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Subject: Final Report Entitled "Qualifying CCBs for Agricultural Land Application"
Project No. 01-CBRC-M23; EERC Fund 5471

Enclosed is the subject final report. If you have any questions, please contact me by phone at (701) 777-5192, by fax at (710) 777-5181, or by e-mail at dhassett@undeerc.org.

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QUALIFYING CCBS FOR AGRICULTURAL LAND APPLICATION

CBRC Final Report

(for reporting period July 1, 2002, through March 31, 2006)

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QUALIFYING CCBS FOR AGRICULTURAL LAND APPLICATION

ABSTRACT

Agriculture application is potentially one of the largest unrealized coal combustion by-product (CCB) utilization options in the United States. Many rural power plants that cannot market CCBs to distant markets may find local farmers to be repeat customers. A case study in Illinois provided the opportunity to study the appropriateness of the use of a mixed CCB from a rural power plant as an agricultural soil amendment. The utility and the Energy & Environmental Research Center (EERC) worked together with additional funding from the U.S. Department of Energy (DOE) Combustion Byproducts Recycling Consortium (CBRC) for this project.

The goal of the effort was to determine the environmental appropriateness of the use of a specific mixed stream of CCBs for agricultural land applications and to develop a draft methodology for generically qualifying CCBs for agricultural land application. The project evaluated a mixed stream of CCBs (bottom ash, fly ash, and sulfite-rich flue gas desulfurization [FGD] material) recovered from wet storage for agricultural land application.

Chapter 1 of this report details the laboratory evaluation of the as-managed mixed CCB stream. This included proton-induced x-ray emission (PIXE) analyses to determine elements of interest, bulk, chemical, and total trace elemental analyses of the solid samples, and ASTM International Method D3987 leaching with a determination of the leachable trace elements. Trace elements frequently present in CCBs were of primary interest in this evaluation. The primary Chapter 1 conclusion is that the data presented and the anecdotal evidence provided by a local farmer indicate that the use of the specific mixed CCB stream is appropriate for use in agricultural land application.

Chapter 2 of this report develops a proposed qualification scheme for CCBs for use in agricultural land application on a national level. The methods used included a review of research studies of agricultural land application of various CCBs; a comparison of available guidelines for agricultural land application of CCBs and other similar by-products; and a comparison of results of the laboratory and field data/information from Chapter 1 with assembled information. This information was used to develop a draft of a qualifying scheme for CCBs only that may be used in future projects and potentially be expanded and detailed to become a tool for the coal ash and agricultural industries to use in understanding the identification of appropriate CCBs for agricultural land application.

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QUALIFYING CCBS FOR AGRICULTURAL LAND APPLICATION

EXECUTIVE SUMMARY

Agriculture application is potentially one of the largest unrealized coal combustion by-product (CCB) utilization options in the United States. Many rural power plants that cannot market CCBs to distant markets may find local farmers to be repeat customers. A case study in Illinois provided the opportunity to study the appropriateness of the use of a mixed CCB from a rural power plant as an agricultural soil amendment. Local farmers expressed interest in using the material because they understood that it could be a source of calcium and sulfur. While field application had been tried in limited locations by one farmer with success, the utility producing the mixed CCB stream felt that a more rigorous investigation was required. CCB use regulations in Illinois include agricultural application of CCBs as an option approved by the Illinois Environmental Protection Agency (IEPA). The utility producer initiated an effort to evaluate the mixed CCB stream of interest to local farmers to understand if the material was allowable for agricultural land application under Illinois regulatory requirements. The utility and the Energy & Environmental Research Center (EERC) worked together with additional funding from the U.S. Department of Energy (DOE) Combustion Byproducts Recycling Consortium (CBRC) for this project.

The goal of the effort was to determine the environmental appropriateness of the use of a specific mixed stream of CCBs for agricultural land applications and to develop a draft methodology for generically qualifying CCBs for agricultural land application. The project evaluated a mixed stream of CCBs (bottom ash, fly ash, and sulfite-rich flue gas desulfurization [FGD] material) recovered from wet storage for agricultural land application.

Chapter 1 of this report details the laboratory evaluation of the as-managed mixed CCB stream. This included proton-induced x-ray emission (PIXE) analyses to determine elements of interest, bulk chemical and total trace elemental analyses of the solid samples, and ASTM International (ASTM) Method D3987 leaching with a determination of the leachable trace elements. Trace elements frequently present in CCBs were of primary interest in this evaluation. Results comparing the total concentrations of trace elements in the CCB of interest, the untreated local soil, and the field-treated local soil are shown in Table ES-1.

The data indicate that both untreated and field-treated soils exhibit similar concentrations of most of the trace elements tested. The concentrations in the as-managed mixed CCB stream are frequently similar to those found in the untreated soils. Some elements, most notably boron, beryllium, mercury, nickel, and zinc were more concentrated in the as-managed mixed CCB stream as compared with the untreated soil; however, concentrations of these elements in the field-treated soil, 3 years after the as-managed mixed CCB application, were not elevated above the concentrations noted in the untreated soil. Further, a comparison of these results with the land application,¹ guidelines developed by the U.S. Environmental Protection Agency (EPA) for

¹ U.S. Environmental Protection Agency. Standards for the Use and Disposal of Sewage Sludge. *Code of Federal Regulations*, Section 40, Part 503, 1993; *Fed. Regist.* **1993**, 58, 9387, amended at 58 FR 9099, Feb 25, 1994; 60 FR 54769, Oct 25, 1995.

Table ES-1. Total Trace Element Results of As-Managed CCB and Soils, µg/g

	As- Managed CCB	As- Managed CCB	As- Managed CCB	Untreated Soil	Untreated Soil	Field- Treated Soil	Field- Treated Soil
Collection Date:	June 2003	Oct 2004	Nov 2004	Oct 2003	Dec 2004	Oct 2003	Dec 2004
Sb	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7	<2.7
As	6.95	6.45	7.55	14.1	14.3	13.7	11.6
Be	6.71	3.88	3.26	1.75	1.97	1.82	1.77
B ^a	386	388	305	<100	<100	<100	<100
Cd	0.994	1.1	1.07	1.03	<0.5	<1	<0.5
Cr	132	57.6	52.7	39.9	47.6	40.6	35.9
Co	22.5	12.8	10.4	10.3	8.28	9.83	6.3
Cu	40.4	18.7	19.7	19.5	23	19.2	13
Pb	13.3	16	16.9	22.5	23.6	19.8	22.5
Hg	<0.1	0.127	0.163	<0.1	0.037	<0.1	0.013
Ni	283	43.5	37.5	<1	25.2	<1	17.7
Se	<2	<2	2.62	<2	<2	<2	<2
Tl	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
V	111	54.6	55	63.1	95	65.6	76.4
Zn	144	106	94.1	56.6	71.6	72.2	62.3

^a Total extractable boron.

placement of sewage sludge (Part 503 Rules), which is used broadly for determining the suitability of a material for land application (USEPA, 1993), determined that the elemental concentrations in the mixed CCB stream were significantly lower than the limits listed in the Part 503 rules.

The primary Chapter 1 conclusion is that the data presented and the anecdotal evidence provided by a local farmer indicate that the use of the specific mixed CCB stream is appropriate for use in agricultural land application.

Chapter 2 of this report develops a proposed qualification scheme for CCBs for use in agricultural land application on a national level. The methods used included a review of research studies of agricultural land application of various CCBs, a comparison of available guidelines for agricultural land application of CCBs and other similar by-products, and a comparison of results of the laboratory and field data/information from Chapter 1 with assembled information. This information was used to develop a draft of a qualifying scheme for CCBs only that may be used in future projects and potentially be expanded and detailed to become a tool for the coal ash and agricultural industries to use in understanding the identification of appropriate CCBs for agricultural land application.

The following conclusions were drawn from the comparison of the laboratory field information detailed in Chapter 1 with the literature search and existing guidelines:

- CCBs can provide benefits when used to amend agricultural soils, but caution must be exercised to ensure environmental protection, crop and soil appropriateness, and human health.

- FGD gypsum has benefits equivalent to natural gypsum and can be applied for the same purposes and at the same rates. Studies under way on the use of FGD gypsum should provide good information to aid in marketing FGD gypsum for agricultural applications, and the criteria for use should be the same for natural and FGD gypsum.
- Total concentrations of inorganic constituents in CCBs are not the best indicator on which to base decisions regarding the suitability of CCBs for use in agricultural land applications.

A proposed preliminary decision tree for qualifying CCBs for agricultural applications was developed by the EERC (Figure ES-1) based on the guidelines and information assembled and using the information presented in Chapter 1 as an example case study.

The EERC makes the following recommendations based on information collected:

- The EERC recommends that industry consider that CCB application to agricultural land should be based on available trace and major/minor elements rather than on total concentrations and should be no more stringent or lenient than other standards regarding the same elements regardless of the source.
- The EERC recommends that continuing work on the use of CCBs in agriculture includes the use of the draft qualification scheme so that scheme can be evaluated to determine if it can become a valuable tool for the agricultural community in determining appropriate application of CCBs.

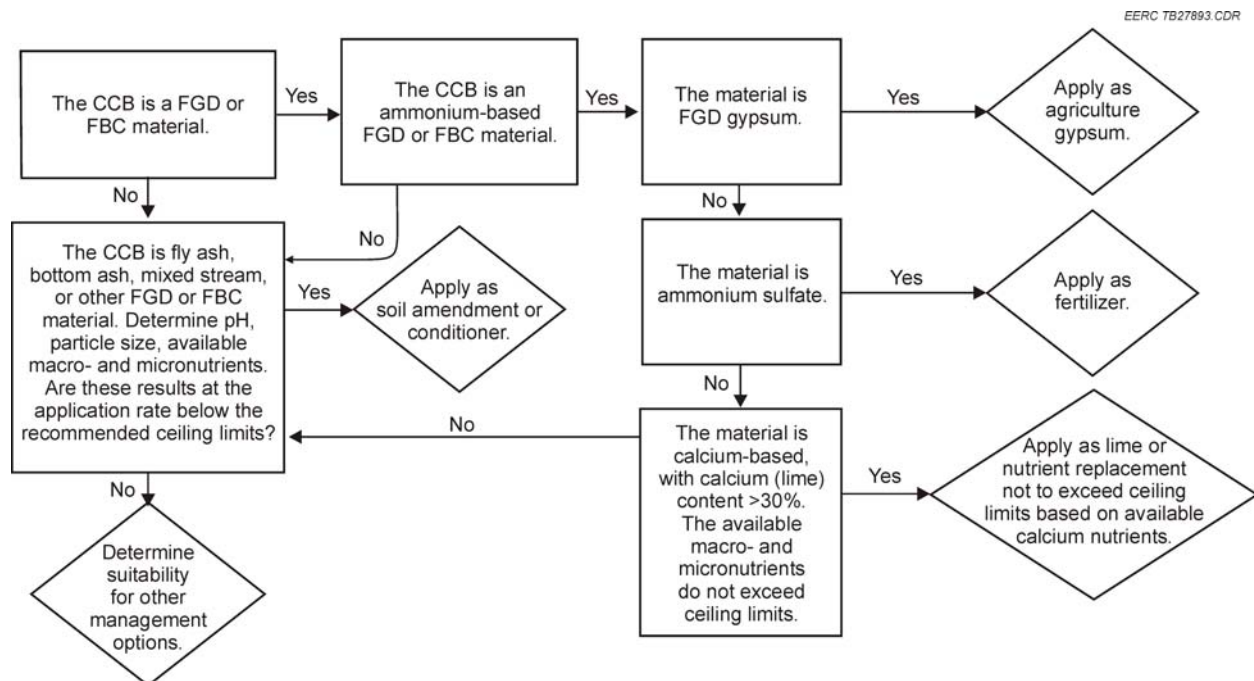


Figure ES-1. Proposed qualifying scheme for CCB use in agricultural land applications.

- The EERC recommends that the discussion of appropriate leaching procedures and the methods to identify appropriate leaching procedures incorporate a discussion of methods to determine elemental availability for input and use in the proposed qualification scheme.

CHAPTER 1. MIXED STREAM CCBs FOR AGRICULTURAL LAND APPLICATION IN ILLINOIS

INTRODUCTION

Fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) material are the four large-volume by-products from the combustion of coal by electric utility power plants. These by-products are collectively referred to as coal combustion by-products (CCBs). In 1999, the U.S. Environmental Protection Agency (EPA) completed a two-phased study of CCBs for the U.S. Congress supporting its Phase 1 conclusion that the characteristics and management of the CCBs listed do not warrant hazardous waste regulation under the Resource Conservation and Recovery Act (RCRA) and that utilization practices for CCBs appear to be safe (U.S. Environmental Protection Agency, 2000). In addition, EPA “encourage[d] the utilization of coal combustion by-products and support[ed] State efforts to promote utilization in an environmentally beneficial manner.” EPA also listed numerous CCB use applications including in agricultural soil amendment as options for the responsible use of these materials. Numerous studies have shown CCBs to be beneficial as agricultural soil amendments (Dick et al., 2004; Li et al., 2002; Chen et al., 2002; Korcak, 1998; Electric Power Research Institute, 1995; Bigham et al., 1993; Stout et al., 1988). With CCBs classified under RCRA Subtitle D for solid wastes, it falls to individual states to regulate the management of these materials.

Illinois is one of the states that opted to include various utilization applications in its regulations, which were promulgated in 1995 (35 ILL. ADMIN. CODE §721.104[b][4]). Illinois includes “CCB used as a functionally equivalent substitute for agricultural lime as a soil conditioner” in its list of beneficial uses for CCBs. In order for farmers to take advantage of locally available CCBs in Illinois, this project was initiated with a focus on determining the appropriateness of a mixed CCB for agricultural application. The project also included work to develop a process for assessing and qualifying CCBs for agricultural use.

FGD materials, typically composed mainly of calcium sulfate/sulfite compounds, are frequently used in agricultural applications. FGD materials vary depending on the type of FGD process, quantity of sorbent used, amount of fly ash present, and oxidation in the treatment process (Berland et al., 2003). These process properties can affect such things as the pH, salts present, trace element concentrations, and sulfate/sulfite concentrations. Forced oxidation of sulfite to sulfate results in FGD gypsum and improves the agricultural usefulness of the material. The mineral gypsum, or calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), from natural or by-product sources improves the tilth of clayey soils, mitigates the toxicity of exchangeable aluminum in acid soils, and improves sodic or saline soils (Sumner, 2005; Fehringer, 2003; Franzen, 2003). Other FGD materials that have not been force-oxidized may also offer similar advantages because the calcium present contributes to soil aggregation by displacing sodium on clay minerals and providing microscopic cementation.

Application of other CCBs (fly ash, bottom ash, and boiler slag) to soils can also provide several potential benefits, such as 1) correcting excessive soil acidity, 2) supplementing soil nutrient supplies, 3) improving moisture retention, and 4) improving infiltration, drainage, and

soil tilth. These effects are important both to plant growth and crop production and in the control of soil erosion by improving the physical and chemical qualities of the plant-rooting zone (Electric Power Research Institute, 1995).

Most CCBs contain soluble forms of calcium, magnesium, sulfur, and certain essential trace elements such as boron, manganese, molybdenum, zinc, selenium, and copper and can provide needed plant nutrients. However, some of these elements and other trace elements present in CCBs raise questions about the environmental appropriateness of the use of CCBs in agricultural applications. Some potentially soluble salts and trace elements that should be evaluated prior to agricultural land application include arsenic, boron, cadmium, lead, and selenium. It is important to evaluate the mobility of constituents present in CCBs in order to determine the appropriateness of individual materials for this type of application.

