2.2 Waste Management

WASTE MANAGEMENT

Semiannual Technical Progress Report
for the Period January 1, 1992 - June 30, 1992

by

Daniel J. Stepan, Research Engineer
Debra F. Pflughoeft-Hassett, Research Chemist
Tina M. Strobel, Research Associate
Rose H. Fraley, Laboratory Technician

Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station
Grand Forks, North Dakota 58202-8213

Technical Monitor: Jerry Harness

for

U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
3610 Collins Ferry Road
P.O. Box 880, M.S. E02
Morgantown, WV 26507-0880

July 1992

Work Performed Under Cooperative Agreement No. DE-FC21-86MC10637

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (continued)

WASTE MANAGEMENT

1.0 GOALS AND OBJECTIVES

The objective of the Waste Management project at the Energy and Environmental Research Center (EERC) is to characterize waters, waste materials, and by-products from advanced coal preparation and utilization processes, evaluate potential uses for these materials, and identify potentially adverse environmental impacts associated with their use and/or disposal. Research is also being done to develop innovative waste management techniques for conventional and advanced coal utilization processes to comply with existing and/or future environmental regulations.

The goal of the Waste Management project is the understanding and application of:

Geological
Physical
Chemical — Processes
Biological
Mineralogical

to all phases of resource management from exploration through development to by-product management.

The activities of the Waste Management project include the following tasks:

- Task 1--Water and Waste Resource Management

  Purpose: to investigate the treatability of hot-water-dried (HWD) coal-water fuel (CWF) process water at the bench-scale.

- Task 2--Coal Combustion Ash Conditioning Study

  Purpose: to evaluate conditioning procedures for advanced coal utilization wastes.

- Task 3--Bituminous Coal Fly Ash Data Collection and Evaluation

  Purpose: to collect and evaluate data concerning the chemical and mineral compositions and physical properties of bituminous coal fly ash.

- Task 4--Waste Depository Scavengers

  Purpose: to evaluate inexpensive methods of sorbing and fixing contaminants that have the potential to migrate from coal ash disposal pits.

2.0 ACCOMPLISHMENTS

The following are the accomplishments of the Waste Management project for this reporting period.

2.1 Water and Waste Resource Management

During this reporting period, testing was performed to evaluate the treatability of process water generated from the hot-water drying of Usibelli coal. The process water was treated using two separate bench-scale systems: an activated sludge system and a two-stage, anaerobic, expanded-bed, granular activated carbon system.

Testing was conducted to determine removal rates of selected parameters, such as five-day biological oxygen demand (BOD_5), chemical oxygen demand (COD), and ammonia (NH_3). Results to date from this activity are presented herein.

2.2 Coal Combustion Ash Conditioning Study

The chemical characterization study of the two atmospheric fluidized-bed combustion (AFBC) residues selected for this task was completed. The subtask investigating trace element mobility within conditioned residues was also completed. Leaching characterization of original AFBC residues was completed. Additional subtasks were outlined for potential future research.

2.3 Bituminous Coal Fly Ash Data Collection and Evaluation

Contacts have been made with numerous electric utilities and ash marketing companies in an effort to obtain information and samples of bituminous coal fly ash for this task. As a result of this effort, 57 samples of bituminous coal fly ash from conventional coal combustion power generation facilities were voluntarily submitted for inclusion in this task.

Physical, chemical, and mineralogical characterization of the bituminous coal fly ash samples, as outlined in the work plan, were completed. Additional characterization information was generated on a large number of the samples represented in the database.

The characterization results were placed in a Lotus® 1-2-3® spreadsheet-style database, and the information was also placed into a database manager. Hard copy and disk versions of each of these database formats will be available.

The bituminous coal fly ash database was merged with the existing database of information on low-rank coal fly ash. The complete coal fly ash database now contains information on over 600 samples of coal combustion fly ash from conventional power generation facilities in North America and worldwide.

A similar spreadsheet style database of characterization information on residues from advanced coal processes was also generated utilizing information from previous research projects at the EERC. This database contains information on samples of various materials. Hard copy and disk versions of this database will also be available. A reproducible x-ray powder diffraction technique for the semiquantitative analysis of advanced coal process residues was developed. This technique utilizes the "Reference Intensity Ratio" method with a zinc oxide (ZnO) internal standard.

2.4 Waste Depository Scavenger Study

The research for this task determined several potentially useful scavenging materials based on attenuation ability, availability, and cost. The scavenging agents targeted for examination included the zeolite mineral clinoptilolite, which is found throughout the western United States in volcanic deposits, bentonite, deposits containing clay minerals, and chars from coal combustion residual material. In laboratory experiments, the clinoptilolite showed the ability to sorb lead and copper from solutions containing high concentrations of these ions.

The initial analytical work indicated that thorough chemical and mineralogical characterization of the individual scavenging materials is necessary. X-ray diffraction (XRD) and x-ray fluorescence (XRF) techniques are useful in determining the initial structure and bulk chemistry of the materials and will provide information on changes that occur during experimentation. Scanning electron microscope/electron probe microanalysis (SEM/EPMA) is also useful in determining the major element composition of the scavenging materials.

3.0 PROJECT RESULTS

3.1 Water and Waste Resource Management

3.1.1 Introduction

The purpose of this task was to assess the characteristics and treatability of the contaminated process water stream derived from the hydrothermal treatment of low-rank coals (LRCs). Coal beneficiation through hydrothermal dewatering has emerged as one of the most promising technologies for upgrading LRCs. Hydrothermal dewatering is a technique used to reduce the water content of high-moisture coals through heating a finely ground coal-water slurry under pressure. The drying temperature is high enough to decompose some carboxyl groups in the coal, forming carbon dioxide. The carbon dioxide then forces the water from the coal pores into the surrounding process water. Reabsorption of water is minimized due to coal surface modification and surface coating with evolved tars and waxes.

Conditions during hydrothermal dewatering, coal chemistry, and coal type have a major impact on the characteristics of coal-water fuel process waters. Many of the contaminants are difficult to remove prior to discharge and may create operational problems if recycled back into the process. Wastewater treatment process selection for coal beneficiation processes is a difficult task. Great emphasis has not been placed on liquid waste management. The need exists for an improved treatability database and a clear methodology for treatment of coal-water fuel waters. Cost-effective production of coal-water fuels can only take place if waste management technologies are developed prior to prototype plant construction. Work on this subtask involves the development of a comprehensive database of process water characteristics and bench-scale testing and evaluation of selected treatment operations.

3.1.2 Research Scope

This task involves bench-scale treatability testing of process water collected during the hot-water drying of coal from the Usibelli coal mine, near Anchorage, Alaska. Based on the information obtained in literature and the chemical and physical characteristics of the contaminated process water, two secondary treatment systems were selected for evaluation, following appropriate preliminary treatment.

3.1.3 Water and Waste Resource Management Study Results

3.1.3.1 Usibelli HWD Process Water Characterization

Modifications to the EERC PDU hot-water drying unit have resulted in two different wastewater streams: condensate and centrate. The condensate stream is generated during the pressure letdown via flash vaporization. The centrate stream is generated during the final centrifugal dewatering step.

Process water used in treatability testing was the centrate stream. A representative sample from the Usibelli HWD CWF process water was collected and submitted to the EERC Analytical Research Laboratory (ARL) for chemical and physical characterization. Table 1 lists the results of characterization analyses of the Usibelli process water.

Approximately 40% of the BOD_5 in the Usibelli centrate can be accounted for in the organic constituents analyzed. Methanol (244 mg/L) contributes the largest percentage to the BOD_5. The remaining portion of the BOD_5 exists in organic constituents that were not analyzed.

Approximately 80% of the total NH_3 in the centrate exists as free NH_3 and would be steam-strippable. However, pretreatment to reduce the centrate NH_3 was unnecessary since NH_3 levels will not be inhibitory to biological treatment systems at these levels.

The $COD:BOD_5$ ratio of the centrate stream is approximately 4:1, suggesting that a large portion of the organic matter in the process water is biorefractory, or nonbiodegradable. Therefore, effluent polishing steps will be required under most discharge or reuse situations.

The condensate stream has an even larger portion of biorefractory organics, as indicated by the $COD:BOD_5$ ratio of approximately 6:1. The organic content of this stream, as measured by COD and phenolics, is nearly three times that of the centrate. A more thorough characterization of the condensate stream is planned. The condensate represents approximately 36% of wastewater flow and has some differentiating physical characteristics, such as the lack of color.

Resource Conservation Recovery Act (RCRA) metals concentrations in the centrate stream are all below maximum contaminant levels.

TABLE 1

Results of Chemical and Physical Characterization Analyses Performed on Usibelli HWD CWF Process Waters

Parameter/Constituent	Centrate (mg/L)	Condensate (mg/L)
pH	7.2	5.2
Alkalinity	850	---
Ammonia (total)	15	9.5
Ammonia (free)	12	0.28
Chloride	10	---
Fluoride	53	---
Cyanide (total)	0.40	0.32
Nitrate	<1.0	---
Nitrite	<1.0	---
Total Kjeldahl Nitrogen	16	---
Phosphate	3.9	---
Sulfate	6.5	---
Sulfide	---	---
Sulfite	---	---
Thiocyanate	<1.0	---
Thiosulfate	<1.0	---
Total Carbon	1,780	---
Total Inorganic Carbon	640	---
Total Organic Carbon	1,140	930
Chemical Oxygen Demand	3,900	11,300
Biochemical Oxygen Demand	1,000	1,900
Acetate	72	---
Formate	---	---
Propionate	36	---
Butyrate	<5	---
Isobutyrate	28	---
Valerate	18	---
Phenolics (4AAP)	30	184
Phenol+o-Cresol	13	---
p-Cresol	0	---
m-Cresol	5	---
Catechol	0	---
Methanol	244	---
Ethanol	0	---
Acetone	11	---
Propanol	0	---
Methylethylketone	0	---
Propionitrile	0	---

Continued ...

TABLE 1 (continued)

Results of Chemical and Physical Characterization Analyses
Performed on Usibelli HWD CWF Process Waters

Parameter/Constituent	Centrate (mg/L)	Condensate (mg/L)
Total Solids	8670	200
Total Volatile Solids	5580	200
Total Suspended Solids	4930	---
Total Volatile Suspended Solids	3580	---
Total Dissolved Solids	3740	---
Total Volatile Dissolved Solids	2000	200
Conductivity (mmhos)	1.70	0.113
Antimony	<0.05	---
Arsenic	0.18	---
Barium	---	---
Beryllium	<0.05	---
Boron	2.0	---
Cadmium	<0.025	---
Calcium	500	---
Chromium	0.30	---
Cobalt	<0.5	---
Copper	<0.17	---
Iron	38	---
Lead	<0.05	---
Magnesium	100	---
Manganese	0.32	---
Mercury	0.005	---
Molybdenum	---	---
Nickel	0.24	---
Phosphorus	1.3	---
Selenium	<0.05	---
Silver	<0.005	---
Sodium	---	---
Thallium	<0.5	---
Zinc	0.81	---

3.1.3.2 Anaerobic Treatment System Testing

3.1.3.2.1 Introduction

Anaerobic systems have traditionally been used to stabilize organic solids from sewage treatment plants. More recently, these systems have become accepted as a viable means of treating high strength wastewaters (Grady and Lim, 1980).

Anaerobic treatment uses microorganisms that thrive in an environment having a substantial amount of organic matter, in which there is no molecular oxygen. The anaerobes hydrolyze the biodegradable organic matter, producing a variety of simpler compounds such as organic acids, CO_2, and H_2. These compounds are then microbially converted to methane (Grady and Lim, 1980).

The biochemical equation for anaerobic metabolism is:

$$\begin{array}{c}\text{Organic}\\\text{Matter}\end{array} + \begin{array}{c}\text{Combined}\\\text{Oxygen}\end{array} \longrightarrow \begin{array}{c}\text{New}\\\text{Cells}\end{array} + \begin{array}{c}\text{Energy for}\\\text{Cells}\end{array} + CO_2 + CH_4 + \begin{array}{c}\text{Other End}\\\text{Products}\end{array} \qquad \text{[Eq. 1]}$$

Combined oxygen includes such sources as NO_3^{-1}, PO_4^{-3}, SO_4^{-2}, and CO_3^{-2}. Gases such as H_2S, H_2, and N_2 are some of the other end products of anaerobic metabolism (Reynolds, 1982).

The conversion of organic matter to methane involves two groups of anaerobes. The first group, nonmethanogenic bacteria, converts the complex organics into low molecular weight organic compounds, such as organic acids, CO_2, and H_2. This group is composed of both fastidious obligate anaerobes and facultative bacteria. The predominant bacterial species in this group are gram-negative, nonspore-forming bacilli (Grady and Lim, 1980).

Methanogenic bacteria make up the second group of anaerobes and are responsible for the production of methane gas. These bacteria are highly substrate specific and depend on the nonmethanogenic bacteria for their supply of substrate. Methanogens are typically obligate anaerobes that tend to be unrelated morphologically, ranging from minute cocci and larger sarcina to individual and chain-forming bacteria. The aspects that these bacteria have in common are that they can only utilize a limited number of substrates (methanol, formic acid, acetic acid, CO_2, CO, and H_2) and that they produce methane gas (Grady and Lim, 1980).

There are several advantages associated with anaerobic treatment processes. Some of the most important include the production of methane, a valuable end product; lower energy requirements, compared to aerobic processes, because no aeration is required; and relatively low sludge production, as compared to aerobic processes. The anaerobes degrade organic compounds, producing a residual sludge which is inoffensive and which can be used as a soil conditioner and low-grade fertilizer (Grady and Lim, 1980).

There are also some disadvantages associated with these anaerobic processes. Because of the symbiotic nature of anaerobic cultures, they are susceptible to system upsets, thus requiring close supervision and control. After an upset has occurred, these systems are sometimes sluggish at returning to their original condition. Also, because of the requirement for heat exchange, capital costs for anaerobic systems may be high. However, when treating high-strength wastewaters is of importance, the advantages of anaerobic processes generally outweigh the disadvantages (Grady and Lim, 1980).

When anaerobic processes are combined with granular activated carbon, the removal rate of organic contaminants is substantially increased. The granular activated carbon serves several purposes. First, it provides a surface for the attachment of the biofilm. Carbon also serves to remove color and odor from the water. The carbon is also responsible for removing the biorefractory, or nonbiodegradable, compounds. The accumulation of the biorefractory constituents continues until the adsorptive capacity of the carbon is exhausted and a breakthrough occurs (Suidan et al., 1987).

3.1.3.2.2 Anaerobic Treatment System Description and Operation

A schematic of the bench-scale, two-stage, anaerobic, expanded-bed, granular activated carbon treatment system used for the treatability testing of HWD Usibelli wastewater is shown in Figure 1.

The columns were initially seeded with an anaerobic culture obtained from the Moorhead, Minnesota, municipal wastewater treatment facility. Five milliliters of a trace mineral and vitamin solution (Table 2) are added to each liter of influent to supply necessary nutrients for the anaerobic bacteria in the column. The filtered process water is then fed through a peristaltic pump into the columns.

The process water is recycled through the columns to maintain expansion of the carbon bed. The carbon bed is supported by stainless steel mesh screens at the bottom of the columns. Screens are also located at the top of the columns to prevent carbon losses from the system.

Methane gas generated through anaerobic decomposition of organic matter escapes through the top of the columns. The volume of gas produced is then measured by water displacement in the gas collection system.

Column effluent flows from the uppermost port on the side of the column header into a 0.650 L (0.172 gal) covered clarifier. Settled solids are removed periodically from the bottom of the clarifier. Column effluent then overflows a weir into a surge tank maintained under a nitrogen atmosphere. In the two-stage system, the water from the surge tank is then fed as influent into the second column. The surge tank acts as a reservoir, maintaining enough volume of water to feed into the second column in the event of operational problems in the first column.

Each column is encased by a second acrylic cylindrical column with a length of 91.44 cm (36 in) and an inside diameter of 6.35 cm (2.5 in) serving as a water jacket to maintain a constant temperature of 98.5°F (36.9°C), conditions ideal for anaerobic metabolism. Distilled water is pumped from a heated water reservoir, through the jackets surrounding the columns, and back to the reservoir.

Table 3 lists the physical parameters and the operating conditions of the fully operational bench-scale, two-stage, anaerobic, expanded-bed, granular activated carbon treatment system. Currently, Columns 2 and 3 are operating in series while Column 1 is operating independently.

Initially, 0.454 kg (1 lb) of granular activated carbon was added to each column. However, due to early operational problems, some carbon was lost in Columns 1 and 2, which accounts for the difference in the mass of adsorbent in Table 3.

Table 4 lists the maintenance performed on the two-stage, anaerobic, expanded-bed, granular activated carbon treatment system. Daily measurements are taken of influent and effluent tank levels, influent and effluent pH, gas production, expanded bed height, water reservoir temperature, nitrogen cylinder pressure, and nitrogen purge flow rate. Influent rates are measured and adjusted daily.

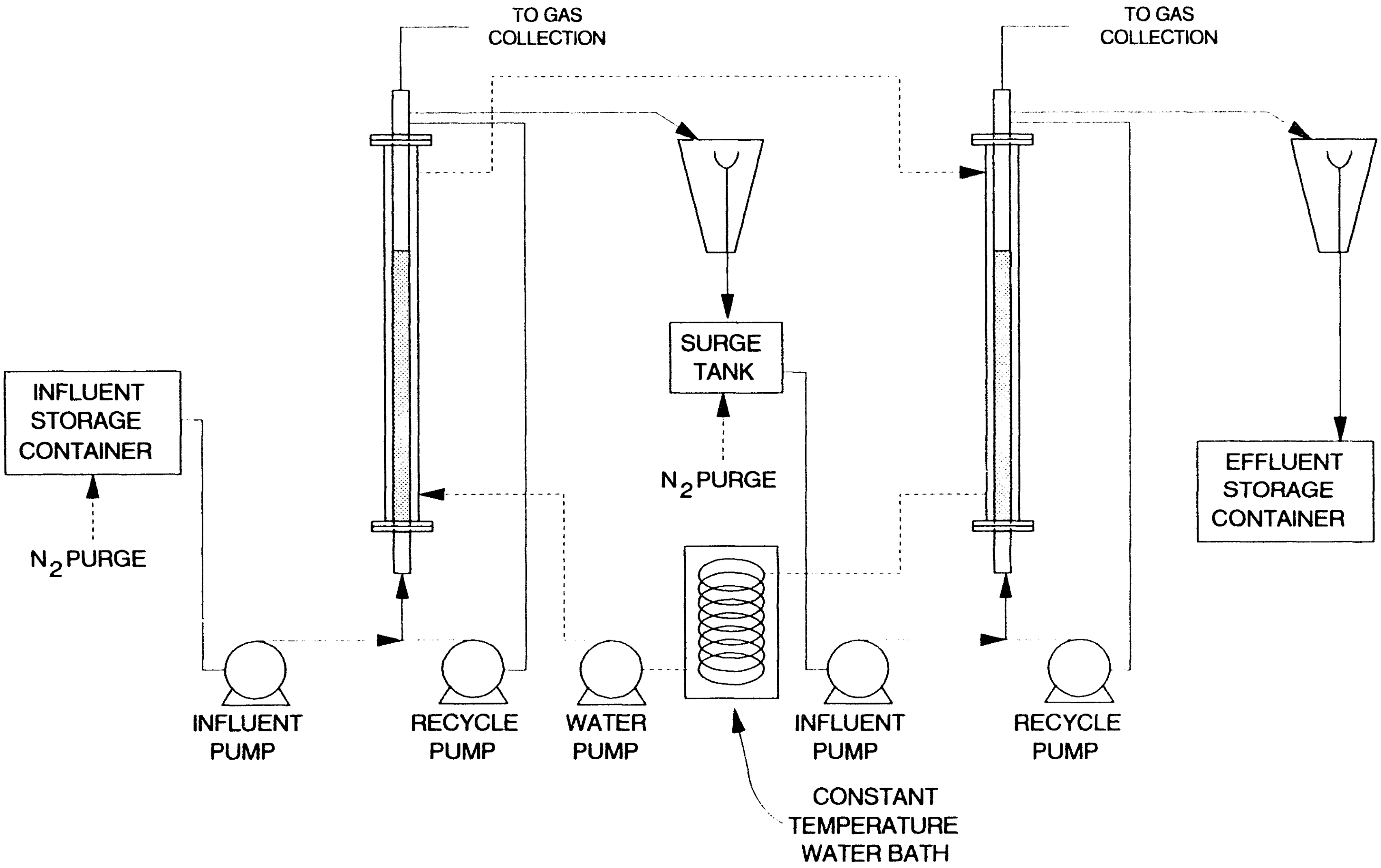


Figure 1. Two-stage, anaerobic, expanded-bed, granular activated carbon treatment system schematic.

TABLE 2

Chemical Composition of the Nutrient Solution

Chemical	Quantity
Nutrient Solution (1 L)	
Aluminum Sulfate Hydrate	0.01 g
Boric Acid	0.01 g
Calcium Chloride	0.10 g
Calcium Sulfate Dihydrate	0.01 g
Cobalt Chloride Hexahydrate	0.11 g
Iron Sulfate Heptahydrate	0.10 g
Magnesium Sulfate Heptahydrate	3.00 g
Manganese Sulfate Hydrate	0.50 g
Nitriloacetic Acid	1.50 g
Potassium Molybdate Dihydrate	0.01 g
Sodium Chloride	1.00 g
Zinc Sulfate Heptahydrate	0.10 g
Vitamin Solution (100 mL solution)*	
p-Aminobenzoic Acid	10.0 mg
Biotin	4.0 mg
Folic Acid	4.0 mg
Nicotinic Acid	10.0 mg
Pantothenic Acid	10.0 mg
Pyridoxine Hydrochloride	20.0 mg
Riboflavin	1.0 mg
Thiamine Hydrochloride	10.0 mg
Thioctic Acid	10.0 mg
Vitamin B_{12}	0.2 mg

* 0.5-mL vitamin solution is added to 1 L of nutrient solution.

