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FLUE GAS CLEANUP

Final Technical Progress Report
for the Period April 1, 1986, through December 31, 1992

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FLUE GAS CLEANUP

1.0 INTRODUCTION

The objective of the Department of Energy's (DOE) Flue Gas Cleanup Program, under the direction of the Pittsburgh Energy Technology Center (PETC), is to promote the widespread use of coal by providing the technology necessary for utilization of coal in an environmentally and economically acceptable manner. The program addresses the reduction of acid rain precursor emissions as well as developing technologies with the potential to meet more stringent emissions control requirements for SO_2, NO_x, and particulate matter. Activities within the Energy and Environmental Research Center's (EERC) Cooperative Agreement Flue Gas Cleanup project have addressed control of all three of these pollutants over the last six years.

Initially, the Cooperative Agreement included separate projects in fine particulate emissions and simultaneous SO_2/NO_x control. The projects were later combined into a single project called Flue Gas Cleanup, which included work in NO_x control and fine particulate control.

From April 1983 through March 1988, the focus of the Cooperative Agreement SO_x/NO_x Control project was investigation of dry sorbent injection for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization. The primary emphasis was furnace injection of calcium-based sorbents with some experiments evaluating back-end humidification (1,2). In April 1988, the emphasis of the project was changed to advanced NO_x control to evaluate the potential of a catalytic fabric filter for simultaneous NO_x and particulate control.

In June 1989, the project name was changed to Flue Gas Cleanup, and the scope of project activities was expanded to include tasks supporting bench-scale work in the fine particulate control area. Work in the fine particulate control area was included as a separate project within the Cooperative Agreement from April 1983 through March 1988 and was also funded as a result of a competitive DOE award during the period May 1988 through December 1989.

In March 1990, the EERC at the University of North Dakota was notified that a proposal entitled "Catalytic Fabric Filtration for Simultaneous NO_x and Particulate Control," which was submitted to DOE/PETC, was selected for funding. Therefore, further catalytic fabric filter development activities were discontinued under the Cooperative Agreement Flue Gas Cleanup project in July 1991. A task was added in the last year of the Cooperative Agreement to assess the effect of coal combustion on visibility impairment in the atmosphere. Therefore, in the last year of the Cooperative Agreement the Flue Gas Cleanup project focused on the visibility study and on bench-scale efforts to investigate the relationships between fine particle emissions from fabric filters and the cohesive properties of fly ash.

2.0 SIMULTANEOUS SO_x/NO_x CONTROL

Earlier pilot and field tests demonstrated the potential to control SO_2 by direct furnace injection of calcium-based sorbents (3-12). However, development of furnace injection of pressure-hydrated lime as a viable technique for SO_2 control required evaluation of several issues, including optimization of sorbent reactivity and investigation of the potential for additives and sorbent recycle to increase sorbent reactivity/utilization. In addition, the effect of furnace sorbent injection and ash/sorbent interactions on sorbent reactivity, rate of ash deposition, deposit strength, particulate collection device performance, and boiler operability required further study.

2.1 Goals and Objectives

The overall objective of the SO_x/NO_x Control project was to expand the scientific and engineering database necessary for the development of innovative processes for the control of SO_x emissions during coal combustion. Dry sorbent injection for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization were investigated. The study addressed factors impacting both sorbent reactivity and operability of the combustion system for new and retrofit applications. Specific factors addressed included 1) sorbent properties, 2) sorbent processing conditions, 3) impact of sorbent injection on boiler performance, and 4) operability of the particulate control device.

The SO_x/NO_x Control project was organized into the following tasks to meet the project objectives: Task A, Sorbent Evaluation; Task B, Enhanced Sorbent Reactivity/Utilization; Task C, Combustion System Operability; Task D, $NO \rightarrow NO_2$ Conversion; and Task E, Process Economics. Detailed summaries of the work completed under the SO_x/NO_x Control project were presented in the Final Technical Reports for the periods April 1, 1986, through March 31, 1987, and April 1, 1987, through March 31, 1988 (1,2).

2.2 Accomplishments

2.2.1 Task A. Sorbent Evaluation

The purpose of Task A was to identify and quantify the effects of sorbent processing on the reactivity of commercial high-calcium sorbents. Sorbent processing includes the calcination and hydration conditions that result in a hydrated lime (calcium hydroxide) product. The sorbent reactivity of pressure hydrates has been shown to equal or surpass that of commercial slaked hydrates. Although processing conditions can lead to changes in the physical properties of a sorbent, the final criterion for determining improved reactivity is the actual performance of a sorbent in controlling SO_2 emissions.

A literature review was conducted to address sorbent characteristics with respect to flue gas desulfurization (FGD) processes with emphasis on furnace injection technology. The literature review showed that limestone properties have been extensively characterized for fluid-bed combustion applications as well as for conventional FGD processes. Comprehensive information on lime and hydrated lime was limited with respect to furnace sorbent injection technology and FGD processes in general.

Based on the results of the literature review, four commercial limestones and their respective calcination and atmospheric hydration products were selected for pilot-scale furnace injection tests. The four materials were Marblehead limestone from the Marblehead Lime Company in Illinois; Longview limestone from the Dravo Lime Company in Alabama; Round Rock limestone, from the Round Rock Division of the Dravo Lime Company in Titus County, Texas; and Mercer limestone from the Mercer Lime Company in Michigan. Sufficient quantities of the commercial preparations of limestone, lime, and atmospheric hydrate were acquired from each supplier to perform calcination, pressure-hydration, and sorbent-reactivity tests. Pilot-scale furnace injection tests and chemical and physical analyses were performed to establish baseline characteristics for the commercial sorbents. The commercial sorbents, experimental calcines, pressure-hydrated calcines, and pressure hydrates produced from the commercial limes were evaluated in the Particulate Test Combustor (PTC) fired on natural gas with anhydrous SO_2 and ammonia injected to produce ~1000-ppm SO_2 and 700-ppm NO_x in the flue gas. The sorbents were pneumatically injected into the combustor at a point where the bulk gas temperature was 1825°F. Sorbent reactivity was determined by SO_2 reduction and sorbent utilization.

Experimental results from the furnace injection tests showed that the commercial hydrate resulted in better sorbent utilization than the limestone or lime for all the commercial sorbent materials. At Ca/SO_2 molar ratios of 1.0, utilization values for the Marblehead hydrate, limestone, and lime were 27%, 17%, and 12%, respectively. Pressure hydrates produced using the Marblehead lime resulted in utilization values of about 35% at a Ca/SO_2 molar ratio of 1.0. Results with the Longview materials were somewhat different. Utilization values for the commercial hydrate and pressure hydrate were similar, 27% at a Ca/SO_2 molar ratio of 1.0. Limestone and lime also exhibited similar results with utilization values of 15% observed at a Ca/SO_2 molar ratio of 1.0.

At a Ca/SO_2 molar ratio of 1.5, utilization values for the Round Rock hydrate, limestone, and lime were 24%, 13%, and 11%, respectively. Pressure hydrates produced using the Round Rock lime resulted in utilization values of approximately 24% at a Ca/SO_2 molar ratio of 1.5. Utilization values for the Mercer commercial hydrate, limestone, and lime were 28%, 15%, and 15%, respectively, at a Ca/SO_2 molar ratio of about 1.5. At a comparable Ca/SO_2 molar ratio, the utilization values for the pressure hydrate prepared with the Mercer lime ranged from 30% to 35%.

Pressure-hydrated limes produced in the bench-scale pressure hydrator using Marblehead and Mercer limes were better sorbents for SO_2 reduction than the commercial Marblehead and Mercer hydrates, respectively, and far better than the corresponding limestones or limes. Utilization values for the Marblehead pressure hydrate, commercial hydrate, limestone, and lime were 35%, 27%, 17%, and 12%, respectively, when injected into a pilot-scale combustor at 1825°F and a Ca/SO_2 molar ratio of 1.0. Utilization values for the Mercer pressure hydrate, commercial hydrate, limestone, and lime were 33%, 28%, 15%, and 15%, respectively, in pilot-scale furnace injection tests at a Ca/SO_2 molar ratio of 1.5.

Pressure-hydrated limes produced in a bench-scale pressure hydrator using Longview and Round Rock limes resulted in sorbent utilization values similar to those observed with commercial Longview and Round Rock hydrates, respectively. However, both the commercial and pressure-hydrated limes were better sorbents for SO_2 reduction than the corresponding limestones or limes. Utilization values for the Longview hydrates, limestone, and lime were 27%, 14%, and 11%, respectively, in pilot-scale furnace injection tests at a Ca/SO_2 molar ratio of 1.0. Utilization values for the Round Rock hydrates, limestone, and lime were 24%, 13%, and 11%, respectively, when injected into a pilot-scale combustor at 1825°F and a Ca/SO_2 molar ratio of 1.5.

Pressure-hydration experiments were performed to evaluate the effect of pressure and water stoichiometry on the reactivity of Marblehead and Longview pressure hydrates. Hydration pressures ranging from 50 psig to 180 psig and water stoichiometries ranging from 1.0 to 1.6 were evaluated. Results from 2 x 2 factorial design experiments showed that hydration pressure and water stoichiometry were not statistically significant with respect to sorbent utilization for either the Marblehead or Longview pressure hydrates, as determined by pilot-scale furnace injection tests.

Marblehead and Longview limestones were calcined at 1850°, 2000°, and 2150°F in a muffle furnace. The Round Rock and Mercer limestones were calcined at 1800°, 2000°, and 2150°F. The resulting calcines showed decreasing surface area with increasing calcination temperature. Sorbent injection tests showed that utilization values for the calcines decreased with increasing temperature for all the limestones. Pressure hydrates prepared from Marblehead and Longview calcines produced at 2000°F demonstrated better utilization than pressure hydrates prepared from calcines produced at 1850° and 2150°F. Pressure hydrates prepared from Round Rock and Mercer calcines produced at 1800°F demonstrated better utilization than pressure hydrates prepared from calcines produced at 2000° and 2150°F.

2.2.2 Task B. Enhanced Sorbent Reactivity/Utilization

Increased sorbent reactivity decreases the amount of sorbent necessary to achieve a specific level of SO_2 control. In addition, reduced sorbent requirements should result in reduced combustion system impacts and lower operating costs, thus improving the economics of furnace injection technology. The use of additives and sorbent recycle have the potential to increase overall sorbent utilization. The objective of Task B, Enhanced Sorbent Reactivity/Utilization, was to determine the effect of selected additives on sorbent reactivity.

Six additives to improve the sorbent reactivity/utilization of calcium-based sorbents were evaluated using commercial Marblehead lime as the base sorbent. The additives included 10% aqueous solutions (by weight) of NaOH, $NaHCO_3$, $NaSiO_3$, $CaCl_2$, and acetic acid, and a 25% solution of ethanol. The $NaSiO_3$ solution was actually a saturated mixture of $NaSiO_2$ in water that was weighed as 10% of the final mixture. The aqueous solutions were used to hydrate the Marblehead lime using 40% excess water under both atmospheric and pressure-hydration conditions. Sodium-based additives were previously identified as improving the utilization of calcium-based hydrates and, therefore, they were included as a basis for comparison with previous work (13-15).

Although the atmospheric hydrates appeared to result in slightly higher utilization than the pressure hydrates in furnace injection tests, the difference was not significant when the standard deviation for the data was considered. Overall, the additives had very little effect on sorbent utilization when compared to the utilization values typically observed for Marblehead pressure hydrate.

2.2.3 Task C. Combustion System Operability

The application of dry scrubbing techniques and specifically furnace injection technology in a commercial boiler is contingent on the overall performance of the combustion system. Introducing a sorbent into the system increases the ash loading which affects ash deposition rate, and also places additional stress on particulate control devices. Pilot-scale combustion tests were performed to characterize the operability of various coal/sorbent combinations. The coals were selected on the basis of marketability, geographical location, rank, and previous use in other furnace injection programs. High-calcium pressure-hydrated lime was prepared in the EERC bench-scale pressure hydrator.

The impact of furnace sorbent injection on ash deposition, electrostatic precipitator (ESP) performance, and baghouse performance was evaluated in pilot-scale combustion tests using Illinois No. 6 bituminous coal/Marblehead pressure-hydrate, Monticello, Texas, lignite/Round Rock pressure hydrate; and Pittsburgh No. 8 bituminous coal/Mercer pressure hydrate fuel/sorbent combinations. Each coal was fired in the ash-fouling combustor to evaluate fouling potential, sorbent utilization, and ESP efficiency. One test was conducted with each coal without sorbent injection to establish baseline characteristics. Two additional tests were performed with sorbent injection, with targeted SO_2 reductions of 50% and 90%, representing SO_2 control levels (prior to the 1990 Clean Air Act Amendments) for retrofit and new installations, respectively. The same test matrix was also performed using the PTC, with emphasis placed on sorbent utilization, particulate characterization, and ESP or baghouse performance.

Ninety percent SO_2 control was not achieved during tests with Illinois No. 6/Marblehead pressure hydrate due to sorbent feeder limitations. After the Illinois No. 6 tests, the sorbent feed system was modified to allow higher sorbent feed rates for tests with high-sulfur coal and/or inferior sorbent materials. A Ca/SO_2 molar ratio of 1.2 was necessary to achieve 50% SO_2 control, and 75% SO_2 was achieved at a Ca/SO_2 molar ratio of 2.2. ESP performance decreased substantially with increased sorbent addition. Particulate collection efficiency decreased from 96% to 67% as sorbent injection increased particulate loadings at the ESP inlet from 1.6 to 6.5 grains/scf. Correspondingly, bulk ash resistivity increased from 10^{12} to 10^{14} ohm-cm. Although sorbent injection increased deposition rate during ash-fouling tests with the Illinois No. 6 coal and the Marblehead pressure-hydrated lime, probe deposits continuously sloughed off the probes indicating that the deposits were weak and could be easily removed with conventional soot-blowing equipment.