In 2005, the American Coal Ash Association (ACAA) reported that over 122 million tons of CCBs were produced in the United States from coal-fired electric generating stations in 2004 (American Coal Ash Association, 2005), with just over 49 million tons of these CCBs utilized. Of these utilized CCBs, close to 216,000 tons were specified as being used in agriculture. This accounts for only 1.7% of all CCBs produced. Clearly, the agricultural market for CCBs is largely untapped, and the CCB and agricultural industries can both benefit if a method for qualifying CCBs for use in agricultural applications can be developed and accepted by regulatory authorities. The work presented in this report was undertaken to facilitate a better understanding of the behavior of CCBs when land-applied for agricultural purposes and to provide a comparison of the concentrations of elements present in CCBs with untreated soil in the region and typical soil ranges. This case study includes information from a specific coal-fired power plant and a specific farm and anecdotal evidence of a farmer's experience with crops grown on CCB-treated soil.

BACKGROUND

This project was developed with input from Ameren Energy Resources Generation (Ameren AERG) and its Duck Creek Power Station near Peoria, Illinois. Using the Duck Creek mixed CCB stream as a case study in agricultural application of CCBs, the project consisted of laboratory tasks designed to evaluate specific CCBs and CCB-amended soils with a site-specific goal of determining the appropriateness of that specific material as an agricultural soil amendment. Additionally, the project was designed to use the site-specific data in conjunction with existing information from the literature to develop an approach to qualify CCBs for agricultural use, which is detailed in Chapter 2 of this report.

The Ameren AERG Duck Creek facility from which materials were obtained and applied to soils produces approximately 59,700 tons of fly ash, 10,500 tons of bottom ash, and 141,000 tons of sulfite-rich wet FGD material annually. These three materials are comingled at the facility and mixed with water to make a slurry containing production proportions of each of the three materials. The slurry is pumped to a holding pond where the mixed stream is excavated, stacked, and allowed to drain. The resulting relatively dry, mixed stream is the source of material used for agricultural application.

Under Illinois regulations, fly ash, bottom ash, slag, and flue gas emission control waste generated primarily from the combustion of coal or other fossil fuels are exempt from regulation as hazardous waste (35 ILL. ADMIN. CODE §721.104[b][4]). In 1995, Illinois enacted legislation specifically authorizing reuse of coal combustion waste (415 ILCS 5/3.135 and 415 ILCS 5/3.140 [P.A. 89-93]). P.A. 92-574 created two classifications of coal ash: coal combustion waste (CCW) and CCBs. CCW is subject to limited management and disposal options. CCBs, on the other hand, may be used in multiple applications as discussed below.

The term CCW includes fly ash, bottom ash, slag, or flue gas or fluid-bed boiler desulfurization by-products generated through combustion of coal. CCW can be classified as a CCB under certain conditions (satisfactory analytical testing results) and reused based on this classification. As modified in 2005 and to be instituted in January 2006 (415 ILCS 5/3.135), CCBs may be reused as follows in Illinois:

1. For the extraction and recovery of materials and compounds within the ash.
2. As a raw ingredient or mineral filler in the manufacture of the following commercial products: cement; concrete and concrete mortars; cementitious products including block, pipe, and precast/prestressed components; asphalt or cementitious roofing products; plastic products including pipe and fittings; paints and metal alloys; kiln-fired products including bricks, blocks, and tiles; abrasive media; gypsum wallboard; asphaltic concrete; and asphalt-based paving material.
3. A) In accordance with the Illinois Department of Transportation (IDOT) standard specifications and subsection (a-5) of this section or B) under the approval of the Department of Transportation for IDOT projects.
4. As antiskid material, athletic tracks, or foot paths (bottom ash).
5. In the stabilization or modification of soils, provided the CCB meets the IDOT specifications for soil modifiers.
6. As a functionally equivalent substitute for agricultural lime as a soil conditioner.
7. In non-IDOT pavement subbase or base, pipe bedding, or foundation backfill (bottom ash).
8. As structural fill when used in an engineered application or combined with cement, sand, or water to produce a controlled-strength fill material and covered with 12 inches of soil unless infiltration is prevented by the material itself or other cover material.
9. For mine subsidence, mine fire control, mine sealing, and mine reclamation.

Certain restrictions apply to reuse of CCBs. The user of CCBs in certain applications (items 3A and 7–9 above) must notify the Illinois Environmental Protection Agency (IEPA) of each project utilizing CCBs, document the quantity of CCBs that will be utilized, and certify that

the CCBs have not been mixed with hazardous waste prior to use and that the CCBs do not exceed Class I groundwater quality standards for metals when tested utilizing ASTM Method D3987-85. Dust generation in fly ash applications must be minimized. CCBs may not be accumulated speculatively. It should be noted that CCBs are not accumulated speculatively if 75% of the CCBs accumulated at the beginning of a calendar year are used during the calendar year. Other CCB applications may be authorized upon IEPA's written determination that the proposed use has no greater adverse environmental impact than the beneficial uses specified in the law.

FIELD APPLICATIONS AND OBSERVATIONS

In keeping with the early IEPA guidance that CCBs may be used "as a functional substitute for agricultural lime as a soil conditioner," the Duck Creek mixed CCB was applied agriculturally in Illinois to better understand the behavior of this material in agricultural settings.

The farmer contributing to this project previously applied the mixed CCB in areas to evaluate the effectiveness in improving plant growth compared with similar soils and crops in the immediate area. The mixed CCB-treated and untreated (unfarmed) soils were geographically located adjacent to one another, with a farm access road and waterway dividing them. A description of the CCB application and history of land use over recent years provided by the farmer as follows:

- **Untreated soil**

The untreated soil grab samples were obtained from an area that was farmed many years ago but is too small for today's larger machinery. Currently, it is a grassy side patch.

- History

- ▶ Sod area
- ▶ Has not been farmed since 1985
- ▶ No fertilizers or crops – just mowed
- ▶ B²-slope – too small of area to farm
- ▶ About 300 yards from mixed CCB-treated area grab sample

- **Mixed CCB-treated soil**

The treated area is soil is from normal crop acres.

- Additive history

- ▶ Fall 1996 – applied 2000 lb/acre mixed CCB
- ▶ Fall 1998 – applied 1400 lb/acre mixed CCB
- ▶ Fall 2000 – applied 1400 lb/acre mixed CCB
- ▶ Fall 2002 – applied 1400 lb/acre high-calcium lime (200 lb/ton available)

- Crop history

- ▶ 2000 corn
 - Herbicide – Dual 1.5 pts, Accent .33 oz, Beacon .33 oz, Clarity 4 oz

- Fertilizer – 12–35–45 plus 50 lb ammonium sulfate
- 35 gal of 28% – 98 lb nitrogen in liquid form
- ▶ 2001 soybeans
 - Herbicide – Roundup 1 qt/acre
 - Fertilizer – 12–35–45
- ▶ 2002 corn
 - Herbicide – Dual 1.5 pts, Accent .33 oz, Beacon .33 oz, Clarity 4 oz
 - Fertilizer – 12–35–45 plus 50 lb ammonium sulfate
 - 35 gal of 28% – 98 lb nitrogen in liquid form
- ▶ 2003 soybeans
 - Herbicide – Roundup 1 qt/acre
 - 200 lb potash (0–0–60)
- ▶ 2004 corn
 - Herbicide – Dual 1.5 pts, Accent .33 oz, Beacon .33 oz, Clarity 4 oz
 - Fertilizer – 12–35–45 plus 50 lb ammonium sulfate
 - 35 gal of 28% – 98 lb nitrogen in liquid form

GOALS AND OBJECTIVES

The goal of the proposed effort was to determine the environmental appropriateness of CCBs for agricultural land applications. Supporting objectives were to:

1. Determine the environmental performance of specific CCBs.
2. Determine the agricultural advantages or effectiveness of CCBs.
3. Determine any potential for impact on groundwater or surface water.

The anticipated deliverables for this effort were proposed to be:

1. A report that could be used by IEPA to facilitate a determination on the appropriateness of a specific mixed ash for agricultural application in Illinois. Chapter 1 of this report has served that purpose.
2. A generic document detailing the process for qualifying CCBs for agricultural application. Chapter 2 of this report was assembled to meet this deliverable.

EXPERIMENTAL

Sampling

The primary samples of interest for this project were an as-managed mixed CCB and soil. The as-managed mixed CCB consisted of fly ash, bottom ash, and sulfite-rich FGD material that had been sluiced to a CCB management pond and later stacked for dewatering. Soil samples, both field-treated with the as-managed dewatered mixed CCB and untreated, were collected from

local farmland. The farmland was last treated with the as-managed mixed CCB in 2000, and samples of the soil were obtained in 2003 and 2004.

For background information, separate samples of fly ash, bottom ash, and sulfite-rich FGD material were obtained before the point of sluicing. In addition, a sample of water from the CCB management pond was obtained for testing. The water and ash samples were collected by plant personnel, and the soil was collected by the farmer of the land. One as-managed mixed CCB sample was quite wet compared to the other samples obtained and was, therefore, dewatered in the laboratory before any analyses were performed.

Proton-Induced X-Ray Emission (PIXE)

A list of trace elements of concern was developed for the project. This list was to include but not be limited to antimony, arsenic, boron, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, thallium, and zinc, with additional elements determined by PIXE analysis. PIXE analysis is a method that determines the elements from sodium through uranium.

Bulk Chemical Analyses

Bulk chemical analyses of the solid samples to determine the major and minor elements were done using x-ray fluorescence.

Total Trace Element Analyses

The solid samples were analyzed for the list of trace elements established above. The samples were dried before analysis if there was a significant amount of moisture present. Samples were digested using EPA Methods 3050 and 3050B (U.S. Environmental Protection Agency, 2005a,b). The total concentrations of the elements were then determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and ICP-mass spectrometry (ICP-MS) using EPA Methods 6010 and 6020 (U.S. Environmental Protection Agency, 2005c,d). A direct mercury analyzer (DMA-80) was used to determine total mercury concentration on most samples and cold-vapor atomic absorption (EPA Method 7471 [U.S. Environmental Protection Agency, 2005e]) was used for the remaining samples.

ASTM D3987 Leaching

The solid samples were leached using ASTM D3987 (ASTM, 2004). This is an 18-hour leachate test using distilled deionized water with end-over-end agitation. The leachates and a sample of CCB management pond water were analyzed for the list of trace elements established above. The leachates were analyzed by ICP-AES and ICP-MS using EPA Methods 6010 and 6020. Mercury concentrations were determined using cold-vapor atomic absorption and cold-vapor atomic fluorescence spectrometry (EPA Method 245.7 [Draft]) (U.S. Environmental Protection Agency, 2005).

The fly ash, bottom ash, and sulfite-rich FGD material samples obtained in conjunction with the first as-managed mixed CCB and soil samples were subjected to ASTM D3987 leaching to provide additional background information.

RESULTS AND DISCUSSION

PIXE

To determine the list of elements of concern, an as-managed mixed CCB and the individually collected fly ash, bottom ash, and sulfite-rich FGD material samples were analyzed with PIXE. In addition to the 13 elements initially agreed upon (see Experimental PIXE Section), beryllium and vanadium were added to the trace element list based on levels noted in the PIXE analyses. Results of the PIXE analyses can be found in Appendix A.

Bulk Chemical Analyses

Results of bulk major/minor chemical analyses for the as-managed mixed CCB and soil samples are shown in Table 1-1. These analyses showed that the field-treated and untreated soil samples are very similar in composition. The field-treated soil did show slightly more calcium, manganese, and sulfur than the untreated soil, as well as a higher loss-on-ignition (LOI) value. The bulk oxide content of the as-managed mixed CCB samples is similar to or less than those of the field-treated and untreated soils for many elements, including silicon, aluminum, magnesium, sodium, potassium, titanium, manganese, phosphorus, strontium, and barium. The elements that are significantly higher in the as-managed mixed CCB than in the soils are iron, calcium, and sulfur. Higher concentrations of calcium and sulfur make CCBs an option for agricultural soil amendment because these are essential plant nutrients required by plants in high amounts. Iron is also an essential plant nutrient. Three years after the final application of the as-managed mixed CCB (2003), sulfur was present at a higher level in the field-treated soil than the untreated soil. However, the following year (2004), the measured sulfur content had decreased to less than that in the untreated soil.

ACAA indicates that elemental concentrations in most U.S. CCBs are present at levels similar to soils (American Coal Ash Association, 1998). Most major, minor, and trace elements present in the as-managed mixed CCB and soils evaluated in this study are at levels similar to soils as reported elsewhere (ACAA, 1998; Kabata-Pendias and Pendias, 1989; Stout et al., 1988) with the following exceptions:

- Elevated boron and sulfur in the as-managed mixed CCB
- Lower nickel levels in both 2003 soil samples
- Lower calcium in the untreated soil samples
- Slightly lower phosphorus in the 2004 untreated soil sample
- Lower sulfur in the 2004 field-treated soil sample

Table 1-1. Bulk Major/Minor Chemical Analyses Results of As-Managed CCB and Soils, % as oxide

	As- Managed CCB	As- Managed CCB	As- Managed CCB	Untreated Soil	Untreated Soil	Field- Treated Soil	Field- Treated Soil
Collection Date	June 2003	Oct 2004	Nov 2004	Oct 2003	Dec 2004	Oct 2003	Dec 2004
SiO ₂	33.32	19.19	17.52	74.42	72.19	71.37	71.88
Al ₂ O ₃	10.96	6.54	6.60	10.24	11.79	10.53	10.43
Fe ₂ O ₃	17.92	10.33	5.89	4.16	5.23	4.25	3.90
CaO	10.73	27.32	30.00	0.77	0.79	1.35	1.02
MgO	0.96	0.74	0.69	0.59	0.99	1.00	0.82
Na ₂ O	0.97	0.52	0.52	0.99	0.93	0.95	0.92
K ₂ O	1.29	0.75	0.74	2.15	2.17	2.13	2.09
TiO ₂	0.57	0.34	0.35	0.78	0.80	0.72	0.76
MnO ₂	0.04	0.05	0.04	0.09	0.10	0.18	0.17
P ₂ O ₅	0.09	0.05	0.09	0.14	0.08	0.13	0.11
SrO	0.02	0.02	0.03	0.01	0.02	0.01	0.02
BaO	0.03	0.02	0.04	0.07	0.06	0.08	0.08
SO ₃	6.59	24.77	29.46	0.07	0.04	0.20	0.01
LOI	16.52	9.34	8.04	5.53	4.82	7.11	7.78
Moisture, as received	12.55	23.52	31.84	14.35	2.05	17.54	15.49

The major and minor components of CCBs, whether individual materials (fly ash, bottom ash, boiler slag, or sulfite-rich FGD material) or mixed CCBs, are usually within concentration ranges, resulting in a benefit to plants.

Results of bulk chemical analyses for the fly ash, sulfite-rich FGD material, and bottom ash samples are shown in Table 1-2. Additionally, Table 1-2 contains a column labeled “calculated concentrations of as-managed CCB.” This column was calculated using the production ratios (approximately 59,700 tons of fly ash, 10,500 tons of bottom ash, and 141,000 tons of sulfite-rich wet FGD material) of the materials produced and combined in the on-site CCB management pond. While it is expected that some variability in the total composition of each material will be observed over time, the data from individual streams and the calculated concentrations of as-managed material provide some insight into the variability of the material that is actually available for agricultural use. When sluicing a mixed stream including materials of different textures and density (such as fly ash, bottom ash, and sulfite-rich FGD material) it is anticipated that heavier, larger particles (most likely bottom ash) will settle from the material earlier than the finer, lighter particles. Research has been done to show the variability of materials in CCB sites where mixed streams have been sluiced, showing that the real-world as-managed samples are not precise composites of the three streams in production ratios. The as-managed samples from 2004 are closer in concentration to the calculated number than the sample from 2003. The mechanical removal of the mixed streams from the pond should not be expected to retrieve a sample of exact composition, and even as material is removed from different locations within the pond, the mix of streams and the composition will vary. This information supports the recommendation that a CCB sample obtained for analysis be taken from a source that is as close to that actually being used or, as it is termed in this report, the as-managed sample. The as-managed sample will allow the analytical work to provide the best information.

