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Project Title: **DEVELOPMENT OF IMPROVED SORBENTS FOR THE
                  MOVING –BED COPPER OXIDE PROCESS**

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ABSTRACT

The overall objective of this program was to develop new and improved regenerable copper-based sorbents for removal of SO_2 and NO_x from flue gas. The sorbents developed in this program were geared towards application in the Copper Oxide Bed Regenerable Absorber (COBRA) process, which is being developed under the joint sponsorship of DCCA and the U.S. Department of energy (DOE). The targeted areas of sorbent improvement included higher reactivity and effective capacity, and better attrition resistance and durability.

To achieve this objective, different formulations of copper-based sorbents in pellet form were prepared. The new sorbents were evaluated for their physical and chemical properties as well as their desulfurization and regeneration reactivities. The alumina-supported copper-based (ALCOA) sorbent, that has been used in the pilot plant scale testing of the COBRA process, was used as the <u>baseline</u> sorbent for comparison with the new sorbents.

In this project, the baseline sorbent 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 by incorporating and impregnating copper into an alumina support 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 somewhat 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 sorbent generally decreased. Therefore, additional work is needed to optimize the sorbent composition and preparation technique to further improve the performance of the sorbent.

EXECUTIVE SUMMARY

In the Clean Air Act Amendments (CAAA) of 1990, 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.

During coal combustion in the pulverized coal combustion process 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 the water vapor in the air and deposit as acid rain. The threat from acid rain is more of a concern in Illinois where over 90% of the high sulfur coal mined is consumed by electric utilities that are based on pulverized coal combustion and, only a very small fraction of the coal-based power plants in Illinois are 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. Given the strict limits on SO_2 emissions (1.2 lbs of SO_2 per million Btu by the year 2000), the high sulfur content of Illinois coal, and the growing concern with the disposal of solid residues from conventional flue gas desulfurization (FGD), the selection of the COBRA technology as one of the most promising technologies to meet CAAA emission standards represents a strategic choice for the Illinois coal research and development program.

Development of the COBRA flue gas cleanup process is well on its way toward commercialization by Sargent & Lundy under the joint sponsorship of DCCA/OCDM and the U.S. DOE as part of the combustion 2000 program. This process has been demonstrated at the nominal half-megawatt scale at the Illinois Coal Development Park in Carterville, Illinois.

The overall objective of this program was to develop new and improved regenerable copper-based sorbents for removal of SO_2 and NO_x from flue gas. The sorbents developed in this program are geared towards application in the COBRA process. The targeted areas of sorbent improvement included higher reactivity and effective capacity, lower regeneration temperature, and better attrition resistance and durability.

To achieve this objective, a number of copper-based sorbents in the form of pellets were prepared. The parameters considered during sorbent preparation included chemical composition as well as physical properties, such as surface area, porosity, and pore size distribution.

The new sorbent formulations were evaluated for their attrition resistance, crush strength, SO_2 removal efficiency and effective sulfur capacity, and regeneration capability. The alumina-supported copper-based sorbent (produced by ALCOA), that has been used in the pilot plant scale testing of the process at the Illinois Coal Development Park, was used as the <u>baseline</u> sorbent to quantify the improvements achieved in this program.

To establish a baseline for comparison of the improved sorbents developed in this program, the baseline sorbent was evaluated for its sulfation performance, regenerability, long term durability, as well as physical and chemical characteristics. The results of these tests indicate that, at the baseline condition used in this project, the effective capacity of the sorbent is about 3% 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. An increase in regeneration temperature of 100°F improves effective capacity by 20% and a decrease in temperature of 100°F results in 40% decrease in effective capacity. Based on the results of multi-cycle durability tests conducted with the baseline 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.

Preparation of improved sorbents (TASK 2) was initiated by channeling initial efforts towards employing alternative sorbent synthesis techniques that have been shown to produce mechanically strong porous solids. A number of batches of alumina support materials were prepared by modified sol-gel techniques. The specific surface areas, copper contents as well as the crush strength of the new sorbents were determined along with those of the baseline sorbent. The results indicate that the crush strength of the alumina support materials produced by various sol-gel techniques is about 7 times higher than that of the ALCOA alumina support, while the crush strength of the copper-based sorbents produced by sol-gel techniques is about 5 times higher than that of the ALCOA sorbent. The results also indicate that while the overall BET surface areas of these sorbents are comparable, a significantly higher fraction of the surface area of the new sorbents is attributed to mesopores (i.e., larger than 50 Å). However, the reactivities of these sorbents in the pellet form (i.e., d=3 mm) were somewhat lower than that of the baseline sorbent, while in the granular form (i.e., d = 0.5-0.8 mm), these sorbents exhibited higher reactivities than that of the baseline sorbent.

Scanning Electron Microscopy (SEM) analyses revealed that ALCOA sorbent has much higher macroporosity compared to these new sorbents, which may explain the lower reactivity of the new sorbents despite their favorable active metal content and surface area. 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 sorbent generally decreased. Therefore, additional work is needed to optimize the sorbent composition and preparation technique to further improve the performance of the sorbent.

OBJECTIVES

The overall objective of this program was to develop new and improved regenerable copper-based sorbents for removal of SO_2 and NO_x from flue gas. The sorbents developed in this program were geared towards application in the Copper Oxide Bed Regenerable Absorber (COBRA) process, which is being developed under the joint sponsorship of DCCA and the U.S. DOE. The targeted areas of sorbent improvement included higher reactivity and effective capacity, and better attrition resistance and durability, leading to improvement in process control and economic utilization of the sorbent.

The specific objectives of this work were to:

- Establish a baseline for the development of improved sorbents.

- Synthesize a number of new sorbents with desired characteristics.

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

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 in the conventional processes, 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 more of a 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 are 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 salable 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.[4,5] The Federal Energy Technology Center (FETC) 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 to be used at moderate temperatures. The sorbent consists of copper oxide (CuO) supported on gamma alumina (γ-Al_2O_3), and is 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.[7-11]

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:

$$CuSO_4 + ½ CH_4 = Cu + SO_2 + ½ CO_2 + H_2O \qquad (2)$$
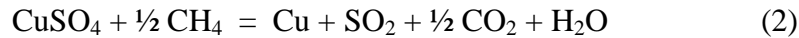
Following sulfate decomposition in the regeneration vessel the sorbent is sent back to the desulfurization unit for re-use. Upon exposure to flue gases, elemental copper is readily oxidized to CuO, thereby fully restoring the sorbent to its original fresh condition.

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 Combustion 2000 program**.[12,13] Shell developed a process in the 1970's, where flue gas from an oil-fired boiler was passed through a fixed-bed of copper oxide sorbent. This technology was later licensed by UOP and applied to a pilot plant that exhibited 90% and 70% removal levels for SO_2 and NO_x, respectively.[5,6] Development of the COBRA flue gas cleanup process is well on its way toward commercialization by Sargent & Lundy under the joint sponsorship of DCCA/OCDM and the U.S. DOE as part of the combustion 2000 program. This process is currently being demonstrated at the nominal half-megawatt scale at the Illinois Coal Development Park in Carterville.

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 Deng and Lin[14-16] who prepared alumina-supported copper oxide in an attempt to increase the CuO loading of the alumina support material, while maintaining high surface area. Their investigations, however, have been limited to laboratory-scale experiments in a thermogravimetric reactor. In addition, the SO_2 removal capability of their sorbents has been evaluated at the relatively high temperature of 500°C. To the best knowledge of the investigators, no life-cycle testing of their sorbents has been reported.

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 believed that there is a potential for reducing net levelized costs by 1 mil per kWh considering all the above cost factors. This would, if it could be realized, make the COBRA process less expensive than other FGD processes even for straight SO_2 removal, without considering the additional benefit of removing NO_x and particulates, which is accomplished by the COBRA process. 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 the sorbent performance to significantly lower the overall cost of the COBRA process.