TABLE 3

Physical Parameters and Operating Conditions for the Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Parameter		Quantity
Column		
Length		91.44 cm (36 in)
Inside Diameter		5.08 cm (2 in)
Outside Diameter		5.72 cm (2.25 in)
Influent/Effluent Header		
Length		10.16 cm (4 in)
Inside Diameter		5.08 cm (2 in)
Outside Diameter		5.72 cm (2.25 in)
Water Jacket		
Length		91.44 cm (36 in)
Inside Diameter		8.89 cm (3.5 in)
Outside Diameter		10.16 cm (4 in)
Influent Feed Rate		
Usibelli Wastewater		1 L/day (0.264 gal/day)
Nutrient Solution		5 mL/day (0.0013 gal/day)
Design Column Recycle Rate		0.660 L/min (0.174 gal/min)
Adsorbent*		
Column 1		0.397 kg (0.875 lb)
Column 2		0.404 kg (0.891 lb)
Column 3		0.454 kg (1.000 lb)
Bed Height		
Column 1	Static	49.3 cm (19.4 in)
	Expanded	53.2 cm (20.9 in)
Column 2	Static	50.2 cm (19.8 in)
	Expanded	54.5 cm (21.5 in)
Column 3	Static	56.4 cm (22.2 in)
	Expanded	63.5 cm (25.0 in)
System Temperature		36.9°C (98.5°F)

* Adsorbent: Calgon F-400 granular activated carbon (16 x 20 mesh).

TABLE 4

Routine Anaerobic System Maintenance Performed During Usibelli Process Water Treatability Study

Control Parameter	Frequency
Measure influent tank levels	Daily
Measure effluent tank levels	Daily
Measure pH of influent and effluents	Daily
Measure expanded bed heights	Daily
Measure gas production	Daily
Measure water reservoir temperature	Daily
Measure nitrogen cylinder pressure	Daily
Measure nitrogen purge flow	Daily
Measure and adjust feed rate	Daily
Replace feed tubing	1/week
Replace recycle tubing	2/week
Measure COD of influent and effluents	2/week
Measure color	2/month
Measure gas composition	1/month

Feed tubing is replaced once a week, while the recycle tubing is replaced once every four days. Color is measured once every two weeks, and gas composition is measured once a month.

Table 5 provides a chronological summary, to date, for the anaerobic treatment system, describing significant events during treatment system operation.

The anaerobic treatment system began operation on 12/10/91 (Day 1) with the start-up of Column 1. Prior to operation, each column was hydrostatically tested by filling both the inner cylinder and outer water jacket with distilled water and allowing it to set for a 24-hour period. One pound (0.454 kg) of granular activated carbon was then added to the column. The column was then seeded with approximately 20 mL of an acclimated anaerobic culture.

Prior to secondary treatment, the process water was filtered through 0.45-μm hydrophilic, polysulfone membrane, high-capacity filters to remove coal particles. Filtering was required because of the high total suspended solids (TSS) in the centrate stream. This pretreatment step is intended to simulate conditions of CWF recovery at an actual operating facility.

Filtered process water was initially fed into Column 1 at 100-mL intervals, increasing by 100 mL every two days, until a rate of 1 L/day (0.264 gal/day) was achieved (Day 38). Gas production was observed on Day 28 of operation. The process water was recycled through the column at a nominal rate of 0.660 L/min (0.174 gal/min). This rate was established to maintain bed expansion, allowing gas bubbles to migrate as discrete particles to the top of the column. Column 1 effluent drained from the column into a clarifier where the solids were gravity-separated from the water. Clarifier effluent

TABLE 5

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
12/10/91	1	Began system operation. Seeded Column 1. Began feeding 100-mL influent daily.
01/01/92	22	Increased influent rate to 200 mL/d.
01/03/92	24	Increased influent rate to 300 mL/d.
01/05/92	26	Increased influent rate to 400 mL/d.
01/07/92	28	Increased influent rate to 500 mL/d. Noted methane production in Column 1. Observed biomass floating above carbon bed.
01/09/92	30	Increased influent rate to 600 mL/d.
01/11/92	32	Increased influent rate to 700 mL/d.
01/13/92	34	Increased influent rate to 800 mL/d.
01/15/92	36	Increased influent rate to 900 mL/d.
01/17/92	38	Increased influent rate to 1000 mL/d.
01/22/92	43	Column 2 placed in series with Column 1. Added 454-g granular activated carbon. Did not seed Column 2 with microbes. Influent rate to Column 2 at 1 L/d of Column 1 effluent.
01/25/92	46	Water recycle pump stopped. Column 1 methane production ceased during this "cold" condition. Worn brushes were replaced in pump. Gas production was observed again as soon as the pump was fixed and recycling warm water.
01/31/92	52	Began routine COD sampling and analyses.
02/14/92	66	Began routine gas sampling and analyses.
02/21/92	73	Began periodic color analyses on influent and Column 1 and 2 effluents.

Continued ...

TABLE 5 (continued)

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
03/10/92	91	Increased COD analyses to twice a week.
04/12/92	124	Influent rate to Column 1 was set too high. The feed container was empty, and air was inadvertently introduced into the column. No adverse effects were observed.
04/22/92	134	Inadvertently added 550-mL influent to surge tank.
04/26/92	138	Column 1 feed container empty. Air was fed into Column 1. Again, no adverse effects were noted. Decreased feed set point to Column 1.
05/11/92	153	Observed gas bubbles in Column 2 as a result of Day 134.
05/19/92	161	Air introduced to both columns. Both Column 1 influent tank and surge tank to Column 2 were empty.
05/21/92	163	Noted disappearance of gas bubbles from Column 1.
05/24/92	166	Gas production in Column 1 reappeared.
05/26/92	168	Air was fed into Column 1 as a result of feed tube halfway out of influent container. No effect on gas production observed. Column 3 prepared for on-line installation.
05/28/92	170	Observed significant gas bubbles in Column 2. This gas production continued. Changed system configuration by replacing Column 1 with Column 3. Column 2 now lead column. Column 1 operating independently.

Continued ...

TABLE 5 (continued)

Chronological Summary of Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Date	Day of Operation	Comments
05/29/92	171	Water jacket leaked, resulting in system heat loss. All columns at room temperature. Gas production observed in Column 1, but not in Column 2. Took Column 3 off-line.
05/30/92	172	Gas production observed in Column 2.
05/31/92	173	Began feeding Column 3 even though the water jacket was not repaired. Noticed heat losses in the system by measuring water jacket temperatures at various locations.
06/12/92	185	Column 1 water jacket began leaking. Column 3 water jacket continues to leak. Drained water from both water jackets and attempted to repair them.
06/15/92	188	Column 3 water jacket repaired.
06/16/92	189	Column 3 fully operational. Column 1 water jacket repaired.
06/17/92	190	Column 1 water jacket fully operational. Observed gas bubbles in Column 3.

overflowed a centrally located weir and was collected in the surge tank. The surge tank allowed sufficient capacity for a two-day supply of water to subsequent columns. A nitrogen-purge was added to the surge tank to prevent air from entering the container.

Column 2 was placed in series with Column 1 on Day 43. Effluent from Column 1, draining into the surge tank, was used as the influent to Column 2. Column 2 was operated under the same conditions as Column 1. Methane production was observed in Column 2 on Day 140.

Columns 1 and 2 were operated in series for 127 days, until Column 1 reached carbon exhaustion, as measured by effluent COD. Column 1 was removed from the two-stage system and is currently being operated independently to observe potential inhibitory effects of biorefractory organics.

Filtered process water is currently being fed directly to Column 2, the lead column, at a nominal influent rate of approximately 1 L/d. The effluent from Column 2 is being collected in the surge tank, of which the contents are being fed into Column 3. Gas production was observed in Column 3 on Day 190. Presently, all three columns are exhibiting gas production.

One of the operational problems encountered with this system included recycle tubing wear and subsequent leaking. To avoid this problem, the recycle tubing is changed once every four days. Another problem encountered was running out of feed and pumping air into the system because the influent rate was set too high. This difficulty is prevented by daily monitoring of the influent rate and adjusting the feed set point as necessary.

One of the more common operational monitoring difficulties with the system was the loss of gas through the effluent line because of pressure differences. It is difficult to measure the gas production accurately when a portion of the gas escapes through the effluent. A daily attempt is made to equalize the pressure in the system so that the gas will flow to the collection system and not be lost through other streams.

Perhaps the most serious problem that has been encountered involved leaking water jackets. Although the jackets were repaired and fully operational within two weeks, the change in temperature from 98.5°F to approximately 70°F may have had a negative effect on the microbial environment, resulting in a decrease of effluent quality.

3.1.3.2.3 Anaerobic Treatment System Results

CHEMICAL OXYGEN DEMAND (COD)

Figures 2 through 4 illustrate the relationship between COD and the system throughput volume. Figure 2 shows Column 1 influent and effluent COD as a function of throughput volume. Breakthrough (400-mg/L COD) occurred at approximately 34 L of throughput, corresponding to 34 bed volumes. Carbon exhaustion was estimated to occur after approximately 150 L of throughput, or 150 bed volumes. Exhaustion was assumed to occur at a column effluent COD of 3200 mg/L, or 1200 mg/L less than the influent COD. The 1200 mg/L difference represents the biodegradable fraction of COD, as measured by BOD_5.

Column 1 was taken off-line after 150-L throughput (carbon exhaustion) and was continued in independent operation to observe any potential microbial inhibition following carbon exhaustion. Effluent COD levels appear to be slowly increasing, without corresponding increases in influent COD, indicating incomplete biodegradation of organics, as measured by BOD_5. Column 1 gas generation rates were also observed to decrease over this same operating period. However, independent operation of Column 1 resulted in operation at a temperature of 6 to 7 degrees lower than the design temperature of 98.5°F, due to necessary placement of the column with respect to the location of the heat exchange reservoir. Reduced operating temperatures are believed to be the reason for reduced anaerobic activity, rather than microbial inhibition. System design modifications will allow for the maintenance of constant temperature across all three operating columns. Subsequent testing is also planned to further evaluate the effects of temperature variations on anaerobic degradation of Usibelli HWD process water.

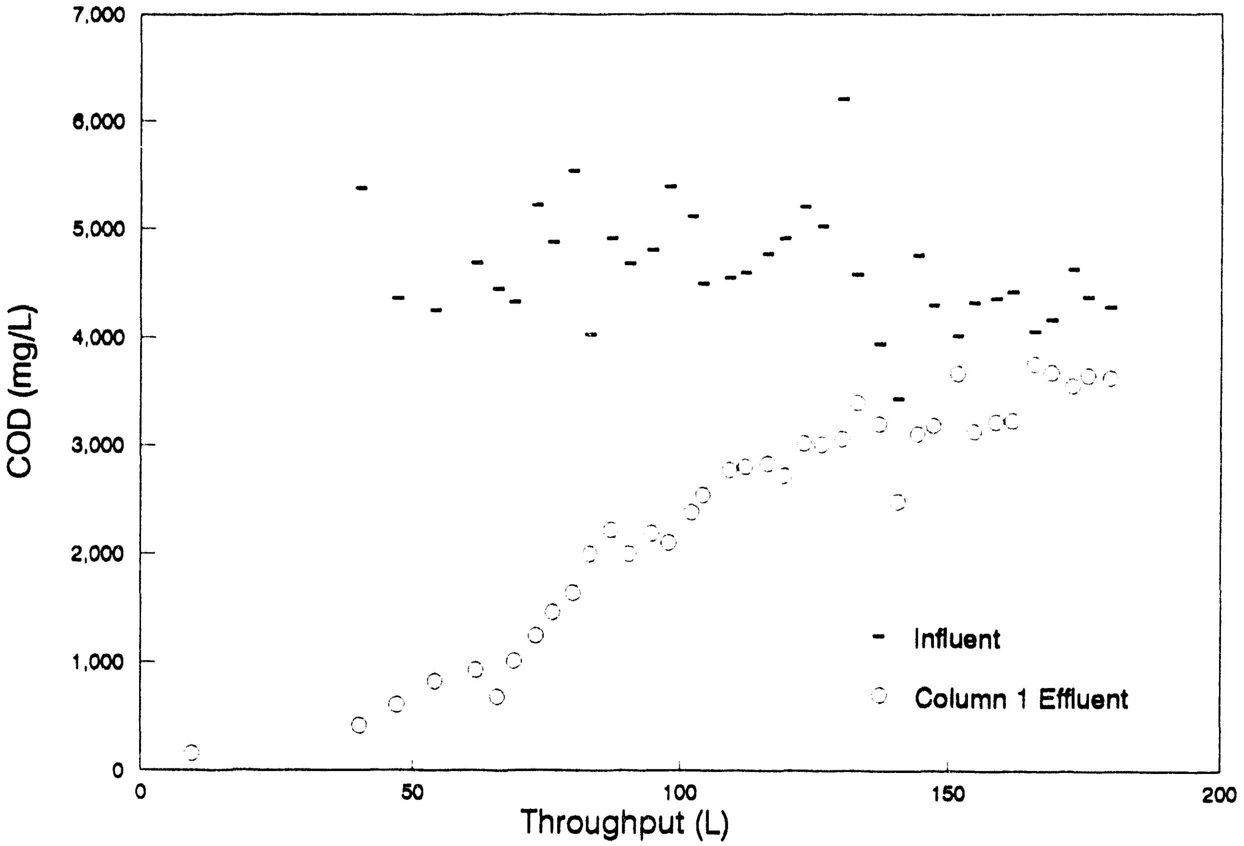


Figure 2. Chemical oxygen demand vs. throughput: Column 1.

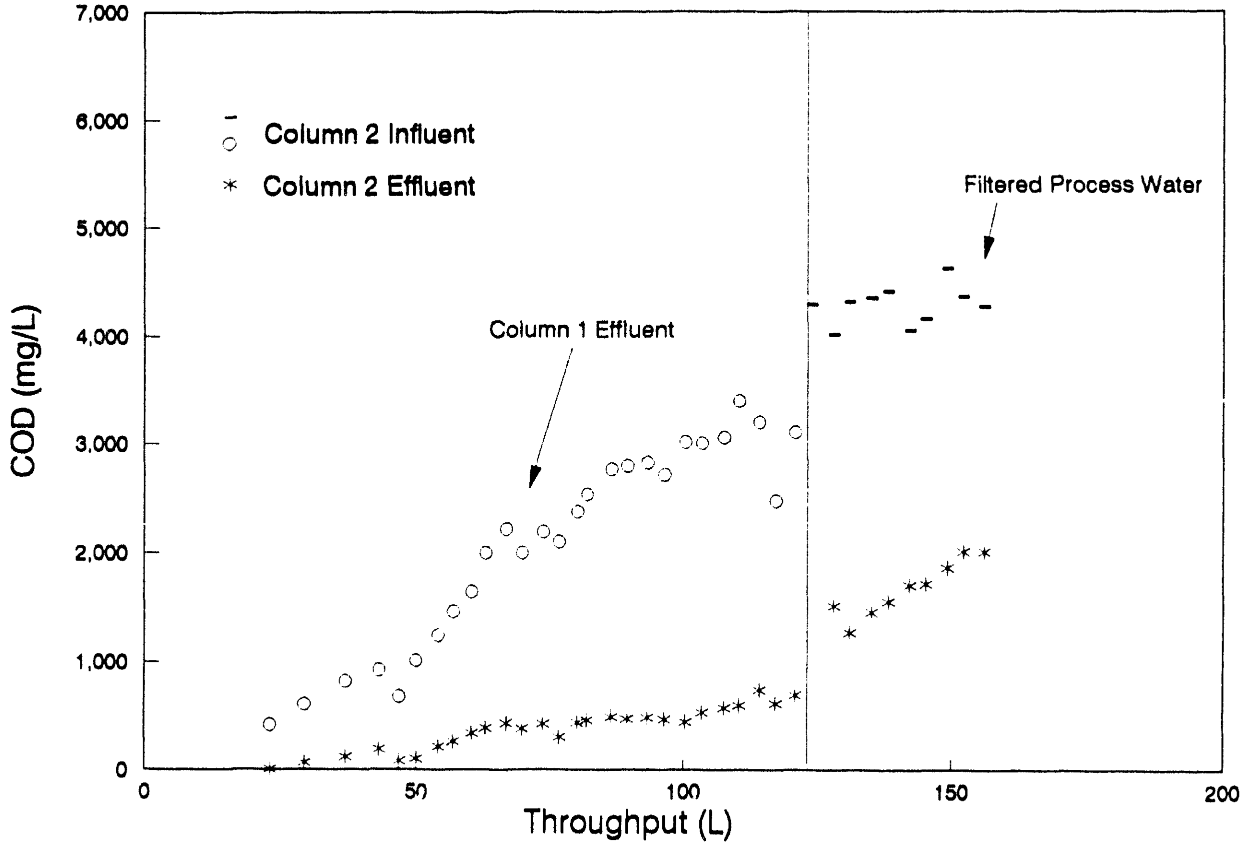


Figure 3. Chemical oxygen demand vs. throughput: Column 2.

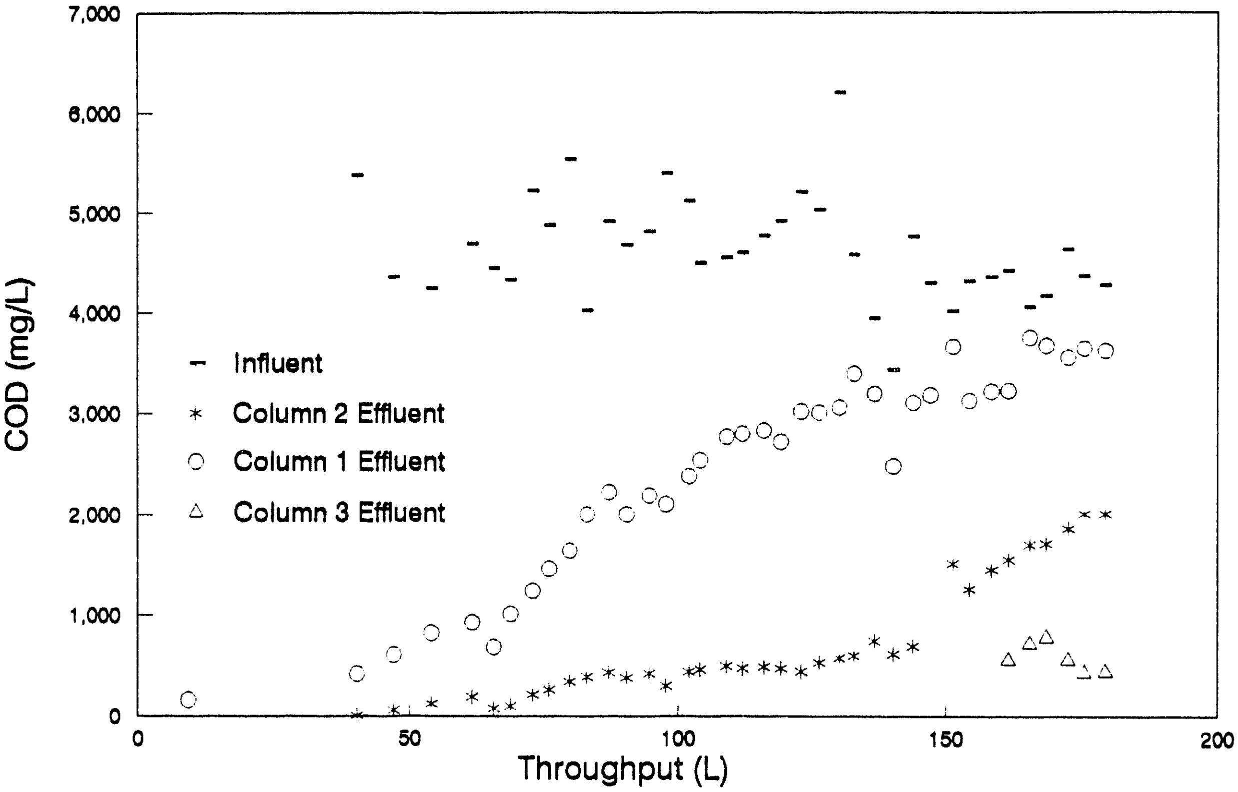


Figure 4. Chemical oxygen demand vs. throughput: overall system.

Figure 3 is a plot of Column 2 COD as a function of throughput. At approximately 125 L of throughput, (Day 169), the system configuration was changed. Column 2 became the lead c [illegible] for two-stage system operation ahead of Column 3. Prior to Day 169 of o [illegible], influent to Column 2 consisted of Column 1 effluent. After that time, [illegible] 2 was fed filtered Usibelli HWD process water. This change is indicated by a significant increase in system influent COD levels. Operation of two columns in series significantly extended the time to effluent COD breakthrough. This increased utilization of adsorption capacity approximately tripled the throughput to breakthrough while roughly only doubling the amount of carbon. Two-stage operation will also allow for complete exhaustion of the column prior to being taken off-line. Overall system operation is illustrated in Figure 4. Limited data for Column 3 were available at the time of preparation of this report.

COLOR

One of the parameters used to evaluate system performance of the anaerobic treatment system was color. The color of the process water was measured visually using a Hach color comparometer, which involves comparing the color of the sample with calibrated plastic color disks. Because turbidity can cause the apparent color determinations to be significantly greater than those of true color, all samples were filtered prior to measurement (American Public Health Association, 1985).