Table 1-2. Bulk Major/Minor Chemical Analyses Results of Individual CCBs, % as oxide

Collection Date	Fly Ash	FGD Material	Bottom Ash	Calculated Concentrations of As-Managed CCB
	June 2003	June 2003	June 2003	
SiO ₂	48.36	1.68	30.75	16.32
Al ₂ O ₃	16.73	0.42	10.68	5.54
Fe ₂ O ₃	18.12	0.50	16.23	6.26
CaO	4.80	41.92	8.03	29.74
MgO	1.03	1.29	0.85	1.19
Na ₂ O	1.57	0.13	0.67	0.56
K ₂ O	2.13	0.04	1.24	0.69
TiO ₂	0.88	0.02	0.53	0.29
MnO ₂	0.08	0.02	0.05	0.04
P ₂ O ₅	0.12	0.07	0.07	0.08
SrO	0.03	0.01	0.01	0.02
BaO	0.04	0.02	0.03	0.03
SO ₃	1.94	53.94	3.75	36.75
LOI	4.17	-0.04	27.11	2.50
Moisture, as received	1.05	0.44	10.28	NA ^a

^a Not applicable.

When reviewing compositional data on CCBs, it is important to understand that reporting of major/minor components as oxides is merely a reporting convention and is not necessarily indicative of the actual chemical forms in the ash. One important example of this is found in the reported calcium oxide concentration. There is likely little free calcium oxide, or lime, present. In fly ash or bottom ash, the calcium usually is present as a component of the glassy phase with numerous elements and is not present as primarily CaO, as reported. In FGD materials, calcium is likely associated with sulfur and is present as calcium sulfite or calcium sulfate. If any calcium oxide is present as lime in any CCBs and is exposed to water by sluicing or storage in a pond situation, that lime will be present as calcium hydroxide or hydrated lime. In a mixed stream such as the material evaluated in this project, both crystalline and amorphous (glassy) phases will be present, and many components will be combinations of elements and are likely to be hydrated because of the exposure to water. However, the bulk compositional data are useful in evaluating CCBs for various use applications because of the voluminous comparative historical data, empirical evaluations, and comparison with other tests and standards.

Total Trace Element Analyses

Results for the total trace element analyses of the as-managed mixed CCB and soil samples are shown in Table 1-3. The total trace element data again provide information on the composition of the as-managed CCBs and the untreated and field-treated soils. Most of the trace elements tested have similar concentrations in the as-managed CCBs and the soils from the site. Arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, and zinc all exhibit concentrations that fall within the range of soil concentrations reported by ACAA (American Coal Ash Association, 1998). Beryllium and boron concentrations measured in the CCB samples were higher than the concentrations of these elements in the untreated and treated soils from the

Table 1-3. Total Trace Element Results of As-Managed CCB and Soils, ppm

Collection Date	As-Managed CCB	As-Managed CCB	As-Managed CCB	Untreated Soil	Untreated Soil	Field-Treated Soil	Field-Treated Soil
	June 2003	Oct 2004	Nov 2004	Oct 2003	Dec 2004	Oct 2003	Dec 2004
Sb	0.981	<2.7	<2.7	1.36	<2.7	<1	<2.7
As	6.95	6.45	7.55	14.1	14.3	13.7	11.6
Be	6.71	3.88	3.26	1.75	1.97	1.82	1.77
B ^a	386	388	305	<100	<100	<100	<100
Cd	0.99	1.1	1.07	1.03	<0.5	<1	<0.5
Cr	132	57.6	52.7	39.9	47.6	40.6	35.9
Co	22.5	12.8	10.4	10.3	8.28	9.83	6.3
Cu	40.4	18.7	19.7	19.5	23	19.2	13
Pb	13.3	16	16.9	22.5	23.6	19.8	22.5
Hg	<0.1	0.13	0.163	<0.1	0.037	<0.1	0.013
Ni	283	43.5	37.5	<1	25.2	<1	17.7
Se	< 2	<2	2.62	<2	<2	<2	<2
Tl	1.5	<1.5	<1.5	<1.5	<1.5	<1.5	<1.5
V	111	54.6	55	63.1	95	65.6	76.4
Zn	144	106	94.1	56.6	71.6	72.2	62.3

^a Total extractable boron.

site. Beryllium was measured to be approximately twice the level in CCBs as compared to the soils from the site. No increase in beryllium content was noted in the treated soils over the untreated soils. The boron level was below the lower level of quantitation in the untreated and treated soils, also indicating that the addition of the boron-containing CCBs did not impact the long-term boron concentrations in the soils. Mercury, nickel, and zinc are higher in the as-managed CCBs also.

Results for the total trace element analyses of the fly ash, sulfite-rich FGD material, and bottom ash samples as well as the CCB management pond water are shown in Table 1-4. The data for these materials are presented only for comparative purposes, as it has been established that the as-managed samples are those that are being applied to agricultural land and are the appropriate samples to use to assess the appropriateness for agricultural use. The trace element concentrations in the CCB management pond water show which elements have leached from the sluiced CCBs in the pond. Pond water tends to accumulate some trace elements, the most prominent of which is boron at this site.

The total trace element concentrations of materials are most valuable for assessing CCBs for agricultural application using guidelines developed by EPA for placement of sewage sludge (Part 503 rules) which is used broadly for determining suitability for land application (U.S. Environmental Protection Agency, 1993). The Part 503 rules were developed specifically for sewage sludge, but individual elements similar to those found in CCBs are included in the guideline. Table 1-5 shows the total trace element concentrations of metals allowed for land application of sewage sludge as denoted in the Part 503 rules. These values are often orders of magnitude higher than those found in CCBs.

Table 1-4. Total Trace Element Results of Individual CCBs and CCB Management Pond Water, ppm

	Fly Ash	FGD Material	Bottom Ash	CCB Management Pond Water
Collection Date	June 2003	June 2003	June 2003	June 2003
Sb	2.36	1.77	1.7	0.0163
As	16.1	<1	7.35	0.0254
Be	11.6	<1	7.06	<0.01
B ^a	1210	131	474	349
Cd	3.79	<1	1.07	0.00189
Cr	196	5.42	138	<0.05
Co	27.2	<1	24.2	<0.1
Cu	74.8	2.74	45.3	0.1
Pb	30.6	1.38	11	<0.002
Hg	0.193	0.137	<0.1	0.000011
Ni	337	3.1	308	<0.04
Se	<2	<2	<2	0.0989
Tl	2.34	<1.5	<1.5	<0.002
V	186	4.81	117	0.013
Zn	401	47.7	216	<0.05

^a Total extractable boron for solid materials.

Table 1-5. Federal Standards for Land Application of Sewage Sludge, ppm

Element	Ceiling Concentration ^a	Monthly Average Concentration ^a
As	75	41
Cd	85	39
Cu	4300	1500
Pb	840	300
Hg	57	17
Mo	75	NA ^b
Ni	420	420
Se	100	100
Zn	7500	2800

^a Dry weight basis.

^b Not applicable.

ASTM D3987 Leaching

Results of the ASTM D3987 leaching of the as-managed mixed CCB and soil samples are shown in Table 1-6. Short-term leaching is considered by the authors to be sufficient to evaluate the leaching characteristics of the as-managed mixed CCB because the pH of the solid material is lower than 11.5, which is a level where secondary hydration reactions occur that affect the leachability of elements in materials such as CCBs (Hassett, 1997; Hassett et al., 1991). Additionally, hydration reactions will likely have gone on in the sluicing and during storage in the ash pond, making long-term leaching, which compensates for these long-term reactions, unnecessary. Boron, which has a high mobility in soil–water systems, is seen to be absent in all

Table 1-6. ASTM D3987 Leachate Results of As-Managed CCB and Soils, µg/L

	As- Managed CCB	As- Managed CCB	As- Managed CCB	Untreated Soil	Untreated Soil	Field- Treated Soil	Field- Treated Soil
Collection Date	June 2003	Oct 2004	Nov 2004	Oct 2003	Dec 2004	Oct 2003	Dec 2004
Sb	<2	<2	4.4	<2	<2	<2	<2
As	7.1	5.1	7.9	6.8	<2	5.4	<2
Be	<10	<0.1	<0.1	<10	<0.1	<10	<0.1
B	9200	16500	21300	<100	<100	<100	<100
Cd	<0.2	0.65	0.97	<0.2	<0.2	<0.2	<0.2
Cr	<50	48.5	50.1	<50	<2	<50	<2
Co	<100	<1	<1	<100	<1	<100	<1
Cu	<50	<1	<1	<50	6.5	<50	8.3
Pb	<2	<1	<1	<2	<1	<2	<1
Hg	<0.01	<0.01	<0.01	0.027	<0.01	<0.01	<0.01
Ni	<40	9.5	14.8	<40	<2	<40	<2
Se	31.1	11.6	61.5	<2	<2	<2	<2
Tl	<2	<2	<2	<2	<2	<2	<2
V	17.8	98.2	101	<2	<2	<2	4.8
Zn	<50	2.2	3.7	<50	<1	<50	3.6
pH	9.62	10.71	10.31	6.79	6.68	7.08	7.14

soil leachates. This gives indirect evidence for the potential for crop improvements in this area by applications of boron-rich materials.

Results of the ASTM D3987 leaching of the fly ash, sulfite-rich FGD material, and bottom ash samples are shown in Table 1-7. An analysis of the CCB management pond water is also included in Table 1-7. Again, these data are presented for comparative purposes only. The high mobility of boron in the pond is evident by its high concentration in the pond water. Boron in the dry materials may end up incorporated into a stringier structure upon hydration and would provide a long-term source of this element for sometime after the initial application.

Field Application and Observations

The farmer contributing to this project was very happy with the results achieved in crop growth with the application of the mixed CCB. Comments from the farmer are provided below:

Local Farmer Comments

Mixed CCB-treated and untreated soils were obtained from a local farmer. Comments from this farmer include the following:

- “It’s great!”
- “Terrific soil conditioner.”
- The soils are easily erodible but the “soft and fluffy” nature of the material “gives the soil integrity.”

The farmer applied the mixed CCB every other year over a 6-year period (three times) and had a stockpile area for the material. Figure 1-1 is a photo of harvested corn stalks that were grown on this mixed CCB stockpile area. The farmer of the land noted that corn grew very well in this stockpile area.

This provides strong anecdotal evidence that at least corn will do well with this material despite the analytical concentrations of boron, indicating potential phytotoxicity. In one EERC study where boron concentrations exceeded the long-term irrigation standard, no adverse effects on plants were noted (Pflughoeft-Hassett et al., 2004). Paul (2000) indicates that boron contamination of ground or surface waters from CCBs is rare, with little or no demonstrated environmental damage.

Table 1-7. ASTM D3987 Leachate Results of Individual CCBs and CCB Management Pond Water Results, µg/L

	Fly Ash	FGD Material	Bottom Ash	CCB Management Pond Water
Collection Date	June 2003	June 2003	June 2003	June 2003
Sb	<2	<2	<2	16.3
As	10.1	2.7	3.4	25.4
Be	<10	<10	<10	<10
B	28700	12100	12000	349000
Cd	0.3	<0.2	<0.2	1.89
Cr	140	<50	6.7	<50
Co	<100	<100	<100	<100
Cu	140	<50	<50	100
Pb	<2	<2	<2	<2
Hg	<0.01	0.321	<0.01	0.011
Ni	<40	<40	<2	<40
Se	136	<2	26.4	98.9
Tl	<2	<2	<2	<2
V	67.6	<2	15.7	13
Zn	<50	<50	<50	<50
pH	11.60	8.32	9.28	8.07

CONCLUSIONS

Based on the laboratory data obtained in this project and on the anecdotal evidence provided by a local farmer, the EERC recommends the use of this mixed CCB in agricultural land application. The EERC recommends analyzing the as-managed mixed CCB yearly for the trace elements tested in this project. Application rate and plant sensitivity, which were not explored in this project, should be taken into account before application of this material. It should be noted that the farmland was last treated with the as-managed mixed CCB in 2000, and samples of the soil were obtained in 2003 and 2004. Thus precipitation would have affected the concentrations of mobile trace elements.



Figure 1-1. Harvested corn stalks grown on previously mixed CCB stockpile.

The crops flourished in the 2003–2004 period after application of the as-managed mixed CCB, so it can be concluded that the addition of the as-managed mixed CCB benefited the plant growth. One explanation is that soil conditions were changed as a result of CCB addition, which could impact root growth over the long term. While the specific soil issue (nutrients, pH, soil tilth, or water-holding capacity) addressed by addition of the as-managed mixed CCB were not identified by the user, the empirical evidence indicated a benefit to the crops planted when the as-managed mixed CCB was added. The only potential trace element issue that could have had a negative impact was boron, which was present in the as-managed mixed CCB at higher concentrations as compared to the untreated soils. There was no evidence that the boron was detrimental to plant growth. It is known that boron is an essential plant nutrient but only trace amounts are needed, and too much boron can be phytotoxic and detrimental to plants. It has been noted in greenhouse and container studies that elevated boron concentrations can be detrimental to plant growth, and limits have been developed for boron concentrations in irrigation water. Boron is highly mobile in water, so it can be hypothesized that the boron present in the added as-managed mixed CCB was washed through the soil into the subsurface and diluted within the soil and subsoil. This hypothesis is supported by the boron concentrations in the treated soils, which were equivalent to the boron concentrations of the untreated soils. Further study of the specific site and crops would be required to determine if the boron in the as-managed mixed CCB provided a source of needed boron or other trace elements for the crops planted.

Existing regulatory standards established for sewage sludge have been used to determine the appropriateness of CCBs and other industrial resources for agricultural land application. The trace element analyses of the as-managed mixed CCB analyzed in this project indicate that the concentrations are at least one order of magnitude lower than the ceiling concentrations in these Part 503 rules.

The primary issue in the use of the as-managed mixed CCB is boron. Boron has accumulated to a high concentration in the CCB management pond water as a result of the leaching of the ash components that occurs during sluicing and storage. Relying on boron concentration limits for long-term irrigation might suggest that the as-managed CCB could exhibit phytotoxicity. The fact that flourishing corn has been shown growing on CCB material indicates that phytotoxicity, at least for that crop species, is not problematic. Boron, which is essential for healthy plant growth, has a very low human and animal toxicity. The reference dose published by EPA is 0.2 mg/kg/day, which for an adult human translates to 35 mg/day of boron. An adult weighing 70 kg would be able to sustain a constant intake of about 16 mg/L of boron for a lifetime without any harm according to EPA.

There are significant differences between the theoretical calculated values for the as-managed CCB and those actually found in the as-managed CCB samples for both major/minor and trace elements. There are several likely explanations for these. The calculated production ratio amounts are likely accurate for the plant but may not be accurate for recovered material as a result of settling differences in the pond. Pond water tends to accumulate some trace elements, the most prominent of which is boron at this site. This supports the recommendation to analyze the material to be used on a regular basis.

Many of the improvements in crop production reported may be due to supplementation of boron on potentially boron-deficient soils. Selenium, also present in the recovered material, is an essential nutrient, can be highly beneficial, and should be looked at as a plus when evaluating the data presented in this report.

REFERENCES

- American Coal Ash Association. *Coal Fly Ash – An Environmental Perspective*; TB-21; Alexandria, VA, Sept 1998; 4 pp.
- American Coal Ash Association. *2004 Coal Combustion Product Production and Use Survey*; Aurora, CO, Sept 9, 2005.
- ASTM International. Standard Method for Shake Extraction of Solid Waste with Water. In *Annual Book of ASTM Standards*; Section 11: Water and Environmental Technology, ASTM D3987-85, 2004.
- Berland, T.D.; Pflughoeft-Hassett, D.F.; Dockter, B.A.; Eylands, K.E.; Hassett, D.J.; Heebink, L.V. *Review of Handling and Use of Wet and Dry FGD Materials*; CARRC Report for Utility Solid Waste Activities Group; Energy & Environmental Research Center: Grand Forks, ND, April 2003.
- Bigham, J.; Dick, W.; Forster, L.; Hitzhusen, F.; McCoy, E.; Stehouwer, R.; Traina, S.; Wolfe, W.; Haefner, R. *Land Application Uses for Dry FGD By-Products: Phase 1 Report*. Electric Power Research Institute, Report No. EPRI TR-105264. Electric Power Research Institute, Palo Alto, CA, April 1993.

