Speciation and Attenuation of Arsenic and Selenium at Coal Combustion By-Product Management Facilities

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Abstract

Following completion of contracting activities, sites were identified for the field leachate characterization study. Sampling and Analyses Plans (SAPs) and Site Access Agreements (SAAs) were developed for each site. A total of ten sites were sampled during this reporting period. Among the trace constituents, boron, silicon, and strontium were present in highest concentrations, with median values above 1 mg/L (1,000 μg/L). Work on the first of three sites for the detailed arsenic and selenium adsorption studies began in 2002, prior to completion of the final DOE award. Kd values ranged from 100 to 12,000 L/kg for arsenic (V), 15 to 160 L.kg for As(III), and 5 to 25 L/kg for Se(VI).

Work in 2004 will focus on leachate sampling at 10 to 15 additional sites, and adsorption studies at two additional sites.

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Executive Summary

Following completion of contracting activities, sites were identified for the field leachate characterization study. Sampling and Analyses Plans (SAPs) and Site Access Agreements (SAAs) were developed for each site. A total of ten sites were sampled during this reporting period: five landfills, four ponds, and one minefill. Trace element concentrations are available for all ten sites, but speciation analyses have not yet been completed. Sample analyses for the first ten sites will be substantially completed by the end of December. Additional field sampling begins in October 2003 and will continue through the summer of 2004.

Preliminary results indicate that all leachate samples were alkaline, with pH ranging from 6.2 to 11.6. Among the trace constituents, boron, silicon, and strontium were present in highest concentrations, with median values above 1 mg/L (1,000 μg/L). Molybdenum and aluminum were next with median concentrations between 0.1 and 1 mg/L.

Work on the first of three sites for the detailed arsenic and selenium adsorption studies began in 2002, prior to completion of the final DOE award. Soil characterization and batch studies for As(III) and As(V) are substantially complete for this site. Batch studies for Se(VI) are about half complete. Stability problems with Se(IV) have hampered progress on that species. Field sample collection was completed for the second site in August 2003. Completion of all batch studies for both sites is expected by February 2004. Column studies are scheduled to begin in the first quarter of 2004. Field sample collection for the third site is also planned for the first quarter of 2004.

As(V) adsorption was non-linear, and decreases significantly above pH 7. As(V) adsorption also showed a consistent matrix effect, decreasing in the presence of sulfate and increasing in the presence of calcium. Arsenic (III) adsorption was more linear, increased slightly above pH 7, and showed less matrix effect than As(V). Kd values ranged from 100 to 12,000 L/kg for arsenic (V), and 15 to 160 L.kg for As(III).

Preliminary results for selenium indicate that adsorption isotherms are approximately linear for both Se(VI). The presence of sulfate generally reduced Se(VI) adsorption, but calcium had no effect. Kd values ranged from 5 to 25 L/kg for Se(VI).

Project Management

Planning

Primary activities in the first several months of the project involved developing detailed project plans, negotiating contracts, and obtaining site access agreements for field sites. Table 1 contains a list of contractors currently participating in the project and their primary roles.

Site access agreements and sampling & analysis plans are required for all of the sites in the field leachate characterization program. The first SAAs were completed in July 2003, and field sampling began in August. Work had already begun at the first site in the arsenic and selenium attenuation phase of the research prior to October 2002.

Table 1
Project Contractors and their Roles

Contractor	Phase	Activities
Natural Resource Technology, Inc	All Phases	Coordinate field work; prepare site access agreements and sampling & analysis plans; develop leachate database; assist with all reporting activities
Trent University	Field Leachate Characterization	Development of field and lab protocols for characterization and speciation; perform field sample collection and laboratory analyses; report preparation
Ish Inc.	As & Se Attenuation	Design of attenuation study; field sample collection; data analyses; report preparation
Purdue University	As & Se Attenuation	Develop and test laboratory protocols for adsorption studies; perform all laboratory characterization; report preparation

Deliverables

- Kickoff Meeting - Pittsburgh, October 29, 2002
- NETL Fact Sheet – 12/1/2002
- Project Status Presentation - *DOE/NETL Mercury Control Technology R&D Program Review*, Pittsburgh, August 13, 2003

Budget and Schedule

The project is currently on budget and schedule. There are no deviations from the proposed work at this time.

