

The Leachability and Speciation of Arsenic and Selenium in Coal Fly Ash

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ABSTRACT

Batch leaching tests were employed to investigate the leaching potential of arsenic (As) and selenium (Se) from two fly ash samples. The effect of pH and solid-to-liquid (S/L) ratio on As and Se leaching was examined in this preliminary study. Maximum As leaching occurred at pH 7-8, and soluble As concentration slightly increased with decrease of S/L ratio. Se displayed consistently increasing leaching with increase of pH, and soluble Se concentration increased with the increase of S/L ratio. Speciation of As and Se in fly ash leachates obtained under both atmosphere and nitrogen conditions was determined using HPLC-ICP-MS. Only one arsenic species, As(V), and one selenium species, Se(IV), were detected in all leachate samples. Total As analysis using ICP-MS agreed well with the speciation analysis with HPLC-ICP-MS, while Se concentration showed a deviation between the two methods, which may be due to formation of undetected species or the higher detection limit with HPLC system. Further study will be conducted for a wide range of fly ash samples and under varying conditions.

INTRODUCTION

Coal fly ash contains concentrations of As and Se that are often higher than background soils^{3, 4}. For bituminous coal fly ash, the As concentrations are typically below 200 ppmw (parts per million by weight) but can range from 1 to 1000 ppmw, depending on coal source and combustion technology⁵. The Se concentration can be as high as 200 ppmw⁶, although it is usually less than 50 µg/g and is typically in the range of 10 to 20 µg/g⁵. US power facilities produced more than 71 million short tons (6.4×10^{10} kg) of coal fly ashes in 2005⁷, which were eventually utilized or disposed in landfills or impoundments. Therefore, understanding the factors that determine the environmental mobility of As and Se from coal fly ash is significant in evaluating the potential impacts of fly ash on ground water quality and developing novel methods to control arsenic and selenium leaching from fly ash.

Previous studies demonstrated that the leaching behavior of As and Se were affected by pH, solid-to-liquid (S/L) ratios, leaching time and temperature⁸⁻¹³. More emphasis has recently been placed on measuring the chemical species of As and Se in

environmental samples, as speciation plays an important role on the toxicity and mobility of the elements of concern¹⁴. For example, As(III) is generally more toxic and more mobile than As(V), the methylated forms (monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)) have been identified as less toxic than the inorganic forms, and arsenobetaine (AsB) is believed to be nontoxic¹⁵. With respect to the two common inorganic Se species, Se(VI) has been reported to be less toxic and more mobile in aqueous environment than Se(IV)¹⁶⁻¹⁹. Previous studies also demonstrated that the predominant species of As and Se in both solid fly ash and the liquid extracts from fly ash were As(V) and Se(IV), respectively²⁰⁻²⁴.

Accurate measurement of arsenic and selenium species in ash leachate can be difficult. Coupled instrumental techniques have been developed for the speciation analysis of As and Se in aqueous samples, which combine a separation process with suitable detection. Separation process can be achieved with ion chromatography (IC)^{21, 25} or high performance liquid chromatography (HPLC)^{26, 20}. Commonly used detectors are atomic adsorption spectrometry (AA)²⁰, inductively coupled plasma atomic emission spectrometry (ICP-AES)²⁵, and ICP-mass spectrometry (ICP-MS)^{27, 28}. The combination of HPLC with ICP-MS was selected in this work due to its high sensitivity, minimal sample pretreatment, and the ability for simultaneous analysis of As and Se.

The overall purpose of the present study is to investigate the leachability and speciation of As and Se in a wide range of fly ash samples under varying conditions. Results are presented here for two fly ash samples collected from a power plant burning a blend of bituminous and subbituminous coal. The use of HPLC-ICP-MS for the speciation analysis of As and Se was also assessed.

MATERIALS AND METHODS

Fly Ash Samples

Two fly ash samples, denoted as 33103-110 (Ash #110) and 33103-111 (Ash #111), were used in this study. The samples were collected from the same unit at a power plant burning a blend of 75% bituminous coal and 25% subbituminous coal. Ash #111 was sampled when brominated powdered activated carbon (PAC) injection was being tested for mercury emission control, while Ash #110 was a baseline sample collected with no PAC injection. Other physical and chemical properties including total As and Se content, loss-on-ignition (LOI), and BET specific surface area are shown in Table 1. Comparing the two ashes, the sample with PAC injection had significantly greater BET area, and higher Se content and LOI. As and Ca contents were not significantly different between the two ashes.

