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Leaching Characteristics of Arsenic and Selenium from Coal Fly Ash: Role of Calcium[†]

Tian Wang,^{‡,§} Jianmin Wang,^{*,‡,§} Yulin Tang,^{‡,§,||} Honglan Shi,[§] and Ken Ladwig[#]

Department of Civil, Architectural, and Environmental Engineering, and Environmental Research Center (ERC), Missouri University of Science and Technology, Rolla, Missouri 65409, College of Environmental Science and Engineering, Tongji University, Shanghai, China 200092, and Electric Power Research Institute (EPRI), 3420 Hillview Avenue, Palo Alto, California 94304

Received January 17, 2009. Revised Manuscript Received April 16, 2009

Understanding the leaching behavior of arsenic (As) and selenium (Se) in coal fly ash is important in evaluating the potential environmental impact of coal fly ash. Batch experiments were employed to systematically investigate the leaching behavior of As and Se in two major types of coal fly ashes, bituminous coal ash and sub-bituminous coal ash, and to determine the underlying processes that control As and Se leaching. The effects of pH, solid/liquid (S/L) ratio, calcium addition, and leaching time on the release of As and Se were studied. Overall, bituminous coal ash leached significantly more As and Se than sub-bituminous coal ash, and Se was more readily leachable, in both absolute concentration and relative fraction, than As for both types of fly ashes. Adsorption/desorption played a major role on As and Se leaching from bituminous coal ashes. However, calcium precipitation played the most important role in reducing As and Se leaching from sub-bituminous coal ashes in the entire experimental pH range. The leaching of As and Se from bituminous coal ashes generally increased with increases in the S/L ratio and leaching time. However, for sub-bituminous coal ashes, the leaching of As was not detected under most experimental conditions, while the leaching of Se increased with increases in the S/L ratio and leaching time. As^V and Se^{IV} were found to be the major species in all ash leachates in this study.

Introduction

The concentrations of arsenic (As) and selenium (Se) in coal fly ash are often greater than those in background soils. For bituminous coal fly ash, the As concentration is typically below 200 mg/kg but can be as high as 1000 mg/kg, depending upon the coal source and combustion technology.¹ The Se concentration can be as high as 200 mg/kg,² although it is typically in the range of 10–20 mg/kg.¹ In 2007, a total of 126.3 million tons (1.15×10^{11} kg) of coal combustion products (CCPs) were generated in the U.S., 56.7% of which were fly ash.³ As and Se have high environmental mobility at an alkaline pH, compared to cationic elements of concern,⁴ and both are regulated in the primary drinking water standard.⁵ Therefore, understanding the leaching behavior of As and Se in coal fly ash is significant in

evaluating its potential impact on the environment. It is also important in developing sustainable ash management and beneficial use strategies.

Previous studies demonstrated that the overall leaching behavior of As and Se from fly ash was affected by pH, solid/liquid (S/L) ratio, leaching time, temperature, and ash type.^{6–11} It was reported that As and Se leaching from acidic ashes was likely controlled by the formation of surface complexes with iron oxide, while the leaching from alkaline ashes was likely controlled by calcium because of the high calcium content in these ashes.^{12,13} Our recent data indicated that, for bituminous coal ash, adsorption played a major role on As and Se leaching.^{14,15} However, raw ash exhibited lesser As leaching than washed ash, indicating that factors other than adsorption also contributed to As binding.¹⁴ Sub-bituminous coal ash released a minimal amount of Se compared to bituminous coal

[†] Disclaimer: Conclusions and statements made in this paper are those of the authors and in no way reflect the endorsement of the aforementioned funding agencies.

* To whom correspondence should be addressed. Telephone: (573) 341-7503. Fax: (573) 341-4729. E-mail: wangjia@mst.edu.

[‡] Department of Civil, Architectural, and Environmental Engineering, Missouri University of Science and Technology.

[§] Environmental Research Center (ERC), Missouri University of Science and Technology.

^{||} Tongji University.

[#] Electric Power Research Institute (EPRI).

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ash.¹⁵ Therefore, a soluble element, suspected to be calcium, reduced As and Se leaching from both types of coal ashes. However, this hypothesis has not been validated.

Both As and Se occur as several different species in the environment, and speciation determines their environmental mobility and toxicity. For example, As^{III} is generally more toxic and more mobile than As^V, while the methylated forms of As, monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA), are less toxic than the inorganic forms and arsenobetaine (AsB) is nontoxic.¹⁶ Se^{VI} is generally less toxic and more mobile in an aqueous environment than Se^{IV}.^{17–20} Previous studies demonstrated that the predominant species of As and Se in fresh fly ash and ash leachates were As^V and Se^{IV}, respectively.^{21–25} However, As and Se speciation may change as the ash weathers, resulting in a change in the overall leaching behavior. As and Se speciation provides key information for the fundamental understanding of the long-term leaching process.

Coupled instrumental techniques have been developed recently for the speciation analysis of As and Se. Separation of different As and Se species was achieved with ion chromatography (IC) or high-performance liquid chromatography (HPLC).^{21,22,26–28} Commonly used detectors are atomic adsorption (AA) spectrometry,²¹ inductively coupled plasma–atomic emission spectrometry (ICP–AES),²⁶ and ICP–mass spectrometry (ICP–MS).^{22,27} The combination of HPLC with ICP–MS has high sensitivity, minimal sample pretreatment, and the ability for simultaneous analysis of As and Se,^{29–32} which could be the only feasible method suitable for detecting trace levels of different As and Se species in fly ash leachates. However, conditions for using this method for ash leachate analysis have not been well-established.

