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

*W. Lee Daniels, Mike Beck and Matt Eick*

*Department of Crop and Soil Environmental Sciences*

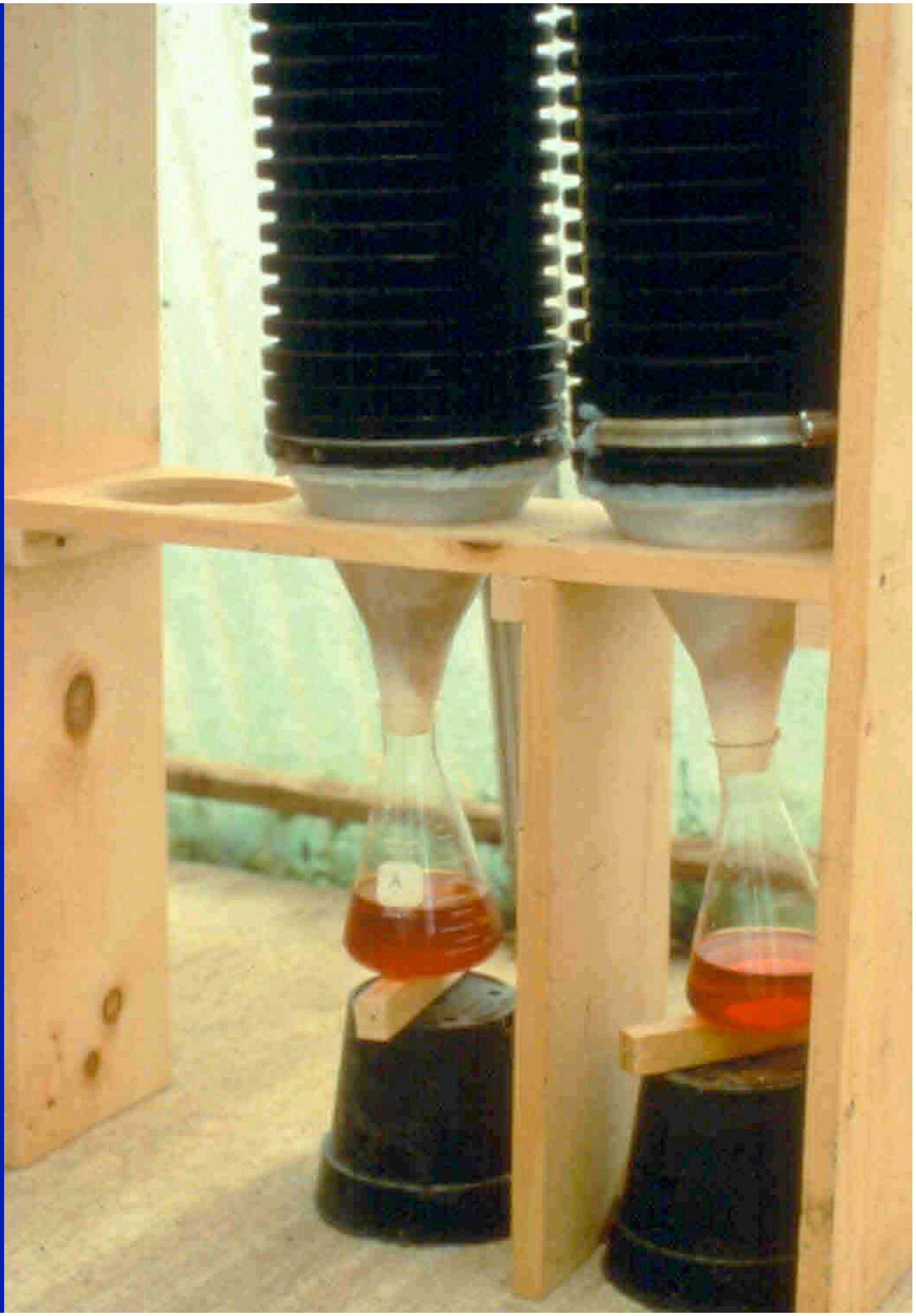
VirginiaTech
1872
VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY

# Overall Study Objectives

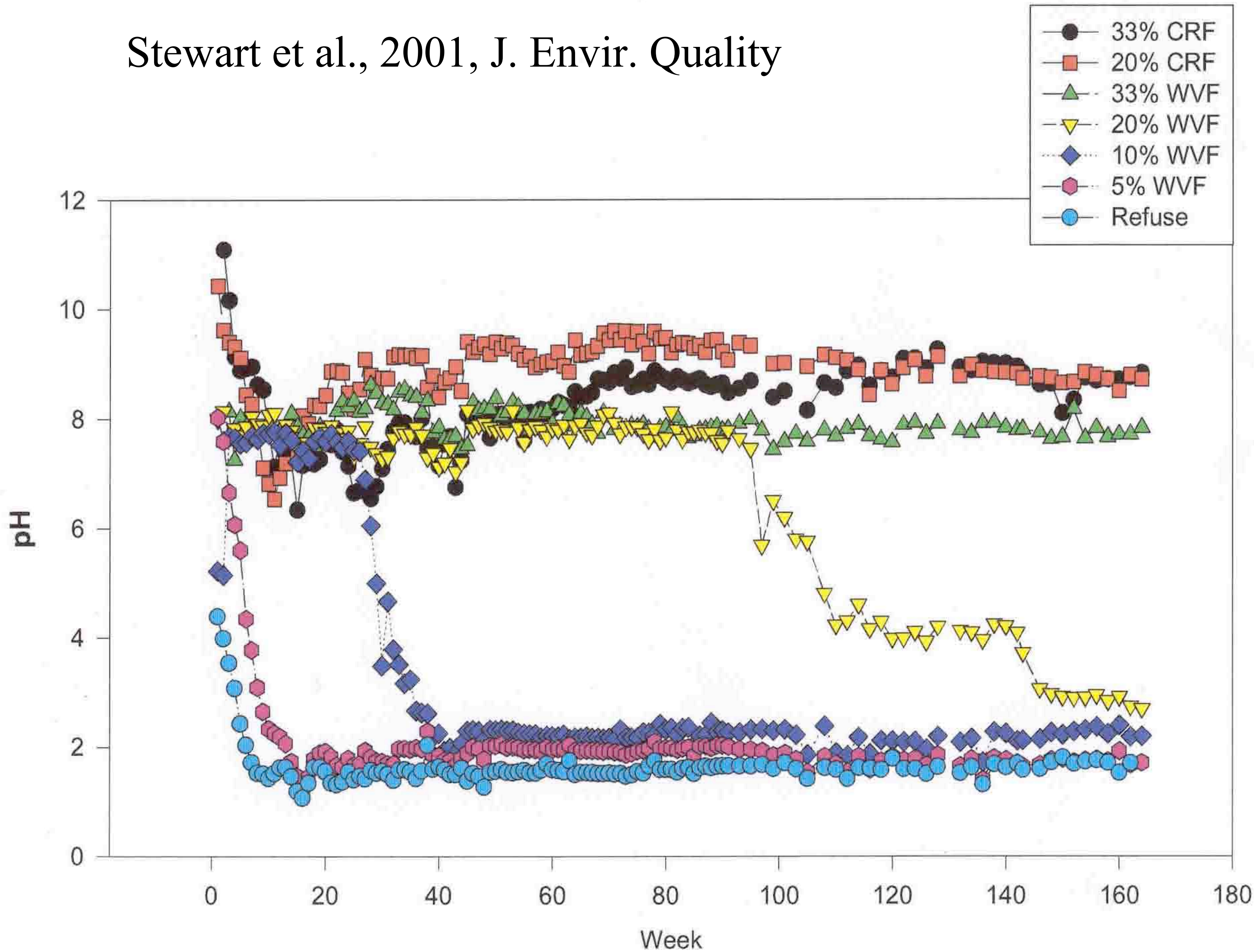
1. To predict the relative bioavailability/leaching risk of As, B, Mo and Se in common SW Virginia coal mining/CCP utilization environments.

