Final Report

Development of Rapid Assessment Protocols for Beneficial Use of Post-2000 Coal Combustion Products in Virginia Coal Mines

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Introduction and Overall Objectives

This document reports and summarizes the results of our study on the development and testing of rapid assessment protocols for beneficial use of coal combustion products (CCPs) on Virginia coal mines. Our previous work on CCP's in the 1990'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. Currently, the public and the environmental regulatory community are placing much greater focus on the potential for As, B, Mo and Se mobility from CCP utilization on/in active coal mines, along with a strong emphasis on defining Hg levels and mobility in coal combustion products in general. As an example, the USEPA recently reaffirmed its 1993 position that exempted CCPs from regulation as RCRA subtitle C (toxic) wastes, but specifically reserved judgment on the use of CCP's in coal mining environments. In April of 2006, in response to citizen and regulatory concerns over the water quality issues, the National Academy of Sciences released its detailed report (NRC, 2006) on potential mine site impacts of CCP utilization. While the report did offer overall support for the beneficial utilization of CCP's in mining environments, it specifically cautioned potential permittees to: (1) Carefully characterize the geochemical properties of both the CCP to be utilized and the mine site; (2) understand and predict long-term reactions and contaminant release patterns; and (3) fully characterize potential site hydrologic impacts. Thus, the prediction of the relative mobility of As, B, Se, Mo, and other potentially water-soluble trace ions is the current focus of our continuing cooperative research program.

As part of our earlier cooperative efforts with the Powell River Project, the Virginia Division of Mined Land Reclamation (VDMLR), and the Virginia Department of Environmental Quality (DEQ) in the 1990's (see Daniels et al., 2002), we began the development of a routine and inexpensive greenhouse bioassay approach to screening the plant growth effects of various land applied residuals. The protocol uses soybeans and tall fescue grown in a mine spoil/soil substrate which is amended with various rates of the CCP proposed for beneficial use. We also developed a relatively simple leaching column approach for evaluating leaching parameters from CCP's blended with coal waste (Stewart et al., 1997; 2001) using relatively large (15 to 25 cm diam.) columns. Both of these techniques showed promise, but we needed to test them across a range of potential CCP's for "fine-tuning" and to develop appropriate response/loading rate guidance functions. We also believed that it would be possible to combine a "pour through" leaching test with the greenhouse bioassay screen that would allow us to simultaneously assess a given CCP for both plant growth effects and "leachable constituents of concern". Therefore, the overall objectives of this study were:

1. To predict the relative bioavailability/leaching risk of As, Se, Hg and B in common SW Virginia coal mining/CCP utilization environments.

2. To develop and refine a simple combined laboratory and greenhouse screening technique that will predict the beneficial use potential of CCPs when used as (a) topical mine soil amendments, (b) geochemically stable backfill materials, and (c) bulk-blended treatments for acidic coal waste materials.

General Research Approach and Specific Tasks

We worked with our industry cooperators and collected 28 representative composite samples of their current CCP streams (Table 1) from regional utilities burning Virginia coals. The 28 primary composite samples were subjected to a suite of chemical analyses and characterization. Based on these results, six CCPs were selected for the greenhouse bioassay study on the plant growth effects of land-application of the various CCPs to mined lands. Acid mine spoil was amended at different loading rates with the CCP's. Concurrently, a laboratory column leaching study was initiated to assess the effect of differing CCP properties and loading rates on leachate quality from acidic coal refuse.

Coal Combustion Products, Mine spoil, and Coal Refuse Analyses

Materials and Methods

- All analyses were conducted in triplicate with the exception of the Toxicity Characteristic Leachate Procedure (TCLP) which is conducted on a large (50g) bulk sample as indicated by USEPA.
- pH and Electrical Conductance (EC) (Rhoades, 1982) were determined in saturated paste extracts from the CCPs. The CCP was mixed with distilled DI water until it formed a glistening paste. The paste was filtered after equilibration and analyzed for pH and EC.
- Hot $CaCl_2$ extractable boron (Bingham, 1982) was determined by boiling 20ml 0.01M $CaCl_2$ with 10g ash for 10 minutes. The filtrate was analyzed by ICP for B.
- Total elemental analysis (U.S. EPA, 1992a) was determined by microwave digestion of 0.5g ash with 3ml conc. HCl and 9ml conc. HNO_3. The extract was brought up to 50ml volume with distilled DI water and analyzed by ICP.
- The sequential fractionation procedure (SEP) by Tessier, et al., (1979) sequentially extracts readily available forms of elements down to more recalcitrant forms of the elements. We modified the method for use on fly ash, high S material by substituting $MgSO_4$ with $MgCl_2$ in the first extraction step. We also omitted the extraction step for elements associated with organic matter. This speciation/partitioning of major and minor elements of environmental concern, including As, Se, Cr, Mo, B, and Hg, uses a series of extractants to dissolve metals associated with particular phases in a complex sample. The sample size used for extraction was 5.0 g at a solution:solid ratio of 5:1. The procedure involves sequential extraction with 1M $MgCl_2$ for soluble/exchangeable metals, followed by extraction with 1M acetic acid/Sodium acetate for carbonates, followed by extraction with 0.2M ammonium oxalate (pH 3) shaken in the dark for 2 hours for amorphous Fe/Mn compounds, followed by 0.04 M hydroxylamine hydrochloride/acetic acid for Fe/Mn crystalline bound forms, and finally, concentrated HCl and HNO_3 for residual bound metals.
- We also used the TCLP test for priority elements (U.S. EPA, 1992b).
- Mehlich-1 extraction (0.05*M* HCl + 0.025*M* H_2SO_4) was utilized for extractable P, Ca, B, and Fe (Mehlich, 1953) followed by ICP emission spectrometry (ICPES, type FTMOA85D, Spectro Analytical Instruments, Inc).

Table 1. Selected chemical properties and TCLP extractable As, Cr, Mo, and Se for 28 different coal combustion by-products

Lab #	Type of CCP	pH Sat. Paste	EC dS m^{-1}	CCE %	Extr. B mg kg^{-1}	Total B mg kg^{-1}	Extr. B as % of total B	TCLP As mg L^{-1}	TCLP Cr mg L^{-1}	TCLP Mo mg L^{-1}	TCLP Se mg L^{-1}
1	Fly ash	5.27	3.19	3.0	9.3	27	34	0.07	0.08	0.18	0.21
2	Fly ash	8.89	2.91	21.5	192.7	781	25	<0.0153	0.01	0.30	0.36
3	Fly ash	9.42	4.01	7.1	29.2	116	25	<0.0153	0.39	0.19	0.11
4	Fly ash	9.30	3.39	3.2	22.5	54	42	0.02	0.31	0.35	0.17
5	Ash	10.69	4.11	13.2	118.6	1022	12	0.04	0.17	0.19	0.10
6	Fly ash	5.83	4.41	3.2	28.6	61	47	0.04	0.42	0.40	0.23
7	FGD	9.14	5.25	41.0	29.2	282	10	0.21	0.30	0.09	0.11
8	Fly ash	12.35	12.12	2.0	46.0	204	23	0.03	0.09	0.09	<0.0118
9	Fly ash	12.26	8.08	51.3	31.0	779	4	<0.0153	0.05	0.07	0.13
10	FGD	8.17	19.72	0	3.4	53	6	<0.0153	<0.0062	0.11	0.02
11	Fly ash	8.85	3.25	0.3	123.4	383	32	0.12	0.03	0.11	0.04
12	FGD	9.26	3.84	52.0	33.7	271	12	0.20	0.15	0.11	0.07
13	Fly ash	9.90	4.56	39.8	39.0	616	6	<0.0153	0.28	0.04	0.10
14	Bottom ash	8.80	1.61	2.5	11.3	47	24	<0.0153	0.05	0.04	0.09
15	Screened ash	8.19	0.66	0.2	2.0	14	15	<0.0153	0.01	0.01	0.02
16	Fly ash	12.58	14.87	46.3	14.1	686	2	0.05	0.01	0.08	0.24
17	Fly ash	12.11	5.12	28.3	24.2	677	4	<0.0153	0.32	0.03	0.11
18	Fly ash	3.57	11.79	0	91.6	220	42	0.38	0.68	0.12	0.32
19	Fly ash	7.18	11.86	1.0	43.7	55	79	0.22	0.02	0.09	0.36
20	Fly ash	8.45	1.26	1.5	3.7	3*	na	0.35	0.01	0.02	0.25
21	Fly ash	9.32	26.85	22.5	16.6	183	9	0.02	<0.0062	0.16	0.14
22	Fly ash	9.36	3.67	1.3	23.3	70	33	0.05	0.01	0.12	0.19
23	Fly ash	8.90	8.01	2.5	14.2	50	28	0.11	0.01	0.12	0.37
24	Fly ash	7.50	2.92	1.8	13.3	8*	na	0.04	0.02	0.07	0.02
25	Fly ash	12.15	11.24	29.8	0.3	22	1	<0.0153	0.05	0.12	0.10
26	Fly ash	10.89	15.63	16.3	2.0	104	2	0.08	0.03	0.12	0.47
27	Fly ash	11.93	4.54	47.7	17.4	701	2	<0.0153	0.26	0.06	0.11
28	Fly ash	11.54	3.15	7.7	3.6	82	4	0.51	0.16	0.23	0.13
					EPA CFR 261 Reg. TCLP Limits:			5.0	5.0	None	1.0

*The total B for these samples appear incorrect as Mehlich-1 extractable and hot $CaCl_2$ extractable B are substantially higher than values obtained for total B content of the CCP. na = not applicable. Values reported as < were below detection limits.

We completed the analyses of the primary composite samples of 28 CCPs as outlined above. The overall results are discussed below along with our rationale for selection of six CCPs that we felt best represented the overall analyzed sample set. These six materials were then subjected to greenhouse plant growth bioassay trial and the laboratory column leaching procedure.

Preliminary CCP Characterization

The data reported in Table 1 demonstrate that we successfully obtained a set of CCPs with wide range of important chemical properties. While the range in pH was 3.57 to 12.35, only 3 CCPs had a pH below 7. The salt content of the CCPs also varied greatly with a range of 0.66 to 26.85 dS m^{-1}, however, the distribution was more uniform across the range than for pH. The liming capacity of the CCPs, ranged from 0 to 52% CCE, and tended to be either low (<10%) or high (>30%), with only 6 CCPs in the 10 to 30% range. Of the 28 CCPs tested, 14 had CCE of <5%. This may be a critical limitation where CCPs are to be used in co-disposal/amendment scenarios with acidic coal refuse or mine spoil. Material #10 (FGD) stands out from the others due to its very low concentrations of most constituents of concern.

The results of the TCLP analysis are also presented in Table 1. Mercury was below detection limits in the TCLP test and was also below detection in all but the residual fraction of the SEP (data not shown), and is therefore omitted from further discussion. However, a major limitation to most lab tests (like TCLP) designed to simulate element release (leaching) is that these tests do not provide information on actual release under a wide range of expected disposal or land application geochemical environments (NRC, 2006). In the case of highly alkaline fly ash or non-acidic coal refuse, for example, the TCLP procedure tests these materials in a moderately acidic (glacial acetic acid) environment. This extraction environment may be drastically different from the conditions governing leachability under actual co-disposal conditions, and we have previously reported (Stewart et al., 2001) significant metal leaching from fly ash materials that easily "passed" the TCLP.

Table 2 presents the total elemental concentrations of As, Se, Cr, and Mo obtained by total digestion of CCP subsamples, and also as the sum of the fractions from the sequential extraction procedure (SEP). The complete results of the SEP for these elements are presented graphically in Appendix 1, Figures A a-g. Our efforts were focused particularly on As, Se, Cr, and Mo as these elements were found to have interesting leaching patterns and potential water quality impacts. Table 3 presents the correlation analysis for the fractional distribution of As, Cr, Mo, and Se with other bulk CCP chemical properties (Table 1 and Appendix A). The data show marked differences among the fractions with strong ash-specific variability. As expected, the release/solubility of the elements tested was generally pH dependent. We found that pH was reasonably well correlated with CCE (r^2 = 0.56), but the fractional distributions of As, Cr, Mo, and Se appear to be more strongly linked to CCE than to pH.

The correlation analysis indicated that CCE was the one chemical property, of all those examined, that was most strongly related to As level and distribution among the various SEP fractions. CCE was negatively correlated to As levels in the first four SEP fractions (r^2 = -0.38 to

-0.53), but positively correlated to the residual fraction (r^2 = 0.78). For CCPs with low total As (< 20 mg kg^{-1}), As resided up to 90% in the residual fraction. For CCPs with high total As (> 100 mg kg^{-1}), however, the As was up to 90% allocated among the labile and moderately labile fractions.

Table 2. Total elemental concentrations of As, Se, Cr, and Mo by single digestion or as the sum of the fractions of the SEP.

CCP		Total Elemental by Microwave Digestion (mg/kg)				Total Elemental by Sum of Fractions (mg/kg)			
Lab #	Type of CCP	As	Se	Cr	Mo	As	Se	Cr	Mo
1	Fly ash	57.4	15.7	72.9	46.0	59.4	12.0	53.6	10.7
2	Fly ash	24.4	30.2	48.1	7.3	21.7	17.1	37.5	6.3
3	Fly ash	25.0	13.8	85.1	43.4	25.3	15.5	68.9	11.2
4	Fly ash	28.55	10.2	79.2	69.6	32.0	9.7	64.4	11.5
5	Ash	17.0	11.0	63.2	56.1	19.9	10.3	50.5	9.2
6	Fly ash	42.1	16.0	101.8	72.0	42.5	14.1	83.0	15.4
7	FGD	24.2	4.1	44.8	10.4	24.1	6.8	32.6	2.4
8	Fly ash	34.9	4.7	81.2	22.0	46.8	10.7	48.1	5.0
9	Fly ash	22.7	18.5	57.1	7.5	15.6	16.6	44.8	3.0
10	FGD	0.8	1.2	0.8	11.4	1.1	1.2	0.7	< 1.0
11	Fly ash	119.1	10.1	86.6	33.3	118.7	15.4	59.1	16.0
12	FGD	27.0	4.4	24.7	3.7	22.6	5.6	18.1	3.1
13	Fly ash	8.7	7.9	52.5	23.8	8.1	9.6	41.7	2.1
14	Bottom ash	45.7	10.0	70.7	3.3	43.2	10.1	55.0	2.4
15	Screened ash	5.0	1.2	20.6	52.8	6.9	5.3	15.4	1.0
16	Fly ash	12.4	9.1	63.8	32.0	12.1	12.1	46.6	3.3
17	Fly ash	8.7	11.0	61.3	15.2	11.4	11.3	51.4	3.7
18	Fly ash	184.3	82.7	153.3	32.2	120.4	48.2	95.9	18.8
19	Fly ash	69.8	9.0	37.6	6.4	64.1	12.4	47.2	7.5
20	Fly ash	59.3	3.6	41.5	0.8	35.3	7.3	6.5	2.9
21	Fly ash	20.7	23.7	28.8	4.1	11.8	17.0	30.8	3.6
22	Fly ash	160.7	3.6	57.1	15.3	153.1	16.3	45.2	18.8
23	Fly ash	94.4	13.8	63.9	9.5	90.5	16.6	63.2	13.1
24	Fly ash	60.0	3.6	50.9	13.7	55.2	1.7	55.4	13.1
25	Fly ash	32.2	3.6	67.2	2.3	14.2	2.6	47.0	3.8
26	Fly ash	24.0	9.7	21.6	2.7	16.4	10.7	22.8	3.4
27	Fly ash	19.0	3.6	71.4	7.2	12.0	17.5	61.0	4.7
28	Fly ash	63.2	12.6	80.5	17.1	57.2	11.1	70.0	11.5
Mean of all CCPs		46.1	12.5	60.3	22.2	40.8	12.2	47.0	7.1

Table 3. Results of correlation analysis for fractional distribution of As, Cr, Mo, and Se with selected chemical properties and other elements of CCPs.

Element	CCE	pH	EC	B**	Al	Fe	Mn	Zn
				Fraction 1				
As	-.38*	Ns	Ns	.28	Ns	Ns	Ns	Ns
	.003			.03				
Cr	.30	.30	Ns	Ns	.42	.53	.39	ns
	.02	.02			.0001	<.0001	.002	
Mo	-.47	Ns	-.26	.32	Ns	Ns	Ns	Ns
	<.0001		.02	.009				
Se	.44	.49	Ns	.37	Ns	.49	Ns	Ns
	.0002	<.0001		.003		<.0001		
				Fraction 2				
As	-.51	Ns	-.25	.33	Ns	Ns	.28	Ns
	0001		.03	.007			.01	
Cr	-.24	Ns	-.25	.32	.36	.53	.48	Ns
	.03		.03	.006	.0005	<.0001	<.0001	
Mo	-.24	-.34	Ns	.28	Ns	.33	Ns	Ns
	.05	.004		.02		.002		
Se	-.35	-.34	Ns	Ns	Ns	Ns	Ns	Ns
	.002	.003						
				Fraction 3				
As	-.53	-.42	Ns	Ns	Ns	.25	Ns	Ns
	<.0001	.0009				.03		
Cr	-.54	-.38	Ns	Ns	.47	.36	.31	.51
	<.0001	.001			<.0001	.0007	.004	<.0001
Mo	-.52	-.67	Ns	.30	Ns	Ns	Ns	Ns
	<.0001	<.0001		.02				
Se	-.41	-.59	.47	Ns	Ns	Ns	Ns	Ns
	.0007	<.0001	<.0001					
				Fraction 4				
As	-.38	-.51	Ns	Ns	.50	Ns	-.47	-.24
	.0008	<.0001			<.0001		<.0001	.02
Cr	-.43	-.50	-.25	.26	.86	.45	Ns	Ns
	.0001	<.0001	.02	.02	<.0001	<.0001		
Mo	-.47	-.65	Ns	Ns	.61	.29	-.22	Ns
	<.0001	<.0001			<.0001	.008	.04	
Se	.45	Ns	Ns	.39	Ns	.26	.65	.62
	.0005			.0004		.03	<.0001	<.0001
				Fraction 5				
As	.78	.28	Ns	Ns	.59	Ns	Ns	.56
	<.001	.02			<.0001			<.0001
Cr	Ns	Ns	Ns	Ns	.47	Ns	Ns	Ns
					.0001			
Mo	-.65	-.54	Ns	Ns	Ns	Ns	Ns	Ns
	<.0001	<.0001						
Se	Ns	Ns	.56	.36	Ns	.35	Ns	.73
			<.0001	.01		.01		<.0001

* Correlation coef. (r^2) followed by the p-value (sig. level)), ns = not significant at $p > 0.05$.
**B as hot $CaCl_2$ extractable B.

The fractional distribution for Chromium (Cr; Appendix A) was most consistent across all CCPs with 60 to 80% of the Cr being in the recalcitrant residual fraction. The distribution for As, Mo, and Se was much more variable the CCPs tested. Yet for all four of these elements, CCE was the one property most often and most strongly correlated with them in all fractions. The bulk soluble salt content (EC) of the CCPs appears to be only related to Se in fractions 3 (amorphous Fe+Mn) and 5 (residual). Table 4 presents results for the Mehlich-1 acid extractable elements for all CCPs. The data again show a broad distribution of properties across all CCPs, yet do not document any obviously high extractable metal levels that in themselves would cause a problem for plant growth.

Using the data sets discussed above, we categorized the 27 materials (excluding #10) into a somewhat modified 2 X 2 matrix of As levels (low and high) by CCE (levels low and high). Electrical conductivity (EC, an indirect measurement of the salt content) was a strong covariate. Low CCE ashes exist with high and low EC, and high CCE materials exist with high and low EC.

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

Five CCPs were initially selected from the larger sample set for a greenhouse bioassay study on the plant growth effects of land-application of CCPs to moderately acidic mine soils at typical soil amendment rates. Similarly, the same CCPs (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.

The main determinants for the selection of the five CCPs for the greenhouse bioassay trial were CCE, total As concentration, and As distribution among the 5 sequential extraction (SEP) fractions. We also chose materials that presented a wide range of soluble B concentrations. Hot $CaCl_2$ extractable B at levels >5 mg kg^{-1} are generally indicated as yield reducing to sensitive crops (Bingham, 1982), The extractable B levels reported for the 28 CCPs (Table 1) cover a range of 0 to 192 mg kg^{-1}. Thus, the bulk addition of 10 or 20% CCPs should, depending on which CCP used, result in conditions such that a sensitive plant like soybeans would be expected to show B toxicity symptoms and associated yield reduction. High B concentrations are often associated with high soluble salt levels (EC). There are marked differences in plant sensitivities to both B and salt levels with tall fescue being greatly more tolerable then soybeans.