The color value of the HWD process water is extremely pH-dependent, increasing as the pH of the water increases. Because the pH of the process water remained relatively constant throughout the measuring period, the increase in effluent color can only be attributed to carbon exhaustion.

Table 6 lists the average influent and effluent color for the three columns. Color units are reported as platinum-cobalt (Pt-Co) units. The bed volumes (L) at each day of operation are provided in parentheses following the values listed for color.

GAS ANALYSIS

Gas composition was measured approximately once a month. Table 7 shows the composition of the gas generated from Column 1 as well as a few physical and thermal properties. The heating value of the gas is of particular importance since the production of methane is one of the advantages of using anaerobic treatment systems.

Overall, twenty of the more common gases are scanned for during the analysis. Of these twenty gases, only five were present in all of the analyses conducted on the gas generated by Column 1, including hydrogen (H_2), carbon dioxide (CO_2), oxygen (O_2), nitrogen (N_2), and methane (CH_4). Future analyses will include the gas generated by Columns 2 and 3.

As observed in Table 7, the ratio of oxygen to nitrogen (20:80) indicates that air was introduced into the method of gas sampling. If air had not been present, the mole percent of methane would be well over 90%. One of the possible, and most likely, pathways in which air was introduced is during the gas sampling procedure. Air may have entered the gas sampling bag during the transfer of gas from the collection system to the bag, or the gas sampling bag itself may allow some air to permeate it, or the seal around the port may not have been tight. To determine the source of error, a different gas collection bag will be used. If this is not the source of error, a new method of gas sampling will be devised.

TABLE 6

Results of Color Analyses for the Two-Stage, Anaerobic, Expanded-Bed, Granular Activated Carbon Treatment System

Average Influent Color: 25,000 Pt-Co Units

	Color		
Day of Operation	Column 1 Effluent	Column 2 Effluent	Column 3 Effluent
80	1200 (53 L)	50 (35 L)	
90	3500 (65 L)	250 (46 L)	
100	20000 (75 L)	200 (60 L)	
150	20000 (131 L)	1000 (109 L)	
170	20000 (146 L)	2500 (123 L)	
190	25000 (172 L)	12500 (148 L)	150 (21 L)

TABLE 7

Column 1 Gas Composition

Day of Operation:	66	99	120	147	196
Component (mole percent)					
Hydrogen	0.05	0.08	0.05	0.05	0.05
Carbon Dioxide	1.25	1.90	2.20	2.66	1.06
Oxygen/Argon	5.38	2.90	6.16	5.18	7.92
Nitrogen	24.61	13.40	26.04	21.95	36.86
Methane	68.71	81.73	65.55	70.16	54.11
Heating Value (Btu/scf)					
Saturated	684.4	814.3	652.8	698.8	538.8
Dry	696.5	828.7	664.3	711.2	548.3
Specific Gravity	0.698	0.644	0.717	0.699	0.760
Average Molecular Weight	20.19	18.63	20.75	20.23	22.01

Figure 5 presents the cumulative volume of gas generated by each column. Gas production in Column 1 was observed as early as Day 28 of operation. However, a measurable quantity of gas was not produced until Day 55. The gas production remained relatively constant, with a few exceptions. For example, because of difficulties in equalizing the pressure, some gas was lost through the effluent discharge line. This is illustrated by a decrease in slope between Days 80 and 90 of operation. Once this situation was corrected, the slope continued to increase consistently until the system configuration was changed. On Day 185, approximately two weeks after Column 1 was removed from two-stage operation and placed into independent operation, the water jacket leaked, exposing the column to room temperatures for about one week. This reduced temperature resulted in a decreased gas production rate which is represented by a decrease in the slope corresponding to Column 1.

Column 2 was placed into operation on Day 43. However, gas production was not observed until Day 172 of system operation. The lag period for gas generation from Column 2 can be attributed to Column 1 effluent being fed to the system. When biodegradable organics were introduced to Column 2, gas generation developed rapidly. The volume of methane produced is directly related to the influent COD (Suidan et al., 1987). On Day 134, untreated process water was inadvertently added to the surge tank. Within a week, gas production was observed in Column 2, continued for approximately three days, and then disappeared. On Day 153, gas was once again observed in the column, but was not generated in sufficient volumes for collection until Day 170, as illustrated in Figure 5.

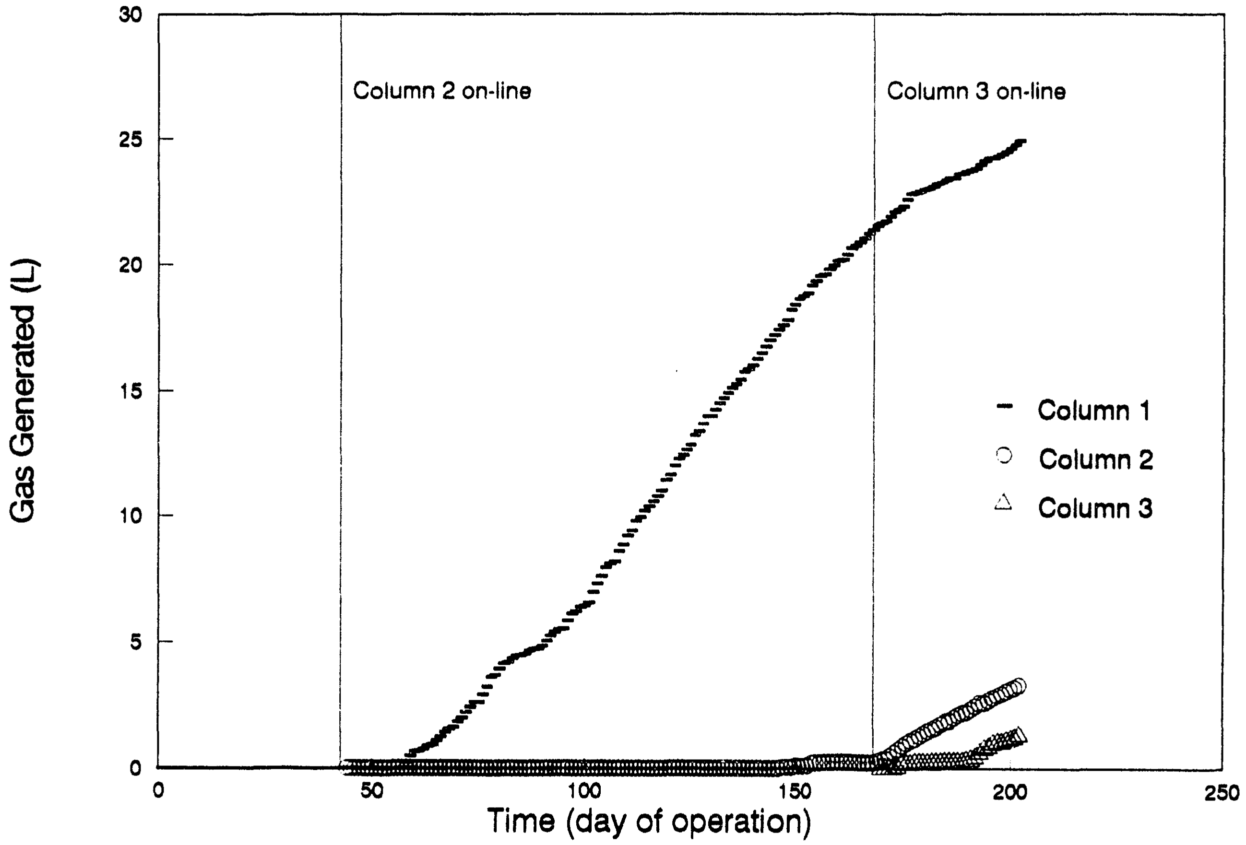


Figure 5. Cumulative gas generated vs. time: overall system.

Figure 6 illustrates the relationship between the COD loading and the gas generated in Column 1. The regression line is represented by the equation: $y = 0.156x + 0.039$. Thus for each 100 grams of COD applied to the system, approximately 16 L of gas are generated. Grady and Lim (1980) have reported theoretical methane generation rate at 16 grams of methane produced for every 64 grams of COD removed from wastewater.

3.1.3.3 Aerobic Treatment System

3.1.3.3.1 Introduction

An activated sludge process was selected for the evaluation of an aerobic system for the treatment of Usibelli HWD process water. Biomass used to seed the reactor was obtained from an activated sludge system operating on mild gasification process condensates.

The activated sludge process utilizes a suspended, mixed growth of aerobic microorganisms that use the organic materials in wastewaters as substrates. These substrates are removed through microbial respiration and synthesis of new cells.

The biochemical equation for the activated sludge process is:

$$\underset{\text{Matter}}{\text{Organic}} + O_2 \longrightarrow \underset{\text{Cells}}{\text{New}} + \underset{\text{Cells}}{\text{Energy for}} + CO_2 + H_2O + \underset{\text{Products}}{\text{Other End}} \qquad \text{[Eq. 2]}$$

Other end products include NH_4^{+1}, NO_2^{-1}, NO_3^{-1}, and PO_4^{-3}.

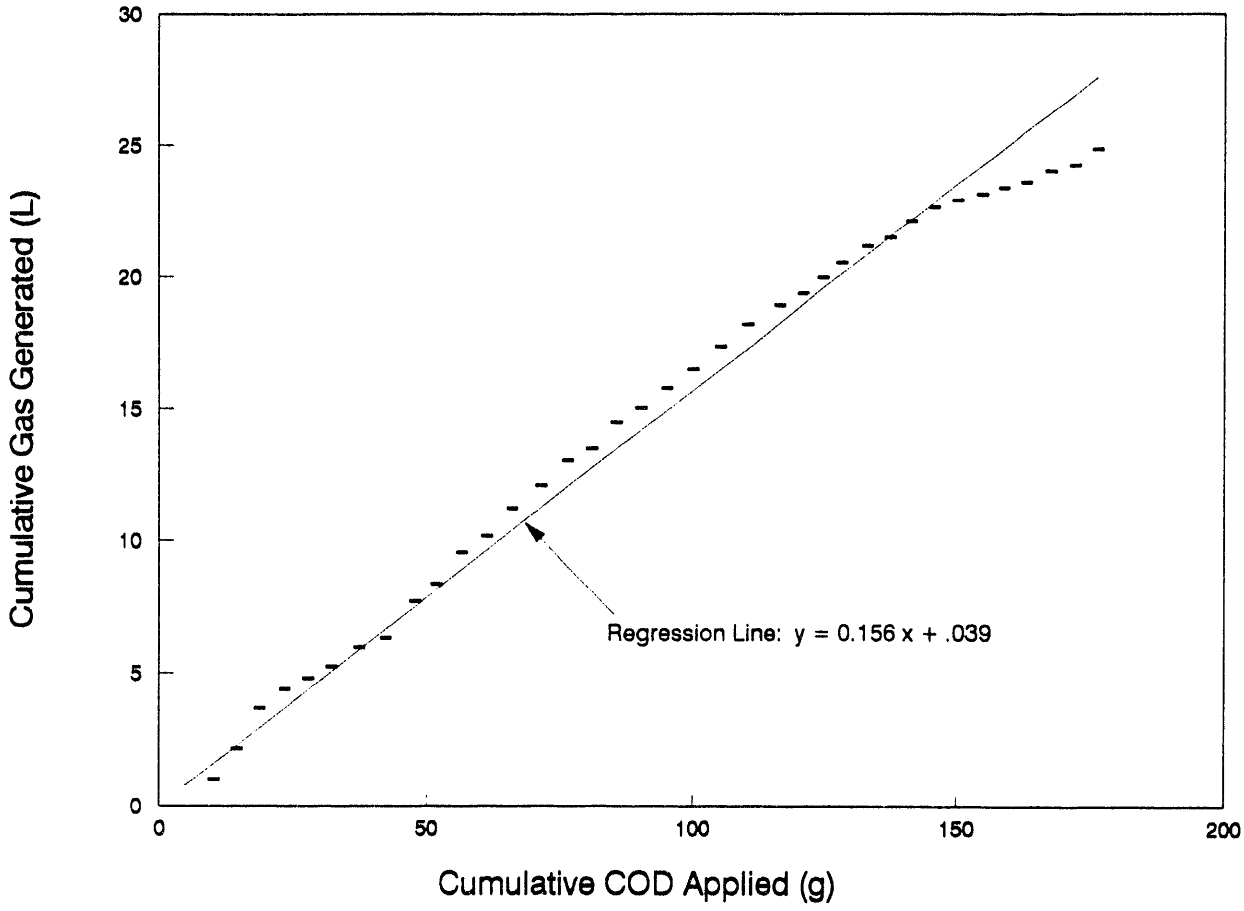


Figure 6. Cumulative gas generated vs. cumulative COD applied: Column 1.

Aerobic organisms can generally be divided into four nondistinct classes including floc-forming organisms, saprophytes, predators, and nuisance organisms. The floc-forming organisms are responsible for gravity settling and removal of the sludge from the treated wastewater. Saprophytes are responsible for degrading the organic matter. This class of bacteria is composed mostly of gram-negative bacilli. Approximately 230 species of predators, usually protozoa which feed on the bacteria, have been reported to occur in activated sludge. Nuisance organisms are usually filamentous bacteria and fungi which inhibit sludge settling (Grady and Lim, 1980).

A mean cell residence time (MCRT), also called sludge age, is used to determine the average time a microbial cell remains in the system. The MCRT, along with the food-to-microorganism ratio (F/M), are used to characterize the efficacy of an activated sludge process. A high F/M coupled with a low MCRT indicate the presence of filamentous growths, nuisance organisms, which create poor settling conditions. A low F/M and a high MCRT generally cause biological solids to undergo degradation and cell dispersion (Reynolds, 1982).

3.1.3.3.2 System Description and Operation

A schematic of the bench-scale activated sludge system used for treatability testing of Usibelli HWD process water is shown in Figure 7. The activated sludge aeration tank consists of a 10-L plexiglass basin with an operating volume of 6 to 8 L. Mixed liquor is maintained in suspension with a mechanical mixer. Oxygen is metered to the system as filtered, humidified, compressed house air through coarse-bubble diffusers.

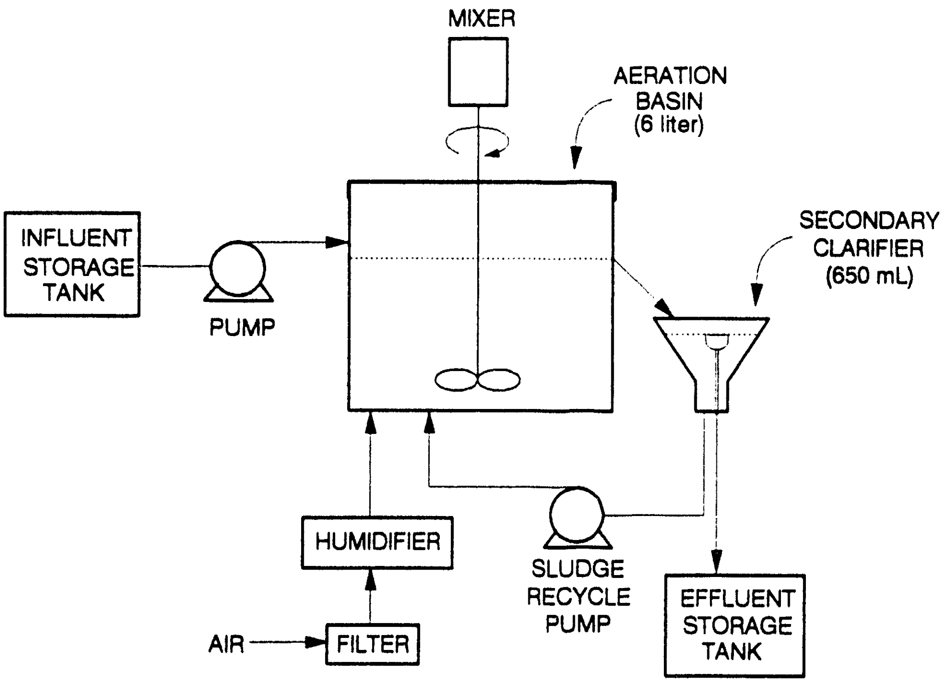


Figure 7. Bench-scale activated sludge treatment system schematic.

Essential nutrients for the growth of microorganisms are nitrogen and phosphorous. Coal-processing wastewaters are typically deficient in phosphorus. However, testing of the HWD Usibelli process water showed it to be deficient in both nutrients. Nitrogen and phosphorus, in the form of ammonium hypophosphate ($[NH_4]_2HPO_4$), were added to the influent to obtain a BOD_5:N:P ratio of 100:5:1.

The MCRT was controlled by volumetric wasting of mixed liquor measured in conjunction with the mass of mixed liquor volatile suspended solids (MLVSS) in the reactor and the concentration of volatile suspended solids lost in the effluent each day. The hydraulic retention time (HRT) was controlled through regulation of the influent rate in relation to the aeration basin volume.

Daily measurements were taken of the influent rate, influent pH, mixed liquor pH, and mixed liquor dissolved oxygen, with adjustments being made as necessary. Settleable solids and dissolved oxygen uptake rate readings were taken on every sampling day. Routine maintenance procedures are listed in Table 8.

Routine analyses were performed once a week on the system. Analyses include measurement of TSS, volatile suspended solids (VSS), COD, BOD_5, and NH_3.

Filtered process water was fed from a 2-L graduated cylinder to the aeration basin with a peristaltic pump. Initially, the system was operated using a continuous-flow configuration whereby mixed liquor flowed by gravity

TABLE 8

Routine Activated Sludge System Maintenance Performed
During Usibelli Process Water Treatability Study

Control Parameter	Frequency
Measure volume in feed tank	Daily
Measure volume in effluent tank	Daily
Measure pH of feed and mixed liquor	Daily
Measure mixed liquor temperature	Daily
Measure mixed liquor dissolved oxygen	Daily
Clean aeration basin and clarifier walls	Daily
Measure dissolved oxygen uptake rate	Variable
Measure mixed liquor settleable solids	Variable
Measure and adjust feed rate	1/week
Replace feed and recycle tubing	1/week
Waste mixed liquor from aeration basin	Variable
Recalibrate pH meter	1/week
Change dissolved oxygen probe membrane	Periodically

to a secondary clarifier with an operating volume of approximately 650 mL. Biological solids settled to the bottom and were recycled to the aeration basin every 20 minutes. Treated effluent and nonsettleable solids overflowed a centrally located weir and were collected in a 6-L effluent storage container.

Table 9 provides a chronological summary, to date, of the activated sludge treatment process. It describes significant events concerning the treatment system.

With this continuous-flow configuration, BOD_5 effluent values were erratic and relatively high. Nutrient addition to the system was increased to assure that these high effluent BOD_5 values were not a result of nitrogen and/or phosphorus deficiency. Additionally, erratic and high losses of VSS to the effluent was occurring. In order to maintain a stable population of microorganisms and allow for better process control, system operation was converted to a fill-and-draw configuration.

Two liters of filtered process water were fed over a 24-hour period into the aeration basin. The mixed liquor volume fluctuated between 6 and 8 L. At the end of the 24-hour period, the contents of the aeration basin were allowed to settle, undisturbed, for 30 minutes. Two liters of supernatant was then withdrawn from the system. This method served to increase the MLVSS and subsequently reduce effluent BOD_5. Results, to date, have shown a significant reduction in effluent BOD_5 values.

Another problem, contributing to poor treatment, observed with the activated sludge system was excessive foaming in the reactor. Foaming is now controlled by adding approximately 2 mL of dilute antifoam, a silicon-based polymer, directly to the reactor. This antifoam is beneficial because it

TABLE 9

Chronological Summary of the Activated Sludge System

Date	Day of Operation	Comments
11/26/91	1	Began activated sludge operation. Seeded reactor with sludge from an activated sludge system treating mild gasification wastewater.
12/10/91	15	Began routine measurement of solids settleability and dissolved oxygen uptake.
12/26/91	31	Excessive foaming observed in reactor.
12/27/91	32	Began adding antifoam to reactor.
01/04/92	40	pH-adjusted mixed liquor from 7.6 to 6.8.
01/07/92	43	Began adding antifoam to influent tank.
01/13/92	49	Began routine analyses for BOD_5, COD, NH_3, and suspended solids.
02/04/92	71	Began adding antifoam directly to reactor.
02/25/92	92	Reduced the frequency and sampling analysis.
03/26/92	122	Began wasting 80 mL/d of mixed liquor.
04/10/92	137	Increased nutrient volume from 1 mL nutrient/L water to 2 mL nutrient/L.
04/16/92	143	Reduced the frequency and sampling analysis.
06/02/92	190	Changed system configuration from continuous to fill-and-draw mode. Discontinued wasting 80 mL/d of mixed liquor.

effectively controls foaming without depleting the oxygen in the mixed liquor, as is common with most antifoaming agents.

3.1.3.3.3 Treatment System Results

Figure 8 shows the relationship between mixed liquor and effluent suspended solids as a function of time. With continued operation, the ratio of MLVSS/mixed liquor suspended solids (MLSS) appears to decrease, indicating a higher fraction of nonvolatile solids. Solids data from operation between days 50 to 100 showed that approximately 50% of the MLSS was MLVSS. Data collected just prior to Day 200 indicate that the MLVSS/MLSS ratio has decreased to approximately 40%.

Figure 9 is a plot of MCRT during the 30-week operating period. The erratic nature of the MCRT can be directly attributed to fluctuations in effluent suspended solids (effluent total suspended solids [ETSS] and effluent volatile suspended solids [EVSS]).

BOD_5 removals of 95% were achieved during activated sludge treatment of Usibelli process water. The average BOD_5 concentration in the influent, 1220 mg/L, was reduced to as low as 31 mg/L, but was not consistent. The treatability target discharge goal for BOD_5, based on New Source Performance Standard (NSPS), was 30 mg/L.