Field Leachate Characterization

Project Status

Trent spent the first several months of 2003 optimizing the laboratory methods for leachate characterization. Trace elements will analyzed using variations of inductively coupled plasma-mass spectrometry (ICP-MS). Possible interferences were identified and procedures for using double-focusing ICP-MS for most trace elements were completed. Arsenic and selenium in particular were problematic for the double-focusing technique due to interferences, and collision cell ICP-MS was adapted for As and Se determinations. Detection limits obtained using these optimized techniques were generally well below 1 μg/L for most elements As and Se speciation will be done using ion chromatographic separation in front of the collision cell (IC-ICP-MS).

Field sampling began in August, and a total of 10 sites were completed by the end of September. Table 2 is a summary of the types of sites and types of samples collected. Most of these site are located in the Midwest. They include 9 ash management facilities and 1 FGD sludge management facility; 5 landfills, 4 ponds, and 1 minefill.

Table 2
Sampling Summary for Field Leachate Characterization

Site #	By-Product	Site Type	Sample Points
1	FA, BA	Landfill	Leachate Wells
2	FA, BA	Landfill	Lysimeters
3	FA, BA	Landfill	Leachate Collection System Leachate Well
4	FA, BA	Landfill	Leachate Collection System
5	FGD	Pond	Leachate Wells Pond
6	FA, BA	Landfill	Leachate Collection System Lysimeter
7	FA, BA	Minefill, wet	Leachate Wells
8	FA	Pond	Cores Pond Drive-Point
9	FA. BA	Pond	Pond
10	FA, BA	Pond	Leachate Well Cores

FA - fly ash; BA - bottom ash

Sampling points varied among the sites. Where available, the primary sampling points were leachate wells, lysimeters, leachate collection systems, or pond water. In some cases, where access to leachate was limited, leachate samples were collected using a hand-driven well point.

All samples were filtered in-line and discharged directly into the various sample bottles for preservation. Field parameters (e.g., pH, conductivity, Eh, dissolved oxygen) were measured on a separate aliquot. Aliquots for speciation were flash frozen in the field using liquid nitrogen, and put in coolers with dry ice for shipping. Aliquots for dimethylmercury analysis were purged in the field onto a solid-phase adsorbent (SPA). The SPA cartridge was dried with a Hg-free inert gas stream, and then sealed and kept cold and dark. All samples were shipped via overnight mail directly to Trent University for analyses.

In a few cases, an auger drill rig was used to obtain by-product core samples. The cores were packed in dry ice and shipped to Trent, where they will be thawed and the porewater extracted for analysis.

Preliminary Results

Sample analysis is currently underway. Preliminary data were received for most of the trace element analyses. The range of the trace element data are shown in Figure 1. Please note that these data are preliminary, not final. As and Se speciation data are not yet available due to a malfunction of the collision cell. The cell has been repaired and the speciation data should be available by the end of December. Mercury speciation analyses will take a little longer to complete.

The leachate samples were predominantly alkaline, with pH ranging from 6.2 to 11.6 (median 8.8) and alkalinity ranging from 11 to 968 mg/L (median 119 mg/L). Redox potential ranged from highly reducing (-232 mV) to mildly oxidizing (+184 mV), with a median value of +49 mV. The most highly reduced sample was from an FGD fill that has been dewatering for several years.

Among the trace constituents, boron, silicon, and strontium were present in highest concentrations, with median values above 1 mg/L (1,000 μg/L). Molybdenum and aluminum were next with median concentrations between 0.1 and 1 mg/L. All other constituents had median concentrations below 0.1 mg/L. Arsenic concentrations ranged from 0.003 to 0.373 mg/L, with a median of 0.022 mg/L. Selenium concentrations ranged from 0.004 to 4.20 mg/L, with a median of 0.012 mg/L. While the maximum selenium concentration was much higher than the maximum arsenic concentration, the median selenium concentration was lower.