Areas of sorbent improvement include lower cost, higher reactivity, higher sulfur capacity, improved attrition resistance, and improved durability. In general, the reactivity of a sorbent is directly related to its key physical properties such as porosity and surface area, while attrition resistance 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

This project was divided into the following three tasks:

Task 1. Evaluation of the Baseline "Commercial" Sorbent

Task 2. Synthesis and Characterization of the "New" Sorbents

Task 3. Evaluation of Desulfurization Reactivity and Regenerability of the "New" Sorbents

Task 1. Evaluation of the Baseline "Commercial" Sorbent

The objective of this task was to fully establish the baseline for the development of improved sorbents for the moving-bed copper oxide process.

The commercially produced regenerable alumina-supported copper oxide sorbent, which has been used in the pilot scale unit at the Illinois Coal Development Park, was selected as the baseline sorbent for comparison with the improved sorbents developed in this program. Samples of fresh, sulfated, and regenerated sorbents were obtained from the pilot plant operation for evaluation in this task. The evaluation included determination of physical and chemical properties, sulfation and regeneration reactivity in the packed-bed and thermogravimetric analyzer (TGA), effects of operating parameters, and long term durability of the sorbent.

In this project, the chemical and physical properties of the baseline sorbent were determined by analysis of fresh (as-received), sulfated, and regenerated samples. The effectiveness of the sorbents for SO_2 removal were determined in the packed-bed reactor system. The baseline tests were conducted at 750°F, with a simulated gas mixture (recommended by Sargent & Lundy) containing 3% O_2, and 2250 ppmv SO_2, while the regeneration tests were carried out at 850°F using natural gas (or methane). Parametric studies were performed to determine the effect of operating conditions on the performance of the baseline sorbent. The parameters studied in this task included sulfation temperature, regeneration temperature, space velocity, and SO_2 concentration. Long-term durability of the baseline sorbent was determined over 20 sulfation/regeneration cycles. The sulfation and regeneration reaction rates were determined in the TGA reactor system. The thorough evaluation of the baseline sorbent

carried out in this task established a firm basis for evaluation of all the new sorbents developed in this program.

In the packed-bed 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 for determination of the SO_2 content of the reactor feed and effluent. The pre-breakthrough SO_2 content of the reactor effluent determines the effectiveness of the sorbents for removal of these species, while the SO_2 breakthrough time represents the effective capacity of the sorbents.

The TGA unit is capable of continuously weighing a sample that is undergoing reaction in a gaseous environment of desired composition at constant pressure. The reaction rate is determined from the rate of change of sample weight using the prevailing chemical reaction chemistry. The gas flow rates used with this system are sufficiently large relative to the reaction rate such that the gas composition is essentially constant. This unit is capable of operation at up to 1000°C and 100 bar using very small quantities of solids and very high gas flow rates, thus eliminating the "starvation condition" and "gas film diffusion" that are very common in TGA experiments. This is especially important when conducting gas/solid reaction tests involving very low concentrations of reactant gases (i.e., <1%). All the hot wetted parts of the unit are made of quartz to eliminate reaction with corrosive and reactive gases.

The baseline operating conditions used in the sulfation and regeneration tests are given in Table 1, while the ranges of the operating variables used in the parametric studies are presented in Table 2. The operating conditions used in the packed-bed tests were selected to closely simulate those in the commercial power plant. The 20-cycle durability test was conducted with the baseline sorbent in the packed-bed reactor, under the baseline conditions indicated in Table 1, to evaluate its performance over an extended period of operation. Chemical and physical analyses of the sorbent included chemical composition (Cu, Al, S-Sulfate, S-Sulfide), and physical properties which included BET surface area, porosity, pore size distribution, density, and crush strength. The results obtained in this task are presented in the section "RESULTS AND DISCUSSION".

Task 2. Synthesis and Characterization of the "New" Sorbents

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

A number of formulations of attrition resistant copper-based sorbent pellets (d = 2-5 mm) were produced in this task. Preparation of improved sorbents was geared towards employing synthesis techniques that have been shown to produce mechanically strong porous solids. Parameters studied include chemical composition, additives (to improve desirable characteristics), and thermal treatment history (i.e., calcination temperature and time). Small quantities of each formulation were prepared for initial screening. Larger

quantities of the "promising" candidate sorbent formulations were produced for further evaluation.

In this project 72 formulations of copper-based sorbents were prepared by modified sol-gel techniques. The sorbents were prepared by wet impregnation with the metal salt or incorporation of the active metal (copper) during the formation of the support material (alumina). Different chemical and physical treatment methods were explored to attain high surface area, high metal loading, while retaining or improving the crush strength of the sorbent.

Ten (10) sorbent formulations were analyzed using standard characterization techniques including, crush strength measurement, BET surface area measurements, mercury porosimetry, X-ray Diffraction (XRD) analysis, and Scanning Electron Microscopy (SEM). BET surface area measurements are common measurements used for determination of the surface area and the pore size distribution in the micro-pore (i.e., <20 Å) and meso-pore (i.e., 20-500 Å) range. Mercury porosimetry can determine pore size distribution, pore volume, and internal pore surface area for the macro-pores (i.e., >500 Å). X-ray Diffraction is important to the study of sorbents because it measures the bulk phases. The SEM/EDX analyses provide close-up pictures of the internal structure of the sorbent as well as spatial distribution of the species within the sorbent. Wet chemical analysis either by Atomic Absorption (AA) or Ion Coupled Plasma (ICP) can measure the loss of sorbent phases after testing in a SO_2 removal reactor.

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

Task 3. Evaluation of Desulfurization Reactivity, Regenerability of the "New" Sorbents

The objective of this task was to identify "promising" candidate sorbent formulations for further development.

The tests in this task were carried out with the promising candidate sorbents in the packed-bed reactor as well as TGA unit, under operating conditions similar to those in Task 1, to provide a basis for comparison with the baseline commercial sorbent.

Based on the preliminary testing of the new sorbents (Task 2), ten (10) promising candidate sorbents were selected for evaluation in this task. The operating conditions for sulfation and regeneration of these sorbents in packed-bed tests are presented in Table 3. The high space velocity of 4000 hr^{-1} was chosen to allow completion of each cycle in a shorter period to avoid undesirable interruptions during a cycle. In addition to ten new alumina- supported copper-based sorbents prepared in this project, two additional bulk copper-based sorbents developed in earlier projects (for H_2S removal) were also evaluated in this task.

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

RESULTS AND DISCUSSION

In order to establish a baseline for the development of improved sorbents for the moving-bed copper oxide process, a large batch of the commercially available regenerable alumina-supported copper oxide sorbent (produced by ALCOA) was obtained for evaluation in this program. This sorbent has been used in the pilot scale unit at the Illinois Coal Development Park.

The performance of the baseline (ALCOA) sorbent was determined under a variety of operating conditions. Series of tests were conducted to determine the effects of various operating parameters on the removal efficiency as well as the effective capacity of the sorbent. The parameters studied in this project included sulfation and regeneration temperature, space velocity, and gas composition. The operating conditions in the baseline tests are given in Table 1 and the ranges of the operating variables used in the parametric study are presented in Table 2. The long-term durability of the ALCOA sorbent was also determined over 20 cycles conducted at the baseline condition.

To establish the baseline conditions for the tests conducted in this program, the initial series of tests was conducted to determine the effect of steam content of the flue gas during the sulfation stage as well as the methane content of the regeneration gas. The results of these tests appear to indicate that the effective capacity of the sorbent using a flue gas containing 7% steam is about 25% higher compared to the result obtained with dry flue gas. Comparison of the results of regeneration tests conducted using pure methane with results from tests conducted using a gas mixture containing 10% methane and 90% nitrogen indicates that regeneration with pure methane will result in a shorter regeneration time without adversely affecting the performance of the sorbent in the following cycle. Based on these initial results, the space velocity of 2,000 hr^{-1} was selected for the baseline condition. This space velocity, which is twice the space velocity expected in the pilot scale unit, will allow completion of each cycle in a shorter period to avoid undesirable interruptions during a cycle.

The SO_2 breakthrough concentration curves in a number of tests conducted at the baseline condition from separate series are presented in Figure 1. The results indicate that the performance of the sorbent can be determined accurately with excellent reproducibility.

