

Potential Use of Surfactant-Modified Zeolite for Attenuation of Trace Elements in Fly Ash Leachate

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ABSTRACT

Large volumes of fly ash and other coal combustion products (CCPs) are produced every year by coal-fired power plants. About 50% of the CCPs produced in the U.S. is buried in impoundment lagoons or dry landfills. Fly ash is generally enriched in several potentially hazardous trace elements, such as As, B, Cd, Co, Cr, Mo, Se, Sr, and V, which can leach from older, unlined disposal sites. Therefore, effective remediation of older CCPs disposal sites is needed to minimize any potential impact of leachate on the groundwater system.

Fly ash samples collected from four power plants were used in this study. Sequential leaching with distilled and deionized water indicated a significant amount of leachable elements in these fly ash samples. For each ash sample, leachate was produced by shaking 30 g of ash in 450 ml of DDI water for 48 hours. The generated leachate solutions were separated from the ash and treated with surfactant-modified zeolite (SMZ). HDTMA-Br modified clinoptilolite was used at different percentages (1% to 20% of 2.67 g of ash) to treat 40 ml of ash leachate. Quantitative comparison of the elemental composition of SMZ-treated and untreated leachate indicated that SMZ is effective in decreasing the concentration of oxyanion and cationic trace elements associated with coal fly ash. In general, up to 30% of the As, Mo, and V; up to 80% of the Cr; and up to 20% of the Se and Sr were removed from the leachate after SMZ treatment. These results support potential use of SMZ in permeable reactive barriers to control the dispersion of heavy metals and metalloids from ash disposal sites.

INTRODUCTION

Worldwide, coal fired power plants produce hundreds of millions of tons of coal combustion products (CCPs) annually, including fly ash, bottom ash, boiler slag, flue gas desulfurization (FGD) materials, and different gasses.¹ Fly ash, the most voluminous fraction of CCPs, is fine particulate matter collected thorough mechanical, electrostatic, and fabric filters from the flue gas produced by the combustion of pulverized coal in the boiler assembly. In 2007, 71.7 million metric tons of fly ash was produced by coal-fired power plants in the US, accounting for 57% of the total CCPs.² Although the beneficial use of fly ash and other CCPs had slightly increased in recent years (44% or 31.6 Mt of fly ash was recycled and used in 2007), the majority of the fly ash is still being buried in impoundment lagoons or dry landfills, along with other unused CCPs.² Fly ash contains numerous trace elements which can potentially pose health hazards in humans; therefore, development of feasible and effective techniques to control the dispersion of

hazardous trace elements from old, unlined CCP disposal facilities to surrounding groundwater and surface water is very important to ensure protection of groundwater and surface water resources.

Several studies have attempted treatment of municipal solid waste (MSW) fly ash to immobilize the heavy metals;³⁻⁶ however, there have been relatively few studies of controlling the mobility of trace elements in coal fly ash.^{7, 8} While working on MSW fly ash rich in sulfates, alkali chlorides, and heavy metals, Auer et al. noted that the addition of reactive calcium aluminates in fly ash resulted in formation of ettringite-like minerals capable of partially incorporating Co, Ni, Cu, Zn, and Cd.³ Therefore, treatment using reactive calcium aluminates can be the first step, followed by addition of other binding materials, for solidification and fixation of heavy metals in sulfate-rich fly ash.³ To stabilize the heavy metals in MSW fly ash, a four step treatment method that includes pH-controlled water washing of soluble salts in fly ash, addition of 10% phosphoric acid, heating of the solid residue to about 800° C, and air hydration after mixing at 1:4 with Portland clinker (Portland cement without calcium sulfate) was developed by Derie.⁴ Crannell et al. were able to stabilize Pb, Cu, Zn, and Cd through the formation of apatite-like minerals with addition of soluble phosphate to the MSW bottom ash.⁵ Similarly, phosphoric acid was used to form insoluble calcium phosphates with apatite structures which incorporate heavy metals present in the water-washed MSW fly ash.⁶ In this study, Hunag and Lo reported a 94.8% decrease in leachability of Pb after treating MSW fly ash with a colloidal aluminate oxide.⁹ A ferrous sulfate treatment method used by Yang et al. to chemically fix arsenic in a contaminated soil¹⁰ was extended by Donahoe et al. to immobilize trace elements in coal fly ash.⁷ It was found that ferrous sulfate treatment at a fly ash:ferrous sulfate solution ratio = 1:30 was most effective in decreasing the synthetic acid rain leachability of several priority trace elements associated with coal fly ash.⁸

The ready availability, low cost, and high cation exchange capacities of natural zeolites make them very useful materials in commercial water treatment applications.¹¹ Zeolites are hydrated aluminosilicate minerals which are characterized by cage-like structures having high internal and external surface areas with net negative surface charges.^{12, 13} Although natural zeolites have been widely used to remove cationic heavy metals from aqueous solutions,¹⁴ they are not useful for removing inorganic oxyanions such as chromate (CrO_4^{2-}).¹⁵ However, the external surface charge of natural zeolites can be altered with a surfactant to make it suitable to adsorb oxyanions of arsenic, chromium, and selenium. When the surfactant concentration is below or at the critical micelle concentration (CMC), it forms a monolayer or 'hemimicelle' at the zeolite-aqueous solution interface through strong Coulombic interactions; a bilayer or 'admicelle' is formed at the interface at surfactant concentrations above the CMC, thereby resulting in a positively-charged external surface suitable for adsorbing anionic counter ions.¹⁵ Bowman et al. showed the ability of a surfactant-modified zeolite (SMZ)-permeable reactive barrier (PRB) to remove metal oxyanions from contaminated groundwater.¹⁶ However, SMZ has not yet been evaluated as a possible PRB material for preventing the down-gradient migration of groundwater contaminants released from unlined fly ash disposal facilities. This study uses batch experiments to evaluate the ability of SMZ to attenuate trace elements associated with coal fly ash leachate.

MATERIALS AND METHODS

Characterization of Fly Ash Samples

Four fly ash samples, labeled HA, HB, MA, and PD, were collected from four coal-fired power plants. The three acidic fly ash samples (HA, HB, MA) are the product of combustion of Eastern Bituminous coals, while the alkaline fly ash sample (PD) is derived from the combustion of Powder River Basin coal. The fly ash samples were air-dried and homogenized prior to use in the experiments.

Fly ash mineralogy was determined by X-ray powder diffraction using a Bruker D-9 Advance X-ray diffractometer. The compositions of the fly ash samples were previously determined by Donahoe et al.⁷ using USEPA Method 3051A, which is a partial digestion method aimed at extracting environmentally available elements from solid wastes using microwave-assisted acid digestion.¹⁷ Ash carbon contents were determined by loss-on-ignition (LOI) tests following the method of Hassett and Eylands.¹⁸

DDI Water Sequential Leaching of Fly Ashes

To evaluate the leachability of trace elements from the fly ash samples, batch leaching experiments were conducted in duplicate. Ash samples were sequentially leached with double-deionized (DDI) water at a 1:15 ratio. For each experiment, 3 g of ash was weighed in a 50 ml centrifuge tube and 45 g of DDI water was added. The mixture was agitated on an orbital platform shaker at 200 rpm for 24 hours, the tube was then centrifuged at 8500 rpm for 30 minutes, and the supernatant solution filtered through a 0.2 μm syringe filter. After each leachate sample collection, 45 g of fresh DDI water was added to the tube and the leaching sequence repeated every 24 hours for a total of 35 days. Immediately after collection, the leachate solutions were acidified to 2% HNO_3 with OPTIMA[®] ultrapure nitric acid and stored in a refrigerator until analysis by inductively coupled plasma optical emission spectrometry (ICP-OES).

