12-2002

Determining the Mobility of Metals Through Coal Combustion Byproducts in Surface Impoundments by Analyzing Leachate From Modified Saturated Hydraulic Conductivity Tests

Michael Joseph Trofinoff
Columbus State University

Recommended Citation

Trofinoff, Michael Joseph, "Determining the Mobility of Metals Through Coal Combustion Byproducts in Surface Impoundments by Analyzing Leachate From Modified Saturated Hydraulic Conductivity Tests" (2002). *Theses and Dissertations*. 35.
https://csuepress.columbusstate.edu/theses_dissertations/35

DETERMINING THE MOBILITY OF METALS THROUGH COAL COMBUSTION BYPRODUCTS IN SURFACE IMPOUNDMENTS BY ANALYZING LEACHATE FROM MODIFIED SATURATED HYDRAULIC CONDUCTIVITY TESTS.

Michael Joseph Trofinoff

Columbus State University

The College of Science

The Graduate Program in Environmental Science

Determining the Mobility of Metals Through Coal Combustion Byproducts in Surface Impoundments by Analyzing Leachate from Modified Saturated Hydraulic Conductivity Tests.

A Thesis in

Environmental Science

by

Michael Joseph Trofinoff

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Master of Science

December 2002

I have submitted this thesis in partial fulfillment of the requirements for the degree of Master of Science.

11NOV02
Date

Michael Joseph Trofinoff

We approve the thesis of Michael Joseph Trofinoff as presented here.

11/11/02
Date

William J. Frazier
William Frazier, Ph.D., Professor of Geology, Thesis Advisor

11/11/02
Date

Thomas B. Hanley, Ph.D., Professor of Geology

11/11/02
Date

R. David Asti, Georgia Registered Professional Geologist, Southern Company Services

11-11-02
Date

David W. Morris
David W. Morris, Manager, Earth Sciences and Environmental Engineering, Southern Company Services

ABSTRACT

Surface impoundments are used extensively throughout the utility industry to store the combustion byproducts, or ash, from coal-fired generating facilities. Following combustion, the metals, naturally contained within coal at low concentrations, may become highly concentrated within the ash. These combustion byproducts are then piped out in a water-ash slurry to the surface impoundments where the ash weathers to a clay-like substance after approximately 10 years. It is feared that these metals that are contained within the ash could possibly leach into the ground and contaminate the local groundwater.

Utilizing a open column percolation test to determine the hydraulic conductivity of the ash, a set of tests were run to see what metals were contained within the test leachate using permitted discharge from the generating facility (Georgia Power Company's (GPC) Plant McDonough, Smyrna, Georgia). The permitted discharge is a slightly alkaline fluid, with a pH range of 7.08-8.03. Toxicity Characteristic Leaching Procedure (TCLP) was then conducted to see what metals would leach from the ash in an acidic (pH range of 4.93 +/- 0.05) environment. The results were then compared to provide a best and worst case scenario for metals leaching from the ash pond into groundwater supplies.

The relatively low levels of metals contained in the leachate from the TCLP tests suggest that after a surface impoundment is no longer utilized, the acidic nature of rainwater would not cause metals to leach into groundwater supplies. Calcium, an important nutrient for plants, was shown in the TCLP tests to be the one metal consistently available from the ash in an acidic environment. This might be the reason

cattails (*Typha* spp.) and pines (*Pinus* spp.) are so numerous within the ash pond's older areas. This large abundance of leachable calcium is due to the large percentage of ash comprised of calcium oxide (CaO), which has a relatively high solubility.

The coal combustion byproducts (CCBs) are commingled within the pond so utilization for beneficial purposes such as concrete aggregate, Portland cement substitute, asphalt shingles, etc. would require separating the CCBs into their components (fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) material). It is recommended that an economic feasibility study be conducted on the ash pond(s) at GPC's Plant Arkwright, a plant that is to cease operations in the near future, to see if it is economically feasible to separate the CCBs in such a way that other industries could use them.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

Though only one name appears on the cover of this thesis, I would be remiss not to acknowledge the many that helped to make it possible...& fun.

Dr. William Frazier, Thesis Advisor; Dr. Thomas Hanley, committee member; Mr. David Morris, committee member; and especially Mr. David Asti, committee member; whose "hands-on" approach helped resolve many issues with Georgia Power Company.

The Department of Science, whose faculty who made it fun to learn.

My fellow graduate students who kept it fun while we weren't learning.

Craig Scott and Dwight A. Davis of Georgia Power for their assistance in analyzing my samples.

Anita Perry of Plant McDonough for her assistance in gathering samples.

Theresa Lee of Geosciences, Columbus, Georgia for her help in cracking my cubes.

Michael H. Leftin, Ph.D., of Integrated Analytical Laboratories of Randolph, New Jersey.

MAJ Greg E. Ebeling of the 926th Engineer Group for the use of his soils laboratory.

The staff of the Simon Schwob Memorial Library, especially the interlibrary loan section.

Mr. Bruce Locke, of Rombout Junior High School, for instilling a "work smarter, not harder" attitude in his seventh grade mechanical drawing students.

My parents, Henry and Gloria Trofinoff, for always emphasizing higher education is not a luxury, but rather a requirement in our modern society.

Most importantly...my wife, Lori, whose constant prodding (a.k.a. nagging) kept this thesis from becoming a fourth bookshelf. Can we please have the cable installed now?

For Alexander, Cameron and Sydney...

...may your generation be less consumptive and wasteful than mine.

In memory of...

Sergeant First Class Barry W. Vance, “Volcano-7”

... a steadfast-professional military engineer, exemplary mentor and gentleman whose love of his country and nature was only exceeded by his love for his wife and son. Your absence from our ranks is sorely missed in this, our nation’s, time of need.

INTRODUCTION

Ash and the Electric Utilities:

Coal-fired electric generating plants are the leading producers of electricity within the United States. Georgia Power Company's (GPC) generating system creates 9,166,174 kilowatts of their capacity, approximately 60%, by coal-fired generating plants (Facts and Figures 2000, Facts & Figures 2001). It is likely that this reliance upon coal as the primary fuel for electric production will continue for the foreseeable future as demand grows and the push to decommission nuclear plants, the second largest electric fuel source, strengthens over the next 25 years.

Coal flows through a typical boiler system as shown in Figure 1. The term coal combustion byproducts (CCBs) refers to all the wastes generated by coal burning: fly ash, bottom ash, boiler slag and Flue Gas Desulfurization (FGD) material. Coal-fired plants produced approximately 90 million tons of CCBs nationally in 1994, of which only 22% was used beneficially (Fly Ash Facts for Highway Engineers, page i). By 1999, that figure had risen to 115 million tons produced nationally (Federal Register). The majority of these CCBs are disposed in surface impoundments, dry landfills, or ash ponds. The Environmental Protection Agency (EPA) reported that as of 1995 only 65% of new ash ponds and 38% of all ash ponds had groundwater monitoring systems in place. Additionally, only 60% of new ash ponds and 26% of old ones had liners (Federal Register).

Metals and Ash:

Aluminum, arsenic, barium, calcium, chromium, copper, nickel, lead, selenium, vanadium, and zinc occur naturally in coal in low concentrations. When the coal is pulverized and burned within a generating plant, these metals are retained within the ash, now at much higher concentrations (EPRI Report TR-101785, Appendix A). Although some of these metals are benign in nature and others may be benign in some forms, they may still produce concerns when mentioned to the public. For example, lead conjures up images of lead based paint peeling off old apartment buildings causing developmental problems for children who eat the paint chips. Chromium, in its hexavalent form, was linked to rare types of cancer as depicted in a recent academy award winning motion picture. In 1879, arsenic was one of the first chemicals linked to cancer when miners were thought to develop lung cancer from inhaling arsenic. Argentina reported large numbers of skin cancer were due to high levels of arsenic in drinking water during the 1930s (Smith, et al. p 2145). The recent adoption of a more stringent drinking water standard for arsenic, 10 μg/l, by the EPA has again brought arsenic into the public conscience.

EPA Regulation of CCBs as Non-Hazardous Waste:

The belief that these metals could leach from the ash ponds and contaminate local groundwater supplies led the federal government to develop standards for CCB disposal. The EPA concluded that CCBs are non-hazardous waste and do not require regulation under subtitle C (hazardous waste)of the Resource Conservation and Recovery Act (RCRA) and provided an exemption under the Bevill Amendment to RCRA in 1993.

National standards were developed under subtitle D (non-hazardous waste) of RCRA in accordance with the amendment. The EPA estimates that should a subtitle C, hazardous waste, approach be warranted in the future it could cost the utility industry $1 billion per year. This cost would likely be passed on to the customers in the form of higher electric rates and higher prices for most goods that require electricity in their manufacture (Federal Register).

Ashes to Clay and Impermeability:

Elemental analysis of conventional coal fly ash and clay soil as shown in Table 1 indicate that there is a high similarity between the two at least chemically (Dienhart, p. 74). Volcanic ash is known to weather to a clay-like substance over time. Studies on the weathering of coal fly ash in ash ponds have shown that some minerals within the ash are naturally altering to a non-crystalline clay and crystalline salts, primarily of Fe and Al. After only a decade of weathering, dissolution of the aluminosilicate particles produces a clay content higher than that within 250-year old volcanic ash (Zevenbergen, et al.). These clays are thought to hold, by adsorption, the metals within the clay structure, whose lower permeability inhibits the leaching of the metals into the groundwater.

Beneficial Uses of CCBs:

CCBs have been used as a substitute for portland cement and small coarse aggregate in concrete since the 1930s. More recently, applications of CCBs in flowable fill, wallboard (a.k.a. sheetrock), paint fillers, asphalt shingles, filler in cast aluminum products, as well as soil admixtures that promote water infiltration and retention have been developed (Dienhart, pps. 15-65). Most of the use of CCBs still involves the concrete industry. Classes for the fly ash have been developed to ensure quality in their use as a component in concrete (Fly Ash Facts for Highway Engineers, page 3-4).

