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Low-Rank Coal Research

Final Report

Volume I. Control Technology, Liquefaction, and Gasification

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April 1987

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For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of North Dakota Energy Research Center
Grand Forks, North Dakota

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SIMULTANEOUS SO_x/NO_x CONTROL

**Final Technical Report for the Period April 1, 1986 - March 31, 1987
including the Quarterly Technical
Progress Report for the Period January through March 1987**

By

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April 1987

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Pittsburgh, Pennsylvania**

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ABSTRACT

The overall project objective is to expand the scientific and engineering data base necessary for the development of innovative processes for the control of SO_x emissions during coal combustion. Investigation of dry sorbent injection concepts for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization were considered in this project.

Task A, Sorbent Evaluation, activities in the first year included a literature review of calcium-based sorbent characteristics and evaluation of two limestones and their respective calcination and hydration products. The literature review addressed sorbent characteristics with respect to flue gas desulfurization processes with emphasis on furnace injection technology. Results of the literature review showed that calcium-based sorbents are well distributed throughout the 48 contiguous states and that an additional 3 to 5 million tons per year of high-calcium lime could be produced from existing capacity for use in SO_2 control processes. Limestone properties have been extensively characterized for fluid bed combustion applications as well as conventional flue gas desulfurization processes. Comprehensive information on lime and hydrated lime was found to be limited with respect to furnace sorbent injection technology and flue gas desulfurization processes in general.

The two commercial sorbent products evaluated in Task A were obtained from the Marblehead Lime Company and the Dravo Lime Company. The Marblehead limestone is mined in Illinois and the Longview limestone is mined by the Dravo Lime Company in Alabama. From each company, sufficient quantities of limestone, lime, and hydrate were acquired to perform the calcination and hydration experiments. Pilot-scale furnace injection experiments and chemical and physical analyses were performed on the commercial sorbents to establish baseline characteristics.

Results of the experiments showed that the commercial hydrate resulted in better sorbent utilization than the limestone or lime for both the Marblehead and Longview materials. At Ca/SO_2 mole 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 mole 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 mole ratio of 1.0. Limestone and lime also exhibited similar results with utilization values of 15% observed at a Ca/SO_2 mole ratio of 1.0. Hydration experiments conducted to determine the impact of pressure and water stoichiometry on sorbent reactivity were not statistically significant. Therefore, for hydration pressures and water stoichiometries ranging from 50 to 180 psig and 1.0 to 1.6, respectively, no change in hydrate reactivity with respect to SO_2 was observed during pilot-scale furnace injection tests.

Task C, Combustion System Operability, involved activities evaluating the impact of furnace injection on ash deposition and electrostatic precipitator performance and flue gas humidification for improved sorbent utilization. Pilot-scale combustion tests were conducted with an Illinois No. 6 bituminous coal and pressure hydrated lime prepared from Marblehead lime. One test was

run without sorbent injection to establish baseline conditions. Two additional tests were run with sorbent injection to achieve 50% and 90% SO₂ control. Ninety percent SO₂ control was not achieved due to sorbent feeder limitations. A Ca/SO₂ mole ratio of 1.2 was necessary to achieve 50% SO₂ control and 75% SO₂ control was achieved at a Ca/SO₂ mole ratio of 2.2. Results of these tests showed this coal/sorbent combination to be low fouling. The ash deposited on the probes continuously sloughed off, indicating that the deposits were weak and should be easily removed with conventional sootblowing equipment. Electrostatic precipitator 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 gr/scf. Correspondingly bulk ash resistivity increased from 10¹² to 10¹⁴ ohm-cm.

Flue gas humidification experiments performed on the pilot-scale combustion system were conducted firing natural gas and using steam as the humidification medium. Roughly 50% sorbent utilization was observed 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%. Increasing sorbent residence time in the duct by injecting at 1250°F resulted in 55% sorbent utilization.

Task D, NO_x→NO₂ Conversion, was a bench-scale fixed-bed reactor study designed to determine mechanisms responsible for the production of NO₂ from NO as it pertains to gas stream cleanup processes. Results from a statistically designed experimental program showed temperature to have the most significant impact on NO₂ production. Other parameters evaluated included oxygen, sulfur dioxide, and moisture content of the flue gas. The rate of NO₂ formation was also found to increase with increased sulfation rate.

1.0 INTRODUCTION

In 1983 the Grand Forks Energy Technology Center of the U.S. Department of Energy was transferred to the University of North Dakota. Since April 1, 1983 the facility has been operating as a nonprofit contract research organization called the University of North Dakota Energy Research Center (UNDERC). Department of Energy programs ongoing at the time of the transfer were continued under a three-year Cooperative Agreement with the Department of Energy. In 1986 a second multi-year Cooperative Agreement (Contract No. DE-FC21-86MC10637) was signed by the Department of Energy. This report documents the results for the SO_x/NO_x Control project for the period April 1, 1986 through March 31, 1987. The highlights of previous work, current program goals and objectives, first year accomplishments on a task basis, and conclusions based on the work completed are summarized.

1.1 BACKGROUND

National attention continues to focus on acid rain and its potential threat to the environment. Scientific groups and individuals across the country generally agree that acid deposition problems exist, but no consensus has been reached as to the severity of the problem, the deposition mechanisms, or the appropriate remedies. Proposals range from immediate enactment of laws to reduce SO₂ and NO_x emissions from combustion sources to additional research studies of acid deposition phenomena.

There is general concern over the emissions of SO_2 , NO_x , and fine particulate matter from stationary coal-fired sources. When coal is utilized in pulverized coal-fired boilers, 70% to 100% of the sulfur and 60% to 80% of the mineral matter in the raw coal are generally converted to SO_2 and suspended fly ash in the flue gas stream, respectively. Emissions of NO_x result from oxidation of both fuel nitrogen and a portion of the nitrogen contained in the combustion air.

New Source Performance Standards (NSPS) for utility boilers limit SO_2 emissions to 1.2 lbs $\text{SO}_2/10^6$ Btu of fuel input and require 70% to 90% SO_2 control depending on heating value and sulfur content of the coal. Current control technology generally employs wet or dry scrubbing with calcium-based sorbents (limestone or lime).

UNDERC has been conducting flue gas desulfurization (FGD) studies since the early 1970's. The first major FGD program pioneered the use of alkaline fly ash in a wet scrubber system to control SO_2 emissions from western coals. Fly ash alkali FGD studies were conducted both on a pilot-scale process development unit and a full-scale utility boiler (1,2,3). Approximately 4200-MW of western U.S. generating capacity currently employ the fly ash alkali process to reduce SO_2 emissions.

Direct injection of sodium-based SO_2 sorbents into combustion systems was also investigated. Nahcolite and trona were evaluated in a pilot-scale combustion system using a fabric filter baghouse (4). Both materials were capable of retaining 80% SO_2 . Similar results were reported by Muzio, et al. (5).

Pilot-scale evaluation of direct furnace injection of high-calcium and dolomitic limestone and quicklime began at UNDERC in early 1978 (6). Sulfur dioxide reduction and sorbent utilization values did not exceed 16% for the limestone injection tests. The relatively low utilization of the limestone was due to an inadequate time/temperature profile necessary for reaction with SO_2 and poor development of the sorbent surface area. Maximum quicklime utilization was 32% at a Ca/SO_2 mole ratio of 1.0 during pilot-scale tests.

In 1981, DOE sponsored a field test on a 50-MW utility boiler to examine direct injection of limestone into boiler flue gas and into a burner operated in a low- NO_x , staged-combustion mode (7). Limestone utilization up to about 16% and SO_2 removal up to 47% were achieved. Samples of the resulting fly ash/calced limestone mixture were subsequently found to be reactive in a spray dryer FGD process.

Recent work at UNDERC has focused on the development of a dry technique for simultaneous control of SO_x/NO_x emissions from coal derived flue gas. The approach combines direct furnace injection of a calcium-based sorbent with particulate collection in a baghouse and a catalytic or noncatalytic NO_x control technique. Specifically, direct furnace injection of high-calcium pressure-hydrated lime and additive-enhanced high-calcium pressure-hydrated lime are being evaluated for SO_2 control.

Pilot-scale combustion tests have evaluated the effectiveness of direct furnace injection of high-calcium pressure-hydrated lime over a range of injection temperatures (1300°-2700°F). At a Ca/SO₂ mole ratio of 1.0, approximately 50% to 55% control of SO₂ emissions was observed (8). At a stoichiometry of 2.0, approximately 80% control was achieved. Residence time and the temperature regime of the sorbent injection location were critical parameters controlling SO₂ reduction and sorbent utilization. A field test of this process, sponsored by the Grand Forks Project Office of the DOE in 1984, demonstrated furnace injection of pressure-hydrated lime for SO₂ control on a utility boiler operated at 44 MW (9). Although the results were not as good as the earlier pilot-scale results, 50% and 70% of the SO₂ was readily removed at Ca/SO₂ mole ratios of 2.0 and 4.0, respectively. Boiler and precipitator performance remained good (e.g., stack opacity levels never exceeded 10%).

Further pilot-scale tests have shown that furnace injection of high-calcium pressure-hydrated lime at a Ca/SO₂ mole ratio of 1.0 can result in 80% SO₂ capture when a baghouse is operated at an approach to saturation temperature of 15°-20°F (~150°F) (10). Improved sorbent utilization has been observed both for high-calcium and for additive-enhanced pressure-hydrated lime at the reduced baghouse temperature. Of the 80% overall utilization, 50% of the sorbent utilization occurred in the flue gas stream as a result of furnace injection and an additional 30% occurred in the baghouse. Baghouse temperature and flue gas moisture content appear critical in achieving these results. Similar results have been observed by other investigators (11), but required operation of the baghouse at an approach temperature of ~7°F and somewhat different process scheme with sorbent injection immediately upstream of the baghouse.

Three specific items must be addressed to complete proof-of-concept development of furnace injection of pressure-hydrated lime as a viable technique for SO₂ control. First, optimization of sorbent reactivity must be completed. Recent pilot-scale tests have shown that two pressure hydrates produced at similar conditions but using different lime sources resulted in roughly a 10% difference in utilization value. Physical and chemical characterization of the sorbents showed no substantial differences although each lime was produced using different calcination methods (rotary versus shaft kilns). Evaluation of several limestones and the effect of calcination and pressure hydration conditions on the resulting pressure-hydrated sorbents' ability to capture SO₂ is a necessary step if furnace sorbent injection is to become an accepted approach to SO₂ control.

Economic evaluations by UNDERC (12) and others (13,14) have shown an advantage for furnace injection over conventional SO₂ control technologies (wet and dry scrubbing). Sorbent cost has always been the most significant factor when evaluating the economics of furnace injection technology. Maximizing sorbent utilization is therefore necessary to minimize furnace injection costs. Second, investigation of additives and sorbent recycle is necessary to determine the potential for increased sorbent reactivity/utilization.

The third item addresses the effect of sorbent/ash interactions and their effect on sorbent reactivity, rate of ash deposition, deposit strength, and particulate collection device performance. Several investigators have documented ash interference and/or enhancement of sorbent utilization. Studies conducted by EPA (15), focusing primarily on eastern coals, documented ash interference. Limited work conducted by UNDERC has shown both enhanced sorbent utilization in the presence of ash and variable sorbent utilization with ash chemistry even when fuel sulfur remained relatively constant (16,17). Based on this limited work, further work is needed to understand the effect of ash/sorbent interactions and the relationship between sorbent reactivity and fuel mineralogy.

Sorbent/ash deposition rates and deposit strength information is also required to fully understand furnace sorbent injection effects on boiler operability. Furnace sorbent injection definitely increases deposition rate due to increased particulate loading, but may reduce deposit strength for certain fuels. While addition of calcium-based materials has generally resulted in weakened ash deposits, this phenomenon has not been correlated with data on fuel mineralogy.

Evaluation of furnace sorbent injection effects on particulate collection device performance is also necessary. Results reported by other investigators (18) have shown ESP upgrades or retrofits are necessary if furnace sorbent injection is to be a viable retrofit SO_2 control technique. However, the previously cited field test conducted by DOE demonstrated limited impact on ESP performance during furnace sorbent injection tests when firing a North Dakota lignite. Stack opacity never exceeded 10% with a baseline of 6%. The degree to which particulate loading and bulk ash resistivity affect ESP performance directly relates to the baseline ash characteristics and ESP design but has not been adequately defined.

2.0 GOALS AND OBJECTIVES

The overall project objective is to expand the scientific and engineering data base necessary for the development of innovative processes for the control of SO_x emissions during coal combustion. Investigation of dry sorbent injection concepts for SO_x control and methods of enhancing SO_x sorbent reactivity/utilization will be considered in this project. The proposed study addresses factors which may impact both sorbent reactivity and operability of the combustion system for new and retrofit applications. Specific factors to be addressed include: 1) sorbent properties, 2) sorbent processing conditions, 3) impact of sorbent injection on boiler performance, and 4) operability of the particulate control device.

2.1 THREE-YEAR OBJECTIVES

2.1.1 Task A. Sorbent Evaluation

The first step of the sorbent evaluation effort will involve reviewing available literature on limestone characteristics. Based on the literature reviewed, four limestones will then be selected for detailed characterization. In addition to the as-mined limestone, samples of commercial products (quicklime and/or hydrates) produced from the limestones will also be obtained. Parametric testing of these materials will evaluate both calcination and hydration conditions. Selection of two limestones will be made in the first year of the Cooperative Agreement. Two limestones and their respective calcination and hydration products will be characterized in the first year with the two remaining limestones characterized in the second year of the program.

- (i) A minimum of two distinct calcination conditions will be evaluated, reflecting those typically found in rotary and shaft kilns. Shaft kilns are typically fired several hundred degrees centigrade higher than rotary kilns and result in hard burn quicklime. Calcination experiments will involve using a muffle furnace system. Initial tests will establish conditions necessary to produce quicklime equivalent to that resulting from commercial calcination. Based on results at these conditions, one or two additional sets of calcination experiments may be run at slightly altered conditions (temperature and/or residence time).
- (ii) Parametric pressure-hydration experiments will study hydration pressure, temperature, and water stoichiometry for each commercial quicklime. A single set of hydration conditions will be used to evaluate experimentally produced quicklime samples. Hydration experiments will be performed in the UNDERC bench-scale pressure hydrator.
- (iii) All pressure-hydrated sorbents produced in the bench-scale pressure hydrator will be evaluated for sorbent reactivity in the particulate test combustor. Each sorbent will be injected into the combustor firing natural gas. Anhydrous SO_2 and NH_3 will be injected to produce 1000 ppm SO_2 and 700 ppm NO_x , respectively, in the flue gas. Sorbent feed rates will be set to maintain a Ca/SO_2 mole ratio of ~ 1.0 . Sorbent reactivity will be determined by SO_2 reduction and sorbent utilization. Nitrogen dioxide (NO_2) and total NO_x will be monitored continuously to determine changes in NO_2 levels due to pressure-hydrated lime injection.
- (iv) Analytical techniques to be used for characterization of materials include multipoint BET surface area, coulter counter, porosimetry, loss on ignition (LOI), x-ray diffraction (XRD), and x-ray fluorescence (XRF) analysis. Atomic absorption (AA) and inductively coupled plasma spectrometry (ICP) will be used as a check on XRF elemental analysis. Complete chemical and physical characterization of the unreacted and sulfated sorbents will be provided.

2.1.2 Task B. Enhanced Sorbent Reactivity/Utilization

An increase in sorbent reactivity/utilization will decrease sorbent costs and improve economics for furnace injection technology. Two approaches will be attempted to achieve increased sorbent utilization. The use of additives to enhance sorbent utilization was initiated under the previous Cooperative Agreement. Evaluation of additional additives will be performed in the second and third year of the new program if and when they are identified. Sorbent recycle is another technique which has potential for increasing overall sorbent utilization. Evaluation of sorbent recycle will begin in the second year with completion in the third year of the program.

- (i) Investigate the use of promising additives in conjunction with the pressure hydrator, and test the enhanced sorbents in a pilot-scale combustion system.
- (ii) Evaluate the potential for sorbent recycle in conjunction with the pressure hydrator, and test the resulting sorbents in a pilot-scale combustion system.

2.1.3 Task C. Combustion System Operability

Furnace sorbent injection studies have shown that deposition rate increases but that deposits are generally weaker and more easily removed with conventional soot-blowing equipment. Furnace sorbent injection obviously increases particulate loading to flue gas cleanup systems and also affects electrical properties of the bulk ash. Increased particulate loadings and high bulk ash resistivity adversely affect emissions levels, especially for ESP's. Ultimately the effects of furnace sorbent injection on ESP performance are the result of the ESP design and the physical and chemical characteristics of the original fly ash. To better establish these impacts, two fuels, a South Hallsville Texas lignite and a Sarpy Creek subbituminous coal, were evaluated under the previous UNDERC/DOE Cooperative Agreement. Evaluation of four additional fuels will begin in the first year with completion planned for the third year of the new Cooperative Agreement. Operational modifications such as flue gas humidification also have potential for improved sorbent utilization. Additional techniques (if any) to be evaluated in addition to flue gas humidification will be determined as work progresses. Evaluation of operational modifications will begin in the first year with completion in the second year of the Cooperative Agreement.

- (i) Four fuels will be selected for evaluation using location (geographical), type (bituminous, subbituminous, lignite), market (current and potential), and previous use in other furnace injection programs as selection criteria.
- (ii) Combustion tests will be performed on a pilot-scale combustion system using an ESP for particulate control. High-calcium pressure-hydrated lime will be prepared in the UNDERC bench-scale pressure hydrator for use during these tests. Sorbent furnace injection rates will be adjusted to achieve 50% and 90% SO₂ control, respectively. Combustion tests without sorbent addition will also be performed to establish baseline data.

- (iii) During combustion tests with each fuel type, a composite coal sample will be collected for inorganic characterization. Inorganic phases will be determined through a combination of chemical fractionation, low-temperature ashing, x-ray diffraction, and scanning electron microprobe analyses. The inorganic characterization data will be used to evaluate the differences noted in the inherent sulfur capture and injected sorbent utilization values for the different fuels.
- (iv) Analytical methods to be used include BET surface area, coulter counter, porosimetry, x-ray diffraction (XRD), x-ray fluorescence (XRF), ultimate, proximate, ash fusion temperatures, bulk ash resistivity, sulfur forms, loss-on-ignition (LOI), and dry sieve. AA and ICP will be used as a check on XRF elemental analysis. This information will provide complete chemical and physical characterization of coal, coal ash, fly ash, ash deposits, and sorbents.
- (v) Flue gas humidification experiments will be performed on a pilot-scale combustion system using both steam and water for humidification. Flue gas will be humidified upstream of a particulate control device (baghouse and/or ESP) at a point in the system where flue gas temperatures are $\leq 1000^{\circ}\text{F}$. High-calcium pressure-hydrated lime will be injected into the furnace to achieve maximum sorbent utilization in the high-temperature ($1400^{\circ}\text{--}2200^{\circ}\text{F}$) flue gas stream. Humidification will then be used to achieve additional SO_2 control in the particulate control device and upstream flue gas duct. Analytical characterization of samples will be identical to those in item (iv) above.

2.1.4 Task D. ~~NO~~ $\rightarrow$ NO_2 Conversion

A bench-scale study will be conducted to identify mechanisms responsible for the production of NO_2 from NO as it pertains to gas stream cleanup processes. Once the mechanisms have been identified an attempt will be made to develop methods to reduce/eliminate NO_2 emissions. This effort will be initiated and completed in the first year of the Cooperative Agreement.

2.1.5 Task E. Process Economics

An engineering/economic evaluation of furnace sorbent injection was completed in the third year of the previous Cooperative Agreement. The evaluation compared 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) application. Sensitivity analyses were performed for sulfur level and sorbent utilization. If progress towards improved sorbent utilization can be made in years 1 and 2 of the new Cooperative Agreement, a new economic evaluation will be prepared in year three.

2.2 CHANGES TO THE FIRST-YEAR PROJECT PLAN

Two changes to the first-year project plan were requested and approved. The first change modified the scope of work for Task A, Sorbent Evaluation. The change resulted in deleting tests which were planned to evaluate hydration temperature. The test plan called for performing pressure hydration experiments to determine the effect of hydrator operation at 25°F above and below the saturation temperature for a specific pressure (150 psig). Similar experiments performed during the previous Cooperative Agreement showed that operation of the pressure hydrator above and below the saturation temperature resulted in hydrates which demonstrated reduced utilization. Operation of the hydrator at 25°F below the saturation temperature typically resulted in a completely hydrated sorbent but the sorbent was wet and difficult to feed during injection tests. Operation of the hydrator at 25°F above the saturation temperature resulted in a sorbent which was not completely hydrated and ultimately demonstrated reduced utilization. Secondly, operating a pressure hydrator at temperatures above saturation can potentially result in a superheat condition which must be avoided for operational and safety reasons. Therefore, deleting tests from the Task A effort was warranted. The six experiments deleted were replaced with replicate experiments of hydration pressure and water stoichiometry conditions to better determine data variability.

The second change involved rescheduling completion of Task D, NO--> NO₂ Conversion. Originally, the Task D completion date was August 31, 1986. Due to personnel availability problems and delays encountered with sample analysis, completion of Task D was rescheduled for January 31, 1987 and subsequently March 31, 1987. Personnel availability problems were encountered when the project manager found it necessary to temporarily reassign personnel to a non-DOE project. Delays encountered with respect to completion of sample analysis were due to personnel leaving UNDERC resulting in a temporary loss of technical capability.

3.0 ACCOMPLISHMENTS

3.1 TASK A, SORBENT EVALUATION

The purpose of this task is to identify and quantify the effects of sorbent processing on the reactivity of commercial high-calcium sorbent preparations. Sorbent processing includes the calcination and hydration conditions resulting in a hydrated lime (calcium hydroxide) product. Research at UNDERC specifically addresses the effect of these conditions on the reactivity of pressure-hydrated lime preparations. Pressure hydrates have been shown to be equal or superior to the commercial slaking process with respect to sorbent reactivity. Although processing conditions can lead to changes in physical properties of a sorbent, the final criteria for determining improved reactivity is the actual performance of a sorbent in controlling SO₂ emissions.

The two commercial sorbent products evaluated in the first year of the Cooperative Agreement were obtained from the Marblehead Lime Company and the Dravo Lime Company. The Marblehead limestone product was mined in Illinois and the Longview limestone was mined in Alabama by the Dravo Lime Company. Sufficient quantities of limestone, lime, and commercial hydrate were acquired from each company to perform the calcination and hydration experiments. Pilot-scale furnace injection experiments and chemical and physical analyses were performed on the commercial sorbents to establish baseline characteristics.

3.1.1 Description of Facilities and Procedures

Muffle Furnace

Calcination experiments were performed in a muffle furnace. The upper limit operating temperature of the muffle furnace was 2200°F. Internal furnace dimensions were 11x11x18 inches. Furnace temperature was measured with an inconel sheathed Type K thermocouple and set with a proportional controller. Refractory trays were constructed at UNDERC to hold the limestone sample to be calcined. The trays were constructed of a standard castable refractory and measured 10x10 inches. The muffle furnace held three trays and each tray held 7 to 8 pounds of pebble limestone.

The calcination procedure involved preheating the muffle furnace to a specific temperature (1800°, 2000°, or 2150°F). When the desired temperature was reached, the refractory trays, filled with limestone, were placed in the muffle furnace. The limestone was calcined for four hours, removed from the furnace, and cooled. Reactivity of the resulting calcine and hydrate prepared from the calcine was subsequently determined by furnace injection tests in the pilot-scale combustion system.

Batch Pressure-Hydrator

A batch pressure-hydrator was designed and fabricated at UNDERC to produce up to 8 lbs of hydrate per run. A schematic of the unit is presented in Figure 1. The reaction vessel consists of an 8-inch diameter schedule 80 carbon steel pipe 12 inches in length, with carbon steel flanges capping both ends. A paddle-wheel stirrer is used to mix the lime and water thoroughly in the vessel, turning at a rate of 2 revolutions per minute. Pressurized water enters the hydrator through 1/8 inch nozzles affixed to the hollow stirrer shaft.

Approximately 6 lbs of quicklime (sized to minus 140 mesh) is placed in the hydrator at the beginning of the run. The solution storage tank is charged with 2.7 lbs of deionized water when high-calcium pressure-hydrated lime is prepared. High-pressure air is used to pressurize the solution tank to 100 psig. When the inside skin temperature of the reactor reaches approximately 350°F, the hydration solution is carefully added under pressure.

Figure 1. Bench-scale pressure hydrator.

Excess water is used to ensure complete hydration of the lime and saturate the reactor with steam. Due to the exothermic reaction of hydration, the reactor temperature rises to about 370°F, and pressure is held constant at about 150 psig. As the hydration reaction proceeds, hydrator pressure is maintained by adding the hydration solution at a controlled rate. After completion of the reaction and during hydrate expulsion, reactor pressure is maintained using a regulated source of nitrogen or compressed air. About 20 minutes after addition of solution to the vessel, the internal temperature begins to decrease, indicating that the reaction is virtually complete. Hydrated lime is then flashed to ambient pressure through a ball valve. Upon expulsion of the hydrate/saturated steam mixture from the hydrator, water trapped inside the pore network of the hydrate particles is released explosively, yielding flash dried, submicron particles with high external surface area. The particles are collected in a nylon fabric filter bag, and stored for subsequent furnace injection tests.

Particulate Test Combustor

The UNDERC Particulate Test Combustor (PTC), shown in Figure 2, was designed for studies of flue gas emission control and particulate characterization. When burning pulverized coal, the resultant fly ash is representative of that produced in a full-scale pc-fired boiler. The mean residence time of a particle in the combustor is three seconds, based on superficial gas velocity. The combustor chamber is 2 feet in diameter and 9 feet high. Heat input is approximately 550,000 Btu/hr, either with natural gas or pulverized coal. Flue gas flow rates are typically 130 scfm.

Figure 2. Particulate Test Combustor (PTC): pulverized coal or gas fired at 550,000 Btu/hr.

Three independent modes of operation are available with the PTC baghouse. The shaker chamber contains 3 bags in each of three compartments: both shaker amplitude and frequency are adjustable. Bag cleaning is accomplished by taking one compartment off-line for shaking. The air-to-cloth ratio (A/C) for these filters is approximately 3 ft/min. The single compartment pulse-jet chamber contains 3 bags and is used at air-to-cloth ratios up to 9 ft/min. Cleaning is performed periodically to control the baghouse pressure drop to 10 inches H_2O . Finally, the low pressure expansion chamber contains 6 cage-mounted bags which are cleaned by reverse-gas flow. The baghouse was designed to operate at temperatures up to 800°F with special fabric filters.

The PTC has the option of using a tubular electrostatic precipitator (ESP) for removing particulates. The ESP consists of an outer shell 8 inches in diameter by 8 feet in length, and a concentrically-mounted wire electrode of 3/16 in diameter. The unit is vertically oriented with flue gas entering from the bottom. The ESP is typically operated at a potential of 30-50 KV.

The PTC is initially heated with natural gas. For gas-fired tests, anhydrous SO_2 and NH_3 are injected into the combustor, to provide baseline concentrations of 1000 ppm SO_2 and 700 ppm NO_x , respectively. After startup and stabilization of the PTC, experiments begin with the pneumatic injection of sorbents into the combustor at a point where the bulk gas temperature measures 1825°F. Sorbent injection is controlled by an adjustable-rate screw

feeder and an air eductor. Injection air contributes approximately 7 scfm or about 5% to the total flue gas. This method of feeding results in precise feed-rate control and provides good dispersion of sorbent particles. Data collected during each test includes: system temperatures, static and differential pressures, flow rates, sorbent feed rate, and flue gas constituent concentrations (CO_2 , H_2O , O_2 , CO , SO_2 , NO_x).

For Task A, Sorbent Evaluation, the PTC was fired on natural gas with anhydrous SO_2 and NH_3 injected to produce 1000 ppm SO_2 and 600 to 700 ppm NO_x in the flue gas. Sorbent injection rates were varied to meet desired test conditions resulting in Ca/SO_2 mole ratios of 1 to 3. Particulate control was accomplished using the pulse-jet chamber of the baghouse.

3.1.2 Results and Discussion

Literature Review

A literature review was initiated in the first quarter of the program year to review available information on limestone, lime, and hydrated lime characteristics and their impact on sorbent utilization with respect to furnace sorbent injection technology. A number of documents were obtained and reviewed which contained information on limestone, its characteristics, and application to flue gas desulfurization processes, including furnace injection. Comprehensive information on lime and hydrated lime was found to be limited with respect to furnace sorbent injection technology and flue gas desulfurization processes in general.

Resource availability is one of the questions which must be addressed when evaluating furnace sorbent injection as a potential technology for SO_2 control in retrofit as well as new facility situations. A study sponsored by the Electric Power Research Institute (EPRI) surveyed the limestone industry and found commercial operations in 44 of the 48 contiguous states (19). Texas was found to be the largest limestone producer, but overall the majority of the limestone quarried in the United States was located in the eastern half of the country. Similarly, lime-producing facilities are well distributed across the country, making calcium-based sorbents readily available for use in SO_2 control processes. The lime industry states that an additional 3 to 5 million tons per years of high-calcium lime could be produced from existing capacity for use in SO_2 control processes (20).

Limestone properties, both chemical and physical, have been extensively characterized for fluid bed combustion (FBC) applications as well as flue gas desulfurization processes. Physical properties such as resistance to attrition, particle size, and pore structure have the greatest impact on sorbent utilization in FBC applications (21).

Physical properties of calcium-based sorbents are also critical in furnace injection applications, with particle size and surface area development having the most pronounced effect on sorbent utilization. Another property which plays a role is pore structure. The chemical form of the calcium-based sorbent also has a significant effect on sorbent utilization such that hydrates result in better utilization than oxides and carbonates.

Ultimately, particle residence time and the bulk gas temperature of the sorbent injection location are the critical parameters controlling SO₂ reduction and sorbent utilization. Limestone utilization with respect to furnace injection is primarily affected by particle size and calcination conditions (residence time and temperature) and can be impacted by mineral matter interactions (22). Calcination conditions affect sorbent surface area development which directly impact sorbent utilization.

Utilization of calcium oxide as a sorbent for furnace injection is also affected by physical properties such as particle size and surface area. Particle size can be directly controlled during preparation and surface area is a function of the calcination conditions (temperature and residence time) under which the oxide was produced. Typically, a smaller particle size and greater surface area results in better sorbent utilization.

Hydrates have been found to be better sorbents for furnace injection than either limestone or lime. Physical properties of hydrates which contribute to better utilization include particle size, pore structure, and surface area. Particle size is a direct result of the hydration process with pressure hydration resulting in the smallest particle size (<1 micron). Pore structure for hydrates is limited due to particle size. Small particle size minimizes pore structure and results in better sorbent utilization due to reduced pore plugging by sulfation. As in the case of limestone, lime and hydrate utilization can be affected by mineral matter interactions due to the presence of fly ash.

Characteristics of Commercial Products

The chemical composition and physical properties of the commercial sorbents are shown in Table 1. The ignition loss exhibited by the limestones and hydrates was consistent with the theoretical losses of carbon dioxide and water, respectively. The analysis of Marblehead lime showed incomplete calcination, while Longview lime was nearly complete. The commercial pebble lime and limestone were pulverized on-site resulting in sorbents with the indicated particle sizes. Since variation in particle size due to pulverization could significantly change sorbent utilization, the data presented in these studies may be valid only for the method of preparation used.

The particle size distribution of pulverized Marblehead and Longview commercial limes are shown in Figure 3. The x-axis presents particle sizes on a logarithmic scale, although the values depicted were chosen at linear intervals. These values represent the center of each of the 14 active discriminator channels of the Coulter counter particle sizer. This figure shows a bimodal particle size distribution for the Longview sorbent, and a more conventional (log-normal) type distribution with Marblehead. Since both materials were processed similarly, this difference may be due to the effects of the commercial calcination processes, resulting in a difference in friability.

TABLE 1

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES FOR
MARBLEHEAD AND LONGVIEW COMMERCIAL SORBENTS

	Marblehead			Longview		
	Limestone	Lime	Hydrate	Limestone	Lime	Hydrate
Ignition Loss, wt%	42.4	1.8	23.6	42.2	0.1	23.2
SiO ₂	0.6	1.3	1.0	0.4	0.6	0.6
Al ₂ O ₃	0.1	0.4	0.3	0.1	0.2	0.2
Fe ₂ O ₃	0.2	0.4	0.4	0.1	0.1	0.1
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0
F ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0
CaO	56.1	94.7	73.6	56.6	97.5	73.9
MgO	0.4	1.0	0.8	0.5	1.4	1.9
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
SO ₃	0.2	0.4	0.3	0.1	0.1	0.1
Total	100.0	100.0	100.0	100.0	100.0	100.0
Surface Area, m ² /g	0.83 ± 0.01	1.44 ± 0.10	15.3	0.82	2.86	17.6 ± 1.7
D ₅₀ , μm	6.3 ± 1.0	5.0 ± 0.6	5.0	8.8	--- ^a	5.8 ± 1.4
Mode, μm	6.3 ± 1.5	3.7 ± 0.0	3.7	7.3	--- ^a	2.9
Number, (N)	2	3	1	1	1	3

^aParticle size analysis did not yield a complete distribution.

Figure 3. Particle size distribution data for Marblehead and Longview lime.

Calcination Conditions

Marblehead and Longview limestones were calcined at 1850°, 2000°, and 2150°F to determine the effect of temperature on the reactivity of hydrated products. The pebble limestone (1/2") was batch calcined in a muffle furnace for four hours. The resulting lime product was analyzed by X-ray diffraction and ignition loss to quantify the extent of decarboxylation. Table 2 shows the chemical composition and physical properties of the calcination products. This data does not indicate any significant differences in composition, although the surface area of the Longview lime was consistently greater. This may be attributed to the smaller particle size. As with the commercial sorbents, the particle size of the calcines is dependent on the pulverizer utilized.

There were significant quantities of carbonate remaining in the product when Longview limestone was calcined at 1850°F. In addition, this calcine was the only one which exhibited a bimodal particle distribution like the one shown in Figure 3.

TABLE 2

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES FOR
MARBLEHEAD AND LONGVIEW CALCINATION PRODUCTS

	Marblehead			Longview		
	Calcined Limestone			Calcined Limestone		
	1850°F	2000°F	2150°F	1850°F	2000°F	2150°F
Ignition Loss, wt%	3.8	2.6	3.6	17.2	1.4	0.8
SiO ₂	0.9	1.1	1.1	0.5	0.7	0.7
Al ₂ O ₃	0.2	0.3	0.2	0.1	0.3	0.0
Fe ₂ O ₃	0.3	0.3	0.3	0.1	0.1	0.1
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.1
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0
CaO	93.4	94.6	93.8	80.9	95.8	96.3
MgO	0.9	0.9	0.9	1.0	1.5	1.7
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0
SO ₃	0.5	0.2	0.1	0.2	0.2	0.3
Total	100.0	100.0	100.0	100.0	100.0	100.0
Surface Area, m ² /g	1.52	1.32	0.87	2.38	1.79	1.72
D ₅₀ , μm	6.0	6.7	7.4	--- ^a	3.5	3.6
Mode, μm	4.7	5.8	6.4	--- ^a	2.9	2.9
Number (N)	1	1	1	1	1	1

^aParticle size analysis did not yield a complete distribution.

Hydration Conditions

The effect of water stoichiometry and pressure during the hydration process was studied using two different experimental approaches. The first approach used a simple "one at a time" design where one variable was changed while keeping all others constant. This method, while capable of finding differences in data, does not have the ability to optimize conditions without performing large numbers of experiments. The second design, a factorial, varies parameters simultaneously to uncover potential interactions using a minimal amount of experiments. The "one at a time" approach was used only with the Marblehead hydrated sorbents since the factorial design was found to be more informative and utilized statistical inference strategies.

Table 3 shows the chemical composition and physical properties of sorbents prepared at six different pressures and four different water stoichiometries using the "one at a time" approach. The chemical analysis showed that the Marblehead lime was homogenous, removing composition as a extraneous variable. The small changes in composition were caused by incomplete hydration, as shown by the ignition loss data. The surface area appears to increase with increasing water stoichiometry and decrease with increasing pressure, while particle size remained invariable.

The furnace injection data generated from the ten sorbent preparations are shown in Table 4. Sorbent utilization was used to measure the response to the preparation conditions. The sorbents were injected at approximately the same Ca/SO_2 mole ratio of 1.0. Even though utilization varies nonlinearly with Ca/SO_2 stoichiometry, the variation in the Ca/SO_2 mole ratios was neglected over the small range studied. Sorbent utilization was calculated both from a mass balance around the PTC (based on flue gas instrumentation and sorbent injection rates) and from the analysis of the baghouse catch by X-ray fluorescence (XRF) spectrometry. As shown in the table, the mass balance and the XRF calculated utilization compared favorably, although neither showed any change in response due to pressure or water stoichiometry. The means of each set of experiments is presented to show overall comparisons between each experimental group.

A 2x2 full factorial (2 levels, 2 variables) designed experiment was performed to estimate the effects (if any) of pressure and water stoichiometry on Marblehead pressure-hydrates. This series of tests was run since a "one at a time" experimental approach may not predict the best possible conditions. Also the results of the factorial experiment would substantiate any findings from the "one at a time" experiment, and provide confidence intervals for the measured responses.

Table 5 presents the ignition loss, chemical composition, surface area and particle size data for the various hydration conditions used in the 2x2 factorial design. The ignition loss data indicates that the water to CaO mole ratio of 1.0 did not sufficiently hydrate the sorbent although X-ray diffraction data did not show the presence of any appreciable CaO crystalline phase. The trends of increasing surface area with increasing water stoichiometry and decreasing pressure seen for the "one at a time" experiments, were also demonstrated with the 2x2 factorial experiments. But in light of the large standard deviations of the replicates, the differences were not significant. It should be noted that the sorbent prepared at 130 psig pressure and a water stoichiometry of 1.3, represents the center point of the experimental range, and is used to determine if the effects of the variables on the response are linear.

TABLE 3

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES FOR MARBLEHEAD PRESSURE
HYDRATES EVALUATED USING A "ONE AT A TIME" EXPERIMENTAL APPROACH

		Pressure Hydration Conditions								
H ₂ O/CaO Mole Ratio:	1.4	1.4	1.4	1.4	1.4	1.4	1.0	1.2	1.4	1.6
Pressure (psig):	50	80	100	120	150	180	150	150	150	150
Ignition Loss, wt%	20.6	21.9	20.5	20.3	19.2	16.7	22.2	22.3	19.2	23.6
SiO ₂	0.9	1.0	0.9	1.0	1.0	1.0	1.0	1.1	1.0	1.1
Al ₂ O ₃	0.2	0.0	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.3
Fe ₂ O ₃	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
TiO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
P ₂ O ₅	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CaO	77.0	75.8	77.2	77.2	78.2	80.7	75.4	75.0	78.2	73.8
MgO	0.7	0.7	0.6	0.7	0.6	0.8	0.6	0.7	0.6	0.6
Na ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
K ₂ O	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SO ₃	0.2	0.2	0.2	0.2	0.4	0.2	0.2	0.2	0.4	0.2
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Surface Area, m ² /g	12.5	8.83	8.57	6.78	8.61	8.24	7.08	6.26	8.61	11.1
D ₅₀ , μm	5.4	6.0	5.7	5.9	5.3	5.9	6.0	5.6	5.3	5.3
Mode, μm	3.7	4.7	3.7	4.7	3.7	4.7	4.7	4.7	3.7	3.7
Number (N)	1	1	1	1	1	1	1	1	1	1

TABLE 4

SULFUR DIOXIDE REDUCTION AND SORBENT UTILIZATION DATA
FOR MARBLEHEAD PRESSURE HYDRATES EVALUATED USING A
"ONE AT A TIME" EXPERIMENTAL APPROACH^a

Number (N)	Pressure (psig)	H ₂ O/CaO (Mole Ratio)	Ca/SO ₂ (Mole Ratio)	SO ₂ Reduction (%)	Sorbent Utilization	
					Mass Balance (%)	XRF Analysis (%)
1	50	1.4	0.94	36.9	39.2	30.5
1	80	1.4	1.15	35.2	30.6	30.4
1	100	1.4	1.22	38.4	31.5	32.7
1	120	1.4	1.18	42.2	35.8	32.8
1	150	1.4	1.10	37.8	34.5	32.8
1	180	1.4	1.20	38.9	32.5	31.8
6	Mean ($\bar{x}$):		1.13 ± 0.10	38.2 ± 2.3	34.0 ± 3.2	31.8 ± 1.1
1	150	1.0	1.13	34.6	30.5	26.2
1	150	1.2	1.14	29.8	26.2	31.6
1	150	1.4	1.10	37.8	34.5	32.8
1	150	1.6	1.13	34.4	30.5	31.8
4	Mean ($\bar{x}$):		1.13 ± 0.02	34.2 ± 3.3	30.4 ± 3.4	30.6 ± 3.0

^aData variation reported as one standard deviation ($\bar{x} \pm 1s$).

TABLE 5

CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES FOR MARBLEHEAD
PRESSURE HYDRATES EVALUATED USING A 2X2 FACTORIAL EXPERIMENTAL DESIGN

		Pressure Hydration Conditions				
		Pressure (psig)/Stoichiometry (H ₂ O:CaO)				
		80/1.0	80/1.6	180/1.0	180/1.6	130/1.3
21	Ignition Loss, wt%	17.6	23.6	19.8	20.3	20.2
	SiO ₂	1.1	0.9	1.0	1.0	1.0
	Al ₂ O ₃	0.2	0.2	0.2	0.2	0.2
	Fe ₂ O ₃	0.4	0.4	0.4	0.4	0.4
	TiO ₂	0.0	0.0	0.0	0.0	0.0
	P ₂ O ₅	0.0	0.0	0.0	0.0	0.0
	CaO	79.8	74.0	77.8	77.2	77.3
	MgO	0.7	0.7	0.6	0.7	0.7
	Na ₂ O	0.0	0.0	0.0	0.0	0.0
	K ₂ O	0.0	0.0	0.0	0.0	0.0
	SO ₃	0.2	0.2	0.2	0.2	0.2
	Total	100.0	100.0	100.0	100.0	100.0
	Surface Area, m ² /g	9.04 ± 3.89	10.07 ± 2.67	7.16 ± 1.24	8.84 ± 2.26	9.50 ± 1.69
	D ₅₀ , μm	5.7 ± 0.5	5.8 ± 0.2	5.3 ± 0.3	5.1 ± 0.1	5.4 ± 0.2
	Mode, μm	4.2 ± 0.5	4.2 ± 0.6	4.0 ± 0.5	3.7 ± 0.0	3.8 ± 0.2
	Number (N)	4	2	3	3	3

The results of the sorbent furnace injection tests are shown in Table 6. This utilization data showed very little variation over the experimental range. The highlights of statistical analysis of the data are summarized at the bottom of the table. The analysis showed that, within the range of the test matrix, pressure and water stoichiometry had no significant effect. This result agrees with the results determined from the previous experiment. Comparing the overall average of the factorial tests with the "one at a time" averages shows only small differences in utilization.

