FINAL TECHNICAL REPORT
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Project Title: **DEVELOPMENT OF ACTIVATED CHAR FOR COMBINED SO_2/NO_x REMOVAL**

ICCI Project Number: 96-1/2.1A-7
Principal Investigator: Anthony A. Lizzio, ISGS
Other Investigators: Sheila Desai, Gwen A. Murphy, Gwen L. Donnals, John M. Lytle, ISGS; Bret H. Howard, John L. Haslbeck, NOXSO
Project Manager: Ronald H. Carty, ICCI

ABSTRACT

The NOXSO Corporation has developed under the DOE Clean Coal Technology Program a dry, post-combustion flue gas treatment system that uses a regenerable sorbent in a fluidized bed to remove SO_2 and NO_x from coal combustion flue gas. The process is especially attractive for use with high sulfur coals because it generates a saleable sulfur by-product, and creates no new waste streams. The actual cost of the sorbent presently used in the NOXSO process, alumina beads impregnated with 2.5% sodium, is greater than the projected cost of an activated char recently developed by the ISGS for cleanup of incinerator flue gas. Thus, an opportunity exists to incorporate ISGS activated char into the NOXSO flue gas treatment process.

The goal of this project, a cooperative effort between the ISGS and NOXSO, was to develop a low cost activated char from Illinois coal that can be used to effectively remove SO_2 and NO_x from coal combustion flue gas. Activated chars were prepared from IBC-102 coal in both granular and powdered form. In single (SO_2 or NO_x) component tests, the SO_2 capacity of one IBC-102 char was greater than that of a commercial activated carbon (Centaur carbon). NO_x removal with this char was one order of magnitude greater than with Centaur carbon. Single and multicomponent (SO_2/NO_x) removal tests performed by NOXSO showed that this char worked better than the NOXSO sorbent in single component tests, whereas the NOXSO sorbent removed more NO_x in multicomponent tests. Additional experiments were performed on IBC-102 char to examine the competitive effects of H_2O and SO_2 on low temperature NO_x removal (120°C). The SO_2 capacity of the char was not affected by NO in the flue gas, however, both H_2O and SO_2 appeared to inhibit NO adsorption. Several new types of chars were prepared to overcome the inhibitory effects of H_2O and SO_2. One char removed 90% of the NO_x for 6 h and 95% of the SO_2 for 14 h at a space velocity of 3000 h^{-1}. There is no commercial activated carbon on the market today that can remove both SO_2 and NO_x from coal combuustion flue gas. Further modification of the char preparation procedure eliminated two of the five production steps in order to lower production costs. These two chars were then tested by NOXSO and their performance compared to that of the NOXSO sorbent. The SO_2 capacity of the lower cost char was four times greater than that of the NOXSO sorbent. The NO_x removal capability of this char was comparable to that of the NOXSO sorbent in the first adsorption cycle, however, the char retained only 20% of its NO capacity in subsequent cycles. Further work is needed to optimize the char regeneration conditions and to incorporate this char into the NOXSO process.

Pages 11 through 36 contain proprietary information.

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/NO_x removal should have a high adsorption capacity for SO_2 and NO_x, rapid SO_2/NO_x adsorption kinetics, low reactivity with oxygen, minimal loss of activity after regeneration, high mechanical strength, and low cost.

In September 1993, the ISGS initiated Phase I of an ICCI research program (Production and Use of Activated Char for Combined SO_2/NO_x Removal, Lizzio et al., 1994; 1995) to investigate the possibility of using activated char derived from Illinois coal to clean combustion flue gas. Activated chars were produced from IBC-102 coal under a wide range of pyrolysis and activation conditions and their SO_2 adsorption capacities were measured. A novel char preparation method was developed to prepare chars with SO_2 capacities significantly greater than those of commercial activated carbons. The work performed in Phase I attracted significant commercial interest, in particular, that of STEAG Aktiengesellschaft, a German firm seeking to market its technology in the U.S. for cleaning flue gas from incinerators. STEAG has pioneered flue gas cleanup in Europe using a low surface area (270 m^2/g) activated carbon made from German brown coal. They are presently seeking out suppliers to provide them with a low cost (< \$300/ton) activated char for their U.S. market. STEAG estimates a market potential of 80,000 tons/year of activated char (160,000 tons of coal) within five years, assuming 10% of U.S. incinerators adopt their technology, to meet needs emanating from anticipated regulation 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.

As part of Phase I activities, laboratory conditions were identified to produce a suitable low cost (< \$350/ton) adsorbent from an Illinois Colchester No. 2 coal. 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 rotary tube kiln. A three step process, which included preoxidation, pyrolysis and activation, was used to produce an activated char with an SO_2 adsorption capacity almost twice that of the char presently used by STEAG. The adsorbent was shipped to Germany and tested on a slip stream of flue gas from a commercial incinerator. Results indicated that the char was effective in removing more than 99.7% of the SO_2, mercury, dioxins and furans from the incinerator flue gas.

