

# Leachate Chemistry of Mixtures of Fly Ash and Alkaline Coal Refuse

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## INTRODUCTION

In the past, acid mine drainage (AMD) associated with coal mining operations and the disposal of coal refuse have been a driving force behind research efforts on the properties of coal combustion products (CCPs) [1]. The results from research over the last 15 years clearly indicate that bulk-blended CCP has the potential to ameliorate AMD production in coal refuse as long as acid-base balance concerns are met [1,2].

Current research efforts are in part driven by the changes in air quality regulation and resultant changes in air emission technologies over the past decade. These advances have led to major changes in the type and properties of CCPs that are now available for back-haul to the Virginia coalfields. Increasing quantities of flue gas desulfurization (FGD) sludges are now being generated as separate CCPs or mixed with fly ash. The advent of low NO<sub>x</sub> boilers has led to significant concentrations of ammonia in many CCPs. As the properties of the CCPs change, their interactions with the disposal environments need to be investigated in order to assess the leachability of potential toxic constituents.

Class F fly ash materials constitute the vast majority of CCPs generated in the mid-Atlantic region at that time. However, alkaline coal refuse, along with class C fly ash, have received little or no attention with respect to their chemical properties and interactions in disposal environments. We have not found any published research that investigated these materials' properties and potential for leachable mass of potentially toxic constituents. While these materials do make up a minor fraction (10-15%) of the total CCPs and coal refuse produced in the mid-Atlantic region, the potential negative environmental impact from just a few locations could be extensive and long-lasting.

Additionally, regardless whether the refuse is alkaline or acid forming, or class C or F fly ash is being utilized, the office of surface mining (OSM), the USEPA, and a recent National Academy of Sciences study [1]) have focused increasingly on the potential mobility of a number of oxyanions and heavy metals (e.g. Selenate, Arsenate, Borate,

and Molybdate) in mining environments. The USEPA is also closely scrutinizing the enrichment of mercury in fly ash and its potential mobility in disposal environments.

Hence, the objectives of this work were to: 1) characterize the chemical properties of an alkaline coal refuse and class C fly ash from south-western Virginia, and 2) to simulate and assess the potential field leaching behavior of heavy metals and oxyanions from the alkaline coal refuse and class C fly ash, and in various likely co-disposal combinations.

## METHODS

Fresh alkaline coarse coal refuse was dried and sieved to obtain the <2.5 cm fraction for use in the column leaching study. The remaining coal refuse fraction (>2.5 cm and up to approximately 15 cm) comprised approximately 25% of the volume of the collected refuse was discarded. Class C fly ash was collected from dry storage hoppers where it is loaded onto trucks for haulage to the landfill facility.

### Chemical Properties of Fly Ash and Coal Refuse

Total elemental analysis was done by acid digestion. The fly ash and coal refuse were analyzed for the calcium carbonate equivalence (CCE). Soluble/leachable boron was determined by the hot  $\text{CaCl}_2$  extraction technique [4], and soluble salt content (electrical conductance, EC) and pH by the saturated paste method [5]. All materials and treatment mixes were analyzed by the Toxicity Characteristic Leaching Procedure (TCLP, U.S. EPA Method 1311). The sequential fractionation procedure (SEP) by Tessier, et al., [6] was used to characterize the elemental distribution in the solid phase of the fly ash. These chemical extractions are used to remove trace elements, including As, Se, Cr, Mo, B, and Hg, from specific solid phases. The SEP uses progressively stronger reagents that solubilize trace elements from increasingly recalcitrant phases. The extracting solutions are intended to simulate the various geochemical processes that immobilize trace elements. While these procedures do not actually identify the true form of a given metal in a soil, they do give fairly consistent clues to metal solubility with redox and pH fluctuations [6].

### Column Leaching Method and Experimental Design

To simulate the potential leaching of oxyanions, heavy metals, and other potential contaminants in a field setting, we constructed a set of leaching columns packed with the different coal refuse and fly ash treatment blends. We utilized (with minor modifications) the leaching column design developed by Jackson [7] and Stewart [8] to equilibrate and subsequently obtain the leachates. The columns were 20cm diameter, 75cm long ABS plastic drainage pipes with a flexible PVC endcap to hold the material.

The experiment consisted of three ash amendment rates (0, 10 and 20% by volume) and two leaching environments (saturated vs. unsaturated). The intent was to simulate

bulk blending fly ash/refuse ratios and appropriate field density conditions. The various treatment blends and the exact amount of material for each column were handled on a weight basis to assure equal material in each column. Table 1 gives the amount of coal refuse and fly ash used for each column, and the amounts ( $\text{mg column}^{-1}$ ) of total As, Cr, Mo, and Se content per column. The depth of the treated mixed zones in the columns was 60 cm, which resulted in a total volume of 19 liters. Simulated rainfall at pH 4.8 (Halvorsen and Gentry, 1990) was used for twice per week leaching of the coal refuse and fly ash mixture treatments. Three replications of each treatment combination were run for a total period of six months.

