

Long-Term Column Leaching of Phase II Mercury Control Technology By-products

Karl Schroeder, Carol Cardone, Fredrick White, Paul Rohar and Ann G. Kim

U.S. Department of Energy, National Energy Technology Laboratory, 626 Cochran's Mill Road, P.O. Box 10940, Pittsburgh PA 15236

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ABSTRACT

An NETL research, development and demonstration program under DOE/Fossil Energy Innovations for Existing Plants is directed toward the improvement of the performance and economics of mercury control from coal-fired plants. The current Phase II of the RD&D program emphasizes the evaluation of performance and cost of control technologies through slip-stream and full scale field testing while continuing the development of novel concepts. One of the concerns of the NETL program is the fate of the captured flue gas mercury which is transferred to the condensed phase by-product stream. The stability of mercury and any co-captured elements in the by-products could have a large economic impact if it reduced by-product sales or increasing their disposal costs. As part of a greater characterization effort of Phase II facility baseline and control technology sample pairs, NETL in-house laboratories have performed continuous leaching of a select subset of the available sample pairs using four leachants: water (pH=5.7), dilute sulfuric acid (pH=1.2), dilute acetic acid (pH=2.9), and sodium carbonate (pH=11.1). This report describes results obtained for mercury, arsenic, and selenium during the 5-month leaching experiments.

INTRODUCTION

Research undertaken by the DOE/ Fossil Energy Innovations for Existing Plants program seeks to improve the performance and economics of mercury control technologies. The on-going Phase II of the RD&D program emphasizes the performance and cost of control technologies through slip-stream and full scale field testing. Because any captured flue gas mercury will be contained in one of the by-product streams, the NETL program is also concerned with the fate of mercury in these by-products. A goal of DOE is to not only maintain but also increase the utilization of coal by-products. These capture-technology byproducts represent a challenge to increased by-product utilization and a large economic impact if sales of ash are lost and disposal costs increase. An important part of this issue is the potential for release of mercury from the capture by-products. Evaluations of the stability of the new by-product streams are necessary. The results will serve to assure generators, potential users, and regulators of the safety and effectiveness of continued by-product utilization.

To evaluate the potential for mercury release, DOE/NETL has funded an extensive investigation of the conditions for, and extent of, release of mercury from CUB under a number of conditions by both in-house and contractor labs. Sample pairs from baseline and mercury capture conditions have been collected from a number of Phase II-participating facilities. The evaluations being performed include the Synthetic Precipitation Leaching Procedure (SPLP, EPA Method 1312), which has been modified to provide for longer equilibration times of up to 30 days, the DOE/NETL Serial Batch Leaching Procedure (SBLP), and NETL column leaching on a select number of sample pairs. The subject of this paper is the column leaching studies.

EXPERIMENTAL

Samples were shipped from the test facility to an off-site contractor. The contractor performed a homogenization of the sample, thereby ensuring that identical sub-samples were examined in each of the evaluations. One of these sub-samples was sent to NETL for leaching tests.

A total of 8 samples consisting of 4 sets of baseline(B) and mercury control(C) pairs were received. Initial tests to determine the likelihood that cementitious properties would clog the columns shows that only 2 of the pairs were amenable to this type of study. The 2 pairs are described in the table below.

Ash Pair	Coal	Pollution control	Mercury control
1B, 2C	Sub-bituminous	Spray dryer / fabric filter	Bromine-activated carbon
7B, 8C	Bituminous	Hot-side ESP	H-PAC

The CUB leaching columns were constructed of 1 meter sections of clear PVC pipe. The pipe had a 5 cm inside diameter and a volume of approximately 2 liters. PVC pipe caps closed each end of the column and had 1/4 inch NPT fittings tapped into them for leachant inflow and leachate outflow. Each column was loaded with 1kg of as-received sample. Other than riffing to ensure representative sub-samples, no other handling and/or size-reduction was performed. The sealed column was hung vertically and connected to the leachant delivery system. A peristaltic pump fed liquid from a reservoir to the top of columns at an average flow rate of approximately 230 mL/day.

Leachant was supplied to the top of the column and allowed to percolate through the bed of material. This was done in an effort to simulate an actual environment in which surface or ground water would encounter a mono-fill of the material in its flow-path. In some cases, decreased permeability of the bed during the course of the leaching resulted in flows much lower than the desired 230 mL/day. This is most obvious for the sulfuric acid leaching data for ash 2C in the data that follows.