Reagent and Standards

Laboratory pure 18 MΩ deionized water was used throughout the experiment. Other reagents, including Arsenic(III), Arsenic(V), Selenium(IV) and Selenium(VI) standard solutions, solid cacodylic acid (dimethylarsenic acid, DMA), and solid arsenobetaine

were obtained from Sigma-Aldrich (St. Louis, MO, USA). Monosodium acid methane was purchased from ChemService (West Chester, PA USA). Reagents used for the HPLC mobile phases including ammonium phosphate (monobasic), nitric acid and ammonium hydroxide (hi-purity), and HPLC grade methanol were purchased from Fisher Scientific. The 5 mg/L intermediate arsenic and selenium standards were made from the stock solutions with deionized water. Calibration standards (5, 10, 50 and 100 µg/L) were freshly prepared by serial dilution of the intermediate standards with mobile phase. The mobile phase was filtered with 0.2 µm membrane filter before use.

Background Leaching Experiment

Two types of background leaching experiments were designed in this study. One was conducted with consistent S/L ratio 1:10 (100 g/L) and various pHs within the range of 2-12, while the other was conducted under natural pH but with different S/L ratios. The objectives were to test the effect of pH and S/L on the leaching separately. For type I experiments, pH was adjusted with 1 N HNO₃ or NaOH. Samples were mixed for 24 hours on a mechanical shaker at 180 osc/min. After shaking, supernatant was filtered through a 0.45 µm syringe filter before soluble As and Se analysis with ICP-MS. The pH was measured using the remaining mixture. For type II experiments, four S/L ratios (1:2; 1:5, 1:10 and 1:20) were applied for each sample. The pH was not adjusted before or during the leaching process. To examine whether arsenic and selenium species can change via contact with air during leaching process, a comparison leaching tests were carried out within a glove box for the type II experiments. The glove box was continuously purged with high purity nitrogen. The oxygen level in glove box was monitored with dry anaerobic indicator strips (Becton Dickinson Company, Sparks, MD). Deionized water and fly ash were purged in the glove box for at least 2 hours before mixing. After mixing for 24 hours, the supernatants were collected inside the glove box and transferred to polypropylene tubes and were ready for speciation analysis with HPLC-ICP-MS.

HPLC Separation with ICP-MS Detection

Isocratic methods were used for arsenic and selenium separation. The HPLC system consisted of a PerkinElmer Series 200 Micro Pump and series 200 auto sampler, with a Hamilton PRP-X100 (4.1 mm x 150 mm, 3 µm 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. Detailed conditions are given Table 2. PerkinElmer ELAN® DRC e ICP-MS was used for arsenic and selenium measurement. The sample introduction system 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 o.d.) and a low dead volume PEEK connector. Operating parameters are given in Table 3.

The Hamilton PRP-X100 column was first tested for the separation of five arsenic species: the isocratic mobile phase containing 5 mM ammonium nitrate and 5 mM

ammonium phosphate with pH = 9.4 was used. A mixed standard with 1 ppb of each species was prepared and analyzed with HPLC-ICP-MS. The signal intensity at m/z 75 was monitored with total analysis time of 11 minutes. The ICP-MS was operated in standard mode. All the other parameters were the same as those listed in Tables 2 and 3. The chromatogram, shown in Figure 1, revealed that five arsenic species were well separated except for As(III) and DMA, which had very close elution times. A longer column may be necessary to fully separate the two species. The HPLC–ICP-MS system was able to monitor multiple ions with different m/z numbers. Arsenic and selenium species were analyzed with the same system simultaneously. A stronger isocratic mobile phase was used for the separation, and a shorter analysis time of 9 min was applied. The ICP-MS was operated in DRC mode, with methane gas flow of 0.25 mL/min. Other parameters are listed in Table 3. After speciation analysis, all leachates were acidified with 1% nitric acid, and reanalyzed with ICP-MS for total arsenic and selenium concentration. For quality assurance purpose, GFAA was also employed for analysis of certain samples.

