

# **Report for 2004MO34B: The Leaching Behavior of Arsenic and Selenium from Fly Ash and Their Potential Impact on Water Quality**

- Conference Proceedings:
  - Wang, T., Wang, J., Chusuei, C., and Ban, H. (2005) Release of Arsenic from Coal Fly Ash Surface. 229th ACS San Diego National Meeting, San Diego, California, USA (March, 2005).
  - Wang, T., Wang, J., Burken, J., and Ban, H. The Leaching Behavior of Arsenic from Fly Ash. 2005 World of Coal Ash, Lexington, Kentucky, USA (April, 2005).

Report Follows

# The Leaching Behavior of Arsenic from Fly Ash

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KEYWORDS: arsenic, fly ash, leaching

## ABSTRACT

The Maximum Contaminant Level (MCL) for arsenic in drinking water will be reduced to 10 ppb from the current 50 ppb level effective January 2006. Fly ash contains arsenic and could be a potential source of arsenic release to the environment. Understanding the leaching behavior of arsenic from fly ash is significant in predicting the arsenic impact on the drinking water quality and in developing innovative methods to prevent arsenic leaching.

The physical-chemical characteristics of three bituminous coal fly ashes (AN/Col #1, AN/Col #2 and AN/NRT #2) were studied using titration method and XPS analysis. AN/Col #1 and AN/Col #2 were obtained from different units burning the same coal. AN/Col #1 employed SNCR (selective non-catalytic reduction) for NO<sub>x</sub> control, and AN/Col #2 did not. AN/NRT #2 was collected from the same unit as AN/Col #2, but a different, higher calcium coal. Three acid sites were found on the surfaces of the fly ash, but only the first acid site, site  $\alpha$ , was considered to be responsible for arsenic adsorption. XPS data indicated that the major elements on ash surface are C, O, Al and Si. Minor and trace elements Ca, As, and Se were also detected. Batch results indicated that pH has significant effect on arsenic leaching. Between pH 3 and 7, arsenic leaching is at a minimum. When pH was less than 3 or greater than 7, a significant amount of arsenic was leached from fly ash. More arsenic was leached out from ash AN/NRT #2 than ashes AN/Col #1 and AN/Col #2. However, the arsenic leaching from AN/NRT #2 was reduced when pH was greater than 9, which may be caused by the precipitation with calcium and other cations. We developed an arsenic adsorption model based on chemical reactions among different arsenic species and surface sites to quantify arsenic partitioning in fly ash. The pH-independent adsorption constants ( $\log K_s$ ) for  $H_2AsO_4^-$  and  $HAsO_4^{2-}$  were determined to be 2.6 and 6.2 respectively. The approach developed in this research is useful for understanding and predicting the release of arsenic from fly ash and other solid materials.

## INTRODUCTION

The USEPA has recently reduced the Maximum Contaminant Level (MCL) for arsenic in drinking water to 10 ppb from 50 ppb, and all drinking water systems must comply with

this new standard by January 2006.<sup>1</sup> Fly ash contains various levels of elements including arsenic.<sup>2,3</sup> For bituminous coal fly ash, the arsenic concentration can range from 1 to 1000 ppm, depending on coal source and combustion technology.<sup>4</sup> In 2003, a total of 122 million tons of Coal Combustion Products (CCPs) were generated in the US, and 58% of the CCPs were fly ash.<sup>5</sup> The release of arsenic from fly ash could lead to concentrations in drinking water that are above the new MCL. Understanding the leaching behavior of arsenic from fly ash is significant in understanding the potential arsenic impact on the drinking water quality, and in developing innovative methods to prevent arsenic leaching.

