ELECTRIC POWER
RESEARCH INSTITUTE

Chemical Fixation of Metals in Fly Ash Using Ferrous Sulfate Treatment

Treatment Data

Chemical Fixation of Metals in Fly Ash Using Ferrous Sulfate Treatment

Treatment Data

1015549

Final Report, September 2008

Cosponsor
Southern Company Services, Inc.
42 Inverness Parkway
Birmingham, Alabama 35242

Project Manager
D. Patel

EPRI Project Manager
K. Ladwig

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 ▪ PO Box 10412, Palo Alto, California 94303-0813 ▪ USA
800.313.3774 ▪ 650.855.2121 ▪ askepri@epri.com ▪ www.epri.com

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

Department of Geological Sciences, University of Alabama

NOTE

For further information about EPRI, call the EPRI Customer Assistance Center at 800.313.3774 or e-mail askepri@epri.com.

CITATIONS

This report was prepared by

University of Alabama
Department of Geological Sciences
Box 870338
Tuscaloosa, AL 35487

Principal Investigators
R. Donahoe
S. Bhattacharyya

This report describes research sponsored by the Electric Power Research Institute (EPRI) and Southern Company Services, Inc.

This publication is a corporate document that should be cited in the literature in the following manner:

Chemical Fixation of Metals in Fly Ash Using Ferrous Sulfate Treatment: Treatment Data. EPRI, Palo Alto, CA and Southern Company Services, Inc., Birmingham, AL: 2008. 1015549.

REPORT SUMMARY

This report provides treatability data from laboratory experiments designed to test chemical fixation as a treatment technology for the immobilization of trace elements associated with coal fly ash. The study is focused on the treatment of fresh fly ash samples with ferrous sulfate solutions, which have been shown to successfully immobilize arsenic in contaminated soil by promoting the formation of insoluble iron-oxyhydroxide phases.

Background

In some cases, fly ash disposal and beneficial use options in structural fills are limited because of the potential for leaching and release of trace constituents. *In situ chemical fixation* refers to the addition of a fixating agent to contaminated soil, or other solid media, to immobilize trace elements. Solutions of soluble iron salts have also been used in numerous applications to sequester aqueous trace elements through co-precipitation with, and/or adsorption by, solid phases that precipitate from the treatment solutions. Often these applications target specific chemicals such as arsenic in contaminated soils. Little work has been done on the simultaneous fixation of several constituents in a coal fly ash matrix.

Objective

- To examine in bench-scale laboratory studies the potential of ferrous sulfate treatment for the long-term immobilization of trace elements in fly ash

Approach

Fly ash samples were collected for this study from four electric power plants located in the southeastern United States. Samples from three plants (HA, HB, and MA) were derived from the combustion of eastern bituminous coals and were generally acidic in nature. The fourth fly ash sample (PD) was derived from the combustion of Powder River Basin coal and was strongly alkaline. All of the fly ashes were treated with both unbuffered and buffered (through calcium carbonate addition) ferrous sulfate solutions at two solid-to-liquid ratios (1:3 and 1:30). The treated samples were then leached repeatedly with a synthetic acid rain (SAR) solution, and the release of eight constituents (arsenic, boron, chromium, molybdenum, selenium, vanadium, nickel, and strontium) was monitored and compared to release from untreated ash samples. The samples were also subjected to a sequential chemical extraction procedure to evaluate possible mechanisms for sequestration.

Results

The ferrous sulfate treatment was an effective method for sequestration of most of the priority trace elements associated with coal fly ash. SAR leaching of the treated and untreated fly ash samples demonstrated that the best overall treatments for trace element sequestration in the coal fly ash samples were the unbuffered ferrous sulfate treatments. The treatment resulted in reductions in the mobilities of all of the trace elements that commonly exist as oxyanions (As, Mo, Cr, Se, and V) in aqueous solutions, as follows:

- Arsenic: 79–90% reduction in mobility for acidic fly ash; 24% mobility reduction for an alkaline fly ash
- Chromium: 89–97% reduction in mobility for acidic fly ash; 82% mobility reduction for an alkaline fly ash
- Molybdenum: 74–99% reduction in mobility for acidic fly ash; 79% mobility reduction for an alkaline fly ash
- Selenium: 67–87% reduction in mobility for acidic fly ash; 41% mobility reduction for an alkaline fly ash
- Vanadium: 55–100% reduction in mobility for acidic fly ash; 70% mobility reduction for an alkaline fly ash

Sequential chemical extraction study of the treated and untreated fly ash samples showed that the primary mechanism for trace element sequestration was transfer of these trace elements from mobile fly ash fractions to be adsorbed and/or co-precipitated on $Fe(OH)_3$ precipitated on fly ash particles during the treatment process. Ferrous sulfate treatment was not effective for B, which commonly occurs as a neutral specie $B(OH)_3$, or for the cationic trace elements Ni and Sr—all of which were apparently mobilized by the treatment solution.

EPRI Perspective

In some states, the use of fly ash in land applications is limited because of the potential for leaching and release of trace constituents. Development of simple fixation methods for reducing the mobility of trace constituents may increase opportunities for use of the ash in these applications. The work presented in this report builds on previous successful application of ferrous sulfate to treat arsenic-contaminated soils from substation sites. The data on the use of ferrous sulfate to limit the mobility of oxyanionic constituents in fly ash are encouraging. Additional work is planned to verify and refine these results, further evaluate the mechanisms for sequestration of the trace constituents, and investigate economics and issues related to field-scale implementation.

Keywords

Fly ash
Trace elements
Fixation
Leaching

ABSTRACT

Large volumes of fly ash and other coal combustion products (CCPs) produced by coal-fired electric power plants located throughout the United States are disposed of in wet ash lagoons and dry landfills. Fly ash makes up approximately 60% of the CCP material and may contain leachable trace elements such as As, B, Cr, Mo, Ni, Se, Sr, and V. Because of potential leaching by rain water and groundwater with time, these impurities may have a negative impact on the environment and therefore present challenges for CCP disposal site management and limit the use of fly ash for beneficial purposes. Thus, simple and effective treatment processes are needed to stabilize trace elements in fly ash to increase its reuse rate and simplify the management of CCP disposal facilities.

This report describes the results of experiments designed to test chemical fixation as a treatment technology for the immobilization of trace elements associated with coal fly ash. The current study is focused on the treatment of fresh fly ash samples with ferrous sulfate solutions, which have been shown to successfully immobilize arsenic in contaminated soil by promoting the formation of insoluble iron-oxyhydroxide phases. Fly ash samples were collected from four electric power plants: three were acidic ashes from bituminous coal combustions; one was an alkaline ash from Powder River Basin coal combustion. These fly ash samples were treated with unbuffered and buffered ferrous sulfate solutions (322 ppm Fe + 28.8 ppm $CaCO_3$) at solid-to-liquid ratios of 1:3 and 1:30. The effectiveness of the treatment was evaluated by sequential leaching of treated and untreated fly ash in batch experiments using a synthetic acid rain (SAR) solution as the leachant. A seven-step sequential chemical extraction procedure (SCEP) was used to evaluate the mechanism(s) by which ferrous sulfate treatment immobilized trace elements in the fly ash samples.

The success of the treatment method depends on the type of fly ash and the trace element of interest. The addition of calcium carbonate as a buffer was found to be detrimental to the chemical fixation of most trace elements associated with the fly ash samples. The unbuffered ferrous sulfate treatment significantly reduced the mobility of oxyanion trace elements—especially at the 1:30 treatment ratio—which produced a proportionately greater amount of $Fe(OH)_3$. The overall reduction in trace element mobility was As by 24–90%, Cr by 82–97%, Mo by 74–99%, Se by 41–87%, and V by 55–100%. Ferrous sulfate treatment of the acidic fly ash samples studied was not effective for Ni, Sr, or B, which were mobilized by the treatment solution. Ferrous sulfate treatment of the alkaline fly ash sample studied slightly reduced B and Sr mobility but increased the mobility of Ni. This study has shown that ferrous sulfate fixation of the oxyanion trace elements (As, Cr, Se Mo, and V) in coal fly ash is stable during prolonged leaching by SAR.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

1

INTRODUCTION

Coal is formed from terrestrial organic plant matter that undergoes thermal maturation during burial in the earth's crust. During the formation of coal (coalification), inorganic minerals such as aluminosilicates, quartz, and phosphates coexist with the organic matter. As a result, heavy metals and other trace elements contained in these minerals are also incorporated into the coal. During combustion, the organic matter is destroyed and trace elements are further concentrated in the residual coal combustion products (CCPs), primarily the fly ash. The distribution and concentrations of the trace elements in fly ash are determined by the composition of the feed coal (McCarthy et al. 1999; Kolker et al. 2000) and by the combustion process used, including any additives for emissions control (EPRI 1987; Hower et al. 1999; Steenari et al. 1999). Trace elements associated with fly ash include arsenic, boron, chromium, molybdenum, nickel, selenium, strontium, and vanadium.

When fly ash is exposed to acid rain or groundwater leaching in older, unlined CCP disposal facilities, trace elements may be released into the environment. The amount and type of trace elements released depend on the properties and composition of the feed coal used, the age of the fly ash in the disposal facility, and also on various environmental conditions, such as pH and redox potential. The presence of trace elements in the environment is potentially of concern because some may be toxic to organisms at low concentrations. Unlike organic pollutants that are susceptible to biological degradation, inorganic trace elements do not degrade to harmless end-products. Major impurities in fly ash include iron and calcium oxides, sulfates, and trace elements such as As, B, Cr, Mo, Ni, Se, Sr, and V (Hansen and Fisher 1980; Eary et al. 1990; Mukhopadhyay et al. 1996; Karayigit et al. 2001). The speciation of these trace elements in fly ash influences their leachability and can be explained by differences in the composition and properties of fly ash such as pH, and the methods employed for the study of the leaching process. Thus, fly ash management requires a simple and cost-effective treatment process to generate a coal combustion product residue that is stable and reusable.

In situ chemical fixation (ISCF) refers to the addition of a fixating agent to contaminated soil, or other solid media, to immobilize trace elements and/or other potentially hazardous chemical compounds. Many studies have been done to chemically treat fly ash to sequester metals using different reagents such as calcium aluminates (Auer et al. 1995), phosphoric acid (Bournonville et al. 2004), chelating surfactants such as ED3A (ethylendiaminetriacetic acid) (Qian et al. 2005), NaOH (Phair et al. 2004), and others. Solutions of soluble iron salts have also been used in numerous applications to sequester aqueous trace elements through co-precipitation with, and/or adsorption by, solid phases that precipitate from the treatment solutions. Voigt et al. (1996) examined the fixation of arsenic in contaminated soils using ferrous sulfate, but found no evidence of the formation of ferric arsenate. Arsenic has also been removed from solution by co-precipitation with ferric chloride (Meng et al. 2000), and processes for removing hexavalent chromium and other heavy metals from waste water using ferrous sulfate, ferric sulfate, or ferric chloride have been developed (Suici et al. 1991; Etzel and Anand 1982). A recent study by Yang (2005) successfully treated arsenic trioxide-contaminated soil with a ferrous sulfate solution to promote the formation of insoluble arsenic-bearing phases.

The objective of this study is to experimentally examine ferrous sulfate treatment to effect the long-term immobilization of trace elements in fly ash. This chemical fixation technique, if proven successful, would provide a potential treatment method for sequestration of trace elements in fly ash, simplifying the management of CCP disposal facilities and promoting higher rates of fly ash utilization for land application and other beneficial uses.

2
METHODS

2.1 Fly Ash Sample Collection and Characterization

Fly ash samples were collected for this study from four electric power plants located in the southeastern U.S. Fly ash samples collected from Plant HA, Plant HB, and Plant MA were derived from the combustion of eastern bituminous coals and were generally acidic in nature. The fourth fly ash sample, collected from Plant PD, was derived from the combustion of Powder River Basin coal and was strongly alkaline. The pH values were measured by equilibrating each fly ash sample with double deionized (DDI) water for 24 hours at the two solid to liquid ratios (S:L) to be used in the batch experiments (S:L = 1:3 and 1:30). The fly ash samples were digested with concentrated nitric acid using EPA Method 3051A for microwave-assisted acid digestion, and the concentrations of the environmentally available major, minor, and trace elements were measured by analyzing the digestate solutions by inductively coupled plasma - optical emission spectroscopy (ICP-OES). The mineralogy of the fly ash samples was determined through powder X-ray diffraction of bulk mounts and fine particle separates using a Brüker D8 Advance X-ray diffraction system with a Våntec-1 detector.

2.2 Ferrous Sulfate Treatment of Fly Ash Samples

The four fly ash samples were treated with a ferrous sulfate (FS) solution having an iron concentration of 322 ppm (6.4 g $FeSO_4 \cdot 7H_2O$ in 4 kg DDI water) at S:L ratios of 1:3 and 1:30. For S:L = 1:3, 50 g of fly ash were treated with 150 g of ferrous sulfate solution on an orbital shaker at 200 rpm for 7 days. For S:L = 1:30, 50 g of fly ash were treated with 1500 g of ferrous sulfate solution on an orbital shaker at 200 rpm for 7 days. All treatment experiments were conducted in duplicate. After treatment, the ash/treatment solution mixtures were centrifuged at 7000 rpm for 15 minutes. The supernatant solutions were collected by filtering through 0.2 μm syringe filters and acidified using Optima® ultra-pure nitric acid. The supernatant solutions were then analyzed for element concentrations by ICP-OES. The treated fly ash samples were allowed to air dry for 7 days.

2.3 Ferrous Sulfate + Calcium Carbonate Treatment of Fly Ash Samples

A second set of batch treatment experiments was conducted using the same ferrous sulfate solution (322 mg/L Fe) plus 1.5 g of solid calcium carbonate (FS+CC). The $CaCO_3$ was added to increase the extent of ferric hydroxide precipitation by buffering the acidic pH of some of the fly ash samples. Otherwise, the same conditions and procedures were used for the buffered experiments as were described in the previous section.

2.4 Sequential Leaching of Treated and Untreated Fly Ash Samples

The effectiveness of the treatment methods was tested by comparing the synthetic acid rain (SAR) leaching behavior of the treated and untreated fly ash samples. The SAR leachant was equivalent to the SPLP solution described by EPA Method 1312B (U.S. EPA 1994a), which is a dilute mixture of sulfuric and nitric acids at a 60:40 ratio and having pH = 4.2. Three grams of treated ash were placed into contact with 45 g SAR leachant in a 50 ml tube and shaken at 200 rpm for 22 hours. The tubes were then centrifuged for 30 minutes at 3,000 rpm and the supernatant solution removed. The leachate solution was filtered through 0.2 µm syringe filters and acidified using Optima® ultrapure HNO_3. Leachate solutions were analyzed by ICP-OES for major, minor, and trace elements. After centrifugation, another 45 ml aliquot of SAR leachant was added to the tube, and the leaching procedure repeated. Leaching was continued until all trace element concentrations (except Sr) dropped to • LOD. The same batch sequential leaching procedure was carried out simultaneously for untreated ash samples for comparison of results.

The change in trace element mobility caused by each treatment method was determined by comparing the amount of trace elements released from the treated fly ash to the amount released by the untreated fly ash during batch sequential leaching. The total (cumulative) amount of each trace element released during the leaching period was calculated by integrating the area under the sequential leaching curve. The mobility reduction of each trace element in the treated fly ash samples was calculated as a percentage with respect to the untreated fly ash samples and corrected for the amount of trace element released during the treatment process.

2.5 Sequential Chemical Extraction Study of Treated and Untreated Fly Ash Samples

The distribution of elements in the FS-treated and the untreated fly ash samples was determined using a sequential chemical extraction procedure (SCEP). After reviewing numerous articles on sequential chemical extraction procedures suitable for geological materials, a seven-step sequential chemical extraction scheme was devised based on the method described by Leleyter and Probst, 1999. The sequential chemical extraction procedure used in this study was designed to separate major, minor, and trace elements associated with the following fly ash fractions:

1. Water Soluble
2. Exchangeable
3. Acid Soluble (Bound to Carbonates)
4. Easily Reducible (Bound to Manganese Oxides)
5. Moderately Reducible (Bound to Amorphous Iron/Aluminum Oxides)
6. Poorly Reducible (Bound to Crystalline Iron/Aluminum Oxides)
7. Oxidizable (Bound to Organics and Sulfides)

The mobility of the elements that are associated with these fractions generally decreases with each extraction step. The seven SCEP steps are described in Table 2-1.

One gram of each FS-treated and each untreated fly ash sample was extracted sequentially in 50 ml polypropylene centrifuge tubes while being agitated on an orbital shaker at 200 rpm. At the end of each extraction step, the tubes were centrifuged at 3000 rpm for 30 minutes; the supernatant solutions were filtered through 0.2 μm syringe filters and then preserved by acidifying with ultrapure Optima® nitric acid for analysis by ICP-OES. Between each successive extraction step, the samples were washed with 20 ml of DDI water for 10 minutes on the shaker at 200 rpm to remove the traces of any remaining extraction solution. The wash solutions from steps 2 through 5 were filtered, acidified, and then analyzed by ICP-OES.

Table 2-1
Seven-Step Sequential Chemical Extraction Procedure

Step	Fraction	Procedure
1	Water Soluble Fraction	1 g sample + 40 ml DDI water shaken at 200 rpm for 16 hrs at 25°C
2	Exchangeable Fraction	Residue from Step 1 + 40 ml 1M NH_4OAc (pH = 4.5) shaken at 200 rpm for 2 hrs at 25°C
3	Acid Soluble Fraction	Residue from Step 2 + 40 ml 0.1M acetic acid shaken at 200 rpm for 16 hrs at 25°C
4	Easily Reducible Fraction	Residue from Step 3 + 40 ml 0.1M $NH_2OH.HCl$ (pH = 2 in 0.01M HNO_3) shaken at 200 rpm for 0.5 hrs at 25°C
5	Moderately Reducible Fraction	Residue from Step 4 + 40 ml 0.25M $NH_2OH.HCl$ in 25% acetic acid shaken at 200 rpm for 16 hrs at 25°C
6	Poorly Reducible Fraction	Residue from Step 5 + 40 ml 0.2M NH_4-oxalate buffer + 0.1M ascorbic acid (pH = 3.25) 30 minutes in water bath at 96°C
7	Oxidizable and Sulfide Fraction	Residue from Step 6 + 10 ml 30% H_2O_2 shaken at 200 rpm and 25°C for 1 hr; extracting 1 hr at 85°C for evaporation; residue + 10 ml 30% H_2O_2 extracting 1 hour at 85°C until solution evaporates to a few ml; add 50 ml of 1M CH_3COONH_4 (pH = 2 in HNO_3 medium), shaken at 200 rpm for 16 hrs at 25°C

3

RESULTS AND DISCUSSION

3.1 Fly Ash Characterization

The pH values of DDI water equilibrated with the untreated fly ash samples for 24 hours are shown in Table 3-1. The pH values measured at the two different S:L ratios are closely comparable for PD fly ash, but show moderate to significant differences for the other three fly ash samples. The fly ashes produced from combustion of eastern bituminous coals are all acidic at a S:L ratio of 1:30, with pH values of 6.31, 5.92, and 4.80 for HA, HB, and MA fly ash, respectively. At a S:L ratio of 1:3, the pH of MA fly ash decreased to 4.42, while the pH of both HB and HA fly ash increased to 6.73 and 7.91, respectively. The fly ash collected from site PD was very alkaline, with a pH of approximately 11.0, corresponding to it having been derived from combustion of PRB coal.

Table 3-1
Fly Ash Equilibrium pH Values

Fly Ash Sample	Solid:Liquid	pH
HA	1:3	7.91
HA	1:30	6.31
HB	1:3	6.73
HB	1:30	5.92
MA	1:3	4.42
MA	1:30	4.80
PD	1:3	10.92
PD	1:30	10.99

Representative XRD patterns for the fly ash samples are shown in Figure 3-1. Figure 3-1(a) shows the diffraction pattern for MA fly ash, and Figure 3-1(b) shows the pattern for PD fly ash. The fly ash samples have virtually identical mineralogy, although relative mineral abundances vary between samples. The major mineral constituents of the fly ash samples are quartz, mullite, and hematite/maghemite.

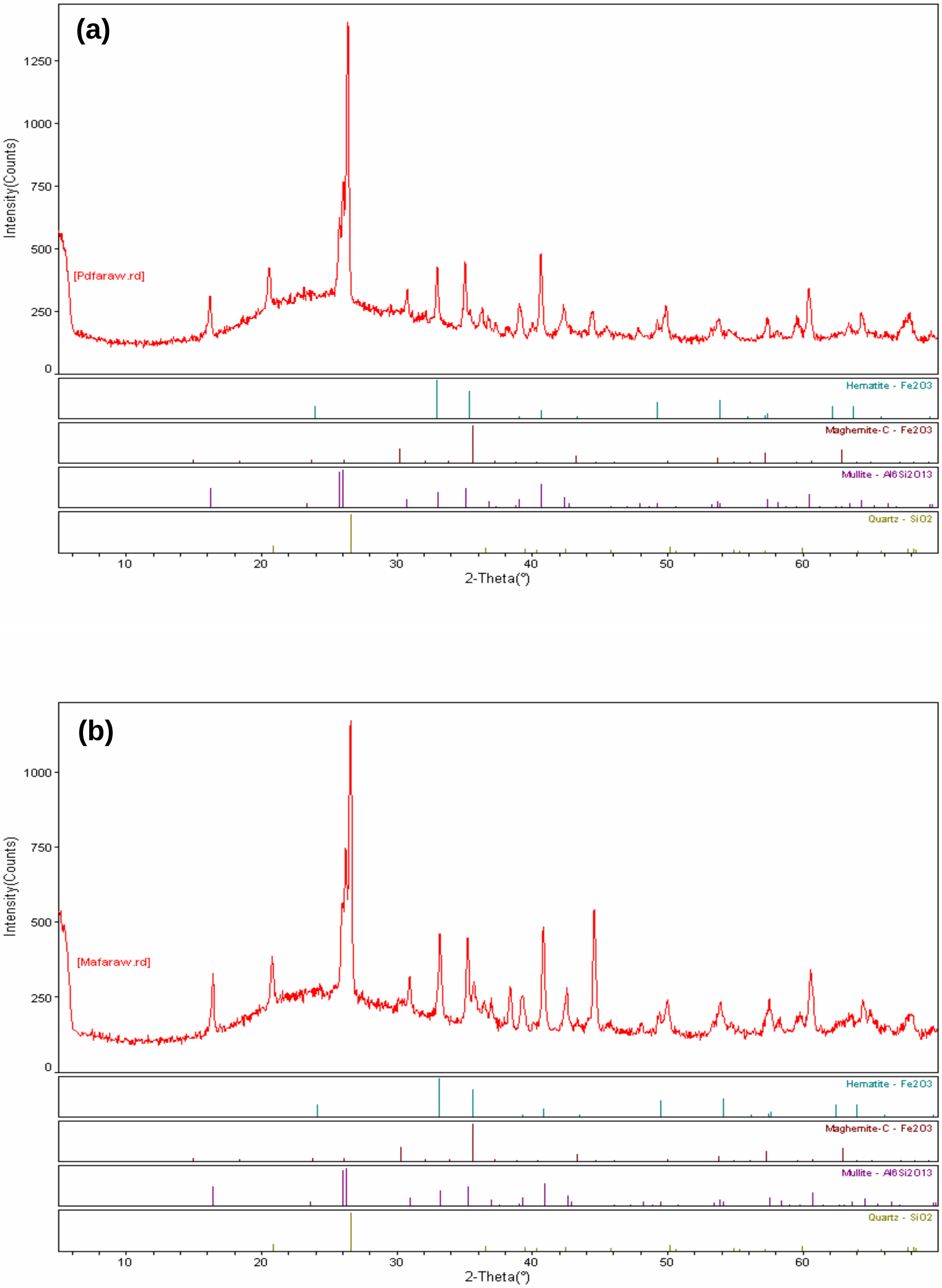
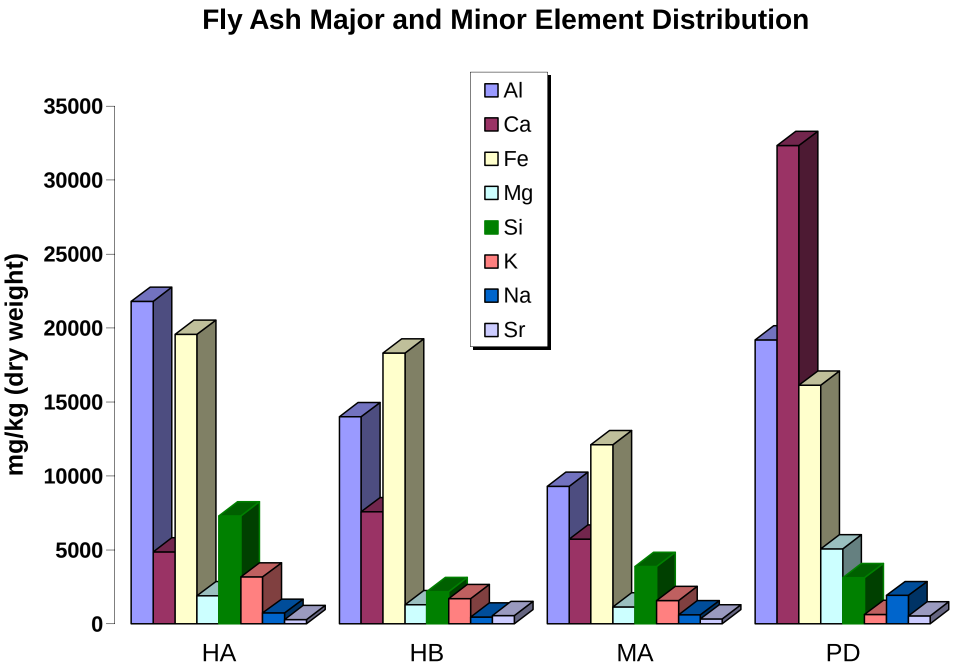


Figure 3-1
XRD pattern for bulk fly ash samples: (a) MA fly ash; (b) PD fly ash

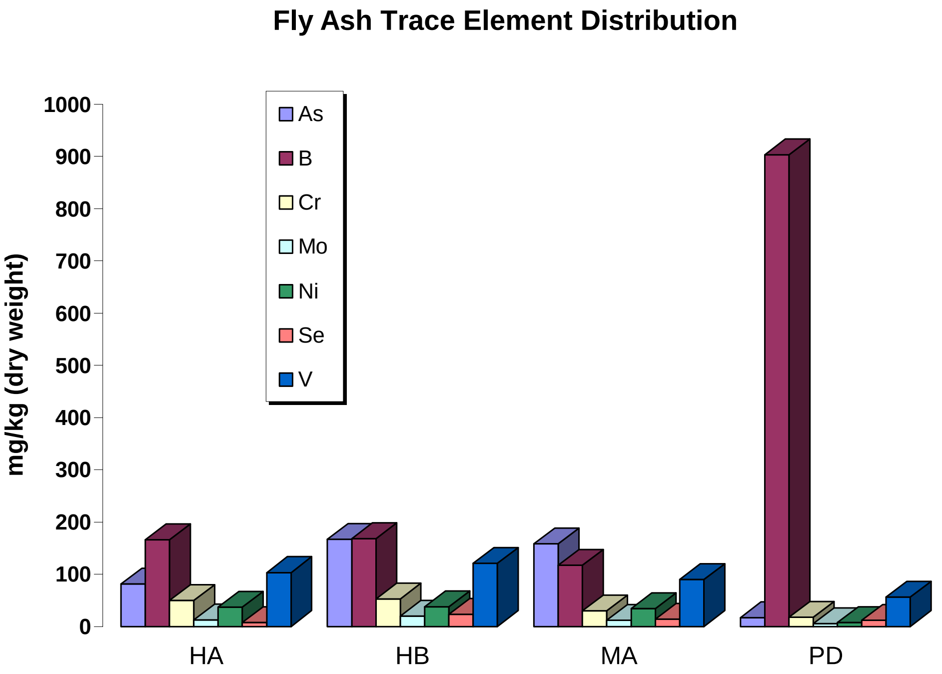
A microwave-assisted acid digestion (MWD) technique (EPA Method 3051A; U.S. EPA 1994b) was used to determine the environmentally available concentrations of major, minor, and trace elements in the fly ash samples. The three acidic fly ash samples (HA, HB, and MA), derived from combustion of eastern bituminous coals, were expected to have similar composition, allowing for minor feed coal composition differences. On the other hand, the PD fly ash derived from Powder River Basin coal was expected to show more significant compositional differences compared to the acidic fly ash samples, because of the different chemistry of the parent coal. Figure 3-2 shows that although absolute element concentrations varied for the acidic fly ash samples, these general composition predictions were borne out. Figure 3-2(a) gives the major and minor element compositions, and Figure 3-2(b) shows the trace element distributions of the four fly ash samples, all expressed in ppm on a dry weight basis. Complete MWD results for the fly ash samples are given in Appendix A.

The environmentally available major element composition of the HA, HB, and MA fly ash samples is dominated by Al and Fe. In contrast, Ca is the dominant major element in PD fly ash (32,000 mg/kg). The highly alkaline pH shown by the PD fly ash may be explained by the high Ca content, which exists primarily as lime (CaO). The Al and Fe contents of PD fly ash are similar to those of HA fly ash, and fall within the ranges of the acidic fly ash samples (10,000 to 22,000 mg/kg). HA fly ash contains the highest amount of Si (7000 mg/kg) among the four ash samples. The concentrations of Mg, K, Na, and Sr are similar among the four fly ash samples and can be grouped together as minor elements. Despite the very high Ca content of PD fly ash, its Sr concentration is similar to those of the low Ca acidic fly ash samples.

The concentrations of the environmentally available trace elements of interest also vary between the fly ash samples. The alkaline PD fly ash has high concentrations of B (900 mg/kg), and has significantly lower concentrations of the other detectable trace elements compared to the acidic fly ash samples. Among the acidic fly ash samples, HB and MA have a higher As concentration (160 mg/kg) than HA (80 mg/kg), while HA and HB fly ash samples have a higher B concentration (165 mg/kg) than MA fly ash (117 mg/kg). All three acidic fly ash samples have similar V concentrations (90 to 105 mg/kg) and have lower Cr, Mo, Ni, and Se concentrations compared to those of the other trace elements.



(a)



(b)

Figure 3-2
Environmentally available concentrations in fly ash samples, as determined by EPA Method 3051A: (a) major and minor element concentrations: (b) trace element concentrations

3.2 Treatment Experiments

Ferrous sulfate treatment of the fly ash samples was designed to immobilize trace elements present in the fly ash through adsorption on, and/or co-precipitation with, ferric hydroxide. Figure 3-3 shows the amount of $Fe(OH)_3$ added to the fly ash samples after the ferrous sulfate (FS) and ferrous sulfate plus calcium carbonate (FS+CC) treatments, as determined by mass balance calculations. For FS treatment at the 1:3 solid:liquid ratio, approximately 1750 mg of $Fe(OH)_3$ were added to 1 kg of each of the fly ash samples; at the solid:liquid ratio of 1:30, approximately 17,300 mg of $Fe(OH)_3$ were added per kg of fly ash, which is ten times more when compared with the 1:3 ratio. Addition of $CaCO_3$ to the treatment procedure slightly increased the amount of $Fe(OH)_3$ precipitated from 1750 to 1900 mg/kg and from 17,300 to 19,000 mg/kg at the 1:3 and 1:30 S:L ratios, respectively. The solid:liquid ratio of 1:30 therefore appears more suitable as a treatment technique due to the higher amount of $Fe(OH)_3$ formed in the fly ash samples. Addition of $CaCO_3$ also appears advantageous in further increasing ferric hydroxide precipitation, although it is much less significant than the S:L ratio.

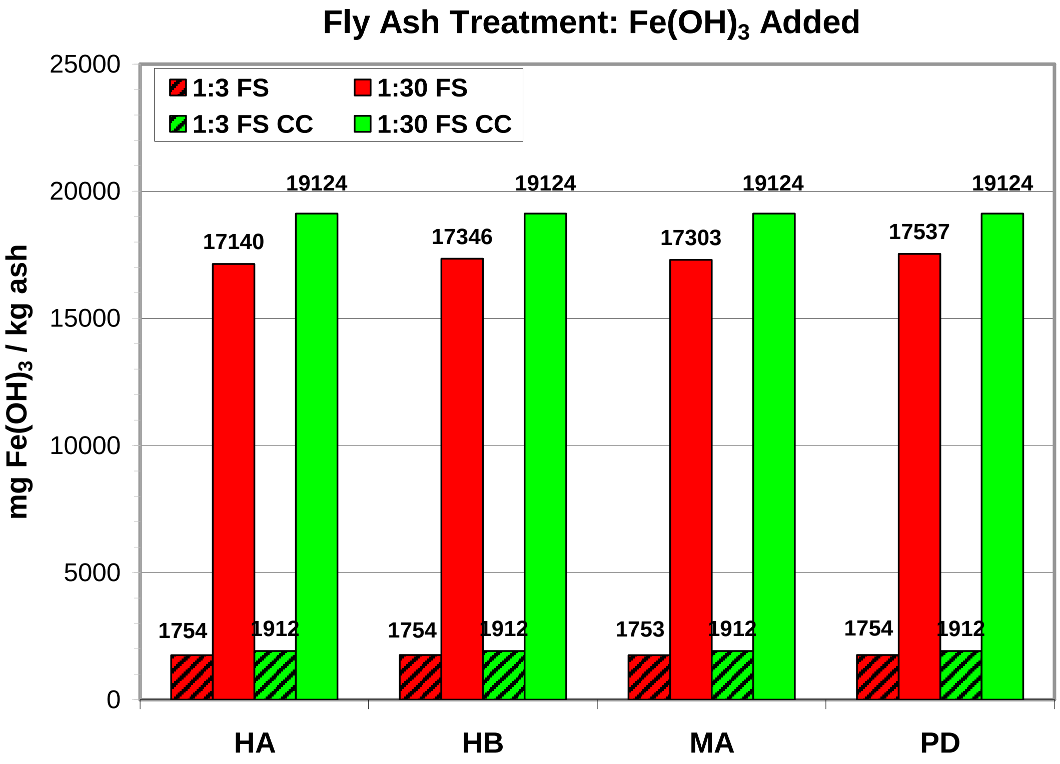


Figure 3-3
Amounts of $Fe(OH)_3$ precipitated in fly ash after ferrous sulfate (FS) and ferrous sulfate plus calcium carbonate (FS CC) treatment

3.2.1 Trace Element Mobility During Treatment

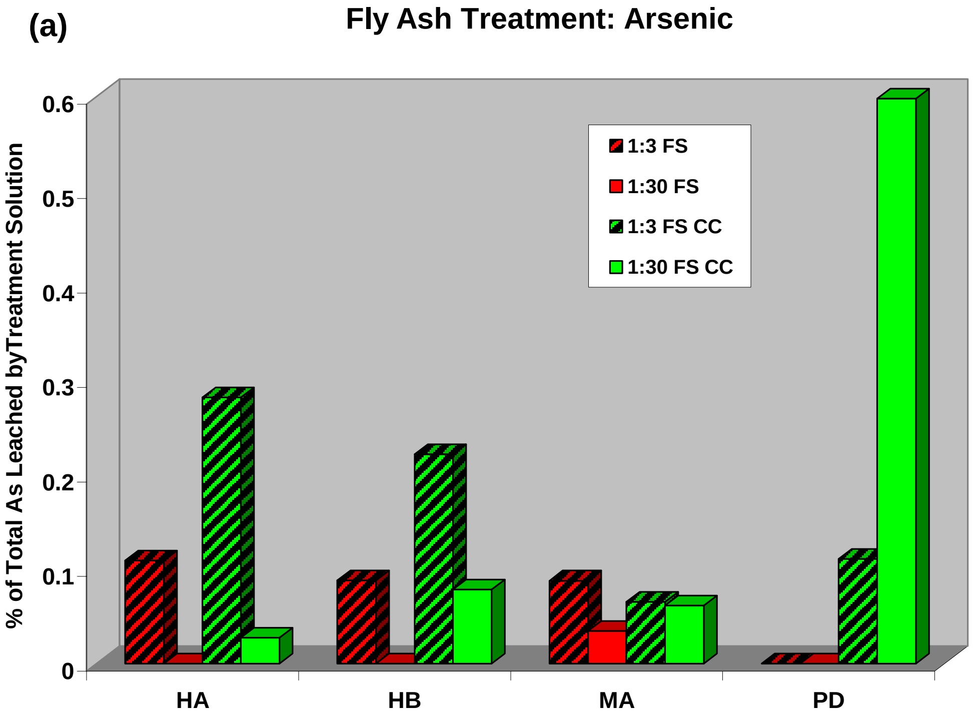
After the seven-day treatment period, the treatment solutions were collected and analyzed by ICP-OES to determine whether any trace elements were mobilized during the fly ash treatment process. Figures 3-4 through 3-7 and Table 3-2 show the percentages of the total MWD trace element (as determined by EPA 3051B) leached from fly ash during treatment by the various solutions studied.