The same 2x2 factorial test matrix was utilized for testing the effects of pressure and water stoichiometry in the preparation of Longview pressure-hydrated lime. Table 7 presents the ignition loss, composition, and surface area for each of the pressure hydration conditions. The surface area data shown in this table displayed a trend that was exactly opposite to that observed with Marblehead sorbents. Surface area decreased with increasing water stoichiometry ratios and increased with increasing pressure. The effect of H_2O/CaO stoichiometry was statistically significant (99% confidence), while pressure was almost significant (95% confidence). Particle size data was not presented in this table because the distribution was bimodal in all cases.

A plot of the particle size distributions for hydrates prepared for the 2x2 factorial experiments is shown in Figure 4. Five Marblehead pressure-hydrate distributions (one for each condition) were combined and averaged. The width of the plot is one standard deviation of variability. Similarly, all 15 of the Longview distributions were combined and plotted on the same figure. Differences in the particle size distributions are shown in this figure. It is interesting to note that these distributions resemble those seen in Figure 3 for the respective limes from which the hydrates were formed. This indicates that the pressure-hydrate particle size distribution, and possibly other factors, may be dependent on the initial pulverization of the lime.

Although there were differences in surface area and particle sizes, the effect of pressure and water stoichiometry on sorbent utilization was insignificant. Table 8 presents the results of the pilot-scale furnace injection tests conducted with the Longview pressure hydrates. Calcium utilization averaged only 25.3% for Longview sorbents, compared to 34.4% for the Marblehead sorbents, based upon the mass balance. With Longview sorbents, the X-ray fluorescence analysis of the baghouse catch showed only 19% calcium utilization. The reason for the discrepancy is unknown. The highlights of the statistical analysis are also presented at the bottom of the table.

Pilot-scale furnace sorbent injection tests were conducted using the commercial sorbent preparations, the experimental calcines, the pressure-hydrated calcines, and the pressure-hydrates produced from commercial lime. By means of a mass balance, the performance of each sorbent was evaluated by the reduction of SO_2 emissions and the utilization of the available calcium oxide. Figures 5 and 6 present the reduction and utilization data for all Marblehead sorbents. The inherent variability in the mass balance makes it difficult to draw definite conclusions, but many trends in the data were apparent. From these figures it can be seen that the pressure-hydrated lime was the most effective sorbent, followed closely by the commercial hydrate.

TABLE 6

SULFUR DIOXIDE REDUCTION AND SORBENT UTILIZATION FOR MARBLEHEAD
PRESSURE HYDRATES EVALUATED USING A 2X2 FACTORIAL EXPERIMENTAL DESIGN^a

Number (N)	Pressure (psig)	H ₂ O/CaO (Mole Ratio)	Ca/SO ₂ (Mole Ratio)	SO ₂ Reduction (%)	Sorbent Utilization	
					Mass Balance (%)	XRF Analysis (%)
4	80	1.0	1.16 ± 0.04	38.6 ± 5.0	33.3 ± 4.3	30.6 ± 3.0
2	180	1.0	1.18 ± 0.07	38.8 ± 4.8	32.9 ± 4.1	33.3 ± 5.2
3	80	1.6	1.06 ± 0.01	35.1 ± 0.2	33.1 ± 0.2	32.2 ± 2.8
3	180	1.6	1.13 ± 0.13	40.1 ± 3.7	35.5 ± 3.2	32.4 ± 4.8
3	130	1.3	1.09 ± 0.17	40.8 ± 2.3	37.4 ± 2.1	32.9 ± 4.3
15	Overall Mean ($\bar{x}$):		1.13 ± 0.10	38.6 ± 3.7	34.4 ± 3.4	32.2 ± 3.7

^aAnalysis Summary:

Signal/Noise Ratios: $t_{\text{pressure}} = 0.503$
 $t_{\text{H}_2\text{O}/\text{CaO}} = 0.604$

t^* (95% Confidence Interval, 10 df) = 2.228

t^* (50% Confidence Interval, 10 df) = 0.604

Pressure and water stoichiometry had no effect on sorbent utilization over experimental range.

Data variation reported as one standard deviation ($\bar{x} \pm 1s$).

TABLE 7

CHEMICAL COMPOSITION AND SURFACE AREA FOR LONGVIEW PRESSURE HYDRATES
EVALUATED USING A 2X2 FACTORIAL EXPERIMENTAL DESIGN^a

		Pressure Hydration Conditions				
		Pressure (psig)/Stoichiometry (H ₂ O:CaO)				
		80/1.0	80/1.5	180/1.0	180/1.6	130/1.3
Ignition Loss, wt%		23.023.1	22.4	23.4	23.2	
SiO ₂	0.6	0.60.6	0.7	0.6		
Al ₂ O ₃	0.1	0.20.2	0.2	0.1		
Fe ₂ O ₃	0.1	0.10.1	0.1	0.1		
TiO ₂	0.0	0.00.0	0.0	0.0		
P ₂ O ₅	0.0	0.00.0	0.0	0.0		
CaO	75.1	74.875.6	74.5	74.9		
MgO	1.0	1.11.0	0.9	1.0		
Na ₂ O	0.0	0.00.0	0.0	0.0		
K ₂ O	0.0	0.00.0	0.0	0.0		
SO ₃	0.1	0.1 0.1	0.2	0.1		
Total	100.0	100.0100.0	100.0	100.0		
Surface Area, m ² /g		9.52 ± 1.22	7.36 ± 0.68	10.9 ± 1.71	3.81 ± 0.67	9.44 ± 1.14
Number (N)	3	3 3	3 3			

^aParticle size data was not presented because the distribution was bimodal in all cases.

Figure 4. Particle size distribution data for Marblehead and Longview pressure-hydrated lime.

The commercial carbonate appeared slightly more reactive than the commercial lime, although the lime data were variable. The experimental calcines and their respective pressure-hydrates are also shown in these figures. The higher calcination temperatures seemed to lower the reactivity of the calcines, but had mixed results with the pressure-hydrated calcines. The overall averages, shown in Table 6 for Marblehead pressure-hydrates, are also presented in these figures for comparison. The error bars associated with this point represent one standard deviation, and is probably typical of the data variability expected in pilot-scale analysis.

The utilization of each sorbent was also determined by the X-ray fluorescence analysis of the baghouse ash. The ash samples were taken directly from the baghouse hopper, and the bags were cleaned by vacuuming between each test. The assumption is made that the sulfation reaction is quenched sufficiently at the baghouse temperatures (300°-400°F) to neglect any sulfation occurring on the bags. The bags were run through a cleaning cycle every 2 minutes to remove the sorbents while the test was in progress.

Figure 7 shows the utilization of the Marblehead sorbents when calculated using X-ray fluorescence data. The same trends shown in Figure 6 were substantiated by the data presented in this figure using an independent method of analysis.

TABLE 8

SULFUR DIOXIDE REDUCTION AND SORBENT UTILIZATION FOR LONGVIEW
PRESSURE HYDRATES EVALUATED USING A 2X2 FACTORIAL EXPERIMENTAL DESIGN^a

Number (N)	Pressure (psig)	H ₂ O/CaO (Mole Ratio)	Ca/SO ₂ (Mole Ratio)	SC ₂ Reduction (%)	Sorbent Utilization	
					Mass Balance (%)	XRF Analysis (%)
3	80	1.0	1.05 ± 0.04	26.9 ± 1.98	25.4 ± 2.78	18.8 ± 0.81
3	180	1.0	1.14 ± 0.05	27.7 ± 2.54	24.4 ± 2.11	18.9 ± 0.57 ^b
3	80	1.6	1.09 ± 0.03	27.1 ± 1.46	24.8 ± 1.75	19.4 ± 1.56 ^b
3	180	1.6	1.25 ± 0.08	33.2 ± 2.18	26.4 ± 0.56	18.8 ± 1.96
3	130	1.3	1.07 ± 0.05	27.0 ± 2.36	25.3 ± 1.21	19.3 ± 0.87
15	Overall Mean ($\bar{x}$):		1.12 ± 0.09	28.4 ± 3.10	25.3 ± 1.71	19.0 ± 1.08

^aAnalysis Summary:

Signal/Noise Ratios: $t_{\text{pressure}} = 0.233$
 $t_{\text{H}_2\text{O}/\text{CaO}} = 0.660$

t^* (95% Confidence Interval, 10 df) = 2.223

t^* (50% Confidence Interval, 10 df) = 0.703

Pressure and water stoichiometry had no effect on sorbent utilization over experimental range.

Data variation reported as one standard deviation ($\bar{x} \pm 1s$).

^bAverage of two numbers only.

Figure 5. Sulfur dioxide reduction versus Ca/SO_2 mole ratio for Marblehead sorbents.

Figure 6. Calcium utilization based on flue gas and sorbent injection data versus Ca/SO_2 mole ratio for Marblehead sorbents.

Figure 7. Calcium utilization based on XRF data versus Ca/SO₂ mole ratio for Marblehead sorbents.

Similar figures were made for data from the Longview sorbent tests. These data are presented in Figures 8, 9, and 10. The commercial hydrate and the pressure-hydrate showed the same level of reactivity, and likewise, the commercial lime and limestone showed identical reactivities. Longview sorbents showed similarities to Marblehead sorbents only with respect to the experimental calcines and hydrated calcines. Each showed that the calcine produced at 1800°F, and the pressure-hydrate made from the 2000°F calcine were more reactive than the other preparations.

Figure 10 shows a small difference in reactivity between the commercial lime and limestone when sorbent utilization is calculated from XRF data. The majority of the other data presented in this figure supported the mass balance derived data.

Mercury porosimetry analysis was performed on the commercial lime, limestone, and hydrate as well as the pressure-hydrated lime, the 2000°F experimental calcine, and the corresponding pressure-hydrate. Figure 11 presents the total volume intruded and the total pore surface area for each of the Marblehead and Longview sorbents. These data showed that the hydrates had more pore surface area than the other sorbents, and that Longview sorbents were consistently higher in surface area than Marblehead with the exception of limestone. A totally opposite trend was observed for the total volume intruded by the mercury. In light of the results of this investigation, with Marblehead sorbents being more reactive, the total surface area is not the best factor for predicting reactivity prior to furnace injection.

Figure 8. Sulfur dioxide reduction versus Ca/SO_2 mole ratio for Longview sorbents.

Figure 9. Calcium utilization based on flue gas and sorbent injection data versus Ca/SO_2 mole ratio for Longview sorbents.

Figure 10. Calcium utilization based on XRF data versus Ca/SO₂ mole ratio for Longview sorbents.

Figure 11. Porosimetry data for both the Marblehead and Longview sorbents.

3.2 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. To better establish these impacts, 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.

Each coal was fired in the Ash Fouling combustor to evaluate the fouling potential, sorbent utilization, and ESP efficiency. One test was run without sorbent injection to establish baseline characteristics. Two additional tests were performed with sorbent injection, where SO_2 levels were reduced by 50% and 90%, representing the target SO_2 control levels for retrofit and new installations, respectively. The same test matrix was also performed using the PTC, with emphasis being placed on sorbent utilization, particulate characterization, and ESP performance.

Inorganic elements in coal are associated with the coal as ion-exchangeable cations, organic complexes or as discrete minerals. Investigation of the relative abundance and modes of occurrence of these inorganic elements is necessary in order to better understand the sources of inorganic elements which participate in reactions during utilization processes such as sulfation. An integrated approach of using both chemical fractionation and quantitative mineralogy was used to determine the sources of inorganics present in Illinois No. 6 coal.

3.2.1 Description of Facilities and Procedures

Ash Fouling Combustion System

A schematic diagram of the ash fouling test furnace is shown in Figure 12. The furnace capacity is approximately 75 lb/hr of pulverized lignite (550,000 Btu/hr). The combustion chamber is 30 inches in diameter, 8 feet high, and refractory lined. Particle laden flue gases pass from the furnace into the 10-inch square refractory-lined duct containing the ash deposition probes. This vertically mounted probe bank was designed to simulate superheater surfaces in the convective pass region of a commercial boiler. The probe bank is located in a hinged door to facilitate inspection and cleaning. Figure 13 details the construction of the probe bank. The bulk flue gas temperature entering the probe bank is maintained at 2000°F, while the surface temperature of the probes is controlled at 1000°F with compressed air. The gas velocity between the tubes is about 25 ft/s.

After leaving the probe duct, the flue gases pass through a series of water-cooled heat exchangers before entering the ESP. The ESP consists of a single-stage rigid-frame electrode design. Two banks of collecting electrode/plate sets are configured in series within the precipitator compartment. The four collecting plates per bank result in a net surface area

Figure 12. Ash fouling combustion system configuration.

Figure 13. Detail of probe bank construction.

of 48 ft², and a specific collection area (SCA) of about 150 ft²/1000 ACFM. Each bank is energized with an independent transformer/rectifier set capable of maintaining 34 KV under normal operating conditions. Collection efficiencies typically range from 95 to 99 percent, when the ESP is not rapped during the combustion test.

Sorbent is pneumatically injected into the top of the furnace using an air eductor and screw feeder combination. A one-half inch stainless steel tube is inserted (vertically) into the center of the top-face of the furnace to transport the sorbent/air mixture. The pneumatic countercurrent delivery of the sorbent provides good particle dispersion within the furnace.

The relative fouling tendencies of the test coals are determined by burning the samples under standard conditions. When starting with a cold furnace, the combustor is preheated for 8 hours with natural gas followed by a 5 1/4-hour test burn on coal. The coal feed rate is adjusted to keep the flue gas temperature entering the upper duct to the probe bank at 2000°F with 25% excess air. Coal samples are taken periodically to form a composite sample. Flue gas oxygen, carbon dioxide, nitrogen oxides, carbon monoxide, and sulfur dioxide are continuously monitored by recording analyzers.

At the completion of the test period, the probe door is opened and photographs are taken of the deposit. The deposit is then removed from the probes in two fractions, an inner and an outer layer, and each is weighed and analyzed separately. Normally the inner white layer weighs less than 10 grams as compared with 100 to 500 grams for the outer sintered deposit.

The weight of ash deposited on the probe bank during a standard test is used to rank the coal by its relative fouling potential. Based upon comparisons between results obtained in the ash fouling combustor and actual operating experience in full-scale utility boilers, the typical relationship between deposit weight and the fouling potential of the fuel is indicated below:

<u>Deposit Weight, grams</u>	<u>Relative Fouling Potential</u>
0-150	Low
150-300	Medium
Above 300	High

Following each test run, proximate, ultimate, and heating value analyses are determined for the composite coal sample collected during the run. Elemental ash analysis is also performed for the composite coal sample, on ash samples from the probe inner and outer layers, and on fly ash collected in the ESP.

Strength of the ash deposits is measured by drop impaction tests. In addition, during removal the hardness and breakability of deposits is rated by the system operating personnel on a scale from 1 to 10 with "1" representing a soft, crumbly, unconsolidated deposit, and "10" a hard and unfragmented deposit. Based on previous studies, the friability as measured by the drop impactor test and operator observations have generally provided the best

estimate for deposit strength. After completion of drop impact tests, the remaining deposits are used to determine strength with a penetrometer. In the penetrometer tests, a weighted 1/16 inch (pointed) probe is used to obtain an average penetration distance at points around the circumference of the deposit. These data, when available, are used for relative comparisons between coals, since no quantitative significance has been established.

The impact test involves dropping a 3.8-oz. weight from a height of 24 inches onto a 1-inch cross-section deposit sample. The fragmented sample is then sieved (using 5.66, 3.66, 0.84, 0.42, and 0.21 mm screens) to obtain friability measurements (similar to the ASTM Tumbler Test, ASTM-441-45). In addition to friability, strength indicators obtained from this test include impulse, impact, crush factor, dust index, and mass mean diameter. The dust index is indicative of the tendency of the deposit to form dust on impact, with values ranging from about 10% for hard deposits to 25% for soft deposits. The mass mean diameter is the average size of the fragmented particle, and usually varies from about 5 mm for hard deposits to 1.3 mm for a very soft deposit.

To assure that the test results from the ash fouling furnace are meaningful for evaluation of ash fouling potential in full-scale utility boilers, calibration tests have been conducted with low-rank coals which are known to produce low and high fouling conditions when used in utility boilers. Comparisons of pilot-scale ash fouling data have been made with information provided by a number of power stations throughout the western U.S.: Monticello (Texas Utilities), Big Brown (Texas Utilities), Four Corners (Arizona Public Service Company), St. Clair (Detroit Edison Company), Jim Bridger (Pacific Power and Light), Big Stone (Otter Tail Power Company), Leland Olds (Basin Electric Power Cooperative), and San Miguel (San Miguel Electric Cooperative). Based on the results of these comparisons, the ash deposit buildup rate on the probe bank was found to be a good indicator of the fouling potential (23).

Laboratory Resistivity Unit

Electrical resistivity measurements of bulk ash were made with the apparatus shown in Figure 14. The resistivity measurement unit was designed and built according to the American Society of Mechanical Engineers Power Test Code 28. Temperature is maintained by an oven consisting of two concentric cylinders separated by three inches of ceramic fiber insulation. The oven can be maintained at any temperature between room temperature and 800°F. Steady state oven temperature is maintained by an automatic controller, while precise sample (ash) temperature is measured by a second thermocouple mounted near the ash layer. The inside atmosphere of the oven is continuously flushed with simulated flue gas at a rate of 13 scfh. Compressed gas cylinders containing pure O₂, CO₂, SO₂, and N₂ are used to synthesize the flue gas through careful mixing of the constituents. Moisture is provided by bubbling the non-reactive gases through a humidity bath controlled to the appropriate temperature. The reactive/non-reactive gas streams are joined just prior to entering the oven.

Figure 14. Schematic of laboratory resistivity apparatus.

A uniform ash layer 5 mm thick is introduced to the conductivity cell. The electrode, designed to place 10 grams per square centimeter pressure on the ash, is placed on the surface of the ash layer. The electrode is energized to 750 volts, producing a constant field strength of 1.5 kV/cm. The oven is heated to a designated temperature and allowed to stabilize for 40 minutes before measuring current through the ash. Using this procedure, a resistivity versus temperature (200° to 750°F) curve is completed in 8 to 10 hours.

Quantitative Mineralogy

The combined Scanning Electron Microscope and Electron Microprobe (SEM/EMPA) has proven to be an effective instrument for the quantitative analysis of minerals in coal (24). The SEM/EMPA system allows for observation and chemical analysis of very fine-grained minerals while preserving both the original chemistry of the minerals and their relationships to the organic constituents. Various procedures and techniques of automated SEM/EMPA analysis have been published which illustrate the benefits of using the SEM for mineralogical analysis (24,25,26).

The UNDERC JXA-35 microprobe is interfaced with a Tracor Northern TN 5500 x-ray analyzer, and was manipulated to perform quantitative analysis of mineral particles in coal. A point-counting method was used to quantify mineral species. Mineral quantities were determined by moving the stage and sample at equal increments and recording the type of material which was encountered under the electron beam spot (i.e. mineral, coal matrix, epoxy).

All minerals encountered were analyzed using energy-dispersive spectrometry (EDS) for 50 seconds and the energy spectra stored for later analysis. Identification of minerals was accomplished by comparing the ratios of elements as determined by EDS with known elemental ratios determined from the mineral's chemical formulas. For example, kaolinite has an aluminum-silicon ratio of 45:55 (weight percent oxide) and typical EDS percentages for kaolinite are approximately 45:55. Since most low-rank coals typically contain only five or six major mineral constituents including the coal matrix, the spectral patterns for these constituents are fairly consistent and easily identified.

Quantitative analysis of the elemental composition of each mineral was performed using the ZAF reduction and correction procedure. This software program considers matrix effects in electron beam excited x-ray spectra and considers the effects of atomic number (Z), absorption (A), and fluorescence (F). Each mineral was subsequently identified by examination of the elemental weight percents and the comparison of these data with known elemental compositions of minerals.

Chemical Fractionation

Chemical fractionation is a method of quantitatively determining the modes of occurrence of the inorganic elements in coal based on the extractability of the elements in solutions of water, 1 molar ammonium acetate, and 1 molar hydrochloric acid. Duplicate 25 gram samples of minus 325 mesh vacuum-dried coal are stirred with 100 milliliters of deionized water to extract water-soluble minerals such as sodium chloride. After stirring for 24 hours at room temperature the water-coal mixture is filtered and the filtrate diluted to 250 milliliters. The filtrate is analyzed by ICP-AES to determine the percent of the elements extracted. The residues are then mixed with 100 milliliters of 1 molar ammonium acetate (NH_4OAc) and stirred at 70°C for 24 hours to extract the elements associated with the coal as ion-exchangeable cations present primarily as the salts of organic acids. After filtering and diluting the filtrate to 250 milliliters, the filtrate is analyzed by ICP-AES to determine the percent of the elements removed. The ammonium acetate extractions are repeated twice to effect the complete removal of the ion-exchangeable cations. After the third ammonium acetate extraction, a sample of the dried residue is analyzed by XRF. The remaining residue of the ammonium acetate extractions is then stirred with 1 molar hydrochloric acid (HCl) at 70°C for 24 hours to remove the elements held in coordination complexes within the organic structure of the coal, as well as acid-soluble minerals such as carbonates, oxides, and sulfates. After filtering and diluting the hydrochloric acid extract to 250 milliliters, the extract is analyzed by ICP-AES. The hydrochloric acid extraction is repeated once. The elements remaining in the coal after the chemical fractionation extractions are determined by difference. The nonextractable elements are associated in the coal as silicates, aluminosilicates, sulfides, and oxides.

3.2.2 Results and Discussion

In the previous Cooperative Agreement, South Hallsville Texas lignite and Sarpy Creek Montana subbituminous coal were evaluated. During the first-year of the current Cooperative Agreement, tests were conducted using Illinois No. 6 bituminous coal and Marblehead pressure-hydrated lime. Table 9 presents the

proximate and ultimate analyses of Illinois No. 6 coal and the X-ray fluorescence analysis of the ASTM coal ash. Proximate analysis indicated the coal moisture and ash content to be about 7.5% and 10.8%, respectively, on an as-fired basis. Ultimate analysis showed sulfur content ranging from 3.2% to 4.0% (moisture-free basis) for the six samples analyzed. Coal ash, as determined by x-ray fluorescence, was found to contain primarily oxides of silica, alumina, and iron (46%, 21%, and 17%, respectively by weight) with small amounts of calcium and sodium (5.8% and 0.5%, respectively by weight) present.

The ash fusion temperatures and composition of the ash collected in the ESP are presented in Table 10. As expected, an increase in fly ash calcium concentration and ash fusion temperatures occurred with increasing levels of sorbent injection (SO_2 control).

Ash Fouling

The ash deposited on the probes in the ash fouling combustor continuously sloughed off and redeposited. Quantitative data on deposit weights and deposition rates could therefore not be determined. Strength tests were conducted on the fragmented deposits found in the duct below the probes. The results of these tests are shown in Table 11.

The high dust index number and small mass median diameter indicate that the deposits were very soft. The subjective "strength rating factor" (SRF) and the high friability number indicates that the deposits were weak and crumbly. Therefore, the deposition rates should not be a problem since the deposits were weak and should be readily removed by conventional sootblowing equipment. Fouling problems would only be expected in systems with extremely tight tube spacing due to the potential for plugging at the high sorbent injection rates.

Sorbent Utilization and ESP Performance

Table 12 presents sorbent utilization and dust loading data for six combustion tests. Both baseline (coal ash alkali) and sorbent utilization data were calculated. Baseline (inherent) SO_2 capture was determined by comparing the apparent flue gas SO_2 concentration to the theoretical SO_2 concentration obtained from complete coal combustion. Utilization was based upon available alkali ($\text{Na}_2\text{O} + \text{CaO}$) in the coal ash. Due to the low available alkali in the ash, there was only 5% to 8% inherent capture of SO_2 . Sorbent utilization was good, resulting in 50% SO_2 capture at a CaO/SO_2 mole ratio of about 1.2 and 75% SO_2 capture at a Ca/SO_2 mole ratio of 2.2. The sorbent utilization was slightly better in the Ash Fouling combustor than the PTC. It should be noted that 90% reduction of SO_2 was not achieved in either combustor due to sorbent feeder limitations. Provisions have been made concerning the sorbent feeder system to accommodate any future high-sulfur coals and/or inferior sorbent materials.

TABLE 9

ANALYSIS OF ILLINOIS NO. 6 BITUMINOUS COAL

SO ₂ Control	Ash Fouling			PTC		
	0%	50%	90%	0%	50%	90%
<u>Proximate, wt% (as rec'd):</u>						
H ₂ O	7.5	6.7	7.7	7.8	7.9	7.6
Ash	10.4	11.7	11.8	9.8	10.5	10.7
Volatile Matter	37.0	34.3	33.5	34.2	33.4	33.4
Fixed Carbon	45.1	47.3	47.0	48.2	48.2	48.3
<u>Ultimate, wt% (mf):</u>						
Carbon	68.58	67.71	67.74	68.36	67.96	68.70
Hydrogen	4.84	4.78	4.68	5.00	4.80	4.81
Nitrogen	1.16	1.15	1.16	1.23	1.24	1.15
Sulfur	3.23	3.77	3.99	3.38	3.53	3.49
Oxygen	10.99	10.99	9.63	11.53	11.07	10.25
<u>Higher Heating Value:</u>						
Btu/lb (mf)	12,392	12,258	12,139	12,556	12,348	12,521
<u>Sulfur Forms, wt% (mf):</u>						
Pyritic	1.18	1.37	1.42	1.10	1.16	1.15
Organic	1.92	2.32	2.53	2.11	2.18	2.20
Sulfate	0.13	0.08	0.04	0.17	0.19	0.14
<u>ASTM Coal Ash, X-ray Fluorescence Analysis (% as Oxides)^a:</u>						
SiO ₂	46.5	44.4	44.9	47.3	47.4	46.4
Al ₂ O ₃	21.2	19.3	19.6	21.4	21.9	20.2
Fe ₂ O ₃	17.2	15.6	16.7	18.3	17.1	18.5
TiO ₂	1.1	1.1	1.0	1.1	1.0	1.1
P ₂ O ₅	0.1	0.3	0.2	0.0	0.1	0.1
CaO	5.2	7.7	7.0	4.5	4.5	5.7
MgO	1.5	1.4	1.3	1.5	1.3	1.4
Na ₂ O	0.8	0.6	0.0	0.0	0.0	0.5
K ₂ O	2.1	2.0	1.9	2.2	2.1	2.2
SO ₃	4.3	7.7	7.3	3.7	4.5	4.7

^aData normalized to 100%.

TABLE 10

X-RAY FLUORESCENCE ANALYSIS AND ASH FUSION TEMPERATURES FOR ESP ASH

SO ₂ Control	Ash Fouling			PTC		
	0%	50%	90%	0%	50%	90%
<u>Percent as Oxides^a:</u>						
SiO ₂	50.5	23.0	23.8	47.9	31.8	15.7
Al ₂ O ₃	22.9	10.6	10.1	20.6	14.0	6.8
Fe ₂ O ₃	12.9	6.7	8.9	16.8	11.6	5.9
TiO ₂	1.3	0.7	0.6	1.0	0.7	0.5
P ₂ O ₅	0.0	0.9	0.6	0.1	0.3	0.6
CaO	5.2	31.9	35.3	6.5	27.5	50.4
MgO	1.6	0.9	0.9	1.4	0.8	0.5
Na ₂ O	0.5	0.0	0.0	0.0	0.0	0.0
K ₂ O	2.4	1.0	0.8	2.2	1.2	0.5
SO ₃	2.8	24.4	18.9	3.5	12.0	19.2
<u>Ash Fusion Temp., °F^b:</u>						
Initial Deformation	2122	2256	2307	2137	2141	2582
Softening	2252	2291	2348	2189	2178	2700
Fluid	2358	2401	2459	2308	2224	2700

^aData normalized to 100%.^bThe furnace temperature limit is 2700°F

TABLE 11

STRENGTH TEST RESULTS^a

SO ₂ Control (%)	Sorbent Addition (g/hr)	Pentrometer ^b (mm)	Index (%)	Friability (%)	MMDIA (mm)	SRF
0	-	-	38	91.2	0.52	4
50	2020	-	35	68.5	0.82	4
90	3904	-	63	96.6	0.27	4

^aDeposits did not adhere to fouling probes.^bDeposits too soft to obtain measurements.

TABLE 12

SORBENT UTILIZATION AND ESP PERFORMANCE
FIRING ILLINOIS NO. 6 BITUMINOUS COAL

SO ₂ Control	Ash Fouling			PTC		
	0%	50%	90%	0%	50%	90%
<u>Sorbent Utilization:</u>						
Theoretical SO ₂ , ppm ^a	2505	3026	3067	2805	2894	2784
Flue gas SO ₂ , ppm ^a	2303	2432	2335	2650	2630	2780
Flue gas O ₂ , % ^a	4.90	4.45	5.17	3.74	4.10	4.33
Additive feed rate, g/hr	--	2020	3904	--	2547	4340
Alkali/SO ₂ mole ratio ^b	0.110	--	--	0.078	--	--
Ca/SO ₂ mole ratio	--	1.06	1.99	--	1.44	2.32
SO ₂ reduction, %	8.06	49.2	78.1	5.53	53.7	72.2
Utilization, %	73.3	46.3	39.1	71.0	37.3	31.1
<u>ESP Performance Dust Loading:</u>						
Inlet, gr/SCF	1.6606	4.9553	6.5525	2.8002	6.1748	8.5492
Outlet, gr/SCF	0.0677	0.7750	2.1512	0.5070	1.2980	5.0216
Efficiency, %	95.9	84.4	67.2	81.9	77.4	41.3
Ash Resistivity at 300°F, ohm-cm	--	--	--	2.4 x 10 ¹²	3.7 x 10 ¹³	1.4 x 10 ¹⁴

^aMoisture-Free basis.

^bFly-ash alkali (CaO + Na₂O) to theoretical SO₂ mole ratio.

The interaction of fly ash/sorbent mixtures with respect to ESP performance was also examined. The inlet flue gas stream to the plate-type ESP utilized by the Ash Fouling combustor was sampled using a 5-stage multicyclone train. The outlet stream was sampled by the standard EPA Method 5 technique. The inlet and outlet streams to the cylindrical ESP utilized by the PTC were sampled once by both methods.

Calculated particulate removal efficiencies are also shown in Table 12. With either ESP, the efficiency was shown to decrease substantially with increased sorbent addition and both ESPs operated at about the same efficiency with respect to the inlet dust loading. The poor performance of the ESP's was due to the low operating voltages (25 KV) required to reduce sparking.

Figure 15 shows plots of resistivity as a function of temperature for ash samples collected when firing the PTC. Baseline ash showed a maximum resistivity of 5.0×10^{12} ohm-cm at 250°F. For tests where sorbent injection was used, maximum resistivity values occurred at a temperature of 375°F, with resistivities of 5.4×10^{13} and 1.8×10^{14} ohm-cm observed. Resistivity was measured in the laboratory, rather than in-situ, using an apparatus which was designed and built according to the American Society of Mechanical Engineers Power Test Code 28. Flue gas SO₃ concentrations cannot be duplicated in the laboratory apparatus, therefore resistivity values reported here are probably high and must be considered qualitative. Based on the resistivity data, an ESP operated above 550°F and without sorbent injection would probably operate satisfactorily using this coal. Satisfactory operation of an ESP at temperatures <550°F would probably require the use of a conditioning agent such as SO₃.

ESP inlet and outlet particulate size distributions were determined by the dust collected in a Flow Sensor 5-stage multicyclone sampler. Depending on flow rates, each cyclone captured a certain mass fraction centered around a mass median diameter, D₅₀, where 50% of the mass (that with diameters greater than D₅₀) is retained by a cyclone, and 50% of the mass (that with diameters less than D₅₀) is passed on to the next cyclone in the train. Logarithmic plots of D₅₀ diameter versus the cumulative percent mass less than D₅₀ are presented in Figures 16 and 17 for the inlet and outlet ESP flue gas streams, respectively. A comparison of the figures shows similar particle size distributions for both inlet and outlet streams. Sorbent injection increased the mass loading in the region above 5 microns, and decreased the mass loading in the region below 1 micron for both the inlet and outlet distributions.

An attempt was made to determine the impact of furnace sorbent injection on respirable particulate loading using a aerodynamic laser particle sizer (APS) manufactured by TSI Inc.. Although measurements were made and data was collected, data retrieval and evaluation was not possible due to electrical interference by the ESP on the computerized data acquisition system. Based on multicyclone data, particulate loading in the range of 0.5 to 10.0 m at the ESP inlet increased by a factor of 3.5 when sorbent was injected to achieve 50% SO₂ reduction. At the ESP outlet a 5 fold increase was observed.

Quantitative Mineralogy

Table 13 lists the results of the quantitative mineralogy procedure for the Illinois No. 6 coal. Over seven hundred counts were recorded for the sample, and volume percentages of the major mineral phases and coal matrix were determined. The volume percentages were converted to weight percentages using published densities of the minerals. The total discrete mineral content was determined to be attributed to discrete mineral phases. Aluminosilicates (kaolinite, illite, and various complex clays) are the dominant minerals present. Many of the alkaline earth elements present in the coal are associated with the clay minerals present. Quartz, pyrite, and calcite are also present in smaller amounts.

Figure 15. Resistivity versus temperature for fly ash samples resulting from combustion of Illinois No. 6 coal.

Figure 16. Cumulative % mass less than the mass median diameter versus mass median diameter of multicyclone fractions for ESP inlet dust sampling.

Figure 17. Cumulative % mass less than the mass median diameter versus mass median diameter of multicyclone fractions for ESP outlet dust sampling.

TABLE 13

ILLINOIS NO. 6 QUANTITATIVE MINERALOGY RESULTS

Mineral	Weight Percent of Coal
Quartz	1.1
Pyrite	1.5
Calcite	0.3
Kaolinite	2.4
Illite	1.7
Montmorillonite	0.3
Unknown Aluminosilicates	<u>1.6</u>
Total discrete minerals	8.9
Ash Content	10.6

Chemical Fractionation

The initial concentrations of sodium, magnesium, potassium, calcium, titanium, iron, strontium and barium were determined by acid digestion of a sample of the raw coal; the initial concentrations of silicon and aluminum were determined by XRF. The percentage of elements removed was determined by ICP-AES analysis of the extracts. Listed in Table 14 are the results of the analyses.

The water extraction removed about one-third of the calcium, about one-fifth of the sodium and strontium, and about ten percent of the magnesium. These elements were probably present in a salt form in the original coal, such as calcium chloride or the salt of water-soluble humic acids. During combustion, they would be volatilized and would be free to participate in numerous reactions.

Roughly half of the calcium and barium, one-fourth the sodium and strontium, ten percent of the magnesium and some silicon and potassium were removed by ammonium acetate extraction. These elements exist predominantly as salts of organic acids in the coal, but portions may exist in association with ion-exchange sites on clays or as ammonium acetate-soluble minerals. These elements are also freed upon combustion and constitute the most reactive fraction of the coal inorganics.

Treatment with hydrochloric acid resulted in the removal of about one-fourth of the iron and barium, about one-tenth of the magnesium and potassium, and traces of all other elements analyzed. These elements exist in organic coordination complexes in the original coal, and as acid-soluble minerals. Most of the elements in these forms will likewise volatilize and be free to react during combustion.

TABLE 14

ICP-AES ANALYSIS OF CHEMICAL FRACTIONATION EXTRACTS

	Initial Concentration g/g	wt% Removed by H ₂ O	wt% Removed by NH ₄ OAc	wt% Removed by HCl	wt% Remaining
Na	330	19.1	22.1	2.1	56.7
Mg	270	11.2	10.2	15.7	62.9
Al	6790 ^a	0	0	3.9	96.1
Si	15120 ^a	0	0.1	2.5	97.4
K	790	0	3.0	6.0	91.0
Ca	1800	35.9	58.6	1.2	4.3
Ti	290	0	0	0.7	99.3
Fe	7700	0	0	27.9	72.1
Sr	12	21.0	23.8	5.1	50.1
Ba	21	0	40.6	28.2	31.2

^aInitial concentrations of silicon and aluminum were determined by XRF.

The remaining inorganic elements are present as discrete minerals (non-crystalline clays, acid insoluble oxides, and aluminosilicates). These elements will undergo little vaporization upon combustion but may act as a surface on which other volatilized species may condense.

The subject of SO₂ capture by alkali contained in the ash resulting from coal combustion is complicated. Calcium and sodium components of the ash are typically the alkali species which are responsible for inherent SO₂ capture by alkali ash. Based on limited data, inherent SO₂ capture is not directly proportional to the quantity of calcium and sodium components in the ash, but rather the availability of ash alkali for sulfation reactions. Alkali availability is believed to be determined by the location of the alkali components in the coal structure. In the case of sodium, association with the organic structure results in sodium volatilization during combustion. A large percentage of the volatilized sodium may result in the formation of sodium sulfate. Sodium associated with the discrete minerals of the coal can also be volatilized and ultimately result in the formation of sodium sulfate or may just as likely remain associated with the discrete minerals and not become available for sulfation reactions.

Calcium species do not volatilize as readily as sodium as a result of coal combustion but their availability for sulfation would also be expected to be dependent on their association with either the organic matter or discrete minerals. Calcium associated with the organic matrix would be expected to result in a high degree of sulfation since calcium present in the organic

matrix would be observed in the form of calcium oxide following coal combustion. Calcium associated with the discrete minerals may also be observed as calcium oxide and available for sulfation reactions or may just as likely remain associated with the discrete minerals and therefore, unavailable for reaction.

Chemical fractionation data presented in Table 14 indicates that 70% of the alkali (Ca and Na) in the ash is associated with the volatile coal constituents for the Illinois No. 6 coal. Pilot-scale combustion data showed that roughly 70% of the ash alkali (Ca and Na) was utilized in sulfation reactions during combustion of the Illinois No. 6 coal. An attempt will be made to correlate chemical fractionation data with inherent SO₂ capture for other coals fired in the same pilot-scale combustion system.

Humidification

Sorbent utilization has been improved by increasing the flue gas moisture content and/or lowering the baghouse temperature (27). This effect has been shown to be a function of the approach to dewpoint temperature (margin). By improving sorbent utilization, operating and maintenance costs will be more favorable for furnace injection technology, resulting in better overall economics.

Six combustion tests were performed firing natural gas in the PTC. Linwood PHL was injected at three different temperatures with and without (steam) humidification. Table 15 presents the utilization of Linwood PHL at various levels of baghouse temperature, sorbent injection temperature, and flue gas moisture. At a baghouse temperature of 300°F and a sorbent injection temperature of 1800°F, humidification had no effect. When sorbents were injected at 500°F, followed by collection in the baghouse operated at 190°F, the moisture level had a considerable effect on utilization due to operation at a lower approach to dew point temperature.

Two temperature ramping tests were performed with sorbent injected at about 1250°F. One test was run under normal conditions with 15% moisture in the flue gas, and one with the flue gas humidified to 25% moisture. The temperature ramping technique uses the on-line heat exchangers to slowly increase the baghouse temperature from just above the dewpoint temperature to about 250°F. The SO₂ reduction and utilization curves plotted in Figures 18 and 19, respectively, show the temperature and moisture dependence of the sorbents. These plots show that humidification merely shifts the curve upscale with respect to temperature so that a given reduction or utilization value is a function of approach temperature rather than baghouse temperature.

The sorbent utilization associated with low temperature baghouse operation is believed to occur in a thin film of residual moisture surrounding individual sorbent particles. Table 16 shows the increase in surface moisture with decreasing sorbent injection temperature. This data is somewhat biased since the baghouse was operated at higher temperatures (300°F) when injecting sorbent at 1780°-1850°F. In all cases, humidification increased surface moisture when compared to the respective baseline test.

TABLE 15

EFFECT OF SORBENT INJECTION LOCATION AND HUMIDIFICATION
ON LINWOOD PHL UTILIZATION

Baghouse Temp. (°F)	Sorbent Injection Temp. (°F)	Flue Gas Moisture (Vol.%)	Mole Ratio (CaO/SO ₂)	SO ₂ Reduction (%)	Sorbent Utilization (%)
300	1850	14.9	1.52	51.6	33.8
300	1780	-- ^a	1.36	49.6	36.4
190	510	15.2	1.40	48.3	34.6
190	475	24.3	1.24	60.4	48.8

^aMoisture content not determined (estimated 20-25%).

Figure 18. Sulfur dioxide reduction versus baghouse temperature for PHL injected at 1250°F.

Figure 19. Sorbent utilization versus baghouse temperature for PHL injected at 1250°F.

3.3 TASK D, NO → NO₂ CONVERSION

Sodium-based sorbents, specifically soda ash, are currently being used for SO₂ control in utility boiler systems using spray dryer technology. Demonstration projects over the last several years have demonstrated 70% to 80% SO₂ control using dry injection of nahcolite and trona upstream of a utility baghouse. In the last two years concern has developed with respect to the association of sodium-based sorbents and the concentration of NO₂ in stack gas resulting in a colored plume. A western utility, which employs a soda ash spray dryer, has experienced plume coloration due to NO₂ concentrations in the stack gas of 40 to 70 ppm (28). A recent utility-scale demonstration of dry sorbent injection, using sodium-based sorbents, resulted in a brown coloration of the stack gas due to NO₂ formation (29). The objective of Task D was to conduct a bench-scale study to identify mechanisms responsible for the production of NO₂ from NO as it pertains to gas stream cleanup processes. Once the mechanisms were identified an attempt was to be made to develop methods to reduce/eliminate NO₂ emissions.

TABLE 16

EFFECT OF FLUE GAS HUMIFICATION ON SORBENT RESIDUAL MOISTURE

Sorbent Injection Temp. (°F)	Flue Gas Moisture (%)	Sorbent Ignition Loss	Baghouse Catch Ignition Loss (%)
510	15.2	22.76	22.55
475	24.3	22.40	48.95
1260	15.3	22.65	20.54
1230	25.5	23.72	26.26
1850	14.9	22.71	2.04
1780	-- ^a	22.89	2.86

^aMoisture content not determined (estimated 20-25%).

3.3.1 Description of Facilities and Procedures

Bench-Scale Fixed-Bed Reactor System

Figure 20 illustrates the bench-scale fixed-bed reactor system used in Task D. Pure gases, stored in high pressure cylinders, were used to synthesize a flue gas mixture. The volumetric flow of each component gas was measured by a rotameter. Verification of the accuracy of the rotameter was done using a dry gas meter. The different gases making up the flue gas were blended from two gas lines. Branch A consisted of gases only slightly soluble in water (i.e., nitrogen and oxygen). The volumetric flow through Branch A was kept constant at 4.0 scfh for the purpose of introducing water vapor into the flue gas stream. The other branch, Branch B, consisted of the more water soluble gases of SO₂, NO and CO₂ with the balance being N₂. The flow rate in Branch B was maintained at approximately 11 scfh throughout the test period. Branch B was preheated to 200°F before mixing with Branch A in order to prevent moisture condensation in the gas line downstream from the point of mixing. The total gas flow in the reactor manifold was 15.0 scfh. When water vapor was present in the gas mixture, the temperature of the total synthetic flue gas flow was maintained above 220°F all the way to the reactor manifold. Gas concentrations of NO and CO₂ at the reactor inlet were maintained at 500 ppm and 15.0% by volume, respectively, for each experiment.

