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

2005/2006 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, 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 ($\leq$ 5 ppb) water quality criteria and higher observed discharge levels in West Virginia. Similarly, the National Research Council (2006) recently issued a report on issues related to management of CCP's in mining environments, which detailed a range of public and agency concerns focused on local impacts to ground water quality. Greater detail on CCP utilization issues and our past research findings are provided in last year's Powell River Project Annual Progress Report.

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.

Research Methods and Procedures

This study was originally proposed as a three-year effort, was initiated in late January of 2004, and will be completed by June of 2007. As reported last year, work over the 2004/2005 project year 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 obtained a much larger sample set (28 ashes; see Tables 1 and 2 in our 2005 report) than originally anticipated. These samples cover a wide range of basic CCP properties and include fly ash, FGD, and bottom ash. Last year's report presented a detailed characterization of the total elemental analysis, sequential fractionation, and other important chemical characteristics of the full sample set.

In this year's (2005/2006) study, we focused on the use of various laboratory methods to estimate the potential mobility of various elements of concern (including As, Mo, Se and B) from CCP treated mine soils and from coal waste/mine spoil/CCP co-disposal fills. We also evaluated the plant growth response to various CCP's in a greenhouse setting. In the coming final year of the project, we will complete all lab and greenhouse analyses and determine which CCP components should be used to limit maximum land application rates for the wide variety of CCP's 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.

As reported in detail last year, the 28 primary composite CCP samples were subjected to the following analyses:

1. pH and Electrical Conductance (EC).
2. Hot $CaCl_2$ extractable boron.
3. Total elemental analysis.
4. 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, B, and Hg.
5. Calcium carbonate equivalence (CCE).
6. Toxicity Characteristic Leachate Procedure (TCLP) for priority metals.

Five CCP's were selected from the larger sample set for a greenhouse bioassay study on the plant growth effects of land-application of CCP's to mine soils at typical soil amendment rates. Similarly, the same CCP's (with one substitution) were selected for a laboratory leaching study to assess the effect of differing CCP properties and loading rates on leachate quality from acidic coal refuse.

Criteria for Selection of 5 CCP's for the Greenhouse Bioassay Trial

The main determinants for the selection of the five CCP's for the greenhouse bioassay trial were bulk soluble salts (EC), and As concentration and distribution among the 5 sequential extraction (SEP) fractions discussed in last year's report. We also chose materials that presented a wide range of soluble B concentrations.

Statistical analyses indicated that CCE was the one chemical property most strongly related to As levels and distribution among the various SEP fractions. CCE was negatively correlated to As levels in the first four more labile fraction (r^2 = -.38 to -.53), but positively correlated to the residual (r^2 = .78) As fraction. For CCP's with low total As (around 12 mg kg^{-1}), the As was up to 90% in the residual fraction. For CCP's with high total As (around 120 mg kg^{-1}), the As was up to 90% distributed among the labile and moderately labile fractions. Therefore, the five CCP products chosen for detailed study were selected to provide the full combination of high/low As vs. high/low EC conditions.

Thus, the selected of CCP's for the greenhouse bioassay trial were as follows:

Ash #	Type of Ash	Ash properties
22	fly ash	high As; low CCE; low EC
28	fly ash	high As; low CCE; mod. high EC
16	fly ash	low As; high CCE; low EC
27	fly ash	low As; high CCE; high EC
7	FGD	relatively low As; high CCE; mod. EC

Methods for Greenhouse Bioassay Trial

The bioassay trial was designed to test the presumed effectiveness of CCP's as surface applied amendment to mine soils for improving pH and water holding capacity. The general design, methods, and techniques used for our greenhouse bioassay (mine soil amendment scenario) are fully documented and cited by Daniels et al. (2002). The procedures were modified to include a "pour-through" procedure where we leached the greenhouse pots with excess leaching waters approximately one month after establishment of the trial, and then collected the leachates for analyses such as pH, EC, As, Se, B and other parameters we deemed important.

- Acidic sandstone mine spoil was collected at an active Powell River/Red River operation, Wise county, Virginia. Laboratory pH = 4.75, with a liming requirement equivalent to 4.5 Mg/ha. The mine spoil was air dried and sieved to pass a 2 mm sieve.

- The trial was conducted using soybeans (*Glycine max*) as an indicator plant sensitive to substrate chemical conditions (EC, pH, elemental toxicity) and tall fescue (*Festuca arundinaceae*) as a test crop exhibiting relative tolerance to low pH, metals, and salts.

- Selected properties of the five CCP's utilized are given in Table 1 below.

Table 1. Properties of five CCP's selected for use in greenhouse bioassay experiments.

			Saturated Paste				Total Elemental Analysis via Micro Digestion				
CCP #	Type	Bd g cm^{-3}	pH	EC dS m^{-1}	CCE %	Ext. B mg L^{-1}	Total B mg kg^{-1}	As mg kg^{-1}	Se mg kg^{-1}	Cr mg kg^{-1}	Mo mg kg^{-1}
28	Fly ash	1.12	11.5	3.1	16.3	3.6	82	57	11	70	11
11	Fly ash	1.50	8.9	3.3	0	185	574	179	15	130	50
16	Fly ash	1.15	12.6	14.9	53	16	789	14	11	73	37
27	Fly ash	1.20	11.9	4.5	57	nd	841	23	4	86	9
7	FGD	0.80	9.1	5.3	49	23	225	19	3	36	8

Experimental Design & Treatments:

- The trials were conducted separately for fescue and soybean. The statistical design was a completely randomized block (RCB) with 4 replications per treatment combination.
- 3 CCP rates: 5%, 10%, 20% (v:v basis, but measured on a weight basis to reduce variability) as well as 100% mine spoil control pots for each crop
- Volume of substrate / pot = 700ml / pot (900g)

3 ash rates X 5 CCP's X 2 crops X 4 replications = 120 pots

Control pots: Control (-) no-lime mine spoil only (4 per crop)
Limed control (-) pots (4.5 Mg/ha equivalent)
Highly limed control (++) pots (9 Mg/ha equivalent)

- Soil substrate moisture was maintained near container capacity.
- Approximately every month, pots were allowed to equilibrate at field capacity for 24 hours and then eluted with excess water to obtain 50ml (± 5ml) of leachate.
- Soybean pots were seeded for 4 plants with thinning to the healthiest plant of each pot 1 month after seeding.
- Fescue was cut, dried, and weighed approximately every 3 weeks.
- Overall fertility was maintained with a 20-20-20 Peter's liquid fertilizer.