The maximum amount of arsenic mobilized by a treatment solution (1:30 FS+CC) was still only 0.6% of the total arsenic (PD fly ash; Figure 3-4a). As expected, all of the treatment solutions removed significant amounts (15-55%) of boron from the fly ash samples. The leachability of boron was much more dependent on the S:L ratio used than on the treatment solution pH. This was particularly important for PD fly ash, which leached more than twice as much of its total boron to the 1:30 treatment solutions, compared to the amounts leached by the equivalent 1:3 treatment solutions (Figure 3-4b; Table 3-2). The fractions of the total boron leached from the acidic fly ash samples (HA, HB, MA) were also comparable for a particular S:L ratio, but were 22-58% higher at the 1:30 treatment ratio.

Essentially none of the chromium was mobilized by any of the treatment solutions from the acidic fly ash samples, while 1.5% and 2.3% of the total MWD chromium in PD fly ash was mobilized by the 1:3 FS and 1:3 FS+CC treatment solutions, respectively (Figure 3-5a). Smaller amounts of chromium were mobilized from PD fly ash at the 1:30 treatment ratio, with the 1:30 FS treatment removing none of the chromium. The 1:3 FS treatment solution did not mobilize molybdenum from any of the fly ash samples except PD fly ash (Figure 3-5b), where 57% of the total molybdenum was removed. Approximately 29-73% of the molybdenum was removed from the ash samples by the 1:3 FS+CC treatment solution, but the 1:30 FS+CC treatment mobilized less molybdenum (5.4-41.4%). No molybdenum was removed from the fly ash samples by 1:30 FS treatment solution.

Small amounts (0.5-8.1%) of the total nickel were mobilized from HA, HB, and MA fly ash by the FS+CC treatment solutions (Figure 3-6a). No nickel was leached from PD fly ash (Ni_{total} = 7.48 ppm) by any of the treatment solutions, and the 1:30 FS treatment did not mobilize any nickel from HA, HB, or MA fly ash (Ni_{total} = 36.9, 37.6, and 34.3 ppm, respectively). All of the treatment solutions, to some extent, leached selenium from each of the fly ash samples (Figure 3-6b), with the 1:3 FS treatment removing the smallest amount (1.2-4.0%) and the 1:30 FS+CC treatment mobilizing the greatest amount (7.9-14.8%).

Strontium was also mobilized from HA and MA fly ash samples by all of the treatment solutions (Figure 3-7a), although no strontium was removed from HB fly ash or PD fly ash by either the 1:3 FS treatment or the 1:3 FS+CC treatment. Minor amounts of vanadium were mobilized by the treatment solutions (Figure 3-7b), with the highest release produced by 1:30 FS+CC treatment of PD fly ash and the lowest by FS treatment (1:30 FS for HB, MA, PD; FS 1:3 for HA).



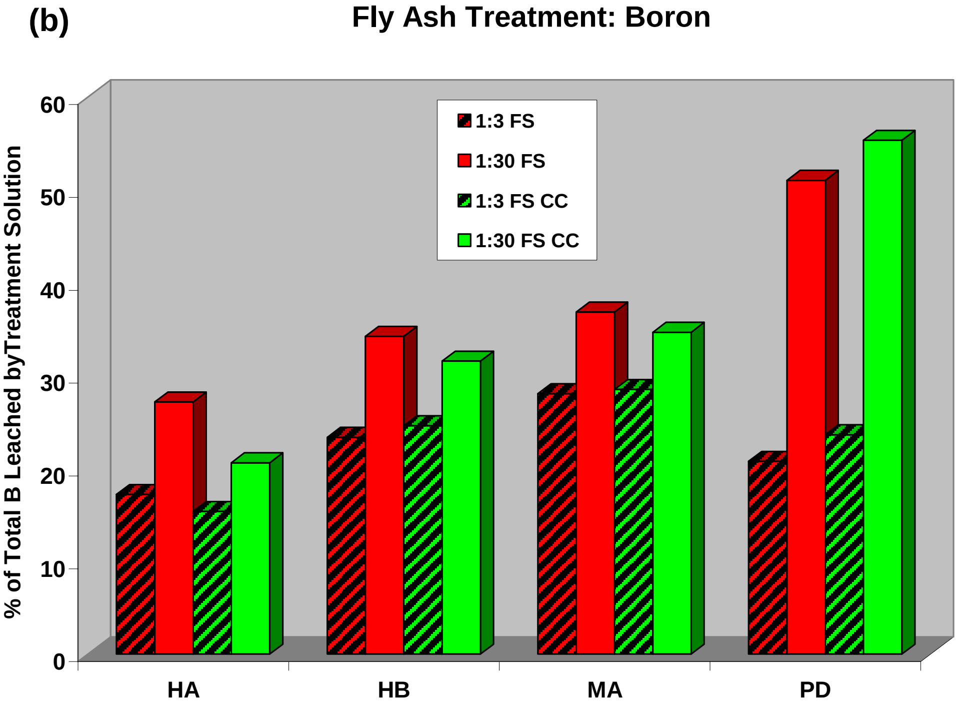
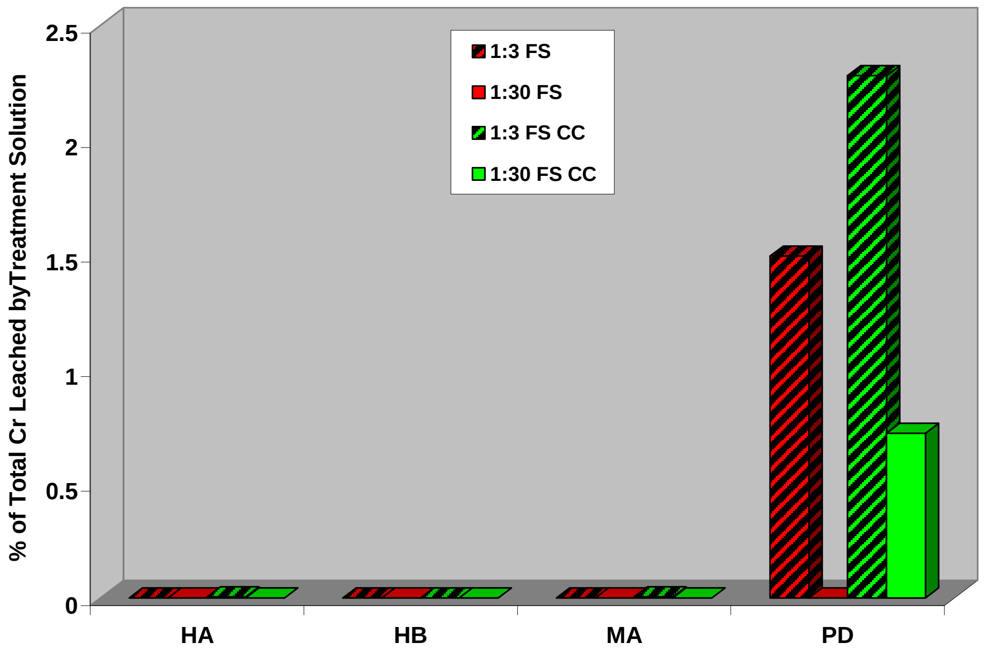


Figure 3-4
Percentage of the total trace element leached from untreated fly ash by the different treatment solutions: (a) arsenic; (b) boron

(a) Fly Ash Treatment: Chromium



(b) Fly Ash Treatment: Molybdenum

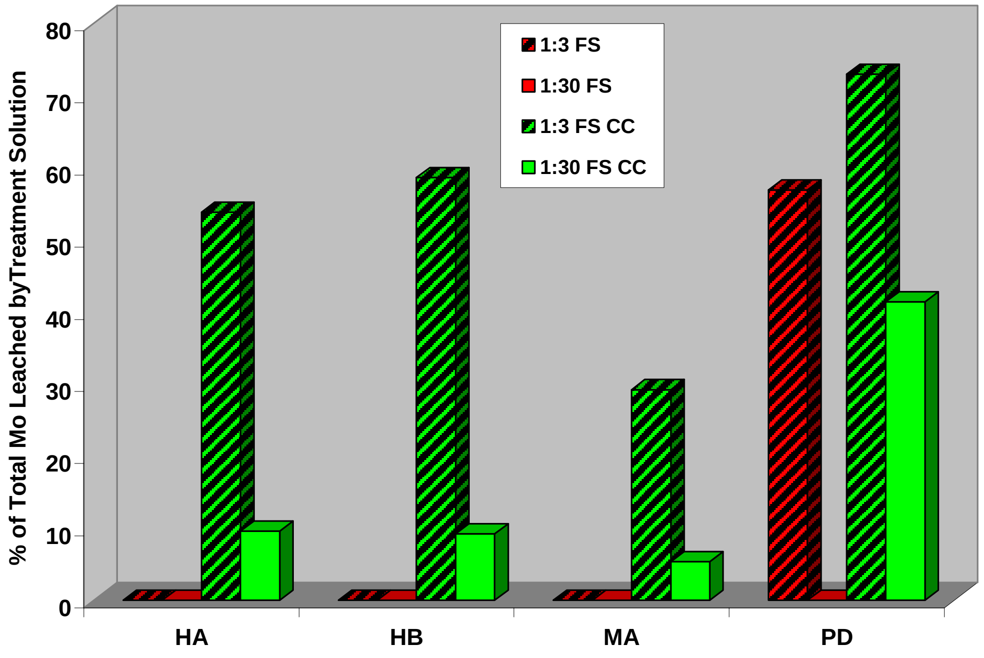
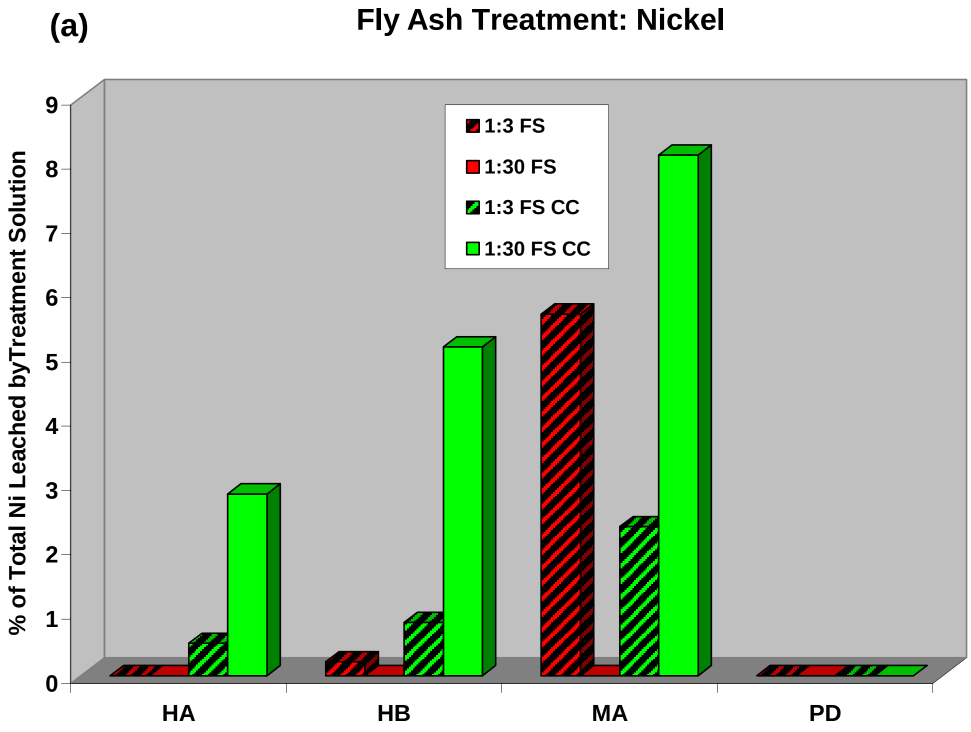


Figure 3-5
Percentage of the total trace element leached from untreated fly ash by the different treatment solutions: (a) chromium; (b) molybdenum



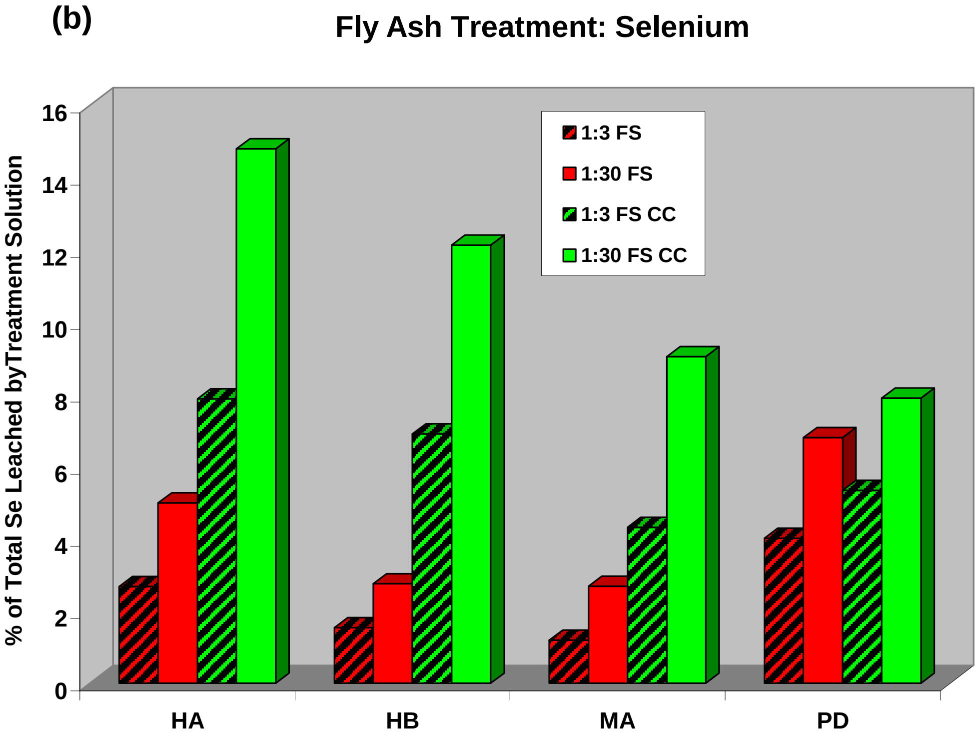
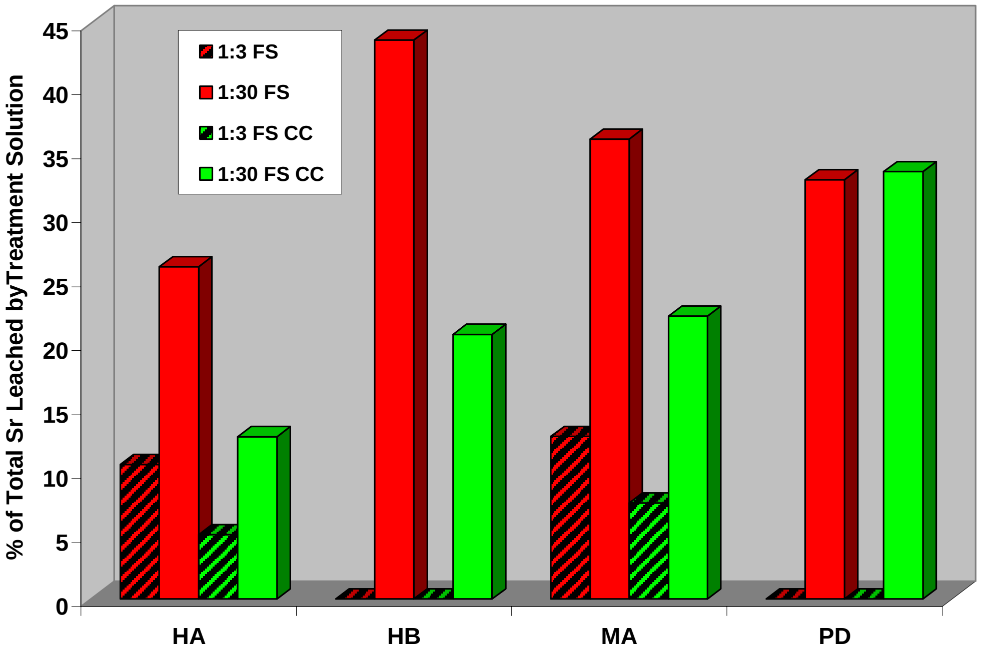


Figure 3-6
Percentage of the total trace element leached from untreated fly ash by the different treatment solutions: (a) nickel; (b) selenium

(a) **Fly Ash Treatment: Strontium**



(b) **Fly Ash Treatment: Vanadium**

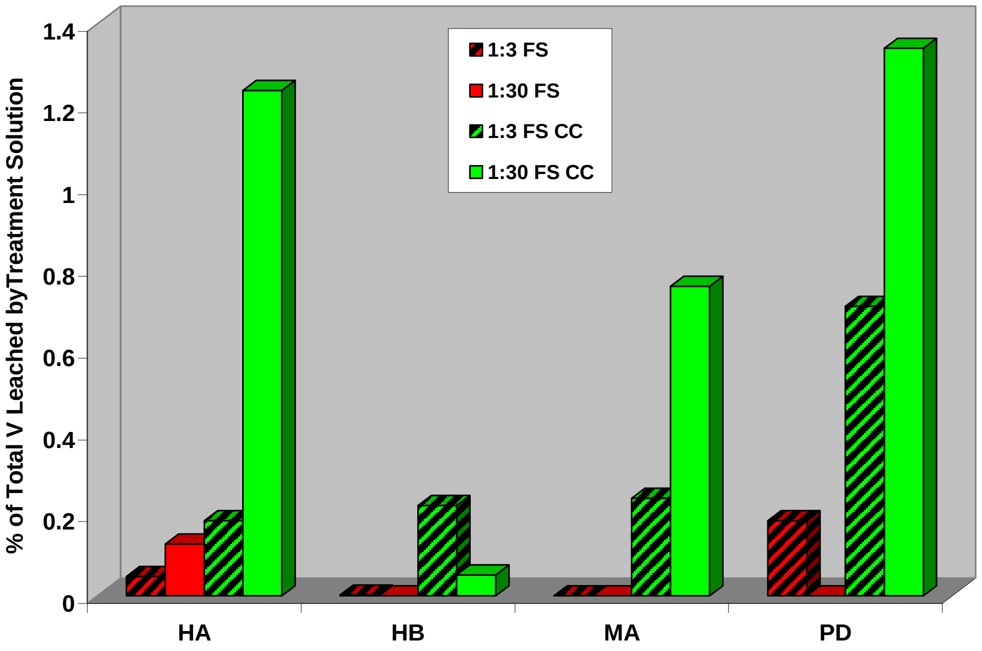


Figure 3-7
Percentage of the total trace element leached from untreated fly ash by the different treatment solutions: (a) strontium; (b) vanadium

In summary, the 1:30 FS treatment released only trace amounts of As, Cr, Mo, Ni, and V from the fly ash samples (Table 3-2), but mobilized large amounts of B and Sr from all of the fly ash samples. Although all of the treatment methods studied removed some Se from all of the fly ash samples, the 1:3 FS treatment released the lowest amounts. The 1:3 FS+CC treatment released the lowest amounts of Sr from the fly ash samples.

Table 3-2
Percentage of Trace Elements Leached by Treatment Solutions

	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC		1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
	Arsenic Percent Leached					**Boron Percent Leached**			
HA	0.11	0.00	0.28	0.03	**HA**	17.21	27.17	15.37	20.62
HB	0.09	0.00	0.22	0.08	**HB**	23.37	34.23	24.60	31.57
MA	0.09	0.03	0.07	0.06	**MA**	28.06	36.85	28.53	34.67
PD	0.00	0.00	0.11	0.60	**PD**	20.78	51.04	23.63	55.35
	Chromium Percent Leached					**Molybdenum Percent Leached**			
HA	0.00	0.00	0.01	0.00	**HA**	0.00	0.00	53.79	9.62
HB	0.00	0.00	0.00	0.00	**HB**	0.00	0.00	58.58	9.21
MA	0.00	0.00	0.01	0.00	**MA**	0.00	0.00	29.19	5.37
PD	1.49	0.00	2.28	0.72	**PD**	56.88	0.00	72.92	41.38
	Nickel Percent Leached					**Selenium Percent Leached**			
HA	0.00	0.00	0.50	2.83	**HA**	2.68	4.99	7.87	14.79
HB	0.22	0.00	0.83	5.12	**HB**	1.54	2.75	6.90	12.13
MA	5.63	0.00	2.32	8.10	**MA**	1.19	2.69	4.32	9.04
PD	0.00	0.00	0.00	0.00	**PD**	4.02	6.80	5.34	7.89
	Strontium Percent Leached					**Vanadium Percent Leached**			
HA	10.52	25.97	5.03	12.69	**HA**	0.05	0.13	0.18	1.24
HB	0.00	43.67	0.00	20.68	**HB**	0.00	0.00	0.22	0.05
MA	12.72	35.93	7.49	22.11	**MA**	0.00	0.00	0.24	0.76
PD	0.00	32.76	0.00	33.40	**PD**	0.18	0.00	0.71	1.34

3.3 Results of Synthetic Acid Rain (SAR) Leaching of Treated and Untreated Fly Ash Samples

The effectiveness and long-term stability of the treatment techniques was tested through prolonged leaching of the treated and untreated fly ash samples using the SAR solution and sequential leaching procedure previously described in the Methods section. Leaching was continued until all leachate trace element concentrations (except Sr) dropped below the limit of detection (LOD). Table 3-3 shows the ICP-OES LOD values for the trace elements of interest, expressed in mg/L.

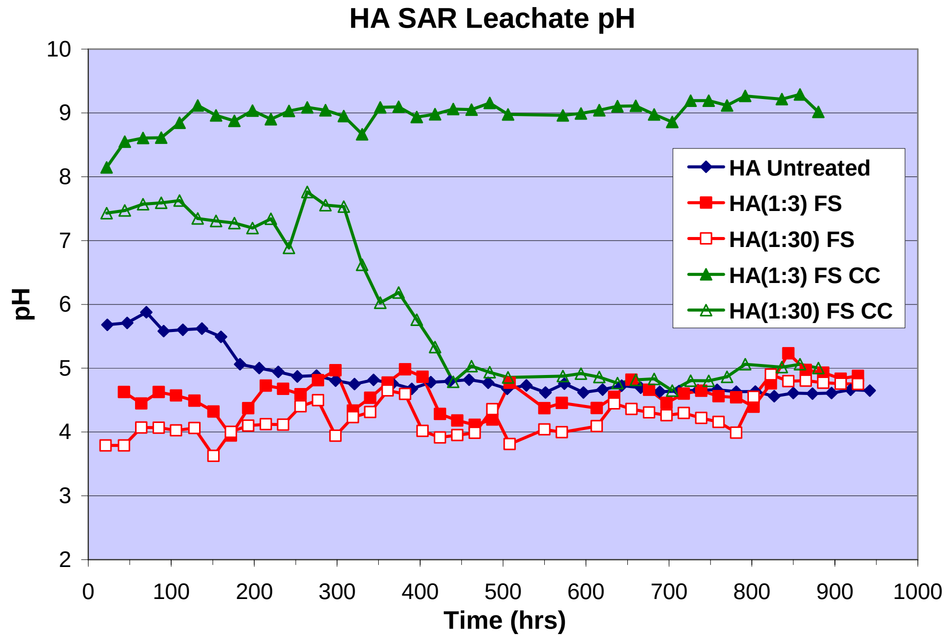
Table 3-3
Trace Element ICP-OES LOD Values

Trace Element	LOD (mg/L)
As	0.009
B	0.102
Cr	0.002
Mo	0.002
Ni	0.001
Se	0.004
Sr	0.001
V	0.07

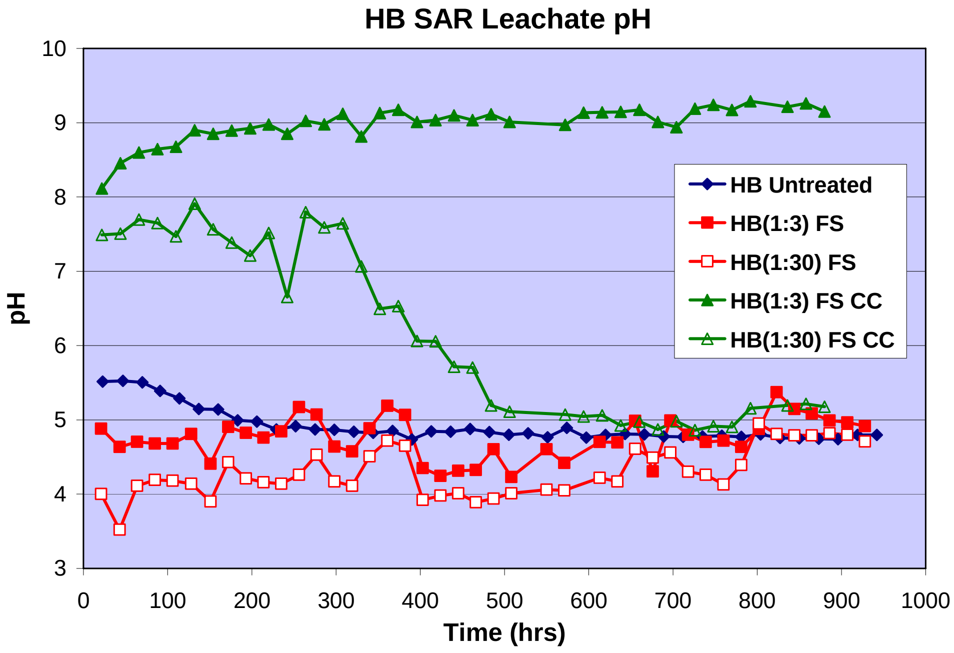
3.3.1 SAR Leachate Solution pH

During SAR leaching of the treated and untreated fly ash samples, the pH of the leachate solutions was monitored. Leachate solution pH values are plotted against leaching time in Figures 3-8 and 3-9.

The pH of the untreated fly ash sample leachate solutions reflected the acidic or alkaline nature of the ash. For example, the untreated acidic ash (HA, HB, MA) leachate solutions stabilized at pH around 4.8. The pH of the leachates of the 1:3 FS and 1:30 FS-treated samples of HA, HB, and MA fly ash showed very similar behavior. The pH of the 1:30 FS-treated ash leachate was lower than the 1:3 FS-treated ash leachate at the beginning of the leaching period due to the greater hydrolysis of Fe(II) in the 1:30 S:L experiments; however, the leachate pH for all FS-treated acidic ash samples rose slowly to converge with that of the untreated ash, demonstrating the long-term buffer capacity of the fly ash. In contrast, the FS-treated PD fly ash leachate maintained pH between 8.2 and 10.3 during SAR leaching because of the alkaline nature of the fly ash, with the pH of the 1:30 FS-treated PD ash leachates being consistently lower than that of 1:3 FS-treated PD. The pH of the FS-treated PD ash leachates also showed greater fluctuations over the leaching period than did the FS-treated acidic fly ash leachates.



(a)



(b)

Figure 3-8
Leachate pH as a function of leaching time for treated and untreated (a) HA fly ash and (b) HB fly ash [Note: The SAR leachant (pH 4.2) was replaced with fresh SAR leachant every 22 hours]

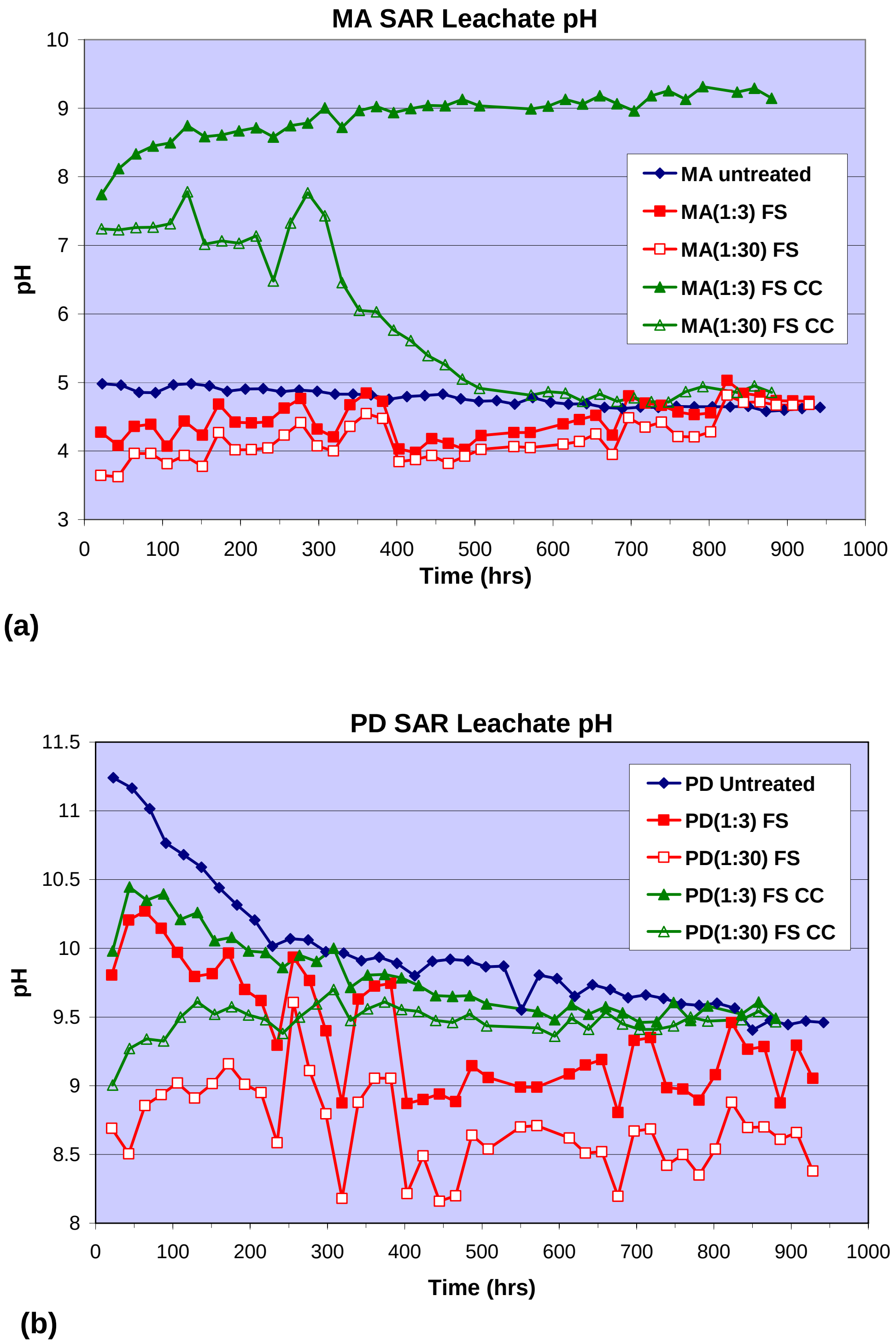


Figure 3-9
Leachate pH as a function of leaching time for treated and untreated (a) MA fly ash and (b) PD fly ash [Note: The SAR leachant (pH 4.2) was replaced with fresh SAR leachant every 22 hours]

The pH of the 1:3 FS+CC-treated acidic fly ash leachates rose from initial values of around 8 to approximately 9.2 over the leaching period. This behavior can be explained by the dissolution of the excess $CaCO_3$ added as a pH buffer. Unlike the 1:3 FS+CC-treated acidic fly ash leachates, the pH of the 1:30 FS+CC-treated ash leachates started at 7-7.5 but decreased with leaching time and converged with the pH of the untreated and FS-treated fly ash leachates after about 15 days of leaching. This behavior can be explained by (1) the greater hydrolysis of Fe in the 1:30 FS+CC-treated fly ash samples and (2) exhaustion of the calcium carbonate buffering. The pH of the 1:3 FS+CC-treated PD fly ash initially rose from 10 to 10.5, then decreased with increased leaching time to converge on 9.5, the pH of the untreated ash leachate. The pH of the 1:30 FS+CC-treated PD fly ash leachate rose from an initial value of 9.0 and quickly stabilized at about 9.5 during the remainder of the leaching period. The pH of the FS+CC-treated PD ash leachate solutions was higher than the corresponding FS-treated PD ash leachate solutions.