For the Monticello lignite/Round Rock pressure hydrate fuel/sorbent combination, a Ca/SO_2 molar ratio of 2.1 to 2.3 was necessary to achieve 50% SO_2 control, and a ratio of approximately 4.8 was required for 90% SO_2 control. The high ash loading due to fuel ash content and sorbent injection resulted in high convective pass deposition rates, but the deposits were friable and of the type that would be easily removable with frequent operation of conventional soot-blowing equipment. ESP performance decreased substantially with increased sorbent addition. Particulate collection efficiency decreased from 95% to 68% as sorbent injection increased particulate loadings at the ESP inlet from 2.6 to 4.5 grains/scf, and the bulk ash resistivity increased from 10^{12} to 10^{13} ohm-cm. Particulate emissions from the baghouse during the PTC tests actually decreased with increasing sorbent injection, but at the expense of increased dust cake resistance and baghouse differential pressure.

For the Pittsburgh No. 8 bituminous coal/Mercer pressure hydrate fuel/sorbent combination, a Ca/SO_2 molar ratio of 1.0 to 1.7 was necessary to achieve 50% SO_2 control, and a Ca/SO_2 molar ratio of 3.0 to 4.0 was required for 90% SO_2 control. Furnace sorbent injection increased ash deposition rate to a moderate level, but the deposits were very friable, indicating that conventional soot-blowing equipment would easily control convective pass deposition. ESP performance decreased from 92% to 71% collection efficiency with increasing sorbent injection as mass loading at the ESP inlet increased from 1.9 to 9.1 grains/scf. Particulate emissions from the baghouse decreased with increasing sorbent injection, but again at the expense of increasing baghouse differential pressure. In this case, the specific dust-cake resistance decreased with increasing sorbent injection, indicating a more cohesive/porous dust cake.

Flue gas humidification experiments were performed using the pilot-scale combustion system fired using natural gas with steam as the humidification medium. In all pilot-scale combustion tests performed, flue gas humidification with steam increased sorbent utilization. Sorbent utilization increased from 30% to 50% with hydrate injection at 500°F, and particulate collection in a baghouse operated at 190°F when flue gas moisture was increased from 15% to 24% by volume. Increasing sorbent residence time in the duct by injecting the hydrated lime at 1250°F resulted in 55% sorbent utilization.

2.2.4 Task D. NO → NO_2 Conversion

Sodium-based sorbents, specifically soda ash, have been used for SO_2 control in utility boiler systems using spray dryer technology. Demonstration projects have resulted in 70% to 80% SO_2 control using dry injection of nahcolite and trona upstream of a utility baghouse. However, concern developed with respect to the association of sodium-based sorbents and plume coloration due to the NO_2 concentration in the stack gas. A western utility, which employed a soda ash spray dryer, experienced plume coloration due to high NO_2 concentrations in the stack gas (16). A utility-scale demonstration of dry sorbent injection, using sodium-based sorbents, resulted in a brown coloration of the stack gas due to NO_2 formation (17). A bench-scale fixed-bed reactor study was undertaken in Task D to identify the mechanisms responsible for the production of NO_2 from NO as it pertains to gas stream cleanup processes and to develop methods to reduce/eliminate NO_2 emissions.

Initially, screening tests were conducted to evaluate the effect of temperature, humidity, SO_2 concentration, and O_2 concentration on NO_2 formation. A full factorial experimental design in four variables and two levels with 2 conditions repeated (for a total of 18 tests) was performed for each of four sorbent materials: sodium carbonate, sodium sulfite, calcium hydroxide, and calcium carbonate. The independent variables were SO_2 concentration (0 ppm and 3000 ppm), O_2 concentration (0% and 6% by volume), H_2O concentration (0% and 20% by volume), and temperature (160°F and 350°F). Only sodium carbonate and calcium hydroxide produced measurable amounts of NO_2. The amount of NO_2 observed during the tests with calcium hydroxide was only slightly above the baseline NO_2 concentration. Formation of NO_2 was observed at 4 of the 16 test conditions using sodium carbonate. Analysis of the data showed that humidity was not statistically significant relative to the other three variables with respect to NO_2 production.

A three-factorial experimental design in two levels was added to Task D in order to 1) determine the most significant variable in NO_2 formation, 2) replicate runs to provide additional data for analysis of variance, 3) screen additional sorbent materials, and 4) provide additional information for determining reaction mechanisms. The variables evaluated were SO_2 concentration (1500 and 3000 ppm), O_2 concentration (3% and 6% by volume), and temperature (250°F and 350°F). Three new sorbent materials were evaluated in addition to sodium carbonate from the first experimental design: calcium sulfite, Montana Dakota Utility (MDU) fly ash, and Colorado Power & Light (CPL) fly ash.

Of the parameters evaluated, temperature, O_2 concentration, SO_2 concentration, and H_2O concentration, only the effect of temperature was statistically significant at the 90% confidence level. Oxidation of NO to NO_2 increased dramatically as the reactor temperature increased from 250°F to 350°F. The rate of NO_2 formation increased with increased sulfation rate. Therefore, materials such as Na_2CO_3, which are highly reactive with respect to SO_2 at the conditions evaluated, resulted in the formation of higher NO_2 concentrations.

2.2.5 Task E. Process Economics

An engineering/economic evaluation comparing furnace sorbent injection with a calcium-based spray dryer system for both a retrofit (50% SO_2 control) and new facility (90% SO_2 control) was completed as part of the previous EERC/DOE Cooperative Agreement. A new economic evaluation was scheduled for completion in the third year of the Simultaneous SO_x/NO_x Control project if substantial improvement in SO_2 control or sorbent utilization was demonstrated in the first two years of the project. Improved sorbent utilization was not achieved, and it was concluded that further pilot-scale furnace injection work was unnecessary under the EERC/DOE Cooperative Agreement. Further work in the area of furnace sorbent injection would be useful only in support of site-specific utility evaluations of the technology. Therefore, a new economic evaluation was not performed, and the focus of the SO_x/NO_x Control project was redirected to advanced NO_x control.

3.0 CATALYTIC FABRIC FILTRATION FOR SIMULTANEOUS NO_x AND PARTICULATE CONTROL

In response to restrictive NO_x regulations in Europe, selective catalytic reduction (SCR) technology has been installed on over 30,000 MW of full-scale utility boiler capacity as a postcombustion NO_x control technique (18). Application of conventional SCR technology to coal-fired systems presents several potential problems, including plugging of the catalyst support structure by fly ash, deactivation of the catalyst by fly ash components and SO_3, deposition of sulfur and ammonia by-products on air-heater surfaces, and waste product handling/reuse/disposal.

The primary difference between the catalytic filter bag developed by Owens-Corning Fiberglas Inc. (OCF) and conventional SCR technology is the catalyst support. Conventional SCR technology uses a honeycomb or plate support structure. The catalytic fabric is prepared by coating the surface of an S-glass (high-temperature) cloth, resulting in a catalyst bonded to the surface of the fabric. The catalytic coating consists of a combination of titanium isopropoxide and vanadium tri-n-propoxide oxide, sometimes called "sol-gel" materials. The sol-gels hydrolyze during air-drying of the coated fabric, resulting in a highly porous layer. The fabric is then cured at low temperature to drive off any residual organics and partially densify the coating. The final product is a highly porous catalytic coating strongly bonded to the surface of the glass fabric.

Initial development of the catalyst-coated woven fabrics was conducted in-house by OCF. Bench-scale evaluation of the catalytic fabrics using simulated flue gas resulted in NO_x reduction as high as 90% at 660°F and a face velocity of 2 ft/min. After several years of development, OCF contracted with the EERC to evaluate the NO_x reduction capability of fifteen catalytic fabrics using a slipstream of flue gas from the PTC fired with Velva North Dakota lignite. Based on the results of the initial tests, the catalytic fabric filter concept demonstrated over 90% NO_x reduction in a flue gas stream, promising catalyst/fabric self-abrasion characteristics and the potential for substantially reduced cost when compared with conventional SCR/fabric filtration technology. Catalytic fabric filter development was discontinued in the fall of 1986 due to lack of funding.

Development of the catalytic fabric filter concept was resumed by OCF and the EERC in April 1988 under the DOE Cooperative Agreement. OCF activities were funded in-house and involved the preparation of catalytic fabric samples for testing at the EERC. The work focused on bench-scale experiments to show continuity with previous work and to screen samples of catalyst-coated fabric under both simulated and actual flue gas conditions.

3.1 Goals and Objectives

The overall objective of the catalytic fabric filter project was the development of a catalytic fabric filter for NO_x and particulate control that will provide high removal efficiency of NO_x and particulate matter, acceptably long bag and catalyst life, and an economic savings over a conventional SCR system and baghouse. The specific goal of the program was the development of a catalytic fabric filter that will provide:

- 90% NO_x removal with <25-ppm ammonia slip.
- A particulate removal efficiency >99.5%.
- A bag/catalyst life of >1 year.
- A 20% cost savings over conventional baghouse and SCR control technology.
- Compatibility with SO_2 removal systems.
- A nonhazardous waste material.

The Catalytic Fabric Filtration project was organized into the following tasks to meet the project objectives: Task A, Catalyst/Fabric Development; Task B, Fabric Screening Tests; Task C, Bag Evaluation and Parametric Tests;

and Task D, Bag Durability and Process Assessment. Tasks A and B were completed as part of the Flue Gas Cleanup project under the Cooperative Agreement. Further development of the catalytic fabric filter concept with respect to bag evaluation and durability and process assessment continued with pilot-scale testing under a competitive award from DOE/PETC with commercial cost-share participants. Detailed summaries of the work completed in Tasks A and B were presented in the Final Technical Reports for the periods April 1, 1988, through June 30, 1989, and July 1, 1989, through June 30, 1990, and in the Semiannual Technical Progress Report for the period January 1, 1991, through June 30, 1991 (19-21).

3.2 Accomplishments

3.2.1 Task A. Catalyst/Fabric Development

The purpose of Task A was to demonstrate continuity with previous work conducted for OCF and to screen several samples of catalytic fabric in a bench-scale fabric filter system using simulated flue gas. Although promising results were obtained previously, continued bench-scale work was necessary to develop the product that would give the best combination of high NO_x removal efficiency, low ammonia slip, high particulate removal efficiency, and long catalyst/bag life. The fabric weave, coating composition, and coating process were adjusted to develop fabrics for further testing. Two series of parametric experiments were completed along with screening tests to evaluate sixteen catalytic fabric samples.

A series of shakedown tests was completed with the bench-scale fabric filter system to determine system operability and repeat previous NO_x reduction results. However, poor NO_x reduction was observed using three fabric samples which previously had produced good NO_2 at reduction. After several more tests, catalyst aging, overheating of the catalytic fabric, and simulated versus actual flue gas were eliminated as causes of the poor NO_x reduction results. Thermal decomposition products (silicon dioxide and siloxanes) from the silicone gasket material used in the fabric filter holder were eventually identified as the reason for the destruction of the NO_x reduction capability of the fabrics.

After the bench-scale fabric filter holder was modified so that the silicone gasket material was no longer required to obtain a good seal, a full factorial parametric test matrix with four factors and two levels was completed using the same fabric sample for all sixteen tests. The independent variables included NO_x concentration, SO_2 concentration, ammonia/NO_x molar ratio, and air-to-cloth ratio. The dependent variables were NO_x removal efficiency, ammonia slip, and SO_3 production. The test matrix was later repeated with Fabric #2, which had performed well (94% NO_x removal and 35-ppm ammonia slip) in the fabric screening tests described later in this section. Fabric #2 was not textured, and no undercoat was applied. It was prepared using seven coats of a 0.2-M solution of V/Ti catalyst. In addition, three center point experiments were performed to test for curvature, and one test condition was repeated four times to increase the number of degrees of freedom.

Statistical analysis of the results of the experiments showed that NO_x concentration, air-to-cloth ratio, and the interaction between NO_x concentration and air-to-cloth ratio had the greatest effect on NO_x removal efficiency. At a low air-to-cloth ratio (1.5 ft/min), an increase in NO_x concentration from 300 to 1000 ppm resulted in an increase in NO_x removal efficiency. When the air-to-cloth ratio was increased to 4 ft/min, an increase in NO_x concentration had no effect on NO_x removal efficiency. Increasing the air-to-cloth ratio from 1.5 to 4.0 ft/min resulted in a decrease in the NO_x removal efficiency independent of NO_x concentration.

The ammonia/NO_x molar ratio, the SO_2 concentration, and the interaction between the NO_x concentration and the SO_2 concentration affected NO_x removal efficiency to a lesser degree. As expected, increasing the ammonia/NO_x molar ratio from 0.8 to 1.1 increased the NO_x removal. But due to the limited range, the statistical significance of the effect was small. Although there was inconsistency in the data, increasing the SO_2 concentration from 300 ppm to 3000 ppm appeared to decrease the NO_x removal efficiency.

Sixteen catalyst-coated fabric samples were evaluated at constant conditions in fabric screening experiments using the bench-scale fabric filter holder and simulated flue gas system. The tests were performed to evaluate the effect of cloth type (textured versus nontextured), fabric undercoat (none, silica/titanium, or silica/zirconium), catalyst quantity (one versus two coats of 1.0-M 25% V and 75% Ti), and catalyst composition (V/Ti, V/Ti/Al, V/Ti/Zr, or CuO) on NO_x removal and ammonia slip. Brunauer-Emmett-Teller (BET) surface area measurements were performed on all fabric samples both before and after exposure to flue gas.