- Chen, L.; Dick, W. *Flue Gas Desulfurization By-Products Provide Sulfur and Trace Mineral Nutrition for Alfalfa and Soybean*. Final Report (April 2000 – April 2002) for U.S. Department of Energy Cooperative Agreement No. DE-FC26-98FT40028; CBRC No. 99ECE08; Ohio State University/Ohio Agricultural Research and Development Center: Wooster, OH, April 2002.
- Dick, W.; Chen, L.; Bigham, J.; Slater, B.; Bok Lee, Y.; Ramsier, C.; Bardhan, S.; Chen, Y.; Nelson, Jr., S. Beneficial Use of CCPs in Agronomic and Horticulture Applications. Presented at Combined ACAA–CBRC–WRAG 2004 Fall Meeting, Denver, CO, Oct 5, 2004.
- Electric Power Research Institute. *Land Application of Coal Combustion By-Products: Use in Agriculture and Land Reclamation*. EPRI TR-103298. Electric Power Research Institute, Report No. EPRI TR-103298. Electric Power Research Institute, Palo Alto, CA, June 1995.
- Fehring, N.E. The Tips, Tricks, Traps, and Uses of FGD Materials in Agricultural Productions. Presented at ACAA 2003 Fall Meeting, Las Vegas, NV, Oct 7, 2003.
- Franzen, D. *Managing Saline Soils in North Dakota*; SF-1087(revised); North Dakota State University NDSU Extension Service: Fargo, ND, Sept 2003; 11 pp.
- Hassett, D.J., Pflughoeft-Hassett, D.F., McCarthy, G.J. Ettringite Formation in Coal Ash as a Mechanism for Stabilization of Hazardous Trace Elements. *In Proceedings of the Ninth International Ash Use Symposium—Volume 2: Stabilization and Aquatic Uses*, Orlando, FL, Jan 22–25, 1991; EPRI GS-7162, Project 3176, 1991, pp. 31–1 to 31–17.
- Hassett, D.J., Enhanced Ettringite Formation: A Treatment Option for the Remediation of Boron- and Selenium-Containing Wastes. *1997 SPE/EPA Exploration and Production Environmental Conference*; Dallas, TX, March 3–5, 1997.
- Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soils and Plants*; CRC Press, Inc.: Boca Raton, FL, 1989; 315 pp.
- Korcak, R.F. Agricultural Uses of Coal Combustion Byproducts. In *Agricultural Uses of Municipal Animal and Industrial Byproducts*; Wright, R.J., Kemper, W.D., Millner, P.D., Power, J.F., Korcak, R.F, Eds.; Conservation Research Report No. 44; U.S. Department of Agriculture, Agricultural Research Service, 1998; pp. 103–119.
- Li, Y.; Zhang, M.; Stoffella, P.; He, Z.; Bryan, H. *Utilization of Fly Ash and Urban Yard Waste as Soil Amendments to Improve Soil Fertility*. Final Report (Oct 1999– April 2002) for U.S. Department of Energy Cooperative Agreement No. DE-FC26-98FT40028; CBRC No. 99ECE11; Tropical Research and Education Center Publication No. TREC-LI02-06; Tropical Research and Education Center: Homestead, FL, May 2002.

- Paul, B.C. *Boron Transport from Coal Combustion Product Utilization and Disposal Sites*. Final Report for U.S. Department of Energy Cooperative Agreement No. DE-FC26-98FT40028; CBRC No. 99ECM04; Southern Illinois University: Carbondale, IL, 2000.
- Pflughoeft-Hassett, D.F.; Dockter, B.A.; Hassett, D.J.; Heebink, L.V.; Solc, J.; Buckley, T.D. *Demonstration of Coal Ash for Feedlot Surfaces*; Final Report; EERC Publication 2004-EERC-02-10; Energy & Environmental Research Center: Grand Forks, ND, Feb 2004.
- Stout, W. L.; Hern, J.L.; Korcak, R.F.; Carlson, C.W. *Manual for Applying Fluidized-Bed Combustion Residue to Agricultural Lands*; ARS-74; U.S. Department of Agriculture, Agricultural Research Service, 1988.
- Sumner, M.E. Uses of Gypsum in Agriculture. Presented at ACAA 2005 Fall Meeting, Atlanta, GA, Sept 27, 2005.
- U.S. Environmental Protection Agency. Method 3050, Acid Digestion of Sediments, Sludges, and Soils. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005a.
- U.S. Environmental Protection Agency. Method 3050b, Acid Digestion of Sediments, Sludges, and Soils. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005b.
- U.S. Environmental Protection Agency. Method 6010, Inductively Coupled Plasma-Atomic Emission Spectrometry. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005c.
- U.S. Environmental Protection Agency. Method 6020, Inductively Coupled Plasma – Mass Spectrometry. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005d.
- U.S. Environmental Protection Agency. Method 7471, Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique). *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005e.
- U.S. Environmental Protection Agency. Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry: Draft. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, Feb 2005.

U.S. Environmental Protection Agency. Regulatory Determination on Wastes from the Combustion of Fossil Fuels; Final Rule. *Fed. Regist.* **2000**, 65 (99), 32214–32237.

U.S. Environmental Protection Agency. Standards for the Use and Disposal of Sewage Sludge. *Code of Federal Regulations*, Section 40, Part 503, 1993; *Fed. Regist.* **1993**, 58, 9387.

CHAPTER 2. QUALIFICATION PROCESS FOR AGRICULTURAL LAND APPLICATION OF CCBs

INTRODUCTION

Agricultural application is one of the largest potential CCB utilization applications. The 2000 EPA decision on the status of CCBs under RCRA indicated that the regulation of CCBs appropriately falls under RCRA Subtitle D for solid wastes, indicating that EPA encourages the beneficial use of CCBs and including the agricultural use of CCBs as one of its identified beneficial uses. EPA specifically noted that agricultural applications of CCBs included their use as a substitute for lime. Additional potential agricultural benefits of CCBs have been identified by numerous researchers, including the following:

- Alleviating soil trace element deficiencies
- Modifying soil pH
- Increasing levels of needed calcium and sulfur
- Increasing infiltration rates
- Increasing depth of rooting
- Increasing drought tolerance

However, concerns have also been noted regarding the land application of CCBs, including the following:

- Excessive trace metal loading
- High soluble salt loading
- High sodium loading
- Sulfite damage to crops
- Leaching of toxic substances into groundwater
- Human exposure to CCBs

These benefits and concerns can be seen as two sides to individual issues, and the agricultural community is familiar with cautions that must be taken when land-applying a wide variety of materials in an effort to improve soil and crop growth. Korcak (1998) states that while potential for the hazards listed exists, it is also true that all of them can be avoided by judicious application of selected CCBs. This is also borne out by a large number of studies that have demonstrated improved crop productivity when a wide variety of CCBs were land-applied. The work reported in Chapter 1 of this report is an example of that. The fact that the characteristics of CCBs can be responsible both for benefits and potential hazards is an admonition to the CCB industry to take a leadership position in developing a method of determining which CCBs are appropriate for agricultural land application and to work with the agricultural community to understand how to gain the best benefit from these materials with responsible application plans. As the CCB industry works toward increased utilization, the use of CCBs in agricultural land applications may offer an option to utilize CCBs that are available in rural areas or that are not well-suited for use in cementitious applications.

BACKGROUND

In 1993, EPA issued a formal regulatory determination that the characteristics and management of the four large-volume fossil fuel combustion waste streams (i.e., fly ash, bottom ash, boiler slag, and flue gas emission control waste) do not warrant hazardous waste regulation under RCRA and that utilization practices for CCBs appear to be safe. In addition, EPA “encourage[d] the utilization of coal combustion byproducts and support[ed] State efforts to promote utilization in an environmentally beneficial manner.” In the second phase of the study, EPA focused on the by-products generated from fluidized-bed combustion (FBC) boiler units and the use of CCBs from FBC and conventional boiler units for mine reclamation, among other things. Following completion of the study, EPA issued a regulatory determination in April 2000 that again concluded that hazardous waste regulation of these combustion residues was not warranted. EPA indicated that sufficient environmental protection could be afforded for the beneficial use of CCBs in agricultural uses by engaging industry to establish voluntary controls on the practice. Based on this indication, it is in the CCB industry’s best interest to undertake a coordinated effort to understand how CCBs can be best used in a beneficial manner in agricultural applications and to work toward the development of a means of qualifying CCBs based on optimizing the benefits while maintaining sufficient environmental protection. The goal of this project was to use a case study of agricultural application of a specific CCB as a means of developing an understanding of the requirements for an industry-based qualifying scheme for CCBs to be used in agricultural soil applications.

Numerous studies have been performed and publications published on the use of CCBs in agricultural land application. These studies have included a rather expansive matrix of CCBs, which were sometimes blended with other industrial, municipal, or agricultural materials; a wide variety of laboratory and field conditions; and applications to many plant types. CCBs that have been investigated include fly ash, FGD materials, which includes FGD gypsum, FBC materials, and bottom ash.

A preliminary summary of previous research provides background information on which much of this study was built. A review of past work on the effect of CCBs on plant growth (Clark et al., 1993) indicates that little agricultural utilization is occurring and that information is limited. Wet sulfite-rich FGD material (scrubber sludge) impoundments have been successfully vegetated using wheat grass, tall fescue, sweet clover, millet, cottonwoods, and red cedars. Wet sulfite-rich FGD materials were successfully used as a source of boron and selenium trace nutrients. FBC materials were variously reported to increase maize and soybean yields and to provide a necessary source of calcium for apples. Research conducted by the Tennessee Valley Authority (TVA) indicated that lime/limestone FGD material can be incorporated into fertilizer formulations (Santhanam et al., 1981).

In controlled greenhouse tests on several different coal products (Clark et al., 1993), the addition of FBC materials to an acid soil of known severe aluminum toxicity served to double the yield of maize at an optimum addition rate of 2% to 3% in the soil mix, but yields decreased at higher use rates. The effect of fly ash addition varied with coal type, with a bituminous Class F fly ash showing its highest growth enhancement at 3% addition, whereas lignitic Class C fly ash continued to increase yields at rates up to 25% of the soil mix. FGD materials generally provided

less growth enhancement, and optimum results were obtained at very low rates of 1% or less of the soil mix, possibly owing to detrimental effects of sulfite contained in these by-products. The use of a wet sulfite-rich FGD material that had been processed to convert sulfite to gypsum enhanced growth rates at addition rates up to 75% of the soil mix, consistent with the known beneficial effect of gypsum application to acid soil.

A major study on land application of FGD and PFBC (pressurized FBC) by-products (Beeghly et al., 1993) was sponsored by the Ohio Coal Development Office, DOE, Electric Power Research Institute (EPRI), Ohio Edison, American Electric Power, Dravo Lime Company, and Ohio State University. By-products from fifteen sources were investigated, representing four major clean coal technologies, including furnace injection FGD (LIMB [limestone injection multistage burner]), duct injection FGD, spray dryer absorber (SDA), and FBC (AFBC [atmospheric FBC] and PFBC). These by-products exhibited high alkalinity expressed as calcium carbonate equivalents of 25%–70%, sulfur contents of 2.4%–10.3%, fly ash contents of 10%–32%, and with the exception of FBC material, a high surface area and fineness. Selected by-products, alone or in combination with sewage sludge, were mixed with acid soils and mine spoils and tested in greenhouse growth studies. Results from different materials and mixtures varied. Example results included the following:

- Growth of tall fescue was enhanced in overburden spoil, but was suppressed in acid underclay.
- Sulfite-bearing material did not harm seed germination.
- LIMB by-product was successfully composted with sewage sludge.

The conclusion reached from the greenhouse tests was that the by-products tested, when used appropriately, are suitable substitutes for traditional soil-liming materials for acid soils. Field tests were performed successfully (Electric Power Research Institute, 1995; Bigham et al., 1993).

The commercial N-Viro soil process (Burnham, 1993) combines agricultural use with waste stabilization by composting CCBs or cement/lime kiln dust as originally used with municipal wastewater treatment sludge. The soil conditioner produced has a low nutrient value (1% N, P, K); a high lime equivalency of 25%–60%; good storage, handling, and spreading properties; and acceptable odor. The product is being produced from sludges produced in several municipalities and is used in agriculture and in cover for landfill. The key to the success of this process is that pathogenic microorganisms are destroyed by the alkalinity and heat associated with the addition of CCBs and possibly quicklime (CaO), followed by temperature-controlled composting and air-drying. Leachability tests at various pH levels have indicated that the heavy metals are below EPA toxicity limits.

The efficacy of using CCBs in agricultural applications cannot be generalized, since it is evident in comparing case studies that success is varied and depends on the suitability of the amendment to the soil and use conditions. For example, composting fly ash with field-collected waste vegetation was found to have no detrimental effect on bean germination in clayey and sandy soil but reduced germination in a high-humus soil (Varallo, 1993). Alkaline treatment is appropriate for eastern acidic soil, but not for many midwestern soils that are already alkaline in

nature. Novel applications in specialized areas may provide some of the more immediate commercial opportunities. FBC materials have been used at high rates of over 100 tons per acre as a mulching agent applied directly to cap the soil surface in orchards and raised-bed tomato rows (Korcak, 1993). Bottom ash has been demonstrated as an acceptable root medium for growing flowers in a hydroponic nutriculture system (Bearce et al., 1993).

Some concerns about the environmental safety of using CCBs in agriculture have been expressed in literature and still existed at the time this project was initiated, despite findings that leachable concentrations of toxic metals are very low (Pflughoeft-Hassett et al., 2004; Hassett and Heebink, 2001; Beeghly et al., 1993; Burnham, 1993; Bennett et al., 1981). While results vary somewhat for different by-products and soil types, the general finding reported is that leachates are nontoxic relative to the eight RCRA (Resource Conservation and Recovery Act) toxic metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) and often approach the more stringent primary standard for drinking water. The mobility of metals depends on the mineral matrix and on pH, and solubility of many constituents can be reduced at the high pH levels associated with alkaline CCBs. Certain beneficial trace plant nutrients present in fly ash, such as boron, selenium, and molybdenum, are assimilated in animal tissues (Lisk, 1981), and selenium deficiency in farm animals has been shown to be correctable by feeding the animals fly ash-grown crops. In coordinated tests on farm crops and animals (Bennett et al., 1981), there has been “little evidence” of detrimental effects on the food chain. One reason for caution is that several standard tests that have been used to develop leachate profiles for trace metals in CCBs, including the EPA extraction procedure (EP) and toxicity characteristic leaching procedure (TCLP) tests for acid solubility do not accurately represent typical utilization environments. In fact, these tests may evidence problems that do not exist or miss potential problems that could occur in practice (Hassett et al., 2005). Even with the EPA indication that CCBs may be useful as soil amendments, states tend to regulate any land application of CCBs as solid waste use constituting disposal, requiring case-by-case permitting (e.g., California [Marshack, 1992]). Well-coordinated research covering a carefully selected classification of by-product materials and utilization settings will be required to provide the confidence level needed for large-scale, unrestricted use of CCBs in agriculture.

The work in this project was intended to focus on the development of a method to qualify CCBs for use as an agricultural amendment. It was proposed that a single qualifying method could be used for any single CCB or CCB blend, but on review of the existing literature, it was determined that the method may also need to provide information on mixtures of CCBs and other materials unless those materials are preapproved for agricultural land application separately from the CCB with which they are applied or blended.