3.3.2 Leaching Behavior and Mobility of Trace Elements

The stability of the fly ash treatment methods was tested by studying the mobility of trace elements during SAR leaching of the treated and untreated fly ash samples. Trace element concentrations in SAR leachates are plotted against time in Figures B-1 through B-4 (Appendix B). Values less than 3xLOD are below the analytical level of quantitation (LOQ), but are plotted to show trace element concentration trends over the leaching period. The total trace element concentration leached was determined from the sum of the aqueous concentration in each SAR aliquot when the leachate trace element concentration was >0.5 LOD, and calculated as ppm dry weight of the ash sample. The total trace element concentrations leached from the treated and untreated fly ash by SAR are given in Table B-1.

The effectiveness of each treatment method was calculated as the percent reduction in total trace element mobility over the leaching period, as compared to the untreated ash, after correction for the amount (if any) of trace element mobilized by the treatment process. The results of this study are shown in Figures 3-10 through 3-17, and calculated values are shown in Table 3-4.

3.3.2.1 Arsenic

The leaching behavior of As was similar for HA, HB, and MA fly ash samples (Figures B-1a, B-2a, B-3a). FS treatment lowered As release from HA and MA fly ash compared to the untreated MA fly ash after approximately 500 hours of SAR leaching. FS-treated HB fly ash released lower As concentrations in the first 400 hours of leaching, compared to the untreated ash. The 1:3 FS+CC treatment technique caused large releases of As from the acidic fly ash samples. In contrast, all treatments lowered the release of As from PD fly ash compared to the untreated ash (Figure B-4a). Peak As release from untreated PD fly ash occurred at around 10 days of leaching.

Figure 3-10 shows the percent mobility reduction of As for the various treatment techniques. The 1:30 FS treatment was the most effective for the acidic fly ash samples (HA, HB, MA), reducing the mobility of As by 71-90%. The 1:3 FS and 1:30 FS+CC treatment techniques were also effective, resulting in a 53-68% and 49-72% reduction in As mobility, respectively. However, the 1:3 FS+CC treatment dramatically increased the mobility of As in the acidic fly ash samples

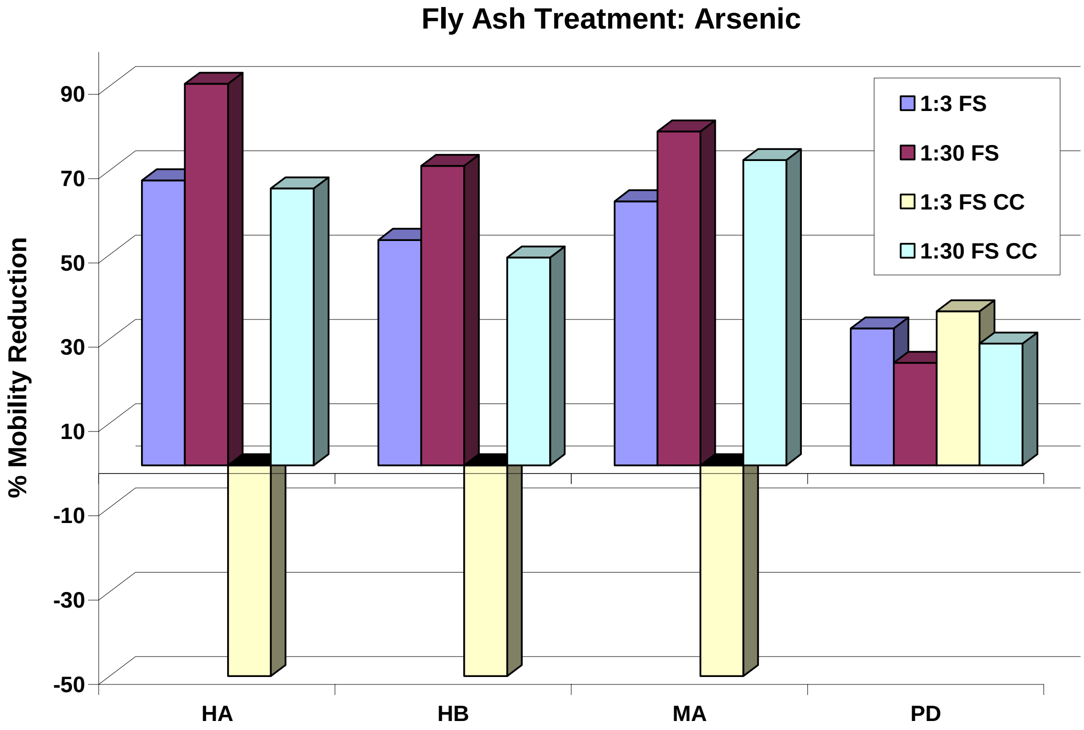


Figure 3-10
Percent reduction in arsenic mobility for treated fly ash compared to untreated fly ash
[Note: Negative scale is truncated]

under SAR sequential leaching. For the PD fly ash all the treatment techniques resulted in similar reductions in the mobility of As, with 24-36% lower As mobility for the treated fly ash compared to the untreated fly ash.

3.3.2.2 Boron

The SAR leaching behavior of B was the same for all the fly ash samples, with immediate release followed by an exponential decrease in concentration with increased leaching time. Figures B-1b, B-2b, and B-3b show that the treated acidic fly ash always released lower amounts of B than the untreated ash, which can be explained by removal of B during treatment. PD fly ash released significantly larger quantities of B over time (Figure B-4b) due to its higher total B concentration (902 ppm). More of the soluble B was removed from the fly ash samples by the 1:30 FS and 1:30 FS+CC treatment solutions than by the 1:3 FS and 1:3 FS+CC treatment solutions (Table 3-2). In general, the amount of B leached during treatment was primarily determined by the treatment S:L ratio; the addition of calcium carbonate buffer had little effect.

Figure 3-11 shows that B mobility in the acidic fly ash was significantly increased by all treatment techniques due to leaching of B during treatment, particularly for MA fly ash, which has the lowest total B concentration and pH. In contrast, all of the treatment techniques, except the 1:30 FS+CC treatment, achieved small reductions (1.9-3.5%) in B mobility for the alkaline PD fly ash. The 1:30 FS+CC treatment resulted in a small overall increase in B mobility. These results are not surprising, given the high solubility of B in coal fly ash (Hollis et al. 1988).

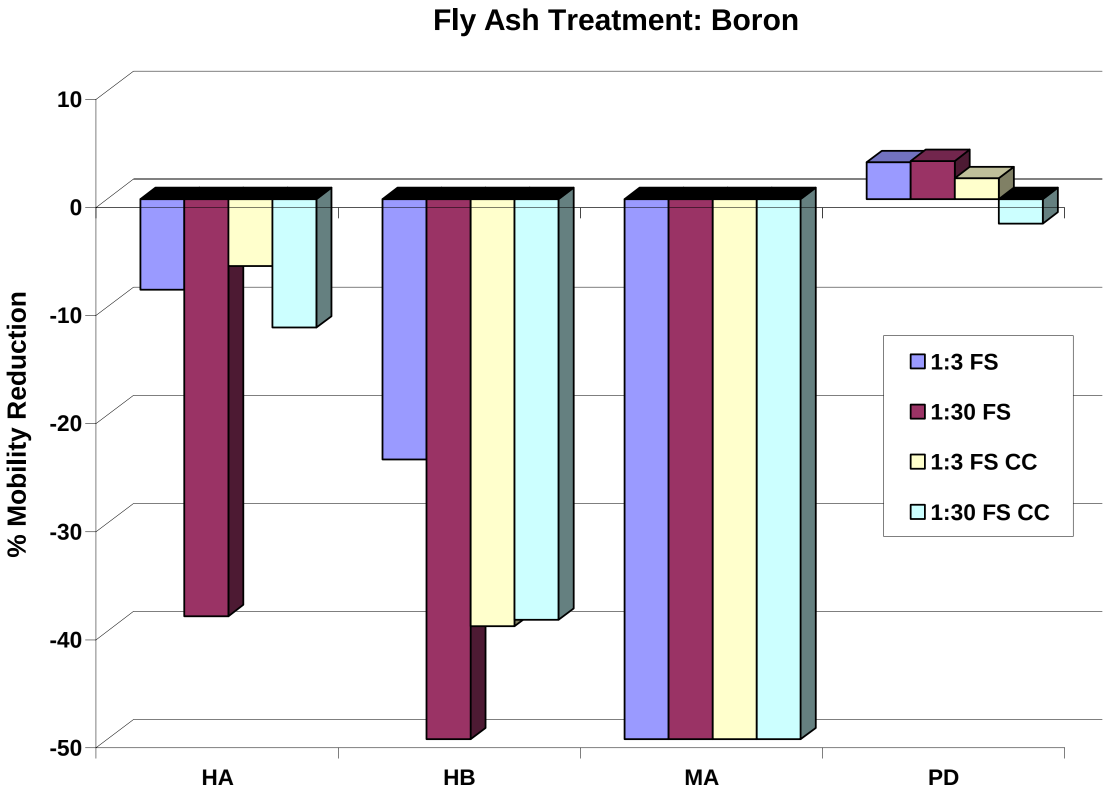


Figure 3-11
Percent reduction in boron mobility for treated fly ash compared to untreated fly ash [Note: Negative scale is truncated]

3.3.2.3 Chromium

The treated and untreated acidic fly ash samples released very low quantities of Cr during leaching (Figures B-1c, B-2c, B-3c). Untreated PD fly ash released the highest quantity of Cr during leaching (Figure B-4c), despite this ash having the lowest total Cr concentration (Table A-1). For PD fly ash, all of the treatment methods resulted in lower Cr release during SAR leaching compared to the untreated ash.

Figure 3-12 shows that all of the treatment techniques substantially reduced the mobility of Cr for all the fly ash samples, with the exception of the 1:3 FS+CC-treated MA ash, which showed

35% higher Cr mobility under sequential SAR leaching. The best result was shown by the 1:30 FS treatment, which reduced Cr mobility by 40-76%.

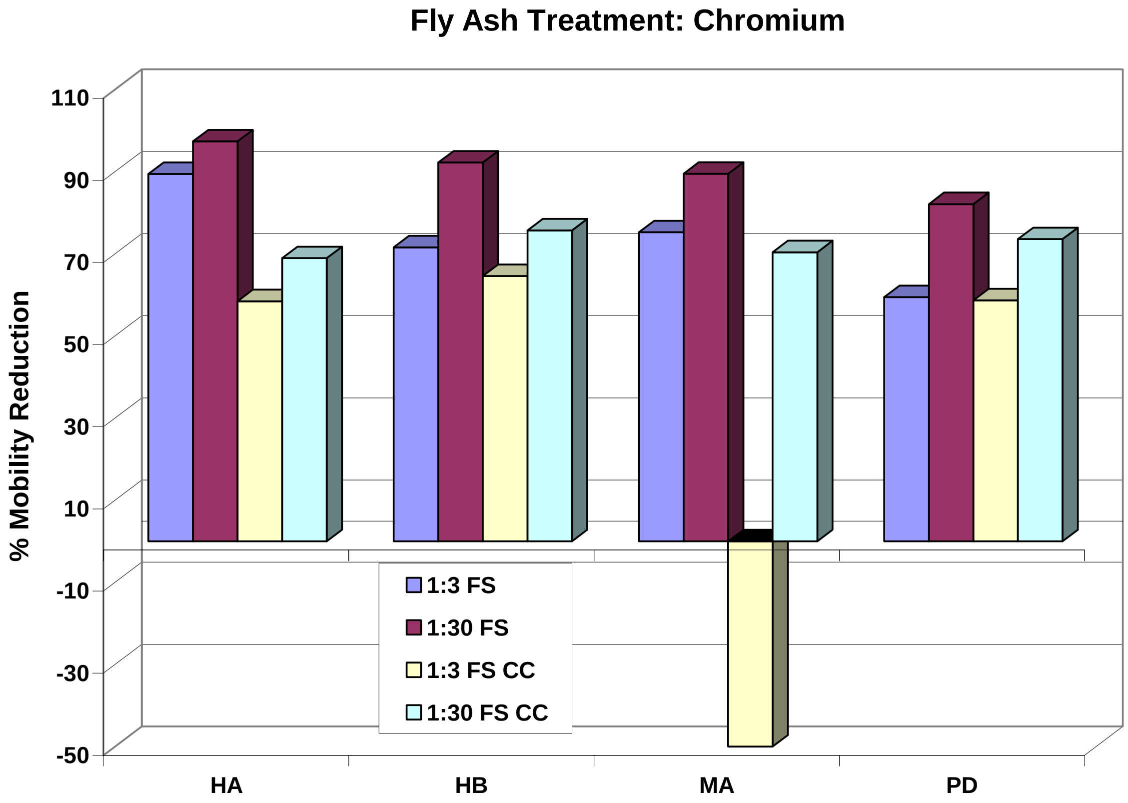


Figure 3-12
Percent reduction in chromium mobility for treated fly ash compared to untreated fly ash [Note: Negative scale is truncated]

3.3.2.4 Molybdenum

All of the untreated fly ash samples except MA show similar Mo leaching behavior with time: rapid initial leaching followed by sharply decreasing concentrations and evidence of cyclical leaching (Figures B-1d, B-2d, B-3d, B-4d). MA fly ash had a lower total Mo concentration than the other ash samples and less of the total Mo was water soluble, which explains the low initial leachate Mo concentrations for untreated MA ash. For HA fly ash, the 1:30 FS+CC treatment slightly decreased Mo leachability compared to the untreated ash. In contrast, the FS+CC-treated HB and MA fly ash initially released more Mo than the corresponding untreated ash. On the other hand, the untreated HA, HB, and PD fly ash samples released the highest quantities of Mo during SAR leaching (Table B-1).

The 1:30 FS treatment was highly effective for the acidic fly ash samples, reducing Mo mobility by 99%, 97%, and 93%, respectively, for HA, HB, and MA fly ash (Figure 3-13). This treatment also was the most effective for PD fly ash, reducing Mo mobility by 78%. The 1:3 FS treatment was also effective for the acidic fly ash samples, reducing Mo mobility by 66-88% (Table 3-4). The 1:3 FS+CC treatment was again found to be detrimental, increasing Mo mobility in all but PD ash. The 1:30 FS+CC treatment also increased Mo mobility for both HB and MA fly ash.

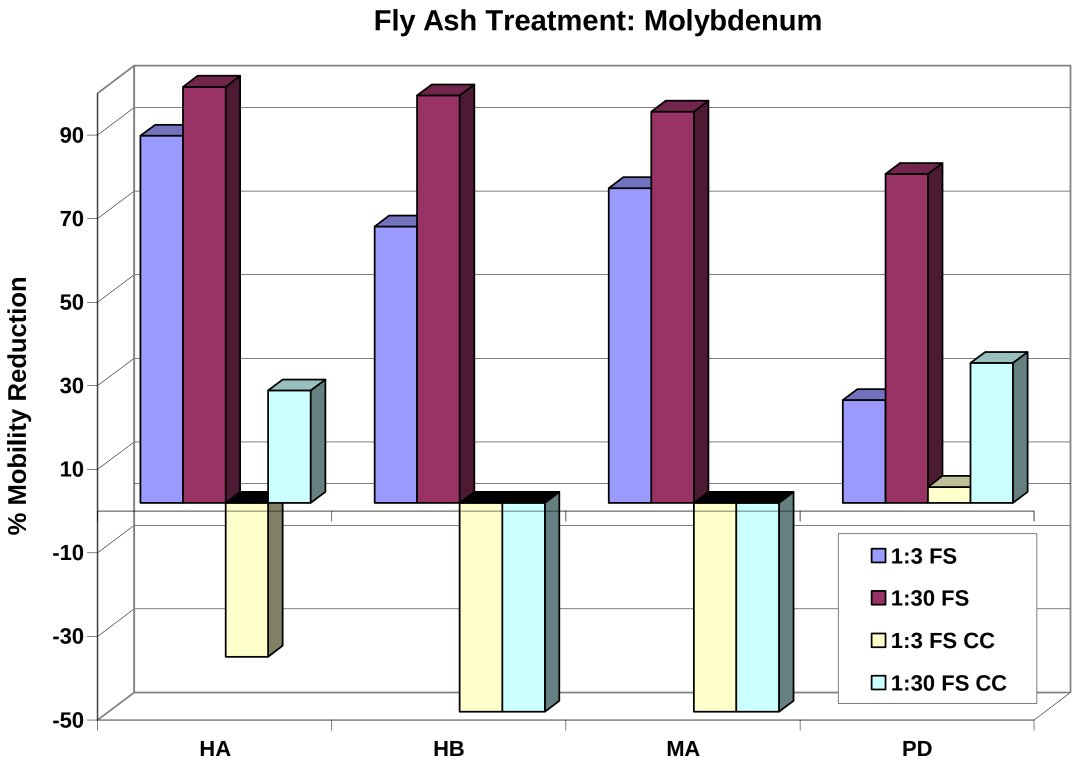


Figure 3-13
Percent reduction in molybdenum mobility for treated fly ash compared to untreated fly ash [Note: Negative scale is truncated]

3.3.2.5 Nickel

The acidic fly ash samples all showed similar leaching behavior for Ni, including cyclic leaching patterns (Figures B-1e, B-2e, B-3e). Untreated HA, HB, and MA fly ash showed high initial release of Ni, followed by rapidly decreasing leachate concentrations. FS-treated acidic ash leachates produced lower initial Ni concentrations than the untreated ash. The lowest initial Ni releases were exhibited by FS+CC-treated acidic ash leachates, but stronger cyclic releases of Ni were observed at around 9 days and between 15-20 days of leaching. FS-treated PD fly ash released very low Ni concentrations during SAR leaching, with occasional values >0.5 LOD (Figure B-4e). In contrast, untreated PD fly ash did not produce any Ni concentrations >0.5 LOD (Table B-1). The 1:3 and 1:30 FS+CC-treated PD ash samples released a large pulse of Ni around the ninth day of leaching (Figure B-4e).

Ni mobility was increased by all of the treatment techniques except the 1:3 FS+CC treatment, which decreased Ni mobility for MA, HB, and HA fly ash by 27%, 63%, and 72%, respectively (Figure 3-14). The negative values calculated for the acidic fly ash samples were produced by the significant amounts of Ni leached from these ash samples during treatment. The large calculated increases in Ni mobility for treated PD fly ash samples were produced by a few >0.5 LOD Ni concentrations in the treated ash SAR leachates. Note that all of these values were <LOQ.

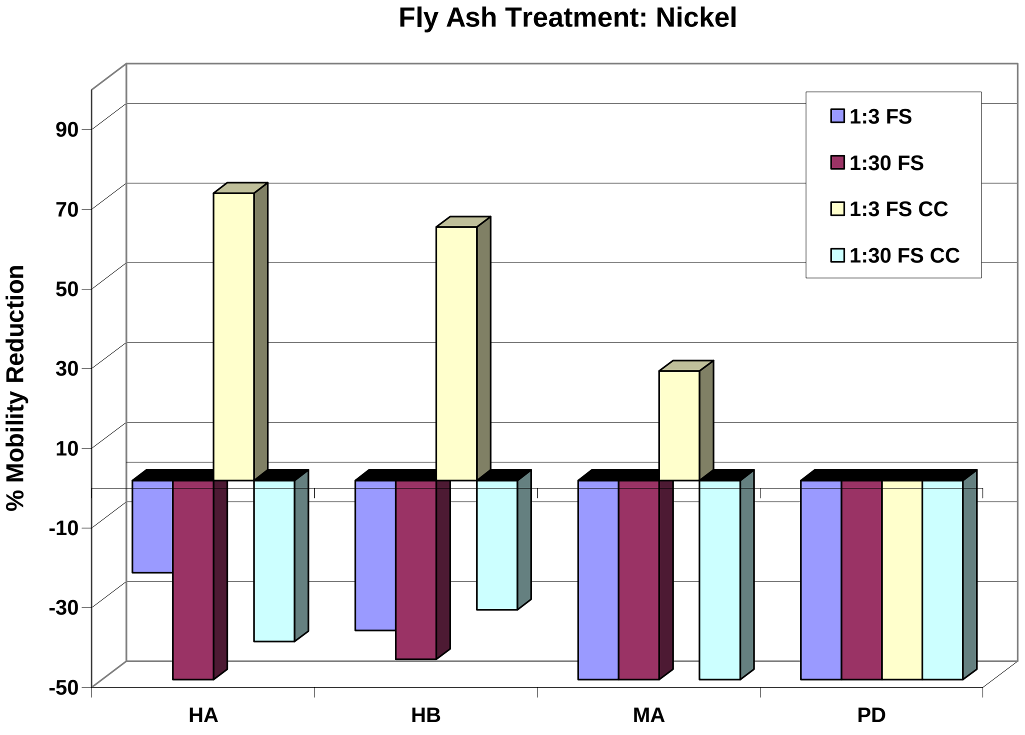


Figure 3-14
Percent reduction in nickel mobility for treated fly ash compared to untreated fly ash [Note: Negative scale is truncated]

3.3.2.6 Selenium

All untreated fly ash sample leachates showed a Se peak at between 25-30 days of SAR leaching (Figures B-1f, B-2f, B-3f, B-4f). The 1:3 FS+CC-treated acidic fly ash samples showed large Se releases compared to the untreated ash. Untreated HA and HB fly ash samples showed similar Se leaching patterns and comparable initial leachate Se concentrations, even though HA fly ash has approximately one-third the total Se concentration of HB fly ash (Table A-1). On the other hand, untreated MA fly ash did not release any Se initially, despite having a total Se concentration almost double that of HA fly ash (Table A-1). Although the Se leaching pattern for untreated PD fly ash was similar to that of Cr, initial leachate Se concentrations exceeded 0.3 mg/L, indicating higher Se mobility.

Figure 3-15 shows that the reduction in Se mobility for the various treatment techniques was similar to that of As, with the most effective treatment for the acidic fly ash samples being the 1:30 FS treatment, which decreased Se mobility by 67-87%. The 1:3 FS+CC treatment caused significant increases in Se mobility for the acidic fly ash samples, but resulted in the greatest reduction in Se mobility (52%) for the alkaline fly ash. All four treatment techniques were successful in reducing the mobility of Se for the PD fly ash.

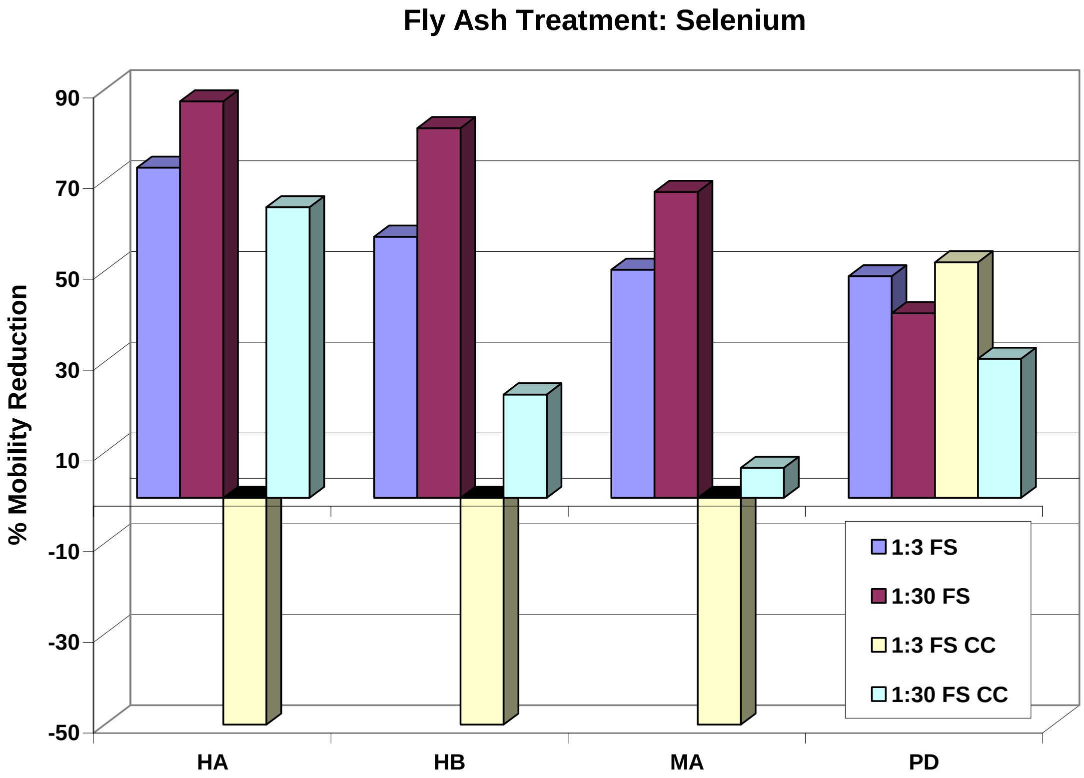


Figure 3-15
Percent reduction in selenium mobility for treated fly ash compared to untreated fly ash [Note: Negative scale is truncated]

3.3.2.7 Strontium

The Sr leachate concentration patterns were similar for all of the fly ash samples, exponentially decreasing from high initial values (Figures B-1g, B-2g, B-3g, B-4g). The high mobility of Sr in the acidic fly ash samples resulted in poor treatability (see below), although treated PD ash samples did show lower leachable Sr concentrations compared to the untreated fly ash.

Figure 3-16 shows that all of the acidic fly ash samples exhibited increased Sr mobility after treatment, except the 1:3 FS-treated HB ash, which showed a 32% reduction compared to untreated fly ash. All of the treatment techniques were effective for PD fly ash, reducing Sr mobility by 6-25%.

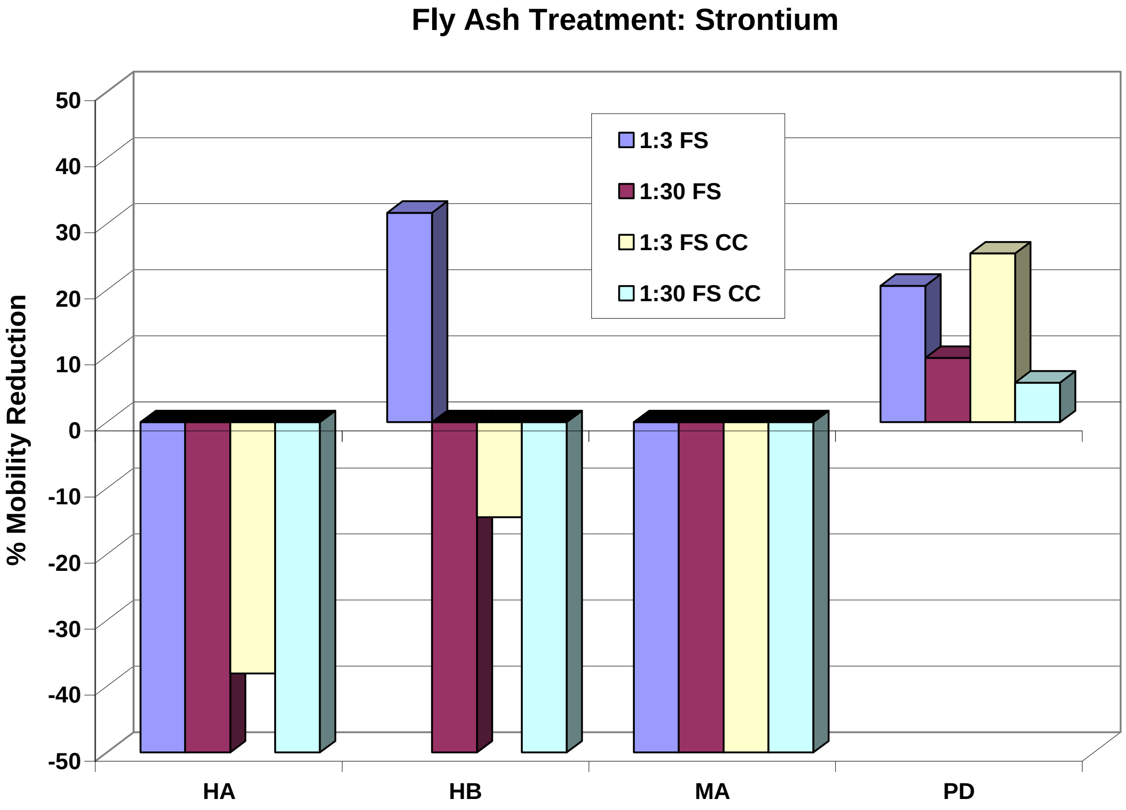


Figure 3-16
Percent reduction in mobility for treated fly ash compared to untreated fly ash for strontium [Note: Negative scale is truncated]

3.3.2.8 Vanadium

Vanadium concentrations in SAR leachate solutions were <LOD for the untreated and FS-treated acidic fly ash samples over the leaching period (Figures B-1h, B-2h, B-3h). All treated HB fly ash samples, the 1:3 and 1:30 FS+CC-treated HA fly ash, and the 1:3 FS+CC-treated MA fly ash occasionally released V concentrations >0.5 LOD, and were therefore included in the % mobility reduction/increase calculations (Table 3-4). The untreated HB fly ash did not release any V concentrations >0.5 LOD during SAR leaching (Table B-1), which produced large apparent releases of V from the % mobility reduction calculations. Vanadium was released by untreated PD fly ash early in the leaching period, but dropped below detection after 6 days (Figure B-4h). The 1:3 FS+CC treatment resulted in a peak V release of around 0.1 mg/L from all of the fly ash samples during the fifth day of leaching.

The 1:3 FS treatment was the most effective for HA fly ash, reducing V mobility by more than 98%, compared to the untreated ash (Figure 3-17). For MA fly ash, the 1:30 FS treatment reduced the mobility of V during SAR leaching by 100%, compared to the untreated ash. All four treatment methods reduced the mobility of V for PD fly ash; the 1:30 FS and 1:30 FS+CC treatments were the most effective, reducing V mobility by 70% and 64%, respectively.

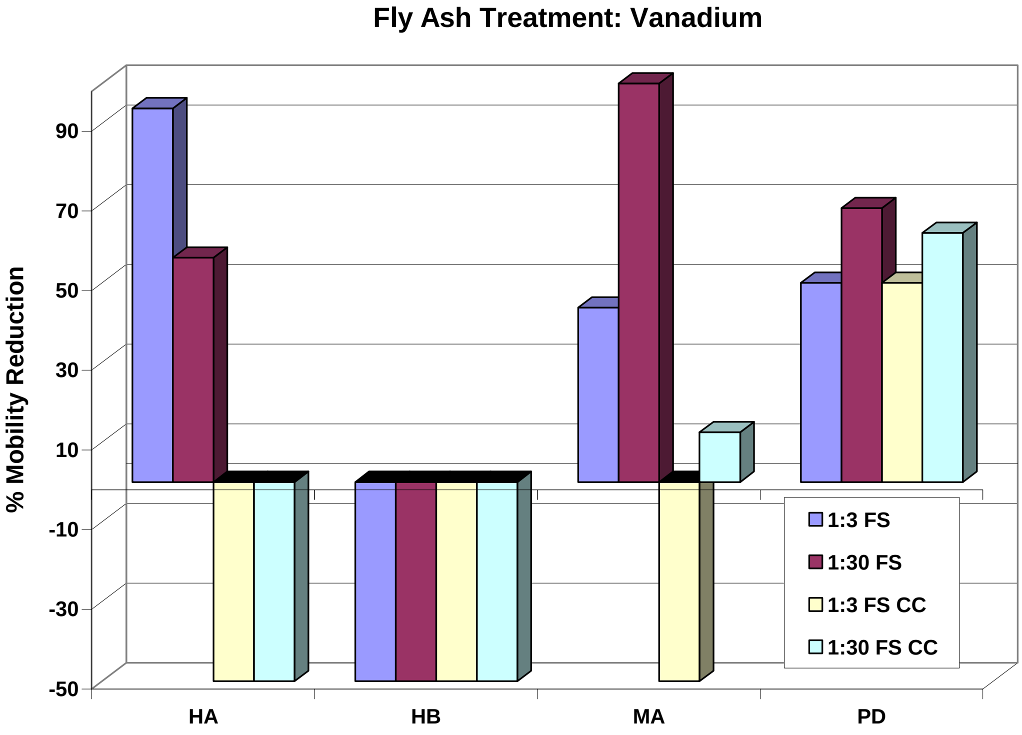


Figure 3-17
Percent reduction in mobility for treated fly ash compared to untreated fly ash for vanadium [Note: Negative scale is truncated]

Table 3-4
Percent Mobility Reduction/(Increase) of Trace Elements.
(*Large apparent increase in mobility reflects SAR leaching data <LOD for untreated ash).

	FS 1:3	FS 1:30	FS CC 1:3	FS CC 1:30		FS 1:3	FS 1:30	FS CC 1:3	FS CC 1:30
	As % Mobility Reduction (Increase)					**B % Mobility Reduction (Increase)**			
HA	68	91	(1130)	66	**HA**	(8)	(39)	(6)	(12)
HB	53	71	(1769)	49	**HB**	(24)	(56)	(40)	(39)
MA	63	79	(1751)	72	**MA**	(189)	(230)	(215)	(198)
PD	32	24	37	29	**PD**	3	4	2	(2)
	Cr % Mobility Reduction (Increase)					**Mo % Mobility Reduction (Increase)**			
HA	89	97	58	69	**HA**	88	100	(37)	27
HB	72	92	65	76	**HB**	66	97	(219)	(59)
MA	75	90	(54)	70	**MA**	75	94	(653)	(197)
PD	59	82	59	74	**PD**	25	79	4	33
	Ni % Mobility Reduction (Increase)					**Se % Mobility Reduction (Increase)**			
HA	(23)	(59)	72	(41)	**HA**	73	87	(83)	64
HB	(38)	(45)	64	(33)	**HB**	58	82	(268)	23
MA	(221)	(243)	27	(179)	**MA**	50	67	(478)	7
PD	(748)*	(731)*	(3529)*	(3360)*	**PD**	49	41	52	31
	Sr % Mobility Reduction (Increase)					**V % Mobility Reduction (Increase)**			
HA	(70)	(164)	(38)	(54)	**HA**	97	55	(671)	(114)
HB	32	(181)	(14)	(67)	**HB**	(9085)*	(6366)*	(193852)*	(28107)*
MA	(70)	(197)	(66)	(103)	**MA**	40	100	(268)	10
PD	21	10	26	6	**PD**	46	70	46	64

3.3.2.9 Discussion

SAR leaching results are summarized in Table 3-4. Although Ni and Sr solubility would be expected to be increased at the pH of the FS treatment solution (pH = 4.2), changes in leachate pH with time do not appear to have had any significant control on trace element mobility trends during SAR sequential leaching of a particular fly ash sample. However, changes in the pH of the leachate caused by the addition of calcium carbonate buffer significantly affected the mobility of the oxyanion trace elements. The increased mobility of As and Se observed for the acidic fly ash samples that resulted from the addition of calcium carbonate to the ferrous sulfate treatment solution can be explained by desorption of these oxyanions from the $Fe(OH)_3$ surface due to the increase in the pH of the leachate solutions. Geochemical modeling indicates the aqueous speciation of boron in the acidic fly ash leachate solutions is $B(OH)_3$. The increase in pH caused by the addition of calcium carbonate buffer therefore would be expected to have little to no effect on the adsorption of this neutral boron species. Precipitation of Ni and Sr carbonate phases would require much higher pH values than were observed in these experiments. The acidic fly ash samples showed the highest Ni sequestration for the 1:3 FS+CC treatment, consistent with increased adsorption of cations by the negatively charged $Fe(OH)_3$ surfaces. The mobility of the oxyanions was not affected by an increase in the pH of the leachates of the alkaline PD fly ash. Hence, the 1:3 FS treatment did not mobilize As and Se from PD fly ash.

