This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

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Prediction of Coal ash leaching behavior in acid mine water: comparison of laboratory and field studies

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ABSTRACT

Strongly alkaline fluidized bed combustion (FBC) ash is commonly used to control acid mine drainage (AMD) in West Virginia coal mines. Objectives include acid neutralization and immobilization of the primary AMD pollutants: iron, aluminum and manganese. The process has been successful in controlling AMD though doubts remain regarding mobilization of other toxic elements present in the ash. In addition, AMD contains many toxic elements in low concentrations. And, each mine produces AMD of widely varying quality. So, predicting the effect of a particular ash on a given coal mine's drainage quality is of particular interest. In this chapter we compare the results of a site-specific ash leaching procedure with two large-scale field applications of FBC ash. The results suggested a high degree of predictability for roughly half of the 25 chemical parameters and poor predictability for the remainder. Of these, seven parameters were successfully predicted on both sites: acidity, Al, B, Ba, Fe, Ni and Zn while electrical conductivity, Ca, Cd, SO4, Pb and Sb were not successfully predicted on either site. Trends for the remaining elements: As, Ag, Be, Cu, Cr, Hg, Mg, Mn, pH, Se Tl and V were successfully predicted on one but not both mine sites.

1. Introduction

Several test procedures have been developed in an attempt to predict the leaching behavior of coal combustion byproducts (CCBs). CCBs include various types of coal ash, flue gas desulfurization solids and boiler slag. The most widely used procedure is the Toxicity Characteristic Leaching Procedure (TCLP), which was designed by the United States Environmental Protection Agency to "determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes."[1] However, this test may only account for fast reactions that take place in short term leaching processes.[2] The results obtained with the TCLP on a limited number of fly and bottom ash samples showed that the range of concentrations of specified constituents was well below regulatory limits.[3] These residues are therefore classified as non-hazardous wastes and can be disposed of on land without risk of contaminating groundwaters to the extent of exceeding drinking water standards. However, Bhumbla et al. (2000) concluded that, environmental concerns about toxic element release from fly ash amended soils have been lessened by evaluation of data from short-term studies in highly

alkaline environments.[4] They point out that all soils in humid regions ultimately become acidic and that the behavior of ash under conditions pertaining over the long term needs to be addressed. They encouraged a better understanding of the mechanisms and rates of trace element release from CCBs so that behavior over the long term can be predicted.

Regulatory agencies, industry and the public need a tool for quantative prediction of leachate composition to properly assess the risks and benefits of a particular CCB application for mine reclamation. Currently applied laboratory extraction procedures yield imprecise estimates of field leachate composition and field studies alone do not provide the causal relationships for the observed behavior. Also, since TCLP and SPLP use standard leaching solutions, they do not predict interactions between the solid waste and components of a specific mine water. Therefore, our research has focused on developing improved laboratory methods for predicting the leaching behavior of CCBs under field conditions. The geochemical reactions of dissolution/precipitation, adsorption/desorption, and oxidation/reduction are recognized as controlling the mobilization of various constituents from solid residues.[5,6]

To address these uncertainties, a leaching procedure has been developed that, through an empirical procedure, recognizes the interactions among mine water chemistry and specific CCBs. This sheds light on the fundamental geochemical reactions critical to interpretation and prediction of leachate chemistry and interactions with various geological materials. Such laboratory studies can be conducted for a wide range of conditions, such as pH, complexations, and ionic strength of leachates and porewaters that would be encountered at different field sites. It is hoped that the result will yield a laboratory procedure that will recognize site conditions and predict in a timely and inexpensive manner the risks and benefits of CCB applications in coal mines. We are attempting to first isolate the modeled system first as an interaction between mine water and the CCB. Subsequent study will include interactions between the resulting leachate and the mine spoil.

