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Project Title: **DEVELOPMENT OF NEW AND IMPROVED SORBENTS FOR THE COBRA PROCESS**

ICCI Project Number: 99-1/1.2A-2
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ABSTRACT

The overall objective of this program was to continue further development of new and improved novel copper-based sorbents for removal of SO_2 and NO_x from flue gas, in support of the Copper Oxide Bed Regenerable Adsorber (COBRA) process. The targeted areas of sorbent improvement included higher reactivity and effective sulfur capacity, higher crush strength, and higher catalytic activity for NO_x reduction, which can lead to improvement in process control and economic utilization of the sorbent.

To achieve this objective, a total of twenty one (21) alumina support materials and forty one (41) new sorbents were formulated using various preparation techniques. The crush strengths of these sorbents were determined. Thirteen (13) new sorbents were evaluated for their SO_2 sorption capacities in apacked bed reactor. The regenerability of seven (7) sorbents that exhibited similar or higher sorption capacities than the baseline sorbent, were determined over three (3) sulfation/regeneration cycles. Based on the results of these tests, the sorbent designated as S43-175 was selected as the "best" formulation for durability studies. A test series consisting of 20 sulfation/regeneration cycles was conducted with this sorbent in the packed-bed reactor. The catalytic activities of the baseline sorbent as well as several new sorbents for NO_x removal were also determined.

Four (4) sorbent formulations exhibited improvement in sulfur capacity <u>and</u> in crush strength compared to the baseline sorbent. The "best" sorbent formulation (S43-175) has 3.5 times sulfur capacity and 1.5 times crush strength compared to the baseline (Alcoa) sorbent. The reactivity of the S43-175 sorbent after 20 cycles is about twice that of the baseline sorbent. The crush strength of the S43-175 sorbent does not appear to be adversely affected by the long-term durability test.

The new sorbents have higher catalytic activities than that of the baseline sorbent. The extent of NO_x removal with the new sorbents in the sulfated form exceeds 99% compared to 88.5% for the baseline sorbent. The extent of NO_x removal does not appear to be affected by the long-term durability test.

EXECUTIVE SUMMARY

During coal combustion, sulfur in coal is released in the form of sulfur dioxide (SO_2) in the flue gas and a small fraction of nitrogen in the form of NO_2 and NO, commonly referred to as NO_x. The SO_2 and NO_x emissions are very damaging to the environment because they combine with moisture to form acids which then fall as acid rain. To protect the environment, legislation was introduced requiring electric utilities to adopt available technology for removal of pollutant gases and particulates from coal combustion flue gases so that the increased use of coal is done in an environmentally acceptable manner.

The threat from acid rain is a greater concern in Illinois where over 90% of the high sulfur coal mined is consumed by electric utilities that are based on pulverized coal combustion, while only a very small fraction of the coal-based power plants in Illinois is currently equipped with Flue Gas Desulfurization (FGD) processes.

The development of the Copper Oxide Bed Regenerable Absorber (COBRA) process, which is based on moving-bed crossflow reactor design for the combined removal of SO_2, NO_x, and particulates, has been pursued in conjunction with the use of Illinois coal. This process has been demonstrated at the nominal half-megawatt scale at the Illinois Coal Development Park in Carterville, Illinois.

The overall levelized cost of the COBRA process is very sensitive to the sorbent price. Any improvement in sorbent performance would reduce capital costs for process equipment as well as for the sorbent itself. Therefore, given the tremendous effect of the sorbent related costs on the overall process cost, it is necessary to conduct a carefully designed systematic study to improve sorbent performance to significantly lower the overall cost of the COBRA process.

Development of improved sorbents for the COBRA process has been pursued in an earlier DCCA/OCDM/ICCI funded project (ICCI project No. 98-1/1.1C-2). In this project, the baseline sorbent (produced by Alcoa) was evaluated in packed-bed experiments. Parametric studies were carried out to determine the effects of operating parameters on the performance of the sorbent. Long term durability of the baseline sorbent was assessed. Physical and chemical properties of the baseline sorbent were also determined. A number of new sorbent formulations were prepared using a modified sol-gel technique. These sol-gel sorbents have significantly higher crush strength and similar surface area compared to the baseline sorbent. However, the reactivities of these sorbents, in the pellet form, were lower than that of the baseline sorbent. To improve the performance of the new sorbents, the chemical composition and the preparation technique were modified. The results indicate that, although the reactivity of the sorbents improved by these modifications, the crush strength of the sorbents significantly decreased. Therefore, additional work was needed to optimize the sorbent composition and preparation technique to further improve the performance of the sorbent.

The overall objective of this program was to continue further development of new and improved novel copper-based sorbents for removal of SO_2 and NO_x from flue gas, in support of the Copper Oxide Bed Regenerable Adsorber (COBRA) process. The targeted areas of sorbent improvement included higher reactivity and effective sulfur capacity, higher attrition resistance, which can lead to improvement in process control and economic utilization of the sorbent.

To achieve this objective, a total of twenty one (21) alumina support materials were formulated using various preparation techniques. To improve the porosity and pore size distributions of the sorbents/alumina supports, a number of boehmite sols were produced using ammonium hydroxide as a hydrolysis catalyst. Various acidic pH levels were tested during gelation of the sols when producing alumina pellets to investigate the effect of pH on the macroporosity of the material. To lower sorbent cost, the aluminum tri-secondary butoxide (i.e., ALTSB, $Al(OC_4H_9)_3$) that was used as the raw material precursor for production of alumina sol was replaced by the less expensive aluminum isopropoxide (i.e., ALISOP, $Al(OC_3H_7)_3$). The sorbent preparation technique was simplified by reducing the number of steps required for producing the sol, resulting in the reduction of the sol production time from 15 hours to 1-4 hours.

The results indicate that, the alumina pellets produced using the simplified technique with shorter preparation time (i.e., 1-4 hr) have higher crush strengths compared to the alumina from a 15-hr sol. The analysis of these materials indicates that the alumina produced by the simplified technique have comparable physical characteristics to those produced earlier.

A total of forty one (41) new sorbents were formulated using the lower cost materials and/or simplified preparation techniques. The crush strengths of these sorbents were determined for comparison with the baseline sorbent produced by Alcoa.

Thirteen (13) new sorbents were evaluated for their SO_2 sorption capacities in the packed bed reactor. The regenerability of seven (7) sorbents that exhibited similar or higher sorption capacities than the baseline sorbent were determined over three (3) cycles. Based on the results of these tests, the sorbent designated as S43-175 was selected as the "best" formulation for durability studies. A test series consisting of 20 sulfation/regeneration cycles was conducted with this sorbent in the packed-bed reactor. The catalytic activities of the baseline sorbent as well as several new sorbents for NO_x removal were also determined.

Among the sorbents developed in this project, four (4) sorbent formulations exhibited more than 23% improvement in sulfur capacity and more than 45% improvement in crush strength compared to the baseline sorbent. The best result was obtained with the sorbent designated as S43-175, which has 3.5 times sulfur capacity and 1.5 times crush strength compared to the Alcoa sorbent. The sorbent designated as 167-WI, which is produced by wet impregnation of a sol-gel alumina, has 25% higher sulfur capacity and 7 times higher

crush strength than the baseline sorbent. This formulation was selected as a "second best" sorbent.

A "life-cycle" test consisting of 20 sulfation/regeneration cycles was conducted with the sorbent designated as S43-175 in the packed-bed reactor.   The results of this series of tests indicate that the effective sulfur capacity of the S43-175 sorbent after 20 cycles is still about twice that of the baseline sorbent, while the rates of decrease in the sulfur capacities for the two sorbents are similar. These results indicate that the rate of "fresh sorbent make-up" needed to continuously maintain the desired level of desulfurization with S43-175 is significantly lower than that of the baseline sorbent. The results also indicate that the crush strength of the S43-175 sorbent is not adversely affected by the long-term durability test.

The catalytic activity of the baseline sorbent for removal of NO_x from flue gas was determined in a series of tests conducted at different operating conditions.   The parameters studied included the effect of bed materials as well as gas composition on the extent of NO_x removal from the gas stream. The baseline tests for this series were conducted at 400°C and 2000 hr^{-1} space velocity using a gas mixture containing 500 ppmv of NO_x and 500 ppmv of NH_3. The results of these tests indicate that the baseline sorbent is capable of removing 69.0% of the NO_x in the regenerated state, while in the sulfated state the NO_x removal will increase to 88.5%. The extent of NO_x removal in the absence of NH_3 is essentially zero confirming that NO_x removal is accomplished through reduction by ammonia. The regenerated sorbent in the reduced form exhibits slightly lower catalytic activity than the oxidized sorbent (64% compared to 69%). The results also indicate that the extent of the extent of NO_x removal is linearly related to the NH_3/NO_x ratio in the flue gas.

Comparison of the catalytic activities of the baseline and new sorbents developed in this program indicates that the new sorbents have higher catalytic activities than that of the baseline sorbent. The extent of NO_x removal with the new sorbents in the sulfated form exceeds 99% compared to 88.5% for the baseline sorbent. The catalytic activity of the S43-175 after 20 cycles was also determined. The extent of NO_x removal was 99.3% indicating that the long-term durability test did not affect the catalytic activity of this sorbent.

OBJECTIVES

The overall objective of the program was to continue further development of new and improved novel copper-based sorbents for removal of SO_2 and NO_x from flue gas, in support of the Copper Oxide Bed Regenerable Absorber (COBRA) process which is currently under development by Sargent & Lundy under the joint sponsorship of DCCA and the U.S. Department of Energy (DOE). The targeted areas of sorbent improvement included utilization of low cost raw materials, higher reactivity and effective sulfur capacity, and higher attrition resistance that can lead to improvement in process control and economic utilization of the sorbent.

The specific objectives of the work were to:

- Synthesize a number of new and improved sorbents with desired characteristics.

- Evaluate new sorbents to identify the "best" sorbent formulation, based on cost, chemical reactivity, regenerability, catalytic activity, as well as all other relevant physical and chemical properties.

- Demonstrate the overall durability of the "best" sorbent in a "life-cycle" test at the optimum process conditions.

INTRODUCTION AND BACKGROUND

Coal-fired power plants currently account for 56% of the electricity used in the United States.[1] With diminishing petroleum supplies, public concern regarding the overall safety of nuclear power, and unavailability of alternative large-scale sources of energy, coal continues to play a leading role in the total energy picture. The most economical use of coal in the future is likely to continue to be the generation of electricity, as has been the case for decades. Significant research has been conducted over the past two decades to increase the efficiency of power generation from coal. However, even if promising new technologies, such the Integrated Gasification Combined Cycle (IGCC), reach the commercialization stage, conventional pulverized coal combustion technology will continue to dominate the market share of the power generation industry.