The other three elements from the SEP (Cr, Mo, and Se) carried less influence in the selection process for varying reasons. Chromium, which may elute at high pH from ash in its hexavalent form (CrO_4^{2-} ;Daniels et al., unpublished data), and is quite toxic, but is quickly reduced to its trivalent form (Cr^{3+}) which is non-toxic and much less soluble/mobile in the environment. Hexavalent Cr is less bioavailable in soils/sediments between pH 5 and 8.5, but its solubility increases dramatically above pH 9.0 (Kabata-Pendias, 2001). Total Se concentrations (1.2 to 184 mg kg^{-1}) were high enough that we expected initial leachate concentrations could be higher than the primary drinking water MCL of 0.05 mg/L, but the highest TCLP extractable Se for any of the 28 CCPs was 50% below the EPA regulatory limit. Selenium is also hyper-accumulated in plants and thus no adverse plant growth effects were expected in the greenhouse

bioassay trials. Molybdenum was present in the labile to moderately labile fractions and was therefore expected to be readily leachable or bioavailable. Molybdenum is also hyper accumulated in plants and thus no adverse plant growth effects are expected in the greenhouse bioassay trials.

Table 4. Mehlich-1 extractable elemental data of 28 coal combustion products (CCPs).

CCP		2 : 1	---------- mg kg^{-1} ----------						
Lab #	Type of CCB	pH	Zn	Mn	B	Cu	Fe	P	Mg
1	Fly ash	6.98	1.9	2.9	9	1.1	78	46	91
2	Fly ash	8.65	0.6	8.1	186	0.1	14	2	232
3	Fly ash	9.10	2.7	10.3	59	3.1	16	8	383
4	Fly ash	9.53	2.1	6.5	32	2.0	100	55	117
5	Ash	9.57	2.5	11.7	309	1.8	13	2	658
6	Fly ash	8.22	1.4	4.2	39	0.3	75	53	139
7	FGD	9.09	0.1	1.0	39	0.1	4	4	1101
8	Fly ash	10.11	1.4	14.2	120	0.7	5	33	142
9	Fly ash	12.02	0.1	0.5	29	0.1	1	2	242
10	FGD	8.94	0.3	2.5	5	0.2	13	2	348
11	Fly ash	9.15	5.5	12.6	183	5.1	373	109	277
12	FGD	8.99	0.3	1.8	55	0.4	43	14	727
13	Fly ash	9.27	0.1	0.2	39	0.1	1	2	204
14	Bottom ash	8.68	1.3	7.7	21	0.1	23	2	214
15	Screened ash	8.64	1.5	12.3	4	1.4	203	37	156
16	Fly ash	11.71	0.1	0.6	21	0.1	11	2	227
17	Fly ash	11.68	0.1	1.5	46	0.1	1	2	341
18	Fly ash	4.10	5.4	6.8	44	0.5	194	97	181
19	Fly ash	7.24	2.3	18	35	2.7	158	60	473
20	Fly ash	7.95	1.6	8.8	8	4.3	152	171	103
21	Fly ash	8.18	0.2	1.0	59	0.3	8	11	147
22	Fly ash	7.01	2.9	4.5	30	7.6	222	73	130
23	Fly ash	8.00	2.4	5.7	20	4.2	150	64	178
24	Fly ash	7.29	3.5	1.7	9	22.2	68	90	73
25	Fly ash	12.09	0.1	0.1	3	0.6	3	4	124
26	Fly ash	8.44	0.1	0.6	22	0.1	0	2	67
27	Fly ash	11.68	0.1	0.1	27	0.1	0	2	372
28	Fly ash	8.47	4.1	7.4	33	2.9	7	2	203
Means across all ashes		9.0	1.6	5.5	52.9	2.2	69.1	34.0	273

Thus, the selection of CCPs for the greenhouse bioassay trial were as follows:

Ash #	Type of Ash	Ash properties
11	Fly ash	High As, low CCE, low EC, high extr. B.
28	Fly ash	High As, low CCE, mod. high EC, low extr. B.
16	Fly ash	Low As, high CCE, low EC, low extr. B.
27	Fly ash	Low As, high CCE, high EC, low extr. B.
7	FGD	Rel. low As, high CCE, mod. EC, med. extr. B.
18*	Fly ash	High As, low CCE, high EC, high extr. B.

*Fly ash #18 was selected as a substitute for # 28 in the leaching column trial to include a low-pH (3.57) CCP. This CCP was omitted from the bioassay trial because its use as amendment to the already acidic mine spoil would not have permitted plant growth.

Table 5 and Figure 1 present the specific fractional break-down of As, Cr, Mo, and Se for the selected CCPs, along with associated EC, pH, and CCE data.

Table 5. Properties of five CCP's selected for use in greenhouse bioassay experiments and the column leaching study.

		Saturated Paste					Total Elemental Micro Digestion				
CCP #	Type	Bd $kg\,L^{-1}$	pH	EC $dS\,m^{-1}$	CCE %	Extr. 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	17.4	841	23	4	86	9
7	FGD	0.80	9.1	5.3	49	23	225	19	3	36	8
18*	Fly ash	0.68	3.57	11.7	0.0	3.6	82	57	11	70	11

Bd = Dry bulk density

*CCP # 18 was substituted for # 27 in the column leaching study

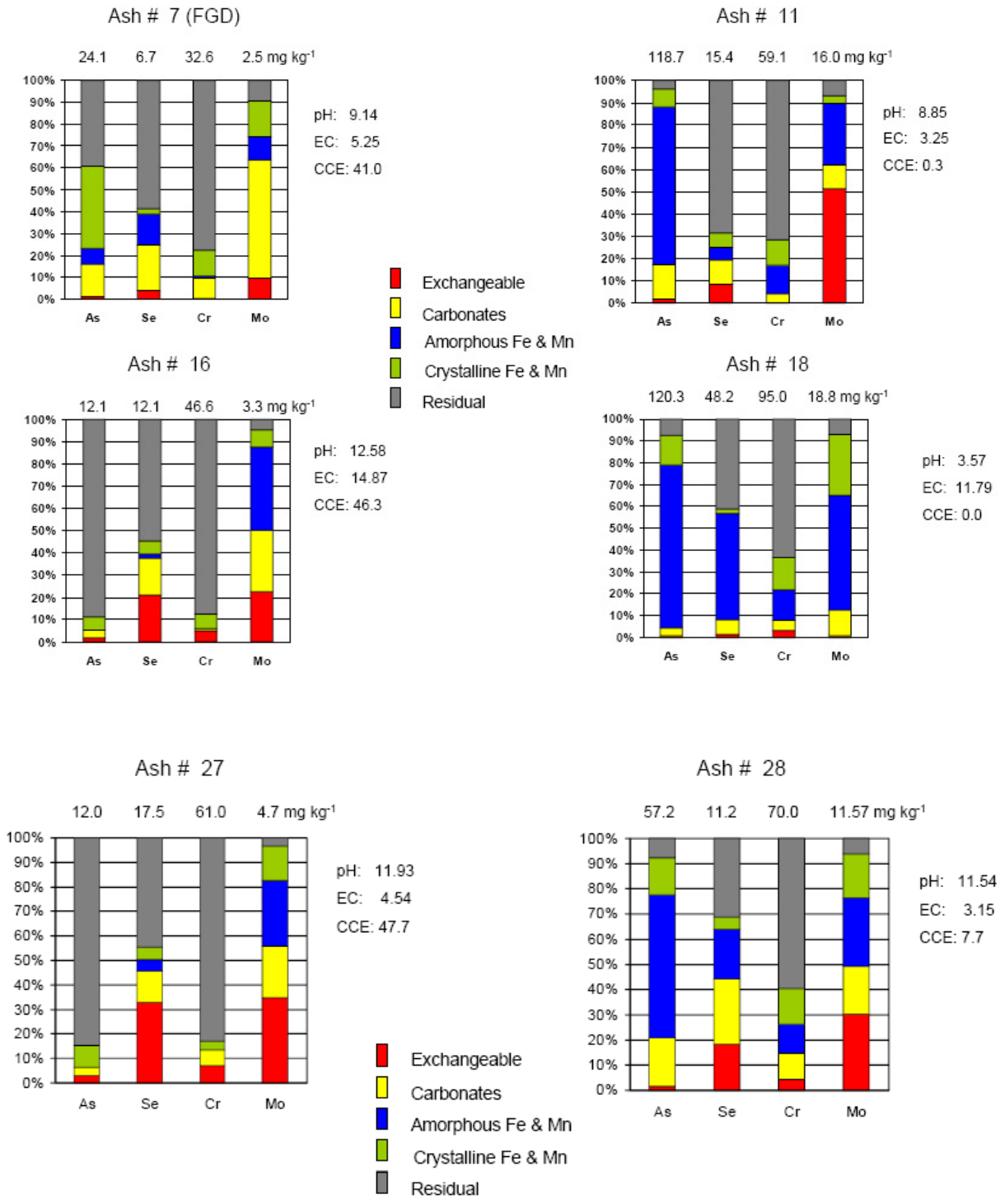


Figure 1. Distribution of As, Cr, Se and Mo in six CCP materials used in experiments. Elements are shown as distributed among five sequential extraction procedure forms.

Methods for Greenhouse Bioassay Trial

The bioassay trial was designed to test the presumed effectiveness of CCPs 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, Cr, Mo, Se, B.

- Acidic sandstone mine spoil was collected at an active Powell River/Red River surface coal mine in Wise County, Virginia. Laboratory pH = 4.75, with a liming requirement equivalent to 4.5 Mg/ha CCE. 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.

Experimental Design & Treatments:

- The trials were conducted separately for fescue and soybeans. The statistical design was a completely randomized block (CRB) 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. This is a modification of the pour-through technique of Wright (1986).
- 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.

- Table 6 gives the Mehlich-1 soil test data for the various treatment mixes used in the bioassay trial

Table 6. 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	24	1.9	4	2	455
#27 – 20%	10.84	2	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

Methods for Leaching Column Study

The selection criteria for five CCPs to be used as an amendment to acid forming coal refuse were the same as those for the bioassay trial with one exception/substitution. For this experiment, CCP # 27 was substituted with CCP # 18. This CCP (#18) 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 CCPs.

- Known acid- forming coal refuse was collected fresh from the Red River Coal Co. prep-plant adjacent to the Powell River Project research area 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 expressed as 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 "reactive and ready" for amendment with CCP's.

Leaching Column Design:

The columns constructed for this experiment (see Fig. 2 below) were of similar design to 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 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.

Figure 2. Photo of leaching column array in laboratory.

Experimental Design & Sampling:

- 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 as calcium carbonate 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.

- Table 7 gives the Mehlich-1 soil test data for the various treatment mixes used in the leaching column trial.

Table 7. Selected chemical properties of coal refuse and CCP amended coal refuse at the onset of the column leaching trial.

Refuse +	2 : 1	---------- mg kg^{-1} ----------						
% of CCP	pH	Zn	Mn	B	Cu	Fe	P	Mg
#7 – 10%	8.40	2.5	6.9	17.5	0.4	30.6	2	694
#7 – 20%	8.84	0.8	3.7	26.0	0.1	2.5	2	879
#11 – 10%	7.14	4.5	6.9	36.9	2.1	270.0	96	232
#11 – 20%	8.07	5.1	9.5	79.0	2.9	406.3	123	222
#16 – 10%	11.81	0.2	1.3	26.9	0.2	16.2	8	379
#16 – 20%	11.89	0.1	0.2	24.4	0.1	1.2	2	323
#18 – 10%	4.56	5.1	6.2	9.0	1.8	195.3	65	229
#18 – 20%	4.31	5.3	5.9	14.1	1.8	170.8	74	174
#28 – 10%	11.52	2.1	3.3	33.6	0.2	10.4	4	440
#28 – 20%	11.72	0.2	0.8	33.6	0.1	1.6	3	429
Refuse 0 lime	5.22*	4.4	4.6	3.6	1.6	155.0	72	243
Refuse limed	7.06	0.7	2.1	0.4	0.1	4.7	3	115

* Refuse was relatively "fresh", and the oxidation/acidification process had just begun, and subsequent sampling would have reflected much lower pH.

Results and Discussion

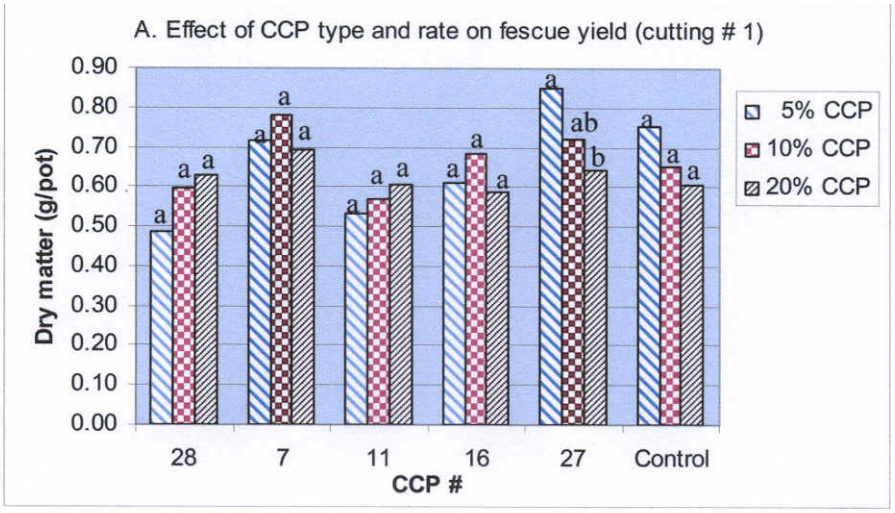
Greenhouse Bioassay Experiment

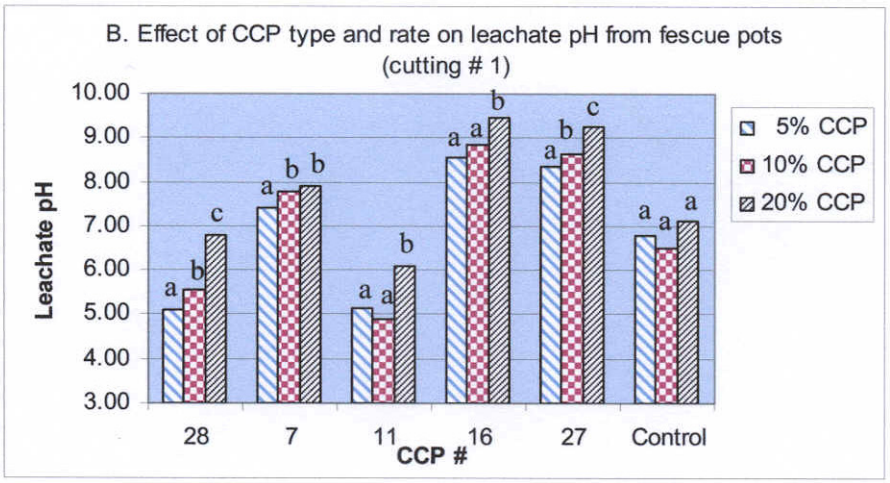
Dry matter yields from the first cutting (30 days) of tall fescue, along with corresponding leachate EC and pH from the pots at that time, are presented in Figure 3. Table 8 reports yields and results of the corresponding pour-through data for the first 3 harvest/pour-through events. Dry matter yield 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 CCPs with 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. The results for the soybean trial are given in Figure 4, and indicated a similar overall response to the varied CCP amendments after 32 days. Yields increased with increasing amendment rates for CCPs # 11 and 28, but there were either no effect, or actual yield decreases for all the other CCPs and for the highest liming rate in the control pots.

The results of the analysis of variance (ANOVA) of the fescue and soybean yield data revealed highly significant (0.001) effects of both CCP source and application rate (Table 9). The same highly significant effects were seen for EC and pH, except that for these two variables, the CCP source by application rate interaction (CCP x rate) was also highly significant. While the CCPs differed widely in their total elemental composition (Table 2) and among the fractional distribution (Fig. 1), 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, either from the added CCP or the amended mine spoil. The limited CCE of CCP #11 and #28 was reflected in the limited liming effect and lower pH of the pour-through leachate solutions.

The pour-through data for the soybean pots (Fig. 4c) showed that EC values significantly exceeded the critical limit (for salt sensitive species) of 2 dS m^{-1} for pots treated with CCP # 7, and, slightly exceeded the limit for #'s 11, 16 and 28. It appears the yield reductions and plant stress symptoms are due to factors such as exceedingly high pH (reduced yield with highest liming rate in control pots), high B, Se, and Mo concentrations, and/or combinations of these factors. Correlation analysis of soybean yield with the pour-through data was significant and positive for pH (0.35, r^2=.003), but negative correlated with Mo (-0.44, r^2=.002) and Se (-0.43, r^2=.006).

Visual symptoms of stress and phytotoxicity (Figs. 5 & 6) on the plants due to different CCPs and amendment rates confirmed the susceptibility of soybeans versus tall fescue. Soybeans showed moderate to severe chlorosis and necrosis in all treatments other than the 5% rate of CCPs # 11 (low in CCE) and #16 (low extractable B). Overall, the affected soybean plants looked very unhealthy and stunted in growth in the 10% and 20% treatments. However, the overall effects of the CCP rates/types on total plant yield (Fig. 4) were not as profound as the observed leaf morphological effects. Tall fescue, on the other hand, displayed symptoms (Fig. 7) for only the 10 and 20% rates of high CCE ashes (# 16 and 27). Furthermore, those symptoms disappeared over time and were not noticeable after the third harvest.





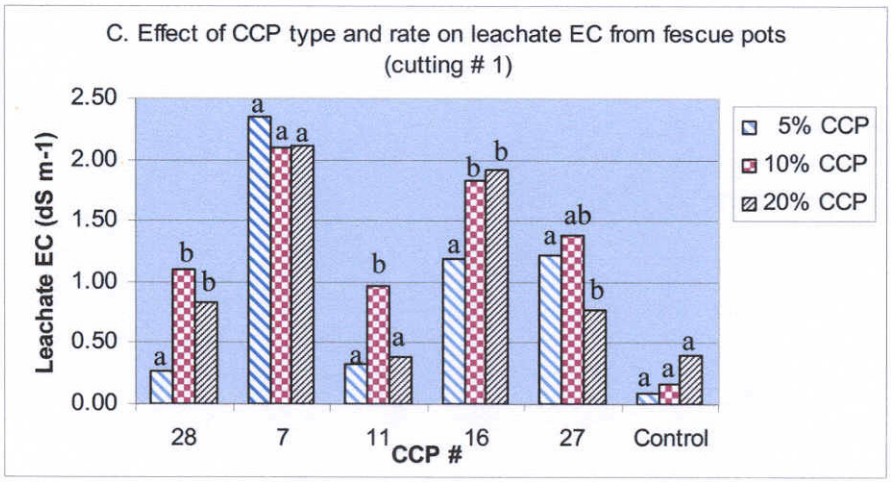


Figure 3. Tall fescue dry matter yield and corresponding pH and EC from pot leachates. Note: for Controls, the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), and 20% to high lime (9 Mg/ha). Bars with differing letters by CCP are different at $p < 0.05$.

