

Chemical Fixation of Trace Elements in Coal Fly Ash

Rona J. Donahoe¹, Sidhartha Bhattacharyya¹, Dan Patel² and Kenneth J. Ladwig³

¹Department of Geological Sciences, University of Alabama, Tuscaloosa, AL 35487-0338; ²Southern Company Services, Inc., 44 Inverness Center Parkway, Bin B426, Birmingham, AL 35242; ³EPRI, 200 South Executive Drive, Suite 201, Brookfield, WI 53005.

KEYWORDS: coal ash, treatment, chemical fixation, trace elements, mobility

ABSTRACT

More than two-thirds of the coal combustion by-products (CCBs) produced in the United States are disposed of in dry landfills or in wet ash lagoons. Most of the older ash disposal sites are unlined and many are unmonitored. The US EPA is currently developing national standards for monitoring groundwater at coal combustion by-product disposal facility (CCBDF) sites in the US. Development of effective techniques for *in situ* chemical fixation of trace elements in ash at closed CCBDFs would save the US electric utility industry billions of dollars in costs associated with excavation and lining of older disposal sites.

Two treatment solutions were experimentally investigated as potential chemical fixation agents for trace elements present in fly ash collected at four different sites located in the Southeastern United States. Both treatment solutions contained the same concentration of ferrous sulfate, but calcium carbonate was added to the second solution to buffer the pH. The effectiveness of the treatment methods was evaluated through sequential batch leaching of treated ash samples using synthetic acid rain (SPLP). The best overall treatment method is FS at the 1:30 solid:liquid ratio. This treatment produces the lowest SPLP mobility for Mo and Sr (all ash samples), for B, Se and V (3 of the 4 ash samples) and for As (2 of the 4 ash samples). Overall reduction in trace element mobility after FS 1:30 treatment was As by 23-73%, B by 43-80%, Cr by 45-77%, Mo by 77-98%, Ni by 12-58%, Se by 49-92%, Sr by 29-58% and V by 41-53%.

The chemical fixation treatment method developed is inexpensive, stable during prolonged leaching by acidic precipitation and easily implemented at closed CCBDF sites. In addition, the fixation technique may make possible increased utilization of CCB materials which have limited reuse potential due to their trace element contents.

INTRODUCTION

A variety of potentially hazardous trace elements are associated with fly ash produced by coal combustion. The distribution and concentrations of the trace elements in fly ash are determined by the composition of the feed coal (¹McCarthy et al. 1999; ²Kolker et al. 2000) and by the combustion process used, including any additives for emissions control.^{3,4,5} Studies have shown that As, B, Bi, Cd, Cr, Cu, Ge, Hg, Mo, Pb, Ni, Se, Sr, Tl, V, W, and Zn are enriched in fly ash compared to the bottom ash.^{6,7,8,9} Through the combustion process, trace element concentrations in fly ash can be enriched up to 30 times relative to the feed coal.¹⁰ Trace element leachability and toxicity depend on their distribution and speciation in the fly ash.

In the disposal environment, fly ash may react with meteoric fluid to release trace elements into groundwater or surface water systems. Numerous experimental leaching studies have been performed to assess the leachability of the trace elements in fly ash.^{3,11,12,13} In many cases, the effluent solutions produced by these laboratory experiments are chemically similar to natural leachate solutions collected from ash ponds. The ash pond pore waters typically have calcium and sulfate as major elements and trace element concentrations that exceed drinking water MCL values.^{14,15,16,17,18,}¹⁹ Despite this, coal combustion by-product disposal facilities (CCBDFs) have not been subject to environmental regulation by the US EPA due to the so-called Bevill Exemption, which exempts coal fly ash from regulation as a hazardous waste as part of the 1980 Solid Waste Disposal Act Amendments to RCRA.²⁰ However, the EPA is currently developing national standards for monitoring groundwater at CCBDF sites in the US. Most of the older ash disposal sites are unlined and many are unmonitored. Development of effective techniques for *in situ* chemical fixation (ISCF) of trace elements in ash at closed CCBDFs would save the U.S. electric utility industry billions of dollars in costs associated with excavation and lining of older disposal sites.

Solutions of soluble iron salts have been used in numerous applications to sequester aqueous trace elements through co-precipitation with, and/or adsorption by, solid phases which precipitate from the treatment solutions. Voigt et al.²¹ examined the fixation of arsenic in contaminated soils using ferrous sulfate, but found no evidence of the formation of ferric arsenate. Yang²² determined that ferrous sulfate treatment of arsenic-contaminated soil accomplished the transfer of arsenic from the easily extractable soil fractions to the fraction associated with poorly crystalline iron oxyhydroxides. Arsenic has also been removed from solution by co-precipitation with ferric chloride²³ and processes for removing hexavalent chromium and other heavy metals from waste water using ferrous sulfate, ferric sulfate or ferric chloride have been developed.^{24,25}

The purpose of this study was to experimentally examine potential methods for ISCF of trace elements associated with coal fly ash. Two treatment solutions were investigated as potential chemical fixation agents for metal and metalloid trace elements present in fly ash collected at four different electric power plants located within the southeastern region of the United States. The effectiveness of the treatment methods was evaluated

through sequential batch leaching of the treated and untreated fly ash samples using a synthetic acid rain solution.

METHODS

Two sets of batch treatment experiments were conducted in which treatment solutions were reacted with each of four different ash samples at two different solid:liquid ratios. The dry, treated ash samples were subsequently leached with a synthetic acid rain solution to evaluate and compare the effectiveness of the treatment solutions to chemically fix trace elements within the fly ash.

Ash Sample Characterization

Four fly ash samples were collected from electric power plants located in the southeastern U.S. The precise site locations are proprietary and will be designated in this paper by two letter sample identification labels: MA, HA and HB fly ash samples were produced from combustion of eastern bituminous coal, while PA fly ash was derived from Powder River Basin (PRB) coal. The mineralogy of the fly ash samples was determined by powder X-ray diffraction (XRD) analysis of bulk ash mounts and fine particle separates. The environmentally available concentrations of major, minor and trace elements in the ash samples were measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES) analysis of the solutions produced by microwave-assisted acid digestion (MWD) of the fly ash following US EPA Method 1351A.²⁶ The pH of the fly ash was measured by equilibrating each sample in doubly deionized (DDI) water for 24 hours at the solid:liquid ratios used in the batch treatment experiments (1:3 and 1:30).

Ferrous Sulfate Treatment

Ash samples were treated with a ferrous sulfate (FS) solution containing 32 ppm iron (6.4g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 4 L DDI water) at solid:liquid ratios of 1:3 (50g ash:150g FS solution) and 1:30 (50g ash:1500g FS solution). After shaking at 200 rpm for 7 days, the ash/treatment solution mixtures were centrifuged at 7000 rpm for 15 minutes. The supernatant solutions were filtered through 0.2 mm syringe filters, acidified using Optima™ ultrapure HNO_3 , and analyzed by ICP-OES. The treated ash samples were allowed to air dry for 1 week.