During coal combustion, sulfur in coal is released in the form of sulfur dioxide (SO_2) in the flue gas and a small fraction of nitrogen in the form of NO_2 and NO, commonly referred to as NO_x. The SO_2 and NO_x emissions are very damaging to the environment because they combine with moisture in the atmosphere to form acid rain. The threat of acid rain formation becomes a significant concern by the utilization of high-sulfur coal. Thus, the removal of SO_2 from flue gases prior to their discharge to the atmosphere is essential to prevent air pollution.

For these reasons, government regulations have been introduced and have become progressively more stringent. In the Clean Air Act Amendments (CAAA) of 1990, for

example, legislation was introduced requiring electric utilities to adopt available technology for removal of pollutant gases and particulates from coal combustion flue gases so that the increased use of coal is done in an environmentally acceptable manner.

The above environmental issues are of greater concern in Illinois where over 90% of the coal mined is consumed by electric utilities that are based on pulverized coal combustion.[2] Furthermore, only a very small fraction of the coal-based power plants in Illinois is currently equipped with flue gas desulfurization (FGD) processes. The high sulfur content of Illinois coal, the imposition of strict limits on SO_2 emissions, unavailability of FGD processes at the majority of existing power plants in Illinois, and the growing EPA concern with the disposal of solid residues from coal combustion and conventional FGD processes, have made flue gas cleanup a major focus for the coal research and development program sponsored by the Illinois Department of Commerce and Community Affairs' Office of Coal Development and Marketing (DCCA/OCDM).

Removal of particulates, SO_2, and NO_x can be achieved through a number of ways that include: (a) pre-combustion cleaning; (b) in-situ cleaning, and (c) post-combustion cleaning.[3] As more high-sulfur coal is used and because of stricter and stricter government regulations, stack gas desulfurization has been practiced more commonly to meet air pollution emission standards. A number of processes have been developed for flue gas desulfurization (FGD). These include dry systems, where a dry solid is used to absorb SO_2 from stack gas, and wet systems, where a solution or slurry is used instead. Some systems are known as throwaway systems because the absorbing substance is discarded. In recovery systems, the absorbing material is regenerated and re-used while the sulfur is recovered in the form of a saleable byproduct.[1]

A concept that has received significant attention is the development of processes for the combined removal of SO_2, NO_x, and possibly particulates from flue gases using dry regenerable sorbents.[4-6] The National Energy Technology Laboratory (NETL) of the U.S. DOE has pursued the development of this concept for the last three decades. The sorbents employed consist essentially of metal oxides supported on an alumina matrix. One of these processes is the copper oxide process, which is based on the use of a dry, regenerable copper-based sorbent at moderate temperatures. The sorbents consist of copper oxide (CuO) supported on gamma alumina (γ-Al_2O_3), and are prepared through impregnation of alumina spheres approximately 3 to 6 mm (1/8 to 1/4 inch) in diameter, that are suitable for a moving-bed desulfurization reactor.[6-11]

Flue gas consisting of N_2, CO_2, H_2O, O_2, SO_2, and NO_x is passed through the desulfurization (or sulfation) vessel containing the sorbent. SO_2 reacts with the reactive component of the supported sorbent, i.e. CuO, and O_2 to form copper sulfate ($CuSO_4$). The desulfurization reaction is carried out at a temperature in the vicinity of 750°F, and may be represented by the following reaction:

$$CuO + SO_2 + \tfrac{1}{2} O_2 \; = \; CuSO_4 \qquad\qquad (1)$$

Following sulfation the sorbent is transferred to a regeneration vessel where it is contacted with a reducing gas, such as methane (CH_4), decomposing the sulfate to elemental copper (Cu) and a byproduct gaseous stream. Both the required regeneration temperature and the composition of the regeneration product gas depend on the reducing gas employed. When methane is used, it has been reported that regeneration can be conducted successfully at 800°F,[4] and the regeneration reaction may be described by the following reaction:

$$CuSO_4 + \tfrac{1}{2}\,CH_4 \;=\; Cu + SO_2 + \tfrac{1}{2}\,CO_2 + H_2O \qquad\qquad (2)$$
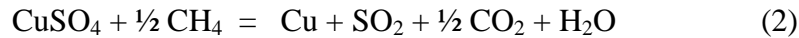
Following sulfate decomposition in the regeneration vessel the sorbent is sent back to the desulfurization unit for re-use. Upon exposure to flue gases, elemental copper is readily oxidized to CuO, thereby fully restoring the sorbent to its original fresh condition.

To reduce the NO_x content of the flue gas, ammonia (NH_3) is injected into the flue gas upstream of the absorber. The copper-based sorbent in the absorber acts as a catalyst for selective catalytic reduction of NO_x in the presence of NH_3 and O_2 by the following reactions:

$$4\,NO + 4\,NH_3 + O_2 \;=\; 4\,N_2 + 6\,H_2O \qquad\qquad (3)$$

$$2\,NO_2 + 4\,NH_3 + O_2 \;=\; 3\,N_2 + 6\,H_2O \qquad\qquad (4)$$
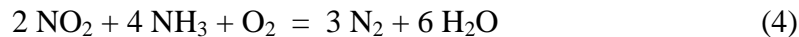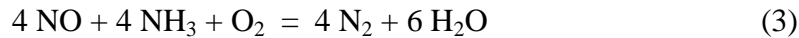
In the absence of oxygen, NO can be reduced by NH_3 --

$$6\,NO + 4\,NH_3 \;=\; 5\,N_2 + 6\,H_2O \qquad\qquad (5)$$
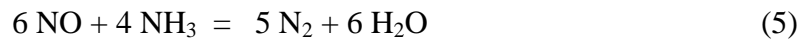
Depending on the operating condition, ammonia can also be oxidized by oxygen to form N_2 and/or NO --

$$4\,NH_3 + 3\,O_2 \;=\; 5\,N_2 + 6\,H_2O \qquad\qquad (6)$$

$$4\,NH_3 + 5\,O_2 \;=\; 4\,NO + 6\,H_2O \qquad\qquad (7)$$
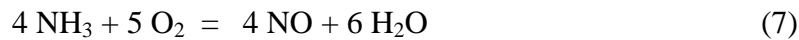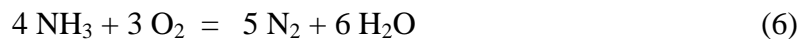
Combined SO_2/NO_x removal from flue gas by copper-based sorbents has been studied by many investigators.[6-19] The results of this studies indicate both SO_2 and NO_x removal efficiencies on the order of 95% can be achieved by copper oxide processes.

The results of various studies on selective catalytic reduction of NO by NH_3 over alumina supported copper-based catalysts suggest that the optimum NO_x removal efficiency can be achieved with NH_3/NO_x ratio in the range of 1.0-1.2.[20-23] These studies also suggest that the fraction of unreacted ammonia leaving the reactor (i.e., ammonia slip) strongly depends on the reactor configuration as well as the operating condition. However, in general, the ammonia slip appears to increase with increasing NH_3/NO_x ratio, especially above 1.

Based on the extensive laboratory and pilot scale data, the moving-bed copper oxide process has been selected as one of the most promising emerging technologies for SO_2 and NO_x removal from flue gases in the **U.S. DOE's <u>Combustion 2000 Program.</u>** A cooperative research and development agreement (CRADA) was established to study the integration of the copper oxide process into commercial power plants design for burning high sulfur Illinois coals and move this promising technology to commercialization. [12,13]

Preliminary economic analysis has indicated that the overall cost of the process is very sensitive to the sorbent cost. Properties of the sorbent such as SO_2 sorption capacity, catalytic activity, crush strength, and long-term durability are the key factors in determining the cost of the sorbent used in a moving-bed application. Any improvement in sorbent performance would reduce capital costs for process equipment as well as for the sorbent itself. Furthermore, replacement of sorbent lost to attrition adds to the O&M costs. Therefore, it is necessary to conduct a carefully designed systematic study to improve the sorbent performance to lower the overall cost of the copper oxide process.

Despite the significant impact of the sorbent cost on the overall economics of the process, no systematic attempt has been made to improve the sorbent to reduce the process cost. A possible exception has been the work of Lin et al.[24,29], who prepared alumina-supported copper oxide sorbents by sol-gel technique in an attempt to increase the CuO loading of the alumina support material, while maintaining high surface area. The results of their investigation indicate that the sorbents produced by <u>sol-gel</u> technique have very high crush strengths. The effective sulfur capacities of these sorbents were determined in a micro-reactor and were shown to be higher than that of a commercially produced UOP sorbent. The experimental evaluation of the sorbent in these studies were limited in scope and did not closely simulate the operating conditions prevailing in the copper oxide process. Furthermore, the effects of the key operating variables on the performance of the sorbent were not addressed. To the best knowledge of the investigators in this program, the catalytic activities of the these sorbents were not determined and no life-cycle test has been conducted to determine the long term durability of the sorbents

Development of improved sorbents for removal of SO_2 and NO_X has been pursued at IGT (now operating as Gas Technology Institute, GTI) in an earlier project sponsored by DCCA/OCDM/ICCI (ICCI project No. 98-1/1.1C-2).[30] The IGT fundamental research group evaluated the alumina-supported copper-based sorbent (that was used in the pilot plant scale testing of the copper oxide process at the Illinois Coal Development Park) to establish a baseline for comparison with the new sorbents. This baseline sorbent is produced by Alcoa. The evaluation included determination of all the relevant physical and chemical properties of the sorbent, such as crush strength, chemical reactivity, and long-term durability.

The results of these tests indicate that, at the baseline operating condition, the effective capacity of the baseline sorbent is about 15 g S/Liter sorbent and that a temperature change of ±100°F can affect the effective sorbent capacity by up to ±20%. The results

also indicate that the effective capacity of the sorbent generally improves with increasing regeneration temperature in the range of 850-950°F. Based on the results of multi-cycle durability tests conducted with the Alcoa sorbent, it appears that the effective sulfur capacity of this sorbent gradually decreases by about 10% after 20 sulfation/regeneration cycles. Furthermore, the results suggest that adsorption and/or formation of aluminum sulfate are probably contributing to SO_2 sorption during the sulfation stage. Under ICCI sponsorship, a number of new sorbent formulations were developed by incorporating and impregnating copper into an alumina support prepared using different preparation techniques. A comparison of the crush strength of various sorbents is presented in Figure 1 indicating that the crush strength of the alumina support materials produced in the earlier ICCI funded project is about 7 times higher than that of the Alcoa alumina support, while the crush strength of IGT's copper-based sorbents is about 3-4 times higher than that of the Alcoa sorbent.

Although, compared to the Alcoa sorbent, the new sorbents developed in the earlier ICCI-funded project have significantly higher crush strength and similar surface area, as shown in Figure 2, the effective sulfur loading of these sorbents in the pellet form is somewhat lower than that of the baseline Alcoa sorbent. Compared to the baseline Alcoa sorbent, the lower reactivities of the new sorbents developed in the earlier ICCI-funded project may be attributed to the significantly lower average pore diameter in these sorbent.