Because each column was loaded with 1 kg of ash, elution volumes, in liters, are numerically equivalent to the liquid / solid ratios (L/S) in liters per kilogram.

Descriptions of the leachants are provided in the table to the left. The de-ionized water (>18.2 MΩ•cm warranty, <10μS conductivity measured) was produced by a Millipore Corporation RO60 Milli-Q Reverse Osmosis (RO) Unit using building RO water as feed. All other solutions used this doubly RO treated water and Trace Metal Grade acids or certified A.C.S. grade anhydrous sodium carbonate to make the leachant.

Leachant	ID	pH
Sulfuric Acid	H ₂ SO ₄	1.2
Acetic Acid	HOAc	2.9
De-ionized Water	Water	6.0
Sodium Carbonate	Na ₂ CO ₃	11.1

Mercury analyses were performed using either a Milestone DMA-80 mercury analyzer for solids or CVAF for leachates. Arsenic and selenium analyses were performed on leachates and digested solid samples using ICP-OES. EPA method 3052 was selected for the digestions to limit the extent of loss of these more volatile elements.

RESULTS

From the mercury assays shown in the table it can be seen that the mercury levels obtained for the two baseline ashes (1B and 7B) are considerably lower than those obtained for the ashes collected during the mercury control test (2C and 8C). As will be

Arsenic, Selenium and Mercury Assays					
Ash	Coal	As (mg/kg)	Se (mg/kg)	Hg (μg/kg)	Hg Capture Ratio
1B	Sub-bit	21.2	6.1	179	7.5
2C		32.4	21.4	1350	
7B	Bituminous	28.3	< 3	48.3	4.1
8C		37.8	10.3	199	

shown below, the increased mercury content of the control ashes did not translate into a correspondingly high amount of leachable mercury.

Arsenic and selenium were also found in both the baseline and control ashes. Although higher amounts of both were found in the control samples, the extent of enrichment was less than seen for mercury.

Column leaching studies were undertaken to determine the extent to which arsenic, selenium, and especially mercury might be mobilized. Because each column was loaded with 1 kg of ash, elution volumes, in liters, are numerically the same as liquid / solid ratios (L/S) in liters per kilogram. The terms are used interchangeably in the discussion that follows.

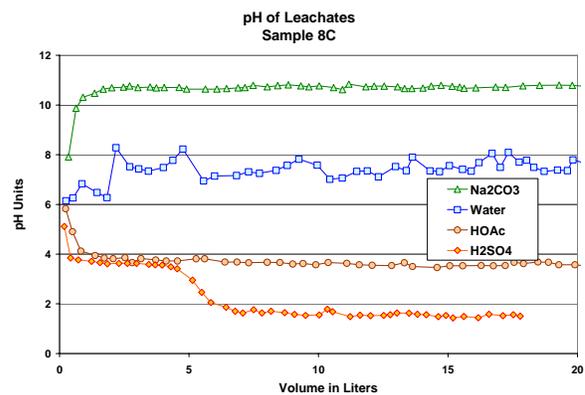
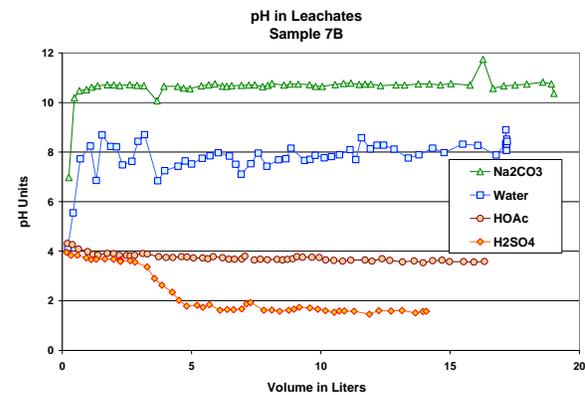
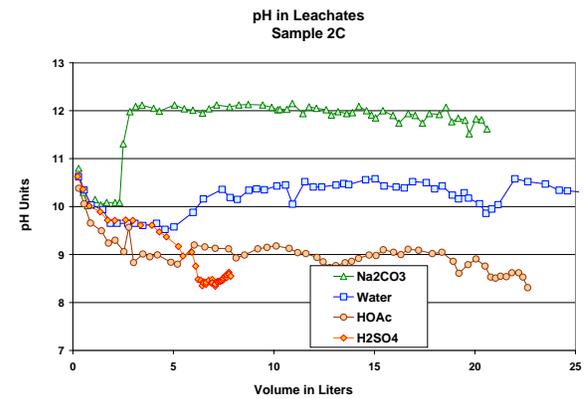
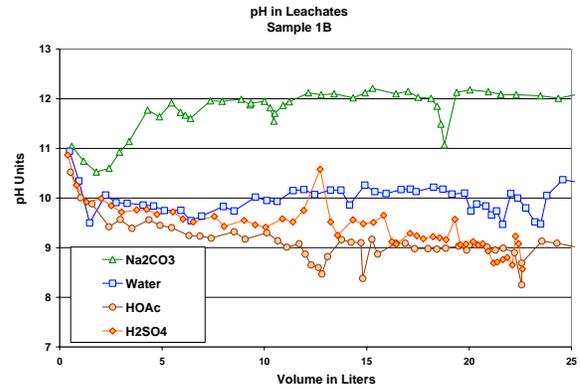
Leachate pH