The average influent total COD during the operating period was 4540 mg/L. Average effluent soluble COD was 3730 mg/L, an 18% removal rate. Figure 10 illustrates influent and effluent COD as a function of time. This concentration is much higher than the target NSPS effluent quality goal of 400 mg/L. High concentrations of refractory COD in the activated sludge effluent will require further treatment.

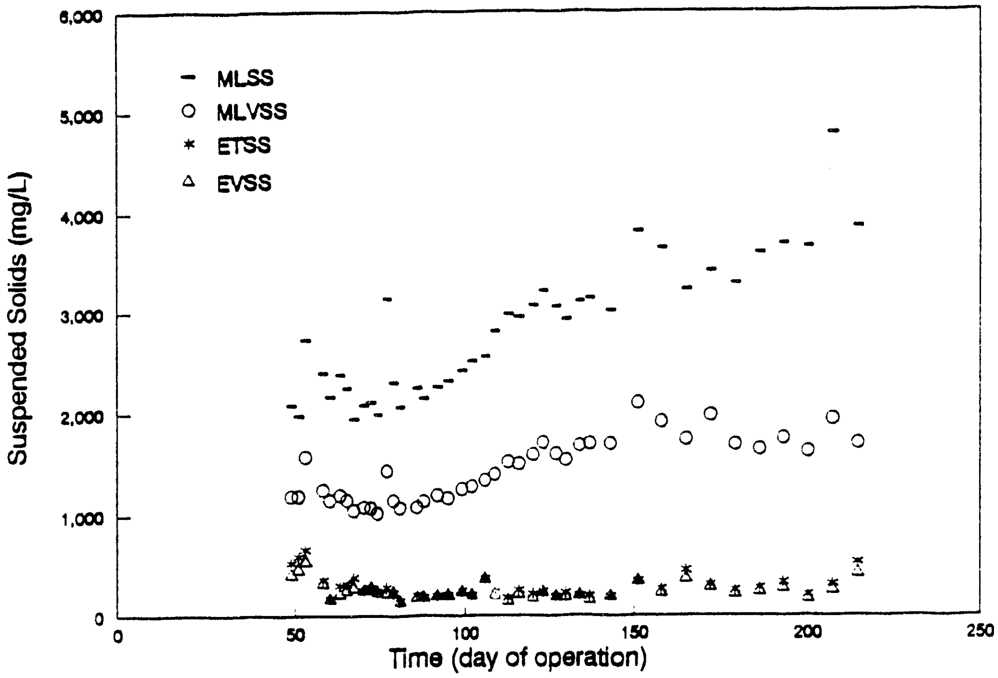


Figure 8. Suspended solids vs. time.

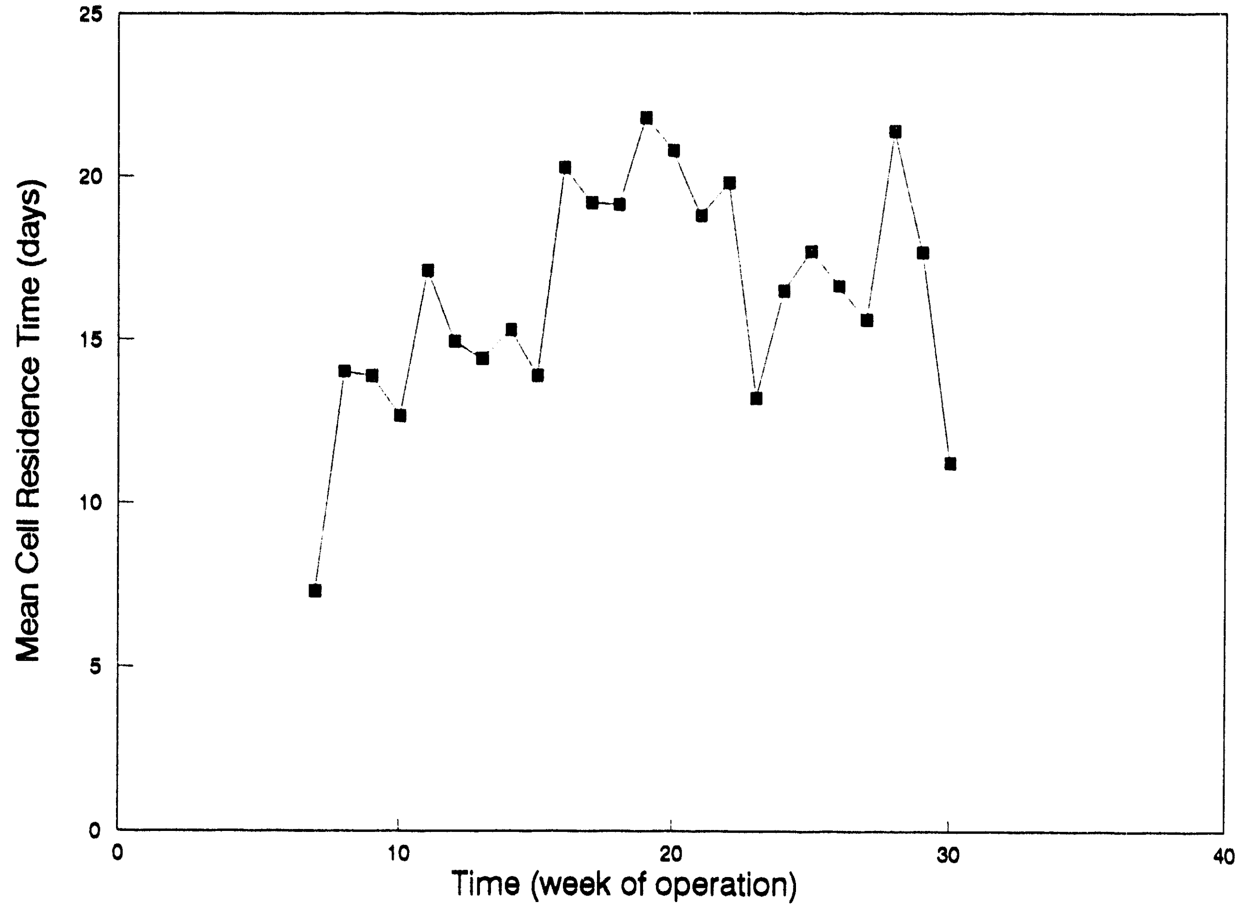


Figure 9. Mean cell residence time vs. time.

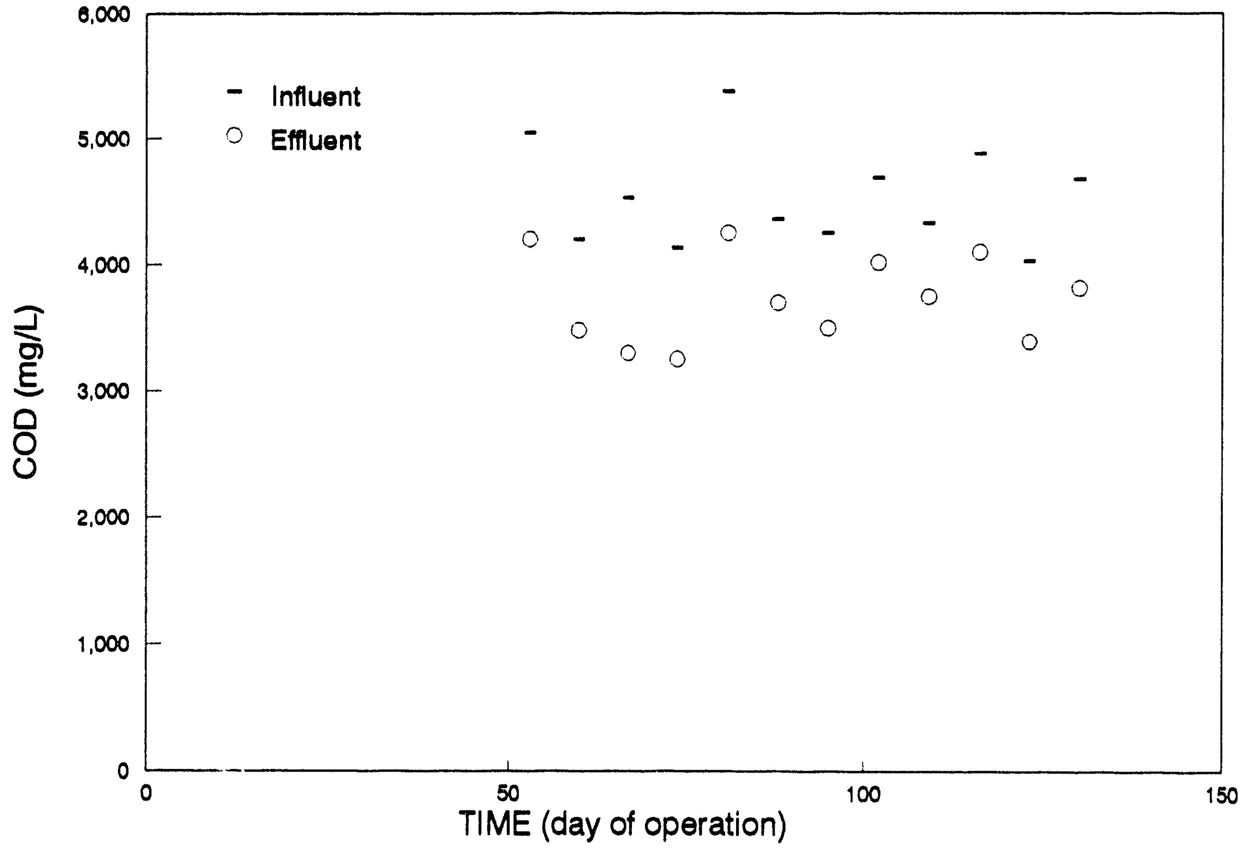


Figure 10. Chemical oxygen demand vs. time.

Figure 11 shows influent and effluent ammonia. Average influent ammonia was 13 mg/L. Effluent ammonia averaged 2 mg/L, resulting in a removal efficiency of 83%. Ammonia removals during activated sludge treatment are most likely the result of air stripping in the aeration basin, rather than biological nitrification. No increase in effluent nitrate was detected.

Table 10 summarizes operating parameters for the activated sludge system during this phase of operation.

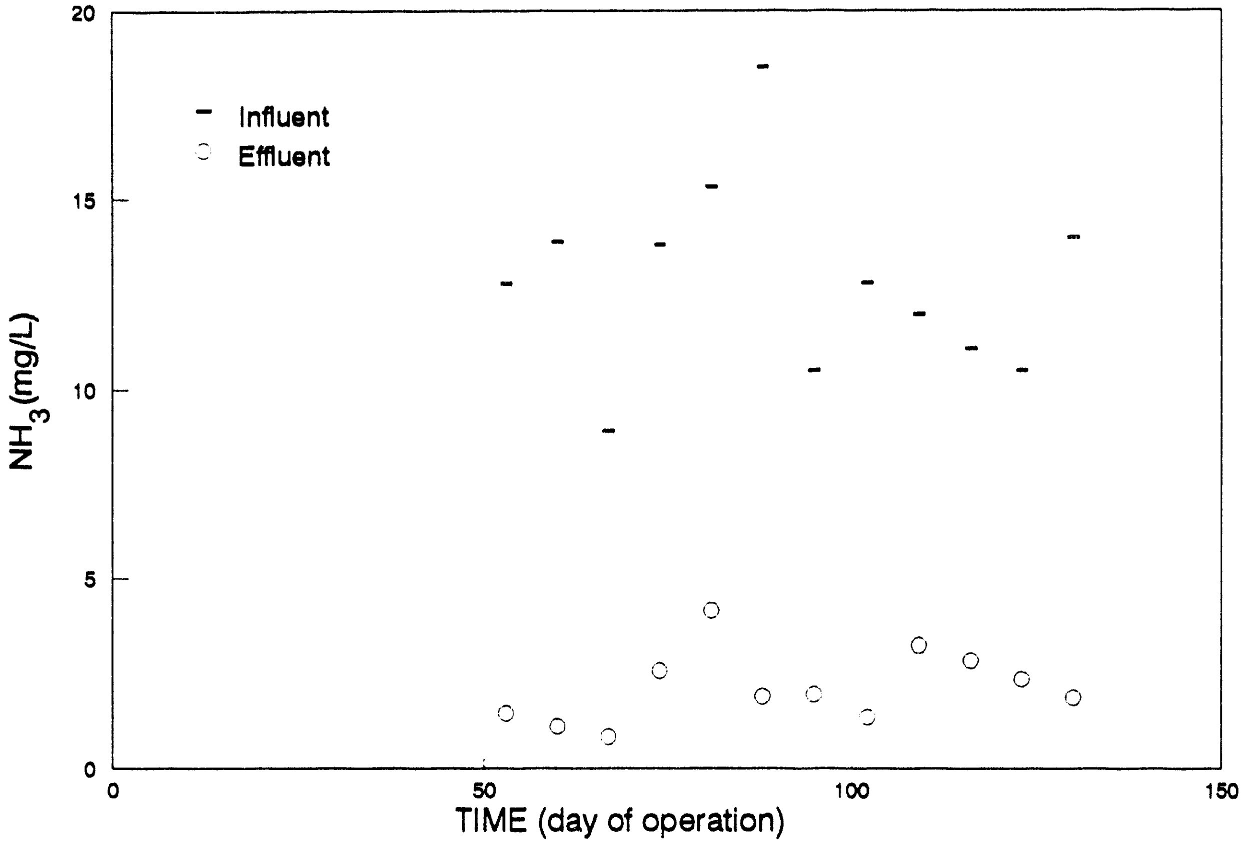


Figure 11. Ammonia vs. time.

TABLE 10

Summary of Operating Parameters
Activated Sludge Treatment of Usibelli HWD Process Water

Hydraulic Retention Time (HRT)	3.3 d
Mean Cell Residence Time (MCRT)	20 d
Food-to-Microorganism Ratio (F/M)	0.0034 g BOD_5/g MLVSS/d
Mixed Liquor Volatile Suspended Solids (MLVSS)	1630 mg/L
Oxygen Uptake Rate	0.112 mg/L/min 141.8 mg/g/hr

3.2 Coal Combustion Ash Conditioning Study

3.2.1 Introduction

Atmospheric fluidized-bed combustion (AFBC) is an advanced coal combustion technology used to control SO_2 emissions. In addition, this process produces lower levels of nitrogen oxides than conventional pulverized coal (PC) units because of lower operating temperatures. Because of SO_2 and NO_x removal during the combustion process, physical and chemical properties of wastes generated differ from those of PC units. Consequently, traditional waste management systems used for PC units may be inappropriate to efficiently condition and dispose of AFBC wastes (Golden, 1988).

This report presents a conceptual design for an innovative ash conditioning system to handle a "self-heating" mixture of 65% char and 35% fly ash produced by an existing AFBC facility. The design is based on the physical and chemical behavior of the ash. Critical waste properties tested include heat of hydration, compressive strength, time of set, rate of hydration, viscosity, bulk and packed density, and gradation.

3.2.1.1 Atmospheric Fluidized-Bed Combustion Process

Atmospheric fluidized-bed combustion (AFBC) is a relatively new technology which may reduce SO_2 emissions associated with acid rain problems currently concerning regulators and the public. There are two basic types of AFBC processes, a bubbling bed and a circulating bed. They are similar in that they both use cyclones to recycle solids back to the fluidized bed. But they differ with regard to fluidization air velocity, combustion particle size, and location of the heat-transfer surface for steam generation. The bubbling-bed process operates at a 4- to 12-ft/sec superficial (air) gas velocity and 0.5- and 0.1-inch coal and limestone particle sizes, respectively. The heat-transfer surface is located both in the fluidized bed and in the convective pass ahead of the cyclone. The circulating-bed process operates with a 15 to 25 ft/sec superficial gas velocity and 0.2- and 0.04-inch coal and limestone particles, respectively. Heat-transfer surfaces are located either at the top of the furnace or as an external heat exchanger. Both processes produce a char stream which is taken from the cyclone system (Golden, 1988; RP 2708-1, 1988).

The AFBC process offers two main advantages over conventional PC technologies: fuel flexibility and high SO_2 removal levels (90%-95%) without postcombustion controls. To achieve the high SO_2 removal level associated with AFBC (a greater than stoichiometric quantity), excess limestone is required to react in the combustion bed. Therefore, a larger quantity of dry solid waste is produced than that of conventional coal-burning technologies. As an example, the removal of 1 kg of sulfur produces approximately 6 kg of spent sorbent at a Ca:S ratio of 2:3. AFBC wastes differ from PC wastes because of the lower combustion temperatures and large limestone addition rates (Golden, 1988; RP 2708-1, 1988; Smith, 1989).

There are three basic AFBC solid waste streams produced during combustion (RP 2708-1, 1988):

- Spent Bed Material (SBM)--waste withdrawn from the bottom of the boiler

- AFBC fly ash--flue gas residue collected by either a fabric filter baghouse or an electrostatic precipitator
- Char--coarser flue gas residue collected by a primary particulate device, typically a cyclone

During the combustion process, crushed coal and limestone of the appropriate particle size are fed into the combustion chamber. A distributor plate distributes a high-velocity air stream throughout the combustion chamber to fluidize the bed. As the coal ignites, it reacts with the limestone which in turn absorbs/reacts with the sulfur contained in the coal.

The combustion heats water running through boiler tubes to produce steam for electric power generation. As the coal burns, flue gas containing fine-solid particles leaves the combustion chamber. A primary dust collection system, usually a multitube cyclone, removes larger particles or char in the 1-μm and larger range. Fine dust particles or fly ash in the 0.001- to 1.0-μm range are removed from the escaping flue gas with either a baghouse or an electrostatic precipitator (Wark and Warner, 1981).

3.2.1.2 AFBC Ash Description

An important characteristic of the AFBC ash for both disposal and utilization is its exothermic behavior upon water addition. Available information indicates that the water added during conditioning reacts with calcium and magnesium oxides and, to a lesser extent, with calcium sulfate in the waste (Golden, 1988). These hydration reactions occur as follows (RP 2708-1, 1988):

1. $CaO_{(s)} + H_2O \longrightarrow Ca(OH)_{2(s)}$ + heat
2. $MgO_{(s)} + H_2O \longrightarrow Mg(OH)_{2(s)}$ + heat
3. $CaSO_{4(s)} + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O_{(s)}$ + heat

The extent to which these reactions will occur, and thus the amount of heat released, depends on plant operating conditions (variations in feedstock, process temperature, etc.) and the AFBC boiler configuration (RP 2708-1, 1988; Smith, 1989; Wark and Warner, 1981; Bland et al., 1989).

A self-heating ash presents various handling problems that are not associated with conventional PC ashes. For example, the heat produced and released during hydration can cause serious problems for ash-handling equipment components such as bearings, bushings, electric connections and motors, and tires. In addition, the steam released creates a nuisance at the conditioning, transport, and disposal areas. Self-heating ashes also tend to dry out during hydration, stiffen, and set up, making conditioning and transport more difficult (Bazzel and Mallory, 1987).

3.2.2 Objective and Scope

In this task, an innovative conditioning process, that was developed for a self-heating AFBC waste, will be described. This conditioning process involves mixing the waste with enough water to satisfy all of the hydration reactions, to allow for moisture losses due to steam release, and to still have enough residual moisture content to produce the maximum compacted density when the waste is placed at the disposal site.

The key objectives of the proposed conditioning system were to 1) mix enough water with the ash to produce the optimum moisture content for maximum compacted density in the fully hydrated material, 2) handle the changing consistency of the ash as it hydrates, 3) promote full hydration of the ash under controlled conditions, and 4) provide short-term storage for the hydrated ash until it can be transported to the landfill for ultimate disposal.

Chemical and mineralogical investigations of the original AFBC residues and samples of conditioned AFBC residues will be included in this study to determine the chemical reactions and mineralogical-phase transformations that may occur during the conditioning process. Major, minor, and trace inorganic constituents of the original and conditioned residues will be studied, and experiments will be designed to investigate the mobility of trace inorganic constituents in the conditioned residues.

3.2.3 Coal Combustion Ash Conditioning Study Results

3.2.3.1 Bulk Chemical and Mineralogical Characterization

Chemical characterization of the AFBC residues was completed, and results of the various analyses are included in Table 11. In this study, proton-induced x-ray emission (PIXE) results (included in the last semiannual report) were used to determine an initial list of trace elements for quantitation in the two residues. That list included all Resource Conservation and Recovery Act (RCRA) elements, even if they were not identified by the PIXE results. Other highly mobile elements were also included for completeness. These trace elements are listed in Table 12.

The chemical characterization protocol included the quantitative analysis of the trace elements listed in Table 12 and the major and minor inorganic constituents. Major/minor inorganic constituents, present in percentage amounts in the samples, were silicon, aluminum, iron, calcium, magnesium, sodium, potassium, titanium, phosphorous, strontium, and manganese. Moisture content, loss on ignition, and carbonate were also determined in the original materials. Complete sets of the chemical characterization results (major, minor, and trace element constituents) are included in Table 11.

Mineralogical characterization by x-ray diffraction of the bulk samples was completed. Results are summarized in Table 13.