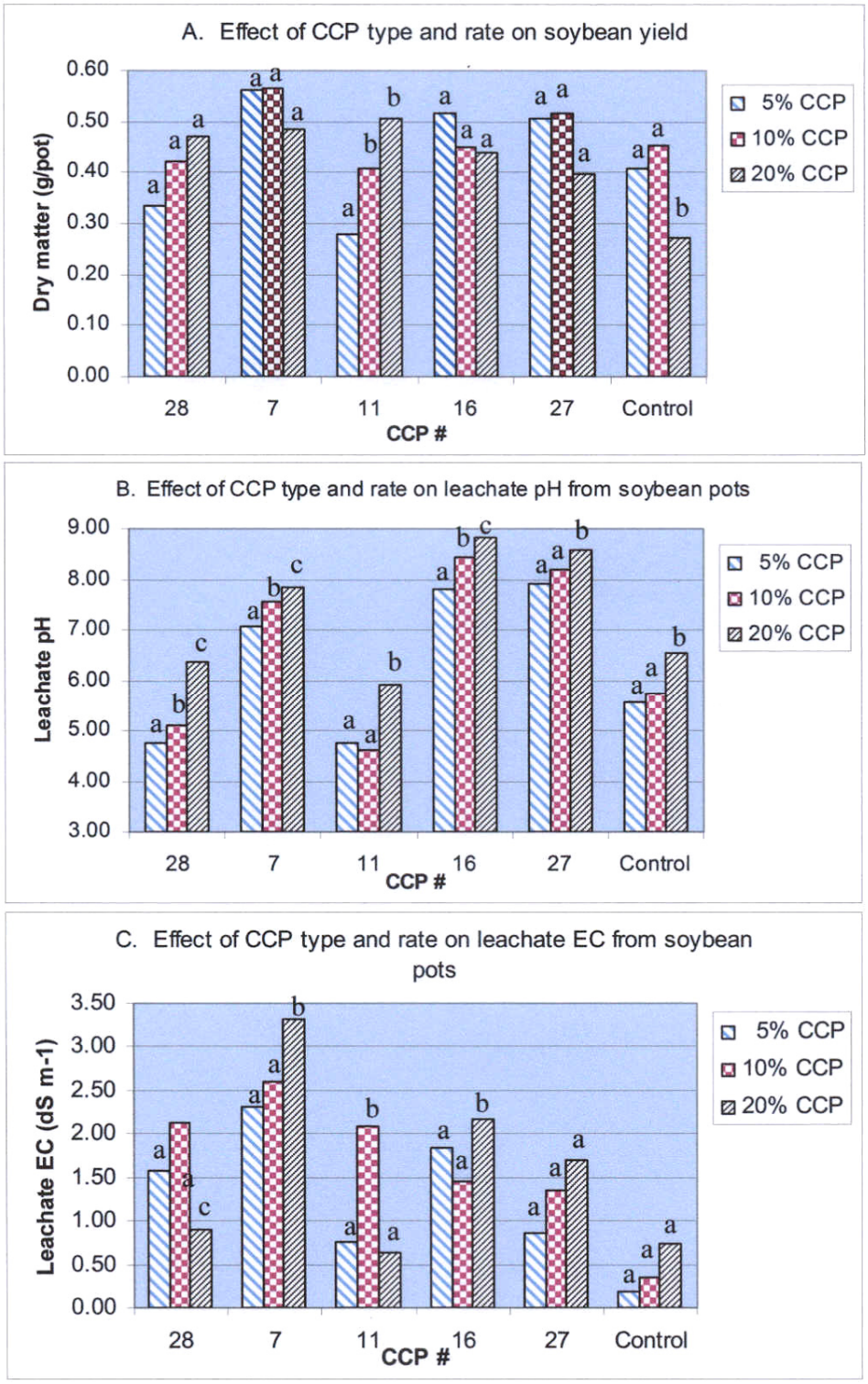


Figure 4. Soybean dry matter yield and corresponding pH and EC from pot leachates. Note: for Controls, the 5% corresponds to no-lime, 10% to low lime (4.5 Mg/ha), and 20% to high lime (9 Mg/ha). Bars with differing letters by CCP are different at $p < 0.05$.

Table 8a. Fescue grass clipping yields (g pot^{-1}) and pour-through leachate pH, EC (dS m^{-1}), and As (mg L^{-1}) from acidic mine spoil amended with various CCPs 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.

		----------Yield----------			---------- 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: Values listed as < denote detection limit for parameter/instrument employed.

Table 8b. Pour-through leachate concentrations (mg L^{-1}) of selected elements from acidic mine spoil amended with various CCPs 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.

		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	0.030	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	<0.03	0.026	<0.024	<0.024
Control++	0	<0.004	<0.004	0.012	<0.008	<0.010	<0.018	<0.03	0.040	0.058	0.026	<0.024	<0.024

Note: Values listed as < denote detection limit for parameter/instrument employed.

Table 9. Analysis of variance (ANOVA) of dry matter yield for tall fescue (cuttings # 1 -3) and soybeans from bioassay trials

Source	df	Fescue 1	Fescue 2	Fescue 3	Soybean 1
		---------- Pr > F value ----------			
Rep	3	ns	ns	ns	ns
CCP	7*	.001	<.0001	<.0001	.004
Rate	3	ns	.004	.03	ns
CCP x rate	8	ns	ns	ns	.02

* df (n-1) = 5 for CCPs and 3 control treatments

Figure 5. Soybean plant growing in acidic mine soil amended with 5% of CCP # 28. Note marginal necrosis and chlorosis of lower leaves; typical of combined soluble salt + B damage.

Figure 6. Soybean plant growing in acidic mine soil amended with 10% of CCP # 16. Note heavy stunting and complete loss/drop of lower leaves; typical of heavy soluble salt + B damage. Also note dropped leaves in pot that were totaled in yield estimates for Fig. 4.

Figure 7. Tall fescue growing in acidic mine soil amended with 20% of CCP # 27 after 30 days. Note slight tip burn due to combined salts+B effect. Soluble salt effects were not noticed at later sampling dates.

The combined plant yield and leachate data from the control samples confirm that the sandstone derived mine soil utilized was a relatively inert substrate with respect the release or leaching of the elements of interest. The slight rise in pH of the no-lime control samples (likely due to the irrigation water and fertilizer solution) indicates its very low buffering capacity. The quartzitic 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 heavy amendment with CCPs. Any release of elements of concern would presumably come from the amending CCP.

Column Leaching Experiment with Acid Forming Refuse

The complete leachate EC and pH data during the first 60 days are given in Tables 10 and 11. Leachate concentrations during the first 46 days for the elements As, B, Cr, Cu, Ni, Se, Zn, Fe, and Mo are given in Appendix B. Leachate concentrations were, depending on the elements and the treatment combination, often below detection limits. The complete elemental release patterns for all treatments are presented in graphical format in Appendix B. The patterns for specific treatment combinations (along with corresponding EC and pH) which are of particular interest or demonstrate general patterns are presented in Figures 8, 9 and 10 a-h. The pH data (Fig. 8 and Table 10) document the strong differences among CCPs in CCE and associated abilities to counteract the strong acidification of the highly reactive coal refuse. High CCE ashes like #16 or #27 raised the pH initially to > 12.0, while #18 had relatively little impact on leachate pH. The pH of the no-lime coal refuse column dropped to below 3.0 within 11 days. Bulk liming the refuse according to the peroxide oxidation potential acidity method kept the pH of the limed-refuse control columns in the 7.2 to 7.9 range for the duration of the experiment.

The oxidation of sulfidic materials and associated formation of acid drainage resulted in more rapid dissolution reactions and significant increases in solution EC (Fig. 9). The importance of controlling acid-base conditions in refuse is reflected in the direct pH control on retention and/or release of specific elements. The dissolution causes very high levels of S and Fe (see Appendix B &C), but of potentially greater concern are the significant releases of As, Cr, Cu, and Zn. However, it appears that even for a CCP with no CCE (e.g. #18), and little direct effect on pH between 10 and 20% addition, that the impact on dissolution/release of Zn, Cr, Cu, and Ni (see Fig. 10 and Appendix B&C) can be significant. The difference was particularly dramatic for Zn (Fig. 10 f) with 38 mg L^{-1} vs. 20 mg L^{-1} release with only a difference in of 0.2 pH units for material #18. Chromium release (Fig. 10 c and Appendix B&C) patterns are clearly controlled by pH. Release of Cr by coal refuse was at or below detection limit (0.006 mg L^{-1}) when the pH was > 7.0, but increased with continued drop in pH. Cumulative Cr release from all CCP amended coal refuse treatments was < 1% of the Cr added by CCP amendments.

Arsenic release was relatively low overall (Appendix B&C and Fig. 10 b). For CCPs # 11 & 18, which had very high total As contents, the cumulative release was <0.3% of total As added. Boron leaching varied widely among CCPs, ranging from < 1 to 135 mg L^{-1} in the first leachate. Boron tended to leach readily and concentrations dropped quickly with successive leaching events. The overall release patterns tended to by paired according to CCP #. While pH

Table 10. Leachate pH from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product.

		Leaching Event #											
		1	2	3	4	5	6	7	8	10	12	14	18
CCP#	Ash	Day of Leaching											
	rate %	1	4	8	11	15	18	22	25	32	39	46	60
7	10	7.38	7.97	8.03	8.13	7.93	7.84	7.79	7.84	7.79	7.72	7.49	7.32
7	20	8.44	8.27	8.34	8.28	8.26	8.15	8.02	7.99	8.17	8.10	7.79	7.74
11	10	4.02	4.01	4.32	4.47	4.35	4.17	4.06	4.05	3.90	3.90	3.89	3.74
11	20	6.17	6.30	6.64	6.69	6.60	6.57	6.60	6.76	6.59	6.48	6.83	6.76
16	10	11.44	10.90	10.92	11.08	11.07	10.97	10.99	10.51	10.95	10.95	10.03	8.63
16	20	12.43	11.89	11.86	11.93	11.81	11.77	11.69	11.65	11.62	11.53	11.14	10.12
18	10	3.57	3.27	3.52	3.67	3.71	3.41	3.32	3.22	3.05	3.03	3.06	2.92
18	20	3.53	3.44	3.57	3.49	3.68	3.55	3.52	3.56	3.44	3.32	3.31	3.28
27	10	10.02	10.02	9.62	10.01	10.02	10.00	9.76	9.52	9.76	9.59	8.79	8.33
27	20	11.70	11.55	11.60	11.65	11.67	11.57	11.50	11.46	11.37	11.36	11.30	10.70
No lime control		3.41	3.36	3.23	2.92	2.73	2.42	2.26	2.21	2.11	2.11	2.11	2.09
Limed control		7.25	7.23	7.71	7.45	7.31	7.32	7.40	7.51	7.36	7.23	7.67	7.93

Table 11. Leachate EC from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product.

CCP#	Ash	Day of Leaching											
	rate %	1	4	8	11	15	18	22	25	32	39	46	60
7	10	5.27	4.16	3.71	3.47	3.11	3.22	3.10	3.13	3.13	2.93	2.80	2.74
7	20	5.40	4.89	3.82	3.46	2.85	2.74	2.84	2.79	2.75	2.59	2.44	2.49
11	10	3.63	3.19	2.97	3.09	2.70	2.66	2.72	2.76	2.86	2.87	2.92	3.04
11	20	4.06	3.37	3.48	3.19	2.84	2.78	2.93	2.86	2.80	2.73	2.35	2.23
16	10	3.17	2.33	2.01	2.08	1.92	2.01	2.00	1.72	1.66	1.54	1.12	1.08
16	20	5.15	4.94	4.35	4.48	3.66	3.69	3.48	3.33	2.82	2.38	1.33	0.77
18	10	5.63	4.75	4.12	4.26	3.80	4.08	4.47	5.08	5.72	5.98	6.14	6.10
18	20	6.14	4.91	4.04	3.87	3.63	3.72	3.93	4.18	4.48	4.29	4.38	4.01
27	10	2.95	2.40	2.38	2.16	1.80	1.82	1.70	1.80	1.56	1.51	1.42	1.22
27	20	2.25	2.43	2.59	2.46	2.40	2.39	2.20	2.00	1.50	1.41	1.06	0.78
No lime control		4.77	4.12	4.20	4.97	6.50	8.87	10.81	12.73	13.16	13.81	13.11	12.29
limed control		3.83	3.40	3.22	3.50	3.00	3.16	3.13	3.21	2.87	2.77	2.60	2.58

Figure 8. Leachate pH from long-term leaching columns of acidic coal refuse amended with 0, 10 or 20% of CCPs.

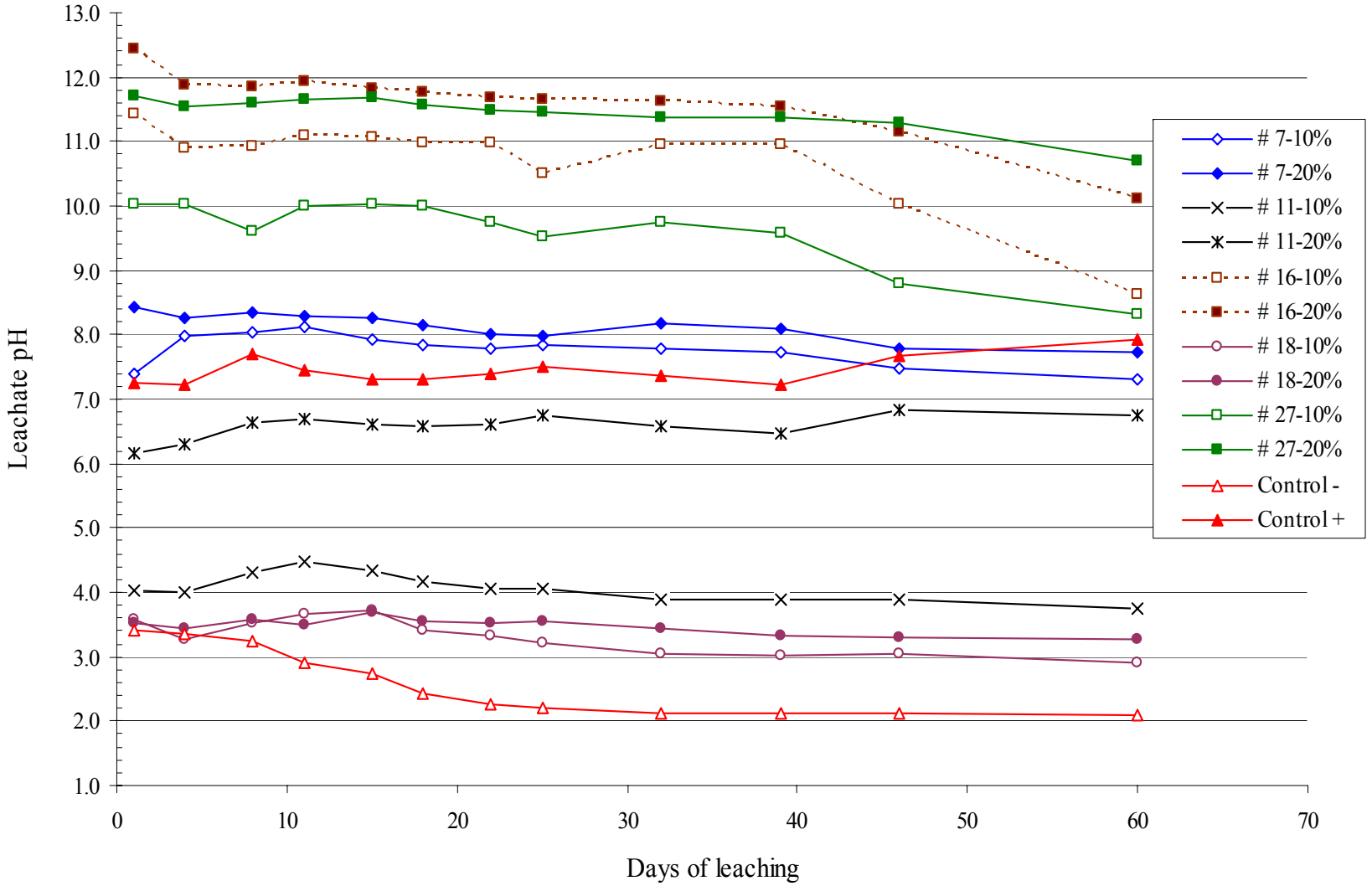


Figure 9. Leachate EC from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

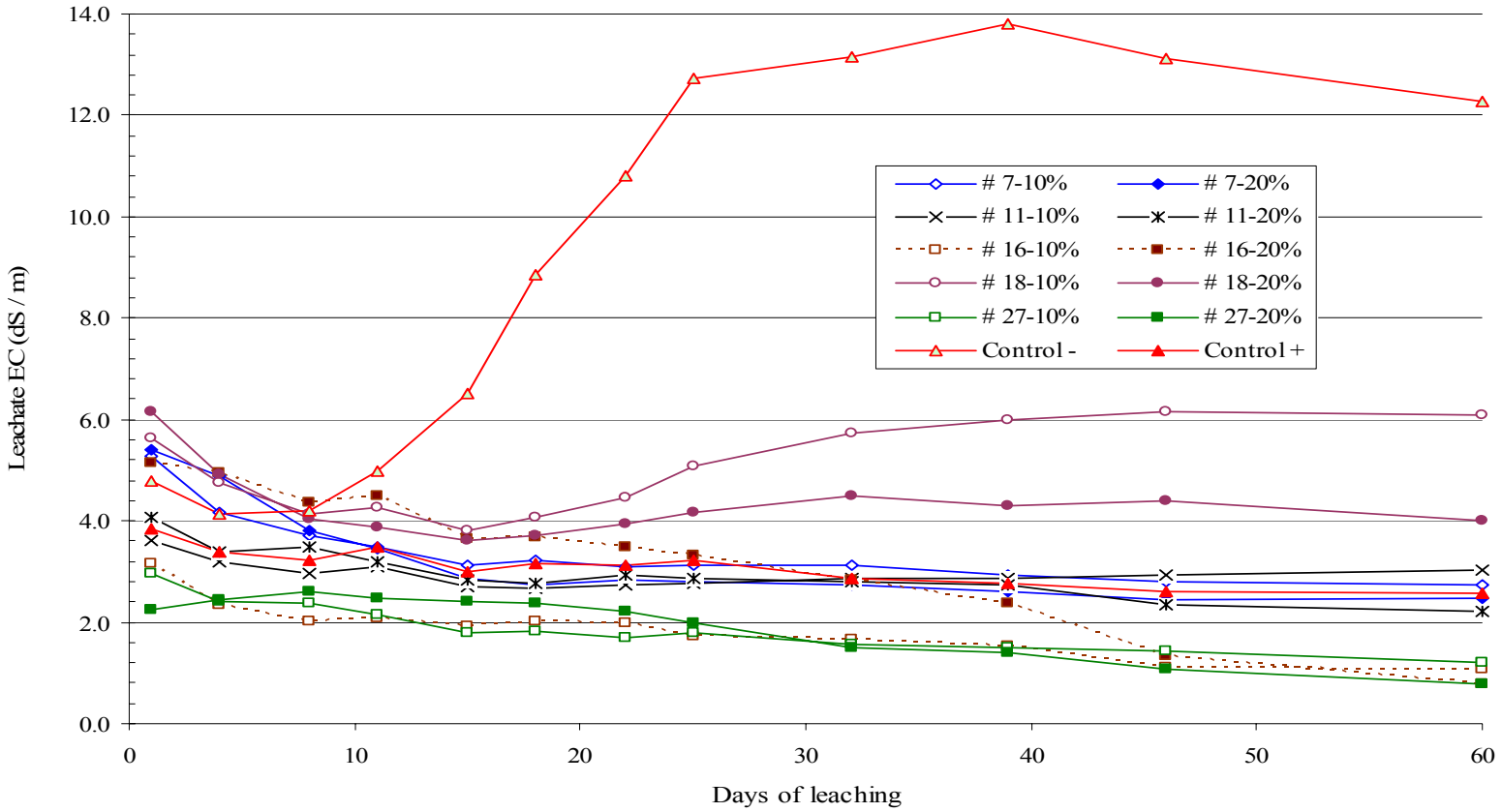
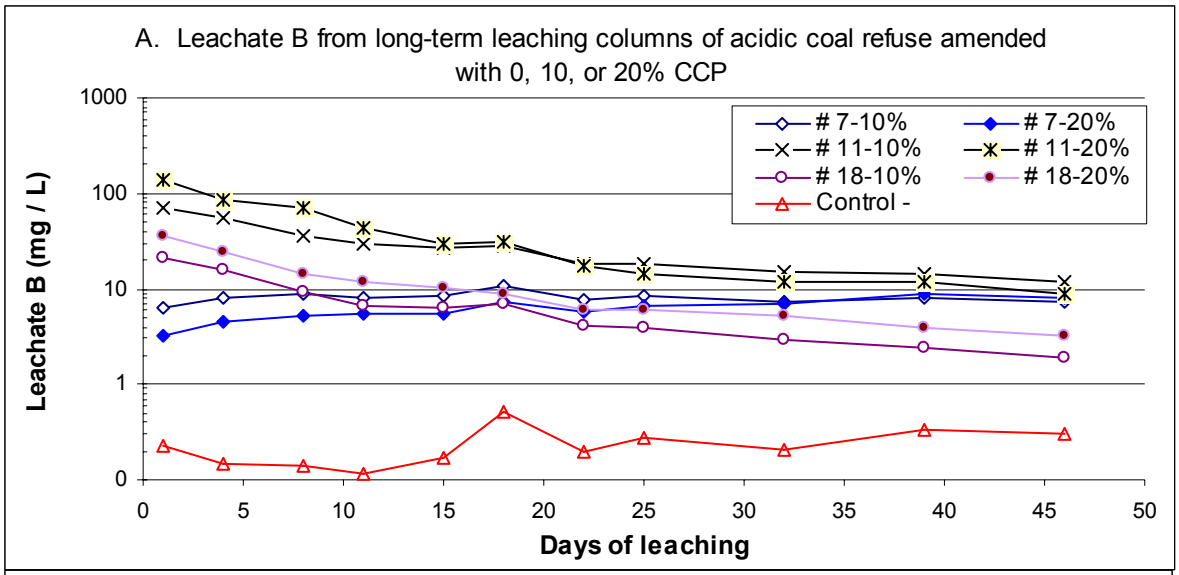
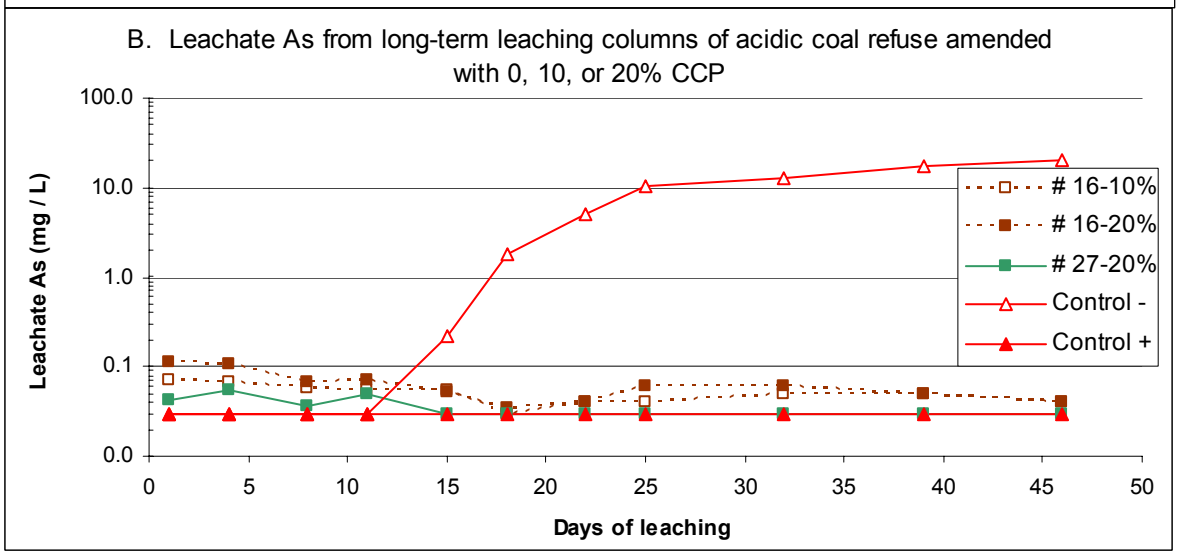


Figure 10 a-c. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% of CCPs.