Methods for Leaching Column Study

The selection criteria of five CCP's to be used as an amendment to the acidic coal refuse were the same as those for the bioassay trial with one exception/substitution. For this experiment, CCP # 28 was substituted with CCP # 18. This CCP has high total As, Se and Cr concentrations, 0 CCE, and a very low pH of 3.57. Including this CCP gave us a maximum range in potential chemical composition and leaching risk once the acid forming coal refuse was amended with the various CCP's.

- Known acid- forming coal refuse was collected fresh from the Red River Coal Co. prep-plant in Wise County, Virginia.

- The refuse was air dried and sieved to maximum 1.25 cm particle size.

- A modified hydrogen peroxide oxidation procedure (Barnhisel and Harrison, 1976) was used to determine the potential acidity (PPA) of the coal refuse. PPA = 34.5 Mg CCE per 1000 Mg material; or agricultural lime demand = 34.5 tons of lime per acre per six inch depth.

- The refuse was repeatedly moistened and allowed to dry out in order to accelerate the oxidation of sulfides. Once the pH of the refuse dropped to 4.5, the material was deemed ready for amendment with CCP's.

- Selected properties of the CCP's are given in Table 2 below.

Table 2. Properties of five CCP's selected for use in greenhouse bioassay experiments.

			Saturated Paste				------ Total Elemental via Micro Digestion ----				
CCP #	Type	Bd	pH	EC	CCE	Extr. B	Total B	As	Se	Cr	Mo
		g cm^{-3}		dS m^{-1}	%	mg L^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
18	Fly ash	0.68	3.57	11.79	0.0	3.6	82	57	11	70	11
11	Fly ash	1.50	8.9	3.3	0.3	185	574	179	15	130	50
16	Fly ash	1.15	12.6	14.9	53	16	789	14	11	73	37
27	Fly ash	1.20	11.9	4.5	57	nd	841	23	4	86	9
7	FGD	0.80	9.1	5.3	49	23	225	19	3	36	8
Coal Refuse		1.92	<3.0		0						

Leaching Column Design:

The columns we built were of similar design as those previously used by our group in CCP leaching studies (Stewart et al., 1997, 2001) but scaled down to approximately 1300 cm^3 sample size. The columns were made from 7.5 cm PVC pipe, 38 cm long, with a rounded endcap at one end. Fine nylon mesh was in the endcap was topped with 2 cm of 1 mm acid-washed glass beads. Test columns were constructed to determine the proper weight ratios of the respective CCP and coal refuse to reflect by-volume CCP amendment of 10 and 20%. Columns were then filled on a by-weight basis to reduce replicate variability. Columns were packed in increments of 100 cm^3. A thin layer of glass beads was added between increments to fill any large voids in order to minimize/eliminate preferential flow. The treatment mixes were topped with 2.5 cm of glass beads in aid infiltration. Leaching water was applied by setting a 6 cm diameter plastic cup with perforated bottom onto the glass beads. This ensured uniform distribution of the leaching water on the head of the column.

Statistical Design & Treatments:

- The statistical design was a completely randomized block (RCB) with 3 replications per treatment combination.

- 2 CCP rates: 10%, 20% (v:v basis, but mixed on a weight basis to reduce variability) as well as 100% coal refuse control (-) columns with no lime added; plus 100% coal refuse control (+) columns with lime added, equivalent to 34.5 Mg/1000 (tons/acre) per the PPA procedure.
- Columns were leached with 100 ml deionized water (equivalent to approximately 2.5 cm or 1" rainfall event) twice per week.
- Leachates were allowed to drain freely for 24 hours into acid-washed polyethylene collection bottles.
- EC and pH were determined on all leachates on the day of collection.
- Elemental concentrations were determined by ICPES analysis on composite samples made up of 6 ml leachate from each replicate of a treatment combination.
- Leachate samples were analyzed for the following elements: As, B, Cr, Cu, Fe, Mo, Ni, S, Se, and Zn.
- Columns were run in the laboratory with room temperature of 22 ^{o}C (±2).
- Columns were moistened to container capacity and allowed to equilibrate for 24 hours prior to the first leaching event.