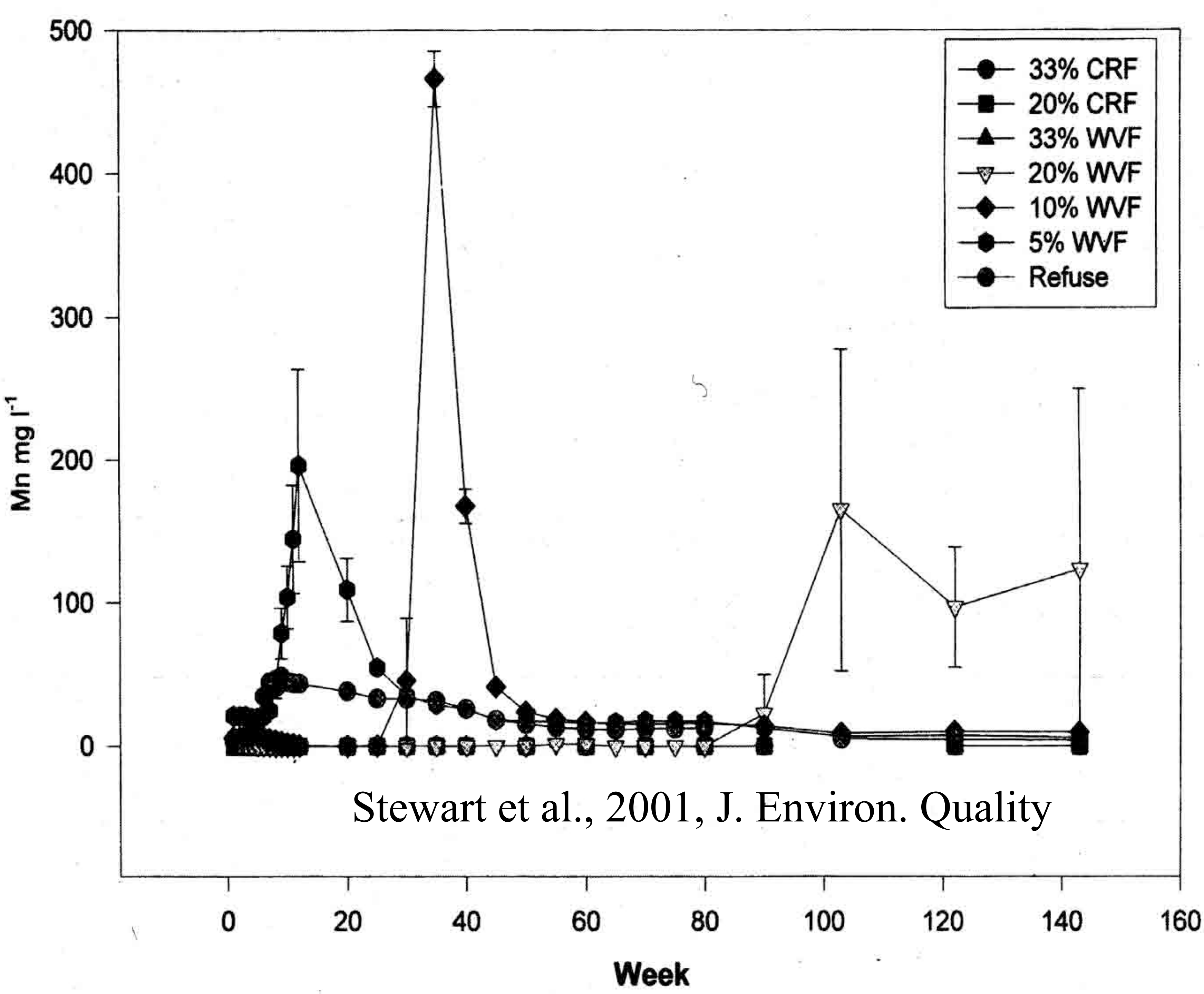
2. To develop and refine a simple combined laboratory and greenhouse screening technique that will predict the beneficial use potential of CCPs when used as (a) topical mine soil amendments, (b) geochemically stable backfill materials, and (c) bulk-blended treatments for acidic coal waste materials.

**Acid mine drainage (pH=2.3; Fe=10,000 ppm) from unsaturated leaching of high S coal refuse (4% pyritic-S).**



Stewart et al., 2001, J. Envir. Quality




33% CRF
20% CRF
33% WVF
20% WVF
10% WVF
5% WVF
Refuse
Mn mg l-1
Week
500
400
300
200
100
0
0
20
40
60
80
100
120
140
160
Stewart et al., 2001, J. Environ. Quality