The leachate pH profiles obtained for the four ashes displayed the major differences usually seen for highly alkaline versus low-alkalinity or acidic ashes. The leachate chemistry of the highly alkaline ashes was determined mostly by the ash chemistry while the leachate chemistry of the acidic ashes was determined mostly by the leachant chemistry.

Samples 1B and 2C were highly-alkaline materials and the pH of the eluate was determined more by the chemistry of the ash than by the nature of the leachant. Leachates from both acetic acid and sulfuric acid gave pH values between 8.5 and 9.5 although the acid solutions had initial pH values of 2.9 and 1.2, respectively. Similarly, the water eluate reflected the natural pH of the ash which is about 10 for both sample 1B and 2C. Only sodium carbonate, which itself is alkaline, gave pH values close to the leachant value of 11.1.

Samples 7B and 8C contained much less alkalinity and the eluate pH rapidly approached that of the leachant in 3 of the 4 cases. In the case of sulfuric acid was there an initial plateau around 4 before the pH dropped to near-leachant values.

The pH profiles for the baseline (7B) and mercury controlled (8C) low-alkalinity ashes were essentially identical but some differences were seen for the highly alkaline ashes (1B and 2C). Most of the difference was due to a displacement of the sulfuric acid pH values from about 9.5 in the baseline case (1B) to about 8.5 for the control (2C). The control also lost permeability earlier in the experiment resulting in less than 10 liters being eluted.

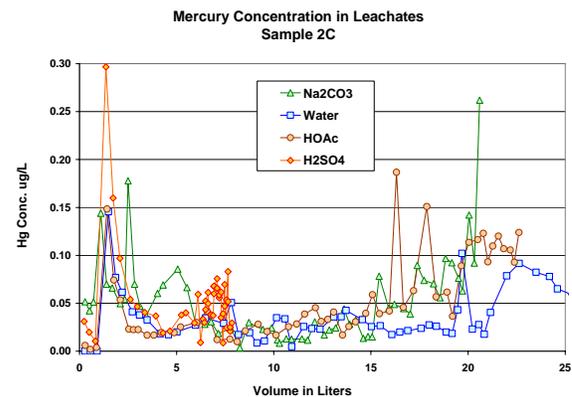
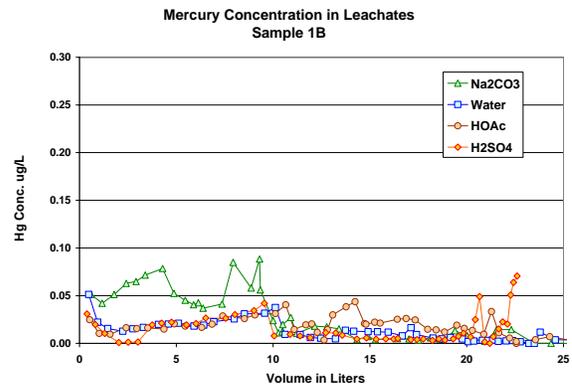