Because of their environmental importance and common occurrence in coal ash leachate, a detailed study is needed to elucidate the underlying mechanisms that control As and Se release. The objectives of this study were (a) to establish

conditions of the HPLC–ICP–MS method for determining trace levels of As and Se species in coal fly ash leachates and determine As and Se speciation in leachates collected under different experimental conditions, (b) to investigate the leaching behavior of As and Se from two major types of coal fly ashes under different conditions, such as pH, S/L ratio, calcium addition, and leaching time, and (c) to validate the role of calcium on As and Se leaching from both types of coal fly ashes.

Experimental Section

Fly Ash Samples. Six coal fly ash samples, three from bituminous coal and three from sub-bituminous coal, were used in this study. Samples 33106-1004 (#1004) and 33106-1005 (#1005) were collected from two different units with cold-side electrostatic precipitators (ESPs) at the same plant; both were pulverized coal units burning Appalachian bituminous coal. Sample #1004 was collected from a unit without selective noncatalytic reduction (SNCR). Sample #1005 was collected from a unit with SNCR for NO_x control. Sample 33106-1009 (#1009) was collected from the same plant and unit as #1004 when burning a different Appalachian bituminous coal with slightly higher calcium content. Samples 25410-1015 (#1015) and 25410-1018 (#1018) were generated at a plant with a cyclone furnace burning a blend of about 80% sub-bituminous coal (Powder River Basin, PRB) and 20% bituminous coal (Illinois Basin), along with varying amounts of pet coke and tires. Sample #1015 was collected from a unit without SNCR, while sample #1018 was collected from a unit with SNCR for NO_x control. Sample 50213-7 (#7) was collected from a third plant burning PRB sub-bituminous coal without SNCR. This plant was equipped with a hot-side ESP.

Ash Characteristics. Important physical and chemical properties, including loss-on-ignition (LOI), specific surface area, total concentrations of major components, such as SiO₂, Al₂O₃, Fe₂O₃, and CaO, and concentrations of As and Se, were determined. LOI was determined by measuring the weight loss of a dried sample at 550 °C. The specific surface area was determined using a Quantachrome Autosorb-1-C high-performance surface area and pore size analyzer (Quantachrome Instruments). Major components in fly ash, SiO₂, Al₂O₃, Fe₂O₃, and CaO, were determined using X-ray fluorescence spectroscopy (XRF) (X-LAB 2000, SPECTRO Analytical Instruments). As and Se were determined using microwave-assisted digestion samples following the United States Environmental Protection Agency (U.S. EPA) method 3052. The sample weight and acid composition were 0.4 g of fly ash + 10 mL of HNO₃ + 5 mL of HF + 5 mL of HCl. Digested samples were collected in 50 mL polypropylene sample tubes, diluted to 50 mL with deionized (DI) water, and then settled for at least 24 h before analysis. The supernatant was further diluted before chemical analysis without settling. Table 1 shows major characteristics and compositions of tested fly ashes.

Reagents and Standards. Millipore DI water was used throughout the research. Other reagents, including As^{III}, As^V, Se^{IV}, and Se^{VI} standard solutions, solid dimethyl arsenic acid, and solid arsenobetaine, were obtained from Sigma-Aldrich (St. Louis, MO). Monosodium acid methane arsonate was purchased from Chem-Service (West Chester, PA). Reagents used for the HPLC mobile phases, including ammonium phosphate (monobasic), nitric acid (trace metal grade), ammonium hydroxide (high purity), and HPLC-grade methanol, were purchased from Fisher Scientific. The 5 mg/L intermediate As and Se standards were made from stock solutions. Calibration standards (5, 10, 50, and 100 µg/L) were freshly prepared by serial dilution of the intermediate standards with the mobile phase. The mobile phase was filtered with a 0.2 µm membrane filter before use.

Batch Leaching Experiments. Two types of batch leaching experiments were conducted in this study. Type-I experiments were conducted under a constant S/L ratio of 1:10 (100 g/L) but with pH conditions ranging from 2 to 12. Type-II experiments were conducted under the natural pH condition but with S/L ratios

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Table 1. Characteristics of Fly Ash Samples^a

sample ID	coal type	LOI (%)	BET area (m ² /g)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	As (mg/kg)	Se (mg/kg)
#1004	bit	6.7	7.6	55.7	29.4	4.6	0.8	49.0	45.6
#1005 (SNCR)	bit	12.7	18.4	50.9	25.4	4.4	0.7	44.9	36.1
#1009	bit	9.8	8.71	53.2	23.7	7.4	1.4	100.9	30.0
#1015	sub	14.8	25.7	25.4	11.1	5.8	20.0	37.2	4.6
#1018 (SNCR)	sub	9.7	15.7	25.1	10.9	7.1	18.2	52.1	5.7
#7	sub	0.2	1.2	34.9	15.1	5.1	22.6	29.1	17.8

^a LOI, loss-on-ignition; bit, bituminous coal; sub, sub-bituminous coal.

ranging from 1:20 to 1:2. For type-I experiments, pH was adjusted using 1 N HNO₃ or NaOH. Samples were mixed for 24 h on a mechanical shaker at 180 oscillations/min. After shaking, all bottles were allowed to settle for 30 min. The supernatant was collected and filtered through a 0.45 μ m syringe filter and acidified with 1% HNO₃ before analysis using ICP–MS for total As and Se concentrations. The pH was measured using the remaining mixture in the bottle. For type-II experiments, four S/L ratios (1:20, 1:10, 1:5, and 1:2) were applied to each sample. The pH was not adjusted before or during the leaching process. Long-term leaching experiments (30 days) were also conducted to determine effects of the leaching time on the release of different As and Se species.

