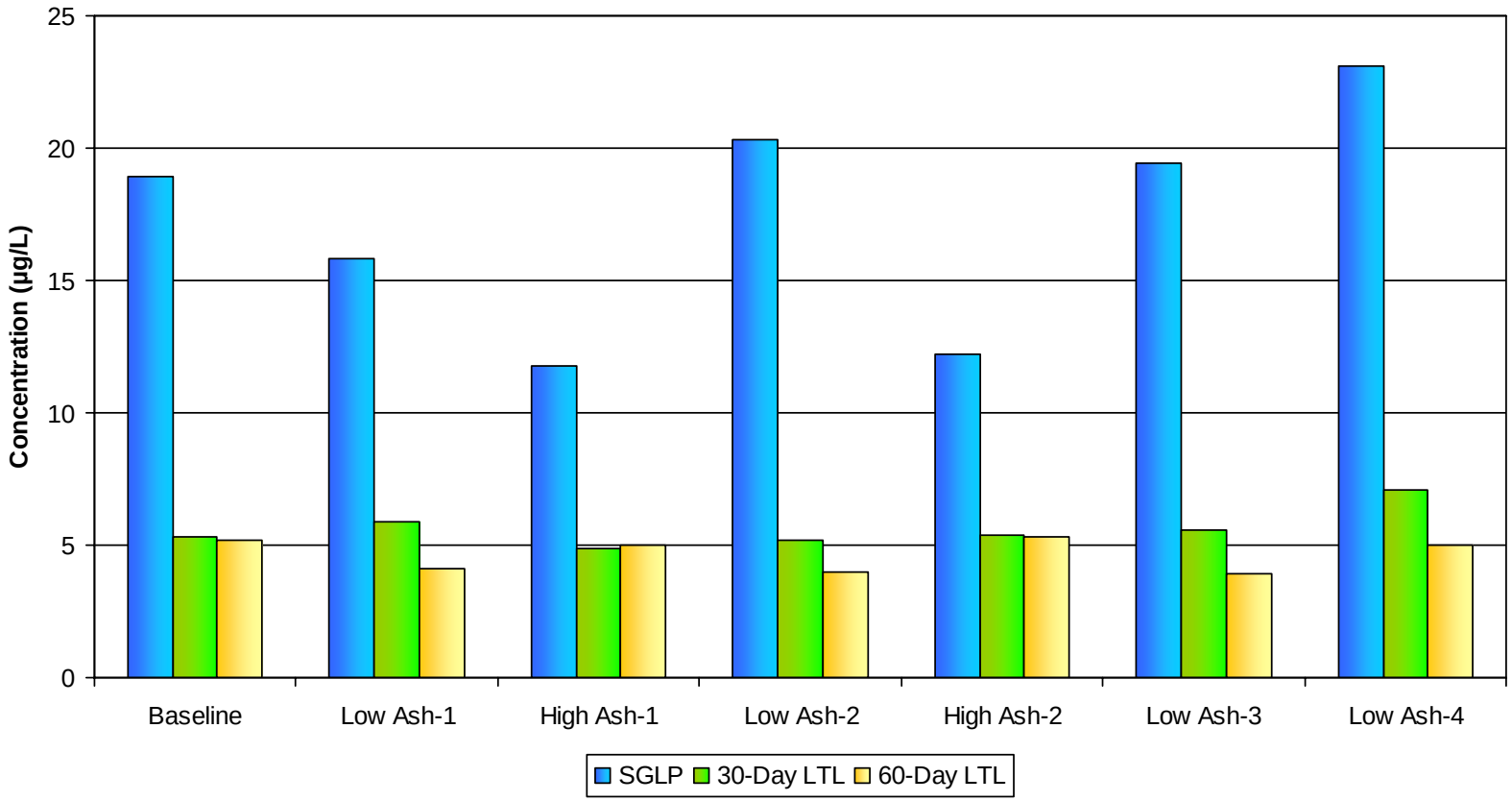
Leaching Results – Selenium



Leaching Results – Chromium

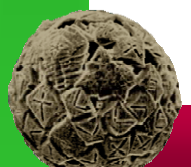


Leaching Results – Nickel



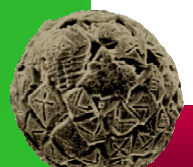
Leaching Summary

- Leachate pH ranged from 11.38 to 12.09.
- Mercury and lead leached below the detection limit (<0.01 and <2 µg/L).
- Leachate concentrations of nickel were lower from fly ash samples WITH Hg control than those WITHOUT Hg control, potentially indicating that leached nickel may be sorbed by the carbon sorbent in situ during the leaching tests.