# USA National Academy of Sciences Study 2006

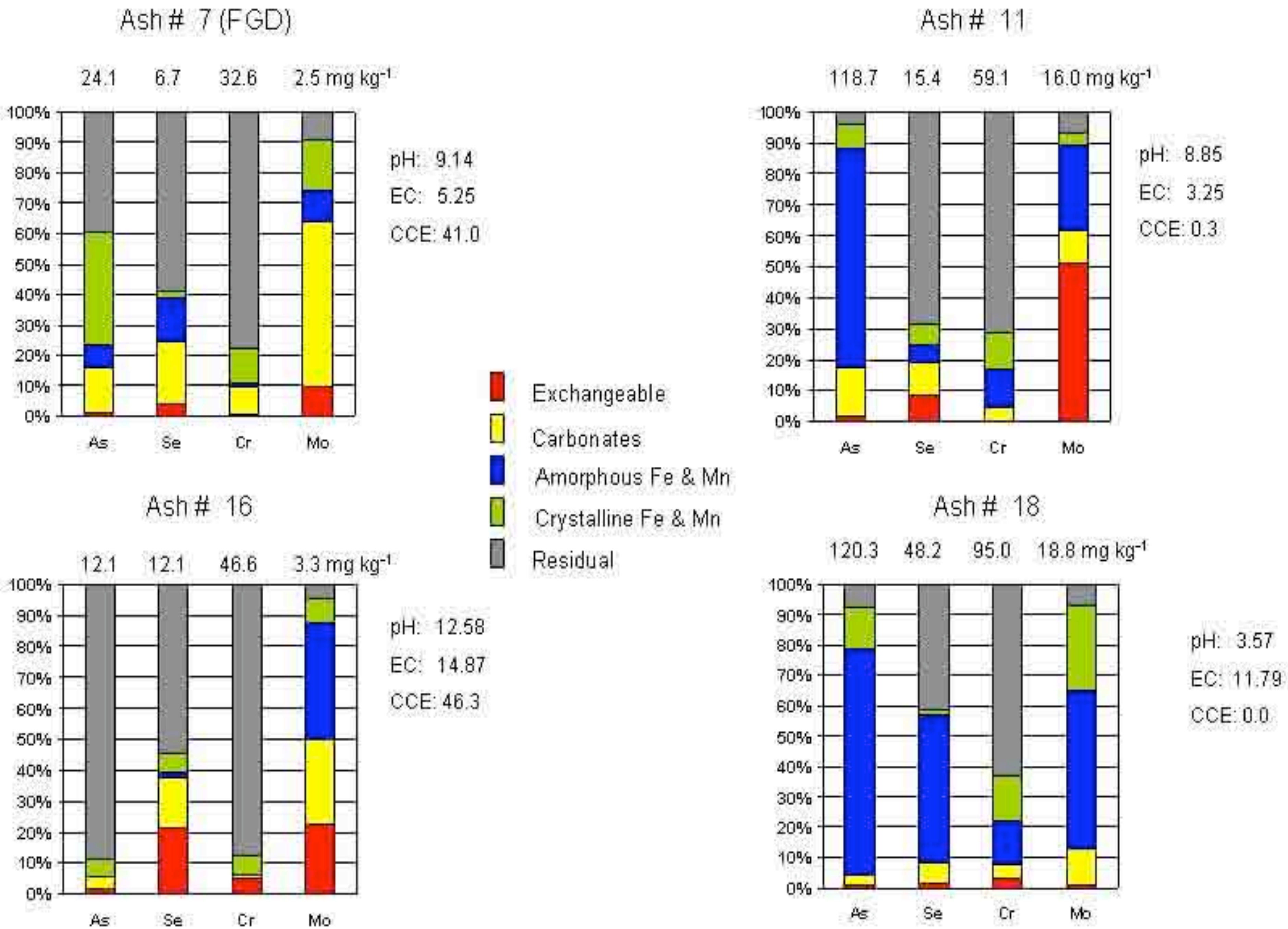
While the report did offer overall support for the beneficial utilization of CCP's in mining environments, it specifically cautioned potential permittees to: (1) Carefully characterize the geochemical properties of both the CCP to be utilized and the mine site; (2) understand and predict long-term reactions and contaminant release patterns; and (3) fully characterize potential site hydrologic impacts.

# Preliminary Characterization

- 28 CCP’s collected regionally; 3 FGD
- Basic analyses included TCLP, sat. paste pH + EC, Ext. B, Total Elemental, and Mehlich-I extractable nutrients and metals.
- Modified Tessier Sequential Extraction Procedure: Omitted OM step and used Cl rather than $SO_4$ for the Exchangeable step.

| | | Saturated Paste | | | | | Total Elemental Micro Digestion | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CCP # | Type | Bd | pH | EC | CCE | Extr. B | Total B | As | Se | Cr | Mo |
| | | kg $L^{-1}$ | | dS $m^{-1}$ | % | mg $L^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | mg $kg^{-1}$ | 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 |

*Ash 18 (low pH) was used in column study in place of ash 27.

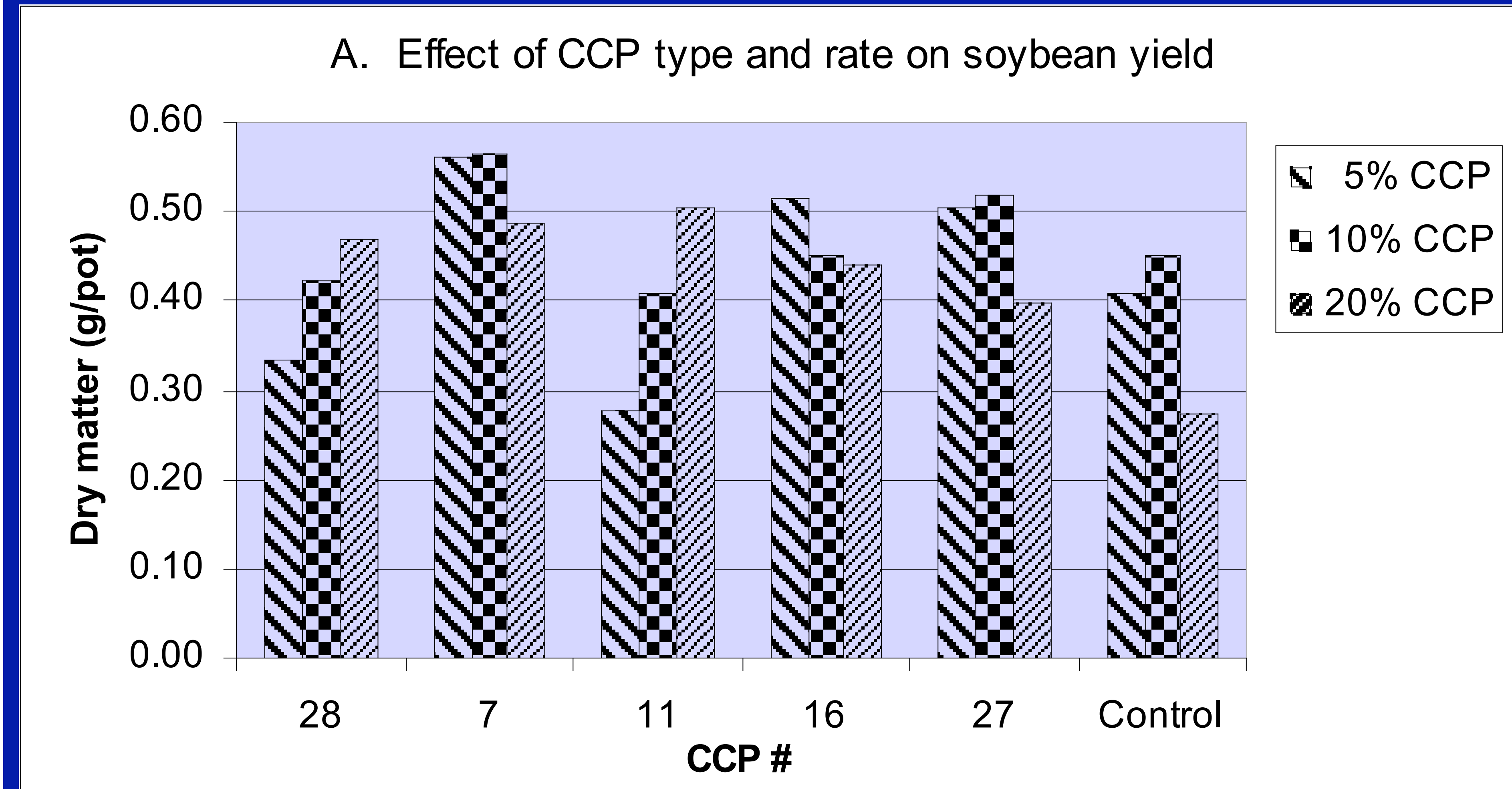

Ash # 7 (FGD)
24.1 6.7 32.6 2.5 mg kg-1
pH: 9.14
EC: 5.25
CCE: 41.0
Ash # 11
118.7 15.4 59.1 16.0 mg kg-1
pH: 8.85
EC: 3.25
CCE: 0.3
Ash # 16
12.1 12.1 46.6 3.3 mg kg-1
pH: 12.58
EC: 14.87
CCE: 46.3
Ash # 18
120.3 48.2 95.0 18.8 mg kg-1
pH: 3.57
EC: 11.79
CCE: 0.0
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
As Se Cr Mo
Exchangeable
Carbonates
Amorphous Fe & Mn
Crystalline Fe & Mn
Residual