The volume percent of water vapor leaving the humidity bath was determined experimentally. The calibration of the water bath was done by a series of tests at various water bath temperatures maintaining a constant gas flowrate to the inlet of the water bath of 4.0 scfh. Water vapor was condensed and collected in a series of cooled impingers. By weighing the water condensate collected, the volume percent of water vapor was determined. The bath may be bypassed as the experimental design specifies and for start-up and shutdown.

Figure 20. Bench-scale fixed-bed reactor system for $\text{NO} \rightarrow \text{NO}_2$ conversion study.

Figure 20 shows the four reactors connected in parallel to an inlet and outlet manifold. An oven enclosing the apparatus was used to maintain the specified temperature. Valve placement on the manifolds permitted flow of gases into each reactor separately.

Each reactor is a right circular cylinder constructed of stainless steel with an inside diameter of 2.69 inches (6.83 cm). Its overall length is 6.0 inches (15.24 cm). Each two piece reactor is flanged in the middle to allow access to the reactor interior. An 80 mesh stainless steel screen was welded to the sides of each reactor to form the bottom of the bed. A glass fiber filter was placed on top of the screen to keep the small particle size material from blowing through the bed during a test. Each reactor was clamped together using a two hinged, beveled teflon compression clamp. The pressure seal for each reactor was provided by a teflon/viton gasket inserted between the two halves.

Upon leaving the reactor assembly, the sample gas was cooled in a sample conditioner removing the moisture in the synthetic flue gas before entering the pump and the gas analyzers.

Oxygen and carbon dioxide concentrations of the "dry" gas mixture were measured by Beckman model 575 and 864 analyzers, respectively. A Dupont model 400 photometric analyzer was used to determine SO_2 concentration at 280 nm. For NO_2 gas analysis, a DuPont model 400 photometric analyzer was converted from monitoring the 280 nm emission line to the 436 nm emission line. A Thermoelectron Model 10 chemiluminescent analyzer was used for NO - NO_x determinations and NO_2 by difference. All gas monitoring instrumentation was calibrated with certified span gases.

A Kaye Data logger was used to collect data from the gas analyzers and thermocouples at one minute time intervals. Strip chart recorders provided constant documentation of all gas analysis instrumentation.

Each of the four reactors were filled to a depth of 0.25 inches with the different materials to be studied. The reactors were installed and the oven was heated to a specified temperature.

If humidification was required, the heater on the water bath was turned on and the gas mixture in branch A was introduced into the water bath at a gas flow rate of 4.0 scfh. At a water bath temperature of 175°F , the total moisture content in the flue gas was determined to be 20% by volume.

After calibration of flue gas analyzers, the synthetic flue gas was directed through the reactor bypass. A computer program was used to calculate the approximate rotameter settings for each component gas. With the help of the gas analyzers, the rotometers were readjusted slightly to tailor the gas mixture to experimental specifications.

When system equilibrium was established, the gas flow was directed from the reactor bypass into one of the reactors. The Kaye data logger recorded the gas analyzer output at a rate of once every 20 seconds while strip chart recorders provided constant readout from the gas analyzers. The time duration of a test was usually between 6 and 10 minutes. After the test, the gas flow was redirected through the reactor bypass to check for variations in baseline conditions.

Experimental Design

The factorial experimental design was developed in two parts. Part I was the initial screening of four parameters (i.e. SO_2 , O_2 , temperature and humidity) and their effect on the formation of NO_2 . A four factorial experimental design was selected to determine the significance of each of the above mentioned independent variables on NO_2 production and any interactions that might exist between those variables. The experimental design format is presented in Table 17 and includes not only the 16 experiments needed for the factorial design but also two replicate experiments for a total of 18.

According to design theory, two extreme points, one high and one low, were selected for each independent factor bracketing the conditions of probable NO_2 formation. The typical conditions for NO_2 reactions were suggested by past experimental work (28). For SO_2 , O_2 and H_2O concentration, the low and high points were 0 and 3000 ppm SO_2 ; 0 and 6 percent O_2 (by volume); and 0 and 20 percent H_2O (by volume). The temperature factor was bracketed at 160°F and 350°F .

TABLE 17
FOUR FACTORIAL EXPERIMENTAL DESIGN
(PART I)

Run Order	SO ₂ Concentration (ppm), X1	Temperature, (°F), X2	O ₂ Concentration (%), X3	H ₂ O Concentration (%), X4
1	0	160	0	0
2	3000	160	0	0
3	0	350	0	0
4	3000	350	0	0
5	0	160	6	0
6	3000	160	6	0
7	0	350	6	0
8	3000	350	6	0
9	0	160	0	20
10	3000	160	0	20
11	0	350	0	20
12	3000	350	0	20
13	0	160	6	20
14	3000	160	6	20
15	0	350	6	20
16	3000	350	6	20
17	3000	160	6	0
18	3000	160	0	20

During Part I four materials, sodium carbonate, sodium sulfite, calcium hydroxide and calcium carbonate, were evaluated using this experimental design format. The total of number of experiments performed in Part I was 72.

Part II of the experiment was added to the overall work in order to 1) determine the most significant variable in NO₂ formation, 2) replicate runs to provide additional data for variance analysis, 3) screen additional materials and 4) to provide additional information in determining reaction mechanisms.

A three factorial design was used in the second set of experiments since statistical analysis of the Part I results revealed that humidity was not a significant variable relative to the other three independent factors studied. Detailed results of the Part I study will be discussed later in this report. Table 18 provides the format used in the experimental design in Part II. The low-high concentrations of SO₂, O₂ and temperature were 1500 ppm and 3000 ppm, 3% and 6% (by volume), and 250°F and 350°F, respectively.

TABLE 18
THREE FACTORIAL EXPERIMENTAL DESIGN
(PART II)

Run Order	SO ₂ Concentration (ppm), X1	O ₂ Concentration (%), X2	Temperature (°F), X3
1	1500	3	250
2	3000	3	250
3	1500	6	250
4	3000	6	250
5	1500	3	350
6	3000	3	350
7	1500	6	350
8	3000	6	350
A	3000	6	350
B	1500	3	350
C	3000	12	350
D	3000	12	250

This three factorial experimental design was applied to three new materials: calcium sulfite, Montana Dakota Utility (MDU) fly ash, and Colorado Power & Light (CPL) fly ash. Sodium carbonate was the only material used in the Part I factorial design and repeated in Part II of the experimental design.

3.3.2 Results and Discussion

Four Factorial Experimental Design

Four materials were screened for NO₂ formation in the four factorial experimental design. They were sodium carbonate, sodium sulfite, calcium hydroxide and calcium carbonate. Only sodium carbonate and calcium hydroxide produced measurable amounts of NO₂ in this set of screening tests.

However, the amount of NO₂ observed for calcium hydroxide was only slightly above the baseline NO₂ concentration. Formation of NO₂ was observed in 4 of the 16 test conditions listed in the experimental design using Na₂CO₃. These four test conditions and results are summarized in Table 19. Sodium sulfite and calcium carbonate produced no measurable concentrations of NO₂ at any of the experimental conditions tested.

A statistical analysis for sodium carbonate was applied to the four factorial design. The results of the analysis, found in Table 20, indicated that of the four factors studied, SO₂ concentration, O₂ concentration and temperature were significant variables in the formation of NO₂. The

TABLE 19
RESULTS OF FOUR FACTORIAL FIXED-BED REACTOR TESTS
DEMONSTRATING NO₂ FORMATION

SO ₂ (ppm)	O ₂ (ppm)	Moisture (%)	Temp. (°F)	Na ₂ CO ₃ NO ₂ ppm	Ca(OH) ₂ NO ₂ ppm
3000	6.0	0.0	350	160	36
3000	6.0	20.0	350	250	30
3000	6.0	0.0	160	23	0
3000	6.0	20.0	160	20	0

statistical significance of an experimental variable is determined by the t_E factor. If the t_E factor, given in Table 20, is greater than the t^* factor, a confidence level may be stated for the existence of a real effect caused by this variable on NO₂ formation. If the t_E factor was less than the t^* factor, the effect of the variable would be considered insignificant being caused merely by random variability of the data. Statistical analysis further revealed a possible three-way interaction of [SO₂], [O₂] and temperature. This is observed in Table 20 under the heading X1X2X3. The t_E for the three-way interaction is 3.80 which is greater than the t^* value of 1.886 at a 90% confidence level with 3 degrees of freedom. Therefore, according to the statistical findings, changing one of these three parameters will effect the behavior of the other two variables in the production of NO₂. The fourth variable, humidity, was found to be statistically insignificant relative to the other three variables with respect to NO₂ production.

In all tests of the four factorial experimental design, NO₂ was formed only when SO₂ sorption was occurring. The materials most reactive with respect to SO₂ at the conditions studied, produced the highest amounts of NO₂. Sodium carbonate, which has a considerably higher rate of SO₂ capture at these temperatures, produced NO₂ at a rate much greater than calcium hydroxide.

Three Factorial Experimental Design

The statistical analysis for each of the four materials tested in the three factorial experimental design is found in Tables 21 through 24. For every material tested, the t_E for temperature is significantly greater than t^* . For example with Na₂CO₃, temperature has a t_E , found in Table 21, of 7.63 and a t^* of 1.638. This indicates that at a 90% confidence level, these calculated effects for temperature are real and not due to the random variability of the data. The magnitude of the t_E number for temperature as compared with the t_E numbers for [SO₂] and [O₂] reveal that temperature is the major variable in the NO₂ reaction. The effect of temperature can also be illustrated graphically. In Figure 21, NO₂ concentration in ppm is plotted

TABLE 20

FOUR FACTORIAL STATISTICAL ANALYSIS OF SODIUM CARBONATE DATA^a

	Mean	SO ₂ Concentration (ppm) X1	Temperature (°F) X2	O ₂ Concentration (%) X3	H ₂ O Concentration (%) X4	X1X2	X1X3	X1X4
Sum (+)	342.99	342.99	311.05	342.99	193.24	311.05	342.99	193.24
Sum (-)	0.00	0.00	31.94	0.00	149.75	31.94	0.00	149.75
$\Sigma(+)+\Sigma(-)$	342.99	342.99	342.99	342.99	342.99	342.99	342.99	342.99
$\Sigma(+)-\Sigma(-)$	342.99	342.99	279.12	342.99	43.50	279.12	342.99	43.50
Effect	21.44	42.87	34.89	42.87	5.44	34.89	42.87	5.44
t _E	2.34	4.67	3.80	4.67	0.59	3.80	4.67	0.59

^at* = 1.638 at 90% confidence level with three degrees of freedom.

TABLE 20 (Continued)

	X2X3	X2X4	X3X4	X1X2X3	X1X2X4	X1X3X4	X2X3X4	X1X2X3X4
Sum (+)	311.05	185.18	193.24	311.05	185.18	193.24	185.13	185.13
Sum (-)	31.94	157.81	149.75	31.94	157.81	149.75	157.81	157.81
$\Sigma(+)+\Sigma(-)$	342.99	342.99	342.99	342.99	342.99	342.99	342.99	342.99
$\Sigma(+)-\Sigma(-)$	279.12	27.37	43.50	279.12	27.37	43.50	27.37	27.37
Effect	34.89	3.42	5.44	34.89	3.42	5.44	3.42	3.42
t_E	3.80	0.37	0.59	3.80	0.37	0.59	0.37	0.37

$a_{t*} = 1.638$ at 90% confidence level with three degrees of freedom.

TABLE 21

THREE FACTORIAL STATISTICAL ANALYSIS OF SODIUM CARBONATE DATA^a

	Mean	SO ₂ Concentration (ppm), X1	O ₂ Concentration (%), X2	Temperature (°F) X3	X1X2	X1X3	X2X3	X1X2X3
Sum (+)	786.56	402.51	362.31	588.71	393.76	411.36	359.16	393.11
Sum (-)	0.00	384.05	424.25	197.85	392.90	375.20	427.40	393.45
$\Sigma(+)+\Sigma(-)$	786.56	786.56	786.56	786.56	786.56	786.56	786.56	786.56
$\Sigma(+)-\Sigma(-)$	786.56	18.46	-61.94	390.86	0.96	36.16	-68.24	-0.34
Effect	98.32	4.61	-15.49	97.72	0.24	9.04	-17.06	-0.08
t _E	7.63	0.36	-1.21	7.63	0.02	0.71	-1.33	-0.01

^at* = 1.638 at 90% confidence level with 3 degrees of freedom.

TABLE 22

THREE FACTORIAL STATISTICAL ANALYSIS OF CALCIUM SULFITE DATA^a

	Mean	SO ₂ Concentration (ppm), X1	O ₂ Concentration (%), X2	Temperature (°F) X3	X1X2	X1X3	X2X3	X1X2X3
Sum (+)	389.84	189.79	239.21	261.61	169.06	178.26	212.64	205.39
Sum (-)	0.00	200.05	190.63	128.23	220.78	211.58	177.20	184.45
$\Sigma(+)+\Sigma(-)$	389.84	389.84	389.84	389.84	389.84	389.84	389.84	389.84
$\Sigma(+)-\Sigma(-)$	389.84	-10.26	28.58	133.38	-51.72	-33.32	35.44	20.94
Effect	48.73	-2.56	7.14	33.34	-12.93	-8.33	8.86	5.24
t _E	7.81	-0.41	1.14	5.34	-2.07	-1.33	1.42	0.34

⁵
⁸ a_t* = 1.886 at 90% confidence level with 2 degrees of freedom.

TABLE 23

THREE FACTORIAL STATISTICAL ANALYSIS OF COLORADO POWER AND LIGHT FLY ASH DATA^a

	Mean	SO ₂ Concentration (ppm), X1	O ₂ Concentration (%), X2	Temperature (°F) X3	X1X2	X1X3	X2X3	X1X2X3
Sum (+)	906.84	508.64	406.96	550.40	443.44	515.00	404.88	454.00
Sum (-)	0.00	398.20	499.88	356.44	463.40	391.84	501.96	452.84
$\Sigma(+)+\Sigma(-)$	906.84	906.84	906.84	906.84	906.84	906.84	906.84	906.84
$\Sigma(+)-\Sigma(-)$	906.84	110.44	-92.92	193.96	-19.96	123.16	-97.08	1.16
Effect	113.35	27.61	-23.23	48.49	-4.99	30.79	-24.27	0.29
t _E	14.43	3.53	-2.97	6.19	-0.64	3.93	-3.10	0.04

59

^at* = 1.886 at 90% confidence level with 2 degrees of freedom.

TABLE 24

THREE FACTORIAL STATISTICAL ANALYSIS OF MONTANA-DAKOTA UTILITIES FLY ASH DATA^a

	Mean	SO ₂ Concentration (ppm), X1	O ₂ Concentration (%), X2	Temperature (°F) X3	X1X2	X1X3	X2X3	X1X2X3
Sum (+)	1089.93	543.52	542.76	702.86	563.25	582.16	445.32	497.13
Sum (-)	0.00	446.31	547.77	387.88	526.58	507.77	644.11	592.8
$\Sigma(+)+\Sigma(-)$	1089.93	1089.93	1089.93	1089.93	1089.93	1089.93	1089.93	1089.93
$\Sigma(+)-\Sigma(-)$	1089.93	197.31	-4.41	314.17	36.57	74.39	-198.29	-95.67
Effect	136.24	49.33	-1.10	78.54	9.14	18.60	-49.57	-23.92
t _E	15.64	5.56	-0.13	9.02	1.05	2.13	-5.69	-2.74

^at* = 1.886 at 90% confidence level with 2 degrees of freedom.

Figure 21. Nitrogen dioxide concentration versus time for Na_2CO_3 at 250°F and 350°F .

versus time in seconds for Na_2CO_3 . The two temperatures are compared at 6% O_2 and 3000 ppm SO_2 . The rate of formation of NO_2 at 350°F has an averaged value of 149.8 ppm/sec compared to 48.2 ppm/sec at 250°F . The same graphs for the other three materials are presented in Figures 22, 23, and 24.

Figures 25, 26, and 27 illustrate that the rate of NO_2 formation for three of the materials studied was similar for $[\text{O}_2]$'s of 3% and 6% by volume. Statistically, the $[\text{O}_2]$ t_E values for Na_2CO_3 , CaSO_3 and MDU fly ash were lower than their corresponding t^* values making them insignificant in the formation of NO_2 under these experimental conditions. Only CPL fly ash had a t_E value for $[\text{O}_2]$ greater than its t^* value. However, the t_E value of 2.97 was not much higher than the t^* value of 1.886.

Sulfur dioxide concentration was observed graphically to have little additional positive affect on NO_2 production above the 1500 ppm level studied. Figure 28 shows the relationship of NO_2 concentration versus time at the two different SO_2 concentrations for Na_2CO_3 . The statistical analysis confirms the graphical representations for both Na_2CO_3 and CaSO_3 having t_E values much smaller than the t^* values. However, the t_E values for the fly ashes studied in the three factorial experimental design showed a statistical significance for SO_2 concentration.

Figure 22. Nitrogen dioxide concentration versus time for CaSO₃ at 250°F and 350°F.

Figure 23. Nitrogen dioxide concentration versus time for MDU fly ash at 250°F and 350°F.

Figure 24. Nitrogen dioxide concentration versus time for CPL fly ash at 250°F and 350°F.

Figure 25. Nitrogen dioxide concentration versus time for Na₂CO₃ at 3%, 6%, and 12% oxygen.

Figure 26. Nitrogen dioxide concentration versus time for CaSO₃ at 3%, 6%, and 12% oxygen.

Figure 27. Nitrogen dioxide concentration versus time for MDU fly ash at 3%, 6%, and 12% oxygen.

Figure 28. Nitrogen dioxide concentration versus time for Na_2CO_3 at 1500 ppm and 3000 ppm sulfur dioxide.

4.0 CONCLUSIONS

Based on the results of work completed during the period April 1, 1986 through March 31, 1987 on the SO_x/NO_x Control project, sponsored by the U.S. Department of Energy under a Cooperative Agreement (Contract No. DE-FC21-86MC10637), several conclusions are presented.

Task A. Sorbent Evaluation

Based on the literature review, substantial information is available on limestone, its characteristics, and application to flue gas desulfurization processes, including furnace injection. As a resource, calcium-based sorbents are widely available in the 48 contiguous states and the lime industry could produce an additional 3 to 5 million tons per year of high-calcium lime from existing capacity for use in SO_2 control processes.

Pressure-hydrated lime produced in a bench-scale pressure hydrator using Marblehead lime was found to be a better sorbent for SO_2 reduction than the commercial Marblehead hydrate and far better than the limestone or lime. Utilization values for the 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 mole ratio of 1.0.

Pressure-hydrated lime produced in a bench-scale pressure hydrator using Longview lime resulted in utilization values similar to those observed with commercial Longview hydrate. Both hydrates were observed to be better sorbents for SO_2 reduction than the limestone or lime. Utilization values for the hydrates, limestone, and lime were 27%, 14%, and 11%, respectively, when injected into a pilot-scale combustor at 1825°F and a Ca/SO_2 mole ratio of 1.0.

Marblehead and Longview limestones were calcined at 1850° , 2000° , and 2150°F in a muffle furnace. 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 both limestones. Pressure hydrates prepared from calcines produced at 2000°F demonstrated better utilization than pressure hydrates prepared from calcines produced at 1850° and 2150°F .

Based on a 2×2 factorial experimental design, hydration pressures and water stoichiometries ranging from 50 to 180 psig and 1.0 to 1.6, respectively, had no significant impact on sorbent utilization, as determined by pilot-scale furnace injection tests, for pressure hydrates prepared from Marblehead and Longview commercial lime.

Task C. Combustion System Operability

When firing an Illinois No. 6 bituminous coal in a pilot-scale combustion system 50% and 75% SO_2 reduction was achieved with furnace injection of Marblehead pressure-hydrated lime at Ca/SO_2 mole ratios of 1.2 and 2.2, respectively.

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 the deposits were weak and should be easily removed with conventional sootblowing equipment.

Electrostatic precipitator performance decreased dramatically with increased sorbent addition for the coal/sorbent combination evaluated. Particulate collection efficiency decreased from 96% to 67% as sorbent injection increased particulate loadings at the ESP inlet from a baseline of 1.6 to 6.5 gr/scf. Correspondingly, bulk ash resistivity increased from a baseline of 10^{12} to 10^{14} ohm-cm.

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 at 1250°F resulted in 55% sorbent utilization.

Task D. NO_x→NO₂ Conversion

Of the four parameters evaluated, temperature, [O₂], [SO₂], and [H₂O], temperature proved to be the most statistically significant. Oxidation of NO to NO₂ increased dramatically as reactor temperature increased from 250° to 350°F. The rate of NO₂ formation was found to increase with increased sulfation rate. Therefore materials such as Na₂CO₃ which are highly reactive with respect to SO₂ at the conditions evaluated, resulted in the formation of higher NO₂ concentrations.

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No.	2. Program/Project Title SOX/NOX CONTROL	3. Reporting Period 04/01/86 through 03/31/87
4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 3/31/86

11. Major Milestone Status	Units Planned	
	Units Complete	
a. Sorbent Evaluation	P	1 ▲ 2 ▲ 3 ▲ 4 ▲ 5 ▲
	C	
c. Combustion System Operability	P	1 ▲ 2 ▲ 3 ▲ 4 ▲ 5
	C	
d. NO → NO ₂ Conversion	P	1 ▲
	C	
f. Annual Report	P	1 ▲
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	
	P	
	C	

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		6. Completion Date 3/31/92

Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Bench-scale calcination experiments	11/15/86	11/30/86	
a.2	Bench-scale pressure hydration experiments	01/31/87	02/28/87	
a.3	Pilot-scale evaluation of pressure-hydrated sorbents	02/15/87	03/15/87	
a.4	Analytical characterization of limestones, calcination products, and hydrates	02/28/87	03/31/87	
c.1	Selection of eastern combustion fuel for combustion system operability evaluation	05/31/86	05/31/86	
c.2	Pilot-scale combustion experiments	08/31/86	08/22/86	
c.3	Inorganic characterization of fuel	09/30/86	11/30/86	
c.4	Analytical characterization of coal, sorbent, coal ash, fly ash, and ash deposits	10/31/86	10/31/86	
c.5	Pilot-scale flue gas humidification experiments	11/30/86	09/15/86	
d.1	Bench-scale NO → NO ₂ conversion experiments	08/31/86	03/15/87	
f.1	Annual report	03/31/87	06/19/87	

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WASTE MANAGEMENT

Final Technical Report for the Period April 1, 1986 - March 31, 1987
including the Quarterly Technical Progress Report
for the Period January through March, 1987

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April 1987

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1.0 Goals and Objectives

The Waste Management project is conducting research to characterize coal combustion solid wastes and to develop innovative liner materials for utility waste disposal sites. The objective of the waste characterization study is to assess the impact of solid waste disposal requirements on the commercial viability of several coal utilization processes being developed at the University of North Dakota Energy Research Center (UNDERC). The objective of the liner study is to develop cost-effective liner materials for utility waste disposal sites using mixtures of coal combustion fly ash, lime and/or cement.

2.0 Accomplishments

This report contains the results of characterization studies performed on 14 different waste materials produced from advanced coal combustion processes being developed at UNDERC. Studies were completed on 10 waste streams from the atmospheric fluidized bed combustion unit (AFBC), 2 waste streams from combustion tests which used pressure hydrated lime injection for SO_2 control and 2 waste streams from combustion tests which used $\text{NH}_3\text{-SO}_3$ injection for enhanced particulate collection. The types of waste samples studied included fly ashes, spent bed materials, primary cyclone ashes, secondary cyclone ashes and ash composites. The test protocol used for the characterization studies consisted of waste analyses for elemental, mineral and trace organic content, waste leachate analyses for trace metals and trace organic compounds, and tests of physical properties relevant to waste disposal.

The results of the waste characterization work indicated that the disposal of waste materials produced from processes being developed at UNDERC should not present any significant or unusual problems.

The waste characterization test results are summarized as follows:

- * None of the 14 materials tested would be classified as hazardous wastes based on their leachate trace metal contents.
- * 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 GC/MS. The minimum detection limit for the test procedure was 20 mg/l in the leachate.
- * The pH values of the ASTM leachates produced from the 14 waste materials ranged from 10.1 to 12.6. The 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.

For the liner development study, six fly ashes were tested to evaluate their suitability as liner construction materials. The fly ash samples were supplied by the Northern States Power Company (Minnesota), the Basin Electric 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 tested for selected chemical and physical properties related to their use for liner materials. Scoping tests were performed with the fly ashes to determine the approximate amounts of additives such as lime, portland cement and water required to produce liner materials. Based on the results of the scoping tests, designed laboratory experiments were performed using variable addition levels of lime, cement and water to determine specific formulas for producing acceptable liner materials from the fly ashes. The formulas were then used to make 4 square foot by 6 inch thick liner slabs to evaluate the properties of the fly ash liners.

The results of the liner development study are summarized as follows:

- * Leaching tests performed on the six ashes showed that none of these materials could be classified as hazardous wastes based on their leachate trace metal contents.
- *The physical properties of the ashes generally indicated that the materials would produce acceptable liner materials.
- *The results of the scoping tests showed that liner materials with permeabilities less than 1×10^{-7} cm/sec could be produced by adding appropriate amounts of portland cement and/or lime to the fly ash liner mixtures.
- * The results of the formulation experiments showed that minimum cement and/or lime additions ranging from 3% to 9.5% (dry weight) were required to produce liner materials with permeabilities significantly lower than 1×10^{-7} cm/sec and unconfined compression strengths which generally exceeded 400 psi.
- * Preliminary results from the liner slab tests indicate that the liner materials do not deteriorate as a result of prolonged contact with fly ash leachate. The permeabilities of the liner slabs have remained below 1×10^{-7} cm/sec after two months of exposure to fly ash leachates and no evidence of liner cracking has been observed.

3.0 Waste Characterization

The test protocol used for waste characterization consisted of waste leaching tests, chemical and mineral analyses and physical property tests. The characterization data was used to evaluate the waste disposal requirements for advanced combustion processes being developed at UNDERC. The principal objective of the evaluation process was to identify any potential regulatory problems which may develop from the disposal of these wastes. The waste characterization protocol is summarized in Table 1.

TABLE 1
THE WASTE CHARACTERIZATION TEST PROTOCOL

- A. Solid Waste Leachate Production
 - 1. EPA-EP batch extraction and inorganic trace element analyses
 - 2. ASTM D-3987 batch extraction and inorganic trace element analyses
 - 3. Trace organic analyses of waste leachates
 - 4. Column leaching tests and inorganic trace element analyses
 - B. Solid Waste Chemical and Mineral Analyses
 - 1. Major and trace inorganic elemental composition
 - 2. Mineral composition
 - 3. Trace organic content
 - C. Solid Waste Physical Properties
 - 1. Permeability
 - 2. Bulk density
 - 3. Specific surface area
 - 4. Loss on ignition
-
-

3.1 Waste Sample Descriptions

A total of 14 different waste samples were characterized at UNDERC during the past year.

Ten waste samples generated from AFBC combustion research performed at UNDERC were characterized using the protocol shown in Table 1. The waste samples were produced with a 1,000,000 BTU/hr, bubbling bed, atmospheric fluidized combustor. The waste materials included spent bed material, primary and secondary cyclone ashes, and baghouse fly ash from a single AFBC.

combustion run. These four samples represent 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 composite ash samples were prepared by blending the wastes in direct proportion to the amounts of material produced during the AFBC combustion runs. The proportions used were 90 wt.% primary cyclone ash, 3 wt.% secondary cyclone ash and 2 wt.% baghouse fly ash.

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. A list of the various AFBC waste samples which were characterized is shown in Table 2. Because of the level of effort required for the column leaching tests, only the composite waste samples were studied with this procedure.

Two fly ash waste samples produced from combustion tests which used pressure-hydrated lime injection for SO_2 control were characterized. 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 NH_3 - SO_3 injection to increase baghouse efficiency were also characterized. The fuel used for these tests was a Monticello, Texas, lignite. The NH_3 - SO_3 fly ashes were collected from a baghouse on 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.

3.2 Waste Characterization Test Methods

The analytical methods used to perform the waste characterization tests are discussed in the following paragraphs. Well documented and standardized methods were selected for each of the tests.

The purpose of the EPA-EP batch leaching test is to determine if a solid waste should be classified as a hazardous waste under the regulations specified in the Resource Conservation and Recovery Act (RCRA). A solid waste may be designated as a hazardous waste based on its leachate trace metal content if the levels exceed the maximum contaminant concentrations listed in Table 3 (1). A detailed description of the procedure for the EPA-EP leaching test is contained in reference 2.

TABLE 2
CHARACTERIZATION TEST PLAN FOR THE UNDERC AFBC SAMPLES

<u>Mine Location/Coal Rank</u>	<u>Chemical-Physical Testing^a</u>	<u>Column Leaching</u>
<u>Sarpy Creek, MT</u> <u>Subbituminous Coal</u>		
Bed Material (Limestone addition)	X	
Primary Cyclone Ash (Limestone addition)	X	
Secondary Cyclone Ash (Limestone addition)	X	
Baghouse Fly Ash (Limestone addition)	X	
Composite Ash Sample (Limestone addition)	X	X
Composite Ash Sample (Ash reinjection)	X	X
<u>Gibbons Creek, TX</u> <u>Lignite</u>		
Composite Ash Sample (Limestone addition)	X	X
Composite Ash Sample (Ash reinjection)	X	X
<u>Navajo, NM</u> <u>Subbituminous Coal</u>		
Composite Ash Sample (Limestone addition)	X	X
Composite Ash Sample (Ash reinjection)	X	X

a. Physical-chemical characterization includes all of the tests listed in Table 1 with the exception of column leaching.

TABLE 3

MAXIMUM CONCENTRATION OF LEACHATE CONTAMINANTS FOR
RCRA HAZARDOUS WASTE CLASSIFICATION

<u>Element</u>	<u>Maximum Concentration (mg/l)</u>
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

The ASTM D-3987 batch leaching test was included in the characterization protocol to evaluate trace metal extraction from the wastes under alkaline leaching conditions. Generally, ASTM-type leachates from western low-rank coal ashes have pH values ranging from 10 to 13. The data obtained from the ASTM leaching test is useful for estimating the impact of coal combustion waste disposal practices on groundwater. In this regard, the RCRA regulations specify that a disposal facility shall not contaminate an underground drinking water source beyond the boundary of the facility. To "contaminate" in this context means to cause trace metal concentrations in the groundwater to exceed their primary drinking water standards. The primary drinking water standards for regulated trace metals are equal to 1/100 of the concentrations listed in Table 3 (3).

Column leaching tests provide information about the rates at which inorganic compounds are extracted from wastes. This type of information is an important supplement to the batch leaching test data because it indicates the time frame during which the waste will have the greatest impact on the surrounding groundwater. The column leaching tests were performed using a test procedure developed at Johns Hopkins University (4). This procedure has been shown in previous studies to be a reliable method for evaluating the time-related leaching behavior of coal combustion wastes.

Updated solid waste disposal regulations are putting more emphasis on determining the types of trace organic compounds that may leach from the waste. For this reason, trace organic analyses were included in the waste characterization protocol. Trace organic compounds in the waste samples and their leachates were extracted and analyzed using methods developed at the Morgantown Energy Technology Center (5). The waste samples were analyzed using a semi-quantitative gas chromatography/mass spectrometry (GC/MS)

scanning procedure. If significant amounts of organics were detected in the samples by the GC/MS scan, additional analyses using gas chromatography were done to quantify the trace organics.

The elemental composition of a waste can be used to evaluate relevant disposal properties such as exothermal hydration potential, abrasivity, and self-hardening potential. Elemental analyses were performed on the waste samples using energy-dispersive x-ray fluorescence.

The mineral composition of a waste can influence both its handling and disposal properties. A fly ash with a high quartz content, for example, tends to be abrasive, while a fly ash with a high lime content tends to be cementitious. The mineral composition of the waste samples were determined by powder x-ray diffraction.

Waste permeability is a measure of the rate at which water passes through the material, and thus indicates the amount of leachate that may be produced after waste disposal. Permeability was measured with a falling-head test apparatus (6).

The bulk density of a waste can be used to calculate volume requirements for future disposal facilities. Bulk density was measured by a conventional volume displacement technique.

The specific surface area of a waste may affect its leaching behavior. In general, the greater the specific surface area, the higher will be the rate at which soluble inorganic constituents will leach from the waste. Specific surface area was measured with a Quantachrome, single-point, monosorb instrument, using the BET liquid nitrogen adsorption principle.

The loss-on-ignition test measures the unburned carbon content of a waste. A high unburned carbon content may inhibit cementitious reactions. These types of chemical reactions are usually beneficial since they can reduce the permeability of a waste after disposal. Loss-on-ignition was measured using ASTM method C 311-68.

3.3 Waste Characterization Test Results

The results of the waste characterization test program are presented in the following sections. Fourteen different waste materials produced from advanced coal combustion processes being developed at UNDERC were evaluated. The characterization results include information about waste leachate production, waste chemical and mineral analyses and waste physical properties.

3.3.1 Leaching Test Results

The results of the EPA-EP leaching tests performed on the UNDERC waste samples are summarized in Appendix A. The purpose of this test is to determine whether a waste could be classified as a hazardous waste under the existing RCRA regulations. The maximum allowable leachate trace metal concentrations, as specified by the regulations, are listed in Table 3. Comparing the leaching data contained in Appendix A to the maximum allowable levels listed in Table 3 shows that all of the wastes tested produced EP

leachate trace metal concentrations which were well below their RCRA limits. Therefore, none of the UNDERC wastes could be classified as hazardous based on their leachate trace metal content.

The results of the ASTM batch leaching tests performed on the UNDERC waste samples are summarized in Appendix B. This test was included in the characterization protocol to evaluate the potential for leaching of trace metals from the wastes under alkaline pH conditions. Waste leaching behavior under alkaline conditions is an important factor for determining the potential impact of the waste on groundwater, since wastes from western low-rank coals typically produce alkaline leachates after disposal.

The RCRA regulations specify that a solid waste should not cause the levels of certain trace metals in usable groundwater deposits to exceed their primary drinking water standards (PDWS). The PDWS are equal to 1/100 of the contaminant concentrations listed in Table 3. To protect groundwater, many states require special disposal practices, such as the installation of a liner at the disposal site, if leachate trace metal concentrations exceed their PDWS by more than a factor of 25.

Selenium was the only trace metal which exceeded its PDWS by more than a factor of 25 in any of the ASTM leachates produced from the UNDERC waste samples. The samples which produced these relatively high leachate selenium concentrations included a Sarpy Creek subbituminous coal fly ash from an AFBC combustion test (Se conc. = 0.48 mg/l) and the two Monticello lignite fly ashes from the $\text{NH}_3\text{-SO}_3$ injection tests (baseline ash Se conc. = 1.76 mg/l and injection ash Se conc. = 0.38 mg/l).

Several important waste management insights are provided by the ASTM leaching data. The test results indicate, for example, that there may be an advantage to combining the various ash streams from the AFBC combustion process before disposal. A comparison between the leachate selenium concentrations from the Sarpy Creek fly ash (0.45 mg/l) and the Sarpy Creek composite ash (0.015 mg/l for the limestone addition tests) shows that the leachate selenium concentration is substantially reduced when the fly ash is diluted with the two cyclone ashes.

Based on the ASTM leachate data obtained from the six composite ashes, it appears that the addition of limestone to the AFBC bed actually reduced the amounts of leachable selenium in the process ash streams. Table 4 compares the selenium concentrations measured in ASTM leachates from three sets of AFBC composite ashes. It is clear from Table 4 that the leachate selenium concentrations obtained from the limestone addition ashes are consistently lower than the leachate concentrations obtained from the reinjection ashes. In two of the three cases, the ASTM leachate concentrations are approximately ten times lower for the limestone addition wastes. Part of the difference in leachate selenium content can be explained by dilution of the ash stream with some of the limestone added to the AFBC bed. Dilution alone, however, cannot account for the large observed differences. A possible explanation for this behavior is that the selenium chemically reacts with the limestone being added to the bed and thus is removed from the combustion gases before it condenses on the ash.

TABLE 4
COMPARISON OF SELENIUM CONCENTRATIONS IN ASTM LEACHATES

<u>Waste</u>	<u>Reinjection Ash Leachate Conc. (mg/l)</u>	<u>Limestone Addition Ash Leachate Conc. (mg/l)</u>
Sarpy Creek Composite Ash	0.07	0.015
Navajo Composite Ash	0.18	0.012
Gibbons Creek Composite Ash	0.43	0.05

The ASTM test results also indicated that $\text{NH}_3\text{-SO}_3$ injection reduced the amount of leachable selenium in the fly ash. The data from the two Monticello ashes showed that the leachate selenium concentration from the $\text{NH}_3\text{-SO}_3$ treated fly ash (0.38 mg/l) was much lower than the leachate selenium concentration from the untreated fly ash (1.76 mg/l). Furthermore, previous leaching tests performed at UNDERC with $\text{NH}_3\text{-SO}_3$ injection fly ashes have produced similar results (7). Based on these results, it appears that $\text{NH}_3\text{-SO}_3$ injection may initiate a mechanism which reduces the solubility of the selenium in the fly ash.

Trace organic analyses were performed on leachates produced from the 14 UNDERC waste samples. Both acid and base/neutral solvent extractions were prepared from each leachate. The extracts were analyzed with GC/MS. The results of the analyses showed that no trace organics were detected in any of the waste leachates. The minimum detection limit for the GC/MS analyses was 20 mg/l in the leachate.

Column leaching tests were performed on the six composite ash samples produced from AFBC test program, one fly ash sample obtained from the lime injection test program and one fly ash sample from the $\text{NH}_3\text{-SO}_3$ injection test program. The column leaching tests were performed using the Johns Hopkins method (4). For each waste sample, approximately 15 to 20 pore volumes were collected in four fractions. A lower number of pore volumes were collected if the leachate flow became limited by the permeability of the sample. The

leachate samples collected from the columns were analyzed for a variety of major and trace elements commonly associated with coal combustion wastes.

The results of the column leaching tests are presented in Figures 1 through 17. These figures show leachate concentration as a function of the number of pore volumes of leachate which passed through the waste sample. Two figures, showing different leachate concentration ranges, are generally included for each waste.

The principal inorganic compound leached from all of the UNDERC wastes using the column procedure appears to be calcium sulfate. Initial calcium concentrations measured in the column leachates ranged from approximately 500 mg/l to 1500 mg/l and initial sulfate concentrations ranged from approximately 700 mg/l to 4500 mg/l. Some other elements detected in the column leachates included sodium, potassium, magnesium, aluminum and silicon. The only trace elements detected in the column leachates were barium and chromium. The maximum barium concentration (15 mg/l) was measured in the leachate from the Sarpy Creek ash produced in the AFBC unit with limestone addition. The maximum chromium concentration (2.9 mg/l) was measured in the leachate from the Monticello fly ash produced with $\text{NH}_3\text{-SO}_3$ injection. The results of the column leaching tests generally show that the bulk of the leachable elements in the UNDERC wastes were removed in the first ten pore volumes passed.

When the data presented in Figures 1 through 17 are related to the actual leaching behavior of the waste in the field, it should be understood that it may take many years for one pore volume of leachate to pass through the waste. In order to make predictions about the impact of a waste leachate on groundwater located in the vicinity of a disposal site, other factors such as site design, local climate and geohydrological setting must also be considered in addition to the column leaching data.

3.3.2 Chemical and Mineral Analyses

The elemental compositions of the UNDERC waste samples are listed in Appendix C, and the mineral compositions are listed in Appendix D. The compositional data indicate that the wastes are principally made up of silicon, calcium and aluminum compounds with lesser amounts of sodium, sulfur and iron also present. The major silicon-containing mineral phase in the wastes appears to be quartz (SiO_2). Much of the calcium appears to be present as anhydrite (CaSO_4) and lime (CaO), and iron is present in the form of hematite (Fe_2O_3) and ferrite spinels (Fe_3O_4).

The presence of quartz as a major mineral phase in 13 of the 14 UNDERC waste samples indicates that these materials are abrasive, and this fact should be considered when designing handling equipment for disposal operations. The presence of lime in several of the waste samples produced with either limestone addition or lime injection indicates that these materials will probably undergo pozzolanic reactions when they contact water. Pozzolanic reactions are important because they may lead to

COLUMN LEACHING RESULTS SARPY CREEK

Figure 1. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Sarpy Creek Composite Ash Produced with Limestone Addition - High Level.

COLUMN LEACHING RESULTS SARPY CREEK

Figure 2. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Sarpy Creek Composite Ash Produced with Limestone Addition.

COLUMN LEACHING RESULTS SARPY CREEK

Figure 3. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Sarpy Creek Composite Ash Produced with Ash Reinjection.

COLUMN LEACHING RESULTS SARPY CREEK

Figure 4. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Sarpy Creek Composite Ash Produced with Ash Reinjection.

COLUMN LEACHING RESULTS NAVAJO

LIMESTONE ADDITION COMPOSITE ASH

Figure 5. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Navajo Composite Ash Produced with Limestone Addition.

COLUMN LEACHING RESULTS NAVAJO

LIMESTONE ADDITION COMPOSITE ASH

Figure 6. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Navajo Composite Ash Produced with Limestone Addition.

COLUMN LEACHING RESULTS NAVAJO

Figure 7. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Navajo Composite Ash Produced with Ash Reinjection.

COLUMN LEACHING RESULTS NAVAJO

Figure 8. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Navajo Composite Ash Produced with Ash Reinjection.

Figure 9. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Gibbons Creek Composite Ash Produced with Limestone Addition.

Figure 10. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Gibbons Creek Composite Ash Produced with Limestone Addition

COLUMN LEACHING RESULTS GIBBONS CREEK

Figure 11. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Gibbons Creek Composite Ash Produced with Ash Reinjection.

Figure 12. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Gibbons Creek Composite Ash Produced with Ash Reinjection.

COLUMN LEACHING RESULTS ILLINOIS #6

LIME ADDITION ESP ASH

Figure 13. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for Illinois #6 Fly Ash Produced with Pressure-Hydrated Lime Injection.

COLUMN LEACHING RESULTS ILLINOIS #6

LIME ADDITION ESP ASH

Figure 14. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for Illinois #6 Fly Ash Produced with Pressure-Hydrated Lime Injection.

COLUMN LEACHING RESULTS FOR MONTICELLO

AMMONIA/SO₃-TREATED BAGHOUSE ASHES

Figure 15. Plot of Column Leachate Concentration (High Levels) vs. Pore Volumes Passed for the Monticello NH₃-SO₃ Injection Fly Ash.