### Column Leachate Data Collection and Analysis

Column leachates for the unsaturated columns were collected into individual bottles 24 hours after the 2.5 cm application of the simulated precipitation, and immediately after the application of the precipitation solution to the saturated columns. We determined EC and pH the day the leachates were collected, after which all samples were acid-stabilized and/or refrigerated depending on laboratory analytical protocol and hold times. The leachate composition of all samples taken over the initial month of leaching was analyzed for the following elements: Ca, Mg, K, Na, S, B, Cd, Cu, Cr, Mn, Mo, Pb, Zn, Hg, As, Se. Subsequent samples were analyzed for a narrower range of elements based on presence/absence in leachates. Elements were analyzed primarily by AAS and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) using EPA approved analytical methods for the various elements.

## RESULTS AND DISCUSSION

As is evident from Table 1, the fly ash contributed significantly to the total amount of As and Mo contained in each column. However, replacement of 10 and 20% of coal refuse with fly ash did not appreciably increase the total Cr or Se of those treatment blends. However, mineralogical differences between coal refuse and fly ash may affect the respective solubility/leachability.

Both materials are alkaline, but the higher pH for fly ash, despite the lower calcium carbonate equivalence (CCE), indicates important difference in mineralogy and reactivity, and the coal refuse is expected to have a greater buffering capacity than the fly ash. Comparing the total elemental analysis of the materials shows that fly ash tended to significantly 'concentrate' potential toxic constituents like As, B, Cr, Cu, Ni, and Se relative to the bulk coal refuse materials. While the As value was slightly higher than expected; the other values were close to expectations for coal fly ash [9].

Table 1. Coal refuse and fly ash content (kg) per column and total As, Cr, Mo, and Se content of column (mg / column)

Treatment	Refuse	Fly ash	As	Cr	Mo	Se
	- kg / column -		----- mg of element / column -----			
100% refuse	36.32	0	409	2098	20.6 (0%)	104 (0%)
10% ash amendment	32.68	2.63	588 (37%)*	2188 (14%)	63.0 (71%)	107 (10%)
20% ash amendment	29.06	5.26	766 (57%)	2279 (26%)	89.0 (84%)	110 (20%)

\* ( ) percent of total elemental content due to ash amendment

Analysis of the TCLP extracts from the ash, refuse and ash/refuse mixes used in the column leaching experiment showed that concentrations of As, Cr, Mo, Se, and Hg were substantially below EPA regulatory limits. Subsequent digestion of the TCLP extracts for total elemental analysis (U.S. EPA method 3015), resulted in considerably higher As and Cr concentrations (by a factor of approximately 10 to 15), but were still far below regulatory limits. The concentrations for Se, Mo, and Hg did not change appreciably.

Little As and Cr were found in the exchangeable phase with the majority of As found in the moderately recalcitrant amorphous oxide fraction, and the majority of Cr found in the very recalcitrant residual fraction. In contrast, significant quantities (33 to 61%) of total Mo and Se were found in the exchangeable phase, respectively. Selenium is particularly concentrated in the most bioavailable fractions (the sum of the exchangeable, carbonate and amorphous fractions), but is nearly absent (below detection limit) in the crystalline and residual fractions. Although trace elements bound or co-precipitated in the carbonate fraction would have low bioavailability at high pH values, their solubility would increase with a decrease in bulk pH over extended periods of time. The high level (58% of total) of As in the amorphous bound phase (Step 3 of SEP) could potentially be of concern, depending on the long-term geochemical stability of these amorphous phases in the final disposal environment. Chromium poses a greatly reduced long-term leaching risk since the majority (64%) of the Cr is bound in the residual fraction (Fig.1).

Based on these SEP results, we expect that As and Cr would have a lower solubility or "leachability" when compared to Mo and Se because they are found in less soluble/bioavailable forms. The TCLP data corroborate the results from the SEP. Although both As and Cr are found at higher total concentrations in the ash compared to Mo and Se, they are found in lower concentrations in the TCLP extracts. The total elemental content of these elements in the ash appears to be generally underestimated if the total elemental content is derived by the summation of the various fractions, rather than by total elemental digestion of a separate ash sample.

## Column Leachate Properties

As expected, the ash-amended columns generated very high leachate pH values (between pH 8.5 and 11.5) that declined slightly but steadily with time. The refuse control produced initial pH values in the mid to high 8's that dropped to 8.1 to 8.2 over time. The unsaturated leachates tended to be higher in pH initially than saturated treatments, but this difference diminished over time and the saturated columns were higher in pH after six months of leaching. The electrical conductance (EC) of the leachates was directly related to the soluble salt load, which is dominated by sulfates. The fly ash-amended refuse columns generated very high EC values in their initial pore volumes that then decreased quickly with time as the bulk sulfates were eluted. After three months of leaching, the EC in all treatments declined to  $< 1.5 \text{ dS m}^{-1}$ , and the ash blended columns were actually slightly lower in EC than the refuse controls. Leachates from the saturated columns had significantly lower EC values than the unsaturated columns.