The effects of sulfation temperature on the performance of the sorbent is presented in Figure 2 indicating that in the temperature range of 650-850°F, the sorbent performance increases with increasing temperature. Compared to the baseline condition of 750°F, a temperature change of ±100°F appears to affect the sorbent capacity by up to ±20%. The regeneration time is generally increased by 100% when regeneration temperature is increased by 100°F in the temperature range of 750°F to 950°F. Figure 3 shows the effect

of regeneration temperature on the effective capacity of the sorbent in the subsequent sulfation test. The results indicate that the effective capacity of the sorbent generally improves with increasing regeneration temperature. Compared to the results obtained at the baseline regeneration temperature of 850°F, a 100°F increase in regeneration temperature resulted in a 20% increase, while a 100°F decrease resulted in a 40% decrease in the effective capacity of the sorbent.

A series of 20-cycle tests was conducted to establish the long-term durability of the baseline sorbent. These tests were carried out at the baseline operating conditions given in Table 1. The results of this series of tests are presented in Figure 4, indicating that the effective absorption capacity of the sorbent gradually decreases during the cyclic process. As shown in Figure 4, the effective capacity of the ALCOA sorbent decreased by about 10% after 20 cycles.

Samples of regenerated sorbents from the 20th cycle were analyzed to determine any changes in the physical properties of the sorbent in the long-term durability test. The BET surface area of the regenerated sorbent reduces from 294 m^2/g to 179 m^2/g during the 20 cycles. Crush strength of the sorbent decreased slightly from 3.22 lb/mm to 2.71 lb/mm. Samples of fresh (as-received), sulfated, regenerated (several samples from different series), and after the life-cycle test were analyzed for their copper, aluminum, and sulfur contents. The results are presented in Table 4 indicating the presence of about 1% sulfur in the form of sulfate in the regenerated sorbents, which may be attributed to possible formation of aluminum sulfate during the sulfation stage. However, comparison of the regenerated sorbents after the 1st and 20th cycles suggests that the aluminum sulfate content of the sorbent is limited to about 1% and does not increase during the course of the cyclic process.

The effect of the space velocity on the performance of the sorbent is presented in Figure 5. The results indicate that an increase in the space velocity from the baseline condition of 2,000 hr^{-1} to 4,000hr^{-1} will result in about 33% reduction in the effective sorbent capacity, while a decrease in the space velocity to 500 hr^{-1} will result in an increase in effective sorbent capacity of 200%, leading to a sulfur loading of greater than 5%. The unexpectedly high sulfur capacity may indicate significant sorption of SO_2 on the sorbent at such low space velocities.

The effect of sulfur dioxide concentration on the sorption capacity of the sorbent is presented in Figure 6. As can be seen in the figure, the effective sorption capacity of the sorbent decreases with increasing sulfur dioxide concentration. At lower sulfur dioxide concentration the sulfur loading of the sorbent was higher than the theoretical capacity of the sorbent, calculated based on the copper content of the sorbent. This result is in agreement with the result obtained from the lower space velocity testing, strengthening the indication of sulfur dioxide-alumina reaction during sulfation.

In order to investigate the role of alumina in the sorption capacity of the baseline sorbent a series of tests were conducted on the fresh sorbent (i.e., as-received sorbent sulfated

during production) and the ALCOA alumina support. Comparison of the results of the sulfation tests involving the regenerated sorbent and the ALCOA support, as shown in Figure 7, indicate that at the space velocity of 2,000 hr^{-1}, about 20% of the sulfur sorbed by the sorbent is probably due to the presence of aluminum oxide. The effective capacity of the alumina support appears to decrease by about 50%, indicating that a significant fraction of the SO_2 sorption by alumina is probably due to adsorption of SO_2 rather than chemical reaction. This is further confirmed by the fact that a significant fraction of the SO_2 sorbed by alumina was released during nitrogen purge of the reactor at the sorption temperature as well as during the heat-up to regeneration temperature. Furthermore, no SO_2 was released after switching the gas to methane. A comparison of the sorption capacities of the alumina support with that of the as-received (sulfated) baseline sorbent is presented in Figure 8, suggesting that most of the sulfur sorbed by the sulfated sorbent can probably be attributed to alumina. Based on the results obtained so far, it is believed that the high sulfur loading observed at the very low space velocity is probably due to adsorption of SO_2 on the sorbent.

In the beginning of this project, two bulk copper-based sorbents developed by IGT in earlier projects, were evaluated for their sorption capacity under the operating condition indicated in Table 3. The results are presented in Figure 9, indicating that the effective sulfur capacities of these bulk sorbents are very low. In general, sorbent reactivity can be correlated with the specific surface area and porosity of the sorbent, while the mechanical strength of the sorbent is generally related to the sorbent composition as well as the thermal treatment of the sorbent during the preparation process. In conventional preparation techniques such as solid oxide mixing, co-precipitation, etc., the mechanical strength of the sorbent can generally be correlated with the calcination temperature. While higher calcination temperature generally results in a stronger sorbent, the surface area and the porosity (and consequently the reactivity) of the sorbent is adversely affected with increasing temperature. Therefore, to achieve high sorbent reactivity and high mechanical strength, it is desirable to use a preparation technique that does not require high calcination temperature during the preparation stage.

Among the alternative sorbent preparation techniques studied, the sol-gel sorbent synthesis techniques that have been shown to produce mechanically strong porous solids was selected and modified for preparation of new sorbents in this program. A number of batches of alumina support and copper oxide sorbents were prepared by sol-gel techniques, which do not require high calcination temperature. Specific surface areas, copper contents as well as crush strengths of the new sorbents and supports were determined along with those of ALCOA materials. A comparison of the crush strengths of the sol-gel based materials with those of ALCOA materials is presented in Figure 10. The results indicate that the crush strength of the alumina produced in this project by sol-gel techniques is about 7 times higher than that of the ALCOA alumina, while the crush strength of the copper-based sorbents produced by sol-gel is about 5 times higher than that of the baseline sorbent. A comparison of the surface areas and the copper concentrations of the new sorbents and those of the baseline sorbent are presented in Table 5. The BET surface area of the sol-gel based materials are comparable to those of

baseline materials. A significant fraction of the surface area in sol-gel based materials is attributed to the mesopores (i.e., pores with diameters larger than 50 Å), while the ALCOA materials have a much higher fraction in the macropore (i.e., pores with diameters larger than 500 Å) range.

The new sol-gel based sorbents were tested for their sulfur dioxide sorption capacity under the conditions indicated in Table 3. As presented in Figure 11, the sorption capacities of these sorbents were somewhat lower than that of the baseline material. Given the high surface area and favorable pore size distribution of the new sorbents, the low capacity may be attributed to possible partial plugging of the pores at the outer surface of the pellets, limiting the diffusion of the reactive gas into the pellets. To investigate this hypothesis, one of the new sorbents was crushed (i.e., d = 500-850 μm) and evaluated at the same operating conditions. As shown in Figure 12, the effective capacity of the new sorbent in crushed form is similar to that of the crushed baseline sorbent with similar copper content and particle size.

To better explain the observed differences in the crush strength and reactivity of the two type of sorbents, Scanning Electron Microscopy (SEM) analyses were performed on both the ALCOA and a selected sol-gel sorbent (IGT S9-50). The SEM micrograph of a number of sectioned pellets of ALOCA and S9-50 (at 12 to 16 times magnification) are shown in Figure 13, indicating that while the ALCOA sorbent generally consists of hollow and layered pellets, the S9-50 generally consists of homogeneous solid materials throughout the pellet. This is consistent with the observed higher crush strength of the new sorbents. The SEM micrograph of a single pellets of ALOCA and S9-50 (at 1250 times magnification) are shown in Figure 14, showing significant differences between the pore size distribution of the two materials. The ALCOA sorbent pellets consist of an aggregate of small particles with high macroporosity, while the S9-50 pellet generally consists of homogeneous mesoporous (50 < d < 500 Å) solid materials, which is consistent with the observed performance of the sorbents in the pellet form (due to pore blockage).