Prior to initiating the fabric screening tests, the simulated flue gas system was modified to include dust injection. Fly ash was not injected continuously during the fabric screening tests. It was initiated at the beginning of each test to develop a differential pressure across the fabric sample of between 2 and 4 inches of water. Fly ash injection was discontinued when the differential pressure reached 4 inches of water to prevent problems with control of the flue gas flow rate.

Results from the fabric screening tests showed that modification of the catalyst composition by adding small amounts of alumina or zirconium refractory components to the original catalyst to expand the operating temperature range substantially reduced the catalytic reactivity of the fabrics tested. Application of a refractory undercoat to improve the abrasion resistance of the glass fabric and to possibly develop greater surface area had no effect on NO_x removal or ammonia slip.

The NO_x removal efficiency and ammonia slip data did not indicate an advantage one way or another for fabric samples prepared using multiple coats of a low-concentration solution versus a single coat of a high-concentration solution. The reactivity of the catalyst-coated fabric was improved by increasing the amount of catalyst on the fabric. Increases in NO_x removal efficiency and decreased ammonia slip were observed when the quantity of catalyst placed on the fabric was increased through the use of multiple coatings of the catalytic solution.

The use of a textured fabric improved the catalytic performance of the catalyst-coated fabrics tested. Fabric comparisons in one case showed an increase in NO_x removal efficiency from 82% to 93% and a decrease in ammonia slip from 56 to 35 ppm. In a second case, comparison of two fabric samples that provided essentially identical NO_x removal values (84% versus 85%), showed that ammonia slip was substantially less for the textured fabric (2 ppm versus 53 ppm).

3.2.2 Task B. Fabric Screening Tests

The purpose of Task B was to evaluate eight of the best performing fabrics from Task A, while filtering fly ash from a pulverized coal-fired combustor. In an actual flue gas environment, the effect of submicron particles, volatile species, and trace elements which may affect catalyst activity could be evaluated. The 0.8-ft^2 fabric filter holder and oven used with simulated flue gas in Task A were used to filter a slipstream of flue gas from the PTC. The criteria for selection of the catalytic fabrics used in Task B were high NO_x removal efficiency and/or low ammonia slip based on Task A results. Four coals were used in the fabric screening tests: a medium-sulfur, washed Illinois #6 bituminous; a high-sulfur Pyro Kentucky bituminous; a Jacobs Ranch subbituminous; and a South Hallsville Texas lignite. Each of the eight fabrics was tested at air-to-cloth ratios of 2, 3, 4, and 6 ft/min with the baseline coal (washed Illinois #6). Ammonia slip and SO_3 measurements were made at each air-to-cloth ratio, with the ammonia/NO_x molar ratio held constant at 0.9.

There was a substantial decrease in catalyst-coated fabric performance with increased air-to-cloth ratio for all the fabrics tested. For the fabric samples tested, the maximum air-to-cloth ratio at which 85%-90% NO_x removal could be achieved was 3 ft/min. Although there was some variability in the data, the NO_x removal efficiency appeared constant with time for the short-term (8-hour) tests completed. Fabric #2 (7 coats of 0.2-M 25% V and 75% Ti, no refractory undercoat, and a texturized weave) appeared to provide the best performance with respect to high NO_x removal efficiency and low ammonia slip. Fabric #13 (1 coat of 1-M 25% V and 75% Ti, 50% Si and 50% Ti undercoat, and texturized weave) also provided good performance.

Both the concentration of vanadium on the fabric and the BET surface area correlate strongly with NO_x removal efficiency. When the catalyst-coated fabric was exposed to flue gas, both the quantity of catalyst on the fabric and the total surface area decreased. However, the percentage decrease in surface area is greater, indicating that a high percentage of the total surface area is located at or near the surface of the catalyst coating. A minimum surface area of 4.5 to 5 m^2/g and a vanadium concentration of 6.5-mg to 7-mg vanadium per gram of fabric are necessary to achieve 85%-90% NO_x reduction at an ammonia/NO_x molar ratio of 0.9.

Following the fabric screening tests, Fabrics #2 and #13 were selected to evaluate the effects of coal type on catalyst-coated fabric performance. Both fabrics were tested using each of the three remaining coals (South Hallsville Texas lignite; Jacobs Ranch subbituminous; and Pyro Kentucky bituminous) at an ammonia/NO_x molar ratio of 0.9 and a flue gas temperature of 650°F. For the first 6 hours of the test, the air-to-cloth ratio was held constant at 3 ft/min. At the end of each test, the air-to-cloth ratio was adjusted to 2 ft/min for 1 hour, and then to 4 ft/min for 1 hour.

Although three of the coals, the two bituminous coals and the subbituminous coal, did not appear to affect the performance of the catalyst-coated fabric samples, the South Hallsville Texas lignite did result in lower

NO_x removal and higher ammonia slip. This was probably caused by pinholes that formed in the dust cake, resulting in flue gas channeling through the fabric.

Two catalyst-coated fabric samples were evaluated in conjunction with the setup and testing of a nitrous oxide (N_2O) analyzer. The catalytic fabrics were evaluated in a slipstream of flue gas from the PTC fired with washed Illinois #6 bituminous coal. Nitrous oxide concentrations were measured at the inlet and outlet of the fabric filter holder to verify that N_2O was not produced as a result of the NO_x reduction reactions occurring on the surface of the catalyst-coated fabric.

Fabric #17 was similar to a previously tested fabric (#2), except that a substantially less expensive vanadium source was used and a high molecular weight organic was added. The new catalyst coating was highly amorphous, reducing the potential for catalyst loss from the fabric surface. The other fabric (#8) was iron on titania, which may increase the temperature window for catalytic activity or cost less than vanadium-based catalysts.

The fabric sample coated with a new and less expensive source of vanadium performed as well as a similar fabric sample coated with the original vanadium catalyst, which may result in substantial cost savings. The fabric sample coated with an iron-based catalyst showed potential. A NO_x removal efficiency of 64% at an air-to-cloth ratio of 2 ft/min was observed without optimizing the iron-based catalyst coating process. The N_2O concentration ranged from 3.5 to 6.0 ppm, which is consistent with results obtained by other researchers for pulverized coal-fired boilers (22,23). There was minimal conversion of NO_x to N_2O (<1 ppm) across the catalyst-coated fabric.

4.0 FINE PARTICULATE EMISSIONS/CONTROL

Present New Source Performance Standards (NSPS) for utility coal-fired boilers limit particulate emissions to 0.03 lb/million Btu and 20% or lower opacity. The control device removal efficiency required to meet this standard varies from about 99% to 99.9%, depending on the heating value and ash content of the coal. Electrostatic precipitators and fabric filters are the technologies that have most often been employed to meet the current standard. Although the best proven control technology for fine particulate matter appears to be fabric filtration, if properly designed, both of these technologies have been successful, in most cases, in meeting the current standard. However, the removal efficiency of both electrostatic precipitators and baghouses is significantly reduced for fine particles less than 2 μm. Furthermore, present emissions standards do not address fine particle emissions. Emissions of fine particles are of concern because these particles are likely to be deposited in the lower respiratory system through normal breathing. The problem is further compounded because hazardous trace elements such as selenium and arsenic are known to be concentrated on these fine particles. Control device removal efficiency is lowest for respirable particles, so a situation exists where the most hazardous particles from coal combustion are collected with the lowest removal efficiency. In addition to causing adverse health effects, fine particle emissions have an impact on atmospheric visibility. Particles which are the most efficient at scattering light are in the 0.1- to 2-μm range. These particles do not readily settle out of the atmosphere and are subject to long-range transport. When present in sufficient concentrations, these fine particles will cause serious visibility impairment. Therefore, the emission of fine particles is an issue because of potential adverse health effects and visibility impairment in the atmosphere.

Early work involving fly ash characterization demonstrated the dependence of fly ash collectability in fabric filters on coal type (24,25). Experiments were initiated to determine if fly ash characteristics could be modified using additives to enhance fly ash collectability. Results showed that fine particulate emissions and baghouse pressure drop could be reduced when small amounts of ammonia and SO_3 were injected into the flue gas upstream of a baghouse (26,27). An assessment report was prepared to compare the technical and economic merits of flue gas conditioning applied to fabric filtration with other existing or emerging methods of fine particulate control (28). From April 1987 through May 1988, the focus of the Fine Particulate Control project was on the completion of bench-scale experiments to study the mechanisms of the flue gas conditioning process. The results showed that flue gas conditioning reduces emissions by enhancing the ability of the fly ash to bridge large pores and pinholes and by inhibiting the reentrainment of ash from the dust cake/fabric interface (29). From May 1988 through December 1989, work continued under a competitive award from DOE/PETC. The objective of the project was to demonstrate the effectiveness of flue gas conditioning for improved fine particulate control in reverse-gas cleaned baghouses. The results showed that the benefits of reduced pressure drop due to flue gas conditioning were retained over multiple cleaning cycles, with no problems with dust cake buildup or bag cleaning (30). During the last three years of the Cooperative Agreement, work focused on bench-scale tests to predict fabric filter performance and to model the conditioning process (20,21,31,32). The tests showed that conditioning increases the tensile stength of fly ash at constant porosity and also reduces the packing tendency. Porosity measurements showed that both aerated and packed porosities are significantly increased for conditioned ashes compared to baseline ashes without conditioning. Bench-scale reentrainment experiments were performed to measure the reentrainment potential of fly ash from the surface of a fly ash filter cake and relate it to the measured cohesive strength. A joint venture project funded by the DOE, the Electric Power Research Institute (EPRI), and the Canadian Electric Association (CEA), completed in October 1992, evaluated the effectiveness of flue gas conditioning for improving the performance of pulse-jet baghouses.

4.1 Goals and Objectives

The objectives of the Fine Particulate Emissions project for the period April 1986 through March 1987 were to 1) make a technical and economic comparison between flue gas conditioning as a method of reducing fine particulate emissions from a fabric filter and other state-of-the-art or emerging technologies, and 2) determine the effectiveness of flue gas conditioning with ammonia and sulfur trioxide (SO_3) for reducing fine particulate emissions from a fabric filter for several coals. Work in the second year of the Cooperative Agreement focused on the fundamental ash properties that control fine particle penetration through a fabric filter including 1) construction and setup of a bench-scale fabric filtration system; 2) tests with reentrained ash at ambient conditions to relate penetration behavior to coal type, ash characteristics, and conditioning; and 3) tests with ammonia and SO_3 injected upstream of the bench-scale filter to determine conditioning effects and the effect of conditioning agent concentrations and temperature. Work in the area of fine particulate emissions was not funded under the third year of the Cooperative Agreement. However, work continued under a competitive award from DOE/PETC to evaluate flue gas conditioning applied to reverse-gas baghouses. The general objective of the fine particulate control effort during the last three years of the Cooperative Agreement was to develop methods to help characterize, control, and model fine particulate emissions from a fabric filter. Characterization goals included the development of methods to measure the cohesive strength and reentrainment potential of fly ashes. Control and modeling goals involved work to relate measured ash characteristics to the level of fine particle emissions from fabric filters.

4.2 Accomplishments

The technical and economic assessment focused on a literature review in the following areas: 1) a review of the basis for fine particulate control, including discussion of the health effects of particulate matter in the atmosphere, the effect of fine particulate emissions on visibility, and current and possible future fine particulate control requirements; 2) a technical and economic evaluation of existing particulate control technologies, including flue gas conditioning applied to fabric filters; and 3) evaluation of the fundamental collection and penetration mechanisms in fabric filtration, basic ash properties which affect fine particulate emissions, and previous results with flue gas conditioning. Pilot-scale experiments were performed to determine the effect of injection temperature and coal type on the overall effectiveness of conditioning.

Results from the pilot-scale tests showed that fine respirable particulate emissions could be reduced by up to 4 orders of magnitude by injecting small amounts of ammonia and SO_3 upstream of a baghouse. This corresponded to an increase in particulate collection efficiency from 90% to 99.999% for some difficult-to-collect ashes. Tests with both lignite and higher-rank coals showed that conditioning is an effective method of greatly reducing fine particulate emissions from a fabric filter. Baghouse pressure drop was also reduced, making the process more economical. Conditioning would add approximately 9% to the cost of operating a conventional reverse-gas baghouse; however, this cost could be more than recovered if pressure drop and/or baghouse size are reduced. Possible applications of flue gas conditioning applied to fabric filtration include retrofit applications where emissions or pressure drop are higher than acceptable or retrofit or new plant applications to meet stricter control requirements.

Bench-scale experiments in the second year of the Cooperative Agreement confirmed previous pilot-scale results which showed that flue gas conditioning is an effective method of reducing fine particle emissions from a fabric filter. Pressure drop is reduced because of an increase in dust cake porosity which results in a reduced specific dust cake resistance coefficient (K_2). Conditioning reduces emissions by enhancing the ability of the ash to bridge large pores and pinholes, by inhibiting the reentrainment of ash from the dust cake/fabric interface, and by reducing K_2, which results in lower pinhole velocity. The mechanisms of emissions reduction are a direct result of increasing the cohesive strength of the ash through the conditioning process. A review of penetration mechanisms showed that there is a theoretical basis for lower emissions with increased bulk cohesive strength. Pressure drop reduction as a result of conditioning occurs due to an increase in dust cake porosity as theoretical and empirical models predict.