3.2.3.2 Results of Trace Element Mobility Investigations

These tasks involved the investigation of trace element mobility in test cylinders of the residues conditioned with different levels of moisture and at four curing times. Slices of these conditioned materials were submitted for the trace element mobility investigations. The various conditioned samples received for these investigations are summarized in Table 14, and Figure 12 indicates the area of the cylinder that was selected and submitted. Two slices, approximately 1 inch thick, were taken from the center of each cylinder. One slice was kept intact for the trace element mobility study,

TABLE 11

Bulk Chemical Characterization Results
Black Dog 1 TVA/Shawnee

Moisture:	%	0.47	0.11
Loss on Ignition:	%	27.9	9.25
SO_3	% Oxide	17.2	16.6
SiO_2	% Oxide	10.7	10.4
Al_2O_3	% Oxide	4.05	3.55
Fe_2O_3	% Oxide	1.97	4.53
CaO	% Oxide	31.2	49.5
MgO	% Oxide	1.98	2.52
Na_2O	% Oxide	0.50	0.07
K_2O	% Oxide	0.20	0.42
P_2O_5	% Oxide	0.24	0.05
TiO_2	% Oxide	0.23	0.05
BaO	% Oxide	0.20	0.03
MnO_2	% Oxide	0.02	0.02
SrO	% Oxide	0.11	0.06
CO_2	% Oxide	1.18	2.34
Arsenic	µg/g	4.1	15.2
Barium	µg/g	1750	259
Boron	µg/g	200	180
Bromide	µg/g	<10	<10
Cadmium	µg/g	<1.0	1.3
Chloride	µg/g	100	180
Chromium	µg/g	21.5	27.7
Copper	µg/g	37.4	13.0
Lead	µg/g	8.4	10.8
Mercury	µg/g	<0.4	<0.4
Molybdenum	µg/g	44.4	27.7
Nickel	µg/g	466	22.1
Selenium	µg/g	2.5	2.7
Silver	µg/g	<1.0	<1.0
Vanadium	µg/g	1210	41.9
Yttrium	µg/g	10.3	6.8
Zinc	µg/g	44.0	131
Zirconium	µg/g	74.3	32.2

TABLE 12

Trace Element Suite for Initial Characterization of AFBC Residues

RCRA Elements	PIXE Elements	Other Elements
Arsenic	Copper	Boron
Barium	Molybdenum	Chlorine
Cadmium	Nickel	Sulfur
Chromium*	Rubidium	
Lead*	Vanadium	
Mercury	Yttrium	
Selenium*	Zinc	
Silver	Zirconium	

* Also identified in PIXE results.

TABLE 13

Bulk Mineralogical Characterization Results

Sample Description	Mineralogical Phases Present	Nominal Composition
TVA/Shawnee	Lime	CaO
	Quartz	SiO_2
	Hematite	Fe_2O_3
	Calcite	$CaCO_3$
	Anhydrite	$CaSO_4$
Black Dog 1	Anhydrite	$CaSO_4$
	Lime	CaO
	Calcite	$CaCO_3$
	Portlandite	$Ca(OH)_2$
	Quartz	SiO_2

TABLE 14

Conditioned AFBC Residues Submitted for Leaching Characterization and Trace Element Mobility Investigations

Residue	Moisture Content (%)	Curing Times (day)
Black Dog 1	37	1, 7, 14, 28
Black Dog 1	47	1, 7, 14, 28
TVA/Shawnee	20	1, 7, 14, 28
TVA/Shawnee	30	1, 7, 14, 28

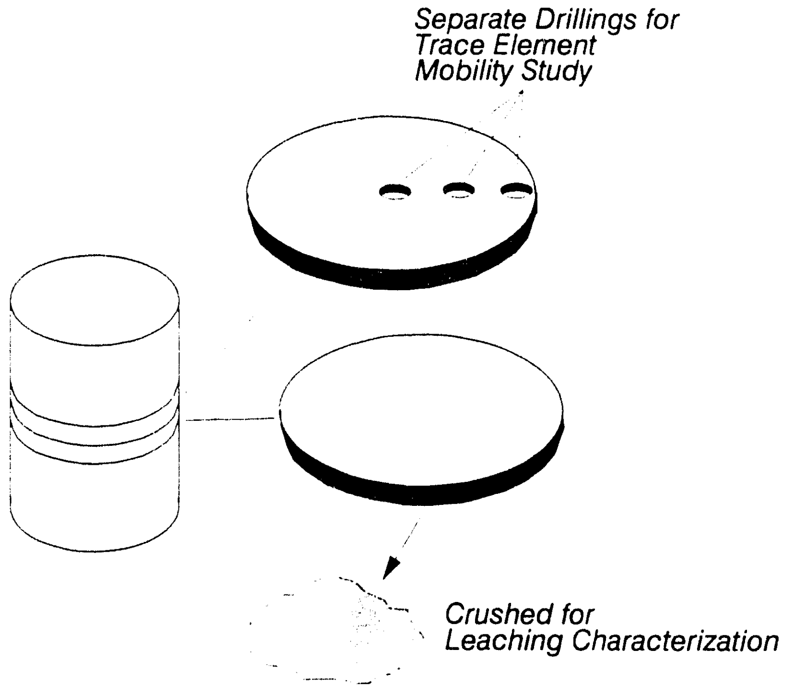


Figure 12. Sampling locations of conditioned residue test cylinders.

and the second was dried and crushed for potential use in future leaching characterization study. A split of the material prepared for the leaching characterization was ground to -60 mesh for mineralogical investigations to be performed in conjunction with the leaching. All these samples have been retained and are being stored pending future funding for a leaching characterization study. The leaching characterization proposed was determined to be beyond the scope of this subtask. Additional sample preparation was required for the trace element mobility studies. The cylinder section that was reserved for this purpose had samples drilled out of specific regions of the slice using a carborundum drill bit. A sample was obtained from the center of the slice, from the edge or perimeter of each slice, and from a concentric ring between the two samples. The sampling locations are shown in Figure 12. This protocol resulted in three distinct samples for each conditioned sample that was submitted. A carborundum bit was chosen because any contamination of the samples by the drill bit would be readily recognized during the mineralogical characterization of these samples. Following this sample preparation procedure, forty-eight samples of conditioned residues were submitted for analysis of total trace elements and major/minor inorganic constituents analysis. These same samples were submitted for x-ray diffraction to identify mineralogical phases present and for comparison of the mineralogy of the conditioned versus nonconditioned material. Mineralogy was determined on the 1- and 28-day cured, conditioned materials at both moisture levels investigated in the engineering study under this task. X-ray diffraction results are listed in Table 15. Chemical analysis results of the residue from Black Dog are included in Tables 16 through 19. Tables 20 through 23 list the chemical analysis results of the residue from TVA/Shawnee. These results are presented in two different formats to ease the interpretation. The first set groups the

TABLE 15

Summary Page Ash Conditioning
NMAL XRD Analysis

1-Day	28-Day
NSP Black Dog Ash 37% H_2O	
Quartz (SiO_2)	Quartz (SiO_2)
Calcite ($CaCO_3$)	Portlandite ($Ca[OH]_2$)
Portlandite ($Ca[OH]_2$)	Anhydrite ($CaSO_4$)
Anhydrite ($CaSO_4$)	Gypsum ($CaSO_4 \cdot 2H_2O$)
	Ettringite ($Ca_6Al_2[SO_4]_3[OH]_{12} \cdot 26H_2O$)
NSP Black Dog Ash 47% H_2O	
Quartz (SiO_2)	Quartz (SiO_2)
Portlandite ($Ca[OH]_2$)	Portlandite ($Ca[OH]_2$)
Anhydrite ($CaSO_4$)	Anhydrite ($CaSO_4$)
Gypsum ($CaSO_4 \cdot 2H_2O$)	Gypsum ($CaSO_4 \cdot 2H_2O$)
TVA Shawnee 20% H_2O	
Quartz (SiO_2)	Quartz (SiO_2)
Calcite ($CaCO_3$)	Calcite ($CaCO_3$)
Portlandite ($Ca[OH]_2$)	Portlandite ($Ca[OH]_2$)
Anhydrite ($CaSO_4$)	Anhydrite ($CaSO_4$)
Hematite (Fe_2O_3)	Hematite (Fe_2O_3)
	Gypsum ($CaSO_4 \cdot 2H_2O$)
TVA Shawnee 30% H_2O	
Quartz (SiO_2)	Quartz (SiO_2)
Calcite ($CaCO_3$)	Calcite ($CaCO_3$)
Portlandite ($Ca[OH]_2$)	Portlandite ($Ca[OH]_2$)
Anhydrite ($CaSO_4$)	Anhydrite ($CaSO_4$)
Hematite (Fe_2O_3)	Hematite (Fe_2O_3)
	Gypsum ($CaSO_4 \cdot 2H_2O$)

TABLE 16

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl µg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr µg/g	Ti mg/g	V mg/g
37% H_2O 1-Day Center	22	1.6	230	93	13	11	3.6	6.3	860	1.1	1.1
37% H_2O 1-Day Middle	21	1.6	230	99	13	11	3.7	6.4	860	1.1	1.2
37% H_2O 1-Day Edge	21	1.6	230	120	13	13	4.2	6.6	840	1.1	1.1
37% H_2O 7-Day Center	23	1.7	250	110	13	12	3.6	6.4	880	1.1	1.2
37% H_2O 7-Day Middle	21	1.7	230	96	13	11	3.9	6.4	810	1.0	1.2
37% H_2O 7-Day Edge	22	1.6	230	120	12	11	3.8	6.2	830	1.1	1.2
37% H_2O 14-Day Center	23	1.7	240	96	14	11	3.8	6.4	830	1.2	1.2
37% H_2O 14-Day Middle	23	1.6	240	93	14	12	4.1	6.5	850	1.9	1.1
37% H_2O 14-Day Edge	25	1.7	230	96	14	12	4.0	6.2	870	2.0	1.2
37% H_2O 28-Day Center	23	1.7	230	86	14	12	3.2	6.4	870	1.8	1.2
37% H_2O 28-Day Middle	23	1.6	230	82	13	11	3.3	6.3	850	1.7	1.1
37% H_2O 28-Day Edge	22	1.6	220	110	14	11	3.7	6.2	870	1.8	1.1
47% H_2O 1-Day Center	24	1.7	240	78	14	13	3.9	6.3	930	2.0	1.2
47% H_2O 1-Day Middle	21	1.7	240	82	14	11	3.7	6.5	870	1.8	1.2
47% H_2O 1-Day Edge	23	1.6	230	100	13	13	3.8	6.4	840	1.9	1.2
47% H_2O 7-Day Center	22	1.7	220	110	13	12	3.5	6.5	840	1.3	1.2
47% H_2O 7-Day Middle	21	1.6	240	100	12	11	3.8	6.5	790	1.1	1.2
47% H_2O 7-Day Edge	22	1.7	240	100	15	13	3.6	6.3	860	2.0	1.2
47% H_2O 14-Day Center	22	1.6	220	120	13	12	3.7	6.3	810	1.3	1.3
47% H_2O 14-Day Middle	21	1.6	230	100	14	12	3.8	6.6	790	1.2	1.3
47% H_2O 14-Day Edge	22	1.7	250	99	13	12	3.7	6.4	840	1.1	1.2
47% H_2O 28-Day Center	22	1.7	240	130	14	12	3.7	6.3	840	1.4	1.2
47% H_2O 28-Day Middle	23	1.7	240	110	14	12	3.8	6.2	860	2.0	1.2
47% H_2O 28-Day Edge	22	1.7	240	110	15	13	3.6	6.4	850	2.0	1.1

TABLE 17

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Mo µg/g	Ni µg/g	Se µg/g	Y µg/g	Zn µg/g	Zr µg/g
37% H_2O 1-Day Center	6.1	21	28	7.5	170	43	410	4.7	11	54	36
37% H_2O 1-Day Middle	5.4	25	30	11	170	50	440	4.7	12	53	37
37% H_2O 1-Day Edge	6.1	23	28	8.1	170	49	440	4.2	11	48	38
37% H_2O 7-Day Center	9.0	24	28	3.9	170	49	440	4.3	11	55	35
37% H_2O 7-Day Middle	7.0	23	28	7.6	170	43	450	4.8	12	46	40
37% H_2O 7-Day Edge	4.6	24	27	8.0	170	44	450	4.4	12	48	38
37% H_2O 14-Day Center	11	24	27	8.8	170	46	450	5.5	12	52	38
37% H_2O 14-Day Middle	6.2	23	27	4.6	160	48	430	3.0	11	50	53
37% H_2O 14-Day Edge	7.6	23	29	5.6	170	44	440	3.5	11	52	31
37% H_2O 28-Day Center	5.5	23	30	9.1	170	48	460	3.6	11	68	40
37% H_2O 28-Day Middle	4.9	24	28	7.5	170	42	440	3.0	11	57	35
37% H_2O 28-Day Edge	5.4	20	28	7.4	160	44	440	3.1	11	56	27
47% H_2O 1-Day Center	5.7	24	30	6.5	180	49	460	4.3	12	53	40
47% H_2O 1-Day Middle	7.0	23	28	6.4	170	48	440	4.8	11	57	33
47% H_2O 1-Day Edge	7.7	22	29	6.3	170	46	450	5.0	12	53	38
47% H_2O 7-Day Center	5.0	22	37	10	160	48	430	4.4	12	47	43
47% H_2O 7-Day Middle	7.1	26	38	10	170	49	440	4.6	13	47	43
47% H_2O 7-Day Edge	6.0	25	39	10	170	50	430	4.3	12	49	40
47% H_2O 14-Day Center	5.8	24	39	12	190	48	450	4.6	12	64	44
47% H_2O 14-Day Middle	6.4	23	39	9.7	170	50	440	3.5	12	54	41
47% H_2O 14-Day Edge	5.4	23	37	10	160	46	390	4.0	12	42	35
47% H_2O 28-Day Center	6.0	25	36	9.4	160	46	430	3.9	12	43	40
47% H_2O 28-Day Middle	5.7	23	35	15	150	48	750	3.5	12	42	41
47% H_2O 28-Day Edge	5.3	21	34	10	150	44	400	4.1	12	42	37

TABLE 18

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl µg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr µg/g	Ti mg/g	V mg/g
37% H_2O 1-Day Center	22	1.6	230	93	13	11	3.6	6.3	860	1.1	1.1
37% H_2O 7-Day Center	23	1.7	250	110	13	12	3.6	6.4	880	1.1	1.2
37% H_2O 14-Day Center	23	1.7	240	96	14	11	3.8	6.4	830	1.2	1.2
37% H_2O 28-Day Center	23	1.7	230	86	14	12	3.2	6.4	870	1.8	1.2
47% H_2O 1-Day Center	24	1.7	240	78	14	13	3.9	6.3	930	2.0	1.2
47% H_2O 7-Day Center	22	1.7	220	110	13	12	3.5	6.5	840	1.3	1.2
47% H_2O 14-Day Center	22	1.6	220	120	13	12	3.7	6.3	810	1.3	1.3
47% H_2O 28-Day Center	22	1.7	240	130	14	12	3.7	6.3	840	1.4	1.2
37% H_2O 1-Day Middle	21	1.6	230	99	13	11	3.7	6.4	860	1.1	1.2
37% H_2O 7-Day Middle	21	1.7	230	96	13	11	3.9	6.4	810	1.0	1.2
37% H_2O 14-Day Middle	23	1.6	240	93	14	12	4.1	6.5	850	1.9	1.1
37% H_2O 28-Day Middle	23	1.6	230	82	13	11	3.3	6.3	850	1.7	1.1
47% H_2O 1-Day Middle	21	1.7	240	82	14	11	3.7	6.5	870	1.8	1.2
47% H_2O 7-Day Middle	21	1.6	240	100	12	11	3.8	6.5	790	1.1	1.2
47% H_2O 14-Day Middle	21	1.6	230	100	14	12	3.8	6.6	790	1.2	1.3
47% H_2O 28-Day Middle	23	1.7	240	110	14	12	3.8	6.2	860	2.0	1.2
37% H_2O 1-Day Edge	21	1.6	230	120	13	13	4.2	6.6	840	1.1	1.1
37% H_2O 7-Day Edge	22	1.6	230	120	12	11	3.8	6.2	830	1.1	1.2
37% H_2O 14-Day Edge	25	1.7	230	96	14	12	4.0	6.2	870	2.0	1.2
37% H_2O 28-Day Edge	22	1.6	220	110	14	11	3.7	6.2	870	1.8	1.1
47% H_2O 1-Day Edge	23	1.6	230	100	13	13	3.8	6.4	840	1.9	1.2
47% H_2O 7-Day Edge	22	1.7	240	100	14	13	3.6	6.3	860	2.0	1.2
47% H_2O 14-Day Edge	22	1.7	250	99	13	12	3.7	6.4	840	1.1	1.2
47% H_2O 28-Day Edge	22	1.7	240	110	15	13	3.6	6.4	850	2.0	1.1

TABLE 19

Chemical Analysis of NSP/Black Dog Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Mo µg/g	Ni µg/g	Se µg/g	Y µg/g	Zn µg/g	Zr µg/g
37% H_2O 1-Day Center	6.1	21	28	7.5	170	43	410	4.7	11	54	36
37% H_2O 7-Day Center	9.0	24	28	3.9	170	49	440	4.3	11	55	35
37% H_2O 14-Day Center	11	24	27	8.8	170	46	450	5.5	12	52	38
37% H_2O 28-Day Center	5.5	23	30	9.1	170	48	460	3.6	11	68	40
47% H_2O 1-Day Center	5.7	24	30	6.5	180	49	460	4.3	12	53	40
47% H_2O 7-Day Center	5.0	22	37	10	160	48	430	4.4	12	47	43
47% H_2O 14-Day Center	5.8	24	39	12	190	48	450	4.6	12	64	44
47% H_2O 28-Day Center	6.0	25	36	9.4	160	46	430	3.9	12	43	40
37% H_2O 1-Day Middle	5.4	25	30	11	170	50	440	4.7	12	53	37
37% H_2O 7-Day Middle	7.0	23	28	7.6	170	43	450	4.8	12	46	40
37% H_2O 14-Day Middle	6.2	23	27	4.6	160	48	430	3.0	11	50	53
37% H_2O 28-Day Middle	4.9	24	28	7.5	170	42	440	3.0	11	57	35
47% H_2O 1-Day Middle	7.0	23	28	6.4	170	48	440	4.8	11	57	33
47% H_2O 7-Day Middle	7.1	26	38	10	170	49	440	4.6	13	47	43
47% H_2O 14-Day Middle	6.4	23	39	9.7	170	50	440	3.5	12	54	41
47% H_2O 28-Day Middle	5.7	23	35	15	150	48	750	3.5	12	42	41
37% H_2O 1-Day Edge	6.1	23	28	8.1	170	49	440	4.2	11	48	38
37% H_2O 7-Day Edge	4.6	24	27	8.0	170	44	450	4.4	12	48	38
37% H_2O 14-Day Edge	7.6	23	29	5.6	170	44	440	3.5	11	52	31
37% H_2O 28-Day Edge	5.4	20	28	7.4	160	44	440	3.1	11	56	27
47% H_2O 1-Day Edge	7.7	22	29	6.3	170	46	450	5.0	12	53	38
47% H_2O 7-Day Edge	6.0	25	39	10	170	50	430	4.3	12	49	40
47% H_2O 14-Day Edge	5.4	23	37	10	160	46	390	4.0	12	42	35
47% H_2O 28-Day Edge	5.3	21	34	10	150	44	400	4.1	12	42	37

TABLE 20

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl µg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr µg/g	Ti mg/g	V µg/g
20% Mix9 1-Day Center	18	0.38	350	110	45	14	0.48	5.3	420	0.87	47
20% Mix9 1-Day Middle	19	0.33	350	110	49	14	0.41	5.4	430	0.93	45
20% Mix9 1-Day Edge	18	0.29	350	110	46	14	0.59	5.5	450	0.88	43
20% Mix7 7-Day Center	16	0.31	350	100	44	14	0.42	5.5	450	0.78	39
20% Mix7 7-Day Middle	16	0.28	350	110	44	14	0.37	5.4	450	0.77	40
20% Mix7 7-Day Edge	16	0.26	360	110	41	14	0.38	5.5	460	0.69	37
20% Mix4 14-Day Center	16	0.27	360	120	41	14	0.37	5.5	430	0.73	38
20% Mix4 14-Day Middle	16	0.34	350	100	41	13	0.35	5.4	430	0.76	37
20% Mix4 14-Day Edge	16	0.24	360	110	40	14	0.37	5.6	440	0.73	37
20% Mix1 28-Day Center	16	0.36	360	90	41	14	0.35	5.6	430	0.67	36
20% Mix1 28-Day Middle	16	0.26	360	94	40	13	0.37	5.5	410	0.68	36
20% Mix1 28-Day Edge	16	0.26	360	96	41	14	0.54	5.6	460	0.70	35
30% Mix8 1-Day Center	15	0.24	300	100	31	13	0.41	5.6	430	0.53	39
30% Mix8 1-Day Middle	17	0.21	320	100	39	14	0.42	5.5	390	0.48	38
30% Mix8 1-Day Edge	16	0.21	320	110	38	14	0.43	5.5	410	0.48	39
30% Mix6 7-Day Center	17	0.22	320	100	37	13	0.38	5.5	450	0.44	39
30% Mix6 7-Day Middle	16	0.19	320	100	34	14	0.41	5.5	390	0.40	39
30% Mix6 7-Day Edge	16	0.30	310	110	42	13	0.41	5.6	430	0.88	38
30% Mix5 14-Day Center	17	0.31	320	100	45	14	0.44	5.5	430	0.88	39
30% Mix5 14-Day Middle	17	0.27	310	100	45	13	0.39	5.6	410	0.88	39
30% Mix5 14-Day Edge	17	0.28	330	96	45	14	0.50	5.6	420	0.86	38
30% Mix3 28-Day Center	17	0.35	340	90	45	14	0.39	5.6	450	0.81	37
30% Mix3 28-Day Middle	16	0.38	350	82	43	14	0.57	5.5	430	0.82	37
30% Mix3 28-Day Edge	16	0.22	340	100	41	13	0.36	5.5	420	0.76	38

