TECHNICAL REPORT
September 1 through November 30, 1994

Project Title: **PRODUCTION AND USE OF ACTIVATED CHAR FOR COMBINED SO_2/NO_x REMOVAL**

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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 SO_2/NO_x removal, and to evaluate the potential application of the products in flue gas cleanup.

In Phase I of this project, chars were prepared from IBC-102 coal under a wide range of pyrolysis and activation conditions. A novel char preparation technique was developed to prepare chars with SO_2 adsorption capacities significantly greater than that of a commercial activated carbon. An attempt was made to relate the physical and chemical properties of the chars to observed SO_2 adsorption behavior. In most cases there was no correlation between SO_2 adsorption capacity and surface area. Temperature programmed desorption (TPD) was used to determine the nature and extent of carbon-oxygen (C-O) complex formation; it was found that SO_2 adsorption was inversely proportional to the amount of C-O complex on the carbon surface. The formation of stable C-O complex during char preparation may have served only to occupy carbon sites that were otherwise reactive towards SO_2 adsorption. A fleeting C(O) complex, formed only during adsorption of SO_2, was postulated to be the reaction intermediate necessary for conversion of SO_2 to H_2SO_4.

During this quarter, further analyses of SO_2 adsorption and TPD data revealed that SO_2 adsorption was directly proportional to the number of unoccuppied (free) adsorption sites on the carbon surface. The SO_2 capacity of a series of prepared IBC-102 chars and commercial activated carbons normalized with respect to the number of free sites varied by less than a factor of two, which indicated an excellent correlation. Based on these results, a mechanism for SO_2 adsorption on carbon and conversion to H_2SO_4 was proposed. To study NO_x reduction by activated char, a packed bed flow through system was designed and constructed. A quadrupole mass spectrometer was installed to monitor the [NO] and [NO_2]; NO breakthrough curves were obtained for a commercial activated carbon at various [NO]. The ISGS is working with two organizations, the Research Triangle Institute (RTI) and Sorbent Technologies Corporation (STC), to produce activated chars optimized for NO_x reduction. Gram quantities of activated char were prepared and shipped to RTI and STC for testing.

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 95% of the SO_2 and over 80% of the NO_x from combustion flue gas. An activated carbon FGD process, typically placed after the precipitator and just before the stack, can be used alone or in conjunction with other methods of FGD to remove SO_2/NO_x from flue gas. This technology has been used in Europe and Japan for cleanup of flue gas from both coal combustion and waste incineration. Presently, no U.S. utility employs a carbon based process to clean flue gas. Carbon based FGD systems can be integrated into both new and existing power plants. The retrofit of an existing utility boiler with such a FGD process could, in addition to improving SO_2/NO_x emissions, lower overall capital and operating costs compared to competitive FGD processes. One of the unique advantages of an activated carbon FGD process is that it removes nearly every impurity found in combustion flue gas including particulates, SO_2/NO_x, mercury, dioxins, furans, and other air toxics. No other existing FGD process has that capability. There are a number of research groups presently involved in the development of novel carbon based processes and materials for flue gas cleanup. The type of carbon used more often than not dictates the economic viability of a given process. A high quality carbon adsorbent for SO_2 removal should have the following properties: high adsorption capacity for SO_2, rapid SO_2 adsorption kinetics, low reactivity with oxygen, minimal loss of activity after regeneration, high mechanical strength, and low cost.

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 research is to determine whether Illinois Basin coal is 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. The initial focus of this study (Phase I) has been to identify process conditions for production of activated char with optimal SO_2 removal characteristics. Chars with varying pore structure and surface chemistry were prepared from an Illinois bituminous coal under a wide range of pyrolysis and activation conditions, and tested for their ability to remove SO_2 from simulated flue gas. A thermogravimetric technique was used to determine the SO_2 capacity (120° C, 1500 ppm SO_2, 5% O_2, 10% H_2O) of the chars. A novel char preparation method, which involved

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nitric acid treatment followed by thermal desorption of carbon-oxygen (C-O) complex, produced activated chars with SO_2 adsorption capacities significantly greater than those of a commercial activated carbon.

An attempt was made to relate the physical and chemical properties of the chars to observed SO_2 adsorption behavior. The N_2 (77 K) and CO_2 (195 K) BET surface areas of the prepared chars were determined. In most cases, there was no correlation between SO_2 capacity and N_2 BET surface area. A better correlation existed with CO_2 BET surface area. The SO_2 capacities of the chars normalized with respect to CO_2 and N_2 BET surface areas varied by a factor 10 and 300, respectively. A temperature programmed desorption (TPD) method was used to determine the nature and extent of carbon-oxygen (C-O) complexes formed on the char surface. TPD data 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 may have served only to occupy carbon sites that were otherwise reactive to SO_2 adsorption. A fleeting C(O) complex, formed only during adsorption of SO_2, was postulated to be the reaction intermediate necessary for conversion of SO_2 to H_2SO_4.

The current project, a continuation of work initiated in Phase I, is a cooperative effort between the Illinois State Geological Survey (ISGS), University of Illinois at Urbana-Champaign (UIUC), and Research Triangle Institute (RTI), and consists of six tasks. In Task 1, a series of activated chars will be prepared from IBC-102 coal with optimal physical/chemical properties for combined SO_2/NO_x removal; a novel oxidation, thermal desorption treatment is utilized to modify the surface chemistry and pore structure of the char. In Task 2, kinetic/equilibrium studies will be performed using themogravimetric analysis and mass spectrometry to evaluate the SO_2/NO_x adsorption properties of the prepared chars. In Task 3, selected chars will be tested in a carbon-based process (RTI-Waterloo) for their ability to remove SO_2/NO_x from simulated flue gas. In Task 4, the physical/chemical properties of the prepared chars will be evaluated. In Task 5, if a suitable activated char is identified, process flowsheets for the production and use of activated char from Illinois coal will be developed, and a preliminary market assessment of the products initiated. In Task 6, technical and management progress reports will be prepared and submitted to the ICCI.

During this quarter, further analyses of SO_2 adsorption and TPD data revealed that SO_2 adsorption was directly proportional to the number of unoccuppied (free) adsorption sites on the carbon surface. The SO_2 capacity of a series of IBC-102 chars and commercial activated carbons normalized with respect to the number of free sites varied by less than a factor of two, which indicated an excellent correlation. To the best of our knowldege, this approach has never been used to explain SO_2 removal by carbon. Based on these results, a new mechanism for SO_2 adsorption on carbon and conversion to H_2SO_4 was proposed. The rate of SO_2 adsorption was expressed as

$$\frac{d[SO_2]}{dt} = k\,[C(O)]\,[SO_2]^n$$

where k is a fundamental rate constant (turnover frequency of the carbon catalyst) and n is the order of the reaction and [C(O)] is the concentration of fleeting complex. For

concentrations of SO_2 less than 1500 ppm, the reaction order was less than one, and for concentrations of SO_2 greater than 1500 ppm, the reaction order approached zero. Arrhenius plots were constructed for SO_2 adsorption on carbon at temperatures between 105 and 240°C; activation energies decreased from -1.7 to -3.0 kcal/mol with increasing adsorption time (from 1 to 12 hours). The negative value of activation energy implies that more than one chemical reaction is occurring during adsorption of SO_2 on carbon and conversion to H_2SO_4. The various reactions which could be occurring include: 1) chemisorption of oxygen on carbon, 2) chemisorption of SO_2 on carbon, 3) reaction of C(O) complex with SO_2 to form SO_3, and 4) reaction of SO_3 with H_2O to form H_2SO_4.

To study NO_x reduction by activated char, a packed bed flow through system was designed and constructed. A quadrupole mass spectrometer was installed to monitor the [NO] and [NO_2]; NO breakthrough curves were obtained for a commercial activated carbon at various [NO]. The ISGS is working with two organizations, the Research Triangle Institute (RTI) and Sorbent Technologies Corporation (STC), to produce activated chars optimized for NO_x reduction. Gram quantities of activated char were prepared and shipped to RTI and STC for testing. In the next quarter, the NO_x reduction capability of activated char prepared from Illinois coal will be evaluated. Selected chars will be tested in the RTI/Waterloo combined SO_2/NO_x removal process, and their SO_2/NO_x removal efficiencies compared to those of commercial activated carbons and selected proprietary carbons. Work with STC will target stationary diesel engines which produce large quantities of NO_x that for the most part remain uncontrolled. STC will evaluate the performance of ISGS activated char in treating the exhaust gas from a stationary diesel engine. Samples of activated char will be prepared and first tested at the ISGS. Samples which show potential for NO_x reduction will be shipped to RTI and STC for further testing.

OBJECTIVES

The main objective of this project is to determine whether Illinois coal is a suitable feedstock for the production of activated char, and to evaluate the potential application of the products in combined SO_2/NO_x removal. Key production variables will be identified to help design and engineer an activated char with the physical and chemical properties to enable the development of an effective SO_2/NO_x removal catalyst.

The project consists of six tasks.