METHODS

As already stated, one goal of this project was to develop a proposed qualifying method for all CCBs and even potentially for CCBs combined with other by-products. Literature reviews and the research described in Chapter 1 of this report lead to the conclusion that the original goal may have been too broad to accomplish. The methods used included a review of research studies of agricultural land application of various CCBs, a comparison of available guidelines for

agricultural land application of CCBs and other similar by-products, and a comparison of results of the laboratory and field data/information from the technical portion of this project with assembled information to develop a draft of a qualifying scheme for CCBs only that may be used in future projects and potentially be expanded and detailed to become a tool for the coal ash and agricultural industries to use in understanding the identification of appropriate CCBs for agricultural land application.

Literature Review

A literature search was not defined as a task under the work plan for this project, but it became apparent that additional resources would be valuable in assessing the potential for and development of a qualifying scheme for CCB use in agricultural land applications. To accomplish this, the EERC assembled appropriate documents focusing on methods of evaluating CCBs and related topics. The literature review was not exhaustive, and the documents assembled were selected to facilitate an understanding of existing guidelines used for CCBs for agricultural land applications and to find comparisons of CCB composition with those guidelines or other materials used as agricultural amendments. Although not part of the original work plan, EERC staff initiated an effort to place the documents assembled in this project into FIRST SEARCH, a coal ash database of documents that was developed under another CBRC project. FIRST SEARCH is available online at www.undeerc.org/carrc/firstsearch and provides links to documents available electronically or instructions on how to access documents that are not available electronically. Some of the documents included in FIRST SEARCH from the literature review performed for this project can be found by author name or searching the abstract text for “agriculture.”

Guidelines for Agricultural Use of CCBs and Other Materials

A search for guidelines for agricultural use of CCBs was included in the literature review, and additional information was assembled from discussions with representatives of or regulations from select state environmental agencies, discussions with utility representatives providing CCBs to agricultural users, and from related publications and online resources providing information on the agricultural use of other by-products or industrial resources. State information was assembled from Illinois because of the specific project objective to address issues of interest for Illinois. Information from other states was assembled from previous EERC projects or from cooperating state agencies or utility partners on this and other EERC projects (Dockter and Jagiella, 2005).

Development of a Proposed Qualification Scheme for CCBs for Use in Agriculture

The EERC used information assembled and previous experience in CCB behavior and constituent mobility to propose a qualification scheme for CCBs that are potentially useful for agricultural land application.

RESULTS AND DISCUSSION

Literature Review

As noted, some documents assembled under this effort were incorporated into FIRST SEARCH. Documents are added to FIRST SEARCH on an ongoing basis based on receipt of permission from various publishers or authors. Key documents that warrant note were the extensive literature reviews and summaries prepared by Adriano et al. (1980) and Carlson and Adriano (1993). These were most useful in developing an initial understanding of the impact of CCBs as agricultural amendments as were many of the documents cited in the background section of this chapter.

While many CCBs have been evaluated for use in agricultural land applications, FGD gypsum merits special consideration because its natural counterpart has already been found to be beneficial for several agricultural purposes. According to the U.S. Geological Survey (2004) Minerals Yearbook, natural gypsum is one of the most widely used minerals and is used as an agricultural soil conditioner among other uses. Synthetic gypsum is produced from several industrial processes including from the cleaning of sulfur gases from flue gas at coal-fired power plants referred to as FGD gypsum. Gypsum, natural or synthetic, is calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Dick (2006) stated that gypsum has the ability to reduce deleterious plant growth effects related to acid soils, is a source of soluble calcium and sulfur (both macronutrients required for plant growth), and is a source of plant nutrients. Gypsum has also been used for many years to improve soil aggregation and inhibit or overcome soil dispersion. Dick (2006) and Clark et al. (2001) also presented information that indicated FGD gypsum can be used to provide these benefits in agricultural land applications.

Other CCBs also have potential to provide benefit when used as an agricultural soil amendment. Horn (1993) summarized the intrinsic value that CCBs have as soil amendments and that many groups have reported, including the following:

1. Plant macronutrients (P, K, S, Ca, Mg).
2. Plant micronutrients (Fe, B, Cu, Zn, Mn, Mo, Co).
3. Animal micronutrients (e.g., Se and some in the microplant nutrient list).
4. Liming value (CaO and MgO, plus the fact that fly ash is already in a finely divided condition).
5. Fine particle size. For example, the fine size of fly ash particles is conducive to rapid chemical reaction. From a physical standpoint, the addition of fine particles to coarse-textured soils increases moisture retention.
6. Coarse particle size. For example, bottom ash can improve physical properties of clay soils.

It is generally agreed that CCBs can provide macro- and micronutrients required for plant growth. It is also generally agreed that CCBs can contain certain trace elements that may be released in concentrations that offer some level of concern for the environment, especially for ground and surface waters; for potential for plant toxicity; and, ultimately, for animal and human toxicity. Clark et al. (2001) indicated that some constraints for use of FGD materials on agricultural land potentially included both insufficient or excessive amounts of CaCO_3 , CaO , and/or Ca(OH)_2 in raising soil pH insufficiently or too much; excessive Ca to cause imbalanced Mg, P, and K in soils/plants; Ca displacement of Al from soil exchange sites to induce Al toxicity in plants; high B to induce B toxicity in plants; excessive sulfite, which is toxic to plants; and excessive amounts of undesirable trace elements (e.g., As, Cd, Cr, Ni, Pb, and Se), which could potentially contaminate water and pose toxicity to plants/animals/microorganisms. EPA specifically called out arsenic as one element that is present in some CCBs at levels that raises questions about the appropriateness of land application of those CCBs. The authors note that several of the elements mentioned as undesirable, such as Cr, Ni, and Se, are actually essential nutrients.

Barker (2000), Electric Power Research Institute (1989), and Stout et al. (1988) performed evaluations of CCB and soil composition, and a comparison of the elemental composition of fly ash, AFBC material, and soils is shown in Appendix B. Additionally, a list of elements studied in various research efforts on the use of CCBs in agricultural applications is included in Appendix C, and a list of the elemental classification used by various groups is included in Appendix D. These summaries provide valuable information that allows the comparison of individual CCBs to existing documented soil data and information on the significance of trace elements that are frequently present in CCBs.

Guidelines and Recommendations for Agricultural Use of CCBs and Other Materials

No federal standards pertaining specifically to agricultural land application of CCBs exist. This lack of federal guidance has led producers and users to apply guidelines developed for other materials to CCBs. Many of the guidelines applied have both suitable and unsuitable components, which may make it difficult to determine the appropriateness of the CCB and to use the existing guidelines to promote the use of CCBs for agricultural use.

Part 503 Rules

Although formulated to regulate land application of biosolids, the 40 Code of Federal Regulations (CFR) 503 (U.S. Environmental Protection Agency, 1994) regulations have become the de facto standard for land application of many materials that may contain potentially hazardous metals (Dick et al., 2000). This regulation requires tracking of additions at application sites to prevent regulated metals from exceeding maximum soil concentrations. The limits indicated by the Part 503 rules are based on total concentrations of the elements of note. Table 2-1 provides a summary of the trace element guidelines included in the Part 503 rules.

Table 2-1. Federal Standards for Land Application of Sewage Sludge (amended from U.S. Environmental Protection Agency, 1993, 1994; Jacobs and McCreary, 2001)

Pollutant	Concentration Limits ^a , mg/kg		Loading Rates ^a , kg/ha	
	CCL ^b	PCL ^c (for EQ ^d and PC ^e biosolids)	CPLR ^f (for CPLR biosolids)	APLR ^g (for APLR biosolids and a 365-day period)
Arsenic	75	41	41	2.0
Cadmium	85	39	39	1.9
Chromium ^h	—	—	—	—
Copper	4,300	1,500	1,500	75
Lead	840	300	300	15
Mercury	57	17	17	0.85
Molybdenum ⁱ	75	—	—	—
Nickel	420	420	420	21
Selenium	100	100	100	5.0
Zinc	7,500	2,800	2,800	140
Applies to:	All biosolids that are land applied	Bulk biosolids and bagged biosolids ^j	Bulk biosolids	Bagged biosolids ^j
From 40 CFR Part 503:	Table 1, Part 503.13	Table 2, Part 503.13	Table 3, Part 503.13	Table 4, Part 503.13

^a Dry-weight basis.

^b Ceiling concentration limits.

^c Pollutant concentration limits.

^d Exceptional quality.

^e Pollutant concentration limits.

^f Cumulative pollutant-loading rate.

^g Annual pollutant-loading rate.

^h CCL and PCL for chromium were deleted from Tables 1 and 3 and PCL for selenium was increased from 36 mg/kg to 100 mg/kg by amendments to Part 503 rule, effective October 25, 1995.

ⁱ The PCL, CPLR, and APLR for molybdenum were deleted from Part 503 rule, effective February 19, 1994. EPA will consider establishing these limits at a later date.

^j Bagged biosolids are sold or given away in a bag or other container.

For biosolids, the material for which the Part 503 rules were developed state that regulations have to be the same as Part 503 and not less restrictive. A 1999 national survey (Goldstein and Block, 1999) indicated that in terms of pollutant limits—looking at ceiling concentration (Part 503, Table 1) and pollutant concentration (Part 503, Table 3)—14 states were more restrictive on either one or both of those tables. Thirty-five states use the same limits. While the survey was specific to biosolids, it is likely that those states with more stringent rules for biosolids would apply similarly restrictive limits if they allow the land application of CCBs or other industrial resources. The reference did not indicate if any states apply biosolid regulations to other industrial resources even though Dick (2006) indicated that the Part 503 rules are commonly applied to CCBs.

A commercial process that combines municipal sludge with other highly alkaline by-products, N-Viro, utilizes the Part 503 rules limits for qualifying CCBs or other materials for use in its process (N-Viro, 2006). N-Viro specifications are noted in Appendix E.

Solid Waste from Air Pollution Control

40 CFR Chapter 1 Part 257.3-5 (U.S. Environmental Protection Agency, 1979) addresses application of solid wastes, defined to include solids, liquids, or semisolids from an air pollution control facility, to land used for the production of food chain crops. However, only cadmium and polychlorinated biphenyls are included in this interim final rule. Requirements for Cd include 1) the pH of the solid waste and soil mixture is 6.5 or greater at the time of each solid waste application, 2) the annual application of Cd from solid wastes does not exceed 0.5 kilograms per hectare (kg/ha), and 3) the cumulative application of Cd from solid wastes does not exceed 5–20 kg/ha based on the background soil pH and the soil cation exchange capacity.

U.S. Department of Agriculture Flowchart for AFBC Materials Selection

Stout et al. (1988) developed a manual for applying FBC material to agricultural lands and included the flowchart shown in Figure 2-1. The flowchart includes steps to determine if the soil needs lime and soil monitoring, but Tasks 2–6 are specific to the FBC material. The flowchart addresses the amount of lime present in the FBC material and the heavy metal and boron loadings. The EERC determined that Tasks 2–6 of this flowchart can serve as a model for developing a decision tree for CCBs as a whole. A description of the calculations detailed by Stout et al. is included in Appendix F. Trace element/metal-loading limits are based on the Part 503 rules limits.

EPRI Recommendations

Horn (1993) describes developing a CCB land application plan as rather awkward as it is fitted to sewage sludge guidelines, which is a very different material. Horn (1993) states that a relaxation of state regulations that restrict field experimentation would allow for more rapid CCB land application testing. The report recommended that a typical evaluation of CCBs to be marketed for land application marketing should include the following factors:

- Particle size
- Macronutrient and micronutrient contents
- Carbon content (LOI)
- Content of metals and other constituents subject to loading limits

It was also indicated that consistency of quality and production over time is important to marketing. Field tests of performance as soil amendments for various crop and soil types characteristic of the market region should be performed, and pretreatment to reduce boron or salinity may be considered in some cases. Horn (1993) indicated that two research areas requiring special attention were 1) an agronomic evaluation of CCB–organic waste mixtures and 2) an evaluation of the application rates of CCB soil amendments alone or as mixtures,

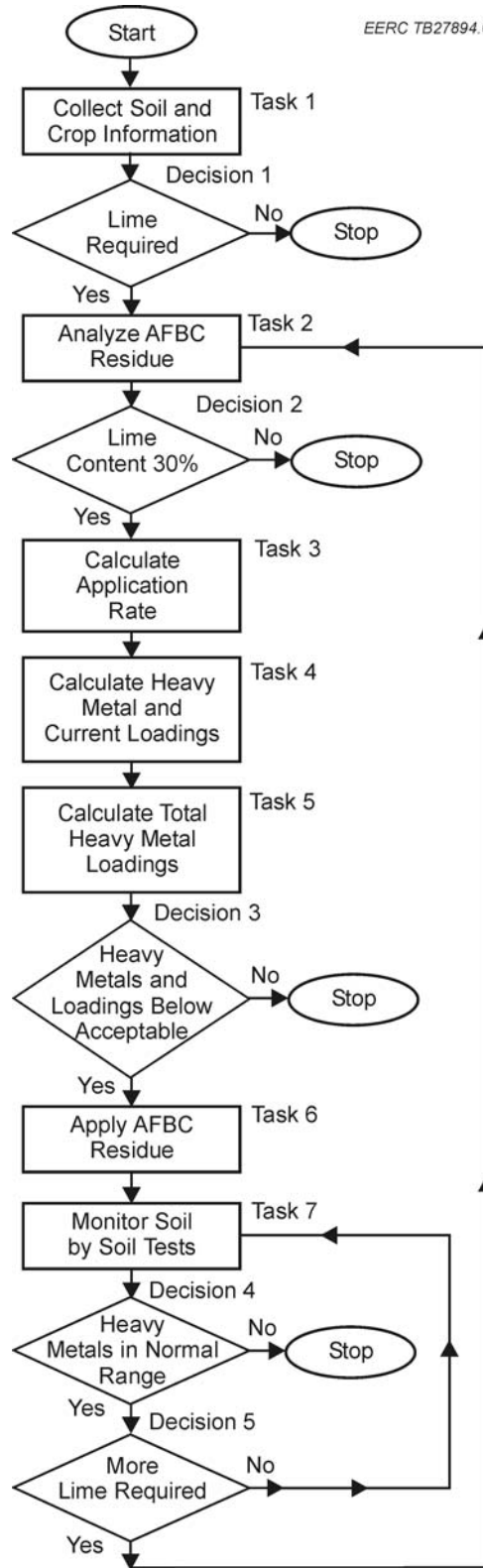


Figure 2-1. Flowchart describing the steps to take to qualify FBC material for use in agricultural applications (adapted from Stout et al., 1988).

considering upper limits dictated by peaks in yield response curves and limits that result from metal-loading limits set by environmental regulations.

Other Recommendations

Other documents that did not specify any type of limits or schemes for evaluating CCBs for use in agricultural applications provided recommendations on the information that should be considered when applying CCBs to agricultural lands.

Adriano et al. (2002) recommended that soil tests for salinity and boron levels should be conducted to confirm the right planting time and that the possibility of risk to livestock health should be integrated into the long-range planning for agricultural production purposes.

Several groups provided classification of elements, many of which are present in varying amounts in CCBs, as macro- and micronutrients for plants. The EERC summarized this information, and that summary is presented in Appendix D. Barak (2006) stated that the dividing line between macronutrients—nutrients required in greater quantities—and micronutrients—elements required in smaller quantities—is drawn somewhat arbitrarily based on the different quantities and concentrations required. As can be seen in the summary in Appendix D, there is good agreement by several research groups on which elements are considered macronutrients. Some research groups refer to these and some other minor or trace elements as essential minerals or nutrients. CCBs frequently contain high concentrations of many of these elements. The questions about the nutrient or essential nature of some of these elements including arsenic, selenium, aluminum, and mercury need to be answered by agronomists and plant scientists. The CCB industry can start to evaluate CCBs proposed for agricultural use for these elements so the potential contribution of these elements to soils and eventually into the food chain from CCBs can be better estimated.