Figure 1 illustrates the model that we are attempting to simulate. It assumes that all metal ions are imported either via the acidic mine groundwater or the CCB. The shaded squares indicate that the metal ions reside in the solid phase and the white squares indicate aqueous compartments. Initially, acid/base neutralization reactions occur between the CCB and the AMD. This step may persist over many years and it is a function of the alkalinity content of the CCB, its permeability and the acid flux generated by the AMD. Contact between AMD and CCB groundwater can liberate ions through dissolution of the CCB and immobilize others as hydroxides, complexes or through adsorption to precipitated metal hydroxides. These hydroxides may dissolve and adsorbed ions may be released as the pH changes. Heavy lines in figure 1 indicate immobilization pathways leading to storage in residual solids. Thin lines indicate transfer to mobile or aqueous phases as dissolved ions.
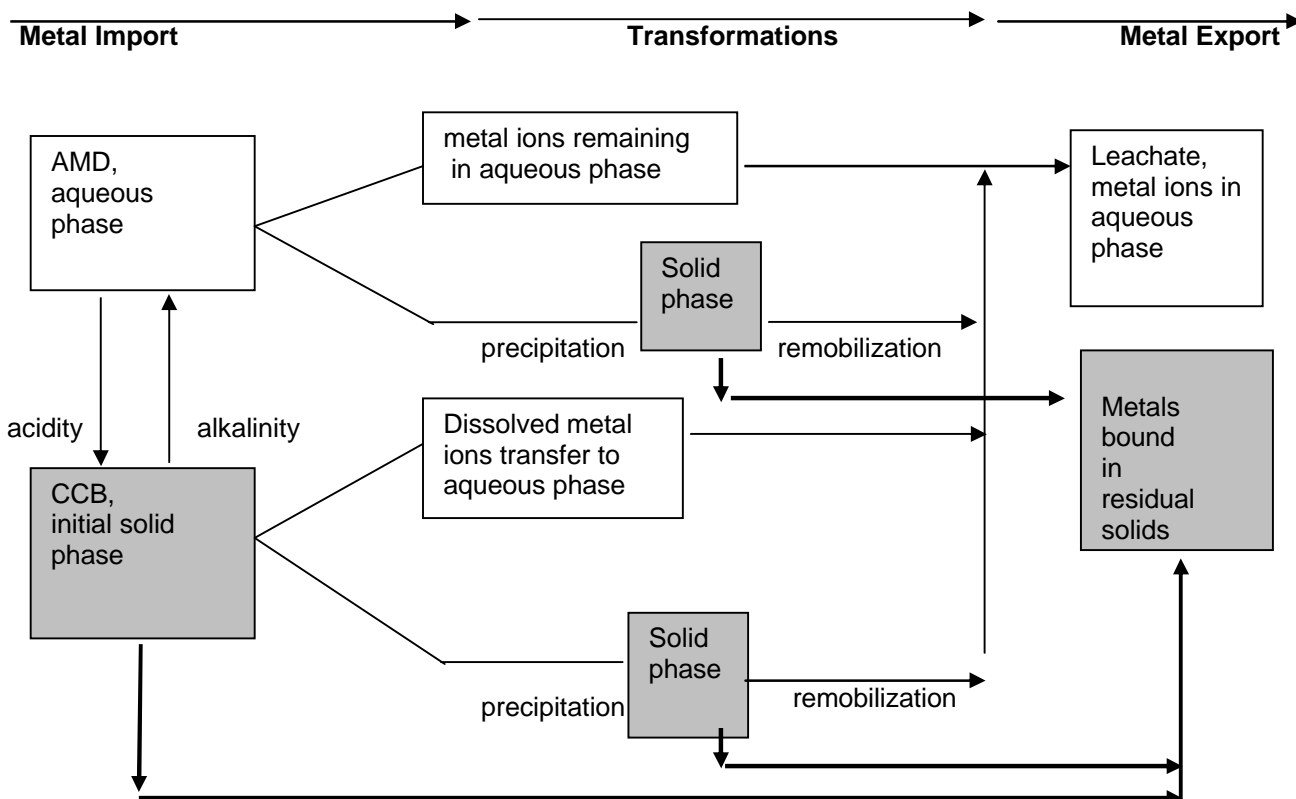
Figure 1. Diagram of the experimental system. *Metals can be imported to the system from either the AMD (aqueous form) or the waste (solid form). Once in the system, metals can either stay in the aqueous phase, precipitate into the solid phase or resolubilize into the aqueous phase.*

The above model does not account for interactions with mine spoil. Rather, this is a first step toward a systematic study of the factors that mobilize and immobilize toxic ions in CCB-minefill settings. Here were only explore the interaction of CCB and the mine's groundwater. Our objective is to test the validity of the laboratory leaching procedure by comparing the results with actual field results using the same CCB and AMD. Throughout we are using the Mine Water Leaching Procedure (MWLP). It was developed to provide a site-specific risk assessment tool for CCB-minefills. The procedure was developed to determine the long-term leaching potential of toxic elements present in industrial wastes when placed in the groundwater found at a specific mine. Of particular concern is the leaching behavior of these materials when placed in acidic environments associated with reclamation of acidic mine spoils.

It is recognized that correlations between leaching studies and field observations are tenuous at best. We hope that by studying the laboratory leaching behavior of individual parameters and by comparing the results to multiple field sites we can begin to distinguish laboratory artifacts and parameters that have predictive value.

Use of CCBs for Coal Mine Reclamation: According to the American Coal Ash Association, 122 million tons of CCBs were produced by the power generating utilities in 2003. Of that total, 2.23 million tons were used in mining applications.[7] CCBs are used as structural fills in mining and are also used to control acid mine drainage, subsidence and for soil reclamation.[8] Class C Fly ash and Class F fly ash mixed with lime exhibit self-cementing properties and can be used to cap surfaces, line pavements and isolate acidic materials in the backfill to prevent AMD formation. In addition, highly alkaline CCBs, such as FGD and FBC residues, are used to directly neutralize acidic materials.

