Properties and Potential Water Quality Effects of Post-2000 Coal Combustion Products

2004/2005 Powell River Project Annual Progress Report

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Introduction and Overall Objectives

In the mid-1990's, we conducted a detailed study of the properties and environmental behavior of coal fly ash in SW Virginia mining environments (Daniels et al., 2002). That cooperative Powell River Project research program focused specifically on coal fly ash materials that were generated in the mid-Atlantic region from coals mined in SW Virginia. However, as discussed below, the basic properties and nature of coal combustion products (CCP's) have changed considerably in the past 5 to 10 years, and further significant changes to properties important for their utilization in mining environments are likely over the next 5 years. For example, the potential for Se release from valley fills and coal waste piles is currently under detailed scrutiny in our region due to very low (≤ 5 ppb) water quality criteria and higher observed discharge levels in West Virginia. Similarly, the USEPA is currently re-evaluating its policy position on utilization of CCP's in mining environments, has recently issued more stringent regulations for As in ground water, and will be proposing new rules on Hg release from coal fired plants. This study was initially funded in January of 2004 with the following multi-year objectives:

1. To determine the basic chemical and physical properties of a large set of modern CCP's generated by combustion of SW Virginia coals, including FGD materials and fly ash produced by emerging air emission control technologies.

2. To estimate the likely effect of changes in coal combustion technologies such as low NO_x boilers and various mercury removal strategies on ash chemical and physical properties.

3. To predict the relative leaching risk of oxyanions such as As, B, Mo and Se in common SW Virginia coal mining/ash utilization environments.

4. To evaluate the full range of CCP products that will likely be available for back-haul utilization and co-disposal for their suitability as (a) topical mine soil amendments, (b) geochemically stable backfill materials, and (c) bulk-blended treatments for acidic coal waste materials.

Background Issues and Related Studies

Acid mine drainage from coal waste piles and other acid forming mine spoils is a major problem in the Appalachian coalfields in general, and a localized problem in the Virginia coalfields. Detailed work by our research group, and others working in the Appalachians, has indicated that coal fly ash is often alkaline, and may be useful as an amendment for acid-forming materials if the appropriate utilization protocols can be developed (Stewart et al., 1997; Daniels et al., 2002). Documented potentially beneficial uses for suitable fly ash materials include its use as a bulk-blended additive to offset acid mine drainage from potentially acidic coal refuse materials and as a topical mine soil amendment at rates of up to 20% by volume (approximately 250 tons per acre, incorporated). We also conducted a detailed study of the geotechnical properties of varying mixture ratios of Clinch River (AEP) fly ash and Moss 3 (Alpha Natural Resources) coarse refuse (Albuquerque, 1994) which indicated, among other findings, that significant reductions in saturated hydraulic conductance are associated with the admixture of dry fly ash into coarse refuse. However, fly ash also contains a number of potentially toxic trace elements which are leachable under certain conditions, particularly if the ash is exposed to highly acidic drainage (Stewart et al., 2001). Thus, our overall findings were generally positive with respect to the beneficial reuse potential of coal fly ash, but they did contain significant cautionary results.

The body of work discussed above was focused entirely upon class F fly ash materials since they constituted the vast majority of CCP’s generated in the mid-Atlantic region at that time. However, changes in air quality regulation and resultant changes in air emission technologies over the past decade have led to major changes in the type and properties of CCP’s that are now available for back-haul to the Virginia coalfields. First of all, increasing quantities of flue gas desulfurization (FGD) sludges are now being generated as separate CCP’s or mixed with fly ash. The advent of low NOx boilers has led to significant concentrations of ammonia in many CCP’s. Mercury removal from flue gas has recently emerged as a federal air emission regulatory priority. Depending on which control technology is utilized, FGD and fly ash will become more enriched in Hg at certain plants, while other plants will utilize injected activated charcoal as a sorbent which may lead to higher ash concentrations of a range of metals in addition to Hg. One major secondary effect of increasing ammonia and carbon levels in CCP’s is that they have substantial negative effects on the marketability of CCP’s for use in cement admixtures or block manufacturing. Thus, the pressure for land application and/or mine utilization would be expected to increase. On a positive note, however, both of these additives could substantially improve the soil amendment properties of CCP’s.

