

FINAL TECHNICAL REPORT  
November 1, 2001, through October 31, 2002

Project Title: **A REGENERATIVE FLUID-BED PROCESS TO CONTROL SO<sub>x</sub>  
AND NO<sub>x</sub>**

ICCI Project Number: 01-1/2.2B-1  
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ABSTRACT

The overall objective of the project was to continue further development of the copper oxide process through extensive evaluation of a novel copper oxide based sorbent developed in the earlier ICCI-funded project (i.e., ICCI project No. 00-1/2.2B-2).

To achieve this objective four (4) different modifications of the “best” sorbent, ICCI-Cu-10 were prepared to identify the key preparation parameters. Four (4) additional sorbent formulations were prepared to determine the optimum sorbent composition. The sorbents were evaluated in a fluid-bed to identify the “best” sorbent. Parametric studies were carried out on the “best” sorbent to determine the optimum operating condition with regard to SO<sub>x</sub>/NO<sub>x</sub> removal, ammonia (NH<sub>3</sub>) slip, and ammonium sulfate formation. To determine the long-term durability of the sorbent, a “life-cycle” test series consisting of 25 sulfation/regeneration cycles was conducted with the sorbent. To assess the economical viability of the process, cost analysis was performed to compare the cost of the regenerative copper oxide (CuO) process for simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub> with the commercial alternatives currently used in the utility industry.

The results obtained in this study indicate that The presence of steam enhances the effective sulfur capacity of the ICCI-Cu-10 sorbent, which gradually decreases in the cyclic process before stabilizing after the 18<sup>th</sup> cycle at 2.2 %, which is very close to the final effective sulfur loading of the sorbent in the “life-cycle” tests conducted in absence of steam. SO<sub>3</sub> did not appear to have any adverse effect on the sorbent performance and, the results obtained with SO<sub>3</sub> are essentially identical to those obtained with the SO<sub>2</sub>. The results also indicate that the sorbent is capable of 100% NO<sub>x</sub> removal at NH<sub>3</sub>/NO<sub>x</sub> ratios at or above 1:1. The NO<sub>x</sub> removal efficiency of the sorbent is not adversely affected by the cyclic process. Furthermore, the ammonia slip was determined to be about 6 ppmv with fresh sorbent, which gradually decreased in the cyclic process. No ammonia slip was detected after the 15<sup>th</sup> cycle. The favorable attrition characteristics and the apparent stabilization of the chemical reactivity of the sorbent in the durability studies, makes this regenerative process economically superior to the existing alternatives in the utility industry at sorbent cost below \$25/lb (\$42/lb with sulfur credit).

## EXECUTIVE SUMMARY

During the pulverized coal combustion process sulfur in coal is released in the form of sulfur dioxide ( $\text{SO}_2$ ) in the flue gas and a small fraction of nitrogen in the form of  $\text{NO}_2$  and  $\text{NO}$ , commonly referred to as  $\text{NO}_x$ . The  $\text{SO}_2$  and  $\text{NO}_x$  emissions are very damaging to the environment because they combine with moisture to form acids which then fall as acid rain.

Conventional FGD processes include “wet throwaway” processes using lime or limestone-water mixture, and “dry throw-away” 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  $\text{NO}_x$  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  $\text{SO}_2$  and  $\text{NO}_x$  removal from flue gases. In these processes,  $\text{SO}_2$  in the flue gas reacts with the reactive component of the sorbent, i.e.  $\text{CuO}$ , and  $\text{O}_2$  to form copper sulfate ( $\text{CuSO}_4$ ). The sulfated sorbent is regenerated by a reducing gas, such as methane ( $\text{CH}_4$ ) decomposing the sulfate to elemental copper ( $\text{Cu}$ ) and a concentrated stream of  $\text{SO}_2$ . In addition to  $\text{SO}_2$  removal via chemical reaction, the sorbent also serves as a catalyst to remove a significant portion of the  $\text{NO}_x$  in the feed flue gas. This step is accomplished by the controlled addition of ammonia ( $\text{NH}_3$ ) 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. Fluidized-bed copper oxide processes offers several advantages over the moving bed processes which include simpler reactor design, and improved gas /solid contacting. Because of the significantly smaller size of the sorbent granules (or powder), instead of low capacity supported pellets, higher capacity bulk sorbent granules can be used. However, highly reactive and attrition resistant sorbents are required to minimize attrition losses and the sorbent make-up rate.

In an earlier CCI funded program (i.e., ICCI project No. 00-1/2.2B-2), the principal investigator of this project has developed highly reactive and highly attrition resistant copper-based sorbent granules for simultaneous removal of  $\text{SO}_x$  and  $\text{NO}_x$  in a fluid bed process using a modified sol-gel based technique, which does not require high thermal treatment temperatures that can be detrimental to the reactivity of the sorbent.

The goal of this program is to develop a regenerative fluid bed process for the combined removal of  $\text{SO}_x$  and  $\text{NO}_x$  from coal combustion flue gases. The overall objective of this project was to continue further development of the copper oxide process through extensive evaluation of the novel copper oxide based sorbent developed in the earlier ICCI funded project.

To achieve the project objectives, four (4) modified formulations of the “best” sorbent identified in the earlier project were prepared and evaluated in a fluid-bed reactor to determine the key preparation parameters. Five (5) other sorbent formulations with varying copper content were then prepared with this optimum preparation technique. The results of evaluation for their SO<sub>2</sub> removal capacities of these sorbents conducted in the fluid-bed reactor confirmed that the “best” sorbent formulation was ICCI-Cu-10, with a nominal sorbent content of 15 %. This sorbent formulation was also tested for its attrition resistance using the ASTM-5757 technique. The results indicated that this sorbent was around 5 times more attrition resistant than the commercially available sorbent.