Work during the last three years of the Cooperative Agreement focused on the development of methods to measure the cohesive properties of fly ash and relate those properties to filtration behavior. The tensile strength, porosity, pore-bridging ability, and reentrainment potential of baseline and conditioned fly ashes were measured to determine if they could be used as predictors of fabric filter performance.

Most of the available methods for measuring the shear or tensile strength of bulk powders were developed for soil mechanics studies, and, therefore, might not adequately describe the behavior of fine powders such as fly ash. After reviewing the available methods for measuring the cohesive properties of bulk powders, an instrument called a Cohetester, manufactured by Hosokawa Micron International, was selected based on successful trial tensile strength measurements of baseline and conditioned fly ashes. The Cohetester gives a direct measurement of the tensile strength of a bulk powder sample. The aerated and packed porosities of the fly ash samples were measured with a Powder Characteristics Tester, also manufactured by Hosokawa Micron International. A description of the Powder Characteristics Tester and the Cohetester, along with test procedures, was given in the Annual Project Report for the period July 1, 1989, through June 30, 1990 (20).

Initial measurements conducted with the Cohetester showed that one of the effects of conditioning on fly ash characteristics is an increase in tensile strength at constant porosity or an increase in porosity at constant tensile strength. When tensile strength was plotted as a function of porosity, the primary effect of conditioning was a shift in the curve upward (higher tensile strength) and to the right (higher porosity). Initial results also showed that the tensile strength measurements may be affected by the ambient relative humidity.

Reentrainment and pore-bridging experiments were performed using precision electroformed nickel sieves with square openings in place of a fabric. Five different pore sizes were evaluated: 300 μm, 150 μm, 75 μm, 40 μm, and 20 μm. Measurement of pore-bridging and reentrainment of conditioned and baseline fly ashes was conducted as a function of pore size and face velocity. Results of the pore-bridging tests showed that conditioning, face velocity, and pore size are critical parameters in determining whether complete pore bridging will occur without reentrainment or pinhole formation. The data were well-behaved in terms of establishing the maximum velocity at which bridging occurs for a given pore size. Pore-bridging and reentrainment tests showed that conditioned ash is more effective at bridging pores over the entire velocity range tested (1, 2, 4, and 8 ft/min). Although the porosity of the conditioned ash is much greater than the porosity of the baseline ash, and the tensile strength at filtration porosities of the conditioned ash is lower than the tensile strength of the baseline ash, the pore-bridging ability of the conditioned ash is superior. An apparent explanation is that the particle-to-particle binding forces are greater with conditioning. Reentrainment tests performed subsequently with size-fractionated baseline and conditioned fly ashes suggested there may be a change in the pore-bridging mechanism when the particle size approaches the pore size.

Additional experiments were performed to evaluate the effect of particle size and relative humidity on tensile strength and porosity. Measurements were conducted using samples stored under controlled conditions in a humidity chamber. The effect of particle size was evaluated using size-fractionated samples of baseline and conditioned Monticello fly ash and two pure powders, ammonium sulfate and calcium sulfate dihydrate.

Test results showed that conditioning, relative humidity, and particle size are important parameters in determining the tensile strength and porosity of bulk powders such as fly ash. Tests at several relative humidities showed that elevated humidity increased the tensile strength at constant porosity for some fly ashes, but that the increase was ash-specific. An increase in relative humidity from 10% to 50% had little effect on the tensile strength and porosity of pure calcium sulfate dihydrate, but did produce a shift in the tensile strength vs. porosity curve for samples of ammonium sulfate. The increase in relative humidity had only a small effect on the baseline Monticello fly ash, but resulted in a major increase in tensile strength for the conditioned fly ash. Therefore, there is an interaction between conditioning and relative humidity.

The primary effect of a smaller particle size was a shift of the tensile strength vs. porosity curve toward higher porosities for the calcium sulfate and conditioned fly ash, and a shift toward both higher tensile strength and higher porosity for the ammonium sulfate. Tensile strength measurements on the size-fractionated Monticello fly ash also showed that a smaller particle size caused a higher tensile strength for either the baseline or the conditioned ash.

Reentrainment tests conducted at higher relative humidities showed that increasing the relative humidity from 15% to 50% did not significantly affect the pore-bridging ability of the baseline Monticello fly ash. However, increasing the relative humidity from 15% to 50% improved the pore-bridging ability of the conditioned fly ash, which was consistent with the tensile strength data. Increasing the relative humidity for the conditioned ash also significantly reduced K_2, which was consistent with the increased aerated and packed porosities at the higher humidities. Since these correlations are for dusts with similar particle-size distributions, they should be valid indicators of fabric filter performance in terms of collection efficiency and dust resistance. For dusts with similar particle-size distributions, the higher the tensile strength, the greater the pore-bridging ability, and the greater the aerated or packed porosity, the smaller the K_2.

Based on the results of the bench-scale experiments, the best predictor of pore-bridging ability is tensile strength, and the best predictor of K_2 is the porosity data. Both tensile strength and porosity measurements correlate with pore-bridging ability and K_2, but for fly ashes with similar particle sizes, tensile strength correlates more strongly with the pore-bridging ability of the dust, and measured porosity correlates more strongly with the K_2 of the dust. This implies that both measurements should be conducted for the best prediction of filter performance. The results indicate that any model for predicting fabric filter performance must include both face velocity and particle size.

Bag cleanability is another aspect of filter performance that depends on the cohesive properties of the ash. For dusts with similar particle-size distributions, the correlations imply that the dusts with the highest tensile strengths and porosities will form dust cakes with the lowest K_2 values. This translates to lower pressure drop only if the residual dust cake weight does not increase. If a dust has too high a tensile strength, it may not be cleaned easily from the bags, and high dust cake weights could result. Nevertheless, the measured tensile strength and porosity of a dust can be used to predict qualitatively pore-bridging ability and dust cake resistance, which are the main indicators of filter performance.

5.0 IMPACT OF COAL COMBUSTION ON ATMOSPHERIC VISIBILITY/SUMMARY OF LITERATURE REVIEW ON ATMOSPHERIC VISIBILITY

In 1977 Congress added Section 169A to the Clean Air Act (CAA), which established as a national goal "the prevention of any future, and the remedying of any existing, impairment of visibility in mandatory Class I Federal areas which impairment results from manmade air pollution." The Environmental Protection Agency (EPA) defines "visibility impairment" as "any humanly perceptible change in visibility (visual range, contrast, coloration) from that which would have existed under natural conditions." The EPA has identified two types of air pollution that impair or reduce visibility. The first is single-source impairment defined by the EPA as smoke, dust, colored gas plumes, or layered haze emitted from stacks that obscure the sky or horizon and are relatable in a single source or a small group of sources. The second type is regional haze which is widespread, regionally homogeneous haze from a multitude of sources, which impairs visibility in every direction over a large area. The EPA has used a phased approach to implement the visibility program. Phase I of the program requires control of impairment that can be traced to a single, existing stationary facility or small group of existing stationary facilities. Section 169B was added to the CAA in 1990 to determine the need for expansion of the visibility protection program. It provides funding for continued research on visibility in Class I Federal areas including 1) expansion of current visibility impairment monitoring, 2) assessments of current sources of visibility impairment using regional air quality models, and 3) studies on atmospheric chemistry and the physics of visibility. Section 169B also calls for the creation of Visibility Transport Regions consisting of one or more states which, because of interstate pollution, contribute significantly to visibility impairment in Class I areas. After the creation of Visibility Transport Regions, Visibility Transport Commissions (VTCs) (whose members include the governors of the affected states) will be formed to address the establishment of clean air corridors, restrictions on new construction, and the development of long-range strategies for remedying regional haze.

Visibility has been the focus of a significant amount of research for over a decade. However, attempts to accurately identify the contributions of various sources to visibility impairment have been hampered by the limitations of air quality models and the lack of understanding of the complex physical and chemical processes that govern the formation of secondary aerosols in the atmosphere.

At the request of the U.S. DOE-PETC, a task assessing the impact of coal combustion on atmospheric visibility was added to the Flue Gas Cleanup project of the EERC/DOE Cooperative Agreement for the period July 1, 1991, through June 30, 1992. A literature review was conducted to evaluate the effect of fine particulate emissions from coal-fired combustion systems on atmospheric visibility. The following questions were addressed as part of the literature review:

1. What are the causes of visibility impairment in the atmosphere? (For example, what sizes and concentrations of fine particulates in the atmosphere will result in significant visibility impairment?)

2. What is the composition of the visibility-reducing fine particulate aerosol, and what are the major sources of these fine particles?

3. What is the contribution of coal combustion to visibility-reducing fine particles in the atmosphere?

4. How are pollutants removed from the atmosphere, and what is the role of atmospheric chemistry in the production of secondary aerosols?

5. How would reduction of SO_2, NO_x, and fine particulate emissions affect visibility?

Visibility impairment in the atmosphere is primarily caused by light attenuation by fine particles ($<2.5\ \mu m$). Secondary fine particulate matter formed in the atmosphere from SO_2 and NO_x precursors is a major source of these fine particles. Other major constituents of fine atmospheric particles are organics, elemental carbon, ammonium ion, soil dust, and water vapor. Water vapor contributes to visibility impairment primarily when the relative humidity is high enough to cause growth in the size of hygroscopic aerosols such as ammonium sulfate. Since coal combustion is a major source of SO_2 (and, subsequently, atmospheric sulfates), some visibility impairment must be attributed to coal combustion. Visibility impairment in the Grand Canyon by secondary sulfates and nitrates from the Navajo Generating Station is a case where the visibility impairment was specifically attributed to a coal-fired power plant. In response, the EPA has required that scrubbers be installed at the Navajo plant to mitigate this visibility impairment. However, the exact contribution of coal combustion to regional haze is generally not known, and the benefits that may be derived from much stricter emission controls on coal-fired power plants are difficult to assess. It appears logical that if SO_2 and NO_x emissions from coal-fired power plants were reduced by 50%, there would have to be an eventual reduction of 50% of the sulfates and nitrates in the atmosphere that originated from coal combustion. However, because of the variable contribution to visibility impairment from coal combustion that might occur in a given location, the overall effect on visual range for that location might be small.

Results from the literature review indicate that there is a complex relationship between emissions from coal combustion and visibility impairment, but that coal combustion may be a significant contributor in some cases. A more detailed summary of the visibility literature review was presented in the Semiannual Technical Project Report for the period January 1, 1992, through June 30, 1992 (32).

6.0 PUBLICATIONS AND PRESENTATIONS

The following is a list of publications and presentations which resulted from work sponsored by DOE under the Flue Gas Cleanup project of the multiyear Cooperative Agreement (Contract No. DE-FC21-86MC10637).

Miller, S.J.; Heidt, M.K.; Laudal, D.L.; Weber, G.F. "Flue Gas Cleanup," Semiannual Technical Project Report for the Period January 1, 1992, through June 30, 1992; DE-FC21-86MC10637, Grand Forks, ND, July 1992.

Heidt, M.K.; Miller, S.J. "Effect of Cohesive Properties on Fine Particle Collection and Reentrainment," Presented at the Eighth Annual Coal Preparation, Utilization, and Environmental Control Contractors' Conference, Pittsburgh, PA, July 27-30, 1992.

Miller, S.J.; Laudal, D.L. "Pulse-Jet Baghouse Performance Improvement With Flue Gas Conditioning," Presented at the Eighth Annual Coal Preparation, Utilization, and Environmental Control Contractors' Conference, Pittsburgh, PA, July 27-30, 1992.

Miller, S.J.; Laudal, D.L.; Heidt, M.K. "Fly Ash Characterization Methods For Prediction of Fabric Filter Performance," Presented at the Second European Symposium on Separation of Particles From Gases, Nürnberg, Germany, March 24-26, 1992.

Miller, S.J.; Heidt, M.K.; Weber, G.F.; Laudal, D.L. " Flue Gas Cleanup," Semiannual Technical Project Report for the Period July 1, 1991, through December 31, 1991; DE-FC21-86MC10637, Grand Forks, ND, January 1992.

Laudal, D.L.; Miller, S.J.; Chang, R. "Enhanced Fine Particulate Control For Reduced Air-Toxic Emissions," Presented at the International Air Toxics Conference, Washington, DC, November 4-6, 1991.

Miller, S.J.; Laudal, D.L.; Chang, R.L. "Flue Gas Conditioning For Improving Pulse-Jet Baghouse Performance," Presented at the Ninth Particulate Control Symposium, Williamsburg, VA, October 15-18, 1991.

Weber, G.F.; Ness, S.R.; Laudal, D.L. "Simultaneous NO_x and Particulate Control Using a Catalyst-Coated Fabric Filter," Presented at the International Joint Power Generation Conference, San Diego, CA, October 6-10, 1991.

Weber, G.F.; Miller, S.J.; Laudal, D.L.; Heidt, M.K. "Flue Gas Cleanup," Semiannual Technical Progress Report for the Period January 1, 1991, through June 30, 1991; DOE Contract No. DE-FC21-86MC10637, Grand Forks, ND, August 1991.

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Miller, S.J.; Laudal, D.L. "Recent Developments in Particulate Control With Low-Rank Fuels," Presented at the Sixteenth Biennial Low-Rank Fuels Symposium, Billings, MT, May 20-23, 1991.

Weber, G.F.; Laudal, D.L.; Aubourg, P.F.; Kalinowski, M. "Catalytic Fabric Filtration for Simultaneous NO_x and Particulate Control," *In* Proceedings of the 1991 Joint Symposium on Stationary Combustion NO_x Control - EPA/EPRI; Washington, DC, March 25-28, 1991.