Given the encouraging results obtained in the previous ICCI-funded program, this project was initiated to continue further development of new and improved novel copper-based sorbents. The targeted areas of sorbent improvement include improvement in sorbent reactivity, sulfur capacity, crush strength, long term durability, as well as catalytic activity for NO_x reduction. However, no attempt was made to address the ammonia slip issue because the extent of ammonia slip is strongly dependent on the reactor configuration. These improvements can lead to improvement in process control and economic utilization of the sorbent.

In general, the reactivity of a sorbent is directly related to its key physical properties such as porosity and surface area, while crush strength is inversely correlated with these parameters. Therefore, the key to the development of improved sorbents is to strike the proper balance among all key parameters.

EXPERIMENTAL PROCEDURES

The work performed in the program was divided into the following tasks:

Task 1. Synthesis and Characterization of New and Improved Sorbents

Task 2. Evaluation of Desulfurization Reactivity, Regenerability, and Catalytic Activity

Task 3. Sorbent Durability Studies

Task 1. Synthesis and Characterization of New and Improved Sorbents

The objective of this task was to prepare new and improved copper-based sorbents with the desired characteristics for testing in Task 2 and Task 3 of this program.

In this task, the most promising sorbent formulations developed in the previous program (i.e., ICCI Project No. 98-1/1.1C-2) were selected for modification to further improve their performance. The parameters include modification of sorbent preparation technique, chemical composition, additives (to improve desirable characteristics), thermal treatment history (i.e., induration temperature and time), and utilization of low cost raw materials. Small quantities of each formulation were prepared for initial screening that was based on the sorbent crush strength. Larger quantities of formulations, which met minimum strength requirements, were produced for further characterization.

The formulations selected in this task were analyzed using standard characterization techniques including, BET surface area measurement, mercury porosimetry, crush strength, and wet chemical analysis.

In this task, in addition to the fresh sorbents, sulfated and regenerated sorbents from tests conducted in Tasks 2 and 3 were also characterized by the standard characterization techniques to provide insight into the changes in the physical and chemical properties of the sorbents during the cyclic sulfation/regeneration process.

Initial efforts were directed towards production of sorbents using simpler and more cost-effective methods. In this regard, the sorbent preparation technique was revised to produce sorbents with higher sorption capacity while maintaining their crush strength (compared to the sorbents produced in the previous ICCI funded project).

A total of twenty one (21) alumina support materials were produced by various preparation techniques. The crush strengths of these support materials were determined for comparison with the baseline support material produced by Alcoa.

To improve the porosity and pore size distributions of the sorbents/alumina supports, a number of boehmite sols were produced using ammonium hydroxide as a hydrolysis catalyst. Various acidic pH levels were tested during gelation of the sols when producing alumina pellets to investigate the effect of pH on the macroporosity of the material.

To lower sorbent cost, the aluminum tri-secondary butoxide (i.e., ALTSB, $Al(OC_4H_9)_3$), that was used as the raw material precursor for production of alumina sol, was replaced by the less expensive aluminum isopropoxide (i.e., ALISOP, $Al(OC_3H_7)_3$).

The sorbent preparation technique was simplified by reducing the number of steps required for producing the sol, resulting in the reduction of the sol production time from

15 hours to 1-4 hours. A number of boehmite sols were prepared using the new simplified technique to produce alumina support materials.

A total of forty one (41) new sorbents were formulated using the lower cost materials and/or simplified preparation techniques. The crush strengths of these sorbents were determined for comparison with the baseline sorbent produced by Alcoa.

The results obtained in this task are presented in the section "RESULTS AND DISCUSSION".

Task 2. Evaluation of Desulfurization Reactivity, Regenerability, and Catalytic Activity

The objective of this task was to identify the "best" sorbent formulation for durability studies in Task 3.

The tests in this task were carried out with the candidate sorbents produced in this program in the packed-bed reactor unit to determine the effectiveness of the sorbents for the removal of the SO_2 and NO_x over one (1) to three (3) cycles. The schematic diagram of the packed-bed unit is presented in Figure 3. The unit essentially consists of a quartz reactor, which is externally heated by two electric furnaces, equipment for feeding and measuring the flow rate of the gases, measuring and controlling the bed temperature, and monitoring the reactor pressure. In these tests, a known quantity of each sorbent is loaded into the packed-bed reactor and the reactor is brought to the desired temperature and exposed to a gas mixture containing the desired level of SO_2. The reactor exit gas is analyzed by a gas chromatograph and a NO_x analyzer for determination of the SO_2 and NO_x content of the reactor feed and effluent. The NO_x and pre-breakthrough SO_2 concentrations of the reactor effluent determine the effectiveness of the sorbents for removal of these species, while the SO_2 breakthrough time represents the effective capacity of the sorbents. As indicated earlier, no attempt was made to address the ammonia slip issue because the extent of ammonia slip is strongly dependent on the reactor configuration.

A series of sulfation tests were conducted at the baseline operating condition to establish the sorption capacity of the baseline sorbent (Alcoa) at a space velocity of 2000 hr^{-1} which allows for a better assessment of the SO_2 sorption capacities of the sorbents by making the differences in capacities more noticeable.

Four (4) new sorbents (i.e., S24-123, S27-124B, 167-WI and S43-175) were evaluated for their SO_2 sorption capacities in a 4 cm^3 bed, while another set of nine (9) new sorbents (i.e., S34-148, S33-142, S25-121, TSR-11, T-4489, S38-157, S37-159, S38-160, 167-WI), were evaluated in a 8 cm^3 bed at 2000 hr^{-1} space velocity. The regenerability of seven sorbents (i.e., S25-121, S27-124B, S33-142, S34-148, S43-175, TSR-11, T-4489) that exhibited similar or higher sorption capacity than the baseline sorbent, were determined over three (3) sulfation/regeneration cycles. Based on the results obtained in this task, the "best" sorbent formulation was identified for durability studies in Task 3.

The catalytic activities of the baseline sorbent as well as several new sorbents for NO_x removal were determined using oxidized as well as sulfated sorbents. Parametric studies were also conducted to determine the effect of bed materials as well as gas composition on the extent of NO_x removal from the gas stream.

The results obtained in this task are presented in the section "RESULTS AND DISCUSSION".

Task 3. Sorbent Durability Studies

The objective of this task was to determine the suitability of the "best" sorbent formulation for long term application in the copper oxide process.

Based on the results of similar tests conducted on regenerable copper-based sorbents for high temperature coal gas desulfurization, it is believed that about 20 cycles are required to develop a conservative estimate regarding sorbent deterioration and rate of "fresh sorbent makeup" needed to continuously maintain the desired desulfurization in the process.

Based on results obtained in Task 2 the sorbent designated as S43-175 was selected as the "best" sorbent formulation for the sorbent durability studies in this task. A test series consisting of 20 sulfation/regeneration cycles was conducted with this sorbent in the packed-bed reactor.

The results obtained in this task are presented in the section "RESULTS AND DISCUSSION".

RESULTS AND DISCUSSION

As indicated earlier, to provide a baseline to quantify the extent of improvement achieved with the copper based sorbents developed in this program, the baseline sorbent (produced by Alcoa) was evaluated over the ranges of operating conditions in the previous ICCI-funded project.[30] The results of these tests indicate that the sorbent has a crush strength of 14.23 N/mm and that, at the baseline operating condition, the effective capacity of this baseline sorbent is about 15 g S/Liter sorbent. During the previous study a number of alumina supported copper oxide sorbents were prepared with varying physical and chemical characteristics. Some of these formulations had higher crush strength but lower capacity compared to the baseline sorbent; other formulations had lower crush strength but higher sorption capacity. Based on the findings of the previous work the sorbent preparation techniques were revised to produce sorbents with both high sorption capacity and crush strength.

A total of twenty one (21) alumina support materials were produced by various preparation techniques. The crush strengths of these support materials were determined

for comparison with the baseline support material produced by Alcoa. To improve the porosity and pore size distributions of the sorbents/alumina supports, a number of boehmite sols were produced using ammonium hydroxide as a hydrolysis catalyst. Alumina pellets produced from these sols were not very strong, indicating that further investigation is needed to modify the preparation technique to improve the physical characteristics of these alumina pellets. To investigate the effect of pH on the macroporosity of the material, various acidic pH levels were tested during gelation of the sols when producing alumina pellets. The crush strengths of the alumina pellets produced are presented in Table 1. The results indicate that the maximum crush strength is obtained at a pH level of about 4 and decreases significantly as pH level decreases to 2.

To lower sorbent cost, the aluminum tri-secondary butoxide (i.e., ALTSB, $Al(OC_4H_9)_3$) that was used as the raw material precursor for production of alumina sol was replaced by the less expensive aluminum isopropoxide (i.e., ALISOP, $Al(OC_3H_7)_3$). The results indicate that the sorbents produced with this lower cost material have comparable physical characteristics to those produced with ALTSB. The sorbent preparation technique was simplified by reducing the number of steps required for producing the sol, resulting in the reduction of the sol production time from 15 hours to 1-4 hours. The crush strengths of a selected number of the support materials prepared in this project are presented in Table 2. The results indicate that, the alumina pellets produced using the simplified technique with shorter preparation time (i.e., 1-4 hr) have higher crush strengths compared to the alumina from the 15-hr sol. The analysis of these materials indicates that the alumina supports produced by the simplified technique have comparable physical characteristics to those produced earlier. Therefore, since the reduction in preparation time is expected to lower the overall production cost of the sorbents, the simplified technique was adopted for preparation of additional sorbents in this project.

A total of forty one (41) new sorbents were formulated using the lower cost materials and/or simplified preparation techniques. The crush strengths of these sorbents were determined for comparison with the baseline sorbent produced by Alcoa.

Four (4) new sorbents (i.e., S24-123, S27-124B, 167-WI and S43-175) were evaluated for their SO_2 sorption capacities in a 4 cm^3 bed, while another set of nine (9) new sorbents (i.e., S34-148, S33-142, S25-121, TSR-11, T-4489, S38-157, S37-159, S38-160, 167-WI), were evaluated in a 8 cm^3 bed at 2000 hr^{-1} space velocity. The results of these tests are presented in Figures 4-11 as well as Tables 3 and 4.

As indicated in Tables 3 and 4, all sorbent formulations produced in this program by sol-gel technique have higher bulk densities (i.e., 0.83-1.00 g/ml) compared to that of the baseline Alcoa sorbent (i.e., 0.63 g/ml). The bulk densities of the sorbent formulations T-44898 and TSR-11, which were produced by different techniques are 1.44 and 0.65 g/ml, respectively. Because the higher densities of the new sorbents contributed to the their higher sulfur capacity on volume basis, the effective sulfur capacities of all the selected sorbents are presented on both volume and weight bases. It should be noted that because

the capital cost of the process is directly related to the reactor volume, comparison on a volume basis appears to be more relevant to the economics of the process.

In general the sulfur capacity is inversely related to the crush strength of the sorbent. Among the sorbents developed in this program, four (4) sorbent formulations exhibited more than 23% improvement in sulfur capacity (per volume basis) and more than 45% improvement in crush strength compared to the baseline sorbent. The best result was obtained with the sorbent designated as S43-175 which has 3.5 times sulfur capacity on volume basis (i.e., 2.6 time on weight basis) and 1.5 times crush strength compared to the Alcoa sorbent.