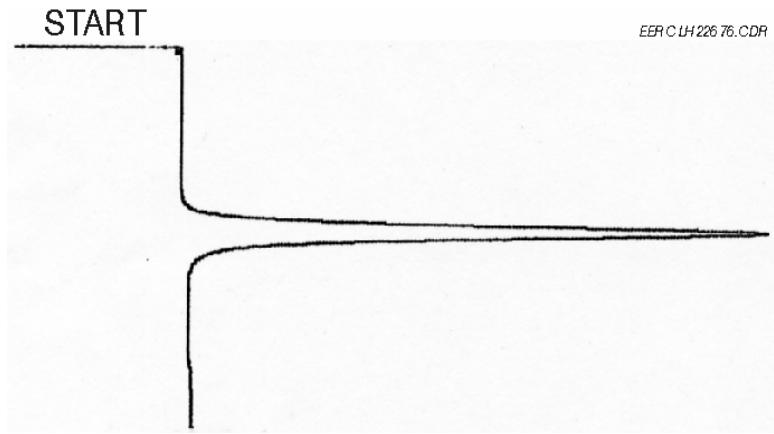
More Leaching Observations

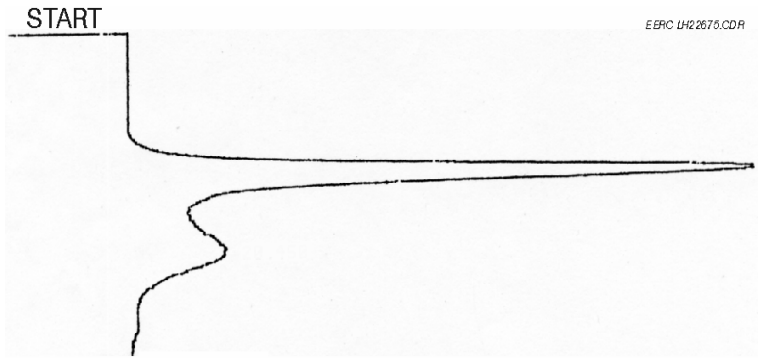
- Leaching results indicate that these materials are nonhazardous using Resource Conservation and Recovery Act (RCRA) limits.
- Results confirm need to include long-term leaching to evaluate alkaline fly ash demonstrated by results for arsenic and selenium.



Elevated-Temperature Results

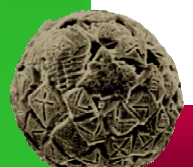
ID No.	First Hg Peak	Total Hg, µg/g
Baseline	**>330°C**	**0.104**
ML-low	>420°C	39.0
ML-high	>450°C	12.7
MD-low	>430°C	35.9
L1D-high	>430°C	12.6
L2D-low	>420°C	44.5
L2D-low2	>380°C	64.5