According to previous research with leaching tests and XPS analysis, arsenic was confirmed to be enriched on ash surface.<sup>6,7</sup> Both As(III) and As(V) were detected in ash, but the latter was present in a much higher fraction.<sup>7,8</sup> Various leachants, including HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, sodium citrate, geopolymer, and EDTA were used to leach the arsenic from fly ash.<sup>7,9,10,11</sup> It was reported that 78-97% of the total As can be removed from fly ash by leaching with 0.5 N H<sub>2</sub>SO<sub>4</sub> or a 1 M sodium citrate at pH 5.<sup>7</sup>

Many factors can influence the leaching of arsenic from fly ash, including pH, solid to liquid ratio, leaching time, temperature, etc.<sup>11,12</sup> Research also suggested that H<sub>2</sub>PO<sub>4</sub><sup>-</sup> can displace arsenate in fly ash and increase arsenic concentration in leachate.<sup>13</sup>

Several mechanisms were proposed to interpret arsenic interactions with fly ash and the surrounding environment. Van der Hoek et al. reported that the leaching of As from acidic ash was sorption controlled and that iron hydroxide was the probable controlling sorbent.<sup>14</sup> However, other study suggested that calcium arsenate is a probable host for arsenic in fly ash.<sup>15</sup>

A surface complexation model was used to quantitatively describe the adsorption of arsenic on acidic fly ash.<sup>16, 17</sup> However, the modeling results were strongly dependent on the initial assumptions, and only amorphous iron hydroxide was considered in modeling. These factors limited the application potential of the model on fly ash.

The objectives of this study are to investigate the physical-chemical characteristics of fly ash, evaluate the leaching behavior of arsenic from fly ash, demonstrate the relationship between the surface characteristics and arsenic adsorption, and quantify the arsenic adsorption behavior by fly ash.

## THEORETICAL ASPECTS

### Ash Surface Speciation

According to Wang, et al.,<sup>18</sup> there are three types of weak acid sites on the fly ash surface. The protonated form of the first acid site, site  $\alpha$ , which has the lowest pK<sub>a</sub> value, is positively charged. Therefore, protonated form of the site  $\alpha$  is most likely the one to adsorb anionic metal ions. The speciation of this acid site can be expressed as:

$$\underline{\text{SOH}}_2^+ = \underline{\text{SOH}} + \text{H}^+; K_H \quad (1)$$

where  $K_H$  is the acidity constant of the surface site  $\underline{\text{SOH}}_2^+$ .

The positively charged surface site concentration can be expressed as:

$$[\underline{\text{SOH}}_2^+] = \alpha_+ S_T \quad (2)$$

where  $S_T$  is the total site  $\alpha$  density, and  $\alpha_+ = \frac{[\text{H}^+]}{[\text{H}^+] + K_H}$

### As(V) Speciation

In water solution, As(V) may exist as the following species:

$$\text{H}_3\text{AsO}_4 = \text{H}_2\text{AsO}_4^- + \text{H}^+; pK_{a1} = 2.26; [\text{H}_2\text{AsO}_4^-] = \alpha_1 [\text{As(V)}]_D \quad (3)$$

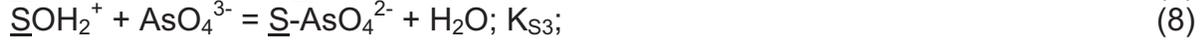
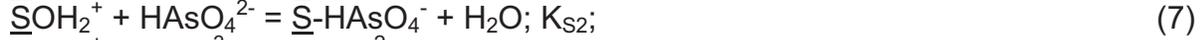
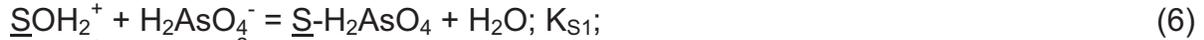
$$\text{H}_2\text{AsO}_4^- = \text{HAsO}_4^{2-} + \text{H}^+; pK_{a2} = 6.76; [\text{HAsO}_4^{2-}] = \alpha_2 [\text{As(V)}]_D \quad (4)$$

$$\text{HAsO}_4^{2-} = \text{AsO}_4^{3-} + \text{H}^+; pK_{a3} = 11.29; [\text{AsO}_4^{3-}] = \alpha_3 [\text{As(V)}]_D \quad (5)$$

Where  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are the fractions of As(V) as  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ , respectively.  $[\text{As(V)}]_D$  is the total dissolved As(V) concentration.