Several series of parametric studies were carried out to determine the effects of various operating parameters on the performance of the sorbent with regards to SO<sub>2</sub>, SO<sub>3</sub>, and NO<sub>x</sub> removal, as well as NH<sub>3</sub> slip from the reactor. The variables studied included reactor temperature, inlet concentrations of the contaminants and space velocity. Based on the results obtained in this study, the optimum operating conditions for the durability studies were determined. The results of these tests proved that the addition of steam to the flue gas increased the sulfur reactivity of the sorbent significantly, with the effective sulfur capacity being twice that observed during the “dry” runs. The results also indicated that the sorbent was capable of reducing 100% NO<sub>x</sub> to nitrogen at NH<sub>3</sub>/NO<sub>x</sub> ratios of greater than or equal to 1. The NH<sub>3</sub>/NO<sub>x</sub> ratios did not appear to have any effects on the ammonia slip, which was observed to be around 6 ppmv for the sulfated sorbent and about 2 ppmv for the regenerated (oxidized) sorbent. The results also suggest that even at high concentrations (2500 ppmv) of SO<sub>3</sub>, the reactor exit gas profile was identical to those obtained with SO<sub>2</sub>. Hence, it was concluded that SO<sub>3</sub> didn’t have any adverse effect on the performance of the 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 cycle after starting at around 5%, gradually decreases during the next 10-15 cycles. The effective sorbent capacity of the sorbent appears to stabilize at 2.2% after the 18<sup>th</sup> cycle. The catalytic activity of the sorbent was also determined during the durability studies. The results indicated that the sorbent was capable of removing 100% NO<sub>x</sub> throughout the 25 cycles. The ammonia slip appeared to decrease in the cyclic process. No ammonia slip was detected after the 15<sup>th</sup> cycle.

A comparative cost study was carried out in collaboration with Gas Technology Institute (GTI) and focused on determination of sorbent cost and make-up rate required to make the proposed regenerative process economically comparable to the commercially available alternatives utilizing wet FGD and SCR. The cost analysis in this task was performed using a computer modeling software [i.e., Integrated Environmental Control Model (IECM)], which is developed by Carnegie Mellon University under the sponsorship of US Department of Energy National Energy Technology Laboratory (U.S.DOE/NETL).

A typical 400 MWe advanced pulverized coal fired power plant, equipped with a wet FGD unit and a hot side Selective Catalytic Reduction (SCR) unit for the removal  $\text{SO}_x$  and  $\text{NO}_x$  was used as the base-case for comparison. A comparative study was performed with two key adjustable parameters (the sorbent cost (\$/lb) and the number of cycles) to determine the combination of parameters required to make the proposed regenerative process economically comparable to the commercially available wet FGD and SCR processes.

The result of the cost study indicate that, if the ICCI-Cu-10 sorbent can maintain an effective sulfur capacity of 2 %, (where it appears to have stabilized), sorbent cost below \$25/lb still make the proposed regenerative process economically superior to the existing alternatives. Furthermore, by taking into account, the appropriate credit from the sales of the concentrated stream of  $\text{SO}_2$ , the proposed process will be economically viable at a sorbent cost of \$42/lb. It should be emphasized that although the estimated cost of the sorbents is expected to be well below the above target values, experimental data from an extended life-cycle test is needed to better assess the economical viability of the proposed process.

## OBJECTIVES

The goal of this program is to develop a regenerative fluid bed process for the combined removal of  $\text{SO}_x$  and  $\text{NO}_x$  from coal combustion flue gases. The overall objective of the proposed work was to continue further development of the copper oxide process through extensive evaluation of the copper oxide based sorbent that has been developed in an earlier ICCI-funded project (i.e., ICCI project No. 00-1/2.2B-2).

The specific objectives of the proposed work were to:

- To optimize the sorbent preparation technique developed in the earlier ICCI-funded project and identify the key parameters for scale up, prior to commercial production.
- Perform Initial evaluation of the sorbents prepared using the optimized technique.
- Determine the effects of key operating variables on the extent of catalytic reduction of  $\text{NO}_x$  and ammonia slip.
- Determine the effects of key operating variables for  $\text{SO}_3$  removal.
- Identify the optimum operating condition with regards to  $\text{SO}_x$  and  $\text{NO}_x$  removal, ammonia slip, ammonium sulfate formation, and regenerability of the sorbent.
- Demonstrate the overall durability of the sorbent in a “life-cycle” test at the optimum process conditions.
- To carry out a detailed cost analysis for comparing the cost of the proposed regenerative process for removal of  $\text{SO}_x$  and  $\text{NO}_x$  with the commercial alternatives currently used in the industry.

## INTRODUCTION AND BACKGROUND

During coal combustion sulfur in coal is released in the form of sulfur dioxide ( $\text{SO}_2$ ) in the flue gas and a small fraction of nitrogen in the form of  $\text{NO}_2$  and  $\text{NO}$ , commonly referred to as  $\text{NO}_x$ . The  $\text{SO}_2$  and  $\text{NO}_x$  emissions are very damaging to the environment because they combine with moisture to form acids which then fall as acid rain.

The high sulfur content of Illinois coal, the imposition of strict limits on  $\text{SO}_2$  emissions, the 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). Some systems are known as throw-away 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.<sup>(1)</sup> The most commonly used system is lime slurry scrubbing, which uses a slurry of  $\text{Ca}(\text{OH})_2$  suspended in water to absorb  $\text{SO}_2$ . 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,<sup>(2)</sup> which must be discarded.

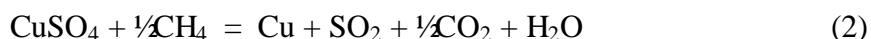
In conventional processes, selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) are employed to reduce  $\text{NO}_x$  content of the flue gas. In these processes, ammonia (or an ammonia precursor) is injected to reduce  $\text{NO}_x$  to nitrogen ( $\text{N}_2$ ). Excess ammonia is used to ensure maximum removal of  $\text{NO}_x$ . Existence of a small fraction of sulfur compound in the flue gas as  $\text{SO}_3$ , poses a major problem for SCR-based processes because  $\text{SO}_3$  can react with unreacted ammonia to form ammonium sulfate and ammonium bisulfate. Formation of ammonium bisulfate, which is a sticky compound, can contaminate fly ash and lead to fouling of the downstream equipment such as air preheater. Also,  $\text{SO}_3$  can react with water to form sulfuric acid, which upon condensation causes corrosion of the downstream equipment. Furthermore wet FGD systems lower plant operating efficiency and reliability, while increasing both capital and operating costs. For these reasons, alternative approaches for flue gas cleaning are needed.

