The Impact of Mercury Control Technologies on Mobility Pathways of Hg, Ni, As, Se, Cd and Pb from Coal Utilization Byproducts

Paper 85

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ABSTRACT

The US Department of Energy/National Energy Technology Laboratory (DOE/NETL) is assessing the fate of mercury removed from flue gas by mercury control technologies (Hg-CT) at coal-fired utilities. Hg-CT are expected to impact the quality of the coal utilization by-products (CUBs) by increasing the concentration of mercury. However, the impact of Hg-CT on other metals has received little study. One of the major test objectives of this study is to determine the impact of Hg-CT on nickel, arsenic, selenium, cadmium, and lead. Results to date show that Hg-CT resulted in an increase of Hg in CUBs for all facilities and Se for several facilities. Thermal release of Hg in CUBs heated to 190°C for 1 hour increased in some facilities using Hg-CT while others were decreased, leading to speculation that the Hg is stabilized in some cases. At 1200°C for 5 minutes, Hg emissions are significantly increased with Hg-CT. High percentages of Se (15-100%) were volatilized from all CUB samples. Microbial leaching resulted in significant methyl-Hg production and mobilization of Ni, As, Se and Cd. The chemical leaching procedure released a very low amount of target metals, except for Se at some facilities.

INTRODUCTION

According to surveys conducted by the American Coal Ash Association (ACAA), 125 million tons of coal utilization by-products (CUBs) such as fly ash and synthetic gypsum were generated in the United States in 2006 from the operation of coal-fired utilities (1). These CUBs are typically landfilled, impounded or utilized in various manufactured products such as wall board, asphalt and cement. A goal for DOE/NETL is to increase the amount of CUBs diverted from landfills or impoundments towards beneficial uses to 50% by 2010 (2). The ACAA estimates that 43% of CUBs were utilized for manufactured products in 2006 (1).

Mercury emissions from coal-fired utilities can be significant, depending on the source of the coal and operating conditions, and have been under scrutiny for many years by federal and state regulatory agencies. The EPA’s Clean Air Mercury Rule has recently been struck down by the Supreme Court leaving coal fired power plants without federal mercury requirements, though several states have mercury requirements. It is likely that when EPA issues new rules, coal-fired utilities will be subject to tighter mercury emission standards. While existing technologies for cleaning flue gas have proven effective for removing mercury from flue gas emissions, additional measures will likely be necessary in order to meet the new requirements.

Numerous mercury control technologies (Hg-CT) have been tested under various operating conditions at multiple facilities. As the mercury is removed from flue gas, it partitions to the solid or liquid by-product stream, potentially impacting the quality of the CUBs. Other metals can be transferred from the flue gas to the CUBs such as nickel, arsenic, cadmium and lead. The purpose of this work is to study the impact of Hg-CT on the mobility of mercury and other metals in CUBs.

EXPERIMENTAL METHODS

CUB samples were collected from 16 coal fired facilities undergoing trials of different mercury removal technologies (see Table 1 for a description of the Hg-CT conditions at each facility). CUB samples collected during baseline conditions were compared to samples collected during the trials. All CUB samples were subjected to various testing procedures designed to mimic the possible end uses of the materials. The testing procedures and associated end uses are summarized in Table 2. All testing and analysis was performed at Frontier GeoSciences (FGS) except for the microbial leaching test, which was performed by the Smithsonian Environmental Research Center (SERC).

Samples were collected in triplicate, tested in triplicate and in some cases analyzed in triplicate to ensure statistically accurate results. In addition to the various testing procedures, total metal concentrations were measured in all CUB samples as a reference point. Mercury, nickel, arsenic, selenium, cadmium and lead were monitored. At all times, samples were handled using ultra-clean methods, including frequent glove changes, manipulating samples in positive laminar flow hoods, and monitoring of the storage space for atmospheric mercury concentration.

Table 1. Mercury Control Conditions

Facility	Sample Type	Fuel Type	Hg Control Type	Injection Rate
A	Ash	PRB	Halogenated ACI	1.4 lbs/Mmacf
B	ESP Ash	FUL	ACI + SEA*	SEA-500 ppm equiv, ACI 2lb/Mmacf
C	Ash	FUL	ACI + SEA2	SEA2 0.033 lb/Mmacf, ACI 0.85 lb/Mmacf
D	Ash	FUL	ACI + SEA2	SEA2 0.033 lb/Mmacf, ACI 0.80 lb/Mmacf
E	Fly ash	Bit. Blend	Halogenated ACI	5 lb/Mmacf
F	Fly ash	PRB/TXL	Halogen Injection	100 ppm Br
G	Fly Ash	LSEB	ACI	3 lb./Mmacf
H	Fly Ash	PRB/TXL	ACI	2lb/Mmacf
I	Ash	PRB	Halogenated ACI	0.7 lb/Mmacf
J	Ash	NDL	Halogenated ACI	1.5 lb/Mmacf
K	Ash	E. Bit.	Halogenated ACI	7 lb/Mmacf
L	FF fly ash	PRB/TXL	Enhanced AC	1.5 lb/Mmacf
M	Fly ash	PRB	C-PAC	4lb/Mmacf
N	FGD slurry	PRB/TXL	Halogen Injection	100 ppm Br
O	FGD JBR overflow	E. Bit.	Nalco 8034	28 mL Nalco 8034 / ug/Nm3 Hg
P	FGD JBR underflow	E. Bit.	Nalco 8034	28 mL Nalco 8034 / ug/Nm3 Hg

*SEA = Sorbent Enhancement Additive

Table 2. Analytical Testing Conducted on CUBs

Test	Procedure	Final Use
Volatilization	40C for 30 days	Soil fill / Landfill
Volatilization	190C for 60 min	Asphalt / Wallboard
Volatilization	1200C for 5 min	Cement
Microbial Methylation	Batch reactor with *D. propionicus*	Soil fill / Landfill / Impoundment
Chemical Leaching	Tumble @ pH 4.2, 60:40 H_2SO_4:HNO_3	Simulates precipitation/ runoff from any use

Total Metals Determination

All solid CUB samples were prepared for total metals determination by a closed vessel bomb digest using hydrofluoric, nitric, and hydrochloric acids. For mercury determination, a split of the digest was removed and diluted with a 5% solution of bromine monochloride and analyzed by cold-vapor atomic fluorescence spectrometry (CV-AFS). The remaining digest was boiled down and exchanged with nitric acid several times for analysis of trace metals by inductively coupled plasma mass spectrometry (ICP-MS).

All samples were digested in triplicate with standard Quality Control (QC) samples normally prepared at FGS for each digestion batch: three preparation blanks, laboratory control sample prepared in duplicate, and a matrix spike/matrix spike duplicate. Because the volatile mercury at low temperature was calculated by difference (see method below), all samples analyzed for volatile mercury at low temperature (ash samples, not FGD slurries) were also analyzed in triplicate to ensure an accurate result for calculating by difference. All samples analyzed by ICP-MS are scanned in triplicate, so additional replicate analysis by ICP-MS was not required.

Microbial Leaching Test

The potential for metal dissolution, volatilization and methylation by microorganisms was assessed by incubating the CUB samples with pure cultures of a sulfate-reducing bacterium, *Desulfobulbus propionicus* 1pr3, a Hg-methylating bacterium. Its ability to methylate Hg and the impact of medium chemistry on methylation rates has been well characterized (3).