3.4 Results of Fly Ash Sequential Chemical Extractions

The 7-step sequential chemical extraction procedure (SCEP) was carried out to fractionate and compare the trace element distributions in the untreated and ferrous sulfate-treated fly ash samples and thereby better understand the mechanism(s) by which FS treatment immobilizes trace elements. The FS+CC-treated fly ash samples were not used for this study because this treatment was not considered viable due to the large scale mobilization of many of the trace elements by SAR sequential leaching. Figures 3-18 through 3-25 show the results of the SCEP for untreated, 1:3 FS-treated, and 1:30 FS-treated fly ash samples. Step 2-5 totals include any trace element removed by the DDI water wash following the extraction step. Mass balance totals for the treated fly ash samples include the amount of trace element leached by the treatment process, if any. Treated ash mass balance totals that fall within 20% of the untreated ash total should be regarded as excellent, considering the cumulative experimental and analytical error inherent with the extraction technique.

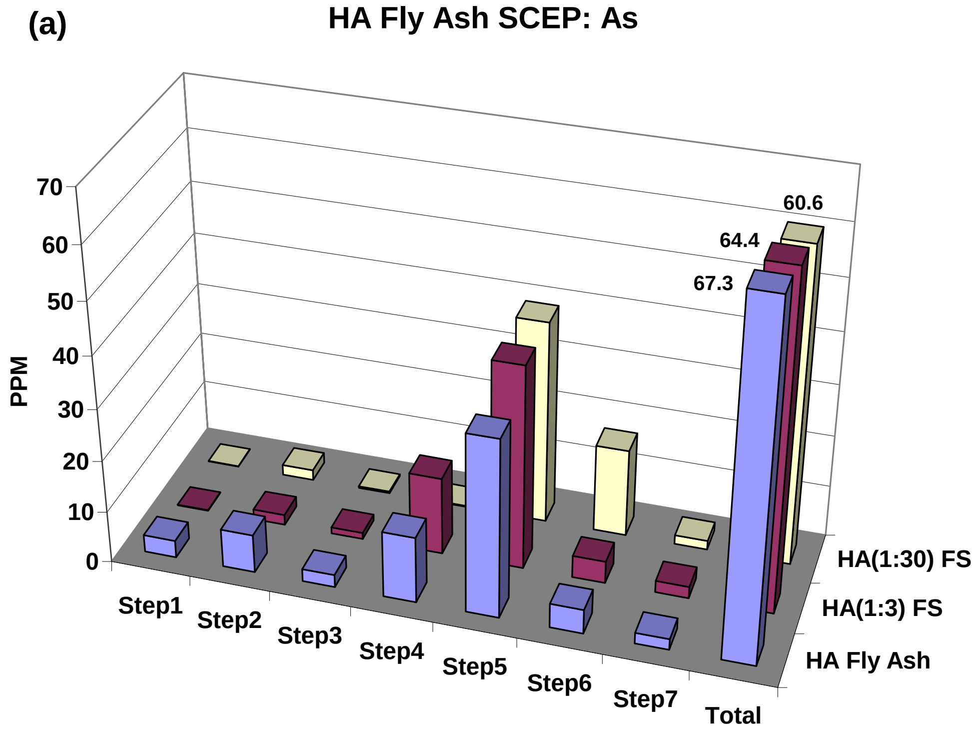
The SCEP separates the fly ash elemental composition into seven different fractions. The water soluble fraction (Step 1) is the most mobile fraction, followed by the exchangeable (Step 2) and the acid soluble (Step 3) fractions. For the oxidizing conditions typical of fly ash disposal facilities, the reducible fractions are the most stable, with the easily reducible fraction (Step 4) being the least stable (but potentially having the highest CEC), and the poorly reducible fraction (Step 6) having the highest stability (but lowest CEC). In a reducing environment, the organic and sulfide fraction (Step 7) would be most stable. A treatment technique can be deemed successful if it transfers the trace elements from more mobile fractions to less mobile fractions.

Figure 3-18 compares the sequential chemical extraction results for the distribution of arsenic in FS-treated and untreated fly ash samples. It can be seen that the 1:3 FS treatment transfers much of the mobile arsenic in the three acidic fly ash samples (Figure 3-18a, b, c) from the water soluble, exchangeable, and acid soluble fractions (Steps 1-3) to the moderately reducible fraction (Step 5), which consists largely of poorly crystalline iron and aluminum oxides. The 1:30 FS treatment also moved As from the easily reducible fraction (Step 4) to crystalline iron and aluminum oxides in the poorly reducible fraction (Step 6). Untreated PD fly ash (Figure 3-18d) had the lowest As concentration and a higher proportion of the total As in the exchangeable fraction (Step 2) and lower proportions in the easily and poorly reducible fractions (Steps 4 and 6) than the acidic fly ash samples. The 1:3 FS treatment appears to have had little effect on the arsenic distribution in PD fly ash, but the 1:30 FS treatment transferred As from the exchangeable and easily reducible oxide fractions to the crystalline oxide fraction (Figure 3-18d). All treated fly ash SCEP mass balance errors are <20% for As.

Figure 3-19(a-c) shows that FS treatment leached most of the B present in the water soluble fraction for all of the acidic fly ash samples, with the greatest removal being accomplished at the 1:30 solid to liquid ratio (Figure 3-4b; Table 3-2). Most of the exchangeable B was also leached from these samples by FS treatment. However, FS treatment made no changes in the B concentrations in the other fractions of HA, HB, and MA fly ash. PD fly ash had approximately an order of magnitude higher B concentration than the acidic fly ash samples (Table A-1). The 1:3 FS treatment moved almost half of the water soluble B from PD fly ash (about 10% of the original B was removed by the treatment process), transferring it to the residual fraction (Figure 3-19d). The 1:30 FS treatment was the most effective, moving most of the B in the water soluble and the exchangeable fractions to the residual fraction. Boron mass balance errors are <10%.

Figure 3-20(a-c) shows that Cr in the acidic fly ash samples was transferred by the 1:3 FS treatment from the water soluble and exchangeable fractions to the reducible fractions. The 1:30 FS treatment also transferred Cr from the acid soluble fraction and concentrated it in the moderately reducible oxide fraction (Step 5). The 1:3 FS treatment of PD fly ash showed little effect on the Cr fractionation, but the 1:30 treatment moved Cr from the exchangeable and acid soluble fractions to the moderately reducible oxide fraction (Figure 3-20d). Mass balances for Cr were within 20%, with the exception of that for the 1:30 FS-treated MA fly ash (36% error).

Untreated HA and HB fly ash have similar Mo distributions, with the highest concentration in the water soluble fraction and small amounts of Mo in the exchangeable (Step 2), easily reducible oxide (Step 4), and poorly reducible oxide (Step 6) fractions (Figure 3-21a,b). Untreated MA fly ash has less water soluble Mo and more Mo in the exchangeable and poorly reducible oxide fractions than the other acidic fly ash samples (Figure 3-21c). Despite this difference, the 1:3 FS treatment removed the water soluble Mo from the acidic fly ash samples and moved it primarily to the exchangeable fraction. The 1:30 FS treatment transferred the water soluble Mo largely to the moderately reducible oxide (Step 5) fraction for HA, HB, and MA fly ash. FS treatment removed a portion of the Mo in the water soluble and exchangeable fractions, but only resulted in a small increase in Mo in the moderately reducible fraction at the 1:30 treatment ratio (Figure 3-21d). Mass balances for Mo are generally poor, which may be explained by fly ash heterogeneity and by propagation of analytical error.



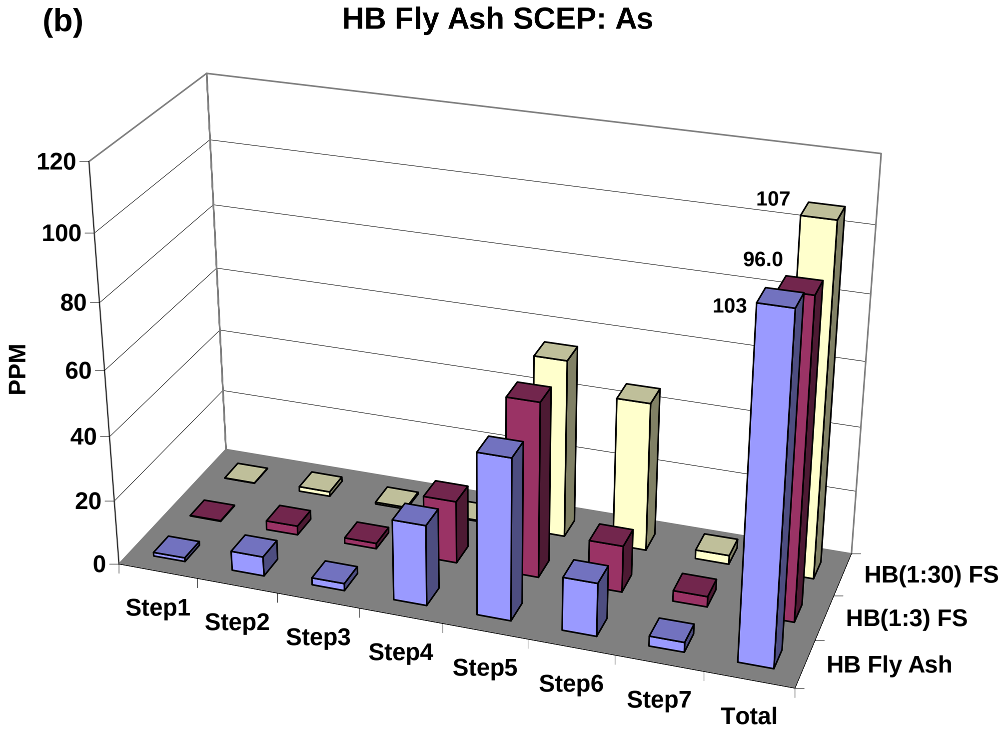
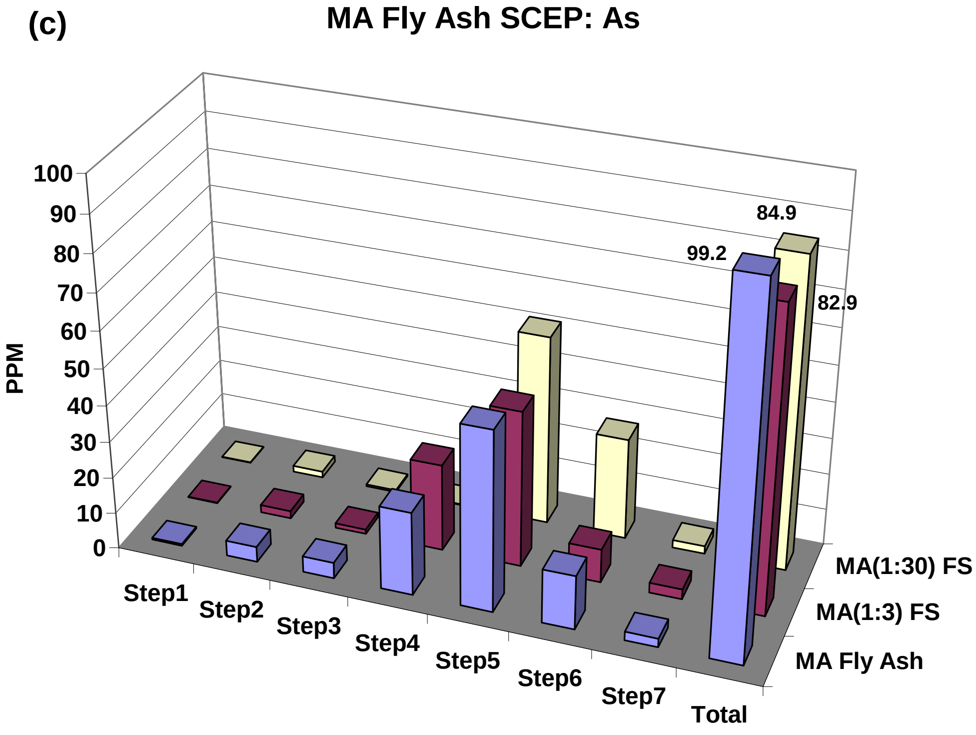


Figure 3-18
Distribution of arsenic in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash



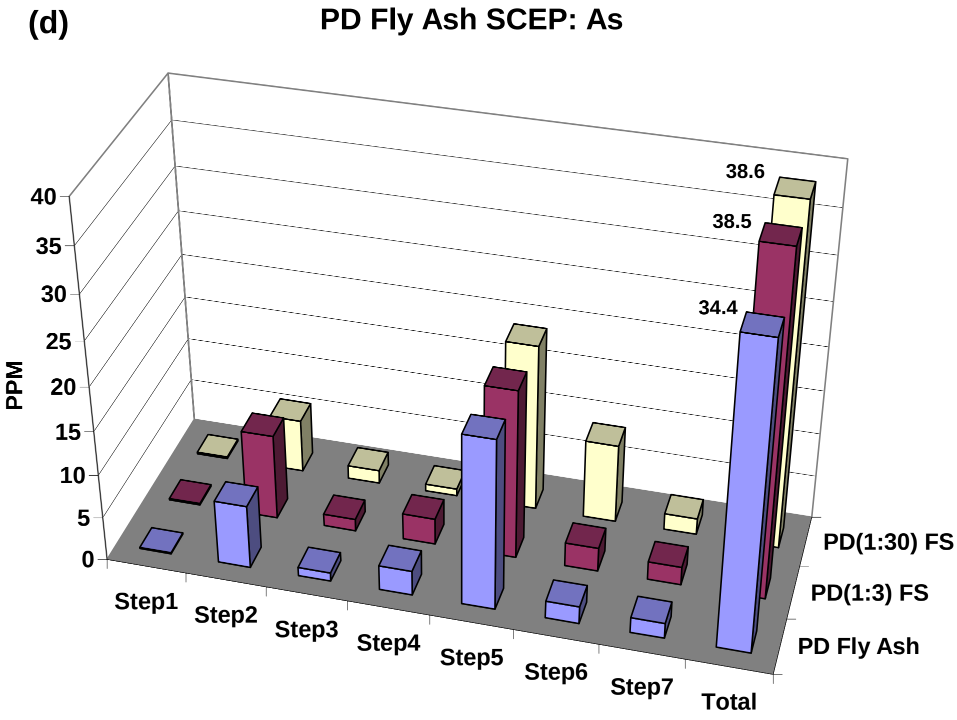
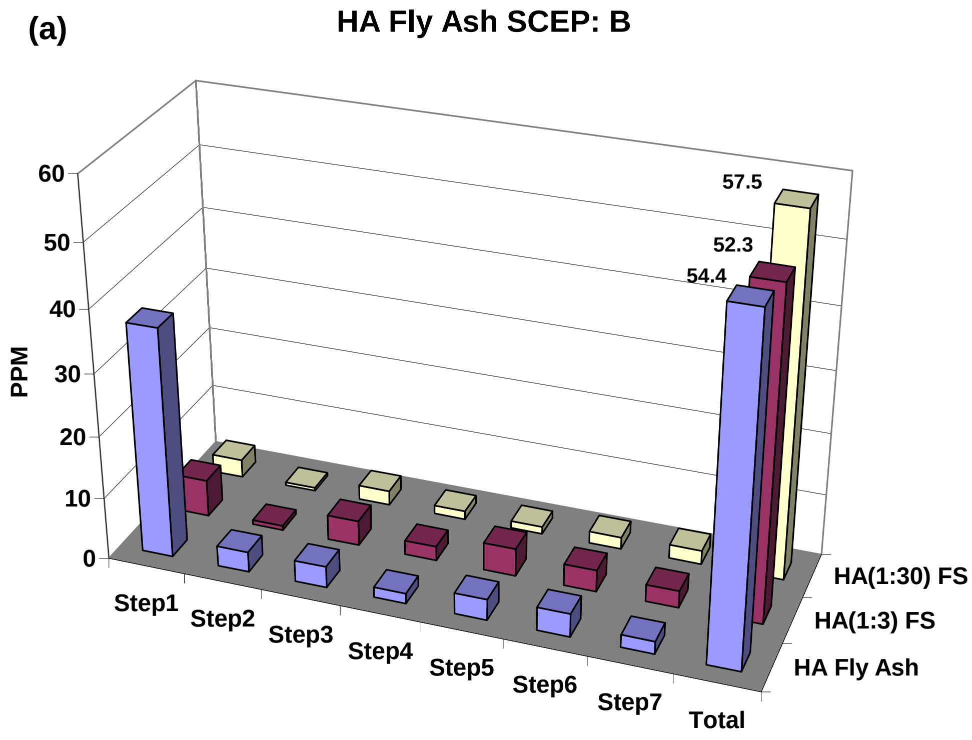


Figure 3-18 (Continued)
Distribution of arsenic in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash



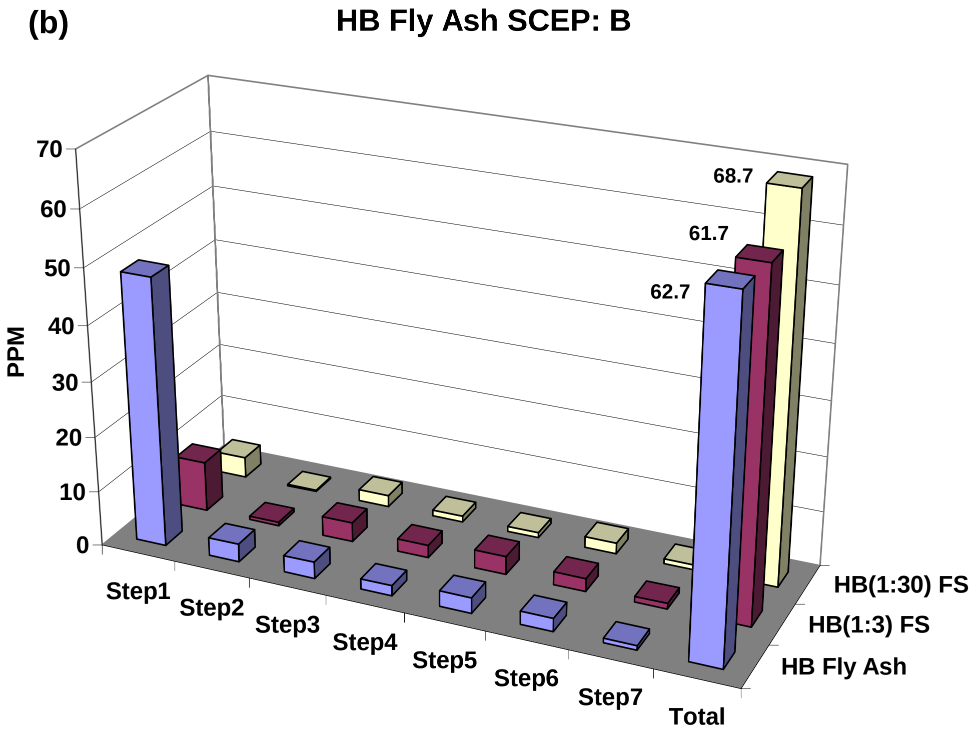
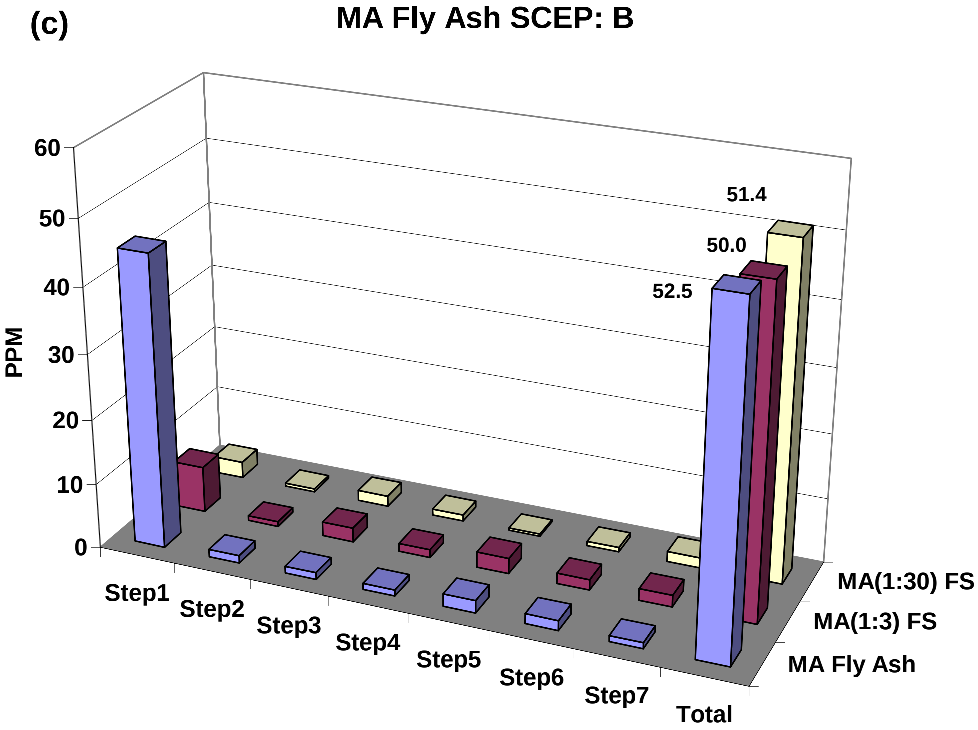


Figure 3-19
Distribution of boron in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash



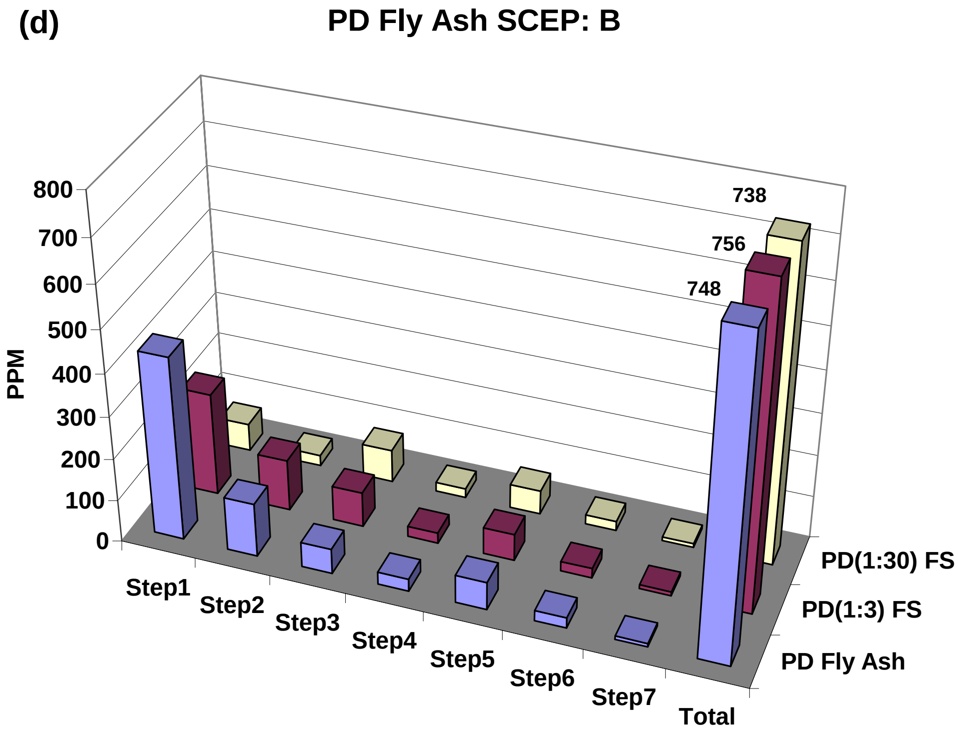
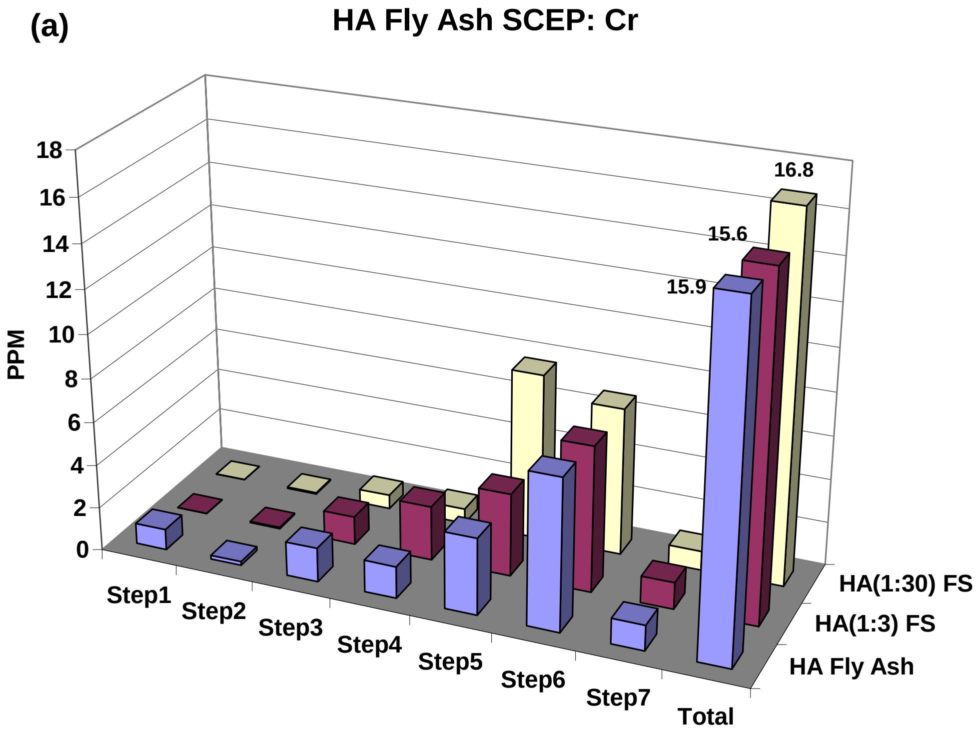


Figure 3-19 (Continued)
Distribution of boron in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash



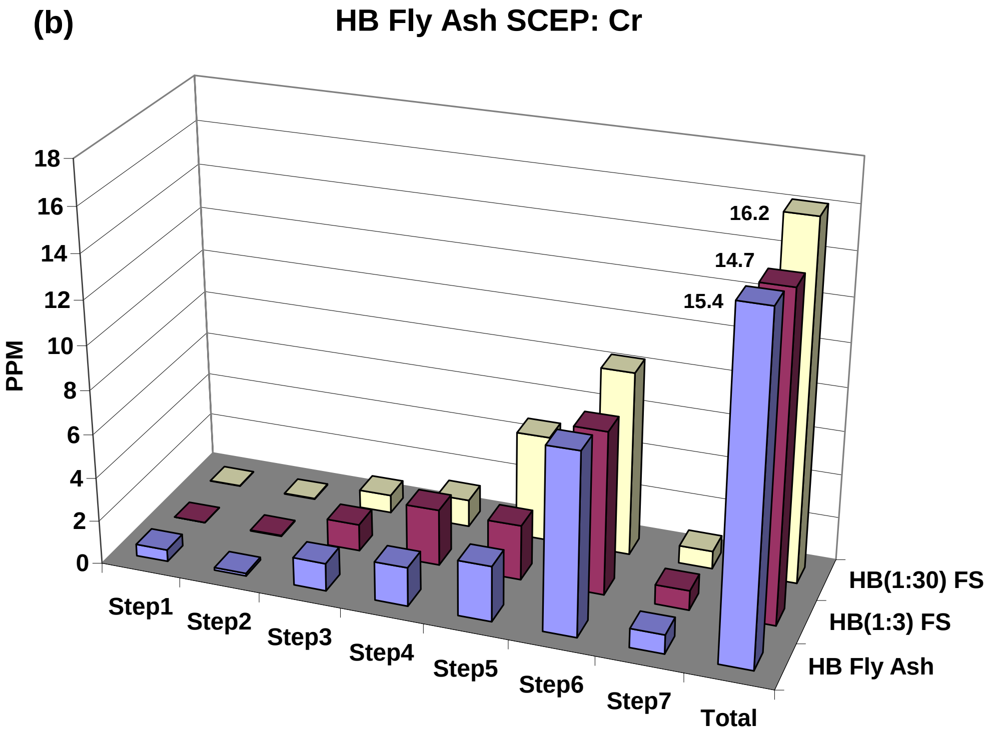
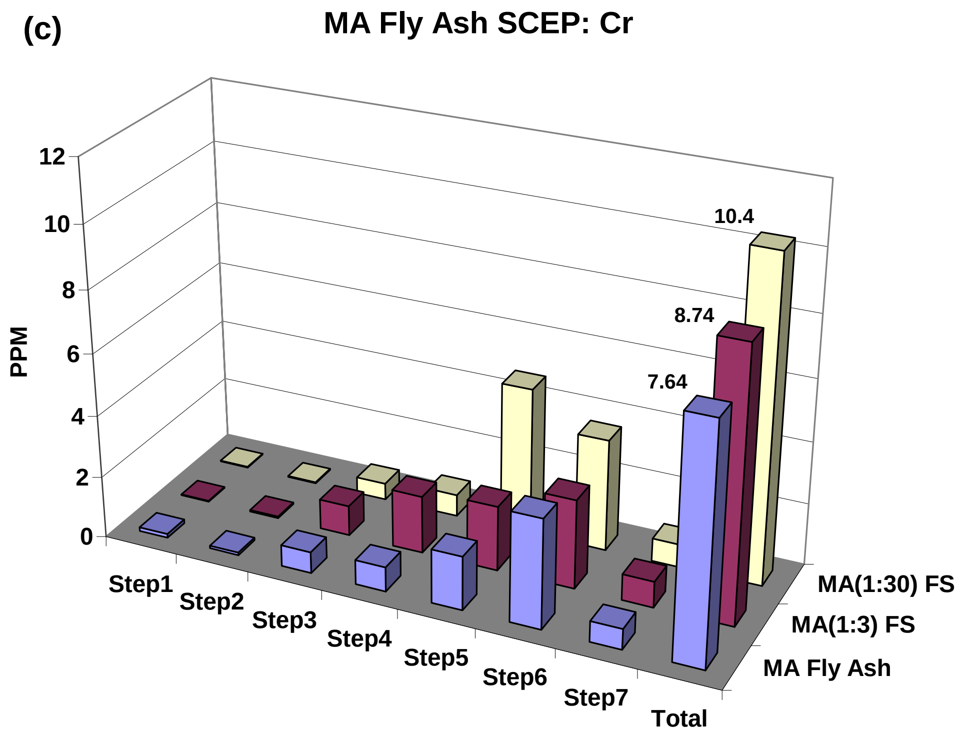


Figure 3-20
Distribution of chromium in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash

(c)



(d)

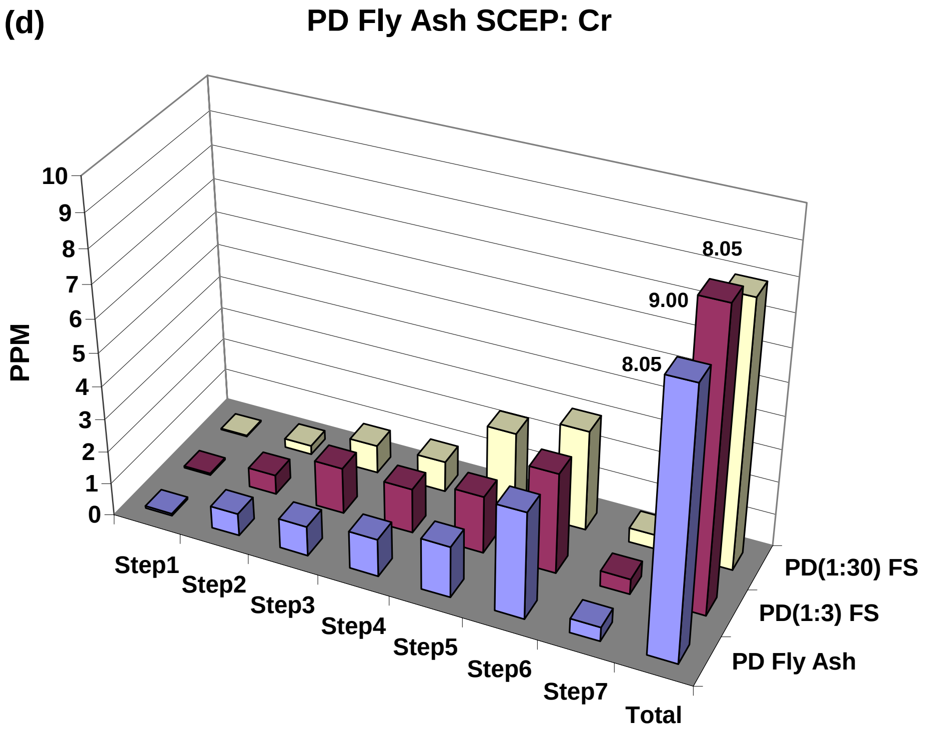
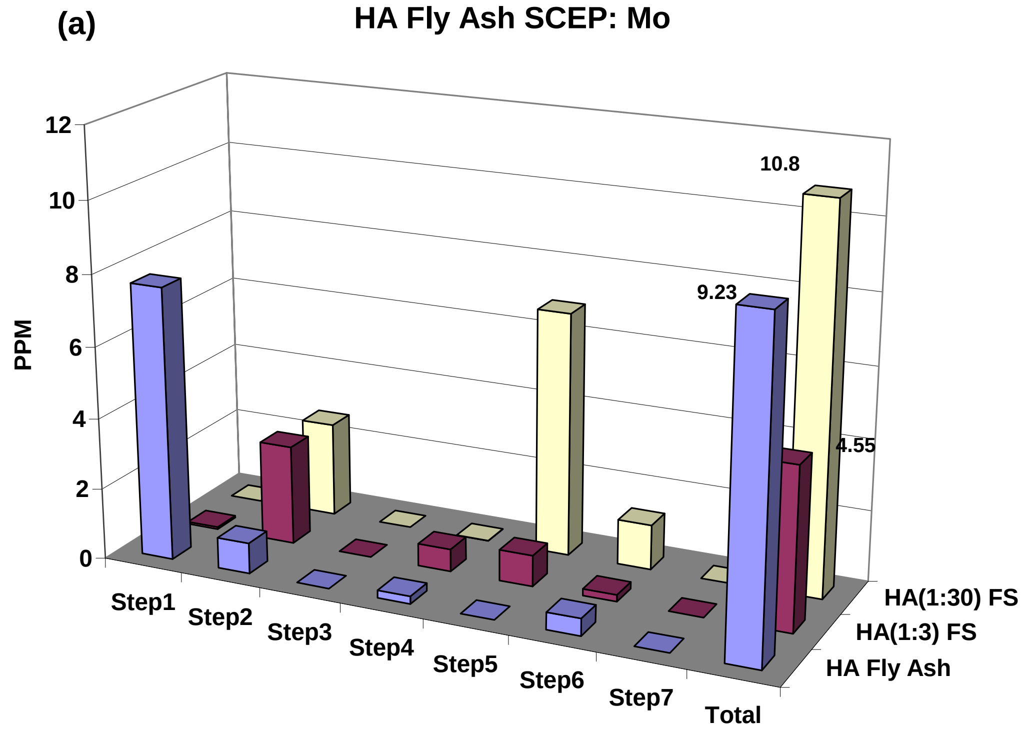