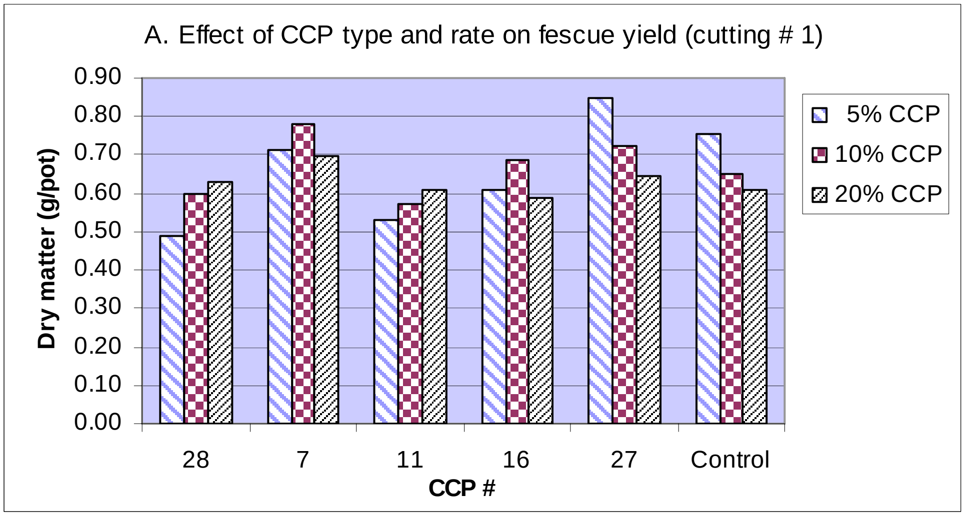
Results and Discussion

Greenhouse Bioassay Experiment

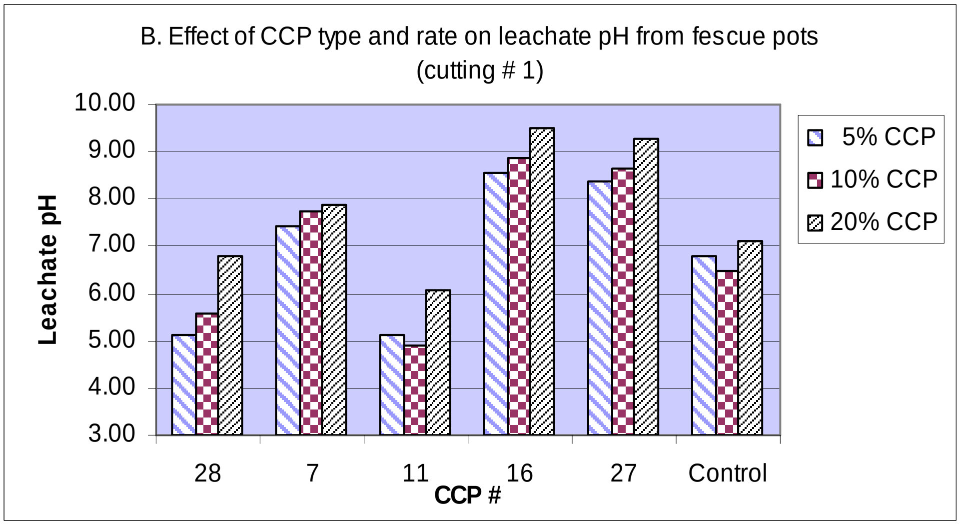
Properties of the various mine spoil and CCP mixtures are presented in Table 3. Dry matter yields from the first cutting of the tall fescue, along with corresponding EC and pH of the leachates from the pots at the time of cutting, are presented in Figs. 1 a-c and Table 4a. Dry matter yield tended to increase with increasing CCP rate as long as the bulk soil pH remained at pH 8.0 or less. Depending on the liming capacity (CCE) of the CCP applied, the 20% application had the greatest positive effect on plant yield (e.g. see CCP # 28 with a CCE of 7.7). However, in case of a CCP with a high liming potential (e.g. #27, CCE = 47.7), a 5% application was most beneficial to dry matter yield. Higher amendment (10 & 20%) rates of CCP with high liming capacities elevated the pH above 8.0 which limited or decreased plant yield.

Analysis of variance (ANOVA) of the fescue yield data revealed highly significant (0.001) effects of both CCP source and application rate. The same strongly significant effects were seen for EC and pH, except that for these two variables, the CCP source X application rate interaction was also highly significant. While the CCP's differ in their total elemental composition (Table 1) and among the fractional distribution (see last year's report), the dominant chemical property with a wide-ranging effect was CCE. This property directly controls the solubility and/or release of the elements of interest, be it from the CCP or the amended mine spoil. The limited CCE of CCP# 11 and 28 is reflected in the limited liming effect and lower pH of the pour-through leachate solution. Data from the soybean trial are still under evaluation and will be reported in full next year in the final project report.

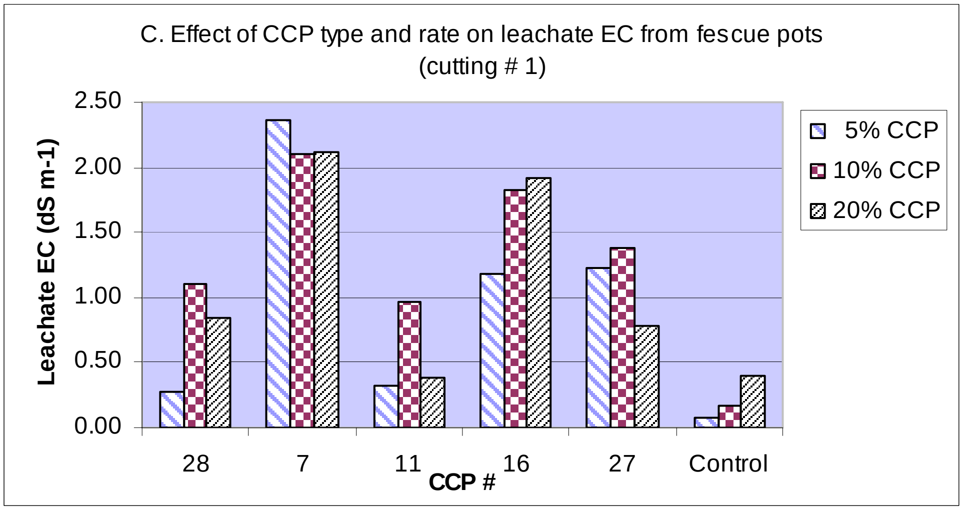
Figures 1a-c. Tall fescue dry matter yield and corresponding pH and EC from pot leachates in response to differing CCP's and application rate. Note: in the control treatments, no CCP was added , but the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), the 20% to high lime (9 Mg/ha).



A. Effect of CCP type and rate on fescue yield (cutting # 1)



B. Effect of CCP type and rate on leachate pH from fescue pots (cutting # 1)



C. Effect of CCP type and rate on leachate EC from fescue pots (cutting # 1)

Table 3. Selected Mehlich-1 extractable chemical properties of mine spoil and CCP amended mine spoil at the onset of the bioassay greenhouse trial.

Substrate	2 : 1	mg kg^{-1}						
% of CCP	pH	Zn	Mn	B	Cu	Fe	P	Mg
Mine spoil	4.75	0.6	7.6	0.9	0.1	12.0	2	32
#7 – 5%	6.72	0.9	126	9	0.1	94	9	307
#7 – 10%	7.07	0.9	97.4	12	0.1	69	4	422
#7 – 20%	7.73	0.8	46.1	19	0.1	21	2	619
#11 – 5%	5.34	0.8	64.6	12	0.1	76	19	85
#11 – 10%	4.90	0.7	23.4	16	0.1	82	24	50
#11 – 20%	4.94	1.7	14.6	40	0.4	177	54	82
#16 – 5%	9.93	1.4	8.4	18	1.9	11	2	424
#16 – 10%	10.72	1.5	6.8	22	1.4	5	2	472
#16 – 20%	11.39	0.1	2.4	26	0.1	1	2	378
#27 – 5%	10.08	2.4	6.6	22	1.8	5	2	429
#27 – 10%	10.42	2.8	6.0	24	1.9	4	2	455
#27 – 20%	10.84	2.0	5.8	33	0.1	1	2	431
#28 – 5%	5.08	0.8	9.1	2	0.2	36	7	41
#28 – 10%	5.59	1.4	12.6	4	0.2	96	19	68
#28 – 20%	6.24	2.2	17	10	1.6	176	32	136

Tables 4 a&b report the yield and chemical properties of the pour-through solutions for the three fescue grass harvests. Concentrations for As, Cr, and Se were very low or below detection, and even the detectable Mo levels were below levels of concern. As expected, boron (B) along with sulfur (as SO_4;data not shown) were the two elements at highest concentration in the leachates. However, correlation and stepwise regression analysis of the yield data with the elemental concentrations from the pour-through solutions shows that these two elements did not negatively affect fescue yield. The stepwise regression analysis did show that fescue yield was affected by pH ($p > 0.0034$), Se ($p > 0.0025$) and As ($p > 0.011$). However, the overall r^2 of the statistical model was relatively weak at 0.38. The effect of As on yield may also be more of a statistical anomaly because concentrations for most As observation were at or below detection limit.