A secondary objective of this research was to see if the CCBs within the research pond could be used in a beneficial manner.

Selection Criteria:

The research conducted by Zevenbergen et al. determined that ten-year old CCBs weathered to a state similar to that of 250-year old volcanic ash. This ten-year mark is the basis for the ash sample selection criteria.

The pond that was sampled is located at Georgia Power Company's Plant McDonough coal-fired generating facility near Smyrna, Georgia. The generating plant consists of two forced draft boilers which have been in operation since 1962 and 1963 respectively. The plant has constructed four ash ponds in its history, currently only ponds #3 and #4 are in use. The two ponds are connected so the discharge entering pond #3 will flow into #4. Pond #4 was the last to be constructed and was finished in the early 1970s.

The ponds have been in active use for over 25 years, so there is ash present whose age is both older and younger than the 10-year mark. The older ash is stable enough to walk on and even supports a variety of plant and animal life. Some of the pine trees within the older ash deposits are at least 10-15 years of age themselves. Pond #3 has gradually filled with ash to the point that a channel had to be dredged through the pond from the discharge pipes to allow the permitted discharge from the plant to carry the ash to the areas still open within the pond (Appendix A). In order to reduce the required redredging of the drainage channel, GPC has implemented a "stacking" program whereby

CCBs are excavated from one portion of the pond and stacked in another so that the permitted discharge may flow freely through pond #3 into pond #4.

Objectives:

The objectives of this research were: first, to determine what metals, if any, would be present in leachate from CCBs that had weathered in surface impoundments; second, to determine if stratification occurs within the surface impoundment; finally, to determine the potential use of these CCBs for applications in other industries.

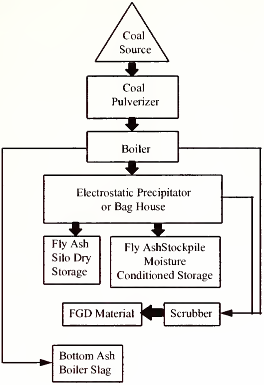


Figure 1. Typical pulverized coal boiler system.
(Dienhart, p. 70)

Table 1. Comparison of Coal Fly Ash and Clay Soil (Dienhart, p. 74).

Compound	**Coal Fly Ash**	**Clay Soil**
SiO_2	46%	42%
Al_2O_3	26%	28%
Fe_2O_3	17%	17%
CaO	3.80%	2.80%
SO_3	2.60%	2.60%
K_2O	1.50%	1.60%
TiO_2	1.10%	1.40%
MgO	1.10%	0.90%
Na_2O	0.60%	1.60%
P_2O_5	0.30%	2.10%

MATERIALS AND METHODS

Sampling Plan:

A total of five sampling points were used to gather CCBs and permitted discharge samples (Appendix B). Two of the CCBs samples were taken from the drainage channel dredged through the pond. The remaining three were taken from the older ash deposits that have since been dried and covered in vegetation. Permitted discharge samples were gathered at each of the two submerged ash-sampling points as well as three other points along the channel (Figure 2). At the permitted discharge sampling point closest to the outlet pipes, a Hydrolab® was used to gather the following data: air temperature, water temperature, pH, specific conductance, dissolved oxygen and percent dissolved oxygen (Figure 3). A tape measure was used to determine depth of the discharge within the drainage channel.

In order to minimize the disturbance of the ash sediment within the pond, and for personal safety, walking in the submerged areas was restricted. Sampling of the submerged areas took place along the sides of the channel. Furthermore, to reduce potential error in the surface water analysis, water samples were taken first, followed by ash samples from the sediment.

Permitted Discharge Samples:

The sampler couldn't walk within the confines of the drainage channel as the required stability was lacking (Figure 4). The sampler remained on the side of the drainage channel and conducted the sampling from the edge. While wearing long-sleeved chemically non-reactive rubber gloves, the sampler submerged one empty 1-liter bottle in

Figure 2. Permitted Discharge Sampling. Walking within the ash pond proved precarious on even apparently stable surfaces. All permitted discharge sampling was conducted from the side of the channel. This sample is permitted discharge #5 and was taken just in front of the discharge pipes at a time when the plant was not discharging into the pond.

Figure 3. Field Testing of Permitted Discharge. A Hydrolab ® is utilized to test the permitted discharge close to the outlets from the discharge pipes. Note the grasses growing within the pond in the background of the photo.

Figure 4. A sampling technician gathers CCBs from location #1 alongside the drainage channel. The fresh CCBs provided no support to sample the permitted discharge just minutes before this photo was taken. The high void ratio and moisture content of the fresh CCBs allowed them to pour out the bottom of the auger during sampling as shown here.

the permitted discharge and unscrewed the cap to fill the bottle. When full, the cap was tightened while submerged. This process was repeated to obtain a second sample; one sample was used during the open column percolation tests while the other was used for the analytical tests. The sampling was done starting at the farthest point downstream and working upstream to avoid contaminating the samples by disturbing the ash.

CCBs Samples:

Because Plant McDonough is still actively using their ash pond, holes were dug with a hand auger to a depth of 18 inches. The top 18 inches of CCBs were arbitrarily disposed of at least one arm's length away from the hole to prevent any CCBs less than ten years old from falling back into the hole (Figure 5). Taking the second auger, the sampler obtained approximately 8-12 inches of CCBs from above the water table within the ash pond. A visual observation of the CCBs was taken to see if any stratification had occurred. CCBs were placed in labeled sealable plastic bags until a composite could be made (Figure 6). Upon completion of all sampling, composite samples were made for each of the five sampling points from the bags that were filled for each specific sampling point. Two eight-ounce jars were filled for each point; one for Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis, the other for Toxic Characteristic Leaching Procedure (TCLP) and open column percolation tests.

Sampling of CCBs also occurred along the wall of an excavated trench which allowed for close visual inspection of the stratification within the CCBs. There were no analytical tests for metals performed on these samples due to the fact that this trench was only safe

Figure 5. Hand Augering for CCBs Samples. David Asti of Southern Company is shown here sampling next to a dewatering trench excavated as part of the CCB stacking program. The stratification is visible within the trench. The thick black layer is the storm runoff from the coal stockpiles. The orange is iron oxide within the CCBs.

Figure 6. Bagging Samples. Pete Robinson, of Williams Environmental Services, removes CCBs from the auger for deposit into a sealable bag with the assistance of David Asti.

to enter and sample well after the initial sampling was conducted and those samples were first analyzed. Moisture content was determined on these samples to see what changes in moisture content related to the stratification of the CCBs (See *Stratification of ash within the pond).*

Permitted Discharge Analysis:

Using ICP-AES as outlined in EPA Method 6010B, the permitted discharge was analyzed for metal content. Analysis preparation requires the samples to be solubilized or digested by an acid prior to analysis. For permitted discharge samples, acid digestion was necessary because the samples were not filtered and acid preserved prior to analysis. The sample is nebulized and subsequent aerosol is then transported to a plasma torch where element-specific emission spectra are produced by radio frequency inductively coupled plasma. These spectra are then separated using a grating spectrometer, and the intensities of the emission lines are monitored by photosensors. Background correction is necessary for trace element analysis. For the complete method please refer to: http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6010b.pdf

CCBs Analysis:

Analysis was done utilizing three methods: the GPC lab used inductively coupled atomic plasma spectroscopy by EPA Method 6010B, and Integrated Analytical Laboratory (IAL) conducted TCLP using EPA Method 1311 and Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) using EPA Method 6020. IAL also performed EPA Method 6010B for calcium and vanadium.

IAL conducted TCLP Method 1311 to obtain extract that was analyzed utilizing ICP/MS Method 6020 for arsenic, barium, cadmium, chromium, copper, lead, nickel, selenium and zinc. The CCB samples were obviously greater than 0.5% solids. The liquids were separated from the solid and stored for later analysis or for combination with the extract when compatible. The solid phase was extracted with an amount of extraction fluid equal to 20 times the mass of the solid phase to be extracted. The extraction fluid utilized was an acetic acid/sodium acetate buffer of pH 4.93+/- 0.05. The extraction fluid and solid phase were placed within a bottle extraction vessel (BEV). All the BEVs were then placed within a rotary agitator for 18 hours. After the extract was separated from the solids it was combined with the liquid phase of the sample and analyzed using ICP/MS.

EPA Method 6020 measures the ions produced by a radio-frequency inductively coupled plasma. The TCLP extract was nebulized and the resulting aerosol conveyed by argon gas into the plasma torch. The ions thus produced are entrained within the plasma gas and then, by means of an interface, introduced into a mass spectrometer. The ions within the plasma were then sorted according to their mass-to-charge ratios. Background correction is necessary for trace element analysis. For the complete methods please refer to:

http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1311.pdf

http://www.epa.gov/epaoswer/hazwaste/test/pdfs/6020.pdf

Open Column Percolation Test:

An open column percolation test was done to see if the leachate passing through the CCBs would exhibit a change in metal concentration. Open column percolation tests of CCBs have been utilized previously in India (Singh and Vibha, and Kumar). Utilizing an open column percolation apparatus constructed of 3/4 inch diameter PVC tube with an endcap into which a 1/6 inch hole had been drilled through to allow for drainage for each sample, CCBs were placed within the tube and lightly compacted with a wooden dowel to a depth of 3 inches (Figure 7). The depth was determined by marking the wooden dowel so that when this mark was even with the top of the PVC tube, there were three inches of CCBs at the bottom of the tube. Initial depth of permitted discharge was consistent with that measured within the drainage channel of the ash pond.