To examine if the speciation of As and Se changed during the leaching experiment under natural conditions, parallel 30 day experiments were carried out under the N₂ gas environment, for ash #1005 and ash #7, at a S/L ratio of 1:2. All sample bottles were set up in a glovebox that was continuously purged with high-purity nitrogen. The oxygen level in the glovebox was monitored with dry anaerobic indicator strips (Becton Dickinson Company, Sparks, MD). DI water and fly ash were purged within the glovebox for at least 2 h before use. After all bottles were set up and tightly sealed, they were taken to a shaker outside the glovebox and shaken for 24 h at 180 oscillations/min. After shaking, all bottles were brought back to the continually N₂-purged glovebox. The bottles were opened within the glovebox, and supernatants were collected and filtered inside the glovebox. The filtered samples were then transferred to polypropylene tubes and sealed for speciation analysis using HPLC–ICP–MS. The maximum time lapse between filtration and HPLC analysis was less than 40 min, to prevent possible speciation change. Samples were maintained at 4 °C or less without freezing, until analyzed. No acidification was applied to all samples before HPLC analysis.

Chemical Analyses. A Perkin–Elmer 3110 flame atomic absorption spectroscopy was used to analyze Ca concentrations in leachates. A Perkin–Elmer Elan DRCE ICP–MS was used to analyze total As and Se. For speciation analysis, a Perkin–Elmer HPLC was used in connection with the ICP–MS system. Isocratic methods were used to separate As and Se. The HPLC system consisted of a Perkin–Elmer Series 200 Micro Pump and a series 200 auto sampler, with a Hamilton PRP-X100 (4.1 \times 150 mm, 3 μ m particle size) anion-exchange column. The isocratic mobile phase contained 10 mM ammonium nitrate and 10 mM ammonium phosphate, and the pH was adjusted to 9.4 with ammonium hydroxide. The sample injection volume was 100 μ L. The sample introduction system of the ICP–MS included a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a Meinhard type-A nebulizer. The effluent from the HPLC column was directly connected to the nebulizer with PEEK tubing (1.59 mm outer diameter) and a low dead volume PEEK connector. The ICP–MS was operated in dynamic reaction cell (DRC) mode, with methane gas flow of 0.25 mL/min and dwell time of 250 ms. Methane was selected as the reaction gas to remove possible interference from the carrier gas argon or other matrix in the sample.

Because the HPLC–ICP–MS system is able to monitor multiple ions with different *m/z* numbers, it was used to simultaneously analyze As and Se speciation. With 10 mM of mobile phase and a flow rate of 1.5 mL/min, all As and Se species were separated within 9 min. The detection limits of As^{III}, As^V, Se^{IV}, and Se^{VI} species were 1–3, 1–3, 3–5, and 3–5 μ g/L, respectively. For each set of samples, the sensitivity of the HPLC–ICP–MS system was found to decrease up to 25% after running for 8 h of operation, probably

because of sample coating on the sampler and skimmer cones. This error was corrected by recalibration with new prepared standards for every eight samples (every 1–1.5 h). Spiking recovery was within 85–110%. After speciation analysis, all leachates were acidified with 1% nitric acid and re-analyzed with ICP–MS for total As and Se concentrations. Speciation results indicated that none of the fly ash leachates contained any organic species of As and Se (data not shown).

Quality Assurance and Quality Control. For type-I leaching experiments, approximately 10–20% of samples (i.e., pH conditions) were selected for duplicate leaching tests and, if results showed a deviation over 20%, more duplicate leaching tests were performed, until a satisfying result was achieved. For type-II leaching experiments, duplicate leaching tests were performed for all samples at different leaching conditions. Standard deviations of the results of duplicate samples were calculated and presented as error bars in corresponding data charts. For chemical analysis, the instruments were recalibrated for each set of samples (up to 20 samples) with reagent blanks and standards, and triple readings of each analyzed standard and sample were recorded and averaged. For each set of samples, at least one laboratory fortified blank (duplicate standard) and one laboratory fortified sample (sample spike) were included and the percent recovery shall be within 80–120%. For microwave acid digestion and ICP–MS analysis, standard coal fly ash SRM 1633b was processed under the same conditions as other samples, and the total element compositions were within \pm 15% of the certified values. Multiple digestion cycles may be necessary to achieve a complete digestion. A slight amount of white residue were observed in some samples even after multiple digestion cycles. However, results indicated that the presence of white residue had no impact on the recovery of As and Se.

Results and Discussion

General As and Se Leaching Profile for Bituminous and Sub-bituminous Coal Ashes. Figure 1 shows leaching results of total As, Se, and Ca for all six ashes under different pH conditions. Figure 1a shows that As leaching from bituminous coal ash samples, #1004 and #1005, was relatively low in a pH range of 3–7 and then increased when the pH increased or decreased beyond this range. For bituminous coal ash #1009, the lowest leaching occurred in a narrower pH range of 3–4. The general leaching behavior exhibited by these three ashes, as a function of pH, is typical for adsorption of anionic elements, such as As, Se, and V.^{9,14,15,17,20,33,34} Because of the high aluminum oxide and iron oxide contents in these ashes (Table 1), it is possible that adsorption is the major mechanism controlling As leaching. The sharp increase in As leaching when pH was less than 3 was probably caused by dissolution of ash particles under very acidic conditions, coupled with an increase in the neutral As species (considered non-adsorbable) in this pH range.¹⁴ The increase in As release when pH was greater than 7 was mostly caused by a decrease in the protonated surface sites that serve as binding sites for anionic As species.¹⁴

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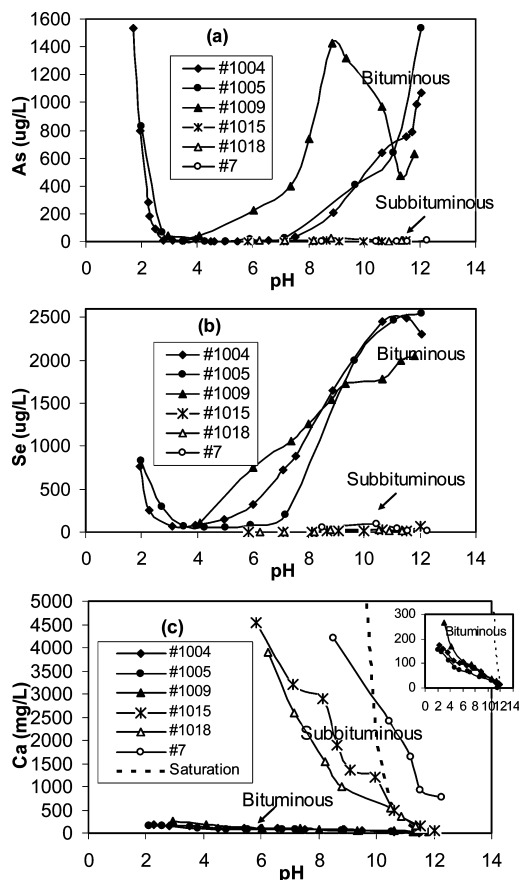