TABLE 21

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Mo µg/g	Ni µg/g	Se µg/g	Y µg/g	Zn µg/g	Zr µg/g
20% Mix9 1-Day Center	13	25	17	12	110	27	24	2.2	8.5	150	22
20% Mix9 1-Day Middle	13	27	18	11	110	28	25	2.3	7.8	150	16
20% Mix9 1-Day Edge	14	26	17	13	110	28	26	2.2	8.3	160	19
20% Mix7 7-Day Center	13	25	18	10	110	26	26	1.6	7.8	180	17
20% Mix7 7-Day Middle	14	26	16	11	110	28	25	1.8	8.4	130	18
20% Mix7 7-Day Edge	14	25	14	8.9	110	28	27	2.4	7.6	150	17
20% Mix4 14-Day Center	14	25	13	11	110	28	25	1.9	8.1	130	19
20% Mix4 14-Day Middle	14	24	13	8.9	110	27	26	1.4	7.3	130	13
20% Mix4 14-Day Edge	15	24	13	9.3	110	27	23	2.0	7.5	140	24
20% Mix1 28-Day Center	14	23	12	9.6	110	30	24	1.3	7.9	150	17
20% Mix1 28-Day Middle	13	23	14	9.2	100	26	24	1.8	7.8	120	14
20% Mix1 28-Day Edge	13	23	13	8.9	100	25	23	2.0	7.1	150	14
30% Mix8 1-Day Center	14	23	12	16	110	27	23	3.8	8.4	140	10
30% Mix8 1-Day Middle	15	24	12	15	110	24	24	4.8	8.6	150	12
30% Mix8 1-Day Edge	13	26	12	15	110	27	26	3.8	8.3	130	3
30% Mix6 7-Day Center	12	27	14	15	110	29	27	3.9	9.1	120	12
30% Mix6 7-Day Middle	14	25	12	15	110	26	25	3.8	8.8	130	12
30% Mix6 7-Day Edge	14	25	17	15	110	29	24	2.7	7.7	130	21
30% Mix5 14-Day Center	15	26	15	11	110	26	23	2.4	7.5	130	21
30% Mix5 14-Day Middle	14	25	13	13	110	29	24	2.4	8.4	120	18
30% Mix5 14-Day Edge	13	24	16	12	100	26	22	2.3	8.2	130	22
30% Mix3 28-Day Center	16	25	18	11	100	27	23	1.6	8.2	130	21
30% Mix3 28-Day Middle	14	24	16	11	110	25	24	2.0	8.1	130	20
30% Mix3 28-Day Edge	13	25	16	11	110	27	25	1.6	8.3	120	21

TABLE 22

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	Al mg/g	Ba mg/g	Ca mg/g	Cl µg/g	Fe mg/g	Mg mg/g	Na mg/g	S %	Sr µg/g	Ti mg/g	V µg/g
20% Mix9 1-Day Center	18	0.38	350	110	45	14	0.48	5.3	420	0.87	47
20% Mix7 7-Day Center	16	0.31	350	100	44	14	0.42	5.5	450	0.78	39
20% Mix4 14-Day Center	16	0.27	360	120	41	14	0.37	5.5	430	0.73	38
20% Mix1 28-Day Center	16	0.36	360	90	41	14	0.35	5.6	430	0.67	36
30% Mix8 1-Day Center	15	0.24	300	100	31	13	0.41	5.6	430	0.53	39
30% Mix6 7-Day Center	17	0.22	320	100	37	13	0.38	5.5	450	0.44	39
30% Mix5 14-Day Center	17	0.31	320	100	45	14	0.44	5.5	430	0.88	39
30% Mix3 28-Day Center	17	0.35	340	90	45	14	0.39	5.6	450	0.81	37
20% Mix9 1-Day Middle	19	0.33	350	110	49	14	0.41	5.4	430	0.93	45
20% Mix7 7-Day Middle	16	0.28	350	110	44	14	0.37	5.4	450	0.77	40
20% Mix4 14-Day Middle	16	0.34	350	100	41	13	0.35	5.4	430	0.76	37
20% Mix1 28-Day Middle	16	0.26	360	94	40	13	0.37	5.5	410	0.68	36
30% Mix8 1-Day Middle	17	0.21	320	100	39	14	0.42	5.5	390	0.48	38
30% Mix6 7-Day Middle	16	0.19	320	100	34	14	0.41	5.5	390	0.40	39
30% Mix5 14-Day Middle	17	0.27	310	100	45	13	0.39	5.6	410	0.88	39
30% Mix3 28-Day Middle	16	0.38	350	82	43	14	0.57	5.5	430	0.82	37
20% Mix9 1-Day Edge	18	0.29	350	110	46	14	0.59	5.5	450	0.88	43
20% Mix7 7-Day Edge	16	0.26	360	110	41	14	0.38	5.5	460	0.69	37
20% Mix4 14-Day Edge	16	0.24	360	110	40	14	0.37	5.6	440	0.73	37
20% Mix1 28-Day Edge	16	0.26	360	96	41	14	0.54	5.6	460	0.70	35
30% Mix8 1-Day Edge	16	0.21	320	110	38	14	0.43	5.5	410	0.48	39
30% Mix6 7-Day Edge	16	0.30	310	110	42	13	0.41	5.6	430	0.88	38
30% Mix5 14-Day Edge	17	0.28	330	96	45	14	0.50	5.6	420	0.86	38
30% Mix3 28-Day Edge	16	0.22	340	100	41	13	0.36	5.5	420	0.76	38

TABLE 23

Chemical Analysis of TVA/Shawnee Drillings for Ash-Conditioning Trace Element Mobility Study

Sample Identification	As µg/g	Cr µg/g	Cu µg/g	Pb µg/g	Mn µg/g	Mo µg/g	Ni µg/g	Se µg/g	Y µg/g	Zn µg/g	Zr µg/g
20% Mix9 1-Day Center	13	25	17	12	110	27	24	2.2	8.5	150	22
20% Mix7 7-Day Center	13	25	18	10	110	26	26	1.6	7.8	180	17
20% Mix4 14-Day Center	14	25	13	11	110	28	25	1.9	8.1	130	19
20% Mix1 28-Day Center	14	23	12	9.6	110	30	24	1.3	7.9	150	17
30% Mix8 1-Day Center	14	23	12	16	110	27	23	3.8	8.4	140	10
30% Mix6 7-Day Center	12	27	14	15	110	29	27	3.9	9.1	120	12
30% Mix5 14-Day Center	15	26	15	11	110	26	23	2.4	7.5	130	21
30% Mix3 28-Day Center	16	25	18	11	100	27	23	1.6	8.2	130	21
20% Mix9 1-Day Middle	13	27	18	11	110	28	25	2.3	7.8	150	16
20% Mix7 7-Day Middle	14	26	16	11	110	28	25	1.8	8.4	130	18
20% Mix4 14-Day Middle	14	24	13	8.9	110	27	26	1.4	7.3	130	13
20% Mix1 28-Day Middle	13	23	14	9.2	100	26	24	1.8	7.8	120	14
30% Mix8 1-Day Middle	15	24	12	15	110	24	24	4.8	8.6	150	12
30% Mix6 7-Day Middle	14	25	12	15	110	26	25	3.8	8.8	130	12
30% Mix5 14-Day Middle	14	25	13	13	110	29	24	2.4	8.4	120	18
30% Mix3 28-Day Middle	14	24	16	11	110	25	24	2.0	8.1	130	20
20% Mix9 1-Day Edge	14	26	17	13	110	28	26	2.2	8.3	160	19
20% Mix7 7-Day Edge	14	25	14	8.9	110	28	27	2.4	7.6	150	17
20% Mix4 14-Day Edge	15	24	13	9.3	110	27	23	2.0	7.5	140	24
20% Mix1 28-Day Edge	13	23	13	8.9	100	25	23	2.0	7.1	150	14
30% Mix8 1-Day Edge	13	26	12	15	110	27	26	3.8	8.3	130	3
30% Mix6 7-Day Edge	14	25	17	15	110	29	24	2.7	7.7	130	21
30% Mix5 14-Day Edge	13	24	16	12	100	26	22	2.3	8.2	130	22
30% Mix3 28-Day Edge	13	25	16	11	110	27	25	1.6	8.3	120	21

various curing times for all points in a slice of the original sample cylinder at a single moisture level. The second set groups the results by location of the drill site in the original cylinder over time at a single moisture level.

The chemical analyses results, in conjunction with the mineralogical results, indicate that the mobility of elemental constituents in conditioned AFBC residues is virtually nondetectable. Results of the total chemical analysis are the same within the variability of the analytical method and the heterogeneous nature of these residues. Statistical analysis of these results was not performed, as general observations were adequate to conclude that the mobility of major, minor, and trace element constituents was very low even at the lowest curing times and moisture contents. Even the most mobile constituents, such as chloride and sodium, showed no trend of mobility in this study. The only mineralogical changes that were noted between 1-day curing and 28 days of curing was the formation of gypsum, which is a hydrated form of $CaSO_4$. Anhydrite, the nonhydrated form of $CaSO_4$, was present in the sample at 1-day curing time in all cases. Only one sample, the Black Dog AFBC at 37% moisture, showed the development of ettringite ($Ca_6Al_2[SO_4]_3[OH]_{12}\cdot26H_2O$) in the sample that had cured for 28 days.

Leaching characterization of these conditioned materials is planned at a future date. The leaching characterization will include short- and long-term leaching procedures. This study will provide extremely beneficial supplemental information when complete.

3.3 Bituminous Coal Fly Ash Data Collection and Evaluation

3.3.1 Introduction

The Western Fly Ash Research, Development, and Data Center (WFARDDC) is a research group funded by a consortium of sponsors interested in the utilization and safe economical disposal of coal by-products. A major research effort since the initiation of the WFARDDC has been the development of a database of information on the physical, chemical, and mineralogical properties of low-rank coal by-products, primarily fly ash. A database, such as the one generated by the WFARDDC, provides a valuable source of scientific and engineering information. The format is useful in identifying trends and specific information pertinent to current and potential utilization applications as well as disposal scenarios and research projects involving coal by-products. The current version of the Western Fly Ash Database contains entries representing more than 500 samples of low-rank coal by-products. WFARDDC researchers have begun a statistical evaluation of the information in this database. Information continues to be entered into the database, and the evaluation process is continuing. The initial evaluation of the database has provided valuable information regarding low-rank coal by-products and has initiated interest in researchers, electric power utilities, coal by-products marketers, and others to extend the database to include similar information on bituminous coal by-products. Bituminous coal fly ash is of particular interest due to the high volume of this material utilized and disposed, primarily in the midwest and eastern United States. A database of information on bituminous coal fly ash has the potential to provide information valuable to the electric utility industry as it strives to meet regulatory mandates, such as the Clean Air Act, by blending coal and utilizing alternate coal combustion methods and by-product collection systems.

The effort to collect and evaluate physical, chemical, and mineralogical information on bituminous coal fly ash will result in a database that can be merged with the current Western Fly Ash Database or be utilized as a stand-alone database. As with the current database, the information will not identify the by-products by electric utility or company affiliation to guarantee anonymity to the participants in this effort.

Interaction with utilities, coal ash marketers and end users, as well as research groups in the areas of coal combustion technologies and environmental systems, has indicated a strong interest in the characteristics of solid by-products or residues from advanced coal combustion technologies. In order to facilitate a scientific and engineering understanding of the characteristics of these materials, this task was expanded to include the development of a database of information on the physical, chemical, and mineralogical characteristics of advanced coal process residues. This preliminary investigation will provide information on which standard engineering and analytical tests are applicable and what new or innovative testing may provide more valuable and predictive information. It will also provide a basis for comparison of the residues generated by various technologies with each other and conventional solid by-products.

3.3.2 Objective and Scope

The primary objective of this task is to collect and evaluate information on the physical, chemical, and mineralogical properties of bituminous coal fly ash and to generate a database of this information. Information of this type that is unavailable through identified sources will need to be generated at the EERC's laboratory facilities. Research staff in the Coal By-Products Utilization Laboratory (CBUL), Analytical Research Laboratory (ARL), and the Natural Materials Analytical Laboratory (NMAL) have extensive experience in both standard testing protocols and numerous research projects on coal conversion by-products, including continuing WFARDDC efforts. These laboratories are equipped with state-of-the-art instrumentation and have extensive analytical and testing capabilities.

The availability of information of interest for the proposed database will be assessed through other research organizations, such as the Electric Power Research Institute, electric power utilities, coal ash marketers, and other groups associated with the coal by-products industry. The inquiries for this information will include mainly sources in the United States; however, foreign sources will be used where readily available. The information will be collected from voluntary participants. Information that is unavailable will be generated at the EERC's facilities from samples of bituminous coal fly ash submitted by identified participants. The evaluation phase of this task allows for the identification of additional information for inclusion in the database as the task continues. A database will be generated; however, the nature of this task implies that the database content and format will evolve over the time frame of the task. A bituminous coal fly ash database will be assembled in a final form for distribution at the conclusion of this task, but it is expected that expansion of the database will continue as has been the case with the Western Fly Ash Database.

An additional objective for the final year of this task is to assemble a database of information on residues from advanced coal processes. The work plan is similar in scope and format to the workplan on bituminous coal fly ash. There will be two major differences in the effort: 1) evaluation of current characterization methods as they apply to advanced coal process residues and development of new methods/techniques where required, and 2) a majority of the samples for inclusion in the database will be obtained from research projects at the EERC or from the Department of Energy (DOE).

3.3.3 Bituminous Coal Fly Ash Data Collection and Evaluation Results

The primary objective of this task--to collect and evaluate information on the physical, chemical, and mineralogical properties of bituminous coal fly ash--is a long-term objective that will continue for the EERC coal by-products research group well past the end of this task. During the time frame of this specific task, the primary objective has been met to the expected level. The primary end result of this effort has been the construction of a database of information on bituminous coal fly ash. The construction of the database also provided opportunities to relate the by-product properties and production to the overall coal-fired electric power generation facility. As a result, several observations can be made that should significantly impact the overall understanding of the coal combustion by-product utilization industry, the by-product disposal practices, the functional relationships within a utility, and the impact of research in these areas. These observations, coupled with the technical expertise required to generate the characterization information for the database and the database itself, should provide useful insight for the research community to address important waste management issues.

A preliminary hard copy version of the Lotus® 1-2-3® spreadsheet format of the bituminous coal fly ash database is included in this report as Appendix A. A key defining the terms used in the spreadsheet is also included in Appendix A. The components of the database as included in this report are the major and minor elemental constituents (expressed as oxides), mineral phases identified in the crystalline portion of the fly ash, selected physical properties and test results relevant to the utilization of fly ash as a mineral admixture in concrete, and information on the operating system and coal source.

The chemical characterization information consists of two groups. The first is the results as dictated by the American Society for Testing and Materials (ASTM) C618 (1991). The chemical composition information required by ASTM to classify fly ash is the total concentration of silicon, aluminum, iron, sulfur, and calcium. Magnesium, sodium, and potassium are included in the ASTM procedures as alternate information. These have also been included in the database for as many samples as possible. Test results from the ASTM designated procedures for moisture (mass of water lost at 105°-110°C), loss on ignition (LOI, mass lost at 750°C), and available alkali (soluble sodium and potassium reported as equivalents of Na_2O) are also included in the database. The second portion of the chemical information in the database includes total concentrations of other minor elemental constituents. These elements were phosphorus, titanium, barium, manganese, and strontium. In keeping with the ASTM convention for reporting the concentrations of major elements in fly ash, all major and minor elemental concentrations were calculated and reported as the common oxides. ASTM also requires the sum of the SiO_2, Al_2O_3, and Fe_2O_3 values for evaluation under C618. This value is also included in the database under "Sum." Table 24 lists all elemental constituents included in the chemical characterization scheme and the common oxide form used for reporting purposes.

TABLE 24

Elemental Constituents Analyzed in Fly Ash and Common Oxides Used for Reporting Purposes

Element	Common Oxide
	ASTM C618 Requirements
Silicon	SiO_2
Aluminum	Al_2O_3
Iron	Fe_2O_3
Sulfur	SO_3
Calcium	CaO
	Alternate ASTM C618 Tests
Magnesium	MgO
Sodium	Na_2O
Potassium	K_2O
	Minor Elemental Constituents
Phosphorus	P_2O_5
Titanium	TiO_2
Barium	BaO
Manganese	MnO_2
Strontium	SrO

In the physical portion of the database, the tests performed were fineness (325 sieve test), specific gravity, pozzolanic activity test with portland cement (28 day), pozzolanic activity with lime (7 day), water requirement, and autoclave expansion. These tests are also included in the ASTM C618 "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan as a Mineral Admixture in Portland Cement Concrete." These procedures were performed in accordance with ASTM C311 (1990).

Fly ash mineralogy was determined by a semiquantitative x-ray powder diffraction protocol developed by Dr. Gregory McCarthy at North Dakota State University (McCarthy et al., 1990). This method uses the "Reference Intensity Ratio," where rutile (TiO_2) is the internal intensity standard. Fly ash is composed of crystalline and amorphous or glassy phases. X-ray diffraction only identifies the crystalline phases. Future research may include the use of scanning electron microscopy point count (SEMPC) to determine the chemistry of the amorphous phases. Crystalline phases, mineralogy codes, and nominal chemical compositions are included in Table 25.

TABLE 25

Crystalline Phases, Mineralogy Codes, and Nominal Chemical Compositions

Crystalline Phase	Mineralogy Code	Composition
Anhydrite	Ah	$CaSO_4$
Tricalcium Aluminate	C3A	$Ca_3Al_2O_6$
Hematite	Hm	Fe_2O_3
Lime	Lm	CaO
Melilite	Ml	$Ca_2(Mg,Al)(Al,Si)_2O_7$
Mullite	Mu	$Al_6Si_2O_{13}$
Merwinite	Mw	$Ca_3Mg(SiO_4)_2$
Periclase	Pc	MgO
Quartz	Qz	SiO_2
Ferrite Spinel	Sp	$(Mg,Fe)(Fe,Al)_2O_4$

Ash fusion was also performed on most samples represented in the database. The ash fusion procedure was performed according to ASTM D1857 (1968), and ash fusion temperatures in both an oxygen atmosphere (O_2) and a reducing atmosphere (CO_2) were generated. The test requires marking various temperatures as a preformed triangular pyramid (cone) passes through certain defined stages of fusing and flow when heated at a specified rate in controlled atmospheres. There are four stages to this fusing:

1. Initial deformation temperature (IT): the first rounding of the apex of the cone

2. Softening temperature (ST): the cone has fused down to a spherical lump in which the height is equal to the width at the base

3. Hemispherical temperature (HT): the cone has fused down to a hemispherical lump at which the height is one half the width of the base

4. Fluid temperature (FT): the fused mass has spread out in a nearly flat layer with a maximum height of 1/16 inch

The ideal cone shape for each of the critical temperature points is shown in Figure 13. Ash fusion temperatures are useful in determining ash behavior in boilers and potentially for use of these materials in high-temperature utilization technologies.

As noted earlier in this section, some important observations regarding the understanding of the coal combustion by-product utilization industry, the by-product disposal practices, the functional relationships within a utility, and the impact of research in these areas, were made over the duration of this task. These observations can be summarized as follows:

- Coal combustion fly ash is an underutilized resource in the United States. Government agencies, utilities, and research organizations need to coordinate efforts to promote ash use in current proven applications and extend ash use to new markets and applications.

- ASTM has set standards and specifications for the use of coal combustion fly ash in specific applications; however, these standards and specifications can be misleading and may be misapplied. Industry and research groups need to continue participation in ASTM committee work to maintain appropriate standards and to develop new and improved standards and specifications where needed.

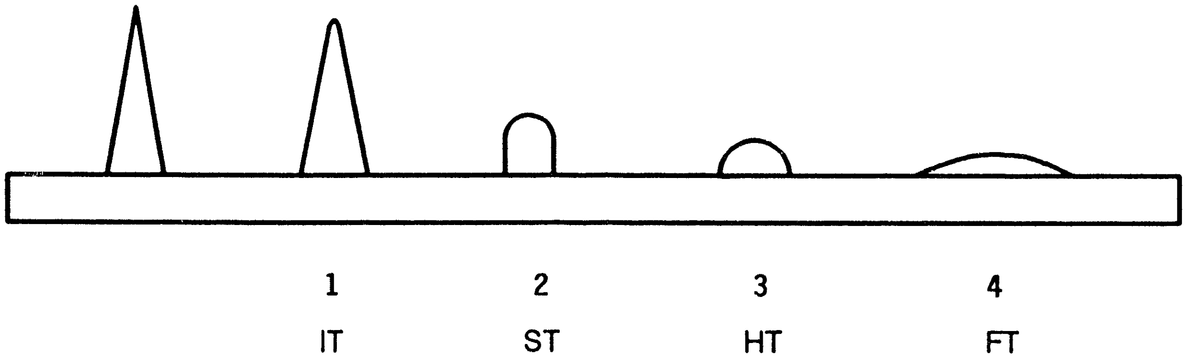


Figure 13. Critical temperature points and associated cone shapes for ash fusion test procedure (ASTM D1857).

- Regulatory agencies should encourage the use of coal combustion fly ash in proven applications. The use of coal combustion fly ash is consistent with the current emphasis on reuse and recycle. The use of this high-quality and lower-cost material can provide an economic advantage in rebuilding and expanding the U.S. infrastructure.

- Coal combustion fly ash should not be categorized as a waste material when it is utilized in engineering or other applications. Coal combustion fly ash should only be designated as a waste in the event the material requires disposal.

- Coal combustion fly ash must not be compared to, or confused with, fly ash resulting from the combustion of other materials, such as municipal solid waste or refuse. It is incorrect and inappropriate to regulate "ash" as a single type of material.