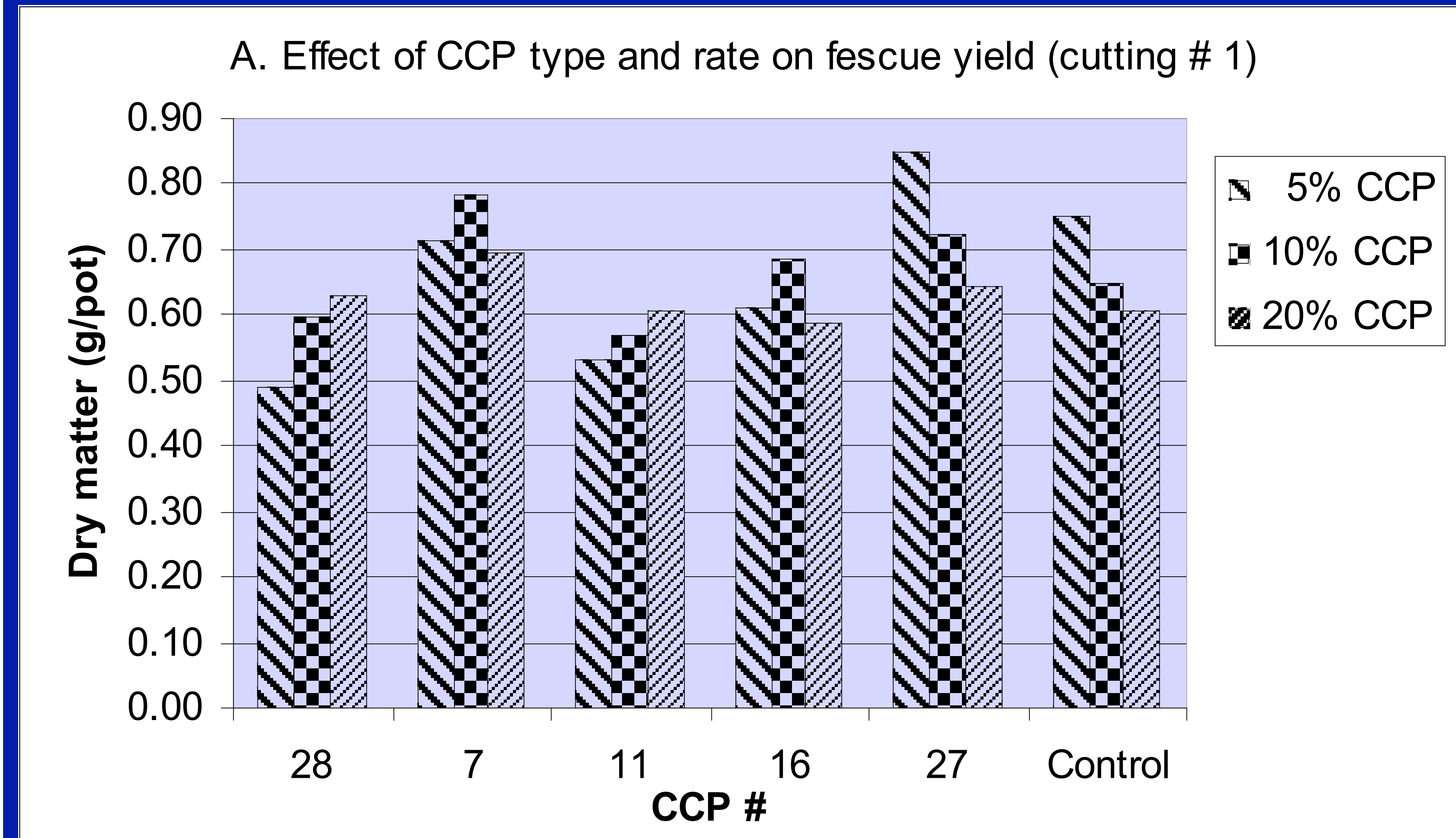
# Greenhouse Bioassay

- Modified version of standard technique we use to screen soil amendments for VDACS.
- CCP's added at 5, 10 and 20% by vol. to acidic brown sandstone mine soil.
- Ran limed and unlimed control pots.
- Also evaluated "pour-through" leachates.
- Seeded to soybean (sensitive) and tall fescue (tolerant).