### As(V) Adsorption Reactions

Assuming that only the negatively charged arsenic species are adsorbed on the positively charged ash surface sites:



Where  $K_{S1}$ ,  $K_{S2}$  and  $K_{S3}$  are adsorption constants of the respective three negatively charged arsenic species. Assuming that the adsorption is in the linear range of the Langmuir isotherm, the concentration of adsorbed As(V) species can be calculated using the following equations:

$$[\underline{\text{S}} - \text{H}_2\text{AsO}_4] = K_{S1} \alpha_{S+} S_T \alpha_1 [\text{As(V)}]_D \quad (9)$$

$$[\underline{\text{S}} - \text{HAsO}_4^-] = K_{S2} \alpha_{S+} S_T \alpha_2 [\text{As(V)}]_D \quad (10)$$

$$[\underline{\text{S}} - \text{AsO}_4^{2-}] = K_{S3} \alpha_{S+} S_T \alpha_3 [\text{As(V)}]_D \quad (11)$$

Therefore, the adsorption ratio of arsenic can be expressed as:

$$R = \frac{[\text{As(V)}]_{\text{ads}}}{[\text{As(V)}]_{\text{D}} + [\text{As(V)}]_{\text{ads}}} = \frac{\alpha_{\text{S}^+} S_{\text{T}} (K_{\text{S1}} \alpha_1 + K_{\text{S2}} \alpha_2 + K_{\text{S3}} \alpha_3)}{1 + \alpha_{\text{S}^+} S_{\text{T}} (K_{\text{S1}} \alpha_1 + K_{\text{S2}} \alpha_2 + K_{\text{S3}} \alpha_3)} \quad (12)$$

where  $[\text{As(V)}]_{\text{ads}}$  is total concentration of adsorbed As(V) species.

## MATERIALS AND METHODS

### Fly Ash Samples

Three ash samples were used in this study. Samples AN/Col #1 and AN/Col #2 were respectively collected from Unit #1 (with SNCR) and Unit #2 (conventional) of a facility burning eastern bituminous coal. Their loss on ignition (LOI) were, respectively, 12.7% and 6.7%. Sample AN/NRT #2, with LOI of 9.8%, was collected from the Unit #2 of the same facility when it was burning a different higher calcium eastern bituminous coal. All these samples were collected from the cold side electrostatic precipitator (ESP).

Raw ash samples were used for basic leaching experiment. All samples were dried at 105 °C for at least 24 hours in an oven before the experiments. Washed ashes were used for surface characterization and arsenic partitioning experiment. The purpose of washing was to remove soluble materials to get a relatively clean surface for the experiments. For the arsenic partitioning experiment, a 0.2 M NaOH solution was used to perform ash washing to maximize the arsenic removal. For other experiments, ashes were washed with DI water. All washing was performed at the solid/liquid ratio of 1:5, and was repeated for 5 times. Aeration was used to agitate the ash – water mixture, and each washing lasted 20 hours. Washed ash was dried in an oven at 105 °C for at least 24 hours before use.

### Batch Equilibrium Titration

A batch equilibrium titration method including mathematical models developed by Wang, et al.<sup>18, 19</sup> was employed in this study to determine the surface site density and acidity constant of the fly ash.

### As(V) Partitioning Experiment

Batch method was employed for arsenic partitioning studies.<sup>18</sup> The solid/liquid ratio was 1/10. Ionic strength was adjusted with 0.01M using stock NaNO<sub>3</sub> solution. For this study, samples were divided into 4 groups, with 1, 2, 5 and 10 ppm As(V) addition, respectively. To make sure the adsorption is in the linear range, the total arsenic concentration should be less than 10 percent of the surface site concentration. The equilibrium time used in this study was 24 hours. After shaking, all samples were settled overnight, the supernatant was then collected for arsenic analysis. The final pH was measured using the rest of the mixture in the bottle.

## Basic Leaching Experiment

Arsenic leaching from raw ash under various pH conditions was investigated using batch methods.<sup>18</sup> Ionic strength was not adjusted in this experiment. At least 10 pH values in the range between 2 - 12 were selected for leaching. Solid/liquid ratio of 1:10 was used in the experiment. Arsenic in the supernatants was analyzed after 24 hrs of shaking. The final pH in each bottle was also measured.