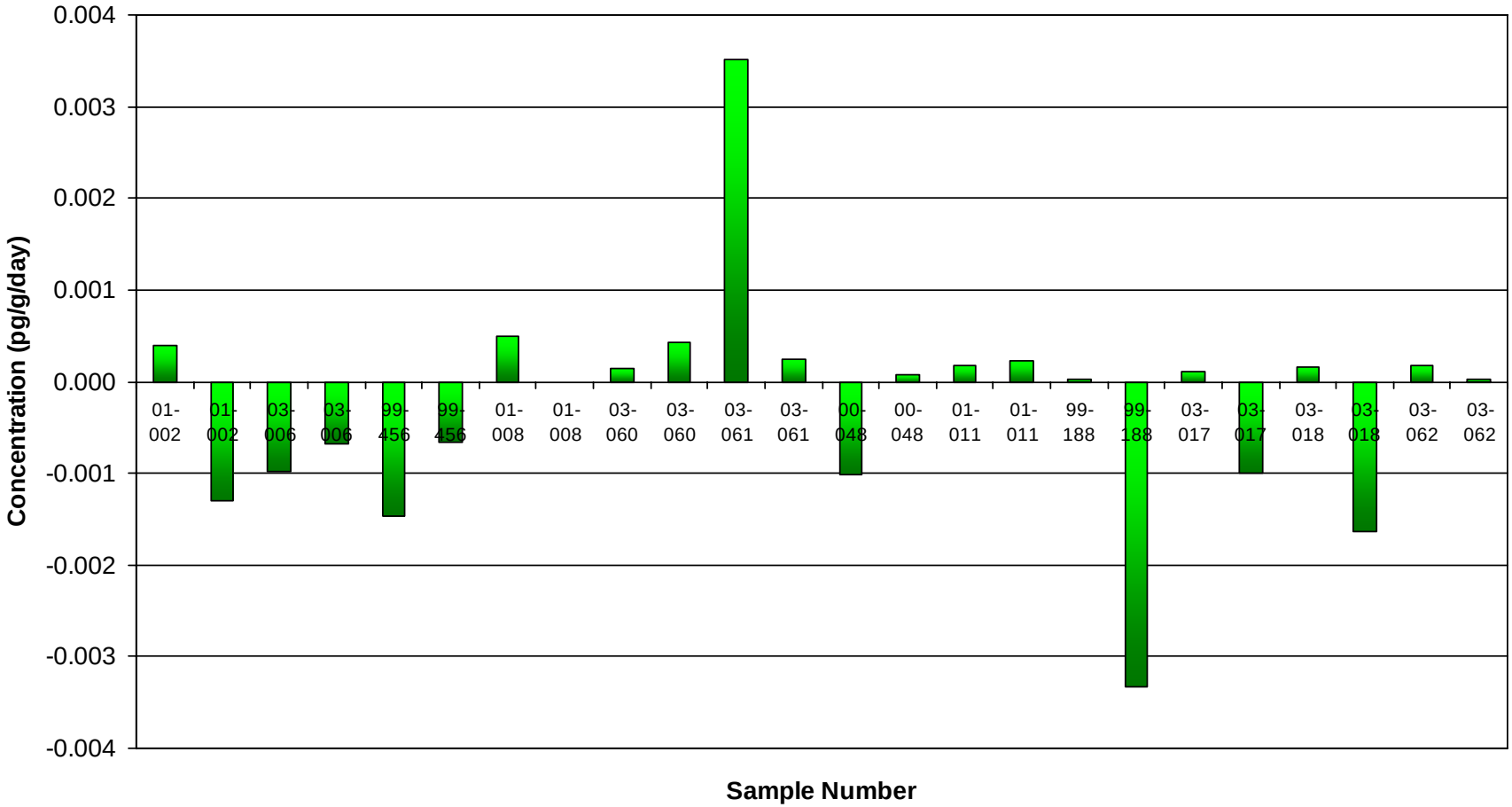


Elevated Temperature Vapor-Phase Transport Observations

- Mercury is released from fly ash and fly ash-AC samples when exposed to elevated temperatures. The temperature at which mercury release is first measured and number of peaks noted varies by sample.
- In example presented, the temperature of first mercury release was higher than previous samples.