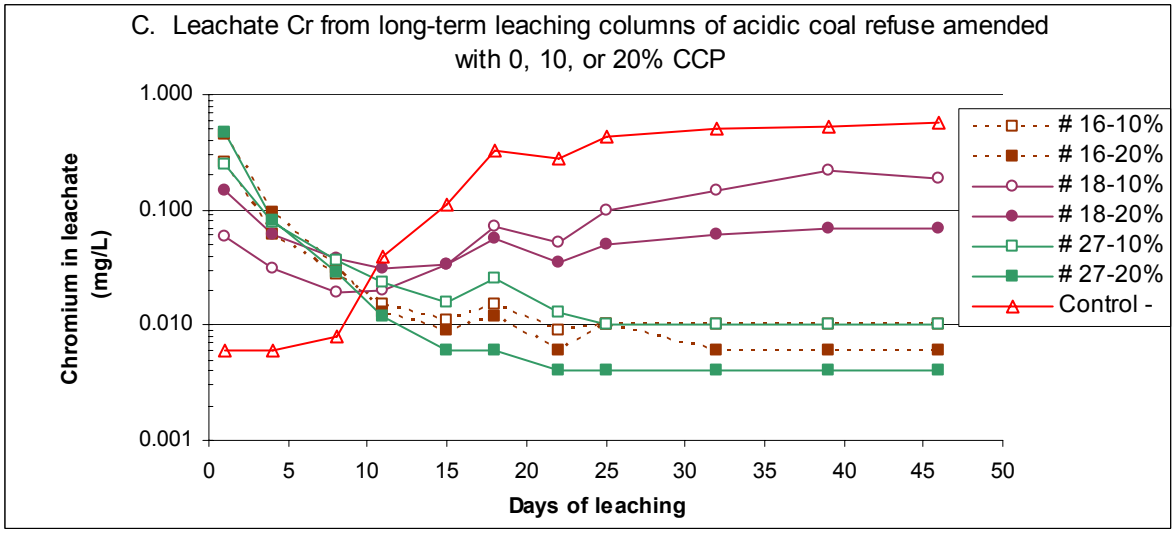
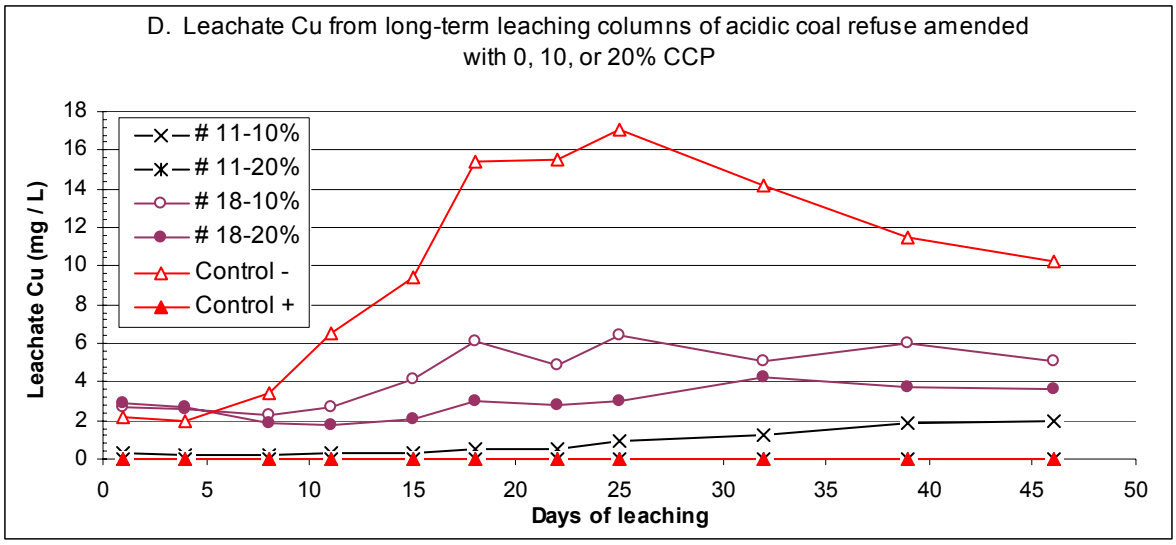
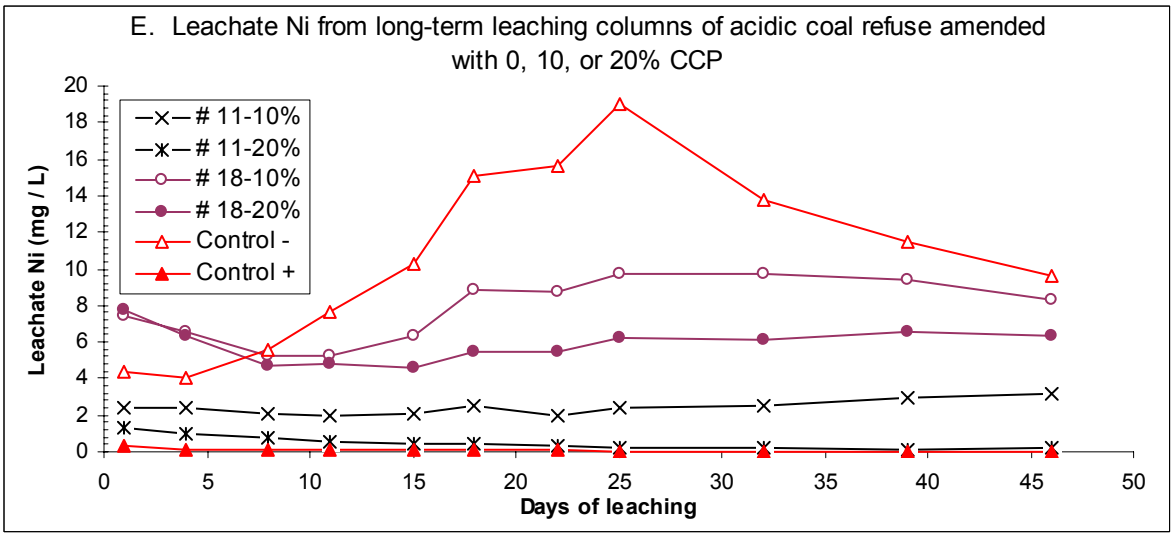


Figure 10 d-f. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCPs.





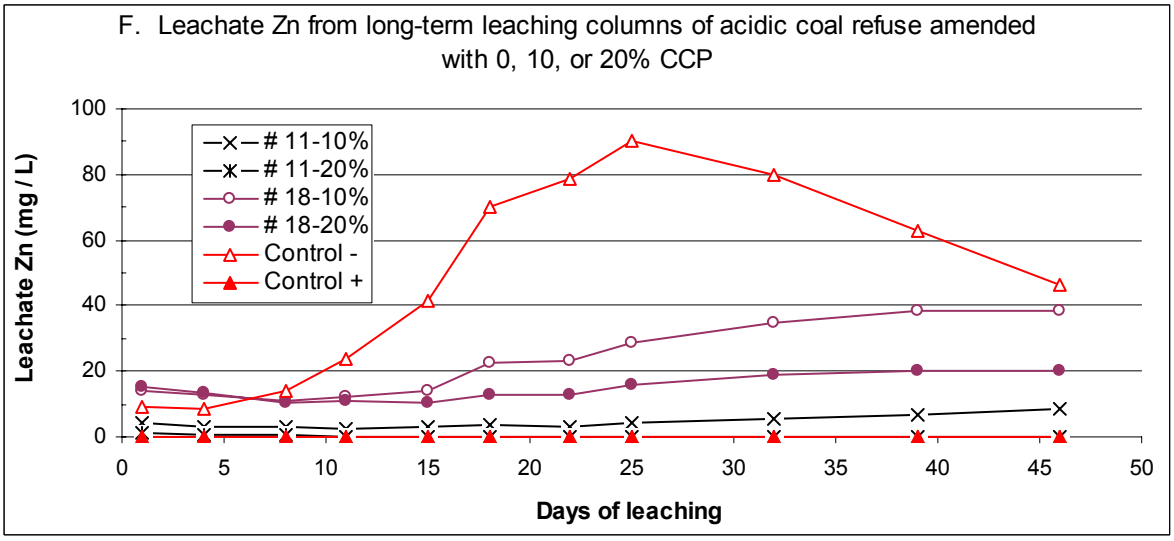
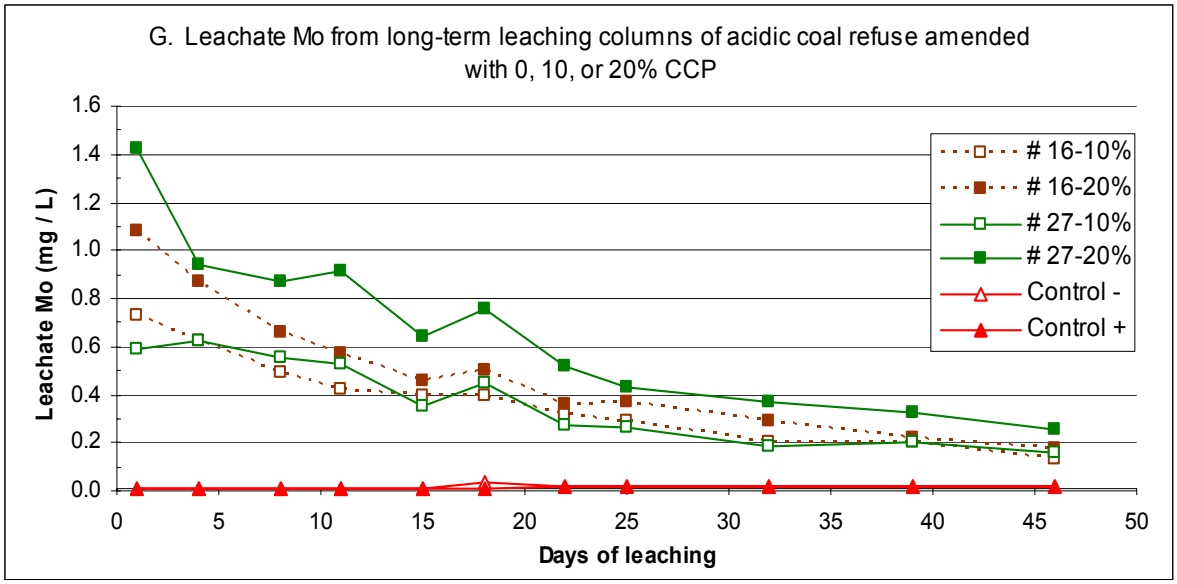
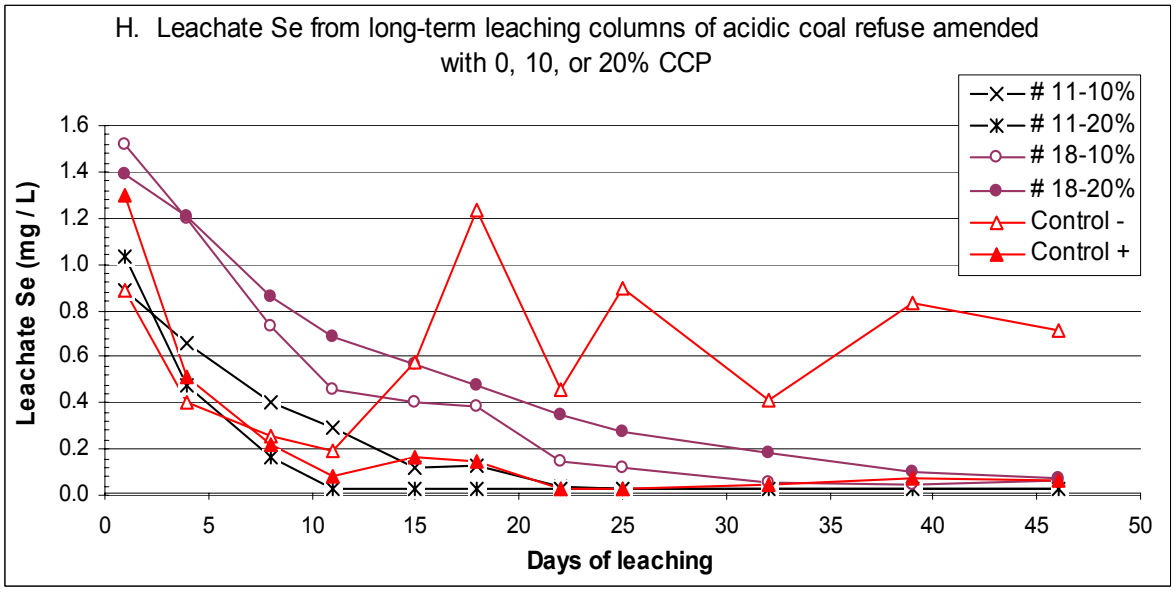


Figure 10 g-h. Leachate chemical properties of selected treatments from acidic coal refuse amended with 0, 10, or 20% CCP





did not seem to readily affect B leachability, B leached as a percent of total applied for a given CCP was always less for treatment rates that resulted in a higher pH. Also, CCP # 27 had by far the highest total B content (Table 1; Appendix B&C), yet it had the lowest mass B release (approximately 1% of the total applied), and the pH of its leachate solution was also the highest at 10 to 11.4. On the other hand, CCP # 18 with a pH of around 3.5, leached 42% of the applied B. The overall release pattern of Mo was controlled by loading rate and not pH per se (Fig. 10 g and Appendix C). CCPs # 11, 16 and 27 did show steady, but declining Mo concentrations with time at relatively high pH. Low pH conditions reduced the Mo release for CCP # 11 (see ash

rate 10% vs. 20%), but for all other CCPs, the % Mo leached as a function of total mass applied decreased as pH increased due to the liming capacity of the CCP. Oddly enough, CCP # 27, with the highest pH also generated the highest % of total Mo leached (34%), while only 0.2 – 8.4% of applied Mo leached from all other CCPs. Selenium release (Fig. 10 h) differed by CCP, but declined steadily toward the detection limit of 0.03 mg L^{-1} for all treatments with the exception of the no-lime control columns. The range of total Se leached was 3.8 to 48.9% of the total applied, but there was no apparent relation of leaching mass loss to total Se concentration.

Overall, the data indicate that dissolution/release rates from weathering refuse (control -) of most elements increased markedly once the pH dropped below 3.0. The addition of alkalinity via agricultural lime (as for the limed-control columns) or from CCPs with adequate CCE largely prevented the pH controlled release of As, Cr, Cu, Ni, and Zn from the acidifying refuse. However, it does appear that B, Mo and Se will leach at relatively higher concentrations during the initial leaching flushes. By comparing the levels and patterns of elemental release from the control columns (limed and no-lime) to those of the CCP amended columns (particularly in conjunction with pH; see Appendix C), we can tentatively attribute leachate elements to primary sources, either from the coal refuse or specific CCP added. Based on the mass CCP and leachate data, the coal refuse appears to be the primary source for the following elements: As, Cr, Cu, Fe, Ni, S, and most Se. The CCPs added were the primary source for B, Mo, and in certain cases, Cr and Se.

Summary of Observed CCP Effects:

B: Coal refuse amended with any CCP had significantly higher B release that the control treatments, regardless of pH. Thus B release must be attributed to the CCPs.

Mo: As with B, the Mo release varied with CCP and rate added, and the control columns had the lowest release, regardless of pH. Thus Mo release must be attributed to the CCPs.

Se: Initial release of Se from certain CCPs (e.g. #18) was higher than from control columns, but once refuse acidification occurred, larger amounts of Se were generated by acid refuse.

Summary of Observed Coal Refuse Effects:

As: Limited As release was noted across most CCPs regardless of As content or net leachate pH. However, once pH of the no-lime control dropped to <2.9, As release went from below detection limit (0.03 mg L^{-1}) to > 20 ppm at a pH of 2.1.

Cr: Chromium initially available from CCPs was quickly leached out and levels appeared to stabilize at or below 0.01 mg L^{-1}. Despite having similar high total Cr contents, the release was near or below detection limit (0.004 mg L^{-1}) after 20 days of leaching despite very different pH environments (see CCP# 11, 18, and 27).

Se: Selenium release tapered off quickly to < 0.1 mg L^{-1} for all treatments if the pH is > 3.0. For each CCP, release decreased with increasing pH. CCP # 18 had at least 3 times the total Se

content, but did not generate higher leachate levels compared to the other CCPs. Once the pH dropped below 3.0, the no-lime control had significantly higher Se than all other treatments.

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

Overall Summary

Coal Combustion Products (CCPS) Analyses

We obtained a sample set of CCPs with a wide range in important chemical properties. The range in pH was 3.57 to 12.35, but only 3 CCPs had a pH below 7.0. The soluble salt content of the CCPs also varied widely with a range of 0.66 to 26.85 dS m^{-1}. The liming capacity of the CCPs ranged from 0 to 52% CCE. Of the 28 CCPs analyzed, 14 had CCE of <5%. This parameter would play a critical role/limitation where low CCE CCPs were used in co-disposal or alkaline amendment scenarios with acid forming coal refuse or mine spoils. Mercury was below detection limits for the TCLP extracts, and below detection limit in all but the residual fraction of the SEP. The CCPs tested here were markedly different in their fractional distribution of As, Cr, Mo, and Se, and the release/solubility of these elements was generally pH dependent. We found that pH was reasonably well-correlated with CCE ($r^2 = 0.56$), but that the fractional distribution of As, Cr, Mo, and Se appeared to be more strongly linked to CCE than to bulk pH per se.

Greenhouse Bioassay Experiment

The fescue and soybean growth data revealed highly significant effects of both CCP type and application rate, and the two species (soybeans vs. fescue) exhibited clear differences in tolerance to growth substrate chemical properties. Using leachate pour-through data from soybean pots along with the data from pre- and post-harvest analysis of the growth substrates, we could not single out any individual element as directly limiting overall soybean yield. Regression and correlation analysis indicated that CCE was the dominant chemical property affecting relative plant growth. CCE directly controls the substrate pH and consequently the solubility and/or release of the elements of interest, be it from the CCP or the amended mine spoil. Plant appearance and visual toxicity symptoms, particularly on soybeans, were a very good and consistent indicator of apparent stress to the plants, while overall biomass yield was not a good indicator.

Column Leaching Experiment with Acid Forming Refuse

The bulk pH environment of the CCP/refuse blends was most critical to the retention/release of the elements of interest. The liming potentials of CCPs differed greatly, with a range in CCE of 0 to 52%. Thus, the liming effect of CCPs is a combined function of the CCE and application rate. The peroxide oxidation potential acidity (PPA) test indicated a necessary liming rate for this coal refuse of 34.5 Mg per 1000 Mg (or tons/acre). Mixing lime with coal refuse at this rate maintained the pH of the limed control columns within the range of 7.2 to 7.9 for the duration of the leaching period. The pH of the no-lime control refuse quickly dropped below 3.0 and stabilized around 2.1. Coal combustion products with adequate CCE are effective

in neutralizing the acidity produced by the oxidizing coal refuse. Using CCPs as a liming/neutralizer source contributed additional Mo and B to leachates, along with some Cr and Se in certain treatments. A small portion of the Cr and Se introduced into the system by the CCPs was leached over the first 6 to 12 leaching events. Se and Cr release from refuse is strongly pH dependent, and increased significantly only when bulk pH levels dropped to < 3.5 for Cr, and < 3.0 for Se. Amending coal refuse with CCPs with adequate CCE was very effective in preventing high concentrations and leaching losses of As, Cr, Cu, Fe, Ni, S, Se, and Zn. Amending acid forming coal refuse generally reduced also the long term evolution of salts (EC), but did generate higher salts in initial leachates.

