

## DEMONSTRATION OF MICRONIZED COAL REBURNING FOR NO<sub>2</sub> CONTROL ON A 175 MW UNIT

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### ABSTRACT

The Tennessee Valley Authority (TVA) has been selected for the Department of Energy's (DOE's) Clean Coal Technology IV program to demonstrate micronized coal reburn technology for control of nitrogen oxide (NO<sub>x</sub>) emissions on a 175 MWe wall-fired steam generator at its Shawnee Fossil Plant. As the technology of the MicroFuel Department of Fuller Power Corporation makes this demonstration feasible, TVA has selected them as the prime contractor for the project and partner in the commercialization of this technology. This retrofit demonstration is expected to decrease NO<sub>x</sub> emissions by 50 to 60 percent. Up to 30 percent of the total fuel fired in the furnace will be micronized coal injected in the upper furnace creating a fuel-rich reburn zone. Overfire air will be injected at high velocity for good furnace gas mixing above the reburn zone to insure complete combustion. Shawnee Station is representative of a large portion of boilers in TVA's and the nation's utility operating base. Micronized coal reburn technology compares favorably with other NO<sub>x</sub> control technologies and yet offers additional performance benefits. This paper will focus on micronized coal reburn technology and the plans for a full-scale demonstration at Shawnee.

### INTRODUCTION

According to recent industry studies, 44 percent of the nation's coal-fired plants will have seen their 30th birthday by the turn of the century. Older fossil plants typically have the following operating characteristics, and many of these conditions lead to high NO<sub>x</sub> production:

- high excess air,
- deteriorating coal fineness,
- poor control of secondary air,
- mill capacity limited from coal switching,
- poor turn-down ratio, and
- cyclic duty operation.

TVA has a high boiler population that falls into this category, yet demand upon this existing fossil generating capacity continues. Therefore, TVA has investigated methods of reducing NO<sub>x</sub> while improving overall boiler performance.

A substantial database has been developed in the reduction of nitrogen oxides (NO<sub>x</sub>) by various

combustion modifications both here and abroad. Accurate control of coal particle fineness and air fuel ratios are essential ingredients in their success. The purpose of this project is to demonstrate the effectiveness of micronized coal (80 percent less than 325 mesh) combined with an advanced coal reburning technology.

Up to 30 percent of the total fuel fired in the furnace will be micronized coal. This fuel will be injected into the upper region of the furnace, creating a fuel-rich zone at a stoichiometry of 0.8 to 0.9. Overfire air will be injected at high velocity for good furnace gas mixing above the reburn zone, insuring an oxidizing zone for an overall furnace stoichiometry of 1.15 (excess air of 15 percent). Micronized coal reburn technology reduces NO<sub>x</sub> emissions with minimal furnace modifications and enhances boiler performance with the improved burning characteristics of micronized coal (Figure 1).

The addition of the reburn fuel into the furnace solves several problems concurrently. Units that are mill limited now have sufficient fuel capacity to restore their lost capacity. Restoration of lost capacity, as a benefit to NO<sub>x</sub> reduction, becomes a very economical source of power generation. Reburn burners can also serve as low-load burners, and units can achieve a turndown of 8:1 without consuming expensive auxiliary fuels. The combination of micronized coal reburn fuel and better pulverizer performance will increase unit performance by increasing carbon burnout.

Micronized coal reburn technology can be applied to cyclone-fired, wall-fired and tangentially-fired pulverized coal units. The overfire air system can also be easily adapted to incorporate in-furnace sorbent injection for SO<sub>2</sub> control.

A baseline test profile of the furnace, along with furnace flow and computer modeling, will be conducted prior to the design and installation of the MicroMill™ systems and micronized coal injector/burners. An extensive test program will document performance during a three-year operational period.

### DOE CLEAN COAL TECHNOLOGY DEMONSTRATION PROGRAM

The Clean Coal Technology Demonstration (CCT) program is a multibillion-dollar national commitment, cost shared by the government and the private sector to demonstrate economic and environmentally sound methods for using our nation's most abundant energy resource, coal. The program will foster the energy-

efficient use of the nation's vast coal resource base. The program will contribute significantly to the long-term energy security of the United States, further the nation's objectives for a cleaner environment and improve its competitive standing in the international energy market.

The objective of the CCT is to demonstrate a new generation of innovative coal utilization processes in a series of "showcase" facilities built across the country. The program takes the most promising of the advanced coal-based technologies and, over the next decade, moves them into the commercial marketplace through demonstration. These demonstrations are on a scale large enough to generate all the data for design, construction and operation that are necessary for the private sector to judge their commercial potential and make informed, confident decisions on commercial readiness.

DOE selected TVA's micronized coal reburning at Shawnee as one of the nine projects to be demonstrated under Round IV of CCT. Since  $\text{NO}_x$  and  $\text{SO}_2$  have been designated by the 1990 Clean Air Act Amendments passed by the U.S. Congress as precursors of acid rain precipitation, controlling  $\text{NO}_x$  has presented challenging problems in achieving a low-cost retrofit control system. To date, there have been several methods used to reduce  $\text{NO}_x$ ; however, each has some disadvantages. Low  $\text{NO}_x$  burners have been fairly successful but may not provide sufficient reduction by themselves. Gas reburning also has been successful, but it requires a steady supply of gas at a reasonable cost. Coal reburning shows promise in providing a  $\text{NO}_x$  control system which can be readily retrofitted and operated at low cost. Coal reburning does not require external modifications to the flue gas duct system nor does it require major modifications to the boiler or a separate type of reburn fuel. In fact, coal reburning may help some power producers who have had to derate their unit due to coal switching that was implemented to meet  $\text{SO}_2$  reduction requirements.

#### Site

**Site Description.** The host site will be one of Units 1-9 at TVA's Shawnee Fossil Plant which was built to help meet the huge electric power requirements of a nearby DOE facility. Construction began in January 1951 and was completed in 1956.

Units 1-9 are 175 MWe (gross) front wall-fired, dry-bottom furnaces burning East Appalachian low-sulfur coal. The plant was originally designed to burn high-sulfur coal; but in the 1970s, the plant was modified to burn low-sulfur coal in order to meet an emission limit of 1.2 lbs.  $\text{SO}_2/10^6$  Btu of heat input without the use of any sulfur dioxide control technology. Each unit has been equipped with a baghouse to control particulate emissions. Flue gas from each unit discharges to one of two 800-foot stacks, also constructed in the 1970s. The nine existing pulverized coal units are representative of a large number of wall-fired units in the industry which will be required to reduce  $\text{NO}_x$  emissions in response to the 1990 Clean Air Act Amendments.

#### Coal Acquisition

TVA has contracts in place to supply Shawnee with low-sulfur bituminous coals from Kentucky and West Virginia. These coals will be used as the primary fuels

for the project. TVA has conducted test burns of western coals such as Powder River Basin (PRB) at a number of sites, including Shawnee, since the late 1970s. PRB coal will be obtained for testing during this demonstration.

## REBURN CONCEPT

### Concept Operation

Micronized coal reburning for  $\text{NO}_x$  control will operate in the same manner as natural gas reburning on coal-fired boilers. In effect, the entire furnace operates as a low  $\text{NO}_x$  burner. The existing burners shall be operated at a lower than normal stoichiometric ratio, with special attention being applied to fuel/air control. Microfine coal with a surface area of 31  $\text{m}^2/\text{gm}$  is fired substoichiometrically in a reburn zone above the top row of the existing burners. Oxidation of high-surface-area micronized coal consumes oxygen very rapidly, converting  $\text{NO}_x$  to molecular nitrogen.  $\text{NO}_x$  conversion requires a residence time of 0.5 to 0.6 seconds. Above the reburn zone, high velocity overfire air will uniformly mix with the substoichiometric furnace gas to complete combustion, giving a total excess air ratio of 1.15. This concept should reduce  $\text{NO}_x$  emissions 50 to 60 percent from current levels of 0.82 to 0.95 lbs/ $10^6$  Btu to an emission level of 0.33 to 0.48 lbs/ $10^6$  Btu.

The proposed project will demonstrate the effectiveness of reducing nitrogen oxide emissions with an advanced coal reburning technology utilizing micronized coal. This technology can be applied in new as well as existing pulverized coal-fired furnaces. The coal used in reburning can be the same coal as used in the main fuel burners. A schematic of this system is shown in Figure 1. In addition, this reburn technology can be combined with various sulfur dioxide ( $\text{SO}_2$ ) control technologies such as fuel switching, dry sorbent injection or other postcombustion technologies.

The addition of MicroMill systems will increase total heat input and will allow classifier settings on existing pulverizers to be adjusted for improved fineness, relating directly to combustion efficiency and lower Loss on Ignition (LOI). Stoichiometry in the lower furnace is maintained at 1.05 (5.0 percent excess air) to assure an oxidizing zone and minimize slagging and corrosion. The stoichiometry at burner level 5, the reburn level, is 0.8 to 0.9; and with the addition of overfire air at level 6, the furnace will have an existing stoichiometry of 1.15 (15 percent excess air), compared to the current operating condition of 1.21 (21 percent excess air). Thus, the micronized coal reburn system not only reduces  $\text{NO}_x$  emissions but also improves boiler efficiency and increases boiler capacity.

### Process Advantages

Reburning is a recognized, effective technology for controlling  $\text{NO}_x$  emissions in a pulverized coal-fired boiler; however, most of the reburning activity to date has been with natural gas or oil as the reburn fuel. The following advantages of micronized coal reburning for  $\text{NO}_x$  control compare favorably with other  $\text{NO}_x$  control technologies.

- Disadvantages of natural gas and oil. Both natural gas and oil have been demonstrated to be effective reburning fuels; however, they are subject to one or more of the following disadvantages:

- availability, especially in winter,
  - unstable/escalating fuel cost,
  - operational problems firing dual fuels, and
  - reduced boiler efficiency due to hydrogen in fuel.
- **Micronized coal as reburn fuel, even with the additional coal handling and micronization cost, is a cost effective alternative to gas and oil due to the substantially lower fuel cost and elimination of problems associated with gas and oil.**
- **Flexibility.** The technology is flexible enough to combine with other NO<sub>x</sub> control technologies and reduce NO<sub>x</sub> emissions to required lower levels.
- **Site specific benefits:**
    - reduced energy replacement costs due to improved ability to operate at a rated load, even with wet coals and/or equipment problems (mills, feeders),
    - reduced capacity costs due to increased power generation,
    - increased fuel flexibility allowing use of lower quality coals while mitigating deratings caused by fuel handling limitations,
    - the ability to operate existing pulverizers at reduced throughput without loss in unit capacity will improve coal fineness and possibly reduce unburned combustible in ash, thus increasing value of the ash as a marketable commodity,
    - improved turndown and stability at low loads without firing supplemental fuels and maintaining superheater outlet temperatures at low loads, and
    - knowledge gained from this demonstration can be used to scale up the micronized coal reburn technology for installation on TVA's Allen Fossil Plant (330 MWe cyclone fired).

#### **NO<sub>x</sub> Control Strategy**

A majority of the 300,000 MWe generated by coal-fired utility units will be impacted by the 1990 Clean Air Act Amendments requiring reduction of NO<sub>x</sub> emissions. It is unlikely that one NO<sub>x</sub> control method will meet the needs of this diverse boiler population. NO<sub>x</sub> control strategies fall into two major categories: combustion modification and postcombustion technologies.

Combustion modification includes low NO<sub>x</sub> burners, reburning and fuel air staging. The postcombustion options are Selective Noncatalytic Reduction (SNCR) using reagents such as ammonia or urea and Selective Catalytic Reduction (SCR) using both reagent injections and catalysts.

In selecting a NO<sub>x</sub> control strategy for a given unit, utility engineers must weigh many factors including the type of unit, operating requirements and unit design ratings versus current operating capabilities. Most utilities will probably select some form of combustion modification as their preferred NO<sub>x</sub> control methods. Many utilities, already familiar with pulverized coal

burners and burner management systems, will elect to install low NO<sub>x</sub> burners as the method of controlling the combustion process.

There is, however, a large population of utility boilers for which reburning is an attractive option. Wet bottom furnaces such as cyclones and some wall-fired furnaces that operate in a slagging mode are obvious choices for reburning, and the addition of a micronized coal reburn system can be utilized in such diverse applications as start-up, low-load operation and restoring lost capacity. In addition, units that operate at very low loads for long periods of time, units that are relegated to cyclic duty and units that have pulverizer load limitations resulting from fuel switching are all very good candidates for micronized coal reburning as a primary NO<sub>x</sub> control method.

#### **SUPPORTING ACTIVITIES**

While the micronized coal reburn system is in a state of technical readiness for full-scale demonstration, there will be several supporting activities to insure a high degree of success for the demonstration. Among these activities are furnace cold-flow and computer modeling. The modeling will be conducted in the first phase and will provide even further evidence of adequacy, availability, suitability and quality of the data and analysis to support the full-scale demonstration.

Diagnostic tests will be conducted to determine temperature and velocity patterns in the furnace, supplementing similar previous tests in another unit at the plant with different burner registers. Boiler performance tests will also be conducted providing flue gas flow rate, gas composition and unburned combustibles. These tests will be used to initiate preliminary design of the reburn injector/burners and overfire air nozzles. A cold-flow model will be built to simulate the existing burner windbox assembly, burners and air registers as well as the furnace flow regime, including the lower and upper furnace past the furnace nose and into the convection section. This flow model will permit determination of the number and location of both the reburn injector/burners and overfire air nozzles. With the cold-flow model existing windbox, burner and furnace flow patterns can be observed. In addition, the model will provide an easy, convenient method to vary the number and location of the reburn injector/burners, overfire air windbox and nozzles to assure dispersion and mixing of the micronized coal in the reburn zone and the overfire air in the burnout zone. The cold-flow model will also be available during Phase 3 of the test program in the event any fine tuning of the reburn system is required. The computer modeling of the furnace will provide not only screening for the cold-flow model but also predict reburn system performance on the furnace and boiler as well as the effect of heat release and mixing in the reburn zone.

Once the flow and mixing characteristics have been determined from the modeling activities, the reburn injector/reburner will be selected or designed. The design will accommodate the unit's flow characteristics while achieving local mixing of the micronized coal-air stream from the injector to achieve combustion at a prescribed fuel-rich condition (0.8 stoichiometry) for reburn operation and at normal fuel-lean conditions for start-up and low-load boiler operation.

## MICRONIZED COAL TECHNOLOGY

### Technology Description

The technology described in this paper is a combination of a technology that produces micro-fine coal reliably and economically with a known NO<sub>x</sub> control technology (fuel reburning). When micronized coal is fired at a stoichiometry of 0.8 to 1.2, devolatilization and carbon conversion occur rapidly.

Micronized coal is defined as a coal ground so the 80 percent of the coal particles are 43 microns or smaller. The MicroFuel® system, consisting of the MicroMill and an external classifier, micronizes coal to a particle range of 10 to 20 microns.

The combined surface area of just one gram of micronized coal particles is 31 square meters, contrasted to a surface area of 2.5 square meters per gram for standard-grind pulverized coal.

The MicroMill system is a patented centrifugal-pneumatic mill with the replaceable rotating impeller as the only moving part. Size reduction is accomplished by the particles themselves striking against one another as they whirl in a tornado-like column of air inside the MicroMill. Centrifugal force retains material in the cone and Rotational Impact Zone (RIZ) as the particles reduce in size prior to being conveyed by the air stream entering the center of the rotating impeller. Figure 2 is a sectional view of the MicroMill, and Figure 3 is a cutaway view of the MF-3018 MicroMill.

Material entering the impeller is swept out of the MicroMill to the classifier, which separates particles by size. Micronized coal particles below 43 microns are discharged directly to the burners, and larger particles are returned to the MicroMill for further size reduction. Figure 4 is a dimensional elevation of a complete MicroMill system.

The net result of micronized coal as a reburn fuel is a uniform compact combustion envelope allowing for complete combustion of the coal/air mixture in a smaller volume than conventional pulverized coal. Heat rate, heat flux, carbon loss and NO<sub>x</sub> formation are all impacted by coal fineness.

### ENVIRONMENTAL ASPECTS

With the exception of significant reductions in NO<sub>x</sub> emission, the environmental impact of the proposed project is inconsequential.

Shawnee currently burns low-sulfur Appalachian coal (1.195 lb. SO<sub>2</sub>/10<sup>6</sup>Btu). Lower-sulfur western coal (0.35 lb. SO<sub>2</sub>/10<sup>6</sup>Btu) will be burned briefly as part of the demonstration. During that period, SO<sub>2</sub> emissions will be further reduced. The use of eastern low-sulfur coals with reduced grindability has made the existing pulverizers marginal. Equipment problems or wet coal will result in further derating of the unit. The introduction of micronized coal reburning as an additional fuel will allow Shawnee to overcome mill limitations and operate at somewhat higher capacity factors.

No significant changes in the emissions of greenhouse gases or air toxics are projected. A minor increase in emissions of CO and hydrocarbons may occur at times

during the demonstration as parametric testing may occasionally result in slightly less than complete combustion. However, existing pollution control equipment should be able to maintain emission levels within regulatory limits. Emissions monitoring will be performed to insure continued compliance.

No new waste products will be generated by the micronized coal reburn process, as no reagents are utilized. Existing requirements for fly ash and bottom ash disposal are expected to remain constant. Current water usage by the unit averages 3.1 million gallons per day for ash sluicing, and no change is projected for the demonstration. Average fly ash particle size will decrease slightly, but existing baghouses will efficiently collect fly ash.

### PREOPERATIONAL AND OPERATIONAL TESTING

Preoperational testing will be conducted to include baseline data acquisition and characterization of existing and newly designed components. Parametric testing will document the effect of the following reburn system variables:

- primary burner zone stoichiometry,
- reburn zone stoichiometry,
- final (burnout zone) stoichiometry,
- reburn zone momentum,
- micronized coal consumption in the reburn zone,
- reburn fuel particle size,
- load,
- coal composition reliability, and
- boiler load response.

All Continuous Emission Monitor (CEM) and boiler operation signals which can be efficiently monitored in real time will be directly stored on disk. The database will permit ready and efficient reduction and analysis of the data, both during execution of the program and during final analysis and evaluation. Information from the long-term test will permit evaluation of system efficiency and reliability under actual operating conditions. Also, the extended operating period will provide data for projecting economic impacts.

### CONCLUSIONS

TVA has a strong history of leadership in the development of new and emerging technologies and the performance of successful R&D programs. TVA believes that this nitrogen oxide emission control technology shows promising benefit to its own system, as well as the utility industry in general, since it is taking a leadership position in sponsoring a micronized coal reburn demonstration.

The combination of micronized coal supplying up to 30 percent of the total furnace requirements and reburning for NO<sub>x</sub> control will provide flexibility for

significant environmental improvement without adding higher operating costs or furnace performance deratings normally associated with environmental controls.

By meeting the objectives of this important coal reburning project, coal will be shown to be its own best friend in controlling NO<sub>x</sub> emissions and providing economical power to the public well into the future.

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## ATTACHMENT A

**Reburn Technology for Boiler NO<sub>x</sub> Control** by R.W. Borio of Combustion Engineering Inc., R.E. Hall of U.S. Environmental Protection Agency, R.A. Lott of Gas Research Institute, A. Kokkinos of Electric Power Research Institute, and S. Durrani of Ohio Edison, presented at the 6th Annual Coal Preparation, Utilization and Environmental Control Contractors Conference.

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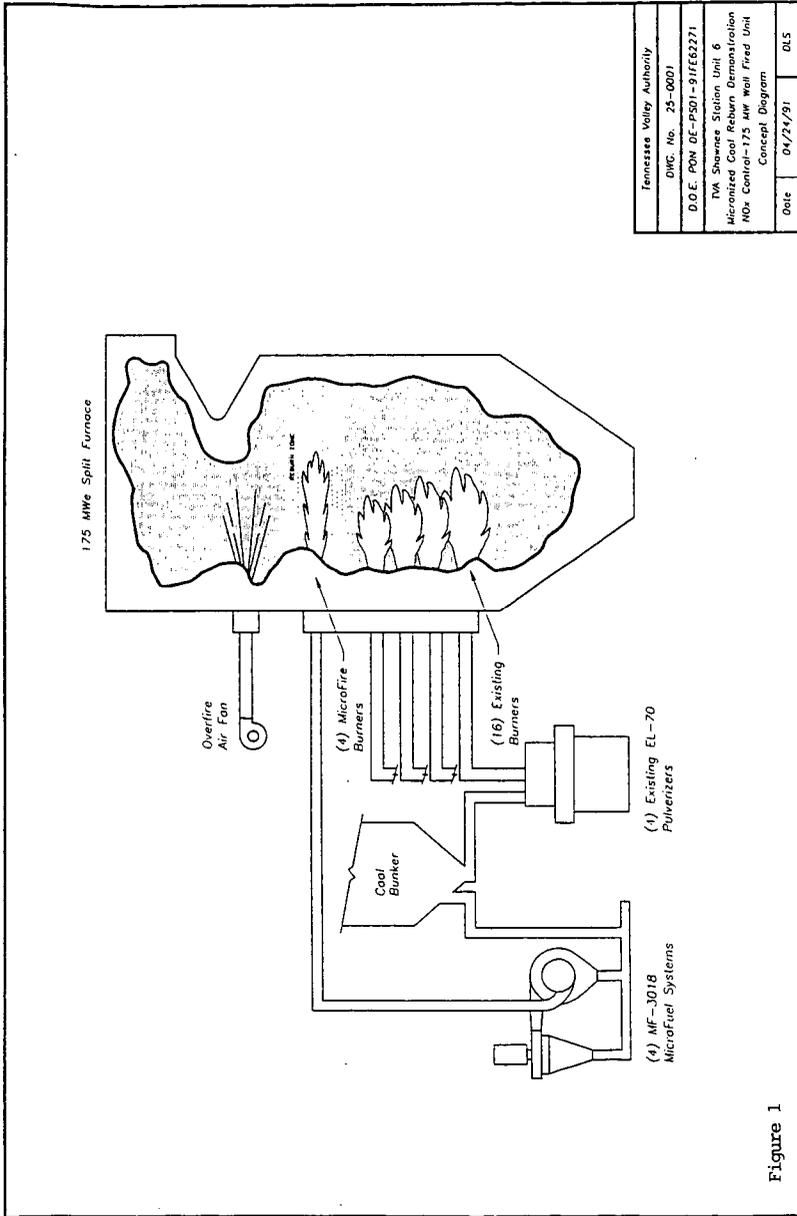
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TVA Shawnee Station Unit 6 Micronized Coal Reburn Demonstration NOx Control-175 MW Wall Fired Unit Concept Diagram	
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Figure 1

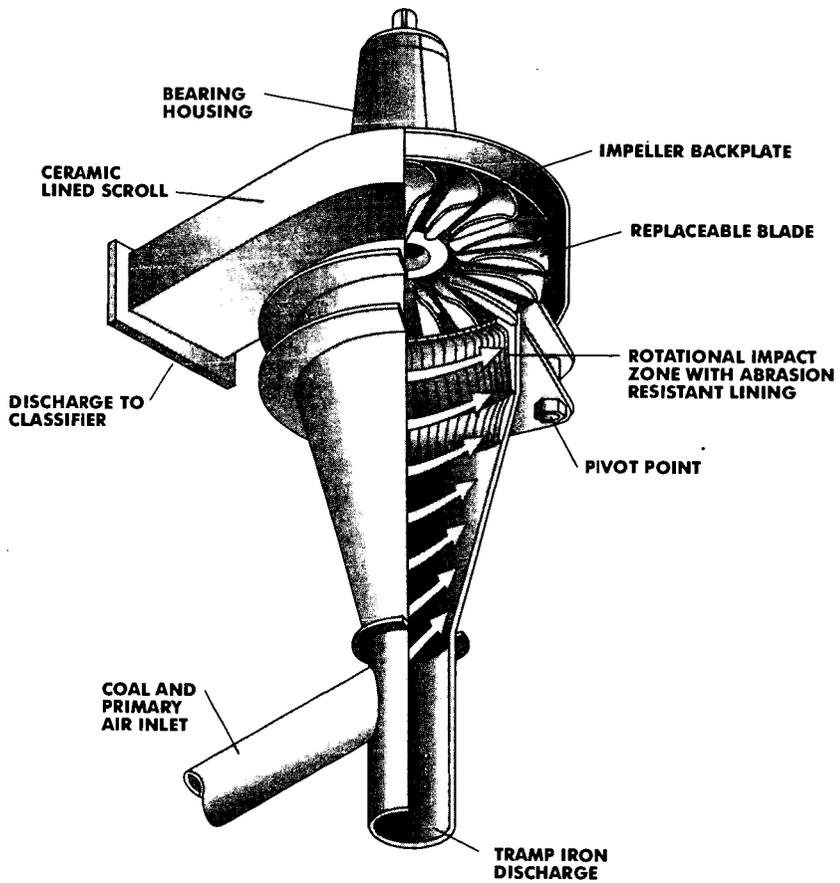


Figure 2

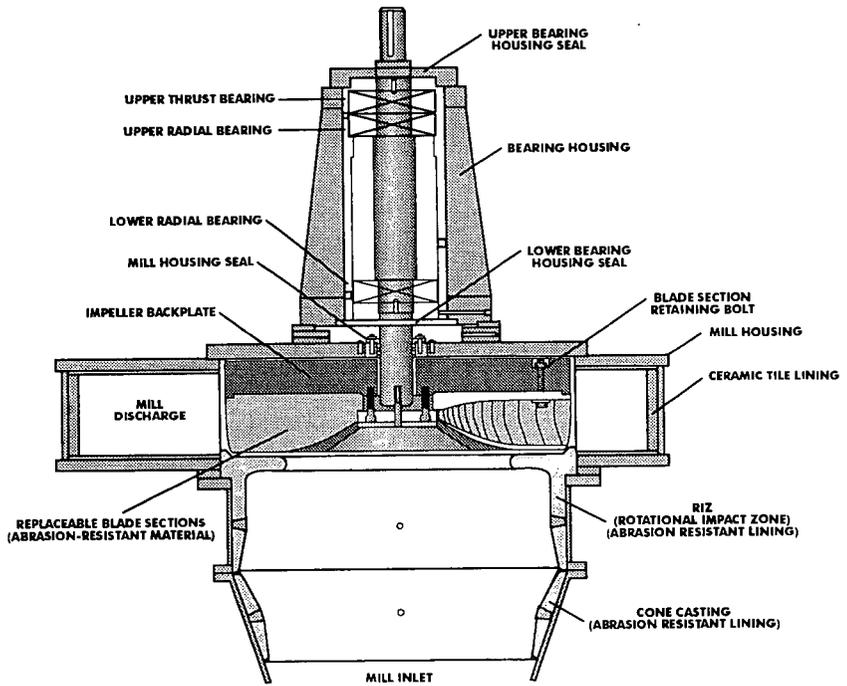


Figure 3



## OPERATING EXPERIENCE WITH THE INTEGRATED DRY NO<sub>x</sub>/SO<sub>2</sub> EMISSIONS CONTROL SYSTEM

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### INTRODUCTION

This paper presents the results to date from the Public Service Company of Colorado (PSCC), U. S. Department of Energy (DOE), and Electric Power Research Institute (EPRI), sponsored Integrated Dry NO<sub>x</sub>/SO<sub>2</sub> Emissions Control System project. This DOE Clean Coal Technology III demonstration project is being conducted at PSCC's Arapahoe Generating Station Unit 4, located in Denver, Colorado. The Integrated Dry NO<sub>x</sub>/SO<sub>2</sub> Emissions Control System consists of five major control technologies that are combined to form an integrated system to control both NO<sub>x</sub> and SO<sub>2</sub> emissions. NO<sub>x</sub> reduction is obtained through the use of low-NO<sub>x</sub> burners, overfire air, and urea-based Selective Non-Catalytic Reduction (SNCR), while dry sorbent injection using either sodium- or calcium-based reagents with humidification is used to control SO<sub>2</sub> emissions. The project goal is to provide up to a 70% reduction of both NO<sub>x</sub> and SO<sub>2</sub> emissions. The combustion modifications were expected to reduce NO<sub>x</sub> by 50% with the expectation that the SNCR system would provide the remaining 20% reduction. Dry Sorbent Injection was expected to provide 50% removal of the SO<sub>2</sub> emissions while using calcium-based reagents. As sodium is much more reactive than calcium, it was expected to provide SO<sub>2</sub> removals of up to 70%.

### UNIT DESCRIPTION

Arapahoe Unit 4 is a 100 MWe down-fired boiler which was built in the early 1950's, and was designed to burn Colorado lignite or natural gas. Currently, the main fuel source is a Colorado low-sulfur (0.4%) bituminous coal. The original firing configuration consisted of 12 intertube burners located on the roof of the furnace. Each burner consisted of a rectangular coal/primary air duct which was split into 20 separate nozzles that injected the coal/air mixture evenly across the furnace roof. Secondary air was injected around each of the individual coal nozzles, and there were no provisions to control the rate of fuel and secondary air mixing. Baseline NO<sub>x</sub> levels for this boiler ranged from approximately 780 to 840 ppmc (ppm, dry corrected to 3% O<sub>2</sub>), depending on load. Arapahoe Unit 4 uses a fabric filter dust collector for particulate control.

### SYSTEM DESCRIPTION

Babcock & Wilcox (B&W) provided the low-NO<sub>x</sub> burners and overfire air system for the Arapahoe Unit 4 project. B&W's DRB-XCL® (Dual Register Burner - axially Controlled Low-NO<sub>x</sub>) burner had been successfully used to reduce NO<sub>x</sub> emissions in wall-fired boilers, but had never been used in a vertically-fired furnace. The burner features dual spin vane registers which allow control of the swirl imparted to the secondary air in both the inner and outer regions of the flame. These registers provide a great amount of control over the rate of combustion, and thus the amount of NO<sub>x</sub> formed. The burners also feature a sliding air damper which allows the total secondary air flow to be controlled independently of the spin vane setting. In many older burner designs, a single register is used to control both the total secondary air flow and the rate of air/fuel mixing.

While low-NO<sub>x</sub> burners alone have proven to be effective for reducing NO<sub>x</sub>, combustion staging can further reduce NO<sub>x</sub> emissions. Overfire air delays combustion by redirecting a portion of the secondary air to a region downstream of the main combustion zone. Three B&W Dual-Zone NO<sub>x</sub> ports were added to each side of the furnace approximately 20 feet below the boiler roof. A numerical modeling study was performed by B&W in order to determine the optimum size and location for the ports. As a result, the NO<sub>x</sub> ports were not spaced symmetrically across the furnace side walls. The ports were also designed to inject up to 25% of the total secondary air through the furnace sidewalls. The dual-zone NO<sub>x</sub>

ports separate the overfire air into two regions. The outer zone features adjustable spin vane registers which disperse air in the region near the wall. The center zone produces an air jet with sufficient momentum to penetrate deep into the furnace. The two-stage injection provides faster mixing and more equal distribution of overfire air into the furnace.

NOELL, Inc. designed and supplied the urea-based SNCR system for the Arapahoe Unit 4 project. The disadvantage of urea injection, as with any SNCR chemical, is that the process operates over a very narrow temperature window. If the temperature is too high, the urea can be converted to  $\text{NO}_x$ . If the temperature is too low,  $\text{NO}_x$  removal efficiencies are reduced, and the emissions of unreacted chemical (ammonia slip) increases. The system at Arapahoe Unit 4 uses NOELL's proprietary dual-fluid injection nozzles to distribute the chemical uniformly into the boiler. A centrifugal compressor is used to supply a large volume of medium pressure air to the injection nozzles to help atomize the solution and rapidly mix the chemical with the flue gas. Two levels of injection nozzles were installed in order to provide the capability to follow the optimum temperature window as its location within the boiler changed with load. A cold-flow modeling study and detailed furnace exit gas temperature measurements were performed in order to determine the optimum location of the two injection levels.

Prior to the installation of the low- $\text{NO}_x$  combustion system, a short test program was conducted to assess the performance of the urea-based SNCR system with the original burners. Early tests at the cooler Level 2 injection location showed the region to be too cold for urea injection, even at full load. Subsequent temperature measurements revealed that the furnace exit gas temperatures were significantly lower (on the order of 150 to 200°F) than those measured previously. Although the reason for the decrease in temperature could not be conclusively identified, it required that the remainder of the test effort be focused on the hotter Level 1 injection location. During the Level 1 tests, it was found that  $\text{NO}_x$  reductions at low load were somewhat less than expected. Recent full-scale SNCR tests<sup>(1)</sup> have shown that aqueous ammonia ( $\text{NH}_4\text{OH}$ ) can provide increased system performance compared to that for urea in certain temperature ranges. A short term test using aqueous ammonia achieved greater  $\text{NO}_x$  reduction than urea at low load. These results made it desirable to investigate  $\text{NH}_4\text{OH}$  injection in more detail during the SNCR tests scheduled after the low- $\text{NO}_x$  combustion system retrofit. However, due to safety concerns, it was preferable to store urea rather than  $\text{NH}_4\text{OH}$  on-site. To this end, NOELL, Inc. designed and installed a system that allows on-line catalytic conversion of urea into ammonia compounds.

A combination of dry technologies is used at Arapahoe Unit 4 to reduce  $\text{SO}_2$  emissions. PSCC designed and installed a dry sorbent injection system that can inject either calcium- or sodium-based reagents into the flue gas upstream of the fabric filter. The reagent is fed through a volumetric feeder into a pneumatic conveying system, and then into a pulverizer where the size of the material can be reduced to approximately 90% through 400 U.S. Standard mesh. The material is then injected evenly into the duct at a point approximately 100 feet upstream of the fabric filter. A bypass can also be installed to convey the calcium-based reagents into the flue gas upstream of the economizer in a region where the temperature is approximately 1000°F.

While significant  $\text{SO}_2$  reductions can be achieved with sodium-based reagents, calcium hydroxide is less reactive. In order to improve  $\text{SO}_2$  removals with calcium hydroxide, a humidification system was installed in the duct upstream of the fabric filter. The system was designed by B&W and consists of 84 I-jet humidification nozzles which can inject up to 80 gpm of water into the flue gas stream. The system was designed to achieve a 20°F approach to saturation at full load conditions.

#### RESULTS

Fossil Energy Research Corporation is conducting all testing of the Integrated Dry  $\text{NO}_x/\text{SO}_2$  Emissions Control System. Currently, the individual testing of the low- $\text{NO}_x$  burners, overfire air, urea injection, calcium duct injection, and calcium economizer injection has been completed. Sodium duct injection testing has started and will continue through January 1994. Testing of the complete

integrated system will continue through mid-1994 with up to four weeks of testing on a high sulfur (2.5%) coal. Although all data have not been reviewed, some preliminary results of the individual technologies comprising the Integrated Dry NO<sub>x</sub>/SO<sub>2</sub> Emissions Control System will be presented.

**COMBUSTION MODIFICATIONS.** Figure 1 shows the original baseline NO<sub>x</sub> emissions compared to the post-combustion retrofit emissions, both with and without the SNCR system in operation. The combination of low-NO<sub>x</sub> burners and overfire air alone resulted in NO<sub>x</sub> reductions varying from 63 to 69% across the load range. The post-retrofit results shown in the figure are for the maximum staging (i.e., maximum overfire air) configuration. In this configuration, approximately 25% of the secondary air is introduced through the NO<sub>x</sub> ports at full load. It was not possible to reduce the overfire air flow to zero as the ports are located in a very hot section of the furnace and, therefore, require a minimum amount of air flow to assure adequate cooling. These NO<sub>x</sub> port cooling requirements limited the minimum overfire air flow to approximately 15% of the total secondary air at full load. Tests at the minimum overfire condition indicate that the low-NO<sub>x</sub> burners are responsible for the majority of the NO<sub>x</sub> reduction over the range of overfire air flow rates tested, as the removals increase only 10% as overfire air is increased from 15 to 25% at full load. At 80 MWe, where the overfire air flow can be reduced to 8% of the secondary air before NO<sub>x</sub> port temperatures become a concern, the increase in NO<sub>x</sub> reduction was only 8% as the overfire air was increased from 8 to 25%. However, it must be noted that it was not possible to totally separate the effects of the low-NO<sub>x</sub> burners and overfire air system, since the overfire air flow could not be reduced to zero.

Flyash unburned carbon levels measured after the retrofit were unchanged from the baseline levels, and did not appear to be greatly affected by the amount of overfire air. CO emissions were also comparable to the baseline levels with maximum overfire air, and tended to increase as overfire air flow was reduced to the minimum values. This was not expected, as low-NO<sub>x</sub> combustion retrofits have been known to result in increases in flyash unburned carbon levels and CO emissions. It is hypothesized that this behavior is due to the penetration and mixing of the overfire air in this down-fired configuration. It is also possible that the lack of an effect on flyash unburned carbon is partially due to the reactive nature of the Western coal utilized by the Arapahoe station. This reactivity allows flexibility in operation of the low-NO<sub>x</sub> burners and overfire air system without resulting in increases in unburned carbon levels. However, as mentioned above, CO emissions were found to be sensitive to changes in combustion system operating parameters.

**SELECTIVE NON-CATALYTIC REDUCTION.** Figure 1 also shows the NO<sub>x</sub> emissions attainable when operating the SNCR system at urea injection rates which limit NH<sub>3</sub> slip at the fabric filter inlet to 10 ppm. The NO<sub>x</sub> removals (measured relative to the 240 to 280 ppmc post-retrofit levels) range from 7 to 45% over the load range of 60 to 110 MWe, respectively. The temperature-sensitive nature of the urea injection process and the limitation of only a single usable injection level is apparent in that the NO<sub>x</sub> removals for a fixed NH<sub>3</sub> slip level are much lower at the reduced loads where the flue gas temperature is also reduced. The reduction in NO<sub>x</sub> emissions due to the combined affects of the low-NO<sub>x</sub> combustion system retrofit and SNCR range from 66 to 82% over the load range of 60 to 100 MWe.

While urea injection allowed reasonable levels of NO<sub>x</sub> removal at higher loads, it was not very effective at reduced loads. A third set of temperature measurements revealed that the low-NO<sub>x</sub> combustion system retrofit resulted in another decrease in furnace exit gas temperatures (this one on the order of 180 to 240°F). In an effort to increase low-load removal, the urea injection system was modified with an on-line ammonia conversion system. This system converts urea to liquid ammonia compounds immediately before injection into the boiler. As ammonia reacts faster than urea and in a lower temperature window, it was expected to provide higher NO<sub>x</sub> removal at lower loads. The results (Figure 2) showed that, when injected into the same location in the Arapahoe Unit 4 boiler, converted urea provided higher NO<sub>x</sub> removals than urea when compared on an equal ammonia slip basis. However, the increased NO<sub>x</sub> removals with converted urea required higher chemical injection rates (ranging from 67 to 133% higher than those for urea injection

at the same load). Therefore, at loads of 80 MWe and greater, urea was the most efficient of the two chemicals.

In addition to creating unwanted ammonia emissions, SNCR can increase nitrous oxide ( $N_2O$ ) emissions.  $N_2O$  emissions with converted urea were lower than those for urea. For converted urea, the fraction of NO reduced which was converted to  $N_2O$  ranged from 3 to 8%, depending on load for a stoichiometric (N/NO) ratio of 1.0. With urea, the conversion ranged from 29 to 35% at a similar chemical injection rate. The  $N_2O$  conversion with urea injection was much higher than that seen before the low- $NO_x$  combustion system retrofit (11 to 16% at a N/NO ratio of 1.0). It is likely that the increase is due to the reduction of the flue gas temperatures in the injection region seen after the retrofit.

**DRY SORBENT INJECTION WITH CALCIUM HYDROXIDE ( $Ca(OH)_2$ ).** Testing of the dry sorbent injection system with  $Ca(OH)_2$  consisted of two phases: duct injection with humidification and economizer injection without humidification. All testing to date has been with a low-sulfur coal and baseline  $SO_2$  emissions in the range of 400 ppmc.

The results of the duct injection tests with humidification at a stoichiometric (Ca/S) ratio of 2.0 are shown in Figure 3. The maximum  $SO_2$  removal of 44% was obtained during a short-term test with the humidification system operating at a 20°F approach to saturation. Immediately after this test, problems developed with the dry flyash transport system, and it is suspected that the low approach temperature operation contributed to the problem. More recently, problems with increased pressure drop across the fabric filter, and deposit build up on the bags occurred after operating the humidification system at a 30°F approach temperature. Currently, studies are still ongoing to determine if these problems were due to steady state operation at the 30°F approach temperature or transient conditions during load changes. At this higher approach temperature,  $SO_2$  removal is reduced to a range of 26 to 36% at a Ca/S ratio of 2.0.

$SO_2$  removals with  $Ca(OH)_2$  injection at the economizer have been much lower than expected. At a Ca/S ratio of 2.0 without humidification,  $SO_2$  removals ranged from 5 to 8%. It was found that distribution of the sorbent with the original injection nozzles was very poor, and only approximately one-third of the flue gas was being treated. Improved nozzles which increased the distribution to approximately two-thirds of the flue gas were installed on one side of the boiler. With the improved distribution,  $SO_2$  removals increased to only 10 to 12% at a Ca/S ratio of 2.0.

**DRY SORBENT INJECTION WITH SODIUM SESQUICARBONATE.** Testing of the dry sorbent injection system with sodium sesquicarbonate ( $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ ) has just recently begun, and only minimal data is available at this time. Figure 4 shows the  $SO_2$  removals as a function of the stoichiometric injection rate ( $Na_2/S$  ratio) over the range of 0 to 1.5. At a  $Na_2/S$  ratio of 1.4,  $SO_2$  removals of 53 to 63% have been achieved to date. It has been further documented during short-term tests that  $SO_2$  removals in excess of 70% can be achieved at  $Na_2/S$  ratios slightly above 2.0. One byproduct of the dry sodium based  $SO_2$  removal process is the oxidation of NO to  $NO_2$ . This can lead to plume coloration and visibility problems. For instance,  $NO_2$  levels have been seen to increase by 6 to 13 ppm (from a baseline level of 1 to 2 ppm) while injecting sodium sesquicarbonate at Arapahoe Unit 4. One potential synergistic benefit of the Integrated Dry  $NO_x/SO_2$  Emission Control System will be the suppression of the NO to  $NO_2$  oxidation with sodium injection by the  $NH_3$  slip from the SNCR system. These benefits will be documented during future testing of the entire integrated system.

#### CONCLUSIONS

The Integrated Dry  $NO_x/SO_2$  Emissions Control System has been in operation for over one and one-half years and preliminary conclusions are as follows:

- $NO_x$  reduction during baseloaded operation of the unit with the low- $NO_x$  burners and overfire air ranges from 63 to 69% with no increase in flyash unburned carbon levels or CO emissions.

- Low-NO<sub>x</sub> burners provided the majority of the NO<sub>x</sub> reduction, while the overfire air system supplied approximately 8 to 10% additional NO<sub>x</sub> reduction over the range of overfire air flow rates tested.
- Urea injection allows an additional 7 to 45% NO<sub>x</sub> removal with an ammonia slip of 10 ppm at the fabric filter inlet. This increases total system NO<sub>x</sub> reduction to 82% at full load, significantly exceeding the project goal of 70%.
- Higher NO<sub>x</sub> reduction is possible using ammonia compounds as the SNCR chemical, but significantly higher stoichiometric ratios are required at loads of 80 MWE and above. However, it must be noted that the performance of the SNCR system with urea was limited by a large unexpected decrease in furnace exit gas temperature at this particular installation and, therefore, any comparison of the performance of ammonia compounds to that for urea must take this into account.
- N<sub>2</sub>O generation is a potential concern with urea injection, but was greatly reduced when ammonia compounds were injected.
- The maximum SO<sub>2</sub> removal attained during short-term tests with calcium hydroxide injection and duct humidification was 44%.
- Preliminary results indicate SO<sub>2</sub> removals with sodium sesquicarbonate injection in excess of 60%.

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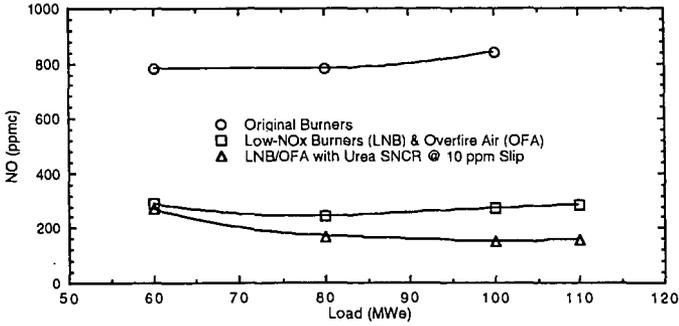


Figure 1. Pre- and Post-Retrofit NO<sub>x</sub> Emissions

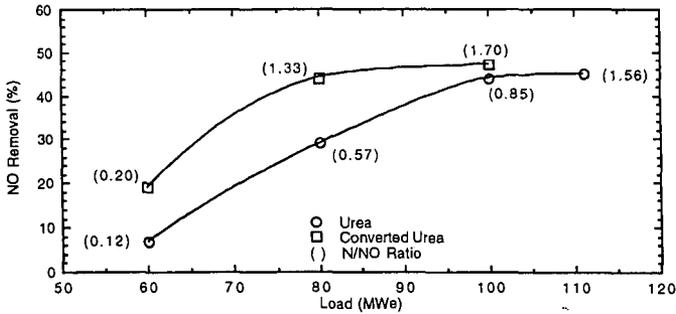


Figure 2. NO<sub>x</sub> Removals for Urea and Converted Urea Injection at a Fixed NH<sub>3</sub> Slip Level of 10 ppm

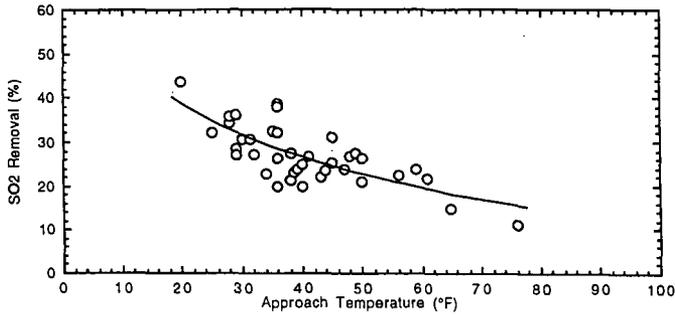


Figure 3. SO<sub>2</sub> Removals with Calcium Hydroxide for Duct Injection with Humidification (Ca/S = 2.0)

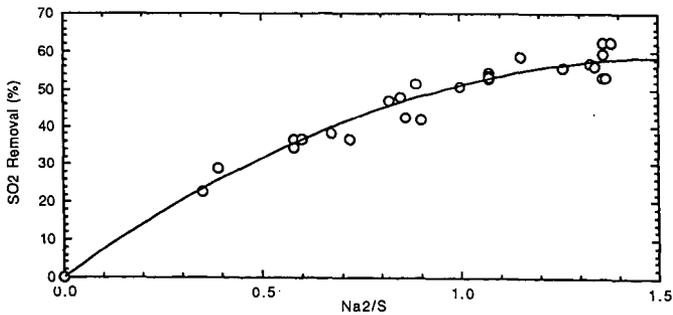


Figure 4. SO<sub>2</sub> Removals with Sodium Sesquicarbonate for Duct Injection without Humidification

GAS REBURNING AND INTEGRATED NO<sub>x</sub> AND SO<sub>2</sub> CONTROL:  
READY FOR COMMERCIAL INSTALLATIONS

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INTRODUCTION

Gas Reburning (GR) is a retrofit NO<sub>x</sub> control technology for boilers and furnaces. This paper presents recent field test results from demonstrations of GR and integrated NO<sub>x</sub> and SO<sub>2</sub> control technologies on three coal fired utility boilers: tangential, wall and cyclone fired. GR was integrated with Sorbent Injection for enhanced SO<sub>2</sub> on two units and with Low NO<sub>x</sub> Burners for enhanced NO<sub>x</sub> control on one unit. Recent test results are presented from all three sites. An economic analysis compares costs for GR and integrated technologies with competing conventional technologies.

GAS REBURNING AND INTEGRATED TECHNOLOGIES

GR is a NO<sub>x</sub> control technology where NO<sub>x</sub> emissions are reduced by reactions with hydrocarbon fragments produced from natural gas (1). Figure 1 shows the application of GR to a front wall fired boiler.

In contrast to conventional firing systems which have a single combustion stage, GR is a three zone process. In the primary zone, the normal boiler fuel (coal, oil, or gas) is fired through conventional (or low NO<sub>x</sub>) burners under low excess air conditions. The firing rate is reduced by 15-20% to accommodate the natural gas. This reduces combustion intensity and NO<sub>x</sub> emissions.

In the reburning zone, natural gas is injected to produce a slightly fuel rich zone (nominally 90 percent theoretical air). The natural gas, principally methane (CH<sub>4</sub>), breaks down to produce hydrocarbon fragments (CH and CH<sub>2</sub>). The hydrocarbon fragments react with the NO<sub>x</sub> produced in the primary combustion zone to reduce it to atmospheric nitrogen (N<sub>2</sub>).

The gases exiting the Reburning Zone contain considerable carbon monoxide (CO) as well as unburned hydrocarbons. These are consumed in the burnout zone by injection of additional combustion air (overfire air), completing the heat release.

Since GR does not require modifications to the main firing system, it is compatible with all types of firing systems. Demonstrations are currently being conducted on tangential, wall and cyclone fired systems. Applications on stokers are also feasible.

By itself, GR can achieve NO<sub>x</sub> control of 60-70% and SO<sub>2</sub> control proportional to the gas firing (typically 15-20%). NO<sub>x</sub> and SO<sub>2</sub> control can be increased by integrating GR with other control technologies. Examples include:

- Low NO<sub>x</sub> Burners (LNB) NO<sub>x</sub> control increases to about 75%. GR-LNB is being demonstrated on a wall fired unit (2).
- Selective Non-Catalytic Reduction (SNCR) The integration of SNCR with GR is termed Advanced Gas Reburning (AGR). The GR system is tuned to optimize the conditions for SNCR improving agent utilization, increasing NO<sub>x</sub> control to about 85%, and eliminating NH<sub>3</sub> slip. AGR has been tested at pilot scale (3).
- Methanol Injection A small amount of methanol injected into the back pass of the boiler converts NO to NO<sub>2</sub> which can be removed in a wet scrubber. The integration of Methanol Injection with AGR, CombiNO<sub>x</sub>, increases NO<sub>x</sub> control to the 90-95% range. CombiNO<sub>x</sub> has been tested at pilot scale (3).
- Sorbent Injection (SI) A calcium based sorbent can be injected in several ways to boost SO<sub>2</sub> control. GR integrated with furnace sorbent injection (GR-SI) can increase SO<sub>2</sub> control to about 50% with conventional sorbents and to over 80% with advanced sorbents, such as

Promisorb. GR-SI is being demonstrated on tangential and cyclone fired units (4).

- SO<sub>2</sub> Scrubber Since the GR modifications affect only the boiler, GR is fully compatible with all types of post combustion emission controls such as SO<sub>2</sub> Scrubbers.

Figure 2 shows the ranges of NO<sub>x</sub> and SO<sub>2</sub> control achievable with these integrated technologies in comparison to conventional technologies without GR (Low NO<sub>x</sub> Burners, SNCR, SCR and SO<sub>2</sub> Scrubber).

#### DATA FROM THREE FULL SCALE DEMONSTRATIONS

EER is demonstrating GR and integrated technologies on three utility boilers in two DOE Clean Coal Technology Projects as shown in Table 1. The host sites are all utility boilers and include the three major firing configurations: tangential, wall and cyclone fired. They cover a capacity range from 33 to 158 MW, a factor of nearly 5/1. As part of the design process, EER projected (and published) performance goals. NO<sub>x</sub> control of over 60% was projected for each of the units.

At all three units the emission control equipment has been installed and tested extensively. The NO<sub>x</sub> control goals have been achieved. Testing has been completed at the Hennepin tangentially fired unit and Illinois Power, the host utility, has elected to retain the equipment. Testing is still in progress at the other three units.

Figure 3 shows how NO<sub>x</sub> decreases as the gas injection rate increases for all three units. It should be noted that the wall fired unit is equipped with low NO<sub>x</sub> burners and the zero gas point corresponds to emissions from the low NO<sub>x</sub> burners. At the Hennepin tangentially fired unit, additional tests were conducted with the unit operating on 100% gas and utilizing the GR system. As shown in figure 3, NO<sub>x</sub> emissions were reduced to 0.05 lb/10<sup>6</sup> Btu. All three demonstrations include long term testing where the emission control systems are operated by plant personnel. The tests have been completed at Hennepin; NO<sub>x</sub> averaged 0.245 lb/10<sup>6</sup> Btu, a 67.3% reduction.

#### ECONOMICS

The capital cost of GR is highly site specific. For a typical installation on a large unit (300-500 MW), the capital cost is typically in the range of 15-30 \$/KW for a easy and difficult retrofits, respectively.

The operating cost for gas reburning is almost entirely related to the differential cost between the gas and the base fuel. No additional operators are required and maintenance is minimal. For coal fired units, gas generally costs more than coal and the differential cost is the largest cost component. For gas fired the fuel cost impact is zero and operating costs are near zero.

In evaluating GR operating costs it is important to account for several benefits of GR other than NO<sub>x</sub> control. These include:

1. SO<sub>2</sub> Reduction in proportion to the fraction of gas fired. The value of the SO<sub>2</sub> reduction will depend on the utility's alternatives for SO<sub>2</sub> control and the SO<sub>2</sub> allowance market price.
2. Reduced Ash Disposal in proportion to the gas firing percentage.
3. Reduced Maintenance and Improved Availability Reducing the amount of coal and ash passing through the power plant components reduces coal and ash related maintenance. Availability via gas use to replace coal during mill outages.

The total cost of emission control can be calculated by adding the capital and operating cost components via the Electric Power Research Institute (EPRI) Technology Assessment Guide (TAG) procedure. An EPRI TAG analysis was conducted for GR and integrated technologies along with conventional emission control technologies including low NO<sub>x</sub> burners, SNCR and SCR. Figures 4 and 5 show the results for coal and gas fired units, respectively. The coal fired

analysis was based on a baseline NO<sub>x</sub> level of 1.0 lb/10<sup>6</sup> Btu and a gas to coal cost differential of 1.00 \$/10<sup>6</sup> Btu. SO<sub>2</sub> credits were evaluated at 300 \$/ton for coals with 1.2 and 6.0 lb/10<sup>6</sup> Btu SO<sub>2</sub> emission potential. As shown in figure 4, the cost effectiveness of the GR technologies is comparable to low NO<sub>x</sub> burners and SNCR but GR achieves substantially higher NO<sub>x</sub> control. For high levels of NO<sub>x</sub> control, where SCR is the only commercially available competing technology, GR-LNB and AGR are much more cost effective.

The gas fired analysis utilized baseline NO<sub>x</sub> levels of 0.3 and 0.5 lb/10<sup>6</sup> Btu. The results shown in figure 5 are generally similar to the coal fired case except that: (1) the overall costs are higher due to the lower initial NO<sub>x</sub> level and no SO<sub>2</sub> credit, and (2) the GR costs have dropped relative to the LNB and SNCR costs since there is no cost differential associated with the gas injected into the reburning zone.

#### CONCLUSIONS

EER has designed, installed and tested GR systems on three utility boilers covering a 5/1 capacity range and involving all three major firing configurations (tangential, wall and cyclone). In all cases the NO<sub>x</sub> control goals were achieved or exceeded with no operational problems. GR can be installed as a stand alone technology to achieve NO<sub>x</sub> control in the range of 60%. Higher levels of NO<sub>x</sub> and/or SO<sub>2</sub> control can be achieved by integrating other synergistic controls. Costs for GR technologies are generally competitive with other technologies which can achieve comparable levels of NO<sub>x</sub> control.

EER has been working on GR technologies for over 12 years. The results from these three Clean Coal Technology demonstrations have provided EER with the design and performance data base necessary to apply GR in the commercial market place. Accordingly, EER is now offering GR and integrated technologies with commercial guarantees for industrial and utility Clean Air Act compliance applications.

#### ACKNOWLEDGEMENT

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The authors wish to thank the personnel at each organization and especially the power plant staff for their direct involvement in the projects.

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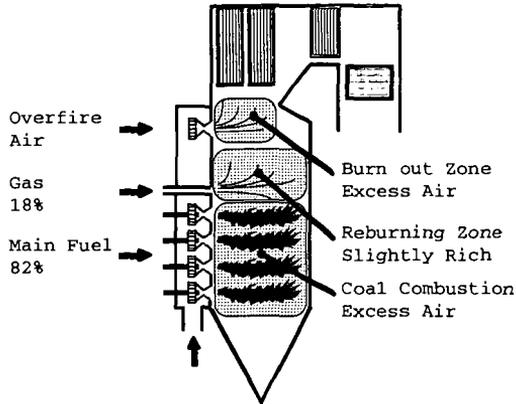


Figure 1. Gas Reburning on a Wall Fired Boiler

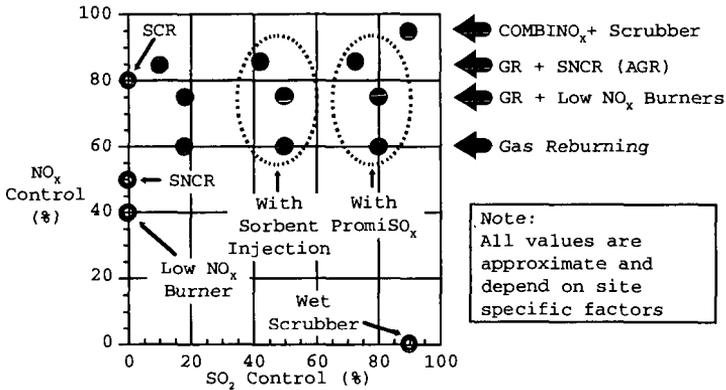


Figure 2. NO<sub>x</sub> and SO<sub>2</sub> Control Comparison

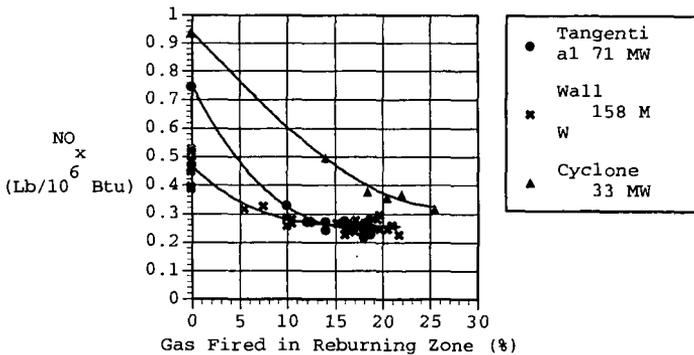


Figure 3. Gas Reburning Data from Three Demonstrations

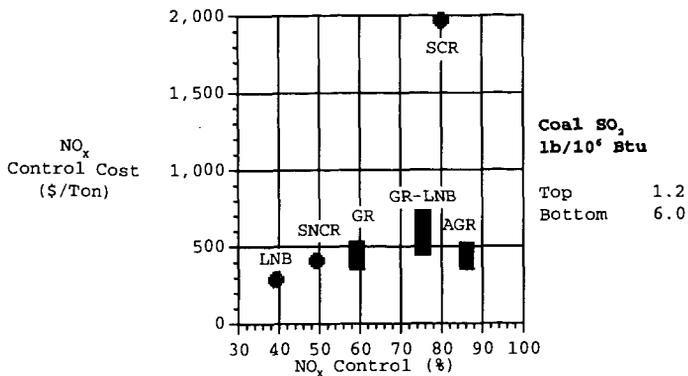


Figure 4. Gas Reburning Economics for Coal Fired Boiler

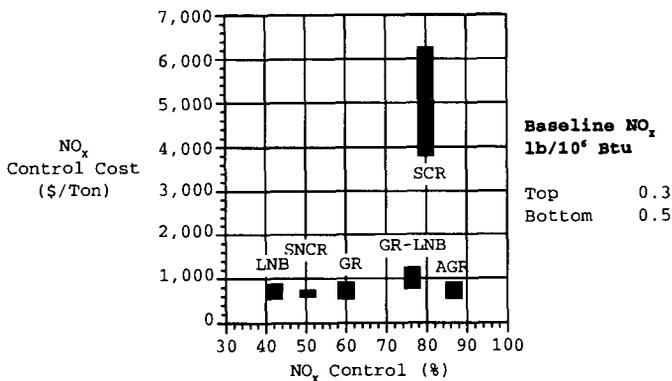


Figure 5. Gas Reburning Economics for Gas Fired Boiler

Table 1. Three Demonstrations

CCT	TECH.	UNIT	CAP MW net	FIRING CONFIG	Status	FUNDING
1	Gas Reburning	Illinois Power Hennepin 1	71	Corner	Comp. 1 Year Test	\$37,000,000 DOE GRI Illinois ENR
	Sorbent Injection	CWLP Lakeside 7	33	Cyclone	1 Yr. Test in Pro	
3	Gas Reburning Low NO <sub>x</sub> Burners	P.S. Colorado Cherokee 3	158	Wall	Para. Comp. 1 Year Test in Pro	\$16,000,000 DOE GRI FS Colorado CIG EPRI EER

## LIFAC SORBENT INJECTION : AN ALTERNATIVE SO<sub>2</sub> CONTROL STRATEGY

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**Keywords :** SO<sub>2</sub> Control, Sorbent Injection, Clean Coal Demonstration

### Introduction

The Clean Coal Technology Program (CCT) has been recognized in the National Energy Strategy as a major initiative whereby coal will be able to reach its full potential as a source of energy for the nation and the international marketplace. Attainment of this goal depends upon the development of highly efficient, environmentally sound, competitive coal utilization technologies responsive to diverse energy markets and varied consumer needs. The CCT Program is an effort jointly funded by government and industry whereby the most promising of the advanced coal-based technologies are being moved into the marketplace through demonstration. The CCT Program is being implemented through a total of five competitive solicitations. This paper discusses the LIFAC sorbent injection technology which was selected in the third round of CCT solicitations.

LIFAC North America, a joint venture partnership of ICF Kaiser Engineers, Inc. and Tampella Power Corporation of Finland, will demonstrate the LIFAC flue gas desulfurization technology developed by Tampella. This technology provides sulfur dioxide emission control for powerplants, especially existing facilities with tight space limitations. Sulfur dioxide emissions are expected to be reduced by up to 85% by using limestone as a sorbent. The limestone is injected into the upper regions of a furnace, where calcining to lime and partial absorption of SO<sub>2</sub> occur. Subsequently, the combustion gas is passed through a unique piece of equipment known as the activation reactor. This is a vertical elongation of the ductwork between the air preheater and ESP where the combustion gas is humidified and SO<sub>2</sub> absorption is completed. The LIFAC technology will be demonstrated at Whitewater Valley Unit No. 2, a 60-MWe coal-fired powerplant owned and operated by Richmond Power and Light (RP&L) and located in Richmond, Indiana. The Whitewater plant consumes high-sulfur coals with sulfur contents ranging from 2.0 - 2.9 percent.

The project, co-funded by LIFAC North America and DOE, is being conducted with the participation of Richmond Power and Light, the State of Indiana, the Electric Power Research Institute, and the Black Beauty Coal Company. The project has a total cost of 21.4 million dollars and a duration of 48 months from the preliminary design phase through the testing program.

The sponsors of this project believe that LIFAC has the potential to be a new and important SO<sub>2</sub> control option for U.S. utilities subject to the Clean Air Act's acid rain regulations. To be considered as a commercially feasible option in this particular emissions control market, LIFAC must demonstrate a high SO<sub>2</sub> removal rate while remaining competitive with other options on a cost per ton of SO<sub>2</sub> removed basis. To this end, the sponsors of this project have designed the demonstration with the following goals in mind:

- Sustained High SO<sub>2</sub> Removal Rate - Incorporated into the test plan are several periods of long term testing which are intended to demonstrate LIFAC's SO<sub>2</sub> removal and reliability characteristics under normal operating conditions.
- Cost - LIFAC must compete with both low capital cost, low SO<sub>2</sub> removal rate options such as sorbent injection and high capital cost, high SO<sub>2</sub> removal rate options such as wet scrubbing. This project will demonstrate LIFAC's competitiveness on a cost per ton of SO<sub>2</sub> removed basis with these currently available alternatives.

- **Retrofit Adaptability** - The host site chosen required a retrofit with tight construction conditions that will prove LIFAC's ability to be installed where other technologies might not be possible. Construction was also to demonstrate LIFAC's ability to be built and brought on-line with zero plant down time other than scheduled outages.
- **System Compatibility** - A major concern of utilities is the degree of compatibility of SO<sub>2</sub> removal systems with their existing operations. This demonstration will show LIFAC's minimal impact on the host site's boiler and associated subsystems.

### **LIFAC Process History and Description**

In 1983, Finland enacted acid rain legislation which applied limits on SO<sub>2</sub> emissions sufficient to require that flue gas desulfurization systems have the capability to remove about 80 percent of the sulfur dioxide in the flue gas. Tampella Power, therefore, began developing an alternative, economical sorbent injection system. Initially, development first involved laboratory and pilot plant tests, then full-scale tests of sorbent injection of limestone. Subsequent research and development by Tampella led to the addition of a humidification section after the furnace which became known as the LIFAC process.

In 1986, the first large full scale test was performed at Imatran Voima's Inkoo powerplant using a 70 megawatt side-stream from a 250 megawatt boiler. A 76 percent SO<sub>2</sub> removal rate with 1.5% sulfur coal was reached. A second LIFAC activation reactor was constructed to handle an additional 125 megawatt side-stream. This newer reactor is achieving removal rates of 75 to 80 percent while using Ca/S molar ratios of between 2 and 2.5 to 1. Also, in 1988 the first tests with high-sulfur U.S. coals were run at the Neste Kulloo Laboratory. A Pittsburgh No. 8 Seam coal containing 3 percent sulfur was tested and an SO<sub>2</sub> removal rate of 77 percent was achieved at a Ca/S molar ratio of 2 to 1.

### **LIFAC Process Description**

The LIFAC system combines conventional limestone injection into the upper furnace region with a post-furnace humidification reactor located between the air preheater and the ESP. The process produces a dry, stable waste product that is removed from both the bottom of the humidification reactor and the ESP.

Finely pulverized limestone is pneumatically conveyed and injected into the upper region of the boiler where temperatures are approximately 1800 to 2200 degrees Fahrenheit. At these temperatures the limestone (CaCO<sub>3</sub>) calcines to form lime (CaO) which readily reacts with the SO<sub>2</sub> to form calcium sulfate (CaSO<sub>4</sub>). All of the sulfur trioxide (SO<sub>3</sub>) reacts with the CaO to form CaSO<sub>4</sub>.

Approximately 25 percent of the sulfur dioxide removal occurs in the boiler with the remaining 75 percent and the unreacted lime passing through the air preheater to the humidification reactor. There the flue gas is sprayed with water that allows the unreacted lime to hydrate to Ca(OH)<sub>2</sub> which more readily reacts with the sulfur dioxide and forms CaSO<sub>3</sub>. A combination of the proper water droplet size and residence time allows for effective hydration of the lime and complete water evaporation to create a dry reactor bottom product.

After exiting the humidification reactor, the flue gas is reheated before entering the ESP. The humidification and lower gas temperature enhance the efficiency of the ESP. Seventy-five percent of the LIFAC-produced spent sorbent and fly ash is collected by the ESP with the other 25 percent collected by the humidification reactor. Both the reactor and ESP ash may be recycled to a point ahead of the reactor to improve sorbent utilization and to improve the SO<sub>2</sub> removal efficiency of the system to the range of 75 to 85 percent. A schematic of the LIFAC process is shown in Figure 1 along with the typical sampling locations used during the demonstration.

### **Process Advantages**

LIFAC is similar to other current sorbent injection technologies but has unique advantages with its use of a patented vertical humidification reactor. And while LIFAC's sulfur dioxide removal efficiency is not as high as traditional wet flue gas desulfurization systems, its cost and simplicity of design, construction and operation offer other advantages over these alternative systems. In particular the advantages of the LIFAC system are:

- **High SO<sub>2</sub> removal rates** - Currently available sorbent injection systems have been unable to sustain high SO<sub>2</sub> removal rates with any consistency. LIFAC has proven in

the past and intends to demonstrate during this project the ability to achieve and sustain high SO<sub>2</sub> removal rates of 75 to 85 percent over long operating periods.

- **By-products** - Wet lime and limestone scrubbing systems create a wet byproduct ash that must be further treated before disposal. LIFAC produces a dry solid waste ash containing calcium sulfide, calcium sulfate and fly ash. This waste is easily disposed of under U.S. regulatory requirements, may be recycled to increase LIFAC's efficiency and may have commercial applications in the cement industry.
- **Compatibility and Adaptability** - LIFAC has minimal impact on the host's site and systems, primarily the boiler, ESP and ID fan. In addition, LIFAC requires little space and few utilities and therefore is easily installed even in small or cramped powerplant sites.

#### **Construction and Systems Integration**

Construction of the LIFAC system has occurred in two phases over a period of one and a half years. The first phase of construction was completed during a routine plant outage in March, 1991. The period was utilized to install tie-ins to the host site's existing systems.

Ductwork and three dampers were installed between the air preheater and ESP to allow flue gas flow to the LIFAC activation reactor. Tie-ins were also made to the powerplant's high-pressure steam, condensate and river-water supplies. The high-pressure steam is required to reheat the flue gas exiting the LIFAC reactor and the water is needed for flue gas humidification inside the reactor. Injection ports were also installed in the boiler walls about 10 feet above the nose elevation.

The second phase of construction began in the Fall of 1991 with the driving of reactor piling and the installation of underground conduit runs. Work continued through to the Summer of 1992 with no need for plant downtime other than normally scheduled outages. During this time the limestone storage area was completed and the injection system was installed on Unit #2. The activation reactor was constructed and then tested with both cold air during a scheduled Unit #2 outage and hot flue gas during a low electricity demand period. Other powerplant tie-ins such as the steam and condensate system were also tested during low demand periods in the evening or on weekends.

#### **Schedule**

The current schedule for the LIFAC demonstration program extends over a four year period from the beginning of preliminary design in August 1990 through the testing program to be completed in early August 1994. However, preliminary test results are now available.

Currently the demonstration project is on schedule. All construction work was completed at the beginning of August 1992. Equipment check-out was performed in July and August and the first limestone delivery was received in early September. Initial tests with limestone injection into the boiler along with post-furnace humidification were conducted in October to December 1992. The project team was prepared to conduct the test plan beginning in early 1993.

#### **Test Plan**

The test plan for the LIFAC demonstration is composed of five distinct phases, each with its own objective. The first of these phases, which has already been completed, consisted of the initial baseline testing portion of the project. Measurements were taken to characterize the operation of the host's boiler and associated subsystems prior to the use of the LIFAC system.

The second, or parametric, phase of testing is currently underway and will be performed to determine the best combination of LIFAC process variables for SO<sub>2</sub> removal. The variables being studied include the limestone injection nozzles' angle and location, the Ca/S molar ratio, the need for supplemental injection air at the boiler, the water droplet size and injection nozzle arrangement in the reactor, the ash recycling ratio and the approach to saturation temperature of the flue gas exiting the activation reactor. The best combination of these variables will be chosen at the conclusion of this phase and used for the remainder of the test program.

Optimization tests will be conducted to examine the effects of different coal and limestone feeds on the SO<sub>2</sub> capture rate. Coals with sulfur contents as high as 3.3 percent will be tested to determine LIFAC's compatibility with high sulfur U.S. coals. Limestones with different compositions will also be tested to determine the LIFAC system's adaptability to local sorbent sources.

Long term testing will also be performed to demonstrate LIFAC's performance under commercial conditions. The LIFAC system will be in operation 24 hours per day for several weeks using the powerplant's baseline coal, high calcium limestone and the optimum combination of process variables.

The final phase of testing is composed of the post-LIFAC tests. The baseline tests will be repeated to gather information on the condition of the boiler and its associated subsystems. Comparisons will be made to the original baseline data to identify any changes either caused by the LIFAC system or independent of its operation.

#### **Preliminary Results**

Parametric testing was initiated at 60 MW to assess the broad impacts of limestone injection, flue gas humidification, and sorbent recycle. Figure 1 shows average reductions achieved throughout the LIFAC process. About 22 percent SO<sub>2</sub> reduction is achieved in the boiler. This is increased to about 52 percent with humidification, and further raised to 75 percent with the use of sorbent recycle from the ESP ash hoppers. These tests were conducted with a fine grind limestone (80% minus 325 mesh) with a Ca content above 90 percent. A Ca/S molar ratio of 2.0 was held near constant and a 4 to 5° Fahrenheit approach to saturation was maintained in the activation reactor.

Figure 2 shows the impacts of varying the Ca/S molar ratio. The majority of the tests have been conducted at 2.0, but the trends are as expected. The higher the Ca/S ratio, the higher the SO<sub>2</sub> reduction. Results show, however, that SO<sub>2</sub> reductions of 75 to 85 percent are possible when spent sorbent is recycled and a 3 to 5° Fahrenheit approach to saturation temperature is maintained.

Figure 3 shows the impact of recycling spent sorbent under various boiler loads. The Ca/S molar ratio was maintained at about 2.0 and the level of humidification is high (4 to 5° Fahrenheit above saturation). Generally, there is an 18 to 25 percentage point increase in SO<sub>2</sub> reduction as a result of sorbent recycle. With recycle, total SO<sub>2</sub> reductions ranged from 75 to 85 percent depending on boiler load.

At this point it has been shown at RP&L and other LIFAC installations that the system can be installed and operated without affecting normal powerplant operations. It will also be shown that the system can economically reduce SO<sub>2</sub> emissions when compared with other flue gas desulfurization technologies.

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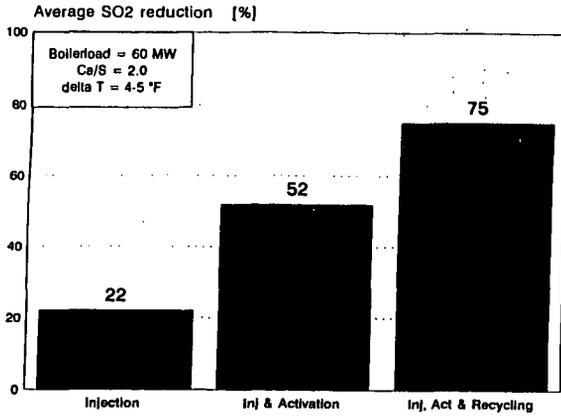


Figure 1. PARAMETRIC EFFECTS

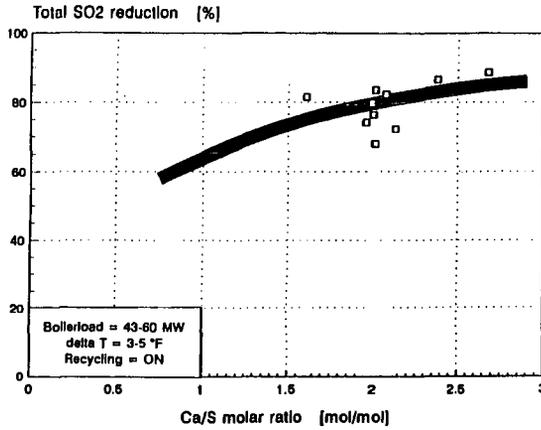


Figure 2. SO<sub>2</sub> REDUCTION vs. Ca/S MOLAR RATIO

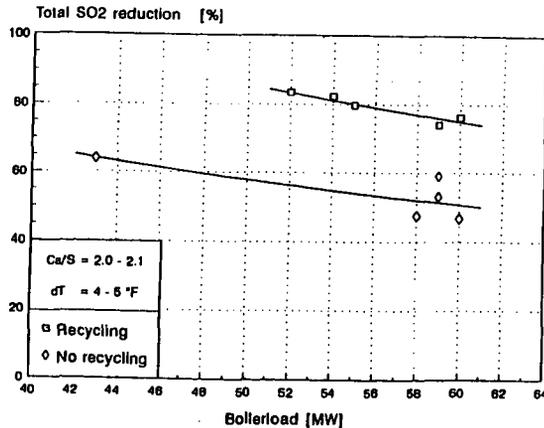


Figure 3. SO<sub>2</sub> REDUCTION vs. BOILER LOAD

## COMPLIANCE BENEFITS OF POWDER RIVER BASIN COAL AND COAL REBURNING

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### ABSTRACT

Cyclone-fired boilers are typically high emitters of  $\text{NO}_x$ , simply as a result of cyclone furnace design requirements. Babcock & Wilcox (B&W) developed the cyclone furnace originally to burn lower grade coals, high in ash and sulfur contents, with unremarkable heating values. To combust the lower grade fuels, the cyclone furnace develops very strong turbulence and extremely fast mixing of fuel and combustion air. A major portion of ash is thrown to the walls where it melts and runs out of the furnace through a slag tap. Large coal particles are trapped in this slag layer allowing complete carbon burn out to be achieved. In this way, the majority of ash and large coal particles are kept out of the main boiler. The resulting high combustion temperatures are conducive to  $\text{NO}_x$  formation. Typically,  $\text{NO}_x$  emissions range from about 0.80 to 1.8 lbs/10<sup>6</sup> Btu, with  $\text{SO}_2$  emissions entirely a function for the fuel.

Standard low  $\text{NO}_x$  burner combustion technologies are not applicable for cyclone-equipped boiler operation. The emerging reburning technology offers cyclone boiler owners a promising alternative to expensive flue gas cleanup techniques for  $\text{NO}_x$  emission reduction. Reburning involves the injection of a supplemental fuel (natural gas, oil or coal) into the main furnace to produce locally reducing conditions which convert  $\text{NO}_x$  produced in the main combustion zone to molecular nitrogen, thereby reducing overall  $\text{NO}_x$  emissions.

B&W has obtained encouraging results from engineering feasibility studies,<sup>(1)</sup> pilot-scale proof of concept testing,<sup>(2)</sup> and a U.S. Department of Energy Clean Coal II project to demonstrate the cyclone coal reburning technology on a full size utility boiler. The host site for the demonstration was Wisconsin Power & Light's (WP&L) 110 MW<sub>e</sub> Nelson Dewey Station. It was at Nelson Dewey that the benefits of fuel switching to a Powder River Basin (PRB) coal as an  $\text{SO}_2$  compliance strategy with coal reburning for  $\text{NO}_x$  emissions reduction became apparent.

The addition of a reburn system capable of providing up to 30% additional fuel input to the furnace means that a utility could switch to lower Btu compliance coal and minimize or eliminate a derate. This paper describes the emissions and impact on boiler operations of coal switching and reburning on Nelson Dewey Unit No. 2.

### INTRODUCTION

The Clean Air Act Amendments of 1990 pose significant challenges to electric utilities to reduce both  $\text{SO}_2$  and  $\text{NO}_x$  emissions. The Act mandates an approximate 3.5 million ton/yr reduction in  $\text{SO}_2$  emissions from 111 selected existing utility boilers by January 1, 1995. An additional 5.3 million ton/yr reduction is also mandated to occur by January 1, 2000 in order to reach a long term  $\text{SO}_2$  emissions cap of 8.9 million ton/yr. Titles I and IV of the Act mandate  $\text{NO}_x$  reduction from stationary sources. Title IV (acid rain) requires the use of low  $\text{NO}_x$  burner technology and Title I (ozone non-attainment) requires reasonable, available control technology (RACT) to reduce  $\text{NO}_x$ . The impact on utilities is that by the year 2000, more than 200,000 MW<sub>e</sub> must be retrofitted with low  $\text{NO}_x$  systems.

The limitations imposed by the Act are particularly challenging, especially for  $\text{NO}_x$  emissions from cyclone-fired boilers. The Coal Reburning for Cyclone Boiler  $\text{NO}_x$  Control Demonstration at WP&L was selected under Round II of the U.S. Department of Energy's Innovative Clean Coal Technology Program to address  $\text{NO}_x$  reduction in cyclone-fired boilers. As an addendum to this demonstration, testing was performed on a Western subbituminous PRB coal. Reburn  $\text{NO}_x$  reduction performance on the Western coal was very encouraging. The use of reburn to minimize or eliminate a unit derate as a result of fuel switching was also demonstrated. Consequently, cyclone reburn can be viewed as a  $\text{NO}_x$  reduction alternative which complements and enhances a coal switching strategy used to comply with  $\text{SO}_2$  regulations.

WP&L's involvement in this project was undertaken for several reasons. The State of Wisconsin enacted acid rain legislation in 1986, which will be fully implemented in 1993. The state law requires significant reduction of SO<sub>2</sub> emissions and the study of potential reduction of NO<sub>x</sub> emissions. To meet SO<sub>2</sub> emission levels at the Nelson Dewey station, WP&L has switched from a medium sulfur bituminous to a low sulfur Western subbituminous coal. In addition, to investigate the potential of reducing NO<sub>x</sub> emissions at Nelson Dewey Unit No. 2, WP&L retrofitted the coal reburning technology.

#### BACKGROUND

Compliance with SO<sub>2</sub> limits will require a utility to exercise a combination of options. These include post combustion flue gas desulfurization (wet scrubbers, dry scrubbers, etc.), repowering with fluidized beds or other technology, acquiring of additional allowances from over compliance at other plants in the utility's system, purchasing additional allowances from other utilities, and fuel switching. Of the 111 named sites more than 64% elected to switch fuels to meet SO<sub>2</sub> compliance.

NO<sub>x</sub> is produced at high temperatures by oxidation of nitrogen from combustion air (thermal NO<sub>x</sub>) and nitrogen in the fuel (fuel NO<sub>x</sub>). Formation of NO<sub>x</sub> is reduced by depressing combustion zone temperatures and by delaying the admission of sufficient oxygen to complete combustion. Compliance with NO<sub>x</sub> limits for the majority of boilers will require use of an internally-staged low NO<sub>x</sub> burner, and optional air staging with overfire air ports.

Reducing NO<sub>x</sub> emissions from cyclone-fired boilers presents a different challenge. Typical delayed combustion techniques are not applicable to cyclones because they rely on developing an oxygen deficient or reducing atmosphere to hamper NO<sub>x</sub> formation. A reducing condition in the confines of a cyclone barrel is unacceptable due to the potential for tube corrosion and severe maintenance problems. Generally, cyclone fuels are typically high in sulfur content which combined with high temperature in a reducing zone create major corrosion problems. Cyclone operation must occur under excess oxygen conditions. High temperatures and severe turbulence within the cyclone barrel attribute to the high NO<sub>x</sub> levels typically observed from cyclone boilers. The 26,000 MW<sub>e</sub> of generating capacity that cyclones represent is about 15% of pre-New Source Performance Standards (NSPS) coal-fired generating capacity, but contribute 21% of NO<sub>x</sub> emitted by pre-NSPS coal-fired units.

#### Reburn Technology Definition

To address the special needs of the cyclone boiler population with respect to NO<sub>x</sub> reduction, B&W developed the coal reburning technology. Reburning is a process by which NO<sub>x</sub> normally produced in the cyclone is reduced (decomposed to molecular nitrogen) in the main furnace by injection of a secondary fuel with a very limited amount of combustion air. The secondary (or reburning) fuel creates an oxygen-deficient (reducing) region where hydrocarbon radicals produced under sub-stoichiometric conditions compete for available oxygen. Any NO<sub>x</sub> in the reburning zone, by virtue of the thermodynamics of the process, is reduced to elemental N<sub>2</sub> while the oxygen is used to continue combustion of hydrocarbon radicals. This process accomplishes the NO<sub>x</sub> decomposition. Because reburning occurs while the cyclone operates in a normal oxidizing condition, its effects on cyclone performance can be minimized.

The reburning process employs multiple combustion zones in the furnace, defined as the main combustion, reburn and burnout zones (Fig. 1). The main combustion zone is operated at a stoichiometry of 1.1 (10% excess air) and combusts the majority of the fuel input (70 to 80% heat input). The balance of fuel (20 to 30%) is introduced above the main combustion zone (cyclones) in the reburn zone through reburning burners. These burners are operated in a similar fashion to a standard wall-fired burner except that they are fired at extremely low stoichiometries. The combustion gases from the reburn burners mix with combustion products from the cyclones to obtain a furnace reburning zone stoichiometry in the range of 0.85 to 0.95 which is needed to achieve maximum NO<sub>x</sub> reduction. A sufficient furnace residence time within the reburn zone is required for flue gas mixing and NO<sub>x</sub> reduction kinetics to occur.

The balance of the required combustion air (totaling 15 to 20% excess air at the economizer outlet) is introduced through overfire air ports. As with the reburn zone, a satisfactory residence time within this burnout zone is required for complete combustion. The added capability to supply fuel to the furnace through the reburn burners is critical to maintaining full load operation while using a lower Btu value PRB fuel.

### Reburn Equipment Optimization for PRB Fuels

In a fuel switching scenario, cyclone furnaces typically experience a 20 to 30% derate due to the volume limited nature of a cyclone furnace in addition to boiler performance. To maintain the original nameplate capacity, an additional 20 to 30% fuel volume is required to compensate for the lower heating value of the PRB coal (8500 Btu/lb versus 11,500 Btu/lb). This increase will not be tolerated by a cyclone furnace and major operational problems will result (high carbon carryover, reduced temperatures in the cyclone and difficult slag removal). To help eliminate this problem, the coal reburning system offers a means to increase fuel volume flow to the boiler.

The coal reburn system includes a pulverizer sized for 20 to 30% of the total fuel input to the boiler. When firing PRB coal, the cyclones continue to operate within design rating (ton/h and heat input) while the pulverizer provides the additional 20 to 30% of the heat input required through the reburn burners to approach full load on compliance coal. In this way, the coal reburn system can reduce or eliminate, on a site specific basis, the derate accompanying a fuel switch to PRB fuel as an SO<sub>2</sub> compliance strategy. The avoided cost of a unit derate can justify the price of a reburn system and at the same time allow the utility to achieve NO<sub>x</sub> and SO<sub>2</sub> compliance goals.

### BASELINE OPERATION

#### Boiler Description

Nelson Dewey Unit No. 2, shown in Fig. 2, is a B&W radiant boiler. The design rate is 100 MW<sub>e</sub> but the current maximum continuous rating (MCR) is 110 MW<sub>e</sub>. The boiler is fired with three cyclone furnaces located horizontally on the front wall with clockwise swirl. Hot combustion gases exit the cyclones at temperatures above 3000F. A target wall in the boiler directs the cyclone flow downward toward the floor of the boiler. The gas then turns upward and passes through slag screen tubes where it enters the main furnace. The lower furnace and slag screen are refractory-lined to keep the slag in a molten state.

The primary demonstration coal for cyclone reburn was Illinois Basin (Lamar) bituminous coal. The majority of the testing was done on this fuel to reflect the large cyclone utility contingent which fires higher Btu, high sulfur bituminous coal. Following the bituminous coal testing, subbituminous PRB coal tests were performed to evaluate the effect of coal switching on reburn operation. This work was important to Wisconsin Power & Light, since switching to the PRB coal for SO<sub>2</sub> compliance was to be implemented by January 1, 1993, within WP&L's system.

#### Baseline NO<sub>x</sub>/CO Emissions

Baseline NO<sub>x</sub> emissions tend to be 10 to 15% lower than those produced with bituminous coal when firing a cyclone boiler with subbituminous coal. The high moisture, low fixed carbon/volatile matter ratio and low fuel nitrogen content are factors which tend to suppress NO<sub>x</sub> formation. Fig. 3 shows that this trend was observed at Nelson Dewey over the boiler's load range (8 to 10% reduced NO<sub>x</sub> emissions).

The higher NO<sub>x</sub> level at 38 MW<sub>e</sub> with Lamar firing is due to single cyclone operation. The higher localized temperatures achieved in firing the single cyclone at a higher capacity results in higher NO<sub>x</sub> levels. Also, the cooling air flow to the idle cyclones increases combustion gas oxygen content which is conducive to NO<sub>x</sub> formulation. Although no baseline data at this load was available during PRB firing, the same trend is expected.

CO emission levels during baseline operation were low while firing either of the two coals. Generally speaking, the CO levels were slightly lower with PRB coal versus Lamar (30 to 45 ppm versus 60 to 70 ppm over the load range).

#### Baseline Boiler Operation with PRB Coal

In addition to the 20 to 30% derate often necessary when switching to higher moisture and lower heating value Western fuels, other related factors must be addressed. These include fouling/slugging problems, higher furnace exit gas temperatures (FEGT), exceeding convection pass metal alarm temperatures, increased attenuater spray flows, furnace overpressure alarms, and higher opacity. Based upon the testing at Nelson Dewey, the maximum load achievable during day to day operation firing PRB coal was about 108 to 110 MW<sub>e</sub> without the reburn system in operation. WP&L's main load limitations were cyclone maximum loading and furnace overpressure alarms. With the reburn system operating, the unit was able to achieve 118 MW<sub>e</sub> while burning PRB coal,

equal to maximum load firing Lamar coal.

It should be emphasized that to address some of the problems characteristic of PRB coal, WP&L had already installed numerous furnace wall sootblowers (air and water blowers available). This was the result of proactive Western fuel firing testing. Also, the cyclone vortex burners were fired by minimizing primary air flow to improve the combustion process within the cyclone barrel. Because of the upgrades and testing experience which WP&L compiled, minimal (if any) problems with fouling/slugging, convection pass metal temperatures, spray flow limitations and opacity levels were encountered during this test project.

#### Baseline Percent Efficiency Loss Due to Unburned Carbon

Baseline percent efficiency loss due to unburned carbon (UBCL) versus boiler steam flow (load) is shown in Fig. 4. Both Lamar bituminous and PRB results are shown. Over the load range, UBCL for PRB coal was lower, particularly at low loads where reduced cyclone temperatures deteriorated combustion performance. With the higher volatile matter content of the PRB coal, these problems were offset at low load. For PRB coal, UBCL ranged from 0% to full load to about 0.3% at very low load. This is not considered a significant impact to overall boiler performance.

#### Baseline Furnace Exit Gas Temperature

Baseline FEGTs were slightly higher during PRB coal firing as compared to the Lamar testing. Fig. 5 shows increases in temperature of about 35, 90 and 10F at full, medium and low loads, respectively. With reburn operation, FEGT's at full load with Lamar coal were reduced by about 150F. FEGT depression with the PRB coal at full load was less, at about 50F. The difference is thought to be due to the reflective nature of PRB ash deposits in the furnace which reduce heat absorption in the furnace. Overall, FEGT with PRB coal and reburn in operation is very close to that of the bituminous coal baseline, offsetting the normally expected FEGT increase with PRB coal. These temperatures are based upon on-line boiler performance model calculations and confirmed via actual in-furnace temperature measurements.

### **REBURNING OPERATION**

#### Reburning Test Parameters

Numerous variables are associated with the reburn system and a test matrix was established to determine optimized operation. The subsequent sections discuss the information collected throughout the parametric evaluations of PRB coal. Complete information on Lamar coal as well as test parameters and ranges tested have been presented in earlier papers.<sup>(9)</sup>

#### Reburning NO<sub>x</sub>/CO Emission Levels

Reburn zone stoichiometry is the most critical factor in changing NO<sub>x</sub> emission levels during coal reburning operation. The reburn zone stoichiometry can be varied by altering air flow quantities (oxygen availability) to the reburn burners, by changing the percent of reburn heat input, the gas recirculation flow rate, or the cyclone stoichiometry.

Fig. 6 shows economizer outlet NO<sub>x</sub> and CO emissions corrected to 3% O<sub>2</sub> while firing PRB coal. A 50% NO<sub>x</sub> reduction was achieved at a reburn zone stoichiometry of about 0.91. As presented in earlier papers<sup>(9)</sup>, the 50% NO<sub>x</sub> reduction point for Lamar bituminous coal was achieved at a reburn zone stoichiometry of about 0.89, a more aggressive reducing atmosphere. The data of Fig. 6 also show that the lowest reburn stoichiometry, 0.85, achieved 62.9% NO<sub>x</sub> reduction. The CO emission levels increased from 45 ppm at baseline to 92 ppm with reburn operation.

It is apparent that reburning is more effective with PRB coal since a less aggressive reburn zone stoichiometry than that used for bituminous coal achieved 50% NO<sub>x</sub> reduction. This infers that either less reburn fuel heat input or higher reburn burner stoichiometries could be used to obtain a given NO<sub>x</sub> reduction with PRB coal.

Comparisons between the PRB and the Lamar coal tests for load versus NO<sub>x</sub> emissions are shown in Fig. 7. PRB operation achieved lower overall NO<sub>x</sub> emission levels and these levels are consistent across the load range. Two factors contribute to the lower NO<sub>x</sub> emissions. First, the baseline NO<sub>x</sub> levels are approximately 10% less with PRB fuel because of inherent fuel characteristics. Secondly, a higher percentage reduction is realized during reburn operation. This is probably due to the higher fuel volatile content

and increased formation of hydrocarbon radicals in the substoichiometric region of the furnace. A change in overall mixing is also a possible explanation. An important observation from Fig. 7 is that NO<sub>x</sub> emissions could be maintained at a constant level over the 110 to 41 MW<sub>e</sub> load range during the PRB testing. The higher volatile content made possible more stable reburn burner flame characteristics at lower loads with lower air rates, than were necessary for flame stability with bituminous coal at low load. This allowed lower reburn zone stoichiometries at low load with corresponding improved NO<sub>x</sub> reduction.

The direct comparison between the Lamar and PRB coal tests are shown in Tables 1 and 2. This direct comparison is based upon operating the reburn system under similar conditions (e.g., same reburn percentage heat input and reburn zone stoichiometries). Optimizing PRB operation further improved overall NO<sub>x</sub> emission levels as shown in the Tables.

Increasing load above 110 MW<sub>e</sub> while firing PRB resulted in higher NO<sub>x</sub> emissions. At 118 MW<sub>e</sub>, the resultant NO<sub>x</sub> level was 275 ppm (0.37 lb/10<sup>6</sup> Btu). This increase in NO<sub>x</sub> level was due to the fact that a lower percentage of reburn heat input could be supplied as a result of reburn feeder limitations. Also, no baseline NO<sub>x</sub> emission levels were obtained at this higher load because the boiler could not accommodate it while firing PRB.

#### Reburning General Boiler Operation

Even though the project testing program is complete, WP&L continues to operate the reburn system. To compensate for the lower heating value of PRB fuel (8500 Btu/lb), WP&L operates the cyclones within design capacity, and uses the reburn system for an additional 30% coal flow. With this strategy, reburn operation minimized or eliminated the derate impact when switching fuels while accomplishing the primary objective of reducing NO<sub>x</sub> emissions. WP&L's typical pre-retrofit low load was about 30 MW<sub>e</sub> and without reburn in operation this level was not affected after the retrofit. Due to reburn flame stability issues and the fact that the cyclones have to maintain a minimum firing rate, the low load condition was increased to 37 MW<sub>e</sub> with reburn in service. Although not ideal, the resultant boiler turndown was 66% with reburn in operation, exceeding the project's goal of 50% turndown.

Table 3 summarizes the remaining general results observed throughout coal reburn operation while firing both of the tested fuels.

#### CONCLUSION

The addition of a reburning system, in combination with a switch to Western subbituminous coal may provide utilities with the optimum strategy for both NO<sub>x</sub> and SO<sub>2</sub> compliance in cyclone-fired boilers. Switching to lower sulfur content coal will lower SO<sub>2</sub> emissions to Phase I compliance levels, and the addition of the reburning system may negate the 20 to 30% capacity derate normally associated with such a switch. In addition, NO<sub>x</sub> emissions are lowered with reburn in operation. The avoided cost of derating a unit could easily justify the price of a reburn system and at the same time allow the utility to achieve NO<sub>x</sub> and SO<sub>2</sub> compliance.

#### Acknowledgements

The authors extend their appreciation to the following people for their help in the management and performance of this study:

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- S. Gebhart, Power Plant Engineer - WP&L
- R. W. Corbett, Technical Project Manager - U. S. Department of Energy

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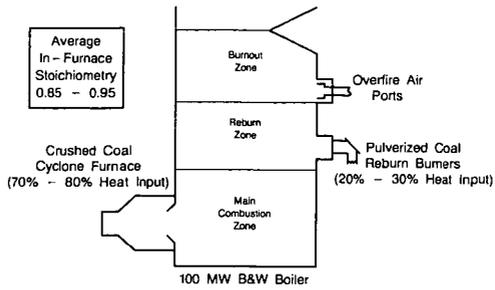


Fig. 1 Cyclone reburn combustion zones.

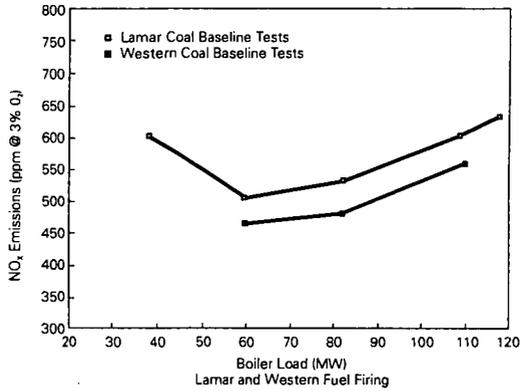


Fig. 2 Wisconsin Power & Light Company Nelson Dewey Station Unit No. 2.

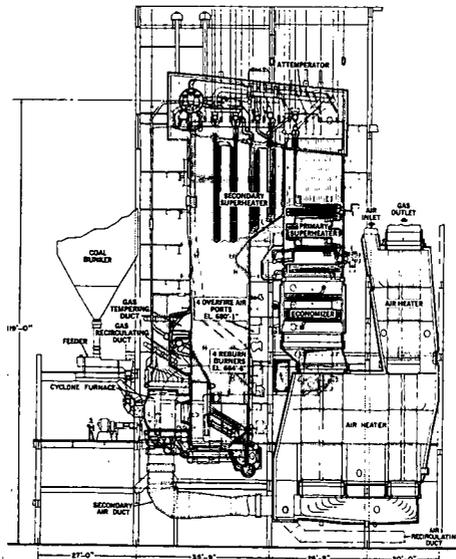


Fig. 3 Baseline NO<sub>x</sub> emissions versus load at Nelson Dewey Unit No. 2.

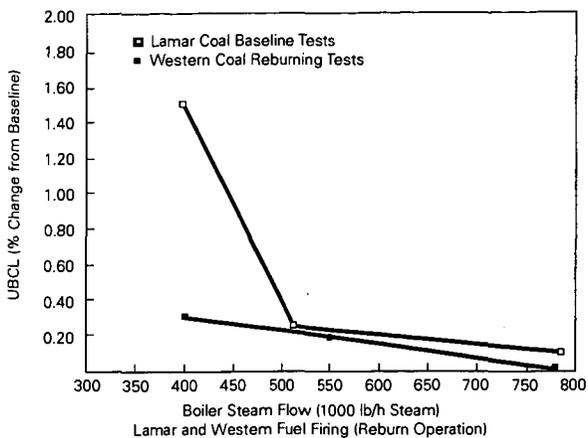


Fig. 4 Unburned carbon (UBCL) efficiency loss (percent change from base) versus load.

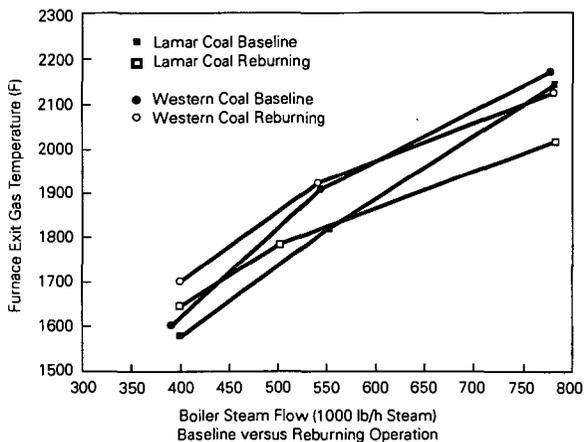


Fig. 5 Furnace exit gas temperature versus load.

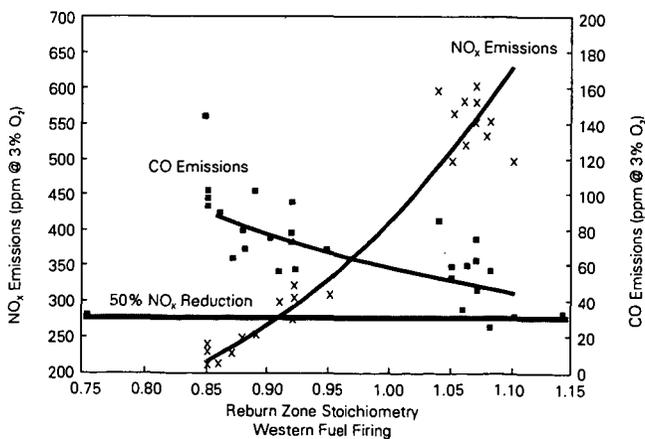


Fig. 6 NO<sub>x</sub> and CO emissions versus reburn zone stoichiometry with PRB coal.

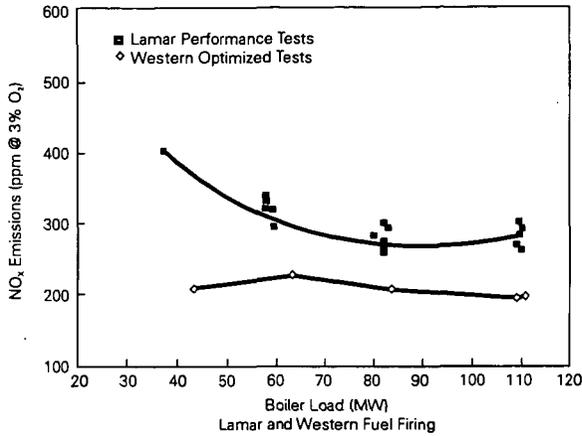


Fig. 7 NO<sub>x</sub> emissions at different loads.

Table 1

Reburn NO <sub>x</sub> Emissions, ppm at 3% O <sub>2</sub> * versus Load					
Load MW,	Baseline Lamar, ppm	Reburn Lamar, ppm	Baseline PRB, ppm	Reburn PRB, ppm	Optimized Reburn PRB, ppm
110	615	290	560	234	208
82	540	285	480	234	215
60	510	325	465	232	220

\* 735 ppm = 1 lb/10<sup>6</sup> Btu NO<sub>x</sub>

Table 2

Reburn NO <sub>x</sub> Emissions as a Percent Reduction from Baseline versus Load			
Load, MW,	Lamar Coal	Reburn PRB Coal	Optimized Reburn, PRB Coal
110	52%	58%	62%
82	47%	51%	55%
60	36%	50%	53%

Table 3

Coal Reburning Effects on General Boiler Operation			
Parameter	Anticipated Results	Actual Lamar Results	Actual PRB Results
Slagging/fouling	No change	No change	No change
Header/tube temperatures	25 to 50F higher	No increase from base	No increase from base
SSH and RH spray flows	30% higher	75% lower	25% lower
Opacity	5 to 10% higher	No increase from base	No increase from base
Furnace corrosion	No change	No change	No change
UBCL (full to low load)	Would increase	0.1 to 1.5%	0.0 to 0.3%
FEGT at full load	Would increase	Decrease 100 to 150F	Decrease 25 to 50F

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# EFFECT OF BUBBLE GENERATING DEVICES ON RECOVERY OF CLEAN COAL FROM REFUSE USING COLUMN FLOTATION

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Keywords: Flotation, beneficiation, clean coal, refuse

## ABSTRACT

Column flotation testing was conducted on the flotation feed slurry obtained from a preparation plant located in the southern Illinois coal basin using three different bubble generating devices, static sparger, gas saver and foam jet. Each of these devices were tested with three different types of frother and various column operating variables to provide maximum combustible recovery, minimum product ash and maximum pyrite rejection. Alcohol frothers were most effective for use with the static sparger, somewhat less effective for the foam jet and ineffective for the gas saver. Glycol frothers were effective for all three bubble generating systems, providing high combustible recovery (>90 percent), low clean coal ash (4-6 percent ash) and high pyrite rejection (70-80 percent).

## INTRODUCTION

Cleaning of fine coal to a very low mineral matter content would have a significant impact on the marketability of high sulfur coals. Most coal preparation plants discard the fine (-28 mesh) coal due to currently available inefficient and uneconomical conventional flotation processes. These fine size refuse slurries are excellent feedstocks for producing low ash, low pyritic sulfur clean coal because the major amount of impurities are liberated.

The column flotation technique has received attention for its ability to provide clean coal containing low mineral matter at high combustible recovery. Yoon,<sup>1</sup> Yang<sup>2</sup> and Christophersen<sup>3</sup> have reported success in removal of high amounts of mineral matter from various fine coals. Parekh et al.<sup>4,5</sup> have reported that using their 'Ken-Flote' column, up to 95 percent of pyritic sulfur was rejected from the Upper Freeport coal at 90 percent combustible recovery.

## EXPERIMENTAL PROCEDURES

Samples of the froth flotation feed were collected from the Kerr-McGee Galatia preparation plant in plastic 55-gallon drums. Representative samples of the slurry were analyzed for percent solids, size distribution and proximate analysis. Baseline flotation tests were conducted using a Denver Model D-12 laboratory flotation machine to determine optimum reagent dosages.

For the column flotation studies, a 5 cm (2-inch) ID, 6 m (20-ft.) tall 'Ken-Flote' column was used (Figure 1). A description of the column has been reported elsewhere.<sup>4,5</sup> Figure 2 shows schematics of the three different types of bubble generating devices tested in this slurry. The static sparger was mounted inside the column and required only the addition of air at 0.276 KPa (40 psig). The gas saver was mounted externally and a mixture of air and reagentized water was forced through it. The 'foam jet' was mounted internally, and a mixture of air and reagentized water was forced through a porous metal plug to generate air bubbles.

The three different types of frothers used in the study and their suppliers were:  
MIBC: Straight chain alcohol (Shell Oil Co.)  
AF76: Mixed alcohols (American Cyanamid Co.)  
M150: Glycol-based (Betz Chemical Co.)

## RESULTS AND DISCUSSION

The particle size and ash analyses of the Galatia flotation feed are summarized in Table 1. The slurry contained 3.5 percent solids with an average particle size of 21.4 microns and had 41.72% ash.

Baseline flotation data obtained using the Denver flotation machine identified optimum fuel oil dosage to be 0.67 Kg/t (1.5 lb/t), while frother dosage was determined to be 0.33 Kg/t (0.75 lb/t) for each of the three frothers tested. With these dosages, combustible recovery ranged from 82 to 87 percent for the three frothers while the clean coal ash content ranged from 12.2 to 15.6 percent.

#### Column Flotation Tests

The column operating parameters that were varied were washwater rate, airflow rate and the type of bubble generating system used. Tables 2, 3 and 4 summarize the best results obtained for each of the frothers tested. These results were derived from a number of tests conducted using statistical design experiments.

The results obtained using MIBC and the three bubble generating devices are summarized in Table 2. The static sparger provided 91.4 percent combustible recovery, 5.97 percent clean coal ash and 66.8 percent pyrite rejection when 0.2 L/min washwater and 1.0 L/min airflow were used. Pyrite rejection improved to 76.3 percent when the foam jet was used for bubble generation, however, combustible recovery decreased to 88.4 percent while clean coal ash improved to 5.10 percent ash. MIBC was not suitable for use with the gas saver (64.9 percent combustible recovery and 3.66 percent clean coal ash).

Results obtained with AF76 are summarized in Table 3. When the static sparger was used with 1 L/min airflow and 0.6 L/min washwater, combustible recovery was 89.9 percent with 5.25 clean coal ash and 75.8 percent pyrite rejection. The foam jet provided slightly higher combustible recovery (91.3 percent) with similar clean coal ash (5.20 percent ash) and pyrite rejection (75.5 percent). Optimum airflow requirement for the foam jet with AF76 was 3 L/min while optimum washwater was 0.2 L/min. As with MIBC, AF76 was not a suitable frother for use with the gas saver providing only 47.2 percent combustible recovery.

All the bubble generating devices provided excellent flotation results with M150 frother as shown in Table 4. The static sparger provided 88.6 percent combustible recovery, 6.21 percent clean coal ash and 64.8 percent pyrite rejection. With the gas saver, combustible recovery improved to 91.0 percent, clean coal ash was reduced to 5.68 percent and pyrite rejection improved to 72.5 percent. The best results were obtained with the foam jet which provided 90.1 percent combustible recovery, 4.80 percent ash in the clean coal and 76.9 percent pyrite rejection.

#### CONCLUSIONS

Based on the experimental data presented, it can be concluded for the Galatia flotation feed that:

- Column flotation provided lower ash (4 to 8%) clean coal product at 90 percent combustible recovery with the three frothers used.
- Column flotation also rejected 50-80 percent pyrite depending on the column operating parameters and the type of frother used. The best results were obtained with the foam jet and M150 frother combination, where 77 percent pyrite rejection was achieved while maintaining 90 percent combustible recovery.
- M150 was an effective frother for all the three bubble generating systems tested, providing high (>90 percent) combustible recovery and low (4-6 percent) clean coal ash content.

#### ACKNOWLEDGEMENTS

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Table 1. Analysis of Kerr-McGee Galatia Flotation Feed

<u>SIZE FRACTION</u> <u>(Mesh)</u>	<u>WEIGHT</u> <u>PERCENT</u>	<u>PERCENT</u> <u>ASH</u>	<u>ASH DISTRIBUTION</u> <u>(Percent)</u>
+200	15.2	7.00	2.5
-200+325	9.4	13.10	2.9
-325+500	8.4	17.45	3.5
<u>-500</u>	<u>67.0</u>	<u>56.66</u>	<u>91.1</u>
Calc Feed	100.0	(41.72)	100.0

Table 2. Optimum Results Obtained with Column Flotation of the Galatia Slurry Using MIBC Frother

BUBBLE GENERATOR	AIRFLOW (lpm)	WASHWATER (lpm)	COMBUSTIBLE RECOVERY %	CLEAN COAL ASH %	PYRITE REJECTION %
SPARGER	1.0	0.2	91.4	5.97	66.8
GAS SAVER	2.0	0.2	64.9	3.66	ND
FOAM JET	1.0	0.2	88.4	5.10	76.3

Table 3. Optimum Results Obtained with Column Flotation of the Galatia Slurry Using AF76 Frother

BUBBLE GENERATOR	AIRFLOW (lpm)	WASHWATER (lpm)	COMBUSTIBLE RECOVERY %	CLEAN COAL ASH %	PYRITE REJECTION %
SPARGER	1.0	0.6	89.9	5.25	75.8
GAS SAVER	2.0	0.2	47.2	3.32	ND
FOAMJET	3.0	0.2	91.3	5.20	75.5

Table 4. Optimum Results Obtained with Column Flotation of the Galatia Slurry Using M150 frother

BUBBLE GENERATOR	AIRFLOW (lpm)	WASHWATER (lpm)	COMBUSTIBLE RECOVERY %	CLEAN COAL ASH %	PYRITE REJECTION %
SPARGER	1.0	0.2	88.8	6.21	64.8
GAS SAVER	1.0	0.2	91.0	5.68	72.5
FOAM JET	2.0	0.4	90.0	4.80	78.9

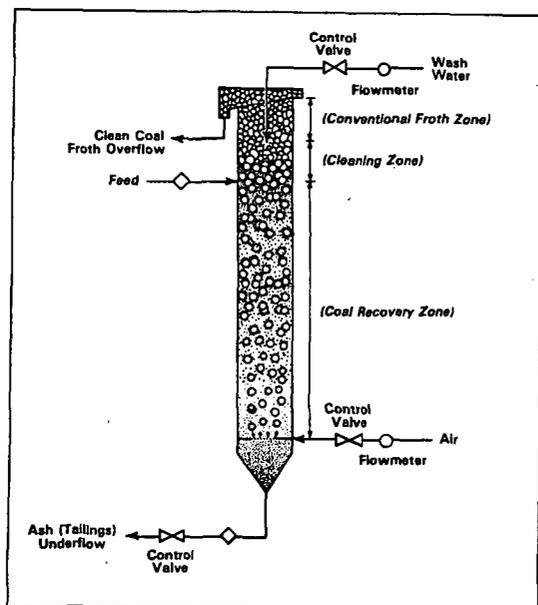
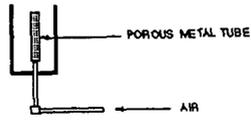
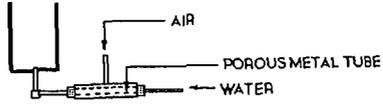


Figure 1. Line Diagram of the 'Ken-Flote' Column Flotation Cell.

SPARGER



GAS SAVER



FOAM JET

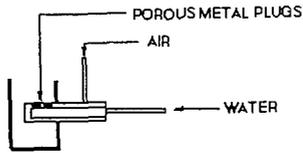


Figure 2. Diagrams of the Three Bubble-Generating Devices Utilized in Column Flotation Testing.

# DEEP CLEANING OF A hvA BITUMINOUS COAL USING A POLYETHYLENE OXIDE/POLYPROPYLENE OXIDE BLOCK CO-POLYMER

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Keywords: Bituminous Coal, Flotation, Block Co-polymer

## ABSTRACT

Deep cleaning of a hvA bituminous coal using flotation process was investigated in this study. A 1/4 inch raw coal containing about 35% ash was subjected to initial flotation tests at nominal feed sizes of -600  $\mu\text{m}$  and -212  $\mu\text{m}$ . In both cases a clean coal product of 13% ash with a combustible matter recovery of about 80% was obtained. Since the ash content was much too high for deep cleaning, a second sample which was the product of a conventional coal preparation plant was used in subsequent studies. It contained about 7% ash. The material was wet ground to nominal feed sizes of -600  $\mu\text{m}$ , -212  $\mu\text{m}$  and -65  $\mu\text{m}$ , respectively, and floated using n-dodecane as collector. The reduction in ash was marginal for the -600  $\mu\text{m}$  and -212  $\mu\text{m}$  coals. However, a clean coal product of 3.9% ash could be obtained with a high yield using -65  $\mu\text{m}$  feed. The product quality was further improved by introducing a mild oil agglomeration stage prior to flotation and by using an ethylene oxide/propylene oxide block copolymer as an additive. The ash content of the clean coal so obtained was 2.5% with a combustible matter recovery of about 76%.

## INTRODUCTION

A super clean coal is considered to be of practical importance in many industrial applications such as liquefaction, coal/water slurries, etc. Liberation of combustible matter from ash forming minerals by size reduction is a necessary step in deep cleaning. In some cases fine grinding to particle sizes less than 100  $\mu\text{m}$  might be required to achieve a satisfactory liberation. With decrease in particle size, the effectiveness of conventional coal cleaning methods mainly involving gravity diminishes. The coal recovery decreases, selectivity becomes poor, and medium recovery becomes a problem. Coal flotation is one of the most promising method for cleaning material at fine sizes. Use of an oily collector and other reagents is often necessary to enhance the hydrophobicity of coal and to promote its flotation. When oil is used alone it might also increase the hydrophobicity of the ash minerals and result in a decrease in the selectivity of the flotation process. It is generally recognized that selectivity of coal flotation does not improve below particle sizes of 100  $\mu\text{m}$  (Crawford, 1936; Davis, 1948; Miller, 1964; Raleigh and Aplan, 1991). Two methods might be used to improve efficiency of separation: I. Decrease floatability of ash forming minerals by the use of dispersants and depressants. II. Increase the floatability of coal by reagents that make coal more hydrophobic. Method I was been demonstrated by Yancey and Taylor, 1935; Zimmerman, 1948; Miller, 1964; Choudhry and Aplan, 1990; Aplan, 1989; Perry and Aplan, 1985, 1988; Arnold and Aplan, 1989.

In this study, Method II was employed to increase the efficiency of coal cleaning by flotation. An ethylene oxide/propylene oxide (PEO/PPO) block co-polymer was used as a reagent to increase the hydrophobicity of flotation in the presence of oily collector. Utilization of a mild oil agglomeration stage prior to flotation was also investigated to further promote the ash rejection.

## EXPERIMENTAL PROCEDURE

### Flotation

A Wemco Model 71260-01 flotation machine was used in the flotation experiments. The stirrer speed was kept constant at 1000 rpm. The solids concentration in the flotation feed was 10% by weight. The flotation pulp was conditioned for 3 minutes to disperse the coal. Dodecane was added in required amounts as the oily collector and the pulp was conditioned for additional 3 minutes. The desired quantity of surfactant was added as an aqueous solution. After conditioning with the surfactant and dodecane, 0.5 kg/T methyl isobutyl carbinol (MIBC) was added as the frother. The slurry was further conditioned for 2 more minutes prior to introduction of air into the cell. The froth was removed at preset time-intervals for a total of 8 minutes. The natural pH of the pulp was 8.0 and no pH adjustments were made throughout the experiments. The flotation products were filtered, dried, weighed and analyzed to determine their ash content.

To prepare the flotation feed, a rod mill was used to wet grind the sample from 1/4 inches to the nominal feed sizes of -600  $\mu\text{m}$  and -212  $\mu\text{m}$ . To prepare the -65  $\mu\text{m}$  feed, a Bleuler mill was employed. The grinding time was determined through prior grinding tests.

### Mild Oil Agglomeration

A mild oil agglomeration of the coal slurry prior to flotation was performed in an attempt to further decrease the ash content. For this purpose, dodecane and a solution of block co-polymeric surfactant was emulsified in a blender for 3 minutes. A coal slurry of 400 ml (1% solid) was added into this solution and blending was continued for 3 more minutes to produce loose agglomerates of coal particles. The slurry was then transferred into the flotation cell and flotation experiments were carried out by addition of frother only.

## MATERIALS

### Coal Samples

The run-of-mine and clean coal samples were obtained from Emerald Mine in Pittsburgh, PA. The coal was a hvA bituminous sample of Pittsburgh seam. The ash and sulfur contents are given in Table 1.

### Surfactants

Two different polymeric surfactants from BASF Cooperation were used in this study to enhance the rejection of ash minerals from coal. These were water soluble and added to the pulp as an aqueous solution. The number of hydrophobic and hydrophilic groups and other properties are given in Table 2. The molecular structure of this type of surfactants is given in Figure 1. Dodecane from Aldrich Chemical Company was used as the oily collector. The frother used in this study was methyl isobutyl carbinol (MIBC) obtained from Shell.

## RESULTS AND DISCUSSIONS

### Flotation of Raw Coal

Initial flotation studies were performed using a raw coal containing 35% ash from Emerald Mine, Pittsburgh at nominal feed sizes of  $-600\ \mu\text{m}$  and  $-212\ \mu\text{m}$  using dodecane as the collector. The results are presented in Figure 2. The decrease in ash was not satisfactory for both the  $-600\ \mu\text{m}$  and  $-212\ \mu\text{m}$  feed materials. A clean coal product of about 12 to 13% ash with a combustible recovery of about 80% was obtained. This observation was in agreement with other studies where no improvement in the product quality was observed with decreasing feed size (Crawford, 1936; Davis, 1948; Miller, 1964, Raleigh and Aplan, 1991). It is possible that even though grinding to a smaller size increased liberation, the problems associated with flotation of fine particles increased. Further cleaning of this sample was not attempted. Instead a clean coal sample from a processing plant with 7.0% ash was used.

### Flotation of Pre-cleaned Coal

#### *Flotation studies in the presence of dodecane*

The second sample tested in this study was a pre-cleaned hvA bituminous coal which was obtained from a conventional coal preparation plant and had an ash content of 7.0%. Similar to the raw coal sample, flotation studies were conducted at various feed sizes in the presence of dodecane as collector. The results of flotation studies are given in Figure 3. As one can see, the reduction in ash was minimal for the  $-600\ \mu\text{m}$  and  $-212\ \mu\text{m}$  feed materials. However, a clean coal product of about 3.9% ash could be obtained with a combustible matter recovery of 75% for the  $-65\ \mu\text{m}$  feed after 2 minutes of flotation. These results show that an increase in selectivity is possible with improved liberation. In order to further decrease the ash content of the sample two surfactants were employed for the  $-65\ \mu\text{m}$  feed material.

#### *Flotation Studies in the Presence of Dodecane and Block Co-polymers Surfactants*

Aliquots of aqueous solutions of the PEO/PPO block co-polymers (BC3 & BC7) and the collector were added simultaneously to the flotation cell. The results are given in Figure 4 for the two polymeric surfactants. For comparison, the flotation data for dodecane alone is also included. It can be seen that the presence of the polymeric surfactants substantially enhanced the ash rejection. A clean coal with an ash content of 2.9% and a combustible matter recovery of 75% could be obtained in the presence of BC3 after 2 minutes of flotation. The corresponding ash was 3.1% for BC7. The amount of ash rejection was found to be a function of both surfactant type and concentration.

## Flotation Studies Preceded by a Mild Oil Agglomeration Stage

In this series of tests, the coal slurry was agitated in a blender to produce loose agglomerates of coal particles. The surfactant, BC7, concentration was same as in previous tests. The agglomerated mass was floated and the results are presented in Figure 4. It can be seen that the product quality improved substantially. A clean coal product of 2.5% could be obtained with a recovery of 75%. A more significant advantage of the pre-agglomeration stage was a substantial increase in rate of flotation. To quantify this effect flotation rates were obtained by plotting flotation yield as a function of flotation time and the data were fitted to a first order model with a rectangular distribution of floatabilities (Huber-Panu et al., 1976; Klimpel, 1980). The mathematical form of this model is given by:

$$R_{t_0} = R_{\infty} \{1 - [(1 - e^{-kt})/kt]\}$$

where  $R_{t_0}$  is the recovery at time  $t$ ,  $R_{\infty}$  is the ultimate recovery and  $k$  is a rate constant. The parameters estimated by the model are given in Table 3. The mean residual square (MRS) errors were somewhat high but the use of alternate models, namely, classical first order, first order with sinusoidal and normal distributions of floatabilities (a summary of these models is given by Miller et al., 1993) gave even higher fitting errors. It can be seen that the ultimate recovery is somewhat similar (around 100%) for all the cases. The flotation rate is between 2 and 3.5  $\text{min}^{-1}$  for the test where flotation was employed only. Use of a mild agglomeration stage significantly accelerated the kinetics of flotation. The flotation rate obtained for this case was 10.66  $\text{min}^{-1}$ . It is interesting to note that this increase in the rate of flotation was also accompanied with a decrease in the ash content, showing the effectiveness of the agglomeration stage.

## CONCLUSIONS

Flotation processing of a hvA bituminous coal was investigated for coals ground to several feed sizes. To improve the influence of PEO/PPO block co-polymers, the selectivity of separation was studied. Based on these tests, the following conclusions were made:

- For the raw coal sample, no improvement in the ash rejection was observed with decrease in feed size. An ash content of 12 to 13% with a combustible matter recovery of about 80% was obtained.
- In case of clean coal, the reduction in ash was marginal for the -600  $\mu\text{m}$  and 212  $\mu\text{m}$  coals. However, for the -65  $\mu\text{m}$  feed a clean coal product of 3.9% ash was obtained with a high yield.
- The clean coal quality was improved further by addition of block co-polymers. The ash content of clean coal so obtained was 2.9% for BC3 and 3.1% for BC7 with a combustible matter recovery of about 75%.
- When a mild oil agglomeration was used prior to flotation the clean coal quality improved further. The clean coal ash content so obtained was 2.5% with a combustible matter recovery of about 76%. In addition, the use of the agglomeration stage resulted in a significant increase in the rate of flotation.

## ACKNOWLEDGEMENTS

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Table 1. A summary of the coal samples used in the study.

Coal samples	Ash (%)	Sulfur (%)
Pittsburgh (Clean coal)	7.0	1.32
Pittsburgh (Raw coal)	35.0	1.85

Table 2. Selected properties of the surfactants used in this study.

Surfactant	Code	Number of hydrophobic groups (PPO)	Number of hydrophilic groups (PEO)	M.W.	HLB*	Surface tension, dyne/cm
Ethylene oxide/propylene oxide block co-polymer	BC3	30	26	2650	11	43.0
	BC7	56	60	5900	13	33.0

\* Hydrophile-lipophile balance.

Table 3. The ultimate yields, flotation rates and mean residuals for fitting the first order kinetics equation with rectangular distribution of floatabilities.

	Dodecane (0.07 kg/T)	BC3 (0.1 g/T)	BC7 (20 g/T)	Aggl. & Flotation
$R_{\infty}$	100.0	99.4	94.3	100.0
k	3.45	2.34	1.97	10.66
MRS*	3.14	8.97	25.56	17.80

\* Mean residual square

Figure 1. Structural formula of PEO/PPO block co-polymers used in this study.

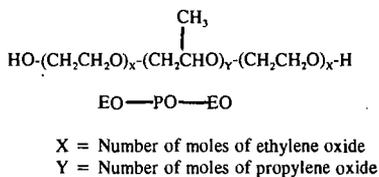


Figure 2. Combustible matter-ash recovery curves for the run-of-mine sample of Pittsburgh seam coal.

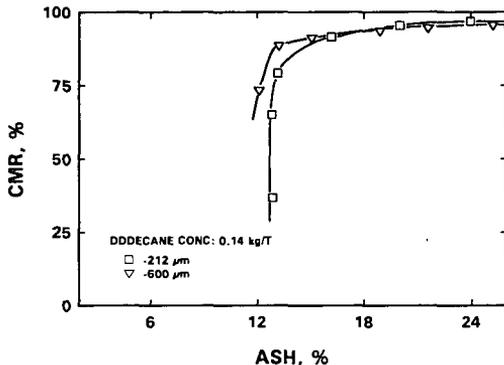


Figure 3. Combustible matter-ash recovery curves for the pre-cleaned sample of Pittsburgh seam coal.

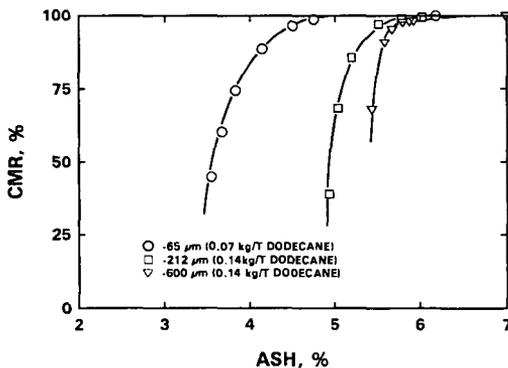
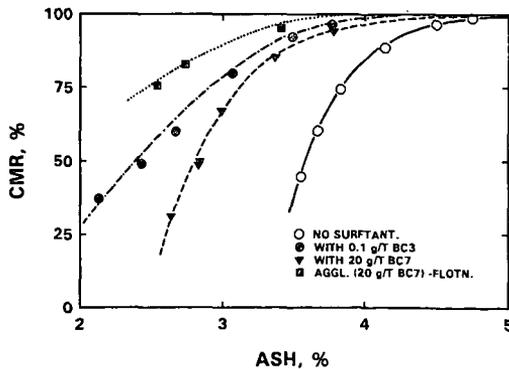


Figure 4. Effect of PEO/PPO block co-polymers on the combustible matter recovery and ash content.



# EFFECT OF CHEMICAL TREATMENTS ON BENEFICIATION OF LOW RANK COALS

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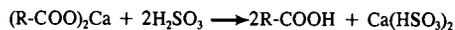
## ABSTRACT

Cleaning of low rank coals is desirable for preparation of feed stock for liquefaction of coal. In this investigation, the effect of chemical pretreatment on the beneficiation of low rank coals was studied. In the first phase of the research, a lignite sample from Texas with an ash content of 12.9% was pretreated with sulfurous acid prior to separation. Treated coal was subjected to flotation or Liquid-Liquid Extraction (LLE) for further cleaning. A final clean coal product of 4.4% ash was obtained with a combustible matter recovery of about 95%. In the second phase, a chemically treated low rank coal sample with 3.3% ash was further cleaned using a mild agglomeration stage prior to flotation. When a non-ionic, block co-polymer surfactant was used with the oily collector, a clean coal product of 1.85% ash could be obtained with a combustible matter recovery of over 85%.

## INTRODUCTION

It is well known that lignites are very difficult to clean from the mineral matter using conventional flotation due to their poor floatability. According to Sun (1954) the floatability index of lignites was 12 taking Ceylon Graphite with an index of 100 as standard. The average floatability index for hvA bituminous coals was 94 on the same scale. The poor floatability was also confirmed by Aplan (1976, 1980 and 1988) who observed that the measured contact angle using captive bubble method was zero for lignites. Use of an oily collector alone does not improve the floatability due to low adsorption of oil on lignites (Sun, 1954; Gayle et al, 1965). This is most probably due to high oxygen content of lignites and the abundance of surface functional groups (Fuerstenau et al, 1983; Gutierrez-Rodriguez and Aplan, 1984 and Schobert, 1990). It was reported that the average oxygen content of lignites could be as high as 30%, carboxylic groups constituting about half this amount (Quast and Readett, 1987). Another important consequence of the presence of the surface functional groups is that these groups act as ion exchange sites for cations such as Na, Ca, Mg and K, and may result in the accumulation of carbonaceous ash. In general 90 - 100% of the Na, 75 - 90% of the Mg, 50 - 75% of the Ca and 35 - 50% of the K in low rank coals may be accumulated by the ion exchange process (Schobert, 1990). These cations which are bonded to the organic portion of the coal as inherent ash are practically impossible to clean using conventional separation techniques.

Chemical treatment of lignites prior to separation may be beneficial due to dissolution of these ion exchange cations, resulting a direct decrease in the ash content. Different types of pretreatment have been suggested in the literature. Mochida et al showed that pretreatment of lignites using HCl improved their conversion during coal liquefaction (1983). Cronauer et al utilized sulfurous acid to chemically clean the lignites (1991). The authors suggested that sulphurous acid converts carboxylic salts to free carboxylic acids through the following reaction:



It was pointed out that sulfurous acid was cheap, less corrosive and easily recoverable. In addition to dissolving the cations from the coals structure, the dissolution process may change the floatability of lignite due to its effect on the surface functional groups.

Objective of this study was to investigate deep cleaning of lignites using a combination of chemical dissolution and physico-chemical separation methods. The study was conducted in two parts. In the first part a raw lignite sample was subjected to chemical treatment using sulfurous acid under a variety of conditions. The treated sample was then further cleaned using Liquid-Liquid Extraction (LLE) method using heptane as the carrier liquid. In the second part a pretreated lignite sample was subjected to cleaning using flotation or mild oil agglomeration followed by flotation, MOAF. A block co-polymer surfactant was also used in this part of the study to improve ash rejection.

## EXPERIMENTAL

### Material

The raw lignite sample used in the first part of the study was obtained from Amoco Company, Naperville, IL and originated from Martin Lake, Texas. The sample had an ash content of 12.9% and was less than 6.35 mm in particle size. A semi-quantitative spectroscopic analysis on the ashed lignite showed that the ash material contained about 10% Ca, 5% Mg and 1% Na. The Si content was around 2%. The sample was ground to a feed size of  $-150\ \mu\text{m}$  to be used in the flotation and LLE studies.

The coal sample used in second part of the study had been pretreated by the Amoco Oil Company with sulfurous acid and had an ash content of about 3.3%. It is referred as Sample No. 2 and had a narrow size distribution of  $212 \times 1650\ \mu\text{m}$ . It was wet ground to various feed sizes for the flotation or mild oil agglomeration-flotation studies.

A polypropylene/polyethylene block co-polymer surfactant was used to enhance the ash rejection during flotation or mild oil agglomeration-flotation studies. This surfactant was previously shown to be very selective in the flotation of a low rank coal (Chander et al, 1993). It was added to the system in an oil-dispersed form. The chemical structure of the surfactant is given in Figure 1.

### Methods

#### *Liquid-Liquid Extraction*

The process of Liquid-Liquid Extraction (LLE) involves selective transfer of hydrophobic particles of organic matter from aqueous phase to an emulsion phase. This process is especially useful at fine sizes (Hsu and Chander, 1988). The tests were conducted in a baffled, 500 ml vessel of standard geometry (Holland and Chapman, 1966). The vessel was slightly tapered at the bottom to allow for easy removal of the separated phases. The total solution volume in a given test was 400 ml. The slurry contained 1% solids by weight and 15% heptane as the organic phase. Following initial conditioning to wet and disperse the lignite, the desired reagents were added and the slurry was conditioned 10 more minutes. Heptane was added and the stirring was continued for preset periods of time at a selected stirrer speed. Finally, the emulsion phase containing the coal particles was allowed to separate out from the aqueous phase containing the mineral matter. Both phases were removed from the bottom of the vessel, filtered, dried and analyzed. Practically all the heptane was recovered from the emulsion phase during the filtering step.

#### *Flotation*

A Wemco model 21260-01 flotation machine equipped with a 1 liter cell was used in the flotation experiments. The impeller speed was kept constant at 1000 rpm in all the flotation tests. The solid concentration was kept constant at 5% when flotation was used alone. For the tests where a mild oil agglomeration step was utilized prior to flotation, the solid concentration in the flotation cell was determined by the amount of solids in the agglomeration stage. The slurry was preconditioned for 3 minutes before any reagent addition. Dodecane and methylisobutylcarbinol (MIBC) were used as the oily collector and frother, respectively. The experiments were carried out at the natural pH of the slurry which was mostly on the acidic side due to prior acid treatment. The flotation products were dried, weighed and analyzed.

#### *Mild Oil Agglomeration Flotation*

A limited number of tests were performed in which a mild agglomeration stage was combined with flotation. This process is referred to as MOAF in this article. In this procedure the conditions were chosen such that the coal particles were agglomerated in a high shear environment to produce loose agglomerates of about one millimeter in diameter. For this purpose dodecane or dodecane-block co-polymer surfactant solution was emulsified in a blender for three minutes. A coal slurry of 400 ml of varying solids content was added into this solution and the blending was continued for 3 more minutes. This procedure produced loose agglomerates of the coal particles. The slurry containing the agglomerates was transferred into the flotation cell and flotation tests were carried out by addition of frother only. In some cases, dodecane-surfactant mixture was added directly to the coal slurry prior to any blending procedure.

## RESULTS AND DISCUSSIONS

### Studies with the Raw Texas Lignite Sample

#### *Pretreatment with Sulfurous Acid*

A 6.0% aqueous solution of  $\text{SO}_2$ , sulfurous acid ( $\text{H}_2\text{SO}_3$ ), was utilized to dissolve the cations from the coal structure. The experiments were conducted at different acid concentrations and temperatures using a nominal  $-150 \mu\text{m}$  feed material. An optimum decrease in the ash content was observed at an acid concentration of 1.0% at  $50^\circ\text{C}$ . Under these conditions the ash content of the lignite sample decreased from 12.9% down to about 6.5% with a combustible matter recovery of almost 100%. A semi-quantitative spectrographic analysis conducted on the as-received and  $\text{H}_2\text{SO}_3$  treated samples showed that there was approximately a ten-fold decrease in the Ca, Mg and Na contents of the lignite sample, supporting the reverse extraction of the cations from the carboxylate structure. The fact that the Na content also decreased substantially is an important result since sodium is known to cause slagging problems in combustion.

Both the as-received and the chemically treated samples were subjected to zeta potential measurements in order to determine the effect of chemical treatment on the electrokinetic behavior. A Lazer Zee Meter from Pen Kem Inc., New York, was used for this purpose. It was observed that the point of zero charge of the as-received sample was around a pH of 2.4. This was in a good agreement with the data in the literature (Arnold and Aplan, 1989). The point of zero charge decreased with increasing concentration of  $\text{H}_2\text{SO}_3$  and found to be around a pH of 1.8 for an acid concentration of 6.0%.

In order to determine the effect of the acid treatment on the floatability of the lignite sample contact angle measurements were conducted using a method first described by Wei et al (1992). In this method a particle was gently placed at the air-water interface and the cross sectional areas of both parts of the particle above and below the interface were measured with a microscope coupled to an image analyzer. The ratio of these areas are related to the contact angle. To prepare the sample for the contact angle measurements a sufficient amount of lignite sample was screened to obtain a narrow size fraction of  $600 \times 850 \mu\text{m}$ . Half of this sample was treated with distilled water whereas the other half was treated with 1.0% sulfurous acid. The samples were dried in a vacuum oven at room temperature. Measurements conducted on about 150 particles for each sample showed that the mean advancing contact angle increased from 62 degrees for the untreated coal to 72 degrees for the  $\text{H}_2\text{SO}_3$  treated coal. This apparent increase in the contact angle suggests that the sulphurous acid treatment results in an increase in the hydrophobicity of the lignite sample.

#### *Flotation*

Flotation experiments were carried out using both the untreated, 12.9% ash, and the  $\text{H}_2\text{SO}_3$  treated, 6.5% ash, samples. The feed size of the both samples was  $-150 \mu\text{m}$ . The concentration of dodecane and MIBC were 20 kg/T and 0.8 kg per ton of coal, respectively. The flotation tests were carried out at the natural pH values of 6.3 for the raw sample and 4.4 for the  $\text{H}_2\text{SO}_3$  treated sample. A quartz depressant,  $\text{Na}_2\text{SiO}_4$ , was also used in the flotation tests. It was observed that the untreated sample could not be benefited using flotation. The ash content of the product was 12.6% after 8 minutes of flotation with a coal recovery of 50.4 in the presence of 0.4 kg of  $\text{Na}_2\text{SiO}_4$  per ton of coal. The flotation response of the treated sample was also not very promising. The ash content of the clean coal product was about 5.5% when the coal recovery was 95%. The high coal recovery obtained in the case of the treated sample was in agreement with the observation stated in the preceding section that acid treatment should enhance the floatability of the lignite sample. Since no satisfactory results were obtained using flotation, LLE method was employed in subsequent tests.

#### *Liquid-Liquid Extraction*

In this series of tests, heptane was emulsified with lignite slurry in a standard vessel. The lignite particles were extracted in the hydrocarbon to form an emulsion phase. Upon completing the transfer of coal particles from aqueous phase into the emulsified heptane phase, the mixing was stopped and the phases were allowed to separate. The emulsion containing the coal particles was separated from the aqueous phase which contained the mineral matter. The LLE experiments were carried out under a variety of test conditions with the sulfurous acid treated lignite sample which contained 6.5%. The variables tested included pH, stirrer speed, mixing time and depressant type and concentration. The best ash rejection was obtained at the natural pH value of the sample and at a stirrer speed of 1800 rpm. The subsequent testing was carried out under these conditions. The result of the mixing time experiments are given in Table I. It can be seen that the ash content of the product does not vary appreciably whereas the combustible matter recovery steadily increases

with increasing mixing time.

Sodium silicate and sodium dicarbonate were used as depressants at different concentrations to increase the efficiency of separation. In the case of  $\text{Na}_2\text{SiO}_4$ , a clean coal product of 4.6% ash with a combustible matter recovery of 94% was obtained at a  $\text{Na}_2\text{SiO}_4$  concentration of 0.13 kg per ton of coal. The results obtained with  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  were slightly better. A clean coal product of 4.4% ash was obtained with a combustible matter recovery of 95% at a  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  concentration of 0.25 kg per ton of coal.

#### Studies with the $\text{H}_2\text{SO}_4$ Treated No. 2 Sample

The sample was processed using conventional flotation or mild oil agglomeration flotation, MOAF in order to further reduce the ash content. The quality of separation was increased in both cases when a block co-polymer surfactant was added into the oily collector. The results of these studies are given in the following paragraphs.

#### *Flotation*

The sulfurous acid treated sample was ground to a nominal feed size of  $-150 \mu\text{m}$  and floated at a natural pH of 2.9. A clean coal product of 2.2% ash was obtained with a combustible matter recovery of 70% when the concentration of the oily collector was 4.0 kg per ton of coal. The ash content did not change with an increase in the oil concentration up to 40 kg per ton of coal. However, the combustible matter recovery slightly increased to 74%. When 0.8 kg of a block co-polymer surfactant was added into 4.0 kg of oil per ton of coal, the combustible matter recovery increased to 87% and the ash content of the clean coal was 2.2%. The ash content of the pretreated coal sample could not be reduced to less than 2.0% when additional flotation studies were performed. Hence, a mild oil agglomeration stage was used prior to flotation step.

#### *Mild Oil Agglomeration Flotation*

Initial MOAF tests were carried out to determine the best particle size for ash rejection. The concentration of the oily collector and the surfactant were 250 kg and 8 kg per ton of coal, respectively. Three different feed sizes of  $-150 \mu\text{m}$ ,  $-60 \mu\text{m}$  and  $-38 \mu\text{m}$  were tested in these experiments. The results are given in Table 2. It was observed that a clean coal product of 2.0% ash could be obtained with a combustible matter recovery of 85% when the nominal feed size was  $-38 \mu\text{m}$ . Neither the ash nor the coal recovery was better for the other two feed sizes. Hence, subsequent studies were carried out using a feed size of  $-38 \mu\text{m}$ . In the next set of MOAF tests, sodium hexametaphosphate (calgon) was added into the coal slurry to promote dispersion of the coal particles. The collector and the surfactant concentrations were kept the same as before. Calgon concentrations of 0.02 kg, 0.1 kg, 0.5 kg and 2.0 kg per ton of coal were tested. The results of these tests are given in Table 3. It can be seen that addition of the dispersant improved the separation appreciably. A clean coal product of 1.94% ash could be obtained with a coal recovery of 92% when 0.5 kg of calgon per ton of coal was added. In order to determine the effect of the block co-polymer surfactant, the concentration of the surfactant was varied keeping the oil concentration constant at 250 kg per ton of coal. The amount of surfactant used was 0, 2, 8, 8 and 25 kg per ton of coal, respectively. The results are given in Table 4. It was observed that increasing the amount of the surfactant in the system decreased the ash content while increasing the combustible matter recovery. The surfactant amount of 25 kg per ton of coal resulted in a better product. In another set of experiments the oil to surfactant ratio was kept constant at 10. The oil amounts in these tests were 125, 250 and 500 kg per ton of coal. The ash contents and the combustible matter recoveries for these tests are given in Table 5.

In the above tests the emulsification of oil-surfactant solution was carried out in the presence of the coal slurry. A different set of experiments was conducted where the oil-surfactant solution was emulsified for 3 minutes prior to the addition of the coal slurry in order to reduce the amount of surfactant and oil used in the process. The coal slurry was added to this emulsified phase and the agglomeration was initiated. The experiments were carried out using the same oil to surfactant ratio of 48. The oil amounts employed in this set were 48, 96 and 192 kg per ton of coal. The results of these experiments are given in Table 6. It was seen that pre-emulsification decreased the amount of surfactant required for separation. A clean coal product of 1.85% ash could be obtained with a coal recovery of 85% using 192 kg of oily collector with 2 kg of surfactant per ton of coal.

### CONCLUSIONS

Deep cleaning of lignite samples was investigated using a combination of chemical dissolution and physico-chemical separation methods. Sulfurous acid,  $\text{H}_2\text{SO}_3$ , was utilized in the dissolution studies. The treated samples were subjected to liquid-liquid extraction, flotation and mild agglomeration-flotation separations to further decrease the ash content.

The findings of this study can be summarized as follows:

1. In the absence of sulfurous acid treatment, lignite could not be beneficiated.
2. Sulfurous acid leaching was very effective in removing salts of Ca, Mg and Na. A clean coal sample of 6.5% ash was obtained from a raw lignite sample with 12.9% ash using a 1.0% solution of sulfurous acid.
3. The acid treatment rendered the low rank coal more hydrophobic most probably due to some chemical changes at the surface during the dissolution of the cations from the carboxylate structure.
4. A clean coal product of 4.4% ash was obtained with 95% combustible matter recovery from a 12.9% ash lignite sample by a combination of sulfurous acid treatment and LLE separation.
5. For a second sample prepared by Amoco Oil Company, the ash content of sulfurous acid treated coal was reduced from 3.3% to 1.85% with a combustible matter recovery of 85%, using the mild oil agglomeration-flotation method.
6. Even though large amount of hydrocarbon was used to obtain the clean coal products of desirable quality, it was possible to recover and recycle most of it.

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Table 1. Results of the LLE tests as a function of mixing time.

Mixing Time (minutes)	Ash (%)	CMR (%)
5	4.63	93
10	4.80	95
20	4.69	96
40	4.90	97
80	4.78	98

Table 2. Results of the MOAF tests as a function of feed size.

Feed size	Ash (%)	CMR (%)
-150 $\mu\text{m}$	2.40	69
-60 $\mu\text{m}$	2.40	63
-38 $\mu\text{m}$	2.02	85

Table 3. Results of the MOAF tests as a function of calgon concentration.

Concentration	Ash (%)	CMR (%)
0.00 kg/T	2.02	85
0.02 kg/T	1.97	93
0.10 kg/T	2.03	88
0.5 kg/T	1.94	92
2.0 kg/T	1.97	92

Table 4. Results of the MOAF tests as a function of surfactant concentration.

Surfactant Concentration	Ash (%)	CMR (%)
0 kg/T	2.23	82
2 kg/T	2.25	82
8 kg/T	2.02	85
25 kg/T	1.96	88

Table 5. Results of the MOAF tests as a function of collector concentration at a fixed collector to surfactant ratio of 10.

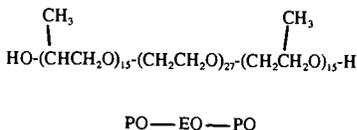
Collector Concentration	Ash (%)	CMR (%)
125 kg/T	2.49	75
250 kg/T	1.96	88
500 kg/T	1.99	91

Table 6. Results of the MOAF tests as a function of collector concentration at a fixed collector to surfactant ratio of 48.

Collector Concentration	Ash (%)	CMR (%)
48 kg/T	2.18	58
96 kg/T	1.95	72
192 kg/T	1.85	85

\* Reagents were Pre-emulsified in a blender before addition of coal slurry.

Figure 1. Structural formula of PPO/PEO block co-polymer used in this study



## ENZYMATIC CONVERSION OF COAL IN NONAQUEOUS MEDIA

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Keywords: coal depolymerization; peroxidases; aqueous-organic media for biocatalysis.

### ABSTRACT.

Two different peroxidases--from horseradish roots and soybean hulls--were studied as potential biocatalysts for modification of coal in aqueous-organic media. Both enzymes were found to cause polymerization of Mequinza lignite in a mixture (1:1 v/v) of DMF and acetate buffer (pH 5). At pH 2.2, incubation of the lignite with soybean peroxidase in 50% DMF resulted in both polymerization and depolymerization.

### INTRODUCTION

It has been demonstrated earlier that both isolated enzymes<sup>1,2</sup> and intact microorganisms<sup>3-5</sup> can selectively modify coal. However, coal bioprocessing has not been highly successful. One of the most difficult problems that remains is the lack of sufficient enzyme-coal interactions that are necessary for substantial depolymerization and solubilization. The insolubility of coal in water severely limits the extents of either microbial or enzymatic degradation. Any truly effective coal depolymerization process, therefore, must take place in a non-aqueous medium that can solubilize at least some fractions of the coal. The use of enzymes in nonaqueous solvents<sup>6,7</sup> has now become common place and numerous enzymes and conditions have been studied in organic media. Specifically, peroxidases are known to be highly active in nonaqueous media, with turnover numbers often enhanced in organic solvents over that in water<sup>8</sup>. Several peroxidases (e.g., chloroperoxidase, lactoperoxidase, and horseradish peroxidase)<sup>1,2</sup> display activity on the oxidation of coal-related compounds including lignin<sup>9</sup>. In the present work, our efforts have focused on study of two different peroxidases as potential biocatalysts for modification of coal structure and for depolymerization of coal in aqueous-organic media. We have evaluated also multi-enzyme systems from whole cells of bacteria in respect of oxidation of a coal model compound.

### MATERIALS AND METHODS

Mequinza lignite (from Spain) was used as a substrate. The lignite was not subjected to any treatment except for thorough grinding. Horseradish peroxidase (EC 1.11.1.7) type II was obtained from Sigma Chemical Co (St. Louis, MO). Peroxidase from soybean hulls (EC 1.11.1.7) was obtained from Enzymol, International (Columbus, OH). The enzymes were used without additional purification. Before incubation with the enzymes, the lignite was fractionated on lipophilic Sephadex LH-60. Gel permeation column chromatography on lipophilic Sephadex LH-60 is traditionally used as a tool to separate molecules of different molecular weight in a non-aqueous medium as well as to determine the molecular weight distribution. Intermolecular associations of coal polymers with the resin, and to each other, were eliminated by employing DMF supplemented with 0.1 M LiCl. The range of molecular weights which can be separated by this technique is 500 - 60000 D.

In a typical experiment, 7.5 mg of the soluble coal fraction was dissolved in 1 ml of pure DMF and 0.8 ml of the aqueous buffer (containing 1 mg of enzyme) was added. The reaction was initiated upon pumping 0.2 mL of hydrogen peroxide into the vial over a period of two minutes. The final concentration of hydrogen peroxide was 0.66-0.8 mM. A control reaction which included all reagents, except enzyme, was initiated concurrently. The incubation mixtures were shaken at 100 rpm at 30°C for 24 h during which time 0.1 mL aliquots were taken. Before analysis of the molecular weight distribution, the samples of the lignite after incubation with peroxidases were dried in vacuum at 45°C and redissolved in 0.1 mL of pure DMF. Supernatant was loaded onto a glass column (24 x 1 cm) packed with Sephadex and eluted at a flow rate 0.1 mL/min. The column was calibrated with polystyrenes with molecular weights of 2, 4, 15, and 50 kD. Fractions (1 mL) were measured via absorbance at 280 nm.

Dibenzothiophene and biphenyl were used as coal model substrates to study oxidation by whole cells of *Beijerinckia* and by the *Beijerinckia* enzyme system in aqueous-organic media. Cells were grown via the method of Laborde and Gibson<sup>10</sup>, harvested and lyophilized. The freeze-dried cells were ground then to a fine powder. NADH was added to the incubation mixture as a cofactor of the oxygenase system for the disrupted cells. In a typical experiment, wet whole cells of *Beijerinckia* (0.3-0.4 g) were incubated with saturated concentrations of the substrates in 10 mL of phosphate buffer (0.05 M, pH 7.2) containing 0.1% of pyruvate and 1-20% (v/v) of organic solvents. In the case of the lyophilized cells (fine dry powder), incubation was carried out in acetate-phosphate buffer at pH 5.0-7.5 containing up to 50% of an organic solvent at a concentration of cells and NADH of 4 mg mL<sup>-1</sup> and 1 mM, respectively. Periodically, aliquots of the reaction mixtures were withdrawn, dried in vacuum at 40°C, redissolved in pure acetonitrile, and analyzed with a Waters  $\mu$ Bondapak C<sub>18</sub> column (3.9 x 300 mm). The mobile phase consisted of an acetonitrile-water mixture; the flow rate was 1 mL min<sup>-1</sup>. Absorbance peaks were monitored at 230 nm.

## RESULTS AND DISCUSSION

### Peroxidase-Catalyzed Polymerization of Lignite

It was previously shown<sup>9</sup> that horseradish peroxidase (HRP) is active in dioxane-water and DMF-water solutions in the one-electron oxidation of phenolic units of kraft lignin, a relatively inert polymeric compound. Horseradish peroxidase suspended in dioxane was also reported<sup>1</sup> to cause the limited solubilization and depolymerization of leonardite, a low rank coal.

In our preliminary investigation we found that peroxidase from soybean hulls (SBP) possesses a much higher oxidative potential in comparison to horseradich peroxidase. Oxidative cleavage of natural coal --Mequininza lignite-- has been attempted using both peroxidases. This lignite represents a highly oxidized, non-bituminous coal.

The lignite powder is poorly soluble in tetrahydrofuran (THF) and dioxane (less than 1% w/w from total amount) and insoluble in water. Both THF and dioxane solubilize only low molecular weight fractions with molecular weight less than 2 kD (data not shown). DMF has been found to dissolve ca. 25% of coal. The solution in DMF contains a broad range of molecular weights as it is seen from Fig. 1, with some coal polymers soluble at molecular weights > 50 kD.

The DMF-soluble coal was fractionated on the GPC column and fraction number 11 (4 kD) was collected for further experimentation. At this molecular weight, both polymerization and depolymerization of the coal fraction can be monitored.

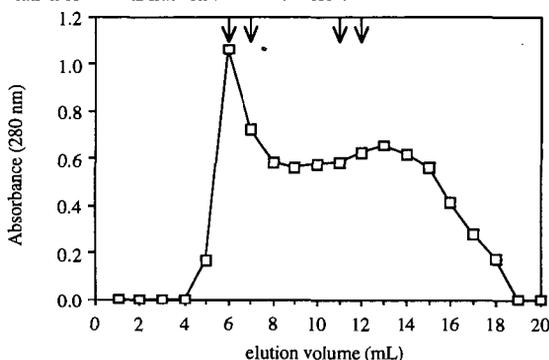


Fig. 1. Gel permeation chromatography of Mequininza lignite fractions soluble in DMF. Arrows indicate molecular weight markers: from left to right, 50, 15, 4, and 2 kD.

Lignite modification reactions were studied using HRP and SBP catalysis with this intermediate molecular weight fraction in 50% DMF at pH 5 (50 mM acetate buffer). In both cases, the incubations resulted in turbid solutions. Control reactions which included water instead of hydrogen peroxide did not lead to formation of turbidity. Sediments were not completely soluble in pure DMF. Figures 2 and 3 depict changes in the molecular weight profile of the lignite fraction for HRP and SBP as catalysts. In both cases, following 24 h, clear polymerization was observed. The highest soluble polymeric products had molecular weights > 50 kD. The DMF-insoluble fractions appear to consist of high molecular weight polymers produced during peroxidase catalyzed oxidative cleavage of coal structure. No evidence of depolymerization was detected. These findings are in accordance with previous literature observations<sup>1,10</sup> that peroxidases are excellent catalysts to oxidize phenolic polymers such as lignins and coals, particularly in the presence of organic solvents.

### Oxidative Power of Soybean Peroxidase -- Depolymerization of Coal in Aqueous DMF Solutions

In related research, we have studied the oxidative ability of SBP. The enzyme is highly active and stable under acidic conditions. At low values of pH, it has been observed that SBP is capable of oxidizing veratryl alcohol (personal communication of J. P. McEldoon). The catalytic activity of SBP on veratryl alcohol was strongly dependent on the pH and the presence of calcium ions. It was found that the pH optimum of veratryl alcohol oxidation is ca. 2.15 with very little oxidation above pH 3. Furthermore, the enzyme is strongly stabilized by CaCl<sub>2</sub> concentrations of up to 0.1 M. Evidently, the low pH results in a significant increase in the oxidation potential of SBP and enables a compound such as veratryl alcohol to be oxidized. Given the high oxidation potential of SBP at low pH, it occurred to us that this enzyme is acting more as a lignin peroxidase than a typical plant peroxidase. In that regard, we proceeded to re-investigate the action of SBP on DMF-soluble lignite at pH 2.2. Figure 4 shows that both polymerization and depolymerization occurred after 24 h incubation of fraction 11 of the lignite with SBP in 50% DMF, 0.1 M tartrate buffer, pH 2.2 containing 0.1 M CaCl<sub>2</sub>. Approximately 10% of the initial lignin precipitated out of the enzyme reaction, indicating that some very high molecular weight material was produced. In the absence of enzyme, no coal modification took place.

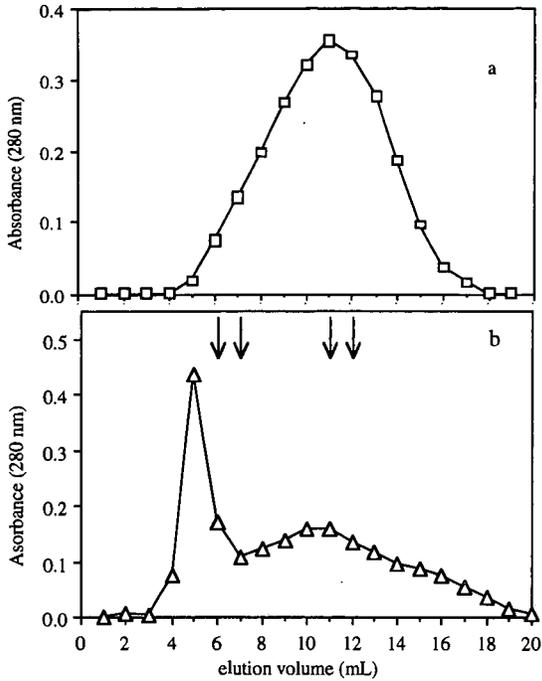


Fig. 2. Gel permeation chromatography of Mequinza lignite fraction No 11 (MW 4 kD) before incubation with horseradish peroxidase (a) and after 24 h incubation at pH 5 in 50% DMF (b).

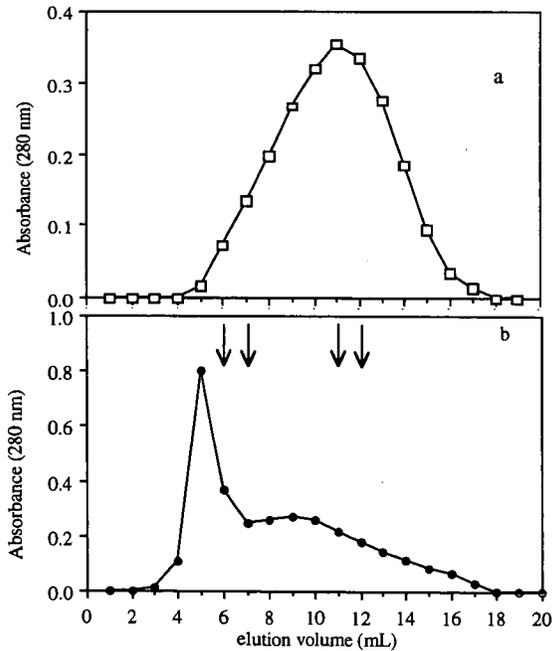


Fig. 2. Gel permeation chromatography of Mequinza lignite fraction No 11 (MW 4 kD) before incubation with soybean peroxidase (a) and after 24 h incubation at pH 5 in 50% DMF (b).

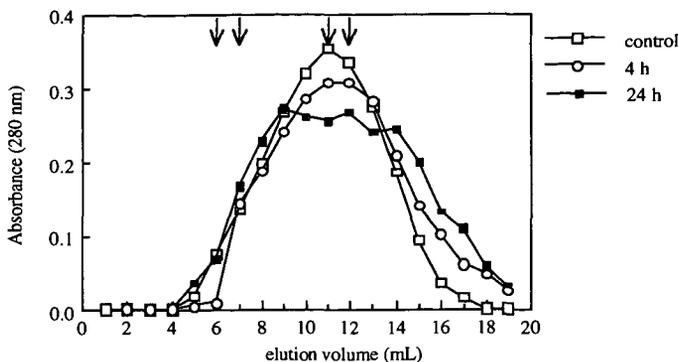


Fig. 4. Gel permeation chromatography of Mequininza lignite fraction No 11 (MW 4 kD) before incubation with soybean peroxidase and after incubation at pH 2.2 (0.1 M tartrate buffer, 0.1 M  $\text{CaCl}_2$ ) in 50% DMF.

We reasoned that a relatively low molecular weight fraction of lignite was more susceptible to polymerization than depolymerization. To test this hypothesis, we examined the action of SBP in 50% DMF (pH 2.2) with a higher molecular weight fraction of DMF-soluble lignite. Figure 5 shows that the high molecular weight fraction (ca. 50 kD) was unaffected in the absence of the enzyme, yet was obviously depolymerized in the presence of SBP.

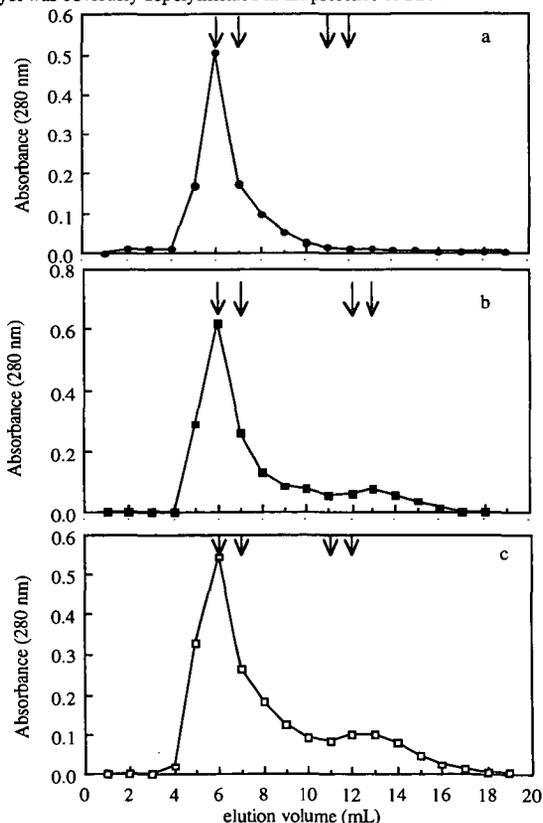


Fig. 5. Gel permeation chromatography of high molecular weight fraction No 6 (MW 50 kD) of Mequininza lignite before incubation (a) with soybean peroxidase and after 4 h (b) and 24 h (c) incubation at pH 2.2 (0.1 M tartrate buffer, 0.1 M  $\text{CaCl}_2$ ) in 50% DMF.

### Activity of Oxygenase Enzymes on Coal Model Compounds

The unique specificities and reactivities of oxygenase enzymes in organic solvents can be exploited for biocatalytic transformation of coal. Mono- and dioxygenases from bacteria consist of a three-enzyme system comprised of an iron-sulfur hydroxylase/oxygenase, a ferridoxin electron transfer protein, and an NAD(P)H reductase. The reaction mechanism of this multienzyme system remains poorly characterized and the use of the isolated enzyme system has been poorly successful. Nevertheless, several promising biotransformations have been performed on coal-related compounds using whole cells. For example, Laborde and Gibson demonstrated<sup>10</sup> that fermentation of dibenzothiophene (DBT) with *Beijerinckia* B8/36 resulted in the accumulation of 1,2-dihydroxy-1,2-dihydrodibenzothiophene and dibenzothiophene-5-oxide in the cell culture. Further treatment of the first product by the *Beijerinckia* sp. led to the accumulation of 1,2-dihydroxydibenzothiophene. We have initially evaluated the catalytic activity of the *Beijerinckia* enzyme system in aqueous-organic media. The whole cells were unable to grow in the solvents, yet retained intrinsic enzyme activity. Conversions (ca. 25%) of both biphenyl and DBT were observed in the media containing up to 50% of DMF or dioxane. Moreover, several unidentified products that were not detected after fermentation of biphenyl and DBT with *Beijerinckia* sp. in aqueous media were found in aqueous-organic mixture. It was also found that the *Beijerinckia* enzyme system from the lyophilized cells is active in non-aqueous media in the presence of NADH. Cofactor regeneration system comprising horse liver alcohol dehydrogenase and ethanol was applied to provide long term activity of the oxygenase system from a fine powder of the freeze-dried cells of *Beijerinckia* sp. in non-aqueous media. Improvement of the ability of the *Beijerinckia* oxygenase enzyme system to catalyze coal model compounds degradation in aqueous-organic media is the subject of continuing investigations.

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## MOLTEN CAUSTIC LEACHING AT LOW CAUSTIC/COAL RATIOS

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**KEYWORDS:** Molten caustic leaching, coal desulfurization, sulfide coal interaction

### INTRODUCTION

Molten caustic leaching (MCL) of coal has been studied under a variety of conditions, many of which studies have been conducted using a large excess of liquid caustic (3:1 caustic/coal or higher) so that, with stirring, coal is suspended in it. This provides a uniform temperature throughout the mixture and is preferred for chemical research. Some development studies have made use of lower ratios of caustic, such as TRW's 20 lb/hr kiln work by Meyers<sup>1,2</sup>, and the studies of Chriswell and Markuszewski at Ames Laboratory<sup>3</sup> and by Kusakabe in Japan<sup>4</sup>. In the Japanese work, Illinois #6 coal was impregnated with mixed KOH and NaOH (52:48 parts by weight) from an aqueous solution to give 51 wt% caustic on the dry coal which after MCL treating, 2 hr at 375°C, produced a coal having only 0.50 wt% total sulfur. Less caustic should help in reducing the cost of an MCL process. Moreover, at high ratios much more caustic is present than necessary to form salts of sulfur and mineral matter in coal. We have calculated that to form the sodium salts of the sulfur and mineral matter present in an 8% ash, 4.2% sulfur, Pittsburgh #8 coal would take about 0.15 parts of sodium hydroxide for one part of dry coal. This does not take into account carbonate formation nor cleavage of carbon-oxygen bonds which also can occur.

The work at Ames National Laboratories has shown that a 2.0:1 ratio can be very effective for desulfurization but that lower ratios tend to give less conversion of sulfur. This group has also demonstrated improved conversion can be obtained by heating in two stages, first to an intermediate temperature, e.g., 250° for an hour, followed by a second-stage, rapidly increasing the temperature to 390°C and immediately cooling, to give desulfurization equivalent to two hours at 390°C. A recent paper reported by Akhtar and Chriswell<sup>5</sup> reveals that treating Illinois #6 coal in boiling water for one hour, makes the coal more reactive in a subsequent MCL treating step. TRW's work demonstrated production of low sulfur coal in continuous flow MCL using standard process equipment, such as, a kiln reactor, filters, and centrifuges made from caustic- and acid-resistant materials. Most of their tests were conducted above 2.0:1 ratio. They have also found a means of counter-current water washing that does not require the usual acidification step<sup>2</sup>.

Because the use of less caustic could offer cost advantages, PCR Technologies prepared a Small Business Innovation Research (SBIR) proposal for studying MCL at low caustic/coal ratios which resulted in a grant awarded by the US Department of Energy<sup>6</sup>. The objectives of this work have been to examine MCL under conditions that could be used for commercial chemical coal cleaning. This has meant using reasonably low levels of acid water and caustic. Tests have been made using coal from three different seams: western Kentucky #9, Illinois #6, and a low- and a high-sulfur Pittsburgh #8. Semiannual reports issued from the grant have shown that significant amounts of desulfurization and demineralization occur at ratios of 0.5:1 to 2:1 but, at most conditions used, desulfurization was not sufficient to meet New Source Performance Standards (NSPS) for the year 2000. NSPS will require certain coal burning facilities to emit no more than 1.2 lbs SO<sub>2</sub>/MMBtu by the year 2000. We have found some single-step sets of conditions at 0.75 ratio with which KY #9 coal and a low-sulfur Pgh #8 coal did meet the 1995 NSPS goal of 2.5 lbs SO<sub>2</sub>/MMBtu. However, using 2:1 caustic/coal ratio, the 1.2 lbs SO<sub>2</sub>/MMBtu level was met with the same two coals. Sulfur removal attained at low ratios in single-step and in two-step MCL tests are compared and experiments showing how the desulfurization level appears to be limited by the presence of sulfide are addressed in this paper.

### EXPERIMENTAL

Most of the experiments described were conducted in an annealed stainless steel, 1-3/8" I.D. pipe reactor containing a 4-3/4" stirrer

blade having a width nearly the diameter of the pipe. During tests, the stirrer was rotated by an induction motor at 5.5 rpm and the reactor held at an angle of 30° from horizontal. Nitrogen gas was passed slowly through the reactor, at atmospheric pressure, while heating the reactor in a hinged furnace. A thermowell passed through a bottom closure and acted as a bearing for the bottom of the stirrer shaft which allowed the MCL reaction temperature to be monitored.

Most often, test conditions were randomized to avoid any sequence or time bias. In a typical test, 18g of 14 mesh x 0 coal and an amount of NaOH beads (20-40 mesh) to give the desired caustic/coal ratio were poured into the reactor and the top screwed in place. The furnace was heated rapidly while the reaction mixture was stirred constantly. Reaction temperatures of 350° to 430°C were reached in about 65 to 85 minutes respectively. The reaction period time was begun as the internal temperature reached 3°C below test temperature and ended when the temperature dropped 3°C below that value. Usually internal temperatures were held within +/-3°C of this value. Cooling was begun in anticipation of the end of the reaction period by turning off the heat, opening the split-hinged furnace, and turning a fan on. The cool-down was about twice as fast as heat-up time. The initial gallon-size samples of high- and low-sulfur Pgh #8 and western KY #9 coals were received from TRW and are coals TRW used in their integrated kiln test program. The IL #6 coal, IBC-101, was received from the Illinois State Geological Survey. A second, larger sample of high-sulfur Pgh #8 coal was obtained through Tra-Det Inc., Wheeling WV. Sodium hydroxide beads (20 x 40 mesh) were used as the source of caustic for these MCL tests. In a few tests, sulfide was added to a caustic/coal mixture, in which case the sulfur source was either Fisher 21.2% aqueous ammonium sulfide solution (9.97 wt% sulfur) or Aldrich 98% sodium sulfide nonahydrate, ACS reagent.

A few larger scale runs were made using a Parr Instrument Co. 6-liter stainless steel stirred reactor so that a partially or completely desulfurized product could be made from 400 to 2000g of the coal. Reactants, including some water, were loaded into the reactor and pressure tested using nitrogen. Tests were conducted either at a fixed pressure, e.g., 400 psig, using a back-pressure regulator with slow flow of nitrogen through the regulator or the reactor was sealed containing at least 30 psig (nitrogen) and allowed to attain whatever pressure occurred at run conditions. For depyriting runs at 250°C, water vapor pressure accounted for most of the pressure observed. Products from the Parr reactor were used as feed for second-stage, atmospheric pressure tests in the pipe reactor.

Products were generally worked up by digesting the cooled mixture of caustic/coal in an amount of hot water equal to four times the weight of coal, filtering the coal and rinsing with up to two weights of hot water. The coal was acidified while dispersed in 2 to 4 weights of water by adding dilute HCl until a pH of 1.2 was maintained for five minutes. (Sulfuric acid would likely be used commercially.) The slurry was then heated to 90°C for 20 minutes with stirring. The hot slurry was filtered and rinsed with two weights of hot water. Moist coal samples were dried at 105° to 110°C.

Coal analyses were conducted by Standard Laboratories, Inc., Cresson, PA. Alkaline wash filtrates were titrated at PCR Technologies to determine total alkalinity (to pH 4.0) and free NaOH (to pH 8.35) in the presence of excess BaCl<sub>2</sub>.

#### RESULTS AND DISCUSSION

High-sulfur Pgh #8 coal was found to be the most resistant to MCL of the three coal seams selected for our study and was chosen for our initial experiments. Over eighty tests were made with this coal in Phase I and II of our grant. A low-sulfur Pgh #8 was also tested in six runs, twenty-one tests were made with IL #6 coal, and over fifty tests with western KY #9 coal. Data (in some cases averages of duplicate runs) for tests at both 0.75:1 and 2:1 caustic/coal ratios are shown in Table 1. Our goal was to obtain a low-sulfur product that would emit 1.2 lbs SO<sub>2</sub>/MMBtu or less on combustion. Even a cursory scan of Table 1 shows that few tests actually achieved this goal and then only from low-sulfur Pgh #8 and KY #9 coals treated at 2.0:1 caustic/coal ratio and temperatures of 390°C or higher.

In MCL treating, pyritic sulfur is much more reactive than organic sulfur and can be removed at a temperature about 100°C lower than is necessary for desulfurizing organic sulfur structures in coal. Thus, effective MCL treating becomes a matter of removing of organic sulfur in the quest for acceptable NSPS coal product. The problem, at first glance might seem to be due to the slow desulfurization reaction rate of organic sulfur in coal. However, longer reaction time often had little effect on desulfurization with these coals. This was more noticeable for those tests using 0.75:1 caustic/coal than 2:1. This could be caused by some organic sulfur structures in coal being more resistant to reaction than others, by steric hindrance of some sulfur moieties, by parts of the solid coal not being in contact with the caustic, by the caustic reacting with coal constituents that used up the caustic, or by a reversible reaction in which a concentration of by-product builds up and prevents further desulfurization at that temperature. Except for high-sulfur Pgh #8, tests at 2:1 ratio definitely caused more desulfurization than did those at 0.75:1. Product from 0.75 ratio runs were obviously wetted and formed solid masses on cooling. Therefore, lower conversion levels should not be due to impervious coal or steric hindrance since higher ratios of caustic/coal increased sulfur removal. Titrations of the water wash filtrates from tests showed that some weak acid salts were formed, but 32 to 80 wt% of free NaOH was still available for tests at 0.75:1 and 55 to 81 wt% at 2:1 ratio. There was ample unreacted caustic remaining to continue the desulfurization reaction. Poor reactivity could best be attributed to more resistant sulfur bonds after the facile carbon-sulfur bonds had reacted or to some form of reversible reaction.

Therefore, an investigation into sulfide as a possible by-product that could interfere with coal desulfurization by a reversible or retrograde reaction was begun. Pyrite in MCL reaction forms sulfide and can quickly build up in the caustic before organic sulfur begins to react. This sulfide concentration effect would be much greater with low ratio tests. Therefore, the first attempt to test whether sulfide in the caustic can reduce the desulfurization of coal was to remove the pyrite from KY#9 coal in a mild MCL reaction and then treat that product in a second-step MCL treat. Both reactions were made with 0.75:1 ratio caustic/coal; the first step was run at 320°C for 50 minutes and the second step at 390°C for only two minutes. Table 2 compares the results with other tests made for various reaction times at 390°C. The first step or "pretreat" test removed 88% of the pyritic sulfur and also about 12% of the organic sulfur. The second step test removed 50% of the remaining organic sulfur and nearly met NSPS year 2000 criteria. For comparison at the same temperature, a 2-minute test removed 34% of organic sulfur and the best level attained, at 50 minutes, removed only 40%. In another approach to investigate the influence of sulfide, hydrogen sulfide was added to a 2:1 ratio of caustic and coal in an amount equivalent to 4-times the weight of total sulfur in KY #9 coal. The H<sub>2</sub>S gas was generated from a weighed amount of (NH<sub>4</sub>)<sub>2</sub>S solution and carried by nitrogen flow into the reactor while holding the MCL reactor charge at 170° to 180°C. Immediately thereafter, the MCL test was run at 390°C. The result was that, although pyrite was effectively removed from the coal, the organic sulfur content remained essentially unchanged. The presence of this much sulfide in the caustic clearly prevented desulfurization of organic sulfur. A hypothesis that MCL desulfurization can be severely affected by the concentration of sulfide in caustic began to unfold.

Another coal, the low-sulfur Pgh #8, was used for a second series of tests to see if it was similarly sensitive to a change in sulfide concentration. Table 3 repeats a few test results of Table 1 for comparison with 2-step MCL treating. In the "pretreat" step, coal was depyrited in the 6-liter reactor using 0.5:1 caustic/coal and enough water to give a 38% solution of the NaOH. Depyriting was conducted for 25 minutes at 250°C and produced a very low pyrite coal with an organic sulfur content elevated about 25% to 1.26 wt%. This depyrited, low-sulfur coal was then used in second-step MCL reactions in the small reactor. Tests were made at 0.25, 0.50, and 0.75 ratios for 25 and 100 minute tests at 390°C. With as little as 0.25 ratio, the NSPS 2000 sulfur dioxide limit was almost achieved and the higher ratio tests were well below the NSPS limit by 25 to 65 %. Two-step MCL treating was necessary to produce NSPS compliance coal when using 0.75 and lower ratios, but it is apparent that there are coals of

moderate to low sulfur content which would respond well to MCL treating at low ratios.

The original high-sulfur Pgh #8 coal was depleted in laboratory tests and a large, fresh sample was needed for larger-scale tests. The original sample had a combined sulfate and pyrite content indicating it had contained 1.57 wt% pyritic sulfur, when fresh, and 2.76 wt% organic sulfur. Our second high-sulfur Pgh #8 sample, obtained from the same mine by Tra-Det, Inc., contained 1.95 wt% pyritic sulfur, 0.05 wt% sulfate sulfur, and 2.45 wt% organic sulfur. In Table 4, data showing a comparison of MCL tests at 2.00:1 ratio for the two coal samples are presented. The Tra-Det sample was somewhat less resistant to treating and met the 1995 NSPS but not that for 2000. Shown next are two-step results from depyriting high-sulfur Pgh #8 coal in the 6-liter reactor and the use of this product in second-step MCL tests. The depyriting was conducted using a 0.62 ratio for 25 minutes at 250°C, during which the reactor was maintained at a pressure of 400 psig. Pyrite conversion was 95% and organic sulfur content increased about 20% when loss of mineral matter, volatiles and pyrite were considered. Using the depyrited, high organic sulfur product as a coal feed, second-step, 25-minute MCL tests were made at 0.25, 0.75 and 2.00 ratios and 390 to 430°C reaction temperatures with interesting results. The 0.25:1 ratio test desulfurized 36% of the organic sulfur but still had more than twice the  $SO_2/MBBtu$  level desired. However, desulfurization with 0.75:1 ratio at 410° and 430°C produced compliance coal product and the 2.00:1 ratio tests, as would be expected, gave even lower sulfur levels at 390°, 410° and 430°C. Two-step, low-ratio treating offers promise for achieving NSPS compliance product even from a high-sulfur coal.

In another experiment, excellent chemical cleaning of Pgh #8 was obtained using a very high ratio, 5.00:1, for 25 minutes at 400°C. However, the following test shows that sulfur removal is reversible when treated in the presence of NaOH and sulfide as in a MCL test. The clean coal contained only 0.73 wt% total sulfur, of which 0.69 wt% was organic. This clean coal was mixed with both NaOH (1.67:1) and  $Na_2S$  (0.50:1) and treated for 25 minutes at 390°C. The amount of  $Na_2S$  added provided 3.69 g  $S^{2-}$ , several times the total sulfur content of untreated Pgh #8 feed coal and demonstrates that sulfide can cause a higher sulfur product to form. The result was that organic sulfur in the sulfided MCL product increased to 1.42 wt%, about twice the amount of organic sulfur in the cleaned coal. The previously clean coal, 0.97 lbs  $SO_2/MBBtu$ , now would produce 2.03 lbs  $SO_2/MBBtu$  on combustion.

If sulfide concentration builds-up sufficiently, a retrograde sulfurizing reaction can occur that will limit or possibly slowly increase the organic sulfur content in coal. Whether the same type of organic sulfur compounds form as are desulfurized has not been determined. Studies of the reactions of organosulfur compounds thought to represent structures in coal<sup>7,8</sup>, such as thiophene, benzothiophene or dibenzothiophene have not been approached as reversible reactions. Often desulfurized products were obtained that also lacked an oxygen. Once that has happened, it is less likely a reaction to incorporate sulfur in a hydrocarbon would occur than it would be to have an exchange between phenolic oxygen and thiophenolic sulfur in the presence of molten caustic. We suspect that the latter type reactions are at play and that some of the phenolics may come from hydrolysis of furan structures in coal.

With coals containing less than 6 wt% sulfur, it is not likely that sulfide could build-up to a high concentration at high ratios so the reverse reaction might not be noticed. However, at low caustic/coal ratios, especially when the coal contains over 2 wt% total sulfur, a desulfurization limitation may occur well before NSPS criteria are reached.

We believe that MCL desulfurization of coal is sensitive to the molar concentration of sulfide ion in the caustic solution. If the molar concentration is low enough, desulfurization can proceed rapidly and only a few minutes, not hours, of MCL reaction time is necessary at temperatures above 370°C. If the sulfide concentration is high, desulfurization cannot proceed regardless if the time or temperature would otherwise be practical for MCL treating. For coals having much pyrite, a low temperature depyriting step followed by a MCL reaction

to remove the requisite amount of residual organic sulfur can achieve compliance coal quality. By considering carefully the amount of sulfur to be removed and the reactivity of the coal, low ratios of caustic/coal could in many instances be used in place of much larger amounts of caustic.

#### SUMMARY

Conditions have been presented showing MCL desulfurization of coals from three coal seams at low caustic/coal ratios. Ratios at 2.00:1 were successfully used in single-step MCL reactions for treating of a 2 wt% sulfur Pgh #8 coal and a 3.4 wt% sulfur western KY #9 coal to achieve NSPS 2000 compliance product, 1.2 lbs SO<sub>2</sub>/MMBtu. Coals having over 4 wt% sulfur were not successfully treated under the same conditions, but a 4.4 wt% sulfur Pgh #8 coal in a two-step reaction at 0.75:1 ratio of caustic/coal did achieve this goal. Several examples of two-step treating have been presented in which the first step is a lower temperature reaction to remove pyrite.

Experiments have demonstrated that desulfurization is sensitive to the presence of sulfide in caustic during MCL treating. Reducing sulfide concentration by depyriting a coal before MCL treating can allow the second-stage MCL treat to be effective even at quite low caustic/coal ratios. Introduction of sulfide into the MCL caustic, can retard desulfurization or at higher levels actually increase sulfur content. The increase is measured as organic sulfur.

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#### DISCLAIMER

References to any specific commercial process, product or service is to facilitate understanding and is not meant to imply endorsement or favoring by PCR Technologies or the US Department of Energy.

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Table 1  
SMALL REACTOR MCL DESULFURIZATION EXPERIMENTS  
SINGLE-STEP REACTIONS

---Run Conditions---			--Analyses, mf basis--			---Sulfur Forms, mf---		
NaOH/Coal	Temp.	Time	Sulfur	Ht Value	SO <sub>2</sub>	Pyritic	Sulfate	Organic
Ratio	C	min	wt%	Btu/lb	lbs/MMBtu	wt%	wt%	wt%
A: High-Sulfur Pgh#8 Coal			4.33	12521	6.91	1.07	0.50	2.76
0.75	370	50	1.89	13535	2.79	0.14	0.32	1.43
0.75	390	150	1.87	14221	2.63	0.02	0.05	1.80
0.75	410	50	2.16	13973	3.09	0.05	0.07	2.04
0.75	430	25	1.92	13205	2.91	0.06	0.31	1.55
0.75	430	100	1.73	13699	2.52	0.07	0.13	1.52
0.75	470	50	1.25	13081	1.91	0.18	0.29	0.79
2.00	350	50	2.65	14157	3.74	0.05	0.06	2.54
2.00	370	50	2.43	14156	3.43	0.05	0.08	2.30
2.00	390	50	2.43	14013	3.47	0.07	0.11	2.26
2.00	390	150	2.06	13980	2.94	0.04	0.20	1.82
2.00	410	50	2.43	13569	3.57	0.04	0.25	2.14
2.00	430	25	2.20	13572	3.24	0.06	0.20	1.93
2.00	430	50	2.54	13184	3.85	0.05	0.35	2.14
B: Low-Sulfur Pgh#8 Coal			2.03	13844	2.93	1.02	0.01	1.01
0.75	390	50	1.07	14082	1.52	0.11	0.03	0.93
0.75	430	*2	1.09	14201	1.53	0.08	0.04	0.97
0.75	430	25	1.03	13900	1.48	0.05	0.05	0.93
2.00	390	50	0.62	14464	0.86	0.04	0.01	0.57
2.00	430	*2	0.53	14446	0.73	0.03	0.00	0.49
2.00	430	25	0.26	14101	0.37	0.02	0.01	0.23
C: IL#6 Coal			4.35	12485	6.97	0.90	0.11	3.34
0.75	350	50	2.77	13500	4.10	0.16	0.10	2.50
0.75	370	50	1.99	13120	3.03	0.10	0.18	1.71
0.75	390	*5	1.82	13935	2.61	0.09	0.05	1.68
0.75	390	50	1.63	13336	2.44	0.06	0.16	1.41
0.75	390	*100	1.71	13711	2.49	0.07	0.06	1.58
0.75	410	50	1.64	13004	2.52	0.04	0.27	1.33
0.75	430	50	1.50	13150	2.28	0.07	0.24	1.19
2.00	350	50	2.87	13764	4.17	0.10	0.05	2.72
2.00	370	50	1.71	13618	2.51	0.03	0.09	1.59
2.00	390	50	1.93	13517	2.85	0.05	0.09	1.79
2.00	410	50	1.00	13308	1.50	0.01	0.21	0.78
2.00	430	50	1.43	13254	2.16	0.07	0.25	1.11
D: W.KY#9 Coal			3.39	12730	5.32	0.90	0.50	2.00
0.75	370	2	1.87	14071	2.66	0.24	0.02	1.62
0.75	390	2	1.48	14055	2.10	0.12	0.04	1.33
0.75	390	25	1.36	13416	2.02	0.06	0.09	1.21
0.75	390	100	1.40	13697	2.04	0.07	0.07	1.26
0.75	410	2	1.42	13975	2.03	0.11	0.04	1.27
0.75	430	2	1.38	13773	2.00	0.08	0.06	1.25
2.00	370	2	1.49	14138	2.11	0.10	0.02	1.38
2.00	390	2	1.09	14216	1.53	0.05	0.02	1.02
2.00	390	100	0.43	12561	0.68	0.04	0.08	0.31
2.00	410	2	0.74	14175	1.04	0.04	0.03	0.67
2.00	430	2	0.64	13803	0.92	0.06	0.07	0.52
2.00	430	25	0.65	13396	0.96	0.04	0.14	0.47

\* Coal pretreated 50 minutes at 320C.

TABLE 2  
MCL EXPERIMENTS WITH KENTUCKY #9 COAL  
EFFECTS OF REMOVING OR ADDING SULFIDE

----Run Conditions----			--Analyses, mf basis--			---Sulfur Forms, mf---		
NaOH/Coal	Temp.	Time	Sulfur	Ht Value	SO <sub>2</sub>	Pyritic	Sulfate	Organic
Ratio	C	min	wt%	Btu/lb	lbs/MMBtu	wt%	wt%	wt%
			3.39	12730	5.32	0.90	0.50	2.00
Single-Step Tests								
0.75	390	2	1.48	14055	2.10	0.12	0.04	1.33
0.75	390	25	1.36	13408	2.02	0.06	0.09	1.21
0.75	390	100	1.40	13697	2:04	0.07	0.07	1.26
Two-Step Test: Step 1 - Removing Sulfide (Mostly Pyrite)								
0.75	320	50	1.91	14190	2.69	0.11	0.04	1.76
Two-Step Test: Step 2 - MCL Treat of Depyrited Coal								
0.75	390	2	0.94	14376	1.31	0.03	0.02	0.89
Single-Step Tests								
2.00	390	2	1.09	14216	1.53	0.05	0.02	1.02
2.00	390	100	0.43	12561	0.68	0.04	0.08	0.31
Single-Step Test - Adding Sulfide to Untreated Coal								
**2.00	390	25	2.14	13853	3.09	0.04	0.11	1.99
** H <sub>2</sub> S added at 170/180C to give 5.89g Na <sub>2</sub> S, leaving 29.96g NaOH; Resulting in 1.66:1 NaOH/coal and 0.33:1 Na <sub>2</sub> S/coal.								

TABLE 3  
MCL EXPERIMENTS WITH LOW-SULFUR PITTSBURGH #8 COAL  
EFFECTS OF REMOVING OR ADDING SULFIDE

----Run Conditions----			--Analyses, mf basis--			---Sulfur Forms, mf---		
NaOH/Coal	Temp.	Time	Sulfur	Ht Value	SO <sub>2</sub>	Pyritic	Sulfate	Organic
Ratio	C	min	wt%	Btu/lb	lbs/MMBtu	wt%	wt%	wt%
Low-Sulfur Pgh #8			2.03	13844	2.93	1.02	0.01	1.01
Single-Step Tests								
0.75	390	50	1.07	14082	1.52	0.11	0.03	0.93
0.75	430	2	1.09	14201	1.53	0.08	0.04	0.97
0.75	430	25	1.03	13900	1.48	0.05	0.05	0.93
2.00	390	50	0.62	14464	0.86	0.04	0.01	0.57
Two-Step Tests: Step 1 - Removing Sulfide (Pyrite)								
0.50	250	25	1.38	14389	1.92	0.08	0.04	1.26
Two-Step Tests: Step 2 - MCL Treat of Depyrited Coal								
0.25	390	25	0.91	14418	1.26	0.04	0.02	0.86
0.50	390	25	0.59	13234	0.89	0.02	0.03	0.54
0.75	390	25	0.60	14525	0.83	0.02	0.07	0.52
0.75	390	100	0.26	13304	0.42	0.01	0.03	0.24

TABLE 4  
MCL EXPERIMENTS WITH HIGH-SULFUR PITTSBURGH #8 COAL  
EFFECTS OF REMOVING OR ADDING SULFIDE

----Run Conditions----			--Analyses, mf basis--			---Sulfur Forms, mf---		
NaOH/Coal	Temp.	Time	Sulfur	Ht Value	SO <sub>2</sub>	Pyritic	Sulfate	Organic
Ratio	C	min	wt%	Btu/lb	lbs/MMBtu	wt%	wt%	wt%
TRW Sample			4.33	12521	6.91	1.07	0.50	2.76
Tra-Det Sample			4.45	13326	6.67	1.95	0.05	2.45
Single-Step Tests - Comparing Two Pgh #8 Samples								
TRW@ 2.00	390	50	2.43	14013	3.47	0.07	0.11	2.26
T-D@ 2.00	390	25	1.83	14391	2.54	0.05	0.05	1.73
TRW@ 2.00	430	25	2.20	13572	3.24	0.06	0.20	1.93
T-D@ 2.00	430	20	1.39	13842	2.01	0.05	0.08	1.26
Tra-Det Sample Used for All Tests Below								
Two-Step Tests: Step 1 - Removing Sulfide (Pyrite)								
0.62	250	25	3.33	13413	4.96	0.09	0.09	3.17
Two-Step Tests: Step 2 - MCL Treat of Depyrited Coal								
0.25	390	25	2.16	14257	3.03	0.03	0.11	2.02
0.75	390	25	1.34	12844	2.08	0.05	0.13	1.16
0.75	410	25	0.79	14028	1.13	0.02	0.10	0.67
0.75	430	25	0.63	13867	0.91	0.03	0.06	0.54
2.00	390	25	0.65	14312	0.91	0.01	0.11	0.54
2.00	410	25	0.34	14109	0.48	0.02	0.08	0.23
2.00	430	25	0.38	13746	0.55	0.04	0.08	0.27
Single-Step Test: High Ratio MCL Treat								
*5.00	400	25	0.73	15066	0.97	0.02	0.01	0.69
Single-Step Test - Adding Sulfide to MCL Cleaned Coal (*)								
1.67	390	25	1.51	14884	2.03	0.03	0.06	1.42
0.50 Na <sub>2</sub> S								

# DESIGN OF MULTI-STAGE LIQUEFACTION PROCESS FOR COMPLETE COAL CONVERSION AND EXTENSIVE UPGRADING

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Keywords: Multi-stage liquefaction, Coal pretreatment, Hydrogen donor, Catalytic upgrading

## INTRODUCTION

Increasing coal consumption to meet the increasing demand of energy in the world should minimize the effects on the environment on the earth. The highest efficiency of energy use and the deepest reduction of pollutants such as SO<sub>x</sub>, NO<sub>x</sub> and solid waste are the key technologies to solve the problems of climate change, acid rain and environmental contamination urgently to prepare their rapid growth. Thus, clean coal technologies are most expected to be developed. The ultimate cleaning of coal can be achieved only after the complete conversion of coal into fluid form by removing completely the pollutant sources of S, N and minerals since they are bound intimately to the organic parts.

The liquefaction has been proved to provide the whole products to be completely free from pollutants and very handy for clean uses. The problems still remain in the low efficiency and high cost. Hence, the authors set up the targets of the current liquefaction technology.<sup>1)</sup>

1. Complete conversion of coal organics into fluid fuels, leaving only minerals to be fully separated in forms free from contaminants.
2. Catalyst recovery from minerals to recycle it and reduce the amount of solid wastes.

To achieve the targets, authors are examining:

1. Coal pretreatment to enhance its reactivity through removal of minerals and oxygen functional groups as well as reagent impregnation.<sup>2,3)</sup> The problems of scale and sludge are expected to be moderated.<sup>4)</sup>
2. Design of hydrogen donor and dissolving solvents.<sup>5,6)</sup>
3. Rapid heating and short contact time at a fairly high temperature for the hydrogen transferring liquefaction.<sup>7,8)</sup>
4. Design of recoverable catalysts of high activity.<sup>9)</sup>

The suppression of preasphaltene formation by controlling retrogressive reactions during the liquefaction, or its activation and digestion if it is produced, and the modification of less reactive components including some of inert macerals are the key objectives in our current study.

## EXPERIMENTAL

An Australian subbituminous (Wandoan) coal, its liquefaction residue (WD-LR) in a 1 t/d process support unit at 450°C under 17 MPa H<sub>2</sub> pressure, and an Australian brown (Morwell) coal were ground to pass 250 μm screen and dried in vacuo for 10 hr at 100°C. Their elemental analyses are summarized in Table 1.

The ground coal was mixed with 10 vol% alcohol / 0.01 N or 1 N HCl, stirred for prescribed times under reflux or at room temperature, filtered, washed with water, and dried at 100°C for 10hr.

Synthetic FeS<sub>2</sub> and commercially available KF-842(Ni-Mo/Al<sub>2</sub>O<sub>3</sub>) catalysts were presulfided at 360°C for 6 hr before their use.

1,2,3,10b-tetrahydrofluoranthene (4HFL) was chosen as a liquefaction solvent because of reasons why it has high dissolving activity when dehydrogenated, high boiling point and thermal stability, and four donorable hydrogens in a molecule. 4HFL was prepared from fluoranthene by hydrogenation at 250°C under 15 MPa using the sulfided NiMo catalyst,<sup>7,8)</sup> followed by vacuum distillation and recrystallization procedure for its purifications.

Liquefaction was carried out in an autoclave (50ml volume). The ground coal (3.0g), the

solvent (4.5g) and catalyst (0.09g) were transferred to the autoclave. The products remaining in the autoclave were extracted with THF, benzene and hexane. The hexane soluble (HS), hexane insoluble but benzene soluble (HI-BS), benzene insoluble but THF soluble (BI-THFS), and THF insoluble (THFI) substances were defined as oil, asphaltene, preasphaltene, and residue, respectively. A small amount (<5%) of solvent derived products, which remained in the HI-BS fraction, was corrected by g.c. analysis. The gas yield was calculated by the difference between the initial (dry ash free base) and recovered residual weights. Thus, the weight loss during the experiment was included in the gas yield.

The first step in two-step liquefaction was carried out in a tube bomb of 20 ml capacity (the heating rate: ca.250°C/min) or autoclave of 50 ml capacity (ca.8°C/min). The coal (3 g) and the solvent (3 or 4.5 g) were transferred into the reactor, which was then pressurized with nitrogen to 1 MPa at room temperature after replacing the air with nitrogen. The tube bomb was then immersed in a molten tin bath at the prescribed temperature and agitated axially. The same procedure was applied to the autoclave liquefaction except for much slower heating rate in an electric furnace.

## RESULTS

### Effects of Deashing Pretreatment on the Liquefaction of Wandoan coal

Products distributions in the non-catalytic hydrogen-transferring liquefaction of Wandoan and its deashed coals are illustrated in Figure 1. 4HFL solvent of three times weight to the coal was very effective to liquefy the non-treated coal into 38% oil and 34% asphaltene by the reaction at 420 °C-30 min under 2 MPa N<sub>2</sub> pressure, leaving 18% preasphaltene and 6% residue. The deashing with 1 N HCl / 10% methanol at 60°C increased very much the oil yield upto 49% with decreased yields of asphaltene, preasphaltene, and residue. Especially, the reductions of asphaltene and residue yields are remarkable by deashing. These results suggest that the deashing pretreatment can accelerate the conversions of THFI residue containing some of inert macerals to soluble fractions, since the coal carries ca. 20 % of total unreactive macerals, as well as those of pre-asphaltene and asphaltene to oil.<sup>(10,11)</sup>

Figure 2 illustrates the products distributions in the catalytic liquefaction of Wandoan and its deashed coals at 450°C with FeS<sub>2</sub> catalyst under 15 MPa H<sub>2</sub> pressure. The liquefaction at 450°C -60 min and 4HFL/coal ratio of 1.5 converted 90% of the coal into soluble products with major products of 48% oil and 38% gas, leaving 9% of THFI residue. The deashing pretreatment at room temperature, regardless of the acid concentration, reduced the residue to 5%, although the enhanced yield of gas led to no increase of oil yield. It is noted that the deashing pretreatment even under much milder conditions with dilute acids can activate the coal, reducing the heavy liquefaction products probably by suppressing their retrogressive reactions.

Figure 3 illustrates the two-stage liquefaction of Wandoan and its deashed coals under reaction conditions of 450°C-7 min at the first step without catalyst and 400°C-20 min under 10 MPa H<sub>2</sub> pressure at the second step with FeS<sub>2</sub> catalyst. The deashing pretreatment at 60°C with 10% methanol/1 N HCl decreased the gas yield very much with 70% oil yield by the mixed solvent of 75% 4HFL / 25% pyrene at the solvent/coal ratio of 1.5, although the yields of heavy products were larger than those of the non-treated coal probably due to shortage of transferable hydrogens at the solvent/coal ratio of 1.5. Highly active catalysts for direct hydrocracking of asphaltene and pre-asphaltene and/or rehydrogenating dehydrogenated solvents are to be designed for further increase of distillate yield at the low solvent/ coal ratio of 1.5 under lower hydrogen pressure of 10 MPa.

### Influences of Deashing on the Liquefaction of Morwell coal

Effects of deashing time under reflux and at room temperature on the non-catalytic hydrogen-transfer liquefaction of Morwell coal are illustrated in Figures 4 and 5, respectively. The deashing under reflux for 24 hr gave inferior product distributions compared to those of the same treatment but for shorter treatment times, indicating that some retrogressive reactions should take place during the deashing under reflux. On the other hand, the deashing at room temperature for 24 hr provided

much better product distributions, giving 40% of oil yield and ca. 60% of oil+asphaltene yield.

Figure 6 shows the product distribution in the two-step liquefaction of deashed Morwell coal which was pretreated in 10% methanol/1 N HCl under reflux and at room temperature for 24 hr. The pretreatment at room temperature gave higher oil yield ca.50% with less preasphaltene yield of 2% than those given by the deashing under reflux conditions. Thus, the complete conversion to oil and asphaltene, which can be fed to the second upgrading stage, can be achievable by the multi-stage liquefaction scheme.

#### Catalytic Upgrading of Wandoan liquefaction distillation residue(WD-LR)

Figure 7 shows products distributions in the catalytic upgrading of WD-CR produced in the I/d process support unit of NEDOL process. The WD-CR consists of 27% HS, 44% HI-BS, 11% BI-THFS, and 18% THFI. The single-stage hydrotreatment at 380°C-40 min with FeS<sub>2</sub> catalyst increased HS yield to 54%. The two-stage hydrotreatment, where the first stage was non-catalytic hydrogen transfer at 4HFL/CR of 1.5 at 450°C-7 min without catalyst followed by the second stage at 400°C-20 min with FeS<sub>2</sub> catalyst, further increased the HS yield to 71% with decreasing yields of BI-THFS and THFI to 2 and 3 %, respectively. However, a large amount (24 %) of HI-BS (asphaltene) still remained even after the two-stage hydrotreatment, indicating that the asphaltene fraction should suffer some retrogressive reactions during the PSU liquefaction process because of higher reaction temperature and/or excessive heating during the vacuum distillation of liquefaction products. Hence, multi-stage approaches are suggested to be designed to suppress the retrogressive reactions for the complete conversion of organic fractions into oil, because the refractory products are very difficult to be upgraded even in the catalytic process.

#### DISCUSSIONS

Current research on the coal macromolecules emphasizes their linearity in terms of their covalent bonds in their chain concerned, suggesting their high solubility in potential. The three dimensional networks of the macromolecules are principally formed by the non-covalent bridges through their chains to determine the properties and reactivity such as solubility and recombination of the thermally fissioned bonds as the solid or highly viscous state of the coal. Hence, the liberation of any non-covalent bridges prior to or during the liquefaction is expected to enhance the solubility of macromolecules and suppress the retrogressive reaction of produced radical species, favoring the progress of liquefaction. Such non-covalent bridges can be found in the asphaltene and preasphaltene which are substantially polymeric, carrying still a number of polar functional groups.

The reasons why the inert macerals are inert in the pyrolytic and liquefaction processes appear multi-fold. Many fusinites are believed to be like char, where a large condensed-aromatic planes have stacked in amorphous manners as if it had been carbonized. However, some of the inertinites consist of organic macromolecular chains strongly bound each other just like some thermosetting polymers such as cellulose. The latter structure can be liberated to be reactive by deshing treatment.

The present study revealed that acid washing to remove cationic ions enhanced the liquefaction to reduce the organic residue. By the acid of solvent of hydrogen donor and dissolving ability, no THF insoluble organic residue is left after the liquefaction of some coals, especially for Australian brown coals.<sup>(1)</sup> The present study revealed that the deashing pretreatments can accelerate the depolymerization of Wandoan subbituminous coal, converting it almost completely to THF soluble fraction even though it has a large amount of inert macerals.<sup>(2)</sup> Such pretreatments significantly reduced the amount from coals which carry a significant amount of inert macerals. Some of inert macerals are activated to be liquefied by the treatment. The acid treatment is also effective to activate asphaltene and preasphaltene by removing trace amount of cationic ions. Such all results indicate major roles of cationic bridges in the coal macromolecules which are one of the major obstacles for their smooth depolymerization.

Other pretreatments such as preheattreatment<sup>(3)</sup> and impregnation of polar reagent<sup>(4)</sup> are

also effective, although their significance is not fully proved. Although more effective conditions or procedures should be explored, the principles to liberate macromolecular assemblies appear correct. The intermolecular bridges are postulated as hydrogen bonds, cationic bridges, charge transferring polar bonds, and  $\pi - \pi$  stacking. Such bridges except for the last one in the high ranking coals are based on the polar groups. Hence, any procedures to remove polar groups and to loosen their non-covalent interactions can be effective. The recombination reactions should be carefully avoided when the polar groups are intended to be removed. The conditions should be carefully controlled.

Selection of solvent in terms of hydrogen donor and dissolving ability as well as optimization of liquefaction conditions in terms of heating rate, temperature and time are carefully designed<sup>15)</sup>, since the progressive and retrogressive reactions always take place competitively and consecutively in the coal liquefaction. The change of solvent according to the reaction progress should be also taken into account. The optimum conditions for the catalysis under high hydrogen pressure may differ from those of non-catalytic thermal process.<sup>16)</sup> Hence, the multi-stages are very reasonable to set up the optimum conditions from the respective stages. Although we have not yet reached to clarify the optimum conditions, we have achieved the highest yields of oil and asphaltene with least amount of organic residue.

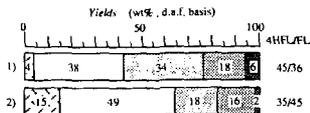
The present authors have proposed two types of recoverable catalysts for the coal liquefaction.<sup>11)</sup> They are separable by their stable ferromagnetism under coal liquefaction conditions and by floating ability to the boundary layer of two solvents. Preliminary results may promise their recovery and catalytic activities. The deashing pretreatment facilitate the recovery and regeneration of the catalyst for its repeated uses.<sup>17)</sup> Further development is now in progress.

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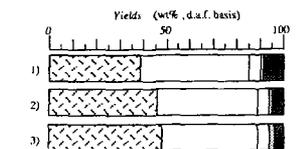
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Table 1 Elemental Analyses of Coals and Liquefaction Residue

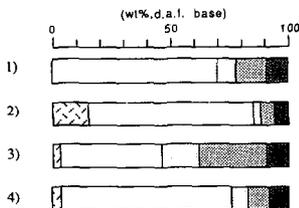
	Wt % (d.a.f. basis)				Ash (Wt %)
	C	H	N	(O+S)diff.	
Wandoan coal	76.3	6.1	1.1	16.5	7.9
Deashed Wandoan coal	76.2	6.2	1.0	16.6	7.0
Wandoan-PSU residue	85.8	5.6	1.5	7.1	29.4
Morwell coal	66.7	4.9	0.6	27.8	2.3
Deashed Morwell coal	63.4	5.0	0.6	31.0	1.7



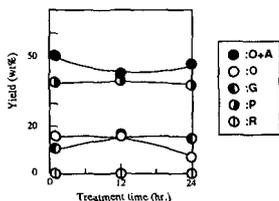
**Figure 1** Effect of deashing on the hydrogen-transfer liquefaction yield from Wandoan coal  
 1) non-treated Wandoan coal,  
 2) Deashed Wandoan coal under reflux in 10vol% MeOH/1 N HCl for 24hr (liquefaction conditions 4HFL/coal=9.0/3.0g), 20 atm N<sub>2</sub>, 420°C-30min



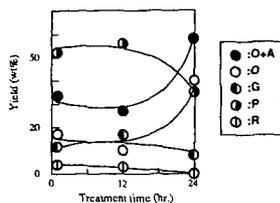
**Figure 2** Effect of deashing on the catalytic liquefaction yield from Wandoan coal  
 1) non-treated Wandoan coal  
 2) 1N-HCl/10vol% EtOH / room temperature / 6hr  
 3) 0.01N-HCl/10vol% EtOH / room temperature / 6hr  
 liquefaction conditions (catalytic liquefaction):  
 4HFL/coal/FeS<sub>2</sub> catalyst = 4.5/3.00/0.09(g),  
 Hz reaction pressure=15 MPa, 450°C-60 min



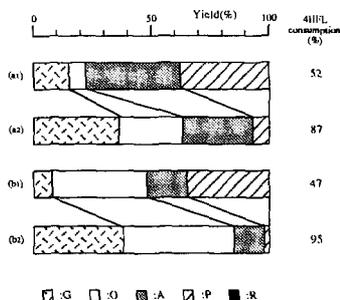
**Figure 3** Influence of deashing on the two-stage liquefaction of Wandoan coal  
 ( 4HFL/Pyren/Coal = 3.4/1.1/3.0 g )  
 1) Gas, 2) Oil, 3) Asp. . . 4) Preas. . . 5) THFI  
 1),2): non-treated coal,  
 3),4): deashed coal under reflux in 10% MeOH/1 N HCl  
 1) Non-catalytic first stage at 450°C-7 min  
 2) Catalytic second stage at 400°C-7 min  
 3) Non-catalytic first stage at 450°C-7 min  
 4) Catalytic second stage at 400°C-20 min



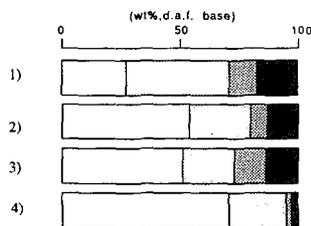
**Figure 4** Effect of deashing time under reflux on the liquefaction yield from Morwell coal  
 (Deashing treatment ; under reflux in 10% MeOH/1 N HCl)  
 (430°C-2min., 4HFL/coal=1.5/1, no catalyst, 20 atm N<sub>2</sub>, tube bomb)



**Figure 5** Effect of deashing time at room temperature on the liquefaction yield from Morwell coal  
 (Deashing treatment ; at room temperature, 10% MeOH/1N HCl)  
 (430°C-2min., 4HFL/coal=1.5/1, no catalyst, 20 atm N<sub>2</sub>, tube bomb)



**Figure 6** Two-stage liquefaction of deashed Morwell coal  
 (a1),(b1) First-stage Non-catalytic Hydrogen-transferred Morwell Coal in the Two-stage Hydro-treatment (430°C-2min, 20 atm N<sub>2</sub>, tube bomb and molten in bath, rapid heating)  
 4HFL/coal=4.5g/3.0g  
 (a2),(b2) Second-stage Catalytic Hydro-treated Morwell Coal in the Two-stage Hydro-treatment (380°C-20 min, 50 cc autoclave, slow heating)  
 (a1),(a2) Deashing treatment ; under reflux , 24hr, 10% MeOH/1N HCl  
 (b1),(b2) Deashing treatment ; room temp., 24hr, 10% MeOH/1N HCl



**Figure 7** Single- and two-stage hydrotreatments of Wandoan liquefaction residue(WD-LR)  
 1) Oil, 2) Asphaltene, 3) Preasphaltene, 4) THFI  
 1) WD-LR as received  
 2) Single-stage hydrotreatment at 380°C-40 min(autoclave) under 10 MPa Hz with FeS<sub>2</sub> and 75% 4HFL/25% pyrene at solvent/WD-LR of 1.5  
 3,4): Two-stage hydrotreatment;  
 3) Non-catalytic first-stage hydrotreatment at 450°C-7 min(rapid heating) under 2 MPa N<sub>2</sub> with 75% 4HFL/25% pyrene at solvent/WD-LR of 1.5  
 4) Catalytic second-stage hydrotreatment at 400°C-20 min(autoclave) under 10 MPa Hz with FeS<sub>2</sub>

# CHANGES IN ORGANIC SULFUR COMPOUNDS IN COAL MACERALS DURING LIQUEFACTION

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Keywords: Coal macerals, liquefaction, sulfur types

## INTRODUCTION

Environmentally sound use of coal for energy production involves effective sulfur removal from the feed coal and/or coal-derived products. Physical cleaning of coal is effective in removing substantial quantities of inorganic sulfur compounds such as pyrite. However, removal of organic sulfur by physical means has not been extremely successful. It is likely that only chemical methods will be useful in substantial removal of organic sulfur. A thorough knowledge of the chemistry of organic sulfur in coal will be valuable in attempts to remove organic sulfur from coal or its liquefaction or pyrolysis products by chemical methods. Since different coal macerals have different liquefaction reactivities, the analysis of sulfur functionalities on separated macerals is deemed to be more meaningful than studying the whole coal. Liquefaction behavior<sup>1</sup> and organic sulfur speciation of the macerals separated from Lewiston-Stockton coal (Argonne Premium Coal Sample bank, APCS-7) by XPS, XANES, and HRMS has been previously described<sup>2</sup>. This paper describes the preliminary speciation of sulfur compounds in the asphaltene fraction of the liquefaction products from these macerals.

## EXPERIMENTAL

Separation of liptinite, vitrinite, and inertinite macerals from APCS 7 coal was achieved by density gradient centrifugation methods<sup>3</sup>. The liquefaction of the macerals was performed in tubing bomb reactors under hydrogen pressure and in the presence of tetralin as a donor solvent. The details of maceral separation and liquefaction procedures have been published earlier<sup>1</sup>. The liquefaction products were successively extracted with hexane, toluene, and tetrahydrofuran (THF). The hexane soluble fraction together with light gases was called oils+gases, hexane insoluble-toluene soluble fraction was called asphaltenes, and toluene insoluble-THF soluble fractions was called preasphaltenes. Desorption chemical ionization (DCI) and desorption electron impact (DEI) mass spectral analyses of the asphaltene and preasphaltene fractions were carried out on a three sector high resolution Kratos MS 50 Mass Spectrometer, operating at 10,000 to 40,000 resolving power<sup>2</sup>. The oil fraction was not analyzed because of the presence of large quantities of tetralin and its reaction products.

## RESULTS AND DISCUSSION

**Table 1** Maceral Characteristics and Product Yields

Maceral	% C (maf)	% Ash	Per 100 Carbons				Wt. % maf		
			H	N	S	O	Oil	Asphaltene	Preasph.
Liptinite	81.7	--	110	1	0.5	8.9	20	54	13
Vitrinite	80.2	0.9	78	1.7	0.3	12	7	33	22
Inertinite	85.4	2.4	46	1.3	0.7	7.5	0	13	12



ACKNOWLEDGEMENT

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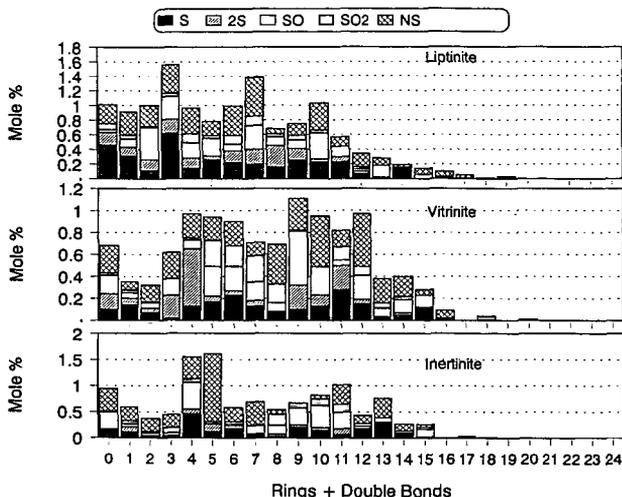


Figure 1. Distribution of sulfur containing molecules from DEIHRMS of the unreacted macerals.

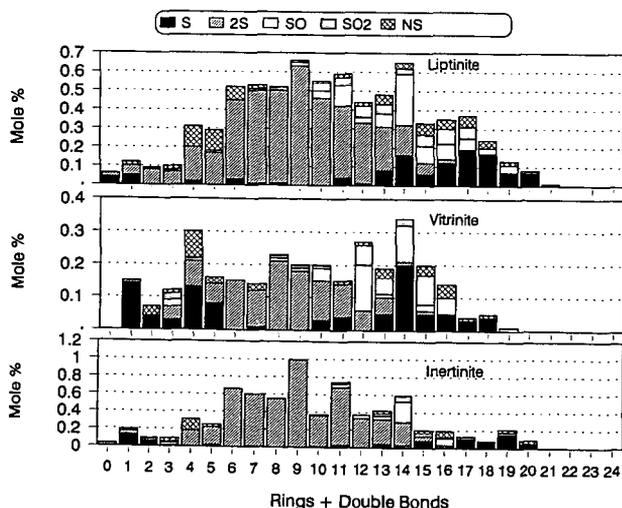


Figure 2. Distribution of sulfur containing molecules from HRMS analysis of the asphaltene products of the liquefaction of the macerals.

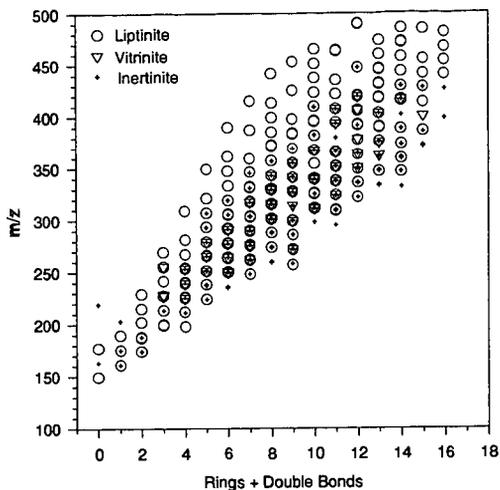


Figure 3. Occurrence of molecules which contain two sulfur atoms in the asphaltene products.

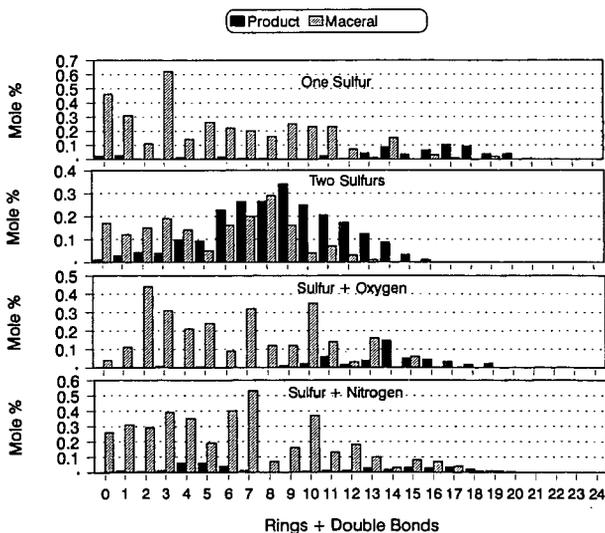


Figure 4. Comparison of sulfur types from the whole maceral and from the asphaltene product of the liptinite. Raw product data were multiplied by 0.54, which is the yield for asphaltene.

CHEMICAL DESULFURIZATION OF COAL:  
PARTITIONING SULFUR TO GAS AS H<sub>2</sub>S

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Keywords: Coal desulfurization, gasification, phosphoric acid

INTRODUCTION

The yields and characteristics of products from mild temperature gasification or pyrolysis of coal have been evaluated extensively in fundamental and process development efforts. At 500°C, the following has been presented as representing the sulfur product distribution from US bituminous coals (1,2):

$$\begin{aligned} \text{Total sulfur in gas} &= 0.31 \times S_{\text{coal}} \\ \text{Total sulfur in tar} &= 0.06 \times S_{\text{coal}} \\ \text{Total sulfur in solid} &= 0.61 \times S_{\text{coal}} \end{aligned}$$

This type of distribution is affected by factors such as coal type, sulfur content and form, particle size, heating rates, temperature of pyrolysis, reactor and process design, and the type of reactants to which the coal is subjected. For example, increasing the pyrolysis residence time usually decreases the sulfur content in the char and increases the tar and gas yields and their sulfur content.

As indicated above, and in other mild temperature gasification studies of low-to-high sulfur coals at temperatures between 400-825°C (3-5), the coal sulfur was distributed nonselectively to all products. As a consequence, the upgrading required to meet environmental regulations has to be applied to more diverse products than the coal from which the products were derived. The severity of such upgrading, and the severity to which coal has to be treated to release all of its sulfur, depends on the chemical form of the sulfur. Recent analytical efforts have begun to define these sulfur forms in coal, the most refractory organic species of which are thiophenic in nature (6,7).

In the current study, the mild temperature pyrolysis of Illinois basin coals mixed with phosphoric acid under continuous-feed, bench-scale fluidized bed conditions at 500°C is reported. The extent of sulfur removal and its partitioning to gas as H<sub>2</sub>S are discussed in relation to its chemical form in the coal. Swelling characteristics of coal/acid mixtures are also discussed relative to operation of the fluidized bed reactor.

EXPERIMENTAL

The two coal samples (labelled as VA and VB) were obtained from the Illinois Basin Coal Sample Program and were both from the Springfield seam (Indiana V), but were sampled at different locations in the seam and at different times. Their composition is presented in Table 1.

The coals were admixed with 50% strength, reagent grade phosphoric acid to attain coal:acid weight ratios of 1.0:0.65 and 1.0:0.96 or with water to produce a coal-only sample having a coal:acid ratio of 1.0:0. These mixtures were dried at 200°C in a nitrogen purged furnace then vacuum dried at the same temperature. The dried samples were stored in sealed containers subsequent to purging with argon until they were treated in a bench-scale reactor.

A schematic of the fluidized bed reactor system is presented in Figure 1. The reactor had a 7.6 cm diameter and was 100 cm in height. Dried coals were loaded into a pressurized hopper located on a precision screw feeder. Coal was dropped from the screw outlet of the feeder into a eductor line which led to the bottom of the gasifier. Gasification tests were as long as four hours in duration with average coal feeds of 0.1-0.3 kg/h.

Nitrogen, nitrogen/air or nitrogen/steam were used as the fluidizing gas during pyrolysis. These gases were pre-heated in a furnace upstream from the fluid bed. Heat traced lines were used to maintain constant temperatures throughout the reactor and its associated output streams. Chars were collected in the down-leg of a cyclone and in an underbed collection flask. A three-stage condensate collection system was used, with the first stage at 140°C, the second stage at 15°C, and the third stage at 0°C.

Subsequent to pyrolysis and before analysis, the chars were hot water filtered to remove excess phosphorus. For these experiments, a stainless steel, 1.4 l pressure filter (Model KST, Lars Lande Manufacturing, Inc.) was insulated and connected to an in-line water heater, a flow meter and a pump.

## RESULTS AND DISCUSSION

Product yields for the two coals were repeatable and similar. On a maf basis, and calculated from (weight feed - weight product)/weight feed, the char yields were near 65% for either 1.0:0.96 or 1.0:0.65 parent coal:acid ratios, and between 70-80% for the same acid ratios when treating physically cleaned coals. These numbers are to be compared with char yields near 60% for coals without added phosphoric acid. The tar yields varied between 0.5-1.5% for coal:acid feeds and near 5% for coal-only feeds. Increasing the phosphoric acid concentration decreased significantly the tar yields.

The duration of the pyrolysis tests using coal-only feeds was slightly greater than one hour, whereas for coal:phosphoric acid feeds the test durations were greater than 2.5 hours. This difference was solely a consequence of difficulties in operating the fluidized bed reactor. For coal-only, agglomeration of the coal in the bubbling bed caused defluidization and bed blockage, and accumulation of tar at the air-side outlet of the cyclone caused pressure increases within the pyrolysis zone and, eventually, bed blockage. Relative to the swelling character of the feed coal, the free swelling index (FSI) was 3.4 whereas the FSI of a 1.0:0.96 mixture was less than one. Previous work examined the effects of HCl on the swelling character of coals (8,9); the present data indicate that phosphoric acid also greatly affects coal thermoplastic properties.

Data presented in Table 1 show the composition of chars produced from the two coals with and without phosphoric acid. Approximately 20% of the sulfur originally in the coals remained in the chars after the 500°C fluidized bed testing of coal:acid mixtures, whereas nearly 70% of the sulfur remained in the char after pyrolysis of coal-only samples. About 90% of the sulfur remaining in the char produced from coal:acid mixtures was organic in nature. The sulfur in the tars accounted for less than 1% of the total amount of sulfur originally in the coals, whereas over 75% of the coal sulfur was selectively partitioned to the gas phase as H<sub>2</sub>S.

Char yields were greater for the coal:acid ratio of 1.0:0.65 than for the 1.0:0.96 ratio, and sulfur removal was increased with increasing acid concentration. This behavior may be a result of competition between alkylating and polymerization functions of phosphoric acid, in combination with the influence of creating char porosity during gasification. For example, the BET N<sub>2</sub> surface area of the char from VA was 445 m<sup>2</sup>/g when using the 1.0:0.96 coal:acid ratio whereas it was 177 m<sup>2</sup>/g when using the 1.0:0.65 ratio. The extent to which sulfur can be removed from coal during hydrolysis has been attributed, in part, to the development of porosity (8). In addition, an increased rate of heating during gasification or pyrolysis influences the softening, swelling and shrinking properties of the coals, and changes significantly the porosity of the char. However, phosphoric acid treatment does not increase the concentration of oxygen in the chars relative to that in the coals.

The amount of sulfur removed from coal:acid mixtures was significantly greater than the amount of sulfur removed from coal-only feeds. The extent to which sulfur was removed is similar to that observed in fixed-bed testing using coal:phosphoric acid mixtures (10), although in the current case the mean residence time of the coal within the reactor was on the order of minutes rather than hours.

Practically total elimination of the pyritic sulfur occurred for all coal:acid mixture feeds. It was also observed that this elimination could be facilitated at temperatures as low as 200°C - i.e. during the initial drying/evacuation before fluidized bed treatment at 500°C. Hence, phosphoric acid decreases the temperature at which pyrite decomposition is initiated. In comparison to the sulfur distribution shown above, which is typical of that obtained during mild temperature gasification, the pyrolysis of coal:phosphoric acid under the same conditions produced the following distribution:

Total sulfur in gas ~ 0.80  $S_{\text{coal}}$   
Total sulfur in tar ~ 0.01  $S_{\text{coal}}$   
Total sulfur in char < 0.20  $S_{\text{coal}}$ .

The form of the sulfur which remained in the Indiana V chars is not known. However, the chemical form of sulfur species in Indiana V coal has been investigated by XANES spectroscopy (11). Even though this XANES-investigated sample was oxidized, about 16% of its sulfur could be identified as a thiophenic species. Such a value is in close agreement with the amount of sulfur remaining in the chars from coal:acid mixtures. Hence, the sulfur in the chars may be predominantly thiophenic species.

Phosphorus remaining in the char after pyrolysis can be removed by hydrolysis since there is reversibility between orthophosphoric acid ( $H_3PO_4$ ) and the pyrophosphoric form ( $H_4P_2O_7$ ) and more polymeric metaphosphate forms. Such removal and the sulfur partitioning suggests a coal utilization scheme as depicted in Figure 2. It would produce valuable elemental sulfur or sulfuric acid from the gas phase  $H_2S$ , minimize byproducts formation, and integrate with advanced topping combustor cycles.

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Table 1. Composition of Indiana V coals (sample A and B) and chars produced during 500°C, fluidized bed pyrolysis.

ANALYSIS(%)	COALS		1.0:0.96 RATIO*		COAL-ONLY
	VA	VB	CHAR A	CHAR B	CHAR B'
Moisture	6.16	5.48	1.88	4.88	3.84
Ash	7.14	8.65	23.61	21.25	10.54
Vol. Mat.	38.37	40.09	22.45	21.54	20.93
Fixed C.	48.30	45.80	52.01	52.22	64.70
Carbon	69.29	67.87	66.77	66.78	74.28
Hydrogen	5.49	5.46	1.86	2.52	3.10
Nitrogen	1.47	1.42	1.61	1.36	1.70
Sulfur	3.45	3.95	0.81	0.95	2.64
Pyritic S	1.50	1.40	0.13	0.18	-
Organic S	1.95	2.51	0.66	0.70	-
Sulfatic S	0.01	0.04	0.02	0.04	-

\*1.0:0.96 = Coal:Acid Ratio (see text).

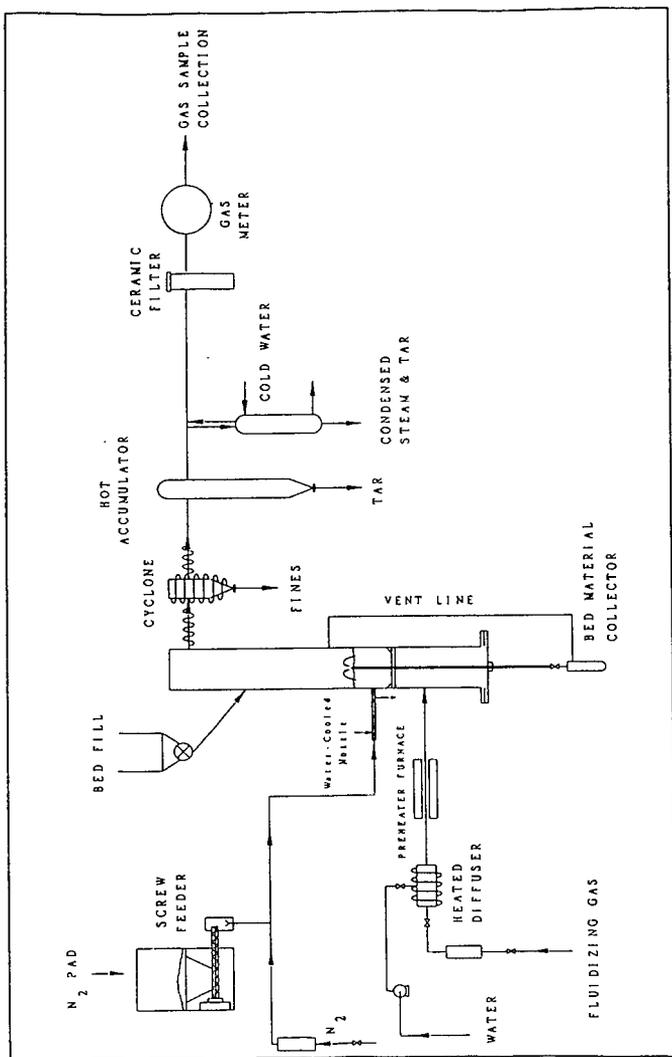


Figure 1. Experimental system used to pyrolyze coal and coal:phosphoric acid mixtures under fluidized conditions.

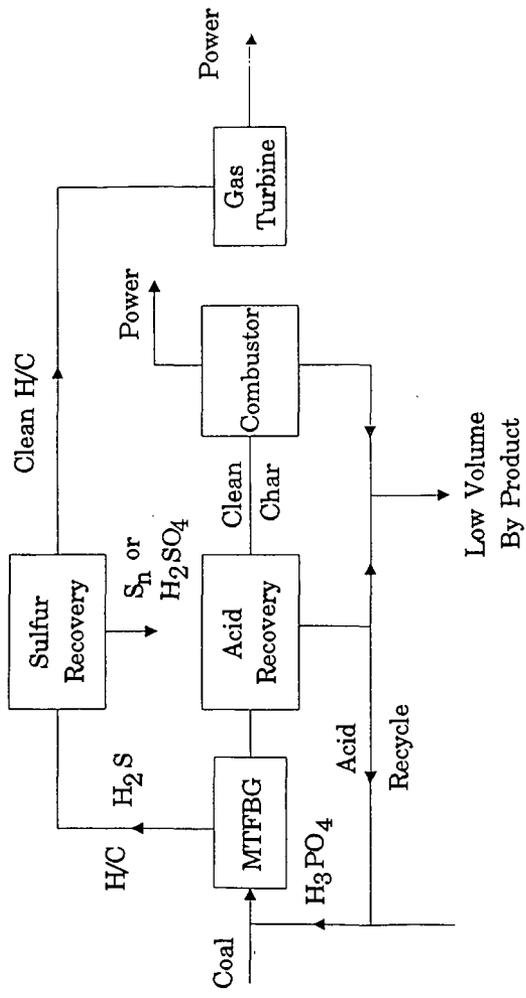


Figure 2. Proposed process using coal:phosphoric acid mixtures.