The leachate data from the control samples (Tables 4 a&b) document that the mine spoil was an inert substrate with respect the release/leaching of the elements of interest. The rise in pH of the no-lime control samples (likely due to the irrigation water and fertilizer solution) indicates its low buffering capacity. The general mineralogical composition of this acidic sandstone mine spoil indicates there will be little release of any element of concern even with drastic pH changes due to the amendment with CCP’s. Any release of elements of concern would come from the amending CCP’s.

Table 4 a. Fescue clipping yields (g pot^{-1}) and pour-through leachate pH, EC (dS m^{-1}), and As (µg ml^{-1}) from acidic mine spoil amended with Various CCP's at 0, 5, 10, or 20% (v:v) and seeded to tall fescue. Observations from 3 pour-through events and associated harvest of grass clippings.

		Fescue Yield (g/pot)			**-------------- pH --------------**			**-------------- EC --------------**			**-------------- As --------------**		
CCP#	CCP rate	1	2	3	1	2	3	1	2	3	1	2	3
28	5%	0.49	0.76	1.24	5.12	5.16	5.84	0.27	0.34	0.33	<0.024	<0.024	<0.024
28	10%	0.60	1.04	1.46	5.56	6.04	6.58	1.11	0.71	0.38	0.026	<0.024	<0.024
28	20%	0.63	0.93	1.44	6.81	7.11	7.77	0.84	0.78	0.55	<0.024	<0.024	<0.024
7	5%	0.72	1.23	1.53	7.42	7.42	7.61	2.36	2.44	2.44	<0.024	<0.024	0.031
7	10%	0.78	1.23	1.50	7.76	7.96	8.05	2.10	2.54	2.61	<0.024	<0.024	0.060
7	20%	0.70	1.06	1.26	7.90	7.96	8.14	2.11	2.49	2.71	<0.024	<0.024	<0.024
11	5%	0.53	0.87	1.03	5.14	6.43	6.23	0.33	0.19	0.25	0.026	<0.024	<0.024
11	10%	0.57	0.94	1.06	4.89	5.80	6.35	0.97	0.56	0.30	0.037	<0.024	<0.024
11	20%	0.61	0.78	1.07	6.08	6.53	7.05	0.39	0.72	0.40	<0.024	<0.024	<0.024
16	5%	0.61	1.29	1.52	8.54	8.33	8.79	1.18	1.85	1.09	<0.024	<0.024	<0.024
16	10%	0.69	1.41	1.45	8.85	8.35	8.58	1.83	2.34	2.26	<0.024	<0.024	0.047
16	20%	0.59	0.87	1.06	9.49	8.73	8.59	1.92	1.18	0.85	<0.024	<0.024	<0.024
27	5%	0.85	1.39	1.42	8.37	8.30	8.58	1.22	0.94	0.69	<0.024	<0.024	<0.024
27	10%	0.72	1.44	1.56	8.64	8.24	8.43	1.38	1.93	0.98	<0.024	<0.024	<0.024
27	20%	0.64	1.20	1.28	9.27	8.40	8.42	0.78	1.48	1.15	<0.024	<0.024	<0.024
control-	0	0.75	0.99	0.97	6.78	6.45	5.61	0.08	0.09	0.12	<0.024	<0.024	<0.024
control+	0	0.65	1.25	1.54	6.49	6.39	6.13	0.16	0.16	0.11	<0.024	<0.024	<0.024
control++	0	0.61	1.01	1.16	7.10	7.57	7.84	0.40	0.31	0.23	<0.024	<0.024	<0.024

Note: Whenever a concentration for a specific element occurs with a < symbol, this represents the detection limit of the analytical instrument.

Table 4 b. Pour-through leachate concentrations (mg L^{-1}) of selected elements from acidic mine spoil amended with various CCP's at 0, 5, 10, or 20% (v:v) and seeded to tall fescue. Observations from 3 pour-through events and associated harvest of grass clippings (Table 4a).

		------------- Cr -------------			**------------- Mo ------------**			**-------------- B --------------**			**-------------- Se --------------**		
CCP#	CCP rate	1	2	3	1	2	3	1	2	3	1	2	3
28	5%	<0.004	<0.004	0.003	<0.008	<0.010	<0.018	0.551	0.523	0.260	0.026	<0.024	<0.024
28	10%	<0.004	<0.004	0.007	0.009	0.015	0.044	4.011	1.382	0.588	0.060	<0.024	<0.024
28	20%	0.006	<0.004	0.003	0.235	0.431	0.337	1.744	1.860	0.475	0.035	<0.024	<0.024
7	5%	<0.004	<0.004	<0.002	0.009	0.013	<0.018	5.318	4.051	1.327	0.048	<0.024	<0.024
7	10%	<0.004	<0.004	<0.002	0.022	0.049	0.048	3.743	6.251	2.355	0.042	<0.024	<0.024
7	20%	<0.004	<0.004	<0.002	0.049	0.071	0.071	5.356	8.056	4.220	0.035	<0.024	<0.024
11	5%	<0.004	<0.004	<0.002	<0.008	<0.010	<0.018	3.752	1.039	0.850	0.026	<0.024	<0.024
11	10%	0.005	<0.004	<0.002	<0.008	<0.010	<0.018	20.091	3.078	1.584	0.026	0.030	<0.024
11	20%	0.004	<0.004	<0.002	<0.008	0.024	0.056	3.274	5.169	2.674	0.032	<0.024	<0.024
16	5%	0.115	0.079	0.025	0.132	0.172	0.147	3.977	13.655	11.344	0.035	<0.024	<0.024
16	10%	0.346	0.127	0.086	0.411	0.220	0.154	4.523	10.679	12.364	0.138	0.077	0.046
16	20%	0.287	0.166	0.067	0.391	0.158	0.090	5.598	5.942	4.782	0.096	<0.024	<0.024
27	5%	0.145	0.029	0.010	0.176	0.244	0.091	9.719	10.752	4.637	0.026	<0.024	<0.024
27	10%	0.416	0.178	0.036	0.371	0.342	0.165	6.073	13.590	11.051	0.072	<0.024	<0.024
27	20%	0.259	0.365	0.124	0.302	0.427	0.202	3.644	9.016	7.888	0.050	<0.024	<0.024
control-	0	<0.004	<0.004	0.002	<0.008	<0.010	<0.018	0.030	0.037	0.057	<0.024	<0.024	<0.024
control+	0	<0.004	<0.004	0.011	<0.008	<0.010	<0.018	0.024	0.031	0.029	0.026	<0.024	<0.024
control++	0	<0.004	<0.004	0.012	<0.008	<0.010	<0.018	0.029	0.040	0.058	0.026	<0.024	<0.024

Note: Whenever a concentration for a specific element occurs with a < symbol, this represents the detection limit of the analytical instrument.