Fly ash generally has a strong influence on spoil pH.[9] Fly ashes are commonly alkaline but may be neutral or acidic as a function of CaO, salts and various amorphous oxides of Fe, which adhere to the exterior of the fly ash spheres.[10] Alkalinity released as CaO is liberated from the dissolving alumino-silicate matrix.[9, 11] Alkaline fly ashes normally contain sufficient neutralization capacity to raise the pH of acid soils.[12] While many class F fly ashes have a high paste pH (10 to 12), their neutralization potential is low so extremely high additions (up to 625 tonnes of fly ash per hectare) may be needed to sustain a neutral pH in acidic coal mine soils.[13, 14, 15] There have been several case studies on the direct neutralization of AMD using highly alkaline CCBs.[16, 17]

CCBs are also used during surface reclamation to improve soil physical and chemical properties of acidic minesoils.[18, 19] A study conducted by Dhaliwal and associates compared the properties of a mineland area reclaimed with fly ash to an adjacent area that received no fly ash. Even after 22 years the fly ash treated mine soil had a higher pH and thicker organic horizon than the adjacent untreated area.[20] Bhumbla used a fly ash/rock phosphate mixture as a topsoil substitute and found that fly ash addition improved certain physical conditions of the mine soils and reduced Al, Fe and Mn toxicities.[21]
Placement of coal combustion byproducts (CCBs) in coal mines raises the prospect of reactions with geochemically aggressive, acidic groundwater in the mine. The CCPs are generally alkaline and are often seen as valuable amendments for groundwater improvement.   However, the weathering behavior of CCPs will change with exhaustion of their alkalinity and regulatory agencies need to know the potential to leach toxic elements over extended time periods.

2. Materials and Methods

Field Sites: Coal ash and acid groundwater (AMD) were collected from two sites where FBC ash had been used to line the acid-generating mine floor rock and also to isolate toxic materials in the backfill of two surface mines in North Central West Virginia. One mine is in Monongalia County (Site M) and the other is in Preston County (Site P). Site M produces a mild AMD with a pH of 4.5, [acidity]: 144 mg/L, [Fe]: 5 mg/L and [Mn]: 0.3 mg/L and [Al]: 23 mg/L. This site is a contour surface mine where a 0.3 m layer of compacted FBC ash was placed on the pit floor prior to backfilling and another 0.3 m layer placed over the pyritic spoil prior to placement of the final soil cover. This method has prevented further AMD formation on the site. We collected our AMD

sample from earlier mining works on the same mine that had not received the FBC ash treatment.

The Site P surface mine recovered coal from a more highly pyritic seam. As a result the AMD is more strongly acidic. The pH is 2.9, [acidity]: 766 mg/L, [Fe]: 169 mg/L, [Mn]: 2 mg/L and [Al]: 39 mg/L. FBC ash placement was similar to Site M. The FBC ash used at both mines came from the same FBC unit. FBC ash had been applied to both sites about 10 years prior to sampling.

Field Sampling: The pH and water temperature were taken with a Hanna Waterproof pH Tester. Sample bottles for water samples were acquired from an State certified analytical laboratory. Two sample bottles were used per sample: one non-acidified bottle for analyzing lab pH, acidity, alkalinity, conductivity and SO_4; and one acidified bottle for analyzing metals such as Fe, Al, Mn, Ca, Mg, As, Ag, B, Be, Ba, Sb, Cd, Cr, Hg, Ni, Pb, Se, Tl, V, and Zn. A non-acidified bottle was used to acquire the first sample. The bottle was rinsed with the sampled water three times before it was entirely filled with the sample. The non-acidified sample was refrigerated until taken to the analytical laboratory. The second acidified bottle was filled with a filtered water sample. A cleansed syringe with a 0.45•m filter was attached and at least 80 mls of water were filtered into the pre-acidified bottle. Samples were taken to the State certified analytical laboratory for analysis within 48 hours

All samples were collected on 20 September 2004. Estimated flows at Site M were about 20 gpm while those at Site P were about 60 gpm   Samples were collected at seeps from both ash treated and untreated locations at each site. Water from the untreated sites was then used as the sites's AMD sample and was used as the leachant for the laboratory leaching tests.