Ferrous Sulfate with Calcium Carbonate Buffer Treatment

A second set of batch treatment experiments were conducted using the ferrous sulfate treatment solution with calcium carbonate (FS+CC) added as a buffer at a 2:1 molar ratio of Ca to Fe. Only a portion of the added CaCO_3 dissolved (35% by weight),

leaving the remainder in the solid phase to provide continued buffering during the treatment and subsequent leaching process. The FS+CC treatment solution was reacted with the ash samples using the same solid:liquid ratios, curing time and procedures described in the previous sub-section. The reacted treatment solutions were acidified and analyzed by ICP-OES. The treated ash samples were allowed to air dry for 1 week.

SPLP Sequential Leaching of Treated and Untreated Fly Ash Samples

A synthetic acid rain solution corresponding to that described by the synthetic precipitation leaching procedure (SPLP), US EPA Method 1312B,²⁷ was used as the leachate in batch sequential leaching experiments designed to test the success of the treatment solutions in reducing the mobility of trace elements associated with the CCB materials. The SPLP fluid is a dilute mixture of water, nitric acid and sulfuric acid with pH = 4.2.

Three grams of treated ash was placed into contact with 45 g SPLP leachate 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 HNO_3 . Leachate solutions were analyzed by ICP-OES for major, minor and trace elements. After centrifugation, another 45 ml aliquot of SPLP fluid was added to the tube, and the leaching procedure repeated. Leaching was continued until all trace element concentrations (except Sr) dropped to \leq LOD. The same batch sequential leaching procedure was carried out simultaneously for untreated ash samples for comparison of results.

RESULTS AND DISCUSSION

Fly Ash Characterization

The pH values of DDI water equilibrated with the fly ash samples for 24 hours are shown in Table 1. The pH values measured at the two different S:L ratios are closely comparable, except those for HA and MA ash, which showed a +0.13 and -0.23 pH unit difference, respectively. The fly ash produced from combustion of eastern bituminous coals are all acidic, with MA fly ash having pH around 4.9, HB fly ash having pH of approximately 5.93 and HA fly ash having pH of about 6.25. 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.

A representative XRD pattern for the fly ash samples is shown in Figure 1. The fly ash samples have virtually identical mineralogy, although mineral abundances vary. The major mineral constituents of the fly ash samples are quartz, mullite and hematite/maghemite.

Table 1. Measured pH values of fly ash samples. See text for explanation of method used.

Fly Ash Sample	Solid:Liquid	pH
HA	1:3	6.18
HA	1:30	6.31
HB	1:3	5.94
HB	1:30	5.92
MA	1:3	5.03
MA	1:30	4.80
PD	1:3	11.05
PD	1:30	10.99

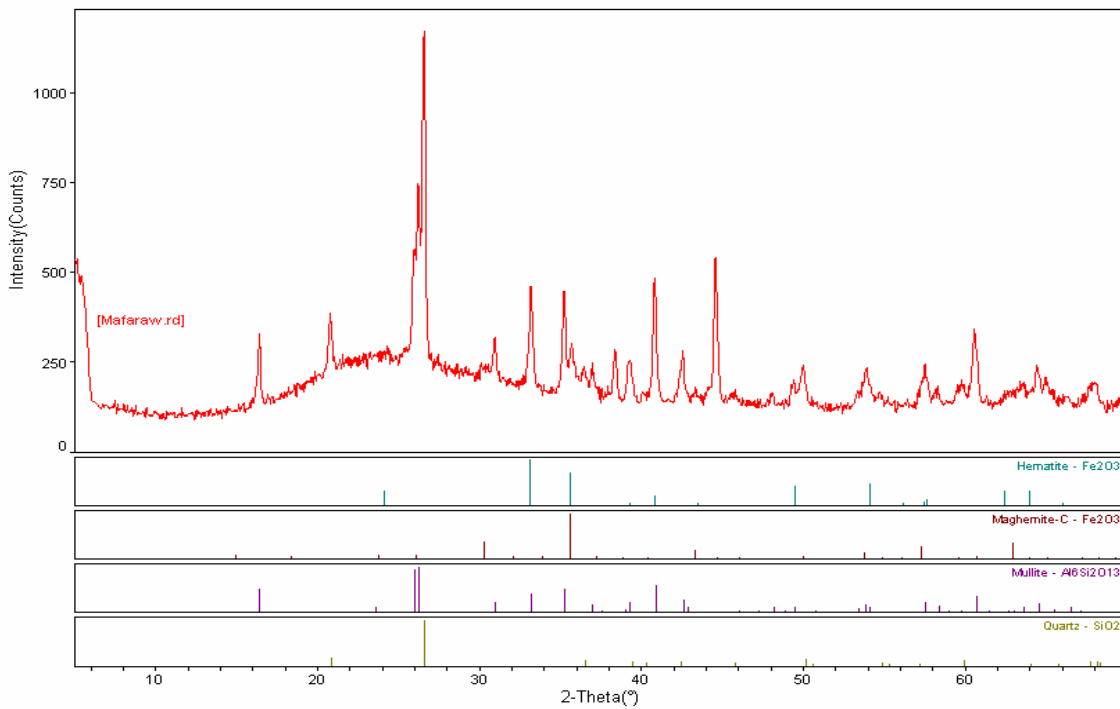


Figure 1. XRD pattern for bulk MA fly ash.

Fly Ash Compositions

The environmentally available concentrations of major, minor and trace elements were calculated for each of the ash samples on a dry weight basis, using the aqueous concentrations of the elements present in the supernatant solutions produced by microwave-assisted acid digestions. The digestion method used (US EPA Method 3051A) is a partial digestion technique aimed at identifying elements with the potential to be released to the environment by leaching processes. The elements present in undigested residual solids (primarily silicate minerals) are not considered to be environmentally available. Figure 2(a) compares the concentrations of major elements and Figure 2(b) compares the trace element concentrations in the four fly ash samples. Trace elements are defined for the purposes of this discussion as those having concentrations < 200 ppm on a dry weight basis.

The alkaline fly ash is significantly different in composition than the three acidic fly ash samples (Figure 2). PD fly ash has the highest digestible Ca and the lowest total trace element concentration of the four ash samples. PD fly ash also has the highest relative proportions of B and Mg and the lowest relative proportions of Si, Al, K and As, compared to the other ash samples. The acidic fly ash samples (HA, HB, MA) share similar major, minor and trace element chemistry. Aluminum is the most abundant major element in HA ash. Iron is a more significant portion (~20%) of the major element distribution for the acidic HA, HB and MA fly ash samples, due to their lower Ca contents compared to the alkaline PD fly ash.

