

FINAL TECHNICAL REPORT
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Project Title: **DEVELOPMENT OF SORBENTS FOR A FLUID-BED PROCESS TO CONTROL SOX AND NOX**

ICCI Project Number : 00-1/2.2B-2

Principal Investigator : Dr. Javad Abbasian, Illinois Institute of Technology (IIT)

ICCI Project Manager : Dr. Ken K. Ho, ICCI

ABSTRACT

The overall objective of the proposed program was to develop highly reactive and attrition resistance copper oxide sorbent for combined SO₂ and NO_x removal from coal combustion flue gases in a fluid bed process.

To achieve this objective, a total of twenty-one (21) new sorbent formulations were prepared using a modified *sol-gel* technique. The nominal copper content of the sorbents ranged from 5% to 33%. The sorbents were evaluated for their SO₂ sorption capacities in a packed-bed as well as fluidized-bed reactors. The best result was obtained with ICCI-Cu-10, which exhibited a 92 % higher sulfur capacity and nine(9) times lower attrition index, compared commercial sorbent.

Parametric studies were carried out with ICCI-Cu-10 sorbent. The parameters studied included space velocity, sulfation and regeneration temperatures, and SO₂ inlet concentration. The “optimum” sulfation and regeneration temperatures were determined to be 450 °C, which also leads to desirable isothermal operation, eliminating the need for external heating of the sulfated sorbent.

The long term durability of the the ICCI-Cu-10 sorbent was determined in a “life-cycle” test series consisting of 25 sulfation/regeneration cycles. The results indicate that the effective sulfur capacity of the sorbent initially increases during the first few cycle, followed by a gradual decrease during the next 10-15 cycles. The effective sorbent capacity of the sorbent appears to stabilize at 2% after the 20th cycle.

The catalytic activity of the sorbent ICCI-Cu-10g for reduction of NO_x from the flue gases was also determined. The results indicated that the fresh sorbent and regenerated sorbent are capable of reducing 91.4% and 92.6% of the NO_x content of the flue gas, respectively, while the sulfated sorbent can reduce more than 99.2 % of the NO_x to nitrogen. The results also indicate that the catalytic activity of the sorbent for reduction of NO_x is not adversely affected by the cyclic process.

EXECUTIVE SUMMARY

During 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 moisture to form acids which then fall as acid rain. The threat from acid rain is made 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 is currently equipped with Flue Gas Desulfurization (FGD) processes.

Conventional FGD processes include “wet throwaway” processes using lime or limestone-water mixture, and “dry throwaway” processes using lime slurries for spray drying or duct injection. However, there are several disadvantages associated with these processes, which include, among others, generation of large quantities of waste, a tendency towards scaling and plugging, erosion, and negligible NO_x removal capability. Therefore, advanced processes that are based on dry regenerable sorbents offer attractive advantages over the conventional FGD processes.

The copper oxide based processes are one of the most promising emerging technologies for SO_2 and NO_x removal from flue gases. In these processes, SO_2 in the flue gas reacts with the reactive component of the sorbent, i.e. CuO , and O_2 to form copper sulfate (CuSO_4). The sulfated sorbent is regenerated by a reducing gas, such as methane (CH_4), decomposing the sulfate to elemental copper (Cu) and a concentrated stream of SO_2 . In addition to SO_2 removal via chemical reaction, the sorbent also serves as a catalyst to remove a significant portion of the NO_x in the feed flue gas. This step is accomplished by the controlled addition of ammonia (NH_3) to the feed flue gases prior to entering the desulfurization unit.

Various reactor designs have been proposed, including fixed bed, fluidized-bed, and moving bed reactors. fluid bed copper oxide processes offers several advantages over the moving bed processes which include much smaller reactor size, simpler reactor design, and improved gas /solid contacting. Because of the significantly smaller size of the sorbent granules (or powder) in the fluid bed process, higher sorbent conversion can be achieved. Furthermore, because of the small size of the pellets, instead of low capacity supported pellets, higher capacity bulk sorbent granules can be used. Significantly higher capacity of the sorbent granules combined with the higher conversion results in tremendous reduction in sorbent requirement. However, highly reactive and attrition resistant sorbents are required to minimize attrition losses and the sorbent make-up rate.

Development of highly reactive and attrition resistant sorbents will expedite the commercialization of an economically more attractive fluid bed copper oxide flue gas desulfurization process, which will result in increased consumption of Illinois coal and creation of substantial number of new jobs and new source of revenue for the State of Illinois.

In earlier ICCI funded programs, the principal investigator of this project has developed highly reactive and highly attrition resistant sorbent granules for H₂S removal in fluid bed using a *sol-gel* based technique. The modified *sol-gel* technique was applied to produce reactive copper oxide pellets with significantly improved crush strength for the moving bed copper oxide process.

The overall objective of the this project was to develop highly reactive and attrition resistance copper oxide sorbents for combined SO₂ and NO_x removal from coal combustion flue gases in a fluid bed process. leading to the development of a more efficient and economically more attractive fluid-bed copper oxide process to control SO₂ and NO_x .

To achieve the project objectives, a total of twenty-one (21) new sorbent formulations were prepared. The nominal copper content of the sorbents ranged from 5% to 33%. To improve the sorbent reactivity toward SO₂, ammonium hydroxide (NH₄OH) was added to the gel matrix. The molar ratio of NH₄OH:HNO₃ was also controlled, as was the dispersion of the NH₄OH solution over the gel matrix. The ammonium hydroxide to nitric acid ratios [i.e., (NH₄OH) : HNO₃] were 0,1, and 2. The attrition resistance of these sorbents was determined and compared with that of the commercially available sorbent. The results indicate that the attrition indexes of the new sorbents developed in this project are 5 to 9 times lower than the commercially available baseline sorbent.

The sorbents were evaluated for their SO₂ sorption capacities in packed-bed as well as fluidized-bed reactors. The results obtained with the seven (7) leading sorbents developed in this project indicate that all the seven sorbents have higher sulfur capacity compared to the commercially available baseline sorbent. The best result was obtained with ICCI-Cu-10, which contains 15% copper. This sorbent has 92 % higher sulfur capacity and nine (9) times lower attrition index compared to the baseline sorbent.

All the above sorbents were produced from aluminum tri-secondary butoxide (i.e., ALTSB, Al(OC₄H₉)₃) precursor. Two additional formulation were produced using aluminum isopropoxide (i.e., ALISOP, Al(OC₃H₇)₃). The copper content of these sorbents was 15%. The results of initial evaluation of these sorbents indicate that the sorbents produced using ASTLB precursor have significantly higher SO₂ sorption capacity, compared to those produced with ALISOP precursor.

The higher effective sulfur capacity exhibited by the ICCI-Cu10 sorbent is believed to be due to higher copper content as well as higher surface area and porosity compared to other sorbents. It should be noted that the lower copper content of the commercially available baseline sorbent is mainly due to the limitation imposed by wet impregnation techniques. Higher copper loading in wet impregnated sorbents generally leads to pore plugging, resulting in lower sorbent reactivity. This was one of the most important features of the *sol-gel* method by which the copper-based sorbents for this project were prepared.

To determine the effects of operating parameters on sorbent performance, parametric studies were carried out with ICCI-Cu-10 sorbent. The operating variables investigated in this project included sulfation temperature (350°-450°C), regeneration temperature (400°-500°C), space velocity (4000-8000 hr⁻¹), and inlet SO₂ concentrations (1200-5000 ppmv). The results of these tests indicate that the effective sulfur capacity of the sorbent significantly improve with increasing sulfation the effective sulfur capacity of the sorbent increase by increasing regeneration temperature in the proceeding cycle. The lower capacity of the sorbent following regeneration at 400 °C (compared to the baseline 450 °C) may be attributed to incomplete regeneration, while the improved performance of the sorbent following regeneration at 500 °C is believed to be the result of changes in the pore structure of the sorbent. It should be noted that although increasing the regeneration temperature to 500 °C, appeared to have beneficial affect on the sorbent performance, it is believed that sorbent exposure to higher temperature can have adverse affect on long-term performance of the sorbent. Therefore, based on the results of the parametric studies, the “optimum” sulfation and regeneration temperatures determined to be 450 °C, which also leads to desirable isothermal operation, eliminating the need for external heating of the sulfated sorbent.