Laboratory leaching procedure: We used the Mine Water Leaching Procedure (MWLP) [22,23] as our laboratory leaching method. It was developed to sequentially leach a particular CCP with the target mine's groundwater to evaluate which elements are likely to be mobilized as alkalinity is exhausted. This provides insight into long-term behavior as well as physical and chemical interactions among the reaction products. This study compared the results of laboratory MWLP leachings with field observations at large-scale CCP applications at acid producing coal mines. Ten grams of coal ash were weighed out and transferred into clean, dry, 2-L plastic reaction bottles. Two liters of AMD were added to each experimental bottle. The bottles were then sealed. The bottles were then agitated for 18 hrs on an end-over-end rotating platform at 30 rpm. After agitation the contents of each bottle were filtered through a 0.7 um glass, borosilicate filter using a stainless steel pressure filtration unit at or below 40 psi. Filtered leachate samples were then analyzed for acidity, pH, electrical conductivity, Al, As, Ag, B, Ba, Be, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Ni, Pb, Sb, Se, SO_4, Tl, V and Zn. Acidity was calculated from pH and major metal concentrations by the formula:

$$Acidity = 50(1000(10^{-pH}) + \sum_{i=1}^{n}(O_{me}[Me]/A_{me})_i) \qquad (1)$$

where: *acidity is given in mg/L CaCO₃ equivalent*

                   O_{me} = *oxidation state of metal ion i*

                   [Me] = concentration of metal ion i in mg/L

                   A_{me}= *atomic weight of metal ion i*

Since pH, Fe, Mn and Al account for virtually all of the acidity in coal mine drainage, the following formula is used:

$$acidity = 50((1000x10^{-pH})+(3x[Fe]/55.8)+(2x[Mn]/54.9)+(3x[Al]/27)) \quad (2)$$

Leaching cycles were repeated until the pH approached that of the mine water. This required only five cycles for the more acidic AMD from Site P while after 15 leaching cycles the Site M samples were still above the pH of the AMD leachant. Method detection limits are given on tables 1 and 2. In order to facilitate calculation, analytical results that were below the detection limit were assigned the detection limit.

3. Results and Discussion

Interpretation of laboratory and field data: The following discussion includes absolute and proportional data. The latter may be easily misinterpreted. For example, net gains in elemental concentrations may be almost infinitely large, particular with parameters that start at near detection limits. Apparently large proportional increases may reflect nearly trivial changes in concentration. For example, an increase from 0.001 to 0.010 mg/L represents a 900% increase yet the parameter may still meet primary drinking water standards. Obviously, the converse applies. On the other hand, decreases in a given parameter obviously cannot exceed 100%. For these reasons, both absolute and proportional data as well as U.S. primary drinking water standards are given to help the reader evaluate the significance of a given change in concentration. In summary, proportional changes in concentration are used to identify statistical trends, they do not imply environmental significance.

The laboratory results reflect a pure system with controlled inputs and outputs. The field data are subject to many confounding factors: unknown degree of contact between groundwater and FBC ash, interactions of the leachate with mine spoil, dilution with other groundwater streams, uncertain groundwater flow paths as well as redox zonation with the spoil. Nonetheless, comparison of the laboratory and field data will help identify those elements whose field behavior is predictable from empirical, laboratory testing and those that undergo significant interactions with the mine spoil

Leaching Studies: Leaching FBC ash with Site M mine drainage caused an immediate rise in pH from 4.5 to 9.6 which then declined very gradually (table 1). Surprisingly, acidity values remained well above alkalinity even with pH values at or above neutral. This coincides with an increase in Mn values throughout the leaching cycles starting at 0.3 mg/L in the leachant, reaching a maximum of 70.3 mg/L at cycle 5

and falling no lower than 47 mg/L by cycle 15. $Mn(OH)_2$ is soluble at a pH below 9.6 so after the leachate pH fell below this level by cycle 5 Mn began appearing in solution. The spike in Mn concentration probably resulted from solubilization of previously precipitated $Mn(OH)_2$ in the filter cake. Formula (1) illustrates how this soluble Mn would account for this increase in acidity.

Changes in leachate chemistry through 5 leach cycles using 10g of FBC ash leached with AMD from the Site M surface mine. The far right column is the net difference between AMD and cycle 15 leachant.

Table 1.