Tests were conducted in batch cultures, under controlled chemical conditions. Medium chemistry was monitored, as well as the dissolution of metals and the production of methyl mercury (MMHg) from the CUBs. *Desulfobulbus propionicus* 1pr3 is an anaerobic, sulfate-reducing bacterium, and therefore all work was done under strict anoxic conditions. Pyruvate (30 mM) was used as the carbon source and 16 mM sulfate was added to maintain sulfate reducing conditions. The pH was maintained in the reactors at approximately 7 with the addition of 200 mM MOPS buffer. Samples were prepared in triplicate with one abiotic control for each sample. Three preparation blanks were processed with each batch of 12 samples to assess the contribution of background metals in the bacterial medium. Production of volatile mercury species were assessed by purging the samples at the end of the growth phase onto Flue-gas Sorbent Total Mercury (FSTM) traps designed to trap mercury.

The microbial leaching was performed at SERC. SERC also monitored pH, sulfide and bacterial counts. The resulting leachates were analyzed for total methyl mercury, dissolved mercury, and dissolved trace metals analysis at FGS.

Volatilization Tests

To assess the potential for volatilization of metals from CUBs, ash samples were subjected to three different temperature profiles described in Table 2. For the high temperature test, some samples fused to the sample holder. When this occurred, the test was performed at 900ºC instead of 1200ºC. The solid portion of FGD slurry samples was only tested at the mid temperature based on the end use of this by-product (synthetic gypsum for wallboard manufacture).

For the mid and high temperature studies, volatile mercury species were collected on FSTM traps. Volatilization of other metals was calculated by difference, measuring the total metals content in the CUBs before and after the volatilization test. For the low temperature studies, volatility of all metals was determined by difference.

For the mid and high temperature studies, a Thermolyne Tube Furnace (model 79300) was used. For the low temperature studies, a homemade low-flow heated chamber was used. All samples were tested in triplicate and three preparation blanks were processed for each batch in the same manner as the samples. For the mid and high temperature studies, a certified reference material (CRM, NIST 1633b) was processed in the same manner as the samples. NIST 1633b is certified for total mercury, not volatile mercury. The purpose of processing this CRM was to compare recoveries between testing batches.

Chemical Leaching Test

The chemical leaching procedure designed for this study is based on EPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP) (4). The extraction fluid is intended to simulate the mobilization of trace metals as a result of precipitation. The SPLP procedure, like its forerunner Toxicity Characteristic Leaching Procedure (TCLP), involves batch extraction (using a rotary apparatus) of a solid phase in extraction fluid, separation of the liquid from the solid phases, and analysis of the filtered leachate for target constituents (Hg, Ni, As, Se, Cd, and Pb). Using the guidelines in method 1312 for Extraction fluid #1, the pH was adjusted to 4.20 ± 0.05 with a solution of sulfuric and nitric acids mixed to a ratio of 60:40. Aliquots were removed after 18 hours, 14 days and 28 days to monitor potential changes in the amount of leached metals over time. Aliquots were analyzed for pH, conductivity, temperature and the metals of interest.

RESULTS & DISCUSSION

Total Metals

The total concentrations of metals in all CUB samples tested so far are presented in Table 3.

In order to assess the impact of Hg-CT on the total metal concentration in CUB samples, the ratio was calculated of metal concentration during Hg-CT operation to metal concentration for baseline conditions (see Table 4). For mercury, most of the ratios were greater than 1, indicating that mercury removed from the flue gas by the Hg-CT is partitioning into the solid by-product. The other metals were not similarly partitioned to the solid phase as a result of Hg-CT, except for Se at several facilities.

Table 3. Total Metals Concentration in CUBs

Facility	**Hg-CT**	**Hg (µg/kg)**	**Std Dev**	**Ni (mg/kg)**	**Std Dev**	**As (mg/kg)**	**Std Dev**	**Se (mg/kg)**	**Std Dev**	**Cd (mg/kg)**	**Std Dev**	**Pb (mg/kg)**	**Std Dev**
A	No	178	2	64.9	6.4	21.3	1.5	16.6	2.0	1.5	0.1	37.3	2.8
A	Yes	1244	11	55.1	0.7	17.0	0.5	14.9	1.0	1.1	0.0	34.8	0.4
B	No	111	22	31.2	1.8	26.0	4.4	5.5	0.8	0.4	0.0	25.7	3.6
B	Yes	197	35	41.4	11.2	37.8	6.1	5.2	0.6	0.6	0.0	23.8	2.4
C	No	5	0	23.6	2.2	18.2	2.0	3.8	0.5	0.4	0.0	17.8	1.1
C	Yes	252	13	23.6	3.4	20.4	1.4	3.1	0.5	0.4	0.1	19.1	0.8
D	No	6	0	24.7	2.2	23.3	0.6	4.9	0.9	0.4	0.0	13.9	9.5
D	Yes	451	22	23.5	2.4	29.1	2.3	5.4	0.2	0.5	0.1	12.8	2.0
E	No	49	3	83.1	0.7	25.4	0.9	1.6	0.0	0.3	0.0	67.4	3.1
E	Yes	195	16	79.7	3.0	22.8	0.9	7.7	0.5	0.3	0.0	60.1	3.0
F	No	135	44	28.4	0.4	8.0	0.5	4.4	0.5	0.6	0.0	30.3	2.1
F	Yes	296	70	30.4	1.2	10.0	1.1	6.6	1.7	0.5	0.0	33.9	2.5
G	No	284	47	101	2	73.9	3.3	17.4	1.7	0.5	0.0	62.5	0.8
G	Yes	358	157	118	6	99.9	28.7	18.3	5.8	0.7	0.2	66.1	13.7
H	No	156	226	46.7	3.0	29.6	3.8	11.3	0.6	1.4	0.1	35.1	4.2
H	Yes	465	222	44.0	6.2	23.0	7.3	9.2	3.5	1.1	0.1	26.9	3.9
I	No	1022	151	61.5	2.6	26.0	0.9	15.2	0.5	1.3	0.1	49.5	2.7
I	Yes	1655	27	55.0	0.7	23.9	0.3	15.1	0.2	1.2	0.0	47.3	0.7
J	No	199	15	35.5	1.4	49.4	2.7	7.3	0.3	0.5	0.0	34.4	1.9
J	Yes	526	83	34.3	0.9	36.4	2.9	7.3	0.6	0.5	0.0	32.8	3.5
K	No	214	67	126	4	139	39	7.7	2.9	1.1	0.3	66.5	15.9
K	Yes	1761	443	113	17	130	73	26.4	18.4	1.3	0.7	64.3	27.6
L	No	320	403	36.4	3.2	55.0	5.5	117	166	1.3	0.1	63.9	4.0
L	Yes	59001	22991	33.0	1.1	95.9	15.6	1222	553	1.3	0.0	60.3	1.0
M	No	68	3	49.9	0.8	16.2	0.5	10.4	0.6	1.1	0.0	34.2	0.3
M	Yes	1414	347	48.6	1.4	19.4	1.9	13.3	2.1	1.0	0.0	35.8	1.0
N	No	2474	832	0.3	0.1	3.0	0.2	72.4	3.0	3.0	0.2	3.0	0.2
N	Yes	2534	450	0.6	0.1	2.3	0.0	42.4	2.7	2.3	0.0	2.3	0.0
O	No	7722	961	46.8	2.2	104	4	216	8	1.8	0.1	55.4	2.6
O	Yes	8911	798	72.7	2.2	134	5	329	14	4.0	0.3	71.6	4.3
P	No	193	17	4.1	0.5	2.9	0.2	12.3	0.6	0.2	0.0	1.2	0.1
P	Yes	315	26	5.3	0.2	5.0	0.5	14.6	1.0	0.2	0.0	2.2	0.3

Table 4. Total Metals: Ratio of Hg-CT to Baseline*

Facility	Fuel Type	Hg Control	Hg	Ni	As	Se	Cd	Pb
A	PRB	Halogenated ACI	**7**	1	1	1	1	1
B	FUL	ACI + SEA	**2**	1	1	1	2	1
C	FUL	ACI + SEA2	**46**	1	1	1	1	1
D	FUL	ACI + SEA2	**72**	1	1	1	1	1
E	Bit. Blend	Halogenated ACI	**4**	1	1	**5**	1	1
F	PRB/TXL	Halogen Injection	2	1	1	1	1	1
G	LSEB	ACI	1	1	1	1	1	1
H	PRB/TXL	ACI	**3**	1	1	1	1	1
I	PRB	Halogenated ACI	2	1	1	1	1	1
J	NDL	Halogenated ACI	**3**	1	1	1	1	1
K	E. Bit.	Halogenated ACI	**8**	1	1	**3**	1	1
L	PRB/TXL	Enhanced AC	**184**	1	2	**10**	1	1
M	PRB	C-PAC	**21**	1	1	1	1	1
N	PRB/TXL	Halogen Injection to FGD	1	2	1	1	1	1
O	E. Bit.	Nalco 8034 addition to FGD	1	2	1	2	2	1
P	E. Bit.	Nalco 8034 addition to FGD	2	1	2	1	1	2

*Bolded values signify conditions where the total metal concentration is significantly higher during Hg-CT operation than during baseline conditions.