Basing regulations on total amounts of potentially problematic trace elements disregards the fact that in CCBs many of the trace elements are located in a glassy matrix and have a very low availability regardless of pH, especially within the pH range that would be found in agricultural settings.

Summary

The guidelines and recommendations assembled generally indicate a ceiling or maximum level of individual elements that may be applied, sometimes over a specific period, for determining the appropriateness of a material for agricultural application. The Part 503 rules for biosolids are most commonly applied; however, the availability of the constituent is not taken into account. It is reasonable to use a guideline or standard that has already been accepted by a large number of regulatory authorities, especially at the state level, where CCB utilization is being regulated. What also must be considered is that regulations and guidelines for other materials may not provide the opportunity to get the highest benefit from CCBs in an application. This may be the case when Part 503 rules are used to calculate the allowable addition of a CCB on agricultural land. This may be the case because the availability of specific constituents from CCBs will likely be very different from the availability of those same constituents in a material

like biosolids. The argument has been made that using standards or limits that overestimate the availability of constituents by assuming that 100% is available is protective of the environment and human health. That argument can be used as a means of working with the agriculture community and regulatory authorities to initiate discussions and potentially the use of CCBs in agricultural applications. However, the CCB industry should also be working toward a better understanding of the availability of CCB constituents so the most benefit can be obtained from their agricultural application.

Development of a Proposed Qualification Scheme for CCBs for Use in Agriculture

A proposed preliminary decision tree for qualifying CCBs for agricultural applications was developed by the EERC (Figure 2-2) based on the guidelines and information assembled and using the information presented in Chapter 1 as an example case study. It should be noted that the EERC-proposed scheme recommends the use of “available” concentrations of nutrients. The EERC proposes that these available concentrations can be determined using appropriate leaching tests. Since pH is a key criterion in determining the availability of inorganic elements, including the nutrients listed, the EERC suggests leaching solutions such as distilled deionized water or low-ionic-strength solutions such as the dilute sulfuric acid used in the synthetic precipitation leaching procedure (SPLP) and typical leaching protocols such as ASTM D3987, SPLP, and the synthetic groundwater leaching procedure (SGLP) with long-term leaching, all of which use a 20-to-1 liquid-to-solid ratio, or other appropriate tests (ASTM International, 2004; U.S. Environmental Protection Agency, 2005; Hassett, 1998; Sorini, 1997). While it is expected that discussion regarding appropriate leaching procedures for many CCB use applications will impact the methods used to determine available concentrations of nutrients and other components of CCBs, the EERC’s position is that it is necessary for industry to work toward a consensus on a method to determine available concentrations of inorganic constituents in order to use CCBs in the most beneficial manner in agricultural applications.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the comparison of the laboratory field information detailed in Chapter 1 with the literature search and existing guidelines:

- CCBs can provide benefits when used to amend agricultural soils, but caution must be exercised to ensure environmental protection, crop and soil appropriateness, and human health.
- FGD gypsum has benefits equivalent to natural gypsum and can be applied for the same purposes and at the same rates. Studies under way on the use of FGD gypsum should provide good information to aid in marketing FGD gypsum into agricultural applications, and the criteria for use should be the same for natural and FGD gypsum.
- Total concentrations of inorganic constituents in CCBs are not the best indicator on which to base decisions regarding the suitability of CCBs for use in agricultural land applications.

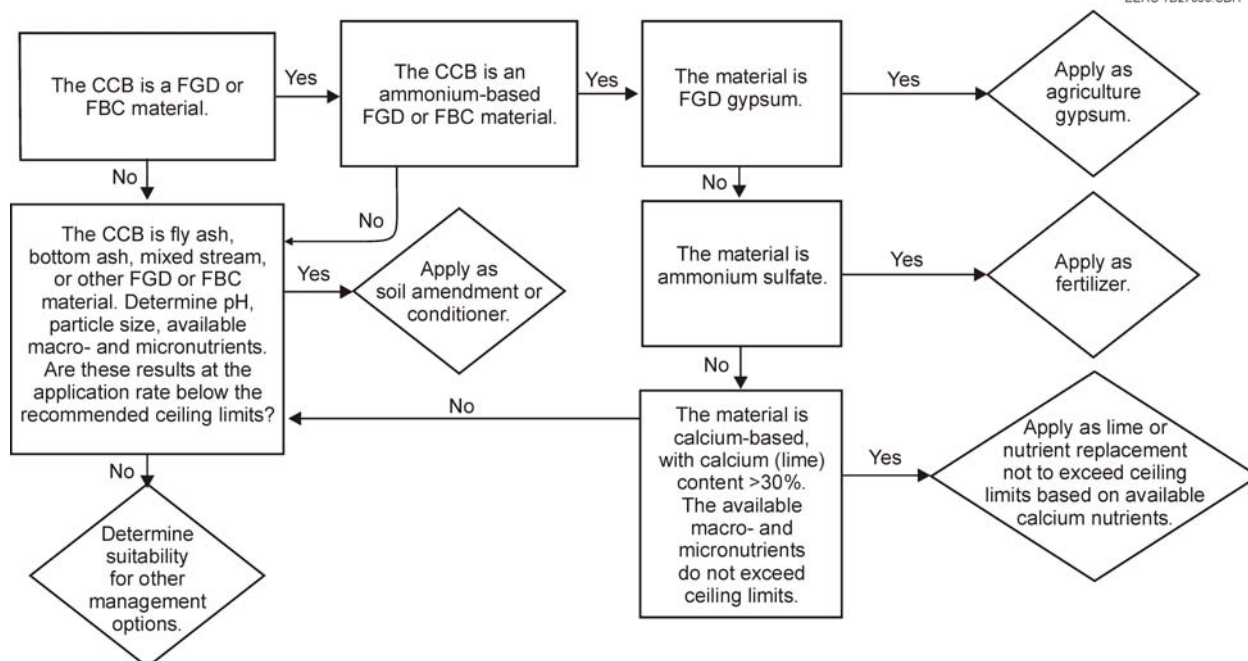


Figure 2-2. Proposed qualifying scheme for CCB use in agricultural land applications.

The EERC makes the following recommendations based on information collected:

- The EERC recommends that industry consider that CCB application to agricultural land should be based on available trace and major/minor elements rather than on total concentrations and should be no more stringent or lenient than other standards regarding the same elements regardless of the source.
- The EERC recommends that continuing work on the use of CCBs in agriculture includes the use of the draft qualification scheme so that scheme can be evaluated to determine if it can become a valuable tool for the agricultural community in determining appropriate application of CCBs.
- The EERC recommends that the discussion of appropriate leaching procedures and the methods to identify appropriate leaching procedures incorporate a discussion of methods to determine elemental availability for input and use in the proposed qualification scheme.

REFERENCES

Adriano, D.C.; Page, A.L.; Elsewi, A.A.; Chang, A.C.; Straughan, I. Utilization and Disposal of Fly Ash and Other Coal Residues in Terrestrial Ecosystems: A Review. *J. Environ. Qual.* **1980**, *3*, 333–344.

- Adriano, D.C.; Weber, J.; Bolan, N.S.; Paramasivam, S.; Koo, B.-J.; Sajwan, K.S. Effects of High Rates of Coal Fly Ash on Soil, Turfgrass, and Groundwater Quality. *Water, Air, Soil Pollut.* **2002**, *139*, 365–385.
- ASTM International. Standard Method for Shake Extraction of Solid Waste with Water. In *Annual Book of ASTM Standards*; Section 11: Water and Environmental Technology, ASTM D3987-85, 2004.
- Barak, P. *Essential Elements for Plant Growth*.
www.soils.wisc.edu/~barak/soilscience326/essentl.htm (accessed March 2006).
- Barker, A.V.; Stratton, M.L.; Rechcigl, J.E. Soil and By-Product Characteristics that Impact the Beneficial Use of By-Products. In Power, J.F.; Dick, W.A., Eds.; *Land Application of Agricultural, Industrial, and Municipal Byproducts*; 2000; pp 169–213.
- Bearce, B.C.; Lentz, D.L.; Woodard, M.A.; Townsend, E.C. Coal Bottom Ash as a Root Substrate for Marigolds in a Closed Loop Nutriculture System. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1, pp 13-1 to 13-16.
- Beeghly, J.H.; Bigham, J.; Dick, W.A. The Ohio-Based Study on Land Application Uses of Dry FGD By-Products. In *Ash Use R&D and Clean Coal By-Products*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 2, pp 59-1 to 59-14.
- Bennett, O.L.; Hern, J.L.; Stout, W.L. Fluidized-Bed Combustion Waste, a Potential Agricultural Soil Amendment. In *Problems and Issues*, Proceedings of the Governor's Conference on Expanding the Use of Coal in New York State; Albany, NY, May 21–22, 1981; Tress, M.H.; Dawson, J.C., Eds.; 1981; pp 43–48.
- Bigham, J.; Dick, W.; Forster, L.; Hitzhusen, F.; McCoy, E.; Stehouwer, R.; Traina, S.; Wolfe, W.; Haefner, R. *Land Application Uses for Dry FGD By-Products: Phase 1 Report*; Electric Power Research Institute, Report No. EPRI TR-105264; Electric Power Research Institute: Palo Alto, CA, April 1993.
- Burnham, J.C. Use of Coal Ash Products as Alkaline Admixtures in the Sludge Stabilization Process. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol.1, pp 1-1 to 1-13.
- Carlson, C.L.; Adriano, D.C. Environmental Impacts of Coal Combustion Residues. *J. Environ. Qual.* **1993**, *22*, 227–247.
- Clark, R.B.; Ritchey, K.D.; Baliger, V.C. Benefits and Constraints for Use of FGD Products on Agricultural Land. *Fuel* **2001**, *80*, 821–828.

- Clark, R.B.; Ritchey, K.D.; Baliger, V.C. Dry Matter Yields of Maize Grown with Coal Combustion By-Products. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1, pp 15-1 to 15-11.
- Dick, W.A. Agricultural and Other Land Application Uses of FGD Gypsum. Presented at Coal Ash Professionals Training Course, Memphis, TN, April 19–21, 2006.
- Dick, W.A.; Chen, L.; Hao, Y. Beneficial Uses of Clean Coal Combustion By-Products: Soil Amendment and Coal Refuse Treatment Examples and Case Studies. In *Proceedings of the Use and Disposal of Coal Combustion By-Products at Coal Mines: A Technical Interactive Forum*; April 10–13, 2000.
- Dockter, B.A.; Jagiella, D.M. *Engineering and Environmental Specifications of State Agencies for Utilization and Disposal of Coal Combustion Products: Volume 2 – Environmental Regulations*; Final Report (Sept 1, 2004 – Aug 31, 2005) for CBRC Project No. 02-CBRC-W12; EERC Publication 2005-EERC-07-05; Energy & Environmental Research Center: Grand Forks, ND, July 2005.
- Electric Power Research Institute. *Coal Ash and the Environment: Characteristics of Fly Ash*. Technical Report RP2485-8, 1989.
- Electric Power Research Institute. *Land Application of Coal Combustion By-Products: Use in Agriculture and Land Reclamation*; EPRI TR-103298; Electric Power Research Institute: Palo Alto, CA, June 1995.
- Founie, A. Gypsum. In *Minerals Yearbook Vol I. – Metals and Minerals*; U.S. Geological Survey, 2004. <http://minerals.usgs.gov/minerals/pubs/commodity/gypsum/gypsumyb04.pdf>.
- Goldstein, N.; Block, D. National Biosolids Overview. *BioCycle* **1999**, Dec, 48–52.
- Hassett, D.J. Synthetic Groundwater Leaching Procedure. In Meyers, R.A., Ed.; *Encyclopedia of Environmental Analysis and Remediation*; John Wiley & Sons, Inc., 1998.
- Hassett, D.J.; Heebink, L.V. *Environmental Evaluation for Utilization of Ash in Soil Stabilization*; Final Report (Aug 11, 1999 – Nov 30, 2001) for U.S. Department of Energy Cooperative Agreement No. DE-FC26-09FT40321 and Electric Power Research Institute No. 1005213; EERC Publication 2001-EERC-08-06; Energy & Environmental Research Center: Grand Forks, ND, Aug 2001.
- Hassett, D.J.; Pflughoeft-Hassett, D.F.; Heebink, L.V. Leaching of CCBs: Observations from over 25 Years of Research. In *2003 International Ash Utilization Symposium*, Special Issue of *Fuel* **2005**, 84 (11), 1378–1383.

- Horn, M.E. *Analysis of Markets for Coal Combustion By-Products Use in Agriculture and Land Reclamation: Summary Report of Four Regional Marketing Studies*; EPRI TR-102575, Project 3207-01; Electric Power Research Institute: Palo Alto, CA, Dec 1993.
- Jacobs, L.W.; McCreary, D.S. Utilizing Biosolids on Agricultural Land. Extension Bulletin E-2781, Michigan State University Extension, Dec 2001.
- Korcak, R.F. Agricultural Uses of Coal Combustion Byproducts. In Wright, R.J., Kemper, W.D., Millner, P.D., Power, J.F., Korcak, R.F, Eds.; *Agricultural Uses of Municipal Animal and Industrial Byproducts*; Conservation Research Report No. 44; U.S. Department of Agriculture, Agricultural Research Service, 1998; pp 103–119.
- Korcak, R.F. Utilization of Fluidized Bed Combustion By-Products in Horticulture. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1, pp 12-1 to 12-9.
- Lisk, D.J. Benefits and Hazards of Using Coal Fly Ash in Agriculture and Aquaculture. In *Problems and Issues*, Proceedings of the Governor’s Conference on Expanding the Use of Coal in New York State; Albany, NY, May 21–22, 1981; Tress, M.H.; Dawson, J.C., Eds.; 1981; pp 13–17.
- Marshack, J., Senior Environmental Specialist, Environmental/Technical Support, California Regional Water Quality Control Board, Sacramento, California. Memo to Pete Fuller, Division of Clean Water Programs, State Water Resources Control Programs, Oct 26, 1992.
- N-Viro. N-Viro Mineral By-Products (MBP) Quality Specification. www.nviro.com/mbp/specs.htm (accessed Aug 2006).
- Pflughoeft-Hassett, D.F.; Dockter, B.A.; Hassett, D.J.; Heebink, L.V.; Solc, J.; Buckley, T.D. *Demonstration of Coal Ash for Feedlot Surfaces*; Final Report; EERC Publication 2004-EERC-02-10; Energy & Environmental Research Center: Grand Forks, ND, Feb 2004.
- Santhanam, C.J.; Lunt, R.R.; Cooper, C.B; Klimschmidt, D.E.; Bodek, I.; Tucker, W.A.; Ullrich, C.R. *Flue Gas Cleaning Wastes, Disposal and Utilization*; Noyes Data Corporation: Park Ridge, NJ, 1981; 646 p.
- Sorini, S.S. A Summary of Leaching Methods. April 1997.
- Stout, W.L.; Hern, J.L.; Korcak, R.F.; Carlson, C.W. *Manual for Applying Fluidized-Bed Combustion Residue to Agricultural Lands*; ARS-74; U.S. Department of Agriculture, Agricultural Research Service, 1988.

- U.S. Environmental Protection Agency. *A Plain English Guide to the EPA Part 503 Biosolids Rule*; EPA/832-R-93/003; Office of Research and Development, U.S. Environmental Protection Agency: Washington, DC, Sept 1994, 176 p.
- U.S. Environmental Protection Agency. Criteria for Classification of Solid Waste Disposal Facilities and Practices. *Code of Federal Regulations*, Section 40, Part 257; *Fed. Regist.* **1979**, *44*, 53460.
- U.S. Environmental Protection Agency. Method 1312, Synthetic Precipitation Leaching Procedure. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*; EPA Publication SW-846, Third Edition, as amended by Updates I, II, IIB, III, and IIIB finalized in the Federal Register on June 14, 2005.
- U.S. Environmental Protection Agency. Standards for the Use and Disposal of Sewage Sludge. *Code of Federal Regulations*, Section 40, Part 503, 1993; *Fed. Regist.* **1993**, *58*, 9387, amended at 58 FR 9099, Feb 25, 1994; 60 FR 54769, Oct 25, 1995.
- Varallo, G. Reclamation of Fly Ash from Electricity Generating Plants Through Cocomposting with Source-Collected Vegetable Waste. In *High-Volume Uses/Concrete Applications*, Proceedings of the 10th International Ash Use Symposium; Orlando, FL, Jan 18–21, 1993; EPRI TR-101774, Project 3176, 1993; Vol. 1, pp 14-1 to 14-10.