At the very low liquid to solid ratios (L/S) of 0.2-0.4 seen at the beginning of these experiments, the leachate pH for each ash tended to be identical, regardless of the leachant, even for the acidic ashes. The alkaline ashes gave a higher pH; a value of 11 was obtained for ash 1B and 10.8 for ash 2C. The acidic ashes gave a lower pH; a value of 4 was seen for ash 7B and 5 for ash 8C. But, in each case a common initial point appears to be shared by all leachates. For the acidic ashes, divergence was very rapid as the L/S increased. Divergence was more gradual for the alkaline ashes. In column experiments, the first leachant delivered to the column becomes depleted in any reagent it may contain and becomes very concentrated in the most soluble constituents of the ash as it percolates through the bed of material. Thus, the chemistry of leachate obtained at very low L/S may be very different from that seen for the bulk material at higher L/S. This is what is seen in the four pH profiles presented here. From a practical perspective, this indicates that the water chemistry can be expected to initially change rapidly in any application where surface or ground water will percolate through the material. From the data presented here, it appears that most transient behavior is complete by the time an L/S of about 5 is attained.

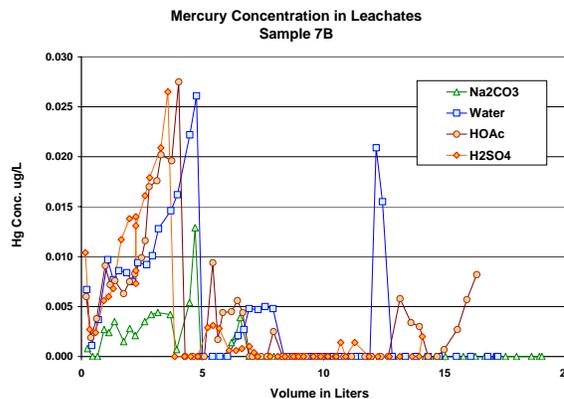
Mercury in the Leachates

Concentrations of mercury in the leachates were low regardless of ash, nature of the leachant, or the liquid to solid ratio. In no case was the 2 ppb (2 $\mu\text{g/L}$) drinking water MCL exceeded.

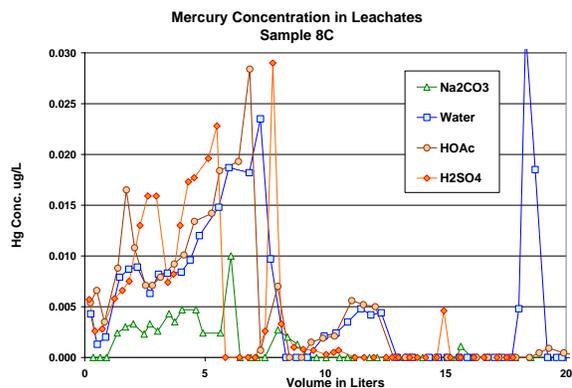
The elution profiles for ashes 1B and 2C were dissimilar with the majority of the mobile mercury appearing in the first 10 liters of eluate for the baseline ash but the control ash showing a minimum at intermediate L/S and elevated mercury levels at higher and lower L/S. The total amount of mercury leached from the control ash was also higher. The pH values for both the control and baseline samples were fairly constant over the same L/S range and nearly identical for identical leachants. The release from the control sample at higher L/S may be more related to long leach times than to the amount of liquid passing through the column. This can be seen in the case of the sulfuric acid leachate. In this case, a loss of permeability that became especially acute after the first 2 months of leaching decreased the flow through the bed of ash so that the data obtained at a sulfuric acid L/S of 6-8 corresponded to up to 5 months of leachate/ash contact time. The mercury values obtained for sulfuric acid at L/S of 6-8 were more akin to the



values seen at higher L/S (ca. 20) but at similar times for the other leachants. This may indicate a slow degradation of the binding capability of the bromine-activated carbon in the highly alkaline environment. Reactions such as aromatic nucleophilic substitutions, which are known to occur for brominated aromatic compounds, may be postulated as being important. However, it is difficult to be specific in the absence of information about the structure of the mercury-binding agent chemical bond.



The elution profiles for ashes 7B and 8C were very similar. The elution peaks occurring at L/S < 5 for ash 7B appear to be replicated for ash 8C except they are broadened to extend up to L/S of about 8. Even the smaller peaks at 5 < L/S < 8 seen for ash 7B can be seen at higher L/S values for ash 8C. Thus, unlike the ash from the bromine-activated technology, the ash from the H-PAC technology appears to display the same chemistry as its baseline counterpart.