	units	method detect. limit	US Primary DW Std.	Site M AMD	Cycle 1	Cycle 5	Cycle 10	Cycle 15	AMD vs. last cycle
pH				4.5	9.6	7.6	6.5	6.6	48%
acidity	mg/L			144.0	3.0	133.0	96.7	86.3	-40%
alkalinity	mg/L			0.0	20.6	13.3	37.8	53.8	
Mg	mg/L	0.1		374.1	247.0	420.9	333.5	333.5	-11%
Ca	mg/L	0.1		534.5	834.6	561.4	511.4	543.6	2%
Fe	mg/L	0.1		5.0	0.3	1.3	0.1	0.1	-98%
Al	mg/L	0.1		23.2	0.3	0.2	0.1	0.1	-100%
Mn	mg/L	0.1		0.3	0.2	70.5	52.7	47.0	15344%
SO4	mg/L	10		2590.7	2587.2	2847.4	2660.6	2908.1	12%
Sb	mg/L	0.00087	0.006	0.00087	0.00087	0.00087	0.00087	0.00087	0%
As	mg/L	0.00410	0.05	0.00410	0.00410	0.00410	0.00410	0.00410	0%
B	mg/L	0.01000	2	0.03120	0.11747	0.10200	0.08307	0.11367	264%
Ba	mg/L	0.00116	0.004	0.00116	0.10292	0.02324	0.01528	0.01650	1323%
Be	mg/L	0.00071	0.005	0.01091	0.00710	0.00710	0.00710	0.00710	-35%
Cd	mg/L	0.00191	0.1	0.00191	0.00191	0.00191	0.00191	0.00191	0%
Cr	mg/L	0.00089	0.015	0.00089	0.00089	0.00089	0.00089	0.00089	0%
Pb	mg/L	0.00135	0.002	0.00135	0.00135	0.00135	0.00135	0.00135	0%
Hg	mg/L	0.00050	0.05	0.00050	0.00050	0.00050	0.00050	0.00154	209%
Se	mg/L	0.01350		0.01350	0.04118	0.02197	0.01350	0.01350	0%
Ag	mg/L	0.00115	1.3	0.00115	0.00115	0.00115	0.00115	0.00115	0%
Cu	mg/L	0.00046		0.02139	0.00046	0.00741	0.00046	0.00046	-98%
Ni	mg/L	0.00242	0.002	0.88031	0.02971	1.09037	0.73447	0.50629	-42%
Tl	mg/L	0.00173		0.00173	0.00173	0.00173	0.00173	0.00173	0%
V	mg/L	0.00089		0.00089	0.00089	0.00089	0.00089	0.00089	0%
Zn	mg/L	0.00352		1.52641	0.00894	0.33229	0.25811	0.20112	-87%
Cond	Umhos/cm			1458	2232	1448	1479	1390	-5%

NM = Not Measured

The far right column in table 1 shows the net change in each parameter during the leaching procedures. Net change is expressed as a percent change in concentration between the raw AMD leachant and cycle 15 leachate. The final cycle was chosen since this was expected to most closely approximate long-term conditions in the field. The most dramatic change was a 15,000% increase in Mn concentration. Ba accounted for the second largest increase. Increases in both B and Hg were about 200%. Note that the

concentrations of elements such as B, Ba and Hg were well below 1 mg/L and that in the case of Hg, levels were near the method detection limit. Other than Mn, all of the parameters that increased under leaching with the mildly acidic Site M water were either volatile or semi-volatile ions that are known to adhere to the outer surface of the ash particles. Thus leaching, rather than dissolution of the ash's alumino-silicate matrix probably accounts for much of the ionic increase. Major decreases occurred in the concentrations of acidity, Fe, Al, Cu, Be, Ni and Zn. Their proportional reductions ranged from 35 to 100%. Nine of the parameters were unchanged reflecting non-detectable levels in both the AMD leachant and the resulting leachates.

Leaching the same FBC ash with the more acidic Site P water yielded a very different picture (table 2). For example, even though a pH of 9.4 was reached on the original leach cycle, its strong acidity caused the original pH of 2.9 to be reached in only five leach cycles. Rather than a strong increase in Mn, it decreased by 11%. The greatest increases were in Al, Zn, Ni, Cr, Cu, Pb, Ba, V and Ag. The greatest decreases were in As, Hg, Fe, Cd, B, Tl, Se and acidity. Fourteen of the twenty-five parameters decreased and pH was unchanged. Perhaps the most interesting result was for As. Its concentration in the untreated site's AMD was 0.025 mg/L and it declined to 0.002 mg/L (the method detection limit) after five leach cycles, never exceeding 0.005 mg/L. This may be the result of an interaction with the high iron content of the Site P AMD since the arsenate oxyanion is strongly adsorbed to precipitated ferrihydrite which has an anion exchange capacity at low pH. Behavior As was below the method detection limit in Site M water both in the AMD and through all leach cycles. Sorption to positively charged ferrihydrite surfaces may explain the decreases in the other elements that form oxyanions such as: Tl, B, Se, SO_4, and Be.