Task 1. Chars will be prepared from IBC-102 coal in a fluidized-bed reactor under controlled pyrolysis and activation conditions. To further develop surface area and porosity, chars will be activated in CO_2 and/or steam. Chemical activation of coal with potassium hydroxide will be carried out to maximize surface area development in the char. The pore structure and surface chemistry of selected chars will be further modified by a nitric acid oxidation/thermal desorption treatment to optimize combined SO_2/NO_x removal.

Task 2. Activated char samples will be tested at the ISGS for their ability to remove SO_2/NO_x from simulated flue gas mixtures. The effects of carbon type, flow rate, $[O_2]$, $[H_2O]$, and adsorption temperature on SO_2 removal and NO_x reduction are examined by thermogravimetric analysis. The kinetics of SO_2 and NO adsorption (in helium) at temperatures between 25 and 200° C are measured and adsorption capacities determined. A laboratory scale adsorption column/mass spectrometry (AC/MS) system is used to perform multicomponent gas adsorption studies. A simulated flue gas mixture (2500 ppm SO_2, 500 ppm NO_x, 2% H_2O, 5% O_2, 15% CO_2, balance He) is passed through a 1 in. ID, 1 ft. AC at a specified flow rate (100 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. In order to gain further insight into the chemistry and kinetics of SO_2/NO_x adsorption, temperature-programmed desorption (5° C/min in helium) coupled with mass spectrometry is used to monitor gas evolution from the spent char during regeneration. The overall performance of the activated char in removing SO_2/NO_x from combustion flue gas mixtures is assessed, and compared to that of a commercial activated carbon.

Task 3. Optimized chars will be tested at the Research Triangle Institute (RTI) for SO_2 removal and NO_x reduction. Standard SO_2 and NO_x removal tests developed by RTI will be performed on selected ISGS chars and a comparison made with results obtained with carbons tested earlier by RTI. Three ISGS activated chars will be tested; the ISGS wil supply to RTI 100 g each of the chars to be tested. Test conditions for SO_2 removal tests

include exposing 85 cm^3 reaction bed of char at a space velocity of 1400 cm^3/cm^3-h, 1 atm, and 100°C to simulated combustion flue gas containing 2500 ppm SO_2, 500 ppm NO, 10% H_2O, 5% O_2, and balance He, and measuring a breakthrough curve until the effluent has 125 ppm SO_2 (5% of inlet). The SO_2 in the effluent is measured using a UV-photometric continuous SO_2 monitor. The carbon is leached offline while still hot with 200 cm^3 of dilute H_2SO_4 (4 N) and quickly replaced in the constant temperature oven at 100°C. The $[H_2SO_4]$ of the resulting solution will be measured. The above procedure will be repeated for at least two additional cycles. Test conditions for the NO_x reduction tests include exposing 85 cm^3 reaction bed of the char at a space velocity of 1400 cm^3/cm^3-h, 1 atm, and 130-160°C to a simulated flue gas doped with ammonia containing 500 ppm NO, 625 ppm NH_3, 10% H_2O, 5% O_2, 10% CO_2, and balance He. For each char, steady state NO reduction data will be measured at four temperatures, i.e., 130, 140, 150 and 160°C, using a chemiluminescent continuous NO/NO_2 analyzer. At one selected temperature for each char, NH_3 slip will be measured using impinger collection followed by an ion selective electrode.

Task 4. Chars will be characterized for their physical and chemical properties such as N_2-BET and CO_2-DR surface area, porosity and pore size distribution, helium and bulk density, attrition resistance, ultimate and proximate analyses, before and after SO_2/NO_x adsorption, to gain further insight into the fundamentals of preparation and properties of activated char. Surface morphology and pore structure of the char will be evaluated by scanning electron microscopy.

Task 5. 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 ISGS activated char will be developed, and a preliminary cost analyses of producing the 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 a specific industrial SO_2/NO_x removal application.

Task 6. Technical and management progress reports will be prepared and submitted to the ICCI. The reports will be prepared quarterly, and a final report at the end of each 12 month contract period. The quarterly reports will provide information about progress to date as well as plans for the upcoming quarter. These discussions will include any variance from cost and scheduling projections.

INTRODUCTION

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, high mechanical strength, and low cost.

Commercial 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. 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 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.

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. 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 modified the Bergbau Forschung (BF) process to meet their SO_2/NO_x removal requirements (Tsuji and Shiraishi, 1991). One of the 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% SO_2 removal and over 80% NO_x removal 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 the carbon. The moving bed of activated coke also 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.

In the U.S., there are several research groups involved in the development of carbon-based processes for flue gas cleanup. Gangwal et al. (1992), funded by the U.S. DOE, developed the RTI-Waterloo process for flue gas cleanup. It is a low temperature process employing carbon based catalysts that operates downstream of the electrostatic precipitator (ESP). The technical feasibility of the process was demonstrated in laboratory scale experiments. A preliminary evaluation of the RTI-Waterloo process was conducted for a 100 MW electric power plant burning a 2.8% sulfur coal. 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). 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 catalyst. The catalyst needed 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 microwaves are used to convert adsorbed SO_2 to sulfur.

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) throughout Europe. The carbon based technology has been given preference over alternative technologies because of its removal efficiency for SO_2, NO_x, particulates, mercury, heavy metals, dioxins, furans, HCl and HF. The carbon used in their process is manufactured from a German brown coal. The carbon has a pore surface area of 270 m^2/g. In their gas 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 selectively treats the pollutants in each layer. The spent activated carbon is cycled back to the incinerator where the noxious components are released again for ultimate removal in the scrubber system. Operating results show that current European emission requirements are met with the STEAG system.

A demonstration test of the STEAG process with the U.S. Environmental Protection Agency is planned in the near future. 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. STEAG estimates a market potential of 80,000 tons/year of carbon adsorbent, assuming 10% of U.S. incinerators adopt their technology, to meet needs emanating from anticipated regulation of emissions from existing incinerators. Because about two tons of coal are required to produce one ton of adsorbent, the potential market is 160,000 tons of coal per year. STEAG designed its process to use readily available, low cost carbon, which is produced in Germany by Rhine-Braun. STEAG desires a dependable supply of low cost U.S. carbon that will work well in its process. STEAG, however, believes commercial activated carbons available in the U.S. may be too reactive due to their high surface area. Hot spots in their system could lead to spontaneous ignition of the carbon. The adsorption of SO_2, NO_x, and O_2 on carbon is an exothermic process. The STEAG process works best with a low activity char, i.e., one with a surface area < 300 m^2/g.

EXPERIMENTAL

Char Preparation

Figure 1 presents a process flowsheet for production of activated char from Illinois coal. The three major processing steps are pyrolysis, activation, and surface modification by an oxygen deposition and thermal desorption treatment. The chars used in this work were prepared from an Illinois No. 2 hvCb coal, sample IBC-102 of the Illinois Basin Coal Sample Program (IBCSP) (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. The coal was exposed to ambient air for a two year period prior to its use in this study. Thus, it is not representative of less oxidized samples typically obtained from the IBCSP. Air oxidation reduces to some extent the propensity of the coal to melt and/or agglomerate during pyrolysis. A physically cleaned 48x100 mesh sample was prepared from the oxidized parent coal, and used throughout as the feedstock for activated char. The proximate and ultimate analyses (moisture-free basis) of the as-received, air-oxidized and clean oxidized coals are given in Table 1. Note the difference in sulfatic sulfur content of the oxidized coal and as-received coal.

Chars were prepared at 500, 700 and 900°C for 0.5 h in a 5 cm 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. Some chars were oxidized in 10% O_2 at a relatively constant rate of reaction in a 2.5 cm ID FBR to increase both surface area and oxygen content. In a typical run, 50 g of char was heated to 390-500°C under

flowing N_2, oxidized for 0.5-0.75 h to obtain a 30% weight loss (conversion), and cooled to room temperature in N_2.

Table 1. Proximate and ultimate analyses of IBC-102 coal.

Analyses	As-Received IBC-102	Air-Oxidized IBC-102	Clean, Oxidized IBC-102
Moisture	14.3	12.5	2.31
Volatile Matter	39.9	39.0	41.3
Fixed Carbon	53.3	55.5	55.2
Ash	6.8	5.5	3.6
Carbon	74.1	73.5	77.4
Hydrogen	5.3	5.1	5.4
Nitrogen	1.5	1.4	1.5
Oxygen	8.9	11.5	10.0
Sulfatic Sulfur	0.1	1.1	0.4
Pyritic Sulfur	2.3	0.6	0.5
Organic Sulfur	1.0	1.3	1.3
Total Sulfur	3.3	3.0	2.2
BTU/lb	13628	13146	13876

Steam activation was performed to further develop the microporosity and surface area of the char. Typically, 50 g char was placed in the 5 cm ID FBR and heated to 860° C in flowing N_2. The N_2 flow was replaced by 50% H_2O/50% N_2 (6 L/min) for 0.75 h to achieve 30% carbon conversion. The activated char was cooled to room temperature in N_2.

A chemical activation method was employed to enhance surface area of the char. Potassium hydroxide (KOH) was loaded onto the coal by impregnation to incipient wetness. Typically, 100 g of KOH was dissolved in 0.1 L distilled water and mixed thoroughly with 100 g of raw coal. The dried coal/KOH mixture was added to the 5 cm ID FBR and pyrolyzed in N_2 at 600 and 800° C for 0.5 h. The sample was cooled in N_2 and washed repeatedly with distilled water to remove leftover potassium and air dried overnight at 110° C.