Figure 3-20 (Continued)
Distribution of chromium in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash



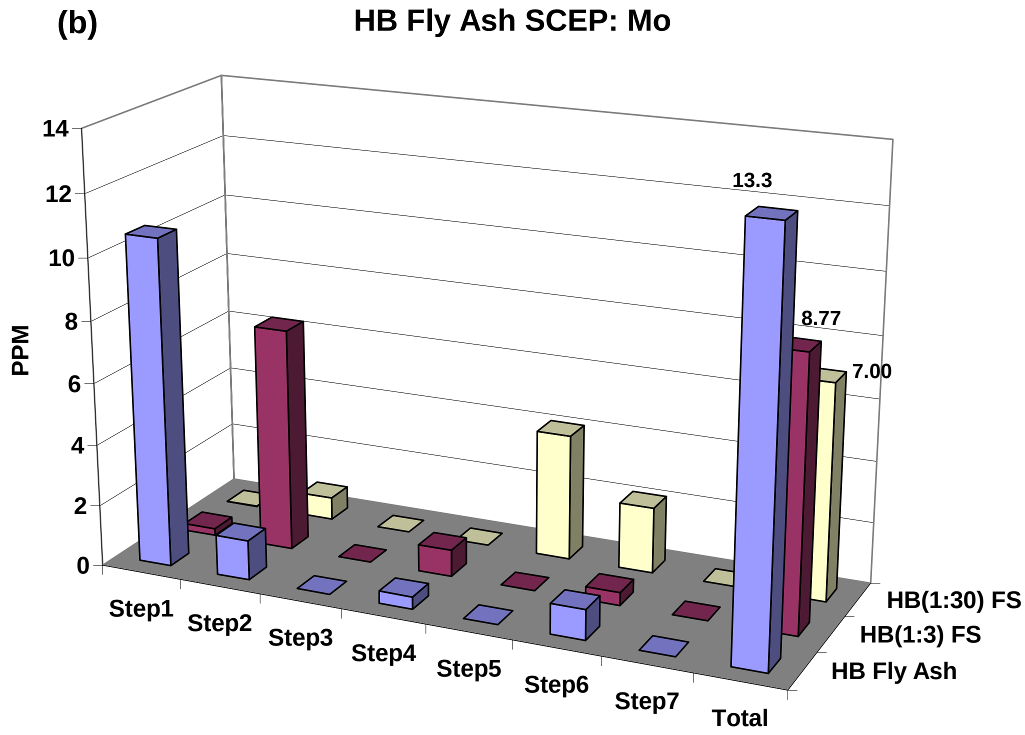
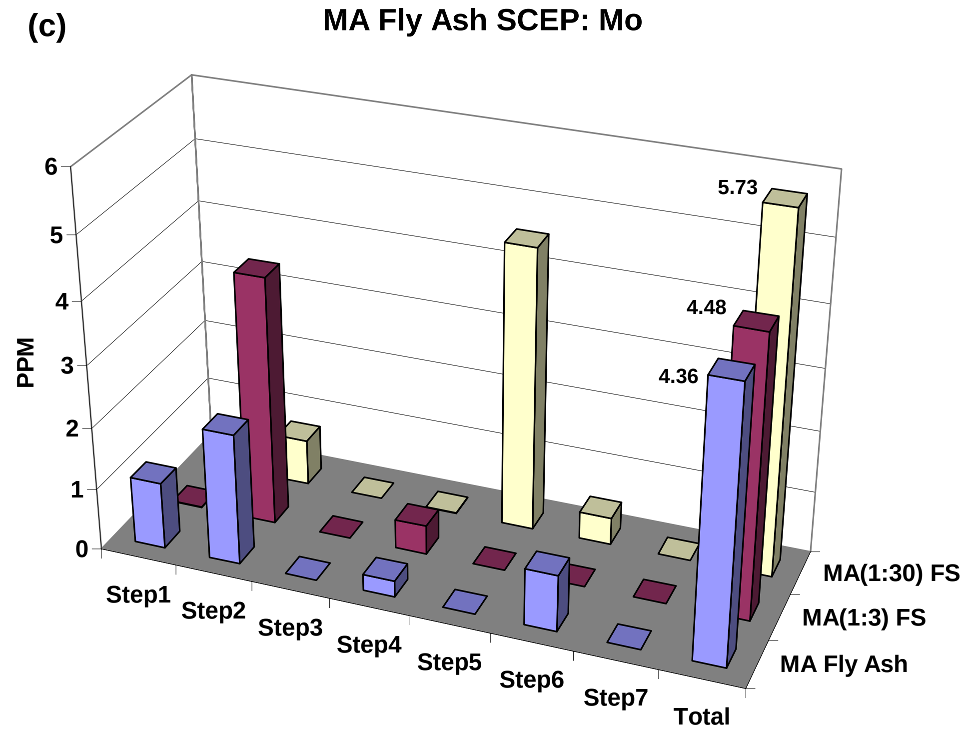


Figure 3-21
Distribution of molybdenum in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash



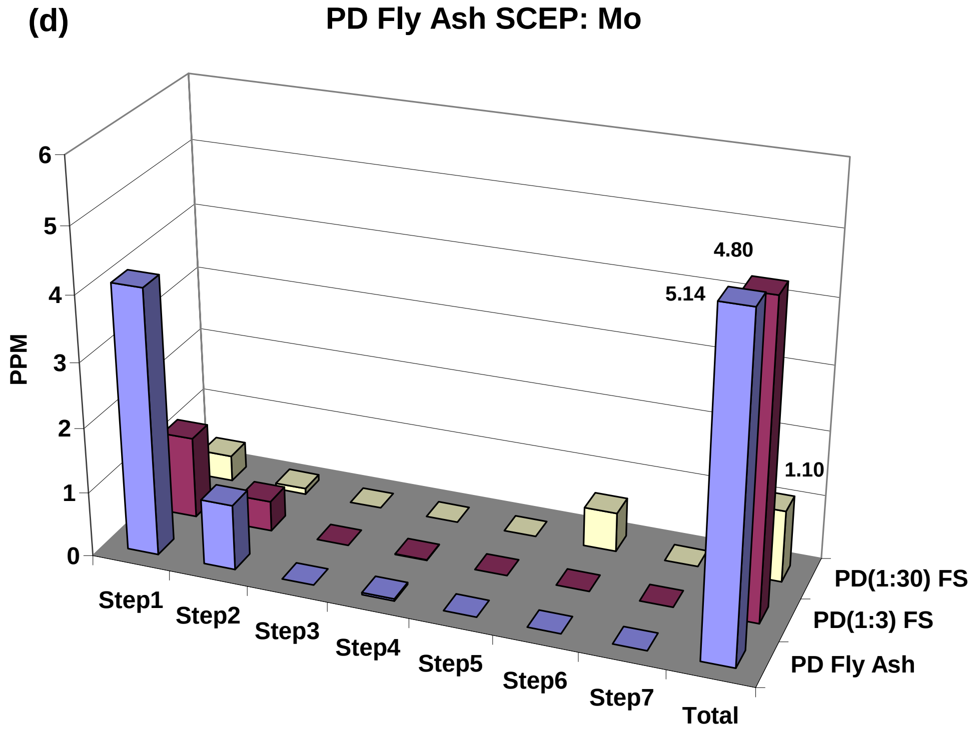
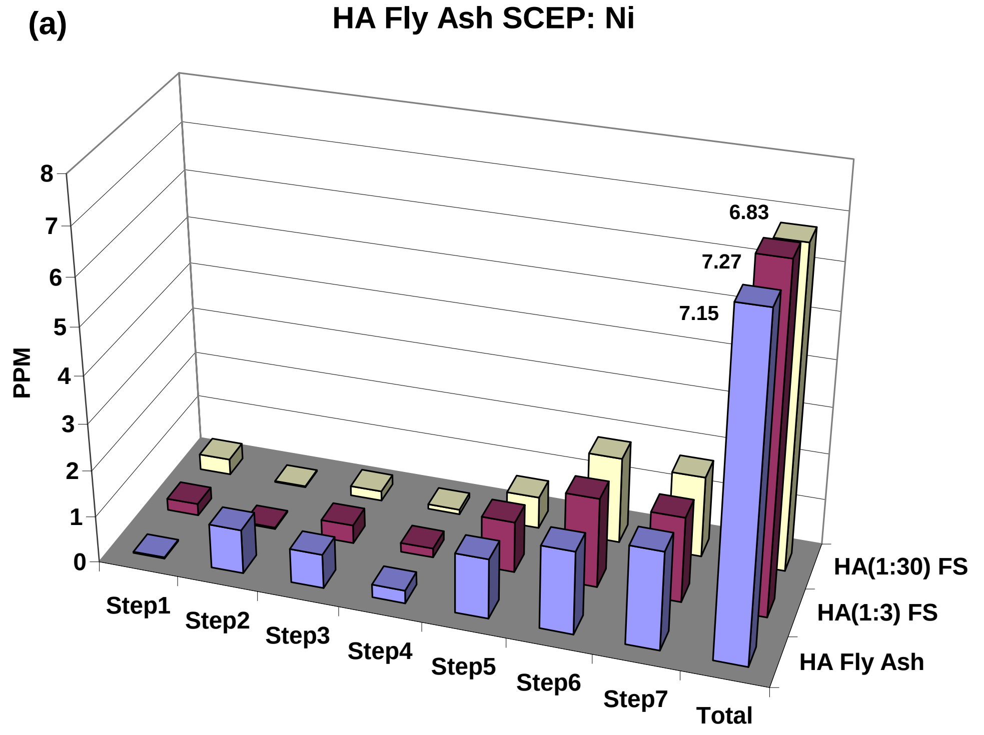


Figure 3-21 (Continued)
Distribution of molybdenum in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash

Nickel is mostly concentrated in the poorly reducible and oxidizable fractions of the acidic fly ash, although untreated MA fly ash has the highest concentration of Ni in the water soluble fraction, whereas both untreated HA and HB fly ash have little water soluble Ni and have higher Ni concentrations in the moderately reducible, exchangeable, and acid soluble fractions (Figure 3-22a-c). Considering the most mobile ash fractions (i.e., Steps 1-3), the SCEP data show an apparent increase in water soluble Ni for FS-treated HA fly ash, compared to the untreated ash. This is also the case for 1:3 FS-treated HB fly ash. Because of this apparent increase, HA and HB fly ash were both calculated to have a net increase in Ni mobility with FS treatment (Figure 3-14), although little to no Ni was leached from HA or HB fly ash during treatment (Figure 3-6a) and FS-treated HA and HB ash released significantly less Ni upon SAR sequential leaching than the untreated ash samples (Figures B-1e and B-2e). The apparent increase in water soluble Ni with FS treatment for these ash samples is therefore likely an artifact produced by sample heterogeneity. FS treatment had little effect on Ni mobility in PD fly ash, although the 1:30 FS treatment appears to have moved small amounts of Ni to the exchangeable and acid soluble fractions at the expense of the easily and poorly reducible oxide fractions (Figure 3-22d), resulting in a net increase in Ni mobility. All Ni mass balances have <20% error and in all but two cases have <10% error.

The 1:3 FS treatment transferred the Se from the water soluble fraction to the easily reducible and poorly reducible fractions for all of the acidic fly ash samples (Figure 3-23a-c). The 1:30 FS treatment moved all of the mobile Se to the poorly reducible oxide fraction for HA and HB fly ash, but a portion was also transferred to the oxidizable fraction for MA fly ash. For PD fly ash, the 1:3 FS treatment redistributed some of the water soluble Se between the exchangeable, acid soluble, and poorly reducible fractions (Figure 3-23d). The 1:30 FS treatment of PD fly ash lowered Se concentrations in the water soluble and the poorly reducible fractions and increased the Se concentration in the oxidizable fraction. Mass balance errors for Se were >20% in all but two cases, due to unexplained loss of Se in the treated ash samples relative to the untreated fly ash.

Figure 3-24(a) shows that FS treatment of HA fly ash caused apparent increases in the concentration of Sr in the water soluble fraction and decreased the Sr concentrations in the easily and moderately reducible ash fractions. The 1:30 FS treatment also removed some Sr from the HA fly ash acid soluble fraction. The concentration of Sr in the water soluble fraction of HB fly ash appears to have been decreased by the 1:3 FS treatment, but does not appear in the treatment solution (Table 3-2). For the 1:30 FS treatment of HB fly ash, loss of water soluble Sr was accomplished mostly through leaching by the treatment solution and also through transfer to the exchangeable fraction (Figure 3-24b). Otherwise, the effects of FS treatment on the distribution of Sr in HB fly ash were similar to those observed for HA fly ash. The effects of FS treatment on Sr mobility in MA fly ash were similar to those observed for HB fly ash (Figure 3-24c), although Sr was mobilized at both S:L ratios. The 1:3 FS-treated PD fly ash showed a transfer of Sr from the water soluble fraction to the exchangeable concentration (Figure 3-24d). The 1:30 FS treatment leached more Sr than the 1:3 FS treatment during the treatment process for all of the ash samples, causing a net increase in Sr mobility (Figure 3-16). Although mass balances for FS-treated PD ash were excellent (<5% error), mass balance errors ranged from 16% to 54% for the other treated fly ash samples.



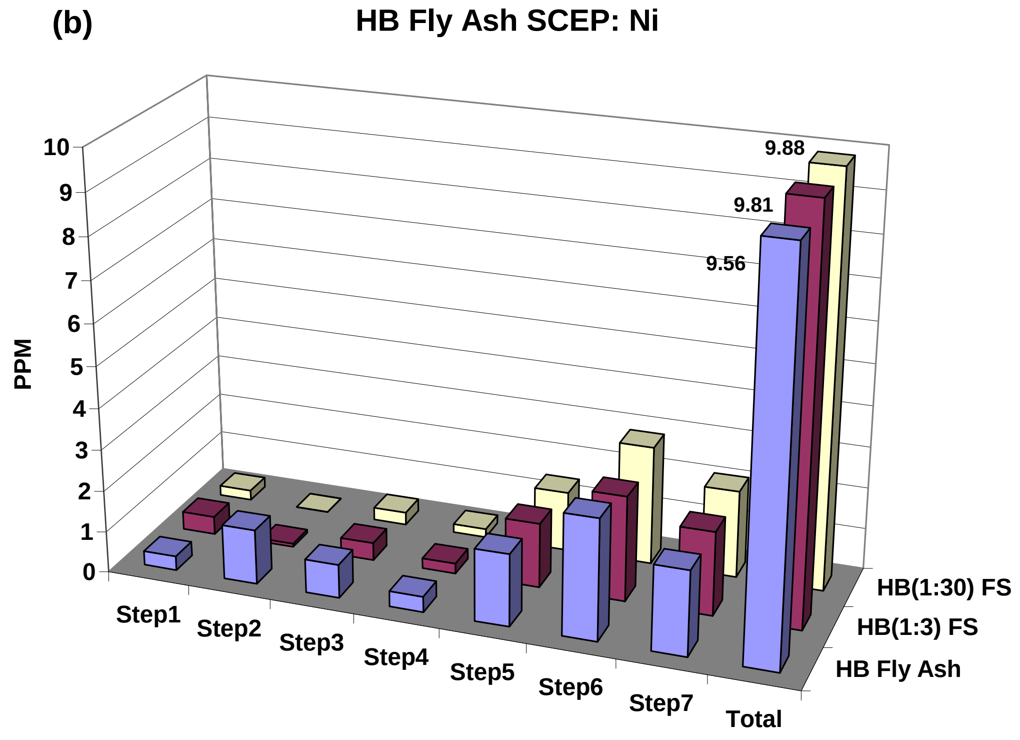
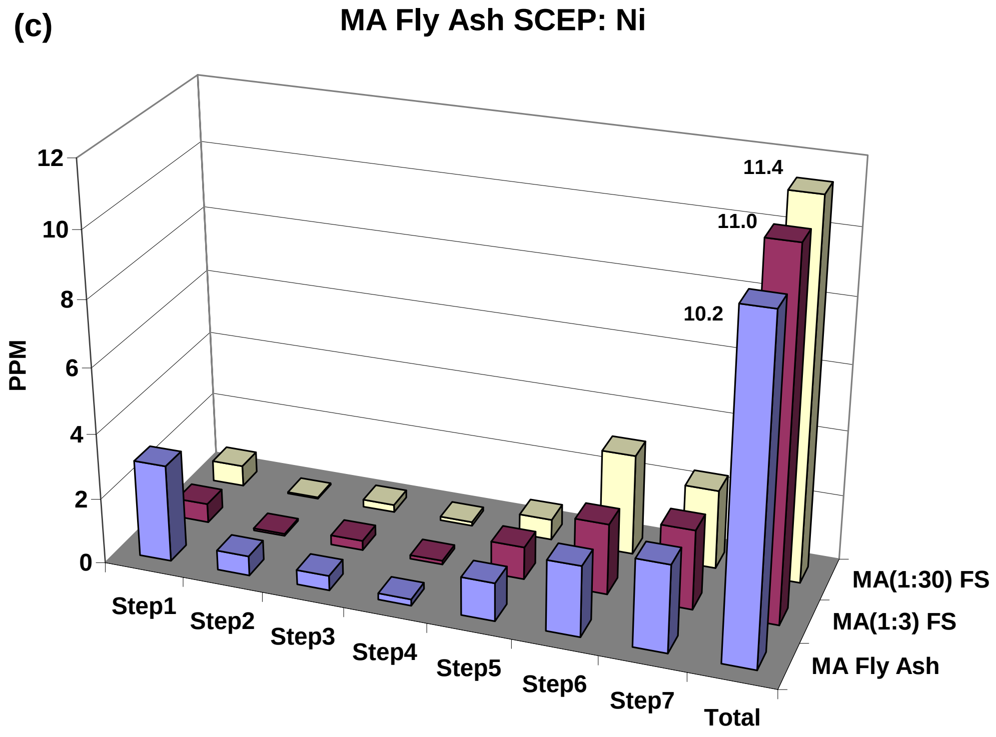


Figure 3-22
Distribution of nickel in FS treated and untreated fly ash, as determined by SCEP: HA fly ash; HB fly ash



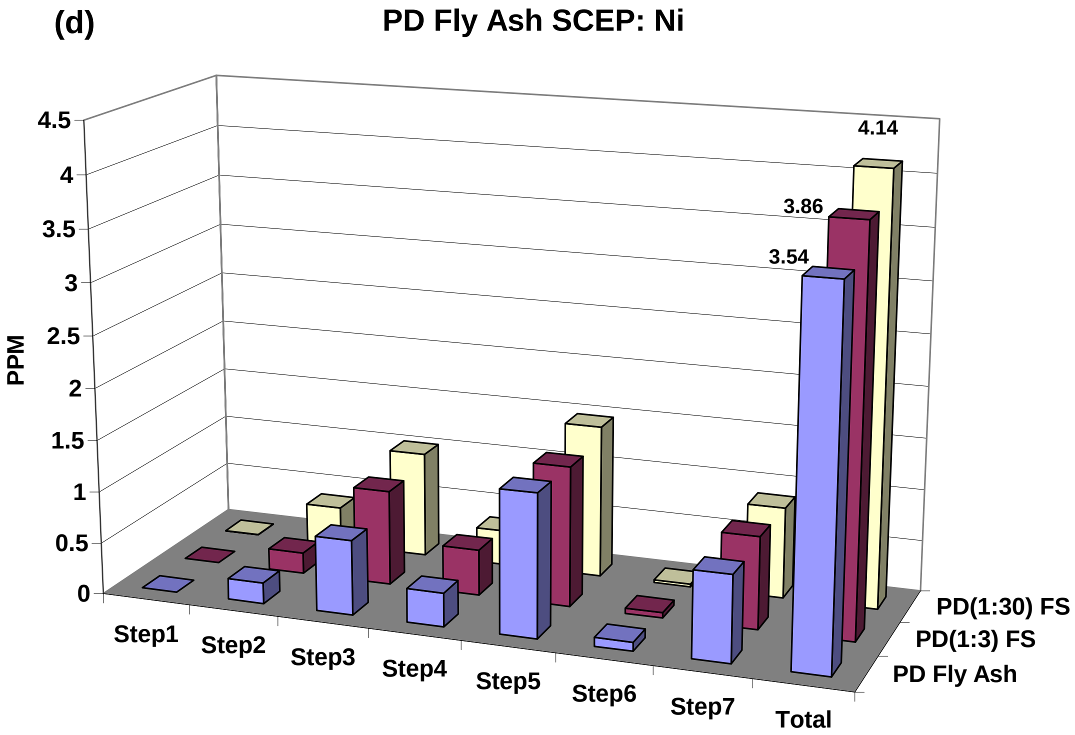
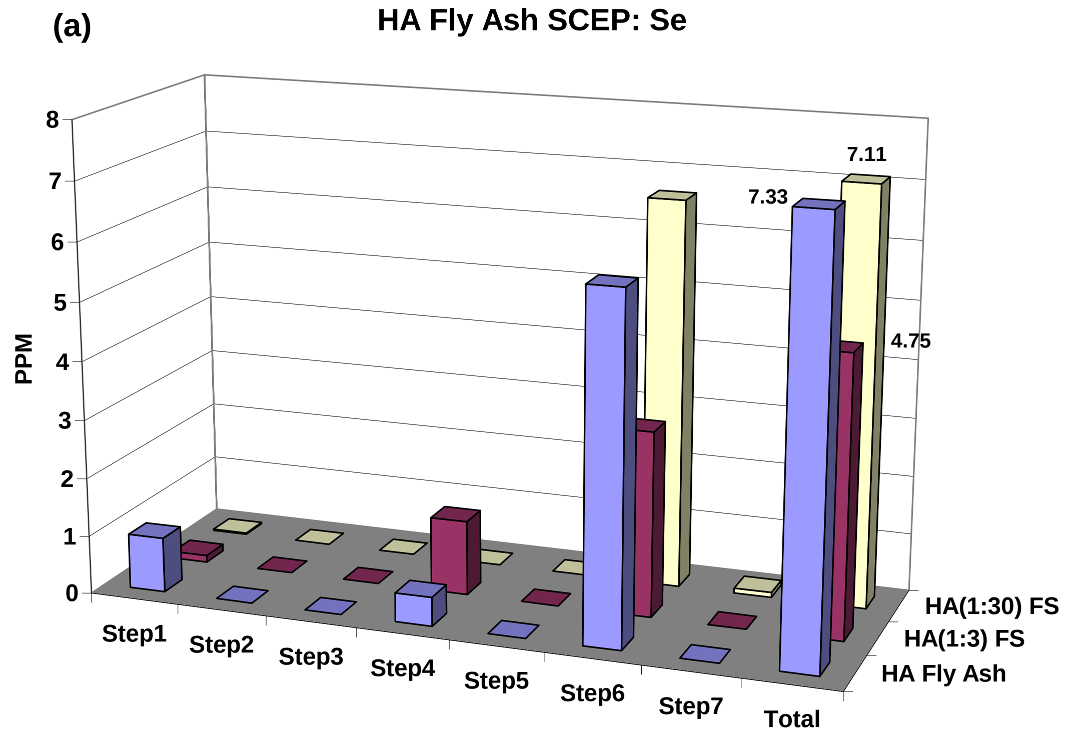


Figure 3-22 (Continued)
Distribution of nickel in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash



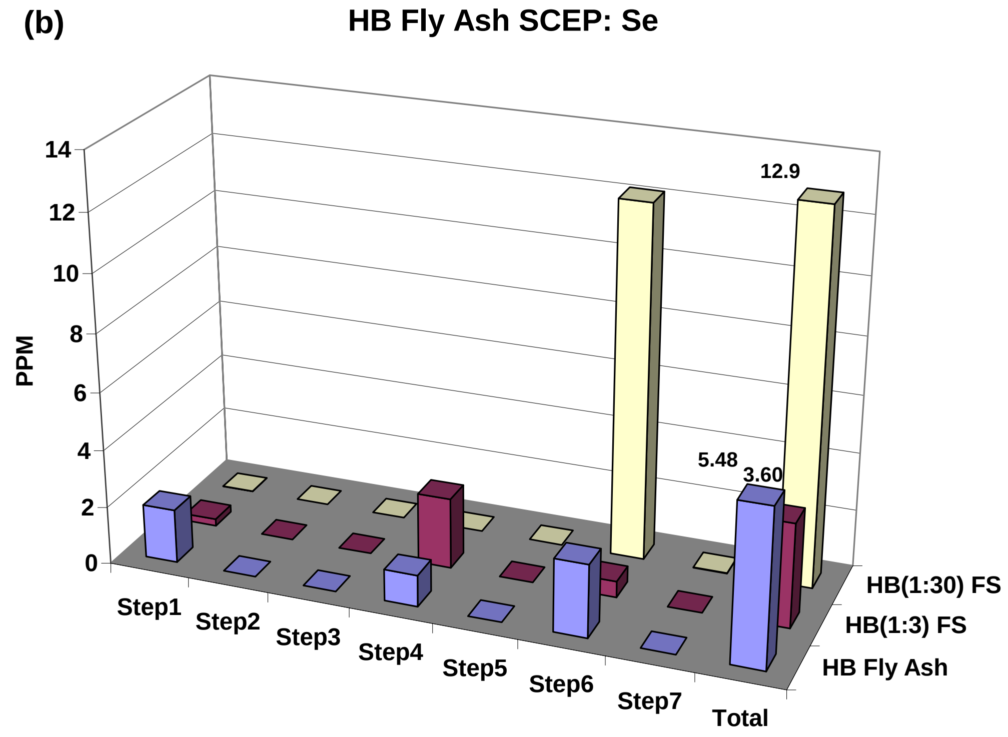
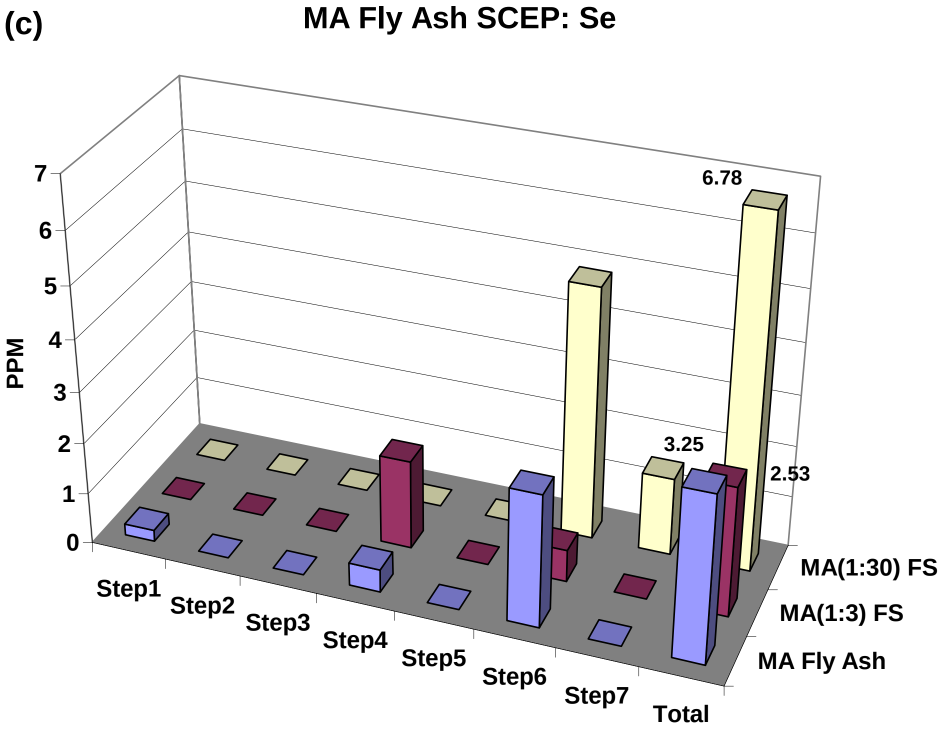


Figure 3-23
Distribution of selenium in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash



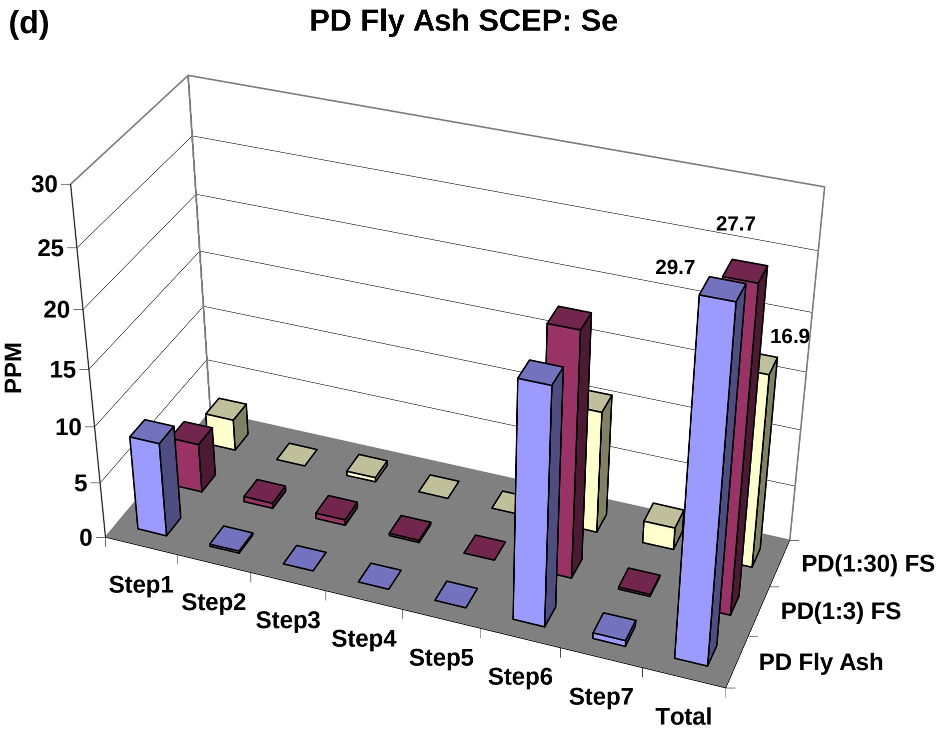
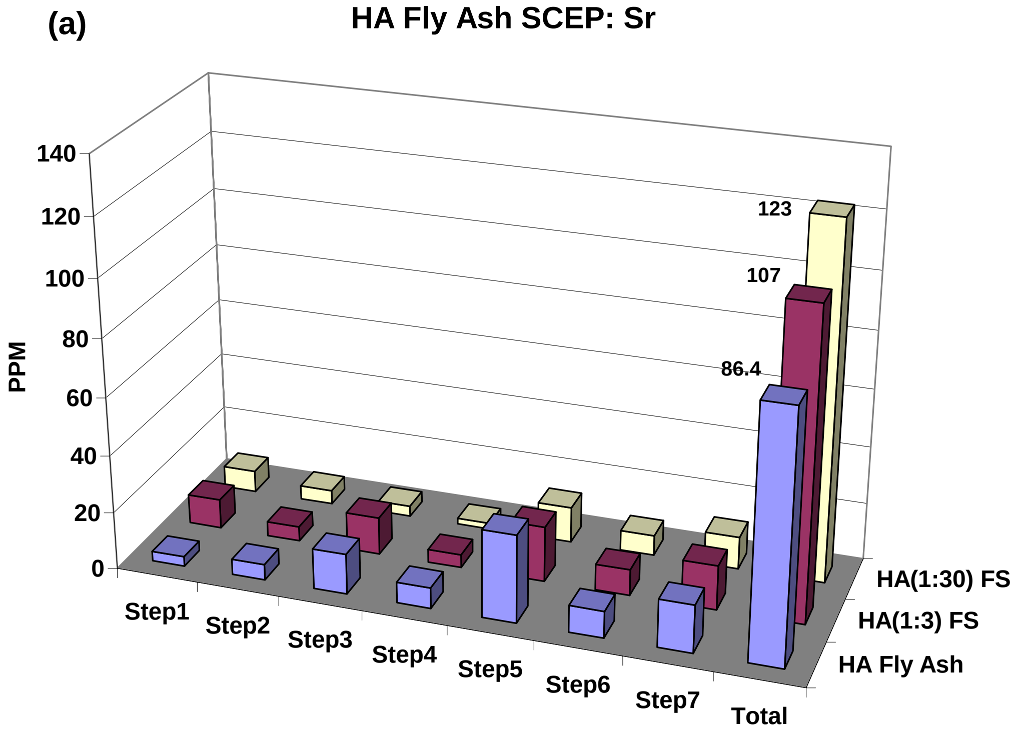


Figure 3-23 (Continued)
Distribution of selenium in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash



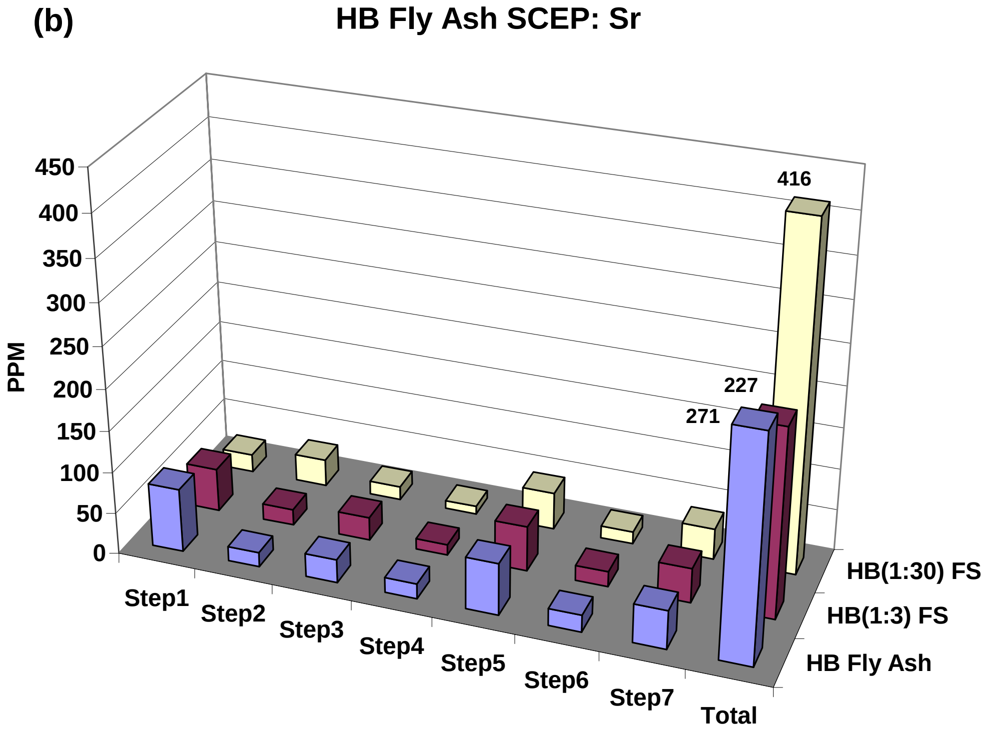
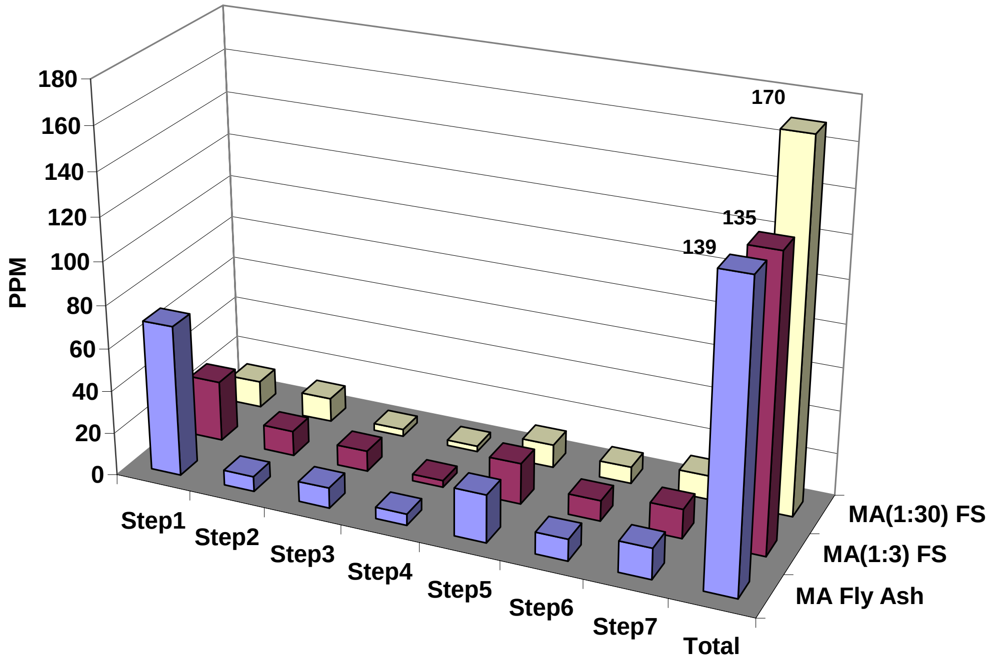


Figure 3-24
Distribution of strontium in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash

(c) **MA Fly Ash SCEP: Sr**



(d) **PD Fly Ash SCEP: Sr**

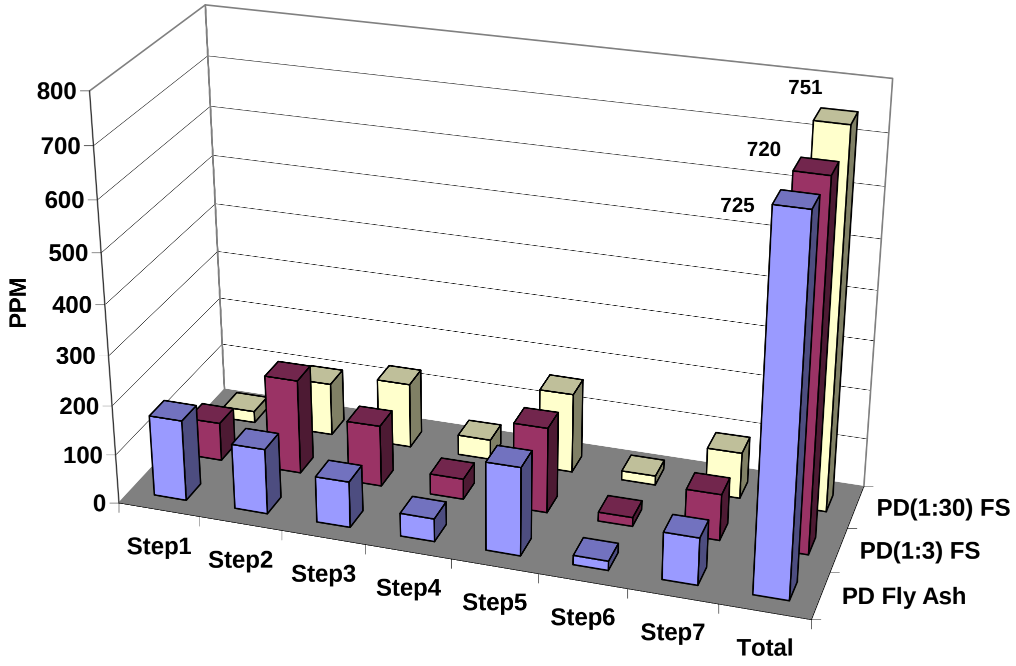


Figure 3-24 (Continued)
Distribution of strontium in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash

The 1:3 FS treatment of HA and HB fly ash samples transferred all or most of the water soluble V to the easily reducible oxide fraction, but some was also transferred to the exchangeable fraction for MA fly ash (Figure 3-25a-c). The 1:30 FS treatment moved water soluble V to the easily and the moderately reducible oxide fractions in HA and MA fly ash samples. In contrast, the 1:30 FS treatment moved almost all of the water soluble V to the exchangeable fraction of HB fly ash. FS treatment lowered the concentration of V in the water soluble fraction of PD fly ash and redistributed it between the exchangeable and poorly reducible oxide ash fractions (Figure 3-25d). V mass balances for FS-treated PD ash and 1:3 FS-treated HA and HB ash samples have <12% error. However, mass balance errors for the 1:30 FS-treated acidic fly ash samples and the 1:3 FS-treated MA ash sample are quite poor, with large apparent increases in total V for 1:30 FS-treated HA and MA fly ash. The poor V mass balances may be due to ash heterogeneity.

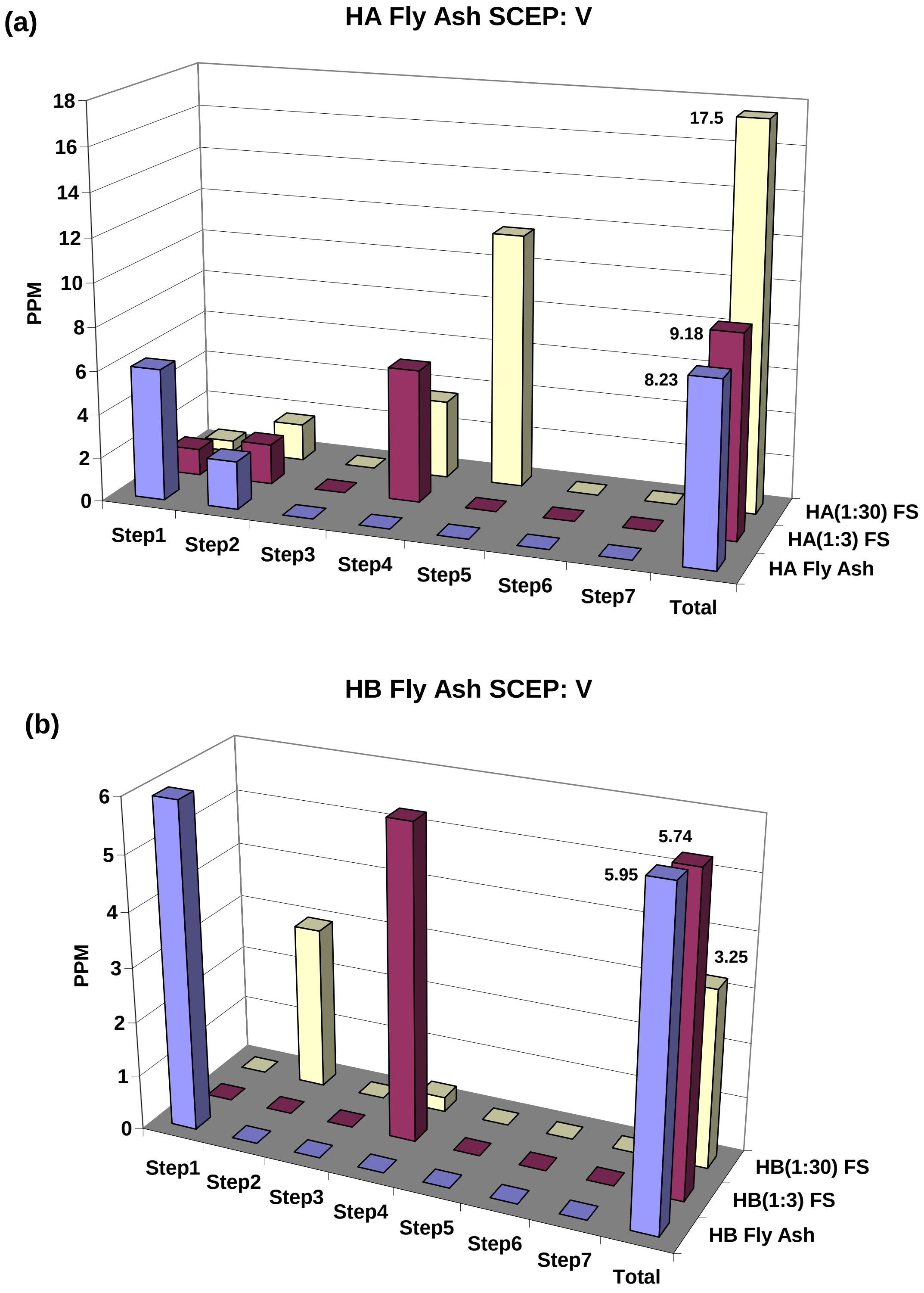
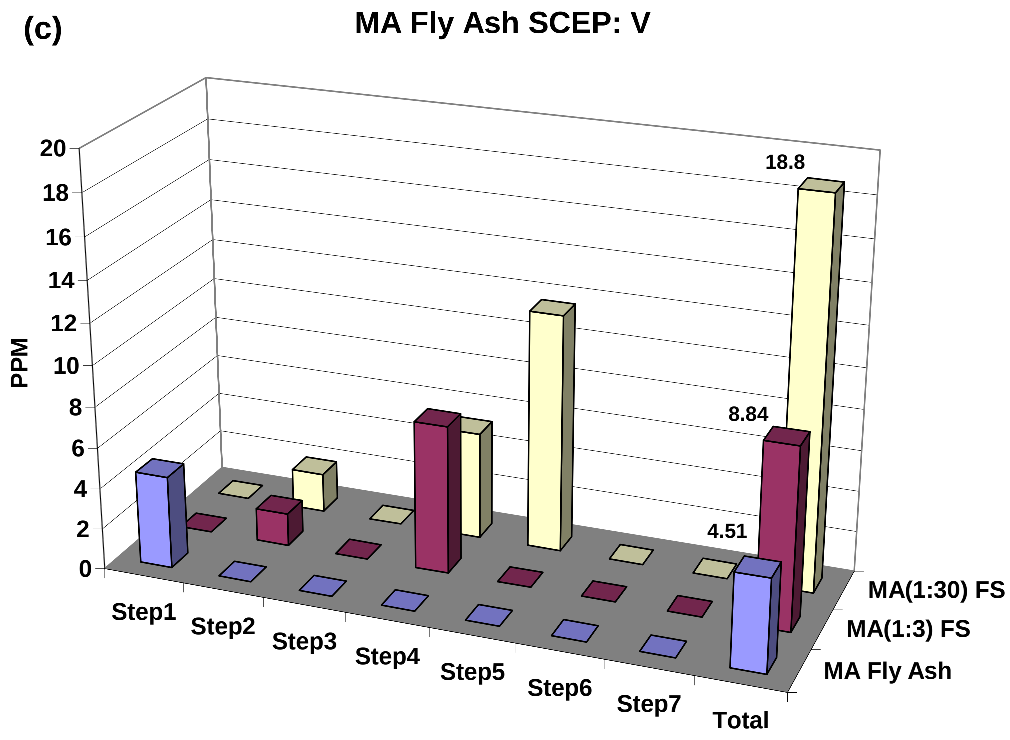


Figure 3-25
Distribution of vanadium in FS treated and untreated fly ash, as determined by SCEP: (a) HA fly ash; (b) HB fly ash



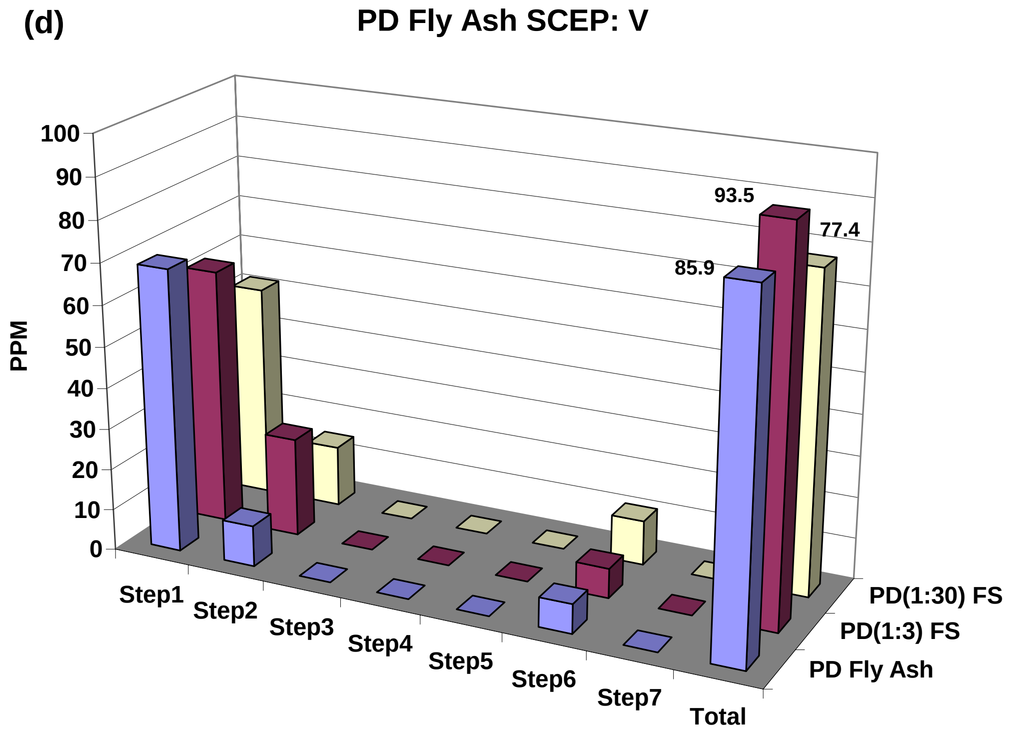


Figure 3-25 (Continued)
Distribution of vanadium in FS treated and untreated fly ash, as determined by SCEP: (c) MA fly ash; (d) PD fly ash

4

SUMMARY AND CONCLUSIONS

This study experimentally tested the ability of a ferrous sulfate treatment solution, at two different solid to liquid ratios and with or without calcium carbonate buffering, to reduce the mobility of eight priority trace elements commonly associated with coal fly ash: As, B, Cr, Mo, Ni, Se, Sr, and V. Three acidic fly ash samples and one alkaline fly ash sample were used in the treatment studies. The mobility of the trace elements was tested through prolonged sequential batch leaching of the untreated and treated ash samples using a synthetic acid rain solution. The leaching experiment results were interpreted through the use of a 7-step sequential chemical extraction procedure.

It was shown that ferrous sulfate treatment is an effective method for sequestration of most of the priority trace elements associated with coal fly ash. Synthetic acid rain leaching of the treated and untreated fly ash samples demonstrated that the best overall treatment technique for trace element sequestration in the coal fly ash samples examined was the 1:30 ferrous sulfate treatment without calcium carbonate buffer. The 1:30 FS fly ash treatment results are summarized in Figure 4-1 and show that the treatment resulted in good to excellent reductions in the mobilities of all of the trace elements that commonly exist as oxyanions in aqueous solutions (As, Mo, Cr, Se, and V) except B, which appears to be exist as an uncharged species. The sequential chemical extraction study of the FS-treated and untreated fly ash samples showed that the primary mechanism for trace element sequestration was transfer of these trace elements from mobile fly ash fractions to be adsorbed and/or co-precipitated on $Fe(OH)_3$ precipitated on fly ash particles during the treatment process.

The major conclusions of this study are:

- Overall, 1:30 FS is the most effective treatment method for sequestration of anionic and neutral trace elements in coal fly ash samples studied. Treatment results by trace element:
    - Arsenic: 79-90% reduction in mobility for acidic fly ash; 24% mobility reduction for an alkaline fly ash
    - Chromium: 89-97% reduction in mobility for acidic fly ash; 82% mobility reduction for an alkaline fly ash
    - Molybdenum: 74-99% reduction in mobility for acidic fly ash; 79% mobility reduction for an alkaline fly ash
    - Selenium: 67-87% reduction in mobility for acidic fly ash; 41% mobility reduction for an alkaline fly ash
    - Vanadium: 55-100% reduction in mobility for acidic fly ash; 70% mobility reduction for an alkaline fly ash

- In general, ferrous sulfate treatment is not effective for the cationic and uncharged trace elements.
    - Increased mobility of boron and strontium was observed for the acidic fly ash samples.
    - Increased mobility of nickel was observed for all fly ash samples studied.
    - Boron mobility was reduced by 3% and strontium mobility was reduced by 10% for 1:30 FS-treated alkaline PD fly ash.
- Ferrous sulfate treatment is not indicated for environments in which reducing conditions prevail, due to the potential for reductive dissolution of the ferric hydroxide precipitated on the ash particles and subsequent release of trace elements.

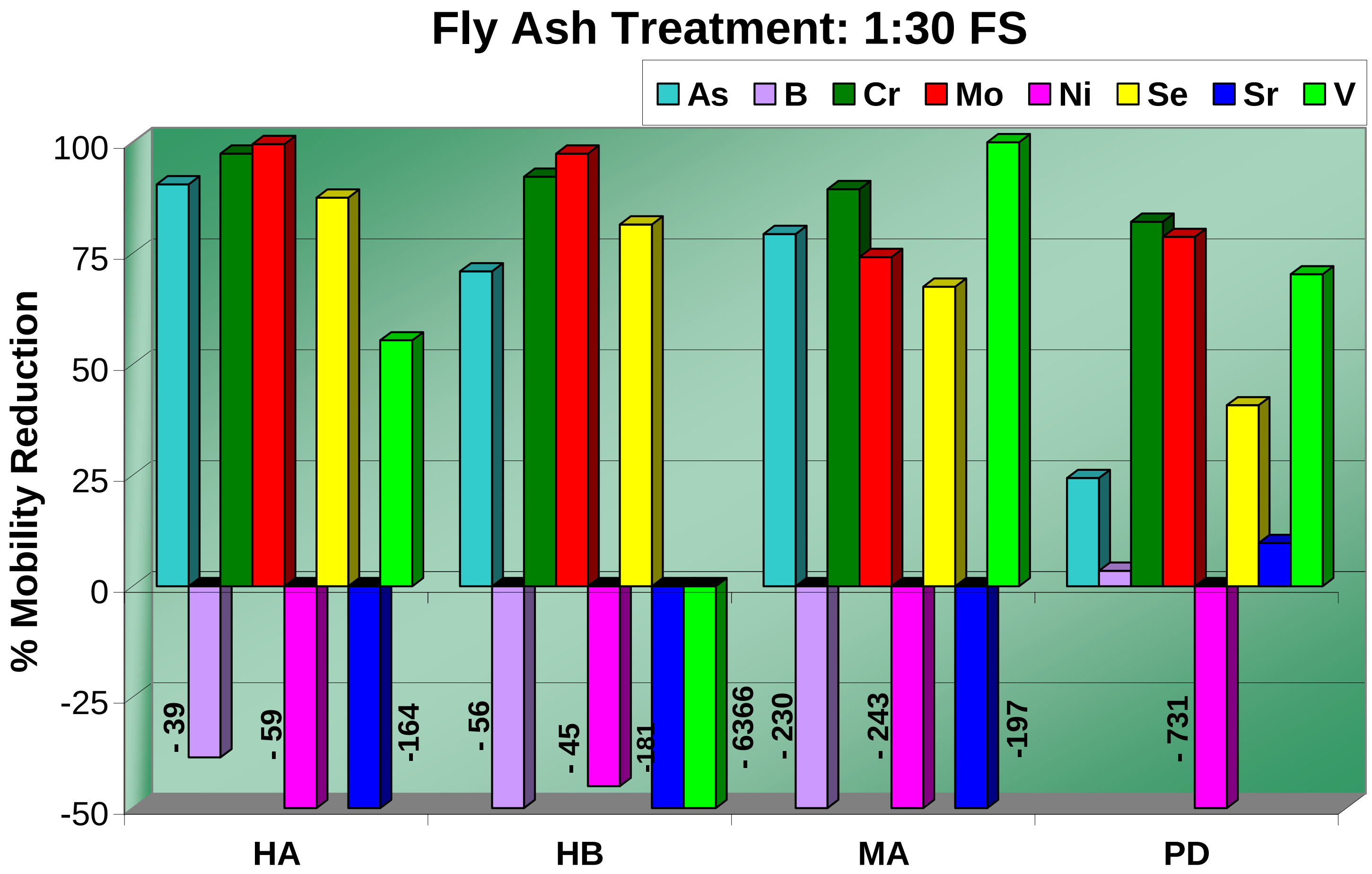


Figure 4-1
Reduction in fly ash trace element mobility observed after 1:30 ferrous sulfate treatment, compared to untreated fly ash. Values have been corrected for any leaching of trace elements by the treatment solution. Negative values indicate net release of the trace element. [Note: Negative scale is truncated]

5
REFERENCES

Auer, S., Kuzel, H. J., Pollmann, H. and Sorrentino, F. 1995. *Investigation on MSW fly ash treatment by reactive calcium aluminates and phase formed*. Cement and Concrete Research. Vol. 25(6), 1347-1359.

Bournonville, B., Nzihou A., Sharrock, P. and Depelsenaire, G. 2004. *Stabilization of heavy metal containing dusts by reaction with phosphoric acid: study of the reactivity of fly ash*. Journal of Hazardous Materials. 116, 65-74.

Eary, L.E., Rai, D., Mattigod, S.V. and Ainsworth, C.C. 1990. *Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements*. Journal Environmental Quality 19, 202-214.

EPRI. 1987. *Chemical form and leachability of inorganic trace elements in coal ash*. EPRI EA-5115, Electric Power Research Institute, Palo Alto, CA, 200 pp.

Etzel, J.E. and Anand, P. 1982. *Method of removing heavy metals from industrial waste streams*. U.S. Patent No. 4343706, U.S. Patent Office, 1982.

Hansen, L.D. and Fisher, G.L. 1980. *Elemental distribution in coal fly ash particles*. Environmental Science and Technology 14, 1111-1117.

Hollis, J.F., Keren, R. and Gal, M. 1988. *Boron release and sorption by fly ash as affected by pH and particle size.* Journal of Environmental Quality 17, 181-184.

Hower, J.C., Robl, T.L. and Thomas, G.A. 1999. *Changes in the quality of coal combustion by-products produced by Kentucky power plants, 1978 to 1997: consequences of Clean Air Act directives*. Fuel 78, 701-712.

Karayigit, A.I., Onocak, T., Gayer, R.A. and Goldsmith, S. 2001. *Mineralogy and geochemistry of feed coals and their combustion residues from the Cayirhan power plant, Ankara, Turkey*. Applied Geochemistry 16, 911-919.

Kolker, A., Finkelman, R.B., Affolter, R.H. and Brownfield, M.E. 2000. *The composition of coal combustion by-products: examples from a Kentucky power plant.* In: The Use and Disposal of Coal Combustion by-Products at Coal Miners: A Technical Interactive Forum. (Eds. C. Vories-Kimery and D. Throgmorton), U.S. Department of Interior, Office of Surface Mining, Alton, IL and Southern Illinois University Coal Research Center, Carbondale, IL, pp. 15-24.

Leleyter, L. and Probst J.L., 1999. *A new sequential extraction procedure for the speciation of particulate trace elements in river sediments.* International Journal of Environmental Analytical Chemistry. 73(2), 109-128.

McCarthy, G.J., Grier, D.G., Wisdon, M.A., Peterson, R.B., Lerach, S.L., Jarabek, R.L., Walsh, J.J. and Winburn, R.S. 1999. *Coal combustion by-product diagenesis II.* Proceedings, 1999 International Ash Utilization Symposium, Lexington, Kentucky, Center for Applied Energy Research.

Meng, X., Bang, S. and Korfiatis, G.P. 2000. *Effects of silicate, sulfate, and carbonate on arsenic removal by ferric chloride*. Water Research 34(4), 1255-1261.

Mukhopadhyay, P.K., Lajeunesse, G. and Crandlemire, A.L. 1996. *Mineralogical speciation of elements in feed coal and their combustion residues from an eastern Canadian coalfield and power plant*. International Journal of Coal Geology 32, 279-312.

Phair, J.W., van Deventer, J.S.J. and Smith, J.D. 2004. *Effect of Al source and alkali activation on Pb and Cu immobilization in fly ash based geopolymers*. Applied Geochemistry 19, 423-434.

Qian, G., Zhang, H., Zhang, X. and Chui, P. 2005. *Modification of MSW fly ash by anionic chelating surfactant*. Journal of Hazardous Materials 121, 251-58.

Steenari, B.M., Schelander, S. and Lindqvist, O. 1999. *Chemical and leaching characteristics of ash from combustion of coal, peat and wood in a 12 MW CFB – a comparative study*. Fuel 78, 249-258.

Suici, D.F., Wikoff, P.M., Beller, J.M. and Carpenter, C.J. 1991. *Process for sodium sulfide/ferrous sulfate treatment of hexavalent chromium and other heavy metals*. U.S. Patent No. 5000859, U.S. Patent Office.

U.S. EPA 1994a. Method 1312B: *Synthetic Precipitation Leaching Procedure*. In: Test Methods for Evaluating Solid Waste, Physical/Chemical methods, 3rd ed., U.S. Environmental Protection Agency, Office of Solid Waste. U. S. Government Printing Office: Washington, DC.

U.S. EPA 1994b. Method 3051A: *Microwave-assisted acid digestion of sediments, sludges and soils*. In: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd edition, U.S. Environmental Protection Agency, Office of Solid Waste. U.S. Government Printing Office, Washington, D.C.

Voigt, D.E., Brantley, S.L. and Hennet, R.J.-C. 1996. *Chemical fixation of arsenic in contaminated soils*. Applied Geochemistry, 11, 633-643.

Yang, L. 2005. *Evaluation of in situ chemical fixation for remediation of arsenic-contaminated soil*. PhD Dissertation, University of Alabama.

A

FLY ASH COMPOSITION DATA

Table A-1
Environmentally Available Concentrations in Fly Ash Samples as Determined by Microwave-Assisted Acid Digestion Using EPA Method 3051A

Element	HA	HB	MA	PD
Ag	n.d.	n.d.	n.d.	n.d.
Al	21,800	14,000	9,310	19,200
As	81.6	167	158	16.7
B	166	168	117	903
Ba	312	246	317	217
Be	n.d.	4.99	4.55	0.164
Ca	4,860	7,580	5,730	32,300
Cd	n.d.	n.d.	n.d.	n.d.
Co	18.9	17.0	13.0	4.63
Cr	50.00	52.5	29.6	17.8
Cu	72.6	79.4	63.3	22.5
Fe	19,600	18,300	12,100	16,100
K	3,160	1,690	1,570	638
Mg	1,890	1,300	1,130	5,060
Mn	74.2	44.6	71.4	61.9
Mo	12.6	19.9	11.8	5.39
Na	722	460	616	1,910
Ni	36.9	37.6	34.3	7.48
Pb	26.5	28.3	23.8	11.5
Se	7.68	23.1	14.0	11.6
Sb	3.66	3.51	2.72	1.50
Si	7,290	2,180	3,880	3,110
Sn	n.d.	n.d.	n.d.	n.d.
Sr	287	557	317	538
Tl	n.d.	n.d.	n.d.	n.d.
Ti	714	634	615	579
V	103	121	90.1	56.0
Zn	67.4	89.2	103	69.0

Concentrations in ppm (dry wt.)
n.d. = not detected
Method reference: U.S. EPA 1994b

B

TRACE ELEMENT CONCENTRATIONS LEACHED DURING SEQUENTIAL LEACHING

Table B-1
Total Trace Element Concentrations Leached (in mg/kg dry weight) from Treated and Untreated Fly Ash Samples During SAR Sequential Leaching. [Note: Only leachate concentrations >0.5 LOD were used in the calculation.]