It is also important to point out that the leachate concentrations of As, Cr, Mo, Se, and other elements reported here reflect what would constitute "worse case" conditions within an actively oxidizing refuse zone that had been bulk blended with CCPs. We do not presume that these levels would represent discharge conditions since numerous attenuation mechanisms would influence each element as it traveled away from these reaction zones and through the bulk of the refuse pile towards discharge. Beyond that, to our knowledge, bulk-blending of alkaline amendments with acid-forming refuse is not common practice at this time.

This study has generated a very large data set, and we are still analyzing various components for important inter-relationships. We will report any new and significant findings to both the Virginia Division of Mined Land Reclamation and the Office of Surface Mining.

Conclusions

The various components of this study represent a multi-faceted attempt to predict relative leachability/bioavailability of As, Cr, Mo, Se, and B from CCPs, and to develop/refine the bioassay method for the screening of CCPs as potential amendments. The results from all three study components indicate that net CCE is the most important characteristic of CCPs that affects bioavailability or leachability for most elements of concern, and that bulk CCE also has the predominant impact on plant growth. The importance of predicting and adding adequate total alkalinity (CCE) to completely offset bulk acidification of CCP/refuse blends has again been demonstrated here. At the higher CCP loading rates necessary for long term neutralization of sulfidic coal refuse, our results do indicate that significant B and Mo could potentially be available for leaching. That being said, it is important to re-emphasize the fact that by adding appropriate levels of alkaline CCPs, the tendency of the refuse itself to generate soluble As, Se, Cu, and other metals is drastically curtailed. The critical issue here would be whether or not sufficient total alkalinity is loaded into the system for long-term and permanent acid control.

Our combined results indicate that a few relatively simple lab measurements (pH, EC, CCE) coupled with a simple soybean bioassay such as reported here can readily predict both the relative effectiveness and potential toxicity of a given CCP when used as either a bulk mine soil amendment or an alkaline additive for acid control. Beyond that, where additional time and resources are available, the modified sequential extraction procedure also shows merit for predicting the relative bioavailability/solubility of a number of elements of concern.

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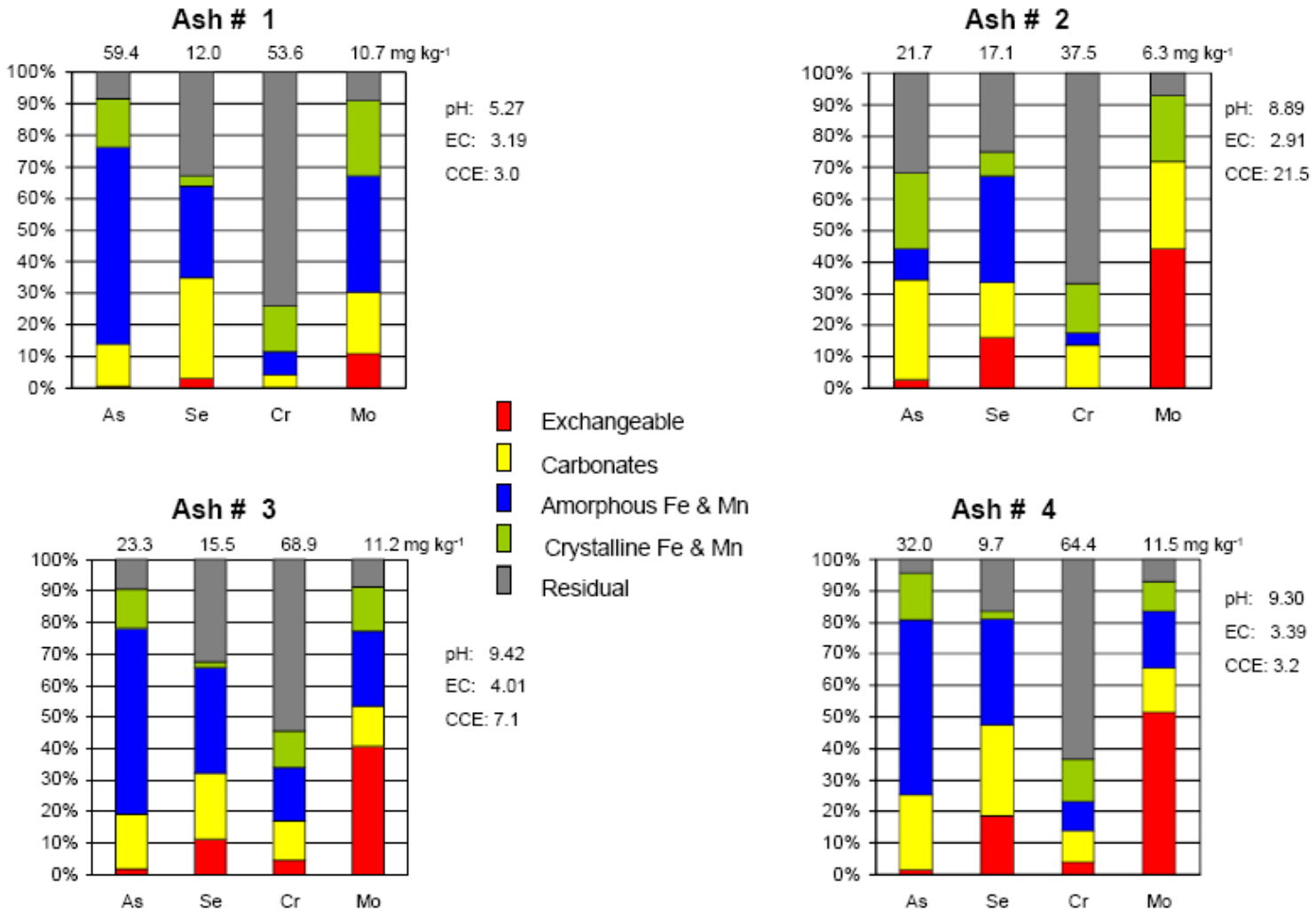
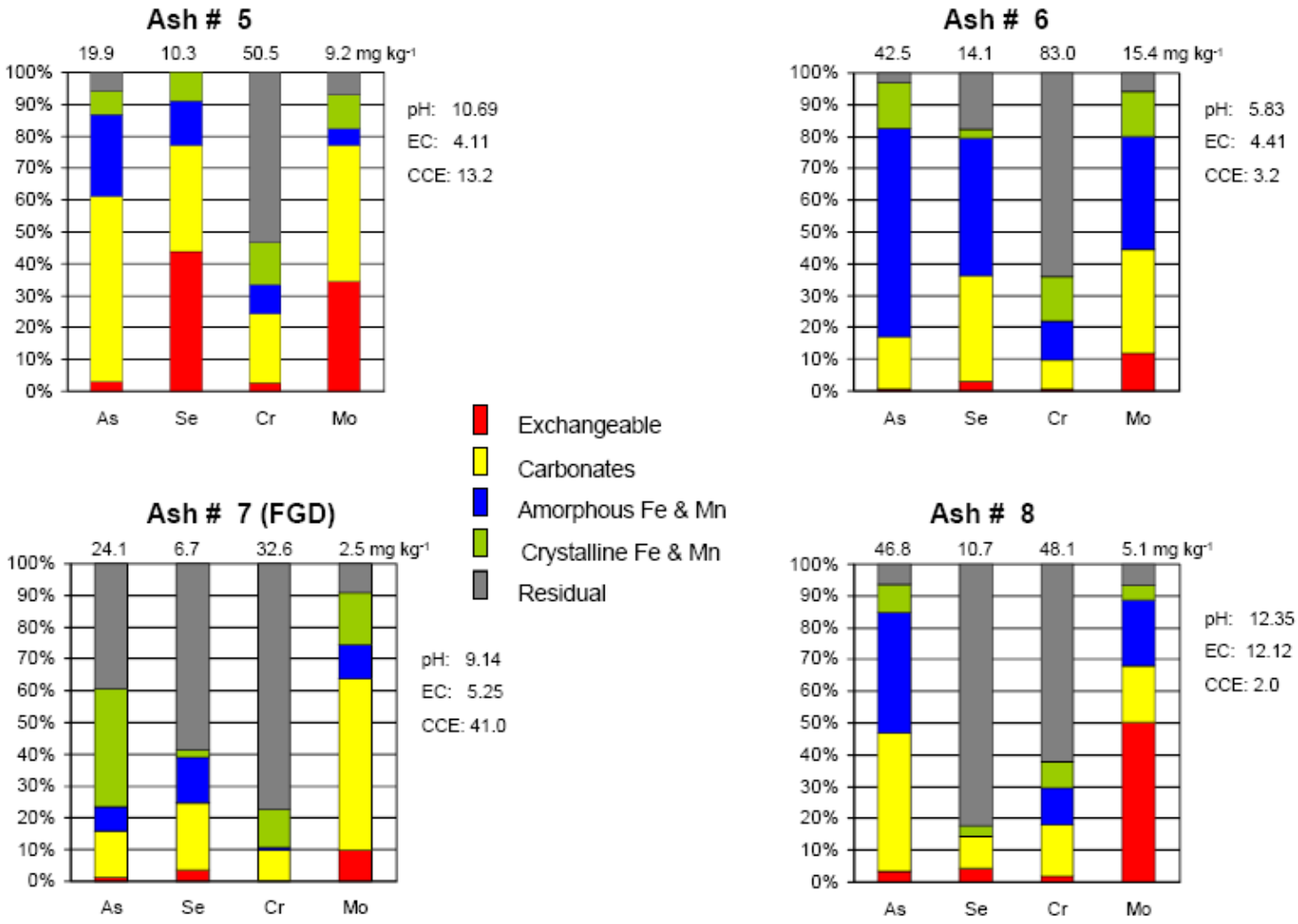
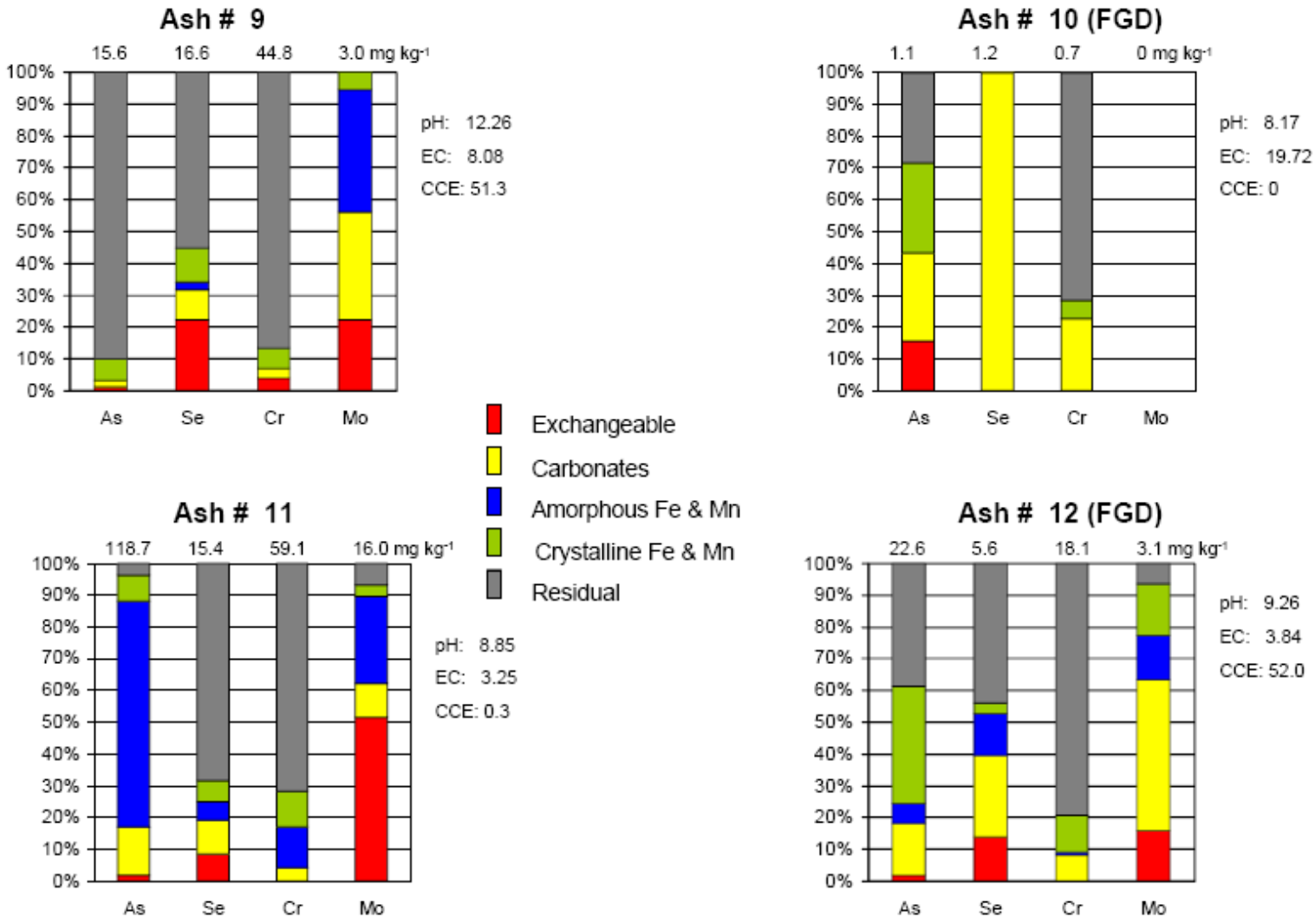
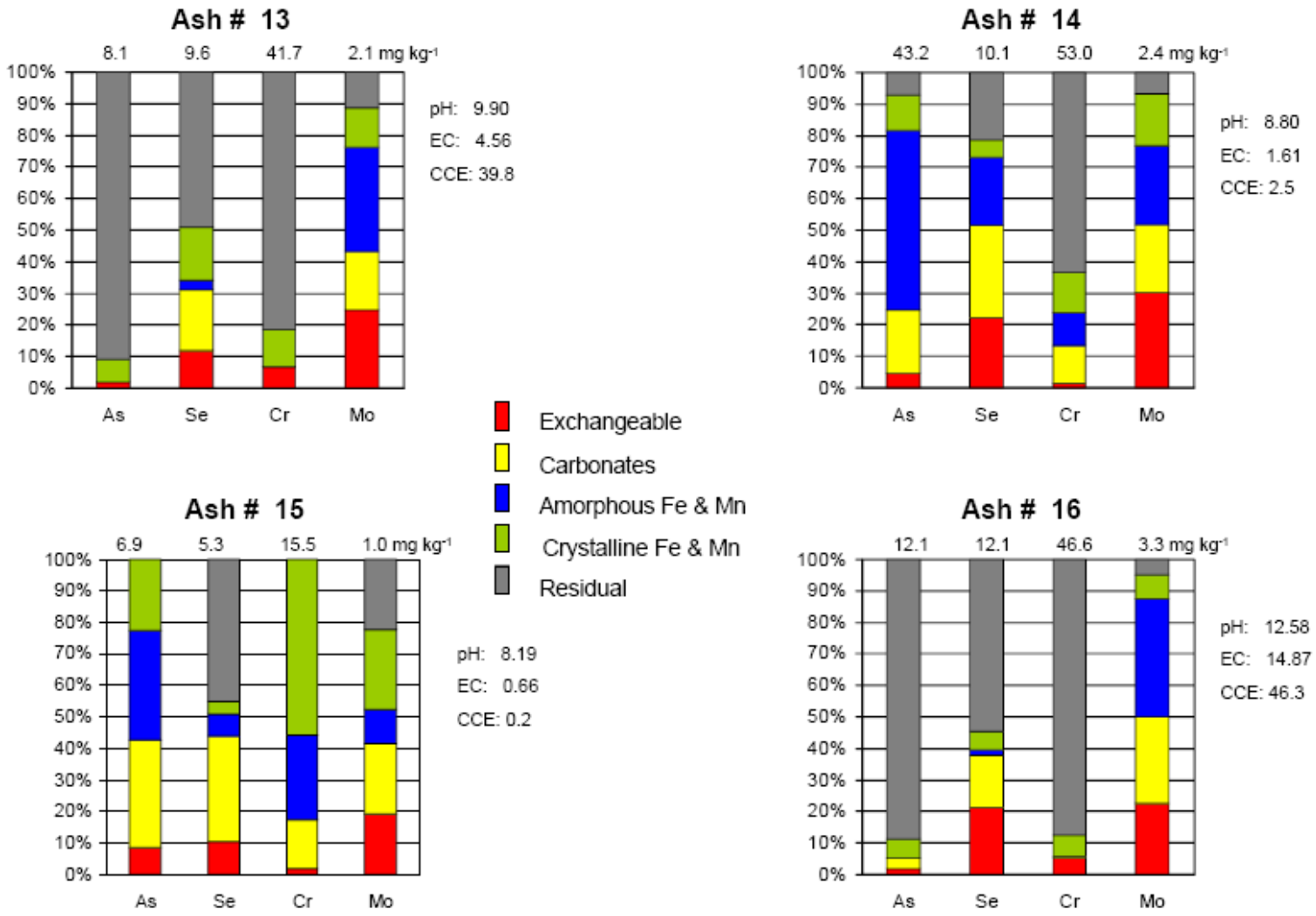
APPENDIX A.

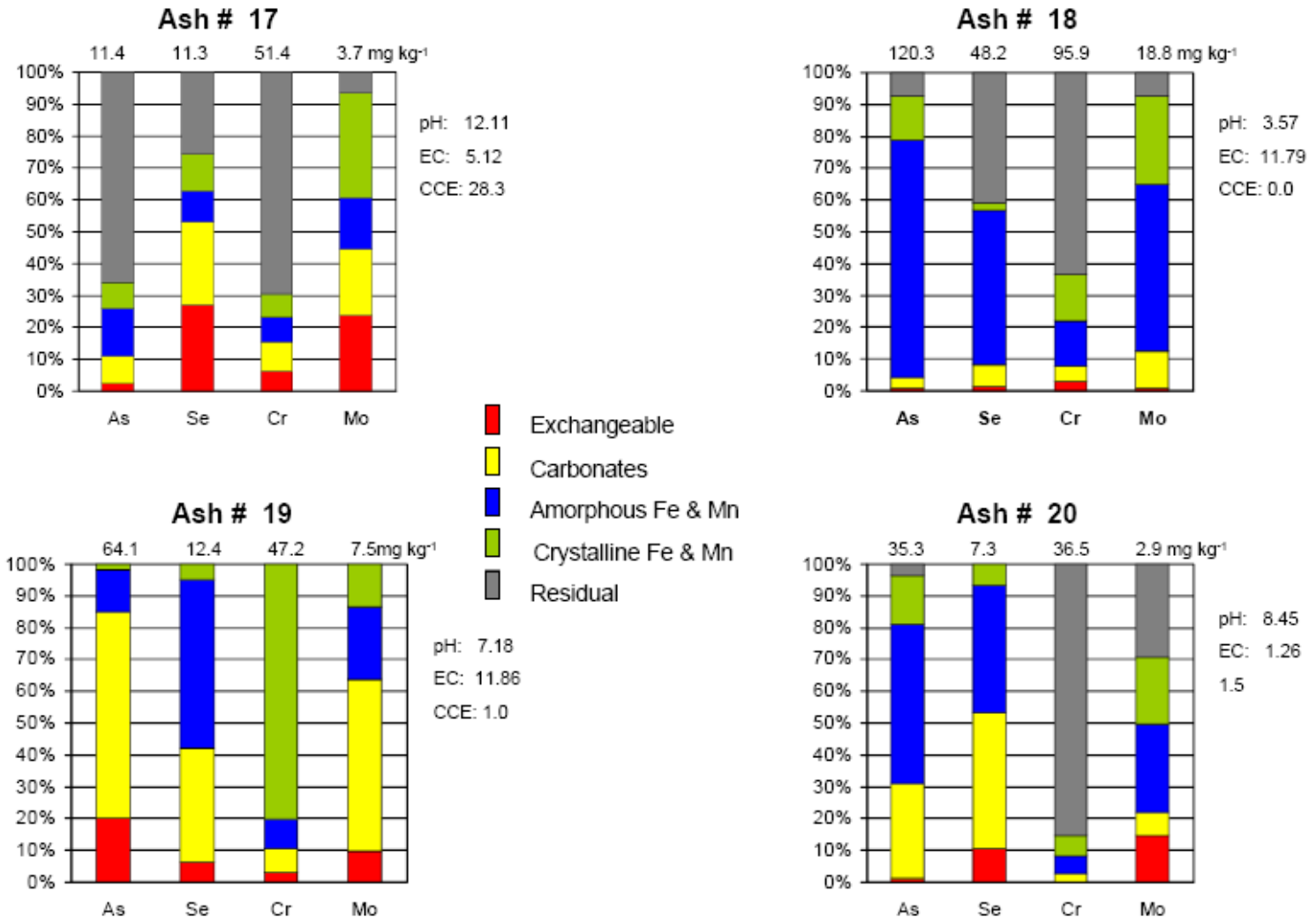
Data of the sequential extraction procedure for 28 CCPs are the mean in three replications.