The open column percolation test utilized permitted discharge fluid from the ash pond instead of the standard 0.01N $CaCl_2$ solution as stated in EPRI Technical Report-101999 for a hydraulic conductivity test and the distilled water used for open column percolation tests by Singh and Vibha, and Sanjay Kumar. The use of permitted discharge more closely replicated leaching within an active ash pond. The leachate from the experiment was collected in 1-liter polypropylene bottles for metal analysis.

Leachate Analysis:

Analysis consisted of EPA Method 6010B, the same procedure that was used for the original metal analysis of the permitted discharge.

Figure 7. Open Column Percolation Apparatus. The amount of leachate within each of the collection bottles is after one week of percolation. The microscopic particle size (most < 45 µm in size) of the CCBs made an effective physical barrier to leaching even with only 3 inches of CCBs in the PVC pipe.

Moisture Content of CCBs:

Each of the five sample jars was opened and stirred with a sample knife to obtain a homogeneous mixture, as the CCBs readily settled out after only 24 hours. Sample cups (tares) were labeled, weighed and recorded on a Soil Moisture Content Sheet (DD Form 1205, 1 FEB 62). Using the sample knife, the CCBs were removed from the jars and placed in the respective tares. These were then weighed and the weights were recorded on the data sheet. The sample knife was rinsed and dried after changing each sample to avoid contamination. The samples were then dried for 24 hours in a Soiltest, Inc. soils oven. The tare and dry CCBs were then removed from the oven, weighed and recorded. Water content was calculated as:

$$\text{water content, } w = (M_w/M_s) \times 100$$

(where M_W = mass of water and M_S = mass of solids)

and recorded on the data sheet. The moisture content was done three times for each of the five CCBs samples and once for each sample taken at depth along the excavated trench wall (Figure 8).

Fly Ash Analysis for use as Soil Stabilization and as a Mineral Admixture in Portland-Cement Concrete:

ASTM Standard D 5239-98, Standard Practice for Characterizing Fly Ash for Use in Soil Stabilization (in poorly graded sands), references ASTM Standard C 430-96 for determining the fineness of the ash by wet sieve analysis based upon the percent weight of the sample retained on a No.325 sieve (45 μm). First, the weight of the No. 325 sieve is determined. The fineness was determined by placing a 1.00 gram sample on a clean and

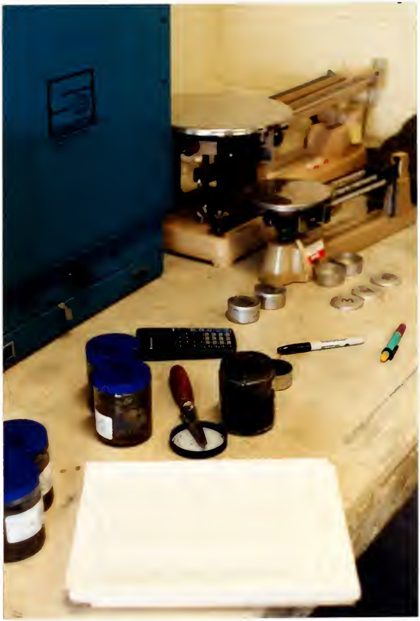


Figure 8. Soils Lab. Moisture content determination of the samples was done in the soils lab at the 926th Engineer Group, Montgomery, Alabama. Here a sample is being placed into tare #3 to be weighed, dried and reweighed. Electronic balances had to be used for certain measurements as the triple balance scale did not provide the precision some procedures required.

dry No. 325 sieve and washing it for one minute with the nozzle about 1/2 inch below the top of the sieve frame and moving in a circular motion. After one minute under the nozzle, the sieve was dried in an oven at low temperatures so as not to soften the solder and still dry the sample. The weight of the sieve with residue was determined and the weight of the dry sieve was subtracted from it to determine the weight of the residue. The weight of the residue was multiplied by 100 plus the correction factor(C) for the sieve, which was +21.2%. This yields the corrected residue. The fineness is then the corrected residue subtracted from one hundred.

Sieve Analysis:

In EPRI Technical Report CS-3314, it is stated that the overall major contributing factor to using coal-derived ash in soil stabilization and as a concrete admixture is the particle size distribution of the ash. Using sieve No.s 4, 10, 16, 20, 30, 40, 60, 80, 100, 200 and 325 particle size distribution was determined so that a comparison could be made with published results on CCBs (Figure 9). The CCBs dried during the moisture content determination procedure were used in the sieve analysis. These 15 samples were placed in a metal bowl. Any CCBs dried together were lightly tapped with the sample knife until they fell apart, so as not to induce an error in the results of the sieve analysis (Figure 10).

Each of the sieves were washed, dried for 15 minutes in the soil oven, then allowed to cool for 20 minutes, then weighed with weights recorded on a Sieve Analysis data sheet (DD Form 1206). A sample was taken from the dried CCBs, weighed and recorded on the data sheet and then deposited in the top sieve of the stack, sieve number 4. The lid

Figure 9. Sieve Analysis of CCBs. A manual agitator was used to shake the sieves during the analysis.

Figure 10. Size Distribution. All 15 samples from the moisture content tests were reused in the sieve analysis. After combining all the dried samples in this metal bowl a sample knife was used to break apart any particles stuck together from the drying process.

was then placed on top of sieve number four and the entire stack of sieves were secured in the manual shaker and continuously agitated for three minutes. The stack was then disassembled and the individual sieves with CCBs were weighed and their weights recorded on the data sheet. The drying of the CCBs in the oven to determine the moisture content caused the CCB particles to stick together even after the sieve analysis. Those particles in the sieves that appeared to be just a conglomerate of fly ash particles were lightly tapped with the sample knife. All the particles that were broken up this way fell through to the next sieve underneath until the #60 sieve. No tapping of the sample knife was used against particles in the #60 or higher sieves for fear of damaging the fine wire mesh. For these sieves, the contents were emptied into a mortar and then lightly tamped with a pestle to break apart the fly ash conglomerates. The contents were then returned to the same sieve that had yielded them previously and another minute of agitation on the manual crank apparatus was conducted. This was done for each sieve up to No. 200. These weights were then used to construct a particle size distribution curve for the CCBs.

Mortar Cubes:

In accordance with EPRI CS-3314, Portland cement was used to construct a six-cube batch of control mortar. The control mortar was made from 250 g Portland cement, 687.5 g standard sand and water. Another six-cube batch of mortar was made, this time with 35% of the absolute volume of the cement being replaced by an equal volume of ash. The fly ash used for these cubes was taken from the CCBs that had passed sieve #200 during the sieve analysis. After 7, 14 and 28 days of curing the cubes are then tested for compressive strength (Figures 11-16). The cubes are first measured with a micrometer to determine the precise size of the side to be loaded by the hydraulic compression machine. Then the cubes are placed within the machine and the cylinder lowered onto the cube so that the load-meter can be zeroed out for the test. The compressive strength of the cube is the load applied to the cube at time of failure divided by the area of the face of the cube that the load was applied on. The Pozzolanic Activity Index (PAI) is calculated by dividing the average compressive strength of the Portland Cement mix by that of the ash mixture. A fly ash with an index of 75% or higher is considered suitable for use in Portland cement concrete.

Stratification of ash within the pond:

As evident in Figure 17, the discharge from the plant varied. At times, both bottom ash and fly ash were being discharged, at other times just one ash and still at another time neither one was being discharged into the pond. Also, sulfur (sulfite, SO_3), injected into the flue gas to reduce the resistivity of low sulfur-coal ash to electrostatic precipitators, when spilled during delivery is deposited into the pond (Figure 18). The storm runoff from the coal storage piles was deposited into the pond as well. This varying discharge meant the CCBs would likely show some stratification. GPC's stacking procedure called for the excavation of CCBs from the pond to be dry stacked in another portion of the pond to increase the volume of the pond and maintain a channel from the outlet across the pond. The initial portion of this excavation was a dewatering-trench which allowed access to depths of 4-5 feet. After entering the trench, vertical

Figure 11. Cleaning the Mortar Cube Molds. The bronze molds for the mortar cubes required cleaning with a wire-brush. A light coat of oil was applied to act as a release agent to help remove the cubes from the mold after one day of curing.

Figure 12. Filling the Molds. After mixing, the mortar was placed into the molds with a hand trowel. Overfilling of the molds was necessary to reduce the voids when tamped.

Figure 13. Tamping the Mortar. Air bubbles within the cubes had to be eliminated or else they would weaken the cubes. A rubber tamper was utilized in accordance with the tamping procedure outlined in ASTM C 109-99.

Figure 14. Tamping Completed. After each of the three layers of mortar is placed within the mold they are tamped. Here are the molds after the third layer is tamped. Notice there is still some excess above the top of the mold. That excess was removed by screeding, or scraped off, across the top of the mold with the tamping tool.

Figure 15. Finished Cubes. After screeding the tops of the cubes with the tamping device these cubes were then cured at room temperature for 24 hours before being moved to a water bath at Geosciences Lab in Columbus, Georgia where they would undergo compressive testing in 7, 14, and 28 days.

Figure 16. Hydraulic Cylinder Compression Machine. The compressive strengths of the 12 cubes were tested in this machine. The readout above the machine shows the total load applied to the face of the cube. This load would be divided by the area of the face of the cube to which the load was applied. The area of the face was calculated using measurements from a micrometer. This particular cube broke at 28 days with a strength of 2,600 pounds per square inch (psi).

Figure 17. Permitted Discharge from Plant McDonough. The discharge pipes shown above are the outlets of the discharge from the plants two boilers. Two of the pipes carry fly ash and two carry bottom ash. Others carry storm runoff from the coal stockpiles. This co-mingling of wastes makes it difficult to utilize the CCBs for beneficial purposes as it would require sieving to separate the fly ash from other wastes. Not pictured here is the sulfite (from the sulfur injection system), found in a pile near the center of the pond, it is another co-mingled waste.