SAR Leaching: Total Arsenic Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	4.05	1.22	0.38	49.62	1.37
HB	4.98	2.17	1.44	92.65	2.39
MA	3.42	1.14	0.70	63.19	0.85
PD	8.50	5.74	6.43	5.37	5.95

SAR Leaching: Total Boron Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	34.49	8.83	2.73	11.1	4.37
HB	42.05	12.84	8.16	17.2	5.27
MA	14.84	10.01	5.84	13.4	3.56
PD	659	449	175	433	174

SAR Leaching: Total Chromium Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	0.78	0.08	0.02	0.32	0.24
HB	0.85	0.24	0.07	0.30	0.21
MA	0.31	0.08	0.03	0.48	0.09
PD	1.91	0.51	0.34	0.38	0.38

SAR Leaching: Total Molybdenum Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	9.42	1.15	0.04	6.09	5.67
HB	6.74	2.28	0.17	9.83	8.86
MA	1.51	0.37	0.10	7.93	3.86
PD	6.30	1.69	1.34	2.13	1.96

SAR Leaching: Total Nickel Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	1.88	0.76	1.12	0.34	1.60
HB	2.62	1.13	1.09	0.64	1.55
MA	1.70	1.10	1.56	0.44	1.96
PD	0.00	0.08	0.08	0.36	0.35

SAR Leaching: Total Selenium Leached (mg/kg)

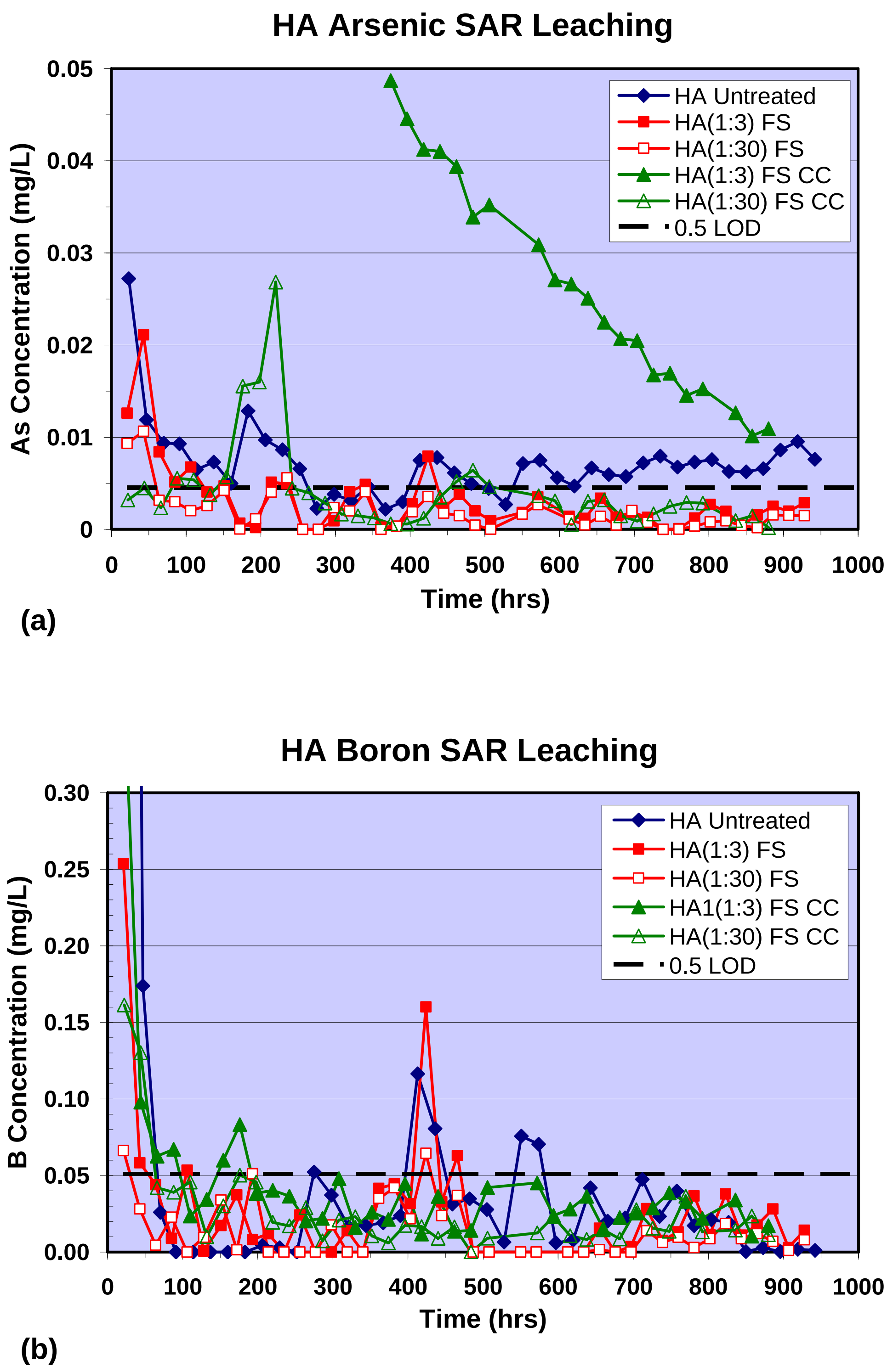
	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	5.08	1.18	0.25	8.69	0.69
HB	5.61	2.02	0.40	19.1	1.53
MA	2.09	0.88	0.31	11.5	0.69
PD	10.3	4.79	5.30	4.32	6.21

SAR Leaching: Total Strontium Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	38.5	35.3	27.2	38.7	22.9
HB	114	77.5	80.1	130	74.0
MA	47.9	42.1	31.4	55.8	27.3
PD	360	285	153	268	159

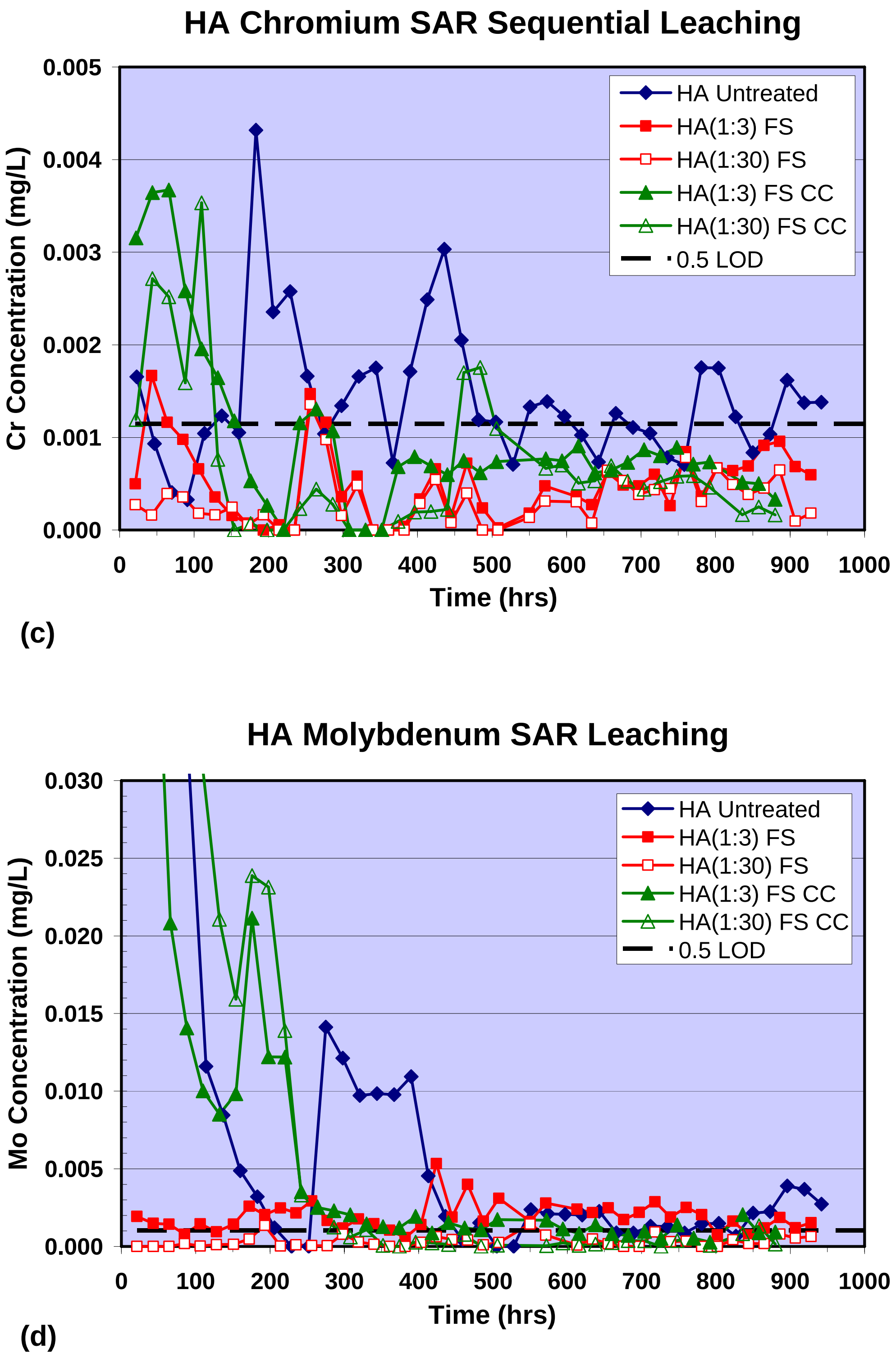
SAR Leaching: Total Vanadium Leached (mg/kg)

	Untreated	1:3 FS	1:30 FS	1:3 FS CC	1:30 FS CC
HA	1.57	0.00	0.56	11.9	2.08
HB	0.00	0.92	0.65	19.1	2.76
MA	3.58	2.14	0.00	12.9	2.54
PD	20.4	10.9	6.04	10.7	6.58


HA Arsenic SAR Leaching

HA Boron SAR Leaching

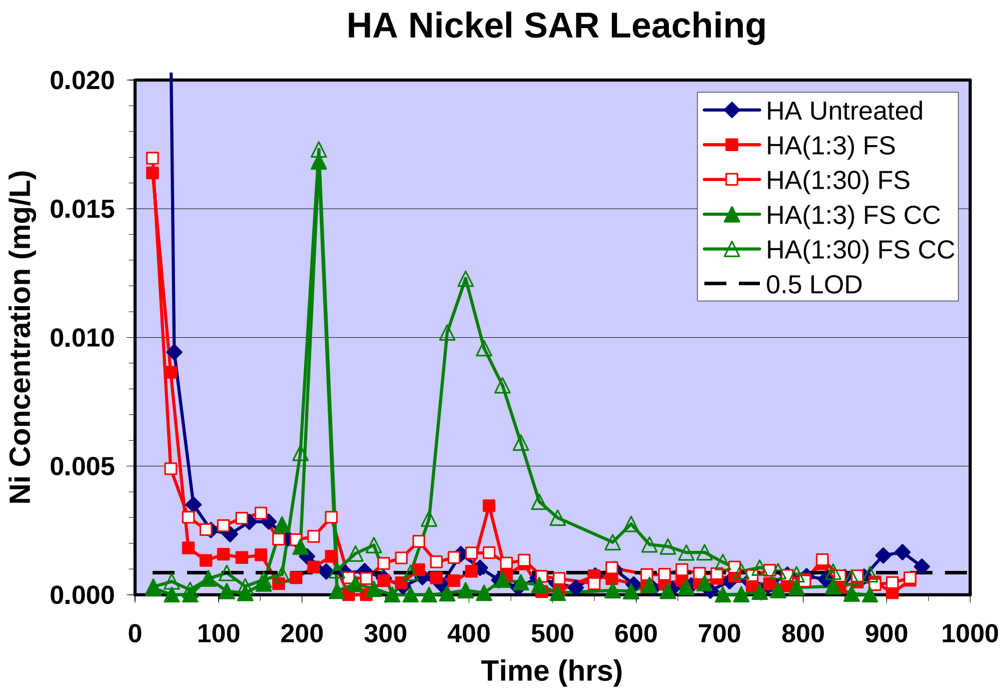
Figure B-1
SAR sequential leaching of HA fly ash: (a) arsenic and (b) boron concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]



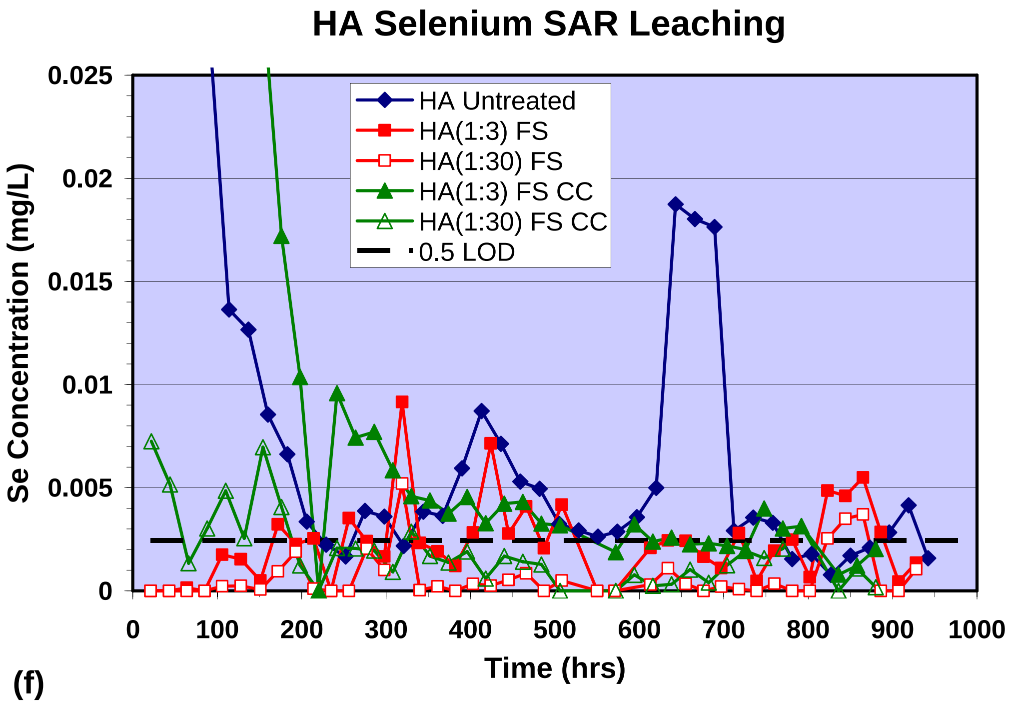
(c)

(d)

Figure B-1 (Continued)
SAR sequential leaching of HA fly ash: (c) chromium and (d) molybdenum concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

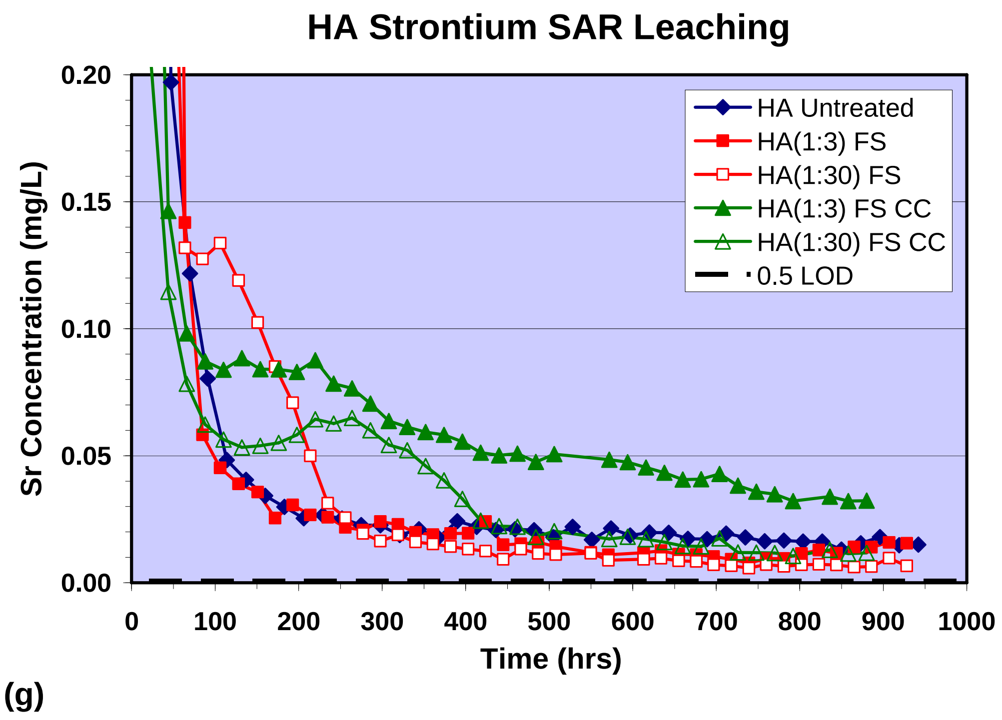


(e)



(f)

Figure B-1 (Continued)
SAR sequential leaching of HA fly ash: (e) nickel and (f) selenium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]



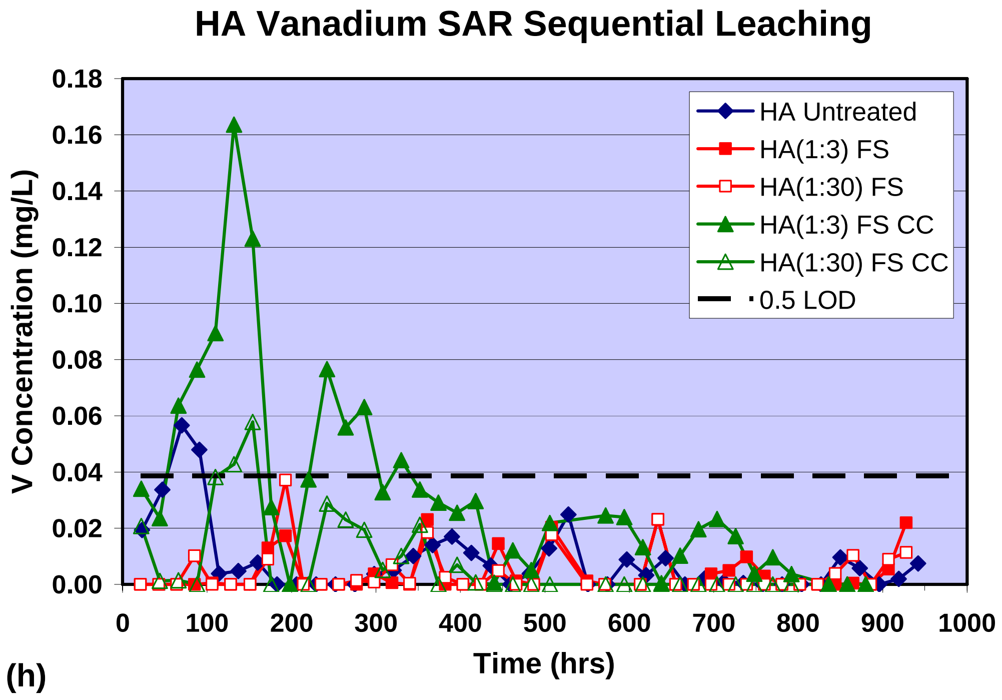
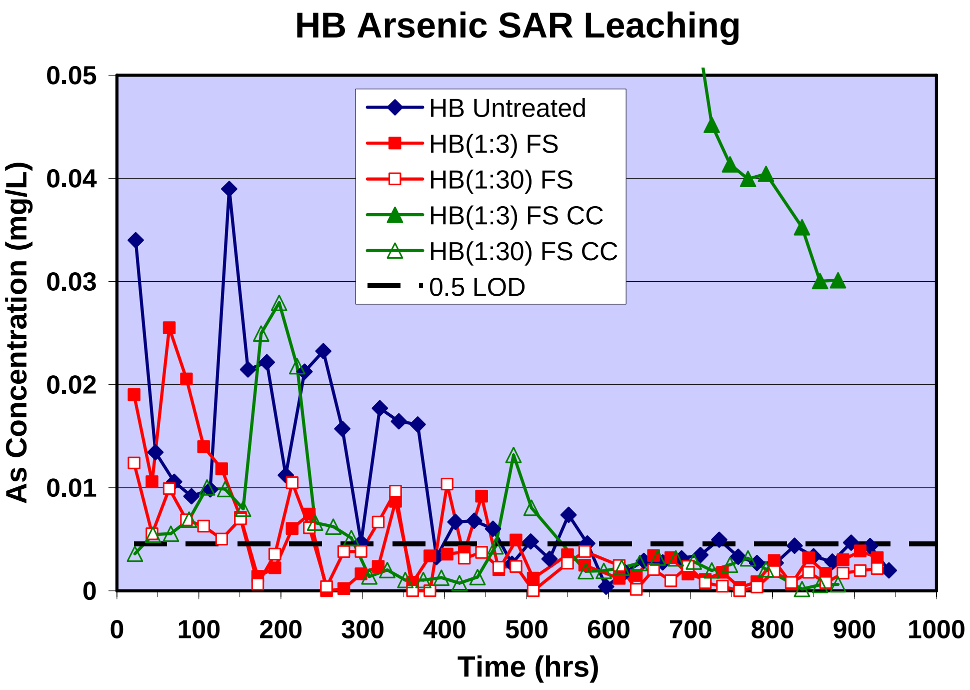
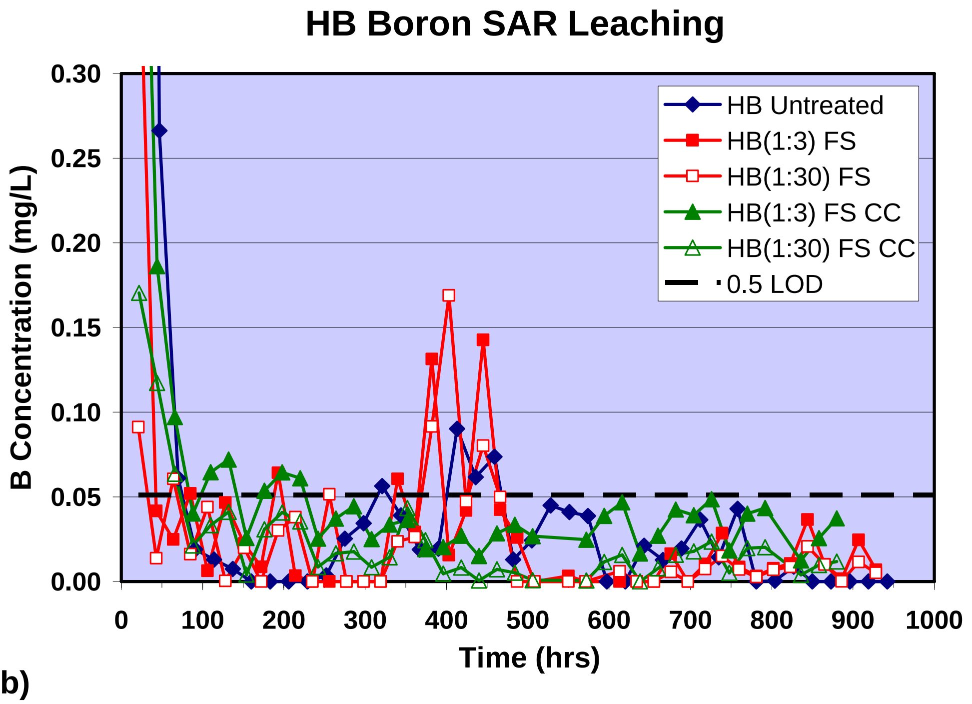


Figure B-1 (Continued)
SAR sequential leaching of HA fly ash: (g) strontium and (h) vanadium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

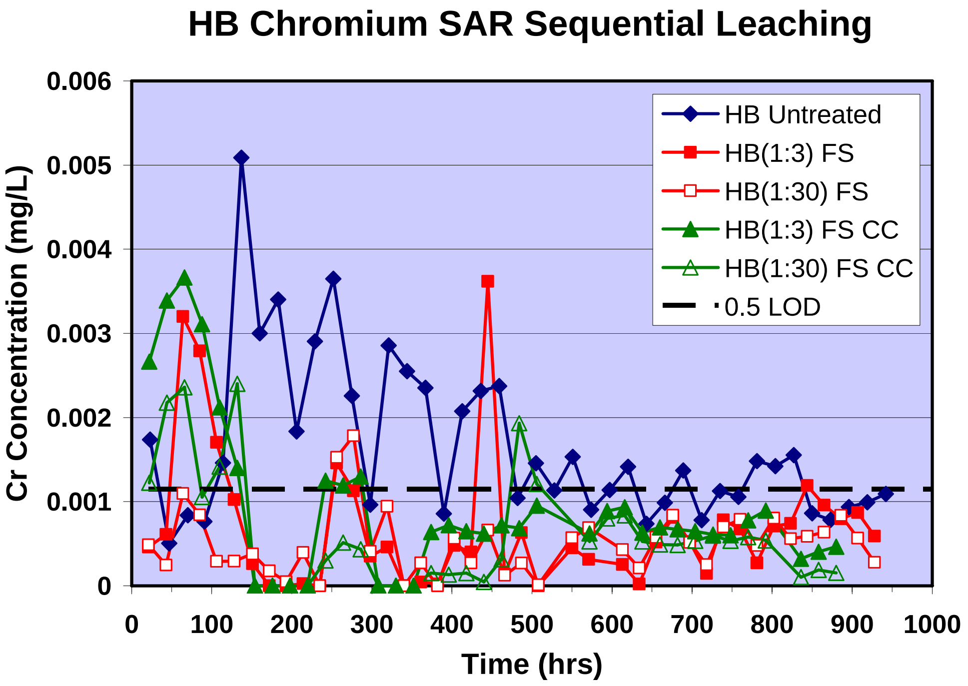


(a)

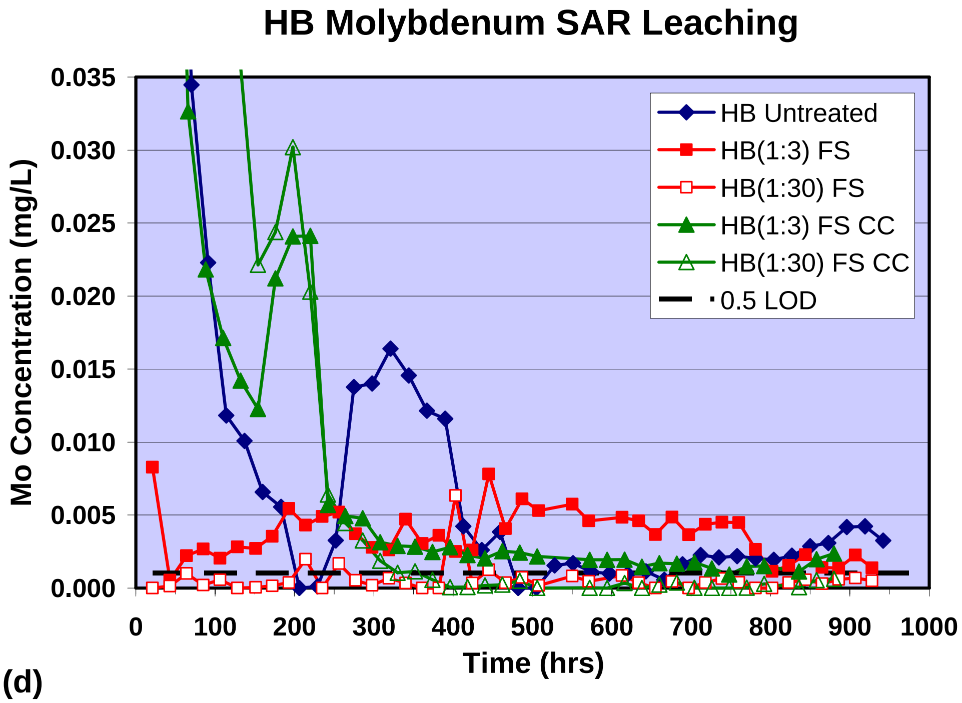


(b)

Figure B-2
SAR sequential leaching of HB fly ash: (a) arsenic and (b) boron concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

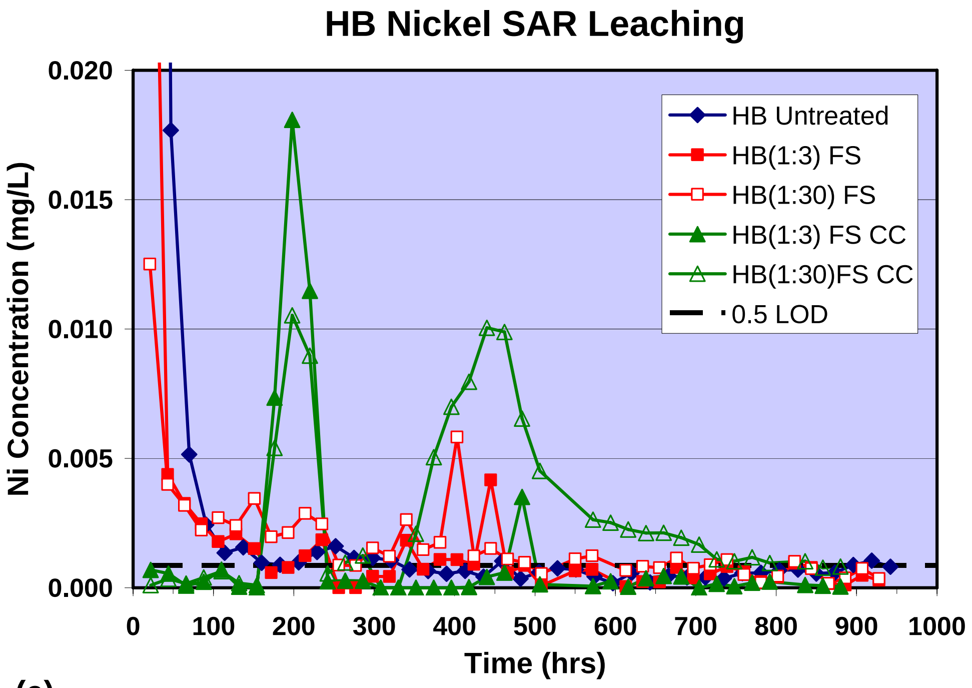


(c)

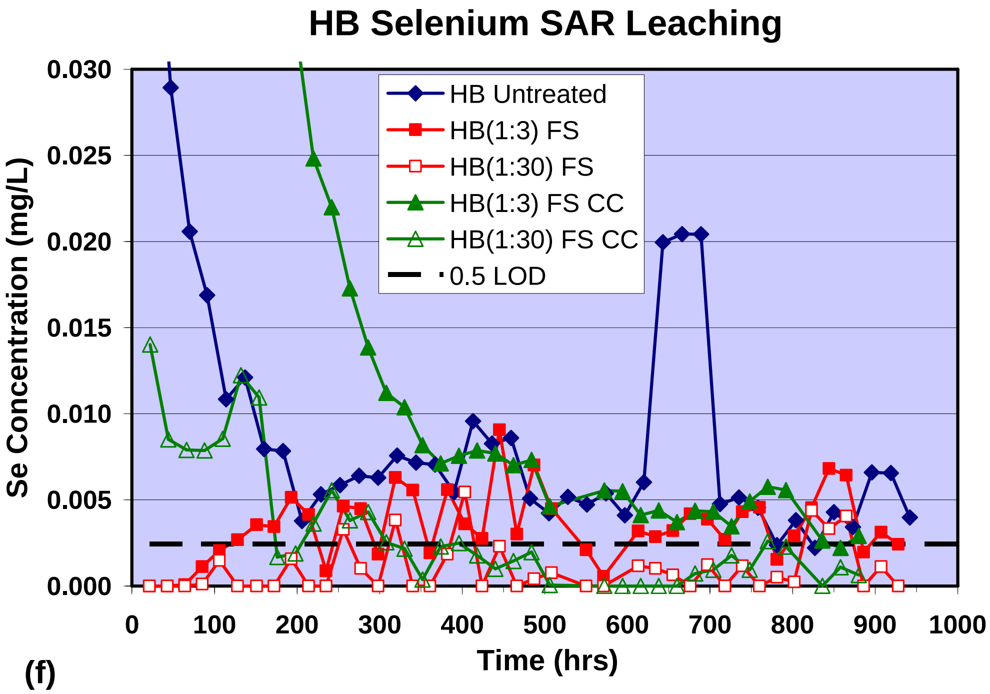


(d)

Figure B-2 (Continued)
SAR sequential leaching of HB fly ash: (c) chromium and (d) molybdenum concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

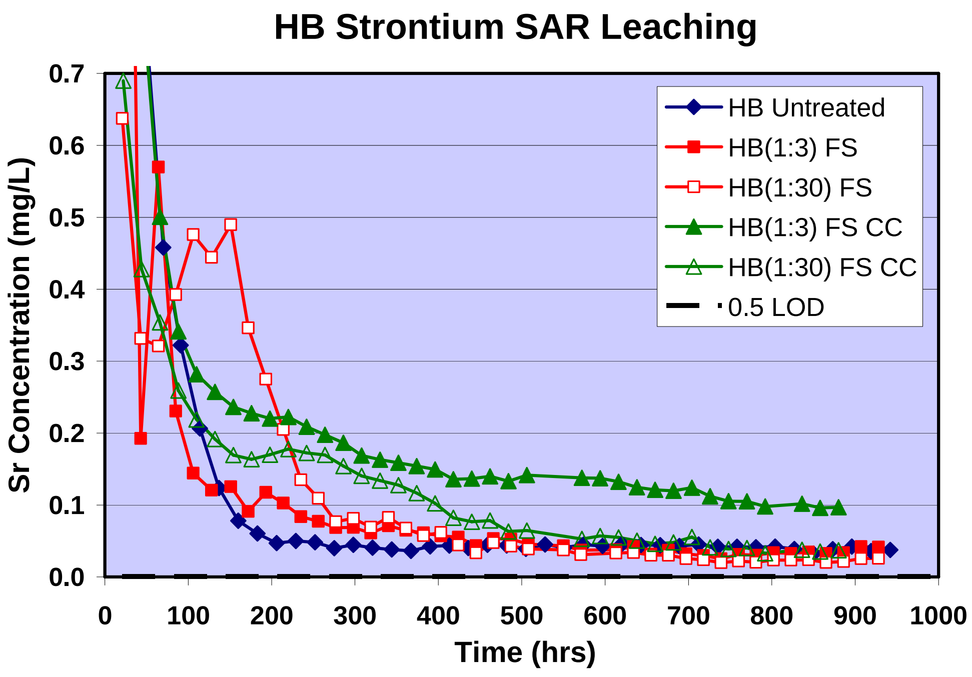


(e)

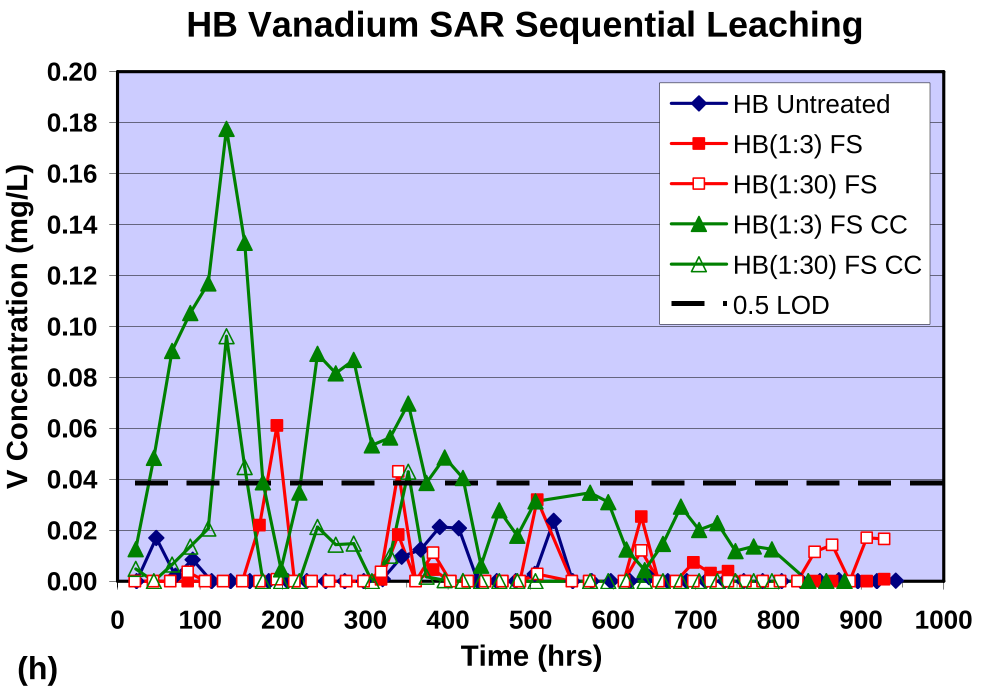


(f)

Figure B-2 (Continued)
SAR sequential leaching of HB fly ash: (e) nickel and (f) selenium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

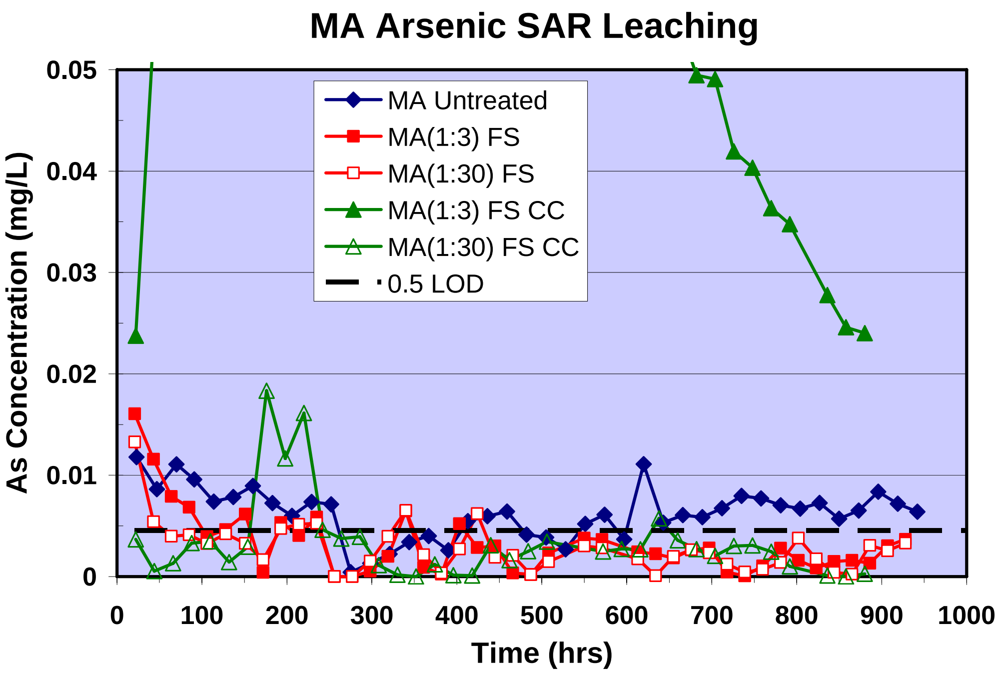


(g)