To improve the performance of the new sorbents, the chemical composition and the preparation technique were modified to change the pore size distribution of the new sorbents. The modifications included:

1. Addition of pore formers and other additives
2. Modification of granulation technique
3. Modification of drying technique
4. Modification of calcination technique.

Among these modifications, addition of chemical additives proved to be more effective in altering the pore size distribution. Modification of the calcination procedure improved the strength of the new sorbents by reducing the stresses on the material during this step.

A set of sol-gel based alumina pellets were produced to observe the impact of the pore formers and chemical additives on the porosity, pore size distribution and crush strength. Among the seven different pore formers and chemical additives tested, two of them caused significant improvement in the crush strength of the pellets (increasing it approximately 100%). One of the additives improved the sphericity of the produced pellets as well as allowing for the production of larger sizes (3-4 mm). Only one of the chemical additives created a significant increase in porosity (from approximately 4% to 23%). Although, the porosity was still not as high as in the ALCOA materials (34% for alumina, 36% for the regenerated sorbent), the sorption capacity of the sol-gel sorbent produced with this additive was comparable to that of the ALCOA sorbent (Figure 15). However, addition of this chemical had an adverse effect on the crush strength of the sorbent. Therefore, additional work is needed to optimize the sorbent composition and preparation technique to further improve the performance of the sorbent.

CONCLUSION(S) AND RECOMMENDATION(S)

In this project the commercial ALCOA copper-based alumina-supported sorbent was evaluated for its sulfation performance, regenerability, as well as physical and chemical characteristics in order to establish a baseline for the formulation of improved sorbents. The results of these tests indicate that, at the baseline operating conditions used in this project, the effective capacity of the sorbent is about 3% at a SO_2 breakthrough concentration of about 250 ppmv. The results also indicate that adsorption and formation of aluminum sulfate are probably contributing to SO_2 sorption during sulfation. The effective capacity of the ALCOA sorbent improves with increasing sulfation and regeneration temperatures and decreasing space velocity and influent sulfur dioxide concentration. The effective capacity of the sorbent decreased by about 10% following 20 cycles of sulfation/regeneration.

Comparison of the physical properties of the new sorbents prepared in this project, using sol-gel techniques, with those of the commercial ALCOA sorbent indicates that the new sorbents have significantly higher crush strength and similar surface area. Most of the surface area in the new sorbents is contributed from mesopores. The lack of macroporosity results in lower sorption capacity compared to the baseline sorbent.

The effective capacity of the new sorbents was improved by using chemical additives, However, the crush strength of the sorbent generally decreased. Therefore, additional work is needed to optimize the sorbent composition and preparation technique to further improve the performance of the sorbent.

REFERENCES

1. Clean Coal Technology, The New Coal Era, DOE/FE-0217P, Nov. 1989, U.S. Department of Energy, Washington, D.C. 20585.

2. Request for Proposals for Research and Development of Illinois Coal, DCCA/OCDM RFP98-1, Date Issued: June 23, 1998.

3. Manahan, S.E. General Applied Chemistry, 2nd Edition, 1982, Willard Grant Press, Boston, MA.

4. Hoffman, J.S., Smith, D.N., Pennline, H.W., and Yeh, J.T. "Removal of Pollutants from Flue Gas Via Dry, Regenerable Sorbent Processes," 1992 AIChE Spring National Meeting, March 29-April 2, 1992,

5. Gas Purification, "Combined NO_x/SO_2 Post-Combustion Processes, pp. 928-934.

6. Gas Purification, "Sulfur Dioxide Removal," pp. 627-634

7. Markussen, J.M. and Pennline, H.W., "Investigation of Sorbent Regeneration Kinetics in the Copper Oxide Process," 1993 SO2 Control Symposium, Washington, D.C., U.S. EPA, 1995, v.4, Paper 93. EPA-600/R-95/015d.

8. Yeh, J.T., Hoffman, J.S., and Pennline, H.W., "Design of a Moving-Bed Copper Oxide Process for Simultaneous SO_2 and NO_x Removal," Air & Waste Management Association, 86th Annual Meeting & Exhibition, Denver, CO, June 13-18, 1993.

9. Hoffman, J.S., Pennline, H.W., Yeh, J.T., Ratafia-Brown, J.A., and Gorokhov, V.A., "Integration of a High Efficiency Flue Gas Cleanup Process into Advanced Power Systems," Proceedings of the 19th International Technical Conference on Coal Utilization & Fuel Systems, Clearwater, FL, March 21-24, 1994, Washington, D.C., Coal and Slurry Technology Association, 1994, pp. 541-552.

10. Yeh, J.T., Hoffman, J.S., and Pennline, H.W., "Study of a Moving-Bed Copper Oxide Process for Simultaneous SO_2 and NO_x Removal," Air & Waste Management Association, 88th Annual Meeting & Exhibition, San Antonio, TX, June 18-23, 1995.

11. Yeh, J.T., Pennline, H.W., Hoffman, J.S., Resnik, K.P., and Vore, P.A. "Life Cycle Tests of the Moving-Bed Copper Oxide Process for SO_2 and NO_x Control," Air & Waste Management Association, 89th Annual Meeting & Exhibition, Nashville, TN, June 23-28, 1996.

12. Darguzas, J.N., Pennline, H., Sloat, D.G., and Penrose, J. "Moving Bed Copper Oxide Desulfurization and NO_x Removal Process Development," Final Technical Report to the Illinois Clean Coal Institute, Sept. 1, 1994 through Jan. 15, 1996.

13. Sloat, D.G., Darguzas, J.N., Gaikwad, R., and Penrose, J.C., "Further Development of a Copper Oxide Desulfurization and NO_x Removal System," Interim Final Technical Report to the Illinois Clean Coal Institute, Sept. 1, 1996 through Aug. 31, 1997.

14. Deng, S.G. and Lin, Y.S. "Sulphation and Regeneration of sol-gel Derived Regenerative Sorbents for Flue Gas Desulfurization," AIChE Symposium Series, 1995, No. 309, Vol. 91.

15. Deng, S.G. and Lin, Y.S. "Synthesis, Stability, and Sulfation Properties of sol-gel-Derived Regenerative Sorbents for Flue Gas Desulfurization," Ind. Eng. Chem. Res. 1996, 35, 1429-1437.

16. Deng, S.G. and Lin, Y.S. "Granulation of sol-gel-Derived Nanostructured Alumina," AIChE Journal, February 1997, Vol. 43, No. 2, 505-514.

DISCLAIMER STATEMENT

Table 1. Baseline Conditions for Sorbent Evaluation

	Sulfation	Regeneration
Temperature, °F	750	850
Pressure, bar	1	1
Space Velocity, hr^{-1}	2000	2000
Gas Composition, vol%		
SO_2	0.25	-
O_2	3.7	-
H_2O	7	-
CO_2	14	-
N_2	75.1	-
CH_4	-	100

Table 2. Ranges of Operating Parameters

Parameter	Sorption	Regeneration
Temperature, °F	650-850	750-950
Pressure, bar	1	1
Space Velocity, hr^{-1}	500-4000	500-4000
Gas Composition		
SO_2, ppmv	1000-4000	-
O_2, %	3.7	-
N_2, %	Balance	-
CH_4, %	-	100
H_2O, %	7	-
CO_2, %	14	-

Table 3. Conditions for New Sorbent Evaluation

	Sulfation	Regeneration
Temperature, °F	750	850
Pressure, bar	1	1
Space Velocity, hr^{-1}	4000	4000
Gas Composition, vol%		
SO_2	0.25	-
O_2	3.7	-
N_2	96.05	-
CH_4	-	100

Table 4. Chemical Composition of ALCOA Sorbent

Sorbent	Cu (%)	Al (%)	S-Sulfate (%)	S-Sulfide (%)
As-received	5.44	36.3	2.84	-
Sulfated	5.47	37.0	4.71	-
Regenerated (1st cycle)	6.01	42.0	1.34	0.04
Regenerated (2nd cycle)	-	-	1.10	0.02
Regenerated (3rd cycle)	-	-	1.03	0.17
Regenerated (after 20 cycle)	-	-	0.90	-