The H_2O activated char was subjected to a nitric acid (HNO_3) treatment (oxygen deposition). Typically, 10 g char was added to 0.2 L 10 M HNO_3 solution, and refluxed (80°C) for 1 h. The HNO_3 treated carbon was washed repeatedly with distilled water to remove excess acid and vacuum dried overnight at 25°C. In some cases, the HNO_3 treated char was heated in N_2 to 525, 725, or 925° C and held for 1 h to desorb carbon-oxygen (C-O) complexes formed by the HNO_3 treatment.

Char Characterization

The kinetics of SO_2 adsorption on prepared 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 N_2 to 360°C to remove moisture and impurities. The sample was cooled to the appropriate adsorption temperature (120°C) under nitrogen. Once the temperature stabilized, the flow of N_2 was switched to a mixture of gases containing 5% O_2, 7% H_2O and the balance N_2. Once there was no further weight gain due to O_2 chemisorption and H_2O adsorption, SO_2 was added in concentrations representative of a typical flue gas for combustion of high sulfur coal (i.e., 2500 ppm 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 in flowing N_2 to regenerate the carbon. Several adsorption/desorption sequences were performed with selected chars to examine the effect of thermal regeneration on SO_2 adsorption capacity.

Temperature programmed desorption (TPD) experiments were carried out in a flow-thru, 2.5 cm 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 at 1000°C to achieve nearly 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 concentrations of CO and CO_2 in the effluent gas.

Surface areas were determined from the amount of N_2 and CO_2 adsorbed at 77 and 195 K, respectively, using a dynamic sorption method in conjunction with a single point BET adsorption equation. Single point N_2 BET surface areas 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 Corporation). Single point CO_2 BET surface areas were determined from CO_2 (195 K, dry ice-ethanol) adsorption data obtained in a custom made U-tube apparatus at a P/P_o of 0.15 (220 torr CO_2 in helium, P_o = 1450 torr).

RESULTS AND DISCUSSION

SO_2 Adsorption

The SO_2 adsorption capacities of the prepared chars were determined in a simulated flue gas containing 5% oxygen and 7-14% water vapor. An adsorption temperature of 120°C was used; there were difficulties with condensation of water vapor in the TGA at temperatures less than 100°C. Figure 2 shows the effect of oxygen and water vapor concentration on the SO_2 adsorption capacity of a char prepared from IBC-102 coal (HNO_3-925°C). There is a significant increase in the SO_2 adsorption capacity of the char when water vapor and oxygen are both included in the flue gas mixture. Figure 2 also shows that increasing the water vapor content from 7 to 14 percent increases slightly the total amount of SO_2 adsorbed after 6 hours. Figure 3 shows that the addition of 10% CO_2 in the flue gas has a negligible effect on the amount of SO_2 adsorbed by the commercial activated carbon.

It was of interest to measure the SO_2 adsorption capacity of materials other than those derived from Illinois coal. Figure 4 shows the kinetics of SO_2 adsorption on several different types of carbon including a Calgon activated carbon (Calgon), char prepared by the Research Triangle Institute optimized for NO_x reduction (RTI), char prepared at the ISGS for use in the STEAG process (ISGS), a char prepared from waste tire (tire char), the char presently used by STEAG in their process in Germany (STEAG), a char obtained from the Coal Technology Corporation

activated in CO_2 for 1 h at 850°C (CTC), and fly ash containing 50% unburnt carbon (ash). The commercial carbon has the largest SO_2 adsorption capacity. It is interesting to note that the tire char has essentially the same SO_2 capacity as the STEAG char which is made from brown coal. The CTC char is produced in the CTC process, which can produce up to 1 ton of metallurgical coke per hour from caking coal using a twin screw feeder reactor. (CTC is currently being considered by the ISGS for large scale production of activated char for the STEAG process.) The CTC char showed very little uptake of SO_2; it may require further activation and/or a coal preoxidation step to increase its SO_2 capacity. The sample of fly ash (actually the concentrate from flotation processing of fly ash) adsorbed less SO_2 than the CTC char.

Effect of Surface Area

There are conflicting reports in the literature on the effect of surface area on SO_2 adsorption by carbon, ranging from "no relation can be found between the SO_2 adsorbed and the BET surface area of the carbons" (Davini, 1989) to "surface area is the most important parameter in order to predict the behavior of a char in the abatement of SO_2 from exhaust gases" (Rubio et al., 1994). Table 2 shows that SO_2 capacity (6 h adsorption) of each char, normalized with respect to N_2 BET surface area (SO_2/N_2), varies by more than two orders of magnitude. In some isolated cases, however, there is a reasonable correlation between SO_2 capacity and surface area, e.g., the KOH activated chars and Calgon carbon.

Table 2 also lists the CO_2 BET surface areas of the prepared chars. The CO_2 molecule which is slightly smaller than the N_2 molecule should be able to diffuse more rapidly into the micropore network at the relatively higher temperature of adsorption; thus, CO_2 surface areas should be more indicative of accessible surface area. Table 2 shows that the SO_2 adsorption capacity normalized with respect to CO_2 BET surface area (SO_2/CO_2) varies by a factor of 13 compared to 316 for the N_2 BET surface area. A better correlation seems to exist between CO_2 surface area and SO_2 capacity. A statistical analysis of the data reveals that the correlation coefficient (assuming a linear relation between SO_2 capacity and surface area) is only slightly better for CO_2 compared to N_2 (0.55 versus 0.49, respectively), both indicating a poor correlation. Other properties of the char may be more important for determining its SO_2 adsorption behavior.

In order to obtain more insight into the fundamental mechanism of SO_2 adsorption on carbon, a series of well characterized activated carbon fibers (ACF), previously prepared in a laboratory of the Materials Science and Engineering Department at the University of Illinois (Economy et al., 1992), were also studied. The starting material for the ACF, commercially available from Nippon Kynol Inc., is a cross-linked phenol-aldehyde polymer activated in steam at 800-1000° C to different levels of conversion. Four ACF were studied with the following N_2 BET surface areas: ACF-10, 600 m^2/g; ACF-15, 1400 m^2/g; ACF-20, 1600 m^2/g; and ACF-25, 1900 m^2/g. The ACF typically consist of 93-95% carbon, less than 1% hydrogen, with the balance oxygen. The ACF are essentially free of inorganic impurities, so the possible effects of inherent mineral matter on SO_2 adsorption need not be considered, as could be the case with coal char (Davini, 1993).

Figure 5 presents the kinetics of SO_2 adsorption for the four ACF studied. The amount of SO_2 adsorbed after six hours varies inversely with the N_2 BET surface area of the carbon. Foster et al. (1992) observed similar behavior for adsorption of ppm levels of n-butane, benzene, or acetone on these same ACF, i.e., low surface area ACF adsorbed more than high surface area ACF. However, at much higher concentration levels (1-3%) of n-butane, the

Table 2. Variation of SO_2 adsorption capacity with N_2 (77 K) and CO_2 (195 K) BET surface areas.

Sample	SO_2 Capacity[1] (mg SO_2/g char)	N_2 Surface Area (m^2/g)	CO_2 Surface Area (m^2/g)	SO_2/N_2 (mg/m^2)	SO_2/CO_2 (mg/m^2)
IBC-102, 500°C, 0.5 h	19	1.2	270	15.83	0.07
IBC-102, 700°C, 0.5 h	33	10.0	315	3.30	0.10
IBC-102, 900°C, 0.5 h	7	1.2	98	5.83	0.07
IBC-102 + KOH, 600°C, 0.5 h	157	500	725	0.31	0.22
IBC-102 + KOH, 800°C, 0.5 h	176	800	1155	0.22	0.15
Commercial Activated Carbon	206	1000	1000	0.21	0.21
IBC-102, 500°C; 10% O_2, 390°C	13	220	422	0.06	0.03
IBC-102, 700°C; 10% O_2, 440°C	37	320	490	0.11	0.08
IBC-102, 900°C; 10% O_2, 500°C	42	230	395	0.18	0.11
IBC-102, 900°C; H_2O, 860°C	176	220	613	0.8	0.29
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, original	26	400	585	0.06	0.04
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 525°C	91	460	693	0.20	0.13
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 725°C	241	500	727	0.48	0.33
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 925°C	287	550	726	0.52	0.39

[1]SO_2 capacity after 6 h.

amount of n-butane adsorbed was directly proportional to the surface area of the ACF. Nitrogen adsorption studies (77 K) showed that the average pore size of the material increased with extent of activation, and that low surface area ACF had a smaller average pore size than high surface area ACF.