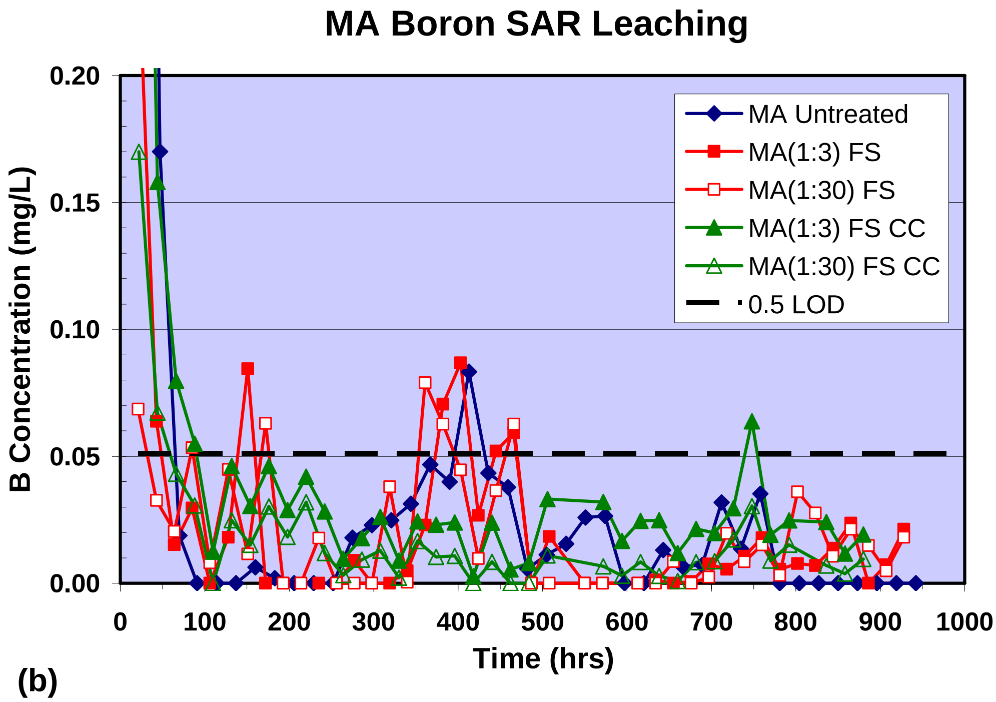


(h)

Figure B-2 (Continued)
SAR sequential leaching of HB fly ash: (g) strontium and (h) vanadium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

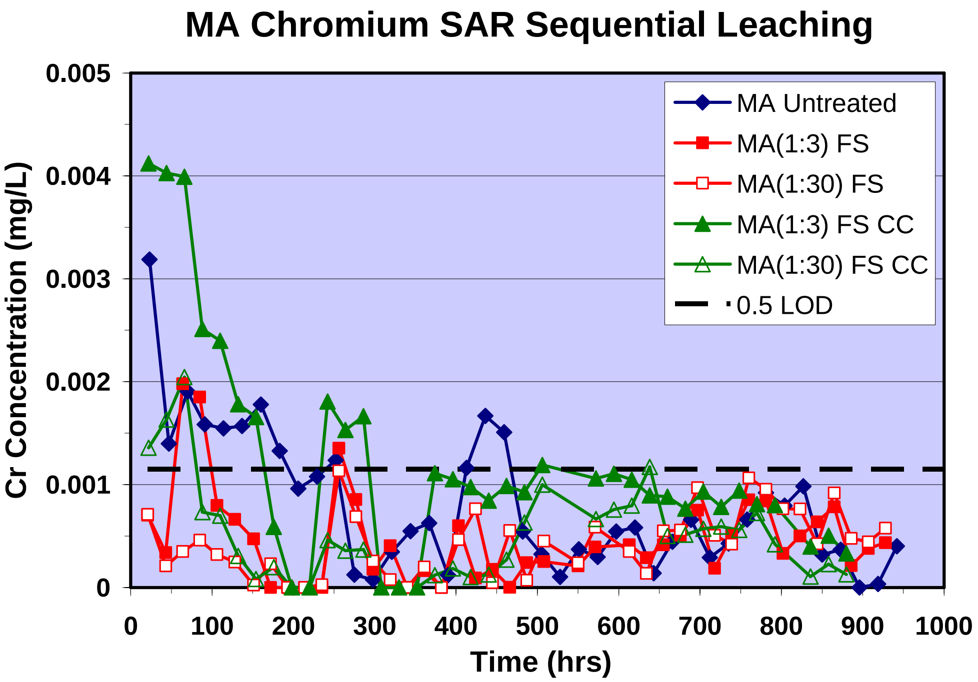


(a)

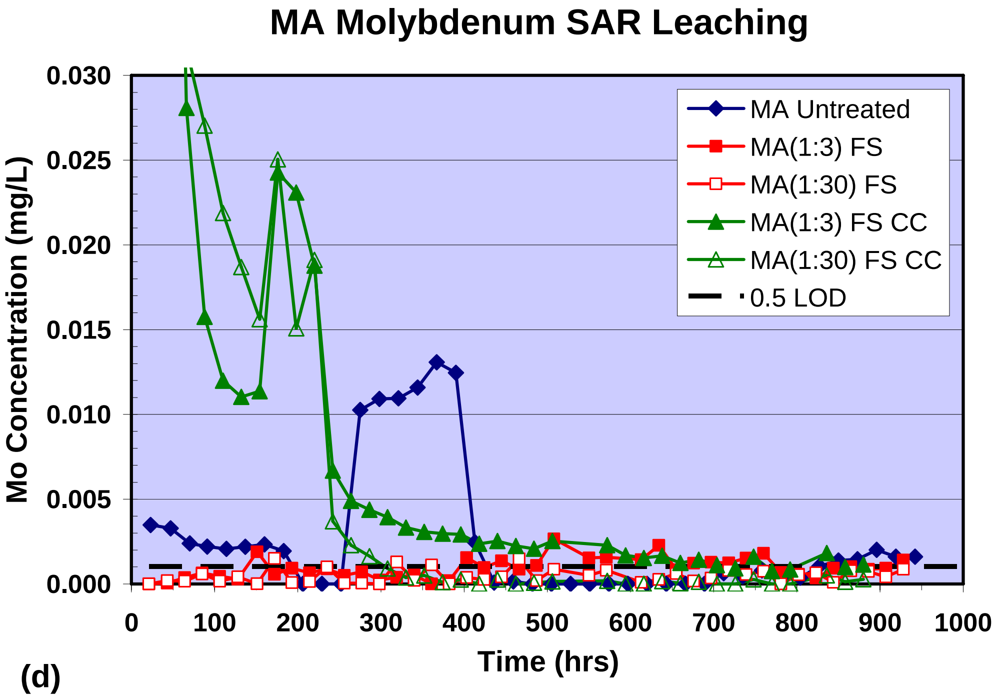


(b)

Figure B-3
SAR sequential leaching of MA fly ash: (a) arsenic and (b) boron concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

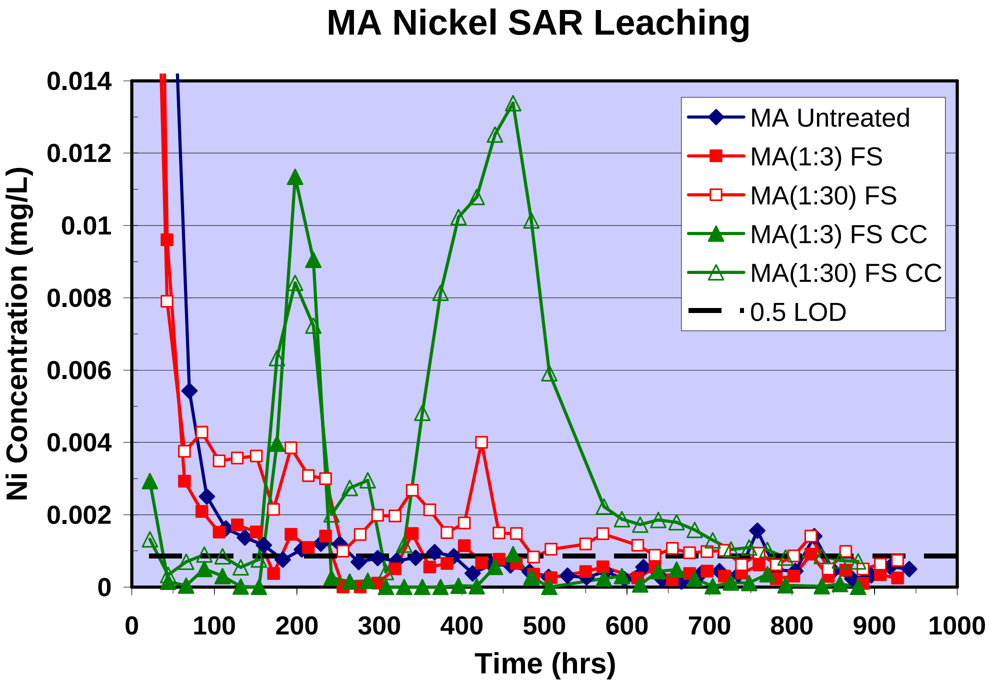


(c)

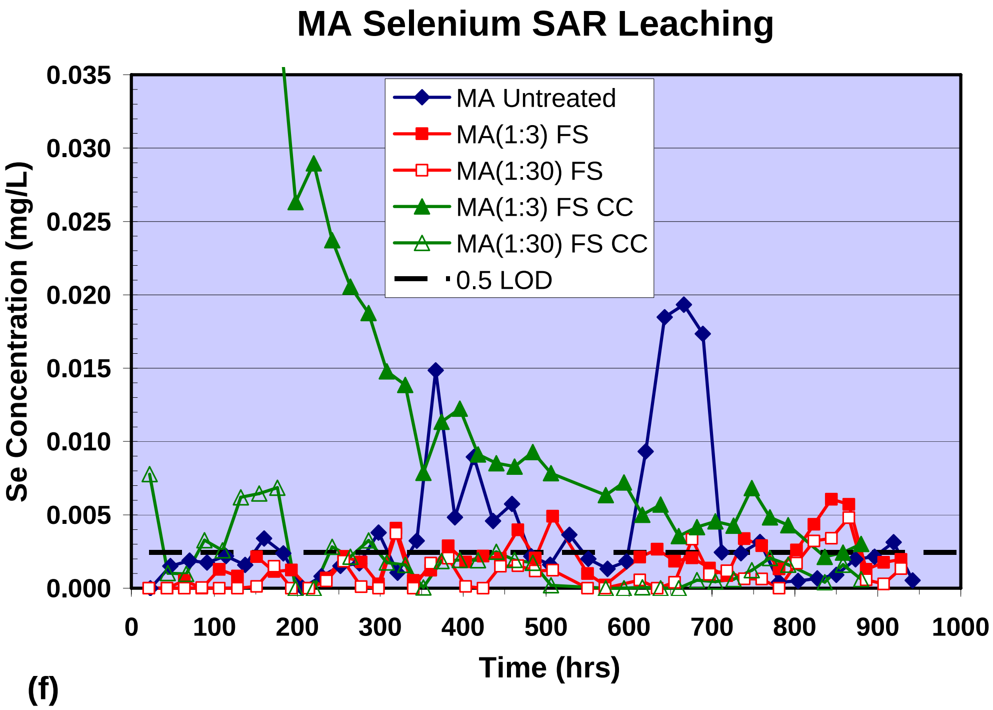


(d)

Figure B-3 (Continued)
SAR sequential leaching of MA fly ash: (c) chromium and (d) molybdenum concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

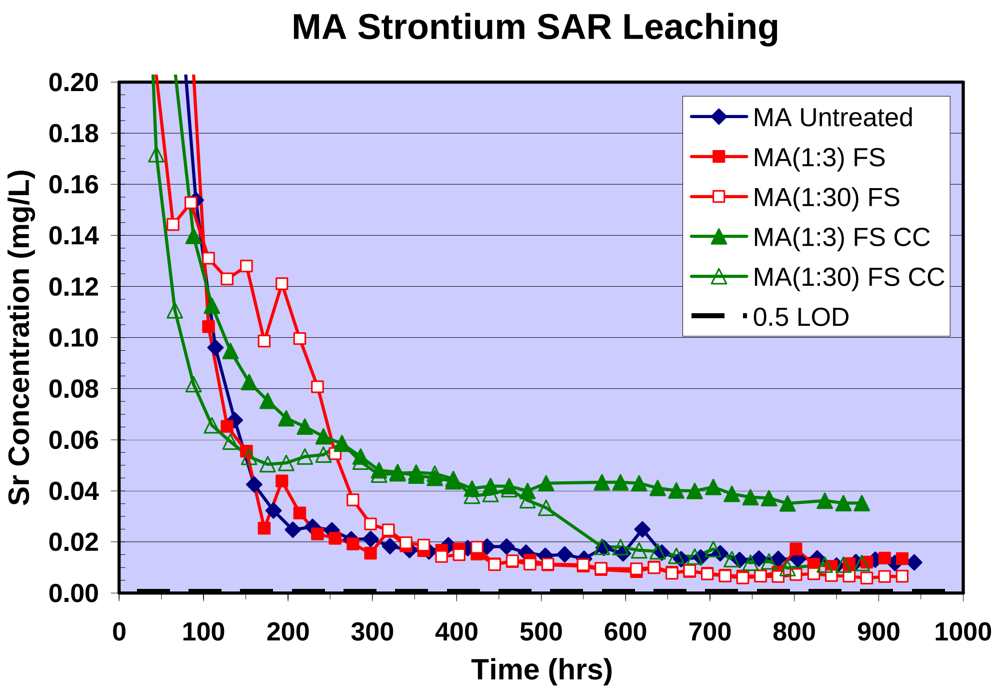


(e)

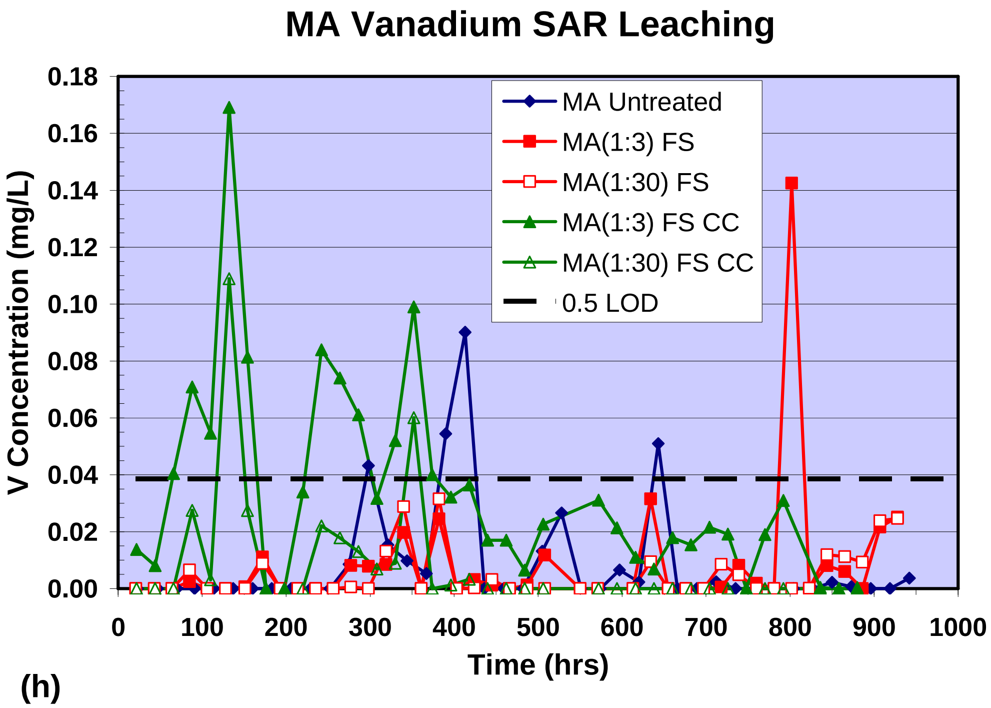


(f)

Figure B-3 (Continued)
SAR sequential leaching of MA fly ash: (e) nickel and (f) selenium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

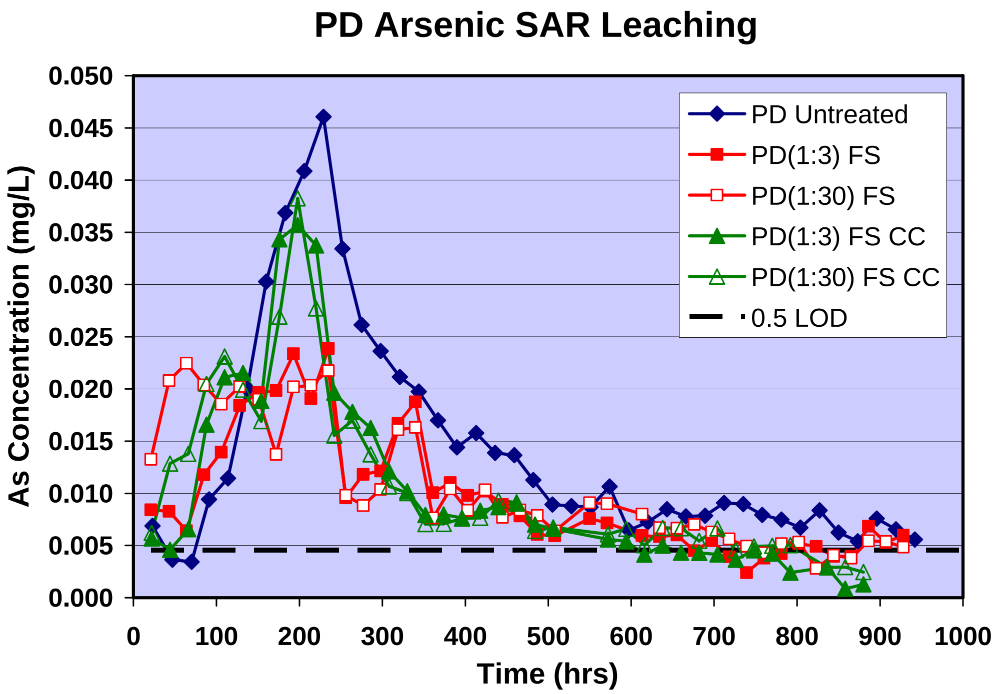


(g)

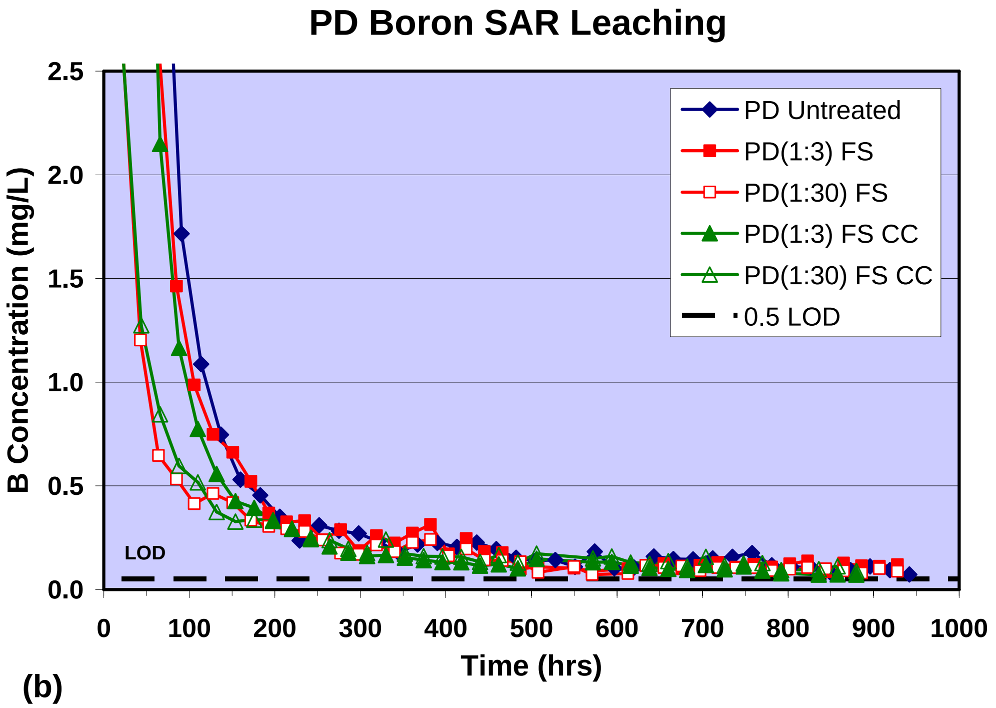


(h)

Figure B-3 (Continued)
SAR sequential leaching of MA fly ash: (g) strontium and (h) vanadium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

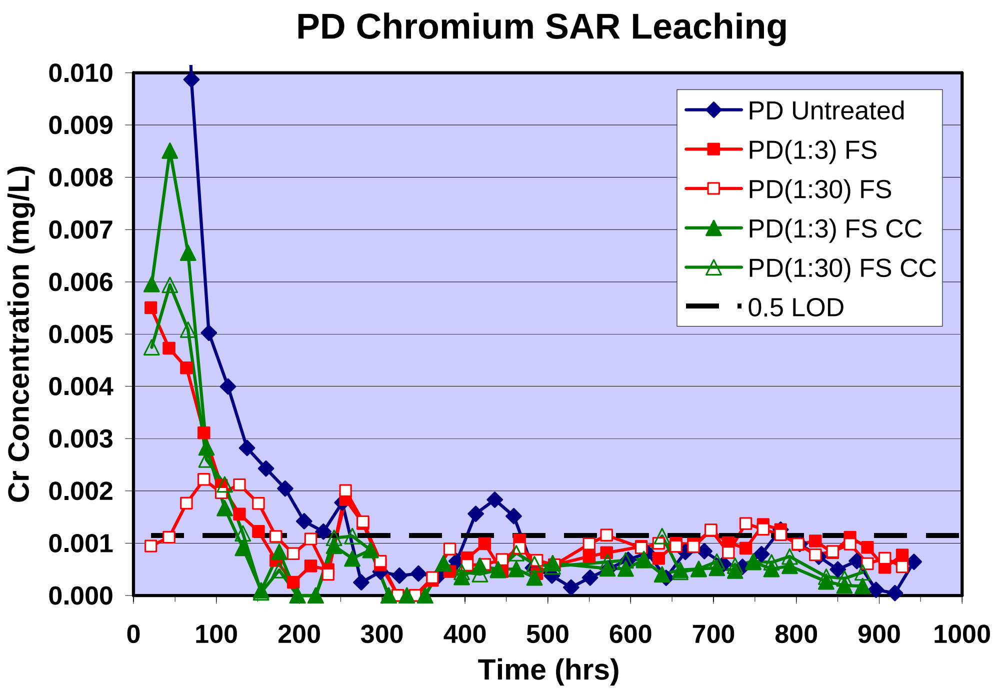


(a)

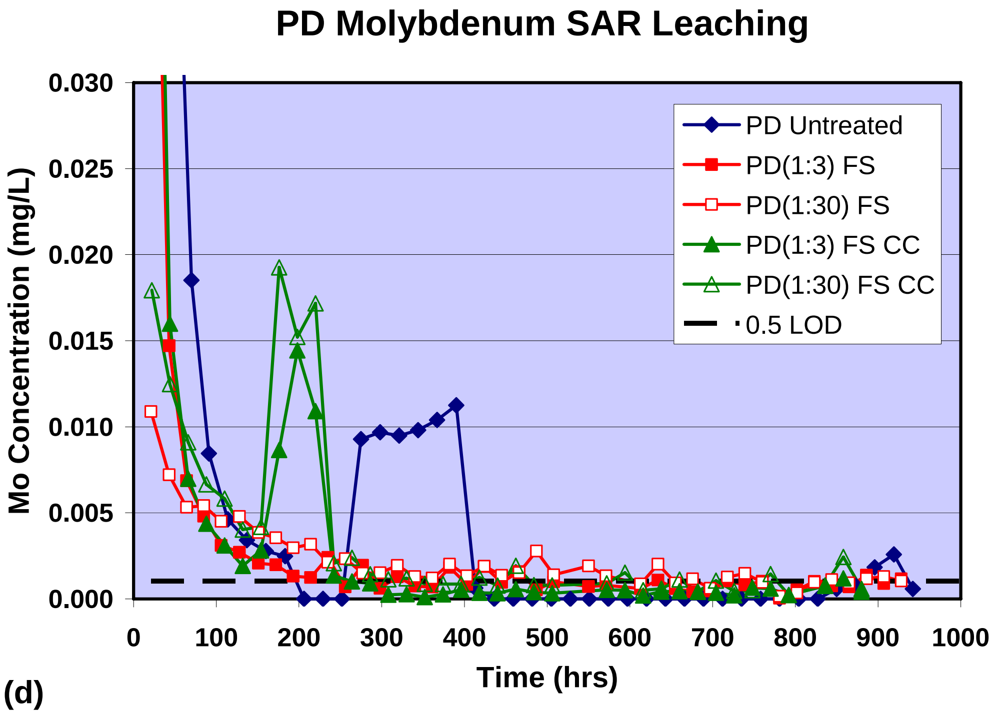


(b)

Figure B-4
SAR sequential leaching of PD fly ash: (a) arsenic and (b) boron concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]



(c)



(d)

Figure B-4 (Continued)
SAR sequential leaching of PD fly ash: (c) chromium and (d) molybdenum concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

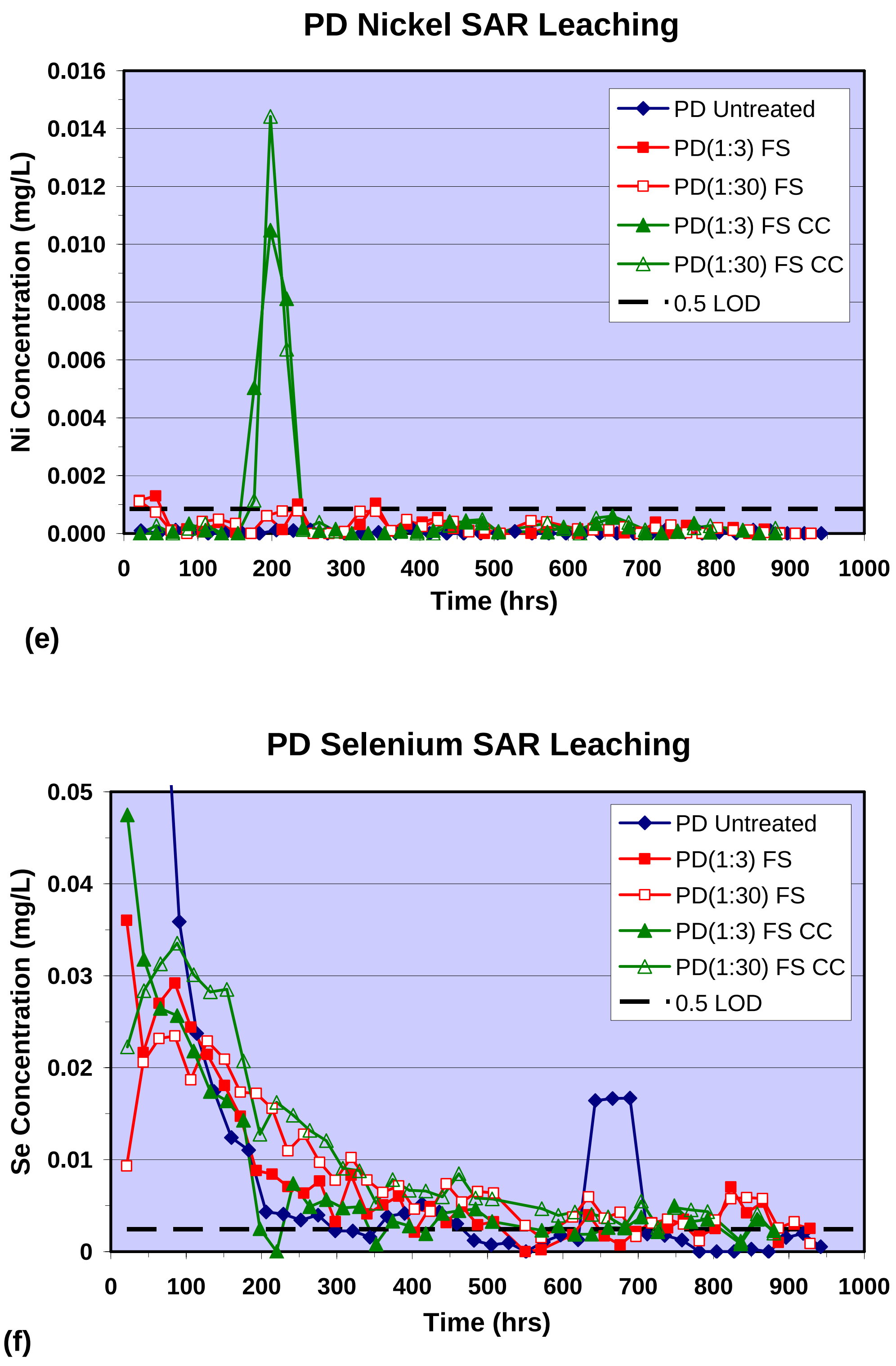
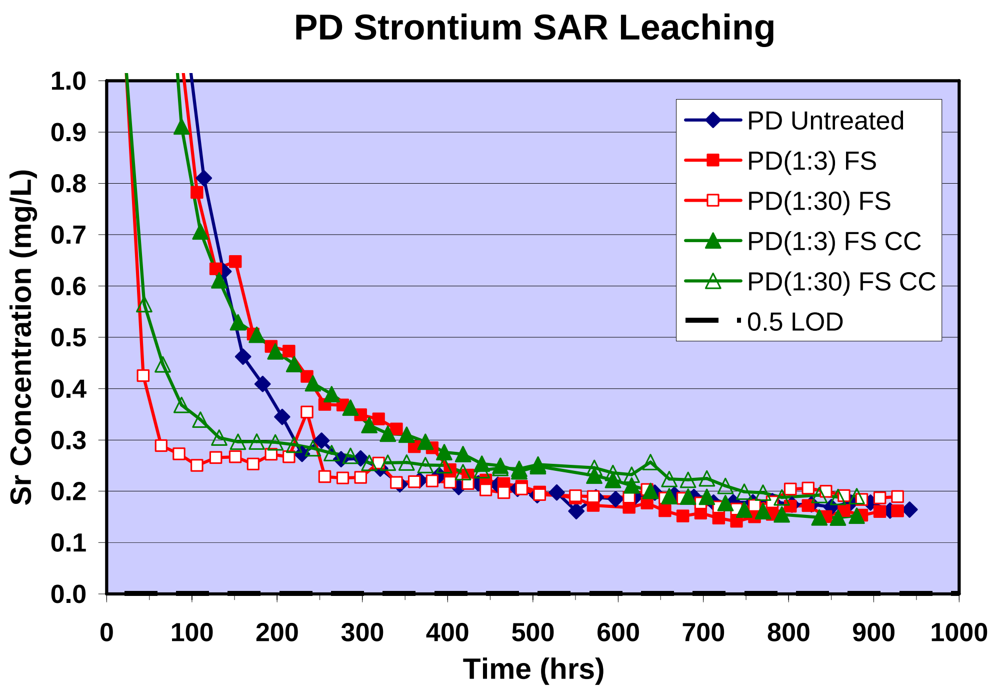
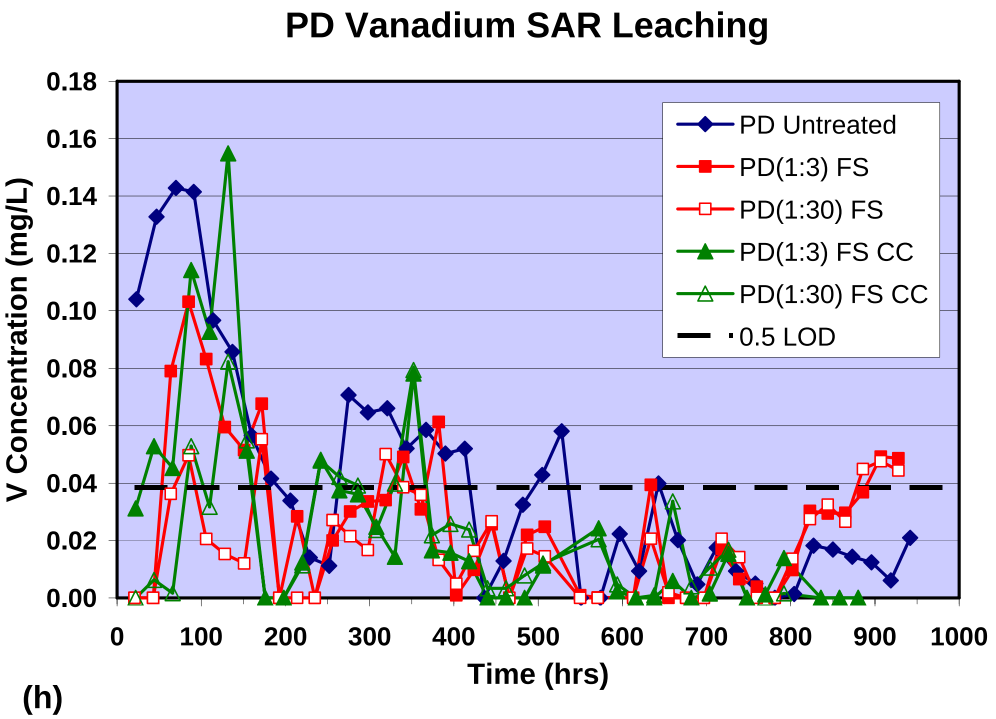


Figure B-4 (Continued)
SAR sequential leaching of PD fly ash: (e) nickel and (f) selenium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]



(g)



(h)

Figure B-4 (Continued)
SAR sequential leaching of PD fly ash: (g) strontium and (h) vanadium concentration versus leaching time. Values <3·LOD are not quantitative, but are plotted to show trends. [Note: y-axis is truncated]

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case-by-case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

The Electric Power Research Institute (EPRI), with major locations in Palo Alto, California; Charlotte, North Carolina; and Knoxville, Tennessee, was established in 1973 as an independent, nonprofit center for public interest energy and environmental research. EPRI brings together members, participants, the Institute's scientists and engineers, and other leading experts to work collaboratively on solutions to the challenges of electric power. These solutions span nearly every area of electricity generation, delivery, and use, including health, safety, and environment. EPRI's members represent over 90% of the electricity generated in the United States. International participation represents nearly 15% of EPRI's total research, development, and demonstration program.

Together...Shaping the Future of Electricity

Program:

Coal Combustion Products – Environmental Issues

♻ *Printed on recycled paper in the United States of America*

1015549

Electric Power Research Institute
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com