**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.**

**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.**

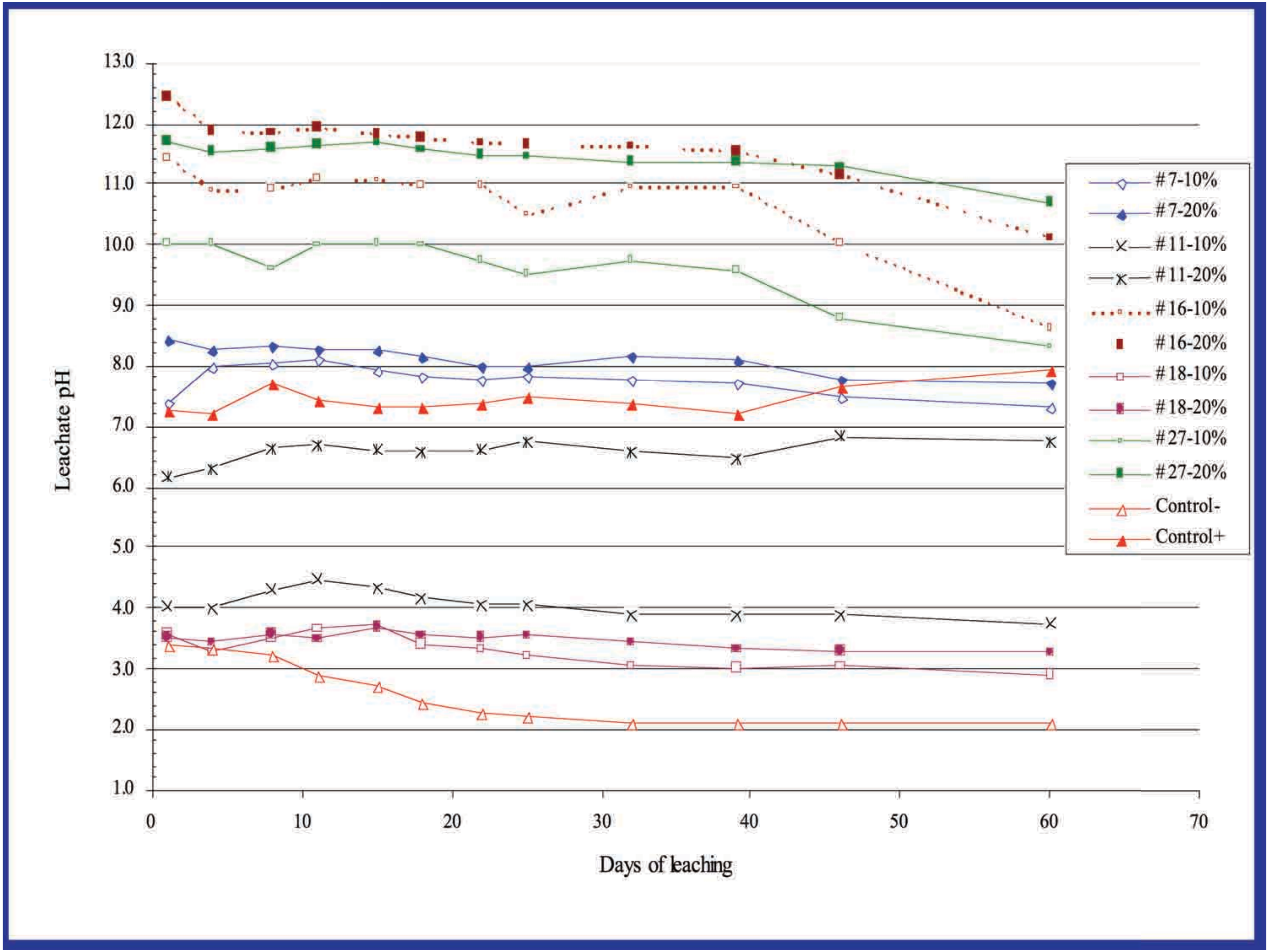

A. Effect of CCP type and rate on soybean yield
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Dry matter (g/pot)
28
7
11
16
27
Control
CCP #
5% CCP
10% CCP
20% CCP


A. Effect of CCP type and rate on fescue yield (cutting # 1)
Dry matter (g/pot)
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
28
7
11
16
27
Control
CCP #
5% CCP
10% CCP
20% CCP

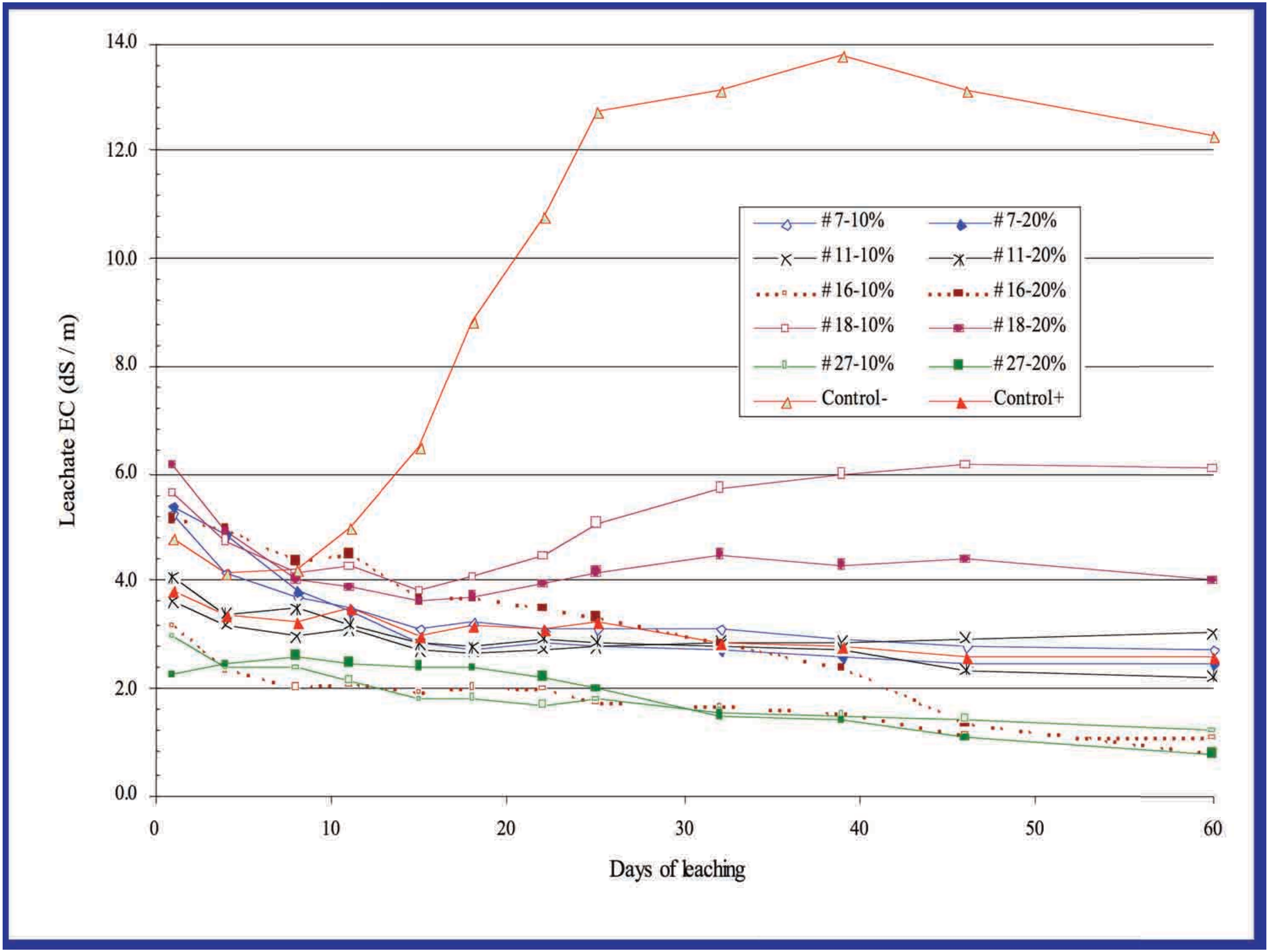
# Lab Leaching Columns Packed with Acid Forming Coal Refuse and Varying Rates & Types of CCPS.