COLUMN LEACHING RESULTS FOR MONTICELLO

AMMONIA/SO₃-TREATED BAGHOUSE ASHES

Figure 16. Plot of Column Leachate Concentration (Intermediate Levels) vs. Pore Volumes Passed for the Monticello NH₃-SO₃ Injection Fly Ash.

COLUMN LEACHING RESULTS FOR MONTICELLO

Figure 17. Plot of Column Leachate Concentration (Low Levels) vs. Pore Volumes Passed for the Monticello NH₃-SO₃ Injection Fly Ash

significant reductions in permeability after the wastes have been land-filled. Lime content can also cause handling problems for wastes if water is added to the material and an excessive heat release occurs due to exothermal hydration reactions.

The organic fractions of the UNDERC waste samples were extracted using a soxhlet apparatus with methylene chloride as the solvent. For each sample, the water content was determined, the total weight of extractable material was measured, and the trace organics in the extract were analyzed using GC/MS.

The results of the organic extractions showed that only one of the wastes, the Sarpy Creek baghouse fly ash, released detectable amounts of organics. Low levels of three polycyclic aromatic hydrocarbons, pyrene (0.2 ug/g ash), fluoranthene (0.31 ug/g ash) and benzo(a)pyrene (0.32 ug/g ash) were quantified using gas chromatography. These types of organics are common by-products of coal devolatilization, and they have been detected in other types of low-rank coal fly ashes (8).

3.3.3 Physical Properties

Selected physical properties of the UNDERC waste samples are listed in Appendix E. For each sample the permeability, bulk density, specific surface area and loss-on-ignition were measured.

The permeabilities of the waste samples ranged from a high value of 8.2×10^{-3} cm/sec for the Sarpy Creek bed material to a low value of 1.6×10^{-5} cm/sec for the Navajo ash produced with limestone addition. It may help to put these permeability results in perspective by noting that the general criteria used to select "impermeable" soils for disposal site liners is 1×10^{-7} cm/sec. Based on a comparison with this criteria, the UNDERC waste samples can be broadly categorized as moderately permeable.

The bulk densities of the UNDERC waste samples ranged from 0.9 grams/ml to 3.1 grams/ml. Bulk density data is useful for estimating volume requirements for designing waste disposal sites.

The specific surface areas of the UNDERC waste samples ranged from 0.2 m²/grams to 16.6 m²/grams. The specific surface area of a waste has been related to its trace metal leaching behavior. The results of previous leaching studies performed at UNDERC have shown that, given two wastes with similar chemical compositions, a higher specific surface area will generally produce higher rates of trace metal release as measured by column leaching tests (9).

The loss-on-ignition test (LOI) provides a measure of the unburned carbon content of a waste sample. Studies have shown that LOI values greater than 7 wt.% may inhibit cementitious reactions which otherwise would tend to decrease waste permeability (10). None of the LOI values measured for the UNDERC waste samples, however, exceeded 7 wt.%.

3.4 Waste Characterization Conclusions

The characterization data generated for the 14 UNDERC waste samples does not indicate that any major regulatory problems will be encountered relating to the disposal of these materials. Furthermore, two of the combustion-related processes being developed at UNDERC appear to reduce the environmental impacts of the solid wastes being produced.

The EPA-EP leaching test results clearly show that the 14 UNDERC wastes could 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 UNDERC 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 UNDERC 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. These concerns could result in increased disposal costs for the wastes if the state regulatory agencies require a liner system at the disposal site to protect the groundwater.

The results of column leaching tests performed on the UNDERC wastes indicate 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 and chromium 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 UNDERC wastes indicates that these materials are abrasive. Appropriate precautions should be taken with the design of waste-handling equipment (conveyors, piping, etc.) to minimize equipment breakdown due to abrasion.

The waste characterization data also indicated that the use of limestone and $\text{NH}_3\text{-SO}_3$ as combustion-related additives tended to reduce the amounts of leachable selenium in the ash materials. A comparison between the ASTM leaching data from the AFBC tests that used limestone addition and the AFBC tests that used ash reinjection clearly indicates this trend. Further, a comparison between the ASTM leaching data from the $\text{NH}_3\text{-SO}_3$ injected and the baseline Monticello ashes indicated a similar trend. 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.

4.0 Fly Ash Liner Development Study

This report section summarizes the activities of the fly ash liner development task of the Waste Management project. The objective of this task is to develop techniques for constructing cost-effective liner materials for utility waste disposal sites using fly ash.

The initial approach used for the liner development study was to prepare liner mixtures with varying levels of fly ash, soil, lime and portland cement at a fixed water addition level. The water addition level used for these tests was selected to produce the maximum compacted dry density for the liner material. Each liner mixture was cured under controlled conditions and tested for permeability and strength. The results of these tests, performed with three different types of fly ash, showed that (1) the liner mixtures prepared in this manner did not meet a permeability criteria of less than 1×10^{-7} cm/sec, (2) the addition of soil to the mixtures either had no effect or had a deleterious effect on the permeabilities of the liner materials and (3) the water addition level used for the liner mixtures appeared to strongly affect their permeabilities. A detailed summary of these initial liner development tests is contained in reference 11.

Based on the results of the initial tests, the scope of the liner study was changed to produce materials with lower permeabilities. To accomplish this, the addition of soil to the liner mixtures was stopped, and the soil addition variable was replaced in the experimental design with a water addition variable. Therefore, the revised test program used variable levels of fly ash, lime, portland cement and water for the liner mixtures. The results of the revised test program are presented in this report. These results clearly show that liner materials with permeabilities of less than 1×10^{-7} cm/sec can be produced using fly ash.

4.1 Liner Development Program Overview

The revised test program for the liner development study was carried out in four discrete tasks. These included waste characterization, permeability scoping tests, liner formulation experiments and confirming slab tests.

The characterization task consisted of analyzing the ash materials used for the study for elemental composition, for leachate trace metals and for selected physical properties. The purpose of the characterization work was to determine how the composition and potential environmental impacts of the fly ashes might affect their use as a liner.

The purpose of the permeability scoping task was to establish ranges for the amounts of lime, cement and water to be used for the follow-on liner formulation experiments. The scoping tests were performed by preparing liner samples with constant levels of lime and cement added and different levels of water added. The liner samples were then tested to determine the relation between permeability and water addition level. Permeabilities were measured with a fixed-wall, constant head test apparatus.

The purpose of the liner formulation task was to determine the minimum amounts of lime and cement required to produce an acceptable fly ash liner material. To do this, fifteen different liner mixtures, prepared with varied amounts of lime, cement and water, were prepared. Each liner sample was tested for permeability, unconfined compression strength and unconfined compression strength after vacuum saturation treatment.

The data collected from the formulation experiments was analyzed using a multiple linear regression procedure. From the regression analyses, quadratic equations were developed to correlate the permeability and strength of the liner materials to their lime, cement and water contents. The quadratic equations were then used to plot contour curves to illustrate the relationships between liner characteristics and liner composition. The minimum amounts of lime and cement required to produce acceptable liner materials were determined from the contour curves.

The final task in the laboratory phase of the liner study was a liner slab test. The purpose of this task was to verify the characteristics of the liner materials developed in the formulation task. A 4 square foot by 6 inch thick fly ash liner slab was prepared for each of the six ash material involved in the study. These slabs were prepared using the minimum amounts of lime and cement indicated by the formulation experiments. The slabs were allowed to cure at room temperature and then placed in a permeability test device.

A representative leachate from each of the unconsolidated ash materials is being used as the permeating fluid for the slab tests. The volume of flow through the liner slab will be measured to determine the permeability, and the trace metal content of the fluid before and after it passes through the slab will be measured to evaluate the potential environmental impact of the liner material.

At the present time, the slab tests are in progress. These tests are taking longer to complete than first anticipated because the permeabilities of the slabs are generally lower than the permeabilities predicted by the formulation experiments.

4.2 Ash Sources for the Liner Study

The fly ash wastes involved in the liner study were obtained from six different utility companies located in five states. The material supplied by the Northern States Power Company (NSP) was a fly ash - scrubber powder mix, originating from NSP's Riverside Station unit #6/7, firing a mixture of Sarpy Creek subbituminous coal and 10-15% coke. The fly ash supplied by the Basin Electric Power Cooperative was produced from a Beulah lignite at the Antelope Valley Station in Beulah, North Dakota. The fly ash supplied by the Texas Utilities Generating Company was produced from a Texas lignite at the Big Brown Station in Fairfield, Texas. The fly ash supplied by the Southwestern Electric Power Company was produced from a Texas lignite at the H. W. Pirkey Power Plant near Marshall, Texas. The material supplied by the Northern Indiana Public Service Company (NIPS) was a 50%-50% mix of fly ash and scrubber sludge which came from the R. M. Schahfer Station in Wheatfield, Indiana. The NIPS fly ash was produced from Illinois #6 bituminous coal and the scrubber sludge was obtained from a lime-based wet scrubber. The fly ash supplied by the Central Illinois Public Service Company (CIPS) was taken from an ash pond located at the Meredosia Station located in Meredosia, Illinois. The CIPS ash was produced from Illinois #6 bituminous coal.

4.3 Ash Characterization Results

Characterization data obtained for the four fly ashes and the two fly ash-scrubber sludge mixtures are presented in Appendix F. The results of an elemental analysis, an EPA-EP leaching test and selected physical analyses are listed for each of the ashes.

Elemental composition data is useful for evaluating the cementitious reactivity of the ash and for estimating the amounts of additives such as lime and portland cement required to produce an acceptable liner material. A calcium content greater than 10% by weight, for example, indicates that the ash will exhibit cementitious properties, a high silicon and aluminum content usually indicates that the ash has good pozzolanic properties, and a low sodium content indicates that the ash has a relatively small water-soluble fraction. The amount of water-soluble material in the fly ash is important because experience has shown that levels exceeding 10% by weight tend to inhibit cementitious reactions (12).

All of the wastes except the Central Illinois ash had calcium contents close to or exceeding 10 wt.%. The Central Illinois ash contained only 3.2 wt.% calcium. The total silicon and aluminum contents of the wastes ranged between 15 wt.% and 32 wt.% indicating low to moderate pozzolanic reactivities. The material with the highest sodium content was the Basin Electric ash. The relatively high sodium content of this ash, however, did not appear to inhibit cementitious reactions, since the Basin ash required the lowest amounts of additives in the formulation tests to produce an acceptable liner material. (See Section 4.5.)

In addition to elemental composition, the unburned carbon content, the specific surface area and the water-soluble fraction were measured for each of the fly ash wastes. The unburned carbon content was measured by the loss on ignition (LOI) test. Unburned carbon content is important because previous

studies have shown that levels exceeding 7% by weight may inhibit cementitious reactions in fly ash (10). The level of unburned carbon did not appear to be a problem for any of the waste materials since all of their LOI values were well below 7 wt.%.

A high specific surface area tends to facilitate cementitious reactions in fly ash. A minimum specific surface area of $0.275 \text{ m}^2/\text{gm}$ has been suggested for fly ash which is to be used as a cementitious binder in soil stabilization work (12). All of the waste materials used for this study, except for the Central Illinois ash, had specific surface areas well over $0.275 \text{ m}^2/\text{gm}$. It was not possible to get a reproducible specific surface area measurement for the Central Illinois ash.

As stated previously, the water soluble fraction of a fly ash to be used for a cementitious binder should not exceed 10% by weight. Water-soluble fraction was measured using a simple leaching technique, and all six ash materials involved in this study were found to have levels well below 10 wt.%.

The six ash materials were tested using the EPA-EP leaching procedure in order to establish their status as non-hazardous wastes. The results of these tests showed that all six wastes produced EP leachates with trace metal concentrations well below the maximum contaminant levels specified by the RCRA regulations for hazardous waste classifications. (See Table 3.)

4.4 Scoping Test Results

A series of liner scoping tests were performed to set ranges for the lime, cement and water additions to be used for liner formulation experiments. The scoping tests were carried out by preparing liner samples with high lime and cement levels and a range of water addition levels. The initial additive levels used for the scoping tests were 4% lime and 4% cement. These levels were selected based on previous experience with fly ash liner mixtures. The water addition levels were selected to produce mixture consistencies ranging from 0 to 100 as measured with a flow table apparatus using ASTM procedure C-593 (13).

Each of the liner mixtures prepared for the scoping tests were compacted with a pressure of approximately 100 psi, cured for 7 days at 100°F and tested for permeability. For the permeability tests, the liner mixtures were compacted in 1.5 inch I.D. by 3 inch PVC tubes which had been scored on the inner surface to provide a good sidewall seal. A "fixed wall" type of permeability test was performed on each of the compacted liner mixtures using 10 psi of constant head differential across the liner sample. Several of the liner samples were also tested using a flexible membrane permeameter to check the results of the fixed wall tests for possible sidewall leakage. The correlation between the fixed wall tests and the flexible membrane tests was generally quite good, and there was no indication that sidewall leakage was occurring in the fixed wall tests.

It was expected that the permeability data from the scoping tests would plot as a U-shaped curve with a minimum permeability corresponding to a specific water addition level. The lime and cement addition levels used for the scoping tests were judged to be acceptable maximum levels for the follow-

on formulation tests if the minimum permeability produced was in the range of 1×10^{-8} cm/sec. If the minimum permeability obtained in the scoping tests was significantly higher or lower than 1×10^{-8} cm/sec, the tests were repeated using higher or lower additive levels, respectively.

The results of the liner scoping tests are listed in Appendix G of this report. The tests showed that it was possible to produce liner materials for all six fly ashes with permeabilities in the range of 1×10^{-8} cm/sec using additive amounts ranging from 3% lime and 3% cement to 6% lime and 6% cement. The U curves obtained for the six ashes are presented in Figures 18 through 23. The water addition levels to be used for the formulation experiments were selected by setting up a range around the point of minimum permeability on the scoping data curve. This range was established by multiplying the minimum permeability obtained in the scoping tests by a factor of 8 and then picking the water addition levels corresponding to this higher permeability value from the U curve. The factor of 8 was based on the relative standard deviation of the permeability test data, and its purpose was to ensure that permeability effects measured in the formulation tests as a function of water addition level would be large enough to distinguish them from effects caused by random experimental error.

Figure 18. Plot of Permeability vs. Water Addition Level for the NSP Liner Material Scoping Tests.

Figure 19. Plot of Permeability vs. Water Addition Level for the Basin Electric Liner Material Scoping Tests.

Figure 20. Plot of Permeability vs. Water Addition Level for the Texas Utilities Liner Material Scoping Tests.

Figure 21. Plot of Permeability vs. Water Addition Level for the SWEF Liner Material Scoping Tests.

Figure 22. Plot of Permeability vs. Water Addition Level for the NIPS Liner Material Scoping Tests.

Figure 23. Plot of Permeability vs. Water Addition Level for the CIPS Liner Material Scoping Tests.

4.5 Liner Formulation Test Results

The results of the scoping tests were used to design a series of liner formulation experiments. The purpose of these experiments was to determine the lowest lime and cement addition levels that produce an acceptable liner material from each of the six fly ashes. The criteria used for evaluating the liner materials were (1) that the material have a permeability less than 1×10^{-7} cm/sec, (2) that the material have an unconfined compression strength greater than 400 psi after a 28-day cure at 70°F and (3) that the material have an unconfined compression strength greater than 400 psi after a 7-day cure at 100°F and vacuum saturation treatment. A target permeability of 1×10^{-7} cm/sec was selected for this study because many states use this as a criteria for designing liners for waste disposal sites. The strength criteria selected for this study were taken from ASTM procedure C-593, which gives specifications for pozzolanic materials to be used with lime.

A Box-Behnken experimental design was used for the liner formulation tests. The general form of this design is shown in Figure 24. This is a three variable design (% lime addition, % cement addition and % water addition) which uses three equally spaced levels for each variable. The responses measured for each liner mixture included permeability, 28-day unconfined compression strength and 7-day unconfined compression strength after vacuum saturation treatment. For this design, a total of 15 liner mixtures were tested for each of the six fly ashes. The mixture representing the centroid of the design space was run three times to estimate experimental error.

BOX-BEHNKEN DESIGN FOR THREE FACTORS

Run	x_1	x_2	x_3
1	-1	-1	0
2	1	-1	0
3	-1	1	0
4	1	1	0
5	-1	0	-1
6	1	0	-1
7	-1	0	1
8	1	0	1
9	0	-1	-1
10	0	1	-1
11	0	-1	1
12	0	1	1
13,14,15	0	0	0

Figure 24. General Form of the Box-Behnken Experimental Design for Three Factors.

The Box-Behnken design was selected for this work because it provides sufficient data to estimate a full response surface for three variables using only 15 test runs; any other design would require at least 18 runs to produce the same result. The variable levels designated -1, 0 and 1 in Figure 24 corresponded to lime and cement levels of 0%, 2% and 4% when the scoping tests indicated that 4% lime and 4% cement addition produced a liner material with a permeability of approximately 1×10^{-8} cm/sec. If 5% lime and 5% cement or 3% lime and 3% cement were required to achieve this permeability in the scoping tests, the -1, 0 and 1 levels in the general design would correspond to 0%, 2.5% and 5% or 0%, 1.5% and 3%, respectively.

The data obtained from the liner formulation experiments were analyzed using the REG computer program, which is a multiple linear regression procedure developed by the Statistical Analysis System (14). The quadratic models developed for unconfined compression strength were obtained by transforming the data to normalize the mean square deviation and comparing the results when strength was raised to various powers. The transformations showed that the smallest normalized mean square deviations between the model and the data were obtained when strength was raised to the .5 power. The

permeability data was modeled as a logarithmic function because this approach was found to give acceptably low mean square deviations between the model and the data. A backward elimination option was used with the regression analyses to eliminate insignificant terms from the quadratic models. The data sets obtained from the liner formulation experiments and the quadratic models generated from the data for liner permeability and strength are contained in Appendix H of this report.

The surface response contour plots were generated from the quadratic models for permeability, 28-day unconfined compression strength and 7-day unconfined compression strength after vacuum saturation treatment. These contour plots can be used to select liner formulas for the six ash materials which use minimum additive levels to meet the specified permeability and strength criteria.

4.5.1 Northern States Power Liner Formulation Results

The contour plots generated for the fly ash - scrubber powder mixture obtained from the Northern States Power Company are presented in Figures 25, 26 and 27. Figure 25 shows the permeability of the liner mixtures as a function of lime and cement addition levels at a fixed water addition level equal to 38% of dry weight of the mix. The results of the formulation experiments indicate that a 38% water addition level produces the lowest liner permeabilities over the range of water addition levels tested. Since the strengths of the NSP fly ash mixtures are well over the 400 psi acceptance criteria, liner permeability is the controlling factor for selecting an appropriate liner formula.

The nominal permeability criteria for the fly ash liners, as specified in the project workplan, is 1×10^{-7} cm/sec or lower. For selection of the liner formulas, it is suggested that a factor equal to 3 times the standard deviation of the replicate permeability measurements obtained for the formulation experiments be added to this criteria to compensate for possible experimental error. This factor provides a 99% level of confidence that the actual permeability of the liner material will be less than 1×10^{-7} cm/sec. Using this safety factor, the minimum effective permeability criteria for the NSP liner material would be 2.0×10^{-8} cm/sec, or expressed as a logarithm, this would be -7.7.

Figure 25 shows that smaller amounts of lime than cement are required to produce an equivalent permeability reduction in the NSP liner material. The figure also shows that, in order to obtain a liner material with a permeability less than 2.0×10^{-8} cm/sec, a lime addition level of approximately 4% by weight is required. Based on an evaluation of the surface response contour plots generated from the formulation data and the permeability and strength requirements for the liner materials, a liner formula is indicated which calls for a mixture of 96% ash material and 4% lime on a dry weight basis with 38% water added on a percent of dry weight basis.

NSP Fly Ash- 38% water
Log of Permeability (cm/sec)

Figure 25. Plot of Permeability vs. Lime and Cement Addition Levels for the NSP Liner Material.

NSP Fly Ash
7-Day Vacuum Saturation Strength (psi)

Figure 26. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Level for the NSP Liner Material.

NSP Fly Ash
28-Day Strength (psi)

Figure 27. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the NSP Liner Material.

4.5.2 Basin Electric Liner Formulation Results

The contour plots for the Basin Electric fly ash are shown in Figures 28, 29 and 30. The water addition level which produced the lowest permeabilities in the liner formulation experiments is 21% of dry weight. The plots show that strengths for the Basin liner mixtures are well above the 400 psi minimum acceptance criteria, and therefore permeability is the major consideration for selecting lime and cement addition levels for a liner formula.

The minimum acceptable permeability for the Basin liner material is 1.2×10^{-8} cm/sec, or expressed as a logarithm, it is -7.9. This effective permeability criteria includes a design safety factor equal to 3 times the standard deviation of the permeability data measured for the Basin Electric formulation experiments. The experimental results for the Basin ash clearly indicate that smaller amounts of lime than cement are required to produce an equivalent reduction in liner permeability. An examination of Figure 28 shows that a lime addition level equal to approximately 3% of the dry weight of the liner mixture is required to produce a material with a permeability of 1.2×10^{-8} cm/sec. Based on the results of an evaluation of the surface response contour plots and the permeability and strength requirements, a liner formula is indicated for the Basin fly ash which calls for a mixture of 97% ash material and 3% lime on a dry weight basis with 21% water added on a percent of dry weight basis.

4.5.3 Texas Utilities Liner Formulation Results

The contour plots for the Texas Utilities fly ash are shown in Figures 31, 32 and 33. The water addition level which produced the lowest permeabilities in the liner formulation experiments is equal to 18% of the dry weight. The plots show that liner strengths tend to be well above the minimum acceptable level of 400 psi and that cement is more effective than lime per unit weight added for increasing the strength of the liner material.

The minimum acceptable permeability for the Texas Utilities liner material is 4.4×10^{-8} cm/sec, or expressed as a logarithm, it is -7.35. This effective permeability criteria includes a design safety factor equal to 3 times the standard deviation of the permeability data measured for the Texas Utilities formulation experiments. Figure 31 shows that, within the additive ranges used for the formulation experiments, a combination of both lime and cement are required to produce a liner material with an acceptable permeability from the Texas Utilities ash. Based on an evaluation of the surface response plots and the permeability and strength requirements for the liner material, a liner formula is indicated for the Texas Utilities fly ash which calls for 94% fly ash, 3% lime and 3% cement on a dry weight basis with 18% water added on a percent of dry weight basis.

BASIN Fly Ash - 21.0% Water
Log of Permeability (cm/sec)

Figure 28. Plot of Permeability vs. Lime and Cement Addition Levels for Basin Electric Liner Materials.

BASIN Fly Ash - 21.0% Water
7-Day Vacuum Saturation Strength (psi)

Figure 29. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the Basin Electric Liner Materials.

BASIN Fly Ash - 21.0% Water
28-Day Unconfined Compression Strength (psi)

Figure 30. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the Basin Electric Liner Materials.

TEXAS U Fly Ash - 18% water
Log of Permeability (cm/sec)

Contour plot of LIME * CEMENT

Figure 31. Plot of Permeability vs. Lime and Cement Addition Levels for the Texas Utilities Liner Material.

TEXAS U Fly Ash
7-Day Vacuum Saturation Strength (psi)

(No Significant Lime Terms)
Contour plot of WATER * CEMENT

Figure 32. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the Texas Utilities Liner Material.

TEXAS U Fly Ash - 18% water
28 - Day Unconfined Compressive Strength (psi)

Contour plot of LIME * CEMENT

Figure 33. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the Texas Utilities Liner Material.

4.5.4 Southwestern Electric Power Liner Formulation Results

The contour plots for the Southwestern Electric Power ash are shown in Figures 34, 35 and 36. The water addition level which produced the lowest permeabilities in the formulation experiments is 18% of dry weight. The plots show that strengths exceeded 400 psi when approximately 3% or more cement was added to the liner mixture.

The minimum acceptable permeability for the SWEF liner material is 5.0×10^{-8} cm/sec, or expressed as a logarithm, it is -7.3. This effective permeability criteria includes a design safety factor equal to 3 times the standard deviation of the permeability data measured for the SWEF formulation experiments. Figure 34 shows that, within the additive ranges used for the formulation experiments, a combination of lime and cement are required to produce a liner material with an acceptable permeability from the SWEF ash. Based on an evaluation of the surface response plots and the permeability and strength requirements for the liner material, a liner formula is indicated for the SWEF fly ash which calls for 93.5% fly ash, 1.5% lime and 5% cement on a dry weight basis with 18% water added on a percent of dry weight basis.

4.5.5 Northern Indiana Public Service Liner Formulation Results

The contour plots for the Northern Indiana Public Service ash material are shown in Figures 37, 38 and 39. The water addition level which produced the highest strengths and lowest permeabilities in the formulation experiments is 19% of dry weight. The plots show that the maximum predicted 7-day unconfined strengths obtained were slightly less than 400 psi and that the maximum predicted 28-day unconfined compression strengths obtained were slightly less than 300 psi.

The minimum acceptable permeability for the NIPS liner material is 4.0×10^{-8} cm/sec, or expressed as a logarithm, it is -7.4. This effective permeability criteria includes a design safety factor equal to 3 times the standard deviation of the permeability data measured for the NIPS formulation experiments. Figures 37 through 39 show that, within the ranges of lime and cement addition used for the formulation experiments, the maximum liner strengths are obtained when 5% cement and approximately 3% lime are used for the liner mixture. This combination of additives also satisfies the permeability requirement for the liner material. Therefore, a liner formula is indicated for the NIPS fly ash - scrubber sludge mix which calls for 92% ash mix, 3% lime and 5% cement on a dry weight basis with 19% water added on a percent of dry weight basis.

4.5.6 Central Illinois Public Service Liner Formulation Results

The contour plots for the Central Illinois Public Service ash are shown in Figures 40, 41 and 42. The water addition level which produced the lowest permeabilities in the formulation experiments is 20% of dry weight. The plots show that liner strengths exceeded 400 psi when approximately 3 wt.% or more cement is added to the liner mixture.

Figure 34. Plot of Permeability vs. Lime and Cement Addition Levels for the SWEP Liner Material.

Figure 35. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the SWEP Liner Material.

Figure 36. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the SWEP Liner Material.

NIPSC Fly Ash-19% water
Log of Permeability (cm/sec)

Contour plot of LIME * CEMENT

Figure 37. Plot of Permeability vs. Lime and Cement Addition Levels for the NIPS Liner Material.

NIPS Fly Ash
7-Day Strength After Vacuum Saturation (psi)

(No Significant Water Terms)
Contour plot of LIME * CEMENT

Figure 38. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the NIPS Liner Material.

NIPSC Fly Ash - 19% Water
28-Day Unconfined Compression Strength (psi)

(No Significant Water Terms)
Contour plot of LIME * CEMENT

Figure 39. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the NIPS Liner Material.

Central Illinois Fly Ash-20% Water
Log of Permeability (cm/sec)

Figure 40. Plot of Permeability vs. Lime and Cement Addition Levels for the CIPS Liner Material.

Central Illinois Fly Ash
7-Day Vacuum Saturation Strength (PSI)

Figure 41. Plot of 7-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the CIPS Liner Material.

Central Illinois Fly Ash 28-Day
Unconfined Compression Strength (psi)

Figure 42. Plot of 28-Day Unconfined Compression Strength vs. Lime and Cement Addition Levels for the CIPS Liner Material.

The minimum acceptable permeability for the SWEP liner material is 4.0×10^{-8} cm/sec, or expressed as a logarithm, it is -7.4. This effective permeability criteria includes a design safety factor equal to 3 times the standard deviation of the permeability data measured for the CIPS formulation experiments. Figure 40 shows that, within the additive ranges used for the formulation experiments, a combination of lime and cement are required to produce a liner material with an acceptable permeability from the CIPS ash. Based on an evaluation of the surface response plots and the permeability and strength requirements for the liner material, a liner formula is indicated for the CIPS fly ash which calls for 90.5% fly ash, 3.5% lime and 6% cement on a dry weight basis with 20% water added on a percent of dry weight basis.

4.6 Liner Slab Tests

For the final task in the laboratory phase of the liner development study, four square foot by six inch thick liner slabs were made from each of the six ash materials involved in the research program. The percentages of fly ash, lime, cement and water were determined from the contour curves developed in the formulation task. The formulas used to make the slabs are listed in Table 5.

TABLE 5
FLY ASH LINER FORMULAS

<u>Ash Source</u>	<u>Liner Composition</u>			
	<u>Lime (wt.%)</u>	<u>Portland Cement (wt.%)</u>	<u>Fly Ash (wt.%)</u>	<u>Water (% of Dry Wt.)</u>
Northern States Power Co.	4	0	96	38
Basin Electric Power Co.	3	0	97	21
Texas Utilities Generating Co.	3	3	94	18
Southwestern Electric Power Co.	1.5	5	93.5	18
Northern Indiana Public Service Co.	3	5	92	19
Central Illinois Public Service Co.	3.5	6	90.5	20

The liner slabs were mixed using the method specified in ASTM procedure C-593. The wet liner material was compacted into a slab in a plastic mold. The slab was made with two lifts of three inches each. Each lift was compacted with approximately 100 pounds of uniform pressure. The finished slabs were then cured at room temperature (approximately 70°F) for 28 days.

After curing, each fly ash liner slab was placed in a "column type" leaching apparatus to measure its permeability and to determine the amounts of extractable trace metals in the liners. These tests have not been completed, but the preliminary results indicate that the permeabilities of the liner slabs are significantly lower than 1×10^{-7} cm/sec.

4.7 Fly Ash Liner Costs

The principal factors which determine the cost of constructing fly ash liners are (1) the amounts of lime and portland cement need to make the liner, (2) the method used to mix the liner, (3) the method used to place and compact the liner, and (4) the amount of fly ash used for the liner (and therefore not requiring conventional disposal).

An analysis was done to determine the costs of the additives required for making fly ash liners. The current prices of hydrated lime and portland cement, delivered to the construction site, were obtained for the six utility sites involved in the fly ash liner study. Based on these prices, the additive costs per cubic foot of fly ash liner material were calculated. The results of the cost analysis are summarized in Table 6. The lime and cement costs per cubic foot of liner material ranged from \$0.12/ft³ to \$0.33/ft³ for the six different types of fly ash.

Mixing the liner material can be done in either a batch mode or a mix-in-place mode. A batch mixing operation typically uses a pug mill or similar mixing equipment. The fly ash, lime, cement and water are placed in the pug mill and vigorously mixed. When mixing is complete, the contents of the pug mill are discharged into a truck for transport to the liner construction site. For a mix-in-place operation, the fly ash, lime and cement are placed on the ground at the disposal site and spread out over the area to be lined. The dry materials are mixed with a mixer-pulverizer, which is similar to a soil tiller. The water is then sprayed onto the dry materials and mixed in with another pass of the mixer-pulverizer.

Each of the mixing modes has certain advantages. Batch mixing, for example, usually permits more accurate control of the amounts of lime, cement and water added to the mix. Batch mixing also provides more thorough mixing action than mix-in-place methods. Mix-in-place methods, on the other hand, are usually less expensive than batch mixing methods. The cost of batch mixing the liner material is estimated to be approximately \$0.30/ft³, and the cost of mixing the liner material in place is estimated to be approximately \$0.15/ft³ (15).

TABLE 6. SUMMARY OF FLY ASH LINER COST ANALYSIS

Ash Source	Liner Formula	Portland Cement Price (\$/ton)	Hydrated Lime Price (\$/ton)	Dry Density of Fly Ash Liner (lbs/ft ³)	Cost of Liner Additives (\$/ft ³)
Basin Electric (North Dakota Lignite)	3% Lime	78	87	97	0.13
Northern States Power (Subbituminous Coal- Dry Scrubber Powder)	4% Lime	61	71	84	0.12
Texas Utilities (Texas Lignite)	3% Lime 3% Cement	55	75	110	0.215
Southwestern Public Service (Texas Lignite)	1.5% Lime 5% Cement	55	75	97	0.19
Northern Indiana Public Service (Illinois # 6 Coal - Scrubber Sludge Mix)	3% Lime 5% Cement	60	70	84	0.215
Central Illinois Public Service (Illinois # 6 Coal Ash taken from a holding pond)	3.5% Lime 6% Cement	60	65	112	0.33

The cost for placing and compacting the fly ash liner material may range from \$0.03 to \$0.06/ft³ (15). Previous experience with the use of fly ash for road construction indicates that the best types of compaction equipment to use for liner construction are pneumatic tired rollers or vibratory steel drum rollers (16).

The normal disposal expenses which are avoided for the fly ash used in the liner can be subtracted from the other construction costs. Fly ash disposal costs are highly site specific but a conservative average cost is approximately \$5/ton (17). Assuming a dry density of 100 lbs/ft³ for the fly ash liner, the cost credit for fly ash utilization is about \$0.25/ft³.

Summing the liner construction costs and ash utilization credit listed above provides a rough cost estimate for liner construction. These costs range from a low figure of \$0.05/ft³, based on the lowest possible costs minus the fly ash utilization credit, to a high figure of \$0.44/ft³, based on the highest possible costs minus the fly ash utilization credit.

4.8 Liner Development Conclusions

The results of the liner development study show that materials with permeabilities significantly less than 1×10^{-7} cm/sec can be produced from a wide variety of fly ashes with the addition of relatively small amounts of lime and/or cement. For each of the six ash materials studied, a specific water addition level was determined which produced a minimum permeability.

It was also possible, with five of the six ashes, to produce liner materials with unconfined compression strengths (with and without vacuum saturation treatment) exceeding 400 psi using relatively small lime and/or cement additions. The one liner material which displayed marginal strength characteristics in the formulation experiments was the Northern Indiana Public Service fly ash-scrubber sludge mixture. From an examination of Figures 38 and 39, it appears that it may be possible to increase the strength of the NIPS liner material by increasing the amount of cement added to the mixture. Higher additive levels were not initially used for the formulation tests because the original ranges were based on the permeability results from the scoping tests.

The principal factors which determine the cost of constructing fly ash liners are (1) the amounts of lime and portland cement needed to make the liner, (2) the method used to mix the liner, (3) the methods used to place and compact the liner and (4) the amount of fly ash used for the liner (and therefore not requiring conventional disposal).

The various costs associated with fly ash liner construction were analyzed for the six ash materials involved in this study. The analysis indicated that fly ash liner construction costs would range from a low figure of \$0.05/ft³, based on the lowest possible costs minus the utilization credit, to a high figure of \$0.44/ft³, based on the highest possible costs minus the utilization credit.

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APPENDIX A: EPA-EP LEACHING TEST RESULTS

Waste Material

<u>Element *</u>	<u>Sarpy Creek Bed Material</u>	<u>Sarpy Creek Primary Cyclone</u>	<u>Sarpy Creek Secondary Cyclone</u>	<u>Sarpy Creek Baghouse Fly Ash</u>
Arsenic	<0.01	<0.01	<0.01	<0.01
Barium	1.0	1.8	0.4	0.75
Cadmium	<0.04	<0.04	<0.04	<0.04
Chromium	<0.05	<0.05	<0.05	<0.05
Lead	<0.002	<0.002	<0.002	<0.002
Mercury	<0.0003	<0.0003	<0.003	<0.0003
Selenium	0.16	<0.003	0.018	0.16
Silver	<0.1	<0.1	<0.1	<0.1

Waste Material

<u>Element *</u>	<u>Sarpy Creek Composite Ash (Limestone Addition)</u>	<u>Sarpy Creek Composite Ash (Ash Reinjection)</u>	<u>Navajo Composite Ash (Limestone Addition)</u>	<u>Navajo Composite Ash (Ash Reinjection)</u>
Arsenic	<0.01	<0.01	<0.01	*0.01
Barium	5.6	0.21	0.16	1.8
Cadmium	<0.04	<0.04	<0.04	<0.04
Chromium	<0.05	<0.05	<0.05	<0.05
Lead	<0.002	<0.002	<0.002	<0.002
Mercury	<0.0003	<0.0003	<0.0003	<0.0003
Selenium	0.003	0.014	0.037	0.009
Silver	<0.1	<0.1	<0.1	*0.1

Waste Material

<u>Element *</u>	<u>Gibbons Creek Composite Ash (Ash Reinjection)</u>	<u>Gibbons Creek Composite Ash (Limestone Addition)</u>
Arsenic	<0.01	<0.01
Barium	0.18	0.06
Cadmium	<0.04	<0.04
Chromium	0.05	<0.05
Lead	<0.002	<0.002
Mercury	<0.0003	<0.0003
Selenium	<0.01	<0.01
Silver	<0.1	<0.1

Waste Material

<u>Element*</u>	<u>Illinois #6 (Baseline)</u>	<u>Illinois #6 (Lime-Injected)</u>
Arsenic	0.072	<0.01
Barium	0.17	0.46
Cadmium	0.04	<0.04
Chromium	1.0	0.23
Lead	0.003	<0.002
Mercury	<0.0003	<0.0003
Selenium	0.012	0.022
Silver	<0.1	<0.1

Monticello, Texas Lignite Baghouse Ashes

Waste Material

<u>Element*</u>	<u>Monticello Baseline Ash</u>	<u>Monticello NH₃-SO₃ Treated Ash</u>
Arsenic	<0.01	<0.01
Barium	0.88	0.52
Cadmium	<0.04	<0.04
Chromium	1.2	1.2
Lead	<0.6	<0.6
Mercury	<0.0003	<0.0003
Selenium	0.097	0.065
Silver	<0.1	<0.1

*All elemental concentrations measured for the EP leachates have units of mg/l.

APPENDIX B: ASTM-D-3987 LEACHING TEST RESULTS

Waste Material

Element *	Sarpy Creek Bed Material (Limestone Addition)	Sarpy Creek Primary Cyclone Ash (Limestone Addition)	Sarpy Creek Secondary Cyclone Ash (Limestone Addition)	Sarpy Creek Baghouse Fly Ash (Limestone Add)
Al	<0.3	<0.3	<0.3	<0.3
As	<0.01	<0.01	<0.01	<0.01
Ba	0.41	0.86	0.22	0.25
B	<0.01	0.37	1.6	0.85
Cd	<0.02	<0.02	<0.02	<0.02
Ca	630	1100	110	310
Cr	<0.05	<0.05	<0.05	<0.05
Fe	<0.02	<0.02	<0.02	<0.04
Mg	<0.1	<0.1	<0.01	<0.1
Mn	<0.05	<0.05	<0.05	<0.05
Mo	<0.4	<0.4	3.5	4.3
K	14	27	150	370
Se	<0.003	0.003	0.006	0.48
Si	0.5	0.3	5.4	29
Na	87	120	1600	3300
Sr	10	41	41	57
pH	12.3	12.5	11.5	11.5

Waste Material

Element *	Sarpy Creek Composite Ash ** (Limestone Addition)	Sarpy Creek Composite Ash ** (Ash Reinjection)	Navajo Composite Ash ** (Limestone Addition)	Navajo Composite Ash ** (Ash Reinjection)
Al	<0.3	<0.3	<0.3	2.2
As	<0.1	<0.1	<0.1	<0.1
Ba	0.43	0.3	1.4	0.09
B	0.47	1.1	<0.1	3.5
Cd	<0.02	<0.02	<0.02	<0.02
Ca	870	440	1100	310
Cr	<0.05	<0.05	<0.05	<0.05
Fe	<0.02	<0.02	<0.02	<0.02
Mg	<0.1	<0.1	<0.01	3.5
Mn	<0.05	<0.05	<0.05	<0.05
Mo	<0.4	0.3	<0.04	0.4
K	60	55	13	5.4
Se	0.015	0.07	0.012	0.18
Si	0.5	3.2	0.6	2.5
Na	430	770	49	50
Sr	78	36	7.2	2.5
pH	12.5	12.2	12.5	10.6

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APPENDICES

Waste Material

Element *	Gibbons Creek** Composite Ash (Ash Reinjection)	Gibbons Creek** Composite Ash (Limestone Addn.)	Illinois #6 (Baseline)	Illinois #6 (Lime- Injected)
Al	<0.3	<0.3	0.6	0.3
As	<0.01	<0.01	0.011	<0.01
Ba	0.02	<0.02	0.75	0.37
B	3.4	0.15	140	51
Cd	<0.04	<0.04	<0.04	<0.04
Ca	540	390	1200	1600
Cr	<0.05	<0.05	0.31	0.14
Fe	<0.03	<0.03	0.14	0.13
Mg	14	<2	<2	<2
Mn	<0.02	<0.02	<0.02	<0.02
Mo	<0.2	<0.2	7.4	0.6
K	4.5	5.2	93	32
Se	0.43	0.05	0.053	0.07
Si	11	<0.5	17	2.8
Na	39	18	280	100
Sr	0.86	6.9	4.2	3.5
pH	10.1	12.6	12.4	12.6

Waste Material

Element *	Monticello Baseline Ash	Monticello NH ₃ -SO ₃ Treated Ash
Al	1.7	1.3
As	<0.02	<0.01
Ba	1.3	1.2
B	10	5.2
Cd	<0.04	<0.04
Ca	420	460
Cr	1.5	1.7
Fe	<0.03	<0.03
Mg	<2	<2
Mn	<0.05	<0.05
K	>2	3
Se	1.76	0.385
Si	4.0	5.1
Na	9.5	18
Sr	13	13
pH	12.2	12.0

* All elemental concentrations for the ASTM D-3987 leachates have units of mg/l except pH.