To determine the long term durability of the sorbent, a “life-cycle” test series consisting of 25 sulfation/regeneration cycles was conducted with the ICCI-Cu-10 sorbent. The results indicate that the effective sulfur capacity of the sorbent initially increases during the first few cycle, followed by a graduate decrease during the next 10-15 cycles. The effective sorbent capacity of the sorbent appears to stablize at 2% after the 20th cycle.

The catalytic activity of the sorbent ICCI-Cu-10g for reduction of NO_x from the flue gases was also determined. The tests were carried out at a temperature of 450 °C and a space velocity of 4000 hr⁻¹, using a simulated flue gas mixture containing 500 ppmv of NO_x and 500 ppmv of NH₃. These tests were performed using fresh, sulfated (after 2nd and 25th cycles), and regenerated (after 25th cycle) sorbents. The results indicate that the fresh sorbent and regenerated sorbent are capable of reducing 91.4% and 92.6% of the NO_x content of the flue gas, respectively, while the sulfated sorbent can reduce more than 99.2 % of the NO_x to nitrogen. The results also indicate that the catalytic activity of the sorbent for reduction of NO_x is not adversely affected by the repeated cycling.

Given that repeated calibration of the NO_x analyzer used in this experiment indicated the instrument was not able to detect the NO_x levels below 8 ppmv, it can be concluded that the NO_x removal efficiency of the sulfated materials is about 99.2 % (± 0.8 %). Therefore, it is conceivable that the sorbent may be capable of completely reducing NO_x content of the flue gases.

OBJECTIVES

The goal of this program was to develop suitable regenerable sorbents for a fluid bed copper oxide process to simultaneously remove SO₂ and NO_x from coal combustion flue gases. The work performed in this project focused on development and evaluation of high capacity, highly reactive and attrition resistant copper based sorbents for fluid bed application.

The specific objectives of this project were to:

- Synthesize a number of high capacity, highly reactive and attrition resistant copper based sorbents (granules or powder).
- Evaluate the sorbents to identify the “best” sorbent formulation, based on attrition resistance, chemical reactivity, regenerability, catalytic activity, as well as all other relevant physical and chemical properties.
- Determine the optimum operating condition for combined removal of SO₂ and NO_x.
- Demonstrate the overall durability of the “best” sorbent in a “life-cycle” test at the optimum process conditions

INTRODUCTION AND BACKGROUND

During coal combustion sulfur in coal is released in the form of sulfur dioxide (SO₂) in the flue gas and a small fraction of nitrogen in the form of NO₂ and NO, commonly referred to as NO_x. The SO₂ and NO_x emissions are very damaging to the environment because they combine with moisture to form acids which then fall as acid rain. The threat from acid rain is made more of a concern by the burning of high-sulfur coal.

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 more of a 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 SO₂ 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 programs.

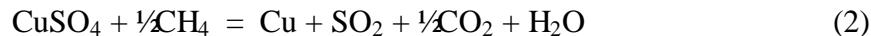
A number of processes have been developed for flue gas desulfurization (FGD). These include dry systems, where a dry solid is used to absorb SO_2 from stack gas, and wet systems, where a solution or slurry is used instead. Some systems are known as throwaway systems because the absorbing substance is 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⁾ The most commonly used system is lime slurry scrubbing, which uses a slurry of $\text{Ca}(\text{OH})_2$ suspended in water to absorb SO_2 . Disadvantages of this approach include the generation of a large amount of sludge, from 30 to 60 million tons per year in the U.S. alone.⁽³⁾

A concept that has received significant attention is the development of processes for the combined removal of SO_2 , and NO_x , from flue gases using dry regenerable sorbents.^(4,5) Example of such processes include the NOXSO process, the fluid- and moving-bed copper oxide processes, and the cerium oxide (CeO_2) process. Other materials that have been investigated include the use of magnesium oxide (MgO) in combination with vermiculite (magnesium-aluminum-silicate).⁽⁶⁾

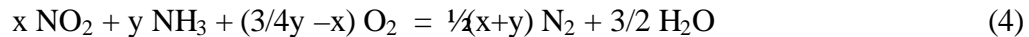
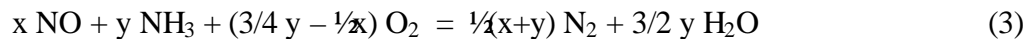
In copper oxide processes, flue gas consisting of N_2 , CO_2 , H_2O , O_2 , SO_2 , and NO_x is passed through the desulfurization (or sulfation) reactor containing the sorbent. SO_2 reacts with the reactive component of the supported sorbent, i.e. CuO , and O_2 to form copper sulfate (CuSO_4). The desulfurization reaction is carried out at a temperature in the vicinity of 400°C , and may be represented by the following reaction:



The sulfated sorbent is regenerated by a reducing gas, such as methane (CH_4), decomposing the sulfate to elemental copper (Cu) and a byproduct gaseous stream. When methane is used, it has been reported that regeneration can be conducted successfully at 450°C ,⁽⁷⁾ and the regeneration reaction may be described by the following reaction:



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. In addition to SO_2 removal via chemical reaction, the sorbent also serves as a catalyst to react a significant portion of the NO_x with a controlled amount of ammonia (NH_3) via selective catalytic reduction (SCR) to form N_2 and H_2O , according to Reactions (3) and/or (4). It has been reported that both CuO and CuSO_4 act as catalysts for NO_x removal from flue gases.⁽⁴⁾



Combined SO₂/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 SO₂ 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 NH₃ over alumina supported copper-based catalysts suggest that the optimum NO_x removal efficiency can be achieved with NH₃/NO_x ratio in the range of 1.0-1.2.⁽²⁰⁻²³⁾

Various reactor designs have been proposed, including fixed bed, fluidized-bed, and moving bed reactors. Fluid bed copper oxide processes offer several advantages over the moving bed processes which include much smaller reactor size, simpler reactor design, and improved gas /solid contacting. Because of the significantly smaller size of the sorbent granules (or powder) in the fluid bed process, higher sorbent conversion can be achieved. Furthermore, because of the small size of the pellets, instead of low capacity supported pellets, higher capacity bulk sorbent granules can be used. Significantly higher capacity of the sorbent granules combined with the higher conversion results in significant reduction in the sorbent requirement. However, all the sorbents developed to date, have been reported to suffer from excessive attrition.⁽¹⁴⁾ Therefore, to make these processes economically viable, highly reactive and attrition resistant sorbents are needed to minimize attrition losses and the sorbent make-up rate.

It has been shown that highly reactive and physically strong sorbents can be produced by *sol-gel* technique.⁽²⁴⁻²⁹⁾ In a recent program, jointly sponsored by USDOE and ICCI, a modified *sol-gel* technique was developed to produce ZnO-based sorbents for H₂S removal, which can achieve the challenging combination of high reactivity and high attrition resistance.⁽³⁰⁾ In another ICCI funded project, the modified *sol-gel* technique was applied to produce reactive copper oxide pellets with significantly improved crush strength for the moving bed copper oxide process.⁽³¹⁾

This project was geared toward using the modified *sol-gel* technique developed in the earlier ICCI sponsored projects to develop and evaluate a number of highly reactive and attrition resistant copper oxide sorbent for combined SO₂ and NO_x removal, leading to the development of a more efficient and economically more attractive fluid-bed copper oxide process to control SO₂ and NO_x.