A concept that has received significant attention is the development of regenerative processes for the combined removal of  $\text{SO}_2$ ,  $\text{NO}_x$ , and possibly particulates from flue gases using dry regenerable sorbents.<sup>(3,4)</sup> The National Energy Technology Laboratory (NETL) of the U.S. DOE has pursued the development of this concept for the last three decades. NETL has examined several dry, regenerable sorbent processes, including the NOXSO process, the fluid- and moving-bed copper oxide processes, and the cerium oxide ( $\text{CeO}_2$ ) process. Other materials that have been investigated include the use of magnesium oxide ( $\text{MgO}$ ) in combination with vermiculite (magnesium-aluminum-silicate).<sup>(5)</sup>

In copper oxide processes, flue gas consisting of  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{SO}_2$ , and  $\text{NO}_x$  is passed through the desulfurization (or sulfation) reactor containing the sorbent.  $\text{SO}_2$  reacts with the reactive component of the supported sorbent, i.e.  $\text{CuO}$ , and  $\text{O}_2$  to form copper sulfate ( $\text{CuSO}_4$ ). The desulfurization reaction is carried out at a temperature in the vicinity of  $400^\circ\text{C}$ , and may be represented by the following reaction:

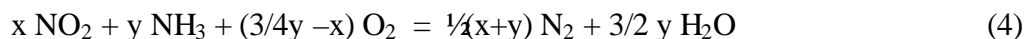
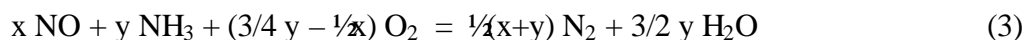


The sulfated sorbent is regenerated by a reducing gas, such as methane ( $\text{CH}_4$ ), decomposing the sulfate to elemental copper ( $\text{Cu}$ ) and a byproduct gaseous stream. The regeneration reaction may be described by the following reaction:



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  $\text{CuO}$ , thereby fully restoring the sorbent to its original condition. In addition to  $\text{SO}_2$  removal via chemical reaction, the sorbent also serves as a catalyst to remove

NO<sub>x</sub> with a controlled amount of ammonia (NH<sub>3</sub>) via selective catalytic reduction (SCR) to form N<sub>2</sub> and H<sub>2</sub>O, according to Reactions (3) and/or (4). It has been reported that both CuO and CuSO<sub>4</sub> act as catalysts for NO<sub>x</sub> removal from flue gases.<sup>(3)</sup>



Combined SO<sub>2</sub>/NO<sub>x</sub> removal from flue gas by copper-based sorbents has been studied by many investigators.<sup>(5-18)</sup> The results of these studies indicate both SO<sub>2</sub> and NO<sub>x</sub> removal efficiencies on the order of 95% can be achieved by copper oxide processes. The results of various studies on selective catalytic reduction of NO by NH<sub>3</sub> over alumina supported copper-based catalysts suggest that the optimum NO<sub>x</sub> removal efficiency can be achieved with NH<sub>3</sub>/NO<sub>x</sub> ratio in the range of 1.0-1.2.<sup>(19-22)</sup>

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 simpler reactor design and improved gas /solid contacting. Furthermore, because of the small size of the pellets, instead of low capacity supported pellets, higher capacity sorbent granules can be used. However, all the sorbents developed to date, have been reported to suffer from excessive attrition.<sup>(13)</sup> 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.

Conventional sorbent preparation techniques require very high thermal treatment temperatures to impart physical strength, and as a result, they often produce sorbents with low reactivity. The desirable sorbent characteristics, such as surface area and porosity were found to diminish with increasing temperature, adversely affecting the reactivity of the sorbent. The goal of this program is to develop a regenerative fluid bed copper-based process for the combined removal of SO<sub>x</sub> and NO<sub>x</sub> from coal combustion flue gases, utilizing highly reactive and attrition resistant sorbents.

## EXPERIMENTAL PROCEDURES

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

- Task 1. Sorbent Preparation and Characterization
- Task 2. Initial Evaluation of the Sorbent
- Task 3. Parametric Studies
- Task 4. Sorbent Durability Studies
- Task 5. Cost Analysis and Comparison

### Task 1. Sorbent Preparation and Characterization

The objective in this task was to optimize the sorbent preparation technique developed in the earlier ICCI-funded project (No. 00-1/2.2B-2) and identify the key parameters for scale up, prior to commercial production.

Because the results obtained in the earlier ICCI-funded project indicated that the sorbent performance is very sensitive to mixing parameters, it was decided to prepare and evaluate four (4) batches of the “best” sorbent using different mixing parameters to determine the key parameters for scale up, prior to commercial production. Furthermore, four (4) additional sorbent formulations with different copper content were prepared and evaluated to determine the “optimum” copper content of the sorbent.

Sufficient quantity of selected sorbent formulations were subjected to physical and chemical characterization, which included mercury Porosimetry, BET surface area, and chemical analysis.

### Task 2. Initial Evaluation of the Sorbents

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

In this task, the effectiveness of various selected sorbents for the removal of SO<sub>2</sub> and NO<sub>x</sub> was determined in the fluid-bed reactor system over one (1) to three (3) cycles. The operating conditions in these tests were similar to the optimum operating condition determined in the earlier ICCI-funded project.

To carry out the tests in this task, a new fluid bed reactor system was designed, fabricated and assembled at the Gas Separation Laboratory at IIT Chemical Engineering Department. The schematic diagram of the fluidized-bed unit is presented in Figure (1). The unit essentially consists of a quartz reactor, which is externally heated by two electrical furnaces, equipment for feeding and measuring the flow rate of the gases, measuring and controlling bed temperature, and monitoring the reactor pressure. In these tests, a known quantity of each sorbent is loaded into the fluid-bed reactor and the reactor is brought to the desired temperature and exposed to a gas mixture containing the desired level of the selected contaminants. The reactor exit gas is analyzed for the determination of the desired contaminants in the reactor effluent. For this purpose, the new system is equipped with a Gas Chromatograph (SO<sub>2</sub> analysis), NO<sub>x</sub> analyzer (NO<sub>x</sub> analysis) and Ion Chromatograph (SO<sub>3</sub> and NH<sub>3</sub> analysis).

To identify the key preparation parameter and its effect on the sorbent performance, four (4) different formulations of the ICCI-Cu-10 sorbent mentioned earlier were tested in the fluid-bed reactor for their SO<sub>2</sub> removal efficiencies. Four (4) additional ICCI-Cu-sorbent formulations prepared using this key preparation parameter were then tested in the fluid-bed unit, to determine (and confirm) the optimum copper content. Following the confirmation of ICCI-Cu-10 (15 % Copper) as the “best” sorbent formulation, a large batch of the sorbent was prepared to carry out the more detailed evaluation. This sorbent formulation was also evaluated for attrition resistance according to the standard ASTM D5757-95 test method.