Miller, S.J.; Laudal, D.L. "Enhancing Baghouse Performance with Conditioning Agents: Basis, Developments, and Economics," *In* Proceedings of the Eighth Particulate Control Symposium; EPRI GS-7050, November 1990, Vol. 2, p 23-1.

Weber, G.F.; Miller, S.J.; Laudal, D.L. "Flue Gas Cleanup," Annual Technical Project Report for the Period July 1, 1989, through June 30, 1990; DE-FC21-86MC10637, Grand Forks, ND, October 1990.

Miller, S.J.; Laudal, D.L. "Enhancing Baghouse Performance With Conditioning Agents: Basis, Developments, and Economics," Presented at the Eighth EPA/EPRI Symposium on the Transfer and Utilization of Particulate Control Technology, San Diego, CA, March 20-23, 1990.

Miller, S.J.; Laudal, D.L. "Flue Gas Conditioning Applied to Fabric Filtration," Presented at the Sixth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, September 25-29, 1989.

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Miller, S.J.; Laudal, D.L. "Flue Gas Conditioning: A Method to Improve Collection Efficiency and Reduce Pressure Drop With Fabric Filters," Presented at the Fifteenth Biennial Low-Rank Fuels Symposium, St. Paul, MN, May 22-25, 1989.

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2.2 Waste Management

WASTE MANAGEMENT

Final Technical Progress Report
for the Period April 1, 1986, through December 31, 1992

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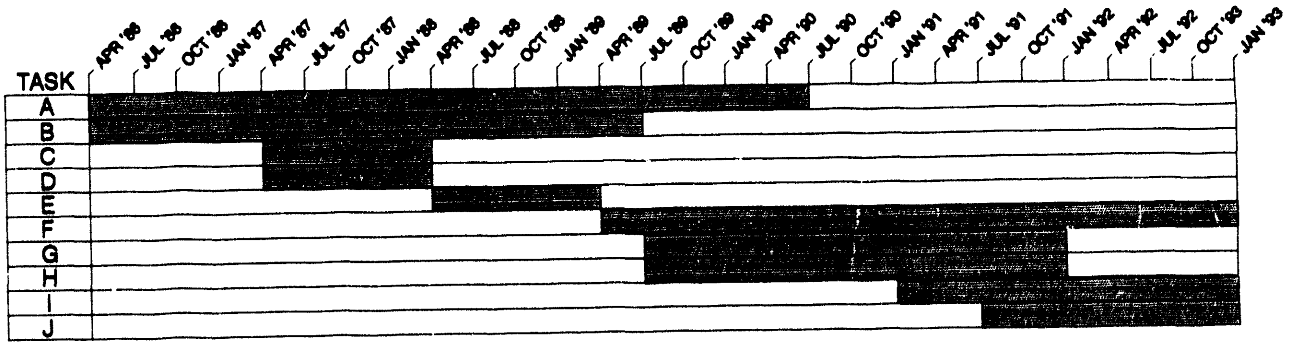
WASTE MANAGEMENT

1.0 INTRODUCTION

The Waste Management project has involved a number of interrelated tasks relating to the characterization, handling and treatment of solid and liquid waste materials and by-products from advanced coal processing and utilization processes. Specific tasks within the Waste Management project have included:

- Waste Characterization
- Fly Ash Liner Development Study
- Numerical Modeling of Disposal-Related Soil Properties
- Leaching Test Evaluation
- Electrostatic Separation of Unburned Carbon from Fly Ash
- Bituminous Coal Fly Ash Data Collection and Evaluation
- Activated Carbon Evaluation
- Coal Ash Conditioning Study
- Characterization and Treatability of Coal-Water Fuel Process Waters
- Waste Depository Scavenger Study

Figure 1 illustrates the time frame in which individual studies were performed.



TASK A: WASTE CHARACTERIZATION
TASK B: FLY ASH LINER DEVELOPMENT STUDY
TASK C: NUMERICAL MODELING OF DISPOSAL-RELATED SOIL PROPERTIES
TASK D: LEACHING TEST EVALUATION
TASK E: ELECTROSTATIC SEPARATION OF UNBURNED CARBON FROM FLY ASH
TASK F: BITUMINOUS COAL FLY ASH DATA COLLECTION AND EVALUATION
TASK G: ACTIVATED CARBON EVALUATION
TASK H: COAL ASH CONDITIONING STUDY
TASK I: CHARACTERIZATION AND TREATABILITY OF COAL-WATER FUEL PROCESS WATERS
TASK J: WASTE DEPOSITORY SCAVENGER STUDY

Figure 1. Time line of tasks performed under the Waste Management project.

2.0 GOALS AND OBJECTIVES

The overall objective of the Waste Management project 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.

3.0 PROJECT TASK SUMMARIES

3.1 Waste Characterization

3.1.1 Introduction

Research in this task was conducted over a period of four years to characterize coal combustion solid wastes for evaluation of the waste disposal requirements for advanced combustion processes being developed at the Energy and Environmental Research Center (EERC).

The test protocol used for the characterization studies consisted of waste analyses for elemental, mineral, and trace organic matter content; waste leachate analyses for trace metals and trace organic compounds; and tests of physical properties relevant to waste disposal.

During the first year, characterization studies were conducted on fourteen waste streams. Ten waste samples generated from the atmospheric fluidized-bed combustion unit (AFBC) at the EERC were characterized. The types of waste samples studied included fly ashes, spent bed materials, primary and secondary cyclone ashes, and ash composites. These four samples represented all of the solid waste streams produced by the AFBC system. In addition, six composite waste samples prepared by blending primary cyclone ash, secondary cyclone ash, and baghouse fly ash were characterized.

The fuels used for the AFBC combustion runs were Sarpy Creek Montana subbituminous coal, Gibbons Creek Texas lignite, and Navajo New Mexico subbituminous coal. The combustion runs used either limestone addition for SO_2 capture or ash reinjection for enhanced carbon burnout.

Two fly ash waste samples produced from combustion tests which used pressure-hydrated lime injection for SO_2 control were also characterized during the first year. The fuel used for these runs was an Illinois #6 bituminous coal. The lime injection fly ashes were collected from the electrostatic precipitator on a 500,000-Btu/hr, pulverized coal combustion unit. One of the samples was produced from a baseline combustion test in which no lime was injected into the system, and the other sample was produced from a combustion test which used a 1.0 lime injection ratio (Ca/SO_2).

Two fly ash waste samples produced from combustion tests which used ammonia-sulfite (NH_3-SO_3) injection to increase baghouse efficiency were also characterized during the first year. The fuel used for these tests was a Monticello Texas lignite. The NH_3-SO_3 fly ashes were collected from a baghouse on a 500,000-Btu/hr, pulverized coal combustion unit. One of the samples was produced from a baseline combustion test in which no NH_3 or SO_3 was injected into the system, and the other sample was produced from a combustion test which used sufficient NH_3 and SO_3 injection to achieve concentrations of 25 ppm and 12 ppm, respectively, in the flue gas.

During the second year, eleven different waste materials, all generated from coal utilization processes in development at the EERC, were characterized. The eleven materials included four wastes from low-temperature coal gasification runs performed for the Hydrogen Production project; six wastes from AFBC tests, which used a coal slurry fuel; and one waste from a coal preparation operation associated with the hot-water drying coal slurry process. The waste materials were tested for leachate trace metals and trace organics, elemental composition, mineral composition, and selected physical properties.

The four gasification waste samples included two gasifier bed materials from hydrogen production runs which used Martin Lake Texas lignite. Both runs were performed at a temperature of 800°C and a 3:1 steam-to-carbon molar ratio. One of the runs used a limestone bed material, and the other run used a silica sand bed material with a trona catalyst. The third gasifier bed material characterized was produced from a hydrogen production run with a Velva North Dakota lignite. This run used a limestone bed, an 800°C gasification temperature, and a 2:1 steam-to-carbon ratio. The fourth gasifier bed material characterized was produced from a hydrogen production run with a Wyodak Wyoming subbituminous coal. This run used a limestone bed, an 800°C gasification temperature, and a 2:1 steam-to-carbon ratio.

The six AFBC waste samples were produced in tests performed at the EERC in a 1,000,000-Btu/hr, bubbling-bed combustion unit. The fuel used was a Sarpy Creek Montana subbituminous coal which was burned in the form of an aqueous slurry. The waste samples studied included a spent bed material (silica sand), a primary cyclone ash, a secondary cyclone ash, a baghouse fly ash, and a composite ash collected from the same combustion run. The sixth AFBC waste characterized was a composite ash produced from a slurry combustion run that used limestone addition directly to the coal slurry to increase SO_2 capture. The AFBC composite ash samples were prepared by blending the various process waste streams in direct proportion to the amounts of material produced during the combustion test. The proportions used were 90 wt% primary cyclone ash, 8 wt% secondary cyclone ash, and 2 wt% baghouse fly ash.

The coal slurry used for the AFBC tests was produced at the EERC with the hot-water-drying process. Wastes collected from slurry combustion runs may have different characteristics than wastes produced from pulverized, dry coal combustion runs because the slurry preparation process removes some water-soluble materials from the coal prior to combustion. To evaluate the differences in waste composition resulting from combustion of the coal in the form of a slurry, the waste characterization data presented in this report was compared to characterization data collected in previous studies from waste samples produced with the same coal burned in a dry form.

The waste sample from the hot-water-drying coal slurry process was produced from a float-sink run performed on a Beulah-Zap North Dakota lignite.

The float-sink operation was part of the coal-cleaning procedure used for the slurry process.

Waste materials characterized during the third year included fly ashes produced from combustion tests performed at the EERC, in which pressure-hydrated lime was injected into the flue gas for SO_2 control, and a solid waste from an EERC diesel engine burning a coal-derived liquid fuel. Three fly ash samples were obtained from combustion tests. The fuel used in the combustion tests was a Pittsburgh #8 bituminous coal. The fly ash samples were collected in an electrostatic precipitator. The samples were obtained from baseline combustion runs during which no lime was injected, and from combustion runs with lime injection, which caused either a 50% or a 90% SO_2 content reduction in the flue gases.

The other waste material studied during the third year was a residual ash from a diesel engine, which was operated at the EERC and designed to burn coal-derived liquid fuels. The fuel used was a light coal tar fraction obtained from the Great Plains Coal Gasification Plant. The diesel waste was basically a high-carbon-content soot collected from the engine exhaust gas.

During the final year of this task, the remaining chemical characterization leaching procedures were completed, as were the analyses of the resulting leachates. Four unreacted limestone bed materials, generated from the Hydrogen Production project, were also chemically characterized.

3.1.2 Goals and Objectives

The overall goal of this task was to assess the impact of solid waste disposal requirements on the commercial viability of several coal utilization processes being developed at the EERC.

3.1.3 Results and Conclusions

The waste characterization test results for the first year are summarized as follows (1):

- None of the 14 materials tested would be classified as hazardous wastes based on their leachate trace metal contents, as determined by the USEPA EP Toxicity test.

- There were no trace organic compounds detected in leachates from any of the 14 waste materials. The trace organic analyses were performed by preparing acid and base/neutral solvent extracts from each waste leachate and then testing the extracts using gas chromatography/mass spectrometry (GC/MS). The minimum detection limit for the test procedure was 20 mg/L in the leachate (2).

- pH values of the ASTM leachates produced from the 14 waste materials ranged from 10.1 to 12.6. Selenium concentrations in three of the ASTM leachates exceeded the primary drinking water standard for selenium by more than a factor of 25.

- The results of column leaching tests indicated that the principal water-soluble component in the wastes was calcium sulfate and that most of this material was extracted in the first ten pore volumes passed through the waste.

- Elemental analyses indicated that the 14 ash samples studied were principally composed of silicon, calcium, and aluminum with lesser amounts of sodium, sulfur, and iron also being present.
- The major mineral phases identified in the waste samples were quartz (SiO_2), anhydrite ($CaSO_4$), and lime (CaO).
- The aqueous permeabilities of the waste samples ranged from 8.2×10^{-3} to 1.9×10^{-5} cm/sec, as measured by the falling head permeability test.

The characterization data generated for the 14 waste samples did not indicate that any major regulatory problems would be encountered relating to the disposal of these materials. Furthermore, two of the combustion-related processes developed by the EERC appeared to reduce the environmental impacts of the solid wastes being produced. The EPA-Extraction Procedure (EPA-EP) leaching test results showed that the 14 EERC wastes would not be classified as hazardous wastes based on their leachate trace metal content. Additionally, there were no trace organics found in the leachates from the wastes at the specified minimum detection limits.

Some state regulatory agencies may be concerned about the relatively high pH values of the ASTM leachates generated from many of the wastes. The selenium concentrations in the Gibbons Creek reinjection ash and the two Monticello fly ashes may also cause concern in some states, from a regulatory standpoint, since they exceed the primary drinking water standard by more than a factor of 25.

The results of column leaching tests performed on the wastes indicated that calcium sulfate was the principal compound extracted. Generally, it appeared that the bulk of the leachable material was extracted from the waste in the first ten pore volumes passed. Barium (15 mg/L) and chromium (2.9 mg/L) were the only trace metals detected in any of the column leachates.

The presence of quartz as a major mineral phase in many of the wastes indicated that these materials are abrasive. Appropriate precautions would be taken with the design of waste-handling equipment to minimize equipment breakdown because of the abrasive nature.