The inorganic species, namely As(III), As(V), Se(IV) and Se(VI), were the focus of this study. Results indicated that the four species can be clearly separated, as shown in the chromatogram of a 50 ug/L standard solution in Figure 2.

RESULTS AND DISCUSSION

Impact of pH on Leaching

Background leaching results of As and Se as a function of pH are shown in Figures 3a and 3b, respectively. For As, both ashes displayed a leaching peak at pH 7 to 8, with maximum concentrations of 1000 µg/L for Ash #110 and 550 µg/L for Ash #111. Minimal release was observed at pH less than 4 or greater than 11. The decrease of As release at high pH may be due to the relatively high Ca content in these two ashes, which can form more adsorbable arsenic species under alkaline conditions. Although Ash #111, with PAC, demonstrated a lower leaching potential for As, further study is necessary to confirm the effect of PAC injection on As leaching.

Compared with As, the soluble concentrations of Se from the two fly ashes were much lower, possibly reflecting the difference in total elemental compositions in these two ashes. The Se concentration increased more or less continuously with increase of pH, which may be attributed to the decrease of selenium adsorption sites with the increase of pH. The two ashes displayed similar Se concentrations in leachates under different pHs, but a lower leaching ratio for Ash #111 compare to the total Se content.

Impact of S/L Ratio on Leaching

Leachate pH

Table 4 shows the pH values for leachates from these ash samples under different S/L ratio and experimental conditions. For both ashes, the final pH of leachate was in the

range of 9-10. Leachate obtained in nitrogen conditions showed slightly higher pH than those obtained in atmosphere, and the pH was slightly increased with decrease of S/L ratio.

Arsenic speciation in fly ash leachate

Figure 4 shows the arsenic and selenium speciation chromatogram for one leachate sample from Ash #110. Only one arsenic species, As(V), and one selenium species, Se(IV), were observed in this leachate. The same two species were observed for Ash #111 leachate.

Arsenic leaching results for Ash #110 and Ash #111 are shown in Figures 5 and 6, respectively. Under all leaching conditions, only As(V) was detected, indicating that under natural pH conditions, arsenic speciation in leachate was not affected by S/L ratio or presence/absence of air in the experimental period. For experiments performed under nitrogen conditions, soluble arsenic concentration in leachate increased with decrease of S/L ratios, i.e. when S/L ratio was changed from 1:2 to 1:20, As(V) concentration increased from 92 ppb to 202 ppb for Ash #110 and from 170 to 275 ppb for Ash #111. Additionally, for lower S/L ratios, less difference was observed between atmosphere condition and nitrogen gas conditions. This inverse relationship between arsenic concentration and S/L ratio suggests that arsenic leaching from these two samples was probably influenced by some soluble constituent in fly ash, i.e. calcium, which will have a greater soluble concentration under higher S/L ratios and may form more adsorbable species with arsenic and reduce arsenic leaching from fly ash. A similar phenomenon was observed for leaching under atmosphere conditions, and concentrations obtained under both conditions were similar, except for those with S/L ratio of 1:2. For Ash #110 and a 1:2 S/L ratio, the arsenic concentration under atmosphere condition was 50% higher than that under nitrogen condition; while for Ash #111 and a 1:2 S/L ratio, the arsenic concentration under atmosphere conditions was much lower than under nitrogen conditions. Total arsenic concentrations analyzed with ICP-MS, also displayed in Figures 5 and 6, agree with the As(V) concentration detected with HPLC-ICP-MS. Therefore, only one arsenic species, As(V) was in ash leachates. The GFAA data (not shown) also validated the total arsenic concentration data obtained based on the ICP-MS.

Selenium speciation in fly ash leachate

Selenium leaching results for Ash #110 and Ash #111 are shown in Figure 7 and 8. Under all leaching conditions, only Se(IV) was detected, indicating that under natural pH conditions, selenium speciation in leachate was not affected by S/L ratio or presence/absence of air in the experimental period. For experiments performed under both atmosphere and nitrogen conditions, soluble selenium concentrations in leachates decreased with the decrease of S/L ratios, i.e. when S/L ratio was changed from 1:2 to 1:20 under atmosphere condition, Se(IV) concentration significantly decreased, from 56 ppb to 9.5 ppb for Ash #110 and from 36 to 7 ppb for Ash #111. The different leaching behavior exhibited by selenium compared to arsenic probably reflects distinct leaching