A new apparatus was constructed at the Gas Separation Lab at IIT to carry out the standard ASTM D5757-95 test. The apparatus system consists of an attriting tube, a settling chamber, a fines collection assembly, and a circular orifice plate containing 3 holes, which is attached to the bottom of the vertical attriting tube within an air delivery manifold. The schematic diagram of the attrition measurement unit is shown in Figure (2).

### Task 3. Parametric Studies

The objective of this task was to determine the optimum operating condition with regards to  $\text{SO}_X$  (i.e.  $\text{SO}_2$  and  $\text{SO}_3$ ) and  $\text{NO}_X$  (i.e.  $\text{NO}$  and  $\text{NO}_2$ ) removal, ammonia ( $\text{NH}_3$ ) slip, and ammonium sulfate formation. This task was divided into three sub-tasks:

#### Subtask 3.1. $\text{NO}_X$ Removal and $\text{NH}_3$ slip

The tests in this subtask focused on determination of key variables on the extent of  $\text{NO}_X$  removal and ammonia slip. The key parameters studied included reactor temperature ( $350\text{-}450^\circ\text{C}$ ),  $\text{NH}_3/\text{NO}_X$  ratio (0.5-3.0), and space velocity ( $4000\text{-}8000\text{ hr}^{-1}$ ). To determine the  $\text{NH}_3$  content of the reactor effluent, the gas was bubbled into water and the solution was analyzed by the IC unit after every 30 min.

#### Subtask 3.2. $\text{SO}_3$ Removal

The tests in this subtask focused on the determination of key variables on the extent of  $\text{SO}_3$  removal. This series of tests were carried out without  $\text{NO}_X/\text{NH}_3$  to determine the effectiveness of the sorbent for  $\text{SO}_3$  removal without interference from the reaction between  $\text{SO}_3$  and  $\text{NH}_3$ .  $\text{SO}_3$  was produced via vaporization of a controlled amount of a diluted sulfuric acid ( $\text{H}_2\text{SO}_4$ ) solution. The key variables studied in this subtask included the reactor temperature ( $400\text{-}450^\circ\text{C}$ ),  $\text{SO}_3$  concentration (1250-2500 ppmv), and space velocity ( $4000\text{-}800\text{ hr}^{-1}$ ). To determine the  $\text{SO}_3$  content of the reactor exit gas, the gas was bubbled into a solution containing sodium hydroxide and hydrogen peroxide and the solution was analyzed by an Ion Chromatograph (IC) unit after every 30 min.

#### Subtask 3.3. Determination of Optimum Operating Condition

This subtask focused on determination of the optimum operating condition with regards to  $\text{SO}_X/\text{NO}_X$  removal, ammonia ( $\text{NH}_3$ ) slip, ammonium sulfate formation. The key variables included the reactor temperature, fue gas composition, and space velocity. The extensive experimental data obtained from the tests performed in subtask 3.1 and subtask 3.2 were analyzed to determine the optimum operating conditions with regards to  $\text{SO}_X/\text{NO}_X$  removal, ammonia ( $\text{NH}_3$ ) slip and ammonium sulfate formation.

### Task 4. Sorbent Durability Studies

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

In this task, the “best” sorbent formulation was subjected to twenty-five (25) cycles of sulfation and regeneration at the optimum operating conditions. The catalytic activity of the sorbent during the sulfation runs was determined throughout the sulfation cycles. The extent of  $\text{NH}_3$  slip analysis was determined after the 1<sup>st</sup>, 5<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup> and 25<sup>th</sup> cycles. The effectiveness of the sorbent for  $\text{SO}_3$  removal was also determined throughout the twenty-five (25) cycle test.

#### Task 5. Cost Analysis and Comparison

The objective of this task was to develop a cost analysis comparing the cost of the proposed regenerative process for removal of  $\text{SO}_x$  and  $\text{NO}_x$  with the commercial alternatives currently used in the utility industry.

This task was carried out in collaboration with Gas Technology Institute (GTI) and focused on determination of sorbent cost and make-up rate required to make the proposed regenerative process economically comparable to the commercially available alternatives utilizing wet FGD and SCR. The cost analysis in this task was performed using a computer modeling software [i.e., Integrated Environmental Control Model (IECM)], which has been developed by Carnegie Mellon University under the sponsorship of the US Department of Energy National Energy Technology Laboratory (U.S.DOE/NETL).<sup>(23)</sup>

### RESULTS AND DISCUSSIONS

#### Task 1. Sorbent Preparation and Characterization

As indicated earlier, the results obtained in the previous study indicated that the sorbent performance is very sensitive to preparation parameters such as mixing speed and time, the molar ratio of  $\text{NH}_4\text{OH}/\text{HNO}_3$  and the dispersion on the  $\text{NH}_4\text{OH}$  solution over the gel matrix. Therefore, in this task four (4) formulations of the “best” sorbent (i.e., ICCI-Cu-10 identified in the earlier project) were prepared using different preparation parameters to quantify the values of the key parameters for scale up. These sorbent sub-batches were designated as ICCI-Cu-10h, ICCI-Cu-10i, ICCI-Cu-10j, and ICCI-Cu-10k respectively.

After the key preparation parameter was identified, four (4) additional sorbent formulations with different copper content were prepared to determine the “optimum” copper content of the sorbents. The nominal chemical compositions and bulk densities of these four (4) new sorbent formulations as well as those of the ICCI-Cu-10 sorbent are summarized in Table 1.

#### Task 2. Initial Evaluation of the Sorbents.

Because the tests in this task were to be conducted in the new fluid-bed reactor system at the Gas Separation Laboratory at IIT, a series of test were conducted to establish the reproducibility of the results using the ICCI-Cu-10 sorbent (previously evaluated at GTI last year). The operating conditions are given in Table 2. The results of these reproducibility tests indicated excellent reproducibility of the experimental data.

The four (4) sorbent formulations produced with different preparation parameters were evaluated in the fluid bed-reactor. The results of the tests indicated that the sorbent performance was only sensitive to rate of addition of ammonia during preparation of the sorbent. The results of evaluation of the sorbents with different copper contents are shown in Figure 3, confirming that the “best” sorbent formulation was ICCI-Cu-10 and that the optimum copper content of the sorbent was about 15 %.