Figure 6 presents the kinetics of SO_2 adsorption for one of the activated carbon fibers (ACF-15, 1400 m^2/g) at six temperatures ranging from 105 to 240°C. It is useful to construct Arrhenius plots (ln rate of SO_2 adsorption versus 1/T) from which activation energies (E_A) can be derived. Figure 7 presents Arrhenius plots for SO_2 adsorption on ACF-15 for five adsorption times (1, 2, 6, 9 and 12 h) and the calculated value of E_A corresponding to each plot. It is interesting to note that E_A is negative in each case and that it decreases with increasing adsorption time. In all singular chemical reactions the activation energy should have a positive value. The negative value of E_A observed here implies that more than one chemical reaction is occurring during adsorption of SO_2 on carbon and conversion to H_2SO_4. The various reactions which could be occurring include: 1) chemisorption of oxygen on carbon, 2) chemisorption of SO_2 on carbon, 3) reaction of C(O) complex with SO_2 to form SO_3, and 4) reaction of SO_3 with H_2O to form H_2SO_4. The contributions of each or any of these reactions could make the overall activation enery negative. A negative activation energy has also been reported for the reaction of NO_x with carbon; the oxidation of NO to NO_2 has an activation energy of -1.7 kcal/mol at temperatures between 25 and 300°C (Singoredjo et al., 1993).

Effect of Chemisorbed 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 (TPD). Typical TPD profiles for IBC-102 char prepared by pyrolysis, pyrolysis/air oxidation and pyrolysis/steam activation are shown in Figure 8. Note the appreciable differences in the peak temperatures and peak heights of the CO and CO_2 evolution profiles of each char. The amount of CO and CO_2 evolved can be determined from the area under the curves. From these values, the amount of chemisorbed oxygen can be calculated. Table 3 lists the SO_2 adsorption capacity, the amount of chemisorbed oxygen and relative amounts of CO and CO_2 evolved during TPD (CO/CO_2 ratio) for the IBC-102 chars. Table 3 shows

Table 3. Variation of SO_2 adsorption capacity with amount of chemisorbed oxygen.

Sample	SO_2 Capacity[1] (mg SO_2/g char)	O_2 (wt%)	CO/CO_2	SO_2/O_2
IBC-102, 500°C, 0.5 h	19	8.8	3.3	0.22
IBC-102, 700°C, 0.5 h	33	1.5	4.8	2.20
IBC-102, 900°C, 0.5 h	7	0.5	---[2]	1.40
IBC-102 + KOH, 600°C, 0.5 h	157	7.4	3.2	2.12
IBC-102 + KOH, 800°C, 0.5 h	176	5.6	1.2	3.14
Calgon Activated Carbon	206	0.5	2.3	41.2
IBC-102, 500°C; 10% O_2, 390°C	13	8.6	3.3	0.15
IBC-102, 700°C; 10% O_2, 440°C	37	8.9	3.4	0.42
IBC-102, 900°C; 10% O_2, 500°C	42	5.2	4.2	0.81
IBC-102, 900°C; H_2O, 860°C	176	1.1	3.4	16.0
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, 2.5 h, 25°C (original)	---[2]	16.4	1.4	---[2]
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 525°C	91	5.9	6.7	1.54
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 725°C	241	1.6	12.8	15.0
IBC-102, 900°C; H_2O, 860°C; 45% HNO_3, desorbed at 925°C	287	0.5	---[3]	57.4
Calgon, 45% HNO_3, 2.5 h, 25°C (original)	---[2]	15.7	1.4	---[2]
Calgon, 45% HNO_3, desorbed at 200°C	46	14.3	0.8	0.32
Calgon, 45% HNO_3, desorbed at 525°C	117	5.6	7.6	2.09
Calgon, 45% HNO_3, desorbed at 725°C	156	3.4	5.5	4.59
Calgon, 45% HNO_3, desorbed at 925°C	214	1.7	5.4	12.6

[1] SO_2 capacity after 6 h.
[2] not determined.
[3] CO_2 concentration below detectable limits.

that the SO_2 capacity normalized with respect to total adsorbed oxygen (SO_2/O_2) varies by more than a factor of 300, indicating a poor correlation. Davini (1990) also observed no correlation between SO_2 adsorption capacity and the total oxygen content of the char. However, he did find a good correlation between SO_2 capacity and the basic (or high temperature) C-O functional groups present in the char. Because SO_2 is an acid gas, a carbon adsorbent with a basic surface could be expected to adsorb more SO_2 (Davini, 1990). The C-O functional groups (carbonyl) which form CO upon thermal desorption in inert gas impart surface basicity, while C-O groups (carboxylic) which form CO_2 are acidic by nature.

In our study, a novel char preparation method (nitric acid treatment/thermal desorption) was devised to install a basic carbon surface which could enhance SO_2 adsorption (Lizzio et al., 1994). Figure 9 shows that the amount and type of oxygen complexes formed on the char surface treated with nitric acid differ markedly from those activated in oxygen or steam (Figure 8). Figure 10 presents the corresponding kinetics of SO_2 adsorption curves for the HNO_3 treated chars. The HNO_3-25°C and HNO_3-525° C chars adsorb less SO_2 than the base char (steam activated). This may be due to the presence of still a relatively large amount of CO_2-forming groups, which could have a detrimental effect on SO_2 adsorption. Note that the surface area of the original HNO_3 treated char (400 m^2/g) is greater than that of the steam activated char (220 m^2/g), but its SO_2 capacity is almost one order of magnitude less (see Table 2). The HNO_3-725° C and HNO_3-925° C chars have SO_2 capacities (24.1 and 28.7%) which surpass that of the commercial carbon (20.6%). It is interesting to note that the char with the smallest amount of C-O complex (HNO_3-925° C) adsorbed the largest amount of SO_2. Assuming 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 reactive or 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 adsorption sites.

An understanding of SO_2 removal by carbon may require knowledge of the concentration of the "otherwise reactive adsorption sites" (free sites), i.e., those sites which form the fleeting C(O) complex prior to adsorption of SO_2. The number of free sites on each of the HNO_3 treated chars can be estimated from the difference in the initial occupied sites for the original HNO_3 treated char (CO_i and CO_{2i}) and the amounts of CO and CO_2 evolved from the surface of the HNO_3 treated chars desorbed at 200, 525, 725 or 925°C (CO and CO_2), as determined by TPD. Table 4 shows that the molar SO_2 capacity normalized with respect to moles of CO-forming free sites ($SO_2/(CO_i-CO)$) and CO_2-forming free sites ($SO_2/(CO_{2i}-CO_2)$), as determined from the data given in Table 3 (SO_2 capacity, wt.% O_2, CO/CO_2 ratio), varies by factors of 1.6 and 2.8, respectively. For these chars, this represents a significant improvement over the previous correlations obtained with N_2 BET surface area (factor of 8.7), CO_2 BET surface area (factor of 9.8), and total chemisorbed oxygen (factor of 37). To the best of our knowldege, this approach has never been used to explain SO_2 removal by carbon. It is interesting to note that there is a better correlation between SO_2 capacity and the CO-forming free sites than the CO_2-forming ones.

It was important to test this concept on another carbon. Figure 11 shows the kinetics of SO_2 adsorption on a series of HNO_3 treated thermally desorbed samples of Calgon

activated carbon (also a steam activated bituminous coal char). It is interesting to note that the original Calgon carbon (no HNO_3 treatment) adsorbs the largest amount of SO_2. Apparently, the HNO_3/thermal desorption treatment did not improve the SO_2 adsorption characteristics of this carbon; perhaps because the pore structure and surface chemistry of the carbon were already optimized for adsorption of contaminants. Figure 12 presents the corresponding CO and CO_2 TPD profiles for the HNO_3 treated Calgon carbon desorbed at 25, 200, 525, 725 and 925°C. Similar trends in TPD profiles were observed for the HNO_3 treated thermally desorbed IBC-102 chars (see Figure 9). Table 4 shows that the SO_2 adsorption capacity normalized with respect to the number of CO and CO_2 forming free sites varies by a factor a 1.7 and 3, respectively, for this series of HNO_3 treated Calgon carbon samples. A similar trend was observed for the HNO_3 treated IBC-102 chars (see Table 4). Thus, in both cases, SO_2 adsorption behavior is directly proportional to the number of free sites as determined by TPD. It is interesting to note that, for each of the seven samples listed in Table 4, the SO_2 adsorption capacity normalized with respect to CO-forming sites is essentially unity.

The following mechanism for SO_2 removal by carbon may explain these results (Lizzio and DeBarr, 1994; Lizzio et al., 1995).

Oxygen Chemisorption	$C + \frac{1}{2}O_2$ -----> C-O or C(O)
Fleeting Complex	C-O -----> C(O)
SO_2 Adsorption	$C(O) + SO_2$ -----> $C\text{-}SO_3$
H_2SO_4 Formation	$C\text{-}SO_3 + H_2O$ -----> $C\text{-}H_2SO_4$
Regeneration	$C\text{-}H_2SO_4$ -----> $C + H_2SO_4$
Overall Reaction	$C + SO_2 + \frac{1}{2}O_2 + H_2O$ -----> $C + H_2SO_4$

Oxygen from the gas phase is chemisorbed onto a carbon active site to form a reactive C(O) intermediate and/or stable C-O complex. Up to this point we have regarded stable C-O complex formation as a predominantly inhibiting process; the mechanism implies that it can also be an intermediate step in SO_2 adsorption and conversion to H_2SO_4. The stable (unreactive) C-O complex, depending on its energy state and neighboring functional groups, can be transformed into a reactive C(O) intermediate (or fleeting complex). Catalytic oxidation of SO_2 to SO_3 involves reaction of SO_2 in the gas phase with the reactive C(O) intermediate. In the presence of water at low temperatures, the SO_3 is converted to H_2SO_4.