The highly alkaline ashes obtained from the sub-bituminous coal (1B and 2C) released more mercury than the bituminous ashes but they also contained higher levels of mercury. If the data are normalized to account for the higher loadings on the control samples, the resulting percent-released values show improved retention for the control samples. For example, 1170 ng/kg of mercury was released from the control technology sample 2C and only 561 ng/kg was released from the baseline sample, 1B. However, the baseline sample contained only 179 µg/kg mercury whereas 2C contained 1348 µg/kg mercury. Thus, the release of 561 ng/kg corresponds to 0.31% of the original mercury in sample 1B but

Mercury Released In Long-Term Column Leaching Experiments				
In nanograms mercury / kg ash (Parts Per Trillion), and Percent of total mercury in the original ash (in parentheses)				
ASH	H ₂ SO ₄	HOAc	H ₂ O	Na ₂ CO ₃
1B	333 (0.19%)	561 (0.31%)	384 (0.21%)	697 (0.39%)
2C	496 (0.04%)	1170 (0.09%)	1020 (0.08%)	1050 (0.08%)
7B	58.0 (0.12%)	69.4 (0.14%)	80.9 (0.17%)	17.3 (0.04%)
8C	79.7 (0.04%)	115 (0.06%)	151 (0.08%)	22.7 (0.01%)

1170 ng/kg corresponds to only 0.08% of the mercury in sample 2C. When comparisons are made in this way, the control technology samples not only contain more mercury, as desired from a stack emission viewpoint, but also retain a larger portion of the captured mercury than the baseline counterparts.

Little can be said about the relative effectiveness of the 4 leachants. The effect of pH was negligible for all ashes and leachants, consistent with results from batch leaching tests. Acetic acid was one of the better leachants providing the highest or second highest amount of leached mercury for all ashes. Sulfuric acid was the poorest, providing the lowest or second lowest amount of leached mercury for all ashes. Water and sodium carbonate showed no regular behavior.

Overall, very little of the mercury contained in the ash samples was solubilized during leaching. The leached mercury was always below 0.5% and often under 0.1% of the amount in the ash. Neither the pH nor the nature of the anion had a noticeable effect on the leachate mercury.

Arsenic in the Leachates

Although the Phase II mercury capture technologies do not explicitly address other pollutants, it is of interest to examine their potential for co-capture and sequestration of elements that may become a concern in the future. Of particular interest are arsenic and selenium, two elements that have been the targets of earlier EPA and EPRI studies.

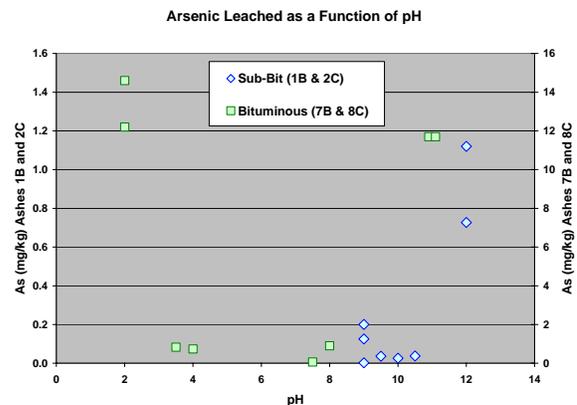
The 2 baseline ashes in this study had similar amounts of As, 21 mg/kg in 1B and 28 mg/kg in 7B. The control technologies increase the amount of As in the control ash by about 10 mg/kg in both cases. In spite of this appearance of similarity, the leaching behaviors of the 2 sets of ashes were very different and appear to be controlled more by the nature of the ash than by the control technology.

Comparison of baseline ash 1B with control 2C and baseline 7B with control 8C shows the leaching chemistry within ash sets is more similar than between ash sets. In the case of the sub-bituminous ash (1B), the addition of the control technology, did measurability reduce the leaching of the As from the ash for 3

Arsenic Released In Long-Term Column Leaching Experiments In milligrams arsenic / kg ash (Parts Per Million), and Percent of total arsenic in the original ash (in parentheses)				
ASH	H ₂ SO ₄	HOAc	H ₂ O	Na ₂ CO ₃
1B	0.036 (0.17%)	0.208 (0.98%)	0.026 (0.12%)	1.12 (5.3%)
2C	0.002 (0.01%)	0.125 (0.39%)	0.037 (0.11%)	0.727 (2.2%)
7B	12.2 (43%)	0.732 (2.6%)	0.898 (3.2%)	11.7 (41%)
8C	14.6 (39%)	0.825 (2.2%)	0.063 (0.17%)	11.7 (31%)