Our previous work on CCP’s (Daniels et al., 2002) focused primarily on the potential water quality benefits and risks of fly ash utilization in various mine environments, with a principal focus upon bulk acid-base balances and heavy metal (Cu, Zn, Fe, Al, Mn, etc.) mobility to local ground-water. However, we did not evaluate the possibility of As, Se, and Mo mobility in ash/refuse leachates in detail for a variety of technical reasons combined with a lack of focused "regulatory concern" at the time. However, the current regulatory climate is placing much greater focus on the potential for As, B and Se mobility from waste disposal and utilization environments on/in active coal mines, along with a strong emphasis on defining Hg levels and mobility in coal combustion products in general. As just one example of the current regulatory climate, the USEPA recently reaffirmed its 1993 position that exempted CCP's from regulation as RCRA subtitle C wastes, but specifically reserved judgment on the use of CCP's in coal mining environments. This delayed decision for mining environments is due largely reports of sulfate and borate migration to local ground-water wells from CCP disposal fills in midwestern surface coal mines. Thus, the prediction of the relative mobility of As, B, Hg, Se, Mo, and other potentially water-soluble trace ions is the particular focus of this research program.

Throughout the1990's, we worked very closely with VDEQ and VDMLR to prepare regulatory guidelines for the beneficial reuse of coal fly ash in mined land environments. As a part of that process we developed the background technical materials and proposed testing standards for the 1994 VDEQ rules, and then we participated in the development of the specific mined land utilization guidelines for VDMLR. While we believe that those guidelines and their underlying assumptions are still quite appropriate for the utilization of the typical coal fly ash materials that we studied in the 1990's, we are not certain of their current applicability to the full range of CCP's and associated properties as discussed above.

Research Methods and Procedures

This study was originally proposed as a three-year effort, was initiated in late January of 2004, and a six-month progress report was provided last year. Work over this past full project year (2004/2005) focused on obtaining broad sample set of CCP's currently generated by coal-fired utilities burning primarily SW Virginia coals. Our two main collaborating utility companies are American Electric Power (AEP) and Dominion Virginia Power. With their cooperation, we have obtained a much larger sample set (28 ashes; see Tables 1 and 2) than originally anticipated. These samples cover a wide range of basic CCP properties and include fly ash, FGD, and bottom ash. In the second full year (2005/2006) of the study, we will focus on the use of various laboratory methods to estimate the potential mobility of various elements of concern (including As, Hg, Mo, Se and B) from CCP treated mine soils or from coal waste/mine spoil/CCP co-disposal fills. In the third year and final year, we will evaluate the plant growth response to various CCP's (including ammoniated and activated C treated materials), and determine which CCP components should be used to limit maximum land application rates for the wide variety of CCP's that likely to be generated in the coming decade. Finally, we will also integrate our complete findings into an overall summary report and synthesis document on the nature of CCP's in relation to mined land utilization on/in coal mines.

Detailed Methods for 2004 to 2005 Project Year

Over the first six months of the study (staring January 2004), we 1) obtained the analytical capability to quantify oxyanions like As, B, Mo, and Se at concentrations < 5 ppb, 2) tested new laboratory procedures for the evaluation of leachable inorganic constituents from CCP's**,** and (3) made contacts with coal fired utilities and obtaining a large suite of regional samples for intensive testing in the coming project year. As mentioned above, we were able to obtain twice the number of ash samples that we had hoped. This will result in more robust and applicable results as we are able to draw upon data from a wider variety of CCP types (fly ash, FGD, bottom ash), with a wider range of chemical properties within each type.

As proposed, we have conducted a detailed preliminary chemical characterization of all samples by the methods listed below. We also developed the capacity for, and analyzed one test sample according to the latest method (Kosson et al., 2002) that is under consideration by the U.S. EPA as the alternative to the TCLP method for the evaluation of CCP's. All samples were subjected to the following procedures:

1. pH and Electrical Conductance (EC) (Rhoades, 1982).
2. Water extractable ions in saturated paste EC extract.
3. Hot $CaCl_2$ extractable boron (Bingham, 1982).
4. Total elemental analysis (U.S. EPA, 1992a).
5. Sequential fractionation analysis (e.g. water soluble, exchangeable, acid-extractable, oxide-bound, total, etc.) to determine the speciation/partitioning of all major and minor elements of environmental concern, including As, Se and Hg (Tessier, et al., 1979).
6. Calcium carbonate equivalence (CCE).
7. Toxicity Characteristic Leachate Procedure (TCLP) for priority metals (U.S. EPA, 1992b).
8. 3-Tier extraction as discussed below (on selected sample) (Kosson, et al, 2002).

