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

ICCI Project Number: 95-1/2.1A-11
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ABSTRACT

The ISGS recently produced a low cost activated char from Illinois coal that removes more than 99.7% of the SO_2, mercury, dioxins and furans from incinerator flue gas. The objective of this project is to further develop activated char suitable for use in simultaneous removal of SO_2 and NO_x from coal combustion flue gas. 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 cost of the sorbent presently used in the NOXSO process, alumina beads impregnated with 5% sodium, is greater than the projected cost of the char developed by the ISGS. An opportunity exists to incorporate ISGS activated char into the NOXSO flue gas treatment process. Commercial demonstration of the NOXSO process is scheduled to begin in December 1997 at the 150 MW Warrick power plant in Newburgh, Indiana. The NOXSO process will initially require one million pounds of sorbent, which will need replacement after each year of operation. The Warrick power plant burns 500,000 tons of high sulfur (3.3%) Illinois Basin coal per year. A successful demonstration of the NOXSO process will forgo usage of low sulfur western coal at this site and demonstrate a technology that can increase clean use of high sulfur Illinois Basin coal.

The ultimate goal of this project, a cooperative effort between the ISGS and NOXSO, is 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. Twenty pounds of cylindrical pellets were made from IBC-102 coal. A steam activated char prepared from these pellets had an SO_2 adsorption capacity similar to that of its granular counterpart. To enhance its SO_2/NO_x adsorption capacity, the pelletized steam activated char was subjected to a liquid phase oxidation/thermal desorption treatment. The SO_2 capacity (120°C) of this char surpassed that of the best carbon catalyst (Centaur carbon). A fixed bed adsorber coupled to a mass spectrometer was used to measure NO_x breakthrough curves for various IBC-102 chars and commerical carbons. The NO_x removal capability (120°C) of the oxidized/thermally desorbed char was an order of magnitude greater than that of the Centaur carbon. NOXSO performed combined SO_2/NO_x removal tests on several ISGS activated chars. In single component tests, the SO_2 and NO_x removal capabilities of the steam activated char and the oxidized/thermally desorbed char compared favorably with those of the NOXSO sorbent, respectively. In multicomponent tests (both SO_2 and NO_x in the flue gas) the NOXSO sorbent performed better than either ISGS activated char with regard to NO_x removal. It appears that similar adsorption sites on the char surface compete for SO_2 and NO_x and that SO_2 more strongly adsorbs on these sites. The regenerability of activated char was also studied. Significantly lower temperatures can be used to regenerate activated char (350°C in air) compared to those needed for the NOXSO sorbent (620°C in methane). Several options are being considered for integrating ISGS activated char into the NOXSO process based on the unique SO_2/NO_x removal properties of activated char.

Pages 17 through 32 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 with funding from the ICCI/DOE initiated Phase I of a 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/NO_x adsorption properties were characterized. A novel char preparation method was developed to prepare chars with SO_2 and NO_x adsorption 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. A meeting was held in Champaign, IL in March 1994, between representatives of the ISGS, ICCI, ICDB and STEAG to discuss the possible use of Illinois char in the STEAG \a\c\t™ process. STEAG, which has pioneered flue gas cleanup in Europe using a low surface area (270 m^2/g) activated carbon made from German brown coal, is 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 (< \$300/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, 10 ft. heated zone, externally fired rotary tube kiln. A novel 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 for testing on a slip stream of flue gas from a commercial incinerator. Recent test results indicate that the ISGS activated char was effective in removing more than 99.7% of the SO_2, mercury, dioxins and furans from the incinerator flue gas.

The successful pilot scale production of low cost activated char by the ISGS has 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 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 5% sodium, is greater than the projected cost of ISGS activated char. The NOXSO process during normal operation for a 500 MW power plant typically consumes 2,000 tons of sorbent per year. It is, therefore, in the best interest of NOXSO to investigate the possibility of using a lower cost sorbent such as activated char made from Illinois coal ($326/ton, Lizzio et al., 1995; Kruse et al., 1996).

The technical and economic feasibility of integrating the SO_2/NO_x removal capabilities of ISGS activated char into the NOXSO flue gas treatment system needs to be determined. The fluidized-bed configuration, which is a key attribute to the NOXSO process, is thought to be the optimal reactor configuration for simultaneous removal of SO_2 and NO_x as well as other air toxics from coal combustion flue gas. Through the installation of one additional fluidized bed of activated char within the main adsorber vessel, process improvement may be realized in terms of removal of vapor phase mercury and other air toxics as well. The commercial market potential for NOXSO technology is significant. Under Phase II of the Clean Air Act Amendments (CAAA), NOXSO expects U.S. and Canadian market requirements for SO_2/NO_x control systems to be as high as 10,000 MW annually in the years 1998-2005, roughly equivalent to thirty installations (300 MW average size) per year.