Table 5. Surface Area and Copper Analysis Results

Sorbent	BET Surface Area (m^2/g)	Surface Area of Pores > 50A (m^2/g)	Cu content (%)
ALCOA alumina	304	68	-
ALCOA sorbent (regenerated)	294	65	6.79
sol-gel alumina	293	180	-
19-WI	193	150	6.72
S3-26B	294	215	3.43
S10-48	251	169	9.57
S9-49A	266	206	8.71
S9-50	213	145	7.89
S8-52	193	117	3.52
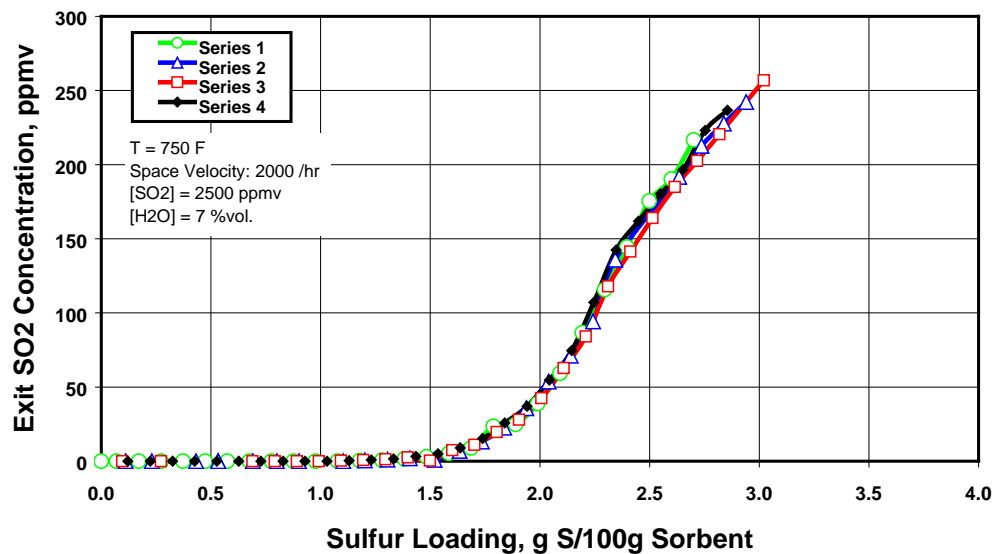
Figure 1. Reproducibility of Sulfur Loading
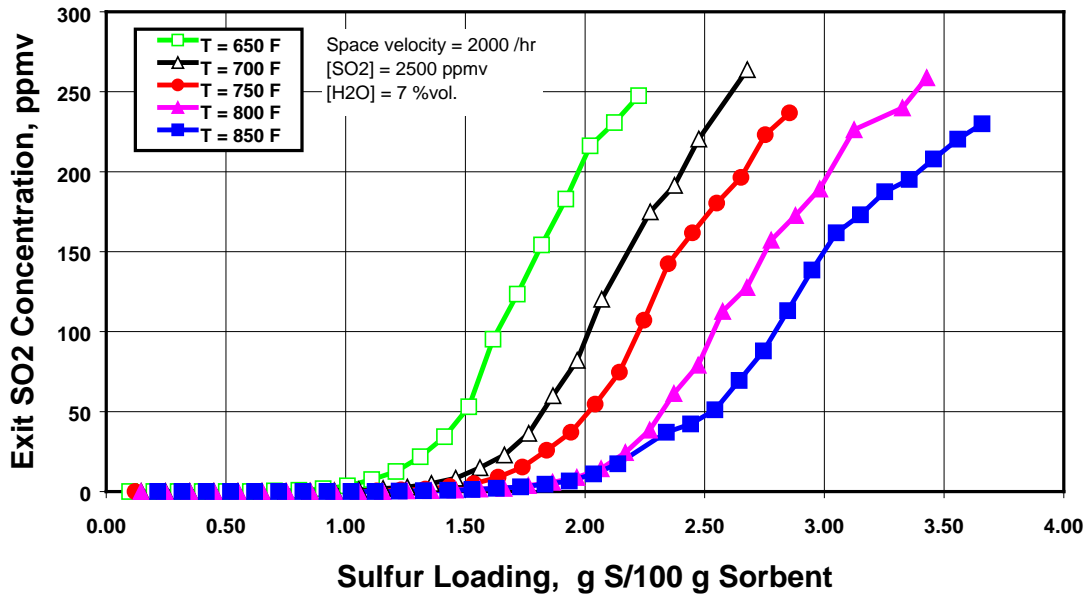
Figure 2. Effect of Sulfation Temperature on the Sorbent Loading
