

# SULFATE AND PHOSPHATE DISPLACEMENT OF ARSENIC FROM FLY ASH AMENDED SOIL

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**Abstract.** Arsenic (As) is the biggest environment contaminant in most of the soils where fly ash is applied. As is usually not mobile and strongly adsorbed onto soil particles. However, in gypsum and phosphorus amended soils As may be much more mobile. A study in repacked columns with soil from Ap horizon was conducted to determine whether or not As becomes mobile when  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  and  $\text{CaSO}_4$  are used as leaching solution, and to compare the competitive interactions between  $\text{PO}_4\text{-AsO}_4$  and  $\text{SO}_4\text{-AsO}_4$ . As concentration in leachate was approximately ten times greater when  $\text{Ca}(\text{H}_2\text{PO}_4)_2$  was used to leach the columns as compare to  $\text{CaSO}_4$ . A concentration of  $800 \mu\text{g As L}^{-1}$  was found in this case, which is sixteen times the limit of  $50 \mu\text{g L}^{-1}$  established by the EPA for groundwater. In fly ash the portion of arsenate non-specifically adsorbed is believed to be much lower than that of arsenate specifically adsorbed. Sulfate anions were able to displace only non-specifically adsorbed arsenate. However, the concentration of As in leaching solution was found to be within acceptable limits. Phosphate can compete with arsenate for all available adsorption sites, non-specific and specific.

## INTRODUCTION

Fly ash, a coal combustion residue, is an amorphous ferro-alumino silicate with a matrix very similar to that of soil. Elevated concentrations of soluble salts and potentially toxic trace elements, including arsenic (As), are present in fly ash as well. Although in some cases the information on leaching of potentially toxic substances from coal combustion residues is available (Carlson and Adriano, 1993), little information on chemical conditions, i.e. anion composition of the soil solution, that affect arsenate mobility in soils is available. The objective of this study was to investigate whether or not arsenate becomes mobile when added to soil in fly ash and to compare the competitive interactions between  $\text{PO}_4\text{-AsO}_4$  and  $\text{SO}_4\text{-AsO}_4$  in miscible displacement experiments under saturated conditions.

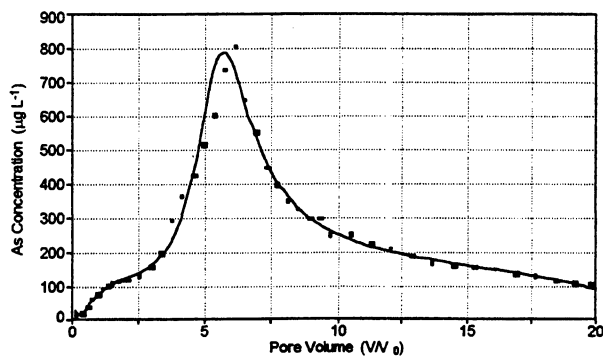
## METHODS

Air dried topsoil materials from a Cecil Ap horizon (clayey,

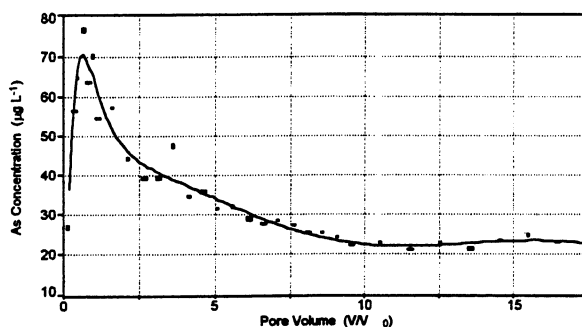
kaolinitic, thermic Typic Hapludults), collected near Watkinsville, Georgia, were packed into the columns. Columns were oriented horizontally and slowly saturated (flow rate  $1 \text{ mL min}^{-1}$ ) with deionized water at a constant flow rate using a peristaltic pump. When steady state conditions were established, the leaching solution ( $\text{CaH}_2\text{PO}_4$  or  $\text{CaSO}_4$ ) was pumped into the column. Electrical conductivity (EC) and pH of the leachate were measured continuously, and leachate fractions of 28 mL were assayed for P and S. Leaching was terminated when the breakthrough curve (BTC) was completed, indicated by similar in- and outflow concentrations. Aliquots were stored in plastic vials at  $0\text{-}5^\circ\text{C}$  prior to analysis. Water content was determined by weighing the columns immediately at the end of each run. From the difference in weight before and after saturation, volumetric water content was calculated. Convection dispersion equation transport parameters were determined from the P breakthrough curves using the CXTFIT code (Parker and van Genuchten, 1984). The deterministic linear equilibrium adsorption model for the flux concentration (mode 2) which has three parameters, mean water velocity (V), dispersion diffusion coefficient (D), and retardation coefficient (R), was used. The experiment consisted of two replicates of four treatments:  $\text{FA}^+$  = with 40 g fly ash per kg of soil;  $\text{FA}^-$  = without fly ash; P = leached with  $1.66 \text{ mmol}_{(e)} \text{Ca}(\text{H}_2\text{PO}_4)_2 \text{ L}^{-1}$ ,  $\text{pH}=5.36$ ; S = leached with  $10 \text{ mmol}_{(e)} \text{CaSO}_4 \text{ L}^{-1}$ ,  $\text{pH}=5.68$ .