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. Initial Evaluation of Sorbents

Task 3. Parametric Studies

Task 4. Sorbent Durability Studies

Task 1. Synthesis and Characterization of the Sorbents

The objective of this task was to prepare highly reactive and attrition resistant copper-based sorbents to be used for testing in Task 2, Task 3, and Task 4 of the project.

In this task, a total of twenty one (21) new sorbents were prepared. The experience and the expertise gained in the earlier ICCI funded projects were applied to produce similar sorbents for combined SO₂ and NO_x removal. The sorbent preparation parameters included selection of precursors, preparation technique, chemical composition, and thermal treatment history.

Initial efforts were directed towards preparation 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 and attrition resistance. To improve the porosity and pore size distribution and eventually the sorbent performance, ammonium hydroxide (NH₄OH) was added to the gel matrix. The molar ratio of NH₄OH:HNO₃ was also controlled, as was the dispersion of NH₄OH solution over the gel matrix. The attrition resistances of these sorbents were determined for comparison with the baseline commercial sorbent.

Small quantities of each sorbent formulation were prepared for initial assessment of the attrition resistance of the sorbent. Larger quantities of formulations, which met minimum attrition resistance requirements, were produced for further characterization. The formulations selected in this task were analyzed using standard characterization techniques including chemical composition, bulk density and BET surface area as well as attrition resistance. The results of physical and chemical characterization in Task 1 were thoroughly analyzed to select several suitable sorbent formulations for testing in Task 2.

Task 2. Initial Evaluation of the Sorbents

The objective of this task was to identify the “best” sorbent formulation for parametric and durability studies in Task 3 and Task 4.

The tests in this task were carried out with the selected candidate sorbents (identified in Task 1) in packed-bed as well as fluidized-bed reactors. The effectiveness of the sorbents for the removal of the SO₂ was determined over one (1) to three (3) cycles. The operating condition in these tests is given in Table (1).

The schematic diagram of packed-/fluidized-bed unit is presented in Figure 1. 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 a typical test, a known quantity of the sorbent is loaded into the reactor and the reactor is brought to the predetermined temperature and exposed to a simulated flue gas mixture containing the desired level of SO₂ and NO_x. A gas chromatograph and a NO_x analyzer are used for determination of the SO₂ and NO_x content of the reactor feed and effluent. The NO_x and

pre-breakthrough SO₂ content of the reactor effluent determine the effectiveness of the sorbents for removal of these species, while the SO₂ breakthrough time represents the effective capacity of the sorbents.

Seven (7) sorbents were evaluated for their SO₂ sorption capacities in a packed-bed reactor. The regenerability of these sorbents was also determined. Following the results obtained in the fixed bed testing, six (6) sorbents were evaluated for their SO₂ sorption capacities in a fluidized-bed reactor. Based on the results obtained in this task, the “best” sorbent formulation was identified for the parametric and durability studies in Task 3 and Task 4.

Task 3. Parametric Studies

The objective of this task was to determine the optimum operating condition for removal of SO₂ and NO_x in the fluid bed copper oxide process.

The tests in this task were carried out in the fluid bed reactor with the “best” sorbent identified in Task 2. The operating variables investigated in this task included sulfation temperature (350°-450°C), regeneration temperature (400°-500°C), space velocity (4000-8000 hr⁻¹), and inlet SO₂ concentrations (1200-5000 ppmv). Based on the results of tests conducted in this task, the optimum operating condition was determined. The optimum operating condition was used in the “life-cycle” tests in Task 4.

Task 4. Sorbent Durability (Life-Cycle) Studies

The objective of this task was to demonstrate the suitability of the “best” sorbent formulation for long term application in a fluid bed copper oxide process. The tests in this task were conducted in the fluidized-bed reactor unit at the optimum operating conditions determined in Task 3.

In this task, the “best” sorbent formulation, identified in task 2, was subjected to twenty five (25) cycles of sulfation and regeneration at the optimum operating condition which was determined in Task 3.

The catalytic activities of the fresh sorbent as well as sulfated and regenerated sorbent after the 1st and 25th cycles for NO_x reduction were also determined. The simulated flue gas in these tests contained 500 ppmv NO_x and 500 ppmv NH₃.

RESULTS AND DISCUSSION

Task 1. Synthesis and Characterization of the Sorbents

As indicated earlier, the main objective in this project was to develop highly reactive and attrition resistant copper-based sorbents for a fluidized-bed process to simultaneously remove SO_x and NO_x from flue gases. A total of twenty-one (21) new sorbent formulations were prepared. The attrition resistance of these sorbents was determined and compared with that of the commercially available sorbent. To improve the sorbent reactivity toward SO_2 , ammonium hydroxide (NH_4OH) was added to the gel matrix. The molar ratio of $\text{NH}_4\text{OH}:\text{HNO}_3$ was also controlled, as was the dispersion of the NH_4OH solution over the gel matrix. The attrition resistances (attrition index) of a selected number of sorbents are shown in Figure 2, indicating that the attrition index of the new sorbents developed in this project are 5 to 9 times lower than the commercially available baseline sorbent.

The physical and chemical properties of a selected number of sorbents are given in Table 2. The nominal copper content of the sorbents prepared in this project ranged from 5% to 33%. The ammonium hydroxide to nitric acid ratios [i.e., (NH_4OH) : HNO_3] were 0,1, and 2. As shown in Table 2, the copper content of the sorbent determined through chemical analysis are generally lower than the nominal composition, which may be attributed to uncalcined copper nitrate. The results also indicate that as the nominal copper content of the sorbent increases above 15%, the BET surface area gradually decreases. The results also appear to suggest that the sorbent porosity also decreases with increasing copper content, as indicated by increasing sorbent density. The lower surface area and porosity in the sorbents is expected to lead to lower reactivity (or sulfur capacity), that will be discussed later.

Task 2. Initial Evaluation of the Sorbents

The sorbents were evaluated for their SO_2 sorption capacities in a packed-bed reactor. The sorbents bed volume in these tests was 10 cc. The operating conditions are given in Table 1. The results obtained with the seven (7) leading sorbents developed in this project as well as that of the baseline commercial sorbent are presented in Figure 3. As seen from this figure, all seven (7) sorbents exhibited improvement in the sorption capacity compared to the commercially available baseline sorbent. The best result was obtained with ICCI-Cu-10, which exhibited a 92 % improvement over the commercial sorbent.

Six (6) sorbent formulations were also evaluated for their SO_2 sorption capacities in a fluidized bed reactor under similar operating condition.. The results of these tests are presented in Figures 4. As indicated in Table 2, the new sorbent formulations produced in this program by the *sol-gel* technique have different bulk densities. Given that higher densities translate to higher sulfur loadings on the volume basis, the effective sulfur capacities of all the selected sorbents are presented also presented on volume basis in Figure 5. It should be noted that although, the cost of the sorbent is generally based on sorbent weight, since 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.

All the above sorbents were produced from aluminum tri-secondary butoxide (i.e., ALTSB, $\text{Al}(\text{OC}_4\text{H}_9)_3$) precursor. Two additional formulations were produced using aluminum isopropoxide (i.e., ALISOP, $\text{Al}(\text{OC}_3\text{H}_7)_3$). The copper content of these sorbents was 15%. A comparison of the sorption capacities of the sorbents produced with different precursors is presented in Figure 7, indicating that the sorbents produced using ASTLB precursor have significantly higher SO_2 sorption capacity, compared to those produced with ALISOP precursor.