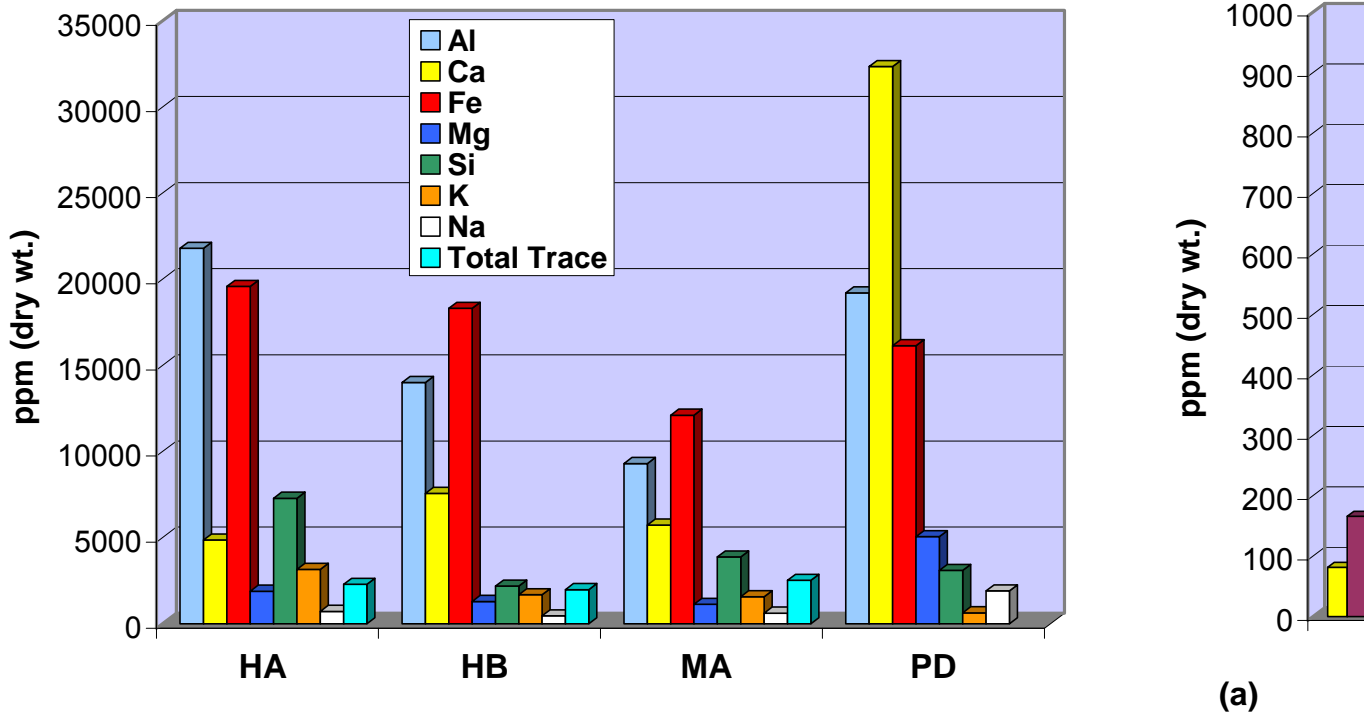


Figure 2. Compositions of the fly ash samples used in this study: (a) major and total trace

elements; (b) minor and trace elements. Element concentrations were calculated on a dry weight basis from ICP-OES analysis of ash digestate solutions produced using US EPA Method 3051.

Treatment Experiments

Mass balance calculations show that approximately 1750 mg of $\text{Fe}(\text{OH})_3$ was precipitated per kg of ash for the solid:liquid ratio of 1:3. Exactly 10x more $\text{Fe}(\text{OH})_3$ was precipitated for the solid:liquid ratio of 1:30 ($\text{Fe}(\text{OH})_3 = 1.75\%$ of sample by weight). A slightly greater amount of $\text{Fe}(\text{OH})_3$ was formed in the buffered experiments (1.91% by weight) due to the promotion of ferric hydroxide formation at higher pH conditions (Figure 3).

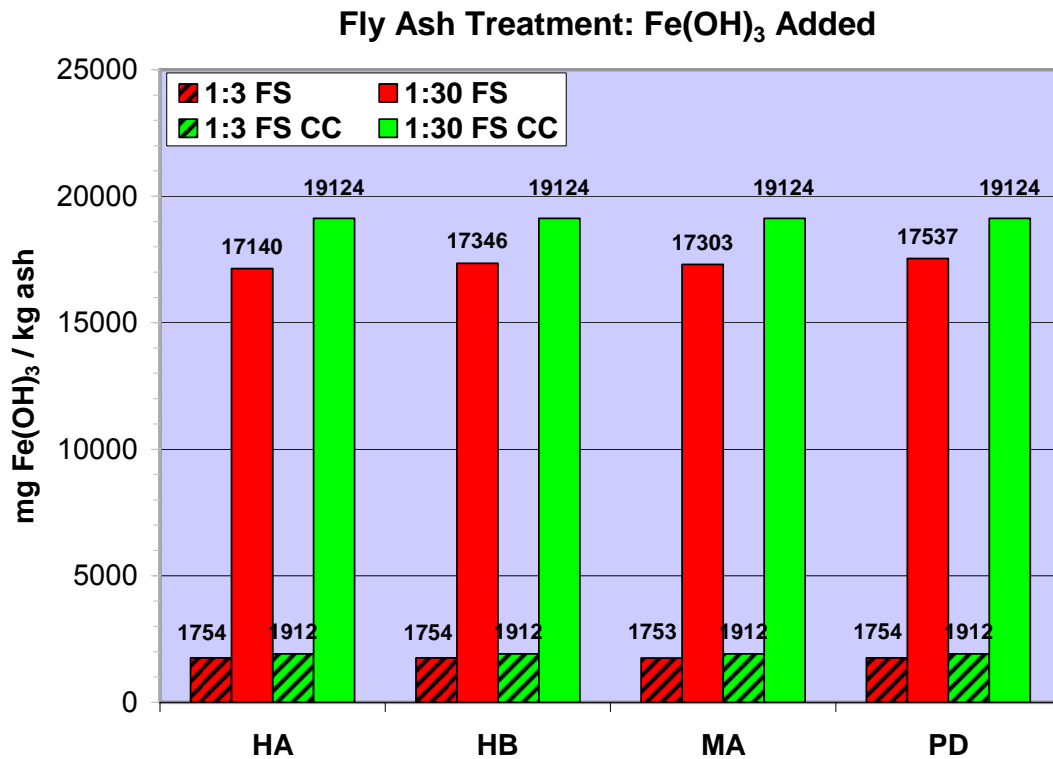


Figure 3. Amounts of ferric hydroxide precipitated in fly ash during ferrous sulfate and ferrous sulfate + calcium carbonate treatment experiments.

The FS 1:30 treatment released only trace amounts of As, B, Cr, Mo, Ni and V from each of the fly ash samples. However, significant amounts of the ash MWD total Se and Sr are released by all of the treatment solutions. The FS 1:3 treatment released the lowest amounts of these elements. The FS+CC treatment leached significantly higher

amounts of all elements from the ash samples during treatment. This was especially important for B in PD ash and for Mo in all of the ash samples.