The waste characterization data indicated that the use of limestone and NH_3-SO_3 as combustion-related additives tended to reduce the amounts of leachable selenium in the ash materials. Since high-selenium leachate concentration is a common problem in western low-rank coal waste, these types of results may be important factors which favor the continued development of these processes.

The waste characterization test results for the second year are summarized as follows (3):

- EPA-EP leachates produced from all eleven of the coal utilization wastes contained trace metal concentrations well below the maximum allowable contaminant levels specified by Resource Conservation and Recovery Act (RCRA).
- No significant levels of trace organic compounds were detected in the leachates produced from the eleven wastes.
- The characterization studies indicated that no significant or unusual regulatory problems should be encountered for the disposal of the eleven coal utilization process wastes which were evaluated.

The characterization data generated for the eleven advanced process wastes did not indicate that any major regulatory problems should be encountered for the disposal of these materials on a commercial scale. The EPA-EP leaching test results clearly showed that the AFBC, hydrogen production, and coal slurry preparation wastes would not be classified as hazardous wastes based on their leachate trace metal contents under the existing RCRA regulations.

The column leaching tests performed on the composite ashes showed that significant reductions in the permeability coefficients of these materials occurred during the course of the tests, particularly for the AFBC ash produced with limestone addition. The permeability reductions were probably caused by pozzolanic reactions between the ash and the limestone-derived reaction products. The observed behavior indicates that the permeabilities of the composite ashes may decrease by several orders of magnitude after the materials have been placed in a permanent disposal site.

The results for the third year are summarized as follows (4):

- With the exception of chromium, EPA-EP leachates produced from the combustion wastes ashes contained trace metal concentrations well below the maximum allowable contaminant levels specified by the regulations of the RCRA for hazardous waste classification.
- No significant trace organic compounds were detected in leachates produced from the hydrated lime injection wastes. It appeared that some organic material was extracted from diesel engine ash, but the materials could not be identified by routine GC/MS analysis.
- The aqueous permeabilities of the 50% and 90% SO_2 reduction fly ashes were both well below the 10^{-7}-cm/sec criteria generally required for clay liner materials.
- The fly ash obtained from the 90% SO_2 reduction test contained a significant amount of unhydrated calcium oxide that caused an extremely exothermal reaction when the material was wetted.

The characterization data generated for the lime injection fly ashes indicates that no major regulatory problems should be encountered for the disposal of these materials. The results of the EPA-EP leaching tests clearly showed that the waste would not be classified as hazardous based on trace metal content under the existing RCRA regulations.

Due to criticisms of the precision and field applications of the USEPA Extraction Procedure (EP) test, the Toxicity Characteristic Leaching Procedure (TCLP) was developed. The TCLP test officially replaced the EP test on September 25, 1990, and was mandated to evaluate wastes for additional contaminants, particularly organics.

The exothermal hydration behavior of the two fly ashes produced with lime injection could require implementation of special handling procedures if this SO_2 control process were implemented on a commercial scale.

The diesel engine waste does not appear to pose any significant handling or disposal problems based on its inorganic trace element content. Although it was not possible to identify any specific trace organics, there did appear to be a significant amount of non-chromatographable material in the methylene chloride extract from the diesel engine waste.

The results for the final year are summarized as follows (5):

- Chemical characterization results show the limestone bed materials to be nonhazardous according to the mandated regulatory leaching test, the toxicity characteristic leaching procedure (TCLP). Concentrations in the leachate for each bed material were determined to be below the hazardous limit as defined by RCRA.

- Results from the synthetic groundwater leaching procedures (SGLP) and the long-term leaching tests show these materials to be nonhazardous for the RCRA elements as well.

It is important to note that these procedures were included in the chemical characterization protocol to more closely approximate the leaching of these materials as a monofill in a natural setting as opposed to a landfill setting. The TCLP was designed specifically to approximate the leaching in a codisposal landfill setting. Materials such as these limestone bed materials are likely to be disposed of in a monofill rather than a sanitary landfill. Additional elements were determined in the various leachates generated. These results may be useful in the future as additional trace elements may be regulated or these materials may be investigated for potential utilization applications.

3.2 Fly Ash Liner Development Study

3.2.1 Introduction

A three-year research project was conducted at the EERC to develop fly ash-based liner materials for waste disposal sites. The research was conducted in three phases. Phase I of the project was a bench-scale laboratory study to formulate liner materials from mixtures of fly ash, hydrated lime, Type-1 portland cement, and water.

In Phase I, six different fly ashes and mixtures of fly ash and scrubber waste from coal-burning power plants in five state were tested to evaluate their suitability as liner construction materials. The fly ash samples were supplied by the Northern States Power Cooperative (North Dakota), the Texas Utilities Generating Company (Texas), the Southwestern Electric Power Company (Texas), the Central Illinois Public Service Company (Illinois), and the Northern Indiana Public Service Company (Indiana).

Each of the six fly ashes was initially characterized for its elemental and mineral compositions, relevant physical properties, and leachate trace metal content. Experiments were then performed to develop a specific liner formula for each ash. The experiments determined the smallest amounts of lime, cement, or a mixture of lime and cement required for addition to each fly ash (at a specified water level) to produce a cemented liner material with a permeability coefficient less than 10^{-7} cm/sec and an unconfined compressive strength greater than 400 psi.

During Phase II, liner slabs with dimensions of 4 square feet by 6 inches thick were prepared using the formulas developed in the Phase I work. The slabs were used to test the durability of the liner materials and to verify the permeability and strength characteristics predicted by the formulation experiments. Each Phase II liner slab was placed in a leachate-compatibility test device and loaded with 6 inches of unconsolidated fly ash and 1.5 feet of water. Each slab was left in the test device for five months. An attempt was made to collect the leachate that passed through the slabs, but no measurable amounts of leachate appeared during the five-month test period. When the slabs were removed from the test device, permeability and strength tests were performed on cores cut from each slab.

Three of the six fly ashes studied in the laboratory were selected for field tests in Phase III. For the field tests, liner sections having dimensions of 40 feet by 40 feet by 2 feet thick were constructed at power plants located in Texas, Indiana, and Minnesota. The physical properties of the liner sections were monitored for approximately one year to evaluate their performance.

Three sets of samples were collected from each field site over a one-year period and sent to the EERC for testing. These samples were tested for permeability coefficient, unconfined compressive strength, textile strength, modulus of elasticity, Poisson's ratio, coefficient of thermal expansion, porosity, and dry density. In addition to the laboratory tests, a double-barrel infiltrometer test was conducted at each of the sites to estimate the permeability of liner using an in-field method.

The Texas fly ash liner test was performed at the H.W. Pirkey Power Plant, owned by the Southwestern Electric Power Company (SWEPCO). The SWEPCO liner section was made with a Texas lignite fly ash. Approximately 5 wt% portland cement, 1.5 wt% hydrated lime, and 18 wt% (dry weight) water were added to the fly ash to produce the liner material.

The Indiana fly ash liner test was performed at the R.M. Schahfer Plant, owned by the Northern Indiana Public Service Company (NIPSCO). The NIPSCO liner section was made with approximately a 50:50 mixture of Illinois #6 fly ash and lime-based scrubber sludge. Approximately 5 wt% portland cement, 3 wt% hydrated lime, and 30 wt% (dry weight) water were added to the fly ash scrubber sludge mix to produce the liner material.

The Minnesota fly ash liner test was performed at the Sherburne County Power Plant, owned by the Northern States Power Company (NSP). The NSP liner section was made with a dry-scrubber powder containing Sarpy Creek, Montana, subbituminous coal fly ash and a lime-based spray dryer residue. Approximately 23 wt% (dry weight) water was added to the scrubber powder to produce the liner material. No lime or cement addition was required for the NSP liner.

3.2.2 Goals and Objectives

The purpose of the fly ash liner study was to develop cost-effective liner materials for utility waste disposal sites using mixtures of fly ash, water, hydrated lime, and/or portland cement.

3.2.3 Results and Conclusions

The results of the Phase I characterizations indicated that the six fly ashes generally exhibited acceptable physical properties for the liner application and that none of the materials could be classified as hazardous wastes based on their leachate trace metal contents. The results of the formulation experiments showed that liner materials with permeability coefficients less than 10^{-7} cm/sec and unconfined compressive strengths close to or exceeding 400 psi could be made from each of the six fly ashes. The minimum lime, cement, or lime and cement addition rate required for the six fly ash liner materials ranged from 3% to 9.5% (of dry weight). The specific moisture addition level used to prepare the fly ash liner mixtures was found to be an extremely important factor in the development of proper permeability and strength characteristics. Generally, the moisture content had to be within plus or minus 2% of the specified value to achieve acceptable results (1).

The results from Phase II indicated that fly ash liner materials were quite stable during the five-month exposure period. The permeability coefficients and strengths measured for the liner cores were all less than 10^{-7} cm/sec and greater than 400 psi, respectively. Additionally, none of the liner slabs developed any visible cracks, dimensional instability, or soft spots during the exposure periods (3).

The results of the SWEPCO field test generally indicated that the Texas lignite fly ash produced an acceptable liner material. Permeability coefficients measured in the laboratory for 12 liner samples varied from 1.4×10^{-7} cm/sec to 3.8×10^{-9} cm/sec, and the permeability coefficient measured in the field was estimated to be less than 10^{-7} cm/sec. The liner material developed an unconfined compressive strength of approximately 1000 psi after curing in the field for one year. The only visible deterioration of the SWEPCO liner section during the field test was the development of some cracks on the liner surface. The cracks appeared to be limited to the top six inches of the liner (4).

The results of the NIPSCO field test indicated that the liner material did not meet the target permeability criteria. Permeability coefficients measured in the laboratory for 12 Indiana liner samples varied from 8.0×10^{-5} cm/sec to 2.0×10^{-9} cm/sec, and the permeability coefficient measured in the field was estimated to be 7.8×10^{-7} cm/sec. The liner material developed an unconfined compressive strength of approximately 700 psi after curing in the field for one year. The only visible deterioration of the liner section during the field test was some crumbling at the liner surface. The crumbling extended about two inches below the surface. Although the permeability of the NIPSCO liner did not meet the target level of less than 10^{-7} cm/sec, it may still be usable for some liner applications since Indiana regulations only require that liners for coal combustion wastes have a permeability coefficient less than 10^{-6} cm/sec (4).

A problem occurred with the NSP liner material used for the field test when shrinkage cracks developed in the initial stage of curing. The shrinkage was reduced by decreasing the amount of water added to the liner mix from 23 wt% to approximately 20 wt% (dry weight). Unfortunately, decreasing the water content of the liner mix caused its permeability to increase. The permeability coefficient estimated from the in-field test was 1.8×10^{-5} cm/sec. The unconfined compressive strength of the NSP liner ranged between 1000 and 2000 psi (4).

It was not possible to determine from the results of the field test whether the shrinkage cracks in the NSP liner were continuous. If the cracks were not continuous through the full depth of the liner, then the material may have been acceptable as a liner (4).

Mineralogical and microscopic characterization of the fly ash liner materials collected at the field-test sites produced valuable information about their composition and microstructure. For the SWEPCO liner, the fly ash particles appeared to be held together by fibrous bridges and surface-to-surface point adhesions. The fibrous bridges may have been composed of ettringite. For both the NSP and the NIPSCO liners, the fly ash particles appeared to be held together by a continuous, interparticle matrix composed primarily of consolidated scrubber material. Significant amounts of ettringite were also detected in these two liner materials (4).

A cost analysis of the liner materials indicated that the main factors which determined the unit cost of the materials were the amounts of lime and cement added and the cost credit allowed for avoided disposal cost for the fly ash. The analysis also indicated that the fly ash liner materials were generally in the same cost range as polymeric membrane liners (4).

An engineering analysis of the fly ash liners indicated that both temperature-induced and load-induced stresses could cause cracking. The results of the analyses suggested that it would be advisable to cover the fly ash liners with several feet of compacted ash as quickly as possible after construction to protect the liner (4).

3.3 Numerical Modeling of Disposal-Related Soil Properties

3.3.1 Introduction

This task was conducted to develop a procedure for identifying inconsistent permeability data obtained from laboratory tests on soil properties from candidate waste disposal sites. Such inconsistent data can result from improper sample collection, sample storage, or laboratory testing. Having the capability to check results for consistency is critical because a single permeability measurement that does not meet the specified regulatory criteria for soil liners may exclude a candidate disposal site from being permitted.

A soils data-screening procedure was developed by compiling a relatively large data set, containing information on the permeability coefficient, liquid limit, plasticity index, and percent passing a #200 sieve, of soil samples collected at five power stations in east-central Texas. The screening procedure was based on a statistical model which predicted the permeability of a soil sample from its plasticity index and percent passing a #200 sieve. To screen the data set, each of the measured permeability coefficients was compared to its predicted permeability coefficient, and the difference between the two values was used as a measure of consistency for the data. If it was found that there was less than a five percent chance that a measured permeability coefficient would have been predicted by the model, it was concluded that the permeability measurement was significantly different from the rest of the data set. This finding could then be used as a basis for removing the inconsistent measurement from the data set.

3.3.2 Goals and Objectives

The purpose of this task was to develop a statistical procedure for checking the consistency of permeability data from candidate waste disposal sites in the Texas lignite region. This procedure can then be used to screen newly acquired soils data to identify test results that appear to be inconsistent with other data collected in this region.

3.3.3 Results and Conclusions

The mean values for log permeability coefficient, liquid limit, plasticity index, and percent passing a #200 sieve were all well within the acceptable ranges of the Texas Department of Water Resources (TDWR) liner criteria. All of the soil properties displayed relatively wide ranges of values, and all of the properties followed skewed distributions (3).