Based on the results mentioned above, a large batch of the sorbent ICCI-Cu-10 was prepared to carry out detailed evaluation, which included parametric studies for determination of the effects of operating conditions and durability studies for assessment of the suitability of the sorbent for long-term application. To eliminate any errors resulting from the non-uniformity of the sorbent bed materials, the large batch of the ICCI-Cu-10 sorbent was riffled into twenty (20) identical smaller sub-batches for detailed studies. Sufficient quantity of the sorbent was analyzed for physical and chemical characterization, which included mercury porosimetry, BET surface area measurement, and chemical composition. The results of these analyses are given in Table (3). The results indicate that this new sorbent is very similar to the sorbent prepared in the earlier project, confirming that the key preparation parameter was correctly identified.

The attrition index (AI) of the sorbent was determined by the standard ASTM D5757-95 test method using the new attrition unit at IIT. A comparison of the results of the attrition tests performed on various sorbents in two attrition units (at IIT and GTI) is presented in Figure 4, indicating that the attrition index of the two ICCI-Cu-10 sorbents are identical. Furthermore, the results also indicate that the Attrition Index (AI) of the sorbents tested at IIT differs from those tested at GTI by a about 1%, which may be attributed to slight difference in the size of the orifices affecting the shear caused by these high velocity jets and resulting in different attrition indexes.

The effect of steam on the performance of the sorbent is shown in Figure 5, indicating that the effective sulfur capacity of the ICCI-Cu-10 significantly increases (5% compared to 2.4% at SO<sub>2</sub> breakthrough concentration of 100 ppmv) in the presence of steam.

The sorbent, ICCI-Cu-10 was also evaluated for simultaneous SO<sub>2</sub> and NO<sub>x</sub> removal using a simulated flue gas containing 2500 ppmv SO<sub>2</sub>, 14% CO<sub>2</sub>, 3.7% O<sub>2</sub>, 10% steam, 500 ppmv NO<sub>x</sub> and 500 ppmv NH<sub>3</sub> and nitrogen. The reactor unit was modified to allow addition of steam, NO<sub>x</sub>/NH<sub>3</sub> mix, and N<sub>2</sub>/O<sub>2</sub>/SO<sub>2</sub> mix through separate feed line to prevent formation of ammonium sulfate. The results showed that the sulfated sorbent was capable of removing 100 % NO<sub>x</sub> at a NH<sub>3</sub>/NO<sub>x</sub> ratio of 1:1. These results formed the basis of the parametric studies carried out in Task 3.

### Task 3. Parametric Studies

The tests carried out in this task was performed in the three following subtasks. The range of operating conditions used in this task is shown in Table 4.

### Subtask 3.1 NO<sub>x</sub> Removal and NH<sub>3</sub> Slip

NO<sub>x</sub> Removal. The parameters studied in this sub-task included reactor temperature, NH<sub>3</sub>/NO<sub>x</sub> ratio, and space velocity. All the tests were performed with sulfated sorbent and inlet NO<sub>x</sub> concentration of 500 ppmv. The effect of the reactor temperature on NO<sub>x</sub> removal is shown in Figure 6, indicating the sulfated sorbent was capable of completely reducing NO<sub>x</sub> to nitrogen in the temperature range of 350-450°C. Figure 7 shows the effect of NH<sub>3</sub>/NO<sub>x</sub> ratio on NO<sub>x</sub> removal, indicating that the NO<sub>x</sub> removal efficiency of the sorbent decreases significantly as the NH<sub>3</sub>/NO<sub>x</sub> ratio is decreased below 1. However, at ratios greater than or equal to 1:1, the NO<sub>x</sub> removal efficiency of ICCI-Cu-10 is 100%. The effect of space velocity on the NO<sub>x</sub> removal presented in Figure 8 indicates that although the NO<sub>x</sub> removal efficiency of ICCI-Cu-10 slightly decreases with increasing space velocity, a very high removal efficiency of 94 % can be achieved at the space velocity of 8000 hr<sup>-1</sup>.

NH<sub>3</sub> slip. The effect of the NH<sub>3</sub>/NO<sub>x</sub> ratio on the extent of NH<sub>3</sub> slip was determined using both the oxidized and the sulfated sorbent. All the tests were carried out at 450°C and a space velocity of 4000 hr<sup>-1</sup>. The results are presented in Figure 9, indicating that the extent of ammonia slip is very low, regardless of the NH<sub>3</sub>/NO<sub>x</sub> ratio.

### Subtask 3.2 SO<sub>3</sub> Removal.

A number of tests were carried out on ICCI-Cu-10 to determine the effects of the operating variables on the extent of SO<sub>3</sub> removal. These tests were carried out without NO<sub>x</sub>/ NH<sub>3</sub> to eliminate any interference from the reaction between SO<sub>3</sub> and NH<sub>3</sub>. The operating variables studied consisted of reactor temperature, SO<sub>3</sub> concentration, and space velocity. The ranges of the operating conditions are given in Table 4. The effect of the inlet SO<sub>3</sub> concentration on the sorbent performance is shown in Figure 10. The results indicate that, even at extremely high SO<sub>3</sub> concentrations, the reactor exit gas concentration profile is identical to those obtained with SO<sub>2</sub>. The effects of temperature and space velocity on SO<sub>3</sub> removal are shown in Figures 11 and 12, indicating that the effect of SO<sub>3</sub> on the performance of ICCI-Cu-10 is essentially identical to the effect of SO<sub>2</sub> over the entire range of operating conditions investigated in this sub-task, leading to the conclusion that the optimum conditions determined for the removal of SO<sub>2</sub> will also be applicable to removal of SO<sub>3</sub> using ICCI-Cu-10.

### Subtask 3.3 Determination of the Optimum Operating Conditions

The optimum operating conditions with regard to SO<sub>x</sub>/NO<sub>x</sub> removal, ammonia (NH<sub>3</sub>) slip, and ammonium sulfate formation was selected based on the results obtained from the tests performed in subtask 3.1 and subtask 3.2 and are presented in Table 5. Because of the negligible ammonia slip and the pre-breakthrough SO<sub>2</sub> concentration of 0 ppmv, it can be assumed that there would be no ammonium sulfate formation downstream of the reactor.

#### Task 4. Sorbent Durability 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 at the operating condition shown in Table 5. The effective sulfur capacity of the sorbent (at SO<sub>2</sub> breakthrough concentration of 100 ppmv) for the “wet” tests (performed in this project) as well as the “dry” tests (performed in the earlier project) are shown in Figure 13. The results of these tests indicate that the enhancing effect of steam on the effective sulfur capacity of the sorbent gradually diminishes after about 20 cycles, and that the effective sulfur capacity of the sorbent at the condition tested appears to stabilize at about 2.2%.