APPENDIX A
PIXE RESULTS

Table A-1. Sample Composition 1

Date:	12/9/2003			
Run:	11			
Job:	2009-03			
Name:	EERC			
Project:	Loreal Heebink			
Target:	Fly Ash			
Element Name	Energy, keV	Det. Limit 95% Conf.	Concentration Mass	Error
*O-----			52.702%	
Na	1.041	0.818%		
Magnesium	1.254	0.175%	0.307%	0.103%
Aluminum	1.487	686.100 ppm	9.029%	0.116%
Silicon	1.740	329.600 ppm	21.007%	0.210%
P	2.014	277.400 ppm		
Sulfur	2.308	171.700 ppm	1.253%	0.035%
Cl	2.623	134.200 ppm		
Potassium	3.314	331.500 ppm	1.592%	0.040%
Calcium	3.692	456.800 ppm	3.828%	0.069%
Sc	4.091	284.800 ppm		
Titanium	4.511	112.300 ppm	0.475%	0.013%
Vanadium	4.952	123.800 ppm	311.741 ppm	50.814 ppm
Chromium	5.415	35.620 ppm	181.083 ppm	21.766 ppm
Manganese	5.899	36.130 ppm	275.300 ppm	22.630 ppm
Iron	6.405	52.070 ppm	9.633%	0.096%
Co	6.930	95.710 ppm		
Nickel	7.478	16.980 ppm	81.681 ppm	11.493 ppm
Copper	8.048	11.160 ppm	91.011 ppm	10.348 ppm
Zinc	8.639	16.740 ppm	427.291 ppm	19.912 ppm
Gallium	9.252	9.482 ppm	43.770 ppm	8.986 ppm
Germanium	9.886	10.940 ppm	45.026 ppm	9.928 ppm
Arsenic	10.544	8.549 ppm	31.633 ppm	9.901 ppm
Se	11.222	11.390 ppm		
Br	11.924	9.402 ppm		
Rb	13.395	59.660 ppm		
Strontium	14.165	80.800 ppm	243.656 ppm	49.097 ppm
Y	14.959	38.680 ppm		
Zr	15.775	68.110 ppm		
Nb	16.615	43.070 ppm		
Mo	17.480	43.710 ppm		
Tc	18.367	41.880 ppm		
Ru	19.279	17.380 ppm		

Continued...

Table A-1. Sample Composition 1 (Continued)

Rh	20.216	22.430 ppm
Pd	2.839	248.800 ppm
Ag	2.984	294.300 ppm
Cd	3.133	336.800 ppm
In	3.286	0.203%
Sn	3.444	796.400 ppm
Sb	3.604	0.200%
Te	3.768	0.214%
I	3.937	890.700 ppm
Cs	4.288	203.900 ppm
Ba	4.466	797.200 ppm
La	4.648	441.600 ppm
Ce	4.841	217.100 ppm
Pr	5.034	167.500 ppm
Nd	5.230	78.680 ppm
Pm	5.431	119.000 ppm
Sm	5.632	55.740 ppm
Eu	5.841	104.200 ppm
Gd	6.050	82.340 ppm
Tb	6.271	644.700 ppm
Dy	6.492	990.000 ppm
Ho	6.725	78.430 ppm
Er	6.945	369.000 ppm
Tm	7.182	339.000 ppm
Yb	7.416	52.450 ppm
Lu	7.655	27.630 ppm
Hf	7.899	27.100 ppm
Ta	8.149	42.540 ppm
W	8.398	26.790 ppm
Re	8.652	112.700 ppm
Os	8.911	33.520 ppm
Ir	9.174	35.680 ppm
Pt	9.443	31.610 ppm
Au	9.712	34.740 ppm
Hg	9.989	28.020 ppm
Tl	10.267	22.540 ppm
Pb	10.551	43.350 ppm
Bi	10.838	21.520 ppm
Th	12.968	76.000 ppm
U	13.616	61.830 ppm

Table A-2. Sample Composition 2

Date:	12/9/2003			
Run:	16			
Job:	2009-03			
Name:	EERC			
Project:	Loreal Heebink			
Target:	Bottom Ash			
Element Name	Energy, keV	Det. Limit 95% Conf.	Concentration Mass	Error
*O-----			53.736%	
Na	1.041	0.484%		
Magnesium	1.254	0.133%	0.359%	0.076%
Aluminum	1.487	432.900 ppm	4.075%	0.062%
Silicon	1.740	385.800 ppm	8.966%	0.090%
P	2.014	188.100 ppm		
Sulfur	2.308	144.500 ppm	9.105%	0.091%
Chlorine	2.622	139.900 ppm	0.542%	0.020%
Potassium	3.314	192.800 ppm	0.635%	0.020%
Calcium	3.692	573.900 ppm	15.265%	0.153%
Sc	4.091	461.500 ppm		
Titanium	4.511	76.330 ppm	0.233%	0.008%
V	4.952	40.870 ppm		
Chromium	5.415	25.050 ppm	105.231 ppm	14.564 ppm
Manganese	5.899	25.860 ppm	225.366 ppm	16.316 ppm
Iron	6.405	23.120 ppm	7.018%	0.070%
Co	6.930	64.140 ppm		
Nickel	7.478	9.531 ppm	36.261 ppm	6.600 ppm
Copper	8.048	5.612 ppm	36.631 ppm	5.711 ppm
Zinc	8.639	9.107 ppm	108.332 ppm	8.125 ppm
Ga	9.250	6.152 ppm		
Ge	9.887	7.960 ppm		
As	10.544	8.343 ppm		
Se	11.222	6.604 ppm		
Br	11.924	10.830 ppm		
Rb	13.395	44.430 ppm		
Strontium	14.165	34.850 ppm	159.547 ppm	25.161 ppm
Y	14.959	17.180 ppm		
Zr	15.775	38.830 ppm		
Nb	16.615	24.950 ppm		
Mo	17.480	18.360 ppm		
Tc	18.367	7.667 ppm		
Ru	19.279	28.270 ppm		
Rh	20.216	13.050 ppm		

Continued...

Table A-2. Sample Composition 2 (Continued)

Pd	2.839	287.000 ppm
Ag	2.984	179.700 ppm
Cd	3.133	208.500 ppm
In	3.286	968.100 ppm
Sn	3.444	474.600 ppm
Sb	3.604	0.259%
Te	3.768	0.313%
I	3.937	0.121%
Cs	4.288	143.900 ppm
Ba	4.466	431.100 ppm
La	4.648	293.100 ppm
Ce	4.841	126.100 ppm
Pr	5.034	87.700 ppm
Nd	5.230	69.000 ppm
Pm	5.431	74.580 ppm
Sm	5.632	42.750 ppm
Eu	5.841	74.720 ppm
Gd	6.050	60.320 ppm
Tb	6.271	439.500 ppm
Dy	6.492	666.800 ppm
Ho	6.725	55.130 ppm
Er	6.945	246.300 ppm
Tm	7.182	220.100 ppm
Yb	7.416	28.650 ppm
Lu	7.655	16.560 ppm
Hf	7.899	17.290 ppm
Ta	8.149	21.280 ppm
W	8.398	17.420 ppm
Re	8.652	45.230 ppm
Os	8.911	17.590 ppm
Ir	9.174	14.950 ppm
Pt	9.443	17.360 ppm
Au	9.712	19.010 ppm
Hg	9.989	19.870 ppm
Tl	10.267	17.830 ppm
Pb	10.551	24.430 ppm
Bi	10.838	16.940 ppm
Th	12.968	90.350 ppm
U	13.616	98.780 ppm

Table A-3. Sample Composition 3

Date:	12/9/2003			
Run:	17			
Job:	2009-03			
Name:	EERC			
Project:	Loreal Heebink			
Target:	FGD Material			
Element Name	Energy, keV	Det. Limit 95% Conf.	Concentration Mass	Error
*O-----			34.666%	
Na	1.041	0.667%		
Mg	1.254	0.100%		
Aluminum	1.487	471.700 ppm	0.200%	0.029%
Silicon	1.740	246.800 ppm	0.431%	0.020%
P	2.014	260.700 ppm		
Sulfur	2.308	386.600 ppm	25.017%	0.250%
Chlorine	2.622	285.400 ppm	0.435%	0.034%
K	3.314	229.400 ppm		
Calcium	3.692	422.900 ppm	39.070%	0.391%
Sc	4.091	387.100 ppm		
Titanium	4.511	18.680 ppm	86.118 ppm	11.428 ppm
V	4.952	5.508 ppm		
Cr	5.415	3.126 ppm		
Manganese	5.899	4.353 ppm	106.609 ppm	3.092 ppm
Iron	6.405	3.534 ppm	0.148%	0.001%
Co	6.930	3.358 ppm		
Ni	7.478	1.538 ppm		
Cu	8.048	1.534 ppm		
Zinc	8.639	2.088 ppm	5.011 ppm	1.200 ppm
Ga	9.250	1.217 ppm		
Ge	9.887	1.264 ppm		
As	10.544	1.298 ppm		
Se	11.222	1.426 ppm		
Bromine	11.924	2.156 ppm	17.616 ppm	1.814 ppm
Rb	13.395	2.018 ppm		
Strontium	14.165	3.832 ppm	106.812 ppm	5.394 ppm
Y	14.959	2.294 ppm		
Zr	15.775	6.526 ppm		
Nb	16.615	3.108 ppm		
Mo	17.480	5.794 ppm		
Tc	18.367	1.935 ppm		
Ru	19.279	4.349 ppm		
Rh	20.216	8.072 ppm		

Continued...

Table A-3. Sample Composition 3 (Continued)

Pd	2.839	398.300 ppm
Ag	2.984	324.300 ppm
Cd	3.133	417.800 ppm
In	3.286	577.300 ppm
Sn	3.444	698.600 ppm
Sb	3.604	0.422%
Te	3.768	0.289%
I	3.937	0.112%
Cs	4.288	67.830 ppm
Ba	4.466	52.310 ppm
La	4.648	39.700 ppm
Ce	4.841	22.180 ppm
Pr	5.034	16.580 ppm
Nd	5.230	13.720 ppm
Pm	5.431	11.450 ppm
Sm	5.632	9.582 ppm
Eu	5.841	15.440 ppm
Gd	6.050	9.273 ppm
Tb	6.271	22.400 ppm
Dy	6.492	31.210 ppm
Ho	6.725	6.215 ppm
Er	6.945	12.530 ppm
Tm	7.182	10.540 ppm
Yb	7.416	5.400 ppm
Lu	7.655	4.925 ppm
Hf	7.899	4.632 ppm
Ta	8.149	4.337 ppm
W	8.398	4.136 ppm
Re	8.652	4.663 ppm
Os	8.911	3.542 ppm
Ir	9.174	3.753 ppm
Pt	9.443	3.620 ppm
Au	9.712	3.704 ppm
Hg	9.989	3.787 ppm
Tl	10.267	3.725 ppm
Pb	10.551	3.674 ppm
Bi	10.838	3.700 ppm
Th	12.968	4.145 ppm
U	13.616	4.978 ppm

Table A-4. Sample Composition 4

Date:	12/9/2003			
Run:	18			
Job:	2009-03			
Name:	EERC			
Project:	Loreal Heebink			
Target:	As-Managed CCB			
Element Name	Energy, keV	Det. Limit 95% Conf.	Concentration Mass	Error
* O-----			53.603%	
Na	1.041	0.494%		
Magnesium	1.254	0.129%	0.464%	0.076%
Aluminum	1.487	269.400 ppm	3.928%	0.059%
Silicon	1.740	407.700 ppm	9.058%	0.091%
P	2.014	178.000 ppm		
Sulfur	2.308	198.800 ppm	9.491%	0.095%
Chlorine	2.622	132.100 ppm	0.889%	0.023%
Potassium	3.314	164.000 ppm	0.629%	0.019%
Calcium	3.692	448.300 ppm	14.529%	0.145%
Sc	4.091	439.300 ppm		
Titanium	4.511	88.180 ppm	0.246%	0.008%
V	4.952	43.370 ppm		
Chromium	5.415	24.700 ppm	105.079 ppm	14.144 ppm
Manganese	5.899	27.790 ppm	252.471 ppm	17.345 ppm
Iron	6.405	31.660 ppm	7.088%	0.071%
Co	6.930	66.130 ppm		
Nickel	7.478	11.230 ppm	39.385 ppm	7.093 ppm
Copper	8.048	7.473 ppm	23.332 ppm	5.173 ppm
Zinc	8.639	6.963 ppm	107.386 ppm	8.279 ppm
Ga	9.250	5.913 ppm		
Ge	9.887	8.428 ppm		
As	10.544	9.112 ppm		
Se	11.222	8.406 ppm		
Bromine	11.924	14.040 ppm	40.347 ppm	9.752 ppm
Rb	13.395	69.610 ppm		
Strontium	14.165	51.020 ppm	189.203 ppm	30.859 ppm
Y	14.959	21.130 ppm		
Zr	15.775	43.800 ppm		
Nb	16.615	24.340 ppm		
Mo	17.480	31.020 ppm		
Tc	18.367	17.090 ppm		
Ru	19.279	39.240 ppm		
Rh	20.216	12.990 ppm		

Continued...