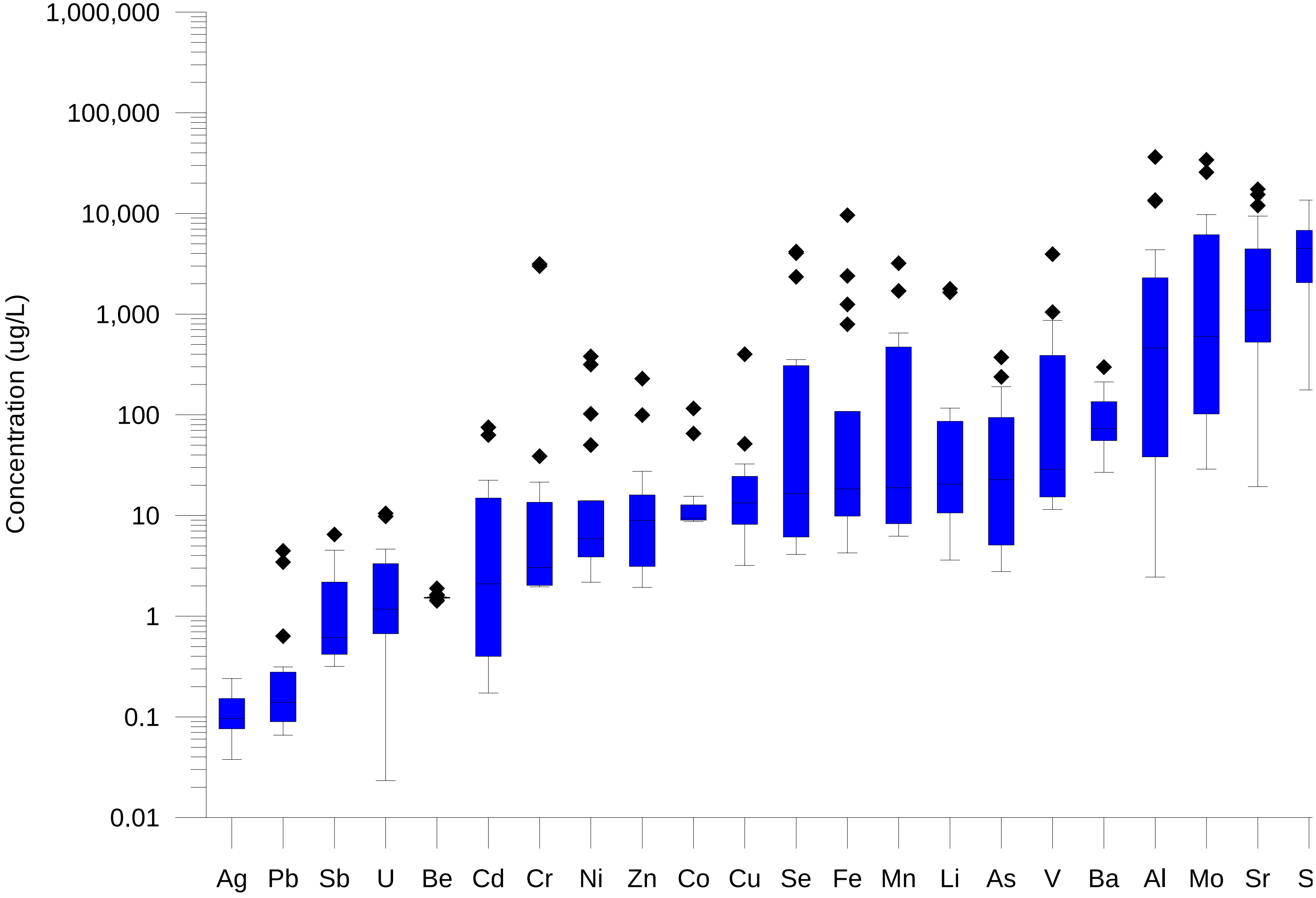

Figure 1 **Range in Trace Constituent Concentrations in Leachate at the First 10 Sites.**
(*Box* represents 25th to 75th percentile; *Bars* represent full data range excluding outliers; *Diamonds* are outliers.)

Arsenic and Selenium Adsorption

Project Status

Two of the three power plant sites were selected for this project. Field samples were collected from the first site in 2002. The first several months of the project were spent developing and testing the equipment and experimental protocols for the adsorption tests. Of critical importance was determining that the various species being tested were stable during the experiments. Most of the arsenic work, and about half of the selenium work is complete for the first site. Samples were collected from the second site in late summer 2003 and lab work has been initiated. Table 3 summarizes the status of the research as of September 30.