mechanisms. Unlike arsenic, direct adsorption/desorption likely was the predominant process controlling selenium leaching from the fly ash samples. For the same S/L ratio, leachate obtained under atmosphere consistently had slightly more soluble selenium than leachate obtained under nitrogen. Since the pH was slightly higher under nitrogen conditions than atmosphere conditions, change in pH does not explain the higher solubility. Total selenium concentrations analyzed with ICP-MS are also displayed in Figures 7 and 8. Total Se concentrations were approximately 30-40% greater than the Se(IV) analyzed with HPLC-ICP-MS. Results obtained with GFAA were consistent with those obtained with ICP-MS. Possible reasons for the lower recovery of Se(IV) from HPLC system were: (1) Other selenium species might be present in leachate samples, but not detectable with HPLC, since the HPLC system had a relatively high detection limit of 5 ppb; (2) even with single Se(IV) species, many samples after dilution had concentrations close to the detection limit, which can cause larger errors on the integration of peak area. Dilution was necessary to reduce TDS to below 0.1% to protect the instrument.

CONCLUSIONS

Background leaching experiments demonstrated that maxima As leaching occurred at pH 7-8. Se displayed consistently increasing leaching with increase of pH. For arsenic, only one species, As(V), was detected in leachates from the two ash samples, and total arsenic analysis obtained using ICP-MS agreed well with the As(V) concentration with HPLC-ICP-MS, indicating that arsenic speciation was not affected by the S/L ratio and presence of air in the one-day equilibrium experiment period. For selenium, only Se(IV) was detected in all leachate samples. However, the discrepancy between Se(IV) concentration and total selenium concentration under both atmosphere and nitrogen conditions suggested that there might be some other selenium species not detected with current instrumental condition. The results suggest that arsenic leaching and selenium leaching may be controlled by different mechanisms, which is still under study.

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Table 1. Sample information.

Sample ID	Coal Type	Mercury Control	Total As (mg/kg)	Total Se (mg/kg)	Total Ca (%)	LOI (%)	BET Area (m ² /g)
Ash #110	Bit/Sub (3:1)	None	40.9	1.5	1.9	13.8	13.46
Ash #111	Bit/Sub (3:1)	PAC	43.1	2.4	1.7	15.1	31.21

Note: Bit/Sum = Blend of bituminous coal and sub-bituminous coal; PAC = powdered activated carbon; LOI = loss-on-ignition.

Table 2. HPLC Isocratic Method and Operating Parameters.

Parameter	Setting
Mobile Phase	10 mM ammonium nitrate and 10 mM ammonium phosphate (monobasic); pH 9.4
Flow Rate	1.5 mL/min
Column	Hamilton PRP-X100
Sample Injection Volume	100 µL
Detection	PerkinElmer ELAN DRC e
Total Analysis Time	9 min

Table 3. ICP-MS Operating Conditions and Parameters.

Parameter	Setting
Spray Chamber	Quartz Cyclonic
RF Power	1500w
Plasma Ar Flow	15 L/min
CeO ⁺ /Ce ⁺	<2%
Dwell Time	250 ms
Methane Flow for DRC	0.25 mL/min
Rpq	0.6

Table 4. pH values of leachate from two ash samples #110 and #111 under different leaching conditions.

S/L	pH (Ash #110)		pH (Ash #111)	
	Atmosphere	Nitrogen	Atmosphere	Nitrogen
1:2	9.34	9.79	8.95	9.12
1:5	9.63	9.98	9.03	9.24
1:10	9.7	9.94	9.04	9.32
1:20	9.84	10.15	9.18	9.41