The higher effective sulfur capacity exhibited by the S43-175 sorbent is due to its higher copper content, smaller pellet size, and most importantly more desirable pore structure. It should be noted that the lower copper content of the baseline sorbent is mainly due to the limitation imposed by wet impregnation techniques. Higher loading in wet impregnated sorbents generally leads to pore plugging, resulting in lower sorbent reactivity. The effect of pellet size on the effective sulfur capacity of the baseline sorbent is presented in Figures 12 and 13, indicating that the effective sulfur capacity of the S43-175 is significantly higher than that expected with the baseline sorbent with similar pellet size. Therefore, it can be concluded that the more favorable pore structure of the S43-175 sorbent heavily contributed to its superior performance.

The sorbent designated as 167-WI, which is produced by wet impregnation of a sol-gel alumina, has 25% higher sulfur capacity and 7 times higher crush strength than the baseline sorbent. This formulation was selected as a "second best" sorbent.

A test series consisting of 20 sulfation/regeneration cycles was conducted with the sorbent designated as S43-175 in the packed-bed reactor. This series of tests was conducted at identical operating condition as the durability test done with the baseline sorbent during the previous ICCI-funded project[30]. The SO_2 breakthrough curves for a selected number of cycles in the durability test are presented in Figures 14 and 15. Although the sorbent reactivity appears to be gradually decreasing, the sorbent reactivity after 20 cycles is still about twice that of the baseline sorbent. Comparisons of effective sulfur capacities of the S43-175 and the baseline sorbent as a function of cycle number are presented in Figures 16 and 17, indicating that after about 15 cycles, the sulfur capacity of S43-175 is about twice that of the baseline sorbent, while the rates of decrease in the sulfur capacities for the two sorbents are similar. These results indicate that the rate of "fresh sorbent make-up" needed to continuously maintain the desired level of desulfurization with S43-175 is significantly lower than that of the baseline sorbent. The crush strength of the sorbent after the 20 cycles is 23.38 N/mm compared to 21.66 N/mm of the fresh sorbent, indicating that the long-term durability test did not adversely affect the crush strength of the sorbent.

The catalytic activity of the baseline sorbent for removal of NO_x from flue gas was determined in a series of tests conducted at different operating conditions. The

parameters studied included the effect of bed materials as well as gas composition on the extent of NO_x removal from the gas stream. The baseline tests for this series were conducted at 400°C and 2000 hr^{-1} space velocity using a gas mixture containing 500 ppmv of NO_x and 500 ppmv of NH_3. The results of these tests are presented in Figure 18, indicating that the baseline sorbent is capable of removing 69% of the NO_x in the regenerated state, while in the sulfated state the extent of NO_x removal increases to 88.5%. The extent of NO_x removal in the absence of NH_3 is essentially zero confirming that NO_x removal is accomplished through reduction by ammonia. The regenerated sorbent in the reduced form exhibits slightly lower catalytic activity than the oxidized sorbent (64% compared to 69%). As shown in Figure 18, the extent of NO_x removal was 30% in the empty reactor, 45% in the presence of alumina support, and 40% in the presence of alumina support calcined at 1300°C. As shown in Table 5, these results indicate that the extent of NO_x reduction in the flue gas that is <u>solely due to catalytic activity of the copper compounds present in the sorbent</u> is in the range of 19% to 43%.

The effect of NH_3/NO_x ratio on NO_x removal is presented in Figure 19, indicating that the extent of NO_x removal is linearly related to the NH_3/NO_x ratio in the flue gas. The catalytic activities of the baseline sorbent as well as several new sorbents for NO_x removal were determined using oxidized as well as sulfated sorbents. A comparison of the catalytic activities of the baseline as well as three (3) sorbents developed in this program is presented in Figure 20 indicating that in both oxidized and sulfated forms, the new sorbents have higher catalytic activities than that of the baseline sorbent. The extent of NO_x removal with the new sorbents in the sulfated form exceeds 99% compared to 88.5% for the baseline sorbent. The catalytic activity of the S43-175 after 20 cycles was also determined. The extent of NO_x removal was 99.3% indicating that the long-term durability test did not affect the catalytic activity of this sorbent. As indicated earlier, no attempt was made to address the ammonia slip issue because the extent of ammonia slip is strongly dependent on the reactor configuration.

CONCLUSION(S) AND RECOMMENDATION(S)

Among the sorbents developed in this program, four (4) sorbent formulations exhibited more than 23% improvement in sulfur capacity (volume basis) and more than 45% improvement in crush strength compared to the baseline sorbent. The best result was obtained with the sorbent designated as <u>S43-175,</u> which has 3.5 times sulfur capacity on volume basis (2.6 times on weight basis) and 1.5 times crush strength compared to the Alcoa sorbent. The reactivity of the S43-175 sorbent after 20 cycles is about twice that of the baseline sorbent, while the rates of decrease in the sulfur capacities for the two sorbents are similar. These results indicate that the rate of "fresh sorbent make-up" with S43-175 is significantly lower than that of the baseline sorbent. The crush strength of the S43-175 sorbent does not appear to be adversely affected by long term durability test.

The baseline sorbent is capable of removing 69% of the NO_x in the regenerated state, while in the sulfated state the extent of NO_x removal increases to 88.5%. The extent of NO_x removal in the absence of NH_3 is essentially zero confirming that NO_x removal is

accomplished through reduction by ammonia. The regenerated sorbent in the reduced form exhibits slightly lower reactivity than the oxidized sorbent (64% compared to 69%). The extent of NO_x removal achieved with alumina support under identical operating condition was 45%. Therefore, it can be concluded that the extent of NO_x removal that is <u>solely due to catalytic activity of the copper compounds present in the sorbent</u> is in the range of 19% to 43%. The extent of NO_x removal appears to be linearly related to NH_3/NO_x ratio in the flue gas.

The new sorbents have higher catalytic activities than that of the baseline sorbent. The extent of NO_x removal with the new sorbents in the sulfated form exceeds 99% compared to 88.5% for the baseline sorbent. The extent of NO_x removal does not appear to be affected by the long-term durability test.

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Table 1. Crush Strength of Alumina Pellets Produced from Different pH Gels

Alumina	pH (during gelation)	Crush Strength (N/mm)
Alcoa*	**-**	**15.03**
S28-136	2	37.99
S28-133	3	97.50
S28-132	4	125.17
S28-135	5	84.92
S28-134	6.5	94.61

* presented for comparison

Table 2. Crush Strength of Alumina Pellets Produced from Various Sols

Alumina Support	Sol Molarity	Precursor	Duration (hr)	Pellet Size (mm)	Crush Strength (N/mm)
Alcoa*	**-**	**-**	**-**	**3.32**	**15.03**
S18-127	1	ALTSB	15	2.16	69.88
S28-128	2	ALTSB	15	2.16	76.24
S31-130	2	ALISOP	15	2.7	69.17
S29B-126	1	ALTSB	4	2.20	85.85
S29A-125	1	ALTSB	1	2.47	90.70
S30-129	2	ALISOP	1	3.61	101.60
S28-137	2	ALISOP	1	2.84	110.89

* presented for comparison

Table 3. Characteristics of the Sorbents Tested with 4 cc Bed Volume

Sorbent	Cu (%)	Particle Diameter (mm)	Density (g/ml)	Crush Strength (N/mm)	Sulfur Loading (g S/L Sorbent)	Sulfur Loading (g S/100 g Sorbent)
Alcoa	6.79	3.22	0.63	14.23	7.89	1.27
S24-123	3.78	1.97	0.83	47.33	7.10	0.86
S27-124B	10.5	1.99	0.90	21.89	18.25	2.03
167-WI	7.6[#]	2.33	0.87	98.88	9.73	1.11
S43-175	10.4	1.81	0.87	21.66	28.20	3.26

[#] Nominal Cu content

Table 4. Characteristics of the Sorbents Tested with 8 cc Bed Volume

Sorbent	Cu (%)	Particle Diameter (mm)	Density (g/ml)	Crush Strength (N/mm)	Sulfur Loading (g S/L Sorbent)	Sulfur Loading (g S/100 g Sorbent)
Alcoa	6.79	3.22	0.63	14.23	11.15	1.74
T-4489	43.8	3.09	1.44	20.60	14.43	2.06
TSR-11	21.2	3.21	0.65	13.10	13.43	1.00
S25-121	3.67	1.88	0.88	86.96	10.76	1.24
S33-142	14.3	1.80	0.98	5.90	23.72	2.44
S34-148	7.64	2.86	1.00	24.91	10.93	1.07
S38-160	4.90	1.94	0.85	53.87	9.84	1.16
S38-157	6.70	2.79	0.90	26.07	5.57	0.62
S37-159	6.82	3.21	0.87	94.08	3.06	0.35
167-WI	7.60[#]	2.33	0.87	98.88	10.38	0.62

