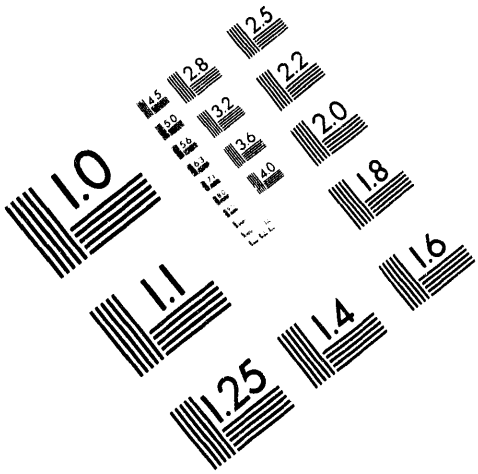

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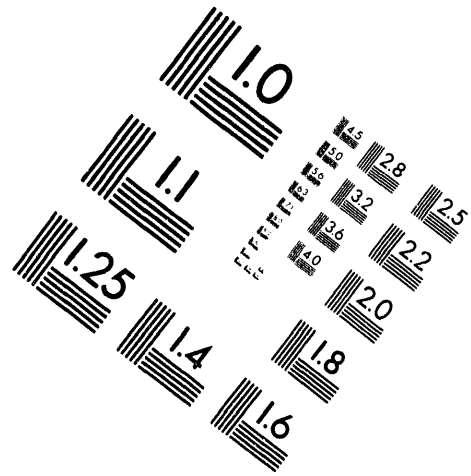

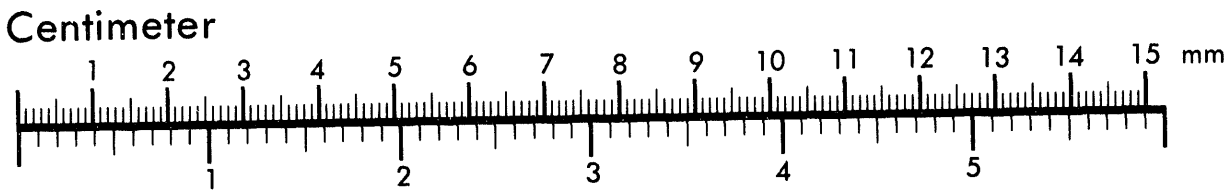

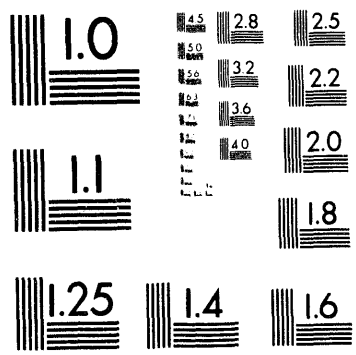

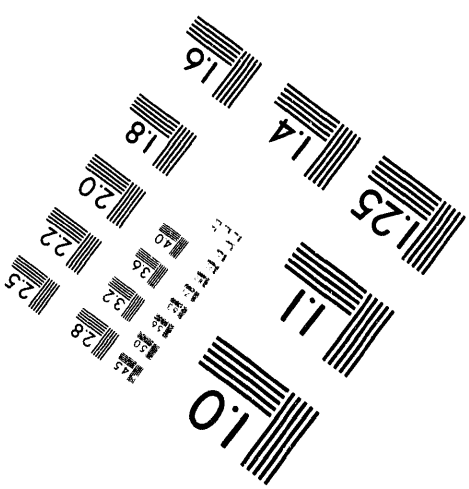

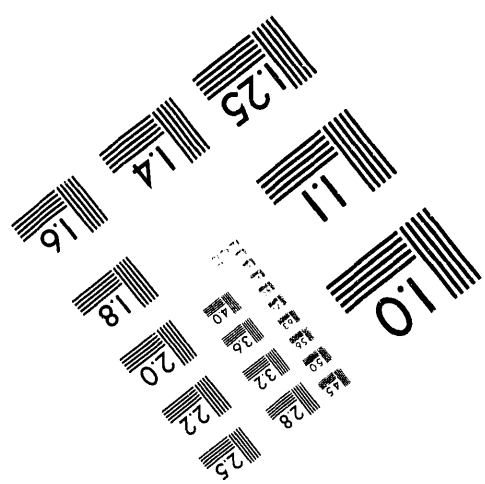

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DOE/PC/92521--T136

TECHNICAL REPORT
December 1, 1993 through February 28, 1994

Project Title:	**PRODUCTION AND USE OF ACTIVATED CHAR FOR COMBINED SO_2/NO_x REMOVAL**
DOE Grant Number:	DE-FC22-92PC92521 (YEAR 2)
ICCI Project Number:	93-1/3.1A-5P
Principal Investigator:	Anthony A. Lizzio, ISGS
Other Investigators:	Joseph A. DeBarr, ISGS Mark J. Rood, UIUC Massoud Rostam-Abadi, ISGS
Project Manager:	Frank Honea, ICCI

ABSTRACT

Carbon adsorbents have been shown to remove sulfur oxides from flue gas, and also serve as a catalyst for reduction of nitrogen oxides at temperatures between 80 and 150°C. The overall objective of this project is to determine whether Illinois coal is a suitable feedstock for the production of activated char which could be used as a catalyst for combined SO_2/NO_x removal, and to evaluate the potential application of the products in flue gas cleanup. Key production variables will be identified to help design and engineer activated char with the proper pore structure and surface chemistry to enable the development of an effective SO_2/NO_x removal catalyst.

During this reporting period, a thermogravimetric technique was developed to determine the kinetics of SO_2 adsorption on a series of chars prepared from IBC-102 coal. Also, a temperature programmed desorption (TPD) method was developed to determine the nature and extent of carbon-oxygen (C-O) complexes formed on the surface of the char. An attempt was made to relate this information to observed SO_2 adsorption behavior. An IBC-102 char prepared with an N_2-BET surface area of 10 m^2/g adsorbed significantly less SO_2 than chars prepared with surface areas > 200 m^2/g. However, for chars with surface areas > 200 m^2/g, the amount of available surface area was not as important as the chemistry of the surface. A steam activated char adsorbed the most SO_2, comparable to the amount adsorbed by a commercial activated carbon. TPD performed on the steam activated char revealed the presence of CO-forming C-O complexes which were basic in nature. The other chars all contained significant amounts of more acidic CO_2-forming complexes. Because SO_2 is an acid gas, a carbon adsorbent with a basic surface should adsorb more SO_2. To enhance SO_2 adsorption, a novel char preparation method was devised to create a basic surface with up to ten times more CO-forming C-O complexes than formed by steam activation.

During the next reporting period, the NO_x adsorption properties of the prepared chars will be determined. Methods will be developed to measure the acid/base characteristics of the carbons to help determine the relationship between SO_2/NO_x adsorption characteristics and pH of the carbon surface.

preference over other alternatives because of its removal efficiency for particulates, heavy metals, organic compounds (dioxins, furans) halogenated hydrogens and SO_2/NO_x. The carbon used is a lignite activated char with pore surface area of 300 m^2/g. In their purification process, the flue gases pass transversely through an activated carbon filter at temperatures between 100 and 150°C. The three-layer carbon bed separates and treats selective pollutants in each layer. Operating results show that current European emission requirements were met with the activated carbon systems. STEAG is presently seeking out U.S. suppliers of activated carbons to provide them with commercial products for testing in a U.S. waste incinerator. A meeting was held in Champaign, IL between representatives from ICDB, ICCI, ISGS and STEAG to discuss the possible use of Illinois coal in their flue gas purification process. STEAG has agreed to send samples of the carbon they currently use to the ISGS for further analyses. The ISGS will attempt to produce a similar type of material from Illinois coal.

The overall objective of this project is to determine whether Illinois Basin coals are a suitable feedstock for the production of activated char which could be used as a catalyst for removal of SO_2/NO_x from combustion flue gas, and to evaluate the potential application of the products in flue gas cleanup. Key production variables will be identified to help design and engineer activated char with the proper pore structure and surface chemistry which will enable the development of an effective SO_2/NO_x removal catalyst.

The project has four tasks.

In Task 1, activated chars are prepared from an Illinois coal (IBC-102) and an existing mild gasification char (MGC), prepared previously in an industrial pilot plant under controlled pyrolysis and activation conditions. Chars are prepared at pyrolysis temperatures ranging from 600-900°C. To increase surface area and SO_2/NO_x adsorption capacity, the IBC-102 char and MGC are further activated in steam or CO_2 or chemically activated using potassium hydroxide as the chemical activant. To enhance catalytic activity of the char for SO_2/NO_x removal, selected chars will be oxidized in air or by nitric acid/thermal desorption treatment.

In Task 2, activated char samples are tested for their ability to remove SO_2 and NO_x from a simulated flue gas. Carbon type, flow rate and adsorption temperature are the principal process variables to be studied. The adsorption capacity and kinetics of SO_2/NO_x adsorption are obtained for selected chars. A laboratory scale adsorption column/gas chromatography/mass spectrometry (AC/GC/MS) system is used to evaluate multicomponent gas adsorption. Temperature programmed desorption (5°C/min in helium) of SO_2 and NO_x from the spent char will provide further insight into the mechanism of combined SO_2/NO_x removal. The overall performance of the char in removing

SO_2/NO_x from simulated flue gas is assessed, and compared to that of commercial carbons.

In Task 3, chemical, physical and morphological studies are performed on activated char samples, before and after SO_2/NO_x adsorption, to discern the effects of combined SO_2/NO_x removal on the adsorption behavior of activated char. The tests to be performed include: proximate and ultimate analyses, N_2-BET (77 K) and CO_2-DR (273 K) surface areas, pore size distribution, helium and bulk density, particle size, and scanning electron microscopy.

In Task 4, if a suitable activated char is identified, the technical and economic feasibility of manufacturing and applying it on a commercial scale will be evaluated. Process flowsheets for the production and use of activated char from Illinois coal will be developed, and a preliminary cost analyses of ISGS activated char initiated.

During this reporting period, a thermogravimetric technique was developed to determine the kinetics of SO_2 adsorption/desorption on a series of chars prepared from IBC-102 coal. A temperature programmed desorption (TPD) method was developed to determine the nature and extent of carbon-oxygen complexes formed on the surface of the char. An attempt was made to relate this information to observed SO_2 adsorption behavior. An IBC-102 char with an N_2-BET surface area of 10 m^2/g adsorbed significantly less SO_2 than chars with surface areas > 200 m^2/g. However, for chars with surface areas > 200 m^2/g, the amount of available surface area was not as important as the chemistry of the surface. Because SO_2 is an acid gas, a carbon adsorbent with a basic surface would be expected to adsorb more SO_2. Of all the IBC-102 chars studied, a steam activated char adsorbed the most SO_2, comparable to the amount adsorbed by a commercial activated carbon. Temperature programmed desorption revealed the presence of CO-forming complexes which are basic in nature. The other samples all exhibited significant amounts of C-O groups which form CO_2 upon thermal desorption indicating a more acidic surface. Based on these results, a novel char preparation method was devised to create a basic surface which would enhance SO_2 adsorption. This procedure loaded on the char up to ten times more CO forming C-O complex than formed during steam activation.

During the next reporting period, the NO_x adsorption properties of the prepared chars will be determined. Methods are being developed to measure the acid/base characteristics of the carbons to help determine the relationship between SO_2/NO_x adsorption characteristics and surface pH. A quadrupole mass spectrometer will be used to detect SO_2 and NO_x species during multicomponent gas adsorption studies. The overall performance of the prepared chars in removing SO_2/NO_x from simulated flue gas will be assessed and compared to that of commercial carbons.

OBJECTIVES

The overall objective of this project is determine whether Illinois Basin coals are a suitable feedstock for the production of activated char, and to evaluate the potential application of the products in a carbon-based system for simultaneous removal of SO_2/NO_x from coal combustion flue gas. Key production variables will be identified to help design and engineer an activated char with properties which will enable the development of an effective SO_2/NO_x removal catalyst.

The project has four tasks:

Task 1. Chars are prepared from an Illinois coal (IBC-102) under carefully controlled pyrolysis and activation conditions. Chars are prepared in 1 and 2-in. ID fluidized-bed reactors (FBR) at pyrolysis temperatures ranging from 600-900°C. To increase surface area and SO_2/NO_x adsorption capacity, selected chars are further activated in steam or CO_2 at 850-900°C to 50-60% carbon conversion. IBC-102 coal is chemically activated using potassium hydroxide as the chemical activant. Potassium is loaded onto the coal or char by an incipient wetness technique and various coal or char/KOH mixtures (1:1, 1:2, 2:1) are prepared. The potassium loaded coal or char is pyrolyzed in the 2-in. FBR at 600 and 800°C, 0.5 h residence time. To enhance catalytic activity of the char for SO_2/NO_x removal, selected chars and activated chars are oxidized in air at 450°C in the 2-in. FBR to increase the oxygen content of the char. Another way will be to add to the char a metal which is known to be an active catalyst for SO_2/NO_x removal.

Task 2. Activated char samples are tested for their ability to remove SO_2 and NO_x from combustion flue gas. Carbon type, flow rate and adsorption temperature are the principal process variables to be studied. The adsorption capacity and kinetics of SO_2/NO_x (SO_2, NO, or NO_2 in helium) adsorption on selected chars at various temperatures (25-200°C) and pressures (200-800 torr) are determined using a volumetric adsorption apparatus and/or thermogravimetric analyzer (TGA). A laboratory scale adsorption column/gas chromatography/mass spectrometry (AC/GC/MS) system is used to evaluate multicomponent gas adsorption. A mixture of SO_2 (2500 ppm) and NO_x (500 ppm) in a simulated flue gas mixture (2% H_2O, 5% O_2, 15% CO_2, 78% N_2) is passed through the AC at a specified and controlled flow rate (20 cm^3/min). Ammonia is introduced into the feed gas in some runs to observe the effects of

selective catalytic reduction. Breakthrough curves for individual gases are determined. When the carbon bed becomes saturated, e.g., inlet [SO_2] = outlet [SO_2], the sorbent is regenerated with heat (200-400°C) and/or vacuum ($1x10^{-5}$ torr) treatment. Temperature programmed desorption (5°C/min in helium) of SO_2 and NO_x from the spent char is used in order to gain additional insight into the kinetics of SO_2/NO_x adsorption/desorption. The overall performance of the char in removing SO_2/NO_x from simulated flue gas is assessed, and compared to that of commercial carbons.

Task 3. Chemical, physical and morphological studies are performed on activated char samples, before and after SO_2/NO_x adsorption, to gain additional insight into the effects of SO_2/NO_x removal on the adsorption behavior of activated char. The tests to be performed include: proximate (moisture, volatile matter, fixed carbon, ash content) and ultimate (carbon, hydrogen, nitrogen, sulfur, oxygen) analyses, N_2-BET (77 K) and CO_2-DR (273 K) surface areas, pore size distribution, helium and bulk density, particle size and electron scanning microscopy. Attrition resistance (mechanical strength) of the spent char is also evaluated.

Task 4. If a suitable activated char is identified, the technical and economic feasibility of manufacturing and applying it on a commercial scale will be evaluated. Process flowsheets for the production and use of activated char from Illinois coal will be developed, and a preliminary cost analyses of ISGS activated char initiated. A collaborative research and development agreement with a suitable industrial partner will be established to facilitate commercial development of the activated char for specific industrial SO_2/NO_x removal applications.

INTRODUCTION

Commercial interest in carbon based flue gas desulfurization technology is growing and these processes have been proven successful at removing up to 100% SO_2 and over 80% NO_x from combustion flue gas. One of the unique advantages of the activated carbon FGD process is that it removes nearly every impurity found in combustion flue gas, including SO_2/NO_x, particulates, heavy metals and other air toxics. No other existing FGD process has that capability. Much of the work performed in the area of activated carbon FGD technology has been centered around understanding the mechanism of SO_2/NO_x removal by carbon. The experimental work to date has, for the

most part, neglected the possibility of improving the physical properties and surface chemistry of the carbon to enhance catalytic activity. A limited number of studies are currently underway in the U.S. on the simultaneous removal of SO_2/NO_x from combustion flue gas using activated carbon. Japanese researchers have developed this technology to the point of commercialization, however, there remains the need for development of sorbents having higher adsorption capacity and mechanical strength.

No data is available on the production or use of activated carbon derived from Illinois coal for simultaneous removal of SO_2 and NO_x from coal combustion flue gas. This relatively unexplored research area, however, shows considerable promise. A recent ICCI sponsored economic evaluation of mild gasification char as a possible feedstock for activated carbon, and as a sorbent for removing pollutants from electric utility flue gas, concluded that "a flue gas deNO_x process using activated mild gasification char is competitive with selective catalytic reduction" and "the activated char scrubber has the potential to create a significant increase in the market for activated carbon." The proposed research, if successful, could affect markets for Illinois coal in three important ways, 1) the development of low cost FGD processes, using Illinois coal-based activated char, would enable electric utilities to continue burning high-sulfur Illinois coal while complying with the 1990 Clean Air Act, 2) the newly developed FGD process would consume activated char made from Illinois coal, thereby increasing utilization of this resource, and 3) if mild gasification char is deemed a suitable feedstock, a market for this char is identified.

Carbon adsorbents may be used to remove sulfur oxides from coal combustion flue gas at temperatures below 120°C, and also as a catalyst for reduction of nitrogen oxides at temperatures between 80 and 150°C (Richter et al., 1985). The type of carbon used is probably the most important process consideration, with respect to both adsorption efficiency and maintenance of efficiency during extended operation. A high quality carbon adsorbent for SO_2/NO_x removal should have the following properties: high adsorption capacity for SO_2, rapid SO_2 adsorption kinetics, high catalytic activity for ammonia-based NO_x reduction, low reactivity with oxygen, minimal activation losses due to regeneration and high mechanical strength.

An activated carbon FGD process could be used alone to remove SO_2/NO_x from the flue gas of coal firing utilities, or in conjunction with other methods of FGD. An activated carbon FGD process is typically placed after the precipitator and just before the stack. This technology has been used in Europe and Japan for removal of SO_2 and NO_x from combustion flue gas. Activated carbon-based FGD processes can be integrated into both new and existing power plants.

Retrofitting an existing utility boiler with such a FGD process should, in addition to improving SO_2/NO_x emissions, lower overall operating costs compared to competitive FGD processes. Richter et al. (1985) describe the flexibility of carbon based SO_2/NO_x removal processes, and their ease of incorporation into existing FGD processes. Four processes were analyzed in detail. Perhaps the most interesting process configuration was an SO_2/NO_x reduction process placed behind a conventional FGD unit (scrubber). With a flue gas of high SO_2 concentration, the flue gas scrubber is able to be operated at a relatively low SO_2 removal rate, and is used only as a preliminary stage for the more efficient carbon based FGD process. As far as NO_2 removal is concerned, Richter et al. (1985) contend that it is easier to integrate a carbon-based NOx reduction process into a power plant FGD scheme than to use a catalyst-based NO_x reduction unit, which needs to be operated at relatively high temperatures (> 250°C). They also suggest that for smaller boilers, and those boilers burning high-sulfur coal, it would be more economical to operate conventional spray sorption methods at low efficiency, and arrange behind them a suitable activated carbon FGD process to remove the majority of the SO_2/NO_x.

A Japanese company (Mitsui Mining Company, Limited) has taken the Bergbau Forschung (BF) process and modified it to meet their SO_2/NO_x removal requirements (Tsuji and Shiraishi, 1991). Their Mitsui-BF dry $DeSO_x/DeNO_x$ process is claimed to be very effective for SO_2/NO_x reduction. One of the main advantages of the Mitsui-BF process over other FGD processes is that both SO_2 and NO_x reduction are performed in a single process. Their process consists of three sections: adsorption, regeneration and by product recovery. It achieves 100% removal of SO_2 and over 80% removal of NO_x by contacting the flue gas with activated coke and injecting ammonia for nitric oxides reduction over a temperature range of 100-200°C. Halogen compounds and trace elements such as mercury vapor and dioxins contained in the flue gas are also removed by chemical or physical adsorption onto the carbon. Furthermore, a moving bed of activated coke serves as a filter for removal of particulates in the flue gas. Elemental sulfur, sulfuric acid, or liquid SO_2 is recovered in the regeneration section.

Mitsui Mining Co. has a licensing agreement with Bergbau-Forschung to investigate, test and adapt the activated carbon FGD system to the facilities in Japan where regulations are more stringent towards SO_2/NO_x pollutants. Mitsui also proceeded to develop technology of their own to produce the activated coke used in their dry $DeSO_x/DeNO_x$ process. Table 1 compares the physical properties and operating performance of their coke and a standard commercial activated carbon. The surface area and SO_2 adsorption capacity of their coke is a factor of three less than that of the (fresh) commercial carbon. Based on the results of laboratory tests, Mitsui

constructed and operated a pilot plant which produced 0.5 tons/day activated coke. Bituminous coal was found to be the ideal feedstock, but lignite and petroleum coke were also used. An activated coke with high mechanical strength was achieved by controlled pyrolysis. A proper micropore structure was developed using a controlled chemical activation process. The ratio of activated coke to binder was critical for producing a final product of high mechanical strength. In some cases, the surface of the activated coke was chemically treated to increase its ability to remove SO_2 and NO_x.

Table 1. Performance characteristics of Mitsui activated coke compared with those of commercial activated carbon (from Tsuji and Shiraishi, 1991).

Characteristics	Mitsui Activated Coke	Activated Carbon
BET Surface Area (m^2/g)	150 - 250	850
Mechanical Strength (%)	95	85
SO_2 Adsorption Capacity (mg SO_2/g)	60 - 120	220 (fresh) 70 (used)
NO_x Removal Efficiency (%)	80 - 85	60 - 70
Price Ratio (-)	1/4 - 1/3	1

Due to recent legislation in the European community, the use of activated carbon for cleaning flue gases from waste incinerators has seen increased interest. A German company (STEAG) has licensed technology for carbon-based systems which have been installed on commercial medical, hazardous and municipal waste incinerators (Brueggendick and Pohl, 1993). In each case the activated carbon technology was given preference over other alternatives because of its removal efficiency for particulates, heavy metals, organic compounds (dioxins, furans) halogenated hydrogens and SO_2/NO_x. The carbon used is a lignite activated char with pore surface area of 300 m^2/g. In their purification process, the flue gases pass transversely through an activated carbon filter at temperatures between 100 and 150°C. The three-layer carbon bed separates and treats selective pollutants in each layer. In the first layer, particulates, heavy metals, furans and dioxins are removed; in the second layer, residual sulfur oxides (SO_2, SO_3) are removed; in the third layer, residual halogenated compounds (HCl, HF) are removed. As the spent carbon is removed the filter is continuously replenished with a fresh supply of carbon. Operating results show that current European emission requirements were met with the activated

carbon systems. STEAG is presently seeking out U.S. suppliers of activated carbons to provide them with commercial products for testing in a U.S. waste incinerator.

In the U.S., there is renewed interest in the development of carbon-based processes for flue gas cleanup. Gangwal and Silveston (1992), funded by the U.S. DOE, developed their novel RTI-Waterloo process for flue gas cleanup. It is a low temperature process employing carbon-based catalysts and operating downstream of the electrostatic precipitator (ESP). The process is capable of removing more than 95% of the SO_2 and 75% of the NO_x from coal combustion flue gas. The flue gas leaving the ESP is first cooled to 100°C. The SO_2 is catalytically oxidized to SO_3 which is removed as medium strength sulfuric acid in a series of periodically flushed trickle-bed reactors containing an activated carbon catalyst. A periodic short duration aqueous or acid flush is used to remove the SO_3 from the carbon as H_2SO_4, which leaves the system. The key to the process is that periodic, rather than continuous, flush simultaneously regenerates the carbon and produces a stronger sulfuric acid than conventional contacting schemes. The flue gas continues to flow at all times. The SO_2 free gas is reheated to 150°C and NH_3 is added. The gas is passed over a fixed bed of a different carbon catalyst to reduce the NO_x to N_2 and H_2O. The technical feasibility of the process was demonstrated in laboratory scale experiments. Based on results, a preliminary evaluation of the RTI-Waterloo process was conducted for a 100-MW electric power plant burning a 2.8% sulfur coal. The economic results obtained for the process were compared to those of competing technologies. The RTI-Waterloo process was found to be competitive with several combined SO_2/NO_x removal processes (conventional FGD/SCR, NOXSO, SNO_x, E-beam). Although the RTI-Waterloo process was capable of removing more than 95% of the SO_2 and 75% of the NO_x while producing a medium strength sulfuric acid product, the major barrier to commercialization of their process was the cost to prepare the carbon. In future work, the carbon catalysts need to be further optimized with respect to cost and long term durability.

EXPERIMENTAL

Char Preparation

Figure 1 presents an overview of the proposed experimental plan for production of activated char from IBC-102 coal. The three major processing steps are: pyrolysis, activation, and surface modification by oxygen deposition/thermal desorption treatment. The goal of this task is to identify process conditions for producing high density, high surface area char with optimal SO_2/NO_x removal characteristics.

The chars used in this work were prepared from an Illinois No.

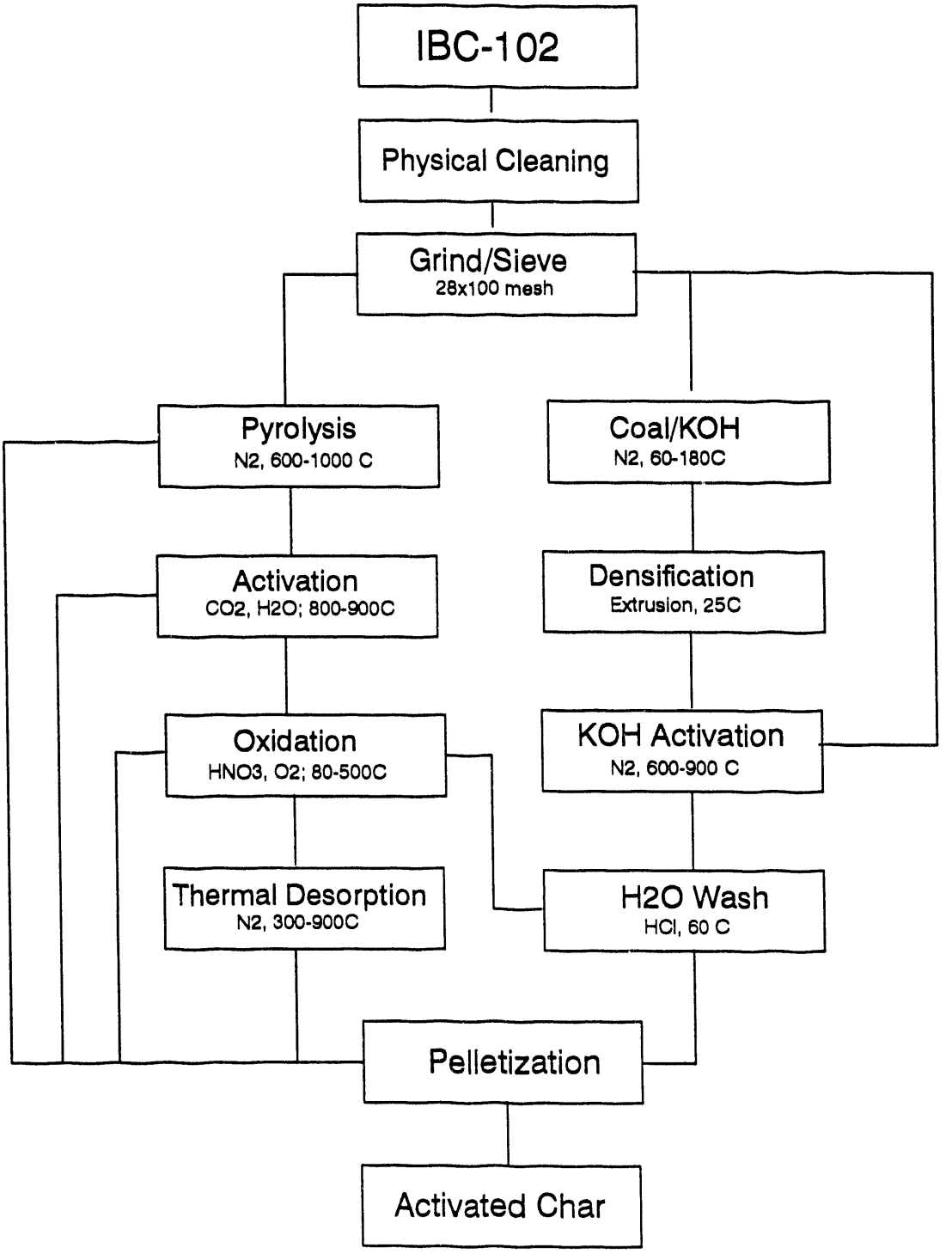

Figure 1. Overview of Experimental Plan.

2. hvC bituminous coal, sample IBC-102 of the Illinois Basin Coal Sample Program (Harvey and Kruse, 1988). This coal was obtained from a western Illinois preparation plant and is relatively low in organic and high in pyritic sulfur. A 48x100 mesh sample was prepared from the parent coal. The IBC-102 coal (-1/8") was sieved prior to grinding to remove any material smaller in diameter than the desired size fraction. The oversized sample was subjected to a step-wise grinding and sieving size reduction technique which involved grinding the sample in a rod mill for 15-120 s intervals, separating the oversized and undersized material from the desired size fraction by sieving on a Ro-Tap sieve shaker, and grinding the oversized material. The cycle was repeated until there was less than 5% of oversized material remaining.

Prior to char preparation, the coal was physically cleaned to remove mineral matter. In a typical run, 400 g 48x100 mesh IBC-102 coal was combined with 4 L H_2O in a Denver model D-2 batch flotation system. A flotation agent (MIBC) was added at an equivalence of 5 lbs/ton. The mixture was stirred by an impeller at a rate of 1400 rpm. After sufficient mixing, air was introduced into the cell and the clean coal particles were collected from the overflow. Additional mineral matter was removed by repeating the procedure using the clean coal as starting material. The clean coal was vacuum filtered and dried in a convection oven at 105°C. The proximate and ultimate analyses (moisture-free basis) of the coal and clean coal are given in Table 2.

Chars were prepared at 500, 700 and 900°C, 0.5 h in a 2-in. ID batch fluidized-bed reactor (FBR). In each run, 200 g IBC-102 coal was fluidized in flowing N_2 (6 L/min) and heated to the desired pyrolysis temperature. A multi-step heating procedure was used to minimize agglomeration of coal particles in the FBR (DeBarr et al., 1991). The physical and chemical properties of the chars were further modified to determine the effect of surface area, oxygen content and type of oxygen on the resulting SO_2/NO_x adsorption capacity of the char.

Selected samples were subjected to oxidation in 10% O_2 to increase both surface area and oxygen content. The chars prepared at different heat treatment temperatures exhibited different reactivities. Preliminary TGA studies were performed to obtain oxidation temperatures which would maintain a relatively constant rate of reaction for each of the samples. In a typical run, 50 g char was placed in the 1 in. ID FBR and heated to 390-500°C under flowing N_2. The sample was oxidized in 10% O_2/90% N_2 for 0.5-0.75 h to obtain a 30% weight loss (conversion), then cooled to room temperature in nitrogen.

Table 2. Proximate and Ultimate Analyses of Coal and Clean Coal Samples.

	IBC-102	Clean IBC-102
Moisture	12.51	2.31
Volatile Matter	39.02	41.26
Fixed Carbon	55.51	55.15
H-T Ash	5.47	3.59
Carbon	73.50	77.35
Hydrogen	5.09	5.43
Nitrogen	1.42	1.49
Oxygen	11.49	9.96
Sulfatic Sulfur	1.11	0.35
Pyritic Sulfur	0.63	0.50
Organic Sulfur	1.28	1.32
Total Sulfur	3.02	2.18
BTU/lb	13146	13876

Steam activation was performed to further develop microporosity and surface area while minimizing oxygen added to the char. Typically, 50 g char was placed in the 1 in. ID FBR and heated to 860°C in flowing N_2. The N_2 flow was replaced by 50% H_2O/50% N_2 for 0.75 h to achieve 30% carbon conversion. The activated char was cooled to room temperature in nitrogen.

A chemical activation method was employed to enhance surface area development and increase the adsorption capacity of the char. The method involved addition of an alkali salt to the raw coal and subsequent heat treatment in inert gas. Potassium hydroxide (KOH) was loaded onto the coal by impregnation to incipient wetness. Typically, 200 g KOH was dissolved in 0.2 L distilled water and mixed thoroughly with the raw coal. 200 g coal/KOH mixture was added to the 2 in. FBR and pyrolyzed at 600 and 800°C, 0.5 h. The sample was cooled in N_2 and washed repeatedly with distilled water to remove excess potassium and air dried overnight at 105°C.

Selected chars were subjected to a nitric acid oxidation treatment. Typically, 10g char was added to 0.2 L 45% HNO_3 solution, heated to 80°C and stirred for 2.5 h. The HNO_3

treated char was washed repeatedly with distilled water to remove excess acid and air dried overnight at 105°C. In some cases the nitric acid treated char was heated in nitrogen to 525°C, 0.5 h to desorb some of the carbon-oxygen complexes formed by the nitric acid oxidation treatment.

Char Characterization

Surface Area

Single-point BET surface areas of prepared chars were determined from N_2 (77 K) adsorption data obtained at a relative pressure (p/p_o) of 0.30 with a Monosorb flow apparatus (Quantachrome Corp.).

Temperature Programmed Desorption (TPD)

Temperature programmed desorption (TPD) experiments were carried out in a flow-thru, 1-in. ID stainless steel fixed-bed reactor system. In a typical run, 0.5 g of sample was heated in flowing nitrogen (0.5 L/min) at 5°C/min to a final temperature of 1000°C. This temperature was held for 1 h to achieve complete desorption of CO and CO_2 from the sample. Rosemount Model 880 CO and CO_2 non-dispersive infrared analyzers were used to continuously monitor the [CO] and [CO_2] in the effluent gas.

SO_2 Adsorption Capacity

The kinetics of SO_2 adsorption on selected chars was determined using a Cahn TG-131 thermogravimetric analyzer (TGA) system. In a typical run, a 30-50 mg char sample was placed in a platinum pan and heated at 20°C/min in flowing nitrogen to 360°C to remove moisture and impurities. The sample was cooled to the specified adsorption temperature (80-120°C) under nitrogen. Once the temperature stabilized, the nitrogen flow was switched to one containing 5% O_2, 10% H_2O and the balance nitrogen. Once the weight stabilized, the SO_2 was added in concentrations representative of a typical flue gas (e.g. 2500 ppmv SO_2). The weight gain versus time was recorded by a computerized data acquisition system. After a given adsorption time, the sample was ramped to 360°C to regenerate the carbon. If desired, several adsorption/desorption sequences were performed with a given char sample to examine the effects of regeneration on SO_2 adsorption capacity.

RESULTS AND DISCUSSION

SO_2 Adsorption

The adsorption of SO_2 on activated carbon can be both chemical and physical, and both may occur over a relatively wide

temperature range, 25-200°C. The degree of each is affected by the presence of oxygen in the flue gas. Various studies have shown that an oxygen-free carbon surface has limited total SO_2 adsorption capacity. The presence of water vapor is also important, because it reacts with the SO_3 formed by reaction of SO_2 with O_2. Physisorption of SO_2 on activated carbon decreases with increasing temperature, e.g., from 8% at 60°C to 0 wt% SO_2 at 250°C (Slack, 1971). In the absence of O_2 and H_2O, adsorption of SO_2 is quite small on the order of 1% by weight from 50-300°C.

The SO_2 adsorption capacities of chars prepared last reporting period were measured by thermogravimetric analysis. The method developed was patterned after one used by Davini (1990). Water and oxygen are essential for catalytic oxidation of SO_2 to SO_3 and H_2SO_4 by carbon. Oxygen from the gas phase is chemisorbed onto a carbon active site to form a carbon-oxygen (C-O) complex. Catalytic oxidation involves reaction between SO_2 in the gas phase with the C-O surface complex. In the presence of water at low temperatures, the SO_3 is converted to the acid, H_2SO_4. The reaction mechanism is shown below:

Oxygen Adsorption	$1/2\ O_2\ (g) + C\ (s) \longrightarrow C\text{-}O\ (s)$
SO_2 Adsorption	$SO_2\ (g) + C\text{-}O\ (s) \longrightarrow C\text{-}SO_3\ (s)$
H_2SO_4 Formation	$C\text{-}SO_3\ (s) + H_2O\ (g) \longrightarrow C\text{-}H_2SO_4$
Overall Reaction	$C + SO_2 + 1/2\ O_2 + H_2O \longrightarrow C\text{-}(H_2SO_4)$

In this study, the simulated flue gas contained 5% oxygen and 10% water vapor. Figure 2 shows the effect of oxygen and water vapor on SO_2 adsorption capacity. There is a tenfold increase in the SO_2 adsorption capacity of the char when water vapor and oxygen are included in the flue gas mixture. These results are in agreement with those of Davini (1990). The optimum SO_2 adsorption temperature was also sought. Figure 3 shows the kinetics of SO_2 adsorption at temperatures between 80 and 120°C for a char prepared in this study (KOH activated char). There is no appreciable difference in the amount of SO_2 adsorbed in this temperature range. An adsorption temperature of 120°C was used in subsequent runs because of difficulties at the lower temperatures with condensation of water vapor in the TGA.

Effect of Surface Area

A series of chars was prepared to determine the effect of surface area and oxygen content on SO_2 adsorption capacity. Table 3 presents N_2-BET surface areas of the prepared chars and a commercial activated carbon. For the three heat treatment temperatures (HTT) studied (500, 700 and 900°C, the

Table 3. Nitrogen BET Surface Area and Oxygen Content of IBC-102 Chars and a Commercial Activated Carbon.

Sample	Surface Area (m^2/g)	CO/CO_2	O_2 (wt%)
IBC-102, 500°C, 0.5 h	1.2	---	---
IBC-102, 700°C, 0.5 h	10.0	4.8	1.5
IBC-102, 900°C, 0.5 h	1.2	---	---
IBC-102 + KOH, 600°C, 0.5 h	500	---	---
IBC-102 + KOH, 800°C, 0.5 h	800	---	---
Calgon Activated Carbon	1000	---	---
IBC-102, 500°C h; 10% O_2, 390°C	215	3.3	8.6
IBC-102, 700°C; 10% O_2, 440°C	315	3.4	8.9
IBC-102, 900°C; 10% O_2, 500°C	231	4.2	5.2
IBC-102, 900°C; H_2O, 860°C	222	3.4	1.1
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, 2.5 h	182	1.4	16.4
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 525°C	---	6.7	5.9

maximum surface area (10 m^2/g) is achieved at a HTT of 700°C. For a HTT of 500°C, some volatile matter remains in the sample, which blocks pore entrances and reduces accessible surface area. At 900°C, the structure of char becomes more ordered (graphitic), which also leads to a reduction in accessible surface area. Oxidation in 10% O_2 significantly increases the surface area of the three chars to 215-315 m^2/g. The 700°C char exhibits slightly higher surface area than the 500 and 900°C chars after air oxidation.

The surface areas of these IBC-102 chars are comparable to those of the lignite cokes used by STEAG in their flue gas purification process (Brueggendick and Pohl, 1993). STEAG is currently attempting to license their technology for flue gas cleanup in the U.S. and are searching for U.S. suppliers of activated carbon to provide their process with a cost-effective adsorbent. The cost requirements are rather stringent since they do not regenerate their carbon, but simply burn it when it becomes saturated with SO_2, NO_x and heavy metals. The overall price of the carbon to be used in their flue gas purification process for a U.S. waste incinerator or utility boiler should be less than $200/ton since it costs STEAG $70/ton to produce it and $130/ton to ship it from Germany to the United States (Rummenhohl, 1994).

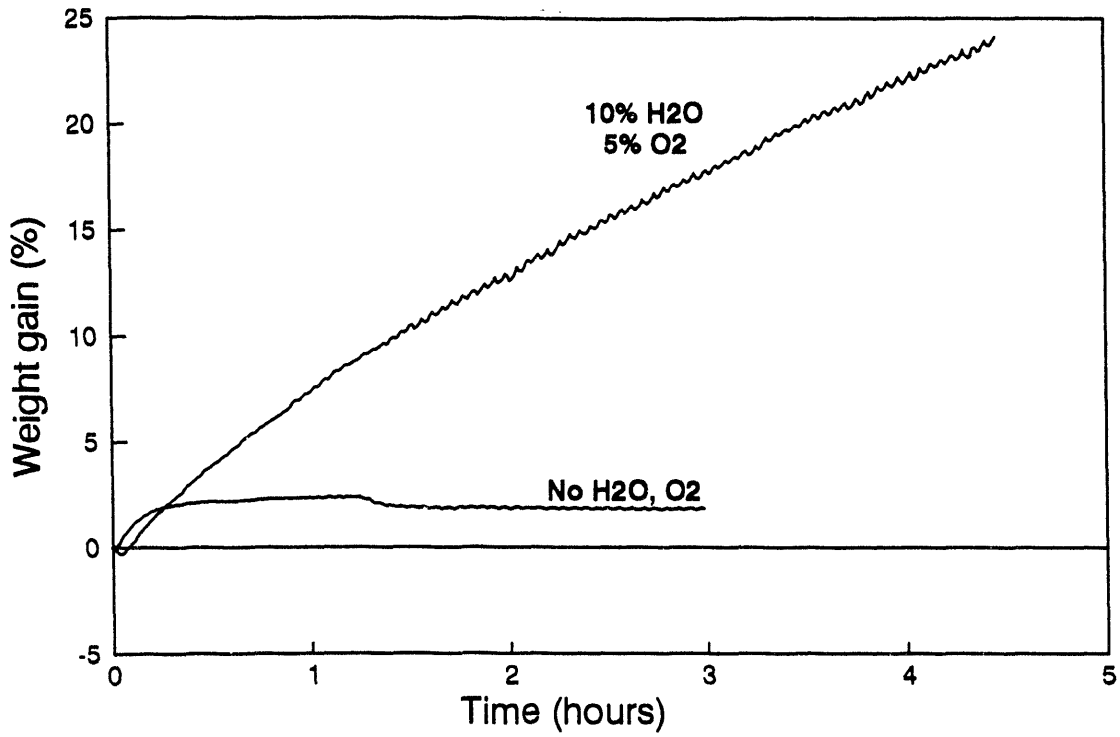

Figure 2. Effect of water vapor and oxygen concentrations on SO_2 adsorption.

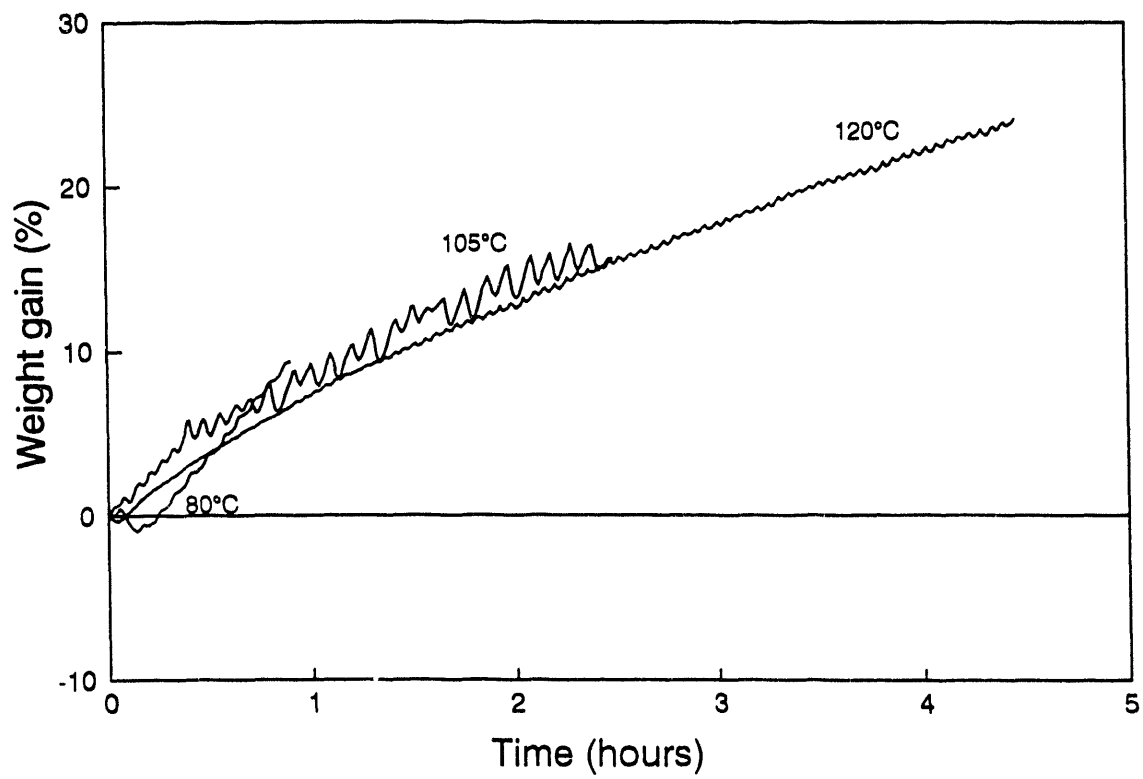

Figure 3. Effect of temperature on SO_2 adsorption.

To date, STEAG has not been successful in locating a U.S. supplier of activated carbon which can meet these performance and cost targets. Based on results obtained in this study, activated char derived from Illinois coal would meet these requirements. It should not cost more than $100 per ton to oxidize to 10-20% conversion a mild gasification char (pyrolysis temperature, 500-600°C) produced from Illinois coal. Energy intensive steam activation, which is the principal method used by industry to activate char, is far more costly than low temperature air oxidation. Table 3 indicates that steam activation is not necessary for production of a char with a surface area of 300 m^2/g. In fact, Table 3 shows that chars produced by steam activation at 860°C and by oxidation at 500°C have similar surface areas (225 m^2/g).

The effect of surface area on the SO_2 adsorption capacity of various chars prepared from Illinois coal and a commercial activated carbon (Calgon F400) is shown in Figure 4. The steam activated char (200 m^2/g) is seen to have the highest initial rate of SO_2 adsorption compared to the other carbons. The char prepared at 700°C, which had the lowest surface area (10 m^2/g), adsorbed the least amount of SO_2 (3.5 wt%) after 7 h adsorption time. The commercial activated carbon, which had the highest surface area (1000 m^2/g), continued to adsorb SO_2 while the other samples became saturated. The commercial carbon adsorbed the greatest amount of SO_2 (35 wt%) after 7 h adsorption time. It is interesting to note that after 3 h adsorption time, the commercial activated carbon and the three chars prepared from Illinois coal having intermediate surface areas (200, 500 and 800 m^2/g) adsorb similar amounts of SO_2, between 15 and 20 wt% SO_2. The chars with surface areas of 500 and 800 m^2/g were prepared by KOH activation at 600 and 800°C. Apparently, once there is an available surface area > 200 m^2/g there is no correlation between SO_2 capacity and surface area. In this case, other properties of the carbon probably become more important for determining the SO_2 capacity of the char.

Effect of Oxygen

An understanding of SO_2 adsorption behavior may require more detailed information about the surface intermediates (carbon-oxygen complexes) formed during char preparation and SO_2 adsorption. The nature and extent of oxygen functional groups on the char surface can be studied by temperature programmed desorption. Temperature programmed desorption (TPD), an experimental technique widely used in the field of heterogeneous catalysis and recently applied in coal gasification studies, may be used to provide useful information not only on the extent, but also on the energetics of desorption of carbon-oxygen (C-O) complexes from the char surface. The objective here is to characterize the energetic

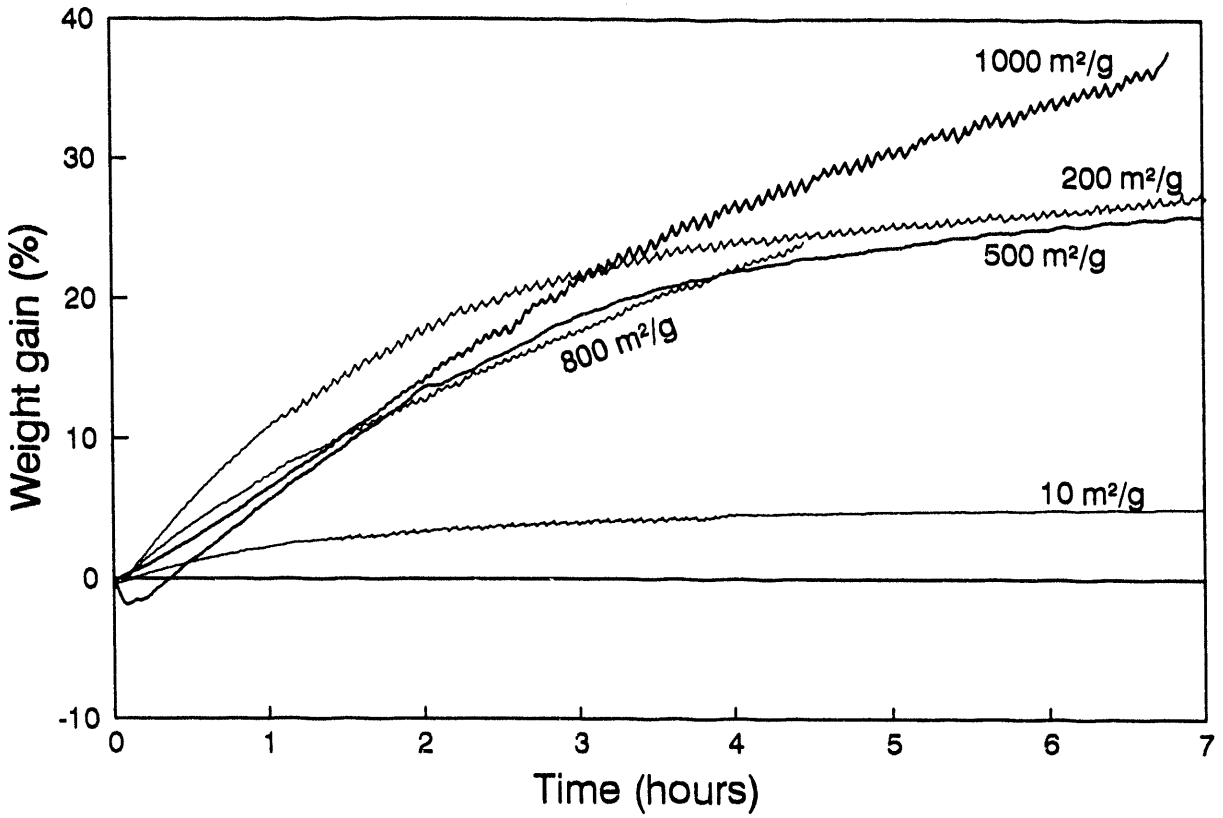

Figure 4. Effect of surface area on SO_2 adsorption.

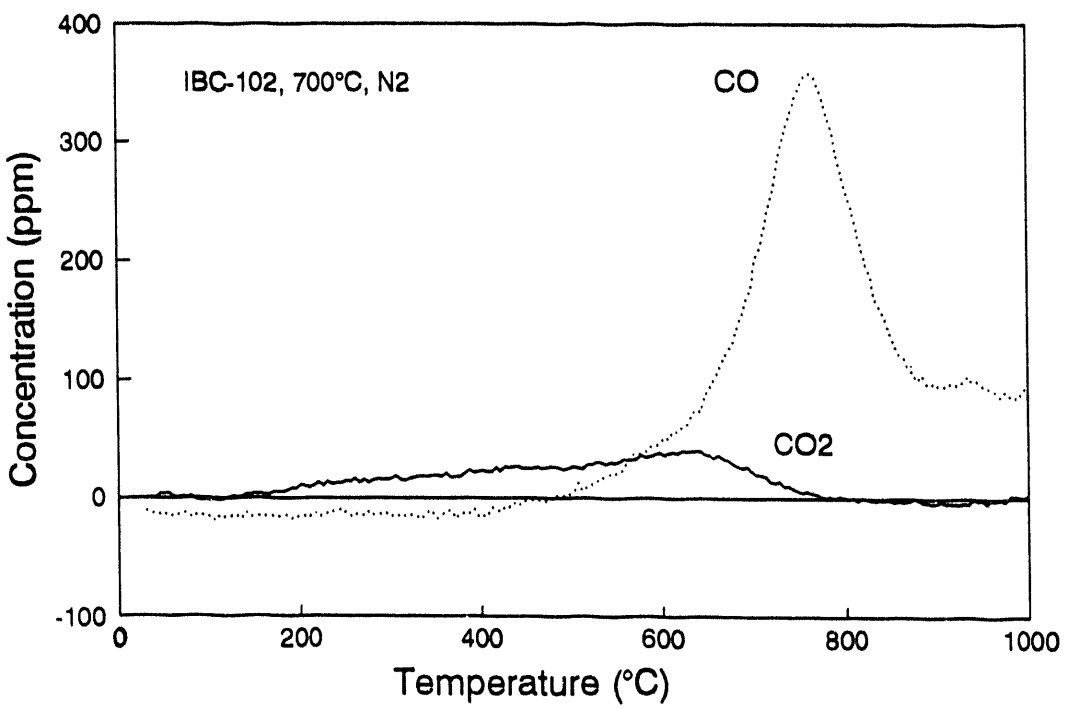

Figure 5. TPD profile of a char prepared at 700°C.

heterogeneity of the char surface and relate it to observed SO_2 adsorption behavior. Typical TPD profiles for selected IBC-102 chars are shown in Figures 5-7. The amount of CO and CO_2 evolved as a function of temperature can be determined from the area under the curves. From these values, the total amount of oxygen present on the carbon surface can be calculated.

Table 3 lists the total oxygen content and the relative amounts of CO/CO_2 evolved during TPD for prepared IBC-102 chars. For carbons with similar total surface areas, oxidation with nitric acid incorporates significantly more oxygen on the carbon than oxidation in air. Davini (1990) observed no correlation between SO_2 adsorption capacity and the total amount of oxygen adsorbed on the carbon. However, a correlation was found between SO_2 capacity and basic C-O functional groups present on the char surface. Because SO_2 is an acid gas, a carbon adsorbent with a basic surface could be expected to adsorb more SO_2. The carbon-oxygen functional groups which form CO upon thermal desorption in inert gas impart surface basicity, while C-O groups which form CO_2 (carboxyl) are acidic by nature. In the present study, based on the results of Davini (1990), a novel char preparation method was devised to create a basic surface which would enhance SO_2 adsorption.

Figures 6 and 8 shows that the type of oxygen complexes formed on the HNO_3 treated carbon are different from those produced by oxidation in air. Significantly more CO_2 is evolved during TPD at lower temperatures for the HNO_3 treated sample than the air oxidized carbon. Compared to the TPD profiles of the air oxidized char (Figure 6), the CO and CO_2 evolution profiles of the nitric acid treated char (Figure 8) show only slight overlap; thus, it may be possible to heat the nitric acid treated char in inert atmosphere to a certain temperature, e.g., 525°C, to remove only the CO_2-forming functional groups and leave behind the CO-forming ones. The end result should be a more basic carbon surface, i.e., one with significantly more CO-forming groups than a surface developed by steam activation of the same char (Figure 6). Indeed, the TPD profile of the HNO_3 sample heated to 525°C (Figure 9) shows that the C-O functional groups remaining on the heat-treated HNO_3 char produce mainly CO upon desorption. The CO_2 evolved from this char at temperatures > 600°C may be attributed to secondary reactions between CO and C-O complexes as CO diffuses from the micropores. An interesting result of this nitric acid/thermal desorption procedure is that it loads onto the char about ten times the amount of the favorable high-temperature CO-forming groups (Figure 9) as compared to the steam activated char (Figure 7). These C-O complexes are thought to be the ones responsible for enhanced SO_2 adsorption (Davini, 1990). Whether an increase in these complexes leads to an increase in SO_2 capacity remains to be determined.

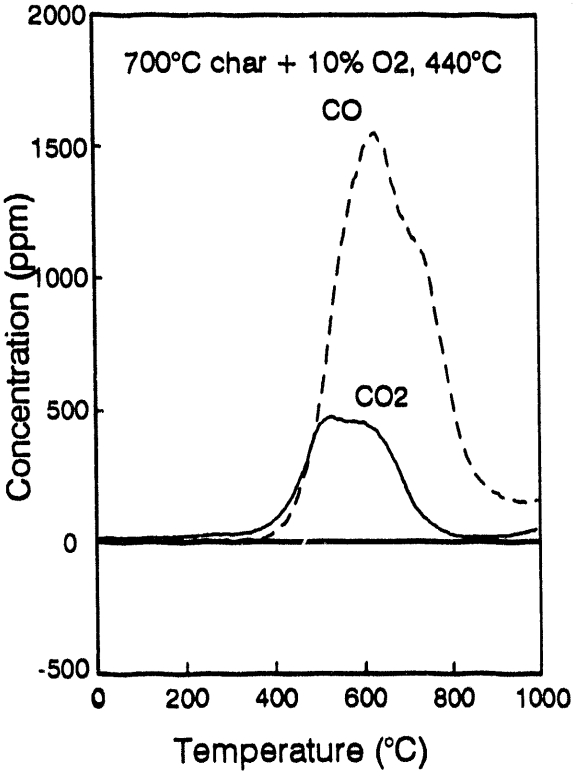

Figure 6. TPD profile of a char activated in O2.

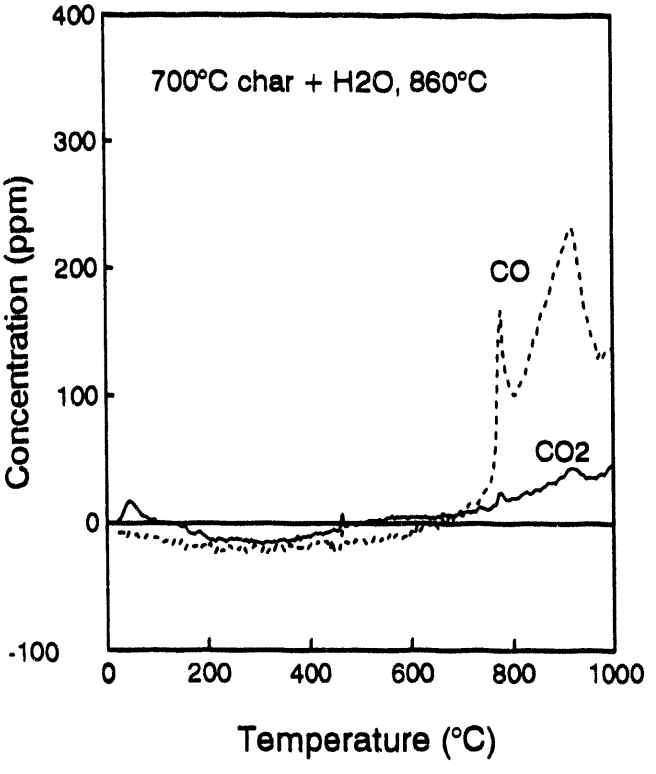

Figure 7. TPD profile of a char activated in H2O.

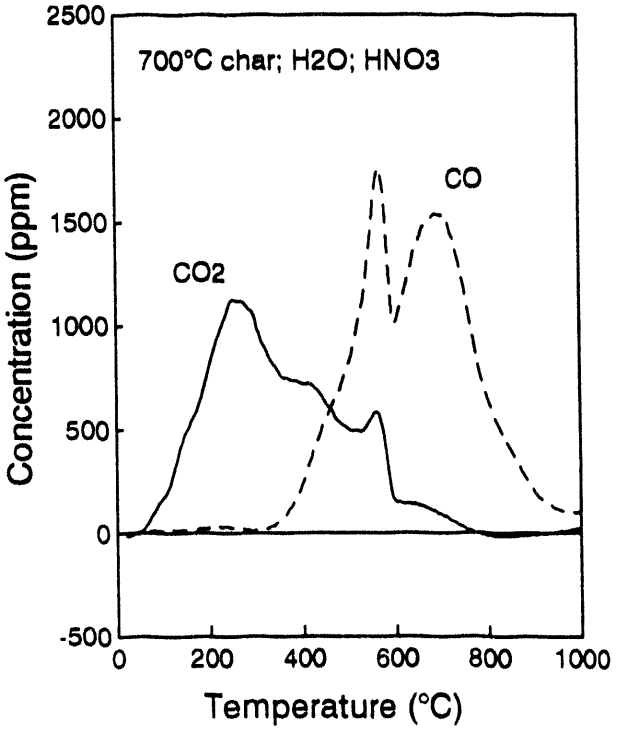

Figure 8. TPD profile of HNO3 treated char.

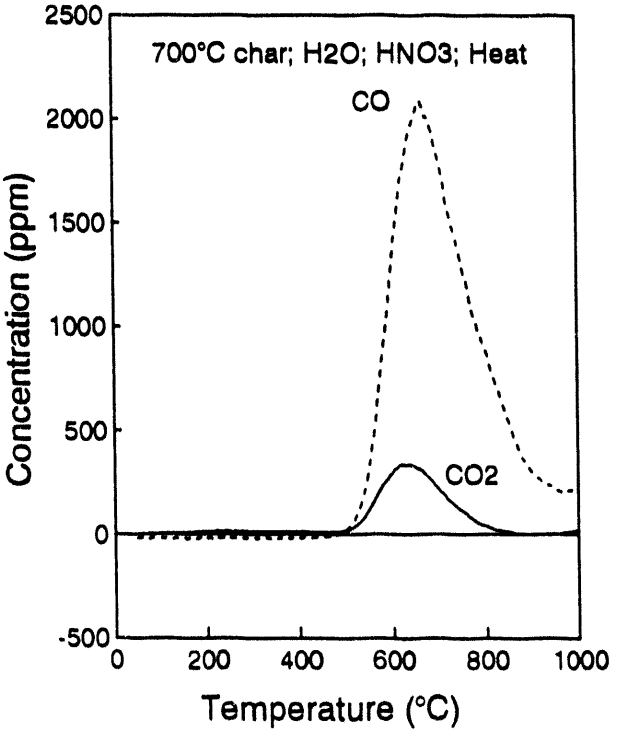

Figure 9. TPD profile of HNO3 treated char after desorption at 525°C.

The kinetics of SO_2 adsorption on the steam activated, HNO_3 treated steam activated, and thermally desorbed HNO_3 treated steam activated chars are presented in Figure 10. The steam activated char is seen to have the highest SO_2 capacity. The thermally desorbed HNO_3 treated char exhibits a higher SO_2 capacity than the HNO_3 treated char; the removal of CO_2-forming groups by thermal desorption has, indeed, enhanced SO_2 adsorption. A comparison of Figures 8 and 9, which are TPD profiles of the nitric acid treated and thermally desorbed nitric acid treated char, shows the effect of 525°C thermal desorption treatment on the energetic heterogeneity of the carbon surface. The CO_2-forming groups which do not enhance SO_2 adsorption have been preferentially removed by thermal desorption at 525°C leaving behind the more favorable CO-forming complexes. It was expected that the thermally desorbed nitric acid treated char would adsorb more SO_2 than the steam activated char since it contained significantly more of these basic C-O functional groups. Figure 10 shows that this was not the case. It is possible that some of the acid remained in the nitric acid treated char because of insufficient washing, which would make the surface acidic. This would negate any benefits gained by removing the CO_2-forming C-O complexes. A method is being developed to measure the pH of the carbon surface. This characterization will aid in determining the relationship between the various treatments used, types of C-O complexes formed, and the SO_2 adsorption capacity of chars. It is also possible that the chosen desorption temperature of 525°C was not high enough to leave behind CO-forming groups of the same thermal stability and type as formed on the steam activated char. A comparison of Figures 7 and 9 indicates a peak CO temperature of 625°C for the thermally desorbed nitric acid treated char compared to 900°C for the steam activated char. A future experiment would involve thermal desorption of all CO_2-forming and some CO-forming groups at a higher temperature, e.g., 700°C, which would shift the CO evolution profile of the nitric acid treated char to higher temperatures. The objective would be to transform the energetic heterogeneity of the char surface as shown in Figure 9 into the one shown in Figure 7, with the only difference being in the amount of CO-forming groups.

Char Regeneration

It is important at some point to determine the regenerative properties of the carbon adsorbent after SO_2 capture since some commercial processes, unlike the STEAG process, do regenerate their carbon. Methods of regeneration that have been used include thermal desorption of adsorbed SO_2 (Davini, 1990) or removal of the acid by washing with water or dilute sulfuric acid to produce medium strength sulfuric acid (Gangwal et al., 1993). Thermal regeneration is used in this study. After an SO_2 adsorption experiment, the spent char is regenerated by heating it to 360°C in nitrogen, holding for

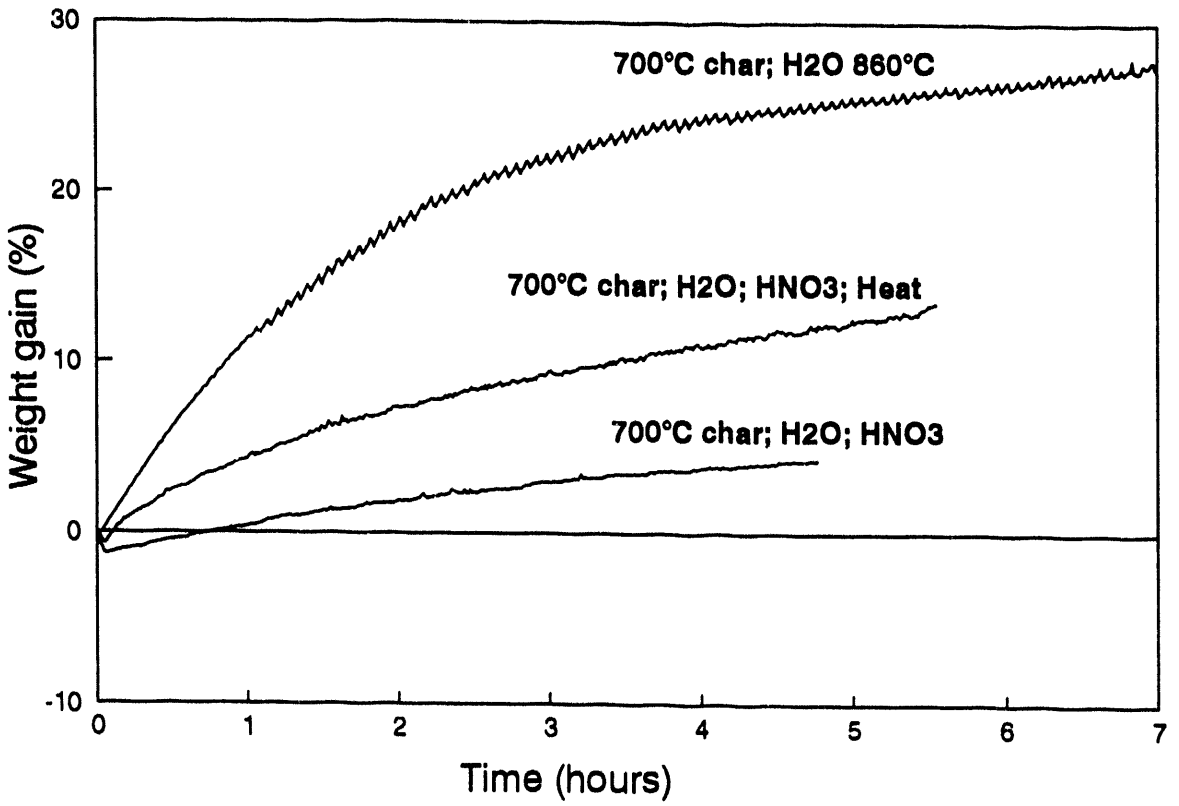

Figure 10. Effect of nitric acid treatment on SO2 adsorption.

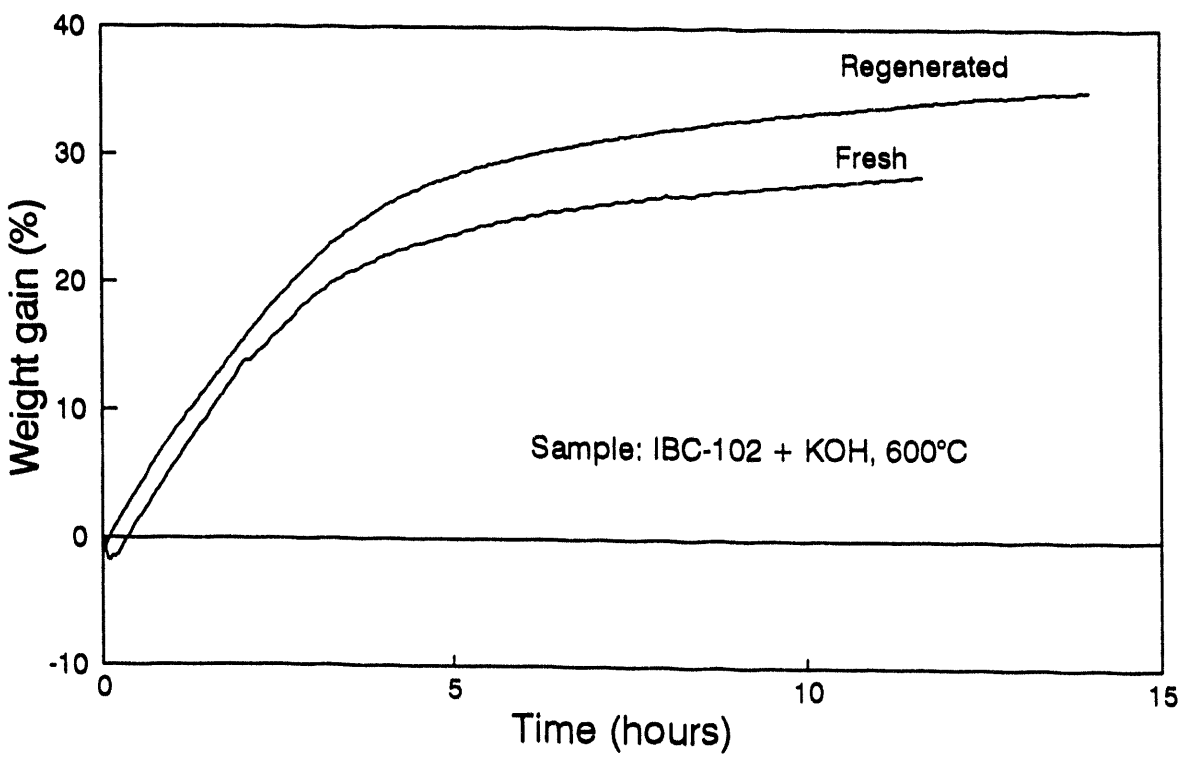

Figure 11. Adsorption of SO2 before and after thermal regeneration.

0.5 h, and cooling to the desired adsorption temperature, 120°C. The kinetics of SO_2 adsorption for a fresh char prepared by KOH activation at 600°C and one that has undergone this regeneration procedure are shown in Figure 11. The regenerated sample exhibits an SO_2 adsorption profile similar in shape to that of the fresh sample, and in this case actually adsorbs slightly more than the fresh sample. The regeneration procedure may have opened up some previously closed porosity, which increased the SO_2 capacity of the char. It was determined that less than 0.5 percent by weight of the original sample was lost during regeneration. This weight loss is due to slight gasification of the carbon during regeneration, i.e., the unstable C-O complexes formed during SO_2 adsorption are liberated as CO and CO_2 during heat treatment in nitrogen at 360°C. The extent of this weight loss may be offset by adsorbed SO_2, which remains strongly bonded to the carbon even after regeneration. Further work is needed to understand the effect of repeated adsorption/desorption cycles on the SO_2 adsorption behavior of IBC-102 char.

Meeting with STEAG

A meeting was held on March 2, 1994 in Champaign, IL between representatives of the ICDB, ICCI, ISGS and STEAG to discuss the possible use of Illinois coal derived char in the STEAG flue gas purification process. STEAG presently uses a lignite coke with a surface area of 300 m^2/g. Due to the high heats of adsorption for the reaction of NO_x with carbon, a carbon with a higher surface area or capacity is not needed or used. STEAG is now trying to locate a U.S. manufacturer of activated carbon which could supply them with activated carbon for their processes installed in the U.S. It was mentioned by ISGS representatives that it would be possible to produce char from Illinois coal with the required surface area in a cost-effective manner. STEAG agreed to send samples of the carbon they currently use to the ISGS for further analyses. The ISGS will attempt to produce a similar type of material from Illinois coal. All indications are that this is feasible and should involve a straightforward pyrolysis/air oxidation procedure. The work performed in this study up to this point has concentrated on developing new methods for production of high capacity carbons for combined SO_2/NO_x removal. For the STEAG process this type of work is probably not applicable. However, there are several other companies presently using carbon-based flue gas desulfurization systems which could benefit from research directed at producing new and improved carbons. Since most of these companies regenerate their carbon, the cost of the carbon is not as much a factor as it is with STEAG. Moreover, the processes now in use by these other companies (e.g., Bergbau-Forschung, Germany; Mitsui, Japan) have heats of adsorption more readily dissipated in moving beds. A high surface area carbon would be beneficial

to their process as it would reduce capital costs and improve process efficiency. In either case, i.e., low or high capacity carbon, the ISGS has the facilities and personnel to produce activated char from Illinois coal with the proper surface area and adsorption characteristics for efficient SO_2/NO_x removal.

CONCLUSIONS AND RECOMMENDATIONS

During this reporting period, a thermogravimetric technique was developed to determine the kinetics of SO_2 adsorption/desorption on chars produced from IBC-102 coal. A temperature programmed desorption method was also developed to determine the nature and extent of carbon-oxygen complexes formed on the surface of the char. An attempt was made to relate this information to the observed SO_2 adsorption behavior.

An IBC-102 char with an N_2-BET surface area of 10 m^2/g adsorbed significantly less SO_2 than chars with surface areas > 200 m^2/g. However, for chars with surface areas > 200 m^2/g, the amount of available surface area was not as important as the chemistry of the surface. Because SO_2 is an acid gas, a carbon adsorbent with a basic surface would be expected to adsorb more SO_2.

Of the IBC-102 chars studied during this period, a steam activated char adsorbed the most SO_2, comparable to the amount adsorbed by a commercial activated carbon. Temperature programmed desorption revealed the presence of CO-forming C-O complexes which are basic by nature. The other samples all contained significant amounts of CO_2-forming complex which indicates a more acidic surface. A method is currently being developed to measure the acid/base characteristics of the carbons to better define the relationship between SO_2 adsorption behavior and surface pH.

Thermal regeneration of a chemically activated char after SO_2 adsorption was studied. The sample was heated to 360°C in inert gas to desorb SO_2. The regenerated char adsorbed more SO_2 than the fresh char. Further work needs to be done to understand the effect of repeated adsorption/desorption cycles on the SO_2 adsorption behavior of the char.

During the next reporting period, the NO_x adsorption properties of the prepared chars will be determined. The surface properties of the prepared chars will be further characterized. An estimate of the micropore size distribution of selected chars will be obtained by analyses of adsorption isotherms of different sized molecules. A quadrupole mass spectrometer will be used to allow detection of SO_2 and NO_x species during multicomponent gas adsorption studies. The overall performance of the prepared chars in removing SO_2/NO_x

from simulated flue gas will be assessed and compared to that of commercial carbons.

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PROJECT MANAGEMENT REPORT
December 1, 1993 through February 28, 1994

Project Title:	**PRODUCTION AND USE OF ACTIVATED CHAR FOR COMBINED SO_2/NO_x REMOVAL**
DOE Grant Number:	DE-FC22-92PC92521 (YEAR 2)
ICCI Project Number:	93-1/3.1A-5P
Principal Investigator:	Anthony A. Lizzio, ISGS
Other Investigators:	Joseph A. DeBarr, ISGS Mark J. Rood, UIUC Massoud Rostam-Abadi, ISGS
Project Manager:	Frank Honea, ICCI

COMMENTS

EXPENDITURES - EXHIBIT B

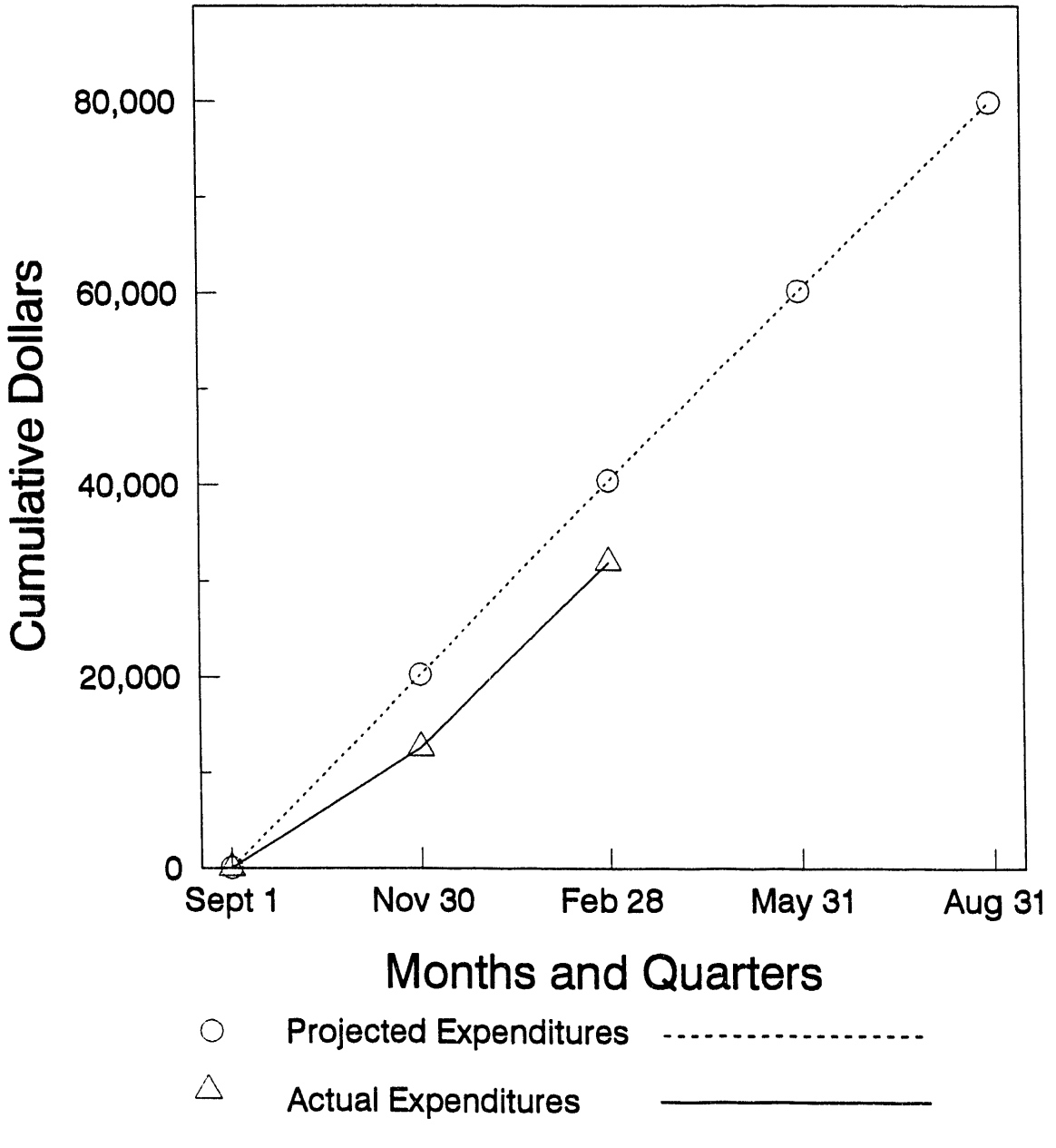
Cumulative Projected and Estimated Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sep. 1, 1993 to Nov. 30, 1993	Projected	10,780	2,415	1,500	0	0	3,720	1,816	20,231
	Estimated	7,150	1,600	710	0	0	1,975	1,144	12,579
Sep. 1, 1993 to Feb. 28, 1994	Projected	21,560	4,830	3,000	0	0	7,450	3,633	40,473
	Estimated								
Sep. 1, 1993 to May 31, 1994	Projected	32,340	7,245	4,000	0	0	11,160	5,448	60,193
	Estimated								
Sep. 1, 1993 to Aug. 31, 1994	Projected	43,120	9,660	5,000	0	0	14,885	7,266	79,931
	Estimated								

***Cumulative by Quarter**

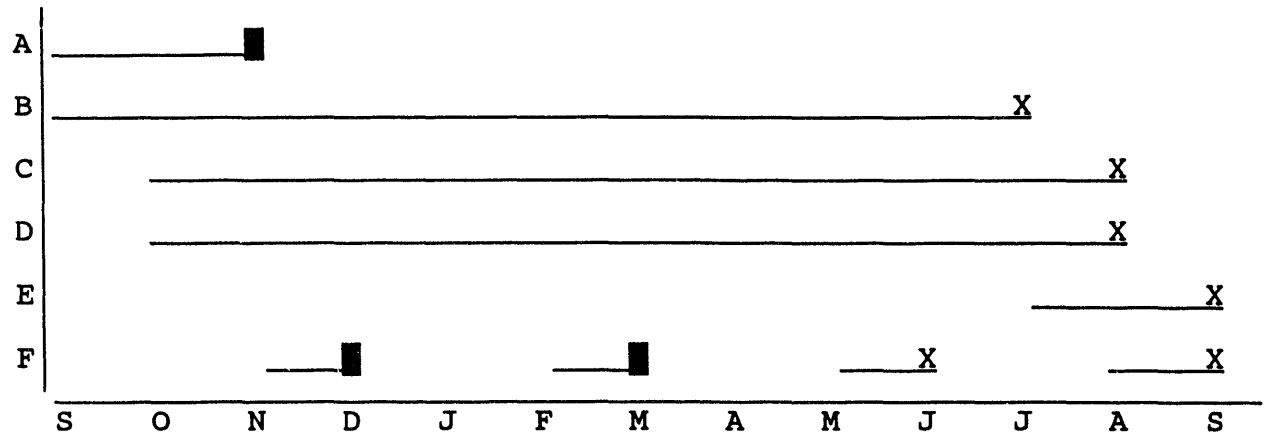
COSTS BY QUARTER - EXHIBIT C

PRODUCTION AND USE OF ACTIVATED CHAR FOR COMBINED SO2/NOX REMOVAL



Total CRSC Award $79,931

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Literature Review
B. Preparation of Activated Char
C. SO_2/NO_x Adsorption/Desorption Tests
D. Physical/Chemical Characterization
E. Technical/Economic/Market Analysis
F. Technical/Project Management Reports Prepared/Submitted

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