Figure 18. Waste sulfur, from the plant's sulfur injection system, is disposed of in the pond. The sulfur, sulfite (SO_3), is injected into the exhaust gases to increase the effectiveness of electrostatic precipitators. The change to a low-sulfur coal about ten years ago forced GPC to use this system to comply with the standards for particulate emission within the Clean Air Act. Waste sulfur is generated usually during delivery when some will spill on the ground and is cleaned up and deposited in the pond.

measurements were made utilizing a tape measure placed alongside the wall of the trench. All measurements were made from the top of the trench (Figure 19).

This sampling was done by measuring down the wall with a tape measure to determine depth below groundlevel. A plastic spoon was then utilized to sample the specific layers. Samples were placed in sealable bags to prevent loss of moisture.

pH of the Permitted Discharge:

In the field, pH determination was conducted only once on permitted discharge #5 using a Hydrolab ®, a series of sensors combined in one instrument to measure pH, temperature, turbidity, conductance, dissolved oxygen and percent dissolved oxygen. In the laboratory at Columbus State University, the Environmental Science Department's Hydrolab® was used to determine the pH of all five samples.

In order to calibrate the Hydrolab ®, the instrument is connected to the display with the stirrer not being connected. The instrument is inverted so the sensors are facing the ceiling with the apparatus secured by a clamp to an instrument stand. This will allow for a plastic sheath to be placed around the sensors to act as a makeshift cup. The standard solutions were placed in this cup to calibrate the sensors. In between calibrating for each of the characteristics (conductivity, pH 7.0, pH 4.0, pH 10.0, 0 NTU Turbidity and 129 NTU Turbidity) three washes of deionized water are used to flush the cup and clean the sensors.

Figure 19. CCB Stratification in Ash Pond. Below three feet eight inches, the CCBs stopped resembling modeling clay and instead became drier and compressed into thin sheets approximately 1/4-1/2 inch in thickness. Few to no roots were found below three feet.

The actual testing of the permitted discharge called for determining the pH. pH was determined for each permitted discharge before and after the bottle was agitated to shake loose the CCB particles on the bottom. This helped to show how the particles in the mixture affected the properties of the permitted discharge.

RESULTS

Leachate in Acidic and Alkaline Environments:

Integrated Analytical Laboratory (IAL) agreed to conduct a total metals analysis on one sample. Ash # 5 was selected for total metals analysis. This total metals analysis, when compared with the total metals analysis conducted by Georgia Power Company (GPC) on Ash #5, shows that two independent labs could produce similar results, thus validating the sampling procedures utilized in the field.

TCLP analysis was conducted on all five ash samples. The acidic nature of the leaching fluid utilized in the TCLP analysis gives an approximation of what would likely leach from the ash if an acidic solution were to leach through the ash pond. The pH of the leaching fluid, ≈ 4.93, is slightly more acidic than current and future rainwater is likely to achieve based upon atmospheric carbon dioxide concentrations but is adequate for establishing characteristics of a low pH leachate. As shown in Table 2, only calcium appears consistently detectable in each of sample. The presence of aluminum and copper in Ash #5, and zinc in Ash #3 are close to the method detectable limits (MDL) for the procedure. Copper is also present in Ash #1 at approximately 2 ½ times the MDL.

As shown in Table 3, the GPC analysis of Ash #5 shows fairly similar results to IAL's with the exception of three elements: aluminum, cadmium, and selenium. The not-detected (ND) results for GPC's cadmium and selenium are because the MDLs for their analysis was higher than the value IAL obtained for those elements utilizing their analysis. IAL detected cadmium at 1.13 mg/Kg which was above their 0.347 MDL and below

Table 2. Integrated Analytical Laboratory's Total Metals and TCLP analysis of Ash. Note, the term "ash" as applied here in the "sample #" represents all CCBs and not just fly ash.

			TCLP					
Method(s)*	**Total Metals** 6020	**MDL**	1311/6020	1311/6020	1311/6020	1311/6020	1311/6020	**MDL**
Date Analyzed	6/17/02		6/14/02	6/14/02	6/14/02	6/14/02	6/14/02	
Sample #	**ASH 5**		**ASH 5**	**ASH 4**	**ASH 3**	**ASH 2**	**ASH 1**	
Aluminum	26000	13.9	2.48	ND	ND	ND	ND	2
Arsenic	90.1	1.39	ND	ND	ND	ND	ND	0.2
Barium	442	13.9	ND	ND	ND	ND	ND	2
Cadmium	1.13	0.347	ND	ND	ND	ND	ND	0.05
Calcium	6140	69.5	84.2	249	15.1	240	21.1	1
Chromium	41.3	2.78	ND	ND	ND	ND	ND	0.4
Copper	70.4	2.78	0.413	ND	ND	ND	0.989	0.4
Lead	51.1	0.695	ND	ND	ND	ND	ND	0.1
Nickel	40.1	1.39	ND	ND	ND	ND	ND	0.2
Selenium	8.75	2.78	ND	ND	ND	ND	ND	0.4
Vanadium	111	2.78	ND	ND	ND	ND	ND	0.4
Zinc	119	2.78	ND	ND	0.443	ND	ND	0.4

Note: All results reported as mg/kg for Total metals, and mg/l for TCLP. Vanadium and Calcium were determined using Method 6010B. MDL represents "Method Detection Limits".

Table 3. Georgia Power Company's Total Metals on Ash utilizing ICP/AES.

Method(s)*	6010B	6010B	6010B	6010B	6010B	
Date Analyzed	3/21/02	3/21/02	3/21/02	3/21/02	3/21/02	**MDL**
Sample #	**ASH 5**	**ASH 4**	**ASH 3**	**ASH 2**	**ASH 1**	
Aluminum	18100	3450	15600	15200	15000	5.6
Arsenic	87	90	93	78	111	11
Barium	379	162	274	261	285	2.6
Cadmium	ND	ND	ND	ND	ND	2.2
Calcium	6240	1580	3020	4960	4020	4.4
Chromium	39	ND	32	40	30	4.1
Copper	60	35	47	44	62	3.2
Lead	37	41	28	31	38	4.6
Nickel	34	ND	31	26	29	4.3
Selenium	ND	ND	ND	ND	11	9.1
Vanadium	99	32	80	101	100	1.6
Zinc	106	24	83	94	72	2.7

Note: Results are reported as mg/kg.

GPC's 2.2 MDL. IAL detected selenium at 8.75 mg/Kg which was above their 2.78 MDL and just slightly below GPC's 9.1 MDL. The aluminum value detected by GPC is significantly lower than IAL's value. This 7900 mg/Kg difference is likely caused by irregularities in the CCBs. To create two samples from one sampling, the CCBs were mixed on site. It is likely that some of the CCBs may have contained a significantly higher aluminum content and were not represented equally in each composite sample.

As shown in Table 4, selenium was not-detected in all of the permitted discharge samples. Permitted discharge #5 was also not-detected for cadmium, lead and nickel. These additional not-detects were likely caused by the significantly lower number of CCB particles within permitted discharge #5. This lower number of CCB particles is due to the lack of discharge from the plant at the time of sampling. The sampling location for permitted discharge #5 was just in front of the discharge pipes from the plant. When the discharge output ceased, the particulate matter within the permitted discharge already in the pond had time to settle out of the mixture.

The numerous not-detects present in leachate #5, see Table 5, are due to the relative lack of CCB particles within permitted discharge #5. The only metal to show in any appreciable concentration consistently was calcium. Calcium was also the only metal to increase in concentration in the leachate from the permitted discharge. Significant increases of several mg/l were reported for each sample. Arsenic and vanadium in Leachate #5 also increased very slightly, less than an mg/l increase each. It is likely that the other metals are still bound to the surface of the CCB particles and have not had sufficient time to be dissolved through weathering or removed by chemical reaction into the solution.

Table 4. Georgia Power Company's Total Metals on Permitted Discharge utilizing ICP/AES.

Method(s)*	6010B	6010B	6010B	6010B	6010B	
Date Analyzed	3/21/02	3/21/02	3/21/02	3/21/02	3/21/02	**MDL**
Sample #	**PD 5**	**PD 4**	**PD 3**	**PD 2**	**PD 1**	
Aluminum	5.2	48	60	42	143	0.57
Arsenic	0.058	0.7	0.78	0.31	1.2	0.053
Barium	0.14	0.82	1.4	0.84	2.6	0.005
Cadmium	ND	0.021	0.019	0.0093	0.016	0.005
Calcium	24	138	128	73	92	0.051
Chromium	0.022	0.21	0.19	0.088	0.24	0.011
Copper	0.059	1.1	0.97	0.43	0.87	0.041
Lead	ND	0.088	0.13	0.1	0.34	0.041
Nickel	ND	0.2	0.2	0.13	0.27	0.028
Selenium	ND	ND	ND	ND	ND	0.12
Vanadium	0.044	0.14	0.23	0.22	0.81	0.009
Zinc	0.091	0.73	0.73	0.4	0.93	0.014

Note: Results are reported as mg/l.

Table 5. Georgia Power Company's Total Metals on Leachate utilizing ICP/AES.

Method(s)*	6010B	6010B	6010B	6010B	6010B	
Date Analyzed	4/24/02	4/24/02	4/24/02	4/24/02	4/24/02	**MDL**
Sample #	**Lch 5**	**Lch 4**	**Lch 3**	**Lch 2**	**Lch 1**	
Aluminum	0.38	14	16	7.5	25	0.057
Arsenic	0.18	ND	0.062	ND	0.25	0.053
Barium	0.061	0.14	0.24	0.22	0.44	0.005
Cadmium	ND	0.02	0.013	ND	ND	0.005
Calcium	40	162	143	102	125	0.051
Chromium	ND	ND	0.017	ND	0.033	0.011
Copper	ND	0.59	0.52	0.096	0.095	0.041
Lead	ND	ND	ND	ND	0.047	0.041
Nickel	ND	0.18	0.17	0.046	0.053	0.028
Selenium	ND	ND	ND	ND	ND	0.12
Vanadium	0.092	0.02	0.045	0.059	0.29	0.009
Zinc	0.042	0.68	0.51	0.18	0.14	0.014

Note: Results are reported as mg/l.