[#] Nominal Cu content

Table 5. NO_x Removal by the Baseline Sorbent at Various Conditions

Sorbent Condition	NO_x Removal	NO_x Removal Due to Cu
Fresh Sorbent	80	35
Regenerated Sorbent	69	24
Regenerated Sorbent Tested without O_2	64	19
Fully Sulfated Sorbent	88	43
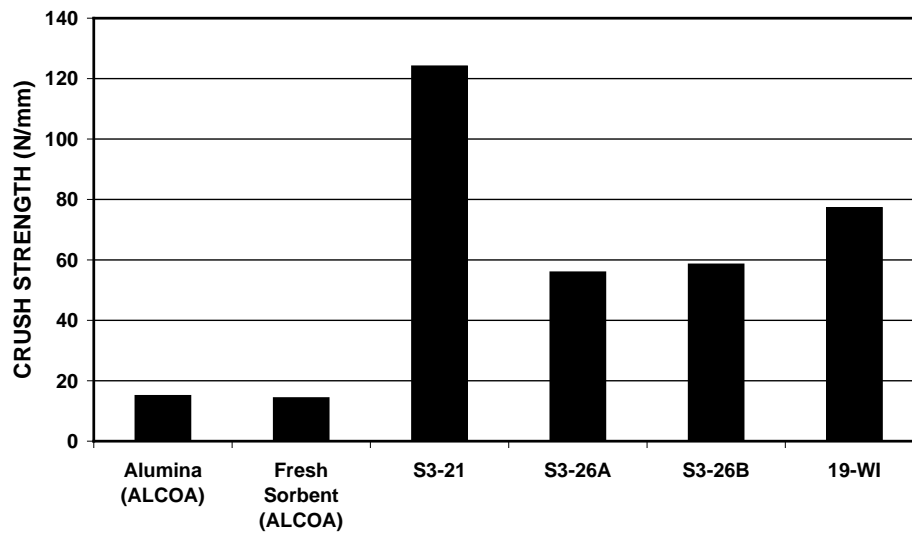
Figure 1. Comparison of Crush Strength of Various Sorbents
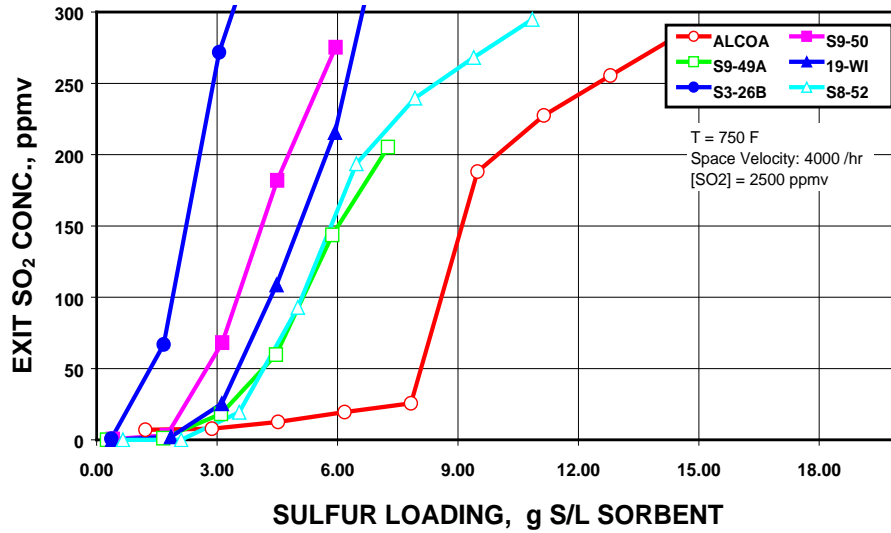
Figure 2. Comparison of Sulfur Reactivities of Various Sorbents
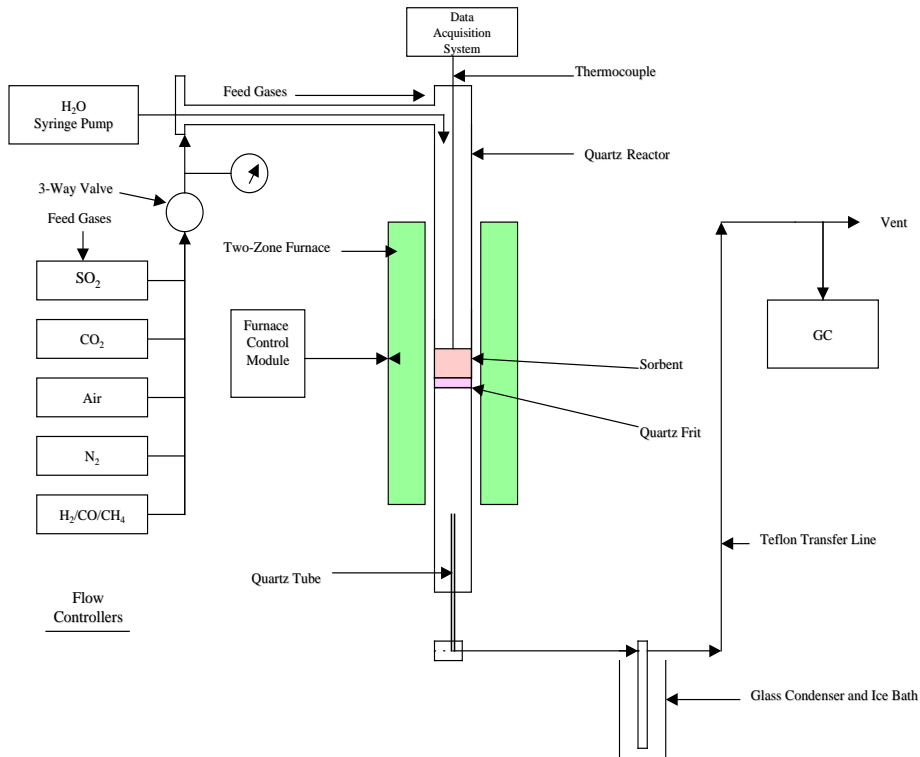
Figure 3. Schematic Diagram of the Packed-Bed Reactor Unit
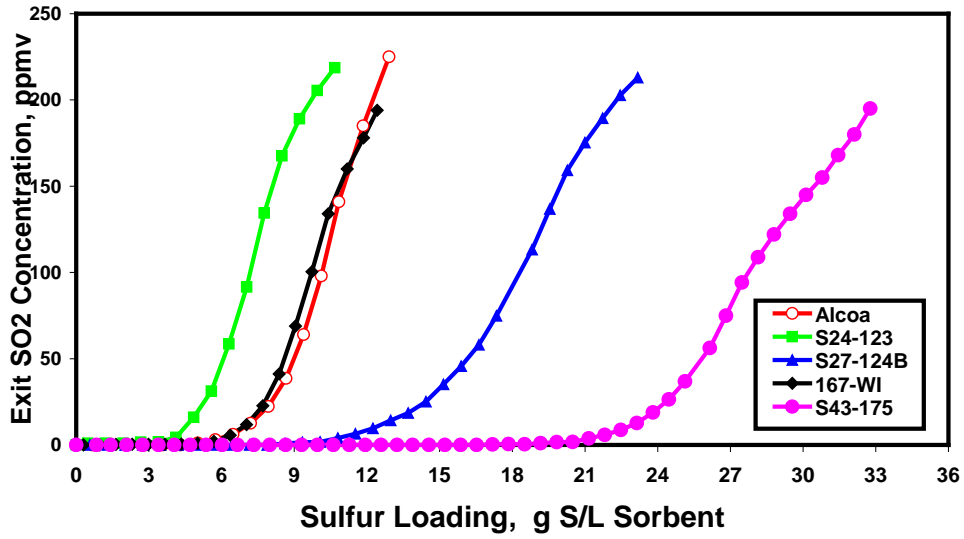
Figure 4. Effective Sulfur Capacities of Various Sorbents (4cc bed-Volume Basis)
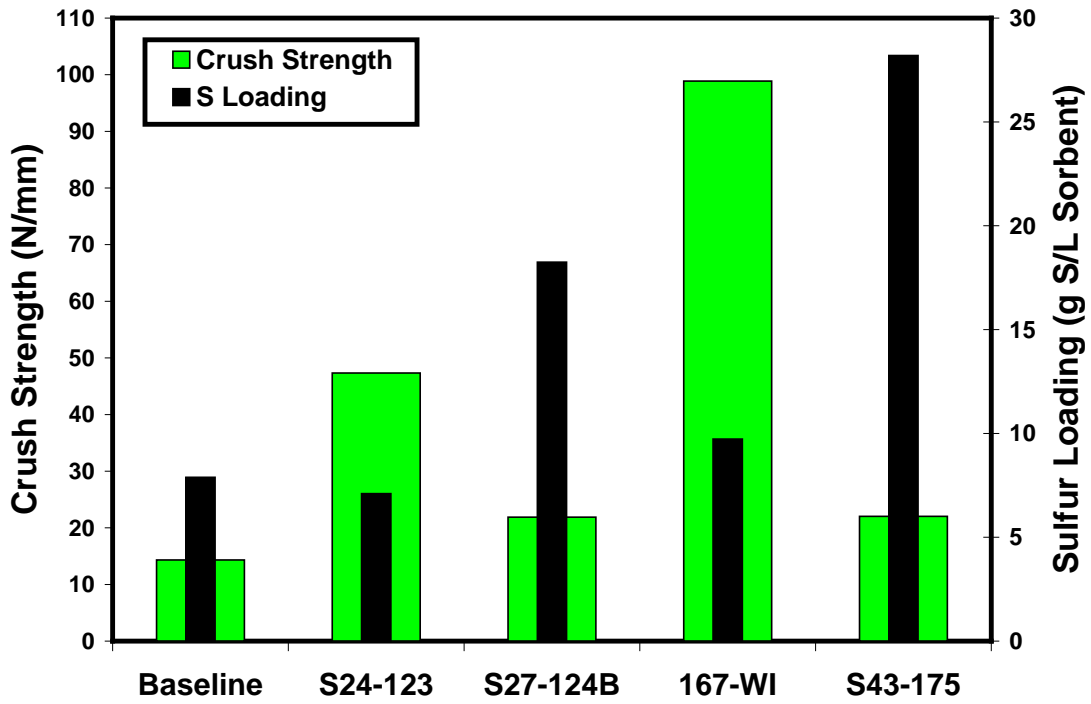
Figure 5. Sulfur Loadings and Crush Strengths of Various Sorbents (4cc bed-Volume Basis)
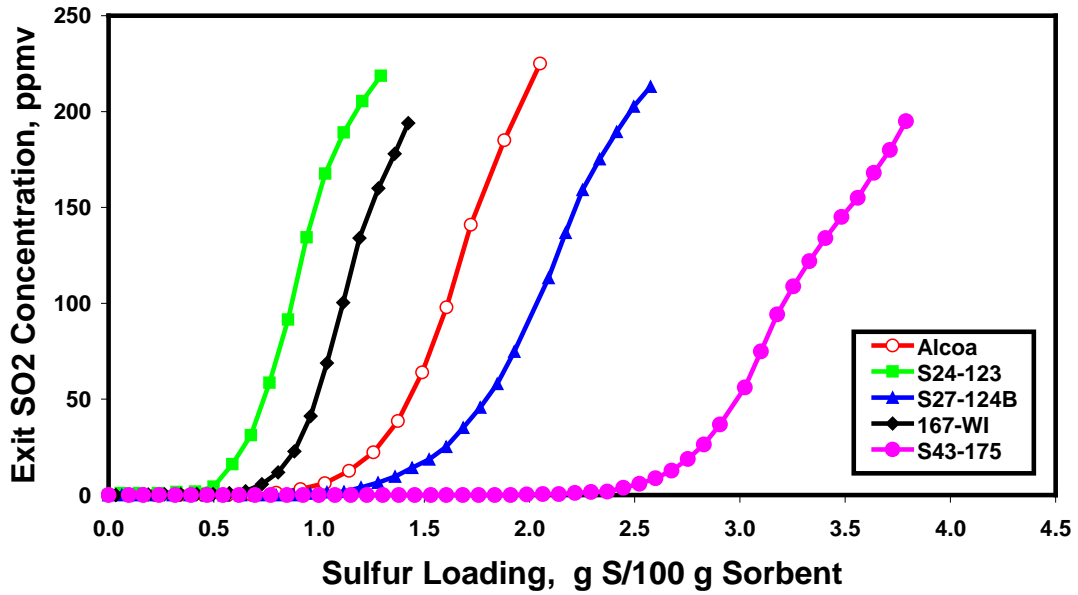
**Figure 6. Effective Sulfur Capacities of Various Sorbents
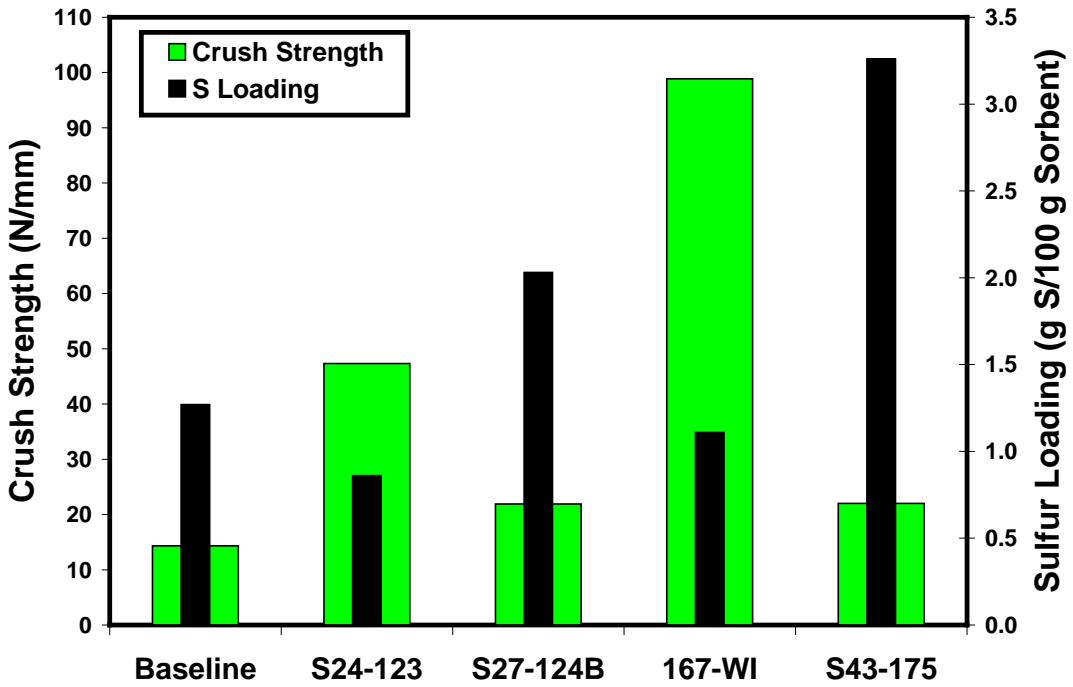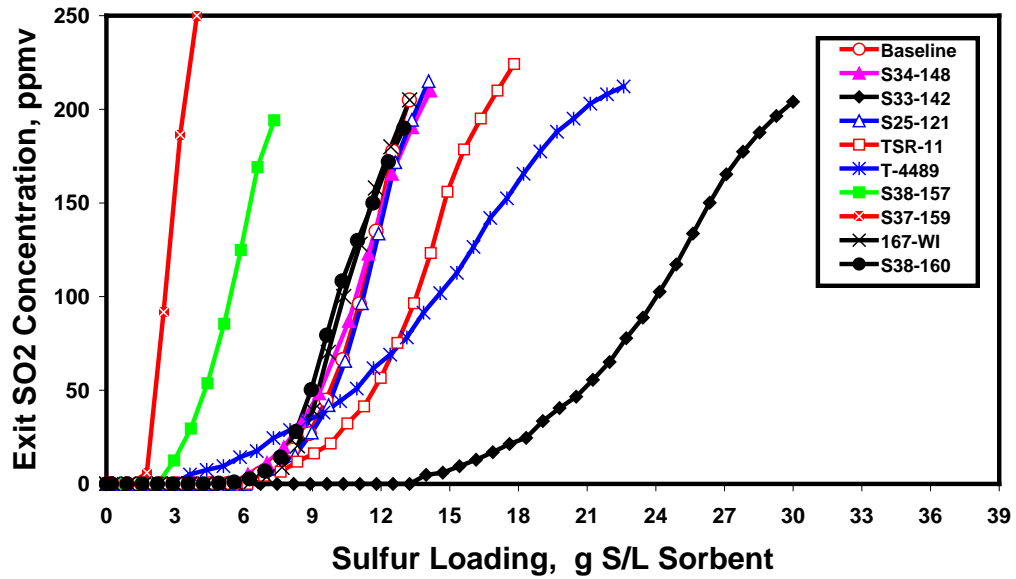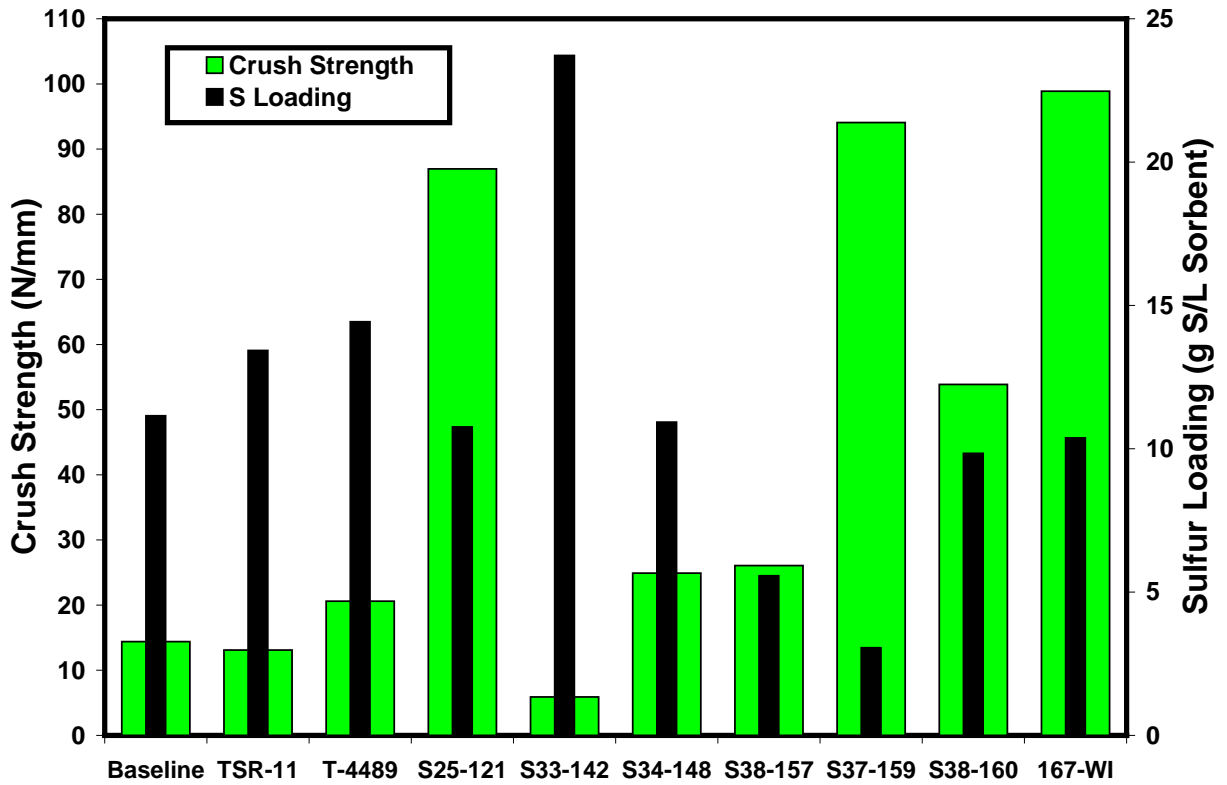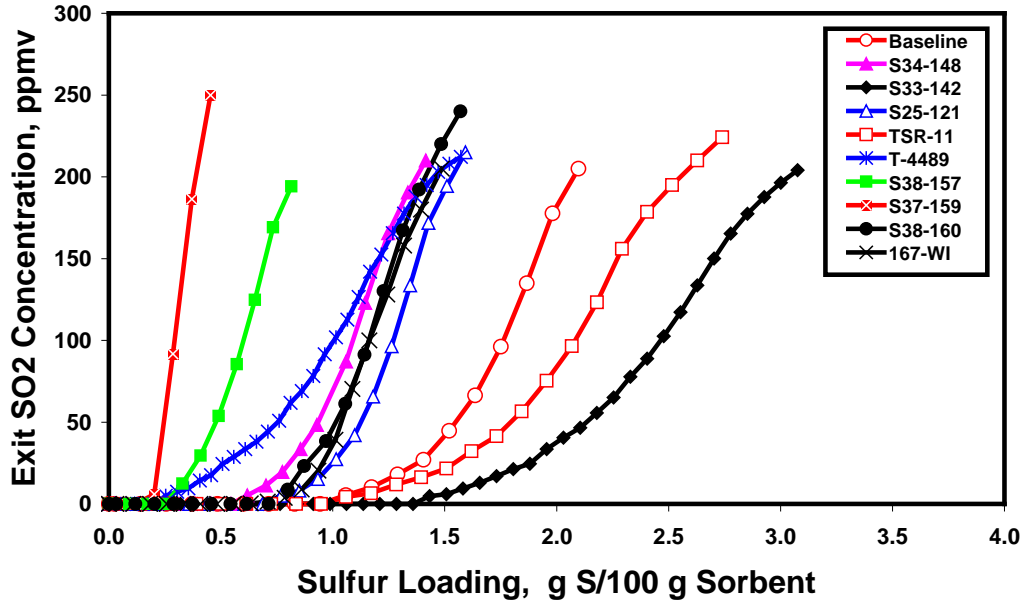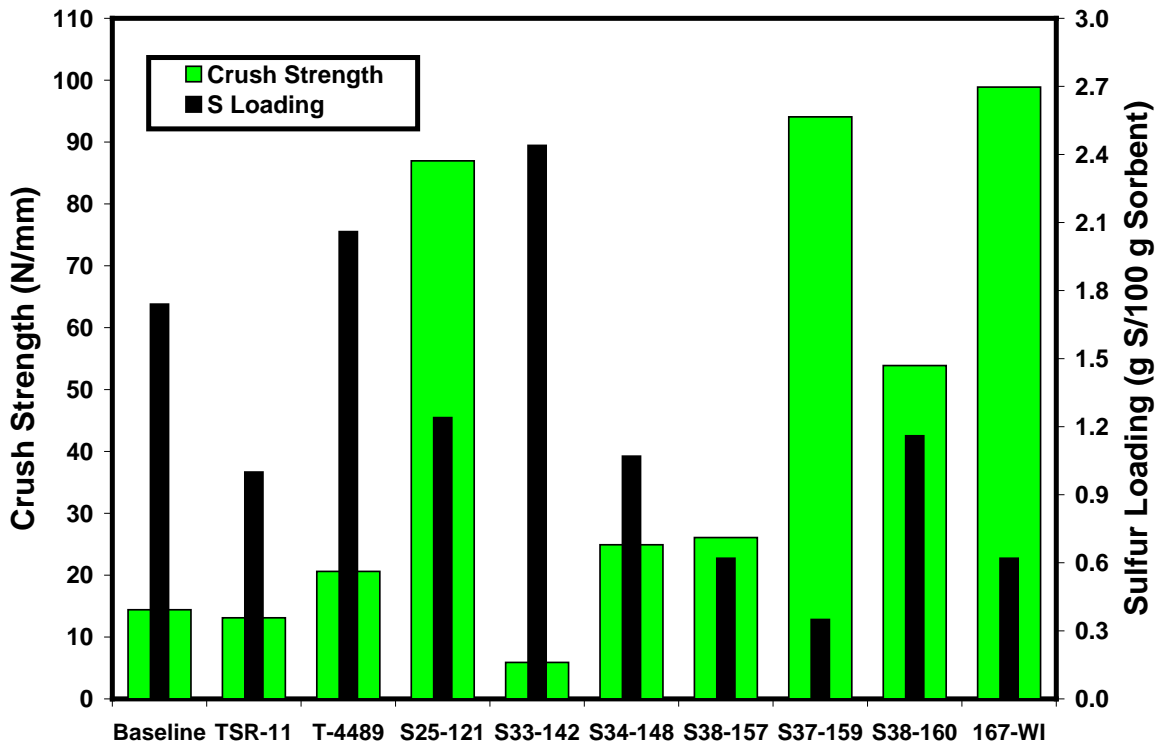(4cc bed-Weight Basis)**