Table 3
Status of the As and Se Adsorption Research as of September 30, 2003

Site 1	**Northeast**
Field Sample Collection	Completed
Soil and Ash Characterization	Completed
Batch Adsorption Tests on Soils	As(III) and As(V) - mostly complete Se(VI) - in progress Se(IV) - difficulties with methodology
Sequential Leaching of Ash	Completed
Column Tests	Not Started
Modeling	Not Started
Site 2	**Southeast**
Field Sample Collection	Completed
Soil and Ash Characterization	In Progress
Batch Adsorption Tests on Soils	Not Started
Sequential Leaching of Ash	Not Started
Column Tests	Not Started
Modeling	Not Started
Site 3	**Not Yet Selected**
Field Sample Collection	Not Started
Soil and Ash Characterization	Not Started
Batch Adsorption Tests on Soils	Not Started
Sequential Leaching of Ash	Not Started
Column Tests	Not Started
Modeling	Not Started

Soil and ash core samples were colleted from both of the first two sites using hollow-stem augers. Samples were placed in coolers and shipped via overnight delivery to Purdue University. Selected sample intervals were used to characterize the physical and chemical properties of the soil and ash. Table 4 contains characterization data for the first site.

Preliminary Results

Arsenic Adsorption

The first set of batch experiments evaluated matrix effects on arsenic adsorption. Batch tests were performed on seven soils, with detailed testing of matrix and pH effects performed on two soils. Four solutions were used to test matrix effects: KCl, K_2SO_4, $CaCl_2$, and $CaSO_4$. The solutions were prepared at two ionic strengths: 0.01M and 0.001M. Figures 2 and 3 illustrate the matrix effects for As(V) and As(III), respectively, for one soil.

Figure 2 clearly shows the non-linearity of the As(V) isotherms for all of the matrices. The isotherms appear to display Langmuir behavior within the aqueous concentration range of the experiments (<1 mg/L). Also of note is that there is a consistent matrix effect. The plots suggest that sulfate depresses As(V) sorption (K_2SO_4 plot line), while Ca enhances sorption ($CaCl_2$ plot line). In the $CaSO_4$ matrix, which is what is expected for ash leachate, the Ca and SO_4 effects cancel each other, producing a net effect similar to that for KCl.

Figure 3 suggests that the adsorption behavior of As(III) for this soil is much different than As(V). The isotherms are more linear for As(III). In addition, while the effect of SO_4 in depressing adsorption is apparent, there is no effect due to calcium, so the net effect of the $CaSO_4$ matrix is to reduce adsorption of As(III).

Figures 4 and 5 show the effect of pH on adsorption of As(V) and As(III), respectively. Again the two species exhibit different behavior, with As(V) adsorption decreasing significantly above pH 8, while As(III) increased slightly above pH 8.

Table 5 shows the calculated range in Kd values for two soils from Site 1, for an initial concentration range (i.e., leachate concentration) of 0 to 1 mg/L, using a $CaSO_4$ matrix. Within this initial concentration range, the Kd values for As(V) varied by about a factor of 3 to 7. Variability across the concentration range is less for As(III), about a factor of 2, reflecting the more linear shape of the isotherms. As expected, Kds were much higher for As(V) than As(III). Also apparent is that there is considerable variability between the two soil samples tested from the first site. The As(V) Kd values for the second soil were a factor of 40 lower than the first soil; As(III) Kd values were about a factor of 5 lower for the second soil. These preliminary results highlight the importance of knowing the leachate concentration and speciation, as well as soil properties when selecting attenuation characteristics for transport modeling at ash management sites.

Table 4
Soil and Ash Characterization Data for Site 1

Sample	ID	pH[£]$_{H_2O}$	pH[¥]$_{CaCl_2}$	% Sand	% Silt	% Clay	CEC (cmol/kg)	AEC (cmol/kg)	DCB Fe (mg/kg)	DC Fe (mg/kg)	Rate of Fe Dissolution (mg/L·min)[ß]	% Base Saturation	% Organic Matter	Bray P1 (ppm)	Clay Minerals
AR1 25-30	Soil	5.3	5.1	33	50	17	15.5	0.08	6494	5928	9.58	68	0.5	38	Illite
AR1 35-40	Soil	5.0	4.7	40	35	25	12.6	0.47	4440	6030	12.49	62	0.5	2	Illite
AR2 10-15	Soil	4.8	4.4	60	23	17	4.7	0.29	24562	31800	40.22	48	1	10	Illite
AR2 16-21	Soil	5.0	4.6	59	28	13	2.45	0.27	13036	11370	18.46	62	0.5	11	Illite
AR3 15-20	Ash	5.7	5.9	46	38	17	NA	0.08	9803	5094	NA	NA	NA	NA	NA
AR3 40-45	Ash	6.1	6.4	68	27	5	5.1	0.08	7597	4980	NA	76	3.5	103	NA
AR3 50-54	Soil	5.0	4.9	9	62	29	13.2	0.08	23344	22470	38.67	64	0.6	14	Illite
AR4 15-20	Ash	5.3	5.4	46	38	17	NA	0.08	7293	4920	NA	NA	NA	NA	NA
AR4 40-46	Ash	5.9	6.0	46	38	17	NA	0.31	7141	5310	NA	NA	NA	NA	NA
AR4 46-50	Soil	5.5	5.5	57	28	15	5.8	0.08	16422	18330	37.6	79	0.9	3	Illite