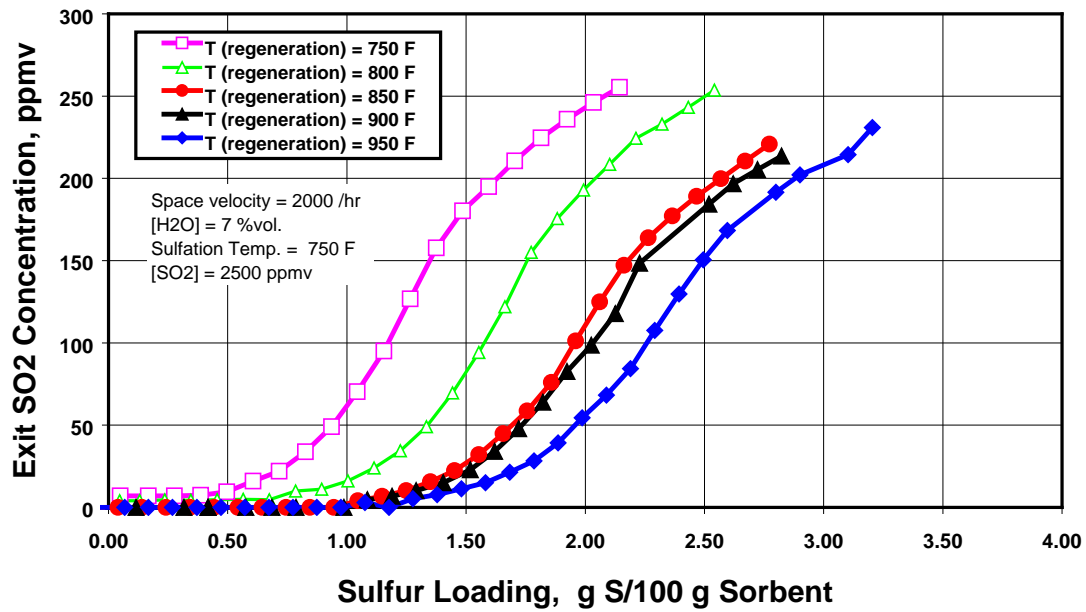
Figure 3. Effect of Regeneration Temperature on Sorbent Loading
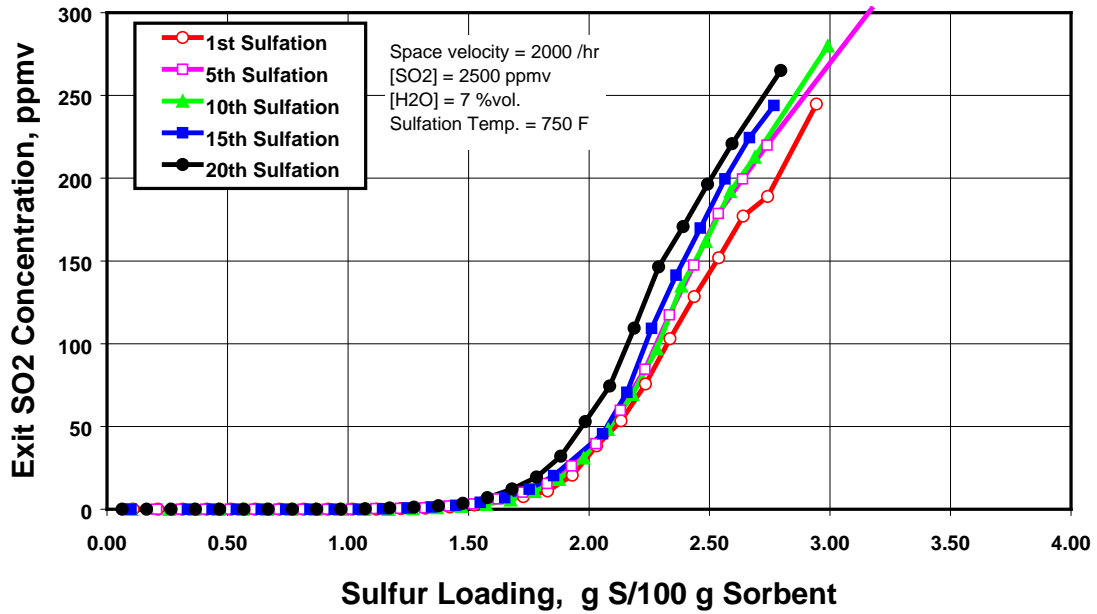
Figure 4. Sorbent Performance in Long-Term Durability Study
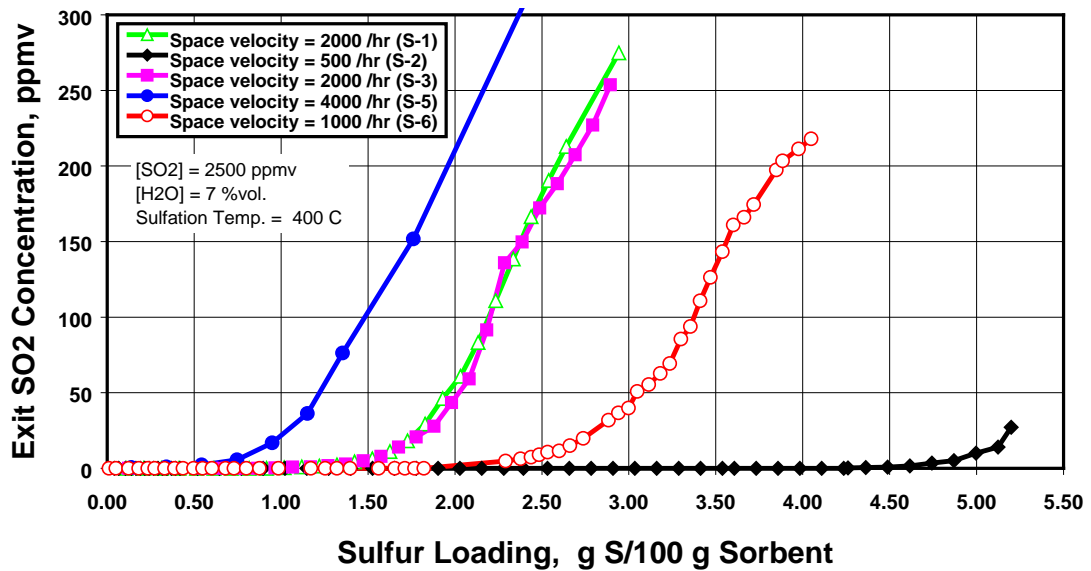
Figure 5. Effect of Space Velocity on the Sorbent Performance
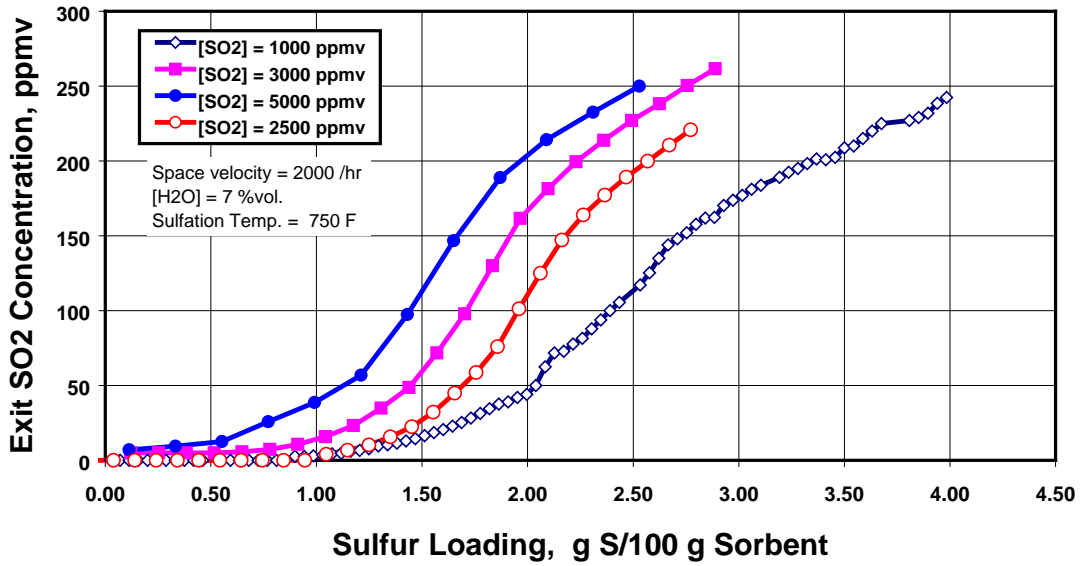
Figure 6. Effect of Sulfur Dioxide Concentration on the Sorbent Performance
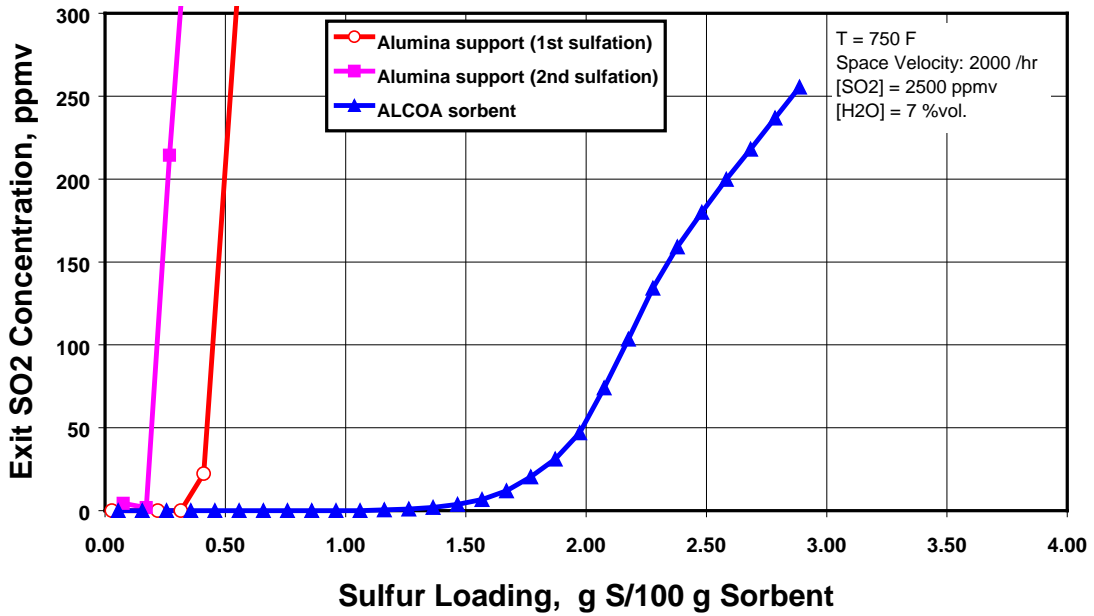
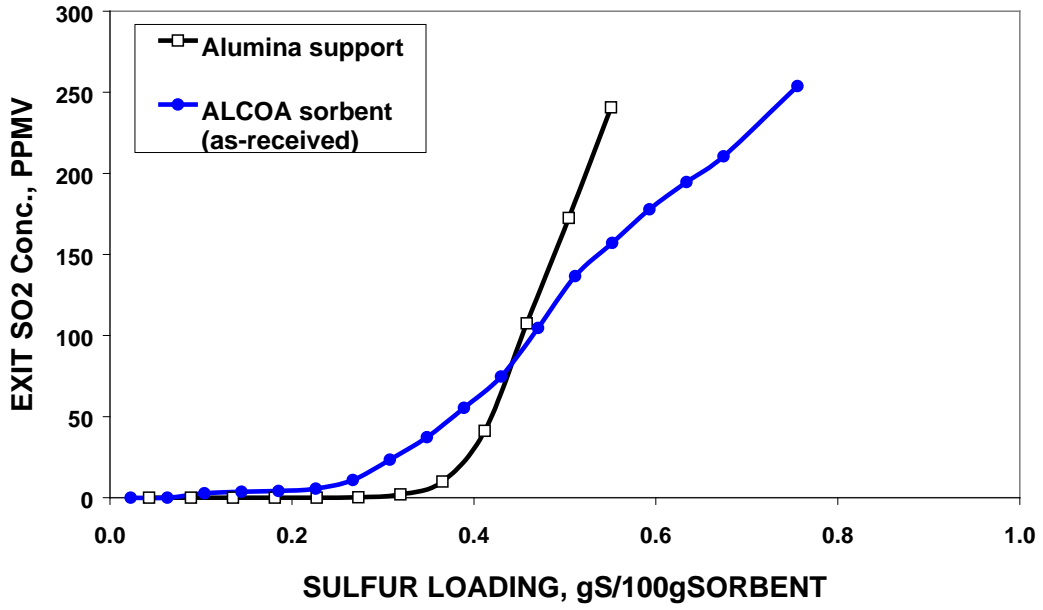**Figure 7.** Performance of Alumina vs. ALCOA Sorbent