A summary of results of evaluation of the sorbents is presented in Table 3. A plot of the effective sulfur capacity (at SO_2 breakthrough concentration of 100 ppmv) as a function of copper content of the sorbents is presented in Figure 6, indicating that the optimum copper content appears to be about 15%.

The results clearly indicate that the sorbent designated as ICCI-Cu-10 which has a sulfur loading of 2.4% on wt. Basis (corresponding to 21 g S/L on volume basis) and an attrition index of 0.92 %-mass/hr is the “best” sorbent formulation developed in this project. The higher effective sulfur capacity exhibited by the ICCI-Cu10 sorbent is believed to be due to higher copper content as well as higher surface area and porosity compared to other sorbents. It should be noted that the lower copper content of the commercially available baseline sorbent is mainly due to the limitation imposed by wet impregnation techniques. Higher copper loading in wet impregnated sorbents generally leads to pore plugging, resulting in lower sorbent reactivity. This was one of the most important features of the *sol-gel* method by which the copper-based sorbents for this project were prepared. As shown in Table 1, the maximum copper loading attained was as high as 33 % (nominal), which was 4.5 times higher than wet impregnated baseline sorbent.

Following the selection of ICCI-Cu-10 as the “best” sorbent formulation, a large batch of the sorbent was needed to carry out the more detailed evaluation, which includes parametric studies to determine the effects of operating condition and durability studies to determine the suitability of the sorbent for long term application. However, because of the unavailability of large mixer and calcining furnace, it was decided to prepare eight (8) identical batches, mix the sized sorbent, and riffle the mixed batch into sixteen (16) identical smaller batches for the detailed evaluation tests.

Task 3. Parametric Studies

Parametric studies were carried out with ICCI-Cu-10 sorbent. The parameters studied included space velocity, sulfation and regeneration temperatures, and SO_2 inlet concentration. The ranges of the parameters investigated are given in Table 4. The SO_2 sorption capacity of the ICCI-Cu-10 sorbent from the first fluidized-bed sulfation cycle in several tests conducted at the baseline condition (see Table 1) with identical samples are presented in Figure 8, indicating that the experimental data obtained in this project can be reproduced with excellent accuracy.

The effect of sulfation temperature on the sorption capacities of the sorbent is presented in Figure 9, indicating that the effective sulfur capacity of the sorbent significantly improve with increasing sulfation temperature. Figure 10 shows the effect of space velocity on the sorbent performance. As expected, the effective sulfur capacity of the sorbent decreases with increasing space velocity. The effect of SO₂ inlet concentration on the performance of the sorbent is presented in Figure 11, indicating that the effective sulfur capacity of the sorbent decreases with increasing SO₂ inlet concentration. Figure 12 shows the effect of regeneration temperature on performance of the sorbent in the subsequent sulfation cycle. The lower capacity of the sorbent following regeneration at 400 °C (compared to the baseline 450 °C) may be attributed to incomplete regeneration, while the improved performance of the sorbent following regeneration at 500 °C is believed to be the result of changes in the pore structure of the sorbent. It should be noted that although increasing the regeneration temperature to 500 °C, appeared to have beneficial affect on the sorbent performance, it is believed that sorbent exposure to higher temperature can have adverse affect on long-term performance of the sorbent. Therefore, based on the results of the parametric studies, the “optimum” sulfation and regeneration temperatures determined to be 450 °C, which also leads to desirable isothermal operation, eliminating the need for external heating of the sulfated sorbent.

Task 4. Sorbent Durability (Life-Cycle) Studies

To determine the long term durability of the sorbent, a “life-cycle” test series consisting of 25 sulfation/regeneration cycles was conducted with the ICCI-Cu-10 sorbent. The results of the 1st, 5th, 10th, 15th, 20th and 25th cycles are shown in Figure 13. The effective sulfur capacity of the sorbent (at SO₂ breakthrough concentration of 100 ppmv) is shown in Figure 14. The results indicate that the effective sulfur capacity of the sorbent initially increases during the first few cycle, followed by a graduate decrease during the next 10-15 cycles. The effective sorbent capacity of the sorbent appears to stablize at 2% after the 20th cycle.

The catalytic activity of the sorbent ICCI-Cu-10g for reduction of NO_x from the flue gases was also determined. The tests were carried out at a temperature of 450 °C and a space velocity of 4000 hr⁻¹, using a simulated flue gas mixture containing 500 ppmv of NO_x and 500 ppmv of NH₃. These tests were performed using fresh, sulfated (after 2nd and 25th cycles), and regenerated (after 25th cycle) sorbents. The results indicated that the fresh sorbent and regenerated sorbent are capable of reducing 91.4% and 92.6% of the NO_x content of the flue gas, respectively, while the sulfated sorbent can reduce more than 99.2 % of the NO_x to nitrogen. The results also indicate that the catalytic activity of the sorbent for reduction of NO_x is not adversely affected by the cyclic process.

Given that repeated calibration of the NO_x analyzer used in this experiment indicated the instrument was not able to detect the NO_x levels below 8 ppmv, it can be concluded that the NO_x removal efficiency of the sulfated materials is about 99.2 % (± 0.8 %). Therefore, it is conceivable that the sorbent may be capable of completely reducing NO_x content of the flue gases.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be made from the results obtained in this study:

- The attrition index of the new sorbents developed in this project are 5 to 9 times lower than the commercially available sorbent.
- The optimum copper content of the sorbent appears to be about 15%.
- The ICCI-Cu-10 sorbent is the best formulation developed in this project, exhibiting 92% higher sulfur capacity and 9 times lower attrition index. Compared to the commercially available baseline sorbent.
- The “optimum” sulfation and regeneration temperatures determined to be 450 °C, which also leads to desirable isothermal operation, eliminating the need for external heating of the sulfated sorbent.
- The fresh sorbent and regenerated sorbent are capable of reducing 91.4% and 92.6% of the NO_x content of the flue gas, respectively, while the sulfated sorbent can reduce more than 99.2 % of the NO_x to nitrogen.
- The catalytic activity of the sorbent for reduction of NO_x is not adversely affected by the cyclic process.

Based on the favorable results obtained in this study, further work is needed to address the following issues:

- Determination of the effects of the key variables on the extent of NO_x removal, ammonia slip, and SO₃ removal. The key variables should include
 - ❖ Reactor temperature
 - ❖ NO_x concentration
 - ❖ NO_x/NH₃ ratio
 - ❖ Gas residence time.

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Table 1. Baseline Operating Conditions

| Operating Variable | Sulfation | Regeneration |
|----------------------------------|-----------|--------------|
| Temperature, °C | 400 | 450 |
| Pressure, bar | 1 | 1 |
| Space Velocity, hr ⁻¹ | 4000 | 2000 |
| Gas Composition, vol% | | |
| SO ₂ | 0.25 | - |
| O ₂ | 3.7 | - |
| CO ₂ | 14 | - |
| N ₂ | balance | - |
| CH ₄ | - | 100 |

Table 2 Physical and Chemical properties of Various Sorbents

| Sorbent | Copper Content (Wt.%) | | Aluminum Content (Wt. %) From Analysis | Nitrogen Surface Area (m ² /g) | NH ₄ OH/HNO ₃ Volume Basis | Bulk Density (g/cc) |
|------------|-----------------------|----------|--|---|--|---------------------|
| | Nominal | Analysis | | | | |
| ICCI-Cu- 1 | 5 | - | - | - | - | 0.7 |
| ICCI-Cu-2 | 10 | - | - | - | - | 1.14 |
| ICCI-Cu-3 | 7 | - | - | - | - | 0.96 |
| ICCI-Cu-4 | 7 | - | - | - | - | 0.97 |
| ICCI-Cu-5 | 7 | - | - | - | 1:1 | 0.90 |
| ICCI-Cu-6 | 12 | 12.4 | 44.1 | 149 | 1:1 | 0.94 |
| ICCI-Cu-7 | 10 | 8.77 | - | - | 1:1 | 0.87 |
| ICCI-Cu-8 | 33 | 26.3 | 34.2 | 135 | 2:1 | 1.13 |
| ICCI-Cu-9 | 21 | 17.2 | 40.3 | 141 | 2:1 | 1.14 |
| ICCI-Cu-10 | 15 | 13.2 | 41.1 | 168 | 2:1 | 0.92 |