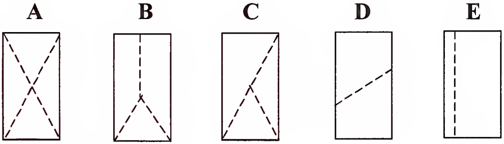
Mortar Cube Strength Analysis:

As shown in Table 6, the results of the mortar cube strength test vary markedly through each of the three time periods. No overall trend depicting increasing strength over time can be derived from these results. The drop off in compressive strength for the F-cube in each batch combined with the high strength of the E-cubes that were tested on the same day indicates major irregularities within the structure of the cubes themselves. This is indicative of numerous voids resulting from poor tamping during the molding of the cubes.

The failure planes of the mortar cubes, as shown in Table 6, also reflect a large number of voids. Generally, for compression tests the cubes will fail along a D-plane, or shear plane. The large number of E-plane failures, columnar planes, indicates that a large enough number of voids were present to weaken the cube. It is possible that this plane was along one of the two planes separating the three layers of mortar placed into the mold when constructing the cubes. The voids would likely occur along this plane since air would be easily trapped within the mortar by the addition of another layer of mortar. The A-plane (cone plane) and C-plane (cone and shear) failures all occurred at 28 days. It is likely that after 28 days of curing these cubes had developed sufficient strength to withstand the columnar failure of the earlier cubes, but still had sufficient voids to break along multiple planes (Figure 20).

Table 6. Mortar Cube Compression Test Results

Ash Batch	Date Tested	Age (days)	Failure Plane	Compressive Load (pounds)	Face Area (in^2)	Compressive Strength (psi)
A	23-Apr	12	E	9473	4.032	2349.4
B	23-Apr	12	E	9329	4.042	2308
C	25-Apr	14	E	9364	4.098	2285
D	25-Apr	14	E	9591	4.004	2395.3
E	9-May	28	C	10580	4.142	2554.3
F	9-May	28	C	9009	4.086	2204.8
Control Batch						
A	23-Apr	12	E	8286	4.036	2053
B	23-Apr	12	E	8156	4.03	2023.8
C	25-Apr	14	E	10883	4.034	2697.8
D	25-Apr	14	E	10334	4.028	2565.5
E	9-May	28	A	13829	4.048	3416.2
F	9-May	28	A	10407	4.002	2600.4



Cone Cone and Split Cone and Shear Shear Columnar

Figure 20. Failure planes for compressive testing of mortar cubes.

Where the Moisture is Present within the Stratification:

By comparing the moisture content results in Table 7 with the sampling plan in Appendix B, it can be seen that the values for the moisture content correspond well with the location of the sampling points. CCB samples 1, 3, and 5 were all located in or adjacent to the drainage channel and thus had slightly higher moisture contents. CCB Samples 2 and 4 were located up-gradient of the drainage channel and noticeably had less moisture.

The noticeable change in color and feel of the CCBs at three feet in depth is likely related to the increase in moisture content of the CCBs at this point and possibly the increase in compaction. No root structure was observed below three feet. The withdrawal of the moisture above three feet from the root structures of the grasses may account for the slightly lower moisture content for this region. The increase in moisture content at approximately 37 inches may be due to the compression of the CCBs below. The compressive force on the older CCBs below likely collapsed the voids within the CCBs, forcing the entrained moisture higher. It was noticed in the field by squeezing the CCBs in your hand that the CCBs below three feet exhibited more brittle characteristics and less malleable ones then those CCBs at 37 inches. The CCBs also appeared to be compacted into layers ¼ to ½ inch in thickness. The color of these compacted CCBs was no longer the dark grey-black of the coal runoff or fly ash, but rather a grey like a battleship grey.

Table 7. Moisture content results on the five CCB sample sites.

CCB Sample # 1				**AVG.**
Run Number	1	2	3	**Moisture**
Tare Number	20	19	1	**Content**
A. Weight of Tare + Wet CCB, (g)	51.3	52.5	61.7	
B. Weight of Tare + Dry CCB, (g)	40.3	41.5	47.8	
C. Weight of water, Ww (A-B), (g)	11	11	13.9	
D. Weight of Tare, (g)	18.1	18.1	18.4	
E. Weight of Dry CCB, Ws (B-D), (g)	22.2	23.4	29.4	
Moisture Content, W (%)	49.5	47	47.2	**47.9**
CCB Sample # 2				**AVG.**
Run Number	1	2	3	**Moisture**
Tare Number	18	17	2	**Content**
A. Weight of Tare + Wet CCB, (g)	55.8	52.7	52.1	
B. Weight of Tare + Dry CCB, (g)	44.8	43.3	42.9	
C. Weight of water, Ww (A-B), (g)	11	9.4	9.2	
D. Weight of Tare, (g)	18.3	18.1	18.3	
E. Weight of Dry CCB, Ws (B-D), (g)	26.5	25.2	24.6	
Moisture Content, W (%)	41.5	37.3	37.3	**38.7**
CCB Sample # 3				**AVG.**
Run Number	1	2	3	**Moisture**
Tare Number	16	15	3	**Content**
A. Weight of Tare + Wet CCB, (g)	49.1	50.9	57.9	
B. Weight of Tare + Dry CCB, (g)	39.1	40.6	46.1	
C. Weight of water, Ww (A-B), (g)	10	10.3	11.8	
D. Weight of Tare, (g)	18.8	18.5	18.2	
E. Weight of Dry CCB, Ws (B-D), (g)	20.3	22.1	27.9	
Moisture Content, W (%)	49.2	46.6	42.2	**46**
CCB Sample # 4				**AVG.**
Run Number	1	2	3	**Moisture**
Tare Number	13	10	4	**Content**
A. Weight of Tare + Wet CCB, (g)	45.5	45.4	61.8	
B. Weight of Tare + Dry CCB, (g)	38.4	38.2	50.6	
C. Weight of water, Ww (A-B), (g)	7.1	7.2	11.2	
D. Weight of Tare, (g)	18.3	18.2	18.3	
E. Weight of Dry CCB, Ws (B-D), (g)	20.1	20	32.3	
Moisture Content, W (%)	35.3	36	34.6	**35.3**
CCB Sample # 5				**AVG.**
Run Number	1	2	3	**Moisture**
Tare Number	9	8	5	**Content**
A. Weight of Tare + Wet CCB, (g)	76.4	70.3	63.5	
B. Weight of Tare + Dry CCB, (g)	56.6	52.4	48.4	
C. Weight of water, Ww (A-B), (g)	19.8	17.9	15.1	
D. Weight of Tare, (g)	18.4	18.6	18.5	
E. Weight of Dry CCB, Ws (B-D), (g)	38.2	33.8	29.9	
Moisture Content, W (%)	51.8	52.9	50.5	**51.7**

Table 8. Moisture content versus Depth of CCBs within the pond.

CCB Sample Depth (inches)	**18**	**30**	**34**
Run Number	1	1	1
Tare Number	16	18	8
A. Weight of Tare + Wet CCB, (g)	66.6	39.9	46.1
B. Weight of Tare + Dry CCB, (g)	50.7	32.9	36.8
C. Weight of water, Ww (A-B), (g)	15.9	7.0	9.3
D. Weight of Tare, (g)	18.4	18.6	18.6
E. Weight of Dry CCB, Ws (B-D), (g)	32.3	14.3	18.2
Moisture Content, W (%)	**49.2**	**48.9**	**51**
CCB Sample Depth (inches)	**37**	**40**	**46**
Run Number	1	1	1
Tare Number	13	20	10
A. Weight of Tare + Wet CCB, (g)	55.4	77.2	66.3
B. Weight of Tare + Dry CCB, (g)	42.1	59.2	53.1
C. Weight of water, Ww (A-B), (g)	13.3	18.0	13.2
D. Weight of Tare, (g)	18.4	18.3	18.4
E. Weight of Dry CCB, Ws (B-D), (g)	23.7	40.9	34.7
Moisture Content, W (%)	**56.1**	**44**	**38**

Sieve Analysis Results:

The sieve analysis was conducted in two trials to see if the results could be duplicated. The material used for the sieve analysis was the dried CCBs from the moisture content analysis. The high percentage of material passing the No. 200 sieve is indicative of the large volume of fly ash comprising the bulk of the CCBs. The average percent passing the No. 200 sieve, including factoring in different initial CCB masses for each trial run, was calculated as follows:

$$\frac{(\text{CCBs} <\#200(\text{trial }\#1)) + (\text{CCBs} <\#200(\text{trial }\#2))}{\text{Initial Sample (trial }\#1) + \text{Initial Sample (trial }\#2)} = \frac{78.2\text{ g} + 154.9\text{ g}}{142.6\text{ g} + 257.2\text{ g}} = \frac{233.1\text{ g}}{399.8\text{ g}} = 58.3\%$$

The error obtained during the sieve analysis was within the acceptable limits. The average percent passing the #325 sieve is the average fineness determined by wet sieve analysis, shown in Table 11, multiplied by the mass of CCBs passing the #200 sieve (233.1 g). 195.4 g of CCBs, or 48.9 %, were able to pass sieve #325 with its 45 µm sized openings.

Table 9. Sieve analysis of CCBs, trial #1.