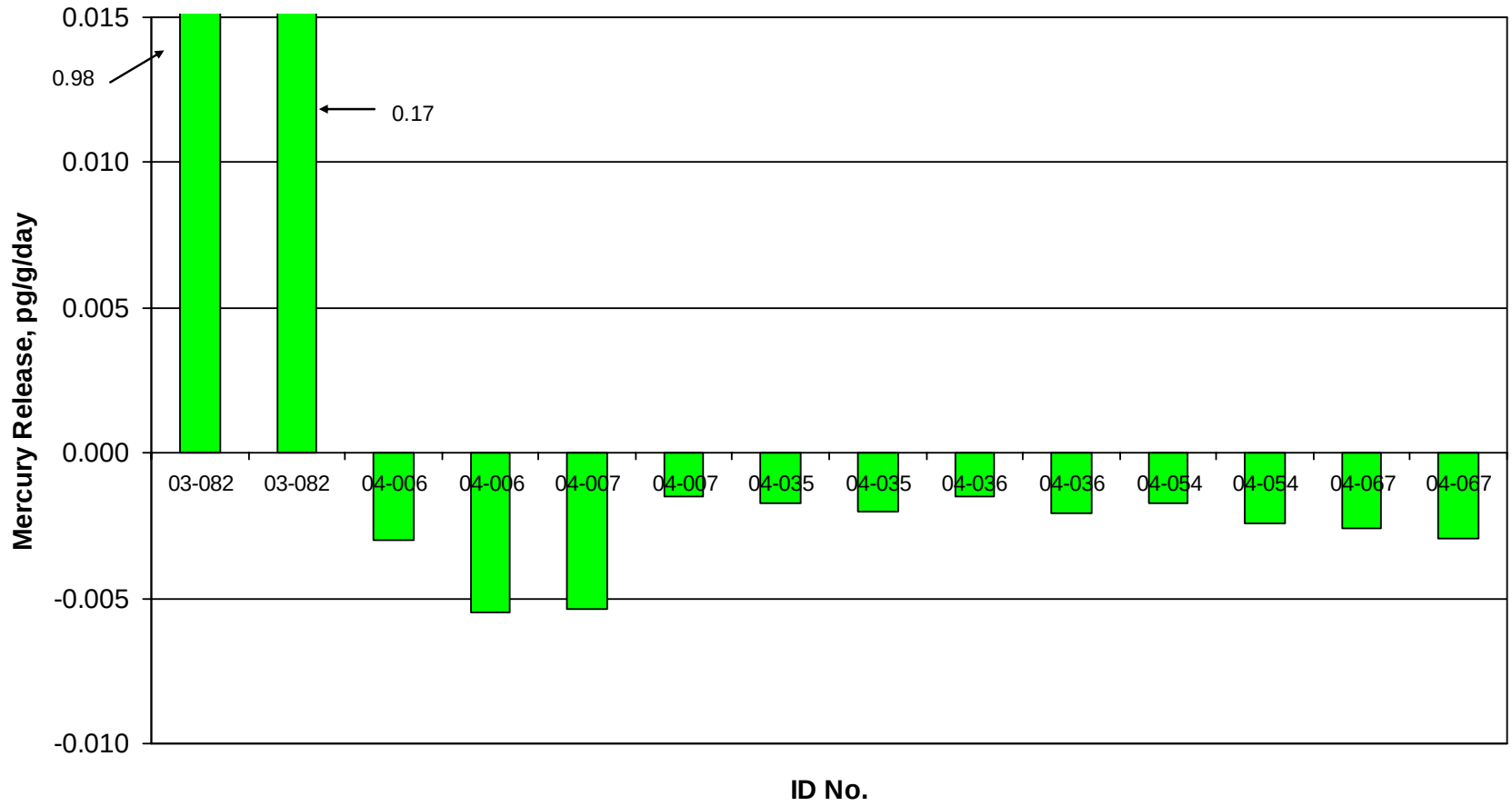
Vapor-Phase Transport
187-Day Release – *Sample Set 1*



Positive values indicate release and negative values indicate sorption.