- Coal-fired electric generation facilities need to consider the production of coal combustion fly ash and other solid residues as an additional product resulting from their operations. This will become particularly advantageous as additional environmental restrictions are placed on air emissions and solid waste disposal. Production of a usable and salable solid residue will be highly advantageous.

- Conventional coal fly ash will likely change in character as advanced coal combustion techniques, clean coal technologies, and new emissions control technologies become more prevalent. These new characteristics need to be investigated for utilization potential immediately to fit them into the current market and develop new markets for the future.

3.3.4 Advanced Coal Process Residues Database Results

A preliminary spreadsheet database of information on residues from various advanced coal processes has been generated. The effort involved required to complete this database is beyond the scope of this task; however, identifying and characterization information available at the EERC, through past and ongoing research projects involving these "new" coal conversion residues, has been collected and placed in a Lotus® 1-2-3® spreadsheet as the initial step toward constructing a complete database similar in scope to the coal combustion fly ash database (which now includes the bituminous coal fly ash database). As the required characterization and identifying information needed for the advanced coal process residues database is identified and obtained, this additional database will be formalized and eventually connected to the coal combustion fly ash database.

Part of the effort required to begin generating reliable and reproducible mineralogical characterization information on advanced coal process residues was to develop a semiquantitative x-ray powder diffraction technique. The protocol was developed by Dr. Gregory McCarthy at North Dakota State University under a subcontract to the EERC. The protocol uses the Reference Intensity Ratio, which requires mixing a fixed amount of an internal standard with each residue. Rutile (TiO_2), the internal standard used for coal combustion fly ash, produced peaks overlapping with analytical peaks of the new phases in the advanced coal process residues. An alternative internal standard, zinc oxide (ZnO), was identified.

3.4 Waste Depository Scavenger Study

3.4.1 Introduction

The initial goal of the Waste Depository Scavenger task was to develop a blend of scavenging materials, such as zeolite and clay minerals and chars, which have a high potential to inhibit the migration of mobile contaminants from certain types of waste depositories. These materials would be incorporated into landfills, possibly within the liners, and would be composed of the most appropriate scavenging agents, depending on the leachate contaminants present in the depository. Appropriate sampling and analysis of these scavenging materials would provide a means to reconstruct contaminant migration in both vertical and horizontal directions.

Constructing large depositories for municipal and industrial waste has become a standard waste management practice. Monitoring potentially hazardous leachate migrating from a waste depository is a critical responsibility to prevent groundwater and soil contamination. Current monitoring techniques, which consist of sampling and analysis of materials around the depository, are inadequate. This type of analysis can be inaccurate due to the heterogeneity of the materials and the virtually undetectable compositional changes with time.

Contaminants emanating from municipal waste include lead, copper, zinc, and, contaminants migrating from fly ash waste include boron, molybdenum, arsenic, and selenium. Remediation of these types of contaminants is expensive and sometimes problematic. Inexpensive waste-cell liners composed of abundant natural materials could be an economical way to immobilize contaminants.

Ion exchange in zeolites has been studied and documented in the literature. Clinoptilolite, a common zeolite, is a framework aluminosilicate mineral with the general formula $(Na,K)_6(Al_6Si_{30}O_{72})\cdot 20H_2O$. Clinoptilolite and many other zeolites occur mainly in microcrystalline sedimentary masses which usually form by the reaction of pore water with volcanic material. Relatively large windows (which are several angstroms wide) or "channels" within the clinoptilolite structure easily hold large ions. The ion exchange capabilities of clinoptilolite have been extensively studied, mainly because of its ability to scavenge cesium^{137} from radioactive waste and ammonium ions from municipal waste (Mercer and Ames, 1978). Clinoptilolite is stable to a pH of less than 2, which is important if the scavenging material will be exposed to weathering processes.

3.4.2 Research Scope

A two-phase test plan was used to determine contaminant migration and sorptive capacity of the scavenger materials. The first phase involved the evaluation of structural and chemical properties of the proposed scavenger materials. The second phase involved the use of batch testing and percolation experiments to determine contaminant sorption of the scavenger. The proper composite mixture of scavenging agents for optimum immobilization of a variety of contaminants will be addressed in the continuation of this research.

Initially, the clinoptilolite was tested for its ability to immobilize ions such as selenium, molybdenum, copper, and lead. Common municipal landfill contaminant ions of lead and copper were chosen for initial experiments because clinoptilolite has a strong affinity for both of these ions. Selenium and molybdenum were chosen for the first percolation experiment because they are common constituents in fly ash leachate. These ions were also selected because they are soluble in water and can be easily detected with the analytical tools at our disposal. Initial funding for this task was limited; therefore, testing of clay minerals for the adsorption of cations and testing of chars or lignites for the adsorption of organics have not been initiated. In subsequent testing, these scavenging materials will be combined and tested for their ability to immobilize a variety of contaminants found in waste depositories.

3.4.3 Results

3.4.3.1 Initial Materials Characterization

Initially, samples of zeolites from the Sentinel Butte and Bullion Creek Formations of western North Dakota were targeted for utilization in these experiments. Mineralogical characterization using XRD indicated that these samples were composed mainly of analcime. Analcime is not capable of efficient ion exchange at ambient temperatures, so this material was not utilized in this research.

Clinoptilolite from East West Minerals Company, Denver, Colorado, was analyzed by XRD to determine other phases present and was found to be nearly homogeneous, with only a minor amount of quartz. The XRD results indicated that the clinoptilolite has a structure similar to sodium-rich zeolites, but SEM/EPMA revealed that the zeolite was more potassium- than sodium-rich (Table 26). This indicates that XRD data should be compared to SEM/EPMA analyses to properly determine the chemical constituents of a crystalline phase. Often XRD peaks may be shifted due to sample preparation techniques or instrumentation settings. Photomicrographs were taken to document the morphology of the crystals.

For the percolation experiments, 20 wt% of the clinoptilolite and 80 wt% of the silica sand was mixed to obtain a permeable material. A portion of the original clinoptilolite/sand mixture was submitted for XRF analysis to determine if trace amounts of selenium or molybdenum were present in the mixture. No molybdenum was detected, but selenium was present in small amounts, probably in quantities less than 10 ppm. The presence of selenium in the clinoptilolite/sand mixture indicates that the material may be suitable for scavenging selenium. The percolation tests will determine if this hypothesis is correct.

TABLE 26

SEM/EPMA Results for Clinoptilolite (Normalized Weight Percents)

No.	SiO_2	Al_2O_3	TiO_2	FeO	MgO	MnO	CaO	Na_2O	K_2O	Label
1	76.06	13.44	0.00	0.47	0.34	0.00	1.09	2.52	6.08	x-91-183.1
2	76.35	13.32	0.00	0.43	0.42	0.00	0.54	2.60	6.34	x-91-183.2
3	75.81	11.93	0.36	3.94	0.46	0.00	1.22	1.03	4.86	x-91-183.3
4	76.61	13.70	0.00	0.41	0.64	0.53	0.48	3.33	4.30	x-91-183.4
5	77.73	12.46	0.00	0.00	0.23	0.35	0.89	1.40	5.75	x-91-183.5
6	71.22	12.25	0.40	4.29	2.97	0.24	1.96	1.77	4.47	x-91-183.6
7	75.81	12.13	0.00	1.57	0.47	0.00	1.73	0.28	6.74	x-91-183.7
8	74.81	10.79	1.24	4.02	0.40	1.01	1.45	0.22	6.07	x-91-183.8
9	77.51	12.18	0.00	0.51	0.42	0.59	1.02	1.79	4.95	x-91-183.9
10	79.93	12.52	0.29	0.76	0.28	0.00	0.53	1.28	3.92	x-91-183.10

3.4.3.2 Batch Experiments

After the initial characterization of the materials, the next phase of this research was to determine the amount of contaminants that the clinoptilolite could immobilize. Initial "batch" testing involved reacting the clinoptilolite with a small portion of a solution containing contaminant species. The first tests used a 1 M (molar) solution of $CuSO_4 \cdot 5H_2O$. This high concentration of copper would not normally be found in a field setting, but was used to allow for easy detection of changes in weight between samples. Copper sulfate was used because of its high solubility in water.

For these batch experiments, one gram of clinoptilolite was added to 10 mL of the copper solution. The sample was then shaken by a mechanical mixer (a Spex mill which is commonly used to attrition samples for XRD analysis) for varying lengths of time to allow the solution and solid to reach equilibrium. The analysis of the samples revealed that when the clinoptilolite and solution were shaken for 1 hour, a noticeable attritioning of grains and the formation of clay-sized particles occurred. Subsequent analysis of these attritioned samples showed that they did not immobilize the copper as efficiently as the samples that had been shaken for only 40 minutes. This difference may be due to the destruction, during shaking, of open channels within the clinoptilolite where the copper would be adsorbed. When nonattritioned, the clinoptilolite can immobilize a large amount of copper from solution.

Lead is another common constituent found in municipal waste leachate and was used for the next set of batch experiments. A 1 wt% solution of $Pb(NO_3)_2$ and distilled-deionized water was reacted with the clinoptilolite using the same "batch" testing method as used for the copper sulfate solution. The reacted and unreacted samples were submitted for inductively coupled argon plasma (ICAP) analysis, which is used to determine the concentration of ions in solution.

The unreacted (control) sample contained approximately 6800-ppm (parts per million) lead in solution (Table 27). The reacted sample indicated that the clinoptilolite immobilized approximately 98% of the lead out of solution. This ability of clinoptilolite to scavenge copper and lead out of solution is a very promising characteristic that may lead to utilization of this material in municipal waste depository liners.

TABLE 27

Results from the Batch Test for Lead

Parameter	Initial (ppm)	Final (ppm)
Na^{+1}	1580	1430
Pb^{+2}	6780	102
NO_3^{-1}	3800	3800

3.4.3.3 Percolation Experiments

The next phase of the project included the completion and setup of one percolation test cell (Figure 14). Sampling ports, which will allow periodic sampling of the percolating solution, were drilled and sealed. Because of the cost of silica beads, an alternative material, a silica sand (97% SiO_2), was chosen to be mixed with the clinoptilolite within the test cell to increase the permeability of the material. The silica sand was analyzed using XRD to determine other constituents, which included plagioclase and potassium feldspars.

The next phase of the waste depository scavenger task will involve the actual percolation experiment. A solution containing 100-ppb selenium and 100-ppb molybdenum with a basic pH (11 to 11.5), to simulate leachate commonly found in fly ash landfills, will be percolated through the clinoptilolite/silica material. Sampling of the solution will occur at regular intervals. Water analyses of the percolating solution will be performed at the ARL using atomic absorption spectroscopy. Several XRD analyses will be performed on the scavenging materials at the completion of the percolation experiment. The XRD results will be compared to the original characterization of the materials to determine changes within the structure of the mineral phases present. These results may indicate if the crystal structure of the clinoptilolite is altered during the percolation experiment.

Some question still remains as to the proper valence states of selenium and molybdenum. For both elements, valence states of +6 were chosen because they represent the most frequently occurring forms of these elements in a fly ash depository, under oxidizing conditions. The selenium/molybdenum solution and the test cell are being prepared for the percolation experiments.

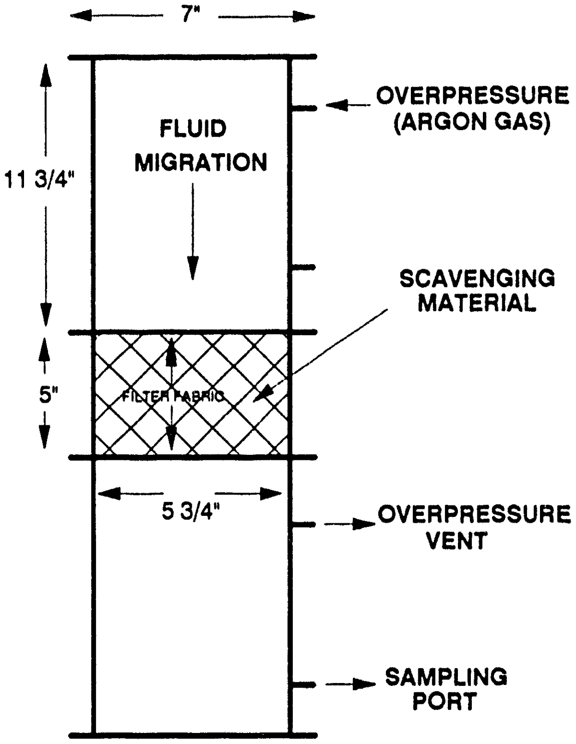


Figure 14. Percolation test cell.

3.4.4 Future Research

The next phase of this project will involve the use of clinoptilolite, a clay, and an activated lignite or char in percolation laboratory test cells. A solution containing several common contaminant constituents in concentrations that would simulate a waste depository leachate setting will be used. The scavenging agents will be packed in layers with more permeable materials interspersed to reduce the time to complete the percolation experiment. The leachate will be collected at regular intervals for water analyses, and the scavenging materials will be analyzed using XRD after completion of the percolation tests.

Development of North Dakota clinoptilolites for use in both present and future experiments will be pursued. Some of the samples collected early in this project from the Killdeer Mountains area of North Dakota were thought to contain bentonite, a clay-containing deposit, but mineralogical characterization by XRD showed them to contain calcite and clinoptilolite. This material could possibly be utilized in future experiments.

Additionally, experimentation to develop methods or treatments to increase the ion-exchange capacity of the scavenging materials in an effort to maximize their efficiency of immobilizing contaminants will be explored. Future research will focus on determining the quantities of contaminants that are permanently immobilized, the quantities that are able to be remobilized from the scavenging agents, and any mineral structural changes that occur during the ion exchange process. This analysis will be useful to characterize the stability of the contaminant-containing scavenging material. The end goal of this task will be to supply the necessary information that will support or oppose the hypothesis that different scavenging materials possess qualities that suit those materials for specific contaminant immobilization. By combining a few selected scavenging materials, an optimum mix will be developed to immobilize several contaminants at a specific site.

4.0 REFERENCES

ASTM C311-90, Method for sampling and testing fly ash or natural pozzolan for use as a mineral admixture in portland cement concrete: Vol. 04.02, Concrete and aggregates.

ASTM C618-91, Specification for fly ash and raw or calcined natural pozzolan for use as a mineral admixture in portland cement concrete: Vol. 04.02, Concrete and aggregates.

ASTM D1857-68, Test method for fusibility of coal and coke ash: Vol. 05.05, Gaseous fuels, coal, and coke.

Bazzel, C.E., and Mallory, R.G., 1987, Disposal of multicyclone and baghouse catch at TVA's 20-MW AFBC pilot plant: Tennessee Valley Authority, West Paducah, KY, p. 967-973.

Bland, A.E., Jones, C.E., Rose, J.G., and Harness, J.L., 1989, Ash management options for AFBC: p. 323-333.

Golden, D., 1988, EPRI R&D on AFBC solid waste management: Current status and future direction.

Grady, C.P.L., Jr., and Lim, H.C., 1980, Biological wastewater treatment: Theory and applications: Marcel Dekker, Inc., New York, NY.

McCarthy, G.J.; Solem, J.K.; Manz, O.E.; Hassett, D.J., 1990, Use of a database of chemical, mineralogical and physical properties of North American fly ash to study the nature of fly ash and its utilization as a mineral admixture in concrete, *In* Day, R.L. and Glasser, R.P., eds., Proceedings of Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal VI: Vol. 178, p. 3-33.

Mercer, B.W., and Ames, L.L., 1978, *Zeolite exchange in radioactive and municipal wastewater treatment*, *In* Sand, L.B., and Mumpton, F.A., eds., Natural zeolites: Occurrence, properties, use: London, Pergamon Press, p. 451-462.

Reynolds, Tom D., 1982, Unit operations and processes in environmental engineering: Brooks/Cole Engineering Division, Monterey, CA,

RP 2708-1, 1988, Concept design guidelines for atmospheric fluidized combustion waste management: EPRI CS-6053 Final Report, December 1988, Prepared by Baker/TSA, Inc., Coraopolis, Pennsylvania, and ICF Technology Inc., Richland, Washington, Sections 3, 5, 7, 8.

Smith, I.M., 1989, Management of AFBC residues: Draft Report, IEA Coal Research, August 1989.

Standard methods for the examination of water and wastewater, 16th Ed.: American Public Health Association, Washington D.C., 1985.

Suidan, M.T. et al., 1987, Anaerobic wastewater treatment, final report: Fossil Energy Publication, DOE/MC/21281-2562, Department of Energy, Nov.

Wark, K., and Warner, C.F., 1981, Air pollution: Its origin and control, 2d ed.: New York, Harper and Row Publishers, p. 219-233.