Microbial Methylation

Methyl mercury (MMHg) production ranged from 0-11% of total mercury in the CUB samples (see Figure 1). The ratios of total MMHg produced during Hg-CT over baseline conditions are shown in Table 5. Absolute methylation was generally higher for CUBs collected during Hg-CT, correlating to the increase in total mercury observed during Hg-CT (Table 4). At three facilities, a decrease in methylation was actually observed during Hg-CT trials even though total mercury increased; albeit mercury increased only slightly for Sites O and P, where injections to an FGD operation were conducted.

Figure 1. Mercury methylation as a Percent of Total Hg

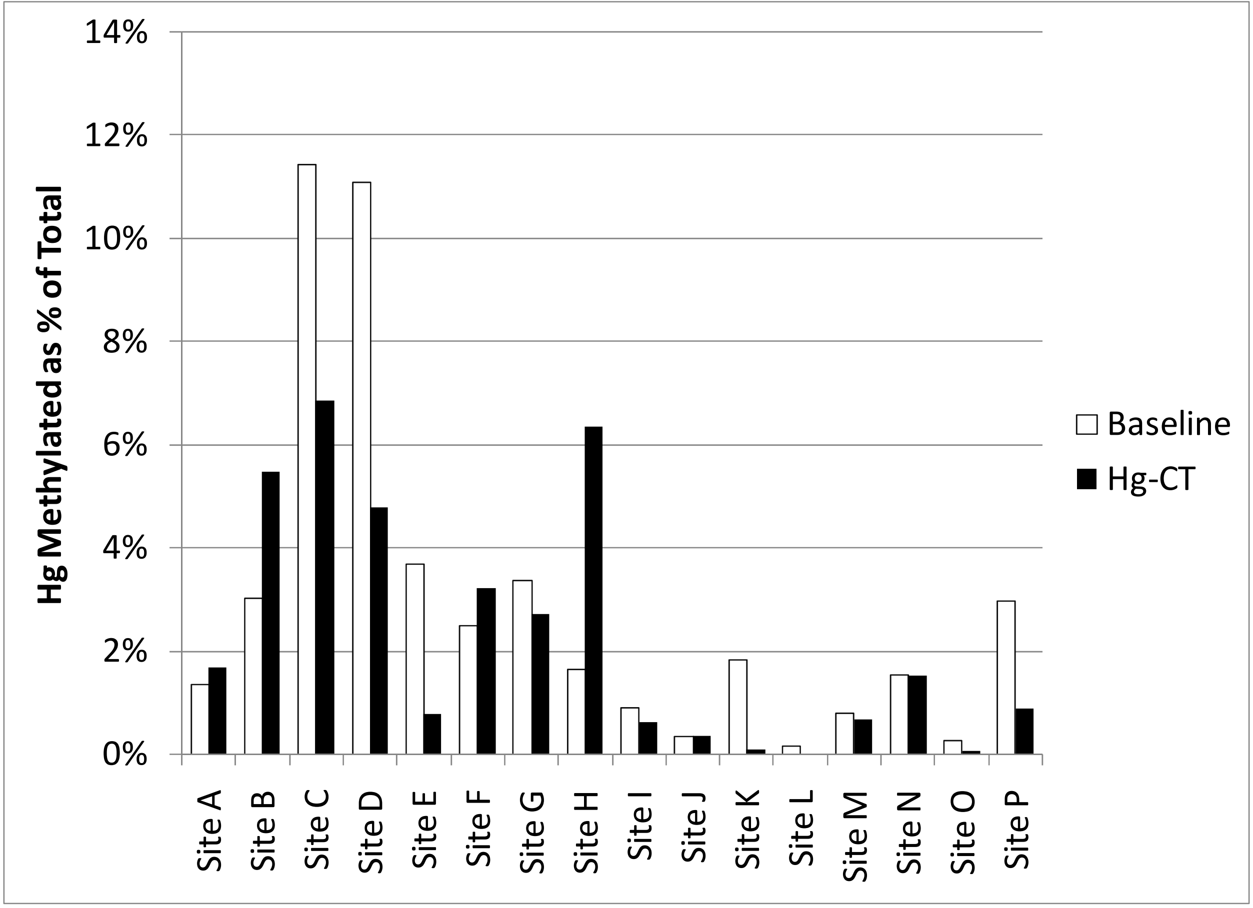


Table 5. Microbially Leached: Ratio of Hg-CT to Baseline*

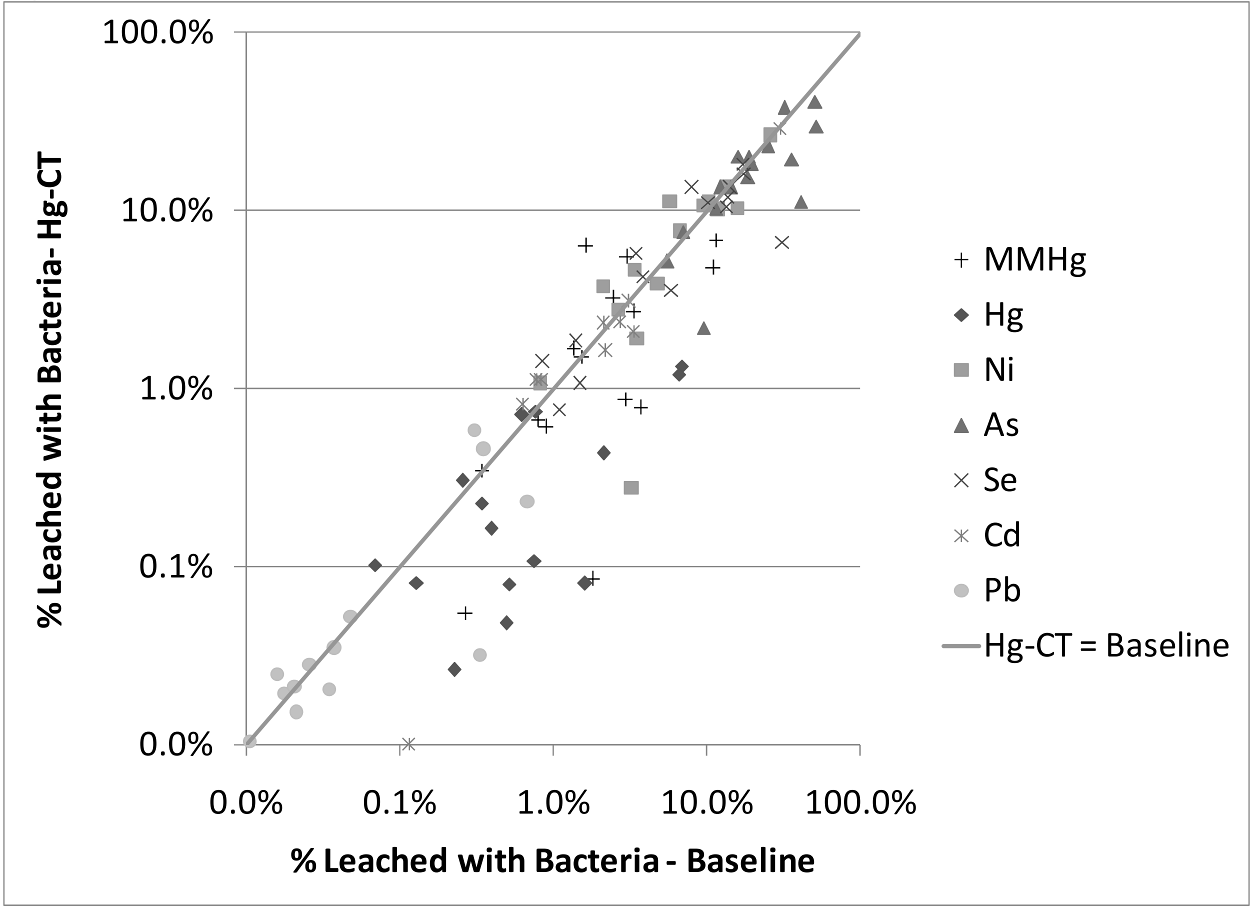
Facility	Fuel Type	Hg Control	MMHg	Hg	Ni	As	Se	Cd	Pb
A	PRB	Halogenated ACI	**9**	1	1	1	1	1	1
B	FUL	ACI + SEA	**3**	1	1	1	2	1	1
C	FUL	ACI + SEA2	**28**	**9**	1	1	1	1	1
D	FUL	ACI + SEA2	**31**	**13**	1	1	ND	1	1
E	Bit. Blend	Halogenated ACI	1	0	0	1	1	ND	1
F	PRB/TXL	Halogen injection	**3**	2	2	1	1	1	1
G	LSEB	ACI	1	1	2	2	1	1	1
H	PRB	ACI	**12**	**4**	1	1	1	1	1
I	PRB	Halogenated ACI	1	1	1	1	1	ND	ND
J	NDL	Halogenated ACI	3	**4**	1	1	2	ND	ND
K	E. Bit.	Halogenated ACI	0	1	1	1	**3**	1	2
L	PRB/TXL	Enhanced AC	**4**	**17**	2	0	**7**	ND	ND
M	PRB	C-PAC	**18**	2	1	1	1	ND	0
N	PRB/TXL	Halogen --> to FGD	1	1	1	1	1	1	1
O	E. Bit.	Nalco 8034 --> to FGD	0	0	1	0	1	0	1
P	E. Bit.	Nalco 8034 --> to FGD	0	0	1	1	1	0	1

*Bolded values signify conditions where the microbially leached metal concentration is significantly *higher* during Hg-CT operation than during baseline conditions. Heavy boxes signify conditions where the concentration is significantly *lower* during Hg-CT operation than during baseline conditions. ND signifies baseline results that were not detected for microbial leaching.

CUB samples exposed to the mercury methylating bacteria, 1pr3, generally produced more MMHg, Hg, and Se during Hg-CT operations than during baseline conditions while the mobilization of other metals was not significantly different between baseline conditions and Hg-CT trials (see Table 5).

Significant amounts of Ni, As, Se, and Cd were microbially leached in CUB samples as a percent of total metal (see Figure 2). The percent of mercury leached was lower than other metals (except Pb), but it is likely that much of the dissolved mercury was converted to methyl mercury.

Figure 2. Percent of Metals Leached with Bacteria: Hg-CT vs. Baseline



Similar trends were observed for the abiotic controls (without bacteria) (see Figure 3), however a comparison of the absolute amount of metals leached in the CUB samples with bacteria and without bacteria (see Figure 4), suggests that several metals were somewhat immobilized by bacteria: Ni, Se, Cd and Pb. MMHg, Hg, and As, however, followed the opposite trend and increased in the presence of bacteria.