This project, a joint effort between the ISGS and NOXSO, seeks to integrate additional SO_2/NO_x control into the NOXSO process via low cost activated char, thereby creating a more cost effective and comprehensive pollution control system. The goal is 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 consists of seven tasks. In Task 1, activated char will be prepared from Illinois coal with optimal physical/chemical properties for combined SO_2/NO_x removal. In Task 2, kinetic and equilibrium adsorption studies will be performed using themogravimetric analysis/mass spectrometry to evaluate the SO_2/NO_x adsorption properties of the chars. In Task 3, a selected char will be tested in a fixed-bed adsorber at the NOXSO Research Center in Clairton, PA for its ability to remove SO_2/NO_x from simulated flue gas mixtures. In Task 4, the physical (surface area, pore size distribution), chemical (functional groups) and fluidization properties (terminal velocity, attrition resistance, crush strength) of the chars will be evaluated. In Task 5, a selected char will be integrated into a 10 in. ID multistage, fluidized-bed adsorber and tested; its SO_2/NO_x removal performance will be assessed and compared to that of the NOXSO sorbent. In Task 6, if a suitable activated char is identified, process flowsheets for the production and use of activated char will be developed. In Task 7, technical and management progress reports will be prepared and submitted to the ICCI.

A pelletized char of considerable mechanical strength is required for the fluidized-bed adsorber in the NOXSO process. Using the California pellet mill at the ISGS, twenty pounds of 6 mm diameter cylindrical pellets were made from IBC-102 coal and a suitable binder. The coal pellets were larger than the NOXSO sorbent (1.6 mm diameter), but showed a 25% size reduction after pyrolysis and steam activation. Based on particle density and size, the fluidization properties of the pelletized steam activated char should compare favorably with those of the NOXSO sorbent. 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 SO_2/NO_x removal capabilities, the pelletized steam activated char was subjected to a liquid phase oxidation/thermal desorption treatment previously developed for granular carbon. The SO_2 adsorption capacity of the treated pelletized IBC-102 char surpassed that of its granular counterpart and a catalytic carbon (Centaur carbon) recently developed by the Calgon Carbon Corporation. The NO_x removal capabilities of IBC-102 char were also evaluated and compared to those of the Centaur carbon. The NO_x removal capacity (120°C) of the oxidized/thermally desorbed char was nearly twenty times greater than that of the Centaur carbon. NO_x removal using this char, however, decreased when initially exposed to air. A new method to preserve the active sites for SO_2/NO_x removal was developed. Preliminary results are promising, but additional work is needed to optimize this novel char preparation technique.

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. Test results showed that 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 the combined SO_2/NO_x removal test. The presence of SO_2 in the flue gas actually catalyzes the removal of NO_x for the NOXSO sorbent, i.e., SO_2 adsorbs on the surface and forms a complex that attracts NO_x. On the other hand, it appears that SO_2 and NO_x compete for similar sites on the char surface and that SO_2 adsorption is stronger. Further work is needed to gain insight into the mechanism of combined SO_2/NO_x removal with carbon. Various sections of the NOXSO process that could benefit from either higher SO_2 or NO_x removal rates, e.g., downstream of the sorbent heater or in the fluidized-bed adsorber itself, are being explored. It appears that less energy is required to regenerate activated char. Regeneration of activated char can be done at much lower temperatures compared to the NOXSO sorbent. Tests indicated that SO_2 adsorbed on activated char at 120°C desorbs at temperatures between 300 and 380°C when heated in air. Regeneration of the NOXSO sorbent requires the use of methane and a temperature of 620°C.

Next year, chars will continue to be developed for SO_2, NO_x and combined SO_2/NO_x removal. Parametric tests to further evaluate the effects of process conditions on the the SO_2/NO_x removal capabilities of activated char will be performed. There are several locations in the NOXSO process besides the fluidized-bed adsorber that could benefit from the proven SO_2 and NO_x removal capabilities of ISGS activated char. The addition of activated char into each location will be addressed and tested accordingly. Two different particle sizes will also be examined. One suitable for the NOXSO fluidized-bed adsorber and one suitable for the gas suspension adsorber being developed by NOXSO and FLS miljø a/s in Copenhagen, Denmark. The fluidization properties and mechanical strength of the tested chars will also be determined.

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