APPENDIX A

BITUMINOUS COAL FLY ASH DATABASE

SOURCE OF COAL	BOILER TYPE\MANUFACTURER	PARTICULATE REMOVAL	COAL TYPE	CBUI NO.	ASTM C 618 Chemical Compositions (wt %)										ADDITIONAL CHEMICAL DATA						
					SiO2	Al2O3	Fe2O3	Sum	SO3	CaO	MgO	H2O	LOI	AA	Na2O	K2O	P2O5	TiO2	BaO	MnO2	SrO
KY, E.VA.	PC TANGENTIAL/RS	ESP\RC	BIT	81.0219	47.70	33.60	12.40	93.70	0.45	1.00	0.90	0.08	3.42	0.41							
EMERY CO.,UTAH		ESP\BUELL	BIT	82.0202	59.30	20.00	3.70	83.00	0.38	6.50	2.30	0.06	2.85								
EAST KENTUCKY		ESP\AMSTAND&CARB.	BIT	82.0354	62.30	17.60	4.30	84.20	1.33	3.30	0.90	0.09	10.22	1.31	1.50	1.10					
EAST KENTUCKY		ESP\AMSTAND&CARB.	BIT	82.0355	65.30	16.70	4.20	86.20	1.20	4.00	1.10	0.06	7.66	1.35	1.60	1.20					
KY, E.VA.	PC TANGENTIAL/RS	ESP\RC	BIT	82.0361	51.20	24.60	9.80	85.60	0.38	1.40	0.90	0.04	4.33	0.39							
BALDWIN, IL		ESP\RC	BIT	83.0062	50.90	19.20	16.50	86.60	1.10	6.20	1.20	0.07	0.78	0.69	0.72	1.95					
EAST KENTUCKY		ESP\AMSTAND&CARB.	BIT	83.0106	54.70	29.90	4.50	89.10	0.27	1.10	0.80	0.19	4.99	0.45	0.27	2.55					
KY, E.VA.	PC TANGENTIAL/RS	ESP\RC	BIT	83.0157	49.20	29.90	8.90	88.00	0.40	1.90	0.80	0.05	5.03	0.46							
KY, E.VA.	PC TANGENTIAL/RS	ESP\RC	BIT	83.0257	48.30	29.90	8.20	86.40	0.43	1.60	0.70	0.09	5.68	0.46							
IL., IN		ESP\BUELL	BIT	83.0509	50.00	22.30	13.70	86.00	1.65	3.60	1.40	0.24	1.36	0.98	0.84	2.74					
E.KY, VA.	PC TANGENTIAL/RS	ESP\RC	BIT	84.0033	49.20	29.50	9.00	87.70	0.50	1.70	1.00	0.10	4.65	0.55							
UTAH		ESP&MULTI\RC	BIT	85.0238	51.40	10.60	8.40	70.40	1.62	21.20		0.40	1.00	0.33							
WYOMING		ESP&MULTI\RC&LC	BIT	85.0239	58.50	18.20	7.40	84.10	0.70	7.40		0.32	0.26	0.38							
PENNSYLVANIA		BAGHOUSE\CARB.	BIT	85.0241	48.00	26.30	10.40	84.70	0.85	1.60		0.16	5.92	0.29							
PENNSYLVANIA		ESP\RC&BUELL	BIT	85.0242	48.50	28.50	13.90	90.90	0.98	1.60		0.24	4.83	0.22							
PENNSYLVANIA		ESP\WESTERN&RC	BIT	85.0243	49.60	28.30	13.30	91.20	1.35	1.40		0.90	3.63	0.21							
BALDWIN, !L		ESP\RC	BIT	85.0327	50.20	18.70	15.80	84.70	1.15	15.80	1.00	0.15	0.62	0.70	0.90	2.00					
PENNSYLVANIA		BAGHOUSE\WF	BIT	86.0235	58.70	26.40	6.20	91.30	0.35	1.00	0.90	0.07	3.37	0.74	0.40	2.50					
PENNSYLVANIA		ESP\WESTERN	BIT	86.0993	47.70	26.90	12.00	86.60	0.09	2.70		0.23	2.25	0.25							
EMERY CO.,UTAH		BH\FLAKT	BIT	86.0998	63.00	19.90	3.60	86.50	0.75	5.40		0.01	2.12	0.62							
ARIZONA		ESP\RC	BIT	86.1175	55.70	21.50	5.40	82.60	0.42	8.00		0.02	1.83	0.67							
EAST KENTUCKY		ESP\AMSTAND&CARB.	BIT	87.0002	65.30	18.20	3.60	87.10	0.38	5.90		0.04	0.88	0.76							
EMERY CO.,UTAH		WET VENTURI	BIT	87.0025	61.00	18.30	3.30	82.60	0.48	5.70		0.03	4.54	0.86							
EMERY CO.,UTAH		BH\FLAKT	BIT	87.0026	59.80	19.80	3.90	83.50	0.78	5.90		0.04	3.30	0.69							
EAST KENTUCKY		ESP\AMSTAND&CARB.	BIT	87.0038	66.50	16.60	4.50	87.60	0.32	5.20		0.05	0.26	0.76							
MANSFIELD, LA		ESP\UOP	BIT	87.0157	52.77	23.63	8.87	85.27	0.36	9.50	2.67	0.02	0.01	1.64	1.09	0.84					
PA., OH., KY., WV.	DRY BOTTOM/B&W	ESP\WESTERN	BIT	90.0198	49.80	25.20	15.20	90.20	0.83	2.27	0.91	0.11	1.92	0.67	0.46	2.20					
CLINCHFIELD COAL		ESP\KOPPERS	BIT	90.0199	49.50	26.30	7.75	83.55	0.98	5.50	1.75	0.06	1.13	1.15	0.50	3.23					
CZECHOSLOVAKIA	N/A	N/A	BIT	90.0200	57.20	25.30	8.48	90.98	0.27	1.95	1.22	0.16	1.00	0.81	0.31	1.44					
WOLFE CREEK	CYCLONE/RS	ESP\BUELL	BIT	90.0201	48.40	30.50	7.97	86.87	1.02	2.39	0.83	0.20	3.35	0.91	0.41	2.11					
N/A	N/A	N/A	BIT	90.0202	52.20	20.10	8.39	80.69	0.75	3.07	1.51	0.11	10.30	0.83	0.15	1.77					
PENNSYLVANIA		ESP\WESTERN	BIT	90.0203	49.00	27.40	11.90	88.30	0.90	2.45	0.91	0.12	2.60	0.60	0.24	2.34					
MARRIBONE	CYCLONE/FW	ESP\BELCO	BIT	90.0204	56.20	32.00	3.13	91.33	0.16	0.66	0.90	0.02	2.65	1.00	0.79	2.72					
IL., WY	PC	ESP\LC	BIT	91.0042	45.57	21.15	7.92	74.64	1.30	15.72	3.28	0.01	0.48	0.70	0.91	1.27	0.70	1.37	0.41	0.04	0.26
IL., WY	PC	ESP\LC	BIT	91.0043	48.58	20.25	9.13	77.96	0.97	12.27	2.84	0.01	1.34	0.87	1.00	1.80	0.40	1.29	0.25	0.05	0.21
IL., WY	CYCLONE	ESP\RC	BIT	91.0052	42.76	17.56	19.20	79.52	1.60	4.49	1.32	0.34	3.52	1.42	1.35	2.95	0.21	1.35	0.07	0.04	0.05
IL., WY	CYCLONE	ESP\RC	BIT	91.0053	39.18	15.16	16.36	70.70	1.60	4.94	1.03	0.16	18.85	0.62	0.70	1.80	0.19	0.95	0.05	0.04	0.04
MARRIBONE	CYCLONE/FW	ESP\BELCO	BIT	91.0086	58.02	32.00	3.17	93.19	0.15	0.65	0.83	0.05	2.07	0.65	0.22	2.69	0.07	1.45	0.06	0.02	0.04
WOLFE CREEK	CYCLONE/C-E	ESP\BUELL	BIT	91.0087	56.47	28.53	6.51	91.51	0.23	0.64	1.19	0.02	4.41	0.84	0.44	3.56	0.05	1.12	0.07	0.03	0.04
WOLFE CREEK	CYCLONE/RS	ESP\BUELL	BIT	91.0088	54.77	30.62	6.62	92.01	0.32	0.86	0.78	0.05	3.56	0.53	0.24	2.26	0.05	1.34	0.06	0.04	0.05
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0130	58.30	26.80	6.27	91.37	0.39	1.30	1.01	0.13	1.68	1.14	0.31	2.73	0.26	1.76	0.10	0.02	0.09
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0131	57.50	26.10	6.16	89.76	0.68	1.26	0.98	0.24	4.77	1.48	0.30	2.63	0.28	1.71	0.11	0.02	0.09
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0132	59.90	25.10	7.58	92.58	0.23	1.73	0.95	0.06	2.91	0.88	0.29	2.47	0.21	1.59	0.10	0.04	0.09
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0133	60.20	25.50	7.81	93.51	0.27	1.70	0.99	0.07	2.23	0.58	0.31	2.55	0.23	1.61	0.10	0.04	0.10
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0134	58.20	25.20	7.06	90.46	3.97	1.08	0.82	0.11	2.12	0.75	0.26	2.28	0.12	1.52	0.10	<0.01	0.08
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0135	59.40	25.40	7.95	92.75	2.74	1.13	0.86	0.10	3.30	1.09	0.24	2.18	0.13	1.52	0.10	<0.01	0.08
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0136	59.40	25.30	8.23	92.93	0.32	1.83	0.93	0.08	1.66	1.21	0.31	2.47	0.09	1.46	0.11	0.01	0.08
OH, KY, WV	PC_OPPOSED WALL\B&W	ESP\BUELL	BIT	91.0137	58.70	24.40	7.62	90.72	0.28	1.66	0.88	0.08	1.45	0.63	0.30	2.48	0.09	1.42	0.10	0.01	0.09
KOREA		N/A	BIT	91.0138	57.87	25.07	4.07	87.01	0.17	3.37	1.02	0.06	5.28	0.35	0.23	1.34					
KOREA		N/A	BIT	91.0139	38.37	20.83	5.38	64.58	0.51	0.47	0.60	1.06	29.60	0.28	0.12	3.01					
E.KY., VA., WV.		ESP\RC	BIT	91.0174	53.40	30.00	5.76	89.16	0.04	2.06	0.98	0.08	0.91	0.61	0.31	2.07					
KY E., VA, WV		ESP&MULTI\BUELL	BIT	91.0179	49.60	26.90	6.69	83.19	0.44	1.44	1.07	0.07	6.82	1.04	0.08	2.61					
E.KY, VA.	PC TANGENTIAL/RS	ESP\RC	BIT	91.0183	53.97	26.05	10.73	90.75	0.40	2.30	1.21	0.10	3.76	0.99	0.45	2.35	0.34	1.15	0.20	0.02	0.16
E.KY, VA.	PC TANGENTIAL/RS	ESP\RC	BIT	91.0184	52.44	26.19	11.81	90.44	0.50	2.64	1.32	0.10	4.57	1.07	0.49	2.36	0.36	1.48	0.20	0.03	0.16
E.KY.		ESP\C-E	BIT	91.0185	53.15	27.95	9.52	90.62	0.45	1.65	1.65	0.16	3.14	1.06	0.38	2.65	0.69	1.45	0.14	0.02	0.15
E.KY.		ESP\C-E	BIT	91.0186	55.04	28.22	8.74	92.00	0.42	1.69	1.14	0.12	2.93	1.04	0.42	2.63	0.63	1.41	0.14	0.02	0.15
PEOPLES REP. CHINA	N/A	N/A	BIT	91.0208	56.18	28.60	5.30	90.08	0.62	3.46	0.89	0.11	5.41	•	0.35	1.14					

CBUI	ASTM C 618 Physical Test Results						wt % Mineral by XRD										OTHER		(in O2 atm.) ASH FUSION TEMPERATURES (in CO2 atm.)								PARTICAL
NO.	>325	CPAI 28 d	LPAI 7 d	H2O Req.	Auto. Expan.	SG	Ah	Mu	Qz	Ml	Hm	C3A	Mw	Sp	Lm	Pc	MINOR	SUM	I.T.	S.T	H.T.	F.T.	I.T.	S.T	H.T.	F.T.	SIZE
81.0219	29.52	78	834	98	0.01	2.30	0.0	12.0	2.9	0.0	2.3	0.0	0.0	3.7	0.0	0.0		21.0									
82.0202	39.02	53		95	0.22	2.07	0.0	11.4	11.8	0.0	0.0	0.0	0.0	0.4	0.3	0.0		23.9									
82.0354	24.22	96	1420	96	0.14	2.23		12.7	9.8	0.0	0.0	0.0	0.0	0.8	0.0	0.0		23.4									
82.0355	24.81	92	1230	94	0.15	2.24	1.2	11.7	10.6	0.0	0.0	0.0	0.0	1.8	0.0	0.0		25.2									
82.0361	28.67	80	850	97	0.02	2.26	0.0	16.4	3.3	0.0	2.4	0.0	0.0		0.0	0.0		22.1									
83.0062	21.11		1173		0.10	2.37	1.0	6.9	5.2	0.0	2.3	0.0	0.0	8.8	0.0	0.0		24.1									
83.0106	16.23	101	1204	93	0.06	2.22	0.0	16.7	4.9	0.0	0.4	0.0	0.0	0.1	0.0	0.0		22.1									
83.0157	26.09	92	1038	98	0.04	2.20	0.0	13.9	3.2	0.0	1.2	0.0	0.0	1.8	0.0	0.0		20.2									
83.0257	40.11	66	955	100	0.04	2.15	0.0	18.1	2.6	0.0	1.5	0.0	0.0	1.3	0.0	0.0		23.5									
83.0509	8.18	108	900	91	0.01	2.43		7.9	5.1	0.0	3.0	0.0	0.0	3.2	0.0	0.0		19.2									
84.0033	28.62	71	990	95	0.11	2.34		14.3	2.6		0.0			4.0				20.8									
85.0238	21.86	67	775	96	fail	2.60	1.2	12.4	24.4	0.3	14.3	0.0	0.0	2.2	1.7	3.1		67.7									
85.0239	14.53	109	1030	91	0.03	2.45	0.7	5.9	11.4	0.0	0.6	0.0	0.0	3.7	0.0	0.0		22.3									
85.0241	22.85	88	934	101	0.02	2.20	0.0	24.3	7.1	0.0	2.5	0.0	0.0	3.6	0.0	0.0		37.5	2741	2780	•	•	2529	2586	2636	2798	
85.0242	19.67	84	955	102	0.02	2.31	0.0	19.4	4.8	0.0	3.1	0.0	0.0	4.3	0.0	0.0		31.7	2745	2779	•	•	2453	2555	2686	2770	
85.0243	19.37	83	982	101	0.03	2.34	0.0	13.9	4.0	0.0	2.6	0.0	0.0	3.5	0.0	0.0		23.9	2643	2683	2760	2798	2344	2515	2600	2728	
85.0327	20.27					2.38	0.5	9.3	6.1	1.6	2.2	0.0	0.0	4.8	1.5	0.0		27.1	2376	2387	2514	2545	2113	2145	2215	2380	
86.0235	12.26	134	990	88	0.03	2.40	0.3	5.3	4.3					1.3		0.0		12.4	2755	•	•	•	2612	2741	2771	•	
86.0993	21.68	105	923	97	0.07	2.38		14.0	4.1	0.0	2.8	0.0	0.0	3.7	0.0	0.0		24.5	2632	2679	2775	•	2403	2482	2612	2727	
86.0998	17.69	80	849	91	0.10	2.21	0.5	15.0	16.4	0.0	0.0	0.0	0.0	0.8	0.3	0.5		35.1	2351	2413	2492	2682	2319	2362	2404	2699	
86.1175	28.22	108	1710	89	0.08	2.21	0.0	8.4	9.7	0.0	0.0	0.0	0.0	0.9	1.0	0.0		19.9					2319	2370	2403	2588	
87.0002	31.72	96	1404	94	0.13	2.30		20.0	8.2		0.0			3.2	0.0			31.4	2372	2456	2481	2716	2336	2380	2433	2635	
87.0025	39.51	64	700	104	0.10	2.17	0.0	9.2	26.0	0.0	0.9	0.0	0.0	0.6	0.4	0.4		39.1	2380	2465	2499	2666	2362	2432	2489	2685	
87.0026	17.71	88	1190	102	0.07	2.21	0.9	16.4	17.5	0.0	0.0	0.0	0.0	0.5	0.2	0.6		37.5	2362	2413	2483	2626	2326	2373	2420	2692	
87.0038	34.56	84	900	95	0.11	2.34		15.1	24.6		0.0			3.2	0.0			42.8									
87.0157	25.50	86		97	-0.04	2.35	0.0	12.1	8.8	0.0	0.4	0.0	0.0	1.2	0.4	0.0		22.9									
90.0198	41.28	70	670	98	0.07	2.30													2575	2600	2647	2726	2163	2256	2442	2530	YES
90.0199	29.60	76	950	95	0.10	2.22													2454	2520	2551	2655	2326	2351	2373	2404	YES
90.0200	85.68	61	570	107	0.11	1.93													2725	•	•	•	2564	2765	•	•	YES
90.0201	17.90	92	850	97	0.05	2.21													2795	•	•	•	2646	2676	2724	•	YES
90.0202	29.40	75	870	102	0.09	2.22													2414	2463	2555	2691	2285	2376	2470	2572	YES
90.0203	36.40	76	890	96	0.17	2.33													2651	2705	2774	•	2513	2562	2615	2787	YES
90.0204	27.80	78	890	96	0.05	2.14													•	•	•	•	•	•	•	•	YES
91.0042	32.29	87	1100	95	0.08	2.43													2363	2388	2433	2500	2252	2278	2314	2418	YES
91.0043	24.72	86	1090	97	0.09	2.43													2350	2374	2429	2486	2207	2236	2286	2332	YES
91.0052	8.38	82	1610	102	0.07	2.65																	2120	2144	2164	2280	YES
91.0053	133.55	46	180	107	0.19	2.18																					YES
91.0086	20.20	78	730	91	0.04	2.28													•	•	•	•	•	•	•	•	YES
91.0087	42.90	69	600	97	0.06	2.04													2787	•	•	•					YES
91.0088	40.60	79	610	98	0.05	2.08													•	•	•	•	2665	2760	2775	•	YES
91.0130	20.38	87	1020	92	0.15	2.26													2784	•	•	•	2779	2790	•	•	YES
91.0131	28.74	82	970	99	0.05	2.28													2790	•	•	•	2706	2750	2784	•	YES
91.0132	77.34	78	320	98	0.07	2.10													2732	2792	•	•	2665	2718	2744	•	YES
91.0133	51.93	77	600	99	0.08	2.18													2738	•	•	•	2659	2707	2757	•	YES
91.0134	32.30	76	870	95	0.07	2.25													2798	•	•	•	2736	2798	•	•	YES
91.0135	44.64	73	750	98	0.06	2.17													2797	•	•	•	2733	2771	•	•	YES
91.0136	36.17	80	570	99	0.08	2.18													2737	2782	•	•	2655	2679	2704	•	YES
91.0137	33.58	85	660	99	0.09	2.34													2744	2786	•	•	2661	2700	2750	•	YES
91.0138	34.79	86	•	103	•	2.19													2518	2721	2769	•	2550	2707	2759	•	YES
91.0139	93.70	86	•	103	0.12	2.19													•	•	•	•	2668	2781	•	•	YES
91.0174	32.53	86	810	92	0.07	2.22													•	•	•	•	2744	2791	•	•	YES
91.0179	25.99	71	750	99	0.02	2.16													2784	•	•	•	2598	2713	2796	•	YES
91.0183	25.43	80	660	93	0.06	2.22													2605	2678	2731	2798	2432	2493	2601	2786	YES
91.0184	18.03	78	810	92	0.06	2.30													2761	2800	•	•	2425	2485	2560	2710	YES
91.0185	25.30	74	850	98	0.07	2.21													2766	•	•	•	2610	2698	2736	•	YES
91.0186	29.46	70	740	98	0.07	2.16													2780	•	•	•	2619	2706	2795	•	YES
91.0208	60.05		•	•	•	2.00													2721	•	•	•	2608	2800	•	•	

FORM EIA 459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127
Page 1 of 2

1. Program/Project Identification No.: DE-FC21-86MC10637

2. Program/Project Title: Waste Management (2.2)

3. Reporting Period: 4-1-92 through 6-30-92

4. Name and Address: Energy and Environmental Research Center
University of North Dakota
Box 8213, University Station, Grand Forks, ND 58202 (701) 777-5000

5. Program/Project Start Date: 4-1-86

6. Completion Date: 9-30-92

7. FY: 91/92

8. Months or Quarters: Quarters

9. Cost Status — a. Dollars Expressed in Thousands — b. Dollar Scale

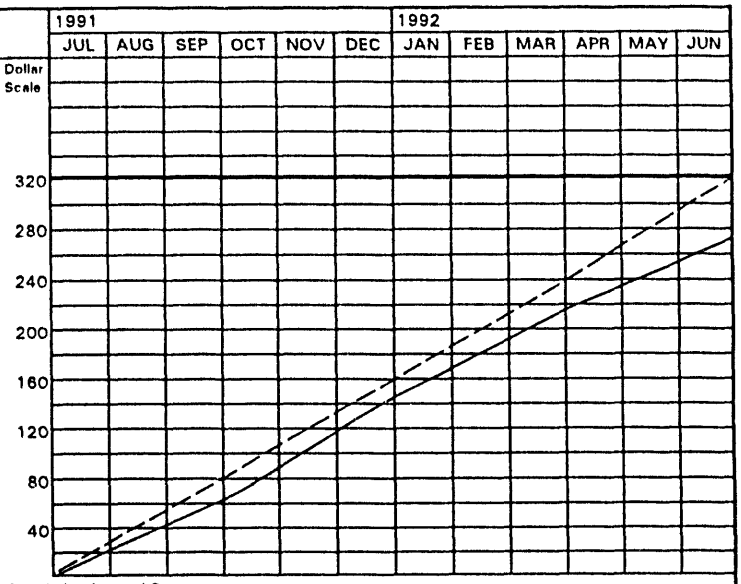
10. Cost Chart

Fund Source		Quarter 1st	2nd	3rd	4th	Cum. to Date	Tot. Plan
DOE	P	80	80	80	80	320	320
	A	61	87	70	54	272	
	P						
	A						
	P						
	A						
	P						
	A						
Total P		80	80	80	80	320	320
Total A		61	87	70	54	272	
Variance		19	(7)	10	26	48	

P = Planned A = Actual

Total Planned Costs for Program/Project

$320

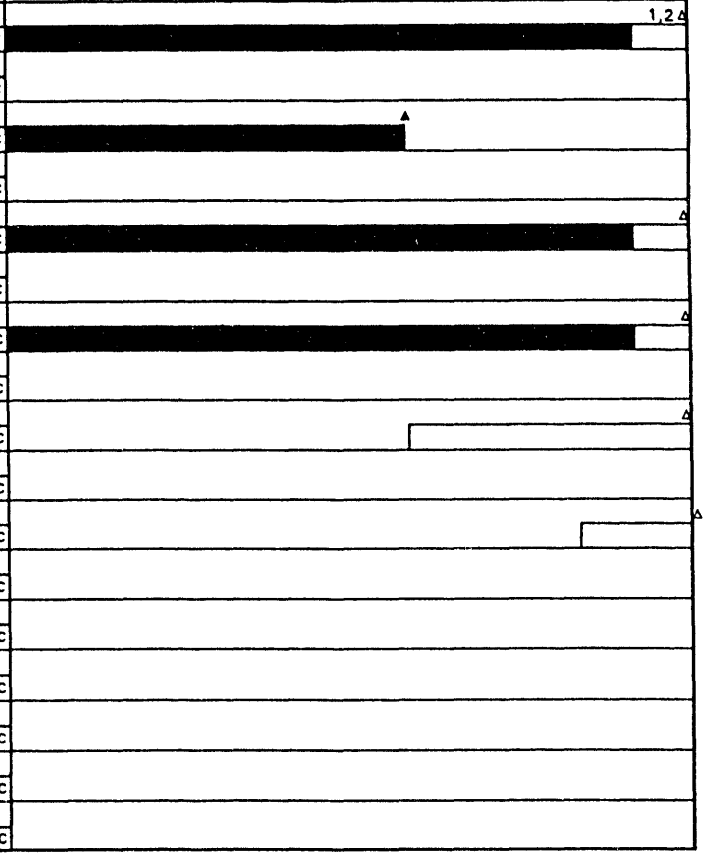


c. Cumulative Accrued Costs

	JUL	AUG	SEP	OCT	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN
Planned			80			160			240			320
Actual			61			148			218			272
Variance			19			12			22			48

11. Major Milestone Status

	Units Planned / Units Complete
A. Water and Waste Resource Management	P C
	P C
B. Coal Combustion Ash Conditioning Study	P C
	P C
C. Collection, Generation, and Evaluation of Bituminous Coal Ash Data Base	P C
	P C
D. Waste Depository Scavenger	P C
	P C
E. Environmental Mercury Associated with Fossil Fuel Utilization	P C
	P C
F. Preparation of Six-Year Final Report	P C
	P C
	P C
	P C
	P C
	P C
	P C



12. Remarks

Due to the EERC fiscal year end, the June books do not close until July 25, 1992. Costs posted through July 8 have been included.

13. Signature of Recipient and Date

Daniel J Stepan 07/28/92

14. Signature of DOE Reviewing Representative and Date

FORM E1A-459E
(10/80)

U.S. DEPARTMENT OF ENERGY

FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
OMB NO. 1900 0127
Page 2 of 2

1. Program/Project Identification No. DE-FC21-86MC10637	2. Program/Project Title Waste Management (2.2)	3. Reporting Period 4-1-92 through 6-30-92
4. Name and Address	Energy and Environmental Research Center University of North Dakota Box 8213, University Station Grand Forks, ND 58202 (701) 777-5000	5. Program/Project Start Date 4-1-86 6. Completion Date 9-30-92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
Task A	Water and Waste Resource Management:			
a.1.	HWD CWF process water treatability testing	6-30-92		
a.2	Activated carbon evaluation	6-30-92		
Task B	Coal Combustion Ash Conditioning Study	1-31-92	2-29-92	
Task C	Collection, Generation, and Evaluation of Bituminous Coal Ash Data Base	6-30-92		
Task D	Waste Depository Scavenger	6-30-92		
Task E	Environmental Mercury Associated with Fossil Fuel Utilization	6-30-92		Task E was not initiated due to lack of funding upon completion of Task B.
Task F	Preparation of Six-Year Final Report	8-31-92		