Figure 3. Percent of Metals Leached in Abiotic Controls: Hg-CT vs. Baseline

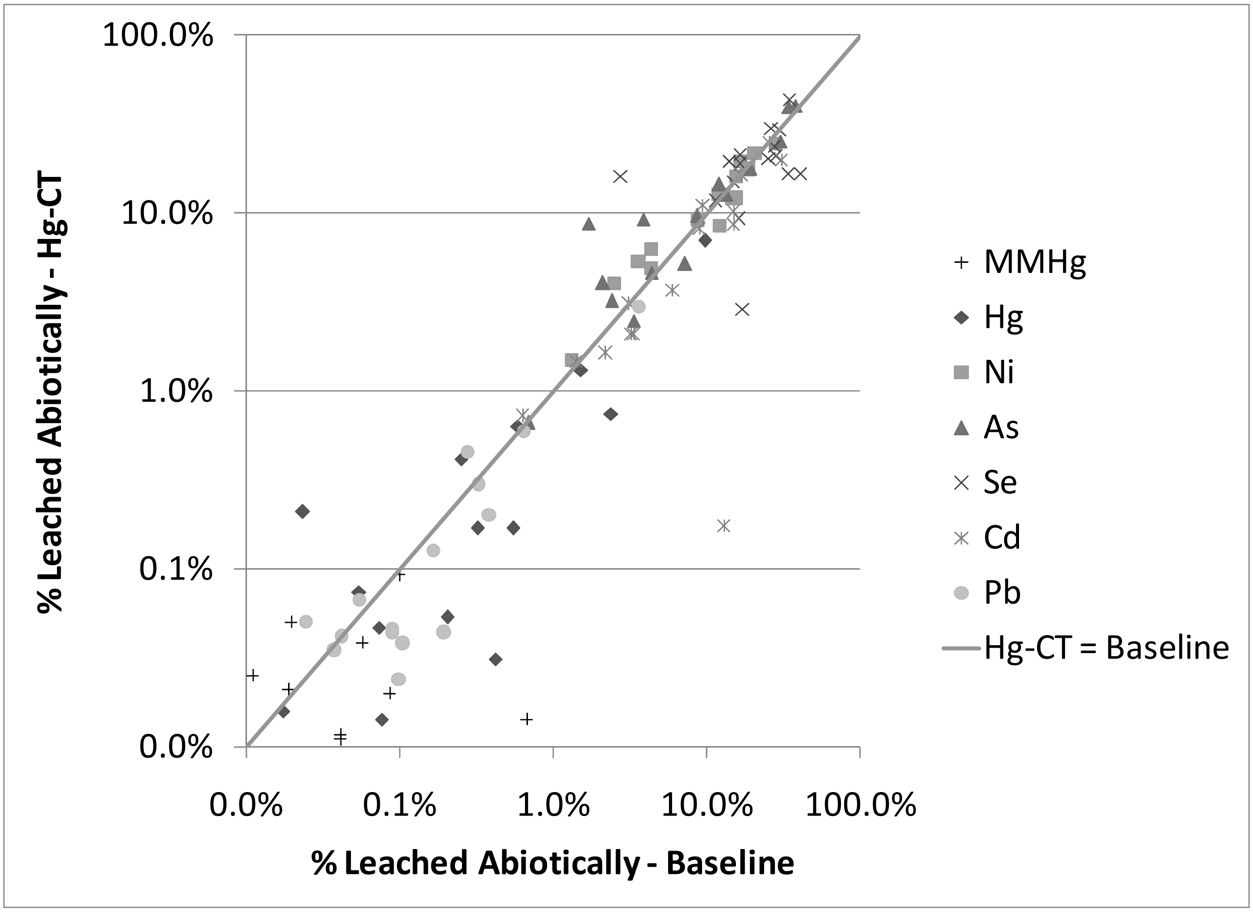
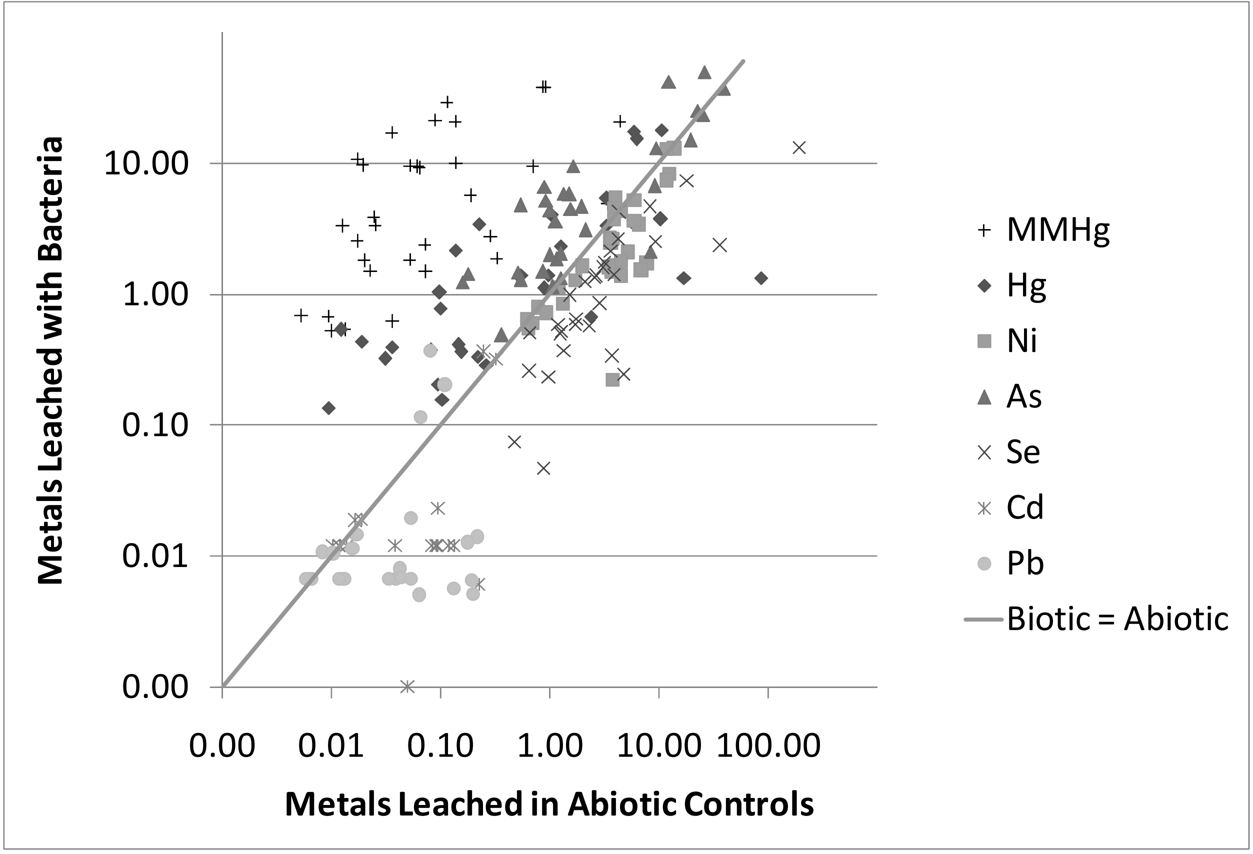


Figure 4. Metals mobilized by bacteria vs. abiotic controls (Hg in µg/kg, other metals mg/kg)



Volatilization

Se was the most volatile metal as a percent of total for all three temperature conditions (see Figures 5-7). Hg was highly volatile under high temperature conditions but not significantly volatile during mid and low temperature conditions. Under low temperature conditions, As was consistently volatilized in all CUB samples at about 10%.

CUB samples subjected to high temperature conditions had increased volatile Hg during Hg-CT trials over baseline conditions at all facilities (see Table 6). There were a few other cases where volatile metals were higher in Hg-CT samples compared to baseline samples, but generally, the baseline samples were the same as or higher than the Hg-CT samples. For many cases, especially for Hg under mid temperature exposure, Hg-CT trials actually resulted in lower concentrations of volatile metals, even when total Hg increased, suggesting immobilization of certain metals as a result of Hg-CT.

Table 6. Volatilized: Ratio of Hg-CT to Baseline*

Facility	Temp	Fuel Type	Hg Control	Hg	Ni	As	Se	Cd	Pb
A	High	PRB	Halogenated ACI	**7**	0	0	1	ND	1
B	High	FUL	ACI + SEA	**2**	1	2	1	**3**	ND
C	High	FUL	ACI + SEA2	**139**	1	ND	1	1	1
D	High	FUL	ACI + SEA2	**176**	1	1	1	1	ND
E	High	Bit. Blend	Halogenated ACI	**3**	2	1	ND	ND	2
F	High	PRB/TXL	Halogen injection	2	1	2	1	1	**3**
G	High	LSEB	ACI	2	ND	ND	1	**4**	ND
H	High	PRB	ACI	2	0	0	1	0	0
I	High	PRB	Halogenated ACI	1	ND	0	1	0	0
J	High	NDL	Halogenated ACI	2	ND	0	1	0	1
K	High	E. Bit.	Halogenated ACI	**7**	ND	ND	**3**	ND	ND
L	High	PRB/TXL	Enhanced AC	**46**	1	**8**	**10**	1	1