In the above reaction scheme, the carbon active sites on the char surface are considered to be the active catalyst. The C(O) intermediate is just that, an intermediate and not a catalyst; the oxygen is transferred to SO_2 to form adsorbed SO_3 via the carbon catalyst. The carbon active site (catalyst) returns to its original state after regeneration. The formation of stable C-O complex deactivates the carbon catalyst. The water that is adsorbed in the pores of the char may act as a regeneration medium. The acid formed on the carbon surface is continuously swept from the surface by water adsorbed in the pores, and goes into solution, as it could in a large scale trickle bed reactor (Gangwal et al., 1993). Thus, the carbon catalyst can undergo numerous cycles of adsorption/desorption. The production of H_2SO_4 proceeds indefinitely until water adsorbed in the pores becomes saturated with H_2SO_4. This mechanism implies that the pore volume of the carbon, i.e., the amount of water retained in the pores, determines the total amount of SO_2 adsorbed by the carbon (DeBarr, 1995).

Table 4. Variation of SO_2 capacity of nitric acid treated IBC-102 char and Calgon carbon with the concentration of free sites.

Sample	SO_2 capacity[1] (moles SO_2)	Chemisorbed oxygen[1] (moles O_2)	CO/CO_2	CO-forming sites[1,2] (moles)	CO_2-forming sites[1,2] (moles)	CO free sites[1,2] (CO_i-CO)	CO_2 free sites[1,2] (CO_{2i}-CO_2)	$\frac{SO_2}{(CO_i-CO)}$	$\frac{SO_2}{(CO_{2i}-CO_2)}$
IBC-102, HNO_3, 25°C	---[3]	0.00512	1.4	0.00421[4]	0.00301[4]	0	0	---[3]	---[3]
IBC-102, HNO_3, 525°C	0.00142	0.00184	6.7	0.00284	0.00042	0.00137	0.00259	1.036	0.548
IBC-102, HNO_3, 725°C	0.00376	0.00050	12.8	0.00086	0.00067	0.00335	0.00294	1.122	1.278
IBC-102, HNO_3, 925°C	0.00448	0.00016	---[5]	0.00031	0	0.00390	0.00301	1.149	1.488
Calgon, HNO_3, 25°C	---[3]	0.00491	1.4	0.00405[4]	0.00289[4]	0	0	---[3]	---[3]
Calgon, HNO_3, 200°C	0.00072	0.00447	0.8	0.00319	0.00255	0.00086	0.00034	0.839	2.119
Calgon, HNO_3, 525°C	0.00183	0.00175	7.6	0.00277	0.00036	0.00128	0.00252	1.430	0.725
Calgon, HNO_3, 725°C	0.00244	0.00106	5.5	0.00179	0.00033	0.00226	0.00256	1.080	0.952
Calgon, HNO_3, 925°C	0.00334	0.00053	5.4	0.00077	0.00014	0.00328	0.00275	1.019	1.216

[1] values based on 1 g char.
[2] calculated assuming that 1 mole O_2 evolved as 2 CO during TPD is equivalent to 2 CO-forming sites, and 1 mole CO_2 evolved as 1 CO_2 is equivalent to 1 CO_2-forming site.
[3] not determined.
[4] initial values of CO_i and CO_{2i}.
[5] CO_2 concentration below detectable limits.

Hartman and Coughlin (1972) found the catalytic oxidation of SO_2 to SO_3 by carbon to be the rate determining step (in the absence of diffusional limitations) in the conversion of SO_2 to H_2SO_4. If the rate determining step is, indeed, catalytic oxidation of SO_2 to SO_3, the rate of SO_2 adsorption could be expressed as

$$\frac{d[SO_2]}{dt} = k\,[C(O)]\,[SO_2]^n$$

where k is a fundamental rate constant (turnover frequency of the carbon catalyst) and n is the order of the reaction. Figure 13 shows the kinetics of SO_2 adsorption on commercial activated carbon at various concentrations of SO_2 ranging from 100 to 3000 ppm. For these reaction conditions and concentrations of SO_2 less than 1500 ppm, the reaction order appears to be less than 1, and for concentrations of SO_2 greater than 1500 ppm, the reaction order approaches zero. It is interesting to note that adsorption equilibrium is not reached even after 40 hours. This indicates that, at these conditions, the H_2O adsorbed in the pores has yet to be saturated with H_2SO_4. The reaction at the catalyst surface between C(O) and SO_2 proceeds until an equilibrium is established between the H_2SO_4 adsorbed on the carbon surface and that dissolved in adsorbed water. At equilibrium, the pore volume of the carbon, or the amount of water adsorbed in the pores, determines its maximum SO_2 adsorption capacity (DeBarr, 1995).

It remains to be determined whether the reactive sites, i.e., those sites which form the fleeting C(O) complex, for SO_2 adsorption and conversion to H_2SO_4, can be titrated directly by available analytical techniques. It may be possible to quantify those sites which adsorb SO_2 by standard low temperature (110-150°C) oxygen chemisorption techniques (Lizzio et al., 1990). The active surface area concept, developed and used to better understand carbon gasification behavior, might prove especially useful since adsorption of SO_2 and conversion to H_2SO_4 occurs in a temperature range similar to that of low temperature oxygen chemisorption. Note that, for the most part, the C-O complexes formed at 110°C would differ from those formed during char preparation (e.g., steam activation, nitric acid treatment). Transient kinetics coupled with isotope labelling of gaseous reactants (Kapteijn et al., 1992) could also be useful in determining the role of the C-O complex in SO_2 removal by carbon.

Char Production for STEAG

STEAG Aktiengesellschaft (Essen, Germany) has pioneered flue gas cleanup using a low surface area (< 300 m^2/g) activated carbon made from German brown coal. STEAG is presently seeking out U.S. suppliers of activated carbons to provide them with a product for testing in a U.S. waste incinerator. STEAG estimates a market potential of 80,000 tons/year of activated char (160,000 tons of coal), assuming 10% of U.S. incinerators adopt their technology, to meet needs emanating from anticipated regulation of emissions from existing incinerators. A meeting was held in Champaign, IL in March 1994, between representatives from the ISGS, ICCI, ICDB and STEAG to discuss the possible use of activated char made from Illinois coal in the STEAG carbon-based combined SO_2/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.

As a part of a previous ICCI/U.S. DOE project (Lizzio et al., 1994), laboratory conditions were identified to produce a suitable low cost (< $300/ton) adsorbent from Illinois Colchester No. 2 coal contributed by Freeman United from its Industry mine. With the assistance of Allis Mineral Systems (Milwaukee, WI), the production steps were carried through two levels of scale up, culminating in the production of 550 pounds of activated char in an 18 in. ID, 10 ft. heated zone, externally fired rotary tube kiln. A three step process, which included preoxidation, pyrolysis and activation, was used to produce an activated char with a N_2 BET surface area of 110 m^2/g and an SO_2 adsorption capacity of 7% by weight, the latter being almost twice that of the STEAG char. The adsorbent was shipped to Germany for testing on a slip stream of flue gas from a commercial incinerator. Early test results indicate that the ISGS activated char was effective. Upon successful completion of these tests, STEAG will ship the pilot plant to the U.S. for cooperative demonstration tests with the U.S. EPA. STEAG is planning to install a commercial unit on a U.S. municipal waste incinerator that will require 12,000 tons of activated char per year.

An economic analysis of the process developed by the ISGS and Allis Mineral Systems, and used to produce 550 pounds of activated char for STEAG, is underway. Preliminary results indicate that it would cost between $280 and $350 to produce one ton of activated char with a plant designed and constructed to produce 80,000 tons/year activated char assuming an 18% rate of return with the plant paid for in five years of operation (Kruse et al., 1994). Further details will be provided in an upcoming report to be submitted to the ICCI (Kruse et al., 1995).

<u>NO_x Reduction</u>

Nitric oxides (NO_x) are also present in flue gas and are composed mainly of nitrogen oxide (NO) and some nitrogen dioxide (NO_2). These can be reduced by reaction with carbon at 80-150° C (Jungten et al., 1988).