Figure 1. Batch leaching results for ashes #1004, #1005, #1009, #1015, #1018, and #7 for (a) arsenic, (b) selenium, and (c) calcium. Experimental conditions: S/L, 1:10; temperature, 20–25 °C; equilibration time, 24 h.

Figure 1a also shows that ash #1009 leached significantly more As over most of the pH range when compared to ashes #1004 and #1005. As leaching from ash #1009 increased with an increase in pH, reaching a maximum level of approximately 1400 $\mu\text{g/L}$ at pH 9 and then decreased with a further increase in pH. As indicated in Table 1, the total As concentration in ash #1009 was more than double that in ashes #1004 and #1005. The increased leaching of As in ash #1009 within a pH range of 4–9 might have been caused by the greater availability of the As in this ash than in the other two ashes.

The acidity constants ($\text{p}K_a$) of arsenic acid are 2.26, 6.76, and 11.29, respectively.³⁵ The AsO_4^{3-} species, which can form many less-soluble compounds or precipitates with Ca,^{36,37} starts to occur when pH is approximately 9, and its concentration increases with the further increase in pH. Because ash #1009 contains about twice as much Ca as the other two ashes (Table 1), the decreased As leaching at a pH greater than 9 could be caused by the greater Ca content in this ash and subsequent precipitation of Ca–As compounds.

Because of the extremely high CaO content in sub-bituminous coal ashes #1015, #1018, and #7 (ranging from 18–23%; see Table 1), it was very difficult to reduce the pH of fly ash mixtures to acidic conditions during the experiment. Therefore, all batch leaching experiments for sub-bituminous coal ashes were conducted from a neutral pH to an alkaline pH. In

comparison to bituminous coal ash samples, all sub-bituminous coal ash samples leached negligible amounts of As in the entire experimental pH range. The low As leaching could be attributed to precipitation with calcium^{36,37} or the formation of ettringite or similar compounds, which can trap anionic elements through substitution for sulfate in their structure under very high pH conditions.^{38–40}

Figure 1b shows Se leaching for both types of coal ashes. Se leaching from bituminous coal ashes was similar to As, except that the lowest Se leaching occurred in a narrower pH range of 3–5 (compared to the pH range of 3–7 for As) and the leaching of Se from ash #1009 did not decrease under high pH conditions, suggesting that Ca–Se precipitation is not controlling the Se concentrations in this sample. Similar to As, adsorption/desorption plays a major role on Se leaching from bituminous coal ash.^{13,15} The sharp increase in Se leaching when pH was less than 3 was probably due to dissolution of ash particles under such an acidic condition and the increase in neutral Se species, which are considered non-adsorbable.¹⁵ The increased Se release when pH was greater than 5 was likely caused by the decrease of protonated surface sites that serve as Se-binding sites.¹⁵ Similar to As, all sub-bituminous coal ash samples leached negligible amounts of Se in the entire experimental pH range. The low Se leaching from sub-bituminous coal ashes could be attributed to the lower available selenium in the ash (see Table 1), precipitation with calcium,⁴⁰ and/or the formation of ettringite or similar compounds and substitution for sulfate in the structure.^{38–40}

Figure 1c shows the Ca concentration in leachates for all ash samples. Concentrations of Ca in all leachates decreased with the increase of pH. The sub-bituminous coal ashes leached significantly more Ca than the bituminous coal ashes because of their much higher Ca content. In comparison to the other two bituminous coal ash samples, ash #1009 leached slightly more Ca because of its slightly greater Ca content. Overall, sub-bituminous coal ashes leached significantly more calcium than bituminous coal ashes. According to Table 1, the CaO content in sub-bituminous coal ashes was approximately 20%. Because of the extremely high Ca content, the soluble Ca concentration in leachates of these ashes might be controlled by the solubility of $\text{Ca}(\text{OH})_2$. The dotted line in Figure 1c shows the calculated saturation concentration of Ca based on K_{SP} of 5.02×10^{-6} for $\text{Ca}(\text{OH})_2$.⁴¹ For sub-bituminous ash leachates, the measured Ca concentration was close to the calculated saturation concentration when the pH was greater than 9. However, for bituminous coal ashes, the Ca concentration in leachates was significantly less than the saturation concentration.

Overall, bituminous coal ashes leached significantly more As and Se but significantly less Ca compared to sub-bituminous coal ashes. Adsorption is the major mechanism controlling As and Se leaching from bituminous coal ashes, while the high calcium contents are believed to have reduced both As and Se leaching from the sub-bituminous coal ashes. The greater calcium content in ash #1009 (compared to the other two bituminous coal ashes) is believed to have reduced As leaching when the pH was greater than 9. Because the Se leaching