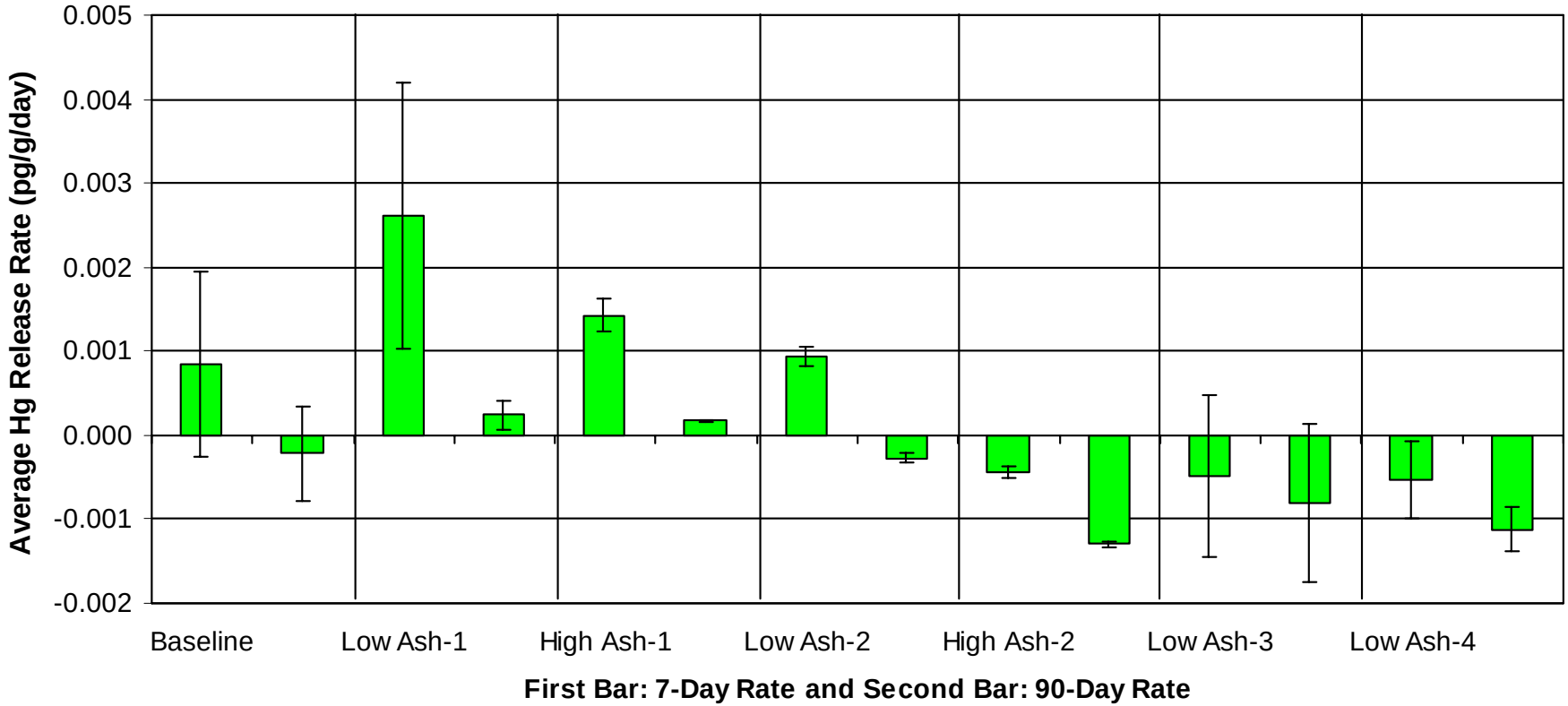
Vapor-Phase Transport

97-Day Release – *Sample Set 2*



Positive values indicate release and negative values indicate sorption.

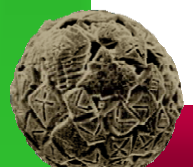
Ambient-Temperature Hg Sorption and Release Over 7 Days and 90 Days



Positive values indicate release and negative values indicate sorption.

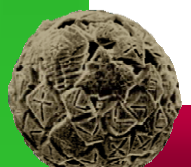
Long-Term Ambient-Temperature Hg Experiments (97 days)

ID No.	Total Hg, µg/g	Average Total Hg Sorbed or Released, µg/g	Average % Sorption or Release	Average Years to Release 100% Hg
Baseline	**0.104**	**-0.0000000139**	**-0.0000134**	**NA**
ML-low	39.0	0.0000000402	0.000000103	259,393,862
ML-high	12.7	0.0000000253	0.000000199	134,078,921
MD-low	35.9	-0.0000000179	-0.0000000498	NA
L1D-high	12.6	-0.000000120	-0.000000950	NA
L2D-low	44.5	-0.0000000759	-0.000000170	NA
L2D-low2	64.5	-0.000000105	-0.000000162	NA