Table A-4. Sample Composition 4 (Continued)

Pd	2.839	339.600 ppm
Ag	2.984	180.900 ppm
Cd	3.133	214.900 ppm
In	3.286	940.400 ppm
Sn	3.444	466.900 ppm
Sb	3.604	0.250%
Te	3.768	0.301%
I	3.937	0.116%
Cs	4.288	144.100 ppm
Ba	4.466	437.900 ppm
La	4.648	304.400 ppm
Ce	4.841	133.400 ppm
Pr	5.034	93.200 ppm
Nd	5.230	65.960 ppm
Pm	5.431	75.750 ppm
Sm	5.632	45.160 ppm
Eu	5.841	82.170 ppm
Gd	6.050	65.470 ppm
Tb	6.271	446.400 ppm
Dy	6.492	676.900 ppm
Ho	6.725	54.610 ppm
Er	6.945	254.100 ppm
Tm	7.182	223.100 ppm
Yb	7.416	32.640 ppm
Lu	7.655	19.590 ppm
Hf	7.899	15.800 ppm
Ta	8.149	21.160 ppm
W	8.398	18.810 ppm
Re	8.652	47.390 ppm
Os	8.911	14.740 ppm
Ir	9.174	15.500 ppm
Pt	9.443	13.360 ppm
Au	9.712	17.760 ppm
Hg	9.989	26.040 ppm
Tl	10.267	20.160 ppm
Pb	10.551	26.080 ppm
Bi	10.838	24.440 ppm
Th	12.968	127.800 ppm
U	13.616	107.400 ppm

APPENDIX B

**CCB AND SOIL ELEMENTAL COMPOSITION
COMPARISON**

CCB and Soil Elemental Composition Comparison, ppm = mg/kg or µg/g

Element	CCB				Soil		Source
	Type	n	Mean	Range	Mean	Range	
Al	FA ^a	39 by XRF ^b	113,000	46,000–152,000	71,000	10,000–300,000	EPRI, 1989
	AFBC	9	10,000	4000–20,000	NR ^c	14,000–40,000	Stout et al., 1988
As	FA	39 by XRF	156	7.7–1385	6	0.1–40	EPRI, 1989
B	AFBC	9	110	95–170	10	2–100	Stout et al., 1988
Ba	FA	39 by XRF	1880	251–10,850	500	10–3000	EPRI, 1989
Ca	FA	39 by XRF	62,000	7400–223,000	13,700	7,000–500,000	EPRI, 1989
	AFBC	9	380,000	240,000–460,000	NR	NR	Stout et al., 1988
	FA	NR	NR	100,000–200,000	NR	NR	Barker, 2000
Cd	AFBC	9	0.5	NR	0.5	0.01–0.70	Stout et al., 1988
Cr	FA	29 by XRF	247	37–651	100	5–3000	EPRI, 1989
	AFBC	9	15	9–23	200	5–1000	Stout et al., 1988
Cu	FA	39 by XRF	185	44.6–1452	20	2–100	EPRI, 1989
	AFBC	9	15	12–19	20	2–100	Stout et al., 1988
Fe	FA	39 by XRF	76,000	25,000–177,000	38,000	3000–550,000	EPRI, 1989
	AFBC	9	11,000	800–16,000	NR	14,000–40,000	Stout et al., 1988
K	FA	39 by XRF	14,300	3000–25,300	14,000	400–30,000	EPRI, 1989
	AFBC	9	2500	500–8000	NR	NR	Stout et al., 1988
	FA	NR	NR	20,000–70,000	NR	NR	Barker, 2000
Mg	FA	39 by XRF	11,800	1,600–41,800	5000	600–6000	EPRI, 1989
	AFBC	9	7100	5000–12,000	NR	NR	Stout et al., 1988
	FA	NR	NR	10,000–80,000	NR	NR	Barker, 2000
Mn	FA	39 by XRF	357	44–1332	850	100–4000	EPRI, 1989
	AFBC	9	485	210–685	850	200–3000	Stout et al., 1988
Mo	FA	36 by XRF	44	7.1–236	2	0.2–5	EPRI, 1989
	AFBC	9	0.19	0.12–0.28	2	0.2–5	Stout et al., 1988
N	FA	NR	NR	300–3000	NR	NR	Barker, 2000
Na	FA	39 by XRF	9087	1300–62,500	6300	750–7500	EPRI, 1989
Ni	FA	39 by XRF	141	22.8–353	40	10–1000	EPRI, 1989
	AFBC	9	21	13–29	40	5–500	Stout et al., 1988
P	AFBC	9	430	380–500	NR	400–3000	Stout et al., 1988
Pb	FA	39 by XRF	171	21.1–2120	10	2–200	EPRI, 1989
	AFBC	9	3	1.5–7.5	10	2–200	Stout et al., 1988
S	FA	39 by XRF	12,643	1300–64,400	700	30–900	EPRI, 1989
	AFBC	9	92,000	72,000–140,000	850	100–1500	Stout et al., 1988
	FA	NR	NR	20,000–60,000	NR	NR	Barker, 2000
Se	FA	30 by XRF	14	5.5–46.9	0.2	0.01–2	EPRI, 1989
	AFBC	9	0.29	0.16–0.58	NR	0.1–2	Stout et al., 1988
Si	FA	39 by XRF	209,000	89,500–275,000	330,000	250,000–350,000	EPRI, 1989
Sr	FA	39 by XRF	1331	204–6820	300	50–1000	EPRI, 1989
U	FA	13 by XRF	19	11.1–30.4	1	0.9–9	EPRI, 1989
V	FA	35 by XRF	272	95–652	100	20–500	EPRI, 1989
Zn	FA	39 by XRF	449	27–2880	50	10–300	EPRI, 1989
	AFBC	9	5	29–105	50	10–300	Stout et al., 1988

^a Fly ash.

^b X-ray fluorescence.

^c Not reported.

Barker, A.V.; Stratton, M.L.; Rechcigl, J.E. Soil and By-Product Characteristics that Impact the Beneficial Use of By-Products. In Power, J.F.; Dick, W.A., Eds.; *Land Application of Agricultural, Industrial, and Municipal Byproducts*; 2000; pp 169–213.

Electric Power Research Institute. *Coal Ash and the Environment: Characteristics of Fly Ash*. Technical Report RP2485-8, 1989.

Stout, W.L.; Hern, J.L.; Korcak, R.F.; Carlson, C.W. *Manual for Applying Fluidized-Bed Combustion Residue to Agricultural Lands*; ARS-74; U.S. Department of Agriculture, Agricultural Research Service, 1988.

APPENDIX C

ELEMENTS STUDIED IN VARIOUS RESEARCH EFFORTS ON THE USE OF CCBS IN AGRICULTURAL LAND APPLICATIONS

Table C-1. Elements Studied In Various Research Efforts on the Use of CCBs in Agricultural Land Applications

Element Studied	Reference(s)	Element Studied	Reference(s)
Aluminum – Al	2–4	Manganese – Mn	2–5
Antimony – Sb	2, 3	Mercury – Hg	3, 4
Arsenic – As	1–4	Molybdenum – Mo	1–4
Barium – Ba	2, 3	Nickel – Ni	2–5
Beryllium – Be	2, 3	Phosphorus – P	1–5
Boron – B	1–5	Potassium – K	1–5
Cadmium – Cd	1–5	Selenium – Se	1–4
Calcium – Ca	1–5	Silicon – Si	2, 3
Chromium – Cr	2–5	Silver – Ag	3
Cobalt – Co	2, 3	Sodium – Na	2–4
Copper – Cu	1–5	Sulfur – S	1–4
Iron – Fe	2–5	Strontium – Sr	2, 3
Lead – Pb	2–5	Thallium – Tl	3
Lithium – Li	2	Vanadium – V	2
Magnesium – Mg	1–5	Zinc – Zn	1–5

1. Carlson, C.L.; Adriano, D.C. Environmental Impacts of Coal Combustion Residues. *J. Environ. Qual.* **1993**, *22*, 227–247.
2. Dick, W.; Bigham, J.; Forster, R.; Hitzhusen, F.; Lal, R.; Stehouwer, R.; Traina, S.; Wolfe, W.; Haefner, R.; Rowe, G. *Land Application Uses for Dry Flue Gas Desulfurization By-Products: Phase 3*; EPRI-TR-112916; Electric Power Research Institute: Palo Alto, CA, Jan 1999.
3. Adriano, D.C.; Weber, J.; Bolan, N.S.; Paramasivam, S.; Koo, B.-J.; Sajwan, K.S. Effects of High Rates of Coal Fly Ash on Soil, Turfgrass, and Groundwater Quality. *Water, Air, Soil Pollut.* **2002**, *139*, 365–385.
4. Stevens, G.; Dunn, D. Fly Ash as a Liming Material for Cotton. *J. Environ. Qual.* **2004**, *33*, 343–348.
5. Sajwan, K.S.; Paramasivan, S.; Alva, A.K.; Adriano, D.C.; Hooda, P.S. Assessing the Feasibility of Land Application of Fly Ash, Sewage Sludge and Their Mixtures. *Advances Environ. Res.* **2003**, *8*, 77–91.

APPENDIX D

EERC SUMMARY OF REFERENCED ELEMENT CLASSIFICATION

Table D-1. EERC Summary of Referenced Element Classification

Element	Classification	References
N	Macronutrient	Adriano (2002) [plant tissue]; Barak (2006); Mason and Adriano (2001) [plant tissue]
	Essential mineral	Barak (2006)
P	Macronutrient	Adriano (2002) [fly ash and plant tissue]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
K	Macronutrient	Adriano (2002) [fly ash and plant tissue]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
Ca	Macronutrient	Barak (2006)
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
	Secondary nutrient	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash and plant tissue]
Mg	Macronutrient	Barak (2006)
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
	Secondary nutrient	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash and plant tissue]
S	Macronutrient	Barak (2006)
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
	Secondary nutrient	Adriano (2002) [plant tissue]
Cl	Macronutrient	Barak (2006)
	Essential mineral	Barak (2006)
B	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient	Adriano (2002) [plant tissue]
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
Cu	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient	Adriano (2002) [plant tissue]
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)
Fe	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient	Adriano (2002) [plant tissue]
	Essential mineral or plant nutrient	Barak (2006); Stout et al. (1988)

Element	Classification	References
Mn	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient Essential mineral or plant nutrient	Adriano (2002) [plant tissue] Barak (2006); Stout et al. (1988)
Zn	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient Essential mineral or plant nutrient	Adriano (2002) [plant tissue] Barak (2006); Stout et al. (1988)
Mo	Micronutrient	Adriano (2002) [fly ash]; Barak (2006); Mason and Adriano (2001) [fly ash and plant tissue]
	Essential micronutrient Essential mineral or plant nutrient	Adriano (2002) [plant tissue] Barak (2006); Stout et al. (1988)
Ag	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
As	Miscellaneous element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Trace element	Mason and Adriano (2001) [plant tissue]
Be	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
Cd	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Heavy metal	Stout et al. (1988)
Cr	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Heavy metal	Stout et al. (1988)
Co	Miscellaneous element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Beneficial mineral	Barak (2006)

Element	Classification	References
Hg	Miscellaneous element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Trace element	Mason and Adriano (2001) [plant tissue]
Ni	Micronutrient	Barak (2006)
	Essential mineral	Barak (2006)
	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Heavy metal	Stout et al. (1988)
Pb	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Heavy metal	Stout et al. (1988)
Sb	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
Se	Essential plant nutrient	Stout et al. (1988)
	Beneficial mineral element	Barak (2006)
	Miscellaneous element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash]
	Nonessential trace element	Adriano (2002) [plant tissue]
	Trace element	Mason and Adriano (2001) [plant tissue]
Tl	Trace element	Adriano (2002) [fly ash]; Mason and Adriano (2001) [fly ash and plant tissue]
	Nonessential trace element	Adriano (2002) [plant tissue]
Al	Miscellaneous element	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash and plant tissue]
	Phytotoxic element	Stout et al. (1988)
Ba	Miscellaneous element	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash and plant tissue]
Na	Miscellaneous element	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash and plant tissue]
	Beneficial mineral element	Barak (2006)
Si	Miscellaneous element	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash]
	Beneficial mineral element	Barak (2006)
Sr	Miscellaneous element	Adriano (2002) [fly ash and plant tissue]; Mason and Adriano (2001) [fly ash]

Adriano, D.C.; Weber, J.; Bolan, N.S.; Paramasivam, S.; Koo, B.-J.; Sajwan, K.S. Effects of High Rates of Coal Fly Ash on Soil, Turfgrass, and Groundwater Quality. *Water, Air, Soil Pollut.* **2002**, *139*, 365–385.

Barak, P. Essential Elements for Plant Growth.
www.soils.wisc.edu/~barak/soilscience326/essentl.htm (accessed March 2006).

Mason, J.; Adriano, D. Coal Ash as Soil Amendment to Enhance Water Balance, Growth, and Harvesting of Turfgrasses. U.S. Patent 6,278,358 B1, Sept 11, 2001.

Stout, W.L.; Hern, J.L.; Korcak, R.F.; Carlson, C.W. *Manual for Applying Fluidized-Bed Combustion Residue to Agricultural Lands*; ARS-74; U.S. Department of Agriculture, Agricultural Research Service, 1988.

APPENDIX E

**N-VIRO MINERAL BY-PRODUCTS (MBP)
QUALITY SPECIFICATION
(available at www.nviro.com/mbp/specs.htm)**

N-VIRO MINERAL BY-PRODUCTS (MBP) QUALITY SPECIFICATION

I. It is the policy of N-Viro that no MBPs which originate from a plant burning hazardous waste will be considered for qualification as N-Viro MBP.

II. Pollutant concentrations

A. Maximum allowable levels of trace elements allowed in N-Viro MBP*

CFR 503, Table 3

Arsenic	41 ppm
Cadmium	21 ppm
Chromium	1200 ppm
Copper	1500 ppm
Lead	300 ppm
Mercury	17 ppm
Molybdenum	75 ppm
Nickel	420 ppm
Selenium	100 ppm
Zinc	2800 ppm

* Those materials that are above the maximum limits will require written permission from N-Viro's Director of Research on a case-by-case basis. With only rare exceptions, final product must be below the allowable levels listed above.

B. Maximum allowable levels of trace elements allowed in any blend component for N-Viro MBP (dry weight basis)

CFR 503, Table 1

Arsenic	75 ppm
Cadmium	85 ppm
Chromium	3000 ppm
Copper	4300 ppm
Lead	840 ppm
Mercury	57 ppm
Molybdenum	75 ppm
Nickel	420 ppm
Selenium	100 ppm
Zinc	7500 ppm

III. Physical characteristics

Particle-size distribution: 60% passing 200 mesh
Blaine-fineness: more than 3000 cm²/gram

Dryness: nonconditioned material preferred. Consult N-Viro for specific information pertaining to conditioned material.

IV. Chemical characteristics

pH: combination of MBP, lime, and sludge will produce required pH (usually >12).

Available lime: sufficient to produce required heat for project or combine with another MBP and/or lime.

Exceptions must be approved by N-Viro in writing.

APPENDIX F

EXAMPLE CALCULATIONS FOR AFBC MATERIAL AGRICULTURAL LAND APPLICATION (adapted from Stout et al., 1988)

EXAMPLE CALCULATIONS FOR AFBC MATERIAL AGRICULTURAL LAND APPLICATION
(adapted from Stout et al., 1988)

Task 1	Soil and crop information					
	Soil type: silt loam					
	Crop: alfalfa					
	Lime requirement: 1.7 tons/acre					
Decision 1	Lime is required for this crop.					
	Proceed to next task.					
Task 2	AFBC material analyses					
	Lime content	60% CaCO ₃				
	B	110 ppm				
	Cd	0.05 ppm				
	Cr	15 ppm				
	Cu	15 ppm				
	Pb	3.2 ppm				
	Ni	21 ppm				
	Zn	55 ppm				
Decision 2	CaCO ₃ is greater than 30%.					
	Proceed to next step.					
Task 3	Calculate AFBC material application rate.					
	Rate = lime requirement/(lime content/100)					
	= 1.7 tons/acre/(60/100)					
	= 2.8 tons/acre					
Task 4	Calculate heavy metal and boron loadings.					
	Loading = element content × rate × 0.002 ^a					
		<u>ppm</u>	×	<u>tons/acre</u>	×	<u>lb/acre</u>
	B	110	×	2.8	×	0.620
	Cd	0.5	×	2.8	×	0.003
	Cr	15	×	2.8	×	0.084
	Cu	15	×	2.8	×	0.084
	Pb	3.2	×	2.8	×	0.018
	Ni	21	×	2.8	×	0.118
	Zn	55	×	2.8	×	0.310
	^a 0.002 is a conversion factor used when the concentration of the elements is expressed in ppm.					
Task 5	Calculate total heavy metal loadings (lb/acre); previous loading was 0.					
		Current and total <u>loading</u>		Maximum <u>loading^b</u>		
	Cd	0.003		4.5		
	Cr	0.084		600		
	Cu	0.084		150		
	Pb	0.018		600		
	Ni	0.118		60		
	Zn	0.310		300		
	^b Values for silt loam soil in Table 2 of Stout et al. (1988).					
Decision 3	Total cumulative heavy metal loadings below maximum and current boron loading below 2 lb/acre.					
	Proceed with application.					
Task 6	Apply AFBC material according to local cropping practices.					
Task 7	Monitor pH and heavy metals in the soil with appropriate soil tests.					
Decision 4	If there is no rapid increase in heavy metal above normal levels in the soil, go to Decision 5; discontinue AFBC material applications.					
Decision 5	If soil needs more lime, return to Task 2; or go to Task 7.					

Stout, W.L.; Hern, J.L.; Korcak, R.F.; Carlson, C.W. *Manual for Applying Fluidized-Bed Combustion Residue to Agricultural Lands*; ARS-74; U.S. Department of Agriculture, Agricultural Research Service, 1988.