No strong correlations were found between permeability and the other soil properties. The best correlation was found between the liquid limit and the plasticity index (3).

The data regression analysis indicated that the plasticity index was the variable which had the largest effect on the permeability model. Percent passing the #200 sieve had the next largest effect, and liquid limit had the smallest effect on the model (3).

The data-screening procedure was designed to identify permeability measurements that are inconsistent with the rest of the reference data set based on the interrelationships exhibited between the various soil properties. This inconsistency does not necessarily mean that a permeability measurement is erroneous; however, it does indicate a high probability that the measurement is in some way different from the other measurements. The screening procedure should be used along with any other available information about the sample to make the final decision whether or not to remove the sample from the data set (3).

3.4 Leaching Test Evaluation

3.4.1 Introduction

This task was conducted as a response to the proposed changes to the solid waste regulations under RCRA Subtitle C amendments, which expanded the Toxicity Characteristic evaluation procedure to include additional chemicals and introduced a new extraction procedure to evaluate toxicity.

A study was performed to evaluate the use of follow-on TCLP tests. This was done by performing replicate leaching tests on two coal gasification tar samples using both Morgantown Energy Technology Center (METC) and TCL procedures. The METC leaching tests were used to identify the various classes of nonvolatile trace organics in the waste leachates, and the TCLP tests were used to quantitatively identify the organics which had specific regulatory criteria.

3.4.2 Goals and Objectives

The goal of this task was to evaluate the use of follow-on TCLP leaching tests in response to changes in the solid waste regulations under RCRA Subtitle C Amendments.

3.4.3 Results and Conclusions

The results of the study indicated that the METC procedure was an effective means of screening the gasifier tar leachates for nonvolatile organic compounds (3).

All of the compounds detected during the METC leaching tests conducted on the "dry" and "oily" tar samples were aromatics, with phenolics present in the highest concentration. The analyses obtained using the METC leaching procedure for the two tars were similar except that the dimethylphenols and naphthalene were detected only in the dry tar leachate (3).

Some of the compounds identified with the METC leaching test were not detected in all of the replicates, but the two classes of regulated nonvolatile organics, phenol and cresols, were detected in all of the replicate leaching tests (3).

Six regulated organics were detected in each tar sample. The TCLP leaching method and the associated analyses appeared to do an excellent job of quantitatively identifying the phenolics which the METC method had indicated were present in the tar leachates (3).

3.5 Electrostatic Separation of Unburned Carbon from Fly Ash

3.5.1 Introduction

An "off-the-shelf" electrostatic separation process was modified for use to reduce the unburned carbon content of fly ash. A bench-scale separator apparatus was constructed at the EERC and a series of test runs were performed to optimize the process. After the process was optimized, a sufficient amount of low loss-on-ignition (LOI) fly ash was collected to determine its air entrainment characteristics.

The fly ash used for the separation tests was obtained from the Allen S. King Power Plant owned by the Northern States Power Company, Minnesota. The King plant burns a mixture of Wyoming and Montana subbituminous coals and Illinois bituminous coal.

The separator apparatus was operated by dispensing fly ash from a vibrating pan through a slit onto a grounded, rotating steel drum. The high LOI ash fraction falls off the drum due to gravity as it rotates. The low LOI ash fraction sticks to the wheel due to electrostatic forces and is scraped off at a separate collection point.

3.5.2 Goals and Objectives

The goal of this task was to reduce the unburned carbon content of fly ash using a modified electrostatic separation process. Specifically, the goal was to produce fly ash with an LOI of less than 3% using the electrostatic separation process.

3.5.3 Results and Conclusions

The results of the separator tests showed that the apparatus was capable of splitting the bulk fly ash, which had an LOI of 7.3%, into two physically separate fractions. One fraction contained approximately 25 wt% of the ash and had an LOI of 3.6% while the other fraction contained the other 75 wt% of the ash. Air entrainment tests performed on the two fly ash fractions indicated that the low LOI fraction required 13.2% less air entraining agent than the bulk fly ash to produce an equivalent entrained air level (4).

It was not possible to achieve the goal of producing a fly ash with a LOI of less than 3% in the test runs that were performed. However, the ASTM C618 fly ash specification for cement replacement only requires that fly ash have an LOI of less then 6%, which the separation process easily achieved (4).

Based on the results of the bench-scale tests, it appears that the electrostatic carbon removal process has commercial development potential, since it is mechanically quite simple and produces significant carbon removal with a relatively low energy input. One drawback of the process is that only about 25% of the bulk fly ash is recovered in the low LOI fraction. However, it may be possible to increase this recovery with further development of the process. Furthermore, some power plants may not be able to sell more than 25% of their fly ash for cement replacement due to market limitations (4).

3.6 Bituminous Coal Fly Ash Data Collection and Evaluation

3.6.1 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.

3.6.2 Goals and Objectives

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.

3.6.3 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 (10).

The components of the database 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 (10).

The chemical characterization information consists of two groups. The first is the results as dictated by the ASTM C618 (1991). The chemical composition information required by the 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 (10).

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) (10).

Fly ash mineralogy was determined by a semiquantitative x-ray powder diffraction protocol developed by Dr. Gregory McCarthy at North Dakota State

University. 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 (10).

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 (10).

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 (10):

- 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.

- 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.

3.6.4 Advanced Coal Process Residues Database Results

A preliminary spreadsheet database of information on residues from various advanced coal processes has been generated. The effort 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) (10).

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 (10).

Future work should include the expansion of the Advanced Coal Process Residues Database. It is crucial to develop a solid understanding of these materials and to be able to compare their properties in order to use and/or dispose of them safely and cost effectively (10).

3.7 Activated Carbon Evaluation

3.7.1 Introduction

Activated carbons have many uses in industry. Most uses are associated with manufacturing and water purification, such as color removal and the removal of toxic or refractory compounds from waste streams. Additional uses are the removal of odorous compounds from industrial gas discharges and the adsorption of solvent vapor after air stripping of contaminated water.

Common materials utilized for the production of activated carbon include lignite and bituminous coals, wood, peat, heavy-petroleum fractions, and waste materials from pulping. In the process of activation, the carbon materials acquire a high surface area that provides a high efficiency of adsorption. Typical operations in the formation of activated carbon include devolatilization at about 590°C, followed by activation with steam or carbon dioxide at approximately 900° to 1010°C. Activation results in weight loss in the range of 30% to 60%. The loss of weight follows the enlargement of the pores during the oxidation that causes the increase in activation. Following activation, the carbon may be crushed, ground, grated, washed to reduce ash content, and dried.

A review of the literature pertaining to methods of characterizing and evaluating activated carbons was performed. Based on this review, methods were selected for laboratory evaluation. In addition, commercial vendors of activated carbons were contacted and several activated carbons were ordered for evaluation.

The analytical methods selected for characterizing and evaluating the chars and the activated carbons included surface area, sieve analysis, iodine number, molasses number, methylene glue number, bulk density, real density, apparent density, particle density, abrasion number, hardness number, and ash content.

Two mild gasification produced chars were collected. These included char samples from Red Harmon and Royal Oak lignites. Testing of these chars for characterization and evaluation was initiated. A mild gasification activated sludge effluent was used to evaluate the treatment efficiency of the lignite chars.

3.7.2 Goals and Objectives

The goal of this task was to characterize and evaluate chars produced from the mild gasification of lignite for use in the commercial activated carbon market or for cost-effective treatment of wastes generated by the mild gasification process.

3.7.3 Results and Conclusions

Preliminary testing of the Red Harmon and Royal Oak lignite chars indicated that they were not well suited for direct use as activated carbon. A comparison of lignite char and activated carbon characteristics is shown in Table 1. The values for effective size and uniformity coefficient for the lignite chars are approximately 60% less than those obtained using the commercial activated carbons. The mild gasification-produced lignite chars tended to be extremely friable and suffered from a high rate of attrition during handling (8).

The Red Harmon char-treated activated sludge effluent showed a chemical oxygen demand (COD) reduction of 17%, from 808 mg/L to 670 mg/L. Color was reduced from 3600 to 3300 APHA PtCo color units using the Red Harmon char, an 8.3% removal rate. Royal Oak char resulted in a COD reduction of 20%, from 808 mg/L to 645 mg/L. Royal Oak char reduced color from 3600 to 2700 APHA PtCo units, a 25% reduction. An identical dosage of Calgon F-400 activated carbon resulted in COD and color removals of 90% and 98%, respectively (8).

As-received mild gasification lignite chars are not well suited for direct use as an activated carbon. Surface area of these chars is less than desired for high-adsorption efficiency. Lignite chars exhibited a high degree of friability and suffered from elevated rates of attrition during handling. However, chars produced may be suitable for use following an activation step. Continuing research under this task will evaluate the effects of activation on mild gasification-produced lignite chars (8).

TABLE 1

Comparison of Lignite Char and Activated Carbon Characteristics

Parameter	Red Harmon Char 12*30	Royal Oak Char 12*30	Calgon[a] F-400 12*40	Norit[a] Hydrodarco 12*40
Surface Area (m^2/g)	211	183	404	271
Sieve Analysis (max %)				
Larger than No. 12	0	0	0.6	9.8
Smaller than No. 30	9.7	5.6	0	0
Smaller than No. 40	0.4	0.2	0.4	0.4
Uniformity Coefficient	1.2	1.2	2.1	2.2
Mean Particle Diameter (mm)	0.7	0.7	1.1	1.2
Effective Size (mm)	0.6	0.6	0.7	0.6
Hardness Number (100 max)	24	68	73	57
Abrasion Number (%)	41	67	73	52
Iodine Number (mg/g)	174	151	1150	640
Apparent Density (kg/m^3)	574	556	480	430
Ash Content (%)	20.4	26.9	7.1	19.6

[a] Values obtained at EERC laboratories.

Samples of the Royal Oak and Red Harmon chars were subjected to activation by steam and by syngas (H_2CO) activation methods. Neither of these methods resulted in a significant increase in surface area. Royal Oak char exhibited only a 4% increase in surface area when subjected to activation with syngas. Steam activation of the Royal Oak char resulted in a decrease in surface area from the original char (8).

Continuing research of activated char should include the examination of the processing and handling of the char material as it is done in the mild gasification process because it is suspected that the char may be exposed to the atmosphere while still hot, resulting in the oxygen of the atmosphere "burning" out the pores of the char particles. Future research should also include examining the effect of altering the temperatures of the mild gas process. Higher temperatures during the carbonization of the material is said to produce a better carbon particle (8).

3.8 Coal Ash Conditioning Study

3.8.1 Introduction

Dry coal utilization wastes are usually noncohesive materials which flow freely if not confined and are readily susceptible to dusting. Water is often mixed with these wastes prior to ultimate disposal to increase cohesion, reduce dusting, and lubricate the particles for better compaction. This operation is referred to as waste conditioning.

Conditioning of conventional fly ash usually requires the addition of between 10% to 15% water. For wastes from advanced processes such as AFBC with limestone addition, conditioning accomplishes an additional function because the water serves to hydrate the excess lime (CaO) created during the combustion process. Thus for conditioning wastes that contain substantial amounts of unhydrated lime, a significantly higher water addition level may be required compared to conventional coal combustion wastes.

In addition to controlling dust and increasing compaction, the conditioning process can also affect the extent to which cementitious and pozzolanic reactions occur in the waste after it has been placed at the disposal site.

During the first year, four coal utilization wastes were characterized to provide baseline elemental composition, mineral composition, and physical property data for the conditioning process evaluation. The advanced process wastes that were studied included a composite cyclone ash and baghouse fly ash from the Tennessee Valley Authority (TVA) Shawnee AFBC unit, an electrostatic precipitator (ESP) fly ash from the NSP Black Dog AFBC unit, and a spent-bed material from the KRW fluidized-bed gasifier. All three wastes were produced from processes that used limestone addition to the bed for sulfur capture.

In addition to the three advanced process wastes, a fly ash from a Riverside conventional cyclone-fired boiler burning a western subbituminous coal (WSC) was included in the conditioning study. This ash was included because it exhibited some of the same types of problematic behavior as the advanced process wastes. Moisture-density tests were also completed on the Black Dog and Riverside fly ashes.

The wastes considered for characterization during the second year included EERC materials from the low-temperature coal gasifier and the circulating fluidized-bed combustor (CFBC). Emphasis for the waste characterization task during the second year was on limestone bed materials from the Hydrogen Production project.

Two sets of conditioned fly ash specimens were prepared for physical, chemical, and mineralogical analyses. The fly ash was obtained from a Black Dog AFBC. The specimens were prepared using two different conditioning moisture levels and four different curing times in order to track changes in the physical, chemical and mineralogical properties of the conditioned ash for the first 28 days of the curing process.

A conceptual design was developed during the last year of this task for an ash-handling process to condition 50 ton/hr of self-heating AFBC ash. In this process, the ash will be mixed as a slurry with 55% moisture added on a dry weight basis. This conditioning moisture level was selected to fully hydrate the AFBC ash and provide a 30% residual moisture content, which previous studies have indicated will be the optimum moisture for producing the maximum compacted density. In this conceptual model, the conditioned ash would then be stored for a short period to allow the steam released by hydration reactions to dissipate and the ash to cool slightly before it would be transported to the ultimate disposal site.

The design of the conceptual ash-conditioning system was developed using certain assumptions. These included a 50-ton/hr conditioning rate, continuous operation, and a maximum transfer distance of 100 ft from the main silo to the feed silo. These assumptions, in conjunction with the physical and chemical characteristics of the ash mixture, were the basis for the design of the system.