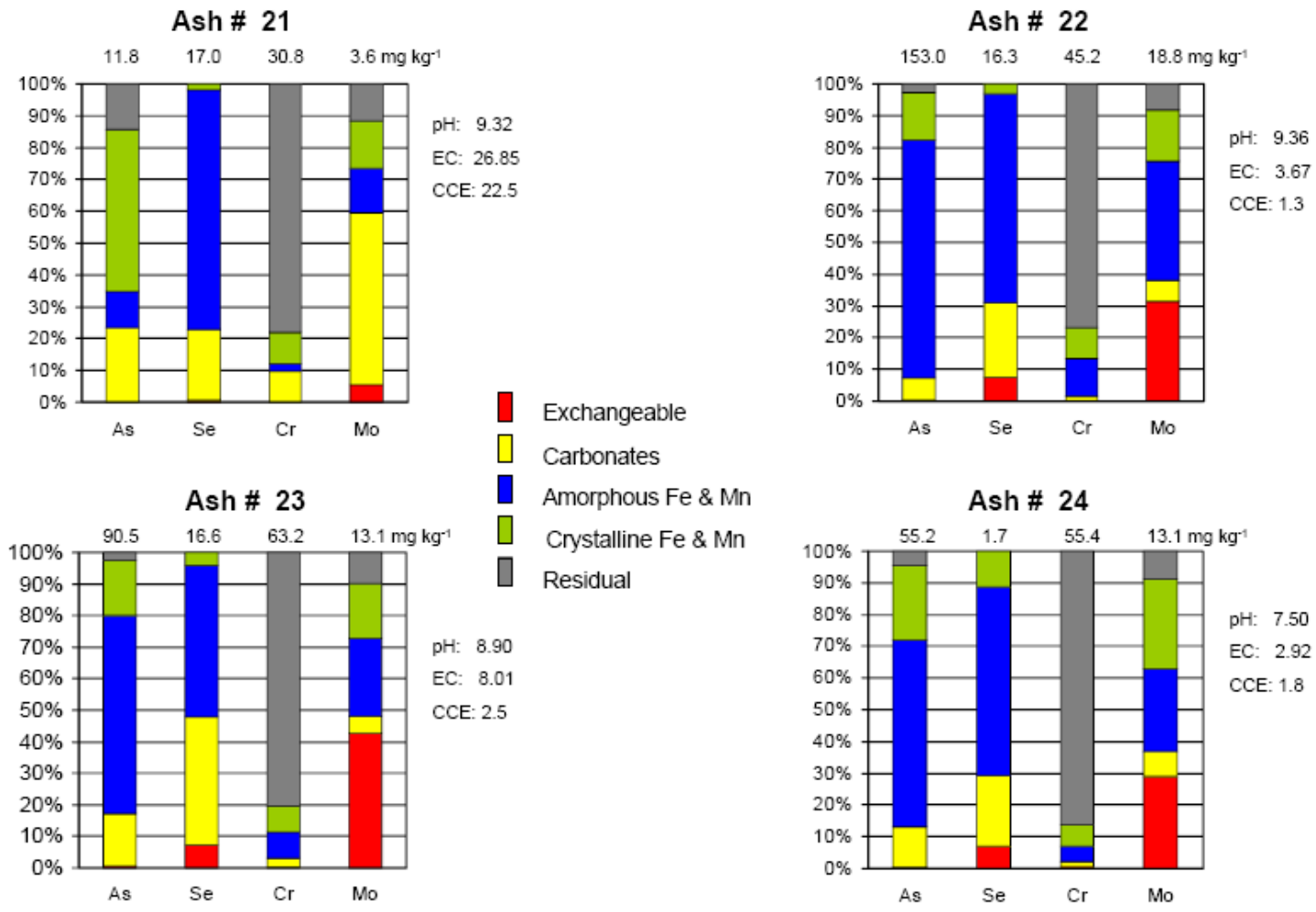

Ash # 1
59.4
12.0
53.6
10.7 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 5.27
EC: 3.19
CCE: 3.0
Ash # 2
21.7
17.1
37.5
6.3 mg kg-1
pH: 8.89
EC: 2.91
CCE: 21.5
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 3
23.3
15.5
68.9
11.2 mg kg-1
pH: 9.42
EC: 4.01
CCE: 7.1
Ash # 4
32.0
9.7
64.4
11.5 mg kg-1
pH: 9.30
EC: 3.39
CCE: 3.2

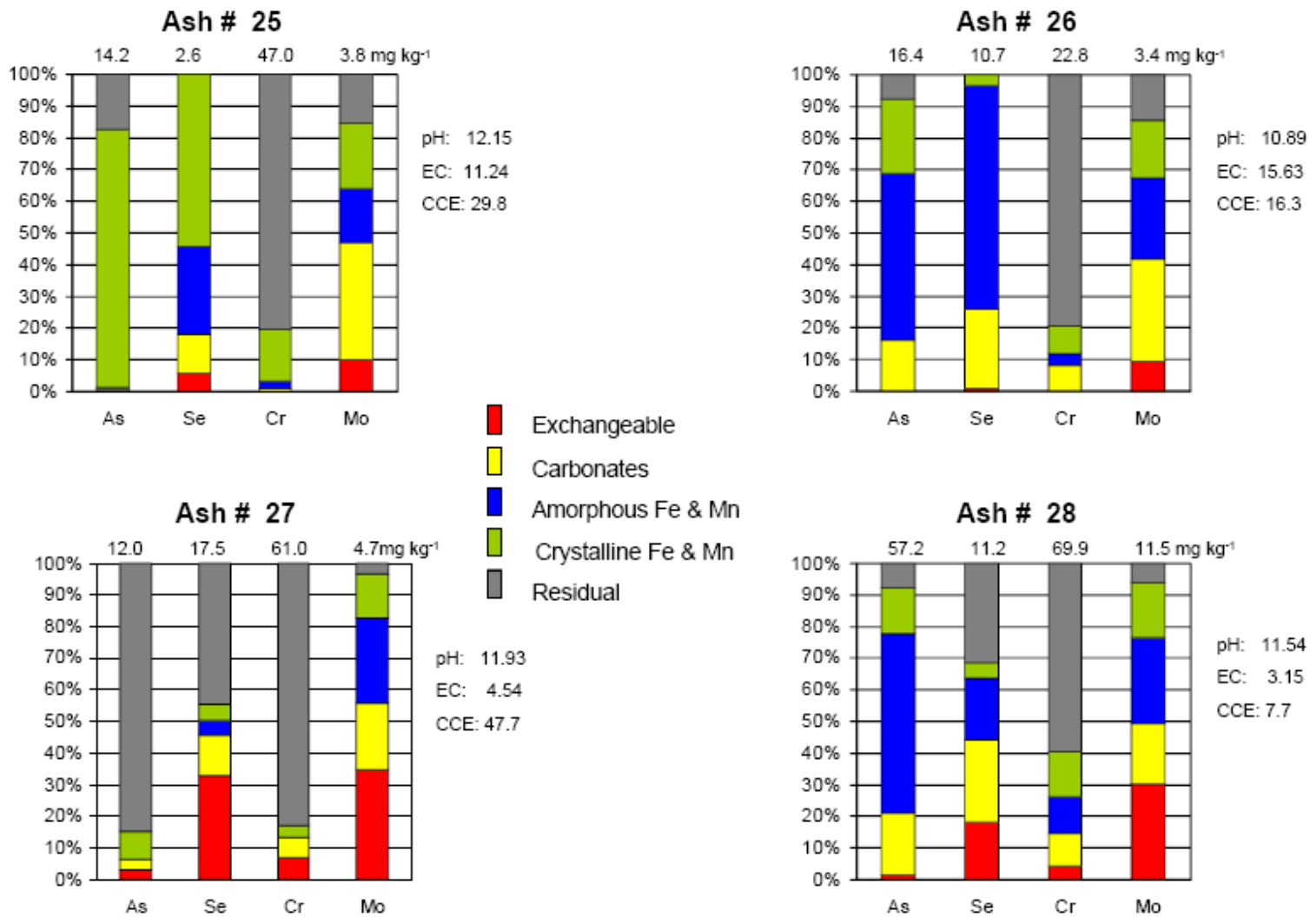

Ash # 5
19.9
10.3
50.5
9.2 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 10.69
EC: 4.11
CCE: 13.2
Ash # 6
42.5
14.1
83.0
15.4 mg kg-1
pH: 5.83
EC: 4.41
CCE: 3.2
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 7 (FGD)
24.1
6.7
32.6
2.5 mg kg-1
pH: 9.14
EC: 5.25
CCE: 41.0
Ash # 8
46.8
10.7
48.1
5.1 mg kg-1
pH: 12.35
EC: 12.12
CCE: 2.0


Ash # 9
15.6
16.6
44.8
3.0 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 12.26
EC: 8.08
CCE: 51.3
Ash # 10 (FGD)
1.1
1.2
0.7
0 mg kg-1
pH: 8.17
EC: 19.72
CCE: 0
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 11
118.7
15.4
59.1
16.0 mg kg-1
pH: 8.85
EC: 3.25
CCE: 0.3
Ash # 12 (FGD)
22.6
5.6
18.1
3.1 mg kg-1
pH: 9.26
EC: 3.84
CCE: 52.0


Ash # 13
8.1
9.6
41.7
2.1 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 9.90
EC: 4.56
CCE: 39.8
Ash # 14
43.2
10.1
53.0
2.4 mg kg-1
pH: 8.80
EC: 1.61
CCE: 2.5
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 15
6.9
5.3
15.5
1.0 mg kg-1
pH: 8.19
EC: 0.66
CCE: 0.2
Ash # 16
12.1
12.1
46.6
3.3 mg kg-1
pH: 12.58
EC: 14.87
CCE: 46.3


Ash # 17
11.4
11.3
51.4
3.7 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 12.11
EC: 5.12
CCE: 28.3
Ash # 18
120.3
48.2
95.9
18.8 mg kg-1
pH: 3.57
EC: 11.79
CCE: 0.0
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 19
64.1
12.4
47.2
7.5mg kg-1
pH: 7.18
EC: 11.86
CCE: 1.0
Ash # 20
35.3
7.3
36.5
2.9 mg kg-1
pH: 8.45
EC: 1.26
1.5


Ash # 21
11.8
17.0
30.8
3.6 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 9.32
EC: 26.85
CCE: 22.5
Ash # 22
153.0
16.3
45.2
18.8 mg kg-1
pH: 9.36
EC: 3.67
CCE: 1.3
Ash # 23
90.5
16.6
63.2
13.1 mg kg-1
pH: 8.90
EC: 8.01
CCE: 2.5
Ash # 24
55.2
1.7
55.4
13.1 mg kg-1
pH: 7.50
EC: 2.92
CCE: 1.8
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual


Ash # 25
14.2
2.6
47.0
3.8 mg kg-1
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As
Se
Cr
Mo
pH: 12.15
EC: 11.24
CCE: 29.8
Ash # 26
16.4
10.7
22.8
3.4 mg kg-1
pH: 10.89
EC: 15.63
CCE: 16.3
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual
Ash # 27
12.0
17.5
61.0
4.7mg kg-1
pH: 11.93
EC: 4.54
CCE: 47.7
Ash # 28
57.2
11.2
69.9
11.5 mg kg-1
pH: 11.54
EC: 3.15
CCE: 7.7

APPENDIX B.

Leachate data for column leaching experiment with acid forming coal refuse. Data are the mean of three replications.

Table B-1. Leachate B from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
Id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	6.27	8.03	8.73	8.24	8.43	10.75	7.77	8.46	7.43	7.99	7.14
7	20	3.20	4.62	5.10	5.40	5.50	7.37	5.74	6.59	6.85	8.98	8.11
11	10	70.94	54.82	35.47	29.94	27.50	28.34	18.22	18.09	15.28	14.45	11.69
11	20	135.2	87.45	70.23	44.17	29.10	31.40	17.83	14.44	12.11	11.74	8.99
16	10	0.96	0.75	0.74	0.75	0.74	0.97	0.67	0.79	0.83	0.91	0.84
16	20	0.67	1.28	1.38	1.28	1.35	1.83	1.25	1.37	1.37	1.43	1.24
18	10	21.59	15.88	9.15	6.60	6.47	6.86	4.04	3.88	2.92	2.46	1.90
18	20	35.20	24.66	14.47	11.88	10.02	8.91	5.93	5.90	5.22	4.00	3.22
27	10	2.13	1.09	0.94	0.96	0.76	1.15	0.81	0.94	1.03	1.21	1.10
27	20	0.42	0.85	1.17	1.49	1.20	1.84	1.33	1.33	1.31	1.44	1.20
No lime control		0.23	0.14	0.14	0.12	0.17	0.51	0.20	0.28	0.21	0.33	0.31
limed control		0.06	0.04	0.04	0.03	0.02	0.04	0.01	0.01	0.04	0.03	0.02

Table B-2. Leachate As from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
7	20	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.04	0.04	0.04
11	10	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.02	<0.03	<0.03
11	20	<0.03	<0.03	<0.03	0.047	<0.03	<0.03	0.05	0.04	0.04	0.16	0.06
16	10	0.070	0.068	0.059	0.054	0.054	<0.03	0.04	0.04	0.05	0.05	0.04
16	20	0.115	0.105	0.068	0.070	0.052	0.035	0.04	0.06	0.06	0.05	0.04
18	10	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.09	0.06	0.05
18	20	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.04	0.05
27	10	<0.03	<0.03	<0.03	<0.03	<0.03	0.039	<0.03	<0.03	<0.03	0.04	0.04
27	20	0.043	0.055	0.036	0.049	0.030	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
No lime control		<0.03	<0.03	<0.03	<0.03	0.215	1.845	5.01	10.45	12.64	17.32	20.18
limed control		<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	0.03	<0.03	<0.03	<0.03	<0.03

Table B-3. Leachate Cr from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
Id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.002	<0.006	<0.006	<0.006	<0.006
7	20	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.002	<0.006	<0.006	<0.006	<0.006
11	10	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.002	<0.006	<0.006	<0.006	<0.006
11	20	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.002	<0.006	<0.006	<0.006	<0.006
16	10	0.254	0.062	0.027	0.015	0.011	0.015	0.009	0.01	0.01	0.01	0.01
16	20	0.444	0.096	0.031	0.013	0.009	0.012	<0.006	0.01	<0.006	<0.006	<0.006
18	10	0.059	0.031	0.019	0.02	0.034	0.072	0.052	0.10	0.15	0.22	0.19
18	20	0.145	0.06	0.038	0.031	0.033	0.056	0.035	0.05	0.06	0.07	0.07
27	10	0.246	0.077	0.036	0.023	0.016	0.025	0.013	0.01	0.01	0.01	0.01
27	20	0.472	0.08	<0.03	0.012	<0.006	<0.006	0.004	<0.006	<0.006	<0.006	<0.006
No lime control		0.00	0.00	0.008	0.039	0.113	0.325	0.283	0.44	0.50	0.53	0.57
limed control		0.00	0.00	0.00	0.00	0.00	0.00	<0.002	0.00	<0.006	<0.006	<0.006

Table B-4. Leachate Cu from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	0.037	0.038	0.009	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
7	20	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
11	10	0.277	0.226	0.252	0.284	0.349	0.509	0.563	0.885	1.259	1.826	2.009
11	20	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.006
16	10	0.010	0.005	0.003	0.003	0.004	0.008	0.009	0.010	0.010	0.011	0.006
16	20	0.012	0.007	0.005	0.003	<0.002	0.004	0.007	0.010	0.008	0.007	0.007
18	10	2.672	2.624	2.279	2.707	4.123	6.092	4.820	6.380	5.084	6.021	5.024
18	20	2.901	2.707	1.869	1.718	2.088	2.997	2.782	3.031	4.230	3.728	3.621
27	10	0.005	<0.002	<0.002	<0.002	<0.002	0.004	0.004	0.005	0.005	0.005	0.003
27	20	0.010	<0.002	<0.002	0.003	<0.002	<0.002	<0.002	0.003	0.004	0.003	0.003
No lime control		2.223	1.965	3.396	6.468	9.395	15.434	15.550	17.090	14.190	11.476	10.290
limed control		<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.005	<0.002	<0.002	<0.002	<0.002

Table B-5. Leachate Ni from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash Id #	Ash rate %	Day of Leaching 1	4	8	11	15	18	22	25	32	39	46
7	10	0.024	0.014	0.011	0.005	0.005	0.028	0.006	0.007	0.006	0.006	0.006
7	20	0.005	<0.004	<0.004	<0.004	<0.004	0.005	0.006	0.006	0.006	0.006	0.006
11	10	2.365	2.362	2.077	2.012	2.097	2.505	1.938	2.352	2.488	2.921	3.119
11	20	1.284	0.992	0.802	0.518	0.393	0.43	0.278	0.211	0.180	0.145	0.175
16	10	<0.004	<0.004	<0.004	<0.004	<0.004	0.013	0.006	0.006	0.006	0.006	0.006
16	20	<0.004	<0.004	<0.004	<0.004	<0.004	0.007	0.006	0.006	0.006	0.006	0.006
18	10	7.424	6.579	5.289	5.30	6.322	8.879	8.760	9.760	9.680	9.380	8.310
18	20	7.719	6.384	4.745	4.851	4.542	5.495	5.470	6.210	6.147	6.560	6.330
27	10	0.011	<0.004	<0.004	<0.004	<0.004	0.013	0.006	0.006	0.006	0.006	0.006
27	20	<0.004	<0.004	<0.004	<0.004	<0.004	0.017	0.006	0.006	0.006	0.006	0.006
No lime control		4.324	4.024	5.626	7.644	10.259	15.083	15.590	19.000	13.810	11.510	9.620
limed control		0.313	0.148	0.105	0.086	0.092	0.086	0.056	0.049	0.036	0.037	0.032

Table B-6. Leachate Se from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash Id #	Ash rate %	Day of Leaching 1	4	8	11	15	18	22	25	32	39	46
7	10	1.292	0.553	0.192	0.026	0.070	0.067	<0.03	<0.03	0.039	<0.03	<0.03
7	20	0.628	0.504	0.226	0.085	0.091	0.157	0.054	0.045	0.072	0.079	0.065
11	10	0.885	0.654	0.398	0.293	0.122	0.124	0.037	<0.03	<0.03	<0.03	<0.03
11	20	1.029	0.476	0.169	0.026	0.026	0.026	<0.03	<0.03	<0.03	<0.03	<0.03
16	10	0.422	0.231	0.115	0.081	0.09	0.162	0.061	0.076	0.047	0.038	<0.03
16	20	0.213	0.161	0.083	0.077	0.074	0.109	0.053	0.070	0.056	<0.03	<0.03
18	10	1.517	1.199	0.734	0.453	0.399	0.385	0.148	0.120	0.057	0.045	0.068
18	20	1.390	1.209	0.857	0.685	0.566	0.472	0.347	0.272	0.186	0.104	0.075
27	10	0.689	0.452	0.275	0.241	0.152	0.212	0.071	0.055	0.033	0.072	0.035
27	20	0.167	0.058	0.059	0.072	0.042	0.159	0.039	0.031	<0.03	0.044	<0.03
No lime control		0.885	0.401	0.257	0.190	0.574	1.234	0.461	0.900	0.410	0.830	0.710
limed control		1.299	0.512	0.221	0.084	0.169	0.143	<0.03	<0.03	0.047	0.073	0.067

Table B-7. Leachate Zn from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
Id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	0.01	0.01	<0.004	<0.004	0.01	0.00	<0.004	<0.004	<0.004	0.005	<0.004
7	20	<0.004	<0.004	<0.004	<0.004	<0.004	0.00	<0.004	<0.004	<0.004	<0.004	<0.004
11	10	4.02	3.29	2.82	2.70	2.79	3.61	3.178	4.196	5.246	6.817	8.633
11	20	0.97	0.62	0.45	0.26	0.21	0.18	0.096	0.079	0.079	0.059	0.113
16	10	<0.004	<0.004	<0.004	<0.004	<0.004	0.00	<0.004	<0.004	<0.004	<0.004	<0.004
16	20	<0.004	<0.004	<0.004	<0.004	<0.004	0.00	<0.004	<0.004	<0.004	<0.004	<0.004
18	10	14.17	13.05	11.00	11.93	14.23	22.35	23.10	28.53	34.63	38.54	38.28
18	20	15.17	13.20	10.12	10.73	10.16	12.80	12.95	15.59	19.12	19.95	20.41
27	10	<0.004	<0.004	<0.004	<0.004	<0.004	0.00	<0.004	<0.004	<0.004	<0.004	<0.004
27	20	<0.004	<0.004	<0.004	<0.004	<0.004	0.00	<0.004	<0.004	<0.004	<0.004	<0.004
No lime control		9.01	8.75	14.16	23.54	41.20	70.36	78.79	90.35	79.58	62.67	46.14
limed control		0.04	0.02	<0.004	0.01	0.02	0.01	<0.004	<0.004	0.010	<0.004	<0.004

Table B-8. Leachate Fe from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash	Ash	Day of Leaching										
id #	rate %	1	4	8	11	15	18	22	25	32	39	46
7	10	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.04	0.02
7	20	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.01
11	10	31.70	3.81	0.10	0.15	0.19	0.87	0.21	0.35	0.79	0.93	1.08
11	20	3.85	0.37	0.22	0.17	0.42	0.19	0.02	0.05	0.12	0.78	0.44
16	10	0.18	0.22	0.12	0.09	0.09	0.01	0.01	0.01	0.01	0.01	0.01
16	20	0.41	0.46	0.26	0.19	0.13	0.05	0.07	0.08	0.05	0.03	0.01
18	10	96.40	15.01	3.85	2.13	3.09	7.14	12.50	28.68	82.28	90.61	127.75
18	20	75.44	17.03	8.85	7.46	3.98	3.42	5.16	6.87	13.34	18.47	23.84
27	10	0.02	0.03	0.02	0.00	0.03	0.00	0.01	0.01	0.01	0.01	0.01
27	20	0.38	0.39	0.28	0.26	0.14	0.02	0.01	0.01	0.03	0.01	0.01
No lime control		55.49	5.67	12.77	111	347	1192	3303	5301	6274	6890	6928
limed control		0.03	0.01	0.00	0.01	0.02	0.02	0.16	0.25	0.35	0.28	0.26

Table B-9. Leachate Mo from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% (v:v) of 4 selected fly ashes and 1 FGD product. Leachate concentration reported as mg L^{-1}.