## Surface Analysis

The XPS analysis was carried out using Kratos Axis 165 X-Ray Photoelectrons spectrometer. Mg K $\alpha$  radiation (1253.6 eV) was employed to provide the x-ray beam. By measuring the photon electron energy in a high-resolution analyzer, information regarding the concentration and oxidation states of the surface elements can be determined.

## Analytical Method

A graphite furnace atomic absorption spectrometer (AAAnalyst 600, Perkin-Elmer Corp., Norwalk, Connecticut, USA) was used to determine arsenic concentrations in the solution. An Orion PerpHecT Triode pH electrode (model 9207BN) and a pH meter (perpHecT LoR model 370) were used for pH measurement.

## Data Analysis

The non-linear regression program Kaleidagraph<sup>TM</sup> was used to conduct curve fitting for the determination of the surface acid characteristics and arsenic adsorption constants, based on the respective models we developed.

# RESULTS AND DISCUSSION

## Surface Acidity

The surface characteristics of three washed ash samples AN/Col #1, AN/Col #2 and AN/NRT #2 were investigated. AN/Col #1 and AN/NRT #2 were washed with DI water only. The AN/Col#2 was washed with both DI water and 0.2M NaOH solution. Figure 1 shows the titration and curve fitting results for all samples. Results indicated that all samples have three types of acid sites on their surface. Table 1 shows the site density and the acidity constant of each site. Since the protonated form of the site  $\alpha$  is positively charged, it may be the most responsible site for adsorption of arsenic anions.

Table 1. Surface site density and acidity constant of washed ash samples AN/Col #1, AN/Col #2, and AN/NRT #2.

Sample	Washing Agent	Site	$\alpha$	$\beta$	$\gamma$
AN/Col #1	DI water	Site density ( $10^{-5}$ mol/g)	$32 \pm 1$	$2.5 \pm 0.8$	$8.6 \pm 2.7$
		Acidity constant ( $pK_H$ )	$3.0 \pm 0.1$	$8.4 \pm 0.5$	$11.6 \pm 0.4$
AN/Col #2	DI water	Site density ( $10^{-5}$ mol/g)	$23 \pm 1$	$3.2 \pm 0.1$	$11 \pm 4$
		Acidity constant ( $pK_H$ )	$2.8 \pm 0.1$	$8.3 \pm 0.5$	$12.0 \pm 0.4$
AN/Col#2*	0.2M NaOH	Site density ( $10^{-5}$ mol/g)	$25 \pm 2$	$8.5 \pm 1.3$	$11 \pm 1$
		Acidity constant ( $pK_H$ )	$3.5 \pm 0.1$	$7.0 \pm 0.3$	$11.1 \pm 0.1$
AN/NRT #2	DI water	Site density ( $10^{-5}$ mol/g)	$47 \pm 2$	$2.5 \pm 1.2$	$16 \pm 20$
		Acidity constant ( $pK_H$ )	$3.4 \pm 0.1$	$8.8 \pm 1.1$	$12.1 \pm 0.9$

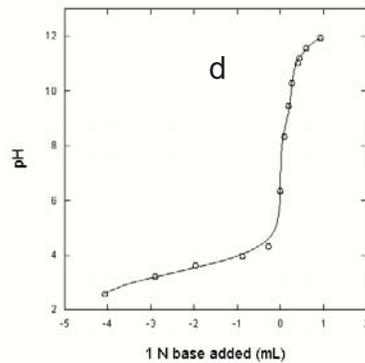
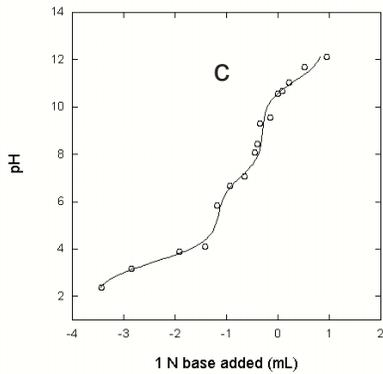
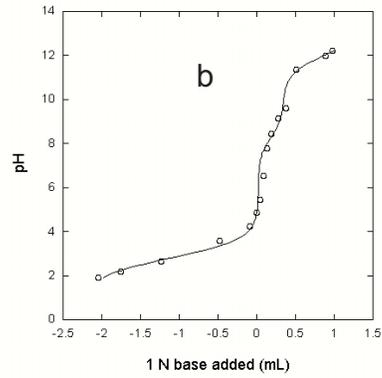
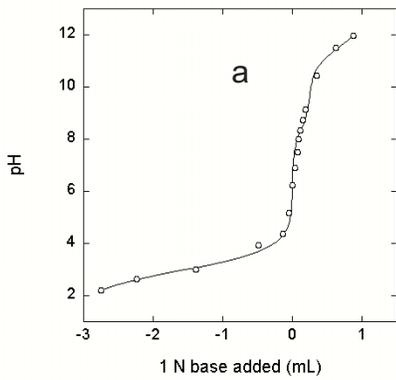