Weight of Original Sample	**Weight after Pre-washing**	**Washing Loss N/A**	
142.6	**N/A**	**Passing Sieve**	
Sieve/weight	Weight Retained on Sieve	Weight	Percent
#4/521.2g	4.5	138.1	96.8
#10/374.6g	5.8	132.3	92.7
#16/342.9g	3.4	128.9	90.3
#20/330.6g	2.1	126.8	88.9
#30/318.5g	2.3	124.5	87.3
#40/399.3g	2.7	121.8	85.4
#60/280.8g	6.5	115.3	80.8
#80/268.9g	7.1	108.2	75.8
#100/265.3g	3.4	104.8	73.4
#200/252.7g	26.6	78.2	54.8
PAN/451.5g	78.1		0
Total weight of fractions= 142.5			
Error = 0.07			

Table 10. Sieve analysis of CCBs, trial #2.

Weight of Original Sample	**Weight after Pre-washing**	**Washing Loss N/A**	
257.2	**N/A**	**Passing Sieve**	
Sieve/weight	Weight Retained on Sieve	Weight	Percent
#4/521.2g	4.8	252.4	98.1
#10/374.5g	5.7	246.7	95.9
#16/342.9g	6.1	240.6	93.5
#20/330.6g	4.5	236.1	91.7
#30/318.5g	4.5	231.6	90
#40/399.3g	14.8	216.8	84.2
#60/280.8g	9.3	207.5	80.6
#80/268.9g	8.1	199.4	77.5
#100/265.3g	4.8	194.6	75.6
#200/252.7g	39.7	154.9	60.2
PAN/451.5g	155.7		0
Total weight of fractions= 258			
Error = -0.31			

Table 11. Wet sieve analysis of material passing No. 200 sieve.

Run	1	2	3
Weight of no. 325 sieve (g)	340.405	340.423	340.566
Weight of sieve and CCB (g)	341.445	341.496	341.607
Weight of CCBs (g)	1.04	1.073	1.041
Weight after Wash (g)	340.689	340.498	340.691
CCBs retained on sieve (g)	0.284	0.075	0.125
Correction Factor	0.212		
Fineness	71.539	92.484	87.473
AVG.	83.832		

pH of Permitted Discharge:

A significant difference in the pH was detected before and after the sample bottles were agitated to create a homogeneous mixture of CCB particles and permitted discharge solution. The relative similarity in the sample #5 measurements is likely due to the lack of particles in the permitted discharge. After agitating the samples, it was visibly evident that they were turbid, despite what the Hydrolab ® recorded. I believe this was because the mixture was so turbid that it well exceeded the range of the sensor and the instrument produced a value that did not register (DNR).

Table 12. Permitted Discharge pH before and after agitation.

Sample #	Conductivity (µS)	pH after	pH before	Turbidity (NTU)	Temperature (celcius)
1	0.698	4.45	7.06	DNR	6.33
2	0.697	4.47	7.18	DNR	6.34
3	0.951	4.32	7.66	DNR	6.33
4	1.098	4.41	8.03	DNR	6.33
5	0.251	6.03	6.12	32.1	6.34

DISCUSSION

Groundwater Contamination in Wisconsin Attributed to CCB Leachate:

Simsiman, et al. found large plumes of contaminated groundwater under an ash pond in Wisconsin. In this case, the large plumes were due to poor site selection and inadequate construction of the system of ponds. Layers of fine to medium sand underlay the site providing a relatively fast infiltration of permitted discharge from the plant to the groundwater flowing through the sand layers (i.e. short retention time in the ponds). The sand layers are the glacial till of the last glaciers to cover North America. Though site specific data (boring logs for monitoring wells and the well water data) for Plant McDonough in Smyrna, Georgia are currently unavailable, the natural geology of the slopes of the Chattahoochee River in this area consists of some clay layers. The pond itself appears to have been constructed with clay. The permeability of this clay is not known, but likely provides a significantly greater barrier to leaching than glacial till comprised of sand.

Simsiman et al. also noted that, using geochemical modeling software (MineQL), the presence of $Al(OH)_3$ and $Fe(OH)_3$ solid phases in groundwater would occur. Furthermore, the presence of these hydrous oxides would retard the migration of arsenic, barium, copper, and zinc by adsorption and co-precipitation. Visible in Figure 4 is an orange band within the CCBs that is likely this iron oxide. The sampling shown in Figure 4 is Ash #3. The TCLP conducted on Ash #3 shows zinc in excess of the MDL by only 0.043 mg/l and no copper was detected. The leachate from the open-column percolation test actually shows a decrease in the amounts of arsenic, barium, copper and zinc from that of the permitted discharge that was utilized in the test. It is likely the oxides present in the CCBs do indeed retard the leaching of the metals from the pond.

One of the largest contaminates in the plumes in Wisconsin was sodium. Simsiman et al. asserted that this was because the plant used sodium carbonate (Na_2CO_3) in the removal of sulfur dioxide (SO_2) from the flue gas. Sodium is an extremely soluble substance, and the use of a sodium carbonate slurry for sulfur removal already puts the sodium ion in solution. Figure 21 is an example of a lime/limestone based flue gas desulfurization process. Plant McDonough does not use a FGD system since it converted to a low-sulfur coal approximately ten years ago. A pile of sulfite was located near the center of the pond system. The sulfite is the result of having a low-sulfur coal fuel source. The electrostatic precipitators are less effective on ash from low-sulfur coals, so sulfite is added to the gases to increase effectiveness of the precipitators and decrease particulate emissions (Figure 22). The large amount of calcium detected in the leachate is due to the percentage of CaO in the ash, sometimes as high as 30% in some sub-bituminous coals (EPRI GS-6129, p.2-16). The high solubility of CaO would also help account for the calcium abundance in the leachate. Comparing the permitted discharge and the leachate analyses (Tables 4 and 5) shows that only calcium increases consistently in all the leachate after percolating through the CCBs. Leachate #5, in which permitted discharge #5 was percolated through ash #5, shows the only other elements (arsenic and vanadium) with an increase in concentrations. These increases are slight.

The principal contributing factor to the reduction in metals in the leachate is likely due to the mechanical removal of CCB particulate matter. Each permitted discharge

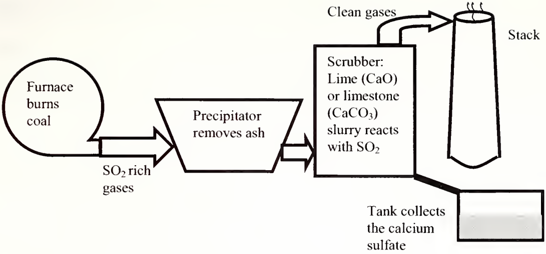


Figure 21. Flue Gas Desulfurization Process (Adapted from Keller's Environmental Geology, 8th Ed.). The calcium reacts with the sulfur oxides to form insoluble calcium sulfides and sulfates.

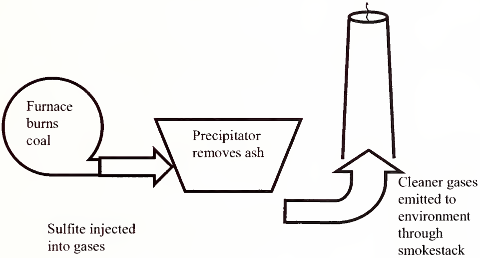


Figure 22. Sulfur Injection System. The sulfite is injected into the exhaust gases from the combustion chamber to increase the effectiveness of the electrostatic precipitators in removing particulate emissions, ash particles (after discussion between R. David Asti and M. Dwayne Allen).

sample was shaken thoroughly prior to pouring it in the open-column percolation apparatus. This was done to dislodge the particles that had settled out in the bottom of the sample bottle and create a homogeneous mixture. Each leachate, following collection, was substantially clearer and lacked the CCB particles of the associated permitted discharge.

Upon disassembly of the open-column apparatus, a significant increase in the thickness of the CCBs was noticed. No specific measurements were taken of the volume increase of the CCBs, but visibly the columns were ½ to ¾ inch longer for Ash #s 1-4. Permitted discharge #5, due to the timing of its collection with a period of no discharge from the plant, had very little particulate matter to begin with and even fewer still after completion of the percolation test. As shown in Table 4, permitted discharge #5 often had an order of magnitude less in concentration for each element than the other samples.

Open-Column Percolation Tests of CCBs in Sindri, India:

Gurdeep Singh and Kumari Vibha utilized an open-column percolation test on the fly ash from the generating plant at the Fertiliser(sic) Corporation of India Ltd., Sindri. Their analysis consisted of fly ash ranging in age from recently produced up to 12 years of age. They mixed the ashes to achieve optimum moisture content by adding distilled water to the material and kneading it until it appeared uniformly mixed. They then packed approximately 60 cm (roughly 14 inches) of a column with this ash. The top 15 cm of the column was left open for the addition of the distilled water, which was used to create the leachate. They reported about 250 ml of water being added twice a week for the three months of the study to achieve the amount of leachate desired.

The samples were acid digested prior to elemental analysis by atomic absorption spectrometry. Their study focused on 19 elements: iron, zinc, manganese, copper, lead, cadmium, nickel, arsenic, cobalt, chromium, magnesium, calcium, selenium, vanadium, boron, barium, mercury, sodium, and potassium. Of these, six (cadmium, selenium, vanadium, boron, barium, and mercury) were below detectable limits throughout the analysis. Calcium, magnesium and iron were found in considerable concentrations; while zinc, manganese and copper were at low concentrations; and the others were detected at minute quantities intermittingly throughout the tests (Table 13).

Table 13. Summary of elemental analysis of leachates from Singh and Vibha.