Column Leaching Experiment with Acid Forming Refuse

Changes in leachate pH, EC and elemental concentrations over the 60-day column study period are presented in Figs. 2a through 2j for selected treatment combinations. Leachate concentrations were, depending on the elements and the treatment combination, at times below detection limits. The elemental release patterns are presented in graphical format for specific treatment combinations which are of particular interest or demonstrate important temporal patterns. Figure 2a and Table 2 document the strong differences between CCP's in CCE and their relative effectiveness to counteract the acidification of the coal refuse over time. The pH of the no-lime coal refuse column dropped to below 3.0 within 11 days. Liming of the refuse to the estimated potential acidity kept the pH of the limed control columns in the 7.2 to 7.9 range.

The oxidation of sulfidic material and its associated formation of acid drainage result in more rapid dissolution reactions and significant increases in solution EC. The importance of controlling acid/base balance conditions in reactive refuse is reinforced by the effects of acidification on retention/release of specific elements. Acid formation and associated mineral phase dissolution generate very high leachate levels of S and Fe (data not shown), but perhaps of greater concern are the significant releases of As, Cr, Cu, and Zn. However, liming with agricultural lime (e.g. as in limed-control columns) or adding CCP's with adequate CCE largely prevented the release of these elements of concern due to acidification.

For differential treatment analysis, we compared the release patterns of elements from the control columns (both limed and no-lime) to those of the CCP amended columns. This allowed us to attribute the elements in the leachate to source, either the coal refuse or a specific CCP. Via this analysis, we conclude that weathering coal refuse was the primary source for As, Cu, Fe, Ni, S, and Se released to leachates. The CCP's were the primary source for B, Cr, and Mo. Following is a summary interpretation of the behavior of each of the major elements of concern:

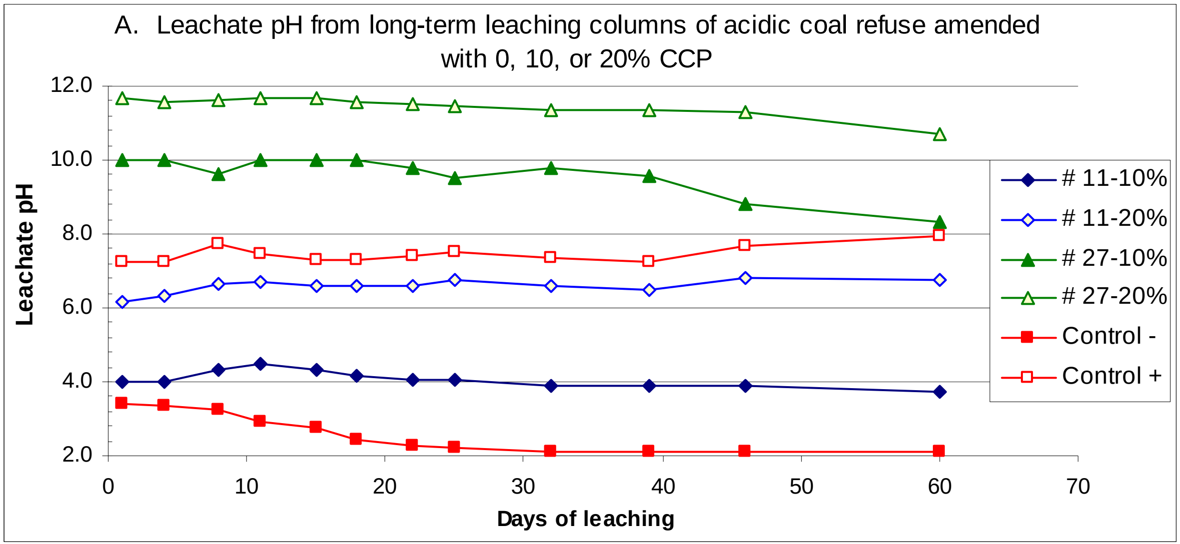
CCP Effects

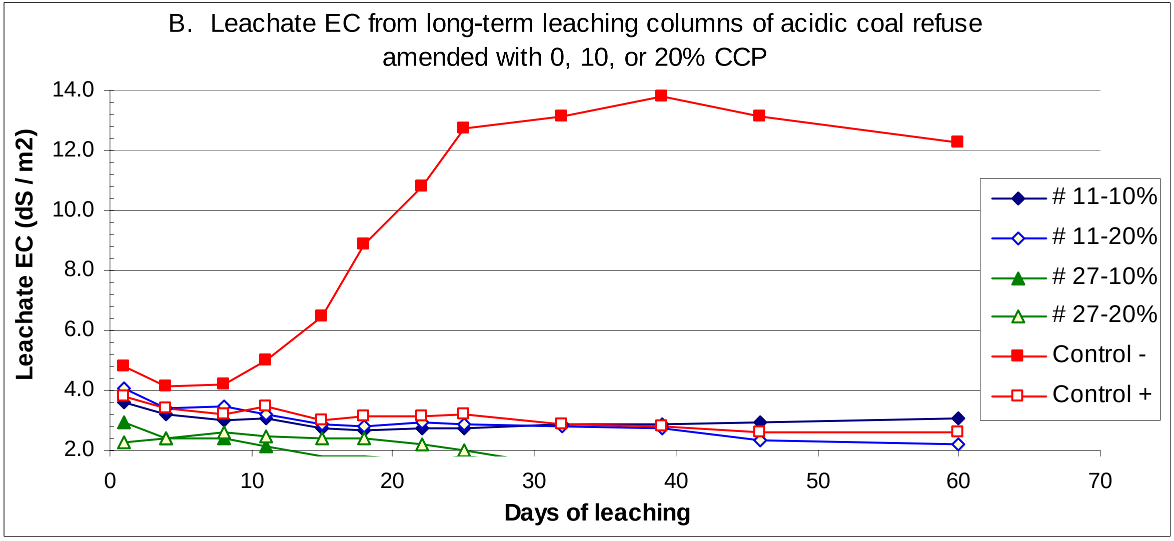
B: Boron contents varied greatly among CCP's, ranging from < 1 mg/L to 135 mg/L in the first leachates. Boron readily leached and was only minimally affected by pH (see comparison of release patterns of CCP # 11 and 18).

Cr: While the refuse does release a minor amount of Cr, it does so only after the pH drops to < 3.0. The overall Cr release from CCP's does not appear to be affected by pH. Despite having similar high total Cr contents, the release was near or below detection limit (0.004 mg/L) after 20 days of leaching despite very different pH environments (see CCP# 11, 18, and 27).