Table 2. Changes in leachate chemistry through 5 leach cycles using 10g of FBC ash leached with AMD from the Site P surface mine. The far right column is the net difference between AMD and cycle 5 leachant.

	units	method detect. limit	US Primary DW Std.	Site P AMD	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	AMD vs. last cycle
pH				2.9	9.4	4.4	4.0	3.2	2.9	0%
acidity	mg/L			766.3	12.4	51.8	482.7	504.8	567.0	-26%
alkalinity	mg/L			0.0	49.4	0.0	0.0	0.0	0.0	
Mg	mg/L	0.1		36.6	16.9	46.4	39.2	37.1	33.8	-8%
Ca	mg/L	0.1		48.8	97.4	110.5	39.2	33.7	45.3	-7%
Fe	mg/L	0.1		168.6	0.5	0.6	0.7	1.2	58.6	-65%
Al	mg/L	0.1		39.0	2.0	7.6	84.7	84.4	58.4	50%
Mn	mg/L	0.1		2.0	0.0	3.4	2.0	1.8	1.7	-11%
SO4	mg/L	10		1529.0	1663.7	1409.3	1479.3	4950.3	1442.0	-6%
Sb	mg/L	0.00087	0.006	0.04800	0.05333	0.05567	0.04667	0.05533	0.04867	1%
As	mg/L	0.00200	0.05	0.02500	0.00233	0.00467	0.00133	0.00233	0.00167	-93%
B	mg/L	0.01000	2	0.24700	0.41300	0.35767	0.28833	0.18900	0.11833	-52%
Ba	mg/L	0.01000	0.004	0.01000	0.01000	0.02000	0.01333	0.01333	0.04000	300%
Be	mg/L	0.00010	0.005	0.00850	0.00123	0.00523	0.01050	0.00983	0.00743	-13%
Cd	mg/L	0.00010	0.1	0.00400	0.00403	0.00560	0.00327	0.00203	0.00177	-56%
Cr	mg/L	0.00010	0.015	0.00570	0.00780	0.00343	0.00547	0.01433	0.01733	204%
Pb	mg/L	0.00300	0.002	0.00400	0.02567	0.04067	0.03367	0.05200	0.05567	1292%
Hg	mg/L	0.00010	0.05	0.00070	0.00030	0.00013	0.00040	0.00023	0.00010	-86%
Se	mg/L	0.00300		0.01600	0.00867	0.00867	0.02733	0.01167	0.01133	-29%
Ag	mg/L	0.00115	1.3	0.00200	0.02000	0.00467	0.00567	0.00767	0.00500	150%
Cu	mg/L	0.00010		0.18400	0.00700	0.12367	0.38600	0.36433	0.23567	28%
Ni	mg/L	0.00200	0.002	0.18800	0.02667	0.45867	0.35233	0.31200	0.26067	39%
Tl	mg/L	0.00100		0.02100	0.01400	0.01600	0.05533	0.02833	0.01200	-43%
V	mg/L	0.00089		0.00300	0.00467	0.00900	0.00800	0.00833	0.01100	267%
Zn	mg/L	0.00100		1.24000	0.00833	2.30000	1.72000	1.42667	1.37333	11%
Cond	Umhos/cm			2910	2423	2117	1834	1983	2500	-14%

Other than Al and Ba, all of the ions mobilized by the strongly acidic Site P water were transition metals. Al increased by 50% suggesting dissolution of the alumino-silicate ash matrix and exposure of the embedded metal ions to mobilization. In contrast, leaching the FBC ash with Site M water resulted in a net loss of Al.

Field Observations: At the Site M surface coal mine, ash application raised the pH from 4.5 to 7.4 changing the groundwater from net acid (144 mg/L) to net alkaline (96 mg/L) (table 3). On the ash site, ten parameters increased and fifteen decreased. The largest proportional increases were in V, Ba, Cr and Ag. Increases also occurred in Mn, B, Sb and Cd. Nearly 100% decreases occurred in Al, Zn, Ni, Fe and Se. Smaller but substantial decreases occurred in Mg, Be, As, SO4, Hg, Ca, Tl and Pb.

Table 3. Comparison of drainage from sites with and without FBC ash application: Site M surface mine.

	units	method detect. limit	US Primary DW Std.	no ash applied	ash applied	net change
pH				4.5	7.4	65%
acidity	mg/L			144.0	3.6	-97%
alkalinity	mg/L			0.0	100.0	0%
Mg	mg/L	0.1		374.1	111.0	-70%
Ca	mg/L	0.1		534.5	238.0	-55%
Fe	mg/L	0.1		5.0	0.4	-93%
Al	mg/L	0.1		23.2	0.1	-100%
Mn	mg/L	0.1		0.3	1.3	311%
SO4	mg/L	10		2590.7	795.0	-69%
Sb	mg/L	0.00087	0.006	0.00087	0.00500	475%
As	mg/L	0.00200	0.05	0.00410	0.00100	-76%
B	mg/L	0.01000	2	0.03120	0.10000	221%
Ba	mg/L	0.01000	0.004	0.00116	0.10000	8521%
Be	mg/L	0.00010	0.005	0.01091	0.00500	-54%
Cd	mg/L	0.00010	0.1	0.00191	0.00500	162%
Cr	mg/L	0.00010	0.015	0.00089	0.05000	5518%
Pb	mg/L	0.00300	0.002	0.00135	0.00100	-26%
Hg	mg/L	0.00010	0.05	0.00050	0.00020	-60%
Se	mg/L	0.00300		0.01350	0.00200	-85%
Ag	mg/L	0.00115	1.3	0.00115	0.01000	770%
Cu	mg/L	0.00010		0.02139	0.02000	-6%
Ni	mg/L	0.00200	0.002	0.88031	0.04000	-95%
Tl	mg/L	0.00100		0.00173	0.00100	-42%
V	mg/L	0.00089		0.00089	0.10000	11136%
Zn	mg/L	0.00100		1.52641	0.05600	-96%
Cond	Umhos/cm			1458	2180	50%