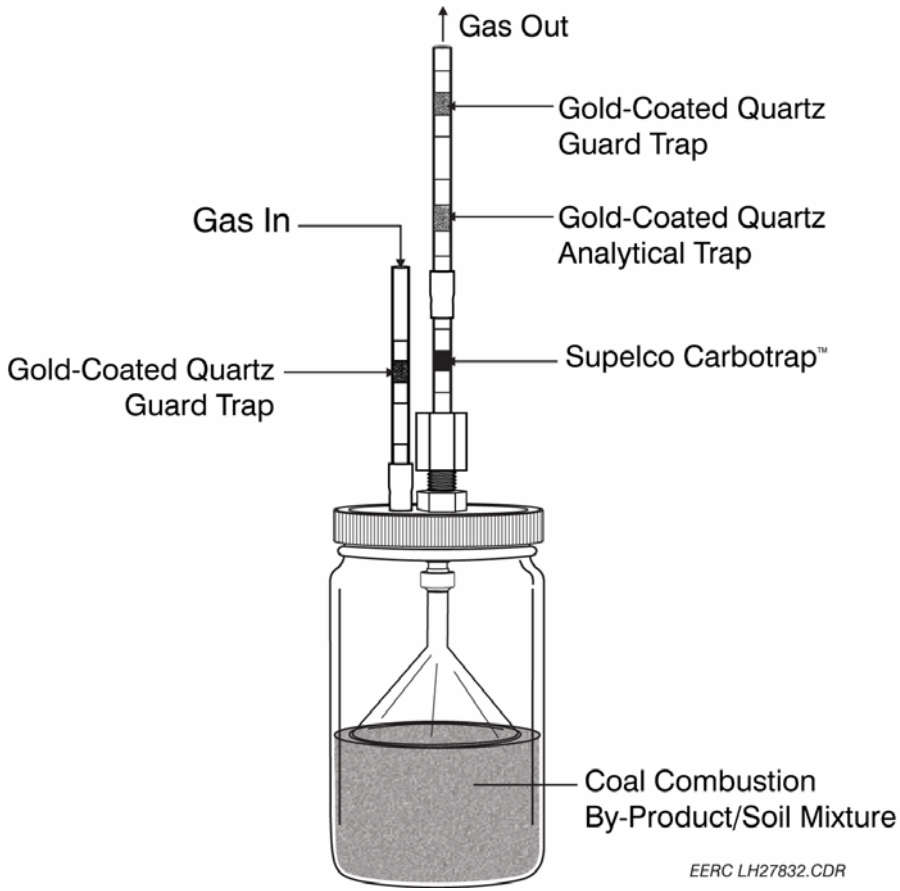
Ambient Temperature Vapor-Phase Transport Observations

- Fly ash-AC samples act as mercury sorbents.
- Fly ash may sorb or release mercury.
- Limited data on FGD materials indicated higher potential for mercury release at ambient temperatures.