of the 4 leachants, but the amounts leached were all small compared to the bituminous ashes. For the bituminous ash, the amount of As leached from the control ash was nearly the same as from the baseline ash in 3 of the 4 cases and all of the values were higher than seen for the sub-bituminous in spite of the similar solid assays. Reference to the pH plots (above) shows that the pH of the leachate cannot explain these differences. While the sulfuric acid leachate for the alkaline ash never approached the low values obtained for the bituminous ashes, the sodium carbonate (pH = 12) and water (pH = 10) leachates from ashes 1B and 2C nicely bracketed the pH of the sodium carbonate leachate (pH = 11) from ashes 7B and 8C. Thus, while the alkalinity of the sub-bituminous ashes may be mitigating the As release in the presence of sulfuric acid, it cannot account for the differences seen at high pH. Thus, the amount of As available for leaching appears to be determined to a large extent by the nature of the ash and less so by the nature of the leachant or the mercury control technology.

While the nature of the ash controls the absolute amount of As that can be released, pH plays an important role in determining the fraction of the available As that is actually released. The pH dependence of the arsenic release can be more readily seen by plotting the data sets on different y-axes as shown on the graph to the right. When presented this way, a distinct minimum in the amount of arsenic



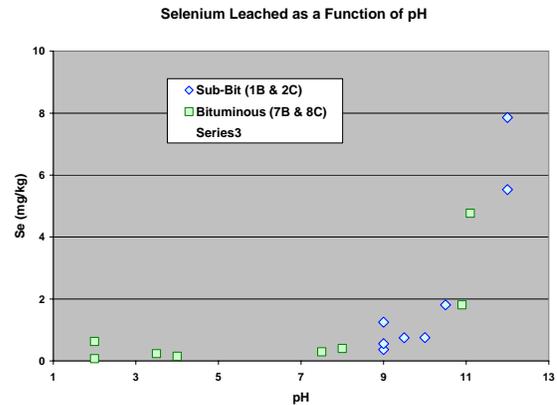
released can be seen at $4 < \text{pH} < 10$. This reinforces the argument that ashes need to be tested at a number of pH values or, at least, at the pH value(s) at which they will be used or disposed of.

Selenium in the Leachates

The 2 baseline ashes in this study had small amounts of Se, just above the detection limit for 1B (6.1 mg/kg) and below the detection limit of 3 mg/kg for 7B. The control technologies increased the amount of Se in the control ash by about 15 and 10 mg/kg, respectively. The leaching behaviors of the 2 sets of ashes appeared to be primarily a function of pH.

Selenium Released In Long-Term Column Leaching Experiments				
In milligrams selenium / kg ash (Parts Per Million), and Percent of total selenium in the original ash (in parentheses)				
ASH	H ₂ SO ₄	HOAc	H ₂ O	Na ₂ CO ₃
1B	0.747 (12%)	1.25 (20%)	0.753 (12%)	7.86 (129%)
2C	0.368 (1.7%)	0.557 (2.6%)	1.81 (8.5%)	5.53 (26%)
7B	0.073 (NA)	0.150 (NA)	0.401 (NA)	1.81 (NA)
8C	0.629 (6.1%)	0.235 (2.3%)	0.297 (2.9%)	4.77 (46%)

The amount of selenium released varied over a large range, both in terms of the absolute amount (0.07-7.8 mg/kg) as well as the percent (2-100%). There was no obvious difference between the bituminous and sub-bituminous ashes as was seen in the case of arsenic (above). Rather, the pH of the leachate appeared to be the dominate factor in accounting for the amount of Se released. This is displayed graphically in the plot to the right. All of the selenium data, regardless of coal type or control technology gave the same trend of increasing selenium mobilization beginning at about pH 8. Only traces of selenium were found in leachates having a pH less than 8.



CONCLUSIONS

Products from 2 Phase II mercury control technologies were found to effectively immobilize the captured mercury over a range of laboratory conditions. Overall, very little of the mercury contained in the ash samples was solubilized during leaching. The leached mercury was always below 0.5% and often under 0.1% of the amount in the ash. Neither the pH nor the nature of the anion had a noticeable effect on the leachate mercury.

Arsenic and selenium were also measured in the leachates. Unlike mercury, a pH dependence was seen for both. In the case of As, release was found to be strongly dependent on the nature of the ash with pH playing a secondary but important role. For Se, pH alone accounted for the extent of release.