## RESULTS

In Figure 1 and 2, changes in As concentration with time, for the treatments  $\text{FA}^+\text{P}$  and  $\text{FA}^+\text{S}$  respectively, are presented. The area under the curves, which gives the total amount of As leached out of columns, was integrated within the domain from 0 to 2.8 L of leachate. For these treatments 698.85 and 84.48  $\mu\text{g As}$  were leached, respectively. For treatment  $\text{FA}^+\text{S}$ , the maximum concentration of As in the leachate was found in the first two pore volumes with a decrease toward a stable equilibrium value thereafter. This result is in accordance with the expectation that sulfate only displaces non-specifically sorbed arsenate, which is weakly held and elutes in the first pore volumes of leachate. For treatment  $\text{FA}^+\text{P}$ , non-specifically sorbed arsenate is removed in the first two pore volumes indicated by the shoulder in the graph, followed



**Figure 1. Changes in As concentration in leachate during leaching with  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .**



**Figure 2. Changes in As concentration in leachate during leaching with  $\text{CaSO}_4$ .**

by a much larger and wider peak with a maximum As concentration  $800 \mu\text{g L}^{-1}$ . However, 17 or more pore volumes are required to reach the steady state. The presence of the first and second peaks demonstrate that phosphate was able to displace arsenate from both non-specific and specific sorption sites with the latter being much greater.

Due to the presence of the high levels of soluble salts in the fly ash the initial EC values in leachate were high. The EC values then decrease attaining equilibrium after two and eight pore volumes for the  $E_s$  and  $E_p$  treatments respectively. This phenomenon is called "salt adsorption phenomenon" (Bellini et al., 1996), in which the simultaneous adsorption of anions and cations of an electrolyte in contact with a variable charge soil takes place. In these soils charge is a function of pH and concentration of soil solution. When P concentration increases new charge sites are created in soil when phosphates ions are sorbed. The cation of the phosphate salt is simultaneously adsorbed to balance the charge. The presence of this phenomenon is clearly shown when the soluble salts in fly ash are leached out (the minima in the curves), and the EC of the leachate decreases below that of the inlet solution. From these results it would appear that the anion of the electrolyte plays the dominant in this phenomenon which can be seen by comparing S and P

treatments.

Similar to what was presented up to now, pH values of the solution became stable after approximately 8 pore volumes, in the case calcium phosphate solution was used. Ligand exchange involves the substitution of an oxyanion species for surface functional groups such as  $\text{OH}_2$  and  $\text{OH}$  (Parfit et al., 1975). That is the probable version for the increase in solution pH from 5.8 to 6.9.

## CONCLUSIONS

As concentration was approximately ten times greater when calcium phosphate was used compare to calcium sulfate. In the  $\text{FA}^+$  treatment non-specifically adsorbed arsenate is believed to be much lower than that specifically adsorbed. It seems as sulfate anions were able to displace only non-specifically adsorbed arsenate. As a consequence the concentration of As in the leaching solution was found to be within acceptable limits. Because phosphate can compete with arsenate for all available adsorption sites (non-specific or specific), the displacement of both arsenate forms by phosphate results in an increase in As mobility in the  $\text{FA}^+$  treatments. Phosphate also displaced arsenate in the control treatment.

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