** Composite ashes were formed by mixing 90 wt.% primary cyclone ash, 8 wt.% secondary cyclone ash and 2 wt.% fly ash.

APPENDIX C: ELEMENTAL WASTE COMPOSITIONS

Waste Material

Element *	Sarpy Creek Bed Material	Sarpy Creek Primary Cyclone	Sarpy Creek Secondary Cyclone	Sarpy Creek Baghouse Fly Ash
Si	34.3%	28.1%	16.6%	10.0%
Al	2.0%	3.7%	10.3%	8.4%
Fe	0.3%	1.3%	1.8%	2.3%
Ca	6.3%	14.6%	16.5%	23.8%
Mg	0.3%	0.5%	2.0%	2.8%
Na	<0.1%	<0.1%	1.6%	1.9%
K	<0.1%	<0.1%	0.3%	0.2%
S	1.9%	1.4%	3.4%	6.6%
P	0.1%	<0.05%	<0.5%	0.2%
Ti	0.1%	0.2%	0.7%	0.8%
Cl	21	105	21	<20
Cr	<20	32	163	67
Mn	83	182	251	287
Ni	<10	<10	<10	<10
Cu	12	22	36	30
Zn	<10	>10	<10	<10
As	<20	<20	74	46
Ba	195	485	795	666
Sr	426	1060	3800	3710

Waste Stream

Element *	Sarpy Creek Composite Ash (Limestone Addition)	Sarpy Creek Composite Ash (Ash Reinjection)	Navajo Composite Ash (Limestone Addition)	Navajo Composite Ash (Ash Reinjection)
Si	19.7%	22.4%	23.1%	29.5%
Al	5.2%	6.8%	10.2%	10.1%
Fe	1.4%	2.4%	2.2%	1.7%
Ca	16.1%	10.1%	11.1%	3.0%
Mg	0.8%	1.1%	0.7%	0.7%
Na	0.5%	1.8%	1.1%	0.4%
K	0.1%	0.3%	0.6%	0.5%
S	2.1%	2.3%	1.2%	0.8%
P	0.05%	<0.05%	<0.05%	<0.05%
Ti	0.3%	0.4%	0.5%	0.4%
Cl	<20	68	58	<20
Cr	34	47	29	30
Mn	98	140	216	98
Ni	<10	<10	<10	<10
Cu	14	28	39	29
Zn	<10	<10	44	20
As	<20	<20	<20	<20
Ba	508	771	401	409
Sr	1140	1540	383	336

Waste Material

Element *	Gibbons Creek Composite (Ash Reinjection)	Gibbons Creek Composite (Limestone Addn.)	Illinois #6 (Baseline)	Illinois #6 (Lime- Injected)
Si	29.4%	18.3%	23.1%	10.6%
Al	9.3%	5.9%	11.6%	5.2%
Fe	2.6%	2.3%	9.2%	5.8%
Ca	6.1%	22.0%	5.1%	26.1%
Mg	0.8%	0.5%	0.8%	0.5%
Na	0.5%	<0.1%	0.7%	<0.1%
K	0.6%	0.3%	2.0%	0.7%
S	0.8%	2.5%	1.2%	7.9%
P	<0.1%	<0.1%	0.02%	0.3%
Ti	0.8%	0.6%	0.7%	0.3%
Cl	47	<20	40	120
Cr	41	25	240	110
Mn	810	530	510	300
Ni	<10	<10	48	34
Cu	45	16	74	23
Zn	80	28	860	390
As	41	<20	45	<20
Ba	290	270	330	240
Sr	460	320	240	150

Waste Material

Element *	Monticello Baseline Ash	Monticello NH ₃ -SO ₃ Treated Ash
Si	24.0%	25.3%
Al	8.5%	8.6%
Fe	3.0%	2.7%
Ca	11.4%	11.4%
Mg	1.5%	1.4%
Na	<0.1%	<0.1%
K	0.4%	0.4%
S	0.5%	0.5%
P	<0.1%	<0.1%
Ti	1.1%	1.1%
Cl	>20	<20
Cr	89	89
Ni	270	270
Cu	56	56
Zn	<10	<10
As	30	<20
Ba	690	680
Sr	1700	1700

* Elemental compositions for the waste streams are in units of either % of dry weight or ug/gram waste.

APPENDIX D: WASTE MINERAL COMPOSITION

Sarpy Creek Bed Material:

Major phase - Quartz (SiO_2)

Trace phase - Anhydrite (CaSO_4)

Sarpy Creek Primary Cyclone Ash:

Major phases - Quartz (SiO_2)
Lime (CaO)

Trace phases - Anhydrite (CaSO_4)
Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)
Calcite (CaCO_3)

Sarpy Creek Secondary Cyclone Ash:

Major phase - Quartz (SiO_2)

Minor phases - Anhydrite (CaSO_4)
Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)

Trace phases - Hematite (Fe_2O_3)
Ferrite Spinels (Fe_3O_4)

Sarpy Creek Baghouse Fly Ash:

Major phases - Quartz (SiO_2)
Anhydrite (CaSO_4)

Minor phases - Lime (CaO)
Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)

Trace phases - Calcite (CaCO_3)
Hematite (Fe_2O_3)

Sarpy Creek Composite Ash: (Limestone Injection)

Major phase - Quartz (SiO_2)

Minor phase - Lime (CaO)

Trace phases - Anhydrite (CaSO_4)
Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)
Calcite (CaCO_3)

Sarpy Creek
Composite Ash:
(Ash Reinjection)

Major phase - Quartz (SiO_2)

Minor phase - Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)

Trace phases - Anhydrite (CaSO_4)
Lime (CaO)
Calcite (CaCO_3)
Ferrite Spinel (Fe $_3\text{O}_4$)
Hematite (Fe_2O_3)

Navajo
Composite Ash:
(Limestone Addition)

Major phase - Quartz (SiO_2)

Minor phase - Lime (CaO)

Trace phases - Anhydrite (CaSO_4)
Calcite (CaCO_3)
Melilites ($\text{Ca}_2\text{Al}_2\text{SiO}_7/\text{Ca}_2\text{MgSi}_2\text{O}_7$)

Navajo
Composite Ash:
(Ash Reinjection)

Major phase - Quartz (SiO_2)

Trace phase - Anhydrite (CaSO_4)

Gibbons Creek
Composite Ash:
(Ash Reinjection)

Major phase - Quartz

Trace phases - CaSO_4 ; Hematite, Ferrite Spinel

Gibbons Creek
Composite Ash:
(Limestone Addition)

Major phases - Quartz, Lime, CaSO_4

Trace phases - CaCO_3 , Hematite, Ferrite Spinel

Illinois #6
(Baseline):

Major phase - Quartz

Minor phases - Mullite, Ferrite Spinel; CaCO_3

Trace phase - Hematite

Illinois #6
(Lime-Injected):

Major phases - Lime; CaSO_4

Minor phase - Quartz

Monticello
Baseline Ash:

Major phases - Amorphous Phases; Quartz

Monticello
 $\text{NH}_3\text{-SO}_3$ Treated Ash:

Major phases - Amorphous Phases; Quartz

APPENDIX E: WASTE PHYSICAL PROPERTIES

	Waste Stream			
	<u>Sarpy Creek Bed Material</u>	<u>Sarpy Creek Primary Cyclone Ash</u>	<u>Sarpy Creek Secondary Cyclone Ash</u>	<u>Sarpy Creek Baghouse Fly Ash</u>
Permeability (cm/sec)	8.2×10^{-3}	4.0×10^{-4}	3.8×10^{-5}	3.8×10^{-3}
Bulk Density (g/ml)	2.4	2.4	2.2	1.5
Surface Area (m ² /g)	0.2	3.8	5.5	5.0
Loss on Ignition (wt.%)	0.77	2.7	2.8	4.8

	Waste Material			
	<u>Sarpy Creek Composite Ash (Limestone Addition)</u>	<u>Sarpy Creek Composite Ash (Ash Reinjection)</u>	<u>Navajo Composite Ash (Limestone Addition)</u>	<u>Navajo Composite Ash (Ash Reinjection)</u>
Permeability (cm/sec)	1.9×10^{-5}	1.2×10^{-3}	1.6×10^{-5}	1.5×10^{-4}
Bulk Density (g/ml)	2.0	2.5	2.6	2.2
Surface Area (m ² /g)	4.4	1.8	6.2	8.0
Loss on Ignition (wt.%)	2.1	0.63	1.1	2.4

Waste Stream

	<u>Gibbons Creek Composite Ash (Ash Reinjection)</u>	<u>Gibbons Creek Composite Ash (Limestone Addn.)</u>	<u>Illinois #6 (Baseline)</u>	<u>Illinois #6 (Lime- Injected)</u>
Permeability (cm/sec)	2.7×10^{-5}	1×10^{-4}	6×10^{-5}	1.9×10^{-4}
Bulk Density (g/ml)	3.0	0.9	1.87	1.85
Specific Surface Area (m ² /g)	16.6	16.0	3.09	4.11
Loss on Ignition (wt.%)	0.62	3.10	2.28	2.98

Waste Stream

	<u>Monticello Baseline Ash</u>	<u>Monticello NH₃-SO₃ Treated Ash</u>
Permeability (cm/sec)	5.6×10^{-3}	4.4×10^{-3}
Bulk Density (g/ml)	2.11	3.10
Specific Surface Area (m ² /g)	0.70	0.67
Loss on Ignition (wt.%)	<0.01%	0.07%

APPENDIX F: DATA SUMMARY - NSP FLY ASH LINER DEVELOPMENT

NSP Fly Ash Composition

<u>Element</u>	<u>Weight %</u>
Sodium	0.23
Magnesium	1.4
Aluminum	7.3
Silicon	12.5
Phosphorus	0.4
Sulfur	7.8
Calcium	18.1
Potassium	0.4
Titanium	0.6
Iron	2.4

Physical Analyses of NSP Fly Ash

Fly Ash Unburned Carbon Content (Loss on Ignition)	5.85 wt.%
Specific Surface Area	4.74 m ² /gm
Fly Ash Water Soluble Fraction	0.8 wt.%

EP Leachate Analyses for NSP Fly Ash

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	<0.01
Barium	<0.02
Cadmium	<0.04
Chromium	0.06
Lead	<0.002
Mercury	<0.003
Selenium	<0.004
Silver	<0.001

Final pH of EP leachate - 6.2

DATA SUMMARY - BASIN FLY ASH LINER DEVELOPMENT

Basin Fly Ash Composition

<u>Element</u>	<u>Weight %</u>
Sodium	4.4
Magnesium	2.6
Aluminum	5.6
Silicon	15.4
Phosphorus	0.2
Sulfur	5.4
Calcium	14.3
Potassium	0.8
Titanium	0.7
Iron	3.7

Physical Analyses of Basin Fly Ash

Fly Ash Unburned Carbon Content (Loss on Ignition)	1.48 wt.%
Specific Surface Area	1.38 m ² /gm
Fly Ash Water Soluble Fraction	3.2 wt.%

EP Leachate Analyses for Basin Fly Ash

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	0.05
Barium	0.5
Cadmium	<0.04
Chromium	<0.05
Lead	<0.002
Mercury	<0.003
Selenium	0.05
Silver	<0.001

Final pH of EP leachate - 7.9

DATA SUMMARY - TEXAS UTILITIES LINER DEVELOPMENT

Texas Utilities Fly Ash Composition

<u>Element</u>	<u>Weight %</u>
Sodium	0.0
Magnesium	1.9
Aluminum	9.6
Silicon	22.2
Phosphorus	0.0
Sulfur	0.9
Calcium	12.3
Potassium	0.7
Titanium	0.9
Iron	4.3

Physical Analyses of Texas Utilities Fly Ash

Fly Ash Unburned Carbon Content (Loss on Ignition)	0.33 wt.%
Specific Surface Area	1.01 m ² /gm
Fly Ash Water Soluble Fraction	0.6 wt.%

EP Leachate Analyses for Texas Utilities Fly Ash

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	0.03
Barium	0.41
Cadmium	<0.04
Chromium	0.44
Lead	<0.002
Mercury	<0.003
Selenium	0.016
Silver	<0.5

Final pH of EP leachate - 5.6

DATA SUMMARY - SWEP FLY ASH LINER DEVELOPMENT

SWEP Fly Ash Composition

<u>Element</u>	<u>Weight %</u>
Sodium	0.0
Magnesium	1.6
Aluminum	8.6
Silicon	21.7
Phosphorus	0.0
Sulfur	0.8
Calcium	9.7
Potassium	0.7
Titanium	0.8
Iron	10.7

Physical Analyses of SWEP Fly Ash

Fly Ash Unburned Carbon Content (Loss on Ignition)	0.12 wt.%
Specific Surface Area	0.49 m ² /gm
Fly Ash Water Soluble Fraction	0.5 wt.%

EP Leachate Analyses for SWEP Fly Ash

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	0.029
Barium	0.48
Cadmium	<0.04
Chromium	0.5
Lead	<0.002
Mercury	<0.003
Selenium	0.015
Silver	<0.5

Final pH of EP leachate - 5.6

DATA SUMMARY - NIPS WASTE LINER DEVELOPMENT

NIPS Waste Composition

<u>Element</u>	<u>Weight %</u>
Sodium	1.23
Magnesium	0.7
Aluminum	5.2
Silicon	10.2
Phosphorus	0.4
Sulfur	10.3
Calcium	16.1
Potassium	0.6
Titanium	0.6
Iron	6.3

Physical Analyses of NIPS Waste

Fly Ash Unburned Carbon Content (Loss on Ignition)	3.89 wt.%
Specific Surface Area	5.42 m ² /gm
Fly Ash Water Soluble Fraction	1.4 wt.%

EP Leachate Analyses for NIPS Waste

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	0.015
Barium	0.2
Cadmium	<0.04
Chromium	0.2
Lead	<0.002
Mercury	<0.003
Selenium	0.1
Silver	<0.5

Final pH of EP leachate - 5.0

DATA SUMMARY - CENTRAL ILLINOIS FLY ASH LINER DEVELOPMENT

CI Fly Ash Composition

<u>Element</u>	<u>Weight %</u>
Sodium	0.0
Magnesium	0.9
Aluminum	8.3
Silicon	14.6
Phosphorus	0.04
Sulfur	0.8
Calcium	3.2
Potassium	1.4
Titanium	0.7
Iron	28.5

Physical Analyses of CI Fly Ash

Fly Ash Unburned Carbon Content (Loss on Ignition)	5.32 wt.%
Specific Surface Area	NA*
Fly Ash Water Soluble Fraction	0.01 wt.%

EP Leachate Analyses for CI Fly Ash

<u>Element</u>	<u>Leachate Concentration (mg/l)</u>
Arsenic	0.18
Barium	0.41
Cadmium	0.19
Chromium	<0.05
Lead	0.22
Mercury	<0.003
Selenium	0.005
Silver	<0.5

Final pH of EP leachate - 5.0

*Reproducible results for the specific surface area of this sample could not be obtained.

APPENDIX G: NSP SCOPING TEST DATA

Test Mixture Composition - 4% lime, 4% portland cement and 92% fly ash

Water Addition Level (% Total Dry Weight)	Permeability (cm/sec)
32	9.0×10^{-6}
35	5.3×10^{-8}
38	1.8×10^{-8}
40	6.4×10^{-8}
44	4.8×10^{-6}

NSP Liner Mixture Test Data

Fly Ash (wt%)	Water (% of dry wt.)	Lime (wt%)	Cement (wt%)	7 Day Strength (psi)	28 Day Strength (psi)	Permeability (cm/sec)
98	35	2	0	688	875	2.8×10^{-7}
98	35	0	2	350	575	5.5×10^{-7}
94	35	4	2	380	575	2.4×10^{-8}
94	35	2	4	563	650	6.9×10^{-8}
100	38	0	0	688	562	2.5×10^{-6}
96	38	4	0	1250	1125	1.0×10^{-8}
96	38	0	4	1000	1413	1.0×10^{-7}
92	38	4	4	3500	3563	2.7×10^{-8}
96	38	2	2	2375	2250	7.6×10^{-8}
96	38	2	2	2313	2313	2.5×10^{-7}
96	38	2	2	1800	1725	1.4×10^{-7}
98	41	2	0	563	750	1.4×10^{-7}
98	41	0	2	1125	1500	4.4×10^{-6}
94	41	4	2	1625	2125	2.8×10^{-7}
94	41	2	4	1875	1313	8.7×10^{-8}

NSP Regression Equations

Permeability:

$$\log P = -6.77 - .69 Z1 - .22 Z2 - .33 Z2^2 + .45 Z1Z2 + .22 Z3 + .26 Z3^2$$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (34.7 + 5.5 Z1 + 5.8 Z2)^2$$

28-Day Unconfined Compression Strength:

$$S28 = (36.2 + 9.4 Z1 + 5.6 Z2)^2$$

where: $Z1 = (\% \text{ Lime} - 2)/2$, $Z2 = (\% \text{ Cement} - 2)/2$, $Z3 = (\% \text{ Water} - 38)/3$

Basin Scoping Test Data

Test Mixture Composition - 3% lime, 3% portland cement and 94% fly ash

Water Addition Level
(% Total Dry Weight)

Permeability
(cm/sec)

18	1.2×10^{-6}
20	9.0×10^{-9}
22	5.0×10^{-9}
24	5.4×10^{-9}
26	1.7×10^{-8}

Basin Liner Mixture Test Data

<u>Fly Ash</u> <u>(wt%)</u>	<u>Water</u> <u>(% of</u> <u>dry wt.)</u>	<u>Lime</u> <u>(wt%)</u>	<u>Cement</u> <u>(wt%)</u>	<u>7 Day</u> <u>Strength</u> <u>(psi)</u>	<u>28 Day</u> <u>Strength</u> <u>(psi)</u>	<u>Permeability</u> <u>(cm/sec)</u>
98.5	19.5	1.5	0	1750	2219	4.3×10^{-8}
98.5	19.5	0	1.5	2151	2751	5.9×10^{-7}
95.5	19.5	3	1.5	2307	2907	2.2×10^{-9}
95.5	19.5	1.5	3	2726	3126	1.1×10^{-8}
100	22.5	0	0	1063	563	2.0×10^{-5}
97	22.5	3	0	1563	2063	6.2×10^{-8}
97	22.5	0	3	2375	2063	1.0×10^{-6}
94	22.5	3	3	2375	3000	5.8×10^{-8}
97	22.5	1.5	1.5	1750	2250	1.3×10^{-6}
97	22.5	1.5	1.5	1938	2438	3.5×10^{-7}
97	22.5	1.5	1.5	2550	2188	1.2×10^{-6}
98.5	25.5	1.5	0	1375	1563	4.8×10^{-7}
98.5	25.5	0	1.5	1375	1688	1.6×10^{-5}
95.5	25.5	3	1.5	2250	3188	1.0×10^{-6}
95.5	25.5	1.5	3	2938	2813	5.2×10^{-6}

Basin Regression Equations

Permeability: $\log P = -6.29 - .97 Z1 + .46 Z2 + 1.1 Z3 + .40 Z2Z3$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (46.8 + 6.0 Z1 + 6.7 Z2 - 3.7 Z2^2 - 3.1 Z1Z2 - 2.4 Z3 + 5.0 Z3^2 + 3.5 Z1Z3)^2$$

28-Day Unconfined Compression Strength:

$$S28 = (44.7 + 2.4 Z1 + 6.6 Z2)^2$$

where: $Z1 = (\% \text{ Lime} - 1.5)/1.5$, $Z2 = (\% \text{ Cement} - 1.5)/1.5$,
 $Z3 = (\% \text{ Water} - 22.5)/3$

Texas Utilities Scoping Test Data

Test Mixture Composition - 4% lime, 4% portland cement and 92% fly ash

<u>Water Addition Level</u> <u>(% Total Dry Weight)</u>	<u>Permeability</u> <u>(cm/sec)</u>
14	1.0×10^{-5}
16	7.6×10^{-8}
18	8.0×10^{-9}
20	1.0×10^{-8}
22	3.0×10^{-6}

Texas Utilities Liner Mixture Test Data

<u>Fly Ash</u> <u>(wt%)</u>	<u>Water</u> <u>(% of</u> <u>dry wt.)</u>	<u>Lime</u> <u>(wt%)</u>	<u>Cement</u> <u>(wt%)</u>	<u>7 Day</u> <u>Strength</u> <u>(psi)</u>	<u>28 Day</u> <u>Strength</u> <u>(psi)</u>	<u>Permeability</u> <u>(cm/sec)</u>
98	16	2	0	313	850	1.6×10^{-7}
98	16	0	2	938	1538	1.2×10^{-6}
94	16	4	2	625	1338	7.8×10^{-8}
94	16	2	4	1625	2788	1.1×10^{-8}
100	18	0	0	313	125	1.7×10^{-6}
96	18	4	0	563	1125	1.9×10^{-7}
96	18	0	4	875	813	5.0×10^{-9}
92	18	4	4	1313	2500	5.0×10^{-6}
96	18	2	2	625	1225	1.3×10^{-7}
96	18	2	2	750	1375	1.3×10^{-7}
96	18	2	2	750	1563	7.8×10^{-8}
98	20	2	0	250	625	2.8×10^{-7}
98	20	0	2	500	625	1.3×10^{-6}
94	20	4	2	563	1188	6.5×10^{-7}
94	20	2	4	938	1563	8.5×10^{-8}

Texas Utilities Regression Equations

Permeability:

$$\log P = -7.04 - .68 Z1 - .35 Z2 + .64 Z1^2 - .51 Z1Z2 + .26 Z3$$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (26.2 + 7.7 Z2 - 2.6 Z3 - 2.0 Z2Z3)^2$$

28-Day Unconfined Compression Strength:

$$S28 = (36.9 + 6.3 Z1 + 9.0 Z2 - 4.6 Z1^2)^2$$

where: $Z1 = (\% \text{ Lime} - 2)/2$, $Z2 = (\% \text{ Cement} - 2)/2$, $Z3 = (\% \text{ Water} - 18)/2$

SWEP Scoping Test Data

Test Mixture Composition - 5% lime, 5% portland cement and 90% fly ash

Water Addition Level (% Total Dry Weight)	Permeability (cm/sec)
16	9.0×10^{-6}
17	5.0×10^{-8}
18	1.7×10^{-8}
19	4.0×10^{-8}
20	9.0×10^{-7}

SWEP Liner Mixture Test Data

Fly Ash (wt%)	Water (% of dry wt.)	Lime (wt%)	Cement (wt%)	7 Day Strength (psi)	28 Day Strength (psi)	Permeability (cm/sec)
97.5	16.75	2.5	0	250	375	7.2×10^{-7}
97.5	16.75	0	2.5	438	812	1.0×10^{-6}
92.5	16.75	5	2.5	438	562	3.1×10^{-7}
92.5	16.75	2.5	5	938	1250	2.7×10^{-9}
100	18	0	0	188	562	2.2×10^{-6}
95	18	5	0	188	438	2.5×10^{-7}
95	18	0	5	750	1038	2.0×10^{-7}
90	18	5	5	1000	1125	4.0×10^{-9}
95	18	2.5	2.5	563	688	2.9×10^{-7}
95	18	2.5	2.5	500	625	1.9×10^{-7}
95	18	2.5	2.5	500	750	1.7×10^{-7}
97.5	19.25	2.5	0	125	125	3.3×10^{-6}
97.5	19.25	0	2.5	250	688	1.7×10^{-6}
92.5	19.25	5	2.5	438	625	1.1×10^{-7}
92.5	19.25	2.5	5	875	875	5.8×10^{-9}

SWEP Regression Equations

Permeability: $\log P = -6.65 - .54 Z1 - 1.0 Z2 + .32 Z1^2 + .48 Z2^2$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (23.0 + 1.5 Z1 + 8.5 Z2 - 1.3 Z1^2 + .8 Z2^2 + 1.8 Z1Z2 - 1.4 Z3 - 1.8 Z3^2)^2$$

28-Day Unconfined Compression Strength:

$$S28 = (27.0 + 6.9 Z2 - 1.9 Z3 - 2.1 Z3^2)^2$$

where: $Z1 = (\% \text{ Lime } - 2.5)/2.5$, $Z2 = (\% \text{ Cement } - 2.5)/2.5$,
 $Z3 = (\% \text{ Water } - 18)/1.25$

NIPS Scoping Test Data

Test Mixture Composition - 5% lime, 5% portland cement and 90% fly ash - scrubber waste mix

Water Addition Level (% Total Dry Weight)	Permeability (cm/sec)
16	2.0×10^{-5}
17.5	6.0×10^{-8}
19	3.5×10^{-8}
20.5	5.0×10^{-8}
22	4.0×10^{-6}

NIPS Liner Mixture Test Data

Fly Ash (wt%)	Water (% of dry wt.)	Lime (wt%)	Cement (wt%)	7 Day Strength (psi)	28 Day Strength (psi)	Permeability (cm/sec)
97.5	17	2.5	0	125	154	4.0×10^{-6}
97.5	17	0	2.5	198	198	1.1×10^{-5}
92.5	17	5	2.5	276	178	2.3×10^{-7}
92.5	17	2.5	5	500	256	2.7×10^{-8}
100	19	0	0	88	62	1.3×10^{-6}
95	19	5	0	187	129	3.5×10^{-8}
95	19	0	5	278	246	4.0×10^{-8}
90	19	5	5	386	278	1.2×10^{-8}
95	19	2.5	2.5	298	189	1.0×10^{-7}
95	19	2.5	2.5	230	234	7.1×10^{-8}
95	19	2.5	2.5	267	129	5.5×10^{-8}
97.5	21	2.5	0	300	231	2.0×10^{-7}
97.5	21	0	2.5	250	285	4.2×10^{-7}
92.5	21	5	2.5	225	218	3.0×10^{-8}
92.5	21	2.5	5	253	296	1.8×10^{-7}

NIPS Regression Equations

Permeability:

$$\log P = -7.15 - .61 Z1 - .52 Z2 - .35 Z3 + .67 Z3^2 + .53 Z2Z3$$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (16.5 + 1.1 Z1 + 2.9 Z2 - 1.4 Z1^2)^2$$

28-Day Unconfined Compression Strength:

$$S28 = (14.6 + 1.0 Z1 + 2.1 Z2 - .93 Z1^2 - 1.1 Z1Z2 + 1.0 Z3 + .87 Z3^2)^2$$

where: $Z1 = (\% \text{ Lime} - 2.5)/2.5$, $Z2 = (\% \text{ Cement} - 2.5)/2.5$, $Z3 = (\% \text{ Water} - 19)/2$

CI Scoping Test Data

Test Mixture Composition - 6% lime, 6% portland cement and 88% fly ash

Water Addition Level (% Total Dry Weight)	Permeability (cm/sec)
17	3.0×10^{-7}
18	5.3×10^{-8}
19	4.0×10^{-8}
20	6.5×10^{-8}
21	8.0×10^{-7}

CI Liner Mixture Test Data

Fly Ash (wt%)	Water (% of dry wt.)	Lime (wt%)	Cement (wt%)	7 Day Strength (psi)	28 Day Strength (psi)	Permeability (cm/sec)
97	17	3	0	363	321	6.3×10^{-7}
97	17	0	3	525	489	5.5×10^{-7}
91	17	6	3	888	904	2.4×10^{-8}
91	17	3	6	1063	1193	6.0×10^{-9}
100	19	0	0	86	102	2.5×10^{-5}
94	19	6	0	742	642	2.0×10^{-7}
94	19	0	6	875	845	2.7×10^{-7}
88	19	6	6	1469	1309	5.0×10^{-9}
94	19	3	3	638	592	7.6×10^{-7}
94	19	3	3	788	829	3.9×10^{-7}
94	19	3	3	675	584	5.8×10^{-7}
97	21	3	0	550	498	5.3×10^{-6}
97	21	0	3	575	520	4.4×10^{-6}
91	21	6	3	613	634	2.8×10^{-6}
91	21	3	6	713	646	8.7×10^{-7}

CI Regression Equations

Permeability:

$$\log P = -6.22 - .67 Z1 - .8 Z2 - .27 Z2^2 + .76 Z3 + .29 Z1Z3 + .31 Z2Z3$$

7-Day Unconfined Compression Strength after Vacuum Saturation:

$$S7 = (25.8 + 4.3 Z1 - 6.0 Z2 - 2.3 Z1Z2)^2$$

28-Day Unconfined Compression Strength:

$$S8 = (25.2 + 4.1 Z1 + 6.2 Z2 - 2.0 Z1Z2)^2$$

where: $Z1 = (\% \text{ Lime} - 2)/2$, $Z2 = (\% \text{ Cement} - 2)/2$, $Z3 = (\% \text{ Water} - 18)/2$

U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

FORM APPROVED
GMS No. 1500 0127

Page ____ of ____

1. Program/Project Identification No.	2. Program/Project Title WASTE MANAGEMENT	3. Reporting Period 4/1/86 through 3/31/87
4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4/1/86
		6. Completion Date 3/31/92

Milestone ID No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Fossil fuel waste disposal literature search	06/30/86	6/30/86	
a.2	Fly ash data base search	06/30/86	6/30/86	
b.1	Fossil fuel user waste disposal survey	07/30/86	7/30/86	
b.2	Prepare a report summarizing the results of the literature and data base searches and user survey	08/30/86	8/30/86	
c.1	Perform laboratory disposal site liner tests	02/28/87	4/30/87	
c.2	Report on liner tests	03/31/87	5/31/87	
d.1	Characterize three pressure hydrated lime injection wastes	12/31/86	12/31/86	
d.2	Characterize three wastes from hot-water-dried coal slurry combustion tests	01/31/87	1/31/87	
d.3	Report on waste characterization studies	03/31/87	3/31/87	

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DIRECT LIQUEFACTION OF LOW-RANK COALS

Annual Technical Report for the Period April 1, 1986-March 31, 1987
including the
Quarterly Technical Progress Report for the Period January through March 1987

by

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DIRECT LIQUEFACTION OF LOW-RANK COALS

ABSTRACT

Research was performed during the year in four major areas: Co-processing of coals and petroleum resids, oil agglomeration, characterization of reactants and products, and aqueous liquefaction.

The UNDERC co-processing research investigated the use of petroleum resids as reactive co-processing solvents. Testing involved Martin Lake and Indian Head lignites, Wyodak subbituminous coal, Lloydminster and Arabian resids, Mayan Crude Oil and Mandan Decant Oil. A screening matrix was performed in the microreactor system which was used to determine a coal/resid pair and solids loading which would be used in further, more detailed testing. The combination of Martin Lake lignite and Arabian resid at a 30% solids loading was chosen for further study. This pair produced the best combination of conversion to THF solubles (49%), good yields of pentane-soluble oil, and low heavy metals content of the coal/resid pairs tested.

Staged co-processing tests were conducted in the hot-charged autoclave system. In this system, heat-up to reaction temperature requires 60 seconds. These studies indicated that when ammonium molybdate was used as a catalyst, improvements in conversion to THF solubles would be noted. However, the product distribution which is obtained through the use of this catalyst is not as desirable as that which is obtained when H_2S is used as a promotor. Therefore, the choice of a co-processing catalyst/promotor appears to depend upon whether maximum conversion or more favorable product distribution is the run objective. Plans have been made to perform an ammonium molybdate test under the same conditions with the addition of H_2S for comparative purposes.

Extensive analyses were performed on both the feeds and the products of the co-processing studies. These involved elemental analyses, thermogravimetric analyses, metals content studies, studies of solubility in pentane, fractionations, NMR analyses and a supercritical fluid chromatography. Two methods of silica gel column fractionation developed at UNDERC, when coupled with high-field NMR chromatography, are very useful for providing insight into the organic structure of petroleum resids and crudes. In addition, supercritical fluid chromatography with flame ionization detection (SFC/FID) may be useful in the analysis of non-volatile resids and co-processing products.

During oil agglomeration studies, it was found that the agglomerating tendencies of Mandan Decant Oil were significantly better than those of any of the other solvents tested when applied to Illinois #6 bituminous and Indian Head lignite. Definite float/sink tendencies were noted during this test, with a large tar ball floating in the solvent and a silty, sink fraction present in the bottom of the container. Further testing with this solvent is warranted to determine optimum agglomerating conditions, as well as the level of ash removal obtained.

In general, it can be said that the aqueous liquefaction runs using Martin Lake lignite/water slurry were physically possible to perform, but in order to obtain optimum performance, an extraction procedure would be necessary. This

is suggested by two things. First, operation of the CPU at temperatures close to or above the critical point of water resulted in downstream plugging due to tar (solvent-refined lignite) agglomeration in the lines. The tar-plugging problem seems to be a result of conversion high enough to produce high levels of tar, but not high enough to produce significant quantities of distillate. High distillate yield would probably require a second stage higher-severity process with catalyst. Secondly, batch studies have shown that the conversions and degree of separation possible using an extraction mode of operation can be high, estimated at 90%. When previous aqueous liquefaction work was performed with a semi-batch autoclave serving as an extractor, the resulting product was a very low-ash (below detection limits), "clean" fuel.

It would appear that the most efficient use of the CPU configuration as it currently exists for aqueous liquefaction would be as the first stage of a two-stage system. The second stage would consist of a catalytic hydrotreating system. In such a case, the CPU would not be expected to produce a high yield of distillate; it would, however, produce a very "clean" feed for second-stage upgrading.

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DIRECT LIQUEFACTION OF LOW-RANK COALS

1.0 INTRODUCTION

Co-processing of low-rank coals (LRCs) with petroleum resids under mild conditions with or without reducing gas present may produce a product that extends petroleum refinery feeds with a partially coal-derived material. These co-processing products may also provide a lower-cost way to introduce coal-derived materials into the commercial market.

Some of the most successful processes described in the literature are catalytic two-stage processes. The petroleum resid, acting as a solvent, aids solubilization of the coal during the first stage, and both the dissolved coal and resid are upgraded during a second-stage catalytic hydrogenation. The use of CO in the first stage increases the yield of solubilized coal when subbituminous coal is processed and would be expected to have a beneficial effect on the solubilization of lignite. Lower-temperature regimes, which are optimal for the use of CO with lignite, will probably be preferred in co-processing. In the second stage, a higher-temperature catalytic hydrogenation results in a maximum yield of distillable products. Although the petroleum resid is not expected to be extensively modified during the first-stage reaction, it would be upgraded by hydrogenation in the higher-severity second stage. The use of CO and H₂S in the first stage may provide a system that makes use of the enhanced reactivity of the lignite and a process-derived, low-cost catalyst. If reduction of oxygen-containing organics in the products is desired, the second stage might require catalytic processes.

2.0 GOALS AND OBJECTIVES

The main objective of the low-rank coal liquefaction project at the University of North Dakota Energy Research Center (UNDERC) is to continue the development of the technical data base necessary for the adaptation of direct liquefaction processes to LRCs, including both lignites and subbituminous coals. Previous UNDERC research work has dealt with catalytic liquefaction, with particular emphasis on the effects of adding H₂S; staged liquefaction; mechanistic/kinetic studies; and determination of the effects of solvent on LRC liquefaction.

During the term of the current Cooperative Agreement, the research will center on co-processing petroleum resids with LRCs to produce liquids for use as petroleum substitutes, either as feedstocks for further refining or as fuel products. Appropriate combinations of geographically-selected resids and LRCs will be screened, and research will be carried out to determine operating characteristics of critical unit processes to provide data on conversion and yield structure, and to determine the properties of the products. The research will lead to information on how best to select suitable coals and resids, as well as provide the initial study of favorable feed interactions, operating conditions, and properties of the products. Achieving specific benefits from co-processing LRCs will be explored. In addition, a study of oil agglomeration as a method of increasing the percent carbon in liquefaction feed by removing ash and moisture will be undertaken.

2.1 Proposed Work for the First Year (4/86-3/87)

2.1.1 Task 1 - Selection of Coal/Resid Combinations and Optimum Processing Conditions

The Goals and Objectives for the first year state that screening tests will be performed in the microreactor system on selected pairs of suitable lignites and resids in order to obtain a data base from which to select the best combination for further study. Selected lignite/resid combinations to be tested include a Gulf Coast lignite, a Great Plains lignite, and Wyodak subbituminous coal as the base case. Further testing will take place in the microreactor system to obtain a working parameter set. The parameters selected for the optimum co-processing of the LRCs and resids will be further tested in batch autoclave reactions. Accurate yield structure data will be obtained from each of these experiments. A limited set of parameter variations, including residence time, pressure of the reducing gas, temperature, and coal/resid ratio will be examined, as well as staged operation and the use of catalyst as required for successful comparison.

The feasibility of preparing a low-ash LRC liquefaction feedstock by using separation/agglomeration techniques will be investigated. These techniques utilize viscous liquids derived from petroleum, bitumen, or coal with LRCs slurried in water. Suitable petroleum streams, those containing unacceptably high metals concentrations, or having other properties making them undesirable for conventional processing, will be chosen for the testing. The process will yield an agglomerated organic coal phase that is separable from the aqueous discharge, which will be high in ash content. If the raw LRCs are found to be too hydrophilic in nature to allow this method of separation, the agglomeration of hot-water-dried coal, which should be less hydrophilic, will be tested.

2.1.2 Task 2 - Characterization of Reactants and Products

Thorough analytical characterizations of the coals, resids, and products of co-processing will be carried out for the selected sets of coals and resids tested in autoclave reactions. Some of the notable successes or failures occurring during the microreactor testing are also to be analyzed to determine, if possible, the reaction chemistry. Special attention will be paid to products arising from petroleum as opposed to those originating from the LRCs, as well as to any mechanistic data which might come from studying these results. Conditions that might favor co-processing of LRCs will be explored. These conditions could include the use of dried or hot-water-dried coal as a feed, devolatilization of the coal, use of CO as the reductant, two-stage processing, and the use of catalysts, including both homogeneous as well as commercial supported heterogeneous catalysts. On-line sampling may be used to test the composition of "intermediates" as a function of time to assist in the determination of better operating conditions.

2.2 Change of Scope

The emphasis of the co-processing research program was shifted from a mechanistic, highly analytical approach to a more engineering-oriented approach. This change in approach had the greatest impact on the Task 2 objectives.

Previously, the program had made use of detailed analytical procedures to obtain an understanding of reaction mechanisms and kinetics as well as to determine reactivities of both the products and the coals and resids tested. Whereas the mechanistic approach dealt with conditions not necessarily optimal for conversion, the engineering-oriented approach will emphasize obtaining the highest conversions possible under a co-processing mode of operation. The addition of catalysts may be necessary to achieve the desired conversions. Analyses will be performed as required to assess the results of the co-processing studies; this may occasionally require the use of a detailed analysis.

UNDERC also assessed the feasibility of replacing costly process or petroleum-derived hydrocarbon solvents with water. In order to assess "aqueous liquefaction", the objective was to test liquefaction at conditions near the critical point of water using a low-rank coal/water slurry. Several reaction conditions, including the use of CO with and without the added promotor H₂S, were to be tested.

3.0 ACCOMPLISHMENTS

3.1 Results of Task 1

3.1.1 Co-processing Studies

3.1.1.1 Materials and Equipment

Three LRCs were studied during co-processing tests at UNDERC: Martin Lake, a Texas lignite; Indian Head, a North Dakota lignite; and Wyodak, a subbituminous coal.

UNDERC co-processing research investigated the use of petroleum resids as reactive co-processing solvents. Two petroleum resids were obtained from UOP Inc. and Lummus Crest Inc. and were designated Lloydminster¹ and Arabian², respectively. A raw crude, designated Mayan³, was also obtained for use in the testing, as were two samples from the Mandan, ND, Amoco refinery, Mandan Reduced Crude and Mandan Decant Oil. Pittsburgh Energy Technology Center (PETC) samples Maya ATB, North Slope, and Boscan Dialyzate were analyzed as well.

Detailed analyses were performed on the coals and resids as a part of Task 2, and the results are therefore reported in Section 3.2.

¹ Vac. UOP No. 71 4049I.

² Lummus Crest Inc., NA1993 Jug No. 5 2670, Run 213 Arab Heavy 650 0+ 41186.

³ HRI 5134 Crude Oil.

When selecting LRCs and resids for the co-processing screening test matrix, the following three criteria were used:

1. Available Data Base -- The feedstocks chosen should have a broad data base extending past the immediate project. This will provide a tie element, permitting integration of data generated during other research either at UNDERC or at other facilities.
2. Reactive Selectivity -- The coals and resids chosen for testing must cover the full range of variables (metals content, yield of oils, etc.).
3. Economic Selectivity -- The resid should be processed in the same geographical area as the coal is "mined" in order to be the most economical in terms of larger-scale utilization.

To rapidly and accurately screen the various LRC/solvent pairs, the testing was carried out in the UNDERC microreactor apparatus. This apparatus consists of a bundle of twelve microreactors, each equipped with a shaker bar to assure continuous mixing of the reactants. Figure 1 is a schematic drawing of a microreactor. The entire microreactor cluster is lowered into a heated, fluidized-sand bath and agitated to assure a constant reaction temperature. Figure 2 illustrates the microreactor cluster. The microreactor system provides a way to rapidly screen reaction conditions, coals and solvents to aid in planning future batch autoclave and CPU co-processing tests. This method of testing twelve points simultaneously ensures generation of reliable, reproducible data. Analytical reproducibilities of 1.5% and 0.25% for distillate yields and THF insolubles, respectively, are possible for samples generated during this type of testing.

The testing took place at the following reaction conditions:

Charge pressure (cold).....	1000 psig
Charge gas.....	Carbon monoxide
Reaction temperature.....	375°C
Reaction time.....	20 minutes
Reactor volume.....	22 ml each reactor
Slurry charge.....	3.5 g
Shaker bar.....	1.5 ml
Catalyst.....	None
Coal loadings.....	10, 30, and 50 wt%

These conditions were chosen for the following two reasons.

1. An extensive data base exists for coal liquefaction reactions at those conditions, enabling comparisons to be drawn between co-processing and the more traditional liquefaction process.
2. These mild conditions are the least amenable to coal conversion, and as such, small differences in the coals and/or solvents would have a more obvious impact on the conversions.

Figure 1. Detail of an UNDERC microreactor

Figure 2. UNDERC microreactor cluster

3.1.1.2 Results of Co-processing Testing

A testing matrix was performed in which the three coals were reacted with the four resids at three different solids loadings of 10, 30 and 50 wt%. Table 1 presents the data resulting from this matrix. An initial review of the data obtained from the testing indicates that, in general, co-processing was not as successful at converting coal to THF solubles as was liquefaction under the same conditions. Previous research had determined the conversion of Indian Head lignite to THF solubles during liquefaction processing with a coal-derived solvent at the conditions used for the co-processing studies to be 56% (1). The best conversion to THF solubles of Indian Head lignite exhibited during the co-processing studies was approximately 40% using Mayan Crude as a solvent with a solids loading of 10%, as shown in Figure 3, a comparison of conversions obtained during UNDERC co-processing tests. The bar graphs shown in Figures 3, 4, and 5 were constructed from reduced data obtained during runs made at the conditions listed previously. Wyodak subbituminous coal was 39% converted to THF solubles during co-processing with Lloydminster solvent and a 10% solids loading, as is also shown in Figure 3. This compares with a 42% conversion of Wyodak coal under the same conditions during previous liquefaction research (1).

Testing during the April-June 1986 quarter showed that Mandan Decant Oil was chemically similar to coal-derived solvents used during liquefaction, and it was therefore expected to behave in much the same manner during co-processing. (For a more detailed discussion of this topic, see section 3.3.) This was not found to be the case. The best conversions to THF solubles which occurred when Mandan Decant Oil was used as a solvent were 36% for Indian Head lignite and 35% for Wyodak coal, both at a solids loading of 30%. These conversions compare with conversions of 56% and 42%, respectively, which were obtained during liquefaction studies using coal-derived solvents.

Of the three coals tested during co-processing, Martin Lake lignite exhibited the highest conversions to THF solubles. Figure 3 shows that a 57% conversion was obtained by reacting Martin Lake lignite with Mandan Decant Oil at a 10% solids loading. Conversions of 48% and 44% were the result of a 10% loading of Martin Lake lignite reacted with Arabian and Lloydminster resids, respectively. The 30% loading of Martin Lake with Mayan Crude produced a 23% conversion to THF solubles, the best with that solvent. Indian Head lignite and Wyodak subbituminous coal were fairly similar in their reactivity during co-processing. For Indian Head lignite, the highest conversion of 40% occurred with Mayan crude at a 10% solids loading, with other conversions generally in the 20% to 35% range, as shown in Figure 3. Figure 3 also shows that a 10% Wyodak loading with Lloydminster resid produced a 39% conversion, and reaction with other solvents produced conversions ranging from 20% to 35%.

TABLE 1

TUBING BOMB CO-PROCESSING SCREENING RUNS

Run #	Coal	Bomb ID	Solvent	Feed Gas Pressure	Temp, °C	Closure, %	Pentane Insolubles, %	% Conversion Based upon THFI ^a
T362	Indian Head	A	Mayan	1000	354	101.5	22.94	17.1
T362	Indian Head	B	Mayan	1000	354	83.4	24.67	40.1
T362	Indian Head	C	Mayan	1000	354	98.1		100
T362	Indian Head	D	Arabian	1000	354	101.9	19.36	31.6
T362	Indian Head	E	Arabian	1000	354	102.0	19.32	30.6
T362	Indian Head	F	Arabian	1000	354	70.8		100
T362	Indian Head	G	Mandan	1000	354	105.6	10.66	42.3
T362	Indian Head	H	Mandan	1000	354	106.4	13.16	27.2
T362	Indian Head	I	Mandan	1000	354	99.5		100
T362	Indian Head	J	Lloydminster	1000	354	104.4	31.37	31.5
T362	Indian Head	K	Lloydminster	1000	354	66.9	33.43	32.3
T362	Indian Head	L	Lloydminster	1000	354	109.6		100
T363	Martin Lake	A	Mayan	1000	452	70.8	22.22	10.4
T363	Martin Lake	B	Mayan	1000	452	86.0	21.10	32.5
T363	Martin Lake	C	Mayan	1000	452	55.2		100
T363	Martin Lake	D	Arabian	1000	452	105.3	19.88	47.9
T363	Martin Lake	E	Arabian	1000	452	104.8	19.44	49.3
T363	Martin Lake	F	Arabian	1000	452	86.8		100
T363	Martin Lake	G	Mandan	1000	452	92.7	10.97	64.7
T363	Martin Lake	H	Mandan	1000	452	100.8	12.64	48.6
T363	Martin Lake	I	Mandan	1000	452	--		100
T363	Martin Lake	J	Mandan	1000	452	70.8	30.44	39.2
T363	Martin Lake	K	Mandan	1000	452	106.2	32.04	46.7
T363	Martin Lake	L	Mandan	1000	452	110.0		100
T364	Wyodak	A	Mayan	1004	368	94.1	23.18	19.4
T364	Wyodak	B	Mayan	1004	368	88.1	23.52	23.1
T364	Wyodak	C	Mayan	1004	368	84.8		100
T364	Wyodak	D	Arabian	1004	368	106.1	19.23	31.6
T364	Wyodak	E	Arabian	1004	368	101.8	20.76	33.8
T364	Wyodak	F	Arabian	1004	368	84.0		100

^a THFI = THF Insolubles

TABLE 1 -- continued

Run #	Coal	Comb ID	Solvent	Feed Gas Pressure	Temp, °C	Closure, %	Pentane Insolubles, %	% Conversion Based upon THFI ^a
T364	Wyodak	G	Mandan	1004	368	--	15.63	
T364	Wyodak	H	Mandan	1004	368	88.9		100
T364	Wyodak	I	Mandan	1004	368	107.0		100
T364	Wyodak	J	Lloydminster	1004	368	100.0	32.57	40.0
T364	Wyodak	K	Lloydminster	1004	368	91.2	32.83	38.0
T364	Wyodak	L	Lloydminster	1004	368	84.3		100
T365	Indian Head	A	Mandan	1001	374	100.0	31.14	36.6
T365	Indian Head	B	Mandan	1001	374	97.3	28.24	36.7
T365	Indian Head	C	Mandan	1001	374	100.2		100
T365	Indian Head	D	Arabian	1001	374	98.5	32.95	38.1
T365	Indian Head	E	Arabian	1001	374	69.7	32.36	35.7
T365	Indian Head	F	Arabian	1001	374	64.7		100
T365	Indian Head	G	Mayan	1001	374	87.0	36.57	38.0
T365	Indian Head	I	Mayan	1001	374	78.5		100
T365	Indian Head	J	Lloydminster	1001	374	91.8	45.92	30.0
T365	Indian Head	K	Lloydminster	1001	374	94.1	47.07	22.7
T365	Indian Head	L	Lloydminster	1001	374	72.7		100
T366	Martin Lake	A	Mayan	1000	377	112.7	33.53	25.9
T366	Martin Lake	B	Mayan	1000	377	84.7	34.20	19.0
T366	Martin Lake	C	Mayan	1000	377	110.9		100
T366	Martin Lake	D	Arabian	1000	377	109.2	33.16	24.3
T366	Martin Lake	E	Arabian	1000	377	110.7	33.51	26.9
T366	Martin Lake	F	Arabian	1000	377	78.5		100
T366	Martin Lake	G	Mandan	1000	377	87.4	28.01	33.8
T366	Martin Lake	H	Mandan	1000	377	110.9	29.70	31.7
T366	Martin Lake	I	Mandan	1000	377	74.7		100
T366	Martin Lake	J	Lloydminster	1000	377	77.3	46.04	12.0
T366	Martin Lake	K	Lloydminster	1000	377	108.5	41.46	37.4
T366	Martin Lake	L	Lloydminster	1000	377	108.5		

^a THFI = THF Insolubles

TABLE 1 -- continued

Run #	Coal	Bomb ID	Solvent	Feed Gas Pressure	Temp, °C	Closure, %	Pentane Insolubles, %	% Conversion Based upon THFI ^a
T367	Wyodak	A	Mayan	997	371	102.1	34.20	23.7
T367	Wyodak	B	Mayan	997	371	101.5	34.64	30.4
T367	Wyodak	C	Mayan	997	371	102.7		100
T367	Wyodak	D	Arabian	997	371	104.8	34.34	25.2
T367	Wyodak	E	Arabian	997	371	99.8	35.57	28.8
T367	Wyodak	F	Arabian	997	371	68.8		100
T367	Wyodak	G	Mandan	997	371	99.0	30.69	34.5
T367	Wyodak	H	Mandan	997	371	103.9	31.71	34.2
T367	Wyodak	I	Mandan	997	371	101.2		100
T367	Wyodak	J	Lloydminster	997	371	100.2	43.92	36.0
T367	Wyodak	K	Lloydminster	997	371	93.9	42.92	36.3
T367	Wyodak	L	Lloydminster	997	371	90.5		100
T368	Indian Head	A	Mayan	1006	373	103.4	45.23	22.1
T368	Indian Head	B	Mayan	1006	373	74.6	47.47	23.7
T368	Indian Head	C	Mayan	1006	373	105.0		100
T368	Indian Head	D	Arabian	1006	373	100.6	46.82	18.8
T368	Indian Head	E	Arabian	1006	373	108.5	43.98	24.0
T368	Indian Head	F	Arabian	1006	373	97.8		100
T368	Indian Head	G	Mandan	1006	373	89.8	49.63	9.4
T368	Indian Head	H	Mandan	1006	373	104.2	44.71	28.3
T368	Indian Head	I	Mandan	1006	373	73.3		100
T368	Indian Head	J	Lloydminster	1006	373	81.0	59.82	2.1
T368	Indian Head	K	Lloydminster	1006	373	101.6	58.06	0.7
T368	Indian Head	L	Lloydminster	1006	373	102.5		100
T369	Martin Lake	A	Mandan	1013	380	113.6	46.85	17.0
T369	Martin Lake	B	Mandan	1013	380	87.8	49.48	58.5
T369	Martin Lake	C	Mandan	1013	380	109.4		100
T369	Martin Lake	D	Arabian	1013	380	81.2	48.07	44.2
T369	Martin Lake	E	Arabian	1013	380	87.5	55.38	28.7
T369	Martin Lake	F	Arabian	1013	380	92.2		100

^a THFI = THF Insolubles

TABLE 1 -- continued

Run #	Coal	Bomb ID	Solvent	Feed Gas Pressure	Temp, °C	Closure, %	Pentane Insolubles %	% Conversion Based upon THFI ^a
T369	Martin Lake	G	Mayan	1013	380	102.8	48.13	17.0
T369	Martin Lake	H	Mayan	1013	380	57.5	50.80	43.3
T369	Martin Lake	I	Mayan	1013	380	57.7		100
T369	Martin Lake	J	Lloydminster	1013	380	89.4	49.99	59.3
T369	Martin Lake	K	Lloydminster	1013	380	61.0	53.80	73.3
T369	Martin Lake	L	Lloydminster	1013	380	86.9		100
T370	Wyodak	A	Mayan	1000	379	101.5	47.94	21.1
T370	Wyodak	B	Mayan	1000	379	67.3	47.51	12.0
T370	Wyodak	C	Mayan	1000	379	101.3		100
T370	Wyodak	D	Arabian	1000	379	103.5	44.08	26.5
T370	Wyodak	E	Arabian	1000	379	--	47.99	-13.3
T370	Wyodak	F	Arabian	1000	379	108.1		100
T370	Wyodak	G	Mandan	1000	379	84.7	50.82	19.7
T370	Wyodak	H	Mandan	1000	379	96.3	45.96	30.3
T370	Wyodak	I	Mandan	1000	379	66.3		100
T370	Wyodak	J	Lloydminster	1000	379	105.5	57.72	20.3
T370	Wyodak	K	Lloydminster	1000	379	101.3	57.13	18.4
T370	Wyodak	L	Lloydminster	1000	379	96.6		100
T371	None	A	Mandan	1000	384	-- ^c	2.5	2.61 ^b
T371	None	B	Mandan	1000	384	--	3.5	2.79 ^b
T371	None	C		1000	384	--		
T371	None	D	Mayan	1000	384	--	15.3	0.75 ^b
T371	None	E	Mayan	1000	384	--	15.4	0.80 ^b
T371	None	F		1000	384	--		
T371	None	G	Lloydminster	1000	384	--	26.8	0.27 ^b
T371	None	H	Lloydminster	1000	384	--	27.2	0.39 ^b
T371	None	I		1000	384	--		
T371	None	J	Arabian	1000	384	--	14.4	0.45 ^b
T371	None	K	Arabian	1000	384	--	13.35	0.44 ^b
T371	None	L		1000	384	--		

^a THFI = THF Insolubles^b THFI of product; not "conversion" calculated using THFI data.^c -- = not calculated

Figure 3. Comparison of conversion of three coals during co-processing screening tests

Figure 4. Comparison of solids loadings of three coals during co-processing screening tests

Figure 5. Comparison of change in yield of pentane solubles for three coals after co-processing screening tests

Data indicate that, in general, a 10% solids loading produces the best results during co-processing. This can be seen in Figure 4. Conversions are decreased for all coals at a solids loading of 50%. The 50% solids loading seemed to have the greatest detrimental effect on Lloydminster resid. Although the 10% solids loading produced slightly higher conversions to THF solubles, it was decided that further testing should utilize a 30 wt% solids loading. It was felt that such a solids loading would produce more reliable results due to the higher coal loading and the fact that 30% solids probably represent more of a real-world approach to co-processing.

A study of the solvent balance following co-processing indicates that great differences in utilization by coal exist between the solvents. As Figure 5 shows, all three coals produced pentane solubles when reacted with Arabian resid. Reactions with the other solvents yielded mixed results; i.e., some showed a net production of pentane solubles, while in other pairs there was a net consumption.

To assess the success of the co-processing tests, the products were analyzed to determine metals content and solubility in pentane. Yields of pentane solubles are somewhat analogous to yields of desired distillate product. Heavy metals which are present in the petroleum resids can deactivate the co-processing catalysts. It is hoped that, during co-processing, the coal will convert the solvent into pentane solubles, leaving the heavy metals in the char bottoms. Both metals content and pentane solubility information were determined for the product slurries. The percent recovered oil and difference oil were also calculated. Recovered oil is the actual weight percent of pentane solubles remaining after the pentane has been removed by rotovaping. Difference oil is a calculated value, equal to 100% minus pentane insolubles. Comparisons of the two values for the products show the recovered oil value as considerably lower than the difference oil value. This decrease in recovered oil values is due to the presence of coal or solvent products which are removed during removal of the pentane. Table 2 lists the yields of pentane solubles of the feeds and products of selected co-processing tests.

Table 2 also lists the metals contents of the feeds and products of the co-processing tests. In general, it can be seen in the table that Martin Lake lignite and Wyodak subbituminous coal reduced vanadium content better than the Indian Head lignite, and Wyodak subbituminous coal was best at lowering nickel and iron content. Based upon these results, the Wyodak subbituminous coal would appear to be the most effective in lowering the metals content of the resids, although Martin Lake lignite was almost as effective. When reacting with either Mayan Crude or Mandan Decant Oil, the Martin Lake lignite seemed to add iron during the co-processing. The Mandan Decant Oil showed an increase in iron content with all coals. This is probably a real increase rather than an anomaly in the data, since previous liquefaction research at UNDERC has indicated that the amount of metals in THF soluble coal liquid products can be greater than the amount present in the solvent feed (2).

TABLE 2

METALS CONTENTS AND YIELDS OF PENTANE SOLUBLES OF FEEDS
AND PRODUCTS OF SELECTED CO-PROCESSING TESTS

Feeds	Metals Content,			Recovered ^a	Difference ^a
	ppm			Oil	Oil
	V	Ni	Fe	Wt%	Wt%
Resids:					
Mayan Crude	315	63	380	77.5	77.1
Arabian	290	140	167	80.5	82.5
Lloydminster	120	37	56	69.1	67.1
Mandan Decant Oil	0	3	45	98.0	97.9
Coals:					
Indian Head	4	7	5950	NA ^b	NA
Martin Lake	24	0	4300	NA	NA
Wyodak	0	0	2600	NA	NA
Products: ^c					
Mayan Crude/ Indian Head	75	19	119	41.3	67.0
Martin Lake	44	21	220	35.2	63.8
Wyodak	47	ND ^d	94	41.7	64.7
Arabian/ Indian Head	55	ND	54	53.3	70.5
Martin Lake	27	14	38	47.7	64.8
Wyodak	52	ND	36	55.8	68.1
Lloydminster/ Indian Head	86	35	180	43.7	60.5
Martin Lake	64	31	ND	41.0	57.1
Wyodak	62	26	29	46.2	53.3
Mandan Decant Oil/ Indian Head	ND	ND	71	56.2	72.5
Martin Lake	ND	ND	170	41.2	64.5
Wyodak	ND	ND	91	57.4	68.8

^a Recovered oil refers to the wt% of oil in the pentane solubles of the product slurry remaining after rotovaping off the pentane. Difference oil is defined as 100% minus the wt% pentane insolubles for a given product slurry sample.

^b NA = not analyzed

^c Product slurry was analyzed after reaction of a 70:30 ratio of resid to maf coal. Actual weight percent of as-received coal varied with coal moisture and ash contents.

^d ND = none detected

3.1.1.3 Coal/Resid Pair Selection

The three selection criteria discussed in Section 3.1.1.1 applied to the selection of coals and resids to be included in the initial testing matrix. Selection of a single coal/resid pair to be used in further co-processing tests was based upon the results of the pentane solubility tests and metals content analyses, as well as conversion to THF soluble products. The characteristics of the individual coals and solvents combined to either complement or inhibit each other's reactivity. Indian Head lignite appeared to react the best with Mayan crude and was inhibited by Lloydminster resid. Martin Lake underwent greater conversion with Mandan Decant Oil, but reacted poorly with Mayan Crude. Conversions of Wyodak subbituminous coal were best when combined with Lloydminster resid and worst with Mayan Crude. On the basis of these results, coupled with the results of the analytical testing and the fulfillment of the three criteria set forth for the co-processing screening test matrix, a 30 wt% solids slurry of Martin Lake lignite with Arabian resid was selected for further testing.

Although the three matrix-selection criteria were set up to select individual coals and resids for the initial screening, it was hoped that the selected pair would meet the same criteria. The first matrix-selection criterion was partially fulfilled because Martin Lake lignite and Arabian resid have each been used during research conducted at UNDERC, and Arabian resid has been used during studies at the Pittsburgh Energy Technology Center (PETC). A broad data base exists, therefore, for Arabian resid.

The second criterion dealt with the range of variables present. To cover all possible results, it was necessary to include a broad range of values in the testing matrix. However, it is desirable that a coal/resid pair be chosen which is representative of the "average" coal and resid. It is hoped that, by doing so, the results of further testing will apply to a wide range of coals and resids. As will be explained in Section 3.3, Martin Lake lignite and Arabian resid did not contain the extremes of any of the variables, but, rather, were representative of the "average" coal and resid.

The third criterion, economic selectivity, is also fulfilled by the selection of the Martin Lake lignite/Arabian resid pair. Several refineries in Texas process Arabian crude, resulting in the production of Arabian resid. Martin Lake is a Texas lignite.

Martin Lake lignite contains more vanadium than the other coals, but no nickel and an intermediate amount (compared to the other two coals) of iron. Arabian resid contained less metals than the other resids, with the exception of Mandan Decant Oil. Although the combination of Martin Lake lignite and Arabian resid did not produce the largest quantities of pentane solubles during the T366 microreactor test (3), the average quantity of pentane solubles produced in all reactions of Martin Lake lignite with Arabian resid compared favorably with other LRC/resid combinations. The Martin Lake lignite/Arabian resid pair produced the best combination of conversion to THF solubles, good yields of pentane soluble oils and low heavy metals content of LRC/resid pairs tested.

3.1.1.4 Autoclave Studies of Staged Co-processing

Co-processing of the selected coal/resid pair was tested in the staged batch autoclave system pictured in Figure 6. The autoclave system consists of a 1-liter first stage reactor, a 1-gallon second stage reactor, and a 2-gallon quench. Four runs were performed. Two runs were made to duplicate base case (i.e., no promotor or catalyst) conditions, one was made with ammonium molybdate catalyst which had been blended with the slurry, and one was made with H_2S . Run conditions for each of the runs were as follows:

Coal.....	Martin Lake lignite
Resid.....	Arabian
Temperature.....	370°-380°C - 1st stage; 425°-435°C - 2nd stage
Reducing Gas.....	3500-4000 psi CO - 1st stage; 2000-2500 psi H_2 - 2nd stage
Residence Time.....	40 min - 1st stage; 10 min - 2nd stage
Heat-up to Reaction	
Temperature.....	60 seconds
Catalyst.....	H_2S - 5% of maf coal charge; Ammonium Molybdate - 1% of MAF coal charge

Figure 7 shows the conversions attained during the autoclave tests. As the graph shows, the run made with ammonium molybdate catalyst exhibited a conversion to THF solubles of approximately 12% more than that attained through the use of H_2S as a promotor, and approximately 18% greater than the average conversion exhibited during the base case tests.

A catalyst carryover effect was noted for the ammonium molybdate catalyst. The research plan called for two base case runs to be performed: one as the initial test and one as the final test to determine run reproducibility as well as possible catalyst carryover. The results of the second base case run did not reproduce the results of the first run. Better results were obtained for this run, which immediately followed the ammonium molybdate-catalyzed run, than were expected, indicating that some of the catalyst remained on the walls of the reactor after the completion of the test. The run was disregarded when comparing the three cases (no catalyst, ammonium molybdate, and H_2S).

The ammonium molybdate test produced the greatest yields of total liquids in the product, including both distillate and residuum, as shown in Figure 8. Figure 9 shows that the ammonium molybdate test produced the least distillates (i.e., light, middle, and heavy oils), whereas the H_2S run produced the most. A rapid heat-up rate, as would occur in a hot-charged system such as the one utilized for these tests, has a definite effect on the products obtained during an ammonium molybdate-catalyzed test. The oxide, rather than the sulfide, which is the more active species, is formed when the heat-up rate is rapid. However, this is dependent upon the availability of a sulfur donor, such as H_2S . Hydrogen sulfide was not present during the ammonium molybdate test; therefore, the heat-up rate of the reaction is superfluous in this case. Plans have been made to perform another ammonium molybdate test under the same conditions with the addition of H_2S .

Figure 6. Flowsheet of UNDERC staged autoclave co-processing system

Figure 7. Conversion as a function of catalyst during staged co-processing of Martin Lake lignite and Arabian resid

Figure 8. Yield of total liquids as a function of catalyst during staged co-processing of Martin Lake lignite and Arabian resid

Figure 9. Distillation of oils as a function of catalyst after staged co-processing of Martin Lake lignite and Arabian resid

Comparison of these figures shows that, because the yield of distillate is greater than the yield of total liquids, THF-soluble residuum was consumed during the processing. Less residuum was consumed during the ammonium molybdate run than during either the base case or H_2S -promoted runs. (Less distillates minus less residuum equals larger total liquid yield.) This is confirmed by Figure 10, which shows the conversion of the THF-soluble residuum for the three runs. As the figure illustrates, H_2S does a better job of converting soluble residuum into distillate than ammonium molybdate. In summary, ammonium molybdate converts more coal, but this is converted into soluble resid and gas, rather than distillate.

More CO was consumed during the ammonium molybdate run than during either the H_2S or the base case runs, as Figure 11 shows. Figure 12 presents the consumption of H_2 . As the figure shows, ammonium molybdate consumed H_2 , while the H_2S and base case runs actually produced small quantities of H_2 . The figure also shows that there was an increase in the yield of C3 and larger hydrocarbons during the ammonium molybdate run than during the other runs; this probably resulted in the increased consumption of H_2 .

The yields of H_2O obtained during the testing are shown in Figure 13. The ammonium molybdate run produced larger quantities of H_2O than did the H_2S or base case runs. Apparently, part of the additional H_2 consumed during this run went toward the production of water.

Figure 14 shows the changes in hydrogen-to-carbon, nitrogen-to-carbon, and sulfur-to-carbon ratios, relative to the base case, that occurred as a result of the co-processing. The change in the hydrogen-to-carbon ratio was greater for the ammonium molybdate run than it was for the H_2S -promoted run, which is to be expected, given the consumption of H_2 during the ammonium molybdate-catalyzed run. During the ammonium molybdate test, both nitrogen and sulfur were consumed, while there was an increase in these elements during the H_2S run.

The products of the ammonium molybdate run contained approximately 5% less pentane solubles than the feeds, while there were increases in pentane solubles of approximately 1% and 9% during the H_2S and base case runs, respectively. This information is shown in Figure 15.

Taking these results into account, it would appear that when ammonium molybdate is used as a co-processing catalyst, conversions will be increased as compared to co-processing either without additives or with H_2S as a promotor. However, the increased conversion also includes increases in both residuum, at the expense of distillate production, and consumption of H_2 . This is probably the result of the higher yield of C3 and larger hydrocarbons. The use of H_2S produces a more desirable product distribution with an acceptable conversion. The decision to utilize one or the other as a catalyst/promotor would depend upon whether the objective was to obtain the best product distribution or the highest possible conversion.

Figure 10. Conversion of THF-soluble non-distillate as a function of catalyst during staged co-processing of Martin Lake lignite & Arabian resid

Figure 11. Consumption of CO as a function of catalyst during first-stage of co-processing of Martin Lake lignite and Arabian resid

Figure 12. Comparison of consumption of H_2 and C_3+ hydrocarbon production as a function of catalyst during second stage of co-processing of Martin Lake lignite and Arabian resid

Figure 13. Yield of water as a function of catalyst during staged co-processing of Martin Lake lignite and Arabian resid

Figure 14. Changes in H/C, N/C, and S/C ratios as a function of catalyst during staged co-processing of Martin Lake lignite & Arabian resid

Figure 15. Loss of pentane solubles as a function of catalyst during staged co-processing of Martin Lake lignite and Arabian resid

3.1.2 Oil Agglomeration Studies

Coal can be reordered into organic and mineral phases. By using an oil, which preferentially wets organics, and water, which preferentially solvates minerals, the organics and the minerals in the coal can be made to agglomerate into separable phases. By decreasing the ash and water contents, oil agglomeration increases the percent carbon in the coal. In LRCs, hydrophilic groups, such as carboxylic groups in the salt form, exist in quantities which can complicate the oil agglomeration of the organics. The removal of these carboxylic groups would result in more organic material, which in turn would aid oil agglomeration. Therefore, oil agglomeration research at UNDERC includes studies of both as-received lignite and lignite in which the carboxylic groups have been altered in order to determine their effects as well as changes occurring in the groups. Alteration of the carboxylic groups is accomplished by two methods: thermal destruction of the groups, and replacement of the alkali cations with hydrogen cations.

3.1.2.1 Materials and Equipment

Two coal, Illinois #6 bituminous coal and Indian Head, North Dakota, lignite, were tested during the oil agglomeration studies. A small-scale test unit was assembled to rapidly analyze the agglomeration that occurs with various coal/solvent/water mixtures. This apparatus is pictured in Figure 16. Its small size will permit the testing of a wide variety of agglomerating conditions.

Figure 16. Micro stirring apparatus for oil agglomeration studies

3.1.2.2 Results

To evaluate the degree of success of the agglomeration tests, an evaluation system was established. This system was based upon the type of agglomeration, the degree of float/sink, and the presence of a definite mineral or silt fraction. A particular value was assigned to each coal/solvent pair, based upon its performance in each area. The areas and values are as follows:

Type of Agglomeration:

- 1 - fine flakes
- 2 - medium, evenly-sized particles
- 3 - irregular particles, small and large
- 4 - tar balls and loose coal
- 5 - a single tar ball

Degree of Float/Sink:

- A - all particles sink
- B - some particles float, some sink
- C - definite float/sink behavior

Presence of Ash/Silt:

- Y - ash or silt layer present
- N - no ash or silt present

Ideally, agglomeration should result in all of the ash/minerals being removed by the water, leaving the organics with the oil. Due to the nature of stirred oil and water mixtures, the organics would form a single, floating ball. The minerals would sink to the bottom of the container. Therefore, for this evaluation system, the best "score" would be 5CY, indicating the formation of a floating "tar ball" made of organics and the presence of a definite sink fraction appearing to be composed of minerals or silt.

Table 3 presents the results of testing Illinois #6 bituminous coal and Indian Head lignite with a number of solvents. As the table shows, the Mandan Decant Oil exhibited significantly better agglomerating tendencies with both the bituminous coal and the lignite than the other solvents tested. Different coal-to-solvent ratios changed the consistency of the ball from sticky to more of a coal-type of consistency. A definite float/sink separation occurred with the coal ball marginally floating and the silt sinking. Further testing with the Mandan Decant Oil will be performed to determine optimum agglomerating conditions and the level of ash removal. It is significant that this solvent was effective, since the Mandan refinery and the lignite are located within 50 miles of each other. The Mayan Crude Oil also gave positive results with the bituminous coal, but has not been tested with the lignite.

TABLE 3

RESULTS OF EVALUATION OF COAL/SOLVENT AGGLOMERATION

Coal Type	Illinois #6 Bituminous	Indian Head Lignite
Coal/Solvent Ratio	0.5/0.7	0.5/0.7
Water pH	1.0	1.0
<u>Solvent</u>		
p-Xylene	1BY	1BN
1-Octanol	2BN	NT ^a
JP-4	1BY	NT
Mandan Decant Oil	5CY	5CY
Arabian Resid	4AN	4BN
North Slope ATB	4AN	NT
Lummus	4AN	NT
Mayan Crude Oil	5CY	NT

^a Not Tested.

One of the goals of the research was to ascertain the effects of carboxylic groups, as well as changes in them, on oil agglomeration. Two methods of alteration of the groups were performed: 1) thermal destruction of the groups, and 2) replacement of the alkali cations with hydrogen cations. These tests were performed using Big Brown lignite rather than Illinois #6 bituminous coal or Indian head lignite. At the conclusion of these alteration studies, it was discovered that sufficient quantities of Big Brown lignite for the remaining agglomeration tests were no longer available, and the remaining tests were conducted using Illinois #6 and Indian Head coals.

By heating a coal/water slurry at a sufficiently high temperature, water is driven from the coal, and carboxylic groups are destroyed. This method of hot-water drying was performed to prepare a Big Brown lignite sample for further agglomeration study. The residence time was increased from the usual 55 minute maximum to 2 hours in an effort to effect a greater decomposition of the carboxyl groups. However, the resulting agglomeration of the coal sample made it unsuitable for additional testing.

To investigate ion exchange as a method of altering carboxylic groups, samples of raw Big Brown lignite were washed with dilute nitric acid at room temperature with minimal protection from air. The results of the proximate and ultimate analyses were similar (4). However, the solid state C-13 NMR spectra indicated that significant oxidation of the coal occurred (5). The aromaticity decreased (in the 120-140 ppm region) and the aliphatic carbonyl, carboxyl-quinone, and double-bonded carbon regions (180, 160, and 80 ppm, respectively) were enhanced in the acid-washed sample as compared with the raw coal. There was slight increase in maf oxygen content from 22.4 to 23.5 wt%, which may be real and caused by the oxidation which occurred during the acid washing.

3.2 Results of Task 2 - Characterization of Reactants and Products

Chemical analyses provide information about feedstocks that is necessary to assess their co-processing value. In addition, they can be used to determine the success of the process through analysis of the products. The value of a feedstock is primarily determined by tests of quality, especially with regard to heavy metal content. Elemental analyses for C, H, N, O and S content are also important to determine possible utilization problems, the presence of catalyst deactivators, and hydrogen consumption, among other things. Quality, as well as quantity, must be determined for the co-processing products.

Complete characterization of the resid samples utilized newly developed methods as well as adaptations of established analyses. Instrumentation that had been calibrated with standards was used for C, H, N and S determinations. Metals content was determined by digestion and inductively coupled argon plasma spectrophotometry (ICP). To determine the organic structure of the resids, silica gel column fractionations were performed on the samples using two methods developed at UNDERC. NMR analysis of the resulting fractions, as well as of the samples prior to fractionation, resulted in the determination of the amounts of aromatic and aliphatic hydrogen present. Thermogravimetric analysis to determine the amounts of light volatiles and water, volatile matter, fixed carbon and ash present in the liquid petroleum

resids was performed using the technique developed for proximate analysis. To separate the components of the petroleum resids, supercritical fluid chromatographic analysis with flame ionization detection was utilized.

3.2.1 Elemental Analysis

The Lloydminster, Arabian, and Mayan Crude resids, as well as the Martin Lake, Indian Head, and Wyodak coals, were analyzed for C, H, N, and S content. A Leco sulfur analyzer and a Control Equipment Corporation CHN analyzer, both of which had been calibrated with standards, were used for the analytical work. The results are presented in Tables 4 and 5.

3.2.2 Thermogravimetric Analysis (TGA) of Resids

The co-processing resids were analyzed by TGA using a technique that results in a proximate analysis of the sample. The results of this analysis are presented in Table 5 and were used as baseline data for comparative purposes after proximate analyses were completed on the co-processing products.

TABLE 4

RESULTS OF MOISTURE AND ULTIMATE ANALYSES OF
COALS USED DURING CO-PROCESSING TESTS

<u>Analysis</u>	<u>Coal</u>		
	<u>Indian Head</u>	<u>Martin Lake</u>	<u>Wyodak</u>
Moisture	26.19	27.07	25.97
Ash	12.13	10.80	7.86
Carbon ^a	61.92	63.65	67.36
Hydrogen ^a	4.13	4.80	4.44
Nitrogen ^a	0.75	1.15	0.88
Sulfur ^a	0.55	1.18	0.47
Oxygen (Ind)	20.52	18.42	18.99

^aMoisture-free Basis

TABLE 5

RESULTS OF PROXIMATE AND ULTIMATE ANALYSES
OF RESIDS USED DURING CO-PROCESSING TESTS

Analysis <u>Wt%</u>	<u>Resid</u>			Mandan Decant <u>Oil</u>
	<u>Mayan Crude</u>	<u>Lloydminster</u>	<u>Arabian</u>	
<u>Ultimate</u>				
C	80.5	83.5	84.2	88.7
H	11.0	10.2	11.1	9.4
N	0.4	0.6	0.2	0.03
S	3.4	6.0	4.6	2.3
<u>Proximate</u> ^a				
Lt. Volatiles/ Water	12.49	1.46	0.01	0.53
Volatile Matter	79.38	86.18	92.24	97.34
Fixed Carbon	8.15	15.37	7.75	0.94
Ash ^c	0.0	0.00	0.00	1.33
T(°C) ^b	496	540	488	323

^a Obtained by TGA

^b Temperature at which maximum weight loss occurs

^c Ash is defined as material remaining after exposure to air at 950°C, and is not equivalent to a standard ash analysis.

3.2.3 Metals Content

Research into the co-processing of coal and petroleum solvents is performed with the hope that the product will be lower in metals content than the feeds. This would result in less poisoning to refinery catalysts during subsequent upgrading. It is hoped that the metals will collect on unconverted coal and thus be easily removed prior to upgrading in a refinery. One method of removal of the undesirable unconverted coal from the co-processing product employs a propane deasphalting process. Analysis of pentane solubles are used to indicate relative yields to be expected from this type of process. As will be seen, available data indicates that the coal/solvent combinations tested produce varied levels of metals removal.

Initially, a method was developed for trace metals determination which involved digestion in nitric acid, boric acid, and hydrofluoric acid in a microwave oven, followed by methane sulfonic acid digestion and, finally, analysis using an inductively coupled argon plasma spectrophotometer (ICP).

The as-received coal and resids were analyzed for metals content. Prior to this, however, samples from the National Bureau of Standards were analyzed to validate the equipment and methods to be used in the analyses. The results of these analyses are shown in Table 6. The analyzed values are within $\pm 12\%$ of the certified values. The results of the analysis of the as-received coal and resid samples were previously presented in Table 2. As the table shows, the coals are low in vanadium and nickel, but high in iron. The resids, except for the Mandan Decant Oil, contain relatively higher amounts of vanadium and nickel, but ten times less iron. To validate the analytical techniques as well as to evaluate the effect of the reactor walls, a set of total product slurry samples was analyzed for their metals content and compared to the metals content of the respective feed slurries. As expected, vanadium and nickel values reflected the resid concentrations of these metals, while the iron contents reflected the coal iron concentrations. Recovery values are presented in the right-hand columns of Table 7. The Mandan Decant Oil contained little vanadium and nickel, resulting in erratic recoveries of these two metals when this solvent was present. In comparing the recoveries of the three metals, iron and vanadium exhibited good recoveries, while more nickel was recovered than was introduced to the system, suggesting that nickel may have been added from the reactor walls.

TABLE 6

RESULTS OF ANALYSIS OF NATIONAL BUREAU OF STANDARDS SAMPLES

Analysis Standard	Date	V ppm	Ni ppm	Fe ppm
1634	Certified	56	29	NR ^a
	Values			
	9/86	55	31	0
	11/86	50	32	120
	1/87	52	43	100
8505	Certified	390	NR	NR
	Values			
	9/86	360	54	77
	11/86	360	50	120
	1/87	430	58	42

^a Certified values were not reported.

TABLE 7

MASS BALANCE OF METALS IN FEED AND PRODUCT SLURRIES FOR INDIAN HEAD COAL

Solvent	Feed MAF/ Solv	Slurry Coal AR Wt%	Metals, ppm			Wt Ratio ^b PS/FS	Product Slurry Metals ^c , ppm			Recovery Metals ^d , %		
			V	Ni	Fe		V	Ni	Fe	V	Ni	Fe
Mayan Crude	10/90	14.7	269	55	1199	1.000	260	91	1200	97	166	100
Mayan Crude	50/50	59.9	129	29	3716	.904	140	48	4100	98	147	100
Lloydminster	10/90	14.7	248	120	1017	.935	260	130	1100	98	101	101
Lloydminster	50/50	61.1	115	59	3700	.763	150	87	4900	99	113	101
Mandan Decant Oil	30/70	40.0	2	2	2407	.822	0	20	3100	--	357	106
Mandan Decant Oil	50/50	61.1	2	5	3653	.967	4	18	4000	158	320	106

^a Feed slurry (FS) consists of as received coal and solvent. The metals content was calculated from the metals content of each component and its wt% in the FS.

^b The wt% ratio of grams of product slurry (PS) recovered to grams of FS charged relates the metals contents of FS and PS. It has been adjusted to give the best overall fit of the data.

^c PS metal content values were measured.

^d The metals recovery was calculated.

For co-processing to be successful, the metals content of the pentane soluble fractions of the product slurries must be low. Table 8 presents pentane solubility and metals content data for a set of coal/solvent combinations. Pentane solubilities were determined after filtration was used to remove the unconverted coal. This should accurately reflect pentane soluble yields, although metals may be a part of the fine particles that passed the filter. It is not known if these particles would end up in products from a propane extraction process, however, since they are small, they probably would. The amount of pentane solubles determined as difference oil and recovered oil in the product slurry can be compared. Difference oil was determined as described in Section 3.2.7; it is equal to 100 minus the wt% of pentane insolubles in the product slurry. Recovered oil is defined as the amount of pentane solubles remaining after removing the pentane during the rotovaping procedure. For the neat solvents, the difference oil and recovered oil values are essentially equal (77.1% versus 77.5%, respectively, for Mayan Crude). This indicates that little material was removed with the pentane during the rotovaping. After co-processing, the recovered oil values were considerably less than the difference oil values for the product slurries. This decrease in recovered oil values for the product slurries is due to the presence of coal or solvent co-processing products which are more volatile. Comparison of gas chromatographic (GC) analysis of recovered oil and unrotovaped pentane solubles (difference oil) shows that a considerable amount of light material was removed during the rotovaping procedure (Figures 17 and 18).

The recovered oil represents the fraction that could be upgraded in present refineries; therefore the metals content of this fraction is important. In general, it can be seen in Table 8 that Martin Lake and Wyodak coals reduced vanadium content better than the Indian Head coal, and Wyodak coal was best at lowering both nickel and iron content. Based upon these results, the Wyodak subbituminous coal would appear to be the most effective in lowering the metals content of the resids, although Martin Lake coal was almost as effective, with two exceptions. When reacting with either Mayan Crude or Mandan Decant Oil, the Martin Lake coal seemed to add iron during the co-processing. The Mandan Decant Oil showed an increase in iron content with all coals. This is probably a real increase rather than an anomaly in the data, since previous liquefaction research at UNDERC has indicated that the amount of metals in THF soluble coal liquid products can be greater than the amount present in the resid feed (2). When the quantities of metals in the recovered oil of non-processed solvent are compared to those in the processed resid, it can be seen that the metals content has not been substantially improved for any of the coal/solvent combinations.

The metals data indicates that, although a substantial reduction in total metals content was observed, sizable quantities remain in the oil fraction of the products, and, in fact, the quantity of iron has been increased.

TABLE 8

YIELDS AND METALS CONTENT OF PENTANE-SOLUBLE FRACTIONS
OF RESIDS AND 30/70 MAF COAL/RESID PRODUCTS

Test ID	Resid/Coal	V ppm	Ni ppm	Fe ppm	Recov. ^a Oil Wt%	Diff. ^a Oil Wt%	Ratio ^c
	Mayan Crude	59	13	0	77.5	77.1	1.005
T365I	Indian Head	75	19	119	41.3	67.0	.616
T366C	Martin Lake	44	21	220	35.2	63.8	.552
T367C	Wyodak	47	ND ^b	94	41.7	64.7	.645
	Lloydminster	82	42	0	69.1	67.1	1.030
T365L	Indian Head	86	35	180	43.7	60.5	.722
T366L	Martin Lake	64	31	ND	41.0	57.1	.718
T367L	Wyodak	62	26	29	46.2	53.3	.867
	Mandan Decant Oil	0	0	10	98.0	97.9	1.001
T365C	Indian Head	ND	ND	71	56.2	72.5	.775
T366I	Martin Lake	ND	ND	170	41.2	64.5	.639
T367I	Wyodak	ND	ND	91	57.4	68.8	.834
	Arabian	28	8	0	80.5	82.5	.976
T365F	Indian Head	55	ND	54	53.3	70.5	.756
T366F	Martin Lake	27	14	38	47.7	64.8	.736
T367F	Wyodak	52	ND	36	55.8	68.1	.819

^a Recovered oil is the wt% of oil in product slurry recovered after rotovaping. The metal values for coal/resid combinations are for the recovered oil. The difference oil was calculated from 100% minus the wt% pentane insolubles for the product slurry and applies only to the single sample used in analysis, as opposed to an average of values as presented in Table 13.

^b None Detected.

^c Ratio of recovered to difference oil.

T 365 I - PENTANE EXTRACT

Before Evaporation of Solvent Under Vacuum

After Evaporation of Solvent Under Vacuum

Figure 17. Chromatograms of the pentane-soluble fraction of the product of the co-processing of Indian Head lignite and Mayan crude

T 366C - PENTANE EXTRACT

Before Evaporation of Solvent Under Vacuum

After Evaporation of Solvent Under Vacuum

Figure 18. Chromatograms of the pentane-soluble fraction of the product of the co-processing of Martin Lake lignite and Mayan crude

3.2.4 Column Fractionation of Resid Samples

Two methods of silica gel column fractionation have been developed at UNDERC. The first, called the "short" method, results in four column fractions, the first two of which contain the most aliphatic material. The subsequent fractions become more polar (7). The second, or "long", method results in twelve increasingly polar fractions (8). The fractions obtained from either method can be investigated by highfield NMR chromatography.

Both methods of fractionation were utilized in the analysis of the resids. Table 9 presents the results of the "short" separation of the resids, while Table 10 lists the results of the "long" separation. The fractions which resulted from the "short" separation were analyzed by NMR spectroscopy. The results of this analysis are included in Table 9.

As Table 9 shows, Fractions 1 and 2 obtained from Lloydminster, Arabian and Mayan Crude contain primarily aliphatic hydrogen, indicating considerable amounts of long-chain hydrocarbon material. For these three resids, a large quantity of aromatic hydrogen is present in Fraction 3, while the amount present in the more polar Fraction 4 is somewhat less. Some long-chain aliphatic hydrogen was present, however, in both Fractions 3 and 4. Fraction 3 exhibited a well-defined NH proton resonance in all of the petroleum-derived materials, indicating the presence of ammonia. Due to the presence of water, however, quantitation of this peak is not possible at the present time.

Mandan Reduced Crude and Mandan Decant Oil (the Mandan, ND, Amoco refinery cat cracker feed and product, respectively) were also analyzed in this manner. The Reduced Crude and the Decant Oil separated well into the four "short" column fractions, which included alkanes (Fractions 1 and 2), aromatic hydrocarbons (Fraction 3) and polars (Fraction 4). NMR analysis showed the cracked Decant Oil to be more aromatic than the feed, the Reduced Crude, as Table 11 shows. In general, the composition of the Decant Oil is very similar to that of a typical LRC liquefaction recycle oil, therefore it was theorized that the Mandan Decant Oil would work well in the co-processing of selected LRCs.

3.2.5 NMR Analysis of Petroleum Resid Samples

The NMR data, presented in Table 11, show that there is not a great deal of aromatic hydrogen present in the petroleum fractions. Complete data for all of the samples analyzed may be found in Appendix A of the April-June 1986 Quarterly Technical Progress Report (4). A solid ^{13}C NMR spectrum was obtained for Lloydminster, the only solid resid. This spectrum, presented as Figure 19, shows the ratio of aromatic carbons to aromatic hydrogens to be approximately 2.6:1, indicating the presence of condensed aromatic ring structures. Aromatic carbon bound to oxygen or other heteroatoms accounted for 1.4% of the carbon in the sample. The aliphatic C:H ratio was found to be 1.76:1 and the overall C:H ratio was determined to be 1.45:1. Approximately 0.9% of the carbon was bonded in carboxyl or ester/amide structures.

TABLE 9

RESULTS OF SEPARATIONS AND ASSOCIATED NMR ANALYSES OF RESIDS USING THE "SHORT" COLUMN TECHNIQUE

<u>Column Fraction Number</u>	<u>Resid</u>				
	<u>Lloydminster</u>	<u>Arabian</u>	<u>Mayan Crude</u>	<u>Mandan Decant Oil</u>	<u>Mandan Reduced Crude</u>
Column Fractions 1 & 2 (aliphatic)					
wt% Fraction	48.2	47.7	44.3	29.9	68.9
% Aromatic	5.3	4.9	2.8	0.8	0.1
Column Fraction 3 (aromatic)					
wt% Fraction	45.0	46.2	39.0	65.7	25.4
% Aromatic	9.3	9.1	8.7	21.3	18.0
Column Fraction 4 (polar)					
wt% Fraction	6.4	5.5	5.8	4.5	4.2
% Aromatic	5.5	4.6	5.9	36.9	14.6

TABLE 10

RESULTS OF SEPARATIONS OF RESIDS USING THE "LONG" COLUMN TECHNIQUE

<u>Column Fraction Number</u>	<u>Resid Weight % Fraction</u>		
	<u>Lloydminster</u>	<u>Arabian</u>	<u>Mayan Crude</u>
1	28.2	37.3	35.5
2	3.3	7.0	12.7
3	1.3	1.4	4.0
4	1.0	0.7	0.3
5	1.0	0.5	0.3
6	1.6	1.4	7.6
7	2.0	0.9	0.6
8	8.7	5.8	3.9
9	91.8	5.5	7.0
10	12.3	17.8	13.6
11	3.0	2.9	3.4
12	3.3	3.9	3.4

TABLE 11

RESULTS OF NMR ANALYSIS OF RESID SAMPLES^a

<u>Resid</u>	<u>% H_{arom}</u>	<u>% H_{aliph}</u>	<u>% C_{arom} (Solid)</u>
Lloydminster	5.7	94.3	22.3
Arabian	5.3	94.7	-- ^b
Mayan Crude	5.0	95.0	--
Mandan Decant Oil	19.5	80.5	--
Mandan Reduced Crude	4.6	95.4	--
Maya ATB	7.6	92.4	--
North Slope ATB	6.1	93.9	--
North Slope VTB	6.9	93.1	--
Boscan Dialyzate Residue	9.8	90.2	--

^a Results not adjusted for water content.

^b Solid NMR not applicable to liquid resid sample.

Figure 19. Solid ^{13}C NMR spectrum of Lloydminster resid

3.2.6 Supercritical Fluid Chromatography

Supercritical fluid chromatographic (SFC) methods for the analysis of organics that are too nonvolatile to be analyzed using gas chromatography are being refined. One method of SFC under development utilizes flame ionization detection (SFC/FID), and the other involves interfacing the SFC column to a mass spectrometer. Although the use of SFC and the associated instrumentation are in the early stages of development, work at UNDERC has thus far resulted in techniques yielding good separation of individual components as well as mass spectrometric data that allows identification of individual species. Because standards of appropriately high molecular weight are largely unavailable, several petroleum- and coal-derived wax samples of a reasonably well-defined chemical nature have been used as "standard" samples. The results of SFC analysis of two commercial waxes, a Fischer-Tropsch wax and an acid montan wax, show that the newly-developed technique is an effective one. The chromatograms of the two waxes were presented previously (4).

The SFC/FID technique was applied to separate the components of the Mayan Crude and the Arabian resid. The chromatograms for these resids are shown in Figures 20 and 21. Individual conditions have yet to be optimized, however it is apparent that SFC may be useful for analyzing heavy resids and co-processing products that cannot be analyzed by ordinary chromatographic methods.

Figure 20. SFC/FID chromatogram of Mayan Crude Oil

Figure 21. SFC/FID chromatogram of Arabian resid

3.2.7 Solubility of Products in Pentane

Information concerning co-processing is valuable to both the coal and petroleum industries; therefore, analyses of the feedstocks and products must relate to the standards of both industries. The petroleum industry quantifies yields of oils by using solvent extractions to remove the non-asphalt fractions. An analogous laboratory technique is the pentane solubility test. To provide a basis for future determinations of product improvements, samples of the solvents were extracted using methylene chloride (MeCl_2) and pentane. The extraction procedure used was as follows. Approximately 20 g of sample was stirred with 1 liter of MeCl_2 for 2 hours without heat. The mixture was filtered using a 40-60TM fritted glass filter. The MeCl_2 insolubles were air dried and weighed. The MeCl_2 was removed from the solubles under a vacuum, and the solubles were mixed with 1 liter of pentane. This mixture was stirred for 4 hours without heat and filtered using a 40-60TM fritted glass filter. The insoluble fraction was dried and weighed. The pentane was removed under vacuum, and the solubles weighed.

The heaviest fraction of a resid is the fraction which is insoluble in both pentane and MeCl_2 , and the lightest is that which is soluble in pentane. Table 12 presents the results of the extractions performed on the resids. As the data show, the Mandan Decant Oil is composed almost exclusively of light oils, while the solid resid, Lloydminster, contains a significant amount of asphaltene and preasphaltene material. Arabian, Mayan Crude, and Mayan 650+ resids were all very similar in composition. This data would indicate that because of its pentane-soluble nature, i.e., greater number of available hydrogen atoms, the Mandan Decant Oil should perform the best of the resids during co-processing testing in which production of a liquefied coal product was the goal. Conversely, it would be expected that Lloydminster would not be a particularly good solvent, based upon these results. Table 13 presents the average pentane-insoluble fractions of the products of the co-processing screening tests. This table shows that the Mandan Decant Oil products, especially at a 30% solids loading, are more soluble in pentane. The table also shows that the Lloydminster products contained more material that was insoluble in pentane.

The same method that was used to determine the yield of pentane solubles was used for analysis of the raw product slurries. However, mass balance closures for the samples ranged from a low of 61% to a high of 93%. In the procedure, the pentane solubles were recovered by rotovaping off the pentane, which removed volatiles as well. The pentane soluble fraction was analyzed by GC before and after removing the pentane, and the results indicated that this was the case. This would account for the low mass balances. Pentane soluble yields determined by difference were used in coal yield calculations.

TABLE 12
RESULTS OF PENTANE SOLUBILITY TEST OF RESIDS

Sample	Weight%				
	<u>Arabian</u>	<u>Lloyd-minster</u>	<u>Mayan Crude</u>	<u>Mandan D.O.</u>	<u>Mayan 650+</u>
Pentane Insoluble MeCl ₂ Insoluble	0.35	0.40	0.35	0.10	0.05
Pentane Insoluble MeCl ₂ Soluble (Asphaltene Preasphaltene)	17.17	32.47	18.76	2.03	22.88
Pentane Soluble (Oils)	80.50	69.09	75.24	97.97	77.47
Total Recovery	98.70	101.96	94.35	100.10	100.40

TABLE 13
AVERAGE PENTANE-INSOLUBLE FRACTIONS OF CO-PROCESSING PRODUCTS^a

Resid	Weight % of Product		
	<u>Indian Head</u>	<u>Martin Lake</u>	<u>Wyodak</u>
<u>30% Solids Loading</u>			
Lloydminster	44.17 ± 4.06	43.45 ± 2.35	44.52 ± 1.97
Arabian	31.50 ± 1.87	33.96 ± 1.10	33.93 ± 1.88
Mandan Decant Oil	28.96 ± 1.92	31.06 ± 3.92	31.21 ± 0.51
Mayan Crude	34.80 ± 2.51	31.32 ± 4.42	34.71 ± 0.54
<u>50% Solids Loading</u>			
Lloydminster	56.44 ± 4.42	51.61 ± 1.97	54.50 ± 5.07
Arabian	43.90 ± 2.96	46.01 ± 10.56	44.24 ± 3.67
Mandan Decant Oil	46.03 ± 3.15	44.54 ± 6.42	49.14 ± 2.76
Mayan Crude	43.59 ± 4.90	46.32 ± 5.60	46.58 ± 1.99

^a Liquids plus solids out.

3.3 Aqueous Liquefaction Test

3.3.1 Materials and Equipment

An aqueous liquefaction test was completed in the continuous processing unit (CPU). The materials and conditions which were initially selected were as follows:

Coal.....Sarpy Creek subbituminous
Temperature.....360°-374°C
Pressure.....4000 psig
Reducing gas.....N₂ or CO; partial pressure of 1000 psig
Residence time.....1 hour
Promotor.....None or H₂S

The materials and reaction conditions which were eventually used were:

Coal.....Martin Lake lignite
Temperature.....350°C
Pressure.....4400 psig
Reducing gas.....N₂ or CO; partial pressure of 1000 psig
Residence time.....0.5 hour
Promotor.....None, H₂S, or sulfur

Problems with pumping and settling of the slurry led to the change in coal to Martin Lake lignite. The choice of coal was made based upon slurry information obtained from the UNDERC hot-water drying unit (8). During hot-water drying, large flow rates caused a reduction in the settling of the slurries to a tolerable rate. The success of the high solids loadings in the hot-water drying unit overshadowed the inherent problems with using the Sarpy Creek coal in the CPU. This is because it was one goal of the CPU run to have a high carbon content in the feed.

The reaction temperature was lowered after operation at temperatures close to the critical point resulted in downstream plugging caused by tar agglomeration in the lines.

The original run plan called for H₂S to be used as a promotor. However, when the H₂S pump failed, sulfur was substituted in an attempt to obtain results within the time and financial constraints that were present.

A 0.5-hour residence time was used rather than a 1-hour residence time in order to overcome flow rate problems. A 1-hour residence time required the pump to operate at only 10% of rated capacity. The compromise on low conversion versus operability was settled at a net residence time of 0.5-hour, which required the pump to operate at approximately 30% to 60% of its stroke capacity.

3.3.2 Results and Discussion

Table 14 presents a summary of the preliminary data from the aqueous liquefaction runs. Run 128-3, using CO and H₂S, resulted in the highest conversion to THF solubles. Due to equipment problems encountered with this run, it should

be reproduced to validate the results which were obtained. The run using N₂ and no promotor, Run 128-1, resulted in the smallest conversion. Figure 22 shows the product distribution for the runs.

TABLE 14
PRELIMINARY RESULTS FROM UNDERC AQUEOUS LIQUEFACTION TESTS

Run #	128-1	128-2	128-3	129-1
Date	12/11/86	12/11/86	12/11/86	12/15/86
Gas	N ₂	CO	CO	CO
Additive	None	None	H ₂ S	Sulfur
Conversion ^b	8.5%	35.2%	67.0%	18.2%
Water Yield	-6.0%	-2.8%	9.7%	8.6%
Gas Yield ^a	1.1%	8.3%	8.3%	4.8%
Ash Yield ^a	0.5%	0.8%	-0.8%	1.0%
Resid/Distillate ^a	12.8%	28.9%	49.8%	21.0%

^a Weight % MAF coal

^b Conversion to THF-solubles

Figure 22. Product distribution of aqueous liquefaction tests using Martin Lake lignite/H₂O slurry

As Table 14 shows, Run Period 128-1, with N_2 as an inert reactant gas, resulted in very low conversion to THF solubles with most of the product in the form of gases and tars. This run was performed as a base case to provide a comparison between past hot-water drying runs and the current effort, and, as such, was successful.

When sulfur was substituted for H_2S as the promotor (during Run Period 129-1), the conversion was not as good as that which generally occurs when H_2S is used. The products of this run contained more resid and less distillate than has been the case with H_2S -promoted runs. One explanation for this result is that the sulfur utilized hydrogen from the water/gas shift reaction, making the hydrogen unavailable for use by the coal.

Research performed with labeled materials 2H and ^{13}CO has shown that when hydrogen is present in the feed as a reductant, it is not incorporated into the product in significant quantities during first-stage liquefaction (9). Likewise, the C or CO from feed containing CO as a reductant is also not incorporated into the product. The logical conclusion is that the increase in utilization of the CO from the feed which was noted during first-stage processing of LRCs is due to the water/gas shift reaction. A sufficiently active hydrogen scavenger, which sulfur may be at these conditions, would tie up active hydrogen produced during this processing. These tests show that the hydrogen acts more as an inert diluent than a hydrogen donor/reductant. With the available active hydrogen tied up in the production of H_2S , the system would behave very similarly to the N_2 run, Run Period 128-1, rather than Run Period 128-3, the CO/ H_2S run.

Conversions to THF solubles for Martin Lake lignite, when reacted with either CO or N_2 in the CPU, exhibited trends very much like those noted during batch aqueous liquefaction testing with a similar low-rank coal, Indian Head (North Dakota) lignite. While the data are not directly comparable per se (different conditions, reaction times and coals were utilized), the general trends in results between the two types of aqueous-phase systems are comparable. The CPU was run co-currently, while the batch autoclave was operated in a semi-batch counter-current fashion. In both cases, conversion increased substantially when CO was utilized during processing, and both were beneficially affected by the addition of H_2S . There is approximately a three-fold increase in conversion in both batch and CPU processing due to the addition of CO. These data suggest that, if the CPU were reconfigured to operate in a counter-current mode, the resulting conversions to THF solubles would be similar to those obtained during the batch autoclave testing of over 80%.

3.3.3 Conclusions and Recommendations

In general, it can be said that the aqueous liquefaction runs were physically possible to perform, but in order to obtain optimum performance, an extraction procedure would be necessary. This is suggested by two things. First, operation of the CPU at temperatures close to or above the critical point of water resulted in downstream plugging due to tar (solvent-refined lignite) agglomeration in the lines. The tar-plugging problem seems to be a result of conversion high enough to produce high levels of tar, but not high enough to produce significant quantities of distillate. High distillate yield would probably require a second stage, higher-severity process with a catalyst.

Secondly, batch studies have shown that the conversions and degree of separation possible using an extraction mode of operation can be high, estimated at 90% (10). When previous aqueous liquefaction work was performed with a semi-batch autoclave serving as an extractor, the resulting product was a very low-ash (below detection limits), "clean" fuel (10).

It would appear that the most efficient use of the CPU configuration as it currently exists for aqueous liquefaction would be as the first stage of a two-stage system. The second stage would consist of a catalytic hydrotreating system. This type of system is illustrated in Figure 23. In such a case, the CPU would not be expected to produce a high yield of distillate; it would, however, produce the very "clean" feed for second stage upgrading.

Figure 23. Flowsheet of process for optimum use of aqueous liquefaction with LRCs

4.0 FUTURE UNDERC CO-PROCESSING STUDIES

Testing will focus on integrated two-stage co-processing both with and without a catalyst. The testing will initially be conducted using the batch facilities at UNDERC. The optimum conditions will then be tested in the continuous processing unit (CPU). The autoclaves are currently set up for this testing. A flow diagram of the system was previously shown in Figure 6. To set the range of conditions for parametric evaluation, a review of past staged testing was performed. Past testing in this mode of operation has produced high conversions to distillate and THF soluble resid using an LRC (from the Indian Head Mine near Zap, ND) and anthracene oil (A04). Figures 24 through 27 (taken from past reports) indicate the response of the tested coal to varied parameters. There is a significant amount of information available in past reports showing that similarly ranked coals generally behave the same during similar processing. For example, if a North Dakota lignite exhibits relatively high conversion during processing, then a Texas lignite will also have a relatively high conversion during the same processing. The rule applies to important parameters that affect overall conversion rather than to specifics such as yields of distillate fractions (e.g., middle oil and heavy oil).

The most important of the responses of LRCs to staged processing are as follows:

1. Figure 24 (9) shows the effect of increasing temperature on autoclave runs which utilize CO during first-stage processing. Overall conversion, defined as one minus the fraction that is insoluble organic matter (IOM), increased over the entire temperature range studied (320° through 400°C). However, at temperatures higher than 375°, no further increase in desirable products (oil and/or soluble residuum) was noted. The result of this testing indicates that the temperature of the first stage should probably not exceed 380°C.
2. Figure 25 (9) illustrates the effect of decreasing CO content/increasing H₂ content in the feed gas. As the percent CO in the feed gas decreases, both overall conversion and yield of C4+ distillate decrease. The decrease in both the yield of C4+ distillate (from 27.8 to 6.9%) and overall conversion (from 87.5% to 75.3%) can be primarily assigned to the increase in soluble residuum (54.6% to 42.5%). Because all of these responses are negative, the use of the highest levels of CO practical should be used during first-stage processing.
3. The effect of increased second-stage residence time is illustrated in Figure 26 (11). As the second-stage time increased from 5 to 30 minutes, the overall conversion increased by approximately 15%, from 70% to 85%. This increase was at the expense of both the distillate and residuum which were to be converted, showing that, without the presence of catalyst or hydrotreated solvent, significant cracking occurs. Therefore, the residence time in the second stage should be low.

Figure 24. Conversion as a function of temperature during liquefaction using CO as feed gas

Figure 25. Effect of decreasing CO content/increasing H₂ content in the feed gas during the liquefaction of Zap lignite

Figure 26. Effect of increasing second-stage residence time during the liquefaction of Zap lignite

Figure 27. Effect of variations in second-stage temperature during the liquefaction of Zap lignite

4. Figure 27 (12) shows the effect of varied second-stage temperature during staged processing. This figure shows that both overall conversion and yield of desirable products (distillate and soluble residuum) increases as second-stage temperature increases. This second-stage temperature should be as high as possible with the production of HC gases as the limiting factor.

To this point, discussion has dealt with tests that were processed under "normal LRC liquefaction" using a coal-derived solvent, as opposed to co-processing. As a result, the conclusions from this earlier work should only be used to set initial parametric ranges that will be used to evaluate the co-processing of LRCs.

The following tables are the result of tests specifically utilizing staged co-processing. This co-processing was performed utilizing catalysts (K_2CO_3 , K_2MoO_4 , and H_2S), subbituminous coal (Highvale-Canadian), and tar sands bitumen (11). The first stage was run on the CPU to produce a large homogeneous sample of first-stage product for subsequent batch processing in the one-gallon autoclaves. The responses of staged LRC co-processing are summarized as follows.

1. Table 15 shows the effect of varied second stage temperature. This shows that the same general trends that are present in staged, direct liquefaction are present in staged co-processing. Increased temperature increased overall conversion (78.8% to 90.6%), distillate yield (33.3% to 54.3%), net equivalent hydrogen production (1.3% to 2.5%) and C1 to C3 gases (1.6% to 6.7%). The increased temperature provided significant increases in the yield of distillate but at the expense of higher gas production. As a result, the data indicated that elevated temperatures should be used for second-stage processing, although it is expected that each feedstock would have a different break-even temperature at which gas production would become too high to be acceptable.
2. Table 16 illustrates the effect of different catalyst systems on the second stage processing of Highvale subbituminous coal and tar sands bitumen. This shows that, for this system, K_2MoO_4 with or without added H_2S outperforms the non-catalyzed system. Hydrogen sulfide can increase the production of distillate in the presence of K_2MoO_4 catalyst. For the non-catalyzed case, the small yield of soluble residuum and large yield of distillate may indicate a synergistic effect during co-processing of coal and tar sands bitumen, however, the conversion to soluble resid is limited. As a result, the non-catalyzed system may not be as attractive as the catalyzed system.

This brief review indicates that, to provide a system that produces the highest overall conversions with low gas production and high yields of desirable products (i.e., distillate and soluble residuum), the following range of conditions should be evaluated:

TABLE 15

LIQUEFACTION OF HIGHVALE COAL WITH VARYING SECOND STAGE TEMPERATURE

Run No.	N150	N149	N138	N145	N148	N142
Coal	ALB2	ALB2	ALB2	ALB2	ALB2	ALB2
Solvent	Bitumen	Bitumen	Bitumen	Bitumen	Bitumen	Bitumen
Additive	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄ /H ₂ S
Run Time, min.	20	20	20	20	20	20
Average Temp.	413	419	425	430	435	440
Max. Press., psig	2660	2680	2620	2695	2660	2740
% H ₂ Feed Gas	99.5	94.7	99.5	99.5	99.5	99.5
Moisture (GMS)	4.4	4.4	4.1	4.3	4.3	4.3
<u>Net Yields</u>						
<u>Wt. % maf Coal Charged:</u>						
C ₁ - C ₃	1.6	2.5	3.4	3.2	5.4	6.7
Gas + H ₂ O	9.1	6.7	7.7	10.0	11.9	15.4
C ₄ + Dist.	33.3	46.9	27.5	49.2	50.0	54.3
Sol. Residuum	36.4	29.3	44.6	29.5	24.1	20.8
IOM	21.2	17.0	20.1	11.3	14.0	9.4
H ₂ Equiv. Consumption	1.3	0.9	1.9	2.0	2.4	2.5
Conversion	78.8	83.0	79.9	88.7	86.0	90.6
Material Balance Closure	97.6	98.9	101.2	99.6	94.4	97.5

TABLE 16

LIQUEFACTION OF COAL WITH DIFFERENT CATALYSTS IN THE SECOND STAGE

Run No.	N149	N155	N156	N151
Coal	ALB2	ALB2	ALB2	ALB2
Solvent	Bitumen	Bitumen	Bitumen	Bitumen
Additive	K ₂ MoO ₄ /H ₂ S	K ₂ MoO ₄	H ₂ S	None
Run Time, min.	20	20	20	20
Average Temp.	419	422	413	420
Max. Press., psig	2680	2625	2620	2770
% H ₂ Feed Gas	94.7	100.0	99.5	100.0
Moisture (GMS)	4.4	4.5	4.3	4.3
<u>Net Yields (Wt.% maf</u>				
<u>Coal Charged):</u>				
C ₁ - C ₃	2.5	2.8	2.4	2.6
Gas + H ₂ O	6.7	6.1	9.7	13.4
C ₄ + Dist.	46.9	35.9	33.7	50.9
Sol. Residuum	29.3	43.7	22.0	3.8
IOM	17.0	14.2	34.6	31.8
H ₂ Equiv. Consumption	0.9	1.4	0.6	0.0
Conversion	83.0	85.8	65.4	68.2
Material Balance Closure	98.9	91.8	98.7	98.7

First-stage Conditions:

Time.....20 to 60 min; Base case - 40 minutes
Temp.....360° to 400°C; Base case - 380°C
Catalyst.....Ammonium Molybdate, H₂S, Shell 424 and Amocat 1C
Reductant.....CO

Second-stage Conditions:

Time.....2 to 30 min; Base case - 10 min
Temp.....420° to 460°C; Base case - 440°C
Catalyst.....Ammonium Molybdate, H₂S, Shell 424, and Amocat 1C
Reductant.....H₂

The full matrix determination will remain flexible but will initially be as follows:

Matrix Series 1:

This matrix will address the questions of first-stage parametric variance. The parameters to be evaluated are residence time and temperature.

Temperature	Minutes		
	20	40	60
400°C	x	x	x
380°C	x	x*	x
360°C	x	x	x

* Centerpoint of matrix for use in subsequent comparisons between matrices.

The second-stage conditions will be held constant at base conditions for runs in this test matrix. All catalyst systems to be evaluated will be tested under at least centerpoint matrix conditions and, pending results of the Matrix 1 tests, more tests will be run as indicated. This series will require 18 tests. The justification for the performance of this testing first is that, for the staged system to work the best (high yields of distillates and low yields of gas), the coal must be converted to heavy product in the first stage and distillate in the second. In other words, most of the conversion should occur in the first stage.

Matrix Series 2:

This matrix series will address the question of parametric evaluation during the second-stage processing. Stage-one conditions will be fixed for this matrix and will be those indicated during the evaluation of the initial test matrix.

Temperature	Minutes			
	2	10	20	30
410°C	x	x	x	x
425°C	x	x*	x	x
440°C	x	x	x	x

*Centerpoint of matrix for use in subsequent comparisons between matrices.

All of the catalyst systems will be evaluated at the base conditions plus any necessary interaction test points resulting from the first test series. This test matrix series will require up to 24 runs.

The base test point will be repeated approximately every three months for internal data validation. In addition, single-stage runs at conditions approximating those used at PETC will be performed during the program. These runs will be used to compare single and 2-stage processes, as well as to provide some data base equivalency between research organizations.

The number of runs in the test series includes unsuccessful runs at a rate of 10%.

5.0 CONCLUSIONS

5.1 Co-Processing

- In general, the petroleum-derived solvents were not as effective in converting coal to THF solubles during co-processing as were coal-derived solvents.
- Pentane solubility testing indicated that Mandan Decant Oil is composed almost entirely of light fraction oils and therefore makes a good co-processing solvent. In addition, the Mandan Decant Oil contains very small quantities of heavy metals, indicating that it could be recycled easily in a co-processing process without fear of catalyst contamination.
- Martin Lake lignite exhibited the highest conversion to THF solubles of the coals tested.
- The Martin Lake lignite/Arabian resid pair produced the best combination of high conversion to THF solubles, good yields of pentane soluble oils, and low heavy metals content of the coal/resid pairs tested.
- Preliminary study of the solvent balance following co-processing indicates that great differences in utilization by coal exist between the solvents. All three coals tested produced pentane solubles when reacted with Arabian resid. Changes in yield of pentane solubles during reaction of the coals with the other solvents depended upon the reaction of the individual coal with the solvent. In general, Martin Lake lignite produced the greatest changes in yield of pentane solubles. When reacted with any of the three coals, Arabian resid always produced pentane soluble oils. This was not the case for any of the other resids which were tested, indicating that Arabian resid reacts more favorably under these conditions.

- Staged co-processing studies indicated that when ammonium molybdate was used as a catalyst, improvements in conversion to THF solubles would be noted. However, the product distribution which is obtained though the use of this catalyst is not as desirable as that which is obtained when H_2S is used as a promotor. Therefore, the choice of a co-processing catalyst/promotor appears to depend upon whether maximum conversion or optimum product distribution is the run objective.

5.2 Oil Agglomeration

- The agglomerating tendencies of Mandan Decant Oil were significantly better than those of any of the other solvents tested. Further testing with this solvent is warranted to determine more favorable agglomerating conditions as well as the level of ash removal attained.

5.3 Characterization of Reactants and Products

- The two methods of silica gel column fractionation developed at UNDERC, when coupled with highfield NMR chromatography, are very useful for providing insight into the organic structure of petroleum resids and crudes.
- Supercritical fluid chromatography with flame ionization detection (SFC/FID) may be useful in the analysis of non-volatile resids and co-processing products.
- The procedure used for determining pentane solubility results in the loss of some of the lightest oils produced by the resid and/or coal during co-processing. Yields of pentane solubles must, therefore, be calculated by difference to be used in coal yield calculations.
- Wyodak subbituminous coal was more effective at reducing metals content than either Martin Lake lignite or Indian Head lignite, although Martin Lake lignite was almost as effective.

5.4 Aqueous Liquefaction Test

- The aqueous liquefaction runs were physically possible to perform, but in order to attain a more favorable performance, an extraction procedure would be necessary. It would appear that the most efficient use of the CPU configuration as it currently exists for aqueous liquefaction would be as the first stage of a two-stage system. The second stage would consist of a catalytic hydrotreating system. In such a case, the CPU would not be expected to produce a high yield of distillate; it would, however, produce a very "clean" feed for second-stage upgrading.

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4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date 4-01-86
		6. Completion Date 3-31-92

7. FY	8. Months or Quarters				(86)												(87)		
86/7	Quarters				A	M	J	J	A	S	O	N	D	J	F	M			
9. Cost Status					b. Dollar Scale														
a. Dollars Expressed in																			
Thousands																			
10. Cost Chart																			
Fund Source	Quarter				Cum. to Date	Tot. Plan													
	1st	2nd	3rd	4th															
DOE	P	215	215	215	215	860	860												
	A	290	221	174	119	804													
	P																		
	A																		
	P																		
	A																		
	P																		
	A																		
Total P		215	215	215	215	860	860												
Total A		290	221	174	119	804													
Variance		(75)	(6)	41	96	56													
P = Planned A = Actual					c Cumulative Accrued Costs														
Total Planned Costs for Program/Project					Planned			215			430			645			860		
					Actual			290			511			685			804		
					Variance			(75)			(81)			(40)			56		

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title LOW-RANK COAL DIRECT LIQUEFACTION		3. Reporting Period 1-01-87 through 3-31-87	
4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202				5. Program/Project Start Date 4/1/86	
				6. Completion Date 3/31/92	
Milestone ID, No.	Description	Planned Completion Date	Actual Completion Date	Comments	
1.a1	Base case testing/data base equivalency	2/87	2/87		
1.b1	Preliminary agglomeration testing	2/87	2/87		
1.b2	Chemical comparison of base case tests	3/87	3/87		
1.a2	Report on base case testing	3/87	3/87		
1.a3	Report on non-catalytic stage coprocessing	9/87			
1.b3	Detail chemical evaluation of non-catalytic coprocessing (C/Res Comb #1)	11/87			
1.a4	Report on non-catalytic coprocessing	12/87			
1.a5	Evaluation of catalytic stage coprocessing (coal/resid combination #1)	1/88			
1.a6	CPU test to validate batch testing	2/88			
1.b4	Detailed chemical evaluation of catalytic staged coprocessing	3/88			
1.a7	Final Task 1 report	3/88			
OPTION 1 (COPROCESSING OF LRC)					
2.a1	Same as Task 1.a3 with 2nd coal/resid	9/87			
2.b1	Same as Task 1.b3 with 2nd coal/resid	11/87			
2.a2	Same as Task 1.a4 with 2nd coal/resid	12/87			
2.a3	Same as Task 1.a5 with 2nd coal/resid	1/88			
2.a4	Same as Task 1.a6 with 2nd coal/resid	2/88			
2.b3	Same as Task 1.b4 with 2nd coal/resid	3/88			
2.a5	Same as Task 1.a7 with 2nd coal/resid	3/88			
2.c1	Agglomeration study	3/88			
OPTION 2 (ChemCoal)				Awaiting Final Option Approval	
2.a1	Engineering study	1 ⁺⁴ ₋₀ /87			
2.a2	CPU refit	2 ⁺⁴ ₋₀ /87			
2.a3	Downstream upgrade	2 ⁺⁴ ₋₀ /87			
2.a4	CPU operation	11/87			

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Milestone ID, No.	Description	Planned Completion Date	Actual Completion Date	Comments
2.a51	Diesel testing (utilization)	12/88		
2.a52	Turbine testing (utilization)	12/88		
2.a53	Agglomeration (utilization)	11/88		
2.a7	Extend projected management	12/88		

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PRODUCTION OF HYDROGEN FROM LOW-RANK COALS

Annual Technical Report for the Period April 1, 1986-March 31, 1987
including the
Quarterly Technical Progress Report for the Period January through March 1987

by

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PRODUCTION OF HYDROGEN FROM LOW-RANK COALS

ABSTRACT

Advanced coal gasification technologies appear to be the most probable alternative for meeting the future demand for large quantities of hydrogen. The greater reactivity of lignites and subbituminous coals, compared to coals of higher rank, make them the probable choice for use in steam gasification. The principal goal of this research project is to establish the feasibility of low-rank coal gasification for low-cost hydrogen production. This research involves a proof-of-concept and the early stages of engineering development using a continuous process unit (CPU). In parallel with this process development work, an evaluation of the relationship between the fundamental properties of low-rank coals and their reactivity under hydrogen-producing conditions is also being conducted.

A CPU utilizing a 6-inch diameter fluid-bed reactor for the determination of the optimum operating conditions for producing low-cost hydrogen was designed and constructed. The CPU was designed to operate at nominally atmospheric pressure in a temperature range of 700° to 800°C and a steam-to-carbon molar ratio range of 2 to 4. The design for the CPU was completed in July, and construction of the unit was completed in March. Shakedown of the CPU was initiated and will continue through May. Parametric testing with the CPU will determine the effects of coal source, catalyst selection, and catalyst concentrations on gas composition and throughput.

A test plan outlining test procedures and methods of analysis was developed for the fundamental properties and reactivity study of low-rank coals. The methods of analysis included TGA for the reactivity studies; and instrumental analyses such as CP/MAS ^{13}C NMR, XRDA, XRFA, and surface analysis techniques such as ESCA and SEM to fully characterize the coals, chars, and gasification residues. Coals selected for the study were Velva (North Dakota) lignite and Martin Lake (Texas) lignite. Catalysts chosen based on previously experimental work were potassium carbonate and trona. Product gas analyses for selected TGA experiments showed that hydrogen can be produced in concentrations predicted by equilibrium via the catalyzed char-steam reaction. Reactivity of the chars increased by factors of two to four at a given temperature with the addition of catalyst due to increases in surface area and active sites. SEM showed that catalyzed chars have a much higher surface area than uncatalyzed chars, and potassium was distributed more uniformly than the trona over the char surface. Also, the highly activated carbon created by the devolatilization of the coal necessitates the prevention of exposure to air if CO functional groups are to be accurately identified by ESCA or quantified by CP/MAS ^{13}C NMR.

1.0 INTRODUCTION

Hydrogen is a key component in petroleum refining, petrochemical processing, and the production of coal-derived synfuels. Hydrogen can also be used directly as a fuel. Over the next 45 years, the demand for hydrogen has been projected to increase by a factor of 19 to 27 (1). Most of the hydrogen currently used in chemical applications and in refining applications is produced either through steam reforming of natural gas or through partial oxidation of petroleum. Advanced coal gasification technologies appear to be the most probable alternative for meeting the future demand for large quantities of hydrogen. Low-rank coals (lignites and subbituminous coals) are the preferred feedstock for such applications because of their low mining cost and higher reactivity relative to higher-rank coals.

The two most important considerations in the design of a process for producing hydrogen from coal are to maintain operating conditions that thermodynamically favor the production of hydrogen and carbon dioxide over carbon monoxide and methane, and to obtain reaction rates that result in sufficient gasifier throughput. Optimization of the conditions for maximum hydrogen content of the product gas requires steam gasification at relatively mild temperature and pressure. Temperatures in the range of 700° to 800°C at atmospheric pressure maximize hydrogen production. In tests at the University of North Dakota Energy Research Center (UNDERC), a dry synthesis gas containing 63% hydrogen was produced by steam gasification of low-rank coal (2). These mild conditions do not, however, promote high reaction rates. As a result, increasing coal reactivity is perhaps the most critical factor in the selection of a gasification process for producing hydrogen from coal. The rate-limiting step in the production of hydrogen from low-rank coals is the catalytic steam gasification of the char. It is important to provide process operating conditions which maximize the rate of this reaction at the mild conditions which maximize hydrogen production.

Fixed-bed gasification is not preferred because of heat and mass transfer limitations on the endothermic steam gasification reaction. Entrained-bed systems are also not preferred because they present difficulties in maintaining long enough solids residence times for reaction without the use of extensive solids recycle. A fluid-bed system operated with catalyzed low-rank coal offers both excellent heat and mass transfer capabilities along with processing flexibility; it is, therefore, attractive for process development. Fluid-bed reactors can achieve more uniform temperature and solids distributions than fixed- or entrained-bed gasifiers, and have high heat transfer characteristics. Further, the use of smaller particles in a fluid-bed system results in less diffusional resistance than a fixed-bed system, more efficient waste heat recovery, and smaller pressure drops. Also, because fluid-bed systems allow coal devolatilization, gasification, and ash removal within a single vessel, they are likely to be used for eventual scale-up of the hydrogen production process.

The physical and chemical nature of low-rank coals offer several advantages for use in this fluid-bed hydrogen production process. The high volatile matter content of lignites supports their use in steam gasification to produce hydrogen, as devolatilization products can be cracked in the hot zone of a fluid-bed to form additional hydrogen. Under suitable reaction conditions raw product gas from such a system would contain essentially only hydrogen, carbon

dioxide, carbon monoxide, and only small quantities of methane and sulfur gases. This was proven in operation of the CO₂ Acceptor process, a fluid-bed system utilizing low-rank coals (3). In addition to producing hydrogen and simplifying downstream gas clean-up, cracking of tars and oils in the gasifier reduces the contaminant concentrations in the process condensate and the attendant waste management problems.

The primary advantage of lignites and subbituminous coals is their greater reactivity relative to coals of higher rank. This increase in reactivity is caused by higher concentrations of active sites, higher porosity, and a more uniform dispersion of alkali impurities that act as inherent catalysts. In steam gasification tests conducted using bench-scale fixed-bed thermogravimetric analysis (TGA), low-rank coal char reactivities were found to be nearly ten times higher than that of a bituminous coal char gasified at the same conditions (4). In addition to the high reactivity determined for low-rank coal chars relative to bituminous coal chars, increases in reactivity were also observed with increasing temperature, within the range of moderate temperatures that maximize hydrogen production, and with the addition of alkali catalysts. An increase in steam gasification temperature from 700° to 800°C resulted in an increase in reactivity from approximately 1.0 (g/hr)/g to 3.5 (g/hr)/g. Reactivities computed for lignite chars catalyzed with a 10 wt% loading of pure sodium carbonate or potassium carbonate ranged from 4.8 to 5.5 (g/hr)/g at 750°C, compared to 1.6 to 2.0 (g/hr)/g for uncatalyzed lignite chars. Catalysis of a bituminous coal char with similar loadings of the alkali carbonates also increased reactivity; however, catalyzed bituminous coal char was found to be five to six times less reactive than similarly catalyzed lignites.

Because of the implications of catalyst cost and associated catalyst recovery costs, several potentially disposable catalysts were also evaluated in bench-scale steam gasification tests (4). Addition of either trona or nahcolite (naturally occurring alkali carbonate minerals) at 10 wt% loadings, resulted in reactivities higher than with equivalent mass loadings of reagent-grade alkali carbonates. The improvement in reactivity obtained using minerals such as trona and nahcolite indicates the value of further testing of impure sources of alkali as disposable catalysts for steam gasification and subsequent hydrogen production from low-rank coals.

The economics of this process are affected by several market factors. The first is the cost and availability of competing feedstocks. When the projected shortages in gaseous and liquid fossil fuels are realized, hydrogen from coal will become the most probable alternative for large-scale production of replacement fuel. The capital costs of hydrogen production via coal gasification have been shown to contribute over 50% of the final product cost (5). The lower feedstock cost and higher reactivity of lignites or subbituminous coal used in a catalytic steam gasification process should more than offset any additional capital cost resulting from additional coal handling requirements. The use of disposable catalysts may also have a major impact on the economics of low-rank coal use.

The properties of low-rank coals and selection of gasifier configuration not only influence gasification economics, but also affect the overall design and economics of the hydrogen-from-coal system. Cracking of devolatilization products in a fluid-bed system offers an environmental advantage, as does the low sulfur content of low-rank coals. The degree to which these benefits are realized in the gasification process will significantly impact the extent of gas and wastewater treatment required. The extent of product gas treatment will also be affected by the selection of end-use applications. End uses for hydrogen range from fuel cells and transportation fuel, to chemical feedstock (such as for methanol and ammonia synthesis), to use in synfuels production, each of which requires different hydrogen purity ranging from 65%-99%. The end uses for, and economics of, producing hydrogen will thus be influenced by the quality of the raw product gas and the extent of gas clean-up required.

A more complete evaluation of the use of low-rank coals in catalytic steam gasification to produce hydrogen is required. To date, much of this work has been performed at the laboratory scale, and has focused only on fundamental reactivity studies. These data must be verified on a larger scale, and a more complete evaluation of the concept must be performed before the technical realities, and also the economic feasibility, of the process can be clearly stated. This report describes the first year's activities and results on the production of hydrogen from low-rank coal research project at UNDERC. The project involves pilot-scale process development in addition to evaluating reactivity and fundamental properties of low-rank coals under hydrogen-producing conditions.

2.0 GOALS AND OBJECTIVE

The objective of this research is to evaluate the technical feasibility of producing low-cost hydrogen by catalytic steam gasification of low-rank coals. This approach takes advantage of the high reactivity, volatile matter, moisture concentration, and inherent alkali content of low-rank coals. This effort will provide a proof of concept and the early stages of engineering development. The research program will include the design, construction, and testing of a 6-inch diameter fluid-bed reactor and determination of the optimum operating conditions for producing low-cost hydrogen. Data collected from this process development work will be used to generate an economic assessment of the process. In addition, gas and wastewater treatment, end use applications, and the integration of thermochemical cycles for enhancement of hydrogen yield will be evaluated as part of a systems approach study to be performed in conjunction with the process economics study.

In parallel with this process development and systems analysis work, an evaluation of the relationship between the fundamental properties of low-rank coals and their reactivity under hydrogen-producing conditions will be conducted. A TGA study will involve reactivities of the low-rank coals computed on both a weight basis and an active site basis, and will be correlated with identified coal properties. Instrumental analysis to be performed on each coal, char and ash that are derived from reactivity studies will include solid ^{13}C Nuclear Magnetic Resonance Spectrometry (NMR), x-ray diffraction, x-ray fluorescence, and Electron Spectroscopy for Chemical Analysis (ESCA) surface analysis.

3.0 ACCOMPLISHMENTS

3.1 Hydrogen-From-Coal Continuous Process Unit (CPU)

3.1.1 CPU Design

A simplified schematic diagram of the final design for the CPU is shown in Figure 1. Steam and a small amount of oxygen are heated to nominally 760°C with an electric superheater and fed into the bottom of the fluid-bed gasifier (FBG). Coal sized to 1/4" x 0 is stored after preparation in a coal hopper with a holding capacity of 450 lbs. The coal is fed to the FBG with a star feeder and screw conveyor mechanism, with the star feeder controlling the rate. The outer shell of the FBG is constructed of 304 stainless steel with a 20-inch outside diameter and a 3/8-inch wall thickness. The FBG is refractory lined with 4.5-inches of insulating refractory and 2 inches of high temperature refractory, making the inside diameter of the reactor nominally 6 inches. The FBG was designed and constructed in three sections: one 5-foot section and two 6-foot sections. The inside working height is 16 feet (4-foot expanded bed height and 12-foot freeboard). Fines are removed from the product gas exiting the FBG by a refractory-lined cyclone. The product gas is quenched to remove condensables via a two-stage gas/liquid separator and a cryogenic trap. The gas is split into two streams before entering the coaxial first-stage water-cooled condensers and the coaxial second-stage glycol-cooled condensers. The coaxial heat exchangers are easy to maintain and provide sufficient gas velocities to prevent hang-up of any condensables. After the cryogenic trap, the product gas is metered and sampled prior to being vented. Feed ranges for the CPU, based on the hydrogen production equilibrium computer code developed at UNDERC (2) for a temperature range of 700°-800°C, steam-to-carbon molar ratio range of 2 - 4, and an average bed superficial velocity of 3 ft/sec, are nominally 13 - 25 lbs/hr coal, 24 - 40 lbs/hr steam, and 5 - 10 lbs/hr oxygen. Design work on the hydrogen-from-coal continuous process unit was completed in early July, and the design for the CPU was reviewed with the Department of Energy (DOE) Contracting Officer's Technical Representative (COTR) for approval to commence construction.

3.1.2 CPU Construction

Final drawings for the piping and instrumentation, and major pieces of equipment to be fabricated on site were completed. Lists of the equipment, instrumentation, and piping for the CPU were compiled, and procurement of equipment, instrumentation, and materials for fabrication not available on-site was initiated. In-house fabrication of equipment for the CPU included construction of the gasifier shell, the coal hoppers, the refractory-lined cyclone, the coal feeders, and the gasifier blowdown pot; along with the collection vessels for the fines removal system, and the gas/liquid separation vessels and heat exchangers for the gas quench system.