NO reduction $\quad 2\,C + 2\,NO + O_2 \text{ -----> } N_2 + 2\,CO_2$

NO_2 reduction $\quad 2\,C + 2\,NO_2 \text{ -----> } 2\,C\text{-}NO_2$

$\quad 2\,C\text{-}NO_2 \text{ -----> } N_2 + CO_2$

When ammonia is added to the flue gas in the presence of carbon, NO can be reduced to nitrogen and steam (selective catalytic reduction). The stoichiometry of the overall reaction indicates that carbon is not consumed in the process.

$$6\,NO + 4\,NH_3 + C \text{ -----> } 5\,N_2 + 6\,H_2O + C$$

If sulfur dioxide is present in the flue gas, ammonium sulfate may be formed which can block pores and reduce the effectiveness of the catalyst.

$$4\ NH_3 + 2\ SO_2 + 2\ H_2O + O_2 \text{ -----> } 2(NH_4)_2SO_4$$

The selective catalytic reduction (SCR) of NO with NH_3 is an example of a reaction which can be catalyzed by carbon. The activity of carbon catalysts for SCR of NO_x can be influenced by both the amount and type of functional groups present on the carbon surface. The surface chemistry can be modified, e.g., by oxidation treatment, to optimize NO_x reduction activity (Tsuji and Shiraishi, 1991; Singoredjo et al., 1993). Recent work has focused on non-catalytic removal of NO_x by selective adsorption on carbon at 70-120° C, followed by desorption of a concentrated stream of NO_x (Ahmed et al., 1993).
Figure 14 presents the kinetics of NO adsorption on selected carbons as determined by TGA. Initial gas concentrations were typical of those in combustion flue gas: 500 ppm NO, 7.5% H_2O, 5% O_2 and balance N_2. The Calgon carbon adsorbed 1% NO at 120° C after 4 h of exposure to the simulated flue gas. To increase NO adsorption capacity, the [NO] was increased to 1400 ppm, the H_2O removed from the gas, and the temperature lowered to 80° C. Under these conditions, the Calgon carbon adsorbed 4% NO. Ahmed et al. (1993) adsorbed as much as 14% NO_x on their carbons, but used NO concentrations of 0.6-2%. Figure 14 shows that the air oxidized, 700°C char adsorbed only 3% NO after 3 h. Further work is needed to optimize the NO_x reduction properties of the carbon.

A packed bed flow through system was designed and constructed to study NO_x reduction by activated char. A quadrupole mass spectrometer (Gastrace-A System, VG Quadrupoles, Fisons Instruments) was installed on the system to monitor gaseous species with an atomic weight between 1 and 300 atomic mass units (amu). The mass spectrometer will be utilized to obtain NO (30 amu) breakthrough curves and TPD profiles of spent chars. A typical NO breakthrough curve for 4.3 g of Calgon activated carbon packed in a 1.5 cm ID stainless steel reactor and exposed to 500 ppm NO in He is shown in Figure 15. The breakthrough curve can be integrated to determine the amount of NO adsorbed. Figure 16 presents a typical NO calibration curve that will allow a quantitative analysis of the breakthrough curve. It will be interesting to compare the NO and SO_2 adsorption capacities of chars obtained by thermogravimetric analysis and by mass spectrometry.

Gram quantities of activated char were prepared for two separate organizations to be tested in their respective NO_x reduction systems. The ISGS is working with the Research Triangle Institute to produce activated chars optimized for NO_x reduction. The two samples prepared for RTI included an IBC-102 coal char loaded with 5% copper and IBC-102 char loaded with 5% copper and 5% cobalt. The cobalt catalyzes oxidation of NO to NO_2 which is believed to be more readily adsorbed than NO. The copper aids in the reduction of adsorbed NO_x to N_2. Additional samples will be prepared next quarter and shipped to RTI for testing.

The ISGS is also working with Sorbent Technologies Corporation (STC) to develop a suitable carbon for NO_x reduction. STC has developed a new system employing coal chars that adsorb NO_x for approximately 24 hours after which the NO_x is driven off during a 20 minute regeneration. The char can then be used again to capture NO_x. The target application is stationary diesel engines which produce large amounts of NO_x that remain for the most part uncontrolled. Stationary diesel engines represent a sizable market for

the new technology and activated char. Another application is the cleanup of exhaust gas from stationary jet engines; STC and the U.S. Air Force has expressed interest in using activated char to accomplish this. To date, six samples of char have been prepared and shipped to STC. The samples include activated char made from Industry mine coal presently being tested in Germany by STEAG, char made from German coal used by STEAG in their process, HNO_3 treated IBC-102 char heat treated to 925°C, Calgon activated carbon, HNO_3 treated Calgon carbon, and HNO_3 treated Calgon carbon heat treated to 925°C. STC will evaluate the performance of these six samples in treating exhaust gas from an existing large stationary diesel engine. The results will be published in upcoming reports to the ICCI.

CONCLUSIONS AND RECOMMENDATIONS

In Phase I of this project, activated chars were prepared from an Illinois coal (IBC-102) under a wide range of pyrolysis and activation conditions. A thermogravimetric technique was used to determine the SO_2 capacity (120° C, 1500 ppm SO_2, 5% O_2, 10% H_2O) of the chars. A novel char preparation method, which involved nitric acid treatment followed by thermal desorption of carbon-oxygen (C-O) complex, produced activated chars with SO_2 adsorption capacities significantly greater than those of a commercial activated carbon. The N_2 (77 K) and CO_2 (195 K) BET surface areas of the prepared chars were determined. In most cases, there was no correlation between SO_2 capacity and N_2 BET surface area. A better correlation existed with CO_2 BET surface area. The SO_2 capacities of the chars normalized with respect to CO_2 and N_2 BET surface areas varied by a factor 10 and 300, respectively. A temperature programmed desorption (TPD) method was used 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 data 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 may have served only to occupy carbon sites that were otherwise reactive to SO_2 adsorption. A fleeting C(O) complex, formed only during adsorption of SO_2, was postulated to be the reaction intermediate necessary for conversion of SO_2 to H_2SO_4.

During this quarter, further analyses of the SO_2 adsorption and TPD data revealed that SO_2 adsorption was directly proportional to the number of unoccuppied (free) active sites on the carbon surface. The SO_2 capacity of a series of IBC-102 chars and commercial activated carbons normalized with respect to the number of free sites varied by less than a factor of two, which indicated an excellent correlation. Based on these results, a new mechanism for SO_2 adsorption on carbon and conversion to H_2SO_4 was presented. To study NO_x reduction by activated char, a packed bed flow through system was designed and contructed. A quadrupole mass spectrometer was installed on the system to monitor the [NO] and [NO_2]. The ISGS is working with the Research Triangle Institute (RTI) and Sorbent Technologies Corporation (STC) to produce activated chars optimized for NO_x reduction. Gram quantities of activated char samples were prepared and shipped to RTI and STC for testing.

In the next quarter, the NO_x reduction capability of activated char prepared from Illinois coal will be evaluated. Selected chars will be tested in the RTI/Waterloo combined

SO_2/NO_x removal process, and their SO_2/NO_x removal efficiencies compared to those of commercial activated carbons and selected proprietary carbons. Work with STC will target stationary diesel engines which produce large quantities of NO_x that for the most part remain uncontrolled. STC will evaluate the performance of ISGS activated chars in treating the exhaust gas from a stationary diesel engine. Samples of activated char will be prepared and first tested at the ISGS. Samples which show potential for NO_x reduction will be shipped to RTI and STC for further testing. Work will also continue towards gaining further insight into the reaction mechanism of SO_2 adsorption on carbon. Significant progress has been made; additional experiments need to be performed to confirm our initial findings. Work with STEAG is also continuing. An economic evaluation of the ISGS process used to produce 550 pounds of activated char for STEAG is underway.

DISCLAIMER STATEMENTS

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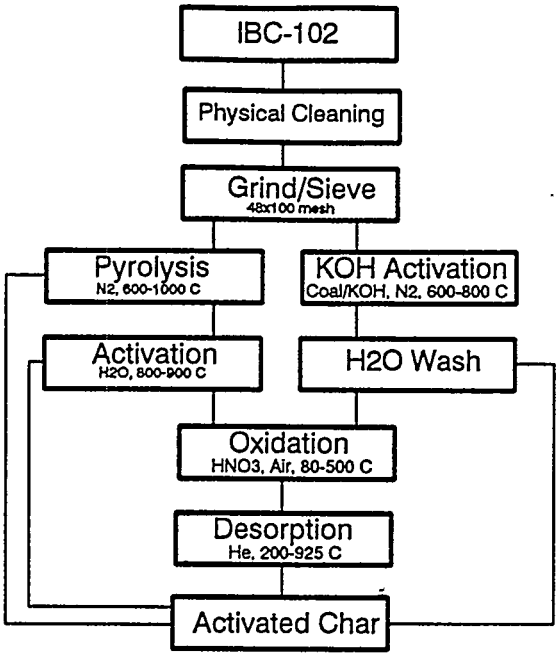

Figure 1. Production of Activated Char from Illinois Coal.

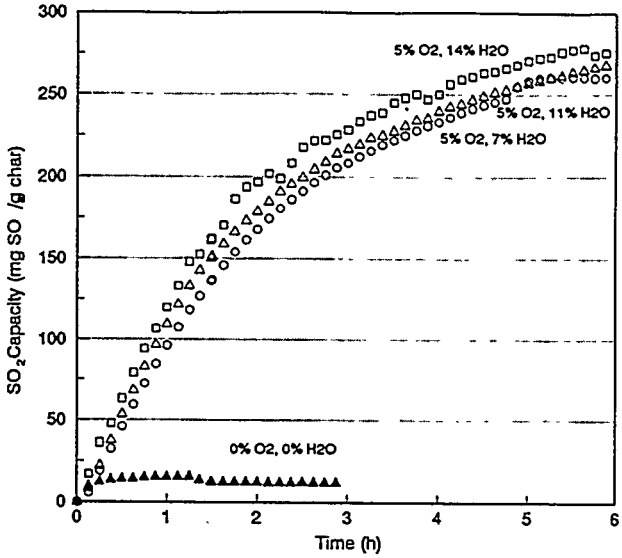

Figure 2. Effect of [O2] and [H2O] on SO2 capacity of IBC-102 char.