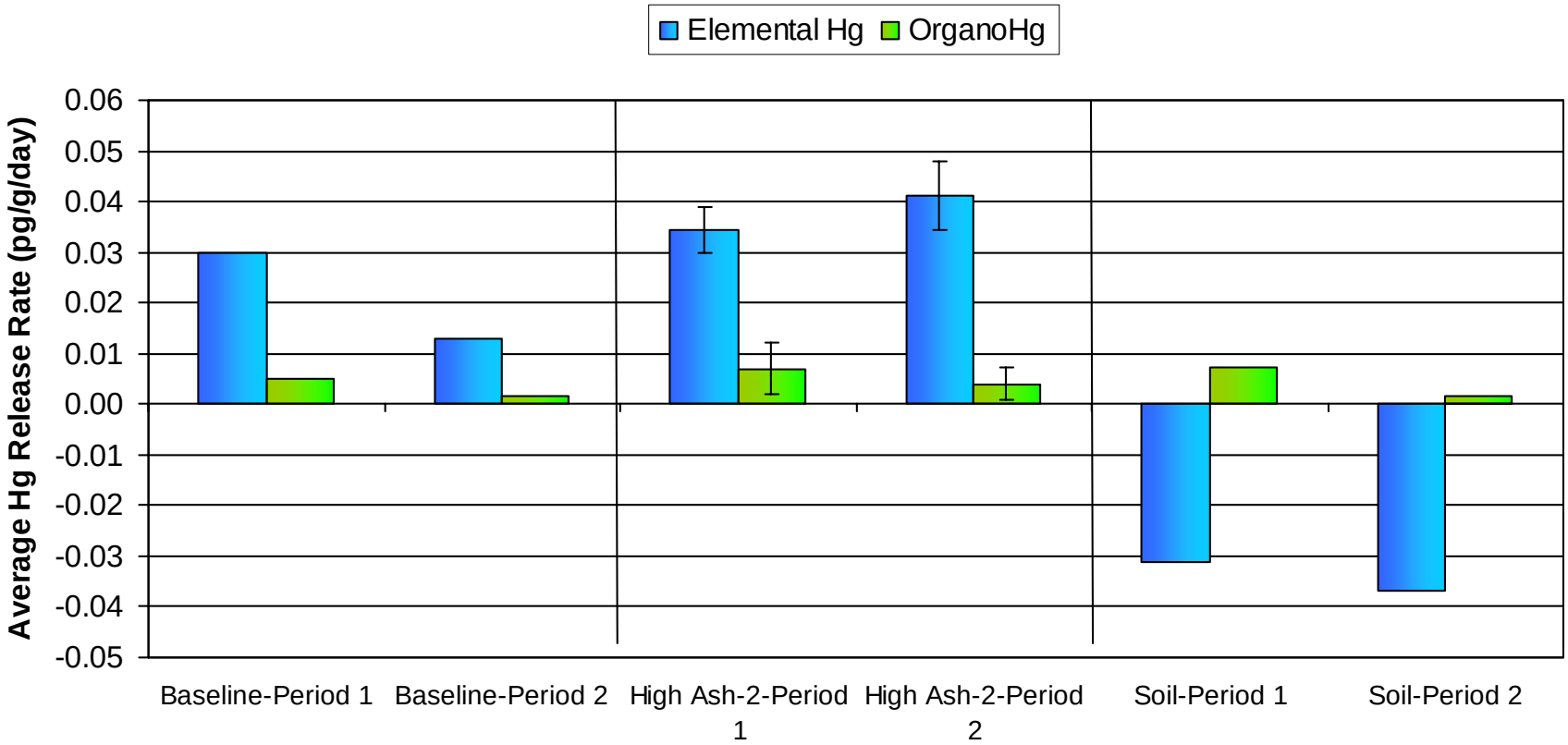


CCB–Soil Microbiological Hg Release Methods

- Similar to long-term ambient-temperature setup
- 20% addition of CCB to soil
  - Moisture added to soil to increase microbial activity
- Elemental and organomercury capture



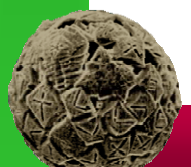
CCB–Soil Microbiological Hg Release Results



Positive values indicate release and negative values indicate sorption.

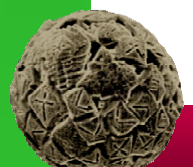
Microbiologically Mediated Mercury Release Observations

- Early experiments indicated that organomercury compounds were present in leachates and vapor generated.
- Recent experiments indicated that organomercury vapor-phase releases were similar in fly ash, fly ash-AC, and soil.
- Elemental mercury vapor-phase releases were higher for fly ash and fly ash-AC than for soil.



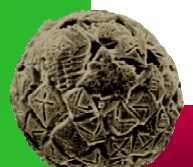
Conclusions

- In addition to mercury, results indicated that selenium may be sorbed on AC.
- Results from release experiments indicated that fly ash and fly ash-AC exhibit similar performance for mercury leaching and elevated temperature vapor-phase release mechanisms.
- Selenium leaching was higher for some fly ash-AC samples than baseline fly ash samples.



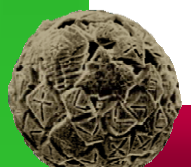
Conclusions

- Ambient-temperature vapor-phase release of mercury from fly ash ranged from a net release to a net sorption of mercury at extremely low levels.
- Fly ash-AC tends to sorb mercury in ambient temperature vapor-phase experiments.
- Organomercury compounds were present in leachates and vapor generated in the experiments performed to evaluate mercury release under microbiologically mediated conditions.



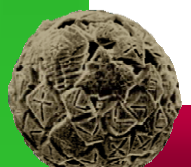
Conclusions

- Mercury associated with fly ash is stable for most current fly ash management options.
- Exposure to elevated temperatures (<250°C) has comparatively high potential to release mercury from fly ash and fly ash-AC.



Conclusions

- The impact of additives used to enhance mercury capture has not been evaluated.
- All types of FGD materials require additional investigation.



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