# Column Leaching Procedures

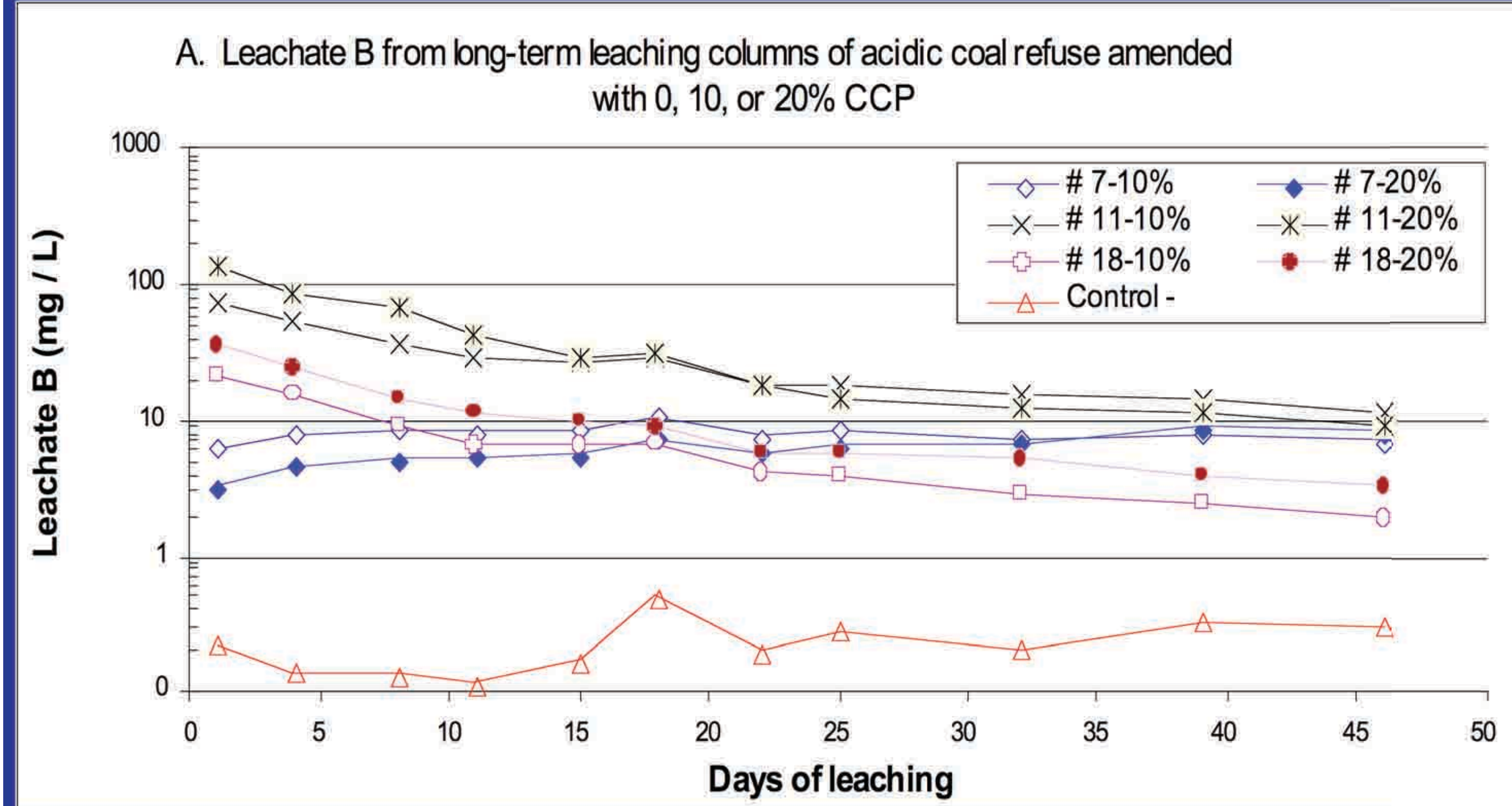
- Acid forming refuse (P.A. = 35 Mg/1000)
- 1.25 max particle size into 7.5 cm diameter
- CCP's added at 10 and 20% by volume
- Dosed with 2.5 cm of simulated rain twice per week
- Limed (to P.A.) and unlimed controls
- EC and pH run immediately; Oxyanions and Metals run later after preservation.



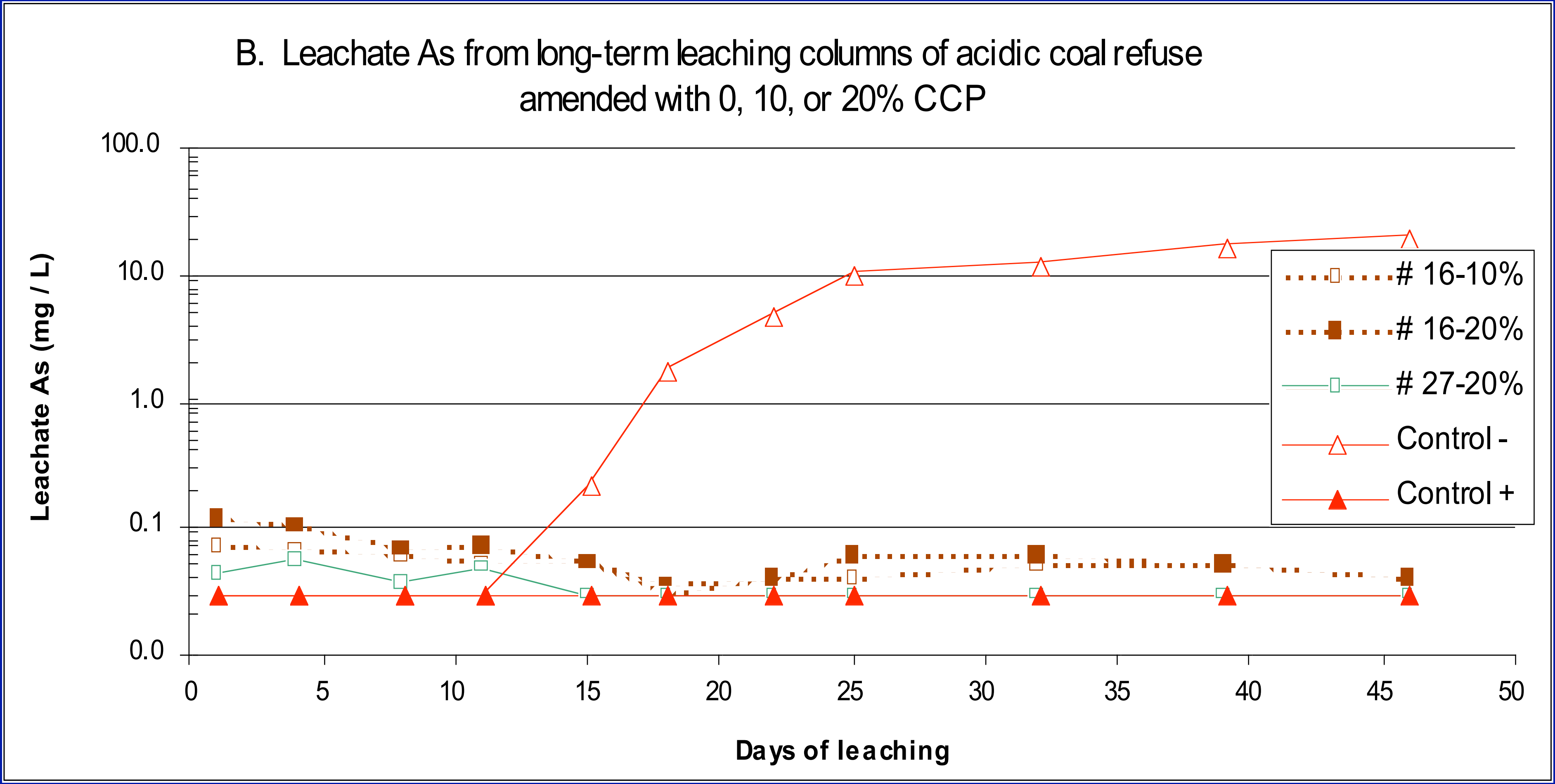
Leachate pH
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10
20
30
40
50
60
70
Days of leaching
# 7-10%
# 7-20%
# 11-10%
# 11-20%
# 16-10%
# 16-20%
# 18-10%
# 18-20%
# 27-10%
# 27-20%
Control-
Control+