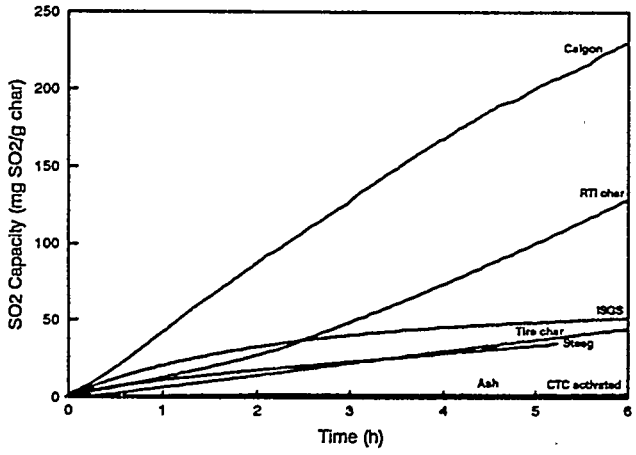

Figure 4. Kinetics of SO2 Adsorption on Various Carbons.

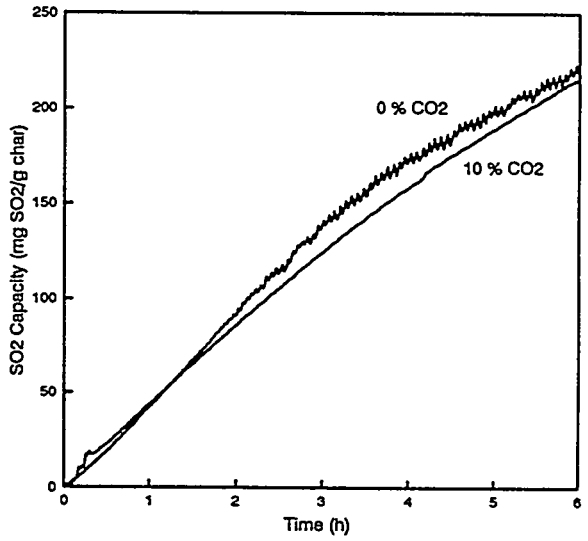

Figure 3. Effect of [CO2] on SO2 Adsorption Capacity of Calgon Carbon.

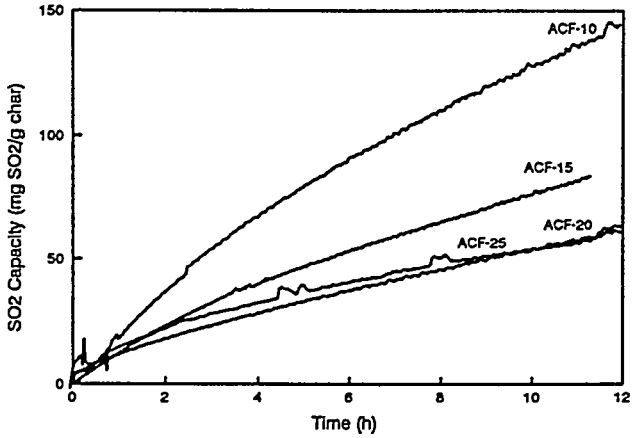

Figure 5. Kinetics of SO2 Adsorption on Activated Carbon Fibers.

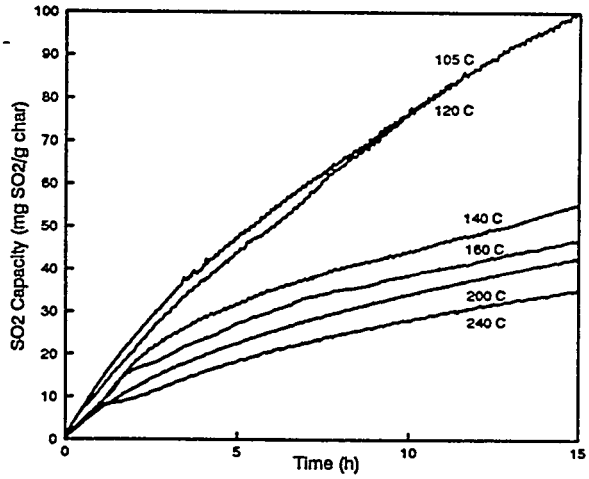

Figure 6. Kinetics of SO2 Adsorption on ACF-15.

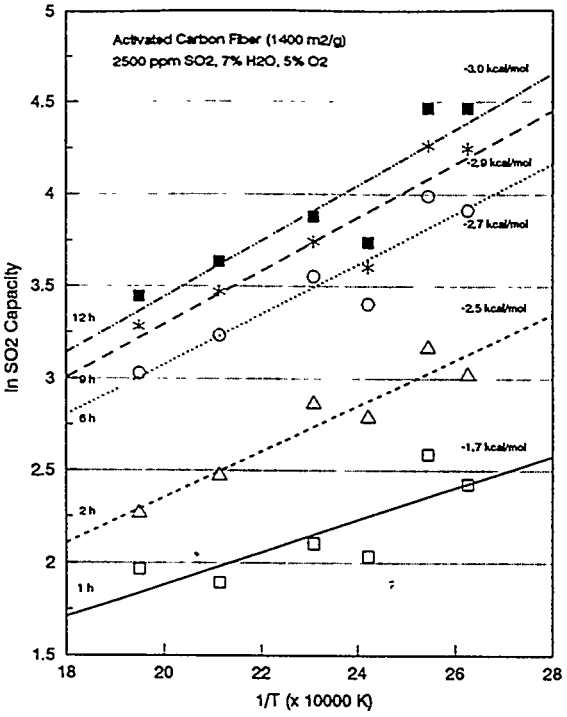

Figure 7. Arrhenius Plots for SO2 Adsorption on ACF-15.

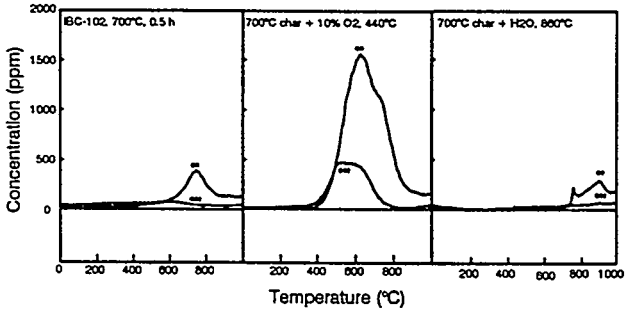

Figure 8. Typical TPD Profiles of IBC-102 Char.

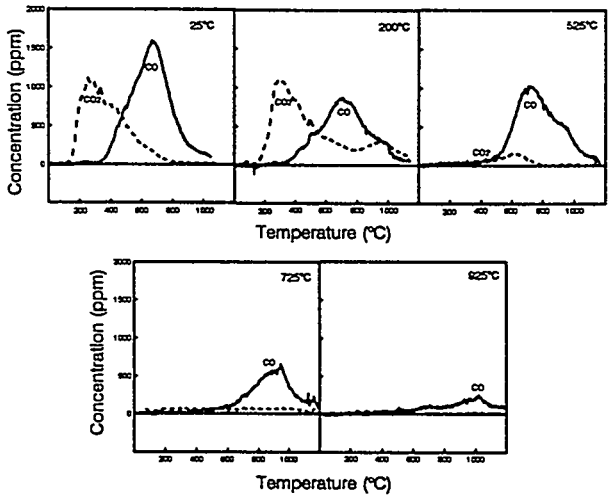

Figure 12. TPD Profiles of HNO3 Treated Calgon Carbon.

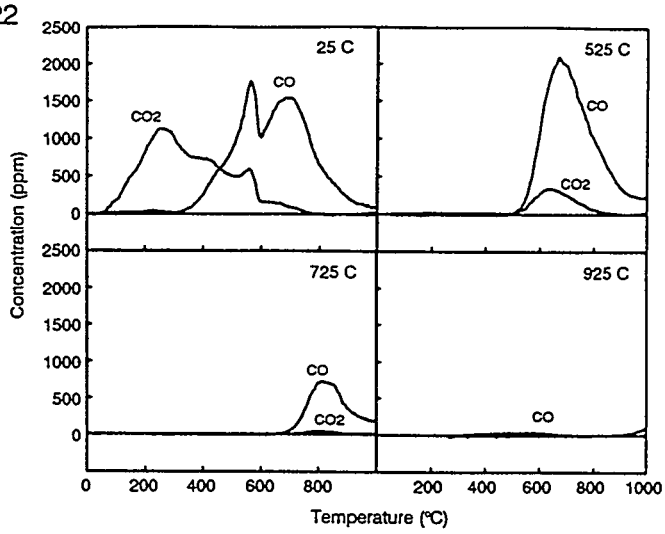

Figure 9. TPD Profiles of HNO3 Treated IBC-102 Char.