Mo: CCP # 11, 16 and 27 did show some steady, but declining Mo with time. Low pH conditions reduced the Mo release for CCP # 11 (see ash rate 10% vs. 20%).

Figure 2 a-c. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCP.


A. Leachate pH from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP


B. Leachate EC from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

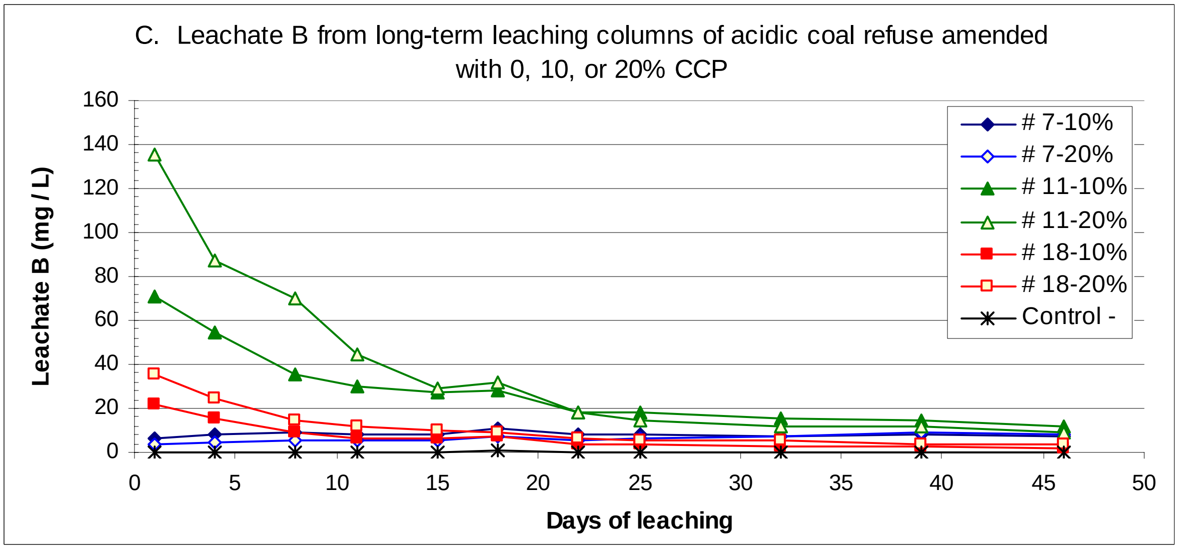
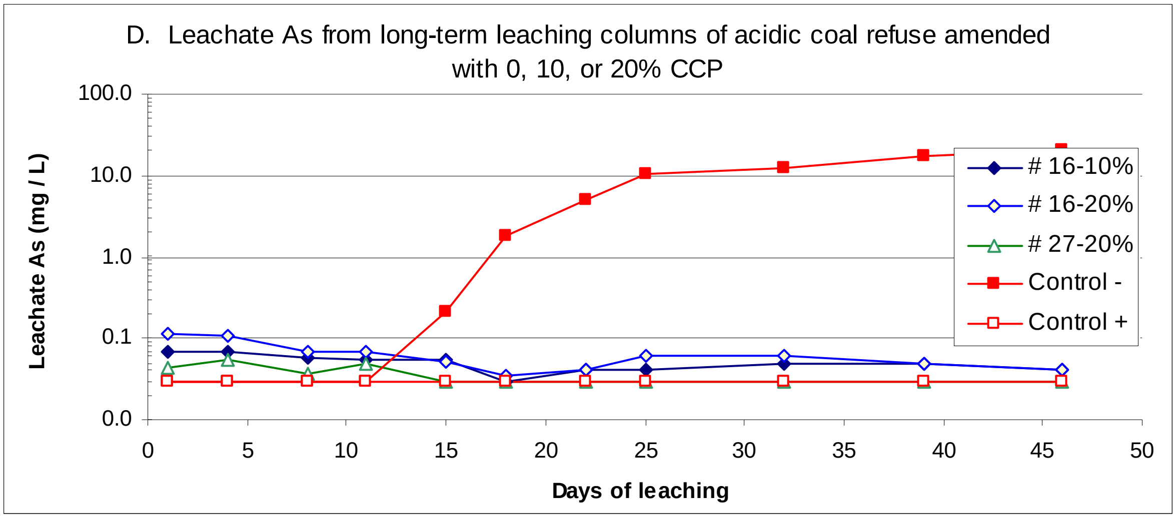
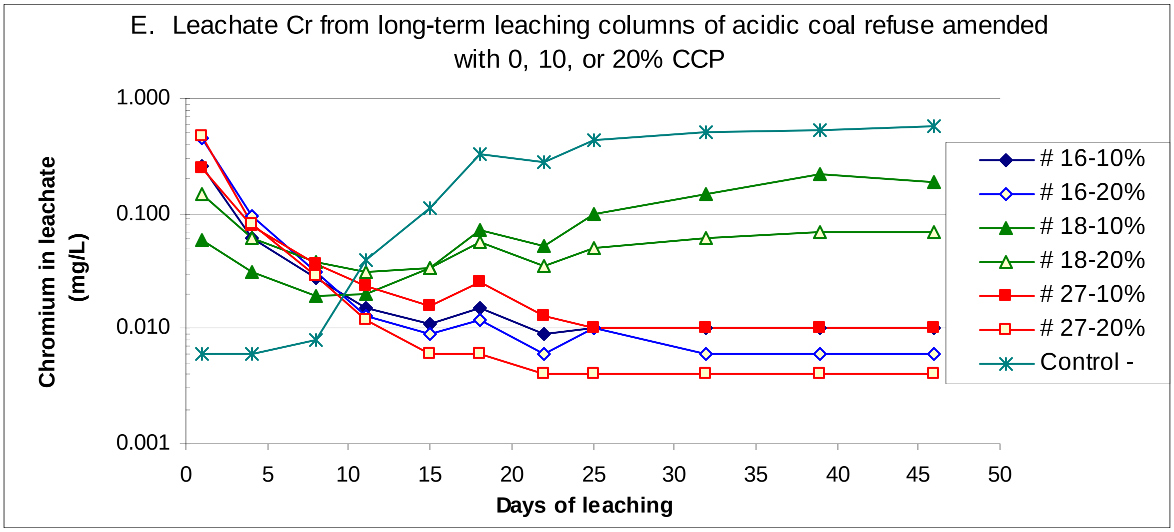

C. Leachate B from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

Figure 2 d-f. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCP.