Ash id #	Ash rate %	Day of Leaching 1	4	8	11	15	18	22	25	32	39	46
7	10	0.042	0.074	0.08	0.081	0.077	0.074	0.072	0.053	0.055	0.032	0.035
7	20	0.027	0.048	0.052	0.05	0.048	0.052	0.050	0.051	0.042	0.048	0.034
11	10	<0.007	<0.007	<0.007	<0.007	<0.007	0.007	<0.007	<0.007	<0.007	<0.007	0.018
11	20	0.129	0.131	0.152	0.137	0.126	0.176	0.145	0.137	0.130	0.107	0.078
16	10	0.73	0.624	0.488	0.418	0.398	0.395	0.320	0.290	0.206	0.201	0.128
16	20	1.084	0.873	0.662	0.573	0.459	0.505	0.362	0.366	0.286	0.216	0.174
18	10	<0.007	<0.007	<0.007	<0.007	<0.007	0.007	<0.007	<0.007	<0.007	<0.007	0.018
18	20	<0.007	<0.007	<0.007	<0.007	<0.007	0.007	<0.007	<0.007	<0.007	<0.007	0.018
27	10	0.585	0.628	0.555	0.524	0.349	0.451	0.273	0.260	0.182	0.198	0.160
27	20	1.424	0.943	0.871	0.916	0.643	0.757	0.520	0.433	0.372	0.324	0.251
No lime control		<0.007	<0.007	<0.007	<0.007	<0.007	0.035	<0.007	<0.007	<0.007	<0.007	<0.007
limed control		<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007	<0.007

APPENDIX C.