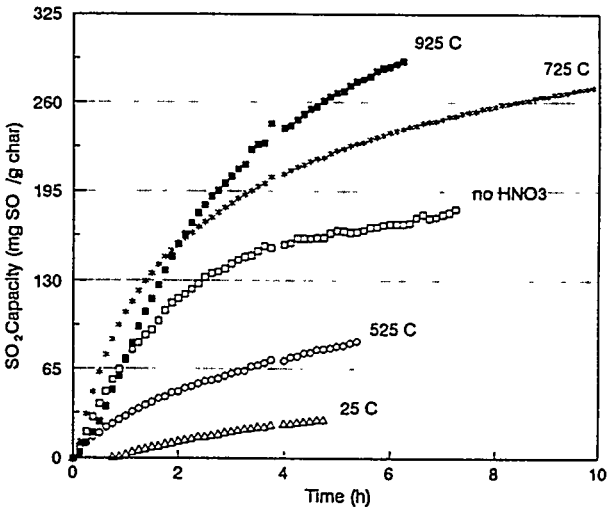

Figure 10. Kinetics of SO2 Adsorption on HNO3 Treated IBC-102 Chars.

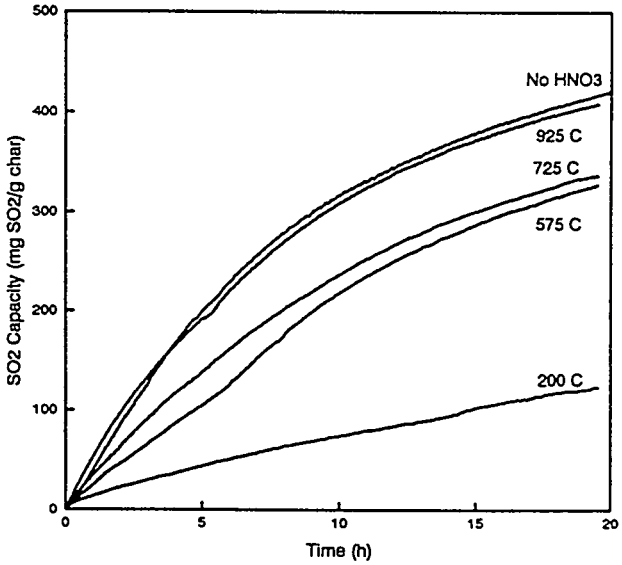

Figure 11. Kinetics of SO2 Adsorption on HNO3 Treated Calgon Carbon.

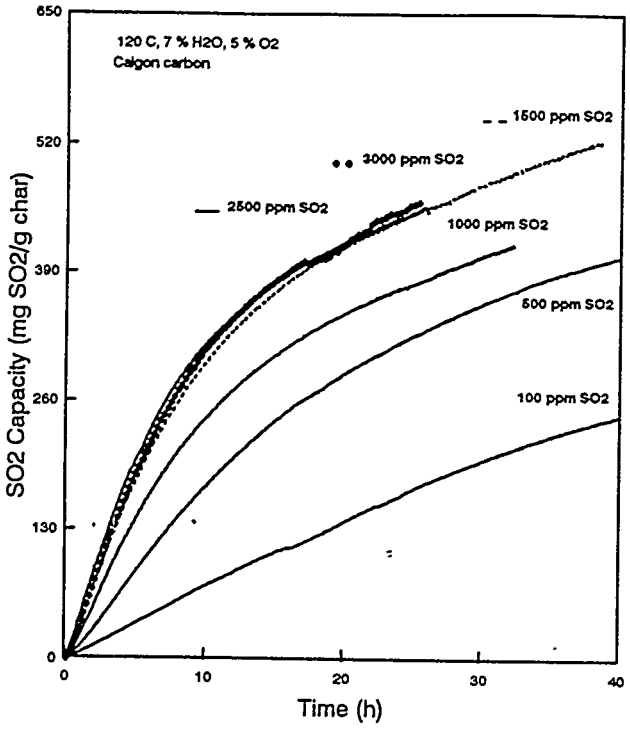

Figure 13. Effect of [SO2] on SO2 Capacity of Commercial Activated Carbon.

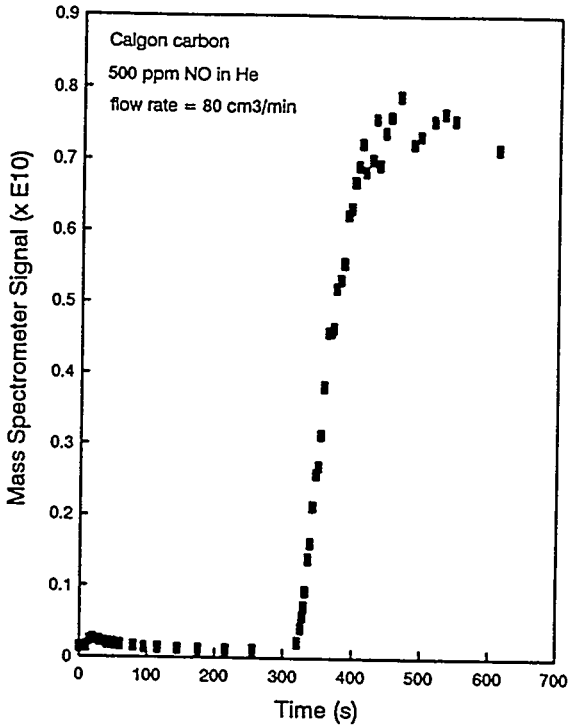

Figure 15. Typical NO Breakthrough Curve.

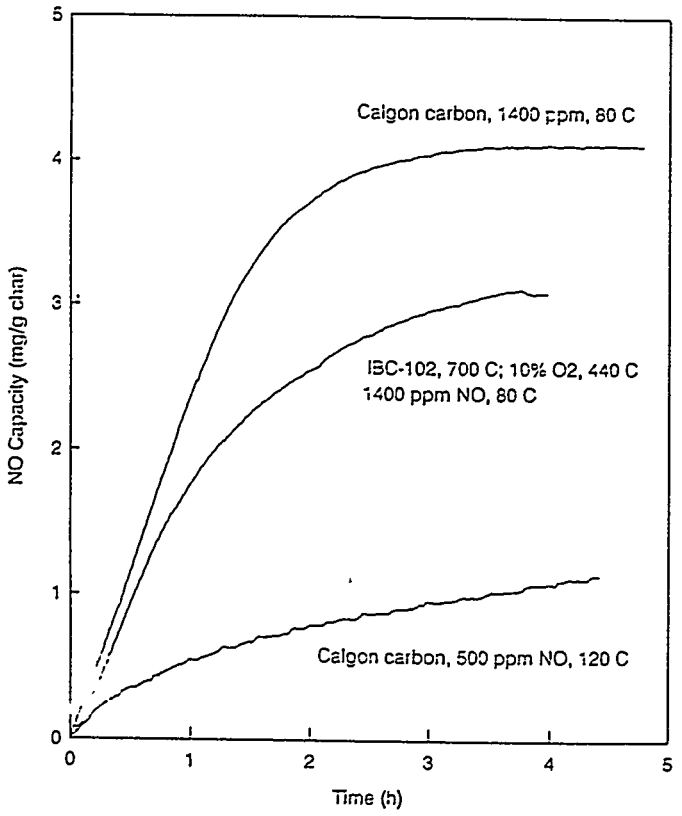

Figure 14. Nitric oxide adsorption on IBC-102 char and Calgon activated carbon.

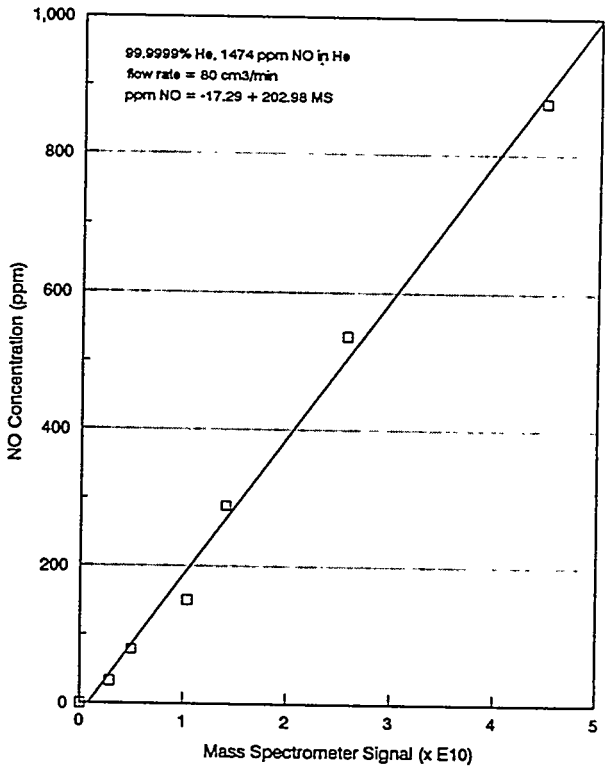

Figure 16. Typical NO Calibration Curve.