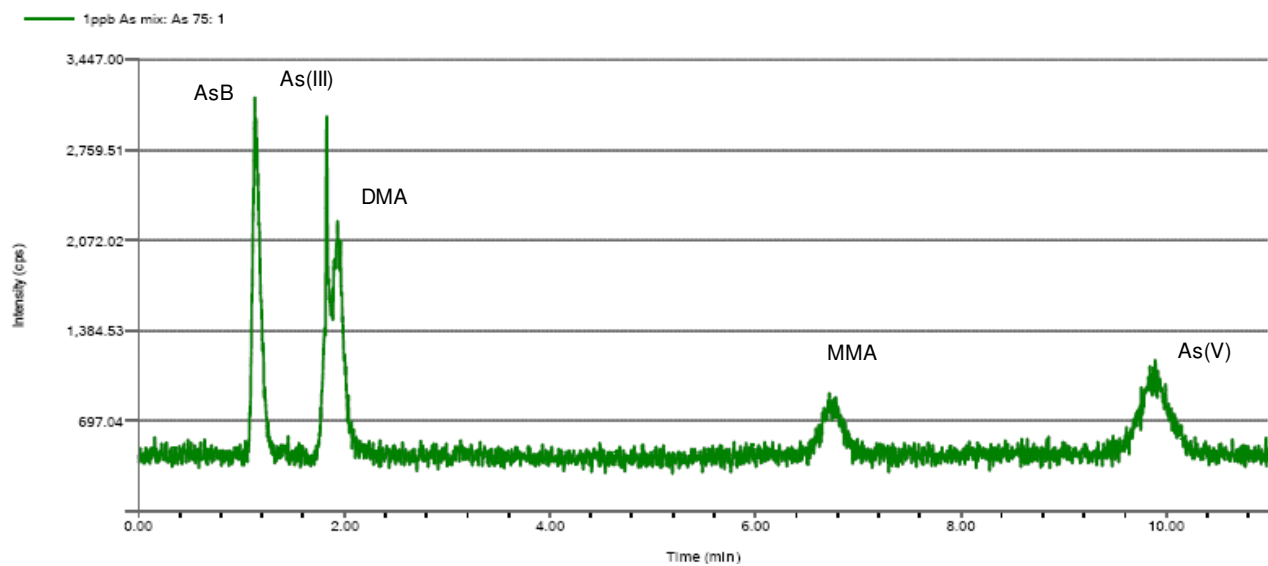


Figure 1. Chromatogram of five arsenic species in the standard solution (1 ug/L each).

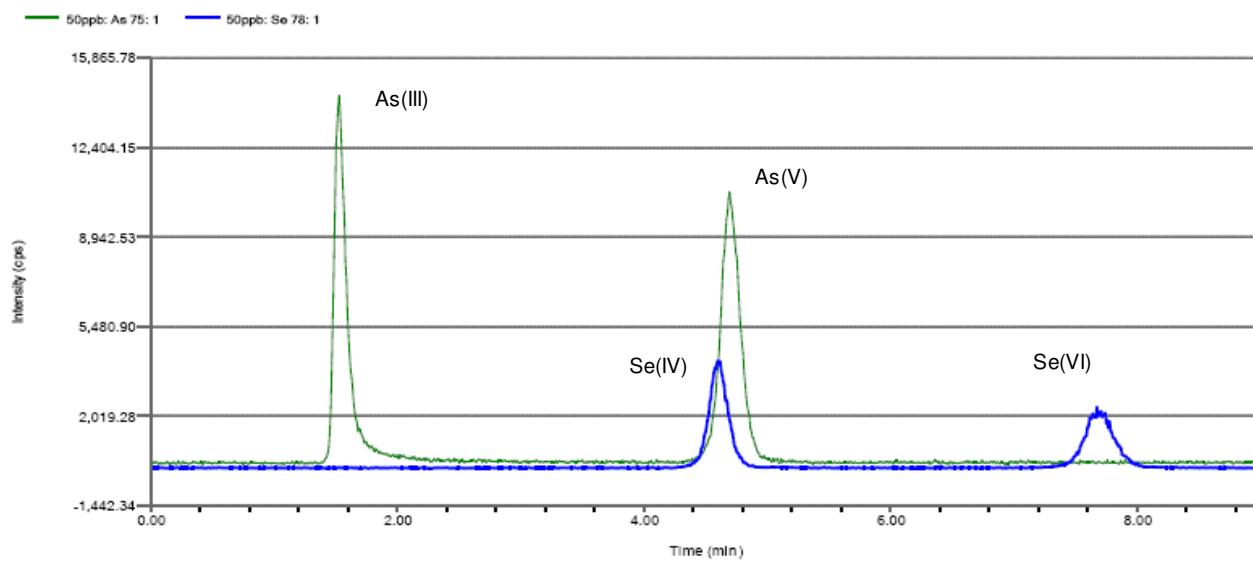


Figure 2. Chromatogram of inorganic arsenic and selenium species (50 ug/L each).