Figure 1 Titration and curve fitting results for washed ashes: (a) AN/Col #1; (b) AN/Col #2 (DI water washed); (c) AN/Col #2 (0.2M NaOH washed); and (d) AN/NRT #2. Ionic strength = 0.01 M (NaNO<sub>3</sub>), temperature = 20 – 25 °C; equilibration time = 24 hours.

### Surface Analysis with XPS

To obtain ash surface composition information and oxidation states of arsenic, the raw ash and washed ash of AN/Col #2 were scanned with XPS. Table 2 shows the relative amounts of each element detected on ash surface. It can be seen that C, O, Al, and Si are major elements on surface, while the amounts of Ca, As and Se are much lower. Quantitative change of these elements before and after washing is also observed. The increase of oxygen may be due to the surface contamination by oxygen in air. The decrease of carbon could be caused by the removal of carbon content during the washing process. For Se and Si, their concentrations on surface increased after washing, which suggests that these elements tend to be under the top layer of the ash surface. The amount of As and Al decreased, suggesting that these elements may be desorbed or dissolved in water during washing. It may also indicate that arsenic tends to be concentrated on the ash surface.

Table 2. Surface composition of ash AN/Col #2 based on XPS analysis.

Element		C	O	Al	Ca	Si	As	Se
Relative Amount (%)	AN/Col #2 Unwashed	7.88	60.8	16.2	0.016	15.1	0.0062	0.019
	AN/Col #2 Washed	3.43	66.4	10.8	0.016	19.3	0.0042	0.033

### Effect of pH on Arsenic Leaching

Effect of pH on arsenic leaching from raw ash AN/Col #1 and AN/Col #2 was investigated using batch leaching methods. Figure 2 shows the soluble arsenic concentration as a function of pH. Figure 2 shows that more arsenic can be released from ash AN/Col #1 than from AN/Col #2. Results also indicate that arsenic can be released when pH is less than 3 or greater than 7, while in the pH range between 3 and 7, very little arsenic is released. This can be explained with arsenate speciation analysis.

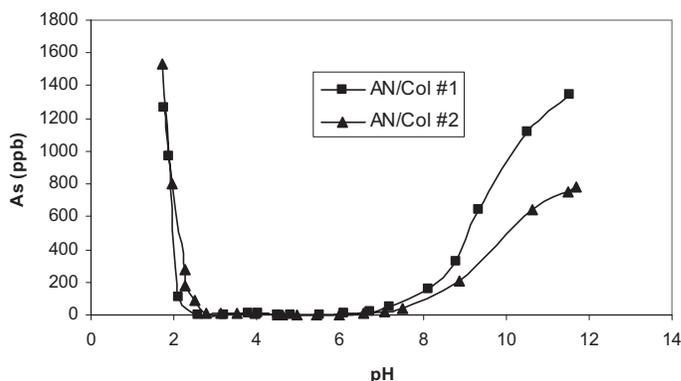


Figure 2. Basic leaching results for As from ash AN/Col #1 and AN/Col #2. Experimental conditions: S/L = 1:10; temperature = 20 – 25 °C; equilibration time = 24 hours.