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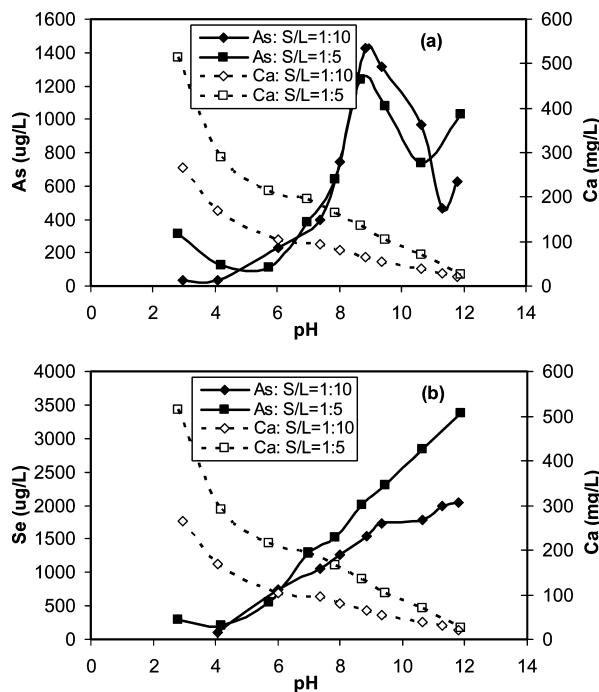


Figure 2. Impact of the S/L ratio on the leaching of As and Se from ash #1009 under different pH conditions. Experimental conditions: S/L, 1:10; temperature, 20–25 °C; equilibration time, 24 h.

behavior for ash #1009 was consistent with the other two bituminous coal ashes, the amount of calcium in ash #1009 was apparently not sufficient to reduce Se leaching from that ash, suggesting that Se is more mobile than As in the presence of Ca.

Impact of the S/L Ratio on As and Se Leaching as a Function of pH. As noted previously, ash #1009 exhibited a different leaching pattern for As than the other two bituminous coal ashes, probably caused by its greater Ca content. Figure 2 shows the leaching results for As, Se, and Ca from ash #1009 for two S/L ratios, 1:10 and 1:5. Figure 2a shows that, when the pH was less than 9, the As leaching curves for S/L of 1:10 and 1:5 overlap. In a pH range of 9–11, the As leaching curve for the S/L ratio of 1:5 is positioned below (lower concentration) that for the S/L ratio of 1:10, while the leached Ca concentration curve for the S/L ratio of 1:5 was positioned above that for the S/L ratio of 1:10. This result suggests that, in the pH range between 9 and 11, As leaching may be controlled by Ca through Ca–As precipitation. Because the acidity constants (pK_a) of arsenic acid are 2.26, 6.76, and 11.29, respectively,³⁵ the AsO_4^{3-} species starts to occur at pH 9. Because it is the major arsenic species that forms precipitation with Ca, a greater calcium concentration reduced the total As concentration when pH was greater than 9.

As leaching again increased above a pH of 11, and more As leached at 1:5 S/L than at 1:10 S/L. Under extremely high pH conditions (pH > 11), Ca forms calcium hydroxide compounds, which reduced the free Ca concentration and, therefore, decreased the formation of Ca–As precipitates. As a result, As leaching increased with an increase in pH. The S/L ratio of 1:5 contained more fly ash and, therefore, had more available As than the 1:10 S/L system, resulting in more As being released.

Figure 2b shows that the leaching of Se increased with the increase of pH. Unlike As, the Se leaching curve for the S/L of 1:5 was above that for the S/L ratio of 1:10 throughout the entire pH range, indicating that Ca precipitation did not play a significant role in Se leaching from ash #1009.

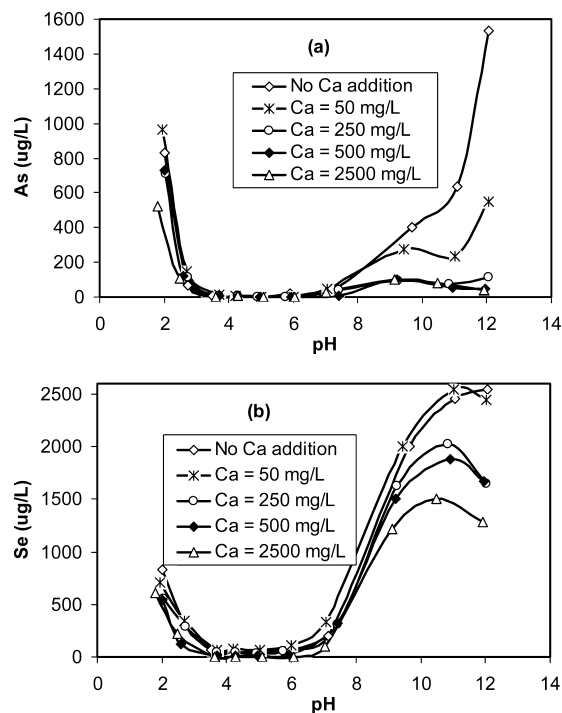


Figure 3. Leaching of As and Se from ash #1005 for different calcium additions. Experimental conditions: S/L, 1:10; temperature, 20–25 °C; equilibration time, 24 h.

Impact of Added Calcium on As and Se Leaching as a Function of pH. A relatively low calcium sample, ash #1005, was used to test the impact of calcium addition on As and Se leaching under different pH conditions. The total added calcium [in the form of $Ca(NO_3)_2$] ranged between 50 and 2500 mg/L. Figure 3 shows the experimental data. Figure 3a clearly shows a decrease in the release of As with an increase in the addition of calcium in the alkaline pH region (pH greater than 8). When the calcium addition was equal to or greater than 250 mg/L, the release of a minimal amount of As was observed. Figure 3b shows that the addition of 50 mg/L calcium did not impact Se release. However, when the calcium addition was equal to or greater than 250 mg/L, the Se release decreased in the alkaline pH range. These results suggest that calcium in fly ash can reduce the leaching of both As and Se under alkaline pH conditions, with a stronger impact on As than on Se. In the previous experiments, the native Ca content in ash #1009 was apparently enough to reduce As release when the pH was greater than 9 but not enough to reduce Se release. All sub-bituminous coal ash samples had significantly more calcium than the bituminous coal ash samples (Table 1), and the leaching of both As and Se were significantly reduced, as indicated in Figure 1.