Mercury (Hg) was not detected (at  $5 \mu\text{g L}^{-1}$  detection limit) in any of the leachates. Arsenic leaching from the coal refuse was negligible. But leachate concentrations of As in both of the ash treatments were significantly elevated above those in the refuse control columns and greater than an order of magnitude above current ( $50 \mu\text{g L}^{-1}$ ) and proposed ( $10 \mu\text{g L}^{-1}$ ) USEPA primary drinking water standards. Interestingly, the highest leachate As levels were seen in the 10% ash blended treatment, rather than the 20% treatment. The release from the 20% ash amendment was steady at around  $200 \mu\text{g L}^{-1}$ . The significantly higher elution of up to  $1 \text{ mg L}^{-1}$  from the 10% fly ash amendment rate, from both the saturated and unsaturated columns, may at first indicate some sort of refuse:ash interaction affecting solid:liquid phase flow dynamics, diffusion differences, or other packing/flow phenomena. However, as the work by De Groot et al. [10] shows, while pH is the main factor controlling leachability, our data also indicated limited solubility of anions at  $\text{pH} > 11$ , and a window of higher solubility in the pH range of 9 to 11. Based on the observed pH values, the 20% and 0% ash amendment rates result in pH above and below, respectively, where As is more readily solubilized. The above findings are a clear indication of the necessity of documenting detailed pH solubility relationships. The general Eh/pH solubility characteristics of heavy metals and oxyanions have been shown to be the controlling factor in the potential leachability of these elements [11].

The release/leaching patterns of Cr, Mo, and Se are similar in that there was an initial flush followed by a rapid drop in leachate concentrations. Selenium levels in all leachates were much higher than the primary drinking water MCL of  $50 \mu\text{g L}^{-1}$  and were directly related to ash loading rate. Over time, the Se levels in the ash blended leachates drop quickly, but remained at or above  $100 \mu\text{g L}^{-1}$ , indicating a potential for prolonged Se release. These data are critical because of the fine separation between Se concentrations being essential and toxic, and the fact that both humans and animals have  $>80\%$  intestinal absorption of Se [12].

Chromium was eluting from the ash-amended columns at levels several times the primary MCL of  $0.1 \mu\text{g ml}^{-1}$ . The release/leaching of Cr was significantly higher for the unsaturated columns when compared to saturated conditions. Leachate Mo levels were also quite high initially and responded to ash amendment rate. Leachates from saturated columns were consistently higher in Mo than their unsaturated counterparts, and leachate levels dropped rapidly after several pore volumes of elution to relatively low levels.

Overall, the SEP data also corresponded well to the column leachate. The difference in release patterns of As and Cr versus the early release of Mo and Se can readily be explained by the predominance of Mo and Se in the more soluble/bioavailable fractions.

The cumulative leachate data, coupled with the total elemental content contained in each column, allowed for the calculation of the percent (%) of As, Cr, Mo, and Se leached from the total input (per column), and to tentatively attribute the primary source of the leached element either to the coal refuse and/or the fly ash. Fly ash significantly increased the total As content of the columns. After 6 months, less than 0.9 ‰ of the As was leached from the coal refuse control columns. However, for the 10% treatment rate, nearly 10% of mass As added with the fly ash amendment was leached. This again points to the critical importance of the chemical conditions of potential disposal environments and their effect on solubility/leachability of potentially toxic elements. While total elemental Cr content is by far the highest for the elements we looked at, total Cr leached was low for all treatment. Given that the fractional distribution of Cr indicates it to be primarily in the residual fraction, Cr leachate concentrations are unlikely to change significantly unless the chemical environment (pH) of the mixes were to change drastically.

The data indicate that large fractions of total Mo and Se may be solubilized and potentially leached. Nearly 10% of the total Mo was leached from the coal refuse after 6 months. This increased to > 50% for the 10 and 20% fly ash treatments. These are considerable quantities, but the fact that Mo is currently not regulated by USEPA makes Mo leaching potentially less of an issue of environmental concern. This may not be the case for Se, however. Compared to As and Cr, considerable quantities of Se were leached from coal refuse alone. Fly ash amendments increased the Se release significantly to approximately 10% of total Se content. More importantly, the release rate for the 10 and 20% fly ash treatments appears to have stabilized after 3 months at levels exceeding regulatory limits.

## CONCLUSIONS

It is important to note that the leaching procedure used here was designed to simulate what could be considered to be “worst case” leaching conditions in a disposal area. The addition of the class C fly ash to the alkaline refuse pile will more than likely increase levels of soluble As, Cr, Mo and Se in waters that are immediately in contact with and leaching through the fly ash and/or ash/refuse mixtures if they are co-disposed in a solid

mix and then leached with natural acidic rainfall over extended periods of time. The dissolution rate and environmental fate of these elements would be affected by (1) the Eh/pH of the disposal environment, (2) residence time and connectivity of the leachates with groundwater in the discharge areas, (3) the nature and mixture rate of coal refuse that is also deposited into the discharge areas, and (4) solution:solid phase interactions as the leachate migrates down the hydrologic gradient within the compacted refuse. The likely fate of these elements down the hydrologic gradient below the ash/refuse disposal zone and to the potential discharge point(s) need to be considered.

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