The regenerated samples in their oxidized states after the 1<sup>st</sup>, 5<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup>, and 25<sup>th</sup> cycles were analyzed to determine the changes in the relevant properties of the sorbent during the cyclic process. The results of the analysis are shown in Table 6, clearly indicating that the surface area of the sorbents decreases significantly with the increasing number of cycles during the initial fifteen (15) cycles, after which it remains virtually constant, leading to the conclusion that pore size distribution of the sorbent is adversely affected by the cyclic process during the initial 15 cycles.

The catalytic activity of the ICCI-Cu-10 sorbent for reduction of NO<sub>x</sub> from flue gases was also determined throughout the “life-cycle” tests. The results at the end of the 1<sup>st</sup>, 5<sup>th</sup>, 10<sup>th</sup>, 15<sup>th</sup>, 20<sup>th</sup> and 25<sup>th</sup> runs are shown in Figure 14. The results indicate that the sorbent is capable of completely reducing NO<sub>x</sub> to nitrogen. The results also indicate that the catalytic activity of the sorbent towards is not adversely affected by the cyclic process.

The results of the ammonia slip analysis conducted are shown in Figure 15. The results clearly show that the ammonia slip decreases with the increasing number of cycles and eventually drops to zero for both the sulfated and regenerated/oxidized sorbent.

#### Task 5. Cost Analysis and Comparison

Cost analysis was performed to compare the cost of the proposed regenerative copper oxide (CuO) process for simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub> with the commercial alternatives currently used in the utility industry.

This task was carried out in collaboration with Gas Technology Institute (GTI) and focused on determination of sorbent cost and make-up rate required to make the proposed regenerative process economically comparable to the commercially available alternatives utilizing wet FGD and SCR. The cost analysis in this task was performed using a computer modeling software [i.e., Integrated Environmental Control Model (IECM)], which is developed by Carnegie Mellon University under the sponsorship of US Department of Energy National Energy Technology Laboratory (U.S.DOE/NETL).<sup>(23)</sup>

This task was initiated by establishing a base-case which was based on the results of cost analysis provided in a 1999 case study report performed under the sponsorship of US

Department of Energy<sup>(24)</sup> on a typical 400 MWe advanced pulverized coal fired power plant, equipped with a wet FGD unit and a hot side Selective Catalytic Reduction (SCR) unit for the removal  $\text{SO}_x$  and  $\text{NO}_x$ . The cost analysis of this plant was performed using the IECM software. Various input parameters for IECM were adjusted based on the information provided in the DOE report to closely match the detailed costs of the power plant including the detailed costs of the wet FGD unit and Hot-Side SCR units with those provided in the DOE report. A similar approach was taken for the analysis of the plant assuming the FGD and SCR units are replaced by the proposed regenerative CuO process. All the other inputs, except those dealing with the combined  $\text{SO}_x/\text{NO}_x$  removal were kept the same. All the design parameters, including the reactor temperatures, space velocity, effective sulfur capacity were calculated using the data obtained from the various tests conducted during the program.

A comparative study was performed with two key adjustable parameters (the sorbent cost (\$/lb) and the number of cycles) to determine the combination of parameters required to make the proposed regenerative process economically comparable to the commercially available wet FGD and SCR processes. The result of this analysis is presented in Figure 16.

It should be noted that the rate of fresh make-up which is inversely proportional to the required number of cycles is dictated by either the rate of sorbent loss due to attrition or the rate of sorbent replacement due to loss of reactivity (or sorbent deactivation), depending on the mechanism that leads to higher make-up rate. Given, the large number of cycles required and the limited data available on the long-term performance of the sorbent, the estimated sorbent make-up rate dictated by sorbent deactivation through extrapolation of the results obtained in the 25-cycle test is extremely sensitive to the extrapolation scheme and may lead to prediction error over two order of magnitude.<sup>(25)</sup> Therefore, until experimental data is available on an extended number of cycles (e.g., 100-500 cycles), the rate of fresh make-up must be estimated assuming the rate of sorbent loss due to attrition to be the controlling mechanism.

To estimate the rate of sorbent loss dictated by attrition, one can assume the expected attrition rates of various solid sorbents in fluid bed processes are proportional to the attrition index (AI) of the sorbent determined by the standard ASTM 5757 method. Therefore, the FCC catalyst was selected as the baseline materials for estimation of the rate of attrition of the ICCI-Cu-10 sorbent. The FCC catalyst, which has an attrition index of 4.1 %, (Figure (6), tested at GTI), has an estimated life of about six month in the FCC fluid-bed process, which represent the extreme upper boundary of the expected rate of attrition of the catalyst. The sorbent ICCI-Cu-10, however, has an Attrition Index, which is 1/4 of that of the FCC catalyst. Hence, the estimated minimum sorbent life dictated by attrition is expected to be two years. Therefore, based on this analysis, if the ICCI-Cu-10 sorbent can maintain an effective sulfur capacity of 2 %, (where it appears to have stabilized), sorbent cost below \$25/lb still make the proposed regenerative process economically superior than the existing alternatives. Furthermore, by taking into account, the appropriate credit from the sales of concentrated stream of  $\text{SO}_2$ , the proposed process will be economically viable at a sorbent cost of \$42/lb. It should be emphasized that

although the estimated cost of the sorbents is expected to be well below the above target values, experimental data from an extended life-cycle test is needed to better assess the economical viability of the proposed process.

## CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained in this study, it may be concluded that:

- The preparation technique for ICCI-Cu-10 has been successfully optimized and the sorbent is ready for commercial production.
- The presence of steam enhances the effective sulfur capacity of the ICCI-Cu-10 sorbent, which gradually decreases in the cyclic process before stabilizing after the 18<sup>th</sup> cycle at 2.2 %, which is very close to the final effective sulfur loading of the sorbent in the “life-cycle” tests conducted in absence of steam. This decrease in the effective sulfur capacity (at breakthrough), can be attributed to the changes in the pore structure of the sorbent material.
- SO<sub>3</sub> has no adverse effect on the sorbent performance and, the results obtained with SO<sub>3</sub> are essentially identical to those obtained with the SO<sub>2</sub>.
- The sorbent is capable of 100% NO<sub>x</sub> removal at NH<sub>3</sub>/NO<sub>x</sub> ratios at or above 1:1. The NO<sub>x</sub> removal efficiency of the sorbent is not adversely affected by the cyclic process.
- The ammonia slip was determined to be about 6 ppmv with fresh sorbent, which gradually decreased in the cyclic process. No ammonia slip was detected after the 15<sup>th</sup> cycle.
- The favorable attrition characteristics and the apparent stabilization of the chemical reactivity of the sorbent in the durability studies, makes this regenerative process economically superior to the existing alternatives in the utility industry at a sorbent cost below \$25/lb (\$42/lb with sulfur credit).