At Site P the pH was 2.9 on the non ash treated location and 4.3 at the ash treated site. Groundwater acidity decreased from 766 mg/L to 308 mg/L. Despite ash treatment this remained an acid dominated groundwater. The largest relative increases in elemental concentrations were in V, Ba, Cr, Ni, Ag, Mn, Ca, Mg, Be, Cd and Zn. Of these Mg, Ca and Ba are semi-volatile alkaline earths known to form soluble salts on the exterior of the fly ash particles. The transition metals: Ni, Ag, Mn, Cd and Zn are present in solution as free metal ions are soluble at low pH and form insoluble hydroxides at high pH. All are soluble at pH 4.3. Decreases of between 60 and 100% were observed for Fe, As, Tl, Se, Hg, acidity, B, Cu and Sb.   Sorption to precipitated ferrihydrite may partly explain the decreased mobility of the anionic species: As, Tl, Se and B.

Table 4.   Comparison of drainage from sites with and without FBC ash application: Site P surface mine.

	units	method detect. limit	US Primary DW Std.	no ash applied	ash applied	net change
pH				2.9	4.3	51%
est. acidity	mg/L			766.3	308.4	-60%
alkalinity	mg/L			0.0	0.0	0%
Mg	mg/L	0.1		36.6	206.0	463%
Ca	mg/L	0.1		48.8	471.0	865%
Fe	mg/L	0.1		168.6	0.2	-100%
Al	mg/L	0.1		39.0	47.6	22%
Mn	mg/L	0.1		2.0	22.4	1049%
SO4	mg/L	10.0		1529.0	1750.0	14%
Sb	mg/L	0.00087	0.006	0.04800	0.00500	-90%
As	mg/L	0.00200	0.05	0.02500	0.00100	-96%
B	mg/L	0.01000	2	0.24700	0.10000	-60%
Ba	mg/L	0.01000	0.004	0.01000	0.10000	900%
Be	mg/L	0.00010	0.005	0.00850	0.03500	312%
Cd	mg/L	0.00010	0.1	0.00400	0.00800	100%
Cr	mg/L	0.00010	0.015	0.00570	0.05000	777%
Pb	mg/L	0.00300	0.002	0.00400	0.00400	0%
Hg	mg/L	0.00010	0.05	0.00070	0.00020	-71%
Se	mg/L	0.00300		0.01600	0.00200	-88%
Ag	mg/L	0.00115	1.3	0.00200	0.01000	400%
Cu	mg/L	0.00010		0.18400	0.07000	-62%
Ni	mg/L	0.00200	0.002	0.18800	1.13000	501%
Tl	mg/L	0.00100		0.02100	0.00100	-95%
V	mg/L	0.00089		0.00300	0.10000	3233%
Zn	mg/L	0.00100		1.24000	3.29000	165%
Cond	Umhos/cm			2910	4310	48%

Though preliminary it seems that the 22 elemental test parameters fall into three broad, activity classes:

Activity class A: semi-volatile cations: Ba, Ca, Mg, Hg
removal mechanism: Other than Hg, these form the cation in salts coating the ash particles.

Primary removal mechanism: cation exchange with spoil clays

Activity class B: oxyanions: B, Se, As, Tl, Cr, V, SO_4,

While these include semi-volatiles, their behavior is likely dominated by their tendency to form oxyanions in aqueous phase. Redox conditions are important in determining their tendency to sorb to ferrihydrites and clays.

Primary removal mechanism: sorption to ferrihydrite at low pH

Activity class C: metal cations: Al, Be, Zn, Ni, Fe, Cu, Mn, Pb, Cd, Sb, Ag
The soluble phases of these metals are dominated by free cations that form insoluble hydroxides with increasing pH. Some like Fe and Mn have multiple oxidation states, the oxidized forms having lower solubilities.

Primary removal mechanism: precipitation as hydroxides at high pH

While hypothetical, systematic investigation of these removal pathways will enhance our understanding of their behavior in mine groundwater settings.