**Figure 7. Sulfur Loadings and Crush Strengths of Various Sorbents
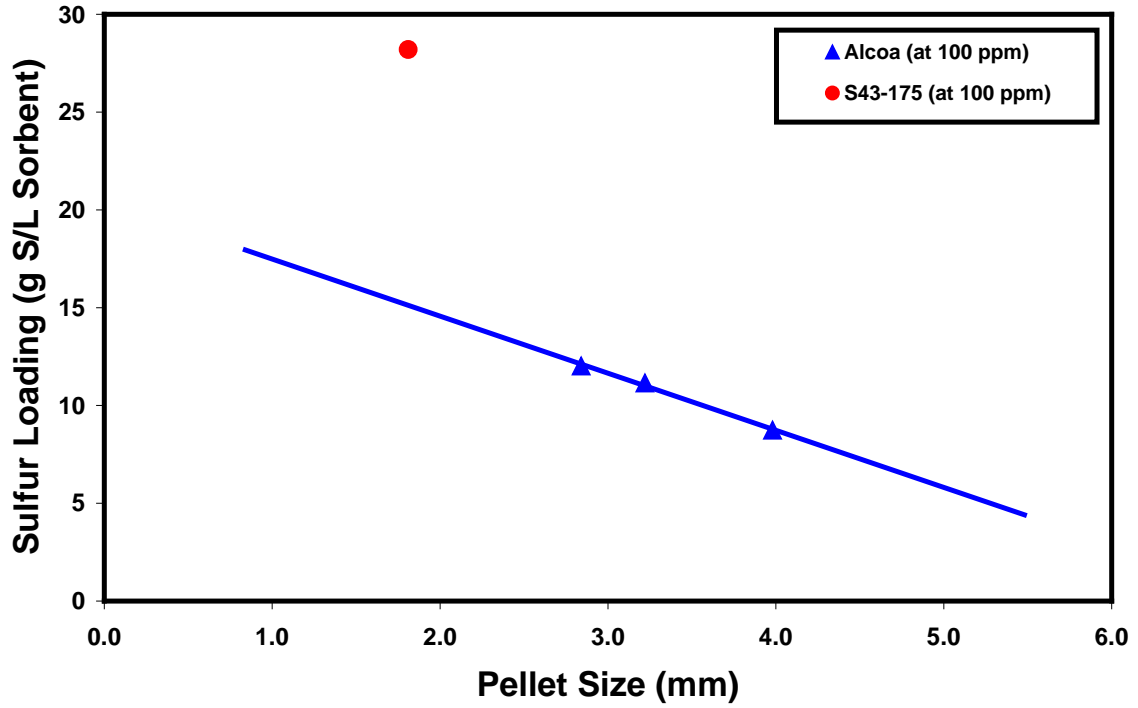(4cc bed-Weight Basis)**