Based on the results obtained in this study, the following additional work is recommended to better assess the economical viability of the proposed process and to move the process toward commercialization:

- Commercial production of the sorbent
- Determination of sorbent performance in extended life-cycle tests
- Determination of the effect of other contaminants, specially mercury
- Evaluation of the process in a continuous reactor system

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**Table 1. Selected Properties of Different ICCI-Cu-Sorbent Formulations**

Sorbent	Copper Content* (%)	Aluminum* Content (%)	Bulk Density (g/cc)
ICCI-Cu-6	12	45	0.93
ICCI-Cu-8	30	33	1.04
ICCI-Cu-9	21	39	0.93
ICCI-Cu-10	15	43	0.92
ICCI-Cu-13	25	17	1.06

\* Nominal Copper Content

**Table 2. Baseline Operating Condition**

Operating Variable	Sulfation	Regeneration
Temperature, °C	450	450
Pressure, bar	1	1
Space Velocity, hr <sup>-1</sup>	4000	2000
Gas Composition, vol%		
SO <sub>2</sub>	0.25	-
O <sub>2</sub>	3.77	-
CO <sub>2</sub>	14	-
N <sub>2</sub>	balance	-
CH <sub>4</sub>	-	100

**Table 3. Comparison of the “Best” Sorbent Formulations**

Sorbent	Copper Content <sup>\$</sup> (wt %)	Aluminum Content <sup>\$</sup> (wt %)	Nitrogen Surface Area (m <sup>2</sup> /g)	NH <sub>4</sub> OH/ HNO <sub>3</sub> (Vol. Basis)	Porosity- from BET (ml/g)
ICCI-Cu-10(1)	15.2	40.0	150	2:1	0.20
ICCI-Cu-10(2)	14.9	43.2	168	2:1	0.21

<sup>\$</sup> From Chemical Analysis

**Table 4. Ranges of Operating Variables in Parametric Studies**

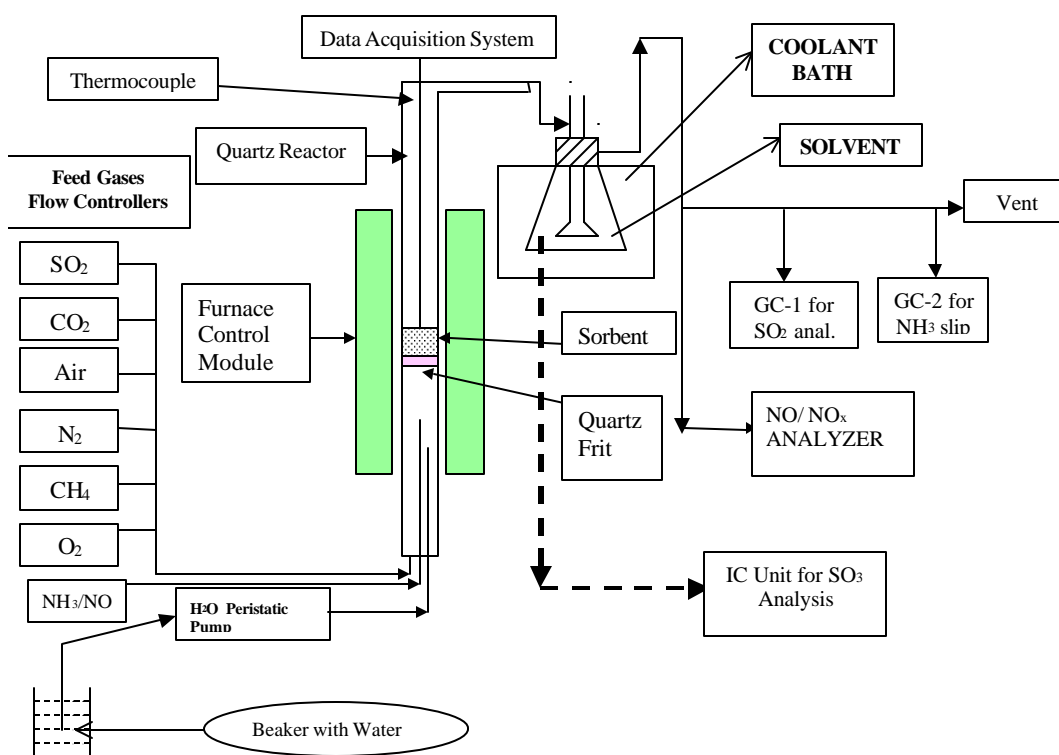
<b>Operating Variable</b>	<b>Sulfation</b>	<b>Regeneration</b>
Temperature, °C	450	450
Space Velocity, hr <sup>-1</sup>	2000-8000	2000-3000
Gas Composition, vol %		
SO <sub>2</sub>	0.125-0.25	-
O <sub>2</sub>	3.77	-
CO <sub>2</sub>	0-14	-
H <sub>2</sub> O	10	-
SO <sub>3</sub>	0-0.25	-
NO <sub>x</sub>	0-0.05	-
NH <sub>3</sub>	0-0.15	-
N <sub>2</sub>	Balance	-
CH <sub>4</sub>	-	100

**Table 5. Optimum Operating Condition**

<b>Operating Variable</b>	<b>Sulfation</b>	<b>Regeneration</b>
Temperature, °C	450	450
Space Velocity, hr <sup>-1</sup>	4000	3000
Gas Composition, vol %		
SO <sub>2</sub>	0.25	-
O <sub>2</sub>	3.77	-
CO <sub>2</sub>	14	-
H <sub>2</sub> O	10	-
SO <sub>3</sub>	0.24	-
NO <sub>x</sub>	0.05	-
NH <sub>3</sub>	0.05	-
N <sub>2</sub>	Balance	-
CH <sub>4</sub>	-	100

**Table 6. Effect of Cyclic Process on the Physical and Chemical Properties of the “Best” Sorbent**

Cycle Number	Copper Content (wt %)	Aluminum Content (wt %)	Sulfur Content (wt %)	Nitrogen Surface Area (m <sup>2</sup> /g)
1	13.1	38.5	1.20	144
5	13.2	39.1	1.28	126
15	12.1	39.1	1.22	113
20	11.4	41.0	1.08	114
25	11.2	40	1.12	111