NA - Not Analyzed

£ - 5 grams soil: 5 mL water (1.5 hours)

¥ - 5grams soil: 5 mL water (1.5 hours)

ß - Rate at 0.5 minutes

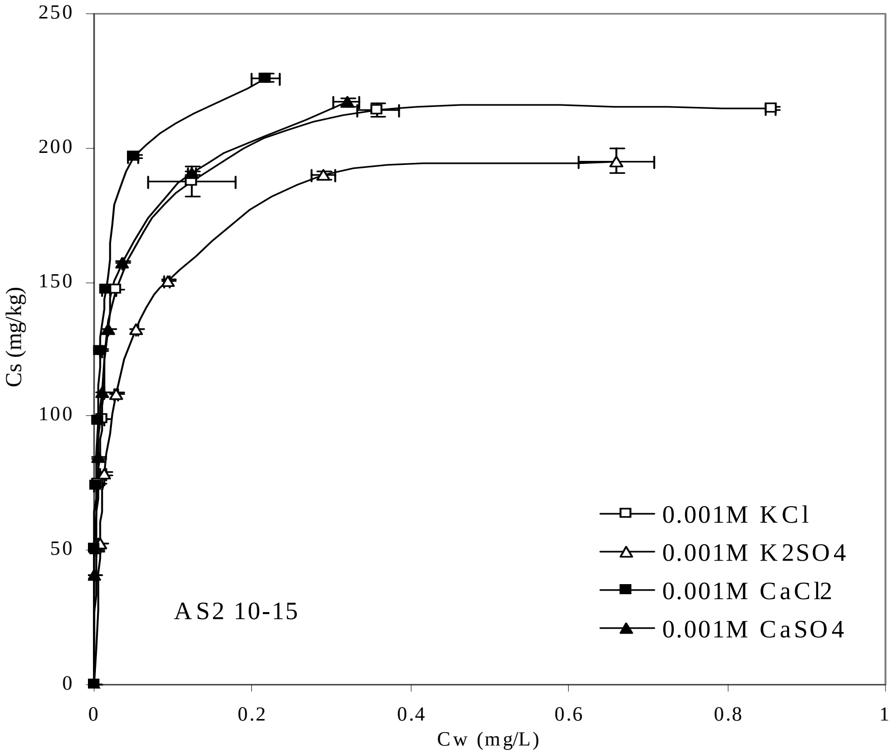

Figure 2 Matrix Effect on As(V) Adsorption Isotherms (Site 1, Soil #1)