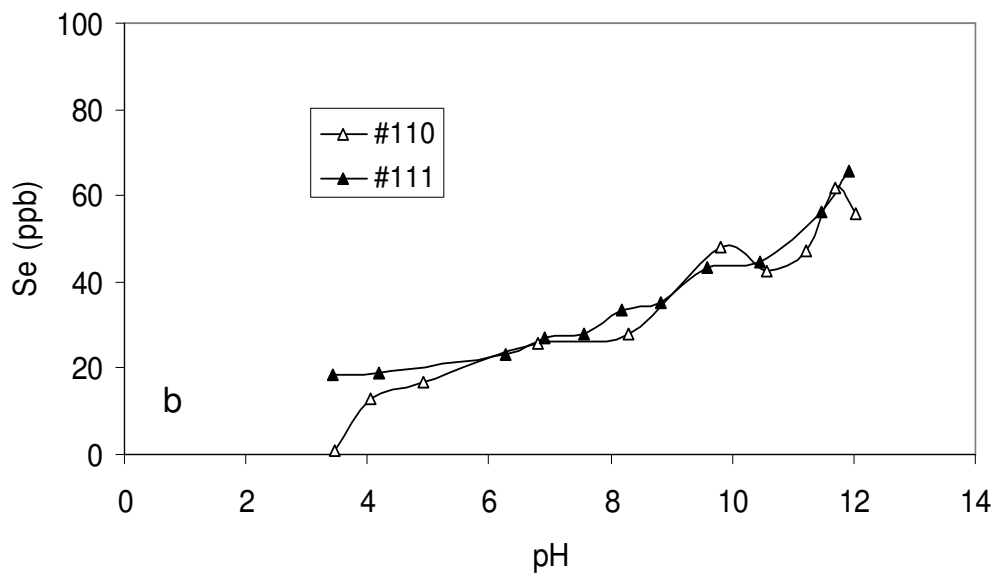
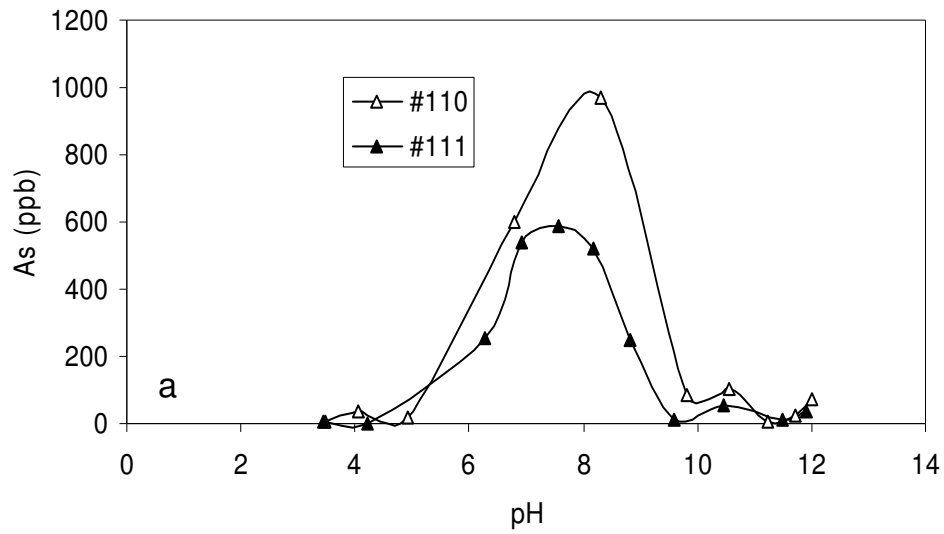


Figure 3. Type I background leaching of (a) Arsenic, (b) Selenium from Ash #110 and #111. Experimental conditions: S/L = 1:10; temperature = 20 – 25 °C; equilibration time = 24 hours.