The proposed conceptual AFBC ash-conditioning system was broken down into four main operations: ash conveying, temporary ash feed storage, and mixer feed; mixer operation; temporary conditioned ash storage for hydration; and conditioned ash transport and 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.

3.8.2 Goals and Objectives

The purpose of this task was to evaluate conditioning procedures for advanced coal utilization wastes and to evaluate trace element mobility within conditioned wastes.

3.8.3 Results and Conclusions

A dominant characteristic of all four wastes was a high calcium content. For the AFBC ashes, much of the calcium was present as free lime. For the KRW and Riverside wastes, however, only a small percentage of the calcium appeared to be in the form of free lime. The AFBC ashes liberated large amounts of heat when mixed with water and displayed a tendency to self-harden. The Riverside ash liberated a moderate amount of heat when mixed with water, but displayed a much greater tendency to self-harden. The KRW waste did not display significant self-heating or self-hardening behavior (5).

The three advanced process coal utilization wastes all had relatively high calcium and sulfur contents due to the fact that limestone was added to the AFBC and gasifier beds for sulfur capture. The Riverside fly ash also had a high calcium content due to the presence of calcium-bearing minerals in the coal rather than to an added sorbent.

Lime was found to be a major component of both the Black Dog and Tennessee Valley Authority (TVA) AFBC ashes. The lime was produced by calcination of limestone in the combustor bed.

The wastes were found to contain essentially no moisture, which was expected since the lime tended to bind any moisture in the waste through hydration reactions. The LOI measured for the Black Dog and TVA AFBC ashes were relatively high compared to conventional coal combustion ash. The extremely low LOI of the KRW gasifier bed material was probably caused by the oxidation of sulfide during the LOI test.

The advanced process wastes, particularly the AFBC ashes, appeared to contain significant amounts of free lime (CaO) as indicated by their high initial pH values and large buffering capacities in the 11- to 12-pH range. In contrast to the advanced process wastes, the conventual Riverside fly ash contained only a small amount of free lime. The Riverside fly ash, however, displayed a large buffering capacity in the pH range of 5.5 to 2.0.

Titration curves indicated that the advanced process wastes had a different gross chemical composition, at least in terms of acid-neutralizable components, compared to the Riverside fly ash. The titration of the KRW spent-bed material liberated a strong odor of hydrogen sulfide, indicating the presence of calcium sulfide in the waste. The results of the KRW titration indicated that the calcium sulfide content was in the range of 5 to 10 wt%.

Moisture-density tests were completed on the Black Dog and Riverside fly ashes. Based on observation made during these tests, it appeared that self-hardening reactions occurred after the water was added and caused the Riverside ash to set up after about 15 minutes. As the ash set up, it changed from a fine powder to a coarse, granular material which was much less cohesive when compacted. The Black Dog ash also hardened after water was added, but to a much lesser extent than the Riverside ash.

It was found that if the amount of conditioning water was less than about 35%, the Black Dog ash heated to 100°C (with an accompanying generation of steam). When the amount of water was greater than 35%, the maximum ash temperature decreased. Apparently the additional water absorbed enough of the heat liberated from lime hydration to keep the temperature from reaching 100°C. The Riverside ash showed a gradual increase in maximum temperature as the amount of conditioning water was increased to about 20%. The difference between the two ashes is probably due to the fact that the heat released by the Black Dog ash was principally caused by lime hydration, while the heat released by the Riverside ash was principally caused by tricalcium aluminate hydration.

Both ashes consumed some of the water added during the conditioning tests. The difference between the water added and the water contained represents the water lost to either hydration reaction, evaporation, or steam generation. For the Black Dog ash, water loss (about 10%) was independent of the amount of conditioning water initially added to the ash, but for the Riverside ash the water loss gradually increased to a maximum of about 10% as the amount of added water increased.

Although the self-heating and water-loss relationships indicated by the conditioning tests appear well defined, caution must be used when applying this type of information to field disposal. The chief difference between laboratory tests and field conditions is the bulk quantities of ash handled. The relatively small amounts of ash used for the laboratory tests will lose both heat and water more readily due to evaporation and steam generation than the large quantities of ash handled in the field. This means that ash handled in the field may get hotter, stay hot longer, and lose less water than the laboratory data indicates.

3.8.4 Bulk Chemical and Mineralogical Characterization

In this study, proton-induced x-ray emission (PIXE) results were used to determine an initial list of trace elements for quantitation in the two residues. That list included all RCRA elements, even if they were not identified by the PIXE results. Other highly mobile elements were also included for completeness.

The chemical characterization protocol included the quantitative analysis of the trace elements 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, LOI, and carbonate were also determined in the original materials.

Mineralogical characterization by x-ray diffraction of the bulk samples was completed.

3.8.5 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. 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, and the second was dried and crushed for potential use in a 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. 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 (10).

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 ($Ca_6Al_2[SO_4]_3[OH]_{12} \bullet 26H_2O$) in the sample that had cured for 28 days (10).

Leaching characterization of these conditioned materials is recommended for future work. The leaching characterization should include short- and long-term leaching procedures. This study will provide extremely beneficial supplemental information regarding trace element mobility in conditioned FBC ash.

The results and conclusions for the conceptual ash-conditioning system, developed during last year of this task are as follows (9):

- The optimum moisture content of the 65/35 char/fly ash mixture was found to be 30% of dry weight (residual moisture). To achieve this moisture content, a water addition rate of 55% of dry sample weight must be used to compensate for moisture loss due to hydration reactions.

- The maximum compacted density of the ash mixture was found to be 77 lb/ft^3 at a moisture content of 30% of dry weight. At this density, a maximum 28-day compressive strength of 366 psi was developed. A permeability of 1.5×10^{-5} cm/sec occurred at the optimum moisture content of 30% of dry weight.

- Since the AFBC ash began to stiffen shortly after the conditioning water was added, a limited amount of time was allowed for mixing. The time from the start of mixing until the ash begins to stiffen was approximately 2 minutes. Therefore, a mixer was selected with residence time less than 1 minute.

- The conditioned ash slurry developed an average short-term (15 minutes to 5 hours), unconfined compressive strength of 16.6 psi. Minimum and maximum short-term compressive strengths were found to be 13.6 and 19 psi, respectively. These data indicated that temporary storage of the conditioned ash would be possible, since these compressive strengths would not hinder the removal of the conditioned ash from the storage areas.

- The conditioning process was chosen to be continuous in order to meet the assumed 50-ton/hr conditioning rate. A continuous process was also required to meet the short mixer residence time required for conditioning.

- In the design, the AFBC ash would be stored in a 23,000-ft^3 combination silo. The ash would be transported from the main silo to the mixer silo with a screw conveyor. The mixer-feed silo would be used to temporarily store the ash mixture. Two 25-ft by 25-ft storage areas would then provide temporary storage for the conditioned ash slurry, allowing the hydration process to be completed, and the ash to cool. The temporary storage areas would be fully enclosed to capture the steam released during the hydration process. After approximately 30 minutes of steaming and cooling, the conditioned ash would be removed from the storage areas with a front-end loader equipped with a 2-yd^3 bucket. The ash would then be placed in a landfill.

- Major, minor, and trace constituents showed no trend of mobility within the conditioned AFBC ash. Hydrated mineral phases were identified in cured conditioned AFBC ash. Leaching characterization is recommended for future work.

3.9 Characterization and Treatability of Coal-Water Fuel Process Waters

3.9.1 Introduction

Coal beneficiation through hydrothermal dewatering has emerged as one of the most promising technologies for upgrading low-rank coals. 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 medium. 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 (CWF) 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 CWF waters. Cost-effective production of CWFs can only take place if waste management technologies are developed prior to prototype plant construction.

3.9.2 Goals and Objectives

The purpose of this task was to characterize and investigate the treatability of hot-water dried (HWD) CWF at the bench scale.

3.9.3 Results and Conclusions

A survey of chemical characterization data for HWD coal process waters was conducted and relevant information was entered into a database management system (6). Several general trends were apparent when a comparison was performed on the chemical characteristics for process waters generated during hot-water drying of a variety of lignite and subbituminous coals. Increasing organic contaminant concentrations occurred with increasing process temperatures. A general increase in 4AAP phenolics, five-day biochemical oxygen demand (BOD_5), COD, and total organic carbon (TOC) occurred with all coal types. Increasing ammonia concentrations were observed with increasing process temperature. A general decrease in sulfate concentrations was seen in all process waters, with increasing temperature. Ash-producing ions, calcium and sodium, followed an increasing trend with increased process temperature. Magnesium concentrations decreased with the increasing operating temperatures. High COD:BOD_5 ratios indicated that high concentrations of biorefractory organics were present in the CWF process water (9).

Based on the results of this survey, several treatability issues were identified (9):

- Coal chemistry and coal type will have a major effect on process water characteristics, treatability, and reuse potential.

- Differences in processing temperature and pressure have a pronounced effect on process water characteristics within a temperature range between 270° and 330°C.

- Thorough characterization of process waters is necessary.

- Biological oxidation will be a key unit process.

- Future discharge and/or reuse criteria need to be defined so that treatment process limitations may be properly evaluated.

- Verification of treatment process stability, reliability, and the development or verification of kinetic parameters should be performed at the bench and pilot scale.

- High COD:five-day biochemical oxygen demand (BOD_5) ratios in HWD CWF process waters indicate high levels of biorefractory organics that will require further treatment of secondary effluent prior to discharge under most situations.

Process water used in treatability testing was collected during the hot-water drying of coal from the Usibelli coal mine near Anchorage, Alaska. A representative sample from the Usibelli HWD CWF process water was submitted to the EERC Analytical Research Laboratory (ARL) for chemical and physical characterization prior to treatability testing (9).

Two secondary treatment systems were selected for evaluation, an anaerobic treatment system and an aerobic treatment system. The anaerobic system combined anaerobic biodegradation with granular activated carbon adsorption in a two-stage expanded-bed reactor configuration. The aerobic system was a conventional activated sludge process (9).

An anaerobic bacterial culture was obtained from the Moorhead, Minnesota, sludge digester, and the aerobic culture was obtained from an activated sludge reactor treating mild gasification wastewater. Testing with these two systems was conducted to evaluate the removals of selected parameters, such as BOD_5, COD, ammonia (NH_3), and color (9).

In the anaerobic system, breakthrough (COD = 400 mg/L) in Column 1 was found to occur 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 (10).

Operation of two columns in series significantly extended the time to system effluent COD breakthrough. Two-stage operation resulted in an increased utilization of adsorptive capacity that approximately tripled the throughput to breakthrough, while only doubling the amount of carbon (10).

The gas generated through anaerobic metabolism was analyzed for composition. The methane content of the gas generated averaged approximately over 70 mole percent. The relationship between COD loading and the gas generated is represented by the equation: $y = 0.156x + 0.0139$. Thus for each 100 grams of COD applied to the system, approximately 16 liters of gas are generated (10).

The aerobic treatment system was based on the concept of activated sludge. BOD_5 removals of 95% were achieved during activated sludge treatment of Usibelli process water. The average influent BOD_5 of 1220 mg/L was reduced to as low as 31 mg/L, but was not consistent. Treatability target discharge goals, based on the new source performance standard (NSPS), were 30 mg/L. The average influent total COD during the operating was 4540 mg/L. Average effluent soluble COD was 3730 mg/L, an 18% removal rate. This concentration is much higher than the target effluent quality goal of 400 mg/L. High concentrations of refractory COD in the activated sludge effluent will require further treatment. Average influent ammonia influent 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 results of air stripping in the aeration basin, rather than biological nitrification. No increase in effluent nitrate was detected (10).

3.10 Waste Depository Scavenger Study

3.10.1 Introduction

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 can include lead, copper, zinc, and contaminants migrating from fly ash waste can include boron, molybdenum, arsenic, and selenium. Remediation of these types of contaminants is expensive and sometimes problematic. Inexpensive waste-cell liners composed of abundant sorptive materials, such as zeolites, chars, and clays, could be an economical way to immobilize contaminants.

3.10.2 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 chemical and mineral properties of the proposed scavenger materials. The second phase involved the use of batch testing and percolation experiments to determine the sorptive abilities of selected materials.

3.10.3 Results and Conclusions

Clinoptilolite, a zeolite mineral with the general formula of $(Na,K)_6(Al_6Si_{30}O_{72})\bullet 20H_2O$, was tested for its ability to immobilize ions of selenium, molybdenum, copper, and lead. Ions of lead and copper were chosen for initial experiments because clinoptilolite has a strong affinity for both of these contaminants, and they are commonly found in municipal landfill leachate. Selenium and molybdenum were chosen for the first percolation experiment because they are common constituents in fly ash leachate (10).

Clinoptilolite obtained from East West Minerals Company, Denver, Colorado, was analyzed by x-ray diffraction (XRD) techniques to determine other phases present. The clinoptilolite was found to be nearly homogeneous and contained only a minor amount of quartz. Scanning electron microscope/ electron probe microanalysis (SEM/EPMA) revealed that the zeolite was more potassium-rich than sodium-rich (10).

Limited batch testing has indicated that clinoptilolite was effective at removing lead from solution, but not an effective scavenging material for Se^{+4} (selenium) or Mo^{+6} (molybdenum) (10).

Further research in this area will include the evaluation of other possible scavenging materials in more complex systems that model field behavior. The evaluation of other scavenging materials, such as chars and clays, and the development of optimum mixtures should also be pursued.

Future research should also focus on determining the quantities of contaminants that are permanently immobilized and quantities that are able to be remobilized from the scavenging agents. This will be an important factor in determining the environmental impact of these materials.

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