As previously discussed, the decrease of As leaching with added Ca was likely caused by the formation of several less soluble Ca–As compounds,^{36,37} especially under high pH conditions when AsO_4^{3-} was the dominant aqueous species in the system. Similar to As^V , Se^{IV} is also a weak acid, with acidity constants (pK_a) of 2.62 and 8.32, respectively.³⁵ Therefore, the fraction of SeO_3^{2-} species in leachates significantly increased when the pH was greater than 8.32. Because the SeO_3^{2-} species can form $CaSeO_3$ precipitates, with K_{SP} of $10^{-7.27}$ at $I = 0$,⁴⁰ the increase in pH-enhanced Se precipitation with added Ca resulted in less soluble Se under alkaline pH and high Ca conditions.

Impacts of the S/L Ratio and Leaching Time on As and Se Leaching from Bituminous Coal Ash. Effects of the S/L ratio (from 1:20 to 1:2) and mixing time (1 and 30 days) on As

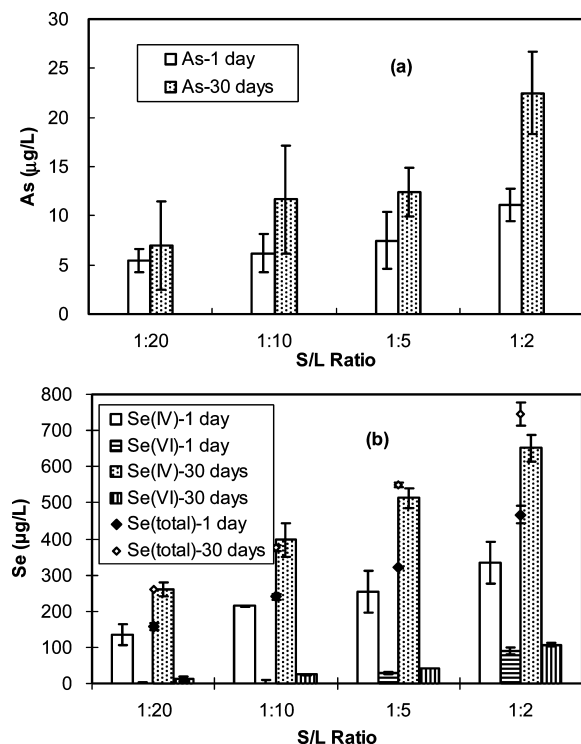


Figure 4. Impact of the S/L ratio and leaching time on (a) As and (b) Se release for ash #1005. Experimental conditions: temperature, 20–25 °C. The final pH values ranged from 5.6 to 6.2.

and Se leaching were determined under natural pH conditions for ash #1005. Figure 4a shows that low concentrations of As were detected in all leachates ($<25 \mu\text{g/L}$) based on ICP–MS. As speciation analysis using HPLC–ICP–MS indicated that only As^{V} was detected in the leachate samples. However, because all samples require a minimum of 3–5 times dilution with mobile phase, the As concentrations of diluted samples fell close to or below the ICP–MS detection limit. Therefore, the HPLC–ICP–MS data on the low As samples failed to provide a satisfying accuracy. Nevertheless, the data qualitatively demonstrated that As^{V} is the only As species in these samples. The low leachability of As from ash #1005, under a natural pH condition of approximately 6, was consistent with the behavior exhibited by the low soluble As from the leachability study in the same pH range (Figure 1). Figure 4a also shows that As leaching increased with an increase in the S/L ratio and leaching time. Because adsorption/desorption plays a major role in the release of As from bituminous coal ash,¹⁴ the total As concentration available for leaching increased with an increase in the S/L ratio. Therefore, the leaching of As is proportionally related to the S/L ratio. The increased release during long-term experiments might indicate a rapid leaching process of As on the ash surface, followed by a slow diffusion process of As from the inner pores of fly ash to the bulk solution. In the case of ash #1009, the leaching of As from it did not increase with an increase of the S/L ratio, as indicated in Figure 2. Because ash #1009 contains about twice as much Ca as ash #1005, the leaching of As might be controlled by a combination of adsorption and calcium precipitation when pH is less than 9 and mainly by calcium precipitation in a pH range of 9–11.

Figure 4b shows the impact of the S/L ratio and leaching time on Se leaching from ash #1005 under natural pH conditions. Both Se^{IV} and Se^{VI} were detected in all leachates, but Se^{IV} was the major Se species. In comparison to results depicted in Figure 4a, this ash leached significantly more Se than As when under natural pH conditions. The total concentration of Se (determined

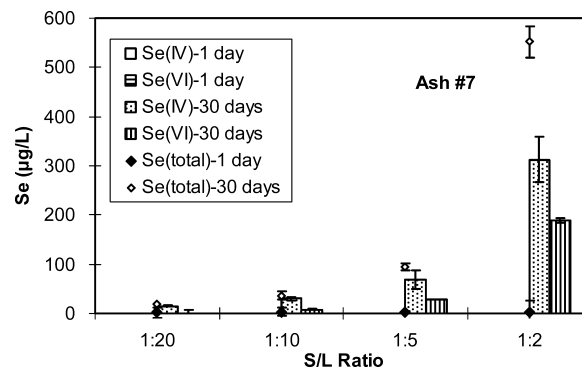


Figure 5. Impact of the S/L ratio and leaching time on Se release and speciation for ash #7. Experimental conditions: temperature, 20–25 °C; leaching time, 30 days. The final pH values ranged from 12.0 to 12.4.

using ICP–MS) agreed with the sum of Se^{IV} and Se^{VI} for these leachates. The Se^{IV} concentration in a 1 day experiment increased from 134 to $334 \mu\text{g/L}$, and the Se^{VI} increased from nondetectable ($<5 \mu\text{g/L}$) to $91 \mu\text{g/L}$ as the S/L ratio increased from 1:20 to 1:2. The linear trend of increasing Se^{IV} and Se^{VI} concentrations, as a function of the S/L ratio, suggests that both Se^{IV} and Se^{VI} leaching were mainly controlled by the adsorption/desorption process.