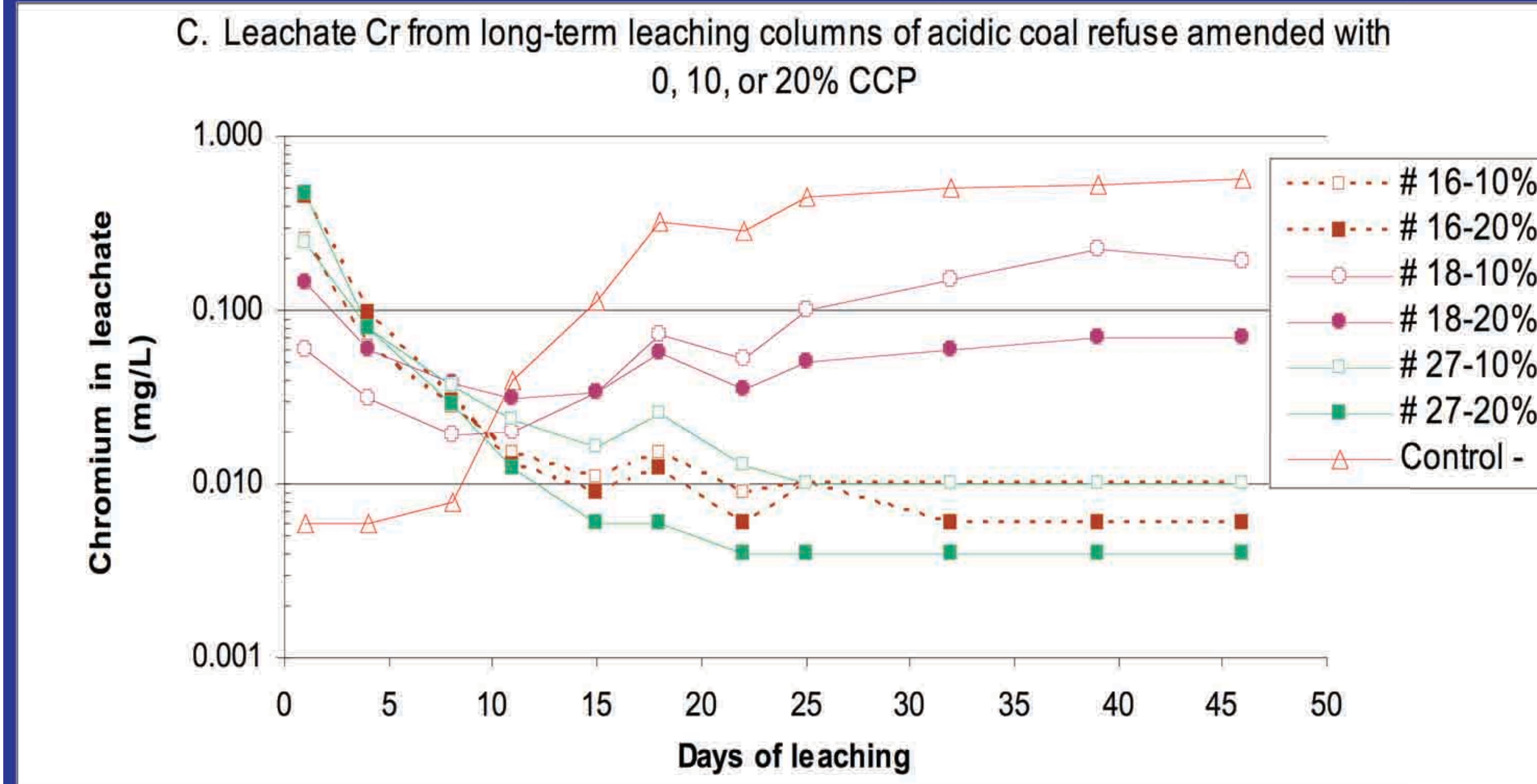
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Leachate EC (dS / m)
0
10
20
30
40
50
60
Days of leaching
# 7-10%
# 7-20%
# 11-10%
# 11-20%
# 16-10%
# 16-20%
# 18-10%
# 18-20%
# 27-10%
# 27-20%
Control-
Control+



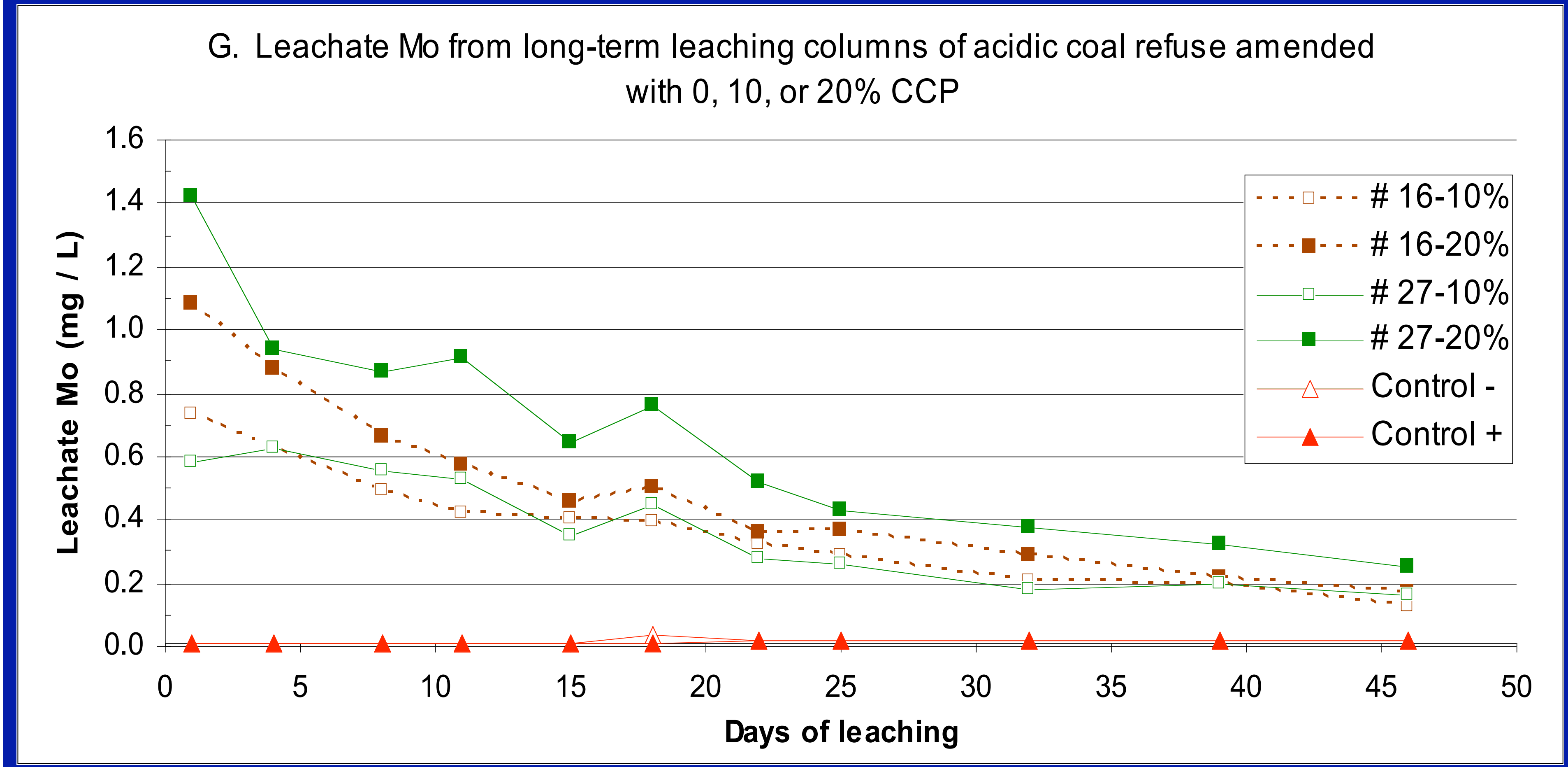
A. Leachate B from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP
Leachate B (mg / L)
1000
100
10
1
0
0
5
10
15
20
25
30
35
40
45
50
Days of leaching
# 7-10%
# 7-20%
# 11-10%
# 11-20%
# 18-10%
# 18-20%
Control -