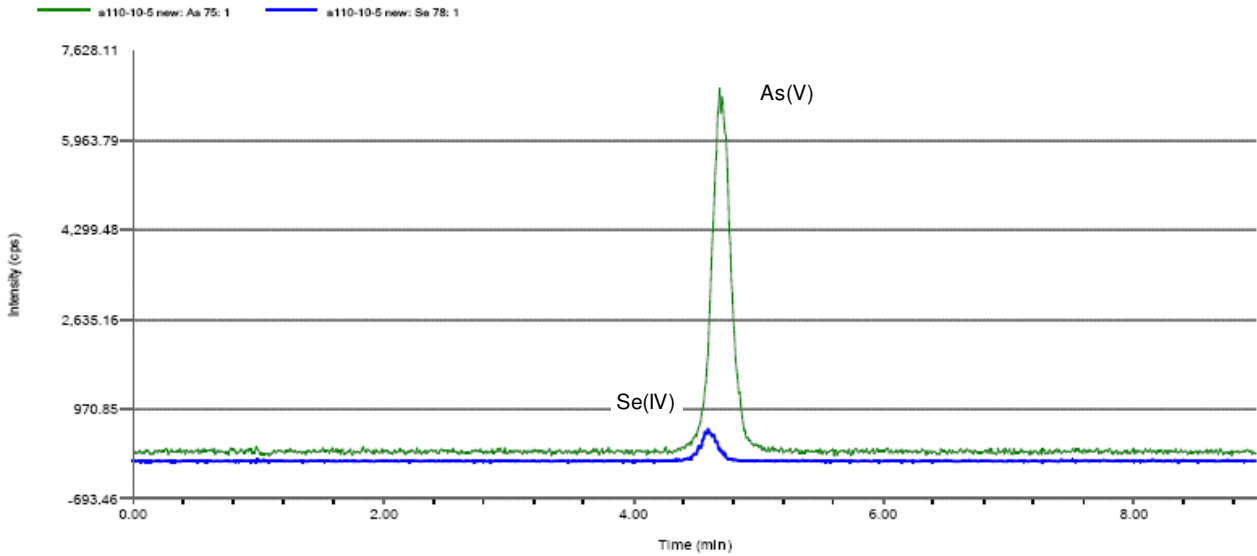


Figure 4. Chromatogram of a fly ash leachate sample (from Ash #110) under atmosphere condition, S/L = 1:10, natural pH = 9.7.

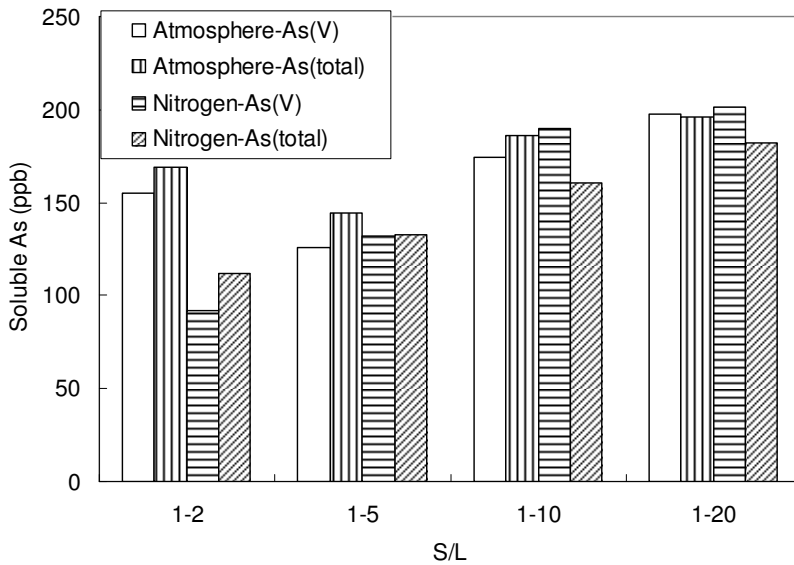


Figure 5. As(V) and total arsenic concentrations in leachate from Ash #110 under different leaching conditions.

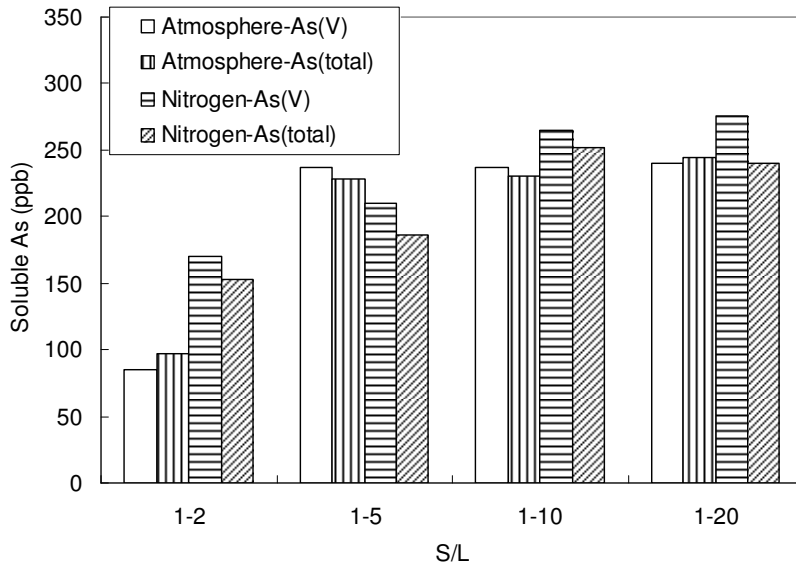


Figure 6. As(V) and total arsenic concentrations in leachate from Ash #111 under different leaching conditions.

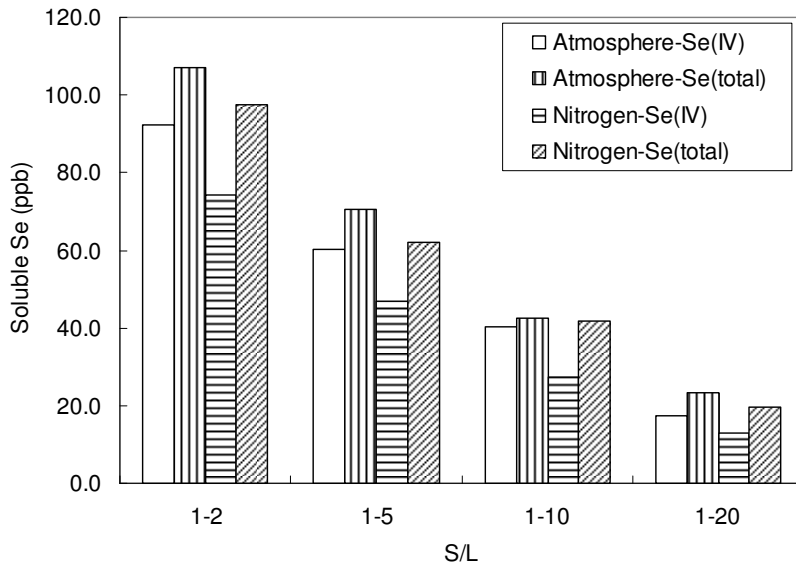


Figure 7. Se(IV) and total selenium concentrations in leachate from Ash #110 under different leaching conditions.

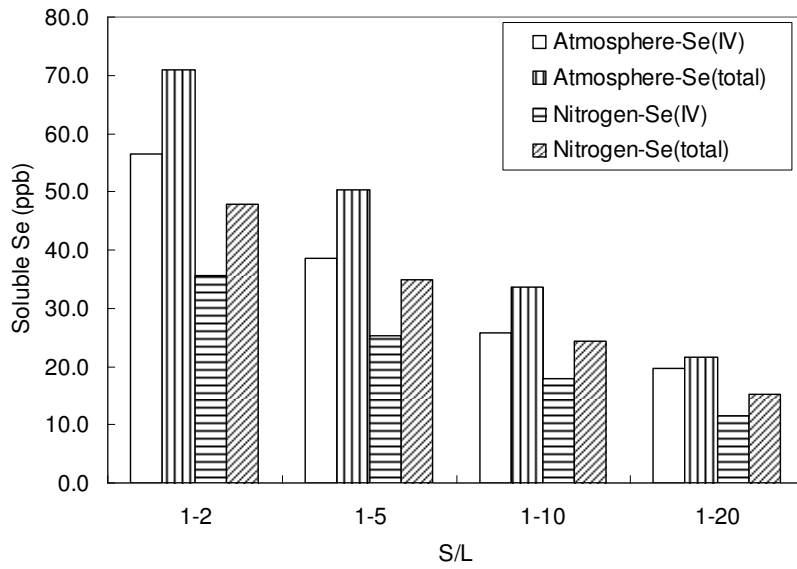


Figure 8. Se(IV) and total selenium concentrations in leachate from Ash #111 under different leaching conditions.