Figure 3 shows the As(V) speciation diagram. When pH is very low (less than 2), the major arsenic species is the  $H_3AsO_4$ , which does not have charge. It appears that the neutral arsenic molecules are not easily adsorbed by ash surface. When pH is increased above 2, the total concentration of anionic arsenic species ( $H_2AsO_4^-$  and  $HAsO_4^{2-}$ ) is also increased. These anions can be strongly adsorbed by positively charged ash surface sites. When pH is further increased above 7, both the ash surface and arsenic are negatively charged, which results in the arsenic release.

Coal ash AN/NRT #2 was also investigated using batch leaching approach. This coal ash had a higher calcium content than the other two coal ashes. Figure 4 shows the leaching results under two S/L ratios. Results indicate that the leachate arsenic concentration for this ash is significantly greater than the other two ash samples. The leaching behavior of arsenic is similar to the other two ashes when pH is less than 9. However, the soluble arsenic concentration decreases with the increase of pH when pH is greater than 9, and increases again with the increase of pH when pH is greater than 11. This behavior may be caused by the precipitation of arsenate compounds. When pH increases, more arsenic is in the free arsenate ion form, which will form precipitates with many cations including calcium. Therefore, the total arsenic concentration decreases with the increase of pH when pH is greater than 9. If we further increase the pH above 11, free cation concentration will be decreased due to the formation of metal-hydroxides. Therefore, some precipitated arsenic can be dissolved due to the decrease of free cation concentration.

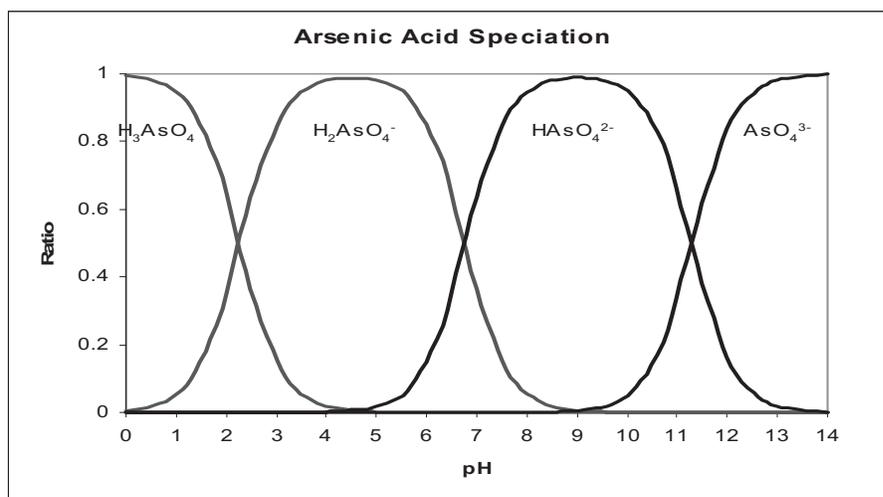


Figure 3. Speciation of arsenic acid.

Figure 4 also shows that, in alkaline pH range, the soluble arsenic concentration is high when the S/L ratio is low. This suggests that, under the low S/L conditions, the total cation concentration is low. Therefore, more arsenic is in soluble form under the saturation condition.

Leist reported that the calcium concentration in the leachate was mirrored in the arsenic concentration, suggestive of As-Ca precipitation.<sup>20</sup> To verify whether As-Ca correlation exists in our system, calcium concentrations in supernatants were measured. The results are also shown in Figure 4. Based on  $K_{sp}$  of  $Ca_3(AsO_4)_2$  and dissolved calcium concentrations, the saturation concentrations of  $AsO_4^{3-}$  and total dissolved arsenic were calculated. However, our calculation results are about 10 times greater than experimental data, which indicates that some other factors may also present in the system affecting arsenic release. This will be investigated in our future studies.

Results also show that when pH is less than 9, the soluble concentrations of arsenic under two ash S/L ratios are overlap. This could be caused by joint effects of adsorption and precipitation. It is speculated that due to the arsenic speciation, there is less chance of precipitation under low pH. The details of this “overlap” phenomenon will be investigated in future.