M	High	PRB	C-PAC	**16**	ND	0	**3**	ND	ND
N	High	PRB/TXL	Halogen --> to FGD	FGD not tested for high temp conditions					
O	High	E. Bit.	Nalco 8034 --> to FGD						
P	High	E. Bit.	Nalco 8034 --> to FGD						
A	Mid	PRB	Halogenated ACI	1	1	1	0	1	1
B	Mid	FUL	ACI + SEA	1	1	2	1	2	1
C	Mid	FUL	ACI + SEA2	**48**	1	1	**11**	1	1
D	Mid	FUL	ACI + SEA2	**29**	1	1	1	1	ND
E	Mid	Bit. Blend	Halogenated ACI	ND	ND	ND	ND	2	ND
F	Mid	PRB/TXL	Halogen injection	0	1	**4**	1	**4**	2
G	Mid	LSEB	ACI	**6**	1	**28**	2	0	1
H	Mid	PRB	ACI	0	0	ND	1	0	0
I	Mid	PRB	Halogenated ACI	1	0	0	1	1	1
J	Mid	NDL	Halogenated ACI	0	ND	ND	1	2	1
K	Mid	E. Bit.	Halogenated ACI	0	ND	ND	ND	ND	ND
L	Mid	PRB/TXL	Enhanced AC	0	1	**4**	**3**	0	1
M	Mid	PRB	C-PAC	0	ND	0	ND	0	ND
N	Mid	PRB/TXL	Halogen --> to FGD	Not analyzed					
O	Mid	E. Bit.	Nalco 8034 --> to FGD	0	ND	ND	ND	0	0
P	Mid	E. Bit.	Nalco 8034 --> to FGD	1	1	ND	ND	1	ND
A	Low	PRB	Halogenated ACI	**10**	1	1	0	0	1
B	Low	FUL	ACI + SEA	0	**7**	2	1	ND	1
C	Low	FUL	ACI + SEA2	0	0	1	ND	ND	1
D	Low	FUL	ACI + SEA2	ND	1	1	ND	ND	ND
E	Low	Bit. Blend	Halogenated ACI	ND	1	1	ND	0	1
F	Low	PRB/TXL	Halogen injection	ND	2	**6**	**3**	**3**	**3**
G	Low	LSEB	ACI	0	1	1	1	**3**	1
H	Low	PRB	ACI	2	1	0	1	1	1
I	Low	PRB	Halogenated ACI	Not analyzed					
J	Low	NDL	Halogenated ACI						
K	Low	E. Bit.	Halogenated ACI						
L	Low	PRB/TXL	Enhanced AC						
M	Low	PRB	C-PAC						
N	Low	PRB/TXL	Halogen --> to FGD	FGD not tested for low temp conditions					
O	Low	E. Bit.	Nalco 8034 --> to FGD						
P	Low	E. Bit.	Nalco 8034 --> to FGD						

*Bolded values signify volatilized metal concentrations that are significantly *higher* during Hg-CT operation than during baseline conditions. Heavy boxes signify concentrations that are significantly *lower* during Hg-CT operation than during baseline conditions. ND signifies baseline results that were not detected for volatilization.