D. Leachate As from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP


E. Leachate Cr from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

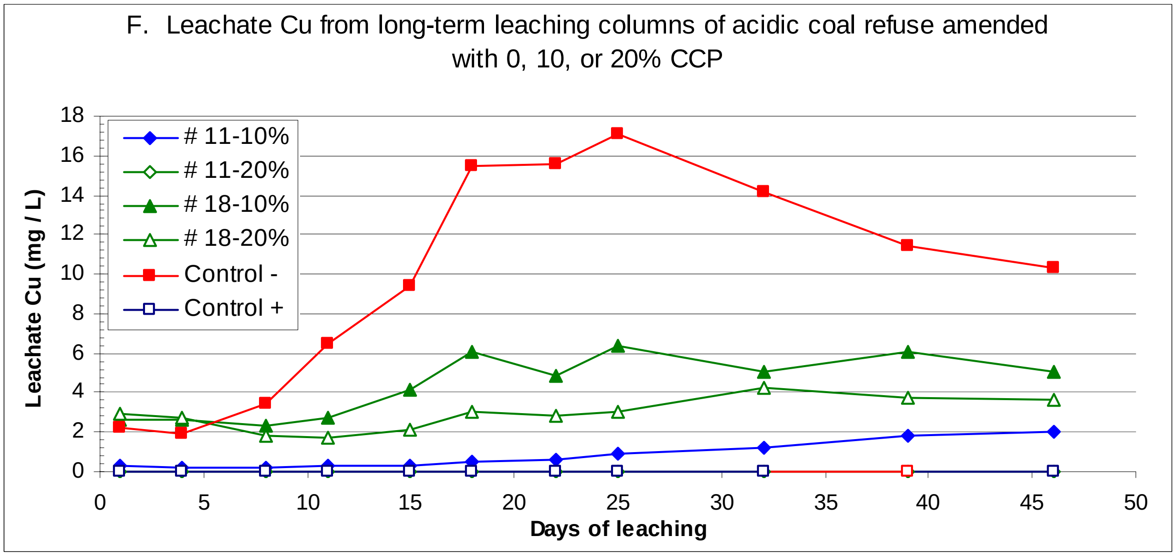
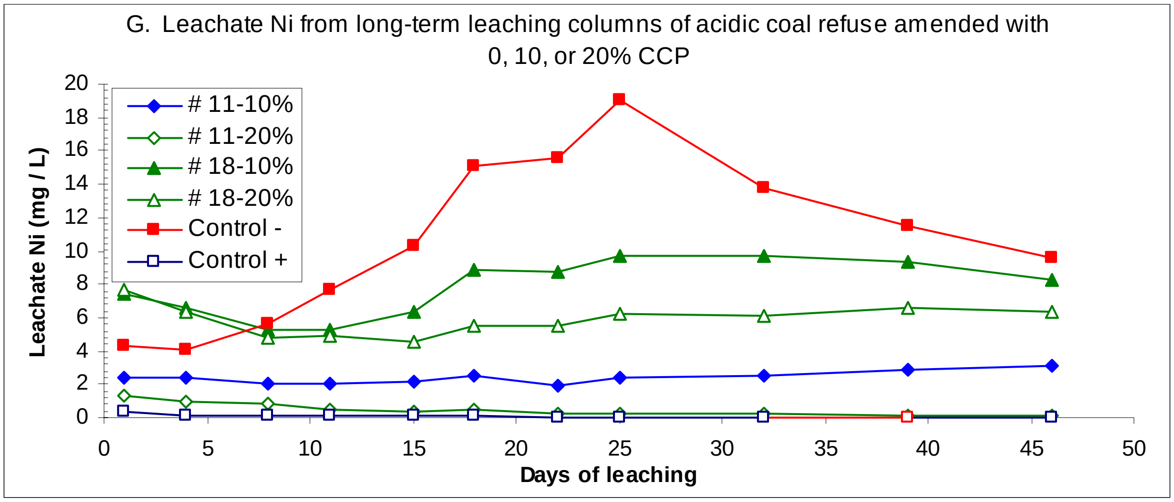
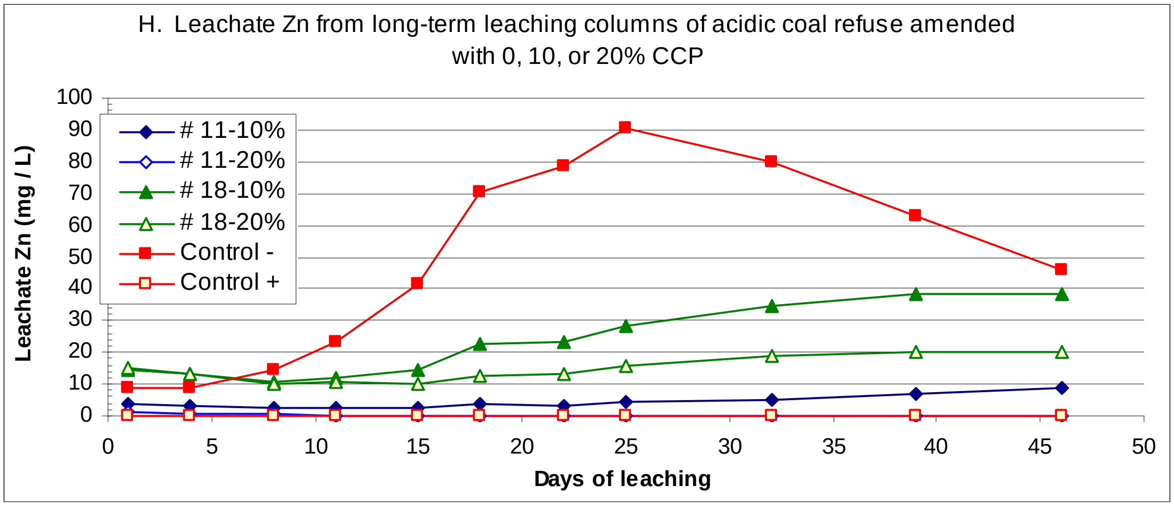