Progress to Date

1) Chemical Characterization and Results:

The chemical characterization of CCPs by detailed sequential fractionation for elements of interest, along with other supplementary chemical properties, can be related to the elements' relative solubility/bioavailability. These data can then be further utilized in geochemical modeling/speciation procedures to determine the likely solubility controlling solid phases, and soluble ion species as affected by leachate pH, Eh and solute conditions. Table 1 documents the various CCP's that we collected and the specific analyses that have been completed. Tables 2 and 3 present summary data for selected chemical properties. These data sets indicate the wide range of CCP’s that we were able to collect and how varied they are in their chemical properties. We have just completed the full laboratory analysis phase of this work, and to date we have not completed a detailed analysis of these data sets. The full range of CCP chemical properties and how they relate to coal source, combustion technologies, and other factors will be discussed in detail in next year’s report.

The sequential extraction procedure by Tessier et al. (1979) uses a series of extractant fluids to dissolve metals and oxyanions associated with particular ligand phases in a complex sample. The procedure involves sequential extraction with 1M $MgCl_2$ for soluble/extractable forms, followed by the extraction with 1M Acetic Acid/NaOac for carbonates, followed by the extraction 0.04 M hydroxylamine hydrochloride/acetic acid for Fe/Mn oxide bound forms, followed by extraction with H_2O_2/ammonium acetate/HNO_3 for organically bound forms, and finally, HF/HNO_3 for residual bound forms. Table 2 presents the sequential extraction data for a subset of samples. In the coming year of this study we will focus on integrating all the data from the various laboratory methods to estimate the potential mobility of various elements of concern (including As, Hg, Mo, Se and B).

2) Evaluating Actual Leaching Potentials

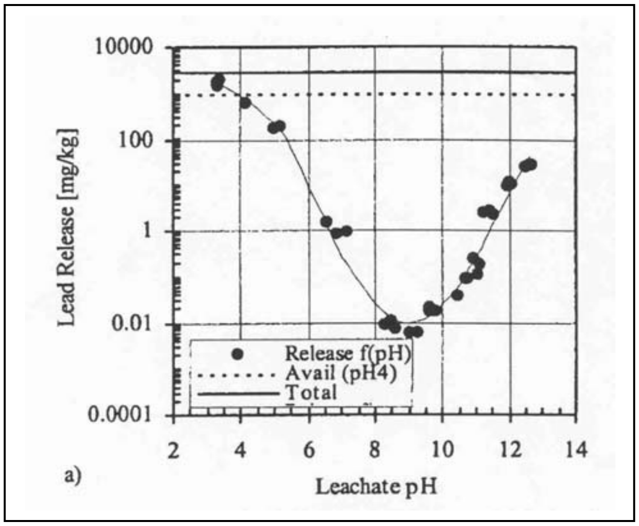
A major limitation to most tests designed to simulate element release (leaching) under specific environmental scenarios is that these tests do not provide information on actual release under a wide range of expected disposal or land application geochemical environments. This is the main criticism of the Toxicity Characteristic Leaching Procedure (TCLP) used by the USEPA for regulatory screening of potentially toxic waste materials. In the case of highly alkaline fly ash or non-acidic coal refuse, for example, the TCLP procedure tests these materials in an acidic (glacial acetic acid) environment. This environment may be drastically different from the conditions governing leachability under actual disposal conditions.

In 2004/2005, we participated in an inter-laboratory study coordinated by USDOE-Pittsburgh that is testing various methods for evaluating leaching. The 3-Tier Leaching Protocol (Kosson et al., 2002) appears potentially suitable in its application to CCPs and coal refuse. The method takes a multi-faceted approach by looking at 1) the solubility and release as a function of pH, 2) the solubility and release as a function of the liquid-solid ratio of the test conditions, and 3) the mass transfer rate from the solidified waste or compacted material.

For example, Figure 1 shows the release of lead (Pb) from a cementitious synthetic waste as a function of pH. The application of the 3-Tier method may provide much more useful information on As, Se, Mo, and Hg release from CCPs and coal refuse than the TCLP method. However, the 3-Tier method is very time-consuming and expensive. Hopefully, by combining data from conventional extractions, the 3-Tier method and the sequential extraction technique discussed earlier, we will be able to determine an optimal approach for estimating environmental leaching risk of these important elements.