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

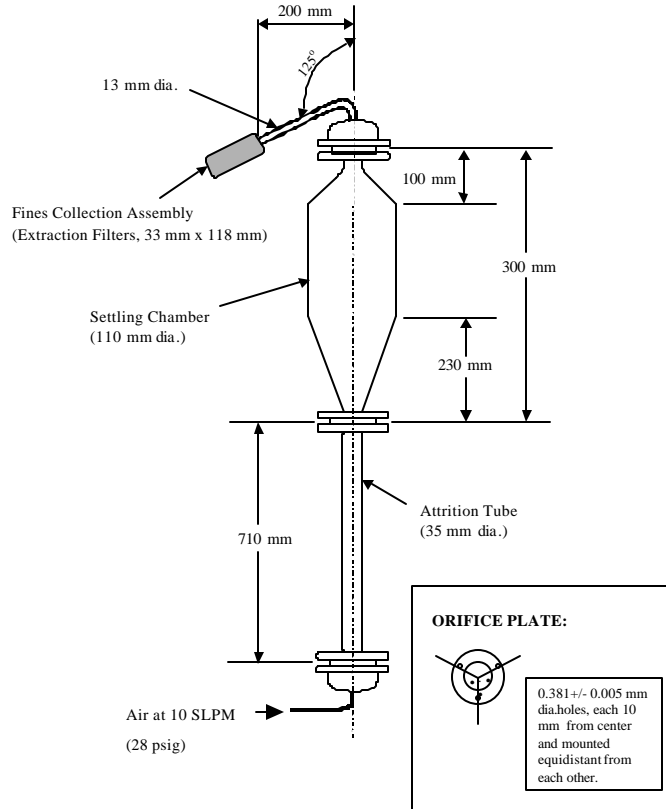


Figure 2. Schematic Diagram of the Air Jet Attrition Apparatus

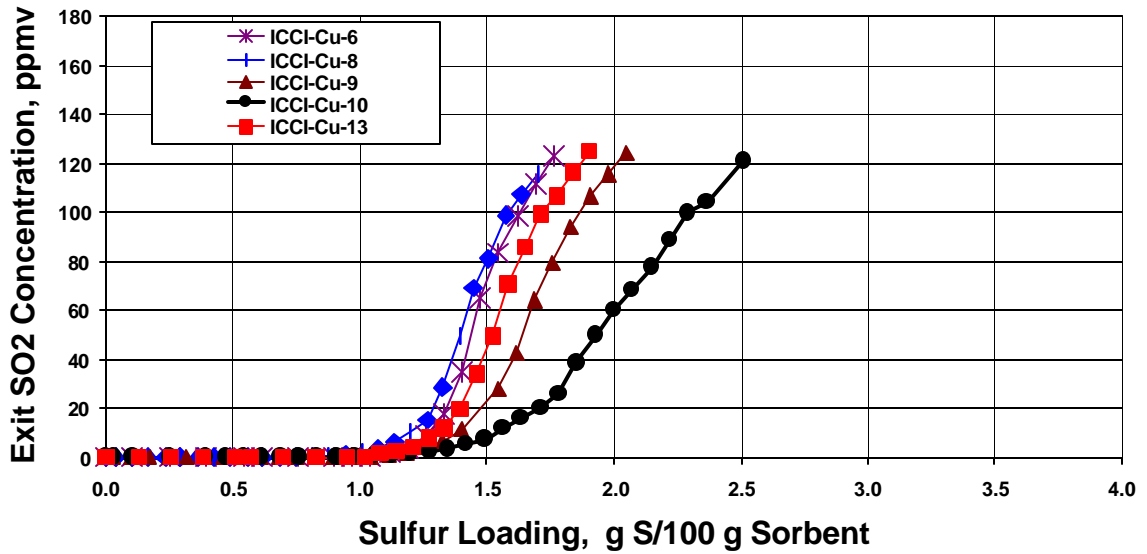


Figure 3. Comparison of the Performance of Different Sorbents

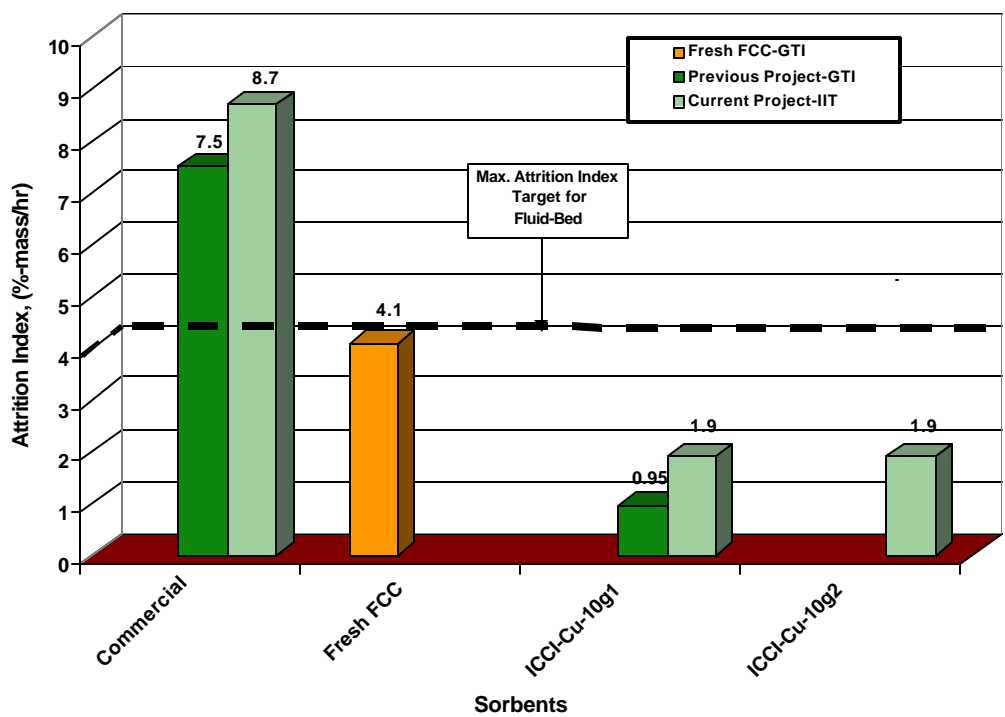


Figure 4. Comparison of Attrition Resistance of Different Sorbents