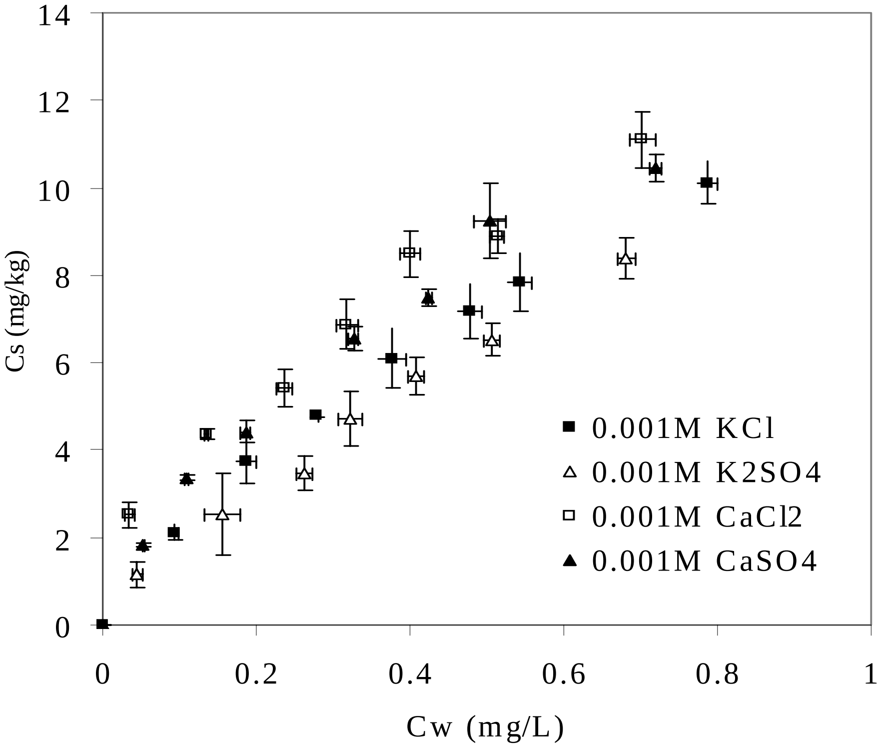

Figure 3 Matrix Effect on As(III) Adsorption Isotherms (Site 1, Soil #2)
Cw = measured final concentration in water
Cs = calculated final concentration in soil

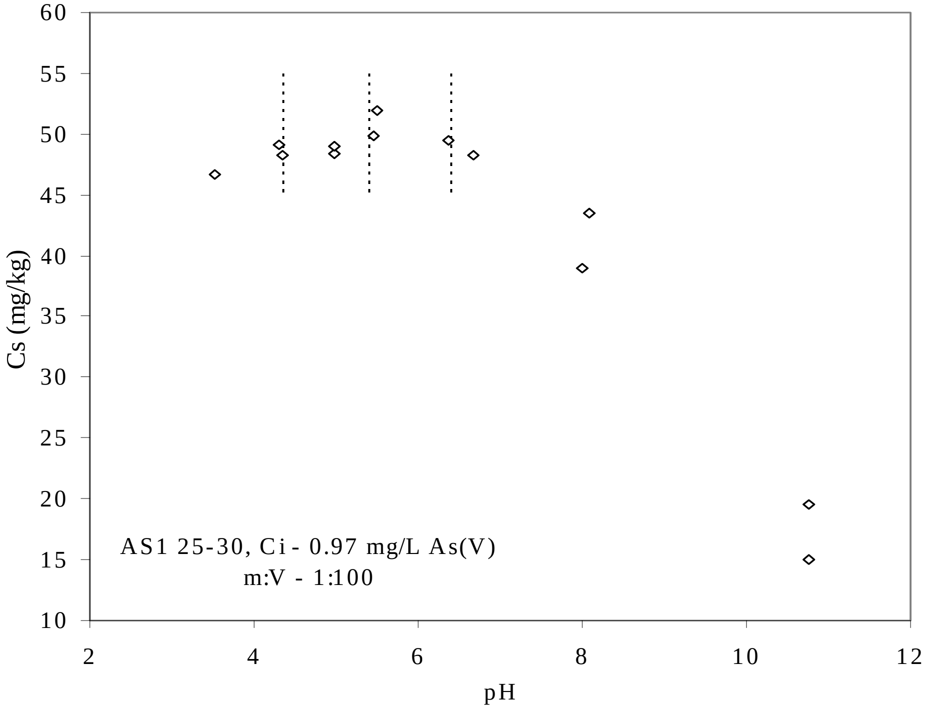

Figure 4 pH Effect on As(V) Adsorption (Site 1, Soil #1)