The pilot scale production of low cost activated char by the ISGS attracted the attention of several organizations interested in utilizing inexpensive carbon to clean flue gas. One such company is the NOXSO Corporation, which has developed under the U.S. DOE Clean Coal Technology Program, a high efficiency, dry, post-combustion flue gas treatment system that uses a regenerable sorbent to simultaneously remove SO_2 and NO_x from coal combustion flue gas. The process has no impact on boiler performance, is compact, easy to retrofit, generates a saleable by-product (sulfuric acid, elemental sulfur, or liquid SO_2), and creates no new waste streams, a distinct advantage over conventional FGD processes. The cost of the sorbent presently used in the NOXSO process, alumina substrate impregnated with 2.5% sodium, is $2,000/ton as compared to a projected $350/ton for ISGS activated char. The NOXSO process during normal operation for a 500 MW power plant typically consumes 2,000 tons of sorbent per year; thus, there could be a significant savings in operating costs if low cost activated char is utilized. The integration of additional SO_2/NO_x control into the NOXSO process via low cost activated char, creates a more cost effective and comprehensive pollution control system. The concept encourages the economical and environmentally acceptable use of Illinois coal in two ways: first, as feedstock in the production of the activated char, and second, by improving the NOXSO process.

The goal of the Phase II program, a joint effort between the ISGS and NOXSO, was to develop an activated char from Illinois coal that can be used in the NOXSO process, either alone or in conjunction with NOXSO sorbent, to effectively remove SO_2 and NO_x and other air toxics from coal combustion flue gas. The project consisted of seven tasks. In Task 1, activated chars were prepared from Illinois coal (IBC-102) by a variety of methods in both granular and powdered form. The physical/chemical properties of the char were optimized to enhance its SO_2/NO_x removal capabilities. In Task 2, the combined SO_2/NO_x removal capabilities of the prepared chars were evaluated by the ISGS. In Task 3, selected chars were further tested by NOXSO in a fixed-bed adsorber for SO_2/NO_x removal and regenerability. In Task 4, the physical/chemical properties of selected chars were determined by the ISGS and NOXSO. In Task 5, gram quantities of an optimized char underwent combined SO_2/NO_x removal tests in a fluidized-bed reactor; its performance was compared to that of the NOXSO sorbent. In Task 6, if a suitable activated char was identified, process flowsheets for the production and use of the char would be developed. In Task 7, technical and management reports were prepared and submitted to the ICCI.

In the first year (1995-1996) of the Phase II program, a California pellet mill was used to produce 20 pounds of 6 mm diameter cylindrical IBC-102 coal pellets. The pelletized steam activated char had excellent mechanical strength and an SO_2 adsorption capacity (120°C) comparable to that of the NOXSO sorbent. To enhance both SO_2 and NO_x removal capabilities, the pelletized steam activated char was subjected to a liquid phase oxidation/thermal desorption treatment. The SO_2 adsorption capacity of this char surpassed that of its granular counterpart and the catalytic carbon (Centaur carbon) recently developed by the Calgon Carbon Corporation. The NO_x removal capacity (120°C) of the oxidized/thermally desorbed char was nearly twenty times greater than that of the Centaur carbon. NOXSO performed single and multicomponent SO_2/NO_x removal tests on several ISGS activated chars. A simulated flue gas containing either or both SO_2 (1,200 ppm) and NO (400 ppm) was used. The oxidized/thermally desorbed char adsorbed more SO_2 and NO_x than the NOXSO sorbent in single component tests, whereas the NOXSO sorbent adsorbed more NO_x in combined SO_2/NO_x removal tests. The challenge became to design a carbon that could remove simultaneously both SO_2 and NO_x from coal combustion flue gas.

This year, additional experiments were performed on IBC-102 char to examine the competitive effects of H_2O and SO_2 on low temperature NO_x removal (120°C). The SO_2 capacity of the char was not affected by NO in the flue gas, however, both H_2O and SO_2 appeared to inhibit NO adsorption. Several new chars were prepared to overcome the inhibitory effects of H_2O and SO_2 on NO_x removal. One char removed 90% of the NO_x for 6 h and 95% of the SO_2 for 14 h at a space velocity of 3000 h^{-1}. There is no commercial activated carbon on the market today that can remove both SO_2 and NO_x from coal combustion flue gas. Through further modification of this novel char preparation method, it was possible to eliminate two of the five production steps without hindering performance. Both new chars were tested by NOXSO and their performance compared to that of the NOXSO sorbent. The SO_2 capacity of the lower cost char was four times greater than that of the NOXSO sorbent and was completely regenerable. The NO_x removal capability of this char was comparable to that of the NOXSO sorbent in the first adsorption cycle, however, the char retained only 20% of its NO capacity in subsequent cycles. Further work would be needed to optimize the char regeneration process conditions. The fluidization properties and crush strength of the char need also be determined. The potential of activated char in carbon injection-like processes such as the one being developed by NOXSO and FLS miljø a/s in Copenhagen, Denmark should also be investigated. NOXSO has the capability to perform large scale tests with activated char in both a 10 in. ID fluidized-bed adsorber and in a gas suspension adsorber, which simulates a carbon injection process with baghouse and recycle. For these tests, hundred pound quantities of activated char would be needed.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.