Parameter/Elements	**Fly Ash S1 Open Column Range**	**Fly Ash S1 Acid Digested Samples**	**Fly Ash S2 Open Column Range**	**Fly Ash S2 Acid Digested Samples**
pH	6.30-8.26	-	6.30-7.41	-
Iron	BDL-0.90	9.37	BDL-0.06	55-162
Zinc	0.013-0.384	0.112	0.011-0.106	0.135
Manganese	BDL-0.724	0.241	BDL-0.047	0.626
Copper	BDL-0.210	0.104	BDL-0.11	0.059
Lead	BDL	0.093	BDL	BDL
Cadmium	BDL	-	BDL	BDL
Nickel	BDL	BDL	BDL	0.561
Arsenic	BDL	BDL	BDL-0.060	BDL
Cobalt	BDL	BDL	BDL-0.055	BDL
Chromium	BDL	BDL	BDL	0.214
Magnesium	12.32-86.24	423.8	2.13-68.21	7.72
Calcium	11.40-140.95	144.6	10.11-97.03	38.4
Selenium	BDL	BDL	BDL	BDL
Vanadium	BDL	BDL	BDL	BDL
Boron	BDL	BDL	BDL	BDL
Barium	BDL	BDL	BDL	BDL
Mercury	BDL	BDL	BDL	BDL
Sodium	BDL-18	5	BDL-8	2
Potassium	BDL-24	5	BDL-5	2

Note: All values are in mg/l. BDL < 0.001 mg/l.

They concluded that the leachate from the ash ponds posed no significant threat to the environment, but recommended that studies on older ash be conducted to determine what leaches out of much older ash. It should also be noted that their tests only looked at the fly ash component of CCBs and not all the CCBs.

Open-Column Percolation Tests of CCBs in Chandrapura, India:

Sanjay Kumar utilized the open-column percolation tests on the fly ash component of CCBs at the thermal power station in Chandrapura, India. The coal utilized at this power station, as well as throughout India, is a low calorific grade, high ash content. It produces 50-70% more ash than some American Coals.

Utilizing two-foot lengths of four-inch diameter PVC pipe, leachate was collected sixty-five times over a period of 274 days. This leachate was then acid digested and analyzed using Atomic Adsorption Spectrometry for: iron, lead, calcium, magnesium, copper, zinc, manganese, sodium, potassium, chromium, nickel, cobalt, cadmium, selenium, aluminum, silver, arsenic, boron, barium, vanadium, antimony, and molybdenum. Of these only calcium and magnesium were detected throughout all the samples, and along with potassium and sodium were the only four detectable in any significant quantities. iron, lead, copper, zinc, and manganese were detected intermittingly in trace quantities (Table 14). The rest were always below detectable limits. Kumar concluded that no significant environmental threat was posed by the leachate and that the ash could be used to reclaim abandoned mines.

Table 14. Summary of elemental analysis of leachates from Kumar.

Elements	**Fly Ash #1 Range**	**Fly Ash #1 Average**	**Fly Ash #2 Range**	**Fly Ash #2 Average**
Iron	BDL-2.92	2.88	BDL-3.12	3.4
Lead	BDL-0.089	0.072	BDL-0.08	0.07
Calcium	10-25	24	28-40	38
Magnesium	11-24	22	20-32	30
Copper	BDL-0.094	0.09	BDL-0.088	0.08
Zinc	BDL-1.082	1.074	BDL-1.10	1.09
Manganese	BDL-0.099	0.085	BDL-0.092	0.086
Sodium	BDL-10	9	BDL-16	14
Potassium	BDL-20	18	BDL-36	34
Chromium	BDL	BDL	BDL	BDL
Nickel	BDL	BDL	BDL	BDL
Cobalt	BDL	BDL	BDL	BDL
Cadmium	BDL	BDL	BDL	BDL
Selenium	BDL	BDL	BDL	BDL
Aluminum	BDL	BDL	BDL	BDL
Silver	BDL	BDL	BDL	BDL
Arsenic	BDL	BDL	BDL	BDL
Boron	BDL	BDL	BDL	BDL
Barium	BDL	BDL	BDL	BDL
Vanadium	BDL	BDL	BDL	BDL
Antimony	BDL	BDL	BDL	BDL
Molybdenum	BDL	BDL	BDL	BDL

Note: BDL-Below detectable limits, BDL = 0.001 mg/l. Concentrations in PPM.

If Not Leachate, How Else Could These Metals Leave the Pond?:

Department of Energy (DOE) scientists at the Savannah River Site have found high levels of heavy metals in animals exposed to CCBs at their site. Elevated concentrations of arsenic, cadmium, selenium, strontium and mercury have been recorded in bullfrog tadpoles and the softshell turtles that consume the tadpoles. The tadpoles live in the ash ponds on the Savannah River Site and absorb the metals there. The turtles then prey upon the tadpoles and leave the ash pond for the nearby Beaver Dam Creek and Savannah River, thereby transporting the metals offsite (Sanders).

The metals are altering the tadpole's mouth morphology, which reduces its ability to consume food. Studies have also shown that tadpoles from the ash pond are less likely to escape a snapping turtle then those tadpoles taken from clean areas, suggesting the metals may be inhibiting muscle development and/or function. Scientists fear these problems may be worldwide due to the global reliance upon coal for electricity (Sanders).

At the Plant McDonough site, during sampling, ducks inhabited ash pond #4 and apparently were submerging to feed on some unseen plants within the pond. Some amphibians were also spotted amongst the cattails in ash pond #3. Ant colonies were also present within ash pond #3. These creatures' ability to absorb and remove metal contaminants from the pond and thus impact the local/regional food chain was not a subject of this research. A biological vector for removal is possible as evident at the DOE Savannah River Site and should be addressed by further research into ash ponds.

CONCLUSIONS

Mobility of Metals:

Of the metals targeted in this study, only calcium showed any appreciable and consistent leachability from the CCBs. Despite the similarity in results from other sites that used open-column percolation tests, the lack of specific geologic information for the site and the unavailability, at this time, of groundwater data from the wells precludes a more thorough validation of the results.

The biological removal of metals from the pond by creatures that utilize it during part of their life cycles was not evaluated during this research. It is recommended that a program be established to capture specimens of the ducks, amphibians, insects and other wildlife inhabiting the area to see what, if any, metals they may be accumulating in their tissues.

Portland Cement Substitute and Soil Stabilization Admixture:

The use of the fly ash component of the CCBs as a Portland cement substitute or soil stabilization admixture needs more evaluation. The performance of both the test and control mortar cubes was affected by the amount of voids in the mortar. Furthermore, the fact that the cubes were not broken on 7 days limited data on the early strength development of the mixes. Current thought is that concrete containing fly ash will continue to gain strength out as far as 90 days (Fly Ash Facts, p. 15). It is therefore recommended that any mortar cube tests conducted for fly ash analysis include strength tests on 7, 14, 28, 45 and 90 days.

Recommendations:

Further studies are recommended on ash ponds to assess the leachability of metals other than and including those targeted here. Georgia Power is in the process of closing a generating plant (Plant Arkwright) near Macon, Georgia. Technology is in place that could utilize these CCBs more effectively. It is recommended that GPC conduct a study to determine the feasibility of mining the CCBs from the ash ponds for beneficial uses such as: asphalt roof shingles, fillers for aluminum casting, plastic manufacture, soil admixtures, flowable fills, and as concrete aggregate. Furthermore, since drilling was not performed at Plant McDonough, it is recommended that analysis of the older CCBs at the bottom of the pond at Plant Arkwright be conducted. Analysis should include total metals content, leachate content, clay-like properties and permeability since it would be these eldest CCBs that have weathered the longest, and reside at the bottom of the pond, that have the most potential for inhibiting leachate from the ponds (Appendix C).

BIBLIOGRAPHY

Dienhart, Gregg J., et al.; *Coal Ash: Innovative Applications of Coal Combustion Products (CCPs)*; American Coal Ash Association; Alexandria, Virginia; 1998; 91 pps.

EPRI Report # CS-3314, Testing and Correlation of Fly Ash Properties with respect to Pozzolanic Behavior; Electric Power Research Institute, January 1984

EPRI Report # EA-5922, Leachate Chemistry at the Montour Fly Ash Test Cell; Electric Power Research Institute, December 1988

EPRI Report # GS-6129, Ash in Concrete Model development; Electric Power Research Institute, January 1989

EPRI Report # GS-6175, Use of Coal Ash in Highway Construction: Georgia Demonstration Project; Electric Power Research Institute, February 1989

EPRI Report # TR-101785, Detailed Physical, Chemical, and Mineralogical Analyses of selected Coal and Oil Combustion Ashes; Electric Power Research Institute, April 1993

EPRI Report # TR-101999, Physical and Hydraulic properties of Fly Ash and Other By-Products from Coal Combustion; Electric Power Research Institute, February 1993

Facts & Figures 2000, Georgia Power Company Corporate Communications, Atlanta, Georgia, 2000, 13 pps.

Facts & Figures 2001, Georgia Power Company Corporate Communications, Atlanta, Georgia, 2001, 13 pps.

Federal Register; Monday May 22, 2000; Part III Environmental Protection Agency, 40 CFR Part 261, Regulatory Determination on Wastes from the Combustion of Fossil Fuels; Final Rule; National Archives and Records Administration, Washington, D.C., 2000

Fly Ash Facts for Highway Engineers (FHWA-SA-94-081); United States Department of Transportation, Federal Highway Administration; American Coal Ash Association, Alexandria, Virginia, August 1995, 70 pps.

Keller, Edward A.; *Environmental Geology*; 8th Ed.; Prentice Hall; New Jersey; 2000; 562 pps.