At this time, we have completed the analysis of one selected fly ash sample by the 3-Tier method. We gained valuable experience in running this procedure and are now able to analyze a subset of our 28 CCP's according to this method. Being able to relate this data to those obtained with TCLP and other chemical characterization, will allow us to evaluate if the new 3-Tier method addresses the shortcomings of the TCLP method as discussed above. As the development of methods become specific to the environmental disposal conditions and waste material tested, the sophistication of the applied techniques puts these tests into the realm of research methods (e.g. 3-Tier procedure) which do not lend themselves to be used as predictive tools for regulatory purposes and management practices. Over the next year we hope to identify possibilities to condense more complicated research methods into shorter, simpler methods that can be used more directly as predictive tools for regulatory purposes and management practices.

Figure 1. Effect of leachate pH on lead release from Kosson et al. (2002).



Expected Results and Benefits for Southwestern Virginia

The appropriate utilization of CCP's on and in southwest Virginia coal mines could directly improve water quality via the offset of acid mine drainage production and increased mine soil productivity. The southwest Virginia coal and transportation industries could also realize substantial efficiencies and improved marketing arrangements through the back-haul of CCP's from coal-fired utilities. However, any such large-scale utilization of CCP's on or in mined landscapes must appropriately balance potential benefits against any long term potentials for water quality degradation via losses of potentially mobile constituents such as As, B or Se.

Finally, we collectively know very little about the abundance and mobility of As, Hg and Se in CCP's, mine spoils and coal processing waste materials in general. This critical information will also be supplied by this research program.

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Supporting Literature/Related Studies

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Table 1. List and type of CCP's analyzed along with completed (X) chemical extractions.

Lab Number	Type of Ash	Saturated Paste EC/pH	Calcium Carbonate Equivalence	TCLP Pretest	TCLP shake and filter	TCLP Digest	Hot $CaCl_2$ Extractable B	Sequential Extraction Procedure	Total Elemental
1	Fly Ash	X	X	X	X	X	X	X	X
2	Not yet known	X	X	X	X	X	X	X	X
3	Fly Ash	X	X	X	X	X	X	X	X
4	Fly Ash	X	X	X	X	X	X	X	X
5	Not yet known	X	X	X	X	X	X	X	X
6	Fly Ash	X	X	X	X	X	X	X	X
7	FGD Stabilized By-Product	X	X	X	X	X	X	X	X
8	Fly Ash	X	X	X	X	X	X	X	X
9	Fly Ash	X	X	X	X	X	X	X	X
10	FGD Sludge	X	X	X	X	X	X	X	X
11	Fly Ash	X	X	X	X	X	X	X	X
12	FGD Sludge	X	X	X	X	X	X	X	X
13	Not yet known	X	X	X	X	X	X	X	X
14	Bottom Ash	X	X	X	X	X	X	X	X
15	Screened Ash	X	X	X	X	X	X	X	X
16	Fly Ash	X	X	X	X	X	X	X	X
17	Fly Ash composite	X	X	X	X	X	X	X	X
18	Fly Ash	X	X	X	X	X	X	X	X
19	Fly Ash	X	X	X	X	X	X	X	X
20	Fly Ash	X	X	X	X	X	X	X	X
21	Fly Ash	X	X	X	X	X	X	X	X
22	Fly Ash	X	X	X	X	X	X	X	X
23	Fly Ash	X	X	X	X	X	X	X	X
24	Fly Ash	X	X	X	X	X	X	X	X
25	Fly Ash	X	X	X	X	X	X	X	X
26	Fly Ash	X	X	X	X	X	X	X	X
27	Fly Ash	X	X	X	X	X	X	X	X
Control	Known Fly Ash	X	X	X	X	X	X	X	X

Table 2. Sequential extraction data for selected CCP samples.