Table 3: Characteristics of the sorbents subjected to Fluidized Bed sulfation tests

| Sorbent | Bulk Density (g/cc) | Sulfur Loading (g S / 100g Sorbent) | Sulfur Loading (g S / L Sorbent) | Attrition Index (%-mass / hr.) |
|------------|---------------------|-------------------------------------|----------------------------------|--------------------------------|
| ICCI-Cu-4 | 0.97 | 0.9 | 8 | - |
| ICCI-Cu-5 | 0.90 | 1.7 | 14 | 1.7 |
| ICCI-Cu-6 | 0.94 | 2.1 | 19 | 0.95 |
| ICCI-Cu-7 | 0.87 | 2.2 | 17 | 0.8 |
| ICCI-Cu-9 | 1.14 | 1.2 | 13 | 1.7 |
| ICCI-Cu-10 | 0.92 | 2.4 | 21 | 0.9 |

Table 4. Ranges of Operating Conditions in Parametric Studies

| Operating Variable | Sulfation | Regeneration |
|---|-----------|--------------|
| Temperature, °C | 350-450 | 400-500 |
| Space Velocity, hr ⁻¹ | 4000-8000 | 2000 |
| SO ₂ inlet concentration, ppmv | 1200-5000 | - |

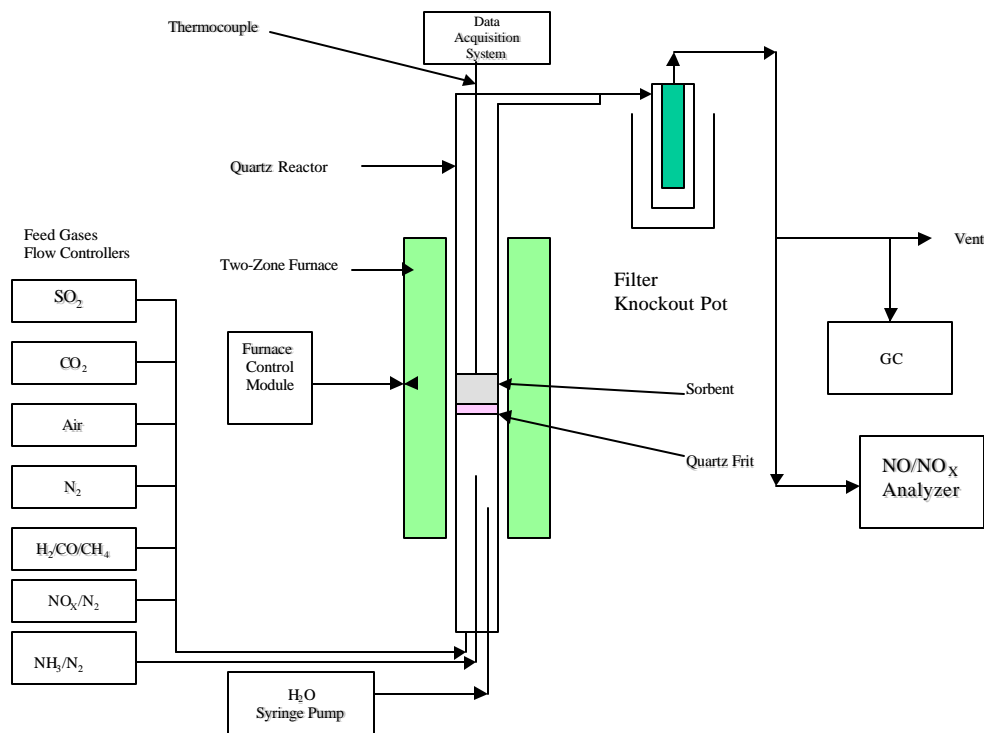
**Figure 1. Schematic Diagram of the Packed-/Fluidized -Bed Reactor unit**

Figure 2. Comparison of Attrition Indices of various sorbents

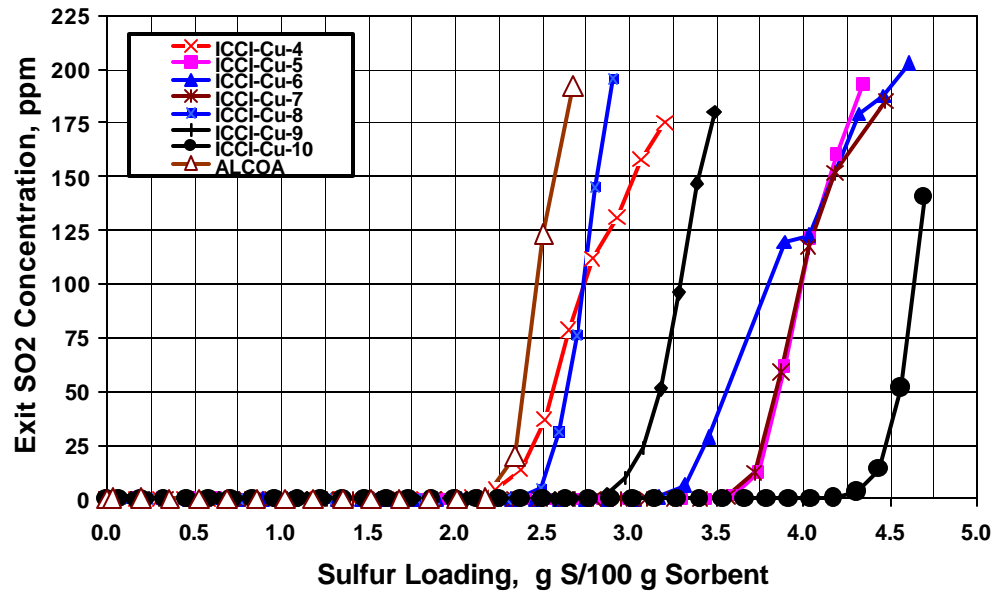


Figure 3. Comparison of Packed-Bed Performance of Different Sorbents

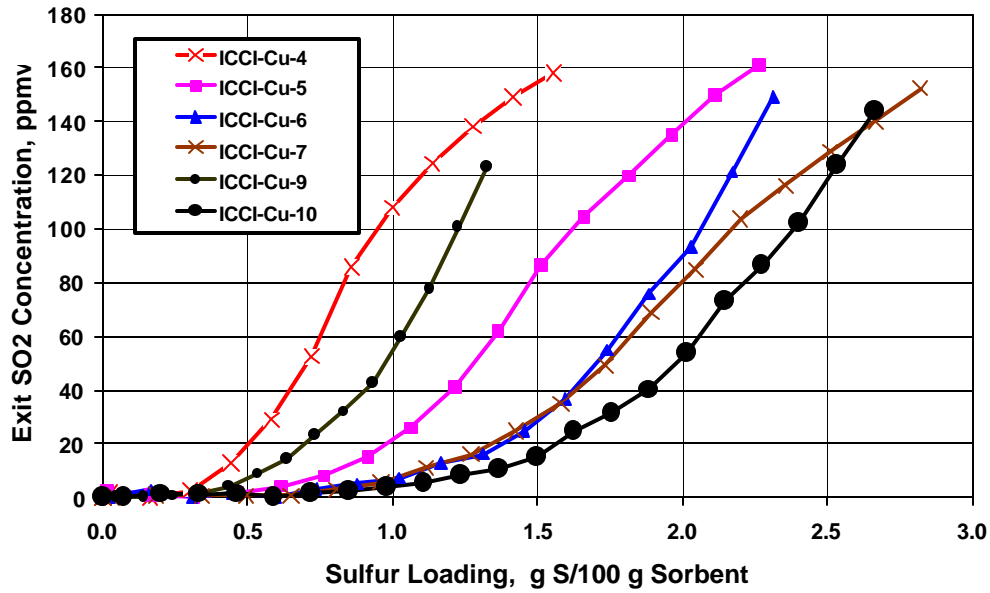


Figure 4. Comparison of Fluid-Bed Performance of Different Sorbents (wt. basis)