Fig C-1. Leachate As from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

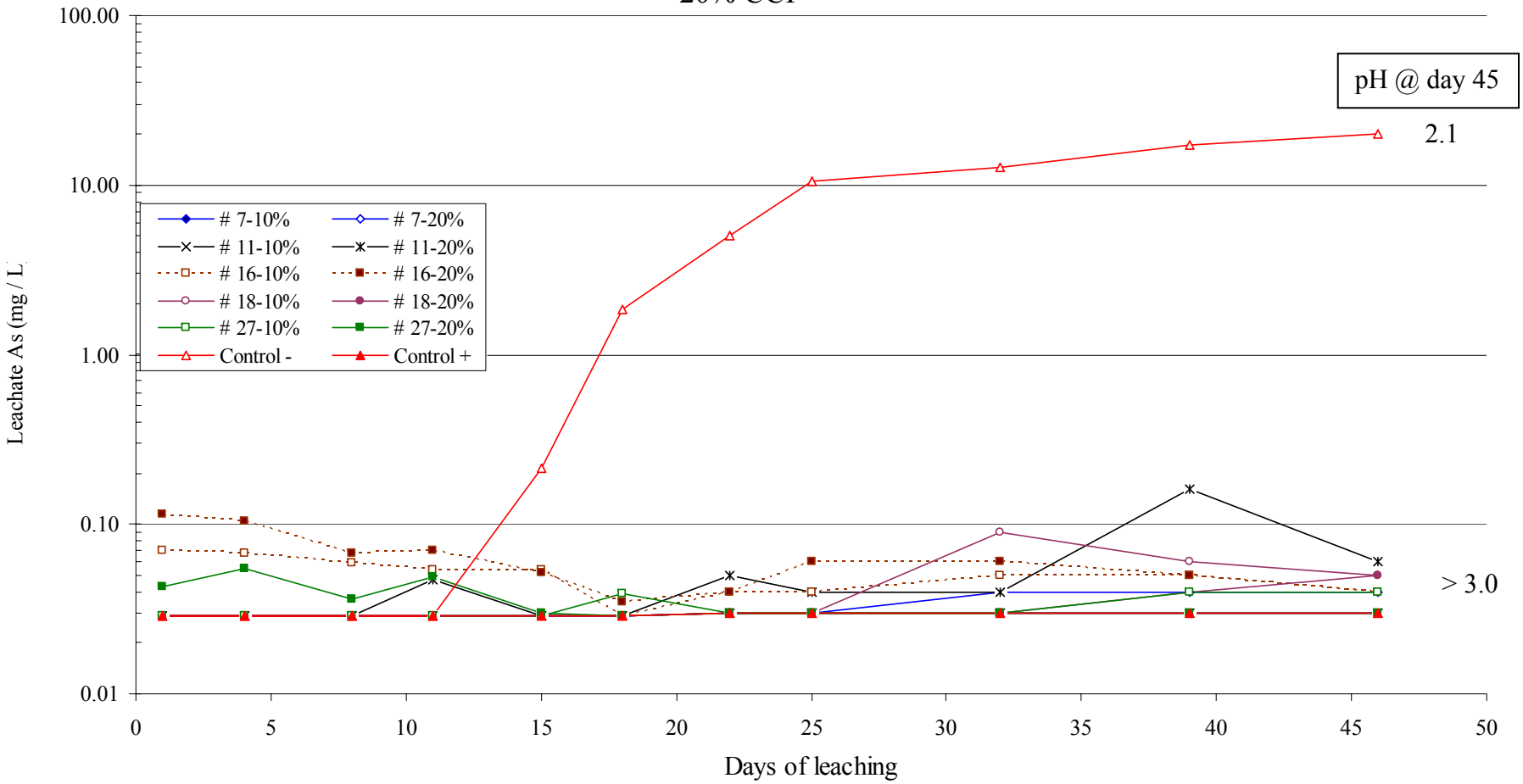


Fig. C - 2. Leachate B from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

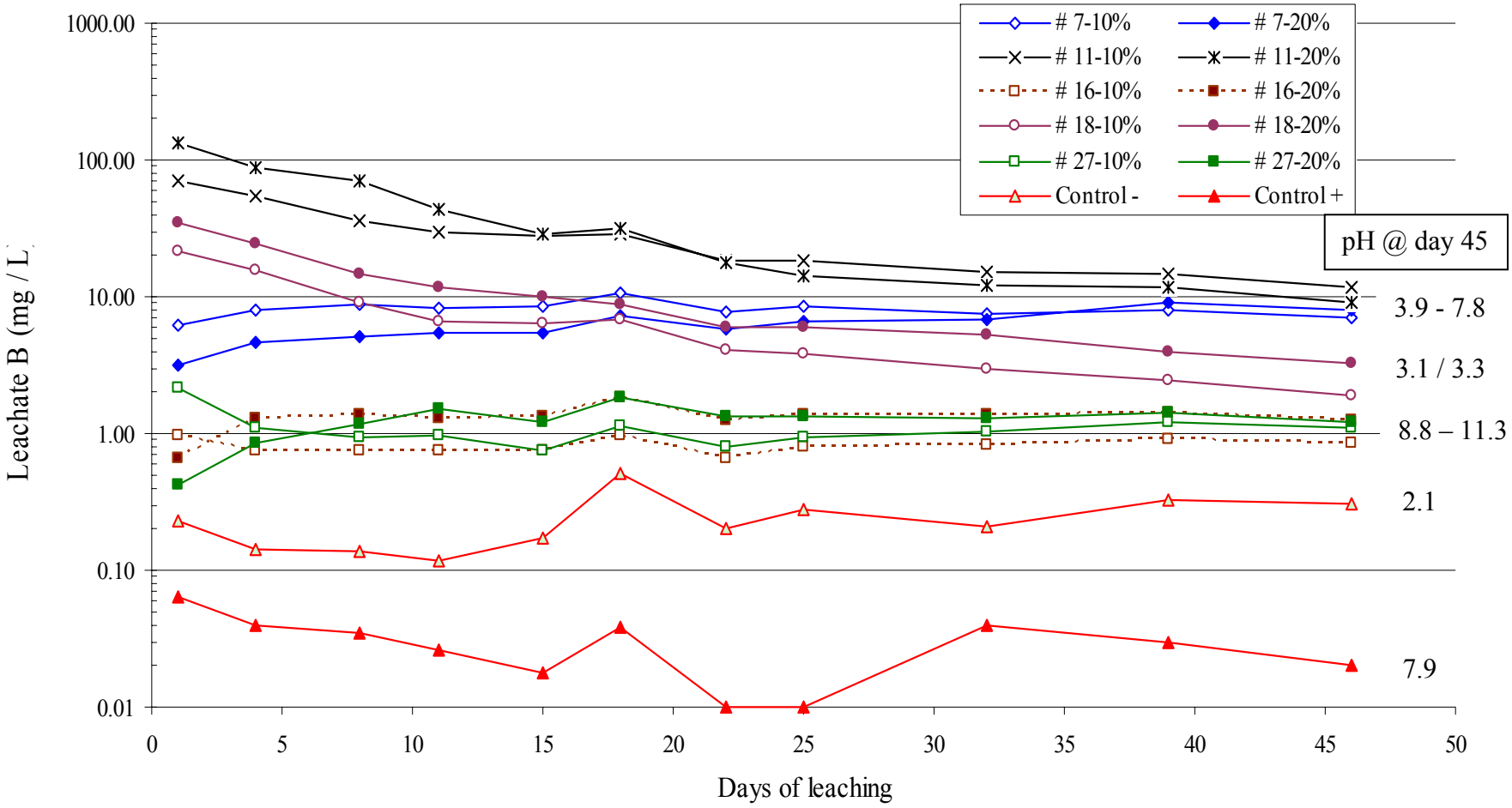


Fig. C-3. Leachate Cr from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

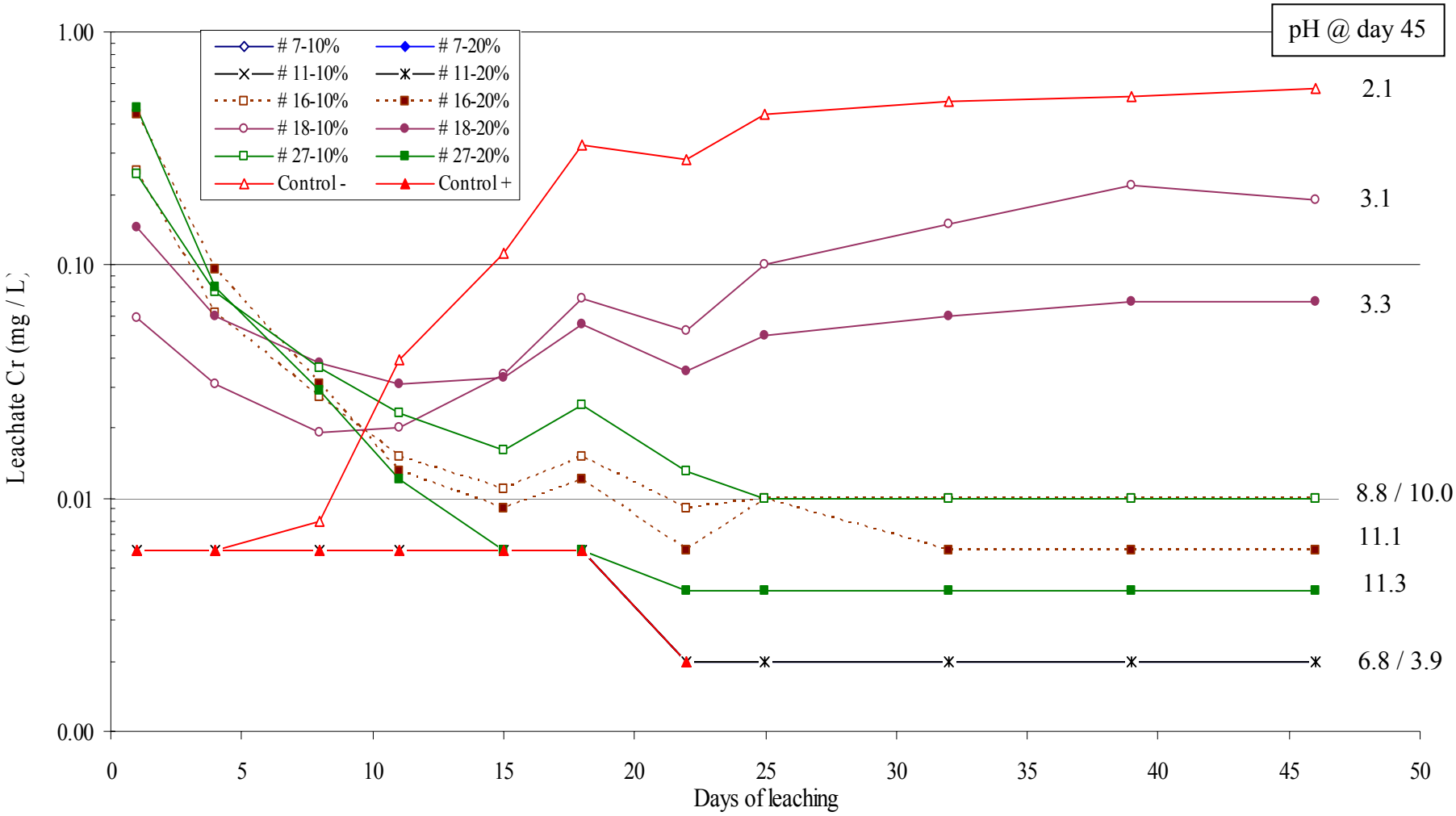


Fig. C-4. Leachate Cu from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

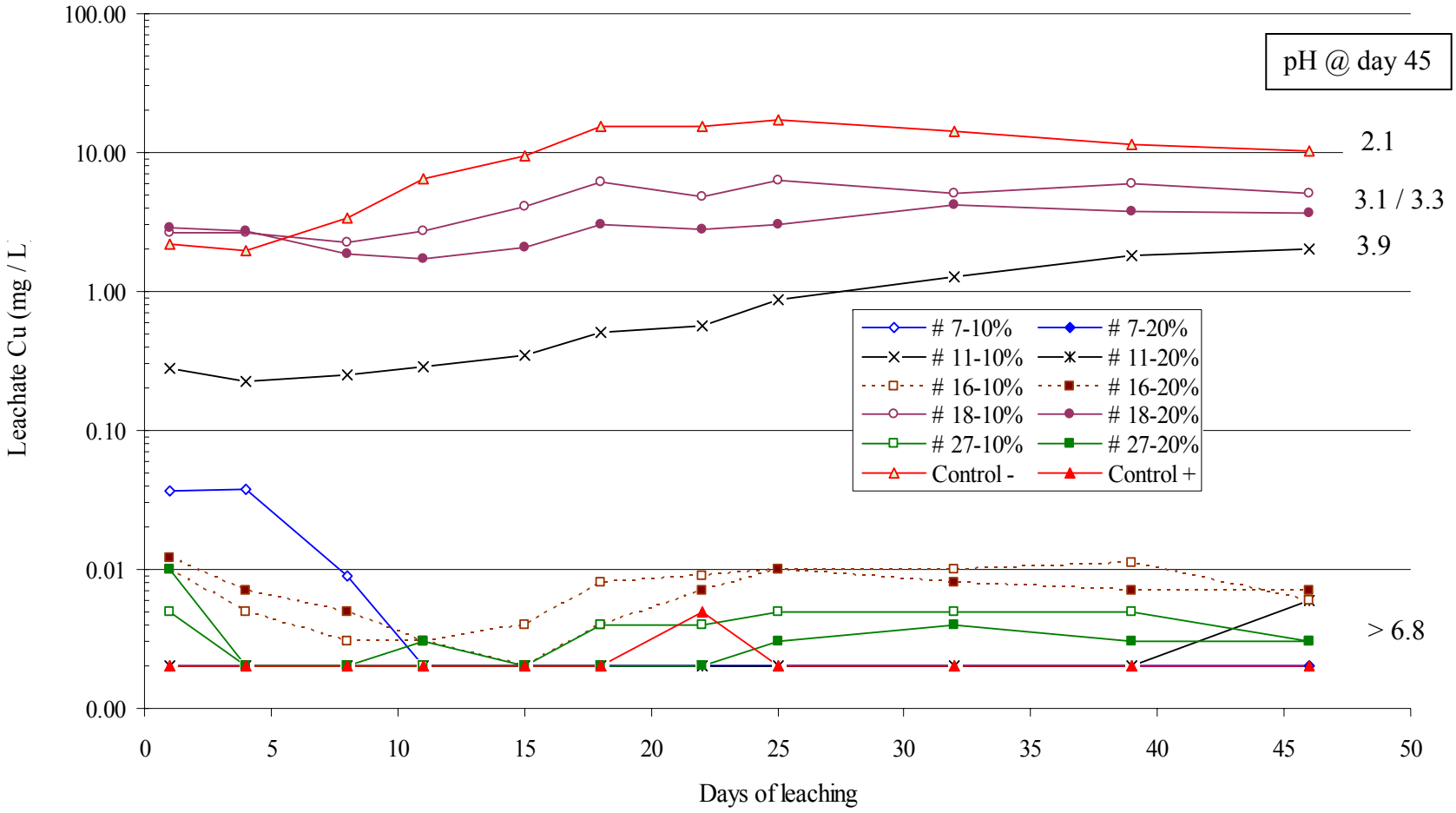


Fig C-5. Leachate Mo from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

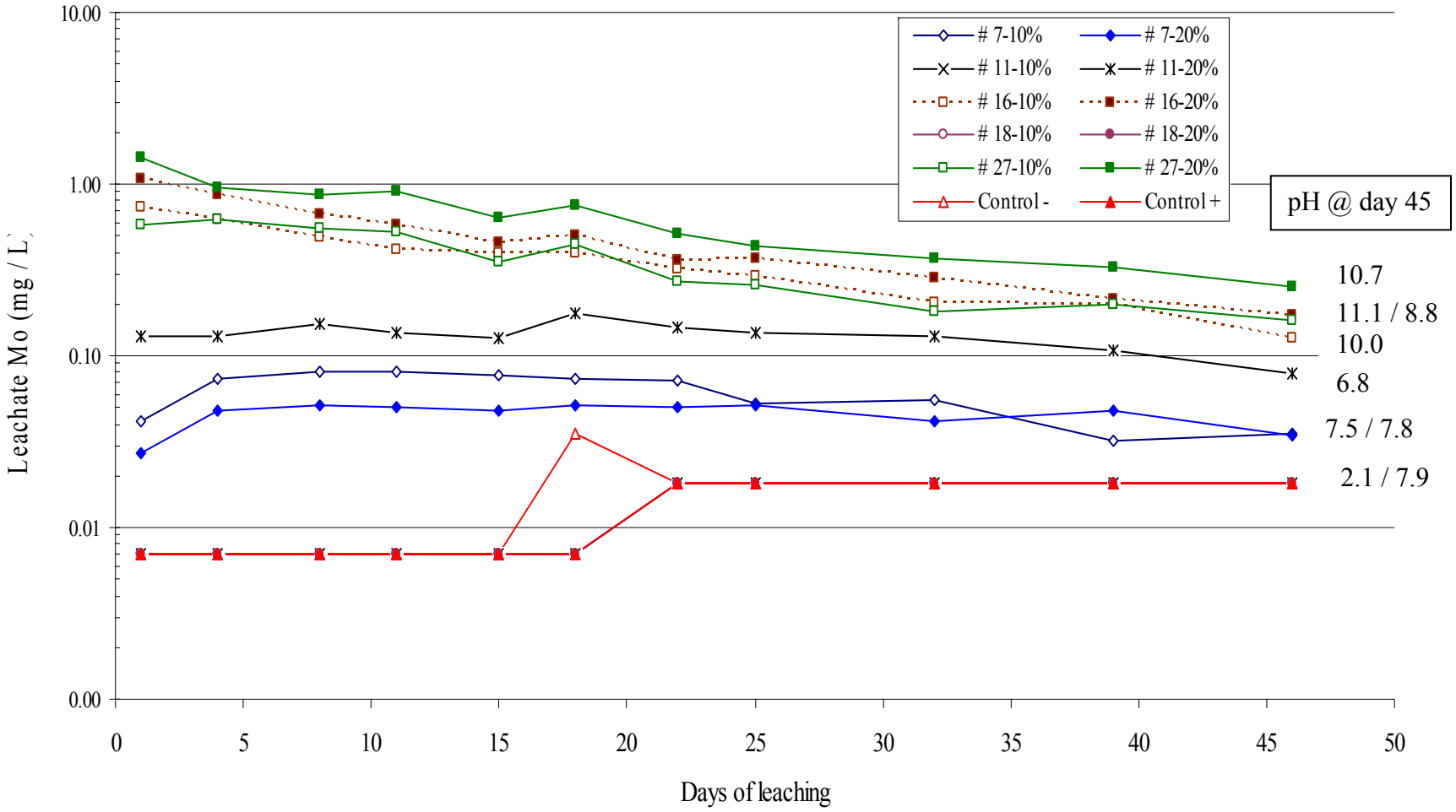


Fig. C-6. Leachate Ni from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

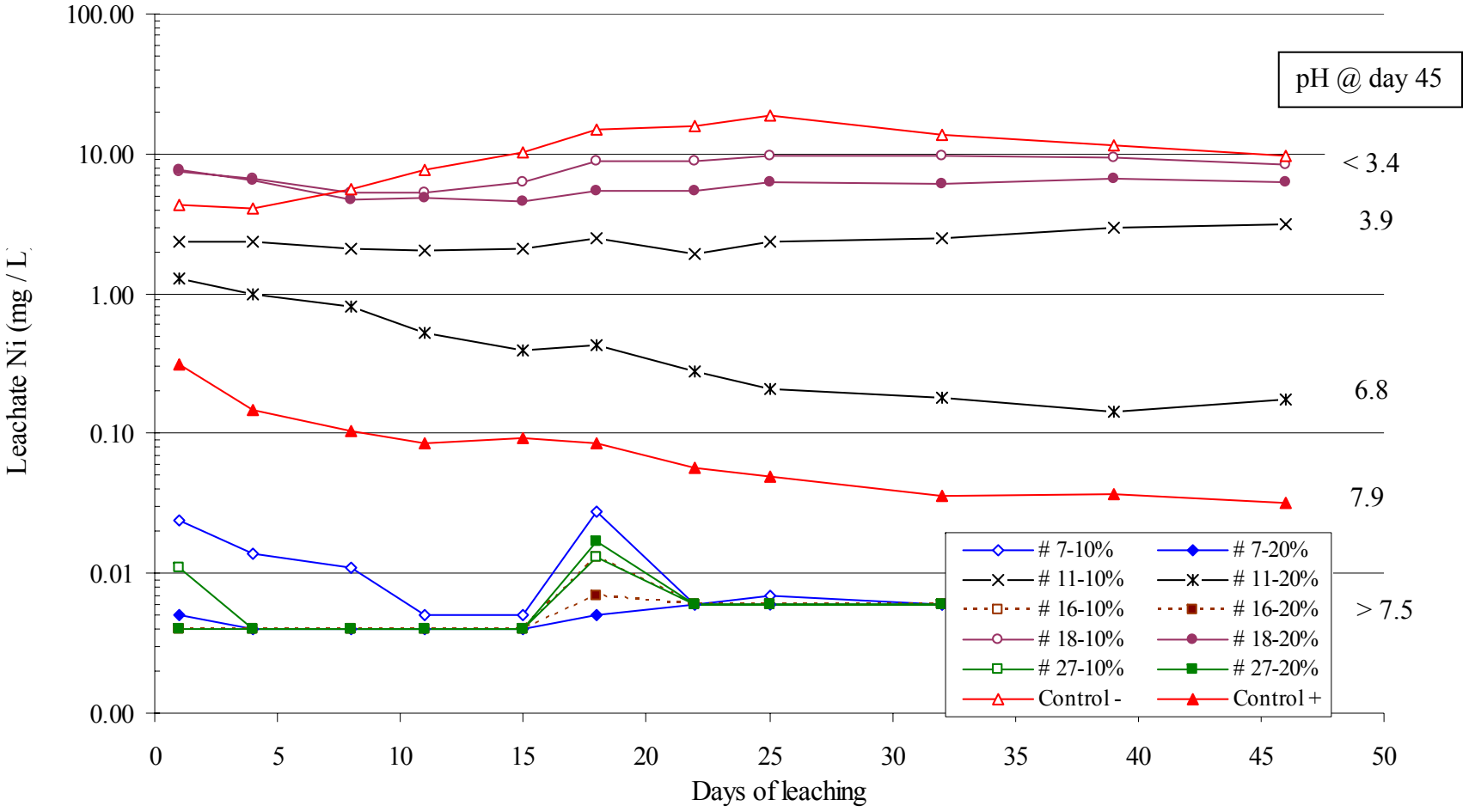


Fig C-7. Leachate Se from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

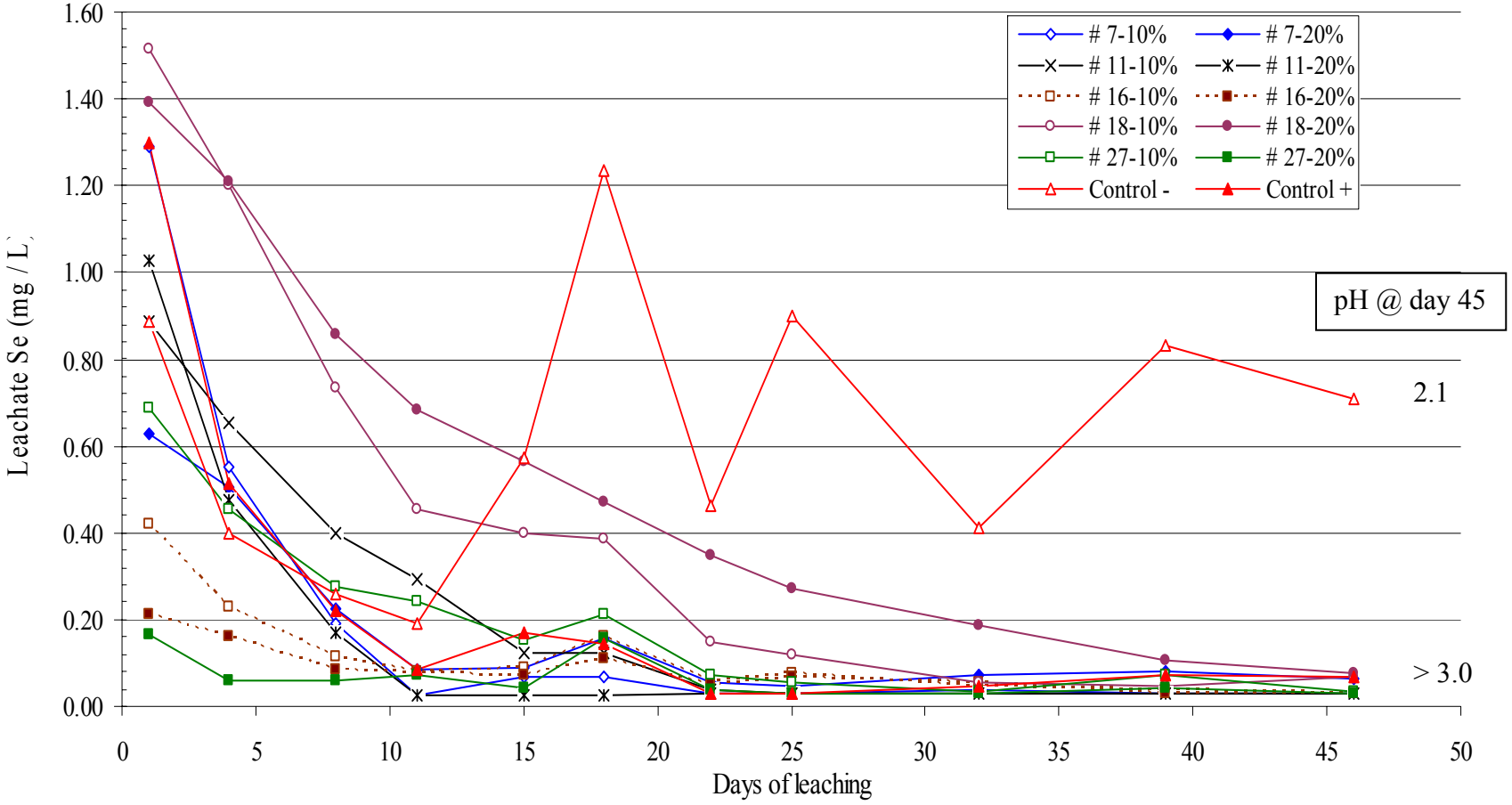


Fig. C-8. Leachate Zn from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

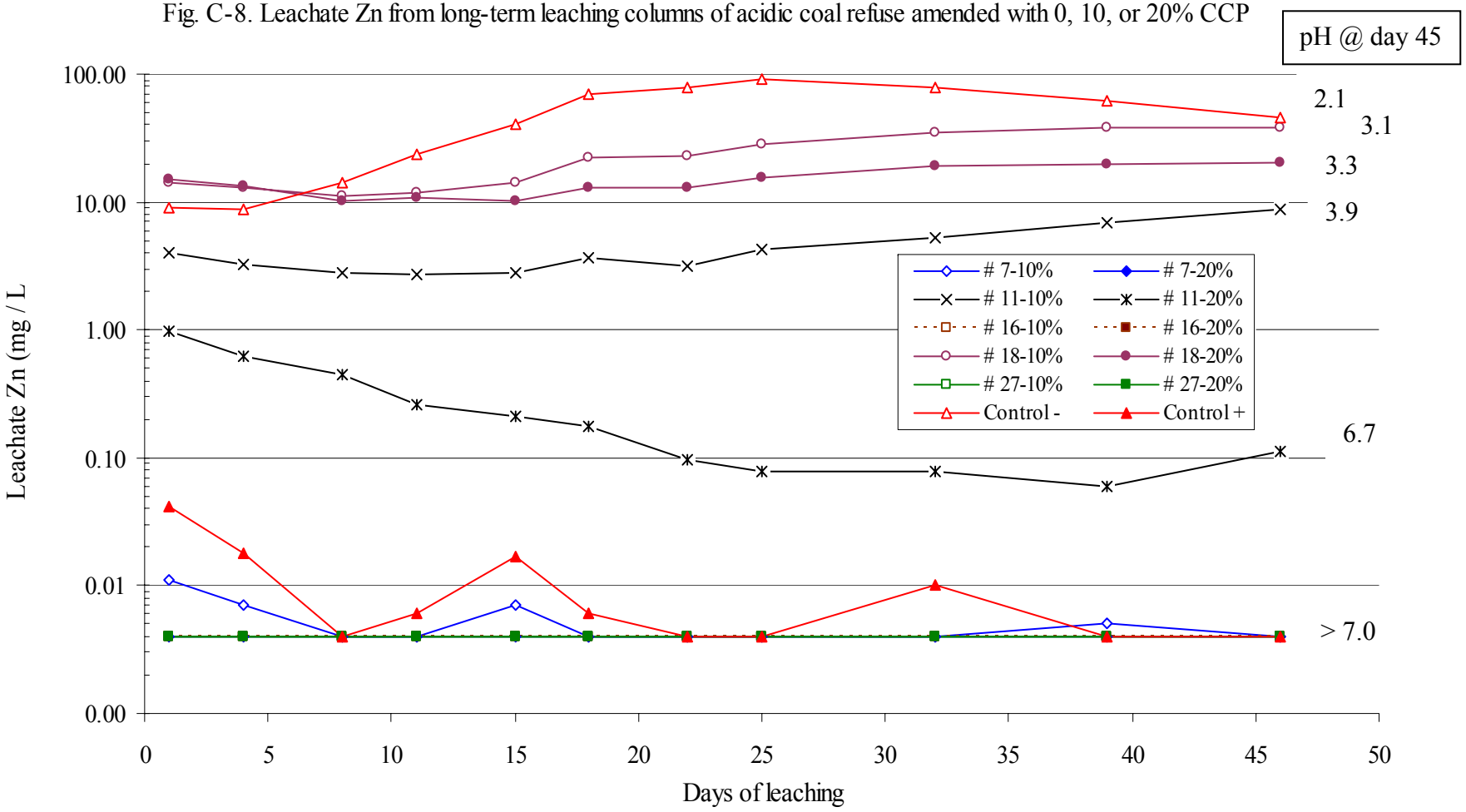


Fig C-9. Leachate Fe from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP

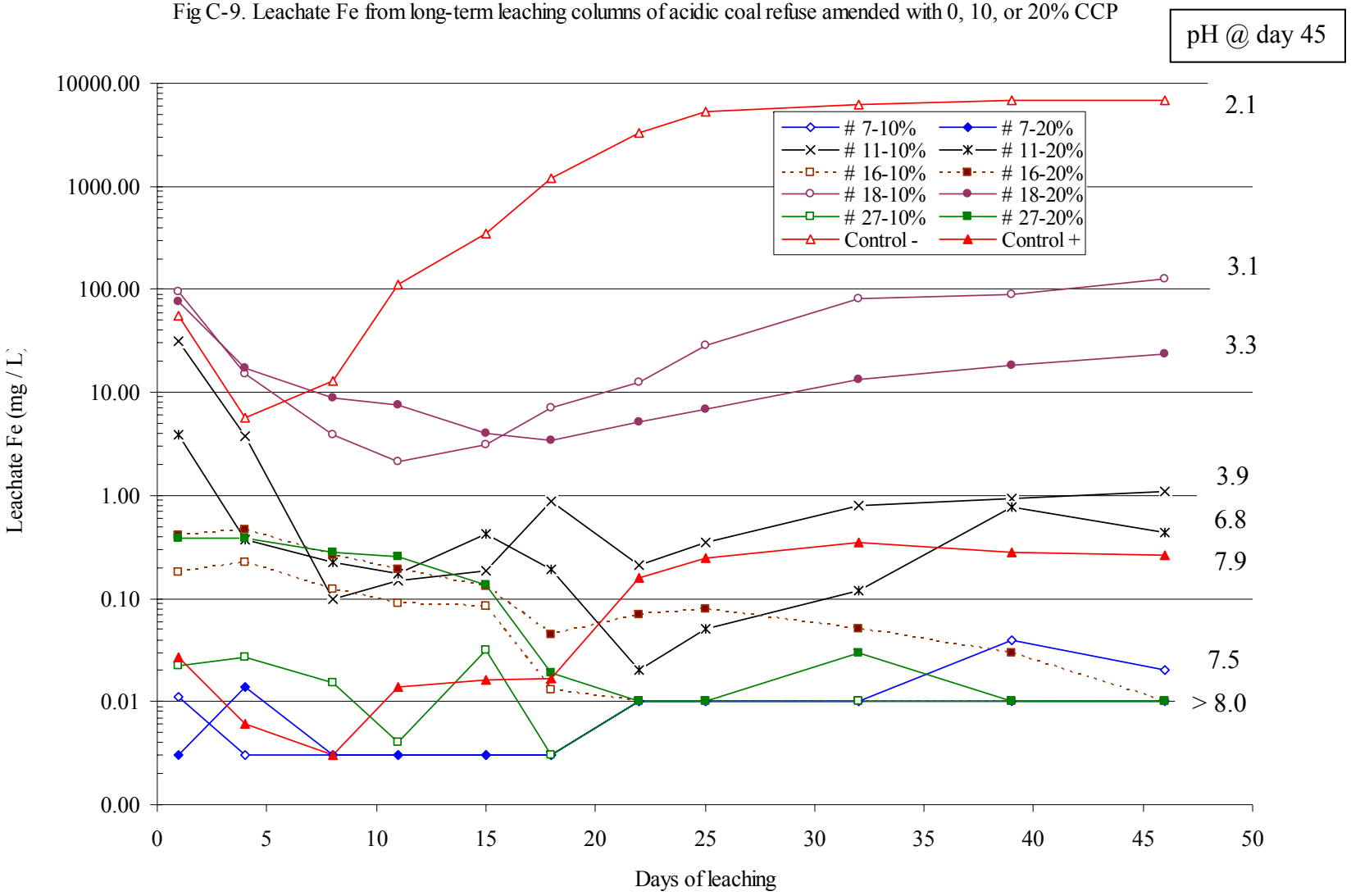
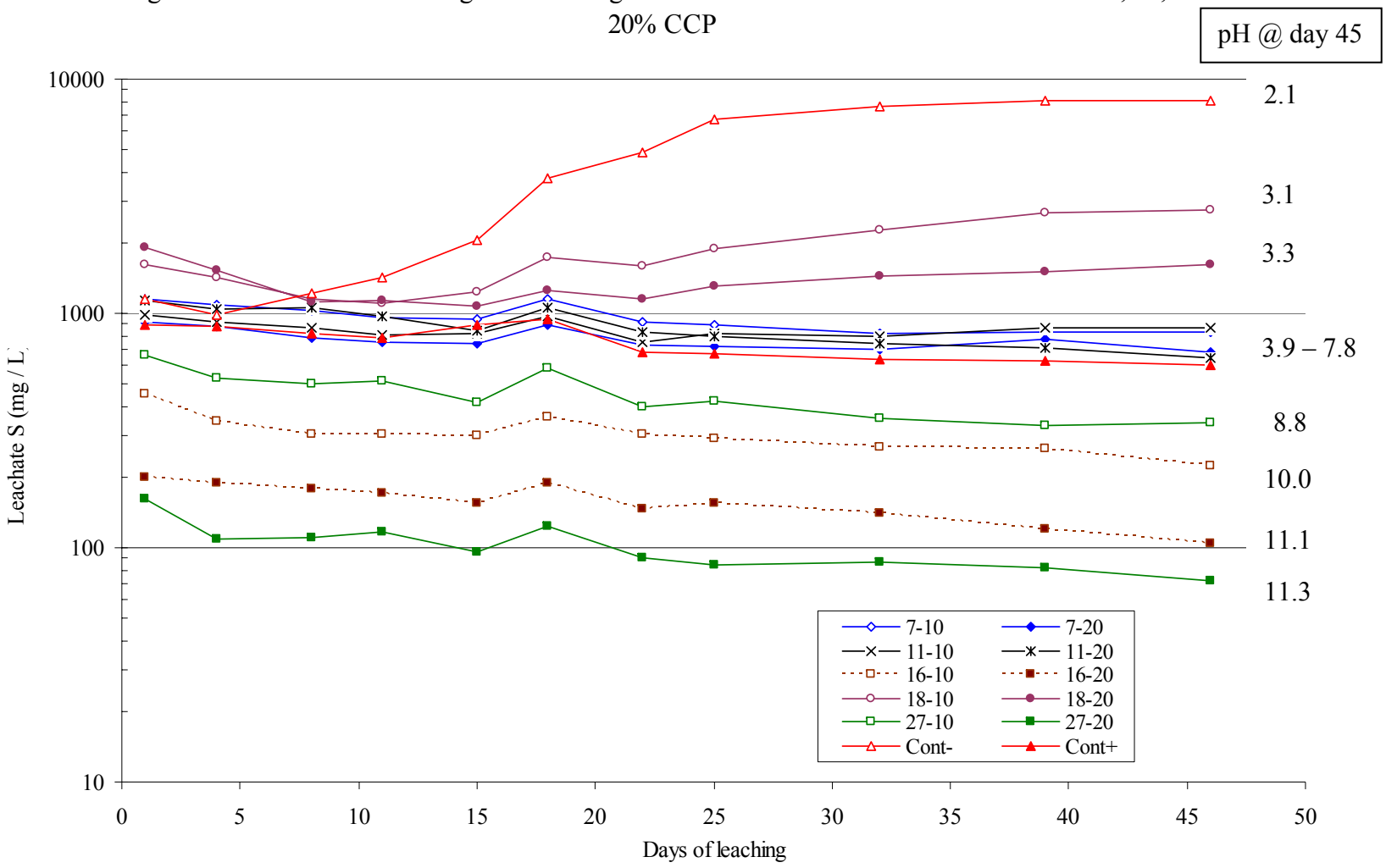



Fig. C-10. Leachate S from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP