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TECHNICAL REPORT
March 1, 1994 through May 31, 1994

Project Title: **PRODUCTION AND USE OF ACTIVATED CHAR FOR
COMBINED SO₂/NO_x REMOVAL**

DOE Grant Number: DE-FC22-92PC92521 (YEAR 2)
ICCI Project Number: 93-1/3.1A-5P
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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 SO₂/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 SO₂/NO_x removal catalyst.

During this reporting period, a meeting was held in Champaign, IL, between representatives from the ISGS, ICCI, ICDB and STEAG Aktiengesellschaft of Essen, Germany to discuss the possible use of activated char derived from Illinois coal in the STEAG carbon-based combined SO₂/NO_x removal process. The ISGS agreed to provide 500 pounds of activated char to STEAG for tests in a demonstration unit to clean flue gas from a U.S. waste incinerator. The STEAG process requires an activated char with a N₂ BET surface area < 300 m²/g, i.e., lower than that of most commercially available activated carbons. An extensive series of tests was conducted to determine process conditions for making such an adsorbent from a Colchester No. 2 coal (Industry Mine coal). Using a 4 in. ID continuous rotary tube kiln (RTK) and a continuous feed charring oven, pound quantities of activated char were produced that matched well the properties of the adsorbent currently used by STEAG. A three step process, which included preoxidation, pyrolysis, and activation, was devised to produce a suitable char from this caking coal. Scale up tests were conducted at Allis Mineral Systems, Milwaukee, WI in an 18 in. ID batch RTK and an 8 in. ID continuous RTK to produce 50 pounds of activated char. During the next reporting period, 500 pounds of activated char will be produced at Allis Mineral Systems in an 18 in. ID, 10 ft. RTK and shipped to Essen, Germany for testing in the STEAG pilot plant facility. Upon successful completion of these tests, the pilot plant will be brought to the U.S. for demonstration testing by the U.S. EPA at a selected waste incinerator site.

U.S. DOE patent clearance is not required prior to publication of this document.

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EXECUTIVE SUMMARY

Worldwide interest in carbon based flue gas desulfurization (FGD) 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 (Tsuji and Shiraishi, 1991). Carbon adsorbents remove sulfur oxides from coal combustion flue gas at temperatures below 120°C, and also serve 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.

One of the unique advantages of an 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. German and 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. 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.

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.

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

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) under carefully 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 is 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 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 SO_2 and NO_x adsorption capacity and kinetics of SO_2/NO_x adsorption are determined using a thermogravimetric analyzer. The spent char is regenerated with heat treatment at 300-400°C. A laboratory scale adsorption column/mass spectrometry (AC/MS) system is used to evaluate multicomponent gas adsorption. 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 to discern the effects of combined SO_2/NO_x removal on the adsorption behavior of activated char. The tests to be performed include: temperature programmed desorption (TPD), 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 for production of ISGS activated char initiated. A collaborative research and development agreement with a suitable industrial partner may be established to facilitate commercial development of the activated char for specific industrial SO_2/NO_x removal applications.

In the previous reporting period, a series of chars was prepared from IBC-102 coal under a wide range of pyrolysis and activation conditions. A thermogravimetric technique was developed to determine the kinetics of SO_2 adsorption on these chars. A temperature programmed desorption (TPD) method was developed to determine the nature and extent of carbon-oxygen (C-O) complexes formed on the char surface. An attempt was

made to relate this information to observed SO_2 adsorption behavior. TPD revealed that SO_2 adsorption was inversely proportional to the amount of C-O complex. The formation of stable C-O complex during char preparation served only to occupy otherwise reactive carbon edge sites. A fleeting C(O) complex, formed only during adsorption of SO_2 , is presumed to be the reaction intermediate necessary for conversion of SO_2 to H_2SO_4 . A novel char preparation method produced activated char with SO_2 adsorption capacities significantly greater than those of commercial activated carbons.

During this reporting period, a meeting was held in Champaign, IL, between representatives from the ISGS, ICCI, ICDB and STEAG Aktiengesellschaft of Essen, Germany to discuss the possible use of Illinois coal char in the STEAG carbon-based combined SO_2/NO_x removal process. 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. STEAG estimates a market potential of 800,000 tons/year of activated char (1.6 million tons of coal) to meet needs emanating from anticipated regulation in the United States of emissions from existing incinerators. The ISGS agreed to provide 500 pounds of activated char to STEAG for tests in a demonstration unit to clean flue gas from a U.S. waste incinerator. The STEAG process requires an activated char with a N_2 BET surface area $< 300 \text{ m}^2/\text{g}$, i.e., lower than that of most commercially available activated carbons. An extensive series of tests was conducted to determine process conditions for making such an adsorbent from a Colchester No. 2 coal (Industry Mine coal). Using a 4 in. ID continuous rotary tube kiln (RTK) and a continuous feed charring oven, the ISGS produced pound quantities of activated char that matched well the properties of the adsorbent currently used by STEAG. A three step process, which included preoxidation, pyrolysis, and activation, was devised to produce a char with the required surface area and mechanical strength. Scale up tests were conducted at Allis Mineral Systems, Milwaukee, WI in an 18 in. ID batch RTK and an 8 in. ID continuous RTK to produce 50 pounds of activated char.

During the next reporting period, 500 pounds of activated char will be produced at Allis Mineral Systems in an 18 in. ID, 10 ft. RTK and shipped to Essen, Germany for testing in the STEAG pilot plant facility. Upon successful completion of these tests, the pilot plant will be brought to the U.S. for demonstration testing by the U.S. EPA at a selected hazardous waste incinerator. Work will continue towards producing activated char with a relatively high SO_2 capacity. These chars are generally desirable for the majority of commercial SO_2/NO_x removal systems (STEAG is an exception). The NO_x adsorption properties of the chars prepared in this study will also be determined. A quadrupole mass spectrometer will be used to detect SO_2 and NO_x species during multicomponent adsorption experiments. The overall performance of the prepared chars in removing SO_2/NO_x from combustion 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 (1×10^{-5} torr) treatment. 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: temperature programmed desorption (TPD), 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. TPD (5°C/min in helium) of SO_2 , NO_x , CO and CO_2 from the char, before and after SO_2 adsorption, is performed to gain additional insight into the mechanism of SO_2/NO_x adsorption/desorption.

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 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_x removal is concerned, Richter et al. (1985) contend that it is easier to integrate a carbon-based NO_x 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 ($> 250^\circ\text{C}$). 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 $\text{DeSO}_x/\text{DeNO}_x$ 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 $100\text{--}200^\circ\text{C}$. 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 $\text{DeSO}_x/\text{DeNO}_x$ 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 ($\text{mg SO}_2/\text{g}$)	60 - 120	220 (fresh) 70 (used)
NO_x Removal Efficiency (%)	80 - 85	60 - 70
Price Ratio (-)	1/4 - 1/3	1

In the U.S., there are several research groups involved 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 the 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.

Another process for cleaning sulfur oxides and nitrogen oxides from combustion flue gas, still in the development stage, involves the use of activated char in conjunction with microwaves (Cha et al., 1992). Sulfur dioxide is adsorbed on activated char and decomposed under microwave energy to sulfur; the nitrogen oxides are decomposed directly under the microwaves to nitrogen. Laboratory tests indicated that up to 98% of the SO_2/NO_x is decomposed to S and N_2 . Dow Chemical has recently bought the rights to this process and is interested in scaling up the process. The process requires a carbon that can withstand many cycles of adsorption and regeneration. The surface area of the carbon increases with every cycle as the microwave energy is used to convert adsorbed SO_2 to sulfur. Since oxygen is also chemisorbed on the carbon surface, CO and CO_2 is evolved. This concurrent gasification may increase surface area of the carbon from an initial value of 10 m^2/g to over 500 m^2/g .

Chang and Rood (1992) used dielectric barrier discharge and combined plasma photolysis to achieve 39% SO_2 and 88% NO_x removal efficiency. Dielectric barrier discharges rely on the gas stream becoming electrically conductive with micropulses of electrons that pass through the gas stream as they travel between two electrodes. These micropulses cause the formation of OH and HO_2 radicals that react with SO_2 and NO to form H_2SO_4 and HNO_3 . Activated char could conceivably be used to more effectively scrub these products from the gas stream without requiring expensive gas-to-particle conversion of the contaminants, and also, could further catalyze removal of unreacted SO_2/NO_x species.

Due to recent legislation in the European community, the use of activated carbon for cleaning flue gases from waste incinerators has seen renewed 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. Operating results show that current European emission requirements were met with the activated carbon systems.

STEAG apparently developed its process to use activated char which was readily available and is produced from a German brown coal by another German company, Rhine-Braun. STEAG has not previously been in the business of making activated carbon, but their planned activities (licensing of technology) in the U.S. appear to dictate involvement in this aspect of the business as well. STEAG desires a U.S. supplier of an activated char that will work satisfactorily in their combined SO₂/NO_x removal process. STEAG, however, believes commercial activated carbons available in the U.S. may be too reactive due to their relatively high surface area, and may form hot spots in their system which may lead to spontaneous ignition of the carbon. The adsorption of SO₂, NO_x, and O₂ on carbon is exothermic. The STEAG process requires a lower activity char having a surface area less than 300 m²/g.

Over the last 15 years, STEAG has developed, designed, engineered, commissioned and operated various activated carbon units with flue gas throughput rates between 6,500 - 155,000 m³/hr. Systems for waste incineration plants with even larger flue gas throughput are currently in the engineering phase. STEAG's proprietary process is protected by a series of patents first issued in 1987. STEAG's approach for making incineration an acceptable option for waste disposal is to pass the flue gas from incinerators through a large guard bed of activated carbon located downstream of a system of wet flue gas scrubbers. These scrubbers remove most, but not all, of the dioxins, furans, trace elements, NO_x and SO₂. The spent activated carbon is cycled to the incinerator where the noxious components are heat-treated again for ultimate removal in the wet scrubbers. STEAG has demonstrated its technology in a number of commercial installations in Germany and the Netherlands, and is now ready to market its technology in the U.S. A demonstration test with the U.S. Environmental Protection Agency is planned. Availability of this proven technology in the U.S. could prompt legislation to set incinerator emissions limits low enough to make incinerators acceptable to the American public.

A unique opportunity exists for the State of Illinois to support testing in the STEAG process of a low grade of activated carbon (activated char) made from Illinois coal. 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. STEAG estimates a market potential of 800,000 tons/year of carbon adsorbent to meet needs emanating from anticipated regulation in the United States of emissions from existing incinerators. Because two

tons of coal are required to produce one ton of adsorbent, the potential market would require 1.6 million tons of coal annually. STEAG, which developed its process to use activated carbon already available in Germany, has not been involved in developing the adsorbent. The STEAG process was developed to use activated carbon produced from a German brown coal by another German company, Rhine-Braun. STEAG has not previously been in the business of making activated carbon, but needs in the U.S. appear to dictate involvement in this aspect of the business. It appears STEAG may be willing to enter a joint venture to assure availability of enough char supply 10 per cent of the potential market. A member of the STEAG board of directors is visiting the U.S. in early June and will meet with ICCI, DENR and ISGS personnel.

EXPERIMENTAL

Char Preparation

Figure 1 presents an overview of the 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 activated char with optimal SO_2/NO_x removal characteristics.

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

Figure 1. Overview of Experimental Plan.

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 N₂ (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 SO₂/NO_x adsorption capacity of the char.

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

Selected samples were subjected to oxidation in 10% O₂ 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 N₂. The sample was oxidized in 10% O₂/90% N₂ for 0.5-0.75 h to obtain a 30% weight loss (conversion), then cooled to room temperature in N₂.

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 N₂. The N₂ flow was replaced by 50% H₂O/50% N₂ for 0.75 h to achieve 30% carbon conversion. The activated char was cooled to room temperature in N₂. 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 N₂ 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% HNO₃ solution, heated to 80°C and stirred for 2.5 h. The HNO₃ 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 Production in the ISGS Rotary Tube Kiln

Pound quantities of activated char were produced in a Model RT-472-104 continuous rotary tube kiln (RTK), manufactured by the Pereny Equipment Company, Inc., of Columbus, Ohio. The RTK consists of a 10.2 cm ID, 1.83 m long rotating tube of HX alloy. The center portion of the tube (1.4 m) is heated by three separate electrically heated furnaces. The sample is introduced into the tube using a screw type feeder.

The RTK removes evolved gases from a tumbling bed of coal with the flow of gases counter to the direction of coal movement through the inclined tube. The feed and discharge ends support a 25 mm ID stainless steel induction tube, a 4 mm ID thermocouple tube and a chain strung loosely from the ends for scraping action. Reaction gases enter the reactor through a 4 mm ID tube near the exhaust end. Evolved gases enter the induction tube through a hole located in the first heated zone, pass the length of the tube, and are burned prior to being released to a fume hood. The residence time of the coal is controlled by the rate of rotation and inclination angle of the tube. Residence times varied from 0.3 to 0.75 h.

In most cases, a three step process was used to produce activated char with the desired surface area and mechanical strength. To prevent agglomeration and melting of the coal, preoxidation of the coal was done in air at temperatures

between 150 and 380°C. Coal pyrolysis was carried out in the continuous feed charring oven. Char activation was carried out in air at temperatures less than 450°C or in CO₂ at 850°C to achieve a specified surface area.

Char Production in the ISGS Continuous Feed Charring Oven

A continuous feed charring oven (CFCO) was also used in the production of activated char. The second step of the three step process, pyrolysis, was carried out in this unit. The CFCO was better suited to handle the large amounts of tar evolved during this step. Coal pyrolysis was done in either N₂ or CO₂ at temperatures between 400 and 500°C. The coal sample was conveyed through a 15.2 cm x 16.2 cm x 69 cm oven on a belt of close-fitting, overlapping, stainless-steel trays (12.7 cm wide) attached to links of a chain drive and heated above and below by tubular electric heating elements. A hopper that controls the bed depth fills the trays as they enter the oven. Evolved gases are removed counter to the direction of the coal and are drawn out an exhaust pipe where volatile materials are burned before being released into the fume hood. All areas outside the heating zone are enclosed in a reasonably tight sheet-metal housing to exclude air. Three gas inlets may be used to maintain a nitrogen purge through all parts of the oven to exclude air and avoid loss of char due to burning. Chars were prepared in the CFCO using feed rates of 1-4 pounds per hour, bed depths of 8-20 mm, temperatures of 400-500°C and residence times of 0.25-0.75 h.

Char Characterization

Surface Area

Single-point BET surface areas of prepared chars were determined from N₂ (77 K) adsorption data obtained at a relative pressure (p/p_0) of 0.30 with a Monosorb flow apparatus (Quantachrome Corporation).

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 CO₂ from the sample. Rosemount Model 880 CO and CO₂ non-dispersive infrared analyzers were used to continuously monitor the [CO] and [CO₂] in the effluent gas.

SO₂ Adsorption Capacity

The kinetics of SO₂ 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% O₂, 10% H₂O and the balance nitrogen. Once the weight stabilized, the SO₂ was added in concentrations representative of a typical flue gas (e.g. 2500 ppmv SO₂). 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. Several adsorption/desorption sequences were performed with selected chars to examine the effect of regeneration on SO₂ adsorption capacity.

RESULTS AND DISCUSSION

SO₂ Adsorption

The adsorption of SO₂ 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 SO₂ adsorption capacity. The presence of water vapor is also important, because it reacts with the SO₃ formed by reaction of SO₂ with O₂. Physisorption of SO₂ on activated carbon decreases with increasing temperature, e.g., from 8% at 60°C to 0 wt% SO₂ at 250°C (Slack, 1971). In the absence of O₂ and H₂O, adsorption of SO₂ is quite small on the order of 1% by weight from 50-300°C.

The SO₂ adsorption capacities of chars prepared previously 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 SO₂ to SO₃ and H₂SO₄ 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 SO₂ in the gas phase with the C-O surface complex. In the presence of water at low temperatures, the SO₃ is converted to the acid, H₂SO₄. The reaction mechanism is shown below:

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 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 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. Table 3 gives the SO_2 capacity of the chars after 6 h. 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 6 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 6 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

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

Figure 3. Effect of temperature on SO_2 adsorption.

Table 3. Characterization of IBC-102 Chars and Commercial Activated Carbon.

Sample	Surface Area (m ² /g)	CO/CO ₂	O ₂ (wt%)	pH	SO ₂ Capacity (mg SO ₂ /g C ¹)
IBC-102, 500°C, 0.5 h	1.2	3.3	8.8	5.2	---
IBC-102, 700°C, 0.5 h	10.0	4.8	1.5	5.6	33
IBC-102, 900°C, 0.5 h	1.2	---	---	---	---
IBC-102 + KOH, 600°C, 0.5 h	500	---	---	3.4 ¹	157
IBC-102 + KOH, 800°C, 0.5 h	800	---	---	9.7	176
Commercial Activated Carbon	1000	2.3	0.5	7.0	206
IBC-102, 500°C h; 10% O ₂ , 390°C	220	3.3	8.6	3.6	---
IBC-102, 700°C; 10% O ₂ , 440°C	320	3.4	8.9	3.5	37
IBC-1.2, 900°C; 10% O ₂ , 500°C	230	4.2	5.2	---	---
IBC-102, 900°C; H ₂ O, 860°C	220	3.4	1.1	9.4	176
IBC-102, 900°C; H ₂ O, 860°C; 45% HNO ₃ , 2.5 h	400	1.4	16.4	3.2	26
IBC-102, 900°C; H ₂ O, 860°C; 45% HNO ₃ , desorbed at 525°C	---	6.7	5.9	---	91
IBC-102, 900°C; H ₂ O, 860°C; 45% HNO ₃ , desorbed at 725°C	---	12.8	1.6	---	241
IBC-102, 900°C; H ₂ O, 860°C; 45% HNO ₃ , desorbed at 925°C	550	1.3	0.5	7.6	287

¹ SO₂ capacity after 6 h.

² Sample rinsed with HCl/H₂O instead of H₂O to remove K after KOH activation.

capacity of the char.

Effect of Oxygen

An understanding of SO₂ adsorption behavior may require more detailed information about the surface intermediates (carbon-oxygen complexes) formed during char preparation and SO₂ 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 heterogeneity of the char surface and relate it to observed SO₂ adsorption behavior. Typical TPD profiles for selected IBC-102 chars are shown in Figures 5-7. The amount of CO and CO₂ 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.

Figure 4. Effect of surface area on SO_2 adsorption.

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

Table 3 lists the total oxygen content and the relative amounts of CO/CO₂ 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 SO₂ adsorption capacity and the total amount of oxygen adsorbed on the carbon. However, a correlation was found between SO₂ capacity and basic C-O functional groups present on the char surface. Because SO₂ is an acid gas, a carbon adsorbent with a basic surface could be expected to adsorb more SO₂. The carbon-oxygen functional groups which form CO upon thermal desorption in inert gas impart surface basicity, while C-O groups which form CO₂ (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 SO₂ adsorption.

Figures 6-8 show that the amount and type of oxygen complexes formed on the HNO₃ treated carbon are markedly different from those produced by air oxidation or steam activation. Significantly more CO₂ is evolved during TPD at lower temperatures for the HNO₃ treated sample than the air oxidized carbon. Compared to the TPD profiles of the air oxidized char (Figure 6), the CO and CO₂ 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 CO₂-forming functional groups and retain 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 7). Figure 8 shows the TPD profiles of the HNO₃ chars thermally desorbed at 200, 525, 725 and 925°C. An interesting result of the HNO₃/thermal desorption procedure is that it can put on the char (HNO₃, 525°C) surface up to ten times more high-temperature CO-forming groups. These C-O complexes are thought to be the ones responsible for enhanced SO₂ adsorption (Davini et al., 1990).

Figure 9 presents the corresponding kinetics of SO₂ adsorption curves for these chars. The 200 and 525°C desorbed chars adsorb less SO₂ than the base char (steam activated). This may be due to the presence of still a relatively large quantity of CO₂-forming groups, which presumably have a detrimental effect on SO₂ adsorption (surface area of the HNO₃ char > steam activated char). It is also possible that trace amounts of the acid remained in the HNO₃ char after washing. This could negate any benefits gained by removing the CO₂-forming complexes. The pH values of selected chars are listed in Table 3. It is also possible that the chosen desorption temperature of 525°C was not high enough to retain CO-forming groups of similar type and thermal stability as those formed on the steam activated char. A comparison of Figures 7 and 8

Figure 6. TPD profile of a char activated in O₂. Figure 7. TPD profile of a char activated in H₂O.

Figure 8. TPD profiles of nitric acid treated chars after desorption.

indicates a peak CO temperature of 650°C for the HNO_3 , 25°C char as compared to 900°C for the steam activated char. Figure 8 shows that thermal desorption at 725°C shifts the CO peak temperature to 825°C. Thermal desorption at 25°C removes nearly all of the C-O complex. Figure 9 shows that the thermally desorbed chars (HNO_3 , 725°C and HNO_3 , 25°C) chars have SO_2 capacities (23.5 and 28.7%) which surpasses that of the commercial carbon (20.6%). It is interesting to note that the sample with the least amount of C-O complex adsorbed the greatest amount of SO_2 (HNO_3 , 925°C). Given that C-O complex is an essential reaction intermediate in the conversion of SO_2 to H_2SO_4 , it may be that TPD does not titrate those C-O complexes responsible for catalytic oxidation of SO_2 to SO_3 , and that a fleeting C(O) complex formed only during low temperature SO_2 adsorption acts as the "catalyst." The formation of stable C-O complex during char preparation may serve only to occupy otherwise reactive carbon edge sites.

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 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 10. 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.

Figure 9. SO_2 adsorption for nitric acid treated chars desorbed at different temperatures.

Figure 10. Adsorption of SO_2 before and after thermal regeneration.

Char Production for STEAG

A unique opportunity exists for the State of Illinois to support testing in the STEAG process of a low grade of activated carbon (activated char) made from Illinois coal. 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. The STEAG combined SO_2/NO_x removal system was developed to use activated carbon that is produced from a German brown coal by another German company, Rhine-Braun. STEAG desires a U.S. supplier of an activated char that will work in its process. A 500-pound batch is needed by early June for tests in a pilot plant assembled in Essen, Germany. After confirmatory tests in Germany on the carbon adsorbent made in the U.S., STEAG will move the pilot plant to the U.S. for demonstration tests.

Activated carbons with high surface areas are generally desirable for most applications. STEAG, however, believes commercial activated carbons available in the U.S. are too reactive due to their high surface area, and may form hot spots in their system because of the exothermic nature of adsorption of SO_2 , NO_x and O_2 contaminants on the carbon. The STEAG process requires a low activity char having a surface area less than $300 \text{ m}^2/\text{g}$. American Norit reportedly produces one of the lowest activity carbons for \$800/ton with a nitrogen surface area of $600 \text{ m}^2/\text{g}$. Commercial manufacturers of activated carbons have indicated that making the desired material is no problem but for unknown reasons are reluctant to become involved in making the lower grade of activated carbon required for the STEAG process. The results of the current study will permit an independent evaluation of the likely costs associated with manufacturing activated char. STEAG prefers that the activated char used in their process cost no more than \$300 per ton.

A sample of the char that is currently used in the STEAG process was supplied to the ISGS. More than 97 percent of the particles were in the 1-5 mm size range. The STEAG char had a N_2 BET surface area of $275 \text{ m}^2/\text{g}$. It is believed that the carbon was produced in a high temperature ($> 850^\circ\text{C}$), one step process. TPD was performed on the STEAG carbon. The results indicated an oxygen content of 3%, which suggests the material was heated treated to at least 850°C (see Table 3).

Several methods of producing activated char from Illinois coal with properties similar to the STEAG char were investigated. Char production runs at the ISGS were performed in a horizontal tube furnace (fixed bed), rotary tube kiln (RTK), and continuous feed charring oven (CFCO). Run conditions are given in Tables 4-6. Initial studies focused on a one step process involving pyrolysis and activation in oxygen at low temperatures. IBC-102 coal was used as the starting material because previous studies indicated chars with surface areas of

about 220 m²/g could be produced from this coal using low temperature oxidation (DeBarr et al., 1994). Tube furnace runs A and B were preliminary efforts to establish operating conditions in the RTK and CFCO and gave chars with surface areas of 100-150 m²/g. Based on these results, pound quantities of chars were produced in the CFCO at various temperatures and oxygen concentrations. However, surface areas were significantly lower than those obtained in the tube furnace, which was attributed to a shorter residence time in the CFCO. Indeed, when the residence time was increased to about 40 minutes by sending a sample through the oven twice (CF-44A), the surface area approached that obtained for tube furnace run B.

It was estimated that 1500 pounds of coal would be needed to produce the 500 pounds of activated char needed for testing at STEAG. Since the coal mine from which IBC-102 coal originates is no longer in operation, a Colchester No. 2 coal (Industry Mine coal), similar in many respects to IBC-102 coal, was obtained from a Western Illinois preparation plant. Subsequent char production runs used a 1x5 mm size fraction of Industry Mine coal as the starting material.

The first attempt to produce an activated char from this coal using a one step oxidation method gave a partially agglomerated product with surface area of only 10 m²/g (CF-46A). This sample was oxidized further in the RTK (RT-S1) to increase surface area, and was then oxidized even further to increased levels of carbon burn-off in the tube furnace (runs 1-3). Figure 11 shows that surface area increases with increasing carbon conversion and approaches a limit of about 160 m²/g when the partially agglomerated product is activated with oxygen. Similar trends in surface area development for CO₂ activation of an Illinois coal char have been observed (Lizzio and Radovic, 1989).

It was found that the agglomerating tendencies of the Industry Mine coal were detrimental to surface area development during activation. A preoxidation step followed by pyrolysis at 450-500°C was necessary to prevent agglomeration. After several attempts using different temperatures, oxygen concentrations and residence times (see Table 4), the preferred method of preoxidation to control agglomeration was 225-250°C for 1-2 h in flowing air. The time and temperature history during pyrolysis was also important in controlling agglomeration. A relatively slow heating rate and a soak time of 1 h at temperatures between 450-500°C was necessary to prevent agglomeration of the coal.

Table 4. Char production tests in the horizontal tube furnace.

Tube #	Sample ID	Tube Furnace (Oxidation +/- Activation)	Yield (%)	Surface Area (m ² /g)
A	48x100 Mesh IBC-102	440°C, 10% O ₂ , 0.5 h	59	106
B	48x100 Mesh IBC-102	420°C, 10% O ₂ , 1 h	52	150
1	RT-S1 ¹	430°C, Air, 0.3 h	64	152
2	RT-S1 ¹	430°C, Air, 0.2 h	80	144
3	RT-S1 ¹	430°C, Air, 0.5 h	58	164
4	Colchester No. 2 (Industry Mine Coal)	650°C, N ₂ , 0.25 h / 440°C, Air, 0.3 h	43	150
5	Tube-4	900°C, N ₂	n/a,	120
6	RT-S2 ¹	825°C, CO ₂ , 0.75 h	59	55
7	Colchester No. 2	325°C, Air, 1 h / 850°C, CO ₂ , 0.75 h	51	179
8	Colchester No. 2 4x8 Mesh / 10x16 Mesh ²	350°C, Air, 1.5 h / 850°C, CO ₂ , 0.75 h	52	175 / 200
9	Colchester No. 2 4x8 Mesh / 10x16 Mesh ²	360°C, 100 % O ₂ , 0.5 h *** Temp ran away / sample ashed - Aborted run		
10	Colchester No. 2 4x8 Mesh / 10x16 Mesh ²	360°C, 100 % O ₂ , 0.5 h / 850 C, CO ₂ , 1 h *** Aborted run -- sample agglomerated		
11	Colchester No. 2 4x8 Mesh / 10x16 Mesh ²	250°C, Air, 4 h / 850°C, CO ₂ , 1 h	n/a	230 / 189
12	Colchester No. 2 -3 Mesh / 4x8 Mesh ²	300°C, Air, 2 h / 450°C, CO ₂ , 1 h / 850°C, CO ₂ , 1 h	55	265 / 235
13	Colchester No. 2 -3 Mesh / 4x8 Mesh ²	350°C, N ₂ , 0.75 h / 375°C, N ₂ , 0.75 h / 850°C, CO ₂ , 1 h		2 / 1
14	Colchester No. 2 -3 Mesh / 4x8 Mesh ²	350°C, Air, 3 h / 850°C, CO ₂ , 1 h	30	334 / 179
15	Colchester No. 2 -3 Mesh / 4x8 Mesh ²	350°C, Air, 0.75 h / 375°C, Air, 0.75 h / 410°C Air, 0.3 h / 850°C, CO ₂ , 1 h	n/a	168 / 116
16	RT-S4 ¹	850°C, CO ₂ , 1 h	66	151
17	RT-S5 / RT-S5A ¹	475°C, CO ₂ , 1 h / 850°C, CO ₂ , 1 h	n/a	236 / 179
18	Allis Minerals #94-037 #1 ⁴	475°C, CO ₂ , 1 h / 850°C, CO ₂ , 1 h	n/a	n/a

¹Samples prepared in rotary tube kiln (see Table 6).²Two samples in boat separated by plate.³n/a - not available.⁴Sample preoxidized in 8-in. kiln at Allis Mineral

Table 5. Char production tests in the continuous feed charring oven.

CF Run #	Sample	Bed depth (mm)	Atmosphere	Time (min)	Temperature (°C)	Surface Area (m ² /g)
41	IBC-102	9	10% O ₂	15	410	---
42	IBC-102	8	10% O ₂	15	425	24.0
43	IBC-102	8	10% O ₂	20.5	450	31.6
44	IBC-102	8	Air	20.5	450	53.2
44A	CF-44	8	Air	20.5	450	121.2
45	IBC-102	8	Air	20.5	500	82.3
46A	Colchester No. 2	20	7% O ₂	13	575	10
47	Colchester No. 2	20	Air	14	250	---
48	CF-47	20	7% O ₂	14	630	---
49A	RT-S6 ¹	20	N ₂	45	475	35
49B	RT-S5A ¹	20	N ₂	45	475	---
49C	Colchester No. 2	20	N ₂	45	475	---

¹Samples prepared in rotary tube kiln (see Table 6).

Table 6. Char production runs in the rotary tube kiln.

RT Run #	Sample	Atmosphere	Temperature (°C)	Time (min)	Surface Area (m ² /g)
S1	CF-46A ¹	17% O ₂	435	20	78.0
S2	Colchester No. 2	Air	150-170	23	---
S3	Colchester No. 2	Air	260-300	28	---
S4	RT-S3	N ₂	370-450	30	---
S5	Colchester No. 2	Air	270-380	48	---
S5A	Colchester No. 2	Air	220	48	---
S6	RT-S5A	Air	220	48	---
S7	CF-49A ¹	50% CO ₂ / 50% H ₂ O	850	48	---
S8	CF-49A ¹	CO ₂	850	48	230
S8A	CF-49A ¹	95% CO ₂ / 5% H ₂ O	850	48	237
S8B	CF-49B ¹	CO ₂	850	48	180

¹Samples prepared in continuous feed charring oven (see Table 5).

Figure 11. Surface area of oxygen activated chars.

It was anticipated that air activation would be difficult to control accurately in a commercial process, so activation in steam and/or CO_2 was subsequently studied. Tests in the tube furnace indicated that if agglomeration of the coal could be prevented, activation in CO_2 for 1 h gave surface areas as high as $334 \text{ m}^2/\text{g}$. Steam activation was also attempted, but the rate of gasification was more difficult to control than with CO_2 . Since the gasification behavior of Illinois coal char in CO_2 was well documented (Lizzio, 1990), the reaction conditions in CO_2 could be readily established.

The final process to produce an activated char with surface area of about $300 \text{ m}^2/\text{g}$ consisted of preoxidation for 1-2 h in air, pyrolysis in N_2 for 1 h at $450\text{--}475^\circ\text{C}$, and activation in CO_2 for 1-2 h at 850°C . Preoxidation of the Colchester No. 2 coal was done in the RTK at 220°C for 1 h (RT-S5A) and 2 h (RT-S6) before the sample was pyrolyzed in the CFCO at 475°C for 0.75 h (CF-49A and CF-49B). The sample which had been preoxidized only 1 h showed only slight agglomeration after pyrolysis while the sample preoxidized for 2 h showed no sign of agglomeration. Upon activation in the RTK using CO_2 , the two samples generated similar surface areas (RT-S8 and RT-S8B). However, it appeared that during activation, the sample preoxidized for 2 h did not maintain mechanical strength as well as the sample preoxidized for 1 h, i.e., there were significantly more fines produced from the 2 h preoxidized coal. Thus, in increasing the coal preoxidation time, a tradeoff exists between decreasing the melting properties of the coal and increasing the amount of fines produced.

The conditions needed to produce the desired char were now established; however, the feed rates used in the RTK and CFCO were too low to allow production of 500 pounds activated char in a reasonable amount of time. Thus, several companies in the area were contacted. One of these, the Allis Mineral Systems, Inc., a subsidiary of the Swedish company, Svedala Industries, Inc., agreed to assist the ISGS in making the 500 pounds of activated char required for testing in Germany. They will also provide cost estimates for producing activated char on a commercial scale. Allis Mineral Systems is an applied research facility located in Milwaukee, Wisconsin that specializes in the use of rotary tube kilns for pilot plant testing of a wide variety of materials including coal. Allis also supports the sale of commercial sized kilns produced by the manufacturer located in Kansas, and provides the necessary services to its customers.

Phase I of the work at Allis involved production of 15 pounds of activated char from 37 pounds of Industry Mine Coal (1x5 mm). A 20 in. ID, 4 ft. (heated zone) batch kiln was used. On May 18, the first test in this equipment was performed. The final product was an agglomerated, coke-like product with a surface area of only $68 \text{ m}^2/\text{gram}$. A tube furnace run performed at the ISGS of a grab sample collected immediately

after 1 h of preoxidation in the batch RTK at Allis also showed severe agglomeration when pyrolyzed at 475°C (run 18). The results suggested that the preoxidation time of 1 h used in the batch kiln was not sufficient to destroy the agglomerating tendencies of the coal. Another problem in the batch RTK developed because the flow rate (5 ft³/min) of inert gas (CO₂) used was not sufficient to remove the large volume of tar produced from heating the 37 pound coal sample to 475°C. The coal particles were essentially bathed in tar during the pyrolysis step. The tar acted as a binder which enhanced the agglomerating and coke-forming properties of the coal.

On May 25, a second test was performed. The coal was preoxidized in the 20 in. ID batch kiln, but for 2 h instead of 1 h. For this test, the pyrolysis and activation steps were performed in a separate 8 in. ID, 4 ft. (heated zone) continuous RTK, using two separate passes. This kiln was heated by a three temperature zone furnace. In the first pass, coal pyrolysis was performed in flowing N₂ (8 ft³/min). The temperature profile in the kiln ranged from 350°C at the feed end to 500°C at the exit. The residence time was 1 h. A sample taken after this step revealed that the coal had undergone significant melting, however particle agglomeration was not observed, i.e., the individual coal particles did not bind together, as was the case in the previous test. A 75 percent char yield was obtained after the pyrolysis step. The activation step was done in CO₂ with a temperature profile of 750°C at the feed end to 870°C at the exit end, and residence time of 1 h. About 36 percent by weight of material was lost during this step due to additional devolatilization and activation. The overall yield of activated char from coal was about 48 percent. The surface area of the final product was only 6 m²/g. We believe that some tar may have redeposited on the char, thus blocking some of the pores and decreasing the surface area. Also, the activation temperature of 850°C may not have been accurately measured since the temperature of the bed was not monitored directly. It may have been that the char never reached a temperature at which activation could occur.

Samples were taken at designated times throughout both the first and second runs. A series of tests were conducted at the ISGS on samples obtained from the second run to determine the reason for the low surface area. First, char particles that showed no visible sign of melting were selected from among the particles in the final product. It is interesting to note, that although there was no particle agglomeration, less than 5% of the particles were completely non melted. The surface area of these non melted particles was determined to be 58 m²/g. This showed that for even the non melted particles, the surface area was still far below the required 200-300 m²/g (STEAG will accept activated char with surface area in that range). This may have been because the sample

was not sufficiently activated or that tars may have redeposited on the char. The 6 m²/g char made at Allis was activated for an additional hour in CO₂ in the tube furnace at the ISGS. This only increased the surface area to 89 m²/g. In the third experiment, the char made at Allis after the pyrolysis step (unactivated char with maximum heat treatment temperature of 450°C) was heated in CO₂ to 850°C and activated for 1 h. The surface area of this material was 151 m²/g. This experiment showed that it was possible to achieve a relatively high surface area with the char produced after the pyrolysis step. Apparently, the activation step at Allis was unsuccessful. Another 37 pound test is planned for May 31 to determine whether a satisfactory material can be produced in the 8 in. ID, 4 ft. RTK. Upon successful completion of this test, the 500 pound production run is scheduled for June 1-3 at Allis Mineral Systems. An indirectly fired, 18-in ID, 10 ft. (heated zone) RTK will be used. The three steps, preoxidation, pyrolysis and activation will be done consecutively in three passes through the kiln.

STEAG representatives have stated that the SO₂ adsorption capacity of the char is a good indicator of how it will behave in the STEAG process. That is, the activated char, if can can adsorb a sufficient amount of SO₂, should be capable of capturing the remaining pollutants in the flue gas. Thus, the SO₂ adsorption capacities of selected chars were measured. The kinetics of SO₂ adsorption for the STEAG char, an ISGS char activated in air (Tube furnace run B), and an ISGS char activated in CO₂ (RT-S8) are shown in Figure 12. The SO₂ adsorption capacity of the ISGS char activated in CO₂ is about four times that of the STEAG char. The SO₂ adsorption capacity of the ISGS char activated in air is only half that of the STEAG char. The relatively low SO₂ capacity of the air activated char might be expected since our earlier results with IBC-102 coal char showed that oxygen chemisorbed on the char surface inhibits SO₂ adsorption. The amount of oxygen adsorbed on the char surface after air activation can be up to one order of magnitude greater than that adsorbed after activation in CO₂ (Lizzio and Radovic, 1989). The SO₂ capacity of the char prepared at Allis Mineral has yet to be determined.

Figure 12. SO₂ adsorption by STEAG char and ISGS chars.

CONCLUSIONS AND RECOMMENDATIONS

In the previous reporting period, a series of chars was prepared from IBC-102 coal under a wide range of pyrolysis and activation conditions. A thermogravimetric technique was developed to determine the kinetics of SO_2 adsorption on these chars. A temperature programmed desorption (TPD) method was developed to determine the nature and extent of carbon-oxygen (C-O) complexes formed on the char surface. An attempt was made to relate this information to observed SO_2 adsorption behavior. TPD revealed that SO_2 adsorption was inversely proportional to the amount of C-O complex. The formation of stable C-O complex during char preparation served only to occupy otherwise reactive carbon edge sites. A fleeting C(O) complex, formed only during adsorption of SO_2 , is presumed to be the reaction intermediate necessary for conversion of SO_2 to H_2SO_4 . A novel char preparation method was developed which produced activated char with SO_2 adsorption capacities significantly greater than those of commercial activated carbons.

During this reporting period, a meeting was held in Champaign, IL, between representatives from the ISGS, ICCI, ICDB and STEAG Aktiengesellschaft of Essen, Germany to discuss the possible use of activated char derived from Illinois coal in the STEAG carbon-based combined SO_2/NO_x removal process. A unique opportunity exists for the State of Illinois to support testing in the STEAG process of a low grade of activated carbon (activated char) made from Illinois coal. 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. STEAG estimates a market potential of 800,000 tons/year of carbon adsorbent to meet needs emanating from anticipated regulation in the United States of emissions from existing incinerators. Because two tons of coal are required to produce one ton of adsorbent, the potential market would require 1.6 million tons of coal annually.

The ISGS agreed to provide 500 pounds of activated char to STEAG for tests in a demonstration unit to clean flue gas from a U.S. waste incinerator. The STEAG process requires an activated char with a N_2 BET surface area $< 300 \text{ m}^2/\text{g}$, i.e., lower than that of most commercially available activated carbons. An intensive series of tests was conducted to determine process conditions for making such an adsorbent from a Colchester No. 2 coal (Industry Mine coal). Using a 2 in. ID horizontal tube furnace, a 4 in. ID rotary tube kiln, and a continuous feed charring oven, the following was learned.

- Preoxidation is essential to prevent agglomeration of the coal and is best accomplished in the $225\text{-}250^\circ\text{C}$ temperature range at 1-2 h residence time. If the preoxidation is insufficient, the coal melts and/or agglomerates during pyrolysis, and a reasonable surface

area is not developed during the subsequent activation step.

- Pyrolysis to remove the volatiles and tar is best done at the lower range of mild gasification, i.e., between 450 and 500°C. This intermediate step is necessary to provide sufficient time (1 h) for the formation of oxygen cross links, which reduce the caking properties of coal.
- Activation of non melted char in CO₂ at 850°C for 1 h developed surface areas ranging from 150 to 330 m²/g. Although steam is more reactive than CO₂, steam was not used because of problems with controlling the rate of reaction at a given partial pressure of steam. Although sufficient surface area was also developed by air oxidation, this method would be difficult to control in a commercial process due to the possibility of spontaneous ignition of the char.

Under these conditions, the ISGS produced pound quantities of activated char that matched well the properties of the adsorbent currently used by STEAG. A three step process, which included preoxidation, pyrolysis, and activation, produced a char with the required surface area and mechanical strength. Two scale up tests were conducted at Allis Mineral Systems, Milwaukee, WI in an 18 in. ID batch RTK and an 8 in. ID continuous RTK to produce 15 pounds of activated char. The first test in the batch RTK was not successful, but valuable information was obtained. The next test, carried out in the 8 in. ID continuous RTK, solved some of the problems encountered in the first run, e.g., coal agglomeration; however, there were some problems in the activation step. Chars were produced with a lower than expected surface area. One more preliminary run is planned in May before the 500 pound production run.

During the next reporting period, 500 pounds of activated char will be produced at Allis Mineral Systems in an 18 in. ID, 10 ft. RTK and shipped to Essen, Germany for testing in the STEAG pilot plant facility. Upon successful completion of these tests, the pilot plant will be brought to the U.S. for demonstration testing by the U.S. EPA at a selected hazardous waste incinerator. Work will continue towards producing activated char with a high SO₂ capacity. These chars are generally desirable for the majority of commercial SO₂/NO_x removal systems (STEAG is an exception). The NO_x adsorption properties of the chars prepared in this study will also be determined. A possible correlation between SO₂ and NO_x adsorption behavior will be investigated. A quadrupole mass spectrometer will be used to detect SO₂ and NO_x species during multicomponent adsorption experiments. The overall performance of the prepared chars in removing SO₂/NO_x from combustion flue gas will be assessed and compared to that of commercial carbons.

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PROJECT MANAGEMENT REPORT
March 1, 1994 through May 31, 1994

Project Title: PRODUCTION AND USE OF ACTIVATED
CHAR FOR COMBINED SO₂/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, Carl W. Kruse,
Massoud Rostam-Abadi, Gwen L.
Donnals, ISGS, Mark J. Rood, UIUC
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	18,885	3,752	1,265	0	0	6,512	3,041	33,455
Sep. 1, 1993 to May 31, 1994	Projected	32,340	7,245	4,000	0	0	11,160	5,448	60,193
	Estimated	31,251	6,605	3,120	0	0	10,915	5,189	57,080
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

CUMULATIVE COSTS BY QUARTER - EXHIBIT C

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

Total ICCI Award \$79,931

OSTI

SEP 21 1994

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SCHEDULE OF PROJECT MILESTONES

Milestones:

- A. Literature Review
- B. Preparation of Activated Char
- C. SO₂/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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