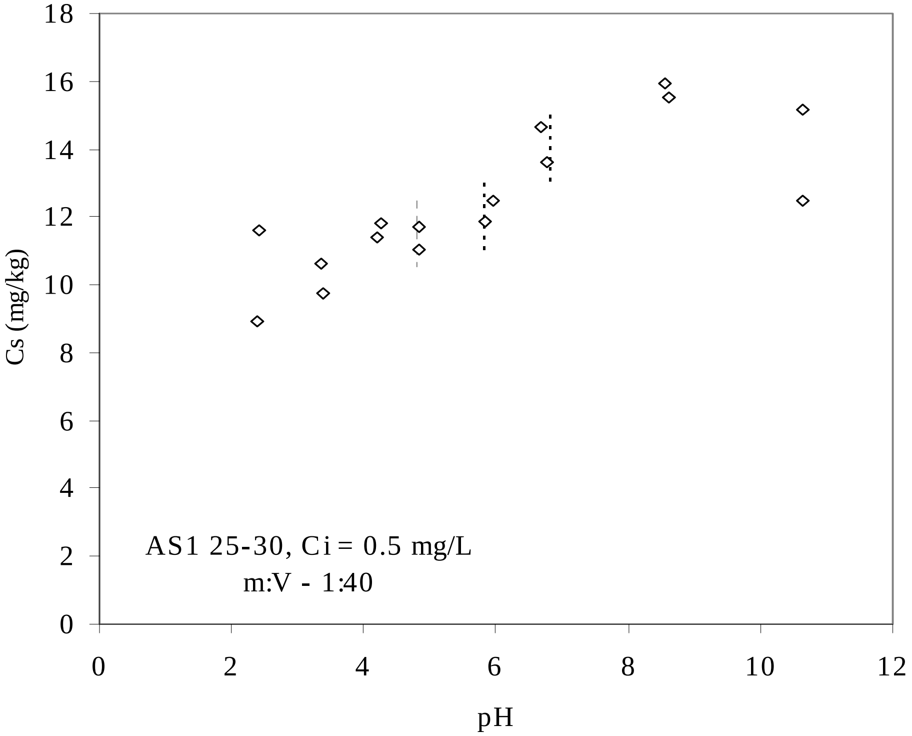

Figure 5 pH Effect on As(III) Adsorption (Site 1, Soil #1)

Table 5
Kd Values (L/kg) for Two Soils from Site 1 over Initial Concentration Range 0 - 1 mg/L

	As(V)	As(III)	Se(VI)
Soil 1	4,000-12,000	80 - 160	10 - 25
Soil 2	100 - 700	15 - 35	5 - 15

Selenium Adsorption

Figure 6 shows matrix effects on adsorption isotherms for Se(VI) for one soil sample. The isotherms are roughly linear for all matrices. As with As(III), the presence of SO_4 reduces Se(VI) adsorption, but Ca has no effect. The net effect is a dampening of adsorption in a $CaSO_4$ matrix. The Se(IV) isotherms also indicate a slight decrease in sorption when solution concentration increased, followed by a flattening of the curve.

Table 5 shows the calculated range in Kd values for two soils from Site 1, for an initial concentration range of 0 to 1 m/L, using a $CaSO_4$ matrix. The Kds were lower and less variable than the arsenic Kds. The values across this leachate concentration range varied by a factor of two to three for a single soil, and a factor of two between soils.

Arsenic Sequential Leaching

Results of 15 sequential extractions (m:V = 1:4) of an ash sample from Site 1 are shown in Figure 7. The figure shows As (total), As(V), As(III), and pH. As(V) concentrations increased during the first 7 or 8 extractions, from about 20 μg/L to 60 μg/L, and then gradually leveled out approaching 70 μg/L. As(III) concentrations were much lower and relatively constant at less than 10 μg/L. Similar results were obtained for a second ash sample from the site. These data suggest that arsenic leaching is probably equilibrium controlled and will continue to occur over a long time scale from this ash. The dominant species is As(V), which is more readily sorbed by the site soils.