F. Leachate Cu from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

Figure 2 g-i. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCP


G. Leachate Ni from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP


H. Leachate Zn from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

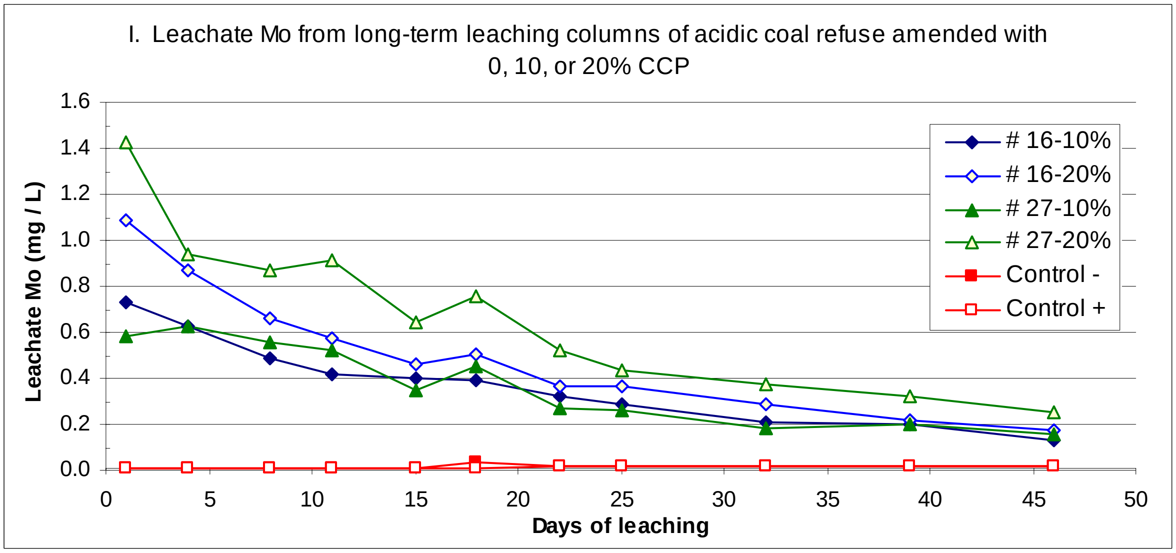
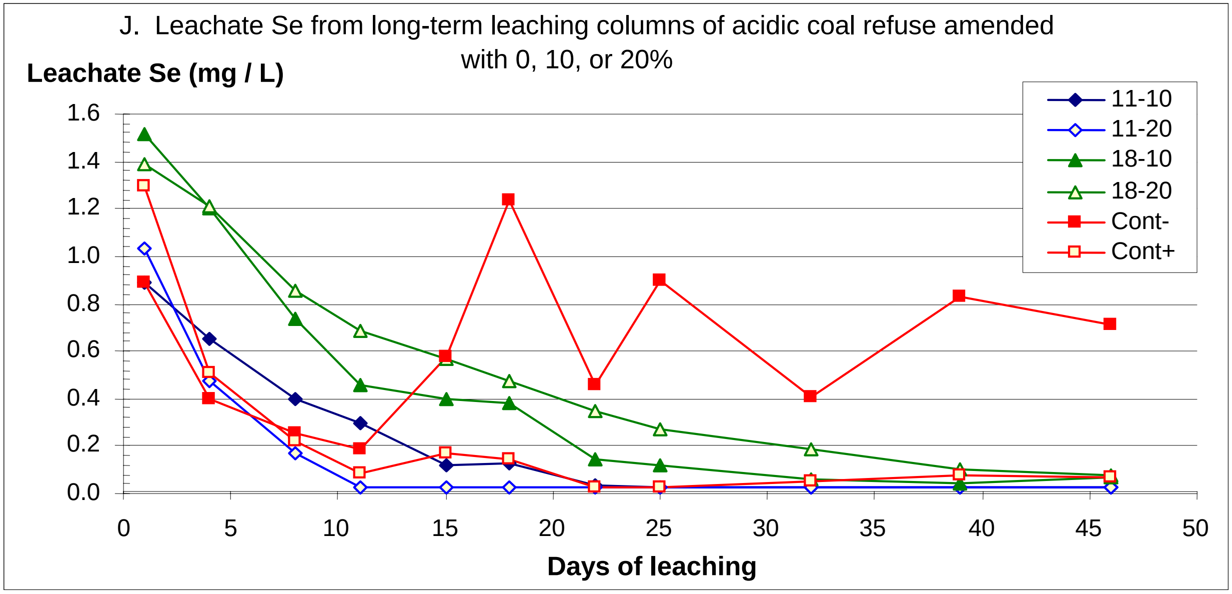

I. Leachate Mo from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

Figure 2 j. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCP



Coal Refuse Effects:

As: CCP # 11 had a high As content, yet no As release was noted at the 10 or 20% amendment rate with respective pH dropping to 3.9 (10% treatment) and 6.8 (20% treatment). After the pH of the no-lime control dropped to <2.9, As release went from below detection limit (0.03 mg/L) to > 20 mg/kg at a pH of 2.1.

Se: Selenium release tapers off quickly at high pH. Low pH over time sustains Se release at < 1 mg/L.

Cu, Ni, Zn: The release of these elements are strongly governed by the pH system. The lower the pH, the higher the release (see particularly CCP # 11, 10% vs. 20%, and refuse control, limed vs. no-lime.

Overall, the pH of the leaching environment is most critical to the retention/release of the elements of interest. Secondly, it is important to point out that a number of these elements (e.g. As and Zn) appear to be leaching from both the fly ash and refuse, and elution by source is also controlled by pH. The liming potential of CCP's differ greatly, with a range in CCE of 0 to 52%. The potential peroxide acidity (PPA) test indicated a required liming rate for this coal refuse of 34.5 Mg/1000 Mg (tons/acre). Applying lime to the coal refuse at this rate has maintained the pH of the limed coal refuse control columns in the range of 7.2 to 7.9, further supporting the accuracy and utility of this lime estimation technique. Coal combustion products with adequate CCE were quite effective in neutralizing the acidity produced by oxidizing coal refuse over the 60 day study period. Using CCP's as liming agents contributed additional leaching of Mo and B. The Cr introduced into the system by the CCP is leached only if the pH level drops to < 3.0. Amending coal refuse with CCP's with adequate CCE was very effective in preventing high solute concentrations and leaching losses of As, Cu, Ni, Zn and Cr.

Overall Summary and Conclusions to Date

The results of our combined studies to date reveal several important overall considerations for safely managing CCP's in mining environments. Overall, it's clear that many present-day CCP's have substantial liming ability; much more than seen in our studies in the early and mid-1990's. The greenhouse trials reported here reveal that CCP's can be quite effective as topical mine soil amendments, but loading rates must be constrained to avoid over-liming or application of excess bulk salts, both of which limit plant growth of even tolerant species like tall fescue. While we are still conducting more detailed analyses of the column leaching data, we are encouraged by our ability to run these trials at a smaller scale in a laboratory setting over a much shorter period of time than in previous studies. We are also encouraged by the obvious bulk liming capacity of a number of the CCP's utilized, and by the relative lack of leaching of elements of environmental concern when the CCP's were utilized at relatively high loading rates.

Over the coming year, we will complete all remaining laboratory and analytical report and combine all findings into combined recommendations for CCP utilization on mined lands.

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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