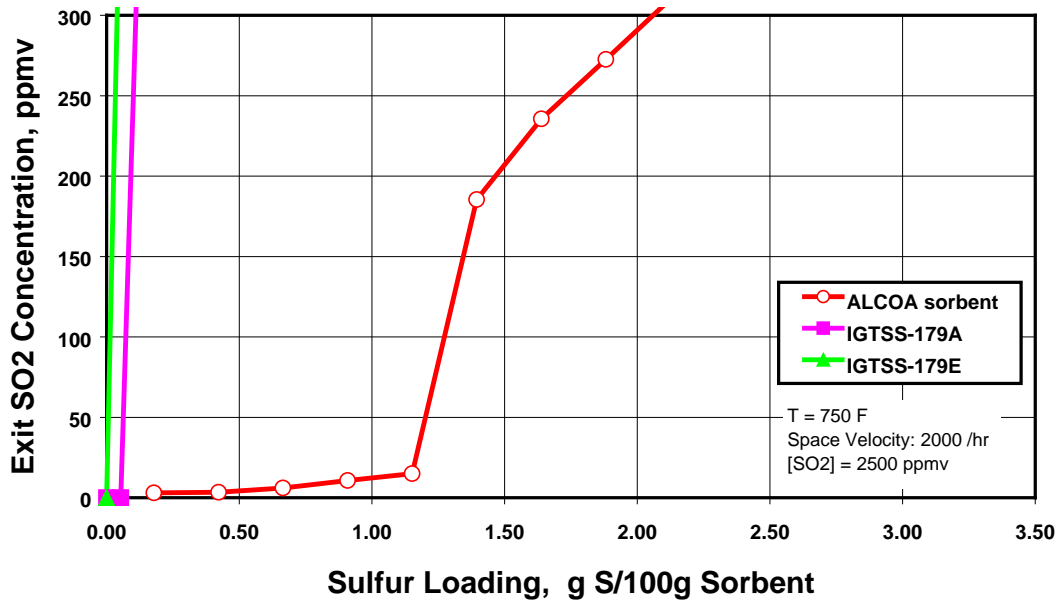**Figure 8.** Comparison of Sorption Capacities of Fresh Sorbent and Alumina Support

Figure 9. Comparison of the Sorption Capacities of Bulk Sorbents with Baseline Sorbent
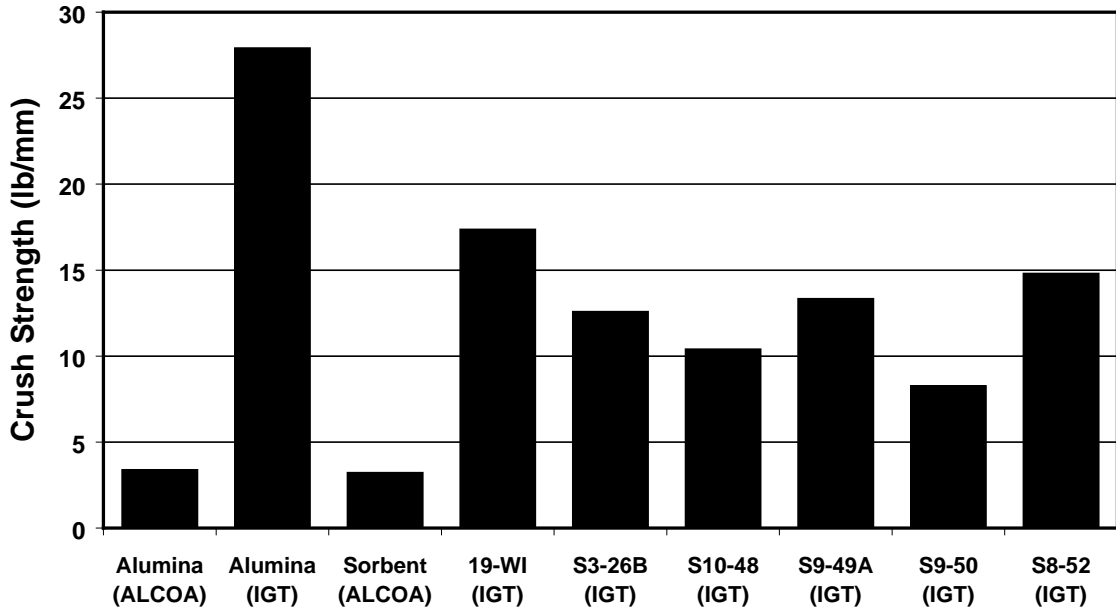
Figure 10. Crush Strength of Sorbents
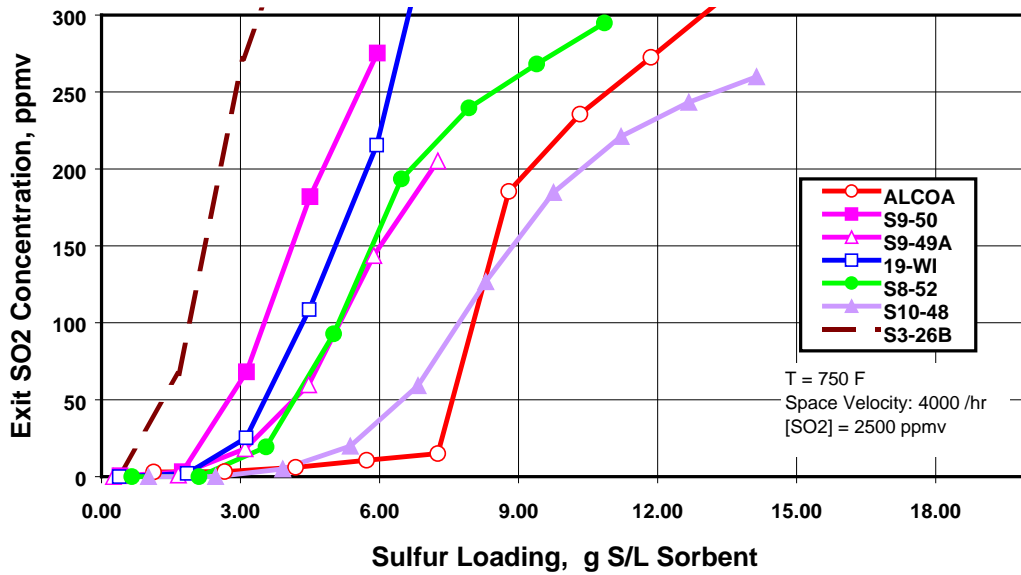
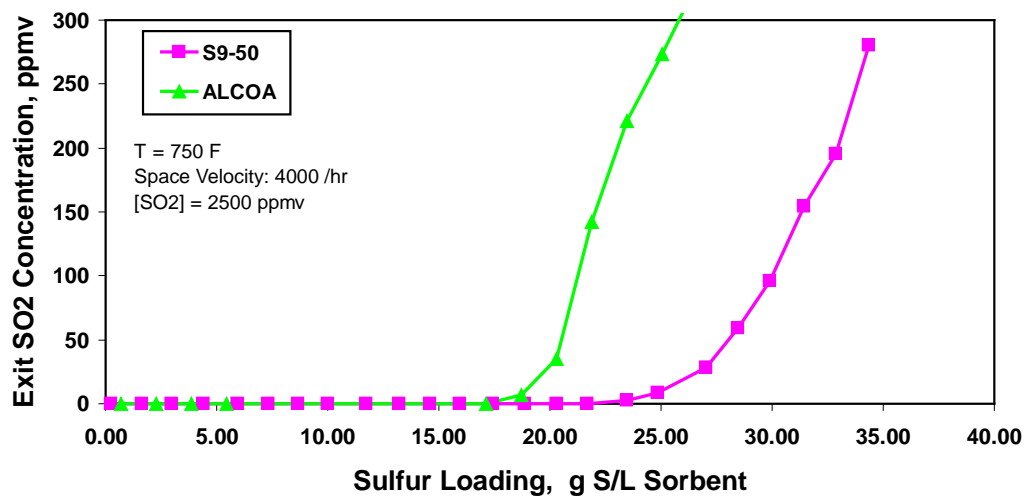**Figure 11.** Sorption Capacities of Various Sol-Gel Sorbents