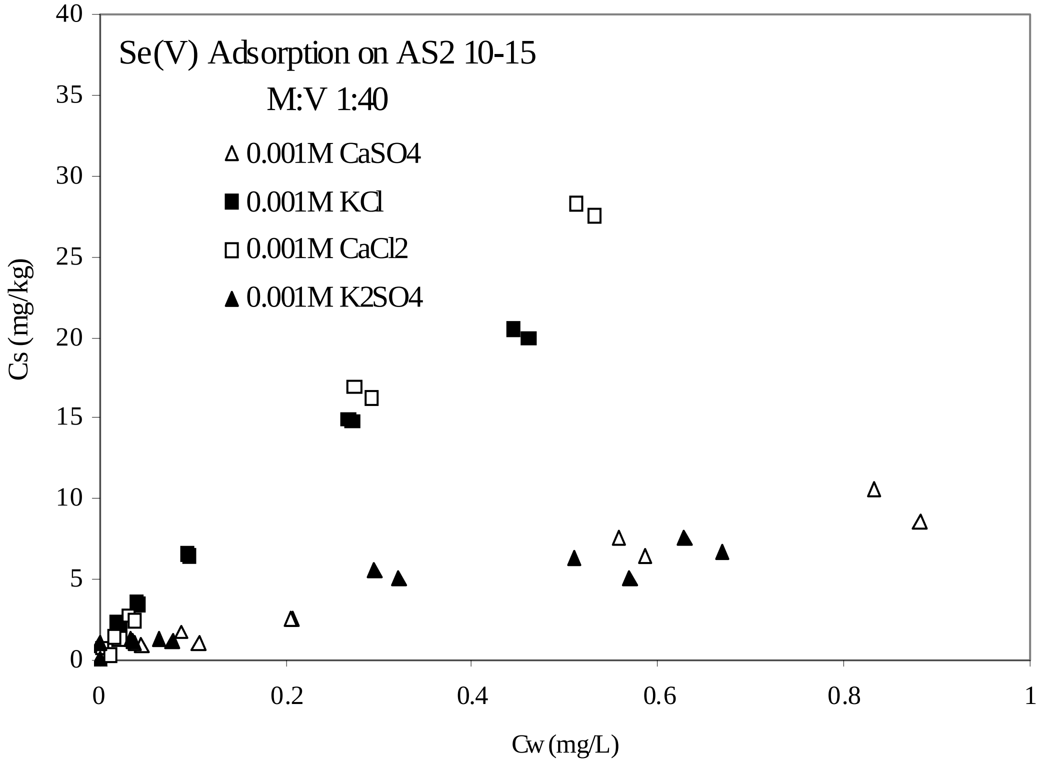

Figure 6 Matrix Effect on Se(VI)) Adsorption Isotherms (Site 1, Soil #1)
Cw = measured final concentration in water
Cs = calculated final concentration in soil

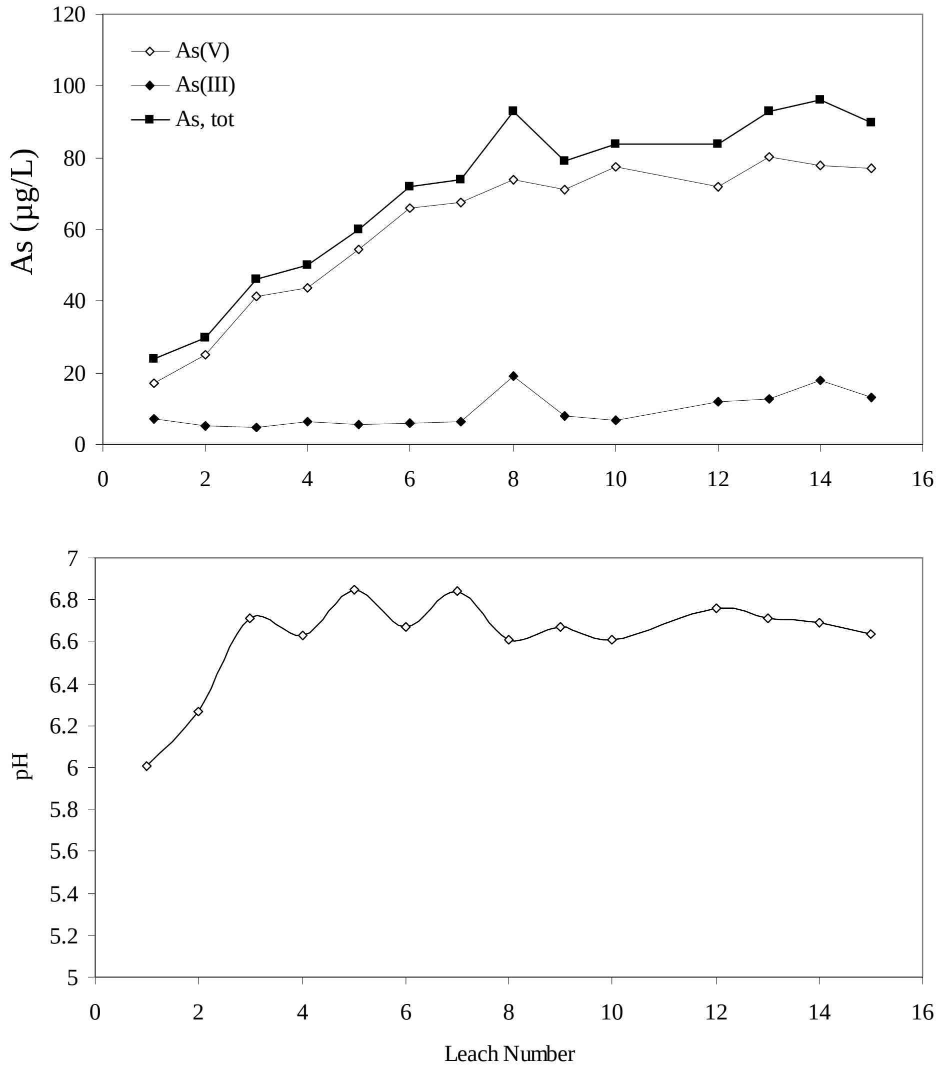

Figure 7 Sequential Leaching Results for Arsenic