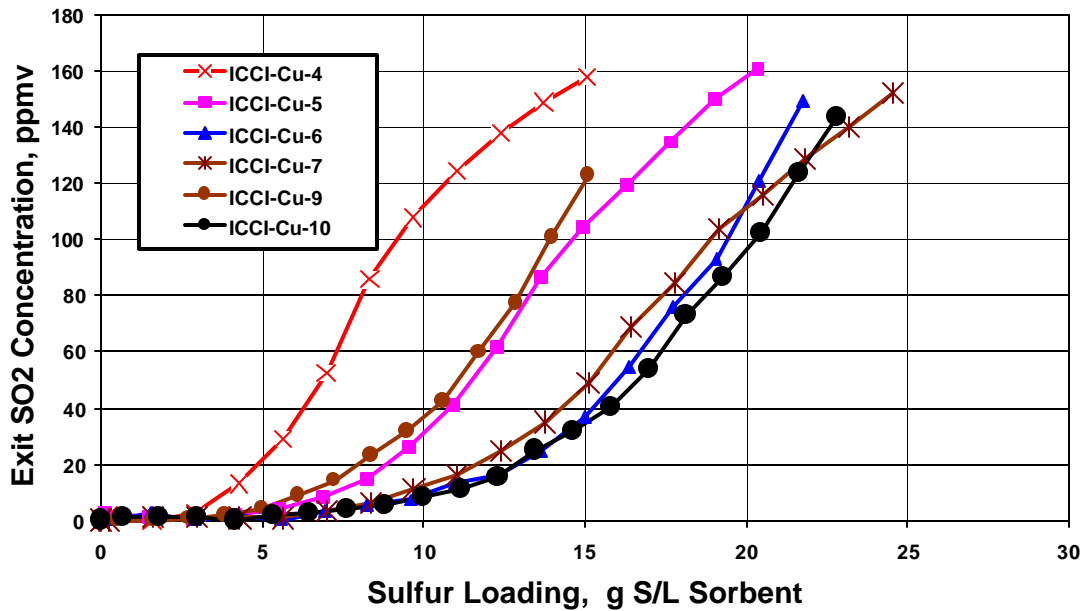


Figure 5. Comparison of Fluid-Bed Performance of Different Sorbents (vol. Basis)

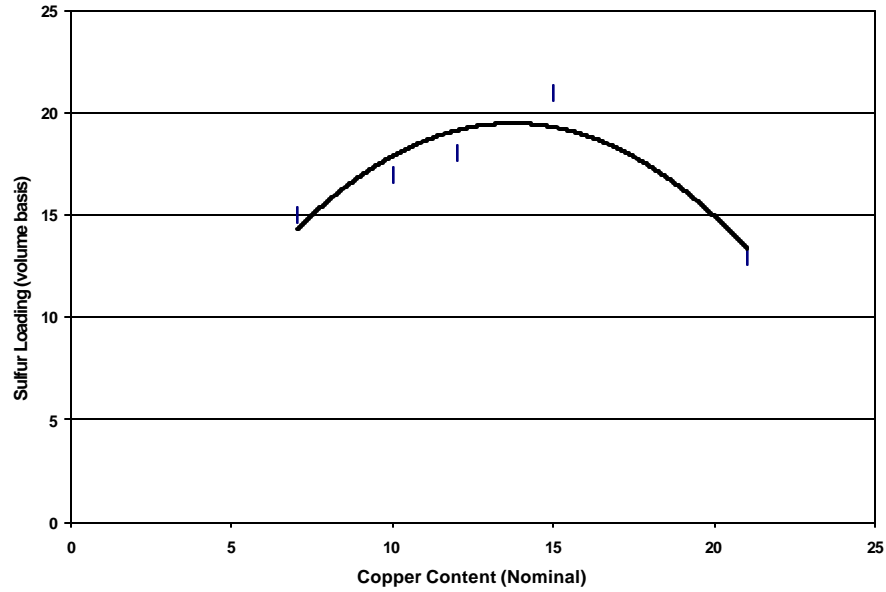


Figure 6. Effect of copper content on Sulfur capacity (vol. basis)

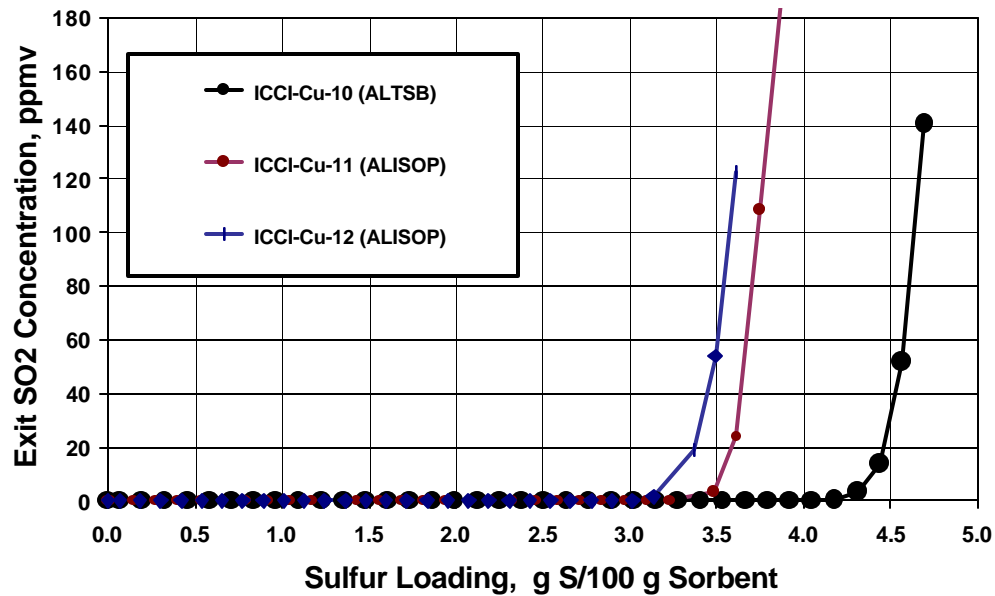


Figure 7. Comparison of Effective Sorption Capacities of Sorbents Prepared from Different Precursors