When the leaching time was extended to 30 days, a significant increase in the amount of Se^{IV} concentration in the leachate was observed for ash #1005, while the Se^{VI} concentration increased only slightly. The different behaviors of Se^{IV} and Se^{VI} indicated that Se^{IV} leaching may consist of two phases, a rapid initial phase followed by a slow release phase, whereas Se^{VI} leaching only needs a short time (i.e., 24 h) to reach equilibrium because it is not strongly adsorbed to the ash.¹⁵

Impacts of the S/L Ratio and Leaching Time on As and Se Leaching from Sub-bituminous Coal Ash. Effects of the S/L ratio (from 1:20 to 1:2) and leaching time (1 and 30 days) on As and Se leaching were determined under natural pH conditions of approximately 12.0–12.4 for ash #7. The concentrations of As in leachates were nondetectable for most samples (data not shown), except for the one collected at the S/L ratio of 1:2 and a leaching time of 30 days, which had $20 \mu\text{g/L}$ of As^{V} . Therefore, the leaching of As was very low from sub-bituminous coal ash, except at the high S/L ratio and long leaching time, which promoted some As release. The overall low leaching of As for sub-bituminous coal ash is controlled by the high calcium content of this ash, as indicated in a previous discussion.

Both Se^{IV} and Se^{VI} were not detectable ($<5 \mu\text{g/L}$) for all leachates during the 1 day leaching experiments. However, both Se^{IV} and Se^{VI} were released during the 30 day leaching, especially under greater S/L ratios (Figure 5), indicating that longer leaching time and greater S/L ratio significantly promoted Se leaching from sub-bituminous coal ash than that from bituminous coal ash. Figure 5 also shows that Se^{IV} was the major species in all leachates. The concentrations of both Se^{IV} and Se^{VI} increased more significantly with the increase in the S/L ratio rather than the pattern exhibited by ash #1005 (Figure 4), suggesting that the S/L ratio played a more important role on Se leaching from sub-bituminous coal ash than that from bituminous coal ash. The leaching pattern in Figure 5 suggests that Se leaching from sub-bituminous coal ash was not controlled by adsorption/desorption. Rather, a major ash component could form precipitation with Se.

Correlation of As and Se Leaching with Calcium under Natural pH Conditions. Because the calcium addition experi-

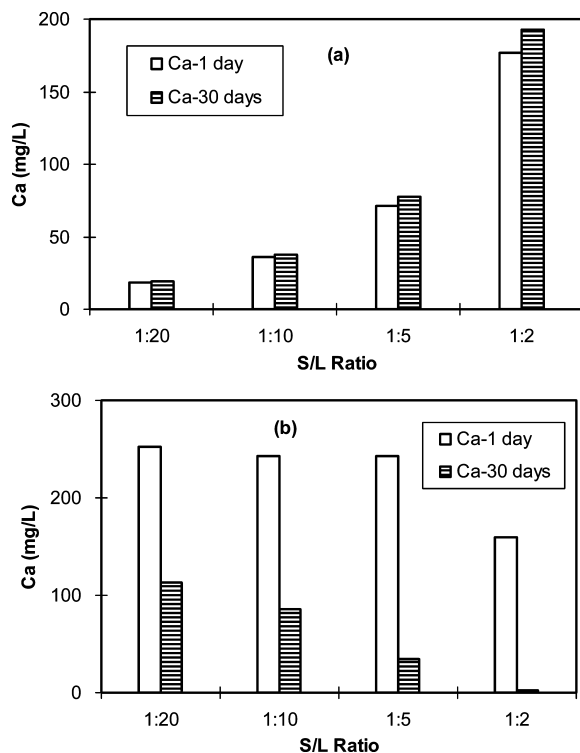


Figure 6. Calcium concentrations in leachates from (a) ash #1005 and (b) ash #7 for different S/L ratios. Experimental conditions: temperature, 20–25 °C. The final pH values ranged from 5.6 to 6.2 for ash #1005 and from 12.0 to 12.4 for ash #7.

ments showed that calcium reduces the release of As and Se, the concentrations of calcium in all leachates were determined (Figure 6). For bituminous coal ash #1005, the calcium concentration for any S/L ratio did not change in the period between the 1 and 30 day tests, indicating that the increase in As and Se leaching during the 30 day test (shown in Figure 4) was not related to calcium. It was more likely caused by the slow diffusion process from within the ash particles. However, for sub-bituminous coal ash #7, the calcium concentrations significantly decreased during the 30-day experiment, with the reduction ranging from 50% at a low S/L ratio to almost 100% at a high S/L ratio (Figure 6). The calcium concentration for the 1 day leaching was likely controlled by the solubility of $\text{Ca}(\text{OH})_2$, as shown in Figure 1c. However, after 30 days, the Ca concentration was significantly reduced as a result of a slow cementation process, in which soluble forms of calcium formed secondary minerals.^{42–44}

As and Ca can form many different low-solubility compounds, such as $\text{Ca}_4(\text{OH})_2(\text{AsO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ca}_5(\text{AsO}_4)_3 \cdot \text{OH}$ (arsenate apatite), $\text{Ca}_3(\text{AsO}_4)_2 \cdot 3(2/3)\text{H}_2\text{O}$,³⁶ $\text{Ca}_3(\text{AsO}_4)_2 \cdot 10\text{H}_2\text{O}$, and $\text{CaNaAsO}_4 \cdot 7.5\text{H}_2\text{O}$.³⁷ Therefore, the leaching of As from sub-bituminous coal ash was expected to be low because of the high calcium content in the ash. The only leachate that contained a detectable As concentration of 20 $\mu\text{g/L}$ was collected from an experiment conducted under a S/L ratio of 1:2 and a leaching time of 30 days. The Ca concentration in this leachate was lower than that of all other leachates for the same ash. Therefore, Ca played a key role in reducing As leaching from sub-bituminous coal ash.