Figure 5. Percent of Metals Volatilized at High Temp (1200ºC or 900ºC): Hg-CT vs. Baseline

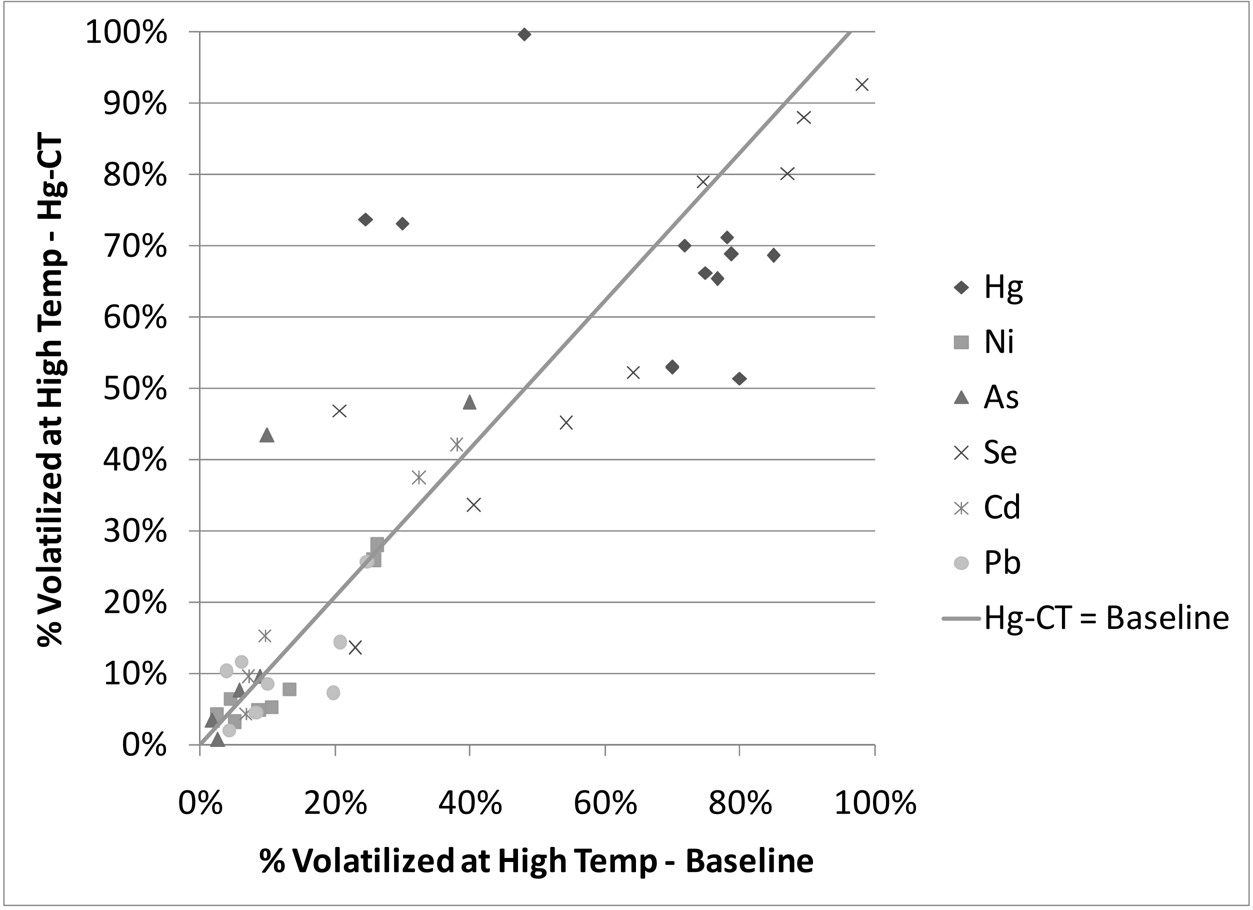


Figure 6. Percent of Metals Volatilized at Mid Temp (190ºC): Hg-CT vs. Baseline

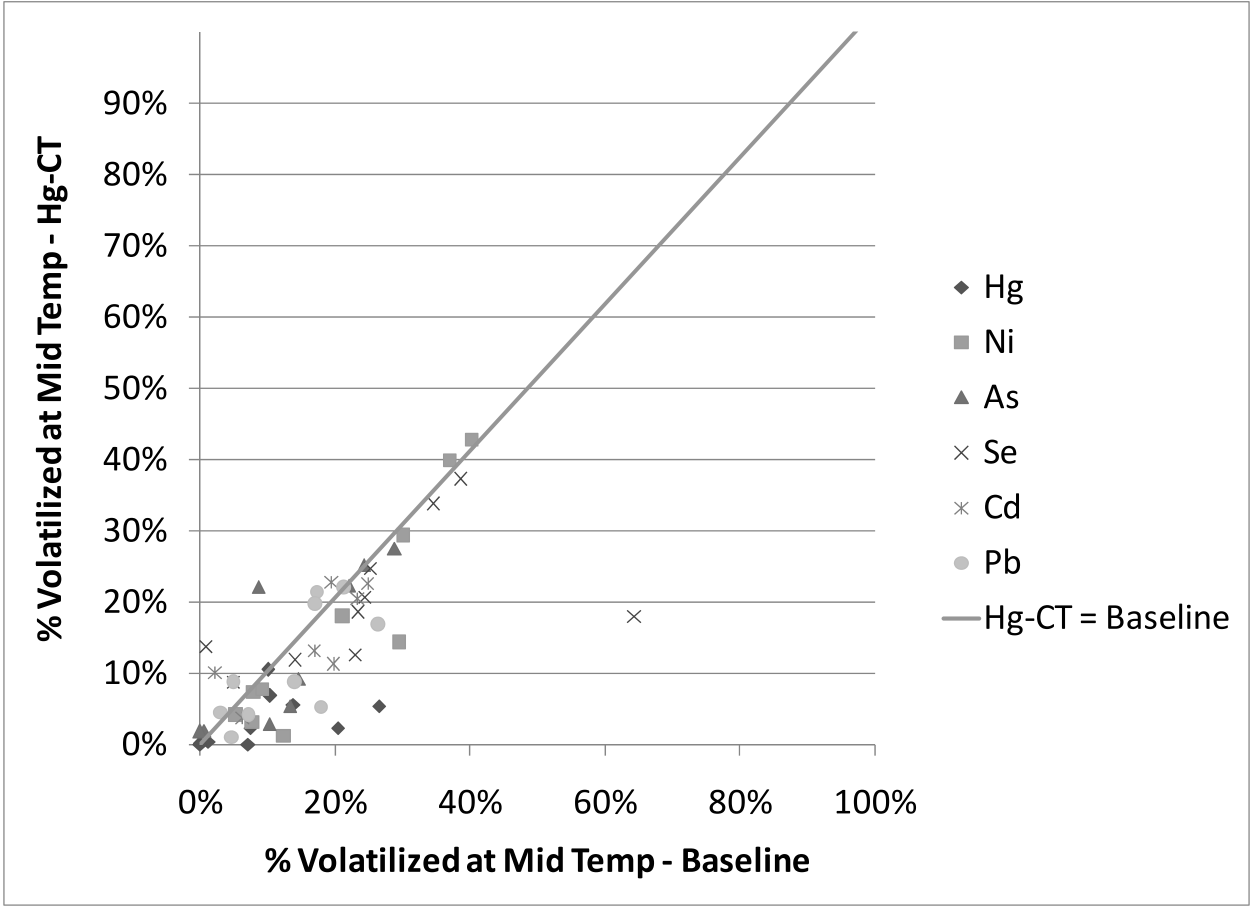
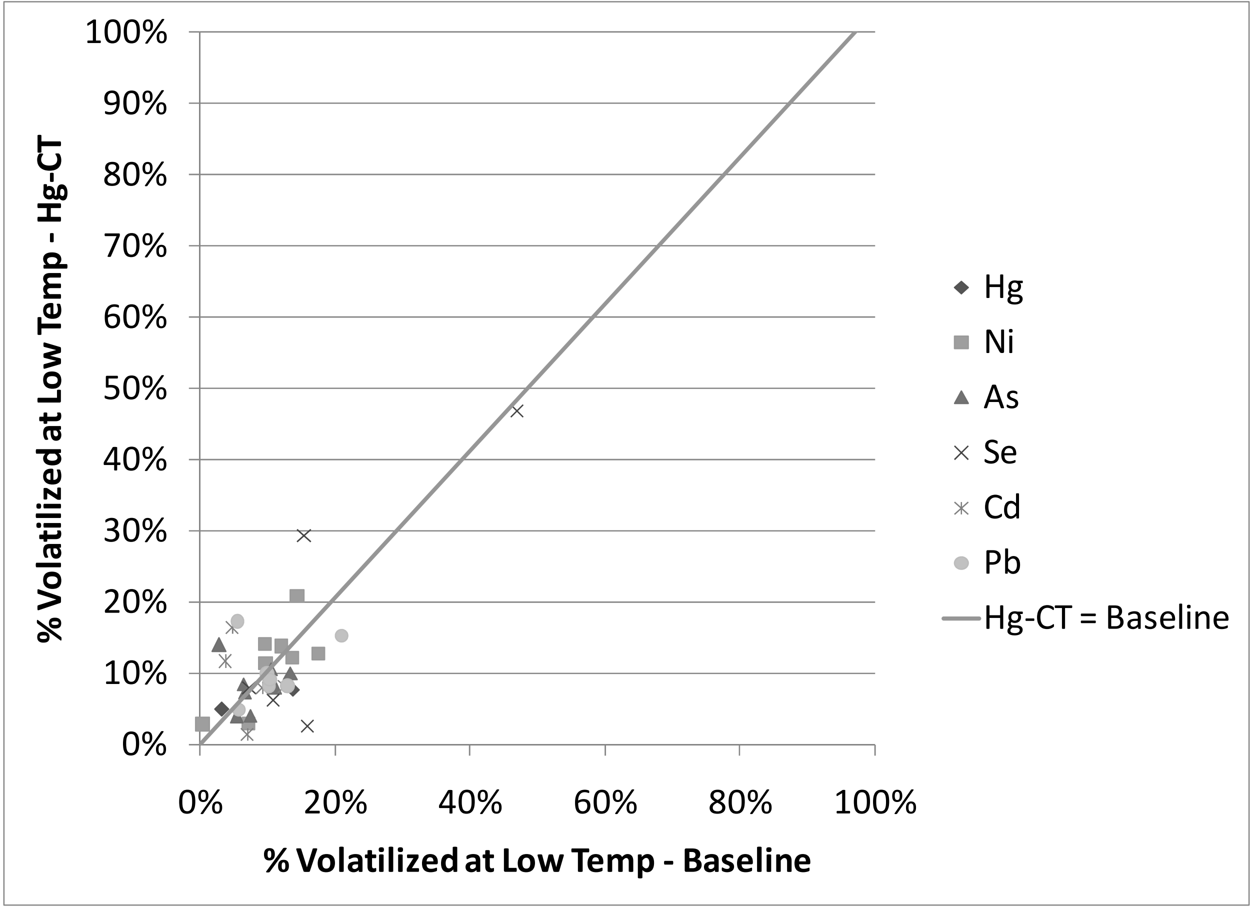


Figure 7. Percent of Metals Volatilized at Low Temp (40ºC): Hg-CT vs. Baseline



Chemical Leaching

Very little (< 5%) Hg, Ni, As, and Pb was leached from any of the CUB samples using a weakly acidic solution (see Figure 8). In contrast, significant Se (as much as 60% Se of the total) was leached from most CUB samples. Two sites using bituminous coal had significant Cd leached (5-20% of the total) from the CUB samples.

In many cases, the amount of metal measured in the leachate over the 28-day leaching period actually decreased (see Figure 9), suggesting formation of insoluble minerals, such as ettringite that can immobilize other metals such as arsenic and selenium.

It is interesting to note that the abiotic controls for the methylation tests showed much greater leaching of most metals than the chemical leaching test, though both tests had the same ratio of CUBs to leaching solution. This is likely due to the different leaching solutions used for each test. The methylation test, including the abiotic controls, were conducted using bacterial media containing a variety of salts, vitamins, trace metals, buffer, and a carbon source while the chemical leaching solution contained only small amounts of sulfuric and nitric acids. We hypothesize that the presence of dissolved ligands such as chloride and pyruvate in the microbial medium used for the methylation tests led to greater dissolution of metals compared to the chemical leaching solution.