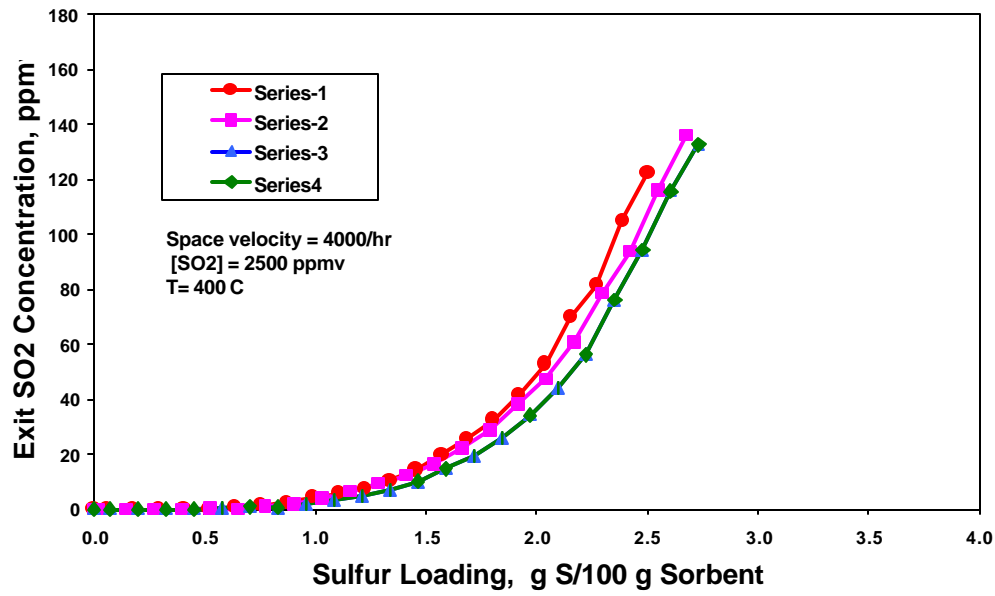


Figure 8. Reproducibility of Data obtained in Sorbent Evaluation Tests

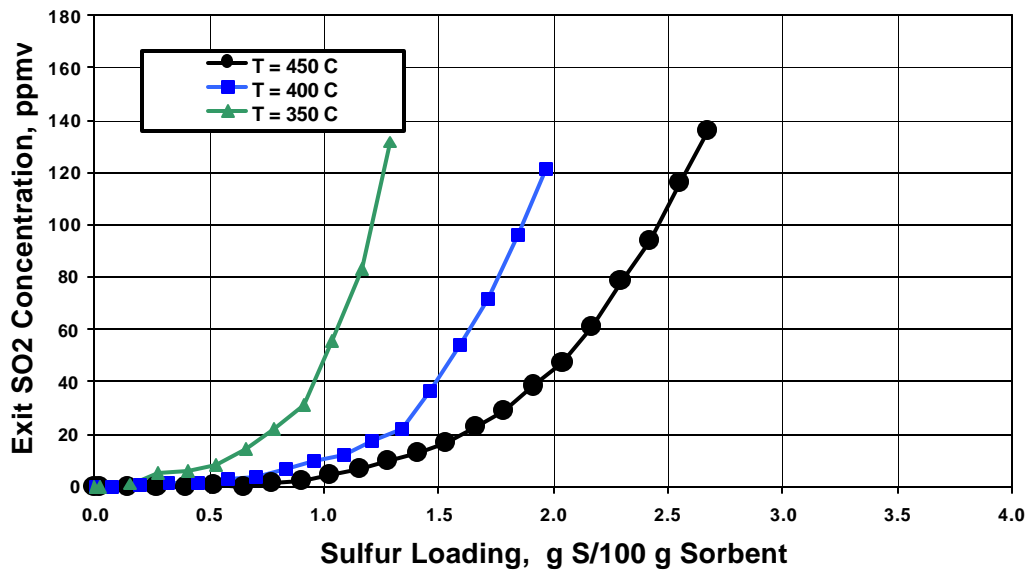


Figure 9. Effect of Sulfation Temperatures on Sorbent Performance.

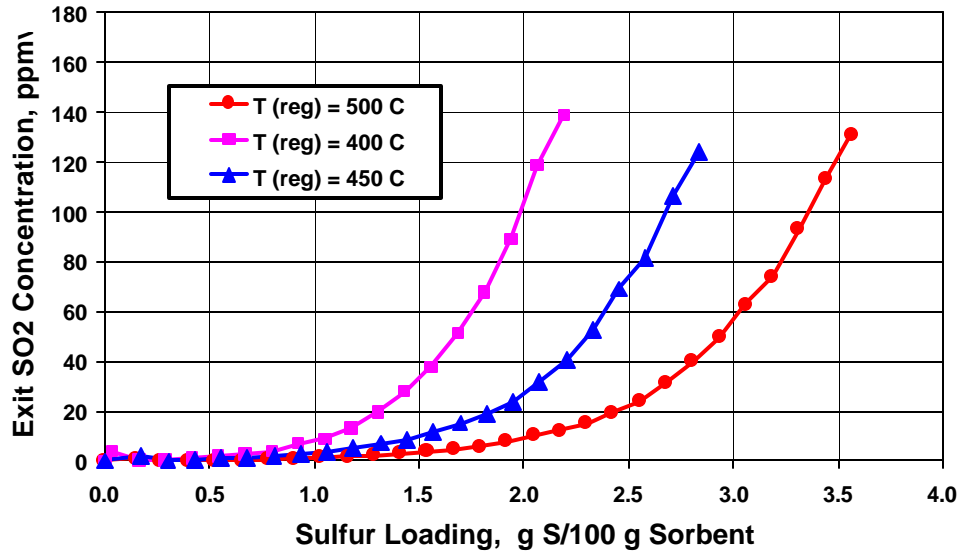


Figure 10. Effect of Regeneration Temperature on Sorbent Performance in Subsequent Cycle