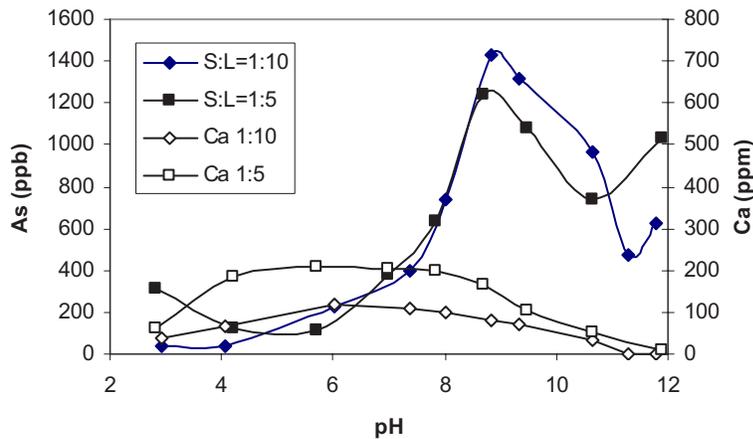


Figure 4. Basic leaching results for As & Ca from ash AN/NRT #2. Experimental conditions: S/L = 1:10; temperature = 20 – 25 °C; equilibration time = 24 hours.

### As (V) Interactions with Washed Ash

In order to determine the significance of adsorption on arsenic leaching, an arsenic partitioning experiment was conducted using washed ash. In this experiment, the NaOH washed ash AN/Col #2 was used for arsenic partitioning studies. Different initial As(V) additions were used: 0, 1, 2, 5 and 10 ppm. Figure 6 shows the arsenic partitioning results. Results indicate that pH has the similar effect on soluble As (V) concentrations for systems containing washed ash and raw ash. The 0 ppm addition data indicate that

the washed ash still contained some leachable arsenic. Results also show that, in a broad pH range, the soluble arsenic concentration is proportional to the arsenic addition, which indicates that the adsorption plays a major role on arsenic partitioning. However, when pH is greater than 9, the soluble arsenic concentration for the 10 ppm arsenic addition scenario decreases with the increase of pH. This could be caused by the arsenic precipitation with the cations but this explanation needs to be further verified. Compared with the basic leaching results in Figure 3, the higher percentage of As(V) is in soluble phase for the washed ash. This could be caused by the removal of other cations during the washing process.

### Modeling for As(V) Partitioning

Equation 12 was used to model As(V) partitioning results. Previously determined parameters including the surface site density and acidity constant were applied to the model. For this study, only site  $\alpha$  was considered, which is most possible to be the arsenic adsorption site. Since a certain amount of arsenic can be released from the ash with 0 ppm addition, a background concentration was estimated to calculate the total arsenic concentration in the system after arsenic addition. The arsenic uptake ratio  $R$  can be expressed as  $[1 - M_d/(M_{add}+M_b)]$ , where  $M_d$ ,  $M_{add}$  and  $M_b$  are the dissolved, added and background arsenic concentrations, respectively. Considering that precipitation may occur at very high pH, only the data with pH condition of lower than 9 was used for curve fitting.

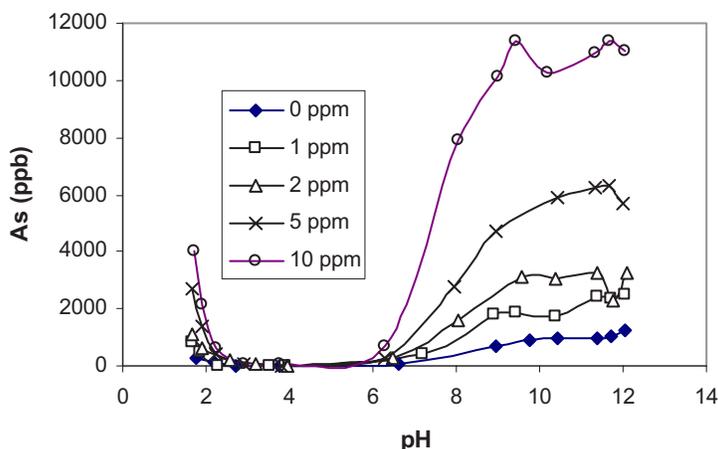


Figure 5. As(V) partitioning results for 0.2 M NaOH washed ash AN/Col #2. Experimental conditions: S/L = 1:10; ionic strength = 0.01M NaNO<sub>3</sub>; temperature = 20 – 25 °C; equilibration time = 24 hours.