HYDROGEN-FROM-COAL CONTINUOUS PROCESS UNIT

Figure 1. Schematic diagram of the Hydrogen-from-Coal Continuous Process Unit

Several vendors of steam superheaters were contacted and asked to provide detailed product performance specifications for their steam superheaters. Bid specifications for the CPU's superheater were based on the heating load electrical requirements. Based on the instrumentation requirements of the CPU, specifications for a data acquisition system were derived. Bid specifications for the data acquisition system and superheater were sent to the appropriate vendors. Final selection of the steam superheater and data acquisition system were made, and each unit was procured. The superheater is a model RCH 6136-1.1-2DSS purchased from Hydro Steam Industries and has a power rating of 11.25 kW with a designed maximum output temperature of 790°C. The data acquisition system selected was a Keithly series 500 model.

The CPU is housed in the gasification tower for UNDERC's 1-ton/hour slagging fixed-bed gasifier. Structural recommendations for supporting the FBG were made prior to initiating preparation of the CPU site. Preparation included removal of the floor grating around the gasifier site and installation of a 2-ton crane and guards around the gasifier site. Prior to assembly of the CPU, the shell for the FBG was assembled on its side, as shown in Figure 2, and hydrostatically pressure checked by an independent laboratory. The gasifier shell was ASME certified by Twin Cities Testing Corporation for a working pressure of 200 psi. The gasifier was disassembled and forms were constructed for pouring the insulating and high-temperature refractories. The gasifier was lined with 4.5 inches of soft insulating refractory and 2 inches of hard high-temperature refractory. The gasifier's middle section was positioned by resting the wings on beam-mounted supports. The wings of the middle section were elevated approximately 10 inches above the support beam to provide sufficient clearance for the bottom bed drain. Figure 3 shows the middle section of the gasifier in place inside the gasification tower. After positioning the middle section of the gasifier the top and bottom sections of the gasifier were positioned and mounted.

The bottom plenum section of the gasifier holds the distributor plate in position, introduces the steam and oxygen into the gasifier, and houses the natural gas preheat burner. The plenum is a short radius elbow constructed of 10-inch diameter schedule 40 carbon steel pipe. The plenum is lined with high temperature refractory and has an inside diameter of approximately 6 inches. The distributor plate utilizes a bubble cap design and is constructed out of 304 stainless steel. The distributor plate was mounted on the bottom plenum section as shown in Figure 4, and the plenum was attached to the bottom section of the gasifier. Once the main sections of the gasifier were in place, the gasifier outlet was plumbed to the refractory-lined cyclone and fines collection vessel.

The gas quench system was assembled and installed inside the gasification tower. Figure 5 is a photograph of the gas quench system in place. The gas/liquid separation vessels and cryogenic trap are constructed of 304 stainless steel. The process side of the coaxial heat exchangers are constructed of 1/2 inch O.D. 304 stainless steel tubing with a 1-inch diameter copper pipe shell. The heat exchangers were mounted, and the cooling water and glycol cooling units were plumbed to their respective heat exchangers.

Figure 2. Fluid-bed gasifier shell prior to hydrostatic pressure test

Figure 3. Middle section of gasifier in place inside UNDERC's gasification tower

Figure 4. Bottom plenum section for fluid-bed gasifier

Figure 5. Gas quench system

The superheater was received in early December, and a mobil stand was constructed for the superheater to provide easier maintenance of the unit. The superheater was mounted on the mobil stand and positioned in place. Saturated steam and oxygen lines were plumbed to the inlet of the superheater, and the outlet was connected to the gasifier. A nitrogen purge line was also plumbed to the inlet of the superheater to provide cooling for the superheater and to replace oxygen while maintaining proper fluidization of the bed during process upsets.

Installation of the coal feed system was initiated by mounting the coal star and screw feeders on the bottom section of the gasifier as shown in Figure 6. The coal hopper was not accessible by the tower crane when the coal hopper was positioned in the coal feed system. Therefore, to allow loading and removal of the hopper using the tower crane a swinging support for the coal hopper was constructed and mounted as shown in Figure 7. The coal feed system was completed with the positioning of the coal hopper and support and the connection of the coal transfer line to the coal feeders.

Additional plumbing of the CPU involved installation of the nitrogen purge lines to the gasifier pressure taps, connection of the cyclone to the gas quench system, connection of the vent and rupture lines for the CPU, and installation of the air and natural gas lines for the natural gas preheat system. The blowdown pot for the gasifier was mounted on a mobil stand and connected to the gasifier. A sample conditioning system was also installed to ensure that the product gas going to the gas analyzers was free of moisture.

The frame for the CPU's control panel was also fabricated on site and positioned adjacent to the control panel for the slagging fixed-bed gasifier. A layout for the control panel was developed, and holes for the instrumentation were cut into the control panel and the instrumentation mounted. Figure 8 is a photograph of the CPU control panel. The control units for the coal feeders and the superheater were mounted on the wall opposite the control panel.

The instrumentation and motors for the CPU were mounted after positioning the major pieces of equipment and were connected to a central junction box inside the tower. For safety purposes, all electrical and instrumentation components inside the tower are explosion proof, and rigid conduit was used for all electrical and instrument leads. The electrical components and instrumentation for the CPU were then tied to the control panel and control units for the feeders and superheater.

3.1.3 CPU Shakedown

Construction of the CPU was delayed due to conflicts in operations manpower scheduling and delays in equipment procurement. Access was limited during construction due to other contractual obligations by UNDERC. This moved the beginning of the shakedown period for the CPU to March 1st. CPU operation training sessions were held to familiarize project personnel with the unit and its operation. Upon completion of the instrumentation connection with the control panel, the instrument loops for the entire CPU were tested.

Figure 6. CPU coal feed system

Figure 7. Coal hopper positioned on swinging support

Figure 8. CPU control panel

Shakedown of the hydrogen-from-coal CPU was initiated with a preliminary shakedown of the gas quench system. The gas quench system was pressure tested for leaks, and nitrogen (at 550°F) was passed through the system to check operation and instrument loops. Shakedown of the CPU continued with the curing of the refractory for the gasifier, overhead lines, and cyclone. During the refractory cure, the superheater, the natural gas preheat system, and the instrument loops for the gasifier and cyclone were checked out. The plenum was removed from the bottom of the gasifier after the curing, and the refractory was inspected and found to be free of major defects. After the refractory cure, an initial shakedown test of the coal feed system was completed. Several modifications were made to the coal feed system to eliminate various problems that were identified in the initial shakedown test. After the modifications, the coal feed system performed reliably and was calibrated for feeding -1/4" x 0 size coal.

Initial start-up test with the CPU will be made with a carbonaceous source that is low in, or free of, volatile matter, such as petroleum coke, to avoid problems with tars until operating procedures are more clearly defined. Bench-scale reactivity experiments on the reactivity of in-house petroleum coke, however, showed that the coke was extremely unreactive and not suitable for use in the start-up of the gasifier for hydrogen production. Efforts to find a more reactive char to minimize start-up problems due to volatile matter were initiated. Shakedown of the CPU is expected to continue through April, with the unit anticipated to be fully operational in May.

3.2 Coal Properties and Reactivity Analysis

The bench-scale study of the fundamental properties and reactivities of low-rank coal was initiated with the development of a test plan outlining test procedures and methods of analysis. The plan includes methods for studying active sites by gravimetric and spectroscopic means and discussion of the instrumental tools to be used for analyzing the coal char and ash. Velva (North Dakota) and Martin Lake (Texas) lignites were selected for the study because they have an existing data base to build on and because of their differences in geographic origin. In addition, Velva lignite exhibited excellent reactivity in the previous work and can serve as a "model" coal for hydrogen production from the char-steam reaction. Proximate and ultimate analyses for the two coals are listed in Table 1. The two catalysts chosen for the catalytic portion of the testing include potassium carbonate and trona. Potassium carbonate was selected based on its well documented catalytic effects, and trona was selected for its good catalytic performance in previous testing and its potential as a disposable catalyst.

3.2.1 Thermogravimetric Analysis (TGA)

The reaction between the low-rank coal chars and steam to produce hydrogen was studied with two different TGA systems. The kinetic study of weight change of char with time for the char-steam reaction was carried out on a DuPont 951 Thermogravimetric Analyzer interfaced with a DuPont 1090 Thermal Analyzer. Samples of approximately 20 mg of -100 x +140 mesh coal, uncatalyzed or catalyzed, were devolatilized under argon flowing at 160 cc/min, and the

TABLE 1
PROXIMATE AND ULTIMATE ANALYSES

	<u>Velva</u>	<u>Martin Lake</u>
Proximate Analyses:		
Moisture, %	29.3	34.8
Ash, wt% mf	13.5	8.7
Volatile Matter, wt% mf	39.3	43.0
Fixed Carbon, wt% mf	47.2	48.3
Ultimate Analyses, maf:		
Hydrogen	4.44	5.20
Carbon	69.28	72.77
Nitrogen	1.09	1.30
Sulfur	0.61	0.90
Oxygen (diff)	24.58	19.83

resulting char reacted with steam ($p(\text{H}_2\text{O}) = 0.1$). Weight, time, and temperature were recorded, and each experiment was terminated when weight loss ceased. Total gas samples (product gas plus carrier gas) were collected over the duration of the run and were analyzed by gas chromatography (GC). Selected experiments were duplicated on a large TGA (described below) for reacting samples larger than 1 g in order to collect gas samples with a larger mole fraction of hydrogen to increase the accuracy of the analysis. Reactivity parameters (k) for 50% carbon conversion were calculated at each of three temperatures (T), and Arrhenius plots of $\ln k$ versus $1/T$ were constructed for calculating energy of activation (E_a) and frequency factor (A) as in previous work (6). Residue remaining after the reaction was analyzed by X-ray Diffraction and X-Ray Fluorescence techniques.

A large capacity (>1 g) TGA module was constructed at UNDERC using a Cahn 1000 electrobalance and a 1200°C vertical tube furnace. A stand was fabricated in-house from non-magnetic stainless steel for the unit and the electrobalance and furnace were mounted on the stand. The large Cahn TGA was interfaced to the programmer/controller of a smaller Cahn model 113C TGA. Shakedown experiments were performed on the large system to determine its physical limitations in terms of sample size, steam flow, temperature ramp rate, cooldown time, and data capacity of the recorder. The shakedown of the system also included preliminary steam gasification reaction at 750°C carried out on uncatalyzed and trona catalyzed Velva char. The char was prepared in-situ in the large Cahn, and the char-steam reaction was run until less than 50% of the fixed carbon remained. Total gas samples (product gas and carrier gas) were collected in 20-liter gas bags and analyzed by GC.

A statistically designed set of bench-scale experiments on the reaction between uncatalyzed and catalyzed Velva and Martin Lake lignite-chars and steam were completed for the temperature range of 650^o-750^oC. This temperature range is lower than that of the previous Hydrogen Production project at UNDERC (4) and will be extended to include temperatures down to 600^oC. Previous data when plotted according to Arrhenius Theory (ln k (reactivity parameter) versus reciprocal absolute temperature) provided linear graphs in the temperature range of 700^o-800^oC (4). This linearity indicated that no change in mechanism occurred over the temperature range investigated. The lower temperature range investigated in this set of experiments was to determine if the mechanism would change at lower temperatures. The overlap at 700^o and 750^oC ensured conditions comparable to the previous experiments at UNDERC.

The inherent mineral matter of the Velva lignite had the effect of increasing the reaction rate over that of the Martin Lake lignite. Addition of either potassium or sodium compounds also increased the rate of the char-steam reaction for both the Martin Lake and the Velva chars. Potassium carbonate and trona admixed with the lignite both gave positive catalysis of the char-steam reaction, as shown by the reactivity parameters listed in Table 2. The reactivity parameter (k in g/hr/g) increased from 1.40 with no catalyst to 3.50 with 10 wt% K₂CO₃ and to 3.23 with 10 wt% trona for Velva lignite at 700^oC. The reactivity parameter also increased from 0.74 with no catalyst addition to 2.31 with 10 wt% K₂CO₃ and 2.37 with 10 wt% trona for Martin Lake lignite at 700^oC.

TABLE 2
REACTIVITY PARAMETERS FOR VELVA AND MARTIN LAKE CHARS

	<u>Reactivity Parameters (k) (G/hr)/G</u>		
	<u>Uncatalyzed</u>	<u>K₂CO₃ Catalyzed</u>	<u>Trona Catalyzed</u>
<u>Velva</u>			
650 ^o C	0.30	1.43	1.28
700 ^o C	1.40	3.50	3.23
750 ^o C	2.10	5.81	7.04
<u>Martin Lake</u>			
650 ^o C	0.36	0.96	1.05
700 ^o C	0.74	2.31	2.37
750 ^o C	1.70	3.95	3.50

The resulting Arrhenius plots are illustrated in Figures 9 and 10 for Velva and Martin Lake chars, respectively. Table 3 shows the calculated apparent energies of activation (E_a) and correlation coefficients from the Arrhenius plots in Figures 9 and 10. The plots show a change in slope over the 650°-750°C range for the uncatalyzed char-steam reaction but no change in slope for the trona catalyzed char-steam reaction. The linearity of the Arrhenius plot for the trona-catalyzed Velva char-steam reaction (Figure 9) is underscored by its correlation coefficient (Table 3) of 0.9995. The linearity is characteristic of a reaction following a single mechanism. The plot of the uncatalyzed

TABLE 3
ACTIVATION ENERGIES AND CORRELATION COEFFICIENTS OF
ARRHENIUS PLOTS FOR VELVA AND MARTIN LAKE CHARS

<u>Coal</u>	<u>Catalyst</u>	<u>Activation Energy, E_a</u>	<u>Correlation Coefficient</u>
Velva	Uncatalyzed	36.6	0.9165
	Trona-catalyzed	32.1	0.9995
	K ₂ CO ₃ -catalyzed	25.9	0.9922
Martin Lake	Uncatalyzed	29.2	0.9947
	Trona-catalyzed	22.7	0.9908
	K ₂ CO ₃ -catalyzed	26.7	0.9989

reaction shows a definite change in slope with a correlation coefficient of 0.9165. This suggests a change in mechanism for the uncatalyzed reaction as the temperature is changed over the 650°-750°C range. On examination of the plot of data from the K₂CO₃-catalyzed reaction it is observed that there is a slight change in slope of the curve between 650°-750°C. However, the correlation coefficient (0.9922) over that temperature range is not unlike that of the range from 700°-800°C (0.9968). In the previous hydrogen production project (4), data from the reaction over the latter temperature range did not indicate a change in mechanism. However, at this point it is unclear as to whether the small slope change represents an alteration of mechanism, and additional data will be required to provide more information from which to draw the final conclusion.

The normalized product gas compositions on the total gas sample collected during the hydrogen production reaction carried out on the large laboratory TGA for uncatalyzed and trona catalyzed Velva char at 700° and 750°C are shown in Table 4. The normalized hydrogen values approximated those predicted by the engineering thermodynamic model, with hydrogen concentrations in the product gas generally over 55%. The values obtained from the samples generated on the large TGA are somewhat more realistic compared to the total gas samples collected from the DuPont TGA since the dilution effect of the carrier gas, and thus the uncertainty in the GC analysis was reduced.

Figure 9. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Velve coal char with steam.

Figure 10. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Martin Lake coal char with steam

TABLE 4

PRODUCT GAS FROM VELVA LIGNITE CHAR-STEAM REACTION
CARRIED OUT IN THE LARGE TGA (MOLE %)

Sample*	Temp., °C	H ₂	CO ₂	CO	CH ₄
With 10 wt% Trona	750	56.23	30.13	13.64	ND
With 10 wt% Trona	700	51.73	43.51	4.55	ND
Uncatalyzed	750	57.70	35.30	6.30	0.72
Uncatalyzed	700	56.20	40.00	2.60	0.90

ND = Absent or below detection limit

* Sample sizes were between 1.0 and 1.4 grams of -100+140 mesh "as-received" coal-catalyst.

Data normalized to exclude carrier gas and air.

3.2.2 Surface Analysis

Catalyzed and uncatalyzed chars subjected to spectroscopic techniques were prepared as in the char-steam reactivity experiments, but were cooled to room temperature under argon. In selected experiments the char was removed from the TGA and stored under argon to prevent exposure to air. These samples were analyzed by ESCA and Cross Polarization/Magic Angle Spinning (CP/MAS) solid ¹³C NMR. Chars were also examined by analytical Scanning Electron Microscopy (SEM) both pictorially and for surface elemental composition. The field was scanned and representative particles were photographed and mapped to determine elemental distribution. All char samples were analyzed for active sites by gravimetric measurement of CO₂ adsorption in a manner similar to that described by Ratcliffe and Vaughn (7).

In preliminary ESCA analyses of Velva chars it was demonstrated that C-O, COOH, and C-N are readily detectable, although the results were not quantitative. Since these sites are thought to be key active sites during the char-steam reaction, their quantitation will give an indication of the relative reactivities of prepared chars. Table 5 shows the ESCA surface carbon/oxygen ratio on the Velva chars prepared at various temperatures. Char prepared at 750°C and exposed to air had a significantly lower surface C/O ratio than that prepared at the same temperature and protected from exposure to air. The latter sample was analyzed at the natural surface, and then at surfaces produced by removal of outer layers of char using ion "sputtering" for the time indicated on Table 5. The low C/O ratio of the exposed sample is due to the adsorption of oxygen on exposure to air due to the highly activated carbon that results during the char formation. The chars formed at the other temperatures given on Table 5 exhibited little increase in C/O ratio with temperature. These results indicate that erroneous surface data can be minimized by maintaining an inert atmosphere over the char samples, and a more accurate analysis can be carried out.

TABLE 5

PRELIMINARY ESCA RESULTS---VELVA LIGNITE CHAR (ELEMENT Z)

Char Temp., °C	Sputter Time, minutes	Element, %			
		C	O	N	C/O
750*	0	74.4	21.0	--	4.73
750	0	82.1	14.3	--	7.69
	10	82.9	13.0	--	8.52
	70	84.3	11.6	--	9.62
700	70	81.9	10.9	0.9	10.03
650	70	80.1	12.3	0.8	8.66
600	70	80.3	12.6	1.0	8.47

*Exposed to air

CP/MAS Solid ^{13}C NMR spectra of Velva chars prepared at temperatures from 600° to 750°C, shown in Figure 11 and 12, lacked aliphatic signals, indicating the removal of aliphatics during the charring process. Aromatic CO groups and carboxyl, amide, and ester groups are absent in the chars as well. The reduction in aromatic signal strength as a function of temperature may result from unobserved carbon signals in CP/MAS due to the decrease in H/C with the char (8).

SEM photographs, Figure 13 and 14, show the surface effect upon charring of adding catalyst to the coals. The ragged, irregular surface and lack of apparent pores in the uncatalyzed char was replaced by the rounded, highly porous surface on the alkali catalyzed char. The degree to which the surface changed with the addition of catalyst differed between the Velva and the Martin Lake chars. The Velva surface contained uniform, evenly spaced nodules of approximately 0.05 μm x 0.10 μm in size. Those of the Martin Lake are neither uniform in size nor evenly spaced over the surface. The reactivities differed similarly with the Velva having the higher reactivity. This suggests that the increase in reactivity of the catalyzed char, which may be due to mechanistic change in the chemical reaction brought about by the alkali, must also be due at least in part to the physical effect of producing a large increase in surface area. The result of this increase in surface area is an increase in available active sites as shown in Figures 15 and 16 for Velva char and Martin Lake char, respectively.

Figure 11. CP/MAS ^{13}C NMR spectra of (a) Velva, North Dakota, lignite; (b) Velva lignite char (750°C); and (c) Velva/trona char (750°C)

Figure 12. CP/MAS ^{13}C NMR spectra of Velva/trona char prepared at (a) 700°C; (b) 650°C; and (c) 600°C.

a) Martin Lake Char - Mag. 6000X

b) Martin Lake/ K_2CO_3 - Mag. 6000X

c) Velva Char - Mag. 6000X

d) Velva/ K_2CO_3 Char - Mag. 6000X

Figure 13. SEM photographs of coal chars and coal/ K_2CO_3 char prepared at 750°C

a) Velva/trona - 750°C - Mag. 780X

b) Martin Lake/trona - 750°C -
Mag. 780X

c) Martin Lake/10% K_2CO_3 - 750°C
Mag. 780X

d) Martin Lake/20% K_2CO_3 - 750°C
Mag. 780X

Figure 14. SEM photographs of coal/catalyst chars prepared at 750°C

Figure 15. Number of active sites per carbon atom in Velva lignite char with and without catalyst

Figure 16. Number of active sites per carbon atom in Martin Lake lignite char with and without catalyst

Mapping the surface for inorganic element distribution showed that the potassium was distributed uniformly over the surface of the Velva particles but not over that of the Martin Lake particles. The uniform distribution of the potassium catalyst on the surface of the Velva char implies a surface wetting by a fluid consisting of, or containing, the catalyst. The trona, however, does not exhibit this mode of distribution. Instead the map showed the sodium surface deposits as being associated with those of silicon and aluminum. The irregularly placed surface nodules of non-uniform size were located near the sodium deposits.

3.2.3 Ash Analysis

The ash obtained from the trona-catalyzed Velva char-steam reaction was analyzed by x-ray powder diffraction (XRD). The XRD results showed that the major minerals found included $\text{NaMg}(\text{CO}_3)_2$, Na_2CO_3 , $\text{Na}_6\text{Al}_4\text{Si}_4\text{O}_{17}$, and Na_2SiO_3 , all of which were expected due to the make-up of the catalyst. Minor minerals identified by XRD included MgCO_3 and MgO . The ash was also analyzed by x-ray fluorescence (XRF), and the results are listed in Table 6. The XRF showed a substantial amount of sodium as expected but also a substantial amount of calcium; however, no calcium minerals appeared on the x-ray diffraction pattern. Further investigation with other ash samples is being pursued.

TABLE 6

ASH ANALYSIS OF VELVA CHAR BY XRFA

Oxide	Uncatalyzed		Trona Catalyzed 750°C
	700°C	750°C	
Si	46.40	43.70	25.50
Al	19.20	19.10	12.30
Fe	3.50	2.50	3.20
Ti	0.70	0.50	0.50
P	0.20	0.40	0.10
Ca	16.30	13.40	13.80
Mg	5.60	6.40	4.10
Na	0.00	2.10	29.90
K	0.70	0.70	0.90
S	7.40	11.20	9.70

3.3 Thermochemical Cycles

A literature search was conducted to identify any possible thermochemical cycles presently documented that may be combined with coal gasification to enrich the hydrogen off-take gas. Thermochemical cycles may economically utilize the heat from coal gasification processes for the thermal portion of the cycle to produce hydrogen in addition to the hydrogen produced from coal

gasification. Thermochemical cycles for the hydrogen production from water prior to 1976 is reviewed by Bamberger, and the review lists 72 published cycles and the maximum temperature for each operation (9). Since 1976 an enormous effort has been made to find useful thermochemical cycles for the production of hydrogen. A library of the various types of processes to produce hydrogen has been compiled, resulting in 200 documents and well over 1000 references.

Based on the literature search, two thermochemical cycles were identified as potential candidates for enriching the hydrogen in the offtake stream of a coal gasification process. These thermochemical cycles are the Westinghouse Cycle (10) and the Mark 13 cycle (11), which are outlined below:

1. The Westinghouse Cycle

2. The Mark-13 Cycle

The adaptation for thermochemical cycles in conjunction with coal gasification processes, however, will require further development to determine the proper integration into the gasification process.

4.0 CONCLUSIONS

- Bench-scale experiments show that H_2 can be produced in concentrations predicted by equilibrium via the catalyzed char-steam reaction.
- Reactivity of low-rank coal chars are increased by factors of two to four at a given temperature with addition of catalyst. The increased reactivity is due to increases in surface area and active sites.
- Scanning electron microscopy shows that catalyzed chars have a much higher surface area than uncatalyzed chars and that potassium was distributed more uniformly than the trona over the char surface.

- The highly activated carbon created by the devolatilization of the low-rank coal necessitates the prevention of exposure to air if CO functional groups are to be accurately identified by ESCA or quantified by CP/MAS ^{13}C NMR.
- A continuous process unit for the demonstration and preliminary engineering assessment of producing hydrogen from the catalytic steam gasification of low-rank coals has been designed and constructed.

5.0 PRESENTATIONS AND PUBLICATIONS

A paper entitled "Catalyzed Steam Gasification of Low-Rank Coals to Produce Hydrogen" was presented at the American Chemical Society National Meeting, September 7 through 12, in Anaheim, California. The paper summarizes the previous bench-scale TGA steam-char kinetics work. Another paper entitled "The Use of Thermogravimetry (TG) in the Kinetic Study of a Coal Char-Steam Reaction to Produce Hydrogen" was presented at the Pittsburgh Conference March 9-13, 1987, in Atlantic City, New Jersey.

6.0 REFERENCES

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

1. Program/Project Identification No. DE-FC21-86MC10637		2. Program/Project Title Hydrogen Production from Low-Rank Coals		3. Reporting Period 1-1-87 through 3-31-87	
4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202				5. Program/Project Start Date 4/1/86	
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Milestone ID. No.	Description	Planned Completion Date	Actual Completion Date	Comments	
a.1	Complete design and construction of CPU	*02/01/87	03/01/87	*Revised 01/15/87	
a.2	Shakedown testing	*05/01/87		*Revised 01/15/87	
b.1	CPU test plan preparation	*04/30/87		*Revised 01/15/87	
b.2	CPU performance evaluation	08/01/88			
b.3	Bed material testing	*06/01/88		*Revised 01/15/87	
b.4	Technical report	10/01/88			
c.1	Properties and reactivity test plan preparation	06/01/86	05/15/86		
c.2	Property and reactivity testing	03/01/88			
c.3	Technical report	08/01/88			

ADVANCED WASTEWATER TREATMENT

Final Technical Report for the Period April 1, 1986 - March 31, 1987
including the Quarterly Technical Progress Report
for the Period January through March, 1987

By

University of North Dakota Energy Research Center
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April 1987

Contracting Officer's Technical Representative: Mr. Leland Paulson

Prepared For
United States Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

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1.0 FIXED-FILM DENITRIFICATION OF PRETREATED GREAT PLAINS GASIFICATION WASTEWATER

1.1 Objective.

The objective of the fixed-film denitrification studies was to demonstrate the applicability of this process for the treatment of gasification condensate.

1.2 Background.

Denitrification is a respiratory reaction very similar to electron transport using oxygen, with the substitution of nitrite or nitrate for the oxygen. In respiration, oxygen is the terminal electron acceptor and is reduced to water. Denitrification is of two types: assimilatory and dissimilatory. Assimilatory denitrification is incomplete denitrification since nitrate is reduced to the level of ammonia only, and is performed by a large number of microbes to obtain nitrogen for metabolism. Dissimilatory denitrification is used by a more select group of microbes as a means of obtaining energy in the absence of oxygen. Dissimilatory denitrification results in reduction of nitrite or nitrate to nitrogen gas (N_2) or gaseous nitrogen oxides (1).

A program of complete nitrogen removal from wastewater requires the following biochemical processes: carbon oxidation, nitrification and denitrification. These processes are usually performed in separate reactors due to their widely different requirements. Although all of these operations function optimally at neutral pH and at, or slightly above room temperature, they are otherwise very different. In carbon oxidation, organic compounds and dissolved oxygen are required for aerobic oxidation to carbon dioxide, water and biomass. In nitrification, inorganic carbon and dissolved oxygen are required, and large amounts of acid and nitrite or nitrate are produced. In denitrification, organic carbon is required, dissolved oxygen must be absent or in low concentrations, and alkali, carbon dioxide, N_2 , and biomass are produced. The microbes involved in carbon oxidation and denitrification have relatively fast growth rates, while the nitrifying bacteria have quite low growth rates.

Since the organic load of the wastewater is reduced considerably prior to denitrification and, since organics are required for denitrification, organics must be added. This problem has been addressed by adding a slipstream of raw wastewater to the denitrification reactor, or adding an exogenous organic compound. A number of exogenous organics have been used such as acetate, ethanol and methanol. Of these methanol is believed to be the best choice, and is most often used.

When methanol is used as the carbon source for denitrification the reaction can be shown by equation 1:

From this equation it can be seen that alkalinity is produced at the rate of one mole of hydroxide per mole of nitrate reduced. For a wastewater with a high nitrate content and poor buffering, this would require the addition of

acid to keep the pH optimal. The optimal pH for denitrification has been reported to be in the range of 6.6 to 8.0 (2).

1.3 Methodology.

A packed-bed column, 28.6 cm (11.25 in.) high and with a 7.6 cm (3 in.) inside diameter plexiglass column, was used for the reactor. This column reactor, shown in Figure 1, was packed with hollow plastic cylinder media (Raschig rings) that had a porosity of 86.5% and a surface area of $3152 \text{ m}^2/\text{m}^3$ ($96 \text{ ft}^2/\text{ft}^3$). The column was operated in a completely flooded mode without recycle of water.

Figure 1. Schematic of the Packed Column Denitrification Reactor.

The reactor was seeded with biomass from an actively denitrifying population. Initial biomass accumulation was performed under aerobic conditions using nitrified wastewater supplemented with glucose, glutamic acid and methanol. After six weeks of operation in this mode, the unit was switched to the anoxic mode of operation. Anoxia was achieved by nitrogen-stripping of feed wastewater. During the operations under anoxic conditions, glucose and glutamic acid addition was halted; however, the addition of methanol was continued. Methanol was added at the rate of 3.75 mg methanol per mg of nitrate-N. This rate is significantly higher than the stoichiometric quantity required, as reported by other investigators of 2.75:1 mg methanol:mg $\text{NO}_3\text{-N}$ (2). This ensured that methanol would not become limiting during the test program.

Three hydraulic loadings were tested successively with the fixed-film denitrification reactor. During pseudo-steady-state for each of these loadings, samples of the feed and effluent were taken and analyzed for nitrite, nitrate, and ammonia.

1.4 Wastewater.

The wastewater used for this research was obtained from the Great Plains Gasification Plant near Beulah, North Dakota. The condensate from the gasification of lignite coal, known as raw gas liquor, is solvent-extracted, and steam-stripped. This solvent-extracted and steam-stripped wastewater is known as stripped gas liquor (SGL). The SGL was transported to UNDERC and biologically treated by activated sludge to reduce the BOD content, then nitrified in an activated sludge reactor. The composition of the SGL before and after nitrification is shown in Table 1. Details of the carbon oxidation and nitrification of the SGL have been previously reported (3,4).

Table 1. Mean Composition of the Great Plains Gasification Associates Stripped Gas Liquor (mg/l except pH).

Component	As-received SGL	Nitrified SGL
COD	2770	126
TOC	870	26
BOD ₅	1150	<10
Ammonia-N	626	<10
Cyanide	5	ND
Nitrite-N	ND	2
Nitrate-N	ND	841
pH	9.3	7.6

1.5 Results and Discussion.

Feed wastewater was initially taken from a large quantity of well-mixed nitrified SGL. Thus, the nitrate content was relatively constant for a major portion of this research, as illustrated in Figure 2. Effluent nitrate-N concentrations closely paralleled the nitrate-N loading, as shown in Figure 3. Steady-state had apparently not been attained during the third loading, between day 123 and the end of operations.

The percent nitrate-N removed from the influent is shown in Figure 4. The earlier operations, at the lowest hydraulic loading (5.6 liters/m²-day), resulted in the highest observed percent removals. The observed percent removals during the intermediate hydraulic loading (11.2 liters/m²-day) were

Figure 2. Influent and Effluent Nitrate-N Concentrations During the Test Period.

Figure 3. Loading of Nitrate-N (kg NO₃-N/1000 m²-day) into and out of the Packed Column Reactor.

Figure 4. Percent Nitrate-N Removed from the Great Plains Gasification Plant (GPGP) Nitrified Stripped Gas Liquor (SGL).

the lowest observed. These removals improved dramatically during the latter part of this loading, increasing from approximately 70% to 93% removal. Interpretation of the removals during the highest hydraulic loading (16.8 liters m^2 -day) are complicated by the following: 1) non-steady-state conditions; 2) decreasing nitrate content of the feed; and 3) the limited amount of data available. In general, it is expected that the removal of nitrate at the highest loading will be less than that observed during the next lowest hydraulic loading.

Table 2 compares the data for the three hydraulic loading rates with the nitrate loadings and the observed removal data. The mean effluent NO_3 -N concentrations, shown in Table 2 for each of the hydraulic loadings, increase with increasing hydraulic load, as expected. Although the mean NO_3 -N for the 5.6 liter/ m^2 -day loading was 18.6 mg/l, concentrations as low as 1.5 mg/l were observed during this loading. Concentrations of NO_3 -N in the effluent were considerably higher at the other hydraulic loadings. However, the trend in the effluent NO_3 -N data indicate a decline with increasing acclimation or biomass buildup. Thus, this reactor could probably achieve much lower effluent NO_3 -N concentrations than were observed at the higher loadings.

Table 2. Fixed-Film Denitrification Reactor Performance.

Hydraulic Loading (liters/m ² -day)	5.6	11.2	16.8
Flow Rate (liters/day)	2.3	4.6	6.9
Hydraulic Retention Time (hours)	13.6	6.8	4.5
NO ₃ N Loading (kg/1000 m ² day)	4.27	8.85	4.86
Influent NO ₃ N (mg/l)	841	788	288
Effluent NO ₃ -N (mg/l)	18.6	179	120
NO ₃ -N Removal (%)	97.8	78.3	83.7

These removal data compare favorably with those obtained by another investigator using similar conditions (5). A packed column reactor, methanol as the carbon source and a high nitrite/nitrate wastewater (1000 mg N/l) were used. Removal efficiency, expressed as mg N/liter-hour, ranged from 8.7 to as high as 506.7 (5). Using the bed volume of the denitrification reactor, estimated efficiencies from this research range from 62 to 108 mg N/liter-hour.

Kinetic coefficients were estimated from this data using the model proposed by Kincannon (6). This model, known as the total organic loading approach, simply compares the loading of substrate removed versus the loading applied to the system. The total organic loading concept has been applied to a number of fixed-film biological processes. The equation used is:

$$L_R = L_{R(max)} * L_0 / (K_s + L_0)$$

where:

- L_R = amount removed, kg/1000 m²-day,
- L_0 = applied loading, kg/1000 m²-day,
- $L_{R(max)}$ = maximum amount removed, kg/1000 m²-day,
- K_s = applied loading at which the removal rate equals one-half $L_{R(max)}$, also known as the proportionality constant.

This equation, which has the same form as the Monod equation, may be rearranged to make a linear plot, as shown:

$$1/L_R = (K_S/L_{R(max)}) * (1/L_0) + 1/L_{R(max)}$$

This equation may then be used to estimate the kinetic parameters by plotting the reciprocal of L_R against the reciprocal of L_0 . The slope of the resulting line is $K_S/L_{R(max)}$, and the y-intercept is $1/L_{R(max)}$.

Figure 5 plots the amount of $\text{NO}_3\text{-N}$ removed versus the amount applied. A simple linear regression of these data yield a slope of 0.55 and a y-intercept of 1.88 with an R^2 of 0.756. The reciprocal plot of these data, used for the kinetic estimates, is shown in Figure 6. The linear regression of these data resulted in a slope of 0.74 and a y-intercept of 0.067, with an R^2 of 0.83. The $L_{R(max)}$ determined from this analysis is 14.82 $\text{kg}/1000 \text{ m}^2\text{-day}$ and the K_S is 10.97 $\text{kg}/1000 \text{ m}^2\text{-day}$.

Figure 5. Plot of Nitrate-N Removed Versus Nitrate-N Applied in $\text{kg NO}_3\text{-N}/1000 \text{ m}^2\text{-day}$ in the Packed Column Denitrification Reactor.

Figure 6. Kinetic Plot for the Packed Bed Denitrification Reactor. The Reciprocal Nitrate Removed is Plotted Against the Reciprocal Nitrate Applied in kg NO₂-N/1000 m²-day.

A removal rate reported for denitrification at a similar temperature of 23°C was 18.6 kg N/1000 m²-day (2). The data obtained in this study compare favorably when taking into consideration the following: 1) this study used wastewater with relatively high concentrations of nitrate, while the other study used municipal wastewater, and 2) the performance of the reactor used in this study (2) was still improving at the completion of this research.

1.6 Summary.

The bench scale packed column denitrification column reactor has demonstrated high removals of nitrate from nitrified Great Plains Gasification Plant stripped gas liquor. Removals as high as 99.8% were obtained at influent NO₃-N concentrations of 841 mg/l. Further improvement in NO₃-N removal rates are expected if operations had continued. Kinetic coefficients were obtained using the total organic loading approach for nitrate-N removal.

2.0 Update on the PDU Downflow Coupled Fluidized-bed Reactor.

2.1 Introduction.

Construction of the process development unit (PDU) has been completed and shakedown testing of the system will be completed soon. A number of changes were made during the construction of this unit that were not anticipated by the initial design (7). Therefore, a complete discussion of the PDU shown in Figure 7, follows.

2.2 Oxidic Reactor.

This reactor has a total height of 2.44 m (8 ft). The material of construction is plexiglass pipe with 0.63 cm (0.25 in) wall thickness. The upper 1.83 m (6 ft) has an inside diameter of 11.4 cm (4.5 in) and the lower 0.61 m (2 ft) has an inside diameter of 14 cm (5.5 in). The larger diameter, lower 0.61 m (2 ft), lowers the cross-sectional velocity of the wastewater flow and prevents media from prematurely washing out of the column. Sample ports are located at 15.2 cm (6 in) intervals beginning at the top of the column. The sample ports are constructed so that a sample can be obtained at any point across the diameter of the column. Recycle wastewater flow passes through a rotameter and enters at the top of the column. It then passes through a distribution nozzle which spreads the flow evenly across the cross section of the column. The wastewater exits the bottom of the column and flows to a clarifier and on to the anoxic surge column.

2.3 Anoxic Reactor.

This reactor has a total height of 2.44 m (8 ft). The upper 1.83 m (6 ft) has an inside diameter of 8.9 cm (3.5 in) and the lower 0.61 m (2 ft) has an inside diameter of 11.4 cm (4.5 in). Recycle wastewater flow, sample ports and material of construction are the same as described for the oxidic reactor. The effluent from this reactor flows to a clarifier and on to the aeration column.

2.4 Aeration Column.

This column is 1.22 m (4 ft) long by 4.44 cm (1.75 in) in diameter. Wastewater enters the aeration column from the anoxic clarifier and from the anoxic surge column. Effluent from the entire fluidized bed system discharges at this point. A stainless steel fritted air diffuser is immersed at the bottom of the column to aerate the wastewater prior to pumping to the oxidic column.

2.5 Anoxic Surge Column.

This column provides a surge volume of 0.94 liters to prevent starvation of the anoxic recycle pump.

2.6 Recycle Pumps.

Two identical recycle pumps are required to fluidize the reactors - one pump for each. Each reactor is fluidized with a positive displacement, progressing cavity Moyno pump which is controlled with a frequency

Figure 7. Schematic of the PDU downflow coupled fluidized-bed reactor.

controller. This arrangement allows for changing flowrates by electronically changing motor speed. The progressing cavity-type pump is very accurate, even under high and variable head, and does not damage biomass. Additionally, progressing cavity pumps are resistant to damage from solids. This may be important if bed material escapes the clarifier.

2.7 Wastewater Feed Pump.

A variable speed peristaltic pump is used to meter wastewater to the reactor.

2.8 Air Supply and Control System.

Primary Air Supply - Air for the aeration column is supplied from a large compressor that supplies the entire research center.

Emergency Air Supply - A 4.72 liter/s (10 scfm) compressor is provided to automatically supply air to the aeration column when the primary air supply falls below a preset pressure.

Air Filtration - Air to the aeration column is passed through a filter to remove oils and particulates.

Air Flowrate Control - Air flow is metered through a pneumatic control valve. A controller receives a 0-100mV signal from the dissolved oxygen meter, which measures oxygen concentration in the effluent from the oxic reactor. The controller processes this signal to position the pneumatic control valve such that the dissolved oxygen concentration remains at a preset value.

2.9 pH Control System.

The pH controller receives a signal from a pH probe inserted in the effluent from the anoxic reactor. A peristaltic pump is controlled in response to this signal to pump sodium bicarbonate into the anoxic clarifier to maintain the desired pH.

2.10 Clarifiers.

There are separate, identical clarifiers for each reactor. The clarifier is a four liter polyethylene funnel with a wall dividing it into two chambers. This arrangement allows separation of the floating media from the wastewater stream prior to entering the recycle pump.

2.11 Wastewater Storage.

Wastewater is stored in a 1890 liter (500 gallon) polyethylene tank which is kept under a nitrogen gas purge to prevent chemical or biological oxidation. Sufficient wastewater for one or two days feed is stored at the reactor site in a 208 liter (55 gallon) nitrogen-purged drum.

2.12 Standby Generator.

A 10 Kw natural gas-fired generator will supply emergency power automatically in the event of an outage of commercial electrical power.

2.13 Heat Exchanger.

A temperature controller regulates the temperature of a water bath in which coils of stainless steel tubing are immersed. Recycle flows for both the oxic and the anoxic reactors pass through individual coils which control the wastewater at a preset temperature of 25°C (77°F).

2.14 Media.

The material that will be used initially for a media is 3M Ceramic Macrospheres. These spheres contain a multiplicity of minute, independent closed air cells surrounded by an impermeable outer shell. Specific gravity of the spheres is about 0.70. The particle size distribution of the lot received at UNDERC ranged from 0.25 to 1.4 mm. Approximately 47% by weight was in the 1.2 mm, 30% in the 0.84 mm and 20% in the 0.60 mm size fractions. The manufacturer reports that the thermal stability of the macrospheres is 1100°C (2000°F). Thus, when biomass must be estimated on the media or for recycle purposes, the media can be thermally regenerated.

3.0 References.

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4. Name and Address University of North Dakota Energy Research Center Box 8213, University Station, Grand Forks, ND 58202		5. Program/Project Start Date <u>4/1/86</u>
		6. Completion Date <u>3/31/92</u>

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U.S. DEPARTMENT OF ENERGY
FEDERAL ASSISTANCE MANAGEMENT SUMMARY REPORT

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Milestone ID No.	Description	Planned Completion Date	Actual Completion Date	Comments
a.1	Fluidized bed bench-scale studies	07/86	7/86	
a.2	Test plan preparation	08/86	8/86	
a.3	Design of the PDU fluid bed system	10/86	10/86	
a.4	Construction of the PDU fluid bed system	12/86	12/86	Equipment being relocated
a.5	System calibration	02/87	4/87	
b.1	Pure oxygen, plug flow column reactor test plan	03/87		
c.1	Study of pretreatment requirements for discharge of gasification wastewater to POTW - Literature search	01/87	1/87	