SPLP Leaching Experiments

Figures 4-7 show the total concentration of trace elements removed from treated and untreated fly ash samples by batch SPLP leaching. Figure 4(a) shows that the FS (1:30) treatment resulted in a 54-72% reduction in As mobility, compared to the untreated HA, HB and MA ash. The addition of CaCO_3 to the treatment solution released 1000-1500 times more As from HA, HB and MA fly ash than was leached from the untreated ash samples. All treatment methods produced comparable results for PD ash, reducing As mobility by 23-39%. All treatment methods resulted in reduced B mobility in all ash samples, except for FS+CC (1:3) which caused a 10% increase in B mobility for MA ash (Figure 4(b)). FS (1:30) and FS+CC (1:30) treatments gave the best results for all ash samples, reducing B mobility by 43-80%. These results are particularly significant for PD ash, which is derived from a high-B PRB type coal.

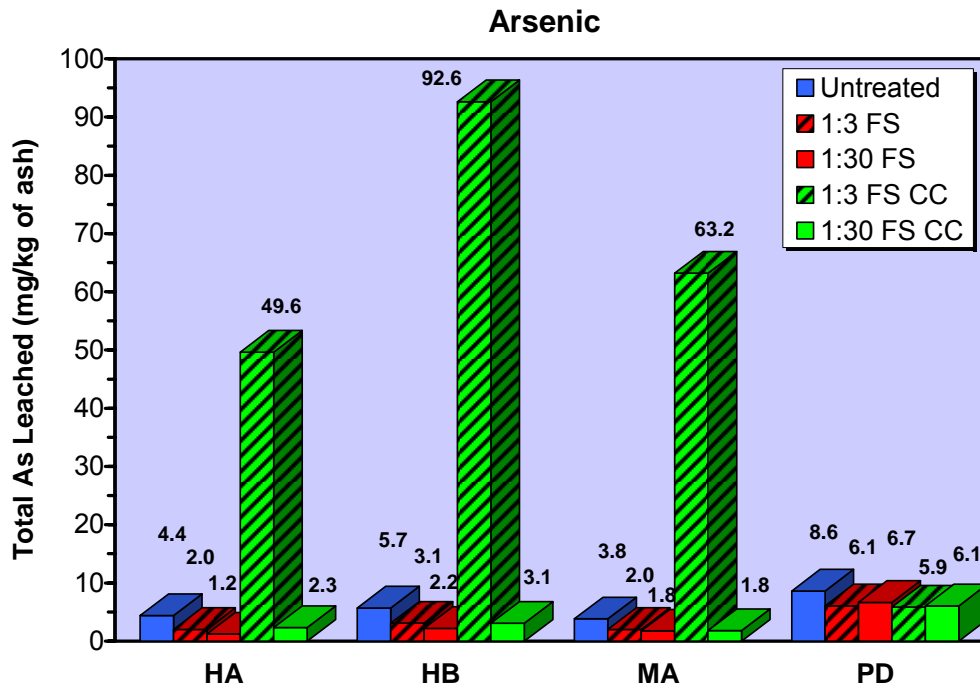
Untreated PD ash released more than twice as much Cr as the other untreated ash samples upon SPLP leaching (Figure 5(a)). All treatment methods gave comparable reductions in Cr mobility for PD ash, regardless of the S:L ratio. For HA, HB and MA fly ash, treatment results for Cr were similar to those for B, although the total reductions in Cr mobility were slightly lower than those achieved for B. It can be seen in Figure 5(b) that FS was the most beneficial treatment for reduction of Mo mobility in all ash samples, with greater reduction achieved for the 1:30 S:L ratio. Addition of CC at the 1:3 S:L ratio resulted in a 44% increase in Mo leaching for HB fly ash and a 500% increase in Mo leaching for MA fly ash, compared to the untreated ash. Comparable reductions in Mo mobility were obtained for FS and FS+CC treatments of PD fly ash, although FS treatment was slightly better.

Figure 6(a) shows that FS+CC (1:3) was the best treatment for HA, HB and MA ash, resulting in 72-78% reduction in Ni mobility. However, FS+CC (1:30) caused a 10% increase in Ni mobility for MA fly ash and was the least effective treatment method for HA and HB ashes. All of the treatment solutions resulted in large releases of Ni from PD ash compared to the untreated fly ash (Figure 6(b)). Even so, the total Ni released from PD ash during sequential SPLP leaching was <0.5 ppm. SPLP leaching patterns for Se are similar to those observed for As, resulting in large increase in Se mobility for FS+CC (1:3) treatment for HA, HB and MA fly ash. The FS (1:30) treatment was again found to be the best for HA, HB and MA fly ash, resulting in 75-92% reduction in Se mobility. All treatment methods resulted in 40-60% reductions in Se mobility for PD fly ash.

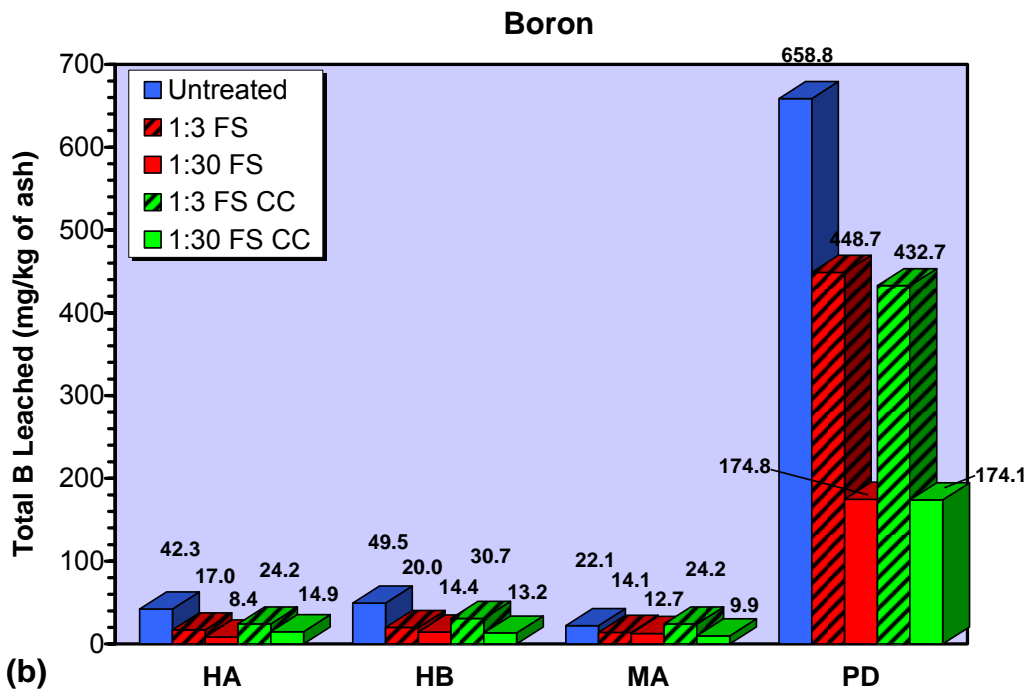
The FS+CC (1:30) is the most effective treatment for reducing Sr mobility in all of the ash samples (Figure 7(a)). However, the addition of calcium carbonate to the treatment solution at the 1:3 S:L ratio increased Sr mobility by 14-16% in HB and MA fly ash and by 1% in HA fly ash. In contrast, FS and FS+CC (1:30) treatment solutions lower Sr

mobility by 56-58% for PD fly ash, which has the largest leachable Sr concentration. Figure 7(b) shows that the addition of CC to the FS treatment solution increased leachable V by 3-5 times in HA, HB and MA ash. All of the treatment methods examined increased V mobility in HB fly ash. All of the treatment solutions reduced V mobility in PD ash, however, the best overall treatment method for the alkaline fly ash is FS (1:30).