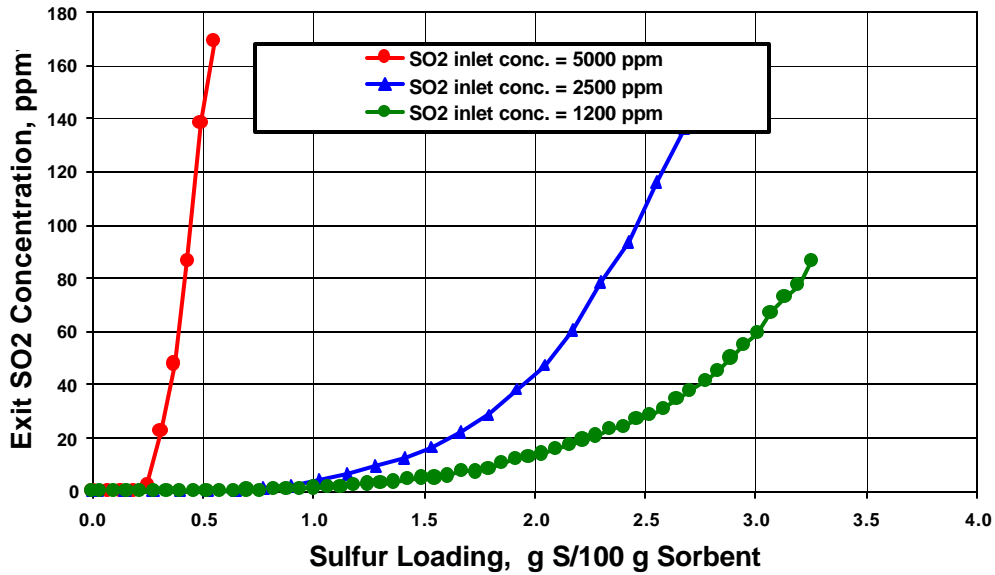


Figure 11. Effect of Inlet SO₂ Concentrations on Sorbent Performance

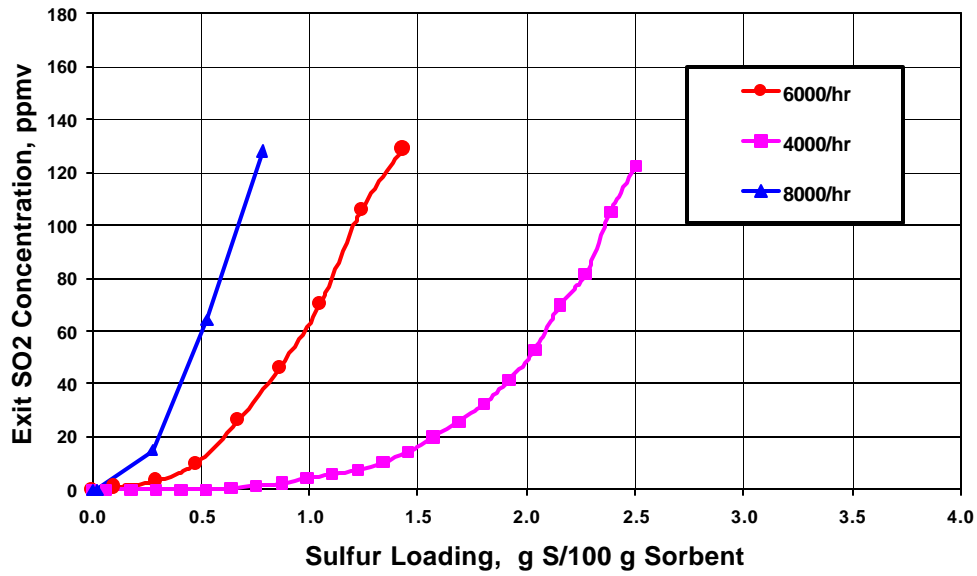


Figure 12. Effect of Space Velocity on the Sorbent Performance

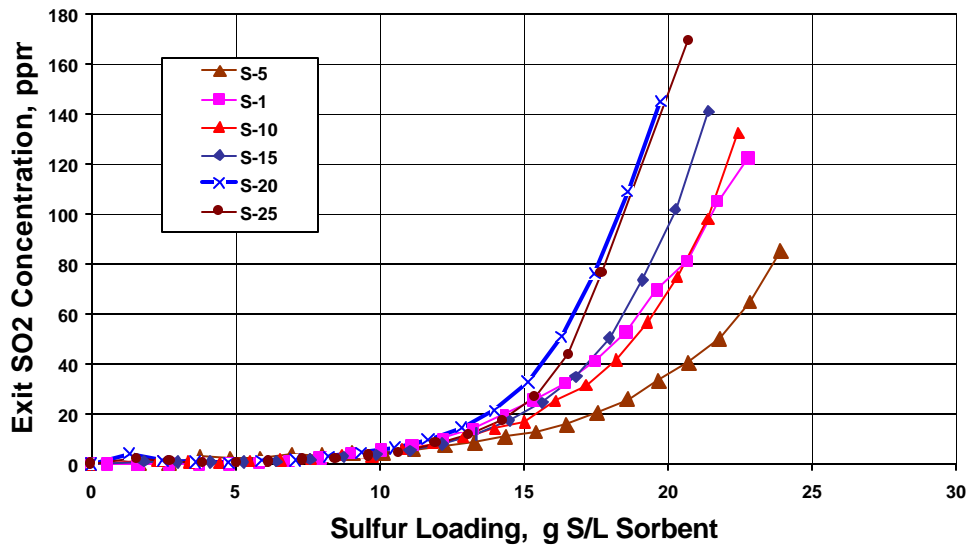


Figure 13. Results of Life Cycle Tests with ICCI-Cu-10

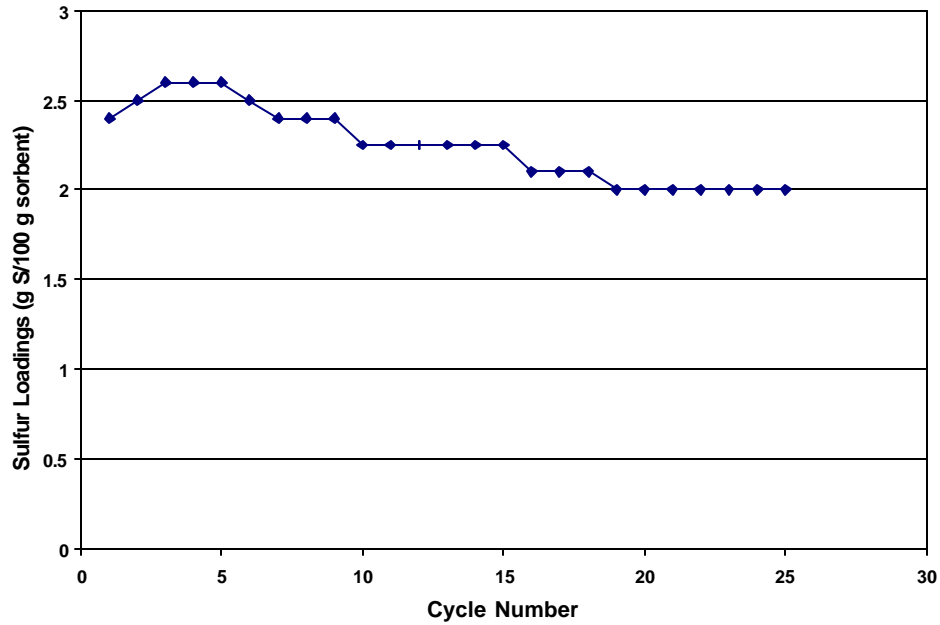


Figure 14. Sulfur Capacities in Long Term Durability Tests

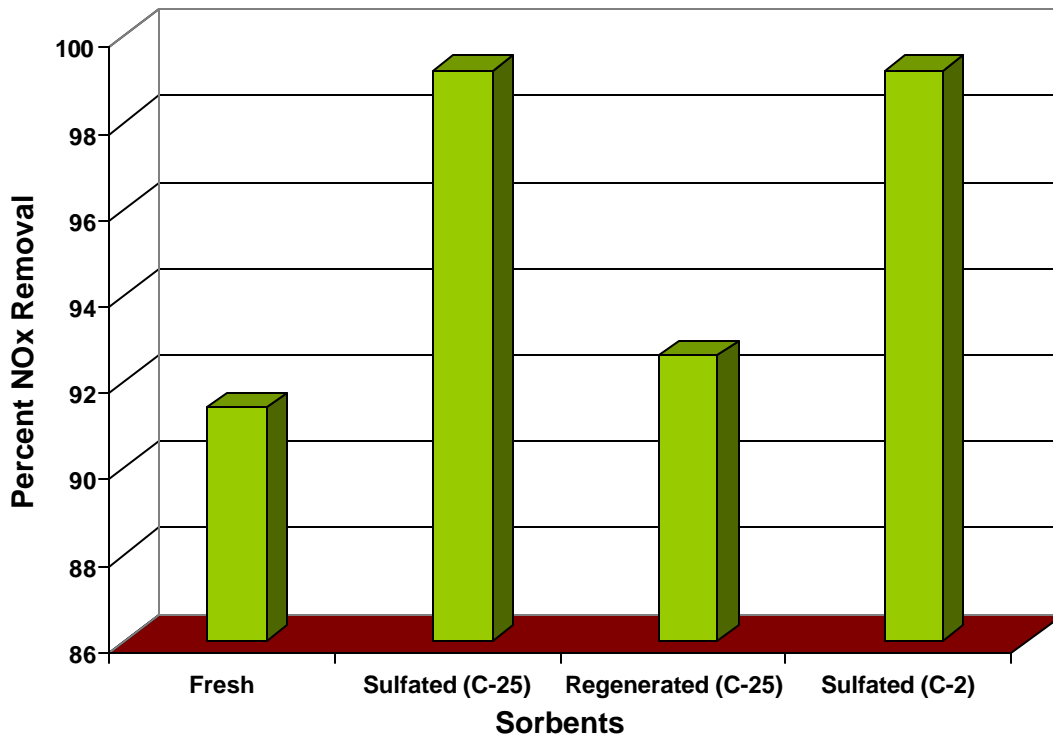


Figure 15. NOx Removal Efficiencies of the ICCI-Cu-10 Sorbents

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