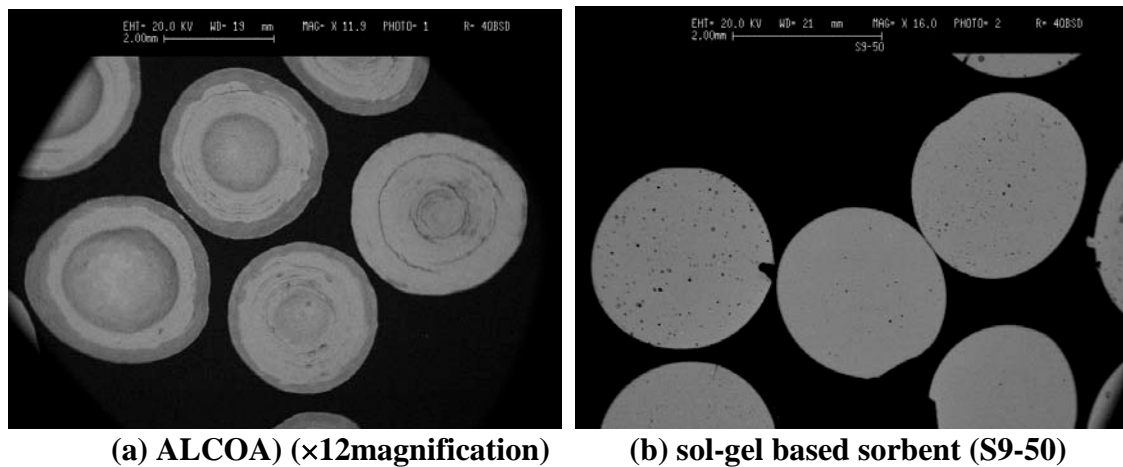**Figure 12.** Comparison of Crushed Sol-Gel and ALCOA Sorbents

(a) ALCOA) (×12magnification)   **(b) sol-gel based sorbent (S9-50)**

Figure 13. SEM Micrographs of Sorbents

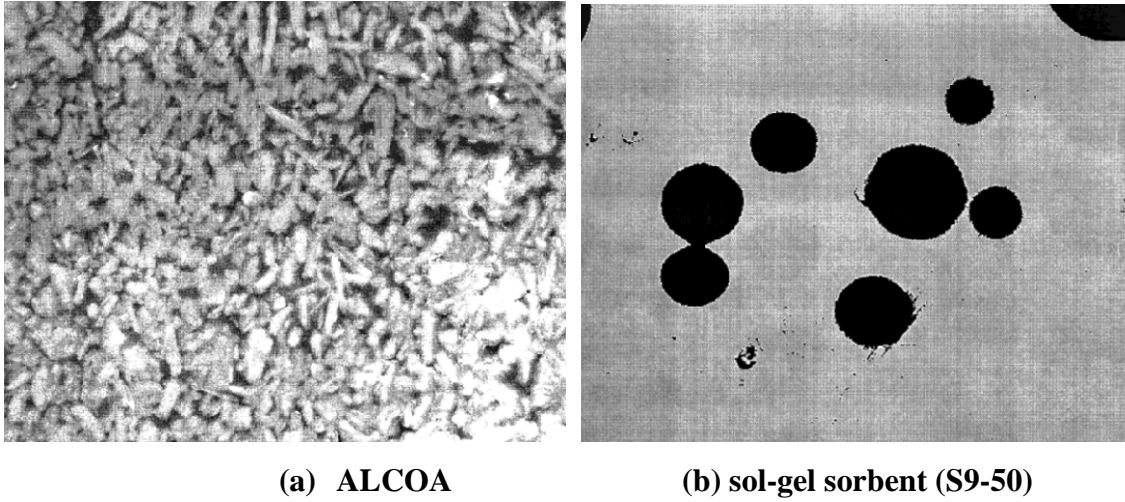(a) ALCOA   (b) sol-gel sorbent (S9-50)

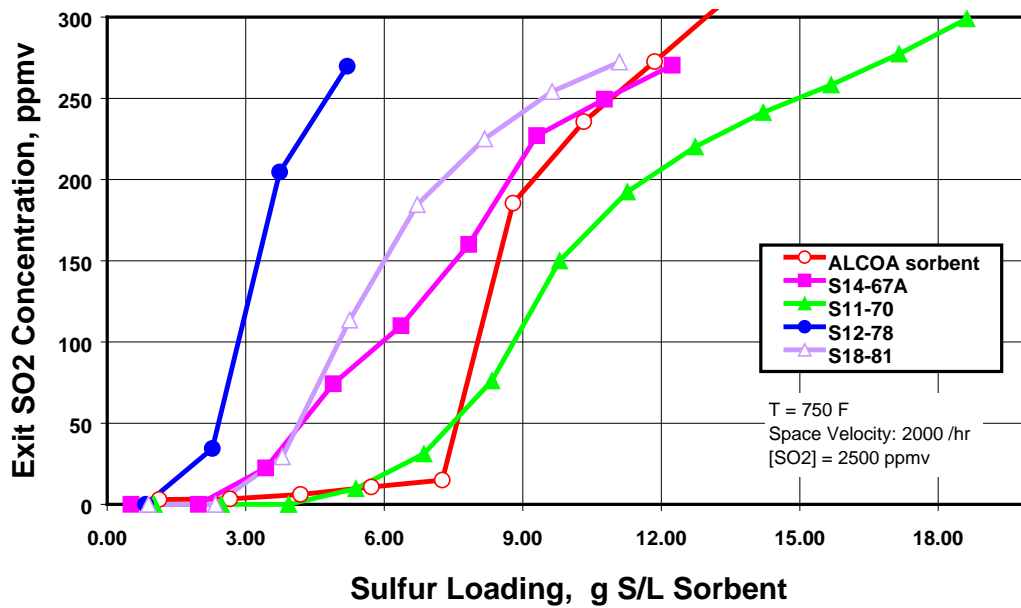**Figure 14.** Comparison SEM Micrographs of Sorbents (×1250 magnification)

Figure 15. Performance of Sol-Gel Sorbents with Additive