Figure 8(a) shows the percent reduction in mobility of arsenic, boron, chromium and molybdenum after treatment of the fly ash samples with FS at S:L = 1:30. The treatment solution reduced the mobility of As by 23-72%, B by 43-80%, Cr by 45-77%, Mo by 77-98%, Ni by 12-58%, Se by 49-92%, Sr by 29-58%, V by 41-53%. Only V (HB) and Ni (PD) showed increased leachability after treatment (Figure 8(b)). It should be pointed out that the total amount of V released from HB ash during sequential SPLP leaching was <2.1 ppm. Likewise, the total Ni released from PD ash during sequential SPLP leaching was <0.17 ppm. Ash heterogeneity can explain these small differences in mobility compared to the untreated fly ash sample. These experiments will be repeated to determine whether the apparent release of V from HB fly ash and the apparent release of Ni from PD fly ash are reproducible.



(a)



(b)

Figure 4. Total concentration of trace elements mobilized by SPLP leaching of treated and untreated fly ash. (a) Arsenic; (b) Boron. Values calculated as mg trace element per kg fly ash, dry weight basis.

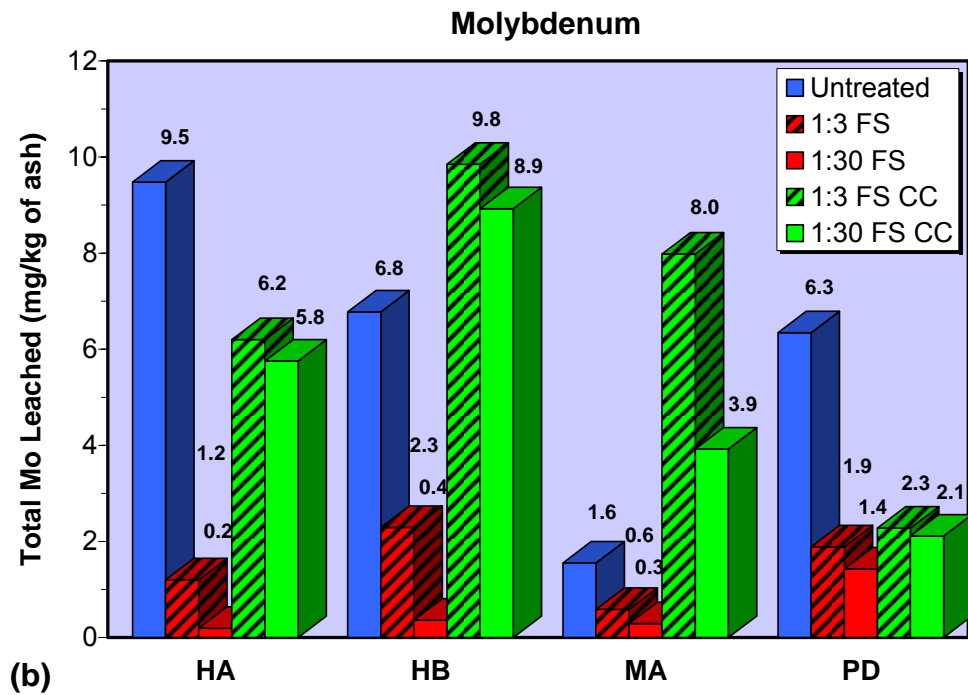
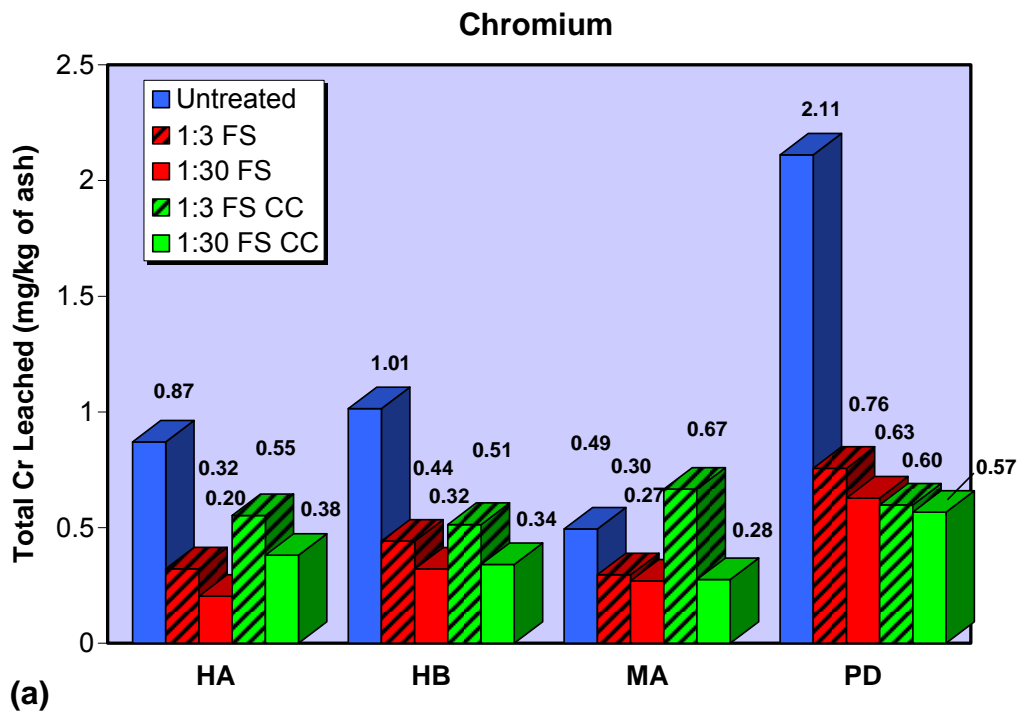
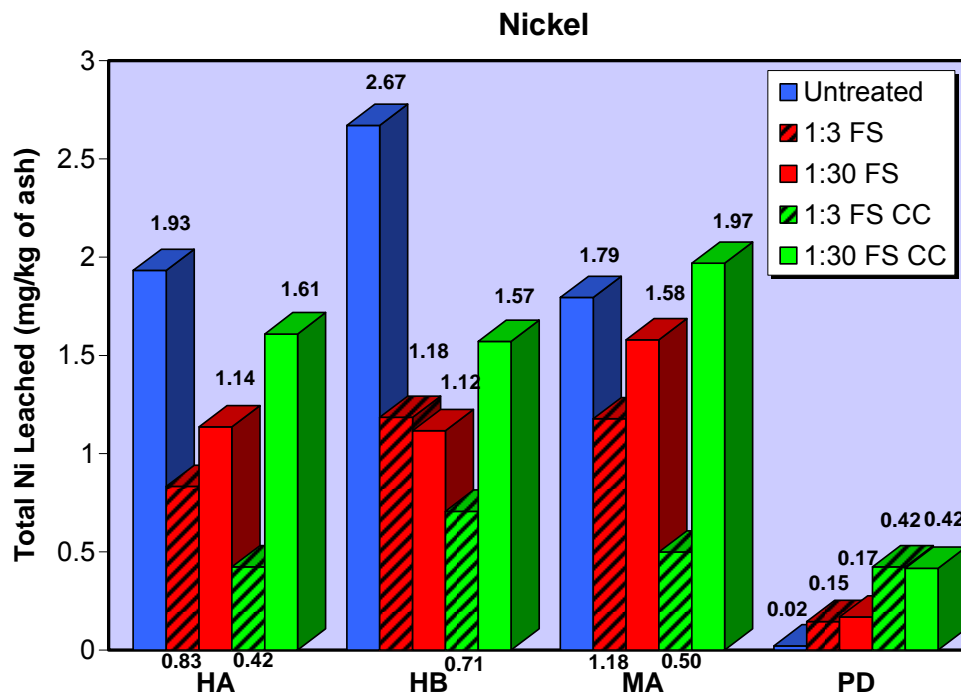
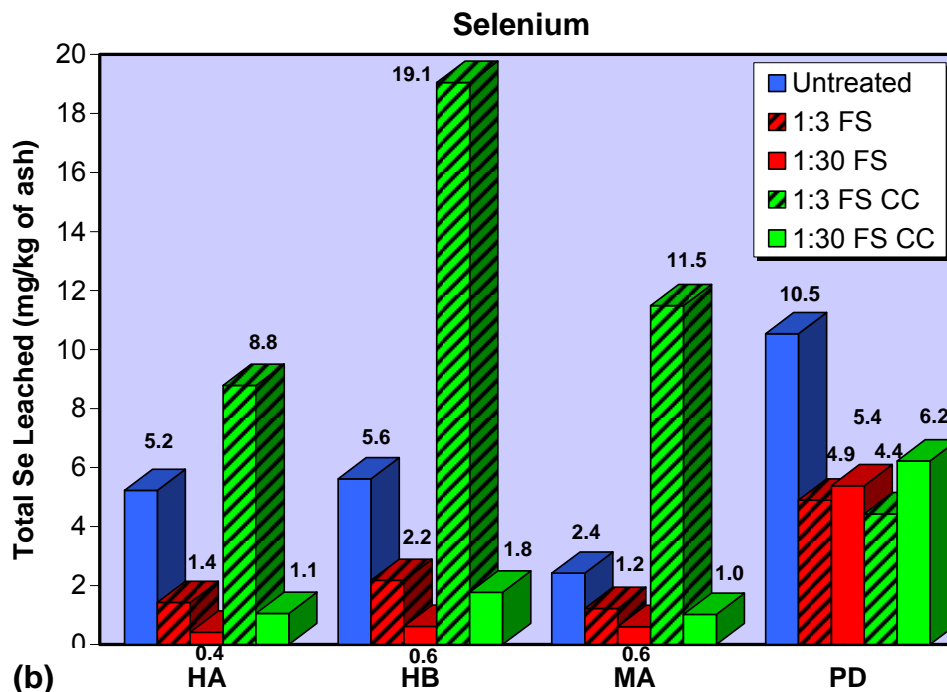


Figure 5. Total concentration of trace elements mobilized by SPLP leaching of treated and untreated fly ash. (a) Chromium; (b) Molybdenum. Values calculated as mg trace element per kg fly ash, dry weight basis.



(a)



(b)

Figure 6. Total concentration of trace elements mobilized by SPLP leaching of treated and untreated fly ash. (a) Nickel; (b) Selenium. Values calculated as mg trace element per kg fly ash, dry weight basis.

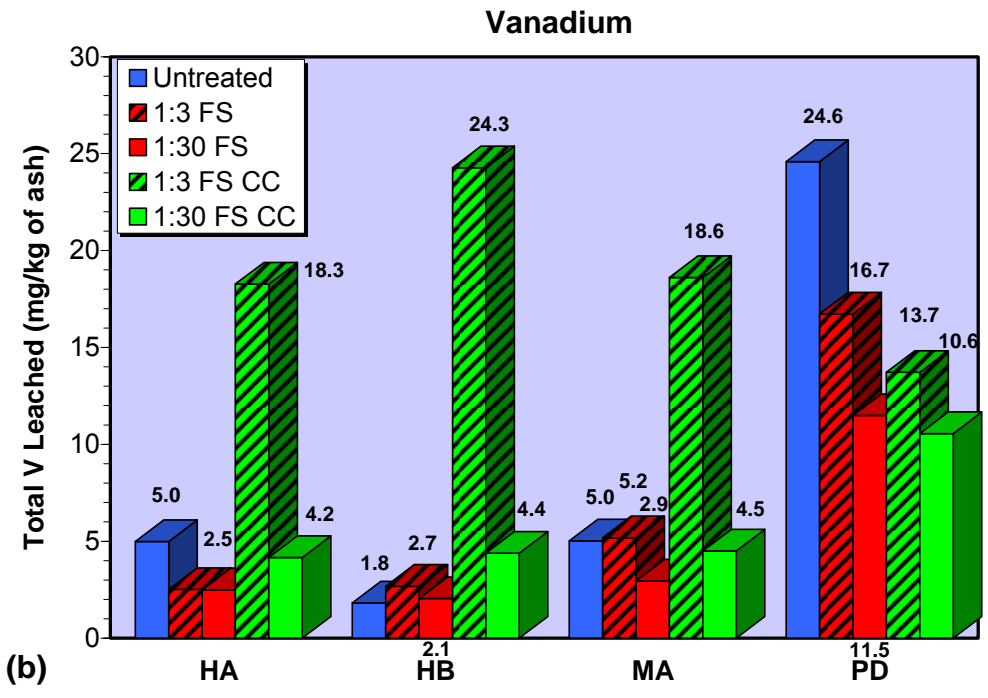
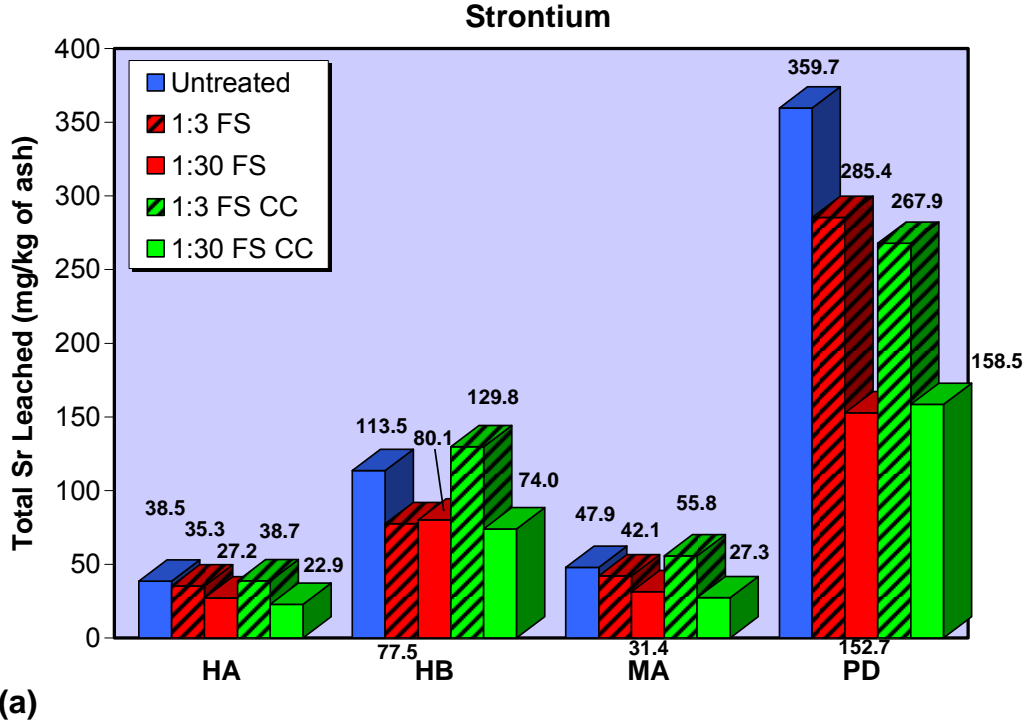


Figure 7. Total concentration of trace elements mobilized by SPLP leaching of treated and untreated fly ash. (a) Strontium; (b) Vanadium. Values calculated as mg trace element per kg fly ash, dry weight basis.

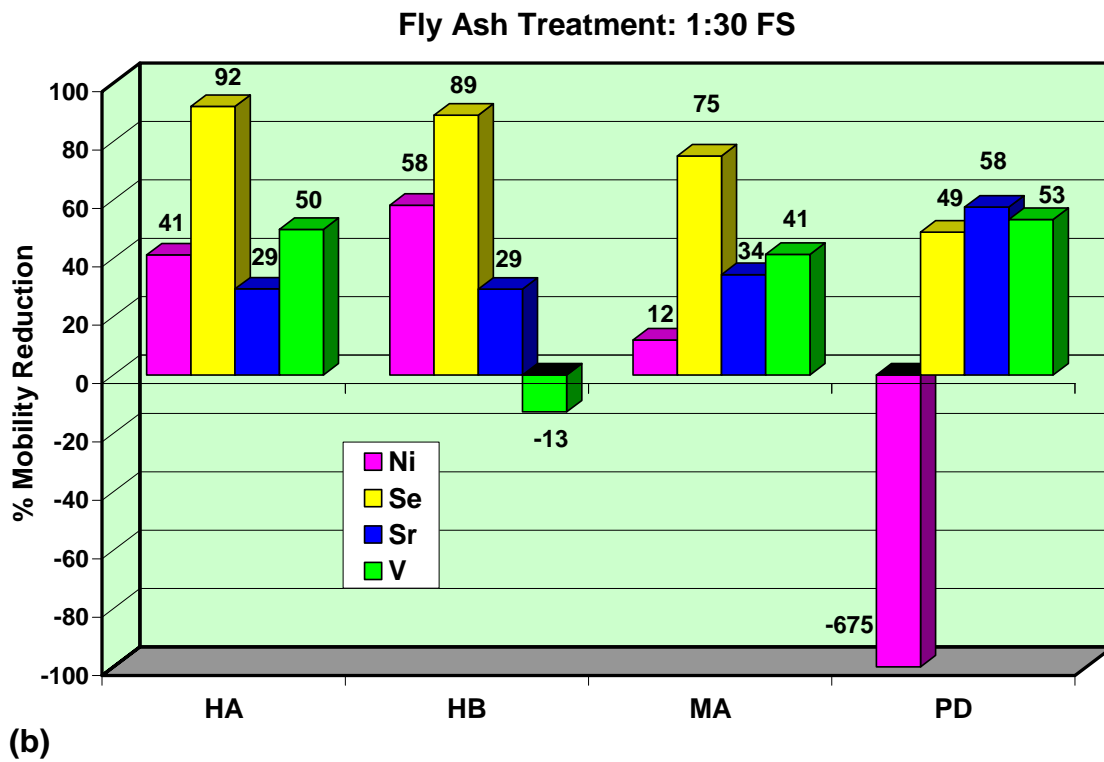
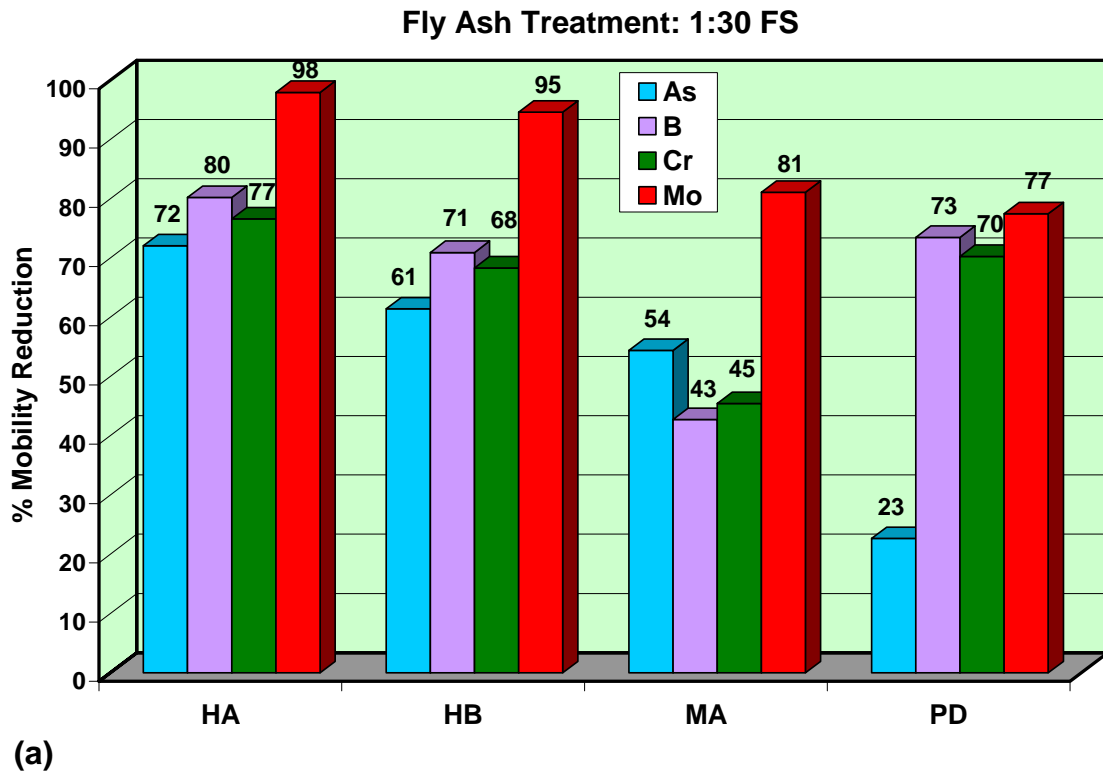


Figure 8. Percent reduction in the mobility of trace elements for FS-treated fly ash at S:L = 1:30, compared to untreated fly ash.

CONCLUSIONS

This study has shown that *in situ* chemical fixation of fly ash is a viable technique for trace element immobilization. Ferrous sulfate treatment of CCB material substantially reduced the mobility of most trace elements, especially at a 1:30 S:L ratio. This treatment solution produced the lowest SPLP mobility for Mo (all ash samples), As (HA, HB), Cr and B (HA), Se (HA, HB, MA), and V (HA, MA). The 1:3 S:L ratio FS+CC treatment was the best for Ni immobilization in the acidic fly ash samples (HA, HB, MA). The FS (1:30) and FS+CC (1:30) treatments were equally effective for immobilization of Sr (all ash samples), B (HB, MA, PD) and V (PD). Addition of CaCO₃ to the treatment solution as a buffer was found to be detrimental, resulting in the release of large amounts of As, Se, V (HA, HB, MA) and Cr (MA) at S:L=1:3, Mo (HB, MA) and Ni (PD) at S:L=1:3 and 1:30.

ACKNOWLEDGEMENTS

This research was supported by funding from the Electric Power Research Institute and from Southern Company Services, Inc. The authors would like to thank E.Y. Graham, J. Schexnayder, Y. Qi and Lauren Williams for their help with analytical and laboratory work.

REFERENCES

- [1] McCarthy, G.J., Grier, D.G. et al. Proceedings, 1999 International Ash Utilization Symposium, Lexington, Kentucky, Center for Applied Energy Research, 1999.
- [2] Kolker, A., Finkelman, R.B., Affolter, R.H. and Brownfield, M.E. In: The Use and Disposal of Coal Combustion by-Products at Coal Miners: A Technical Interactive Forum. (Eds. C. Vories-Kimery and D. Throgmorton), US Department of Interior, Office of Surface Mining, Alton, IL and Southern Illinois University Coal Research Center, Carbondale, IL, 2000, pp. 15-24.
- [3] Wu, E.J. and Chen, K.Y. EPRI EA-5115, Electric Power Research Institute, Palo Alto, CA, 1987, 200 pp.
- [4] Hower, J.C., Robl, T.L. and Thomas, G.A. Fuel, 1999, 78, pp. 701-712.
- [5] Steenari, B.M., Schelander, S. and Lindqvist, O. Fuel, 1999, 78, pp. 249-258.
- [6] Hanson, L.D. and Fisher, G.L. Environmental Science & Technology, 1980, 14, pp. 1111-1117.
- [7] Eary, L.E., Rai, D., Mattigod, S.V. and Ainsworth, C.C. J. Environ. Quality, 1990, 19, pp. 202-214.

- [8] Mukhopadhyay, R.K., Lajeunesse, G. and Crandlemire, A.L. *International Journal of Coal Geology*, 1996, 32, pp. 279-312.
- [9] Karayigit, A.I., Onocak, T., Gayer, R.A. and Goldsmith, S. *Applied Geochemistry*, 2001, 16, pp. 911-919.
- [10] Giere, R., Carlton, L.E. and Lumkin, G.R. *American Mineralogist*, 2003, 88, pp. 1853-1865.
- [11] Warren, C.J. and Dudas, M.J. *Journal of Environmental Quality*, 1985, 14, pp. 405-410.
- [12] De Groot, G.J., Wijkkstra, J., Hoede, D. and van der Sloot, H.A. In: *ASTM Special Technical Publication*, ISSN 0066-0558, American Society for Testing Materials, 1989, pp. 170-183.
- [13] Van der Hoek, E.E., Bonouvrie, P.A. and Comans, R.N.J. *Applied Geochemistry*, 1994, 9, pp. 403-412.
- [14] Dreesen, D.R., Gladney, E.S., Owens, J.W., Perkins, B.L. Wienke, C.L. and Wangen, L.E. *Environmental Science & Technology*, 1977, 11(10), pp. 1017-1019.
- [15] Chu, T.Y.J., Ruane, R.J. and Krenkel, P.A. *J. Water Pollution Control Fed.*, 1978, 50(11), pp. 2494-2508.
- [16] Theis, T.L. and Richter, R.O. *Environmental Science & Technology*, 1979, 13(2), pp. 219-224.
- [17] Turner, R.R. *Environmental Science & Technology*, 1981, 15(9), pp. 1062-1067.
- [18] Howell, J.R., Redwine, J.C. and Donahoe, R.J. *Secondary Mineral Formation in Weathered Ash: Implications for Metals Sequestration*. Electric Power Research Institute Technical Report #1005261, EPRI, Palo Alto, CA, 2003.
- [19] Alberts, J.J., Newman, M.C. and Evans, D.W. *Water, Air & Soil Pollution*, 2004, 26(2), pp. 111-128.
- [20] RCRA Solid Waste Disposal Act Amendments, 1980, 40 CFR 261.4(b)(4).
- [21] Voigt, D.E., Brantley, S.L. and Hennes, R.J.-C. *Applied Geochemistry*, 1996, 11, pp. 633-643.
- [22] Yang, L. *Evaluation of In Situ Chemical Fixation for Remediation of Arsenic-Contaminated Soil*. Ph.D. Dissertation, The University of Alabama, 2005.

[23] Meng, X., Bang, S. and Korfiatis, G.P. Water Research, 2000, 34(4), pp. 1255-1261.

[24] Suici, D.F., Wikoff, P.M., Beller, J.M. and Carpenter, C.J. U.S. Patent No. 5000859, U.S. Patent Office, 1991.

[25] Etzel, J.E. and Anand, P. U.S. Patent No. 4343706, U.S. Patent Office, 1982.

[26] U.S. EPA Method 3051A 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., 1994.

[27] U.S. EPA Method 1312B 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., 1994.