The Se concentration increased during the 30 day tests with ash #7 (Figure 5). It was reported that Se and Ca formed CaSeO_3

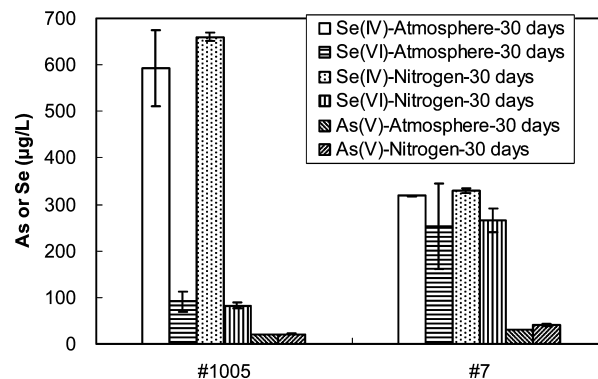


Figure 7. Speciation of As and Se in leachates from ash #1005 and ash #7 under natural and nitrogen conditions. Experimental conditions: temperature, 20–25 °C; S/L, 1:2. The final pH values were 5.9 for ash #1005 and 12.2 for ash #7.

precipitation.^{40,45,46} The calculated ion products of $[\text{Ca}][\text{SeO}_3]$ for all leachates were in a range from $10^{-6.1}$ to $10^{-6.7}$ for different S/L ratios, which is slightly greater than the reported K_{sp} value of $10^{-7.27}$ ($I = 0$ and 25 °C).⁴⁰ This suggests that the Se in leachates in the 30 day tests was controlled by CaSeO_3 precipitation, and therefore, Se concentrations in the leachates increased as the Ca concentrations decreased. The increased Se leaching with the increase of the S/L ratio was also caused by a decrease in the Ca concentrations in the leachates.

Impact of the Natural Condition on As and Se Leaching and Speciation. This experiment was designed to determine whether or not the natural condition, in the presence of air, changed the speciation of As and Se during the leaching process. To obtain the leaching information for different As and Se species originally present in fly ash without the interference of air, a N_2 -purging technique was employed. In the N_2 environment, the potential oxidation of As and Se to their higher oxidation states caused by oxygen in the air can be avoided. All leaching experiments, in the presence of air and with N_2 purging, were conducted for 30 days. Figure 7 shows As and Se leaching and speciation data for ashes #1005 and #7, without pH adjustment (natural pH). To obtain data that reflect the high solids concentration in the field scenario, the highest possible S/L ratio of 1:2 for batch experiments was used. For ash #1005, the final pH values in the presence of air with and with N_2 purging were 5.9. For ash #7, the final pH values for both conditions were 12.2. For As leaching, only As^{V} was detected for all leachate samples and the total As concentration measured using ICP–MS (and GFAA for 50% of the samples) agreed with the As^{V} concentration. The results in the presence of air agreed with those obtained in the N_2 environment. Therefore, As^{V} was the only species in all leachates, and the As speciation was not affected by the presence/absence of air.

Both Se^{IV} and Se^{VI} were detected in all leachate samples. For ash #1005, the total Se concentration (analyzed using ICP–MS) agreed with the sum of Se^{IV} and Se^{VI} concentrations (determined using HPLC–ICP–MS) for the same sample. The concentrations of Se^{IV} and Se^{VI} in both types of leachates (with air or nitrogen) were consistent with each other. Therefore, the presence of air during the 30 day leaching process did not convert Se^{IV} to Se^{VI} . This result agreed with a previous study that Se^{IV} was the dominant species in field leachates for bituminous coal ash.¹² Similarly, concentrations of Se^{IV} and Se^{VI} in both types of ash #7 leachates were also consistent, although

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a relatively larger error was observed during the analysis. This higher error was caused by the higher dilution rate required to reduce the dissolved solid concentration for this sample during speciation analysis. As a result, all Se^{IV} and Se^{VI} in leachates were directly from the solid phase, and there is no significant conversion between Se^{IV} and Se^{VI} during the 30 day leaching experiments under natural conditions. Because field leachates from sub-bituminous coal ashes, including ash #7, mainly contained Se^{VI} ,¹² a 30 day leaching period may be too short to produce significant change in Se speciation. A more detailed study for a longer period of time using field-weathered samples is needed to determine Se speciation change in field settings.

Conclusions

Bituminous coal ash and sub-bituminous coal ash have significantly different leaching characteristics. In general, bituminous coal ashes leach significantly more As and Se than sub-bituminous coal ashes, and adsorption/desorption play a major role on As and Se leaching. The leaching of As and Se from bituminous coal ashes generally increases with increases

in the S/L ratio and leaching time. For sub-bituminous coal ashes, the leaching of As is minimal under most experimental conditions and the leaching of Se increases with increases in the S/L ratio and leaching time. The calcium precipitation plays the most important role in minimizing As and Se leaching from sub-bituminous coal ashes. Results also indicate that Se is more leachable than As, and As^{V} and Se^{IV} are major species in all ash leachates in this study. There is no significant conversion between As^{V} and As^{III} and between Se^{IV} and Se^{VI} during the 30 day leaching experiment under natural conditions.

Acknowledgment. This work was supported by the Electric Power Research Institute (EPRI) and the U.S. Department of Transportation through the National University Transportation Center (NUTC) at the Missouri University of Science and Technology. The authors also thank Mr. Jack Quade and Ms. Cynthia Bosnak at Perkin-Elmer, Inc., for their help in metal speciation analysis using HPLC–ICP–MS, and Ms. Barbara Harris at the Missouri University of Science and Technology, for her help in proofreading this paper.

EF900044W