Figure 8. EffectiveSulfur Capacities of Various Sorbents
(8cc bed-Volume Basis)

Figure 9. Sulfur Loadings and Crush Strengths of Various Sorbents
(8cc bed-Volume Basis)

**Figure 10. Effective Sulfur Capacities of Various Sorbents
(8cc bed-Weight Basis)**

**Figure 11. Sulfur Loadings and Crush Strengths of Various Sorbents
(8cc bed – Weight Basis)**

Figure 12. Effect of Pellet Size on Sorbent Performance (Volume Basis)
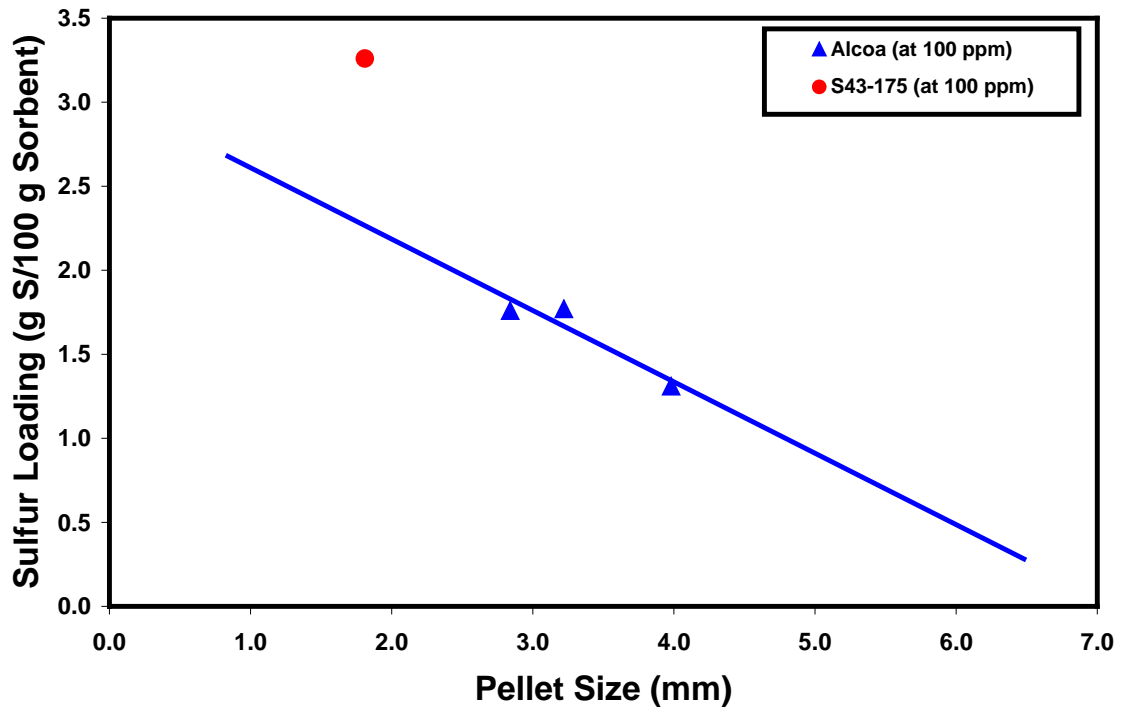
Figure 13. Effect of Pellet Size on Sorbent Performance (Weight Basis)
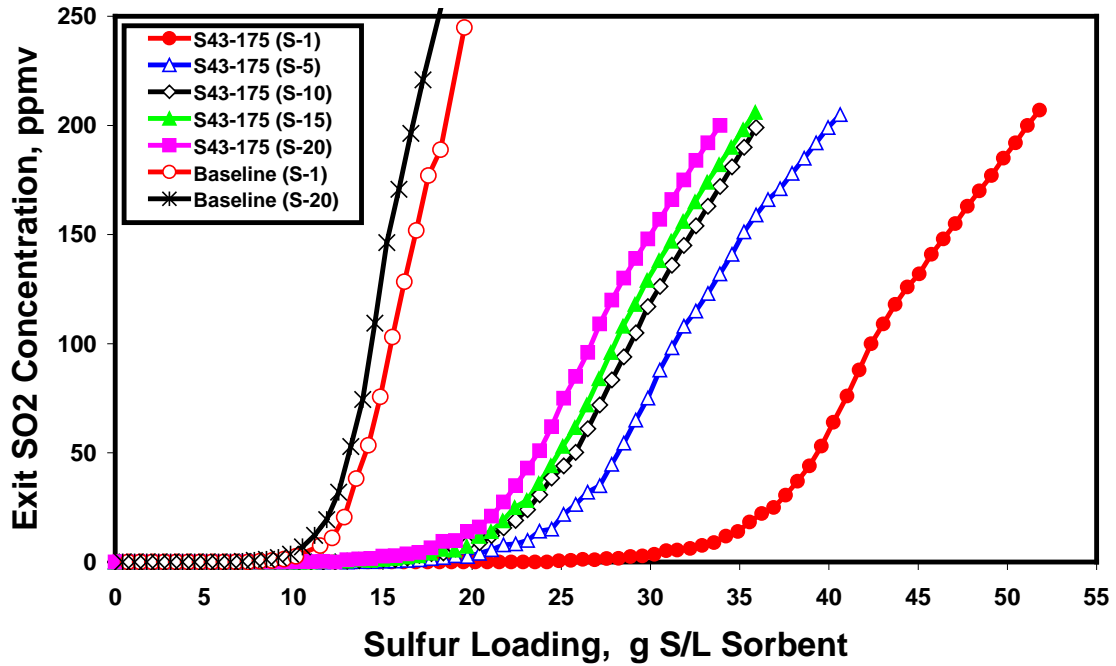
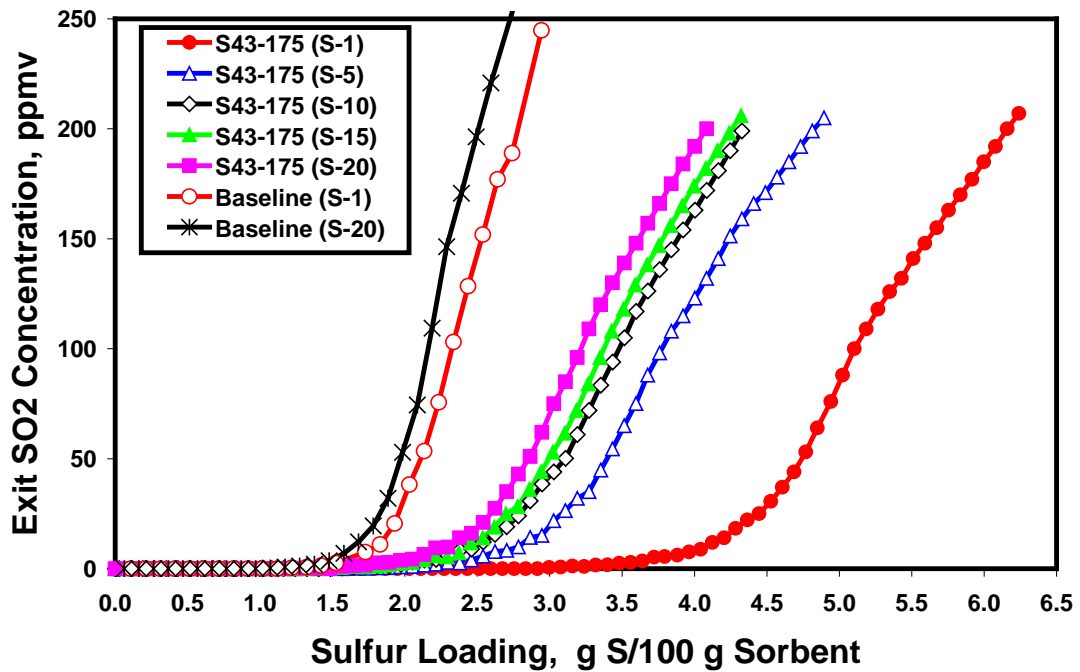**Figure 14. Comparison of Long-Term Durability of New and Baseline Sorbents (Volume Basis)**