Kumar, Sanjay; "A Case Study of Chandrapura Thermal Power Station-Leaching Study of Trace Elements from Fly Ashes"; Journal of Scientific and Industrial Research, vol. 59, September 2000, pps. 852-855

Sanders, Jane M.; "DOE Ecologists Identify Coal Ash-related Problems"; Environmental News Network, July 15, 1997; obtained from www.enn.com/enn-news-archive/1997/07/071597/07159704.asp

Simsiman, Geronimo V., et al.;"Effect of Ash Disposal Ponds on Groundwater Quality at a Coal-Fired Power Plant"; Water Resources, vol. 21, No. 4, 1987, pps. 417-426

Singh, G. and K. Vibha; "Environmental Assessment of Fly Ash in its Disposal Environment at FCI LTD., Sindri"; Pollution Resources, vol. 18, No. 3, 1999, pps. 339-343

Smith, Allan H., et al.; "Arsenic Epidemiology and Drinking Water Standards", Science, vol. 296, June 21, 2002, pps. 2145-2146

Zevenbergen, Chris, et al.; "Clay Formation and Metal Fixation during weathering of Coal Fly Ash"; Environmental Science and Technology, vol. 33, No. 19, 1997, pps. 3405-3409

APPENDIX A, Satellite Image of Plant McDonough Ash Pond (1993)

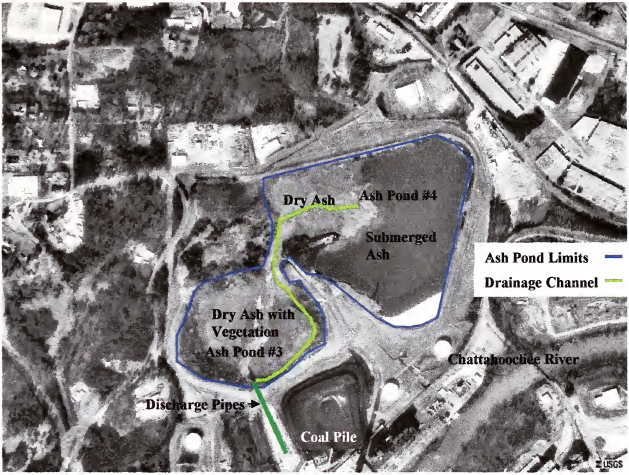


Image downloaded from http://terraserver.homeadvisor.msn.com

APPENDIX B, Sampling Plan for Plant McDonough Ash Pond

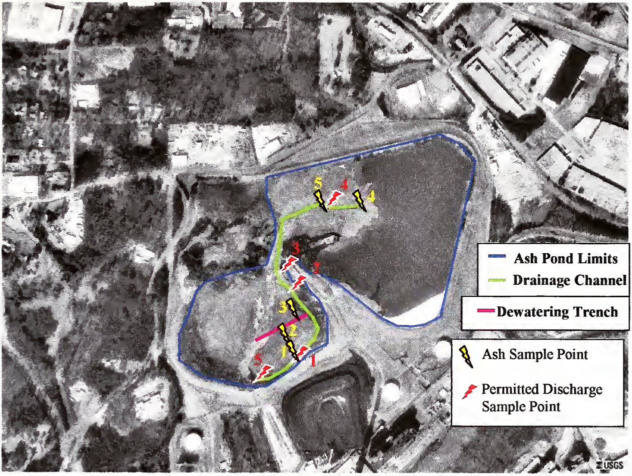


Image downloaded from http://terraserver.homeadvisor.msn.com

APPENDIX C, Proposal for Further Analysis of Surface Impoundments

DETERMINING THE ECONOMIC FEASIBILITY OF MINING COMINGLED COAL COMBUSTION BYPRODUCTS IN SURFACE IMPOUNDMENTS FOR USE IN OTHER INDUSTRIES

PROPOSED BY: MICHAEL J. TROFINOFF

Introduction

Coal-fired electric generating plants create vast amounts of coal combustion byproducts (CCBs) and though some may be used for beneficial purposes, the vast majority is disposed in impoundments (ash ponds). The naturally occurring, non-toxic amounts, of heavy metals in coal are concentrated in the CCBs at levels that exceed health standards. The belief that these metals could potentially leach from the ash ponds and into groundwater supplies have caused the U.S. EPA to develop national standards under subtitle D of Resource Conservation Recovery Act (RCRA) to address the CCBs disposed in landfills and surface impoundments.

Studies on the weathering of the coal fly ash component of CCBs in disposal areas have shown that minerals within the ash are naturally altering to noncrystalline clay due to weathering processes. After a decade of weathering, dissolution of the glass produces a clay-content higher than in 250-year-old volcanic ash (Zevenbergen, et al., 1999). These clays trap the metals within the clay structure, whose lower permeability inhibits leaching of the metals into the groundwater.

The Georgia Power Company is currently in the process of closing the coal fired generating facility known as Plant Arkwright located northwest of Macon, Georgia.(See Tab A) The opportunity to study the ash pond and the dry storage area at Plant Arkwright should be taken advantage of to expand the current base of knowledge on CCB leachate. Furthermore, the co-mingling of all CCBs makes the beneficial use of such material for other industries difficult. The opportunity exists to determine the economic feasibility of mining co-mingled CCBs from a storage area for use in other industries. Since the co-mingling of CCBs is the preferred method of storage by GPC it would be beneficial to examine this before further ash ponds need to be constructed in order to minimize the corporation's environmental impact.

Objectives

The objective of this study is to increase the body of knowledge on the metal content of leachate from CCBs in ash ponds and dry storage areas:

- Determine the metal content of leachate using EPA Method #6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) from open-column percolation tests containing the CCBs from the ash pond and dry storage area at Plant Arkwright. The columns of ash being created from the Shelby Tube samples.

- Address the metal content of the weathered CCBs based upon the stratification of the ash pond. Use EPA Method #6010B, Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), to determine the metal content of each layer within the ash pond. This will show how the metal content varies with the age of the CCBs during weathering.

Determine the economic feasibility of mining the co-mingled CCBs for use in other industries:

- What amount of resources would be required to convert (separate by mechanical sieving) co-mingled CCBs into their components (fly ash, bottom ash, boiler slag, flue gas desulfurization (FGD) material) for eventual use by such industries as roof shingles, sheet rock, filler material for cast aluminum products, concrete aggregate, and Portland cement substitute.

Materials and Methods

Sampling Plan:

One examination pit will be excavated in the ash pond and in the dry storage area to adequately determine the depth of the CCBs within the two facilities prior to sampling with the Shelby tubes. These pits will be dewatered to allow the safe entry of personnel into the pits to sample the specific layers of CCB stratification for metals analysis. The Shelby tubes will then be used to retrieve CCB samples for use in the open-column percolation test.

The Shelby tubes and CCBs will then be transported to the GPC Lab near Smyrna, Georgia where the open-column percolation test will be conducted over a period of one year.

CCB Sampling in the Pits:

The excavated pits will likely require pumps to dewater them prior to the safe entry of personnel to conduct sampling. Once the pit is safe to enter, the samplers will document the stratification of the facility with measurements (depth of layer, layer thickness, color, organics, etc.) detailing the visible delineation of the layers of CCBs. Two 8 ounce samples will be taken for each layer.

Open-Column Percolation Test:

Upon arrival at the GPC Lab, the contents of the Shelby tubes will be slid into the PVC tubes for the open-column test. The endcaps will be attached with the drainage holes already being drilled through each one and the tubing in place and secure. The columns should be mounted upright over the collection bottles. The pH of the solution used for the tests should be representative of the pH of rainwater in the region as this would be the only moisture likely to enter a CCB storage facility at a closed generating site. The test solution should be checked daily and added as required to maintain a minimum depth of four inches in the column above the CCBs. The drainage tubing at the bottom of the column should run into the sample bottles. Recommended a clip be placed nearby to allow for easy clamping of each tube for a clean switch of the sample bottles. Each Monday for one year, the samples should be removed, measured for volume (to determine permeability), then analyzed for metals.

Leachate Analysis:

Using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) as outlined in EPA Method # 6010B the leachate will be analyzed for metal content.

Preparation of samples requires them to be solubilized or digested by an acid prior to analysis. For leachate samples, acid digestion should not be necessary if the samples are filtered and acid preserved prior to analysis. The sample is nebulized and subsequent aerosol is then transported to a plasma torch where element-specific emission spectra are produced by radio frequency inductively coupled plasma. These spectra are then separated using a grating spectrometer, and the intensities of the emission lines are monitored by photosensors. Background correction is necessary for trace element analysis.

For the complete method please refer to:

http://www.epa.gov/epaoswer/hazwaste/test/6010b.pdf

CCB Analysis:

Analysis will be done using EPA Method # 6010B. Ash will require an acid digestion process.

The CCBs from the pits will be analyzed to determine the metal content of the CCBs as they weather to verify what, if any, changes in metal content occur.

Sieving the CCBs:

The excavated material from the pits will be sieved to separate the CCBs by particle size. The finest particles belong to the fly ash, and likely represent the bulk of the material. The amount of resources necessary to separate this known volume of material, the volume of the excavations, could then be used to project the costs for the entire facility and will determine if it is feasible to attempt to segregate co-mingled CCBs. This cost should be compared with that associated with transporting it to other facilities for storage in their ash ponds, the loss of service life in those ash ponds due to the incoming ash, and the costs of constructing new ash ponds or "stacking" CCBs at those sites at a minimum.

Schedule:

Week One: Mobilize equipment, excavate pits, and initiate pit dewatering. Conduct sieve operations.

Week Two: Continue dewatering and sieve operations as required and sample the CCBs within the pits. Analyze pit samples. Determine best locations to conduct Shelby tube sampling and sample.

Week Three: Construct open-columns and initiate tests.

Weeks Four-Fifty Five: Analyze leachate from open-column tests.

Weeks Fifty Six-Fifty Nine: Analyze data, write report (draft).

Budget:

Drilling:

20 Shelby tubes = $3,000.00

Excavation:

Requires tracked excavator = $500/week
Operator = $33/hr.

Sieve Equipment:

Unknown at this time…

Lab Analysis:

20 leachate samples/week/52 weeks:
1040 leachate samples (EPA Method #6010B) @ $50.00 each = $52,000.00
Estimate 25 samples per pit, 2 pits, 50 samples = $2,500.00

Open-column Percolation Test:

PVC Tubes, 4 in. dia., 5 feet sections, 20 sections = $65.00
PVC Endcaps, 20 each = $70.00
Flexible tubing, 20 feet = $20.00

Total = $64,000.00 (includes 10% overage)

Tab A to Appendix C