Figure 8. Percent Chemically Leached: Hg-CT vs. Baseline

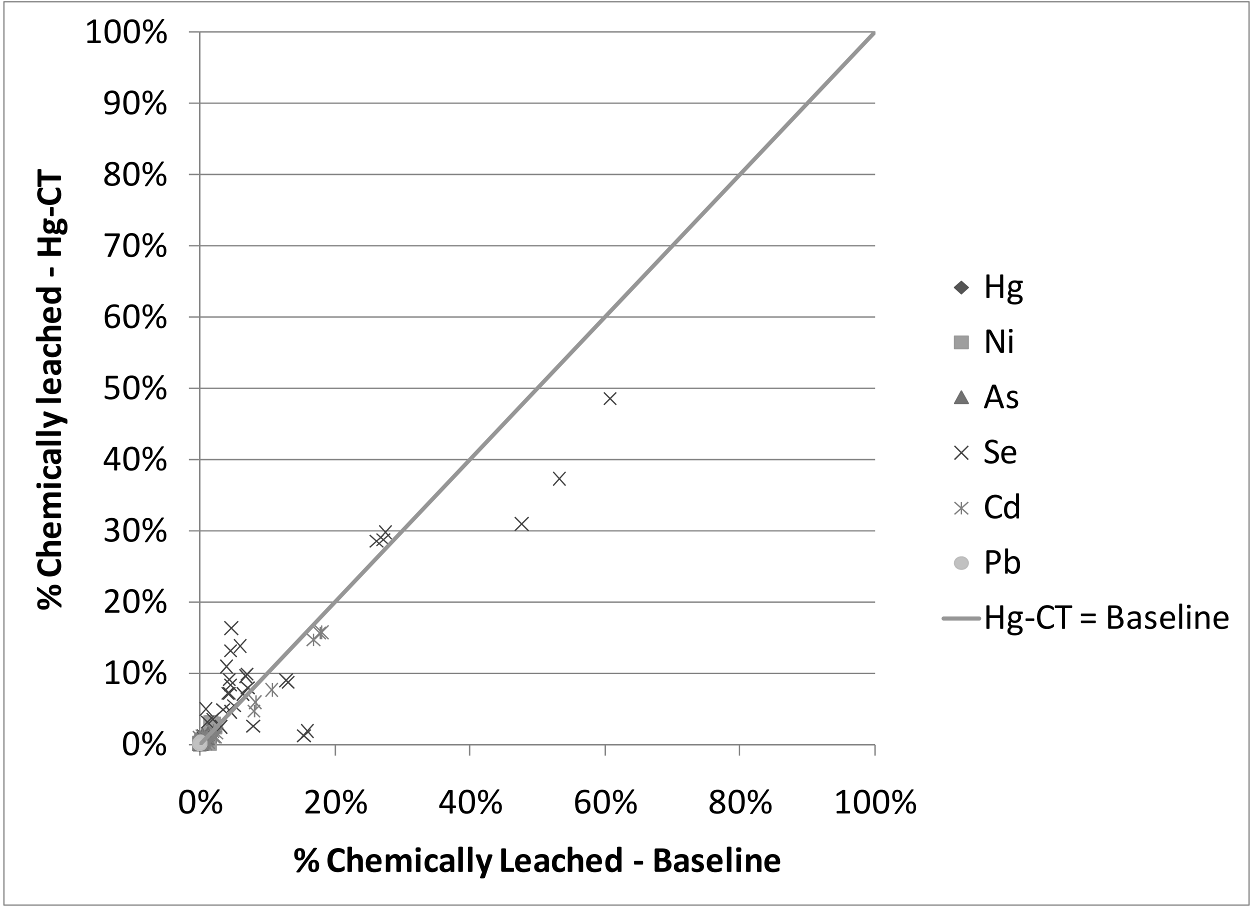
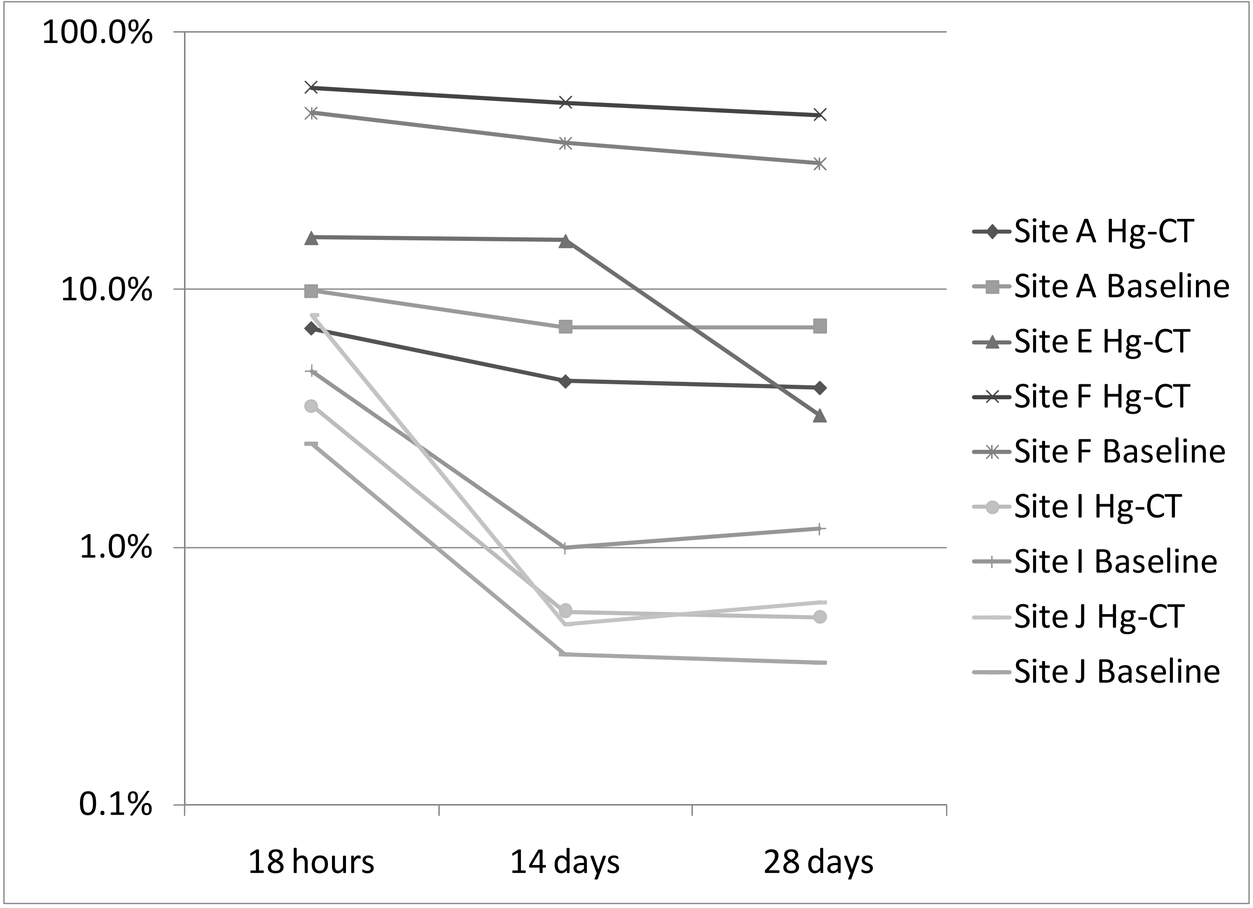


Figure 9. Selenium in selected leachate samples over 28-day leaching period



SUMMARY

As expected, the concentration of total mercury increased in the CUBs during Hg-CT trials as a result of mercury removal from the flue gas. However, the concentrations of most other metals were not significantly affected as a result of Hg-CT, except for Se at 3 facilities.

Overall, the operation of Hg-CT did not significantly change the mobility of Ni, Cd and Pb in the CUBs; however, Hg-CT operations did have impacts on Hg methylation and volatilization at several sites as well as As and Se volatility at a number of sites.

In FGD slurry solids, the total concentration of most metals and their mobility were relatively high compared to the ash samples. However, the use of Hg-CT did not have a noticeable impact on the total concentration or mobility of any of the metals in FGD slurry solids.

Methylation of Hg increased in samples collected during Hg-CT trials, but not more than the total concentration of Hg increased between baseline and Hg-CT samples. This suggests that the increase in methylation is likely due to the increase in total Hg concentration in the CUBs and not the result of the mercury being more bioavailable for methylation with Hg-CT operation. Bacteria produced or mobilized MMHg, Hg, and As in CUB samples but appeared to immobilize other metals such as Ni, Se, Cd and Pb.

Significant Se is volatilized under all temperature conditions, with a general trend of volatilization occurring in the expected temperature order: high>mid>low. Significant Hg is volatilized under high temperature conditions, with even more volatile mercury measured during Hg-CT operations than during baseline conditions. Under low temperature conditions, significant amounts of total Ni and As were volatilized. With the exception of mercury volatilized under high temperature conditions, it appears that Hg-CT immobilizes metals from volatilization.

Exposure of CUB samples to a weakly acidic solution leached very little Hg, Ni, As, or Pb. Se was highly leachable in most samples, though the operation of Hg-CT did not seem to make Se more leachable, except for Site L. A relatively high amount of Cd was leached at two sites using bituminous coal; Hg-CT did not affect the amount of Cd leached.

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KEY WORDS

Coal utilization by-products, CUBs, coal-fired power plants, synthetic gypsum, mercury, mercury control technology, mercury methylation, selenium, arsenic, nickel cadmium, lead, SPLP