Based on the soluble arsenic concentrations in Figure 5, the amount of arsenic addition, and the estimated background arsenic concentration, the arsenic partitioning can be calculated. Figure 6 shows the arsenic partitioning ( $R$ ) as a function of pH (points). It shows that, regardless of the amount of arsenic addition, the percentage of arsenic on

the ash surface is constant for a given pH. It indicates that all experiments were conducted within the linear range of the Langmuir isotherm.

Kaleidagraph™ was used to perform the curve fitting and determine the adsorption constants of two species  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$ . Because the species  $\text{AsO}_4^{3-}$  is significant only under very high pH conditions when the surface sites are negatively charged, the chance of  $\text{AsO}_4^{3-}$  adsorption by positively charged surface sites is minimum. Therefore, the adsorption of  $\text{AsO}_4^{3-}$  was not considered in the model. The solid curve in Figure 6 is the model result. Table 3 shows the calculated adsorption constants, their standard errors, and the correlation factor for the curve fitting. The good agreement between experimental data and the theoretical model indicates that this model is successful and practical for simulating arsenic partitioning under different pH conditions.

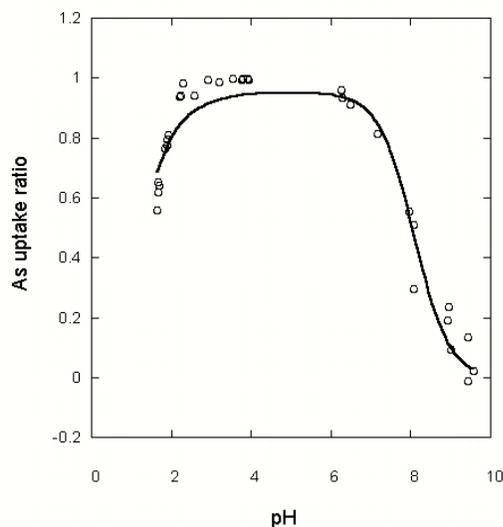


Figure 6. The adsorption results of As(V) onto washed ash AN/Col #2. Experimental conditions: metal concentrations = 1 - 10 mg/L; S/L = 1:10; ionic strength = 0.01M ( $\text{NaNO}_3$ ); temperature = 20 – 25 °C; equilibration time = 24 hours.

Table 3 Adsorption constants between As(V) and ash AN/Col #2

Species	$\log K_s$	Standard Error	$R^2$
$\text{H}_2\text{AsO}_4^-$	2.64	0.06	0.95
$\text{HAsO}_4^{2-}$	6.20	0.06	

## CONCLUSIONS

Results indicate that there are three acid sites on ash surfaces, among which the first acid site is most likely responsible for adsorption of arsenic. The model developed in this study based on arsenic speciation analysis can be used to quantify the As (V)

partitioning. The adsorption constants ( $\log K_s$ ) for  $\text{H}_2\text{AsO}_4^-$  and  $\text{HAsO}_4^{2-}$  are determined to be 2.6 and 6.2, respectively. Results also indicate that adsorption and precipitation may concurrently exist to control arsenic leaching.

## ACKNOWLEDGEMENTS

This work was supported by the Electric Power Research Institute (EPRI), by the Department of Interior (USDOI) through Missouri Water Research Center (MWRC) (Award Number 01HQGR0089), and by the Environmental Research Center for Emerging Contaminants (ERCEC) at the University of Missouri-Rolla (UMR). Assistance from Mr. Ken Ladwig, Project Manager at EPRI, was greatly appreciated. Conclusions and statements made in this paper are those of the authors, and in no way reflect the endorsement of the funding agencies.

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