Step/Extractant	Sample #	Cr	As	Mo	Mn	Se	Al	Fe	Ni	Cu	Zn
		mg / kg									
1	19	0.01	.*	0.20	0.07	0.12	1.94	0.21	0.05	0.07	0.05
$MgCl_2$	20	0.24	0.66	5.57	0.16	1.20	3.25	0.29	0.06	0.15	0.11
Exchangeable	21	0.03	0.40	0.42	0.19	0.78	2.63	0.34	0.05	0.07	0.06
	22	0.02	0.22	3.23	4.84	0.79	2.79	0.29	0.18	0.10	0.02
	23	0.29	0.15	3.81	0.14	0.13	3.39	0.22	0.13	.	0.03
	24	0.59	.	0.40	0.03	0.15	1.99	0.15	0.08	0.08	0.03
	25	.	.	0.32	0.06	0.08	2.51	0.23	.	0.12	0.03
	26	0.01	0.26	5.89	1.41	1.23	2.87	0.37	0.19	0.14	0.16
	Control	0.63	0.17	4.59	0.06	2.42	252.8	0.60	.	0.12	.
2	19	2.95	2.77	1.94	10.82	3.80	226	267	6.56	19.70	17.00
Na-Acetate	20	1.79	15.05	0.71	3.86	6.73	189	38	1.47	1.93	1.92
Carbonates	21	0.99	10.57	0.22	4.29	3.10	63	17	0.52	2.90	1.13
Bound Forms	22	1.35	12.84	0.41	14.63	4.41	114	42	0.85	4.46	2.09
	23	0.96	7.02	1.03	1.77	0.37	75	17	1.42	10.50	2.66
	24	0.36	0.10	1.40	1.99	0.32	54	2.67	0.57	0.06	0.30
	25	1.87	2.64	1.11	7.18	2.70	104	212	3.26	10.90	9.49
	26	0.64	10.71	1.24	2.62	3.84	141	37	1.23	4.20	2.37
	Control	10.84	14.82	2.82	8.56	2.64	277	133	1.19	7.15	2.78
3	19	0.81	1.35	0.50	0.71	12.82	153	167	0.57	0.34	0.53
NH_4-oxalate	20	5.05	56.85	3.23	6.94	7.99	734	503	1.74	5.09	1.36
Amorphous **Fe-Mn Bound**	21	2.01	17.61	0.80	11.96	2.90	391	583	0.80	4.13	.
	22	3.64	41.45	2.32	12.37	6.58	374	350	0.85	3.82	0.25
	23	2.69	32.62	3.44	1.52	1.01	406	255	0.84	8.37	1.33
	24	1.22	0.08	0.65	1.60	0.72	32	4	0.22	0.4	.
	25	0.84	8.67	0.88	0.43	7.56	1083	420	0.36	3.59	.
	26	5.48	115	7.08	4.70	10.77	1024	625	2.07	8.56	1.55
	Control	8.70	33.9	3.38	10.78	3.24	1069	906	0.71	3.55	0.61

Table 2
Continued

Step/Extractant	Sample #	Cr	As	Mo	Mn	Se	Al	Fe	Ni	Cu	Zn
		mg / kg									
4	19	3.00	6.02	0.53	3.96	.	2385	1054	4.10	18.33	8.24
Hydroxylamine in	20	5.37	15.79	2.28	18.27	.	2685	2190	5.48	14.71	7.98
25% acetic acid	21	2.31	5.35	0.61	31.7	.	2041	2101	3.26	7.19	4.14
Crystal. Fe-Mn Bound Forms	22	4.41	8.44	0.98	16.67	.	1942	2371	4.37	10.44	7.64
	23	3.61	12.78	3.70	4.32	.	2224	1228	2.55	10.85	12.67
	24	7.49	11.57	0.77	21.59	.	7310	2331	4.24	8.27	20.55
	25	2.00	3.87	0.62	4.89	.	1975	1521	4.53	8.48	6.64
	26	4.35	23.25	3.01	12.91	.	3358	2787	5.71	16.02	9.03
	Control	7.13	7.04	1.56	19.84	.	3283	1838	2.20	6.52	5.59

.* Below detection limit

Table 3. Electrical conductance (EC), pH , CaCl$_2$ extractable B, and total elemental analysis for selected CCP samples.

Sample	EC dS / m	pH	Extr. B	B	Cr	As	Mo	Se	Ni	Cu	Zn	Cd
			mg / kg									
19	11.86	7.17	43.7	116.9	35.1	57.7	7.52	13.55	24.97	42.10	18.60	1.03
20	1.25	8.45	3.7	35.8	32.7	33.8	2.82	.*	31.50	40.53	17.54	.
21	26.85	9.32	16.6	168.5	31.6	13.7	4.14	18.46	36.90	68.66	42.87	.
22	3.67	9.36	23.3	98.8	118.1	169.9	24.67	14.79	72.91	136.54	65.33	2.28
23	8.01	8.01	14.2	49.5	57.2	71.9	8.46	15.66	35.87	66.47	31.27	1.38
24	2.92	7.50	13.3	32.3	132.1	52.9	14.90	.	38.33	76.55	56.74	0.65
25	11.2	12.15	0.3	31.7	91.5	21.6	5.34	.	59.54	44.83	78.84	.
26	15.63	10.89	2.0	101.9	19.3	18.3	4.29	9.94	27.41	35.81	24.52	.
Control				60.4	120.3	59.7	14.34	10.87	32.87	77.12	37.22	0.81

* Below detection limit