It is important to note that even after 15 leach cycles the Site M leaching procedure still had not exhausted the alkalinity in the ash sample. Site M water had a pH of 4.5 and after the final leaching the pH was 6.6, while the Site P water had returned to its original pH of 2.9 after five leach cycles indicating exhaustion of the ash's inherent alkalinity. This may account for some of the differences in results between the two laboratory leaching results.

Comparison of Laboratory and Field Results: The effects of ash on laboratory and field concentrations were compared to identify which field trends (increasing or decreasing) were correctly predicted by the laboratory leaching procedure (table 5). Trends in twelve of the twenty-five parameters were correctly predicted at Site M. Fourteen of twenty-five parameters were correctly predicted at Site P. Seven parameters were successfully predicted on both sites while six were not successfully predicted on either site. The remaining elements were successfully predicted on at least one of the two field sites. Considering the many other factors that influence field leachate quality, these results indicate significant promise for predicting the effects of CCB minefills on a mine's water quality. Future study will undertake a detailed statistical analysis in the field and the laboratory to identify an improved risk assessment method. Also, sequential extraction of the residual solids would assist in interpreting the sequestration mechanisms. Approached systematically, we will begin to understand the effects of mine water on CCBs and the effects of spoil composition and hydrology on the resulting leachates.

Table 5. This table illustrates the ability of the MWLP leaching procedure to predict increasing (positive values) or decreasing (negative) trends. Field and laboratory data representing Sites M and P are given. Where the MWLP correctly predicted increasing or decreasing trends in the field data, the row was assigned a 'yes' while those trends that were not correctly predicted were assigned a 'no'. Activity classes represent: A-semi-volatile cations, B-oxyanions, C-metal cations.

	Site M Surface Mine (mildly acidic AMD)					Site P Surface Mine (strongly acidic AMD)			
	Activity class	MWLP results	Field data	predicted trend?		Activity class	MWLP results	Field data	predicted trend?
Al	C	-100%	-100%	yes	Fe	C	-65%	-100%	yes
acidity		-40%	-97%	yes	As	B	-93%	-96%	yes
Zn	C	-87%	-96%	yes	Tl	B	-43%	-95%	yes
Ni	C	-42%	-95%	yes	Se	B	-29%	-88%	yes
Fe	C	-98%	-93%	yes	Hg	A	-86%	-71%	yes
Mg	A	-11%	-70%	yes	acidity		-26%	-60%	yes
Be	C	-35%	-54%	yes	B	B	-52%	-60%	yes
Cu	C	-98%	-6%	yes	Al	C	50%	22%	yes
pH		48%	65%	yes	Zn	C	11%	165%	yes
B	B	264%	221%	yes	Ag	C	150%	400%	yes
Mn	C	15344%	311%	yes	Ni	C	39%	501%	yes
Ba	A	1323%	8521%	yes	Cr	B	204%	777%	yes
Se	B	0%	-85%	no	Ba	A	300%	900%	yes
As	B	0%	-76%	no	V	B	267%	3233%	yes
SO4	B	12%	-69%	no	Sb	C	1%	-90%	no
Hg	A	209%	-60%	no	Cu	C	28%	-62%	no
Ca	A	2%	-55%	no	Pb	C	1292%	0%	no
Tl	B	0%	-42%	no	SO4	B	-6%	14%	no
Pb	C	0%	-26%	no	Cond		-14%	48%	no
Cond		-5%	50%	no	pH		0%	51%	no
Cd	C	0%	162%	no	Cd	C	-56%	100%	no
Sb	C	0%	475%	no	Be	C	-13%	312%	no
Ag	C	0%	770%	no	Mg	A	-8%	463%	no
Cr	B	0%	5518%	no	Ca	A	-7%	865%	no
V	B	0%	11136%	no	Mn	C	-11%	1049%	no

Trends for elements in activity classes A and C: semi-volatile cations and metal cations respectively were evenly divided with respect to predictability. However, trends for all but one of the oxyanions comprising activity class B were not predicted by leaching procedure with Site M AMD while all but one were successfully predicted for Site P. This may be explained by the high iron content of Site P water and the availability of ferrihydrite as a scavenging agent for oxyanions at pH 2.9.

4. Conclusions

This study attempts field verification of the results of a laboratory leaching procedure that uses mine water to sequentially leach coal ash. In addition we attempted to begin the process of identifying which chemical parameters could be predicted in the laboratory.

The Mine Water Leaching Procedure is a sequential leaching procedure that was developed to determine the long-term leaching behavior of industrial wastes in acidic mine environments. The complex hydrology, redox and geochemical conditions found within the backfills of most surface mines are difficult, if not impossible to reproduce in a laboratory setting.   However, preliminary comparisons of MWLP leachates with field leachates indicates that this procedure may be a valuable tool for predicting the overall trend of leaching behavior for CCBs placed in unique acidic environments.

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