Figure 15. Comparison of Long-Term Durability of New and Baseline Sorbents (Weight Basis)
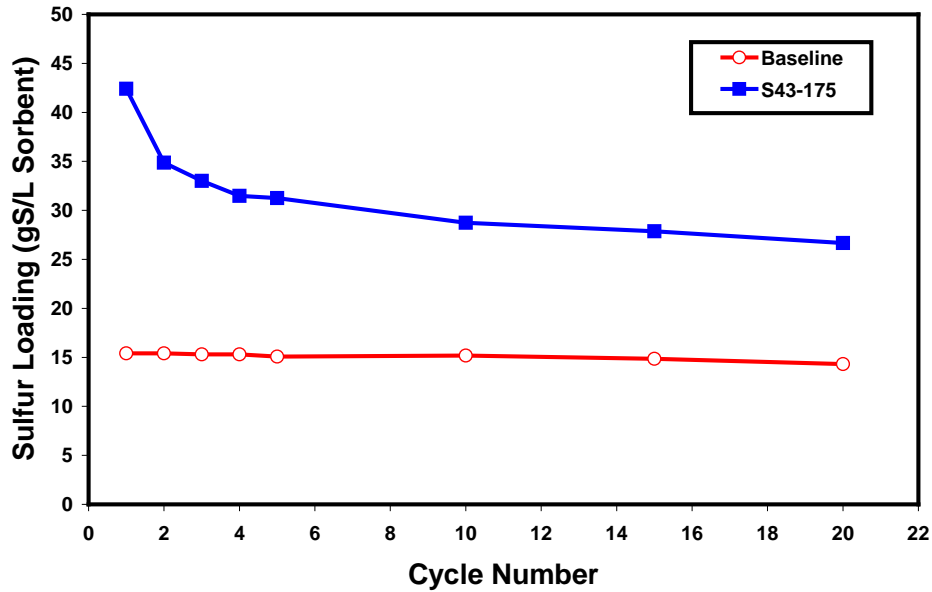
Figure 16. Comparison of Sulfur Capacities of the Baseline and New Sorbent in Long-Term Durability Test (Volume Basis)
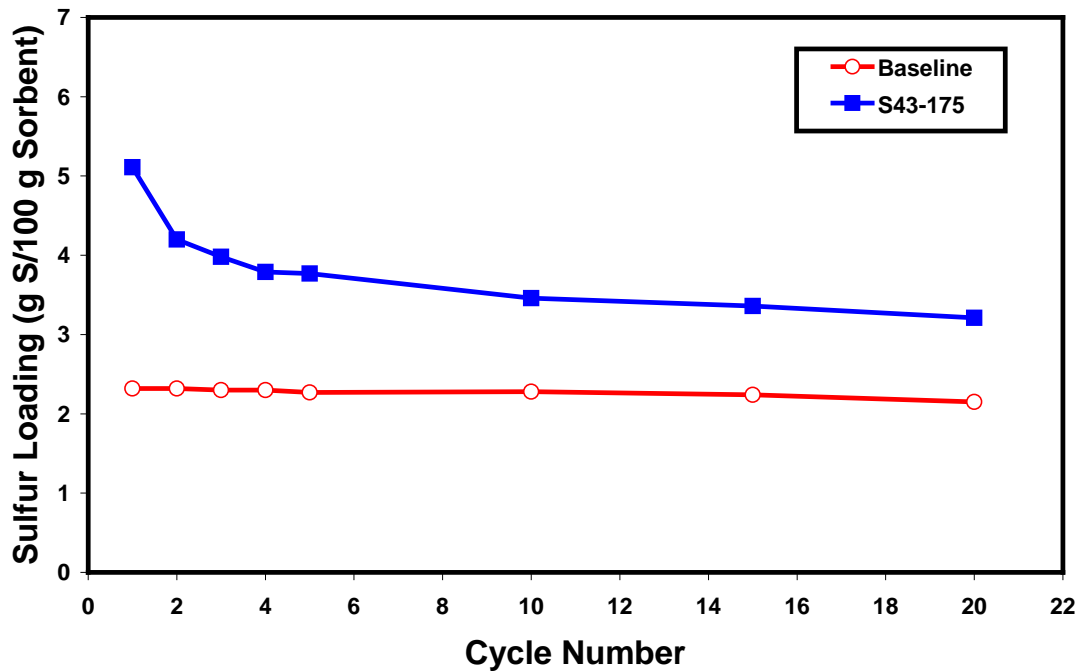

Figure 17. Comparison of Sulfur Capacities of the Baseline and New Sorbent in Long-Term Durability Test (Weight Basis)
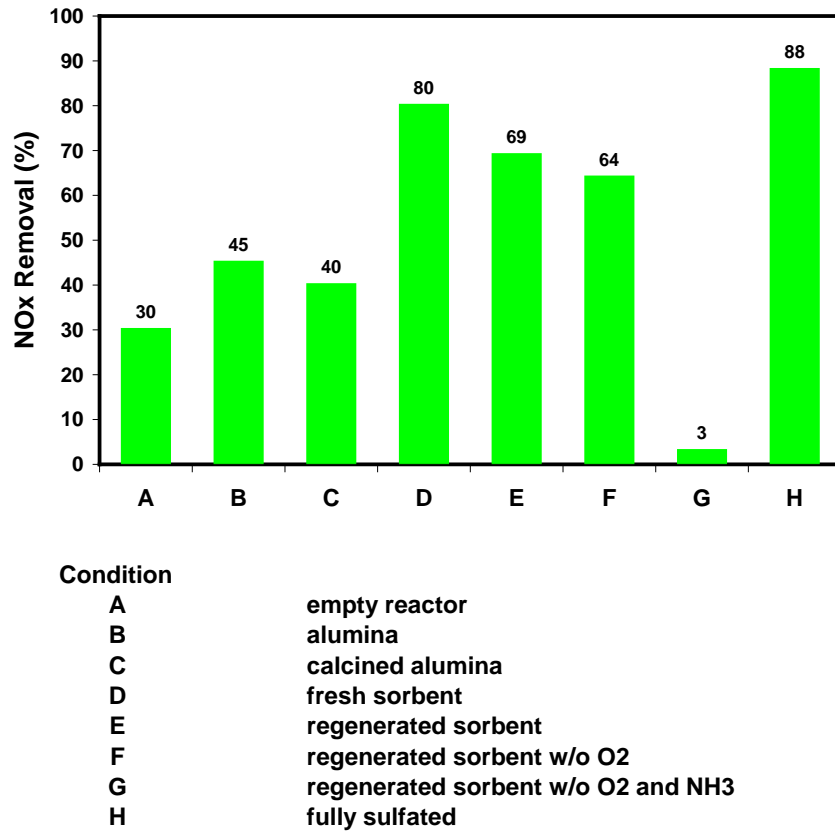
Condition	
A	empty reactor
B	alumina
C	calcined alumina
D	fresh sorbent
E	regenerated sorbent
F	regenerated sorbent w/o O2
G	regenerated sorbent w/o O2 and NH3
H	fully sulfated

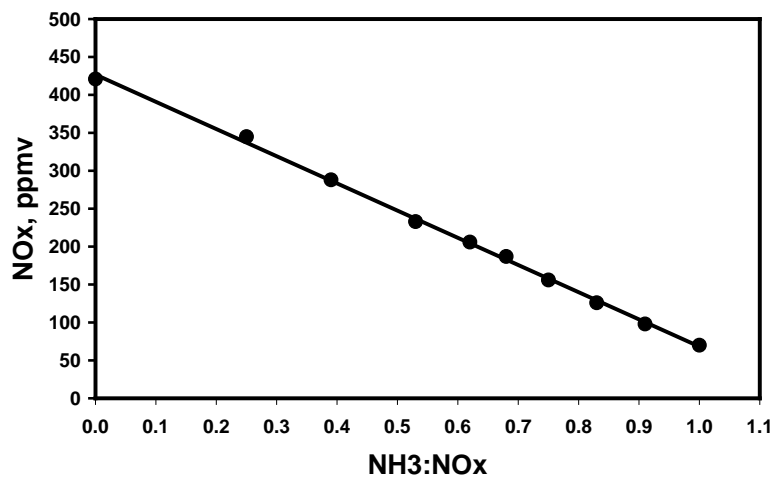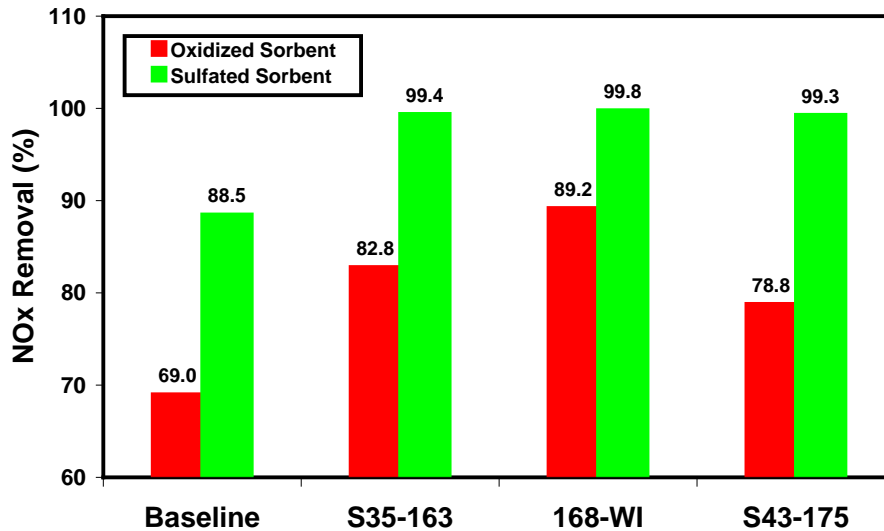**Figure 18. Effects of Operating Parameters on the Extent of NO_x Removal with Baseline Sorbent**

Figure 19. Effects of NH_3/NO_x Ratio on the Extent of NO_x Removal with Baseline Sorbent

Figure 20. Comparison of NO$_x$ Removal Efficiencies of Various Sorbents

DISCLAIMER STATEMENT

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