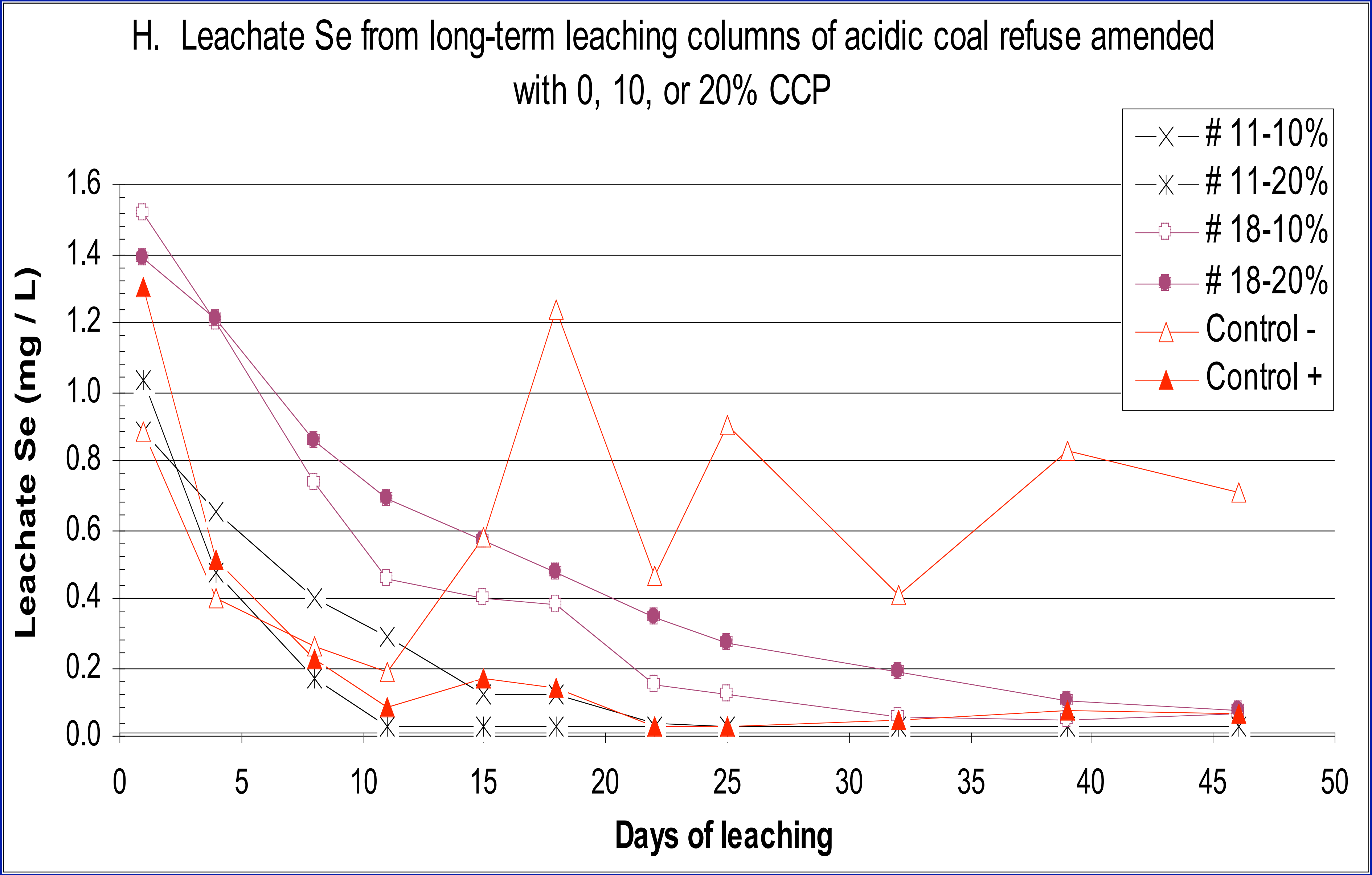


B. Leachate As from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP
Leachate As (mg / L)
100.0
10.0
1.0
0.1
0.0
0
5
10
15
20
25
30
35
40
45
50
Days of leaching
# 16-10%
# 16-20%
# 27-20%
Control -
Control +



C. Leachate Cr from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP
Chromium in leachate (mg/L)
1.000
0.100
0.010
0.001
0
5
10
15
20
25
30
35
40
45
50
Days of leaching
# 16-10%
# 16-20%
# 18-10%
# 18-20%
# 27-10%
# 27-20%
Control -


G. Leachate Mo from long-term leaching columns of acidic coal refuse amended
with 0, 10, or 20% CCP
Leachate Mo (mg / L)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
35
40
45
50
Days of leaching
# 16-10%
# 16-20%
# 27-10%
# 27-20%
Control -
Control +


H. Leachate Se from long-term leaching columns of acidic coal refuse amended with 0, 10, or 20% CCP
# 11-10%
# 11-20%
# 18-10%
# 18-20%
Control -
Control +
Leachate Se (mg / L)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0
5
10
15
20
25
30
35
40
45
50
Days of leaching

# Column Caveats

- Column leaching studies offer great advantages in that they allow for both kinetic data and substrate interaction effects.
- As run, these are probably “worse case” predictors and only estimate water quality as it might occur in the inner portions of the refuse:CCP fills.
- Any of these mobile constituents would be subject to sorption/attenuation down gradient (we have a current parallel study on this)

# Conclusions

The chemical properties of CCP's, particularly levels of soluble salts, CCE, and potentially soluble oxyanions continue to vary widely and must be carefully assessed and matched to utilization site geochemical and hydrologic conditions.

# Conclusions

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.

# Conclusions

**Similarly, if the CCP utilization/disposal environment is allowed to become strongly alkaline, CCP fills or layers should be expected to be internal sources of high pH soluble oxyanions such as arsenate, borate and selenate *if* those constituents are elevated in the inbound CCP materials. These would leach very early in the system.**

# Conclusions

**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.**

# Conclusions

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.

# Conclusions

While not currently a common practice, utilization of CCP's as a topical amendment to mine soils and coal waste for soil improvement and revegetation purposes is viable, but application rates will be limited to less than 10% (100 Mg/ha) for most CCP's due to deleterious effects of soluble salts on initial plant growth.

# Conclusions

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.

# Acknowledgments

This project was funded by the USDI-OSM Applied Research Program. We appreciate the assistance of Lois Uranowski and Kim Vories (OSM) and Butch Lambert (VDMLR) in this effort. The Powell River Project (thanks to Carl Zipper) provided early and ongoing support for CCP X mining research related to this program.