Surfactant-Modified Zeolite (SMZ)

The natural zeolite used in this study was obtained from the St. Cloud mine located in Winston, NM. It consists of clinoptilolite (74%), smectite clay (5%), quartz/cristobalite (10%), feldspar (10%), and illite (1%).¹⁹ The external cation exchange capacity of this zeolite has been reported by Sullivan et al. in the range of 70 to 90 meq/kg.^{19, 20} For this study, St. Cloud clinoptilolite was powdered using a mortar and pestle and sieved to ≤ 200 mesh prior to surface modification. A 0.04 M quaternary amine hexadecyltrimethylammonium bromide (HDTMA-Br) solution was prepared by adding 2.904 g of HDTMA-Br crystals to 200 ml DDI water. HDTMA-Br is a long-chain cationic surfactant with a critical micelle concentration of 0.9 mM.²¹ At higher concentrations, HDTMA-Br selectively exchanges with inorganic cations on the external surface of the zeolite, up to the external cation exchange capacity, and forms a stable surfactant bilayer with anion exchange properties.^{13, 15, 22} About 50 g of zeolite were mixed with 188 ml of 0.04 M HDTMA-Br solution in a 250 ml polypropylene bottle and agitated for three days. After being allowed to settle for 24 hours, the clear supernatant solution was discarded and the solid residue was collected by vacuum filtration through a 0.45 μm nylon membrane. The solid residue was

returned to the treatment bottle and agitated with 200 ml of DDI water for 24 hours to remove the excess HDTMA-Br. The washed solid was collected by vacuum filtration, the wash solution was discarded, and the surfactant-modified zeolite was air dried at room temperature.

Fly Ash Leachate Solutions

Fly ash leachate solutions were prepared using a solid-to-liquid ratio at 1:15. For each fly ash sample, 30 g was placed in a 500 ml polypropylene bottle and 450 g of DDI water was added. The ash-water mixtures were agitated at 200 rpm for 48 hours and then allowed to settle for 4 hours. After settling, the leachate solutions were passed through 0.2 μm syringe filters and collected in clean polypropylene bottles. Approximately 20 ml of each leachate solution was placed in a 30 ml bottle, acidified to 2% HNO_3 using ultrapure OPTIMA[®] nitric acid, and kept refrigerated until analysis by ICP-OES.

SMZ Treatment of Leachates

Different amounts of SMZ were equilibrated with fly ash leachate in duplicate batch experiments to evaluate its ability to remove the trace elements present. For SMZ treatments, 40 ml of each fly ash leachate were mixed separately with 0.027 g, 0.133 g, 0.267 g, 0.400 g, and 0.533 g of SMZ which represents, respectively, 1%, 5%, 10%, 15%, and 20% by weight of the 2.667 g of fly ash which were used to generate leachate at a 1:15 solid:liquid ratio. The required amount of SMZ was weighed in a 50 ml centrifuge tube and 40 ml of fly ash leachate were added. Experimental blanks were also prepared. The tubes were agitated at 200 rpm for 24 hours and then centrifuged at 8500 rpm for 30 min. The supernatant solutions were passed through 0.2 μm syringe filters, acidified to 2% HNO_3 with ultrapure OPTIMA[®] nitric acid, and stored in a refrigerator until analysis by ICP-OES.

RESULTS AND DISCUSSIONS

Fly Ash Characterization

The fly ash samples consist mostly of spherical glass particles, uncombusted carbon, and minor amounts of crystalline phases. X-ray diffraction data for these fly ash samples indicated similar mineralogy with different proportions of quartz, mullite, and hematite/maghemite.⁷ Combustible carbon contents, as determined by LOI tests, are 6.74%, 6.37%, 14.7%, and 3.66%, respectively, for HA, HB, MA, and PD fly ash samples.

The environmentally available concentrations of major, minor, and trace elements in these fly ash samples are given in Figures 1 and 2. Aluminum, Ca, and Fe are the dominant elements in all of the fly ash samples. PD fly ash, which is basic, is very rich in Ca compared to the three acidic fly ashes. MA fly ash has the lowest Al and Fe concentrations of the four ash samples. Trace elements such as As, B, Ba, Cr, Cu, Mo, Ni, Pb, Se, Sr, Ti, V, and Zn are also present at varied concentrations in all of the fly ash samples (Figure 2). Boron is highly enriched in PD fly ash, compared to other fly ash samples. However, As, Co, Cr, Cu, Ni, Pb, and V concentrations are lower in PD fly ash than in the other fly ash samples.

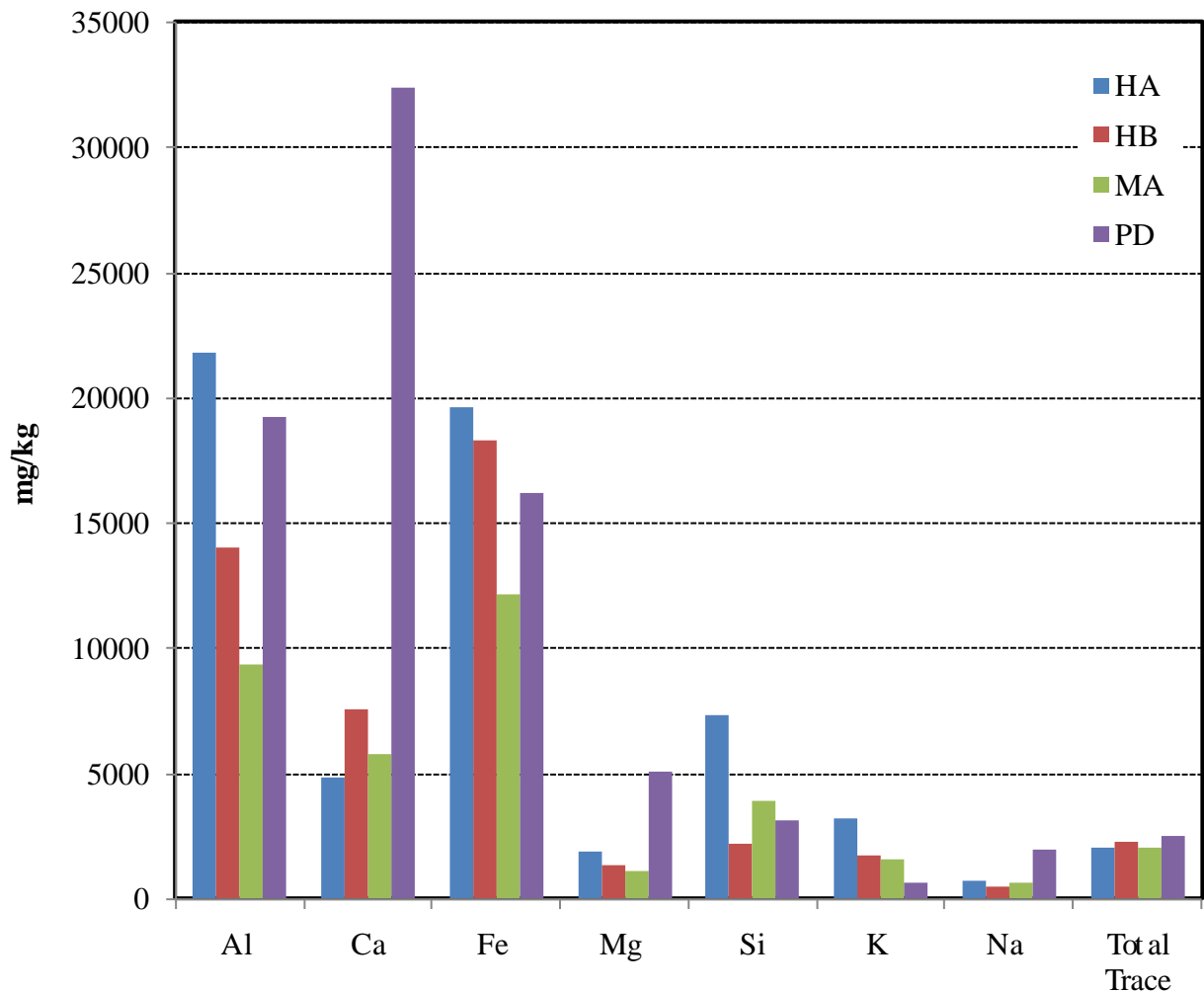


Figure 1. Environmentally available major element concentrations in the different fly ash samples. (From Donahoe et al.)⁷

Sequential Leaching of Fly Ashes

Figure 3 shows the change in pH during DDI water sequential leaching of the four fly ash samples. PD fly ash is alkaline, producing initial leachate pH values greater than 11. However, within the first 10 days of leaching, leachate pH decreased by more than a unit, followed by an asymptotic decrease over the remaining 25 days to a final pH of approximately 9.4. The three acidic fly ash sample leachates showed initial increases in pH, followed by decreasing pH. HA fly ash leachate increased rapidly in pH over the first 3 leaching cycles, then hovered around neutrality for the next 3 weeks, then decreased to fluctuate around 6.3 for the final 10 days of leaching. HB and MA fly ash leachates showed very similar pH trends; leachate pH slowly increased to approximately 7 during the first two weeks, then gradually decreased to fluctuate around 6.4 for the final 10 days of leaching.

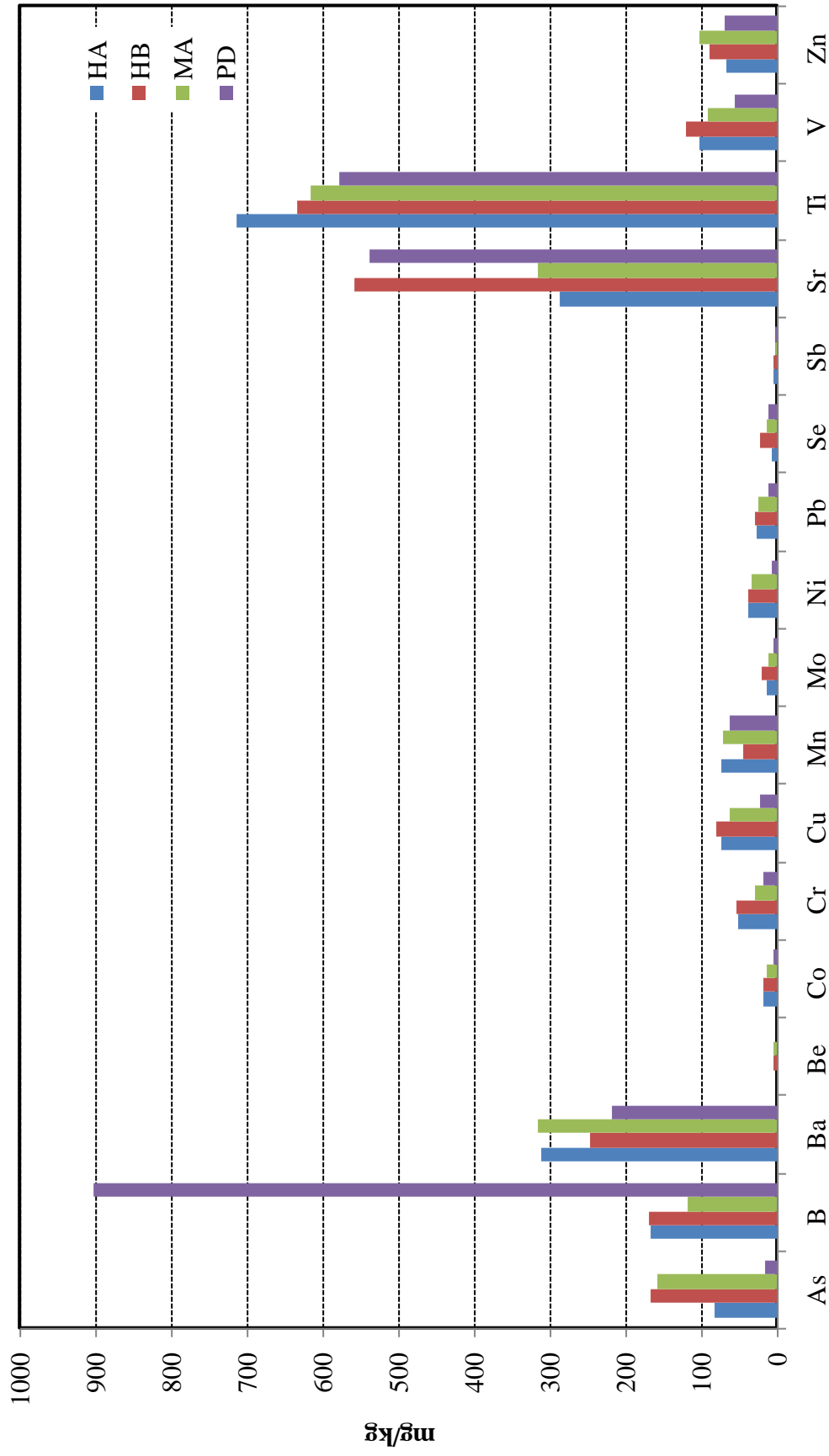


Figure 2. Environmentally available trace element concentrations in the different fly ash samples. (Data taken from Donahoe et al.)⁷

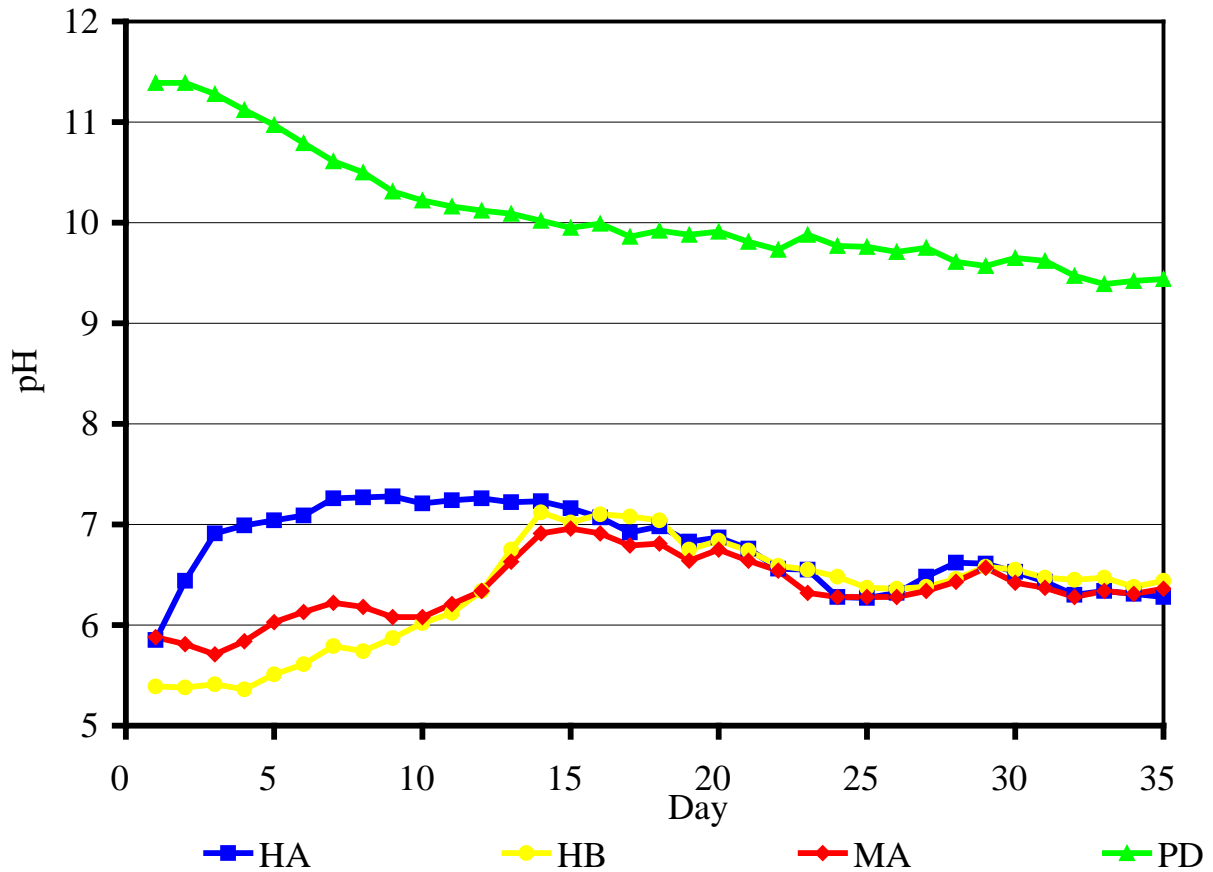


Figure 3: Leachate pH during DDI water sequential leaching of the fly ash samples

Figure 4 shows representative sequential leaching plots for a major element (Ca) and a trace element (As). High initial Ca concentrations decrease exponentially in subsequent sequential leaching cycles for all fly ash samples. Most of the Ca leached from the acidic fly ash samples was removed by the first four leaching cycles. Cumulatively, PD fly ash released almost five times more Ca than the acidic fly ash samples (Figure 4a). Leachate As concentrations showed a different leaching behavior than Ca. For all fly ash samples, As release was kinetically controlled. For HA fly ash, leachate As concentrations peaked in the 3rd leaching cycle and gradually decreased thereafter. In contrast, several additional leaching cycles were required for the other fly ash leachates to reach peak concentrations. For MA, PD, and HB fly ash, peak arsenic concentrations occurred at the 7th, 12th, and 17th leaching cycle, respectively. Cumulatively, HA fly ash released the most As over the course of the experiment (35 sequential leaching cycles), followed by MA, PD, and HB. In general, DDI water leached a significant amount of trace elements from the fly ash samples over a prolonged time period.

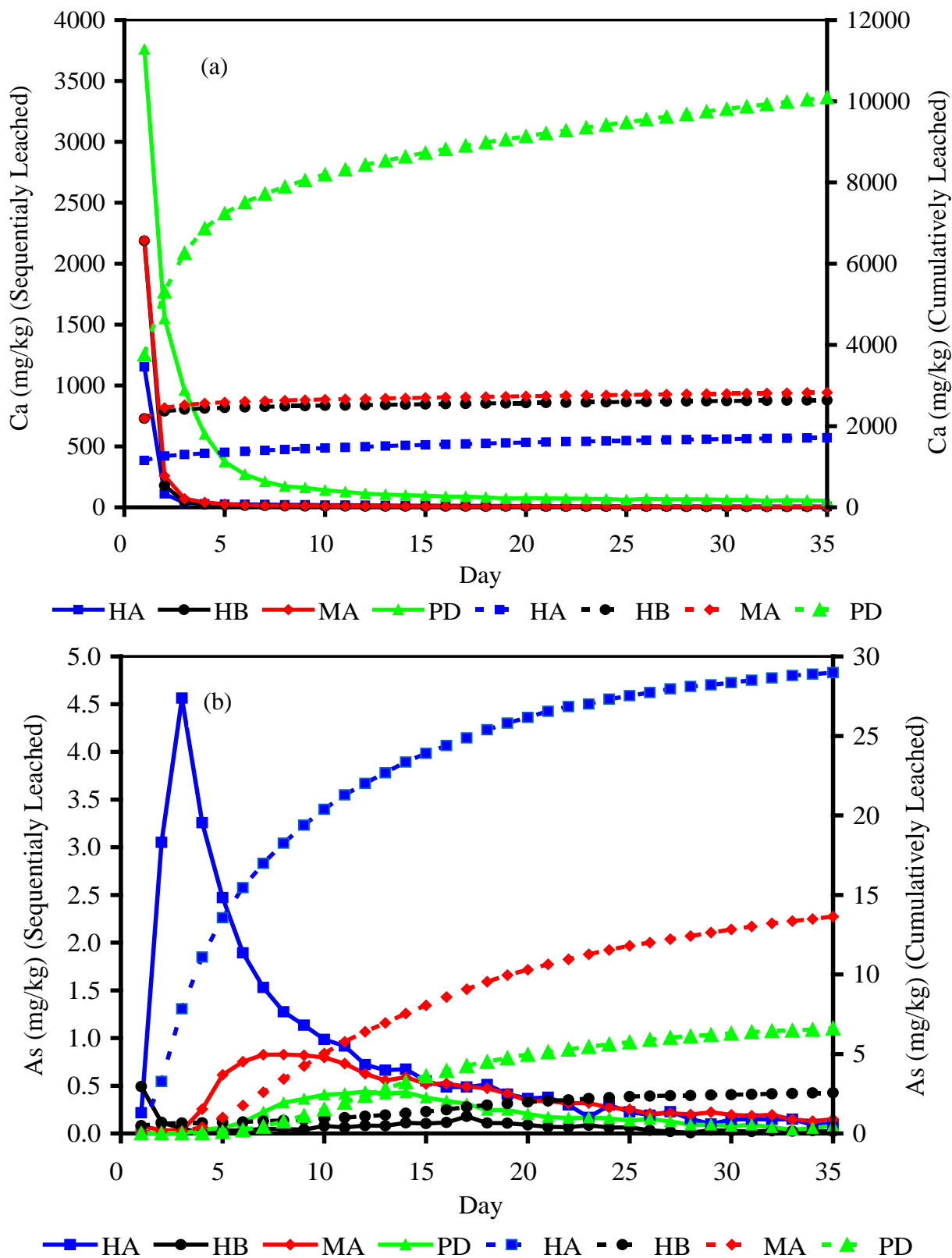


Figure 4: DDI water sequential leaching of fly ash (a) Ca and (b) As (solid lines give sequential leachate concentrations; dashed lines give cumulative concentration leached)

Figures 5 and 6 illustrate the percentage of environmentally available elements (see Figures 1 and 2), as determined by microwave-assisted acid digestion¹⁷, leached during 35 cycles of DDI water sequential leaching. Almost no environmentally available Al (except PD ash), Fe, Be, Cu, or Ti were leached. Among the major elements, sequential leaching removed more than 30 percent of the environmentally available concentrations of Ca, Na, and Si (PD only) from the fly ash samples. Significant amounts of some of the trace elements were also removed by sequential leaching from individual fly ash samples. For example, 35% (HA) and 39% (PD) of the As; 26% (HB), 32% (MA), and 71% (PD) of the B; 55% (HB) and 59% (PD) of the Ba; 50-89% of the Mo; 28-100% of the Sb; and 22% (HB), 26% (MA), and 64% (PD) of the Sr were removed by sequential leaching. For PD fly ash, more than 50% of the environmentally available B, Ba, Mo, Sb, and Sr were leached. Only 0-10% of environmentally available Co, Cr, Mn, Ni, Pb, Se (except HB), V (except MA), and Zn (except HB) were removed during DDI water sequential leaching.

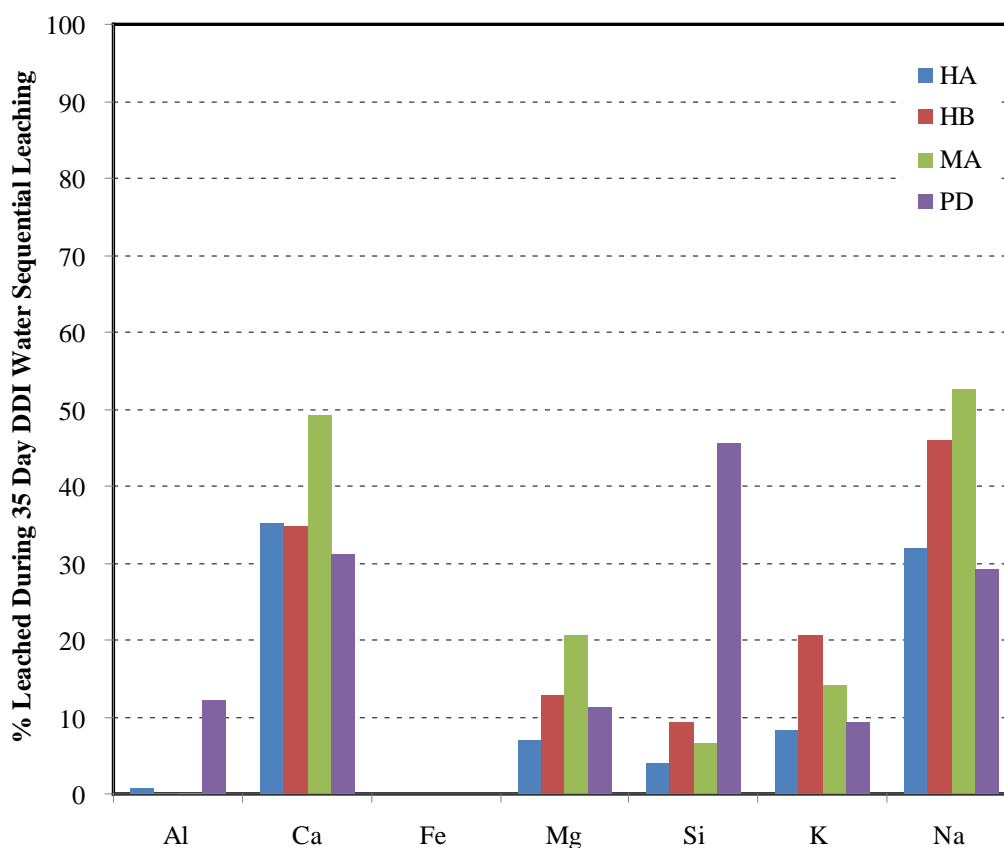


Figure 5: Percentages of environmentally available major elements leached during 35 days of DDI water sequential leaching

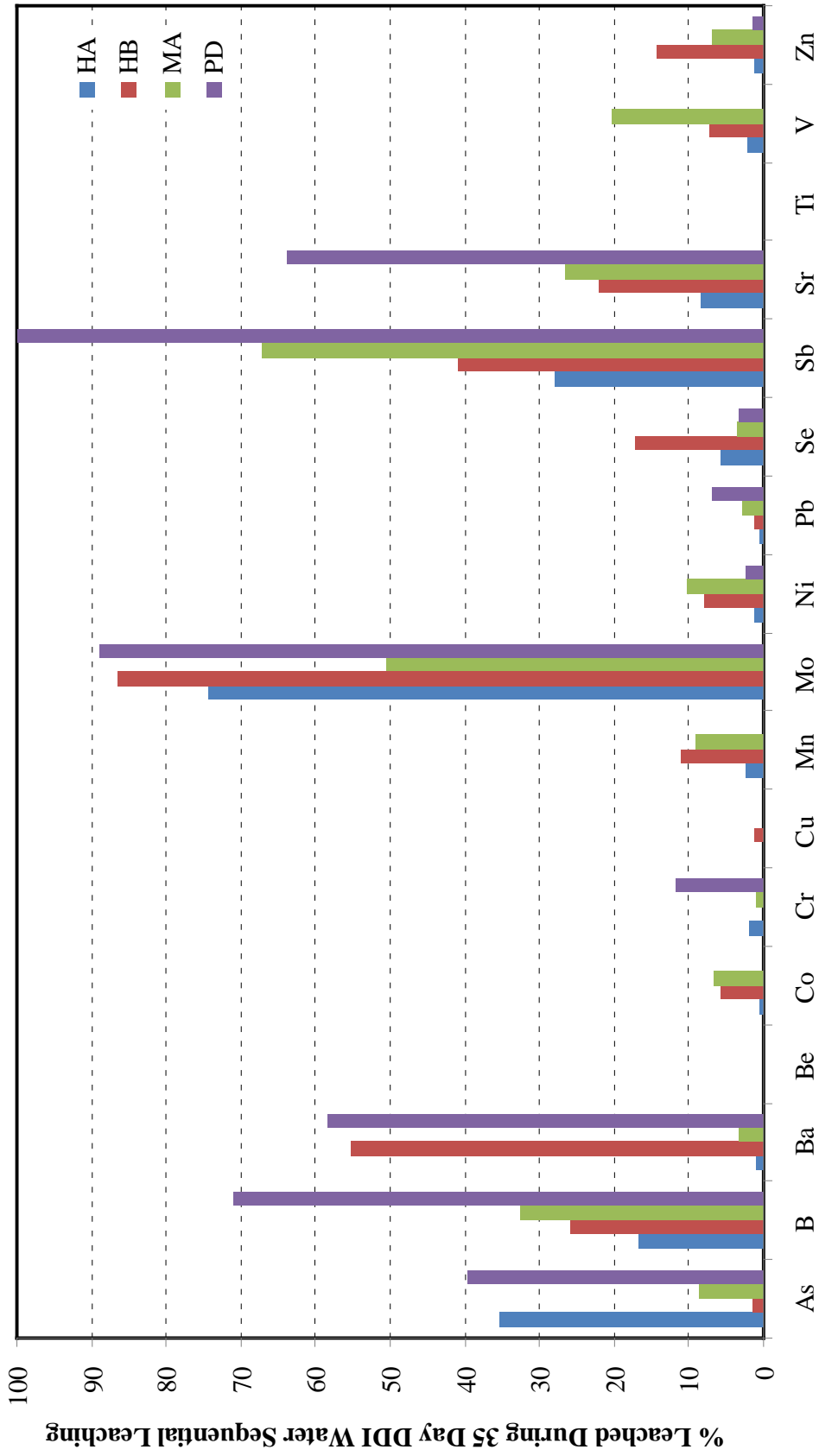


Figure 6: Percentages of environmentally available trace elements leached during 35 days of DDI water sequential leaching

Fly Ash Leachate Solutions

Figure 7 shows the compositions of the leachate solutions generated by 48 hour equilibration of the fly ash-DDI water mixtures at a 1:15 ratio for use in the SMZ batch treatment experiments. For all leachates, Ca was the dominant element, followed by K, Na, Mg, Sr, Si, and B (Figure 7a). Compared to leachate generated from the other fly ash samples, PD fly ash leachate had two orders of magnitude higher Al concentration, but two orders of magnitude lower Mg concentration. All fly ash leachates were also very rich in sulfate (≥ 280 mg/L, data not shown). The concentrations of trace elements in the fly ash leachate solutions are shown in Figure 7b. Comparison of Figure 7b and Figure 2 shows that US EPA Method 3051A is not a reliable predictor of the DDI water leachability of trace elements from coal fly ash.

SMZ Treatment of Leachates

Because the negatively charged external surface of clinoptilolite becomes positively charged by the formation of a surfactant double layer after the surface modification, anionic species can adsorb on the SMZ surface.¹⁵ However, the size of the cationic HDTMA⁺ is larger than the internal structural channelways of clinoptilolite, therefore the internal surface remains negatively charged and favors the adsorption of cationic aqueous species.¹⁵ Therefore, solutions containing both cationic and anionic aqueous species can show significant remediation after SMZ treatment.

Figures 8 through 11 show the percentage change in concentration of selected elements in the fly ash leachate solutions after SMZ treatment. For most of the leachates, the concentrations of several priority trace elements such as As, Cr, Mo, Ni, Sr, and V were decreased significantly by SMZ treatment. Similarly, treatment also decreased leachate Al, Ba, Ca, K (except PD), Ni, and Zn concentrations to varying extents. However, concentrations of Mg, Na (except MA and PD), and Si increased in the supernatant solution after SMZ treatment, indicating cation exchange reactions released these elements from the clinoptilolite surface during treatment. For PD fly ash leachate, the K concentration was increased and the Na concentration decreased by SMZ treatment (Figure 11). Leachate B concentrations were unaffected by SMZ treatment.

Treatments using higher weight percent SMZ resulted in greater reduction in the concentrations of several leachate constituents. Increased removal of elements with increasing SMZ content during treatment was observed for Cd (HB only), Cr, Mo (except MA), and Sr (except HA). However, for other some elements (e.g. As, Se, and V), there was no significant improvement in removal from leachate with addition of more than 10% SMZ.

For HA, HB, and MA fly ash leachates, As concentrations were reduced by 28%, 22%, and 24%, respectively, after 10% SMZ treatment. For HA, HB, MA, and PD fly ash leachates, Cr concentrations were decreased by 29%, 69%, 51%, and 14%, respectively. Similarly, 10% SMZ treatment decreased leachate Mo, Ni, Se, Sr, and V concentrations by up to 16%, 15%, 22%, 15%, and 13%, respectively.

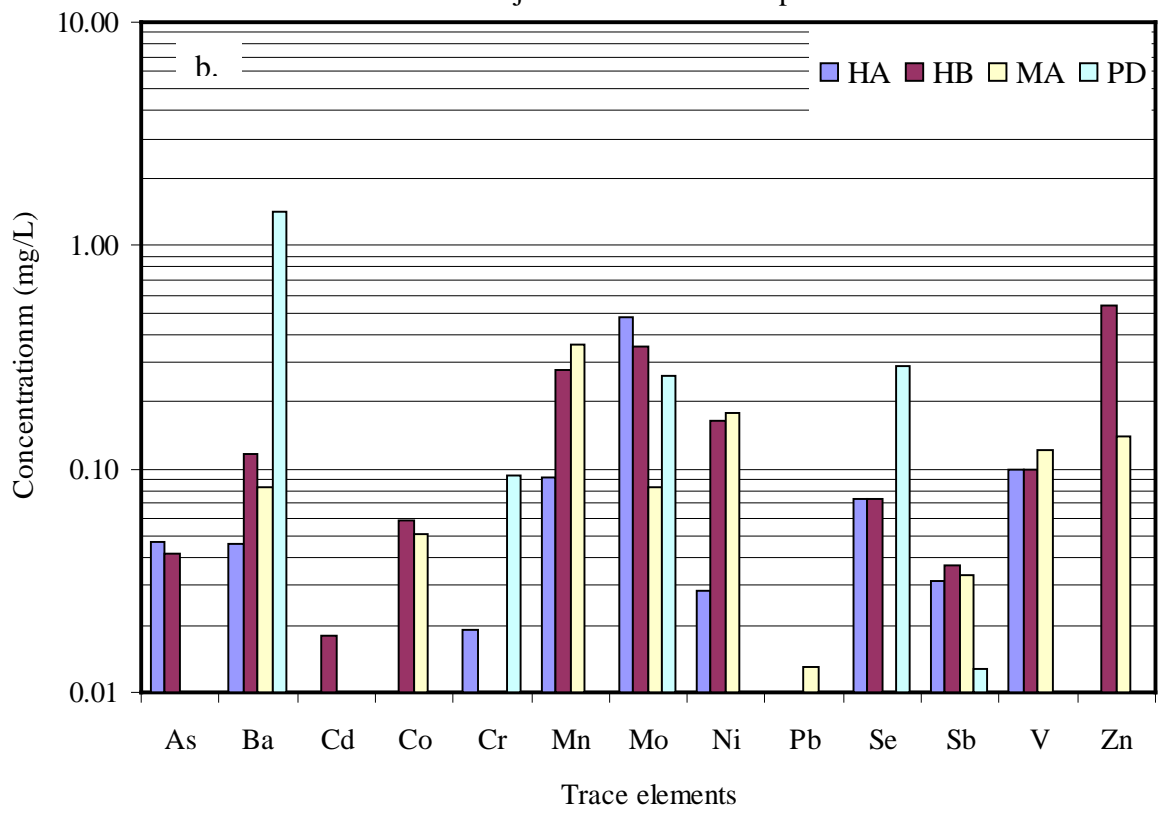
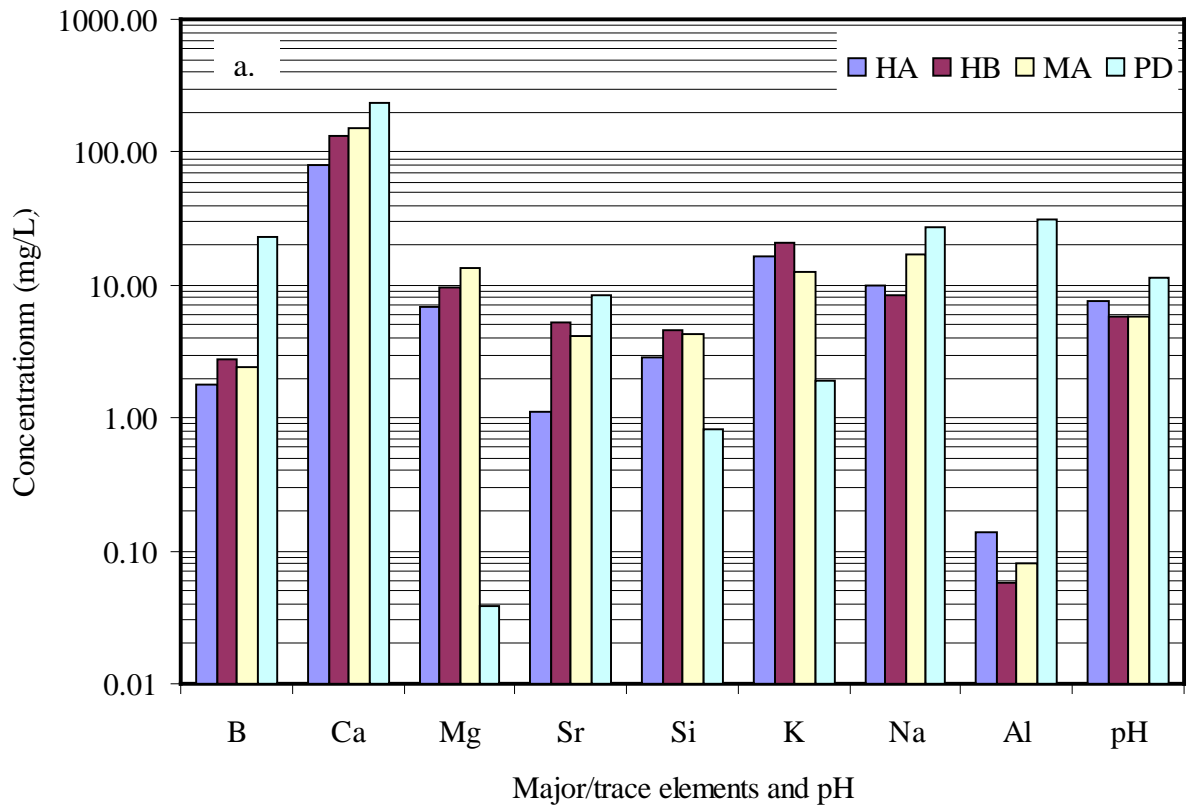


Figure 7: Major and trace element concentrations in fly ash leachates (Note the logarithmic y-axis scale.)

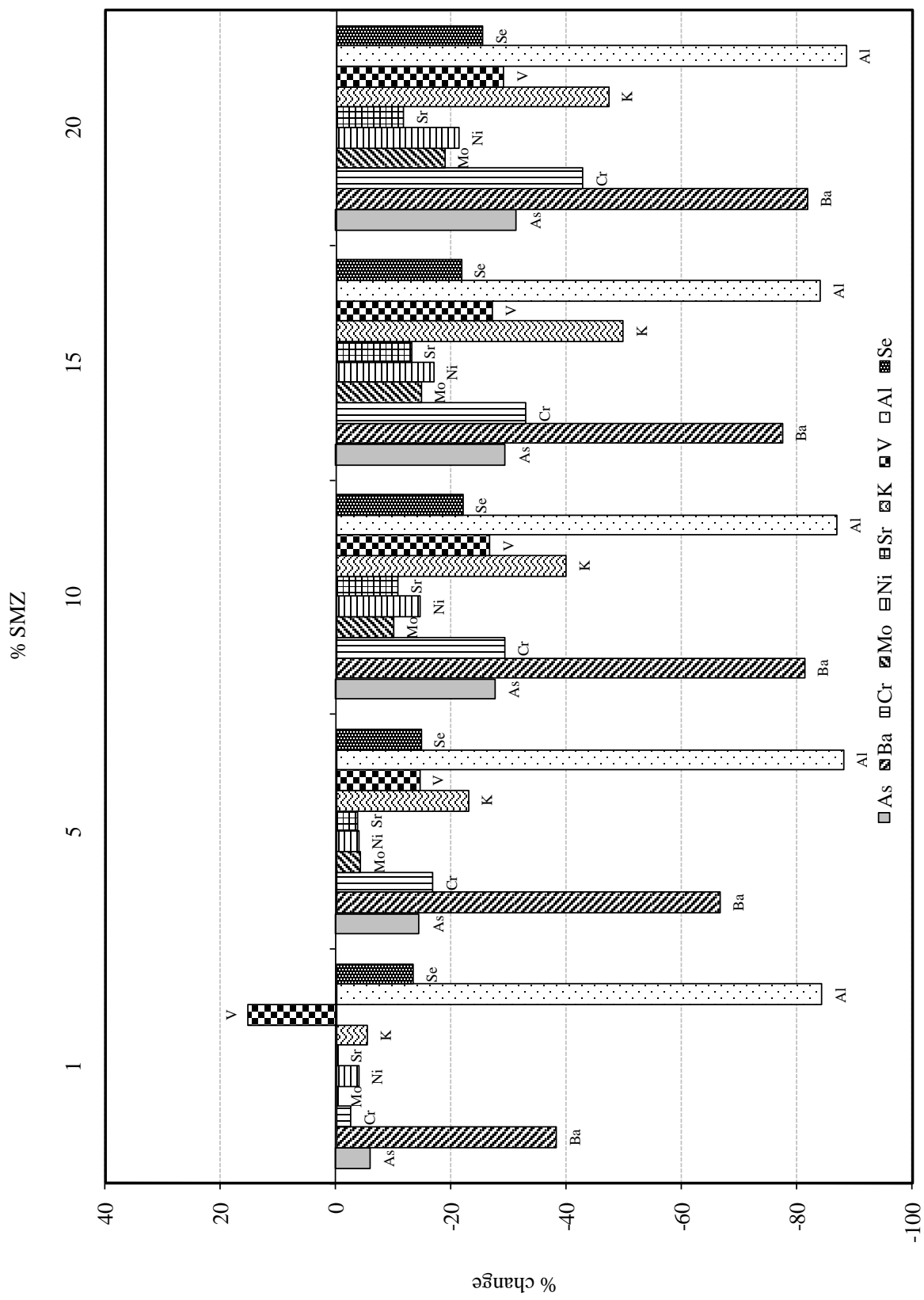


Figure 8: Percent reduction of element concentrations in HA fly ash leachate after treatment with 1, 5, 10, 15 and 20% SMZ

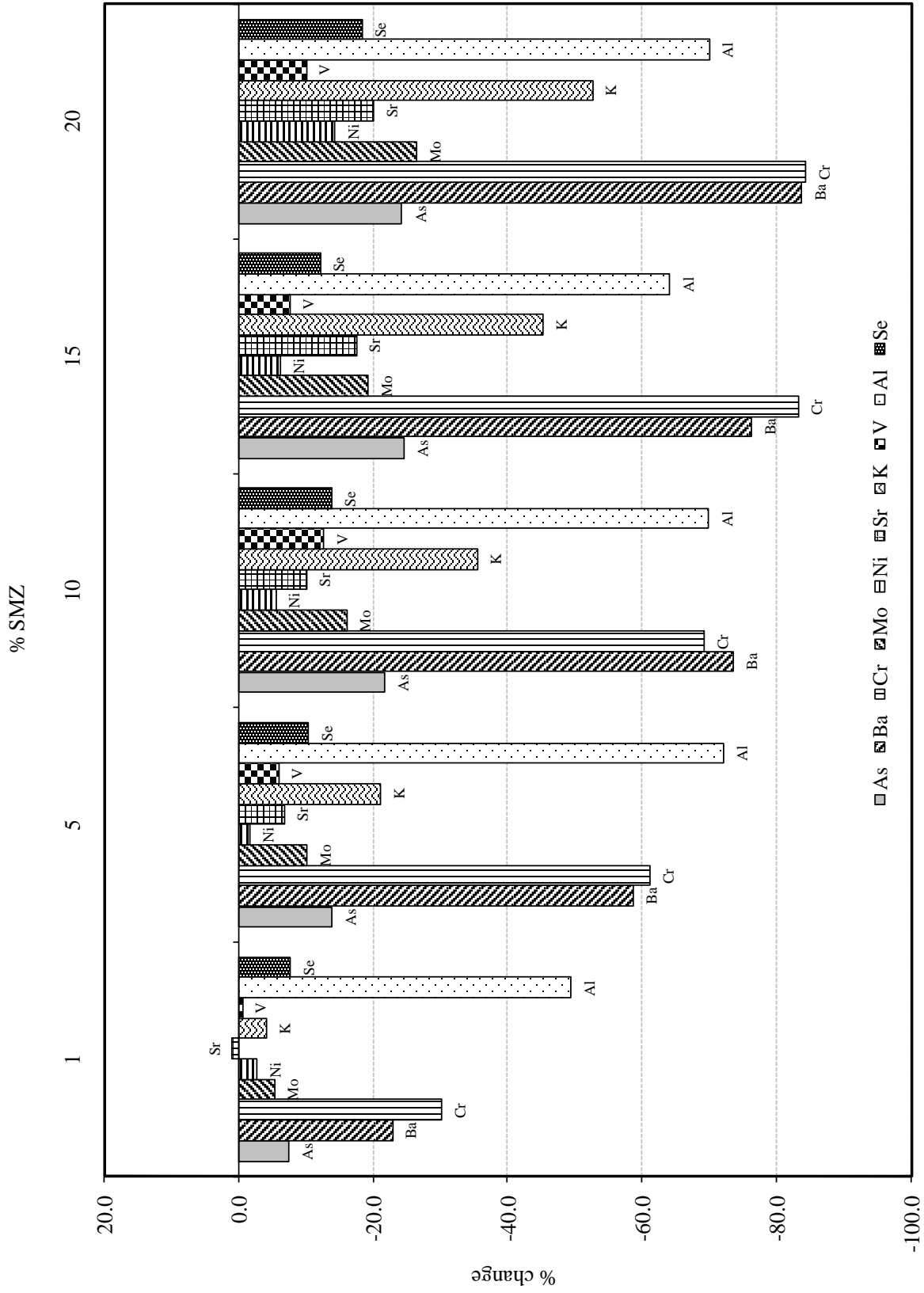


Figure 9: Percent reduction of element concentrations in HB fly ash leachate after treatment with 1, 5, 10, 15 and 20% SMZ

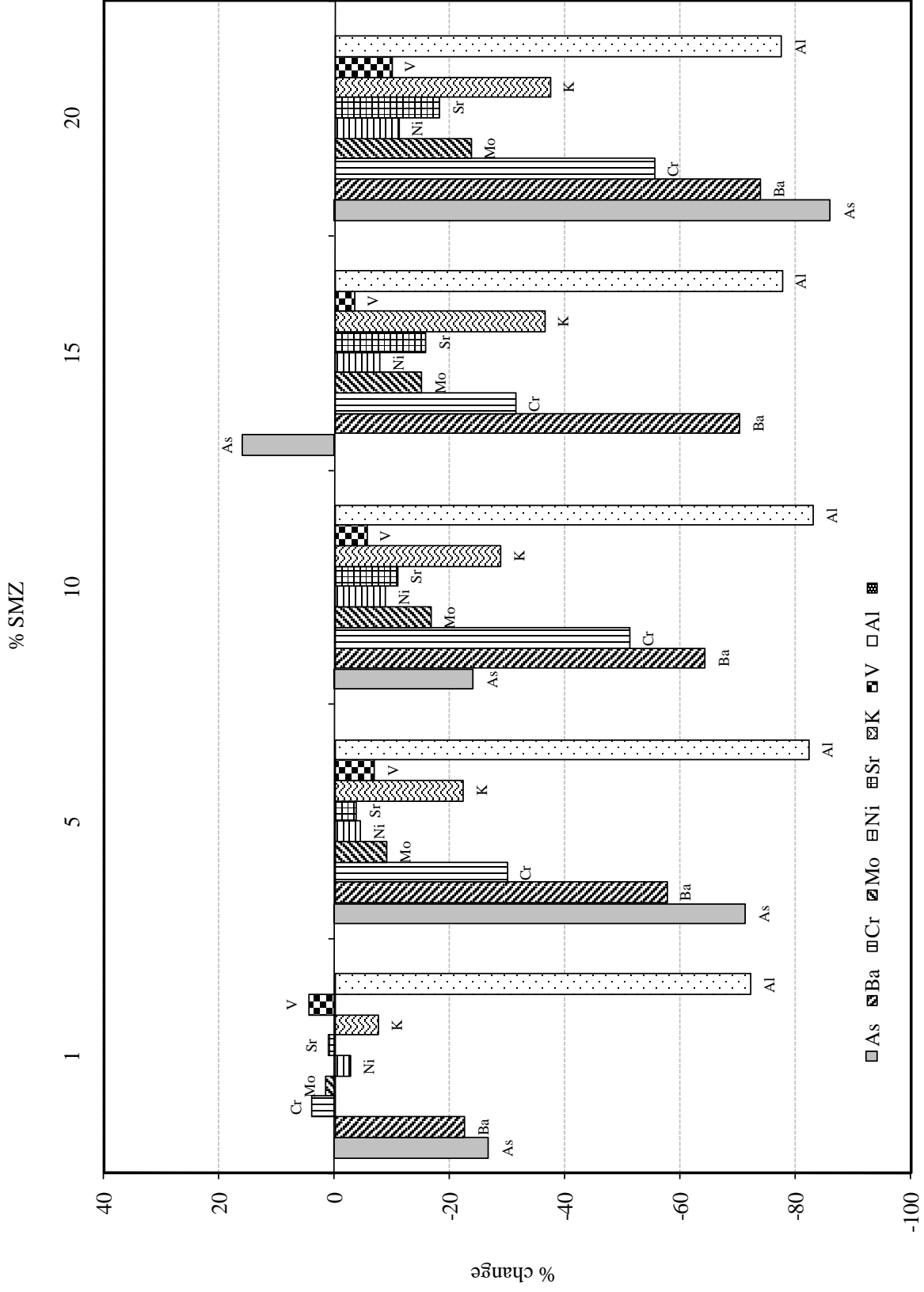


Figure 10: Percent reduction of element concentrations in MA fly ash leachate after treatment with 1, 5, 10, 15 and 20% SMZ

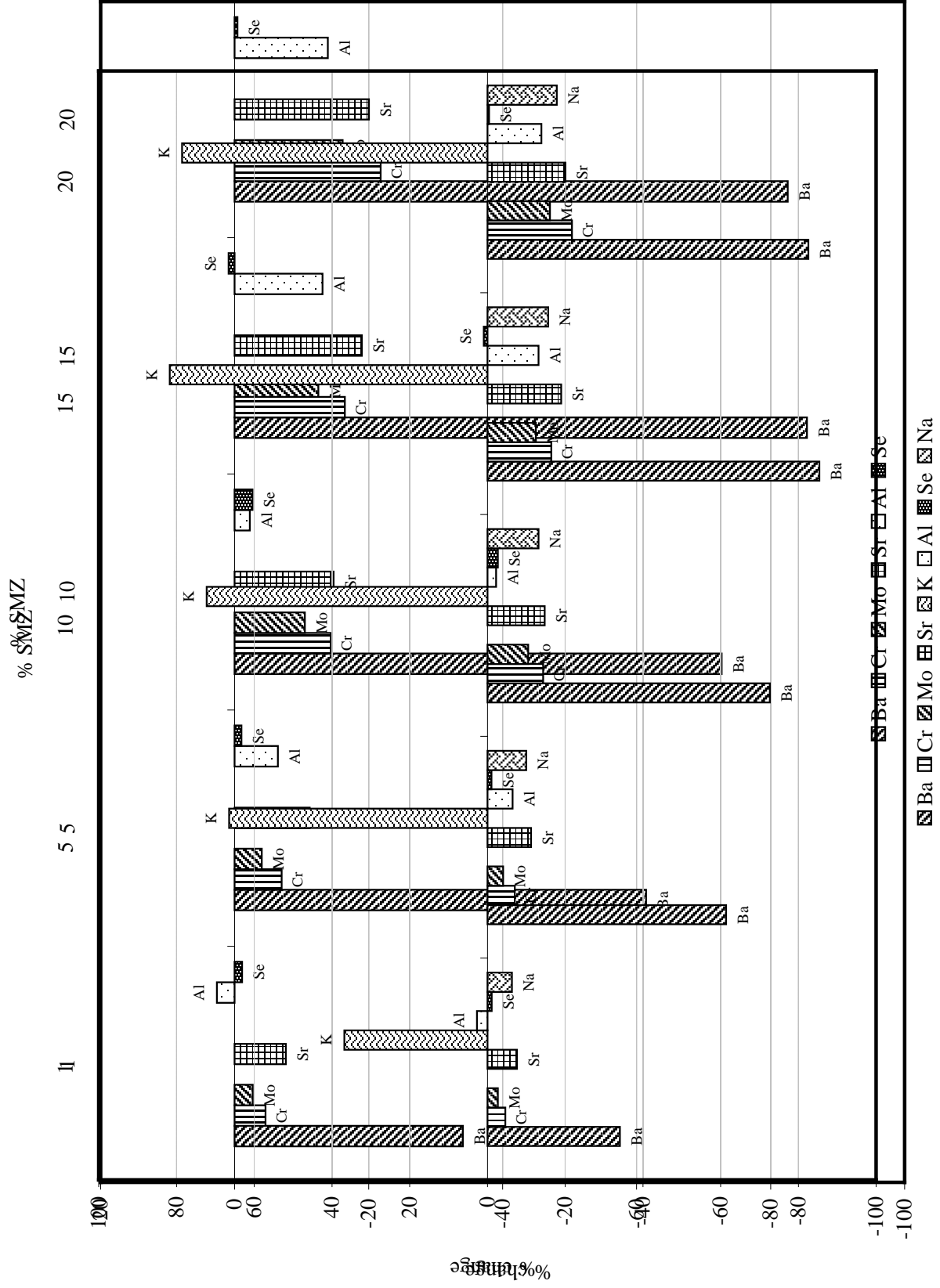


Figure 11: Percent reduction of element concentrations in PD fly ash leachate after treatment with 1, 5, 10, 15 and 20% SMZ

CONCLUSIONS

Coal fly ash samples used in this study showed significant amounts of water-leachable trace elements, illustrating the need for effective methods for in-situ treatment of coal ash leachate solutions. Batch treatment experiments using fly ash leachates and different additions of SMZ showed SMZ to be successful in decreasing the concentrations of several priority elements in fly ash leachate. The results of this study suggest a potential use for SMZ in removing hazardous elements from fly ash leachate plumes. The next phase of this research will utilize column experiments to evaluate the potential effectiveness of SMZ as a PRB material for controlling the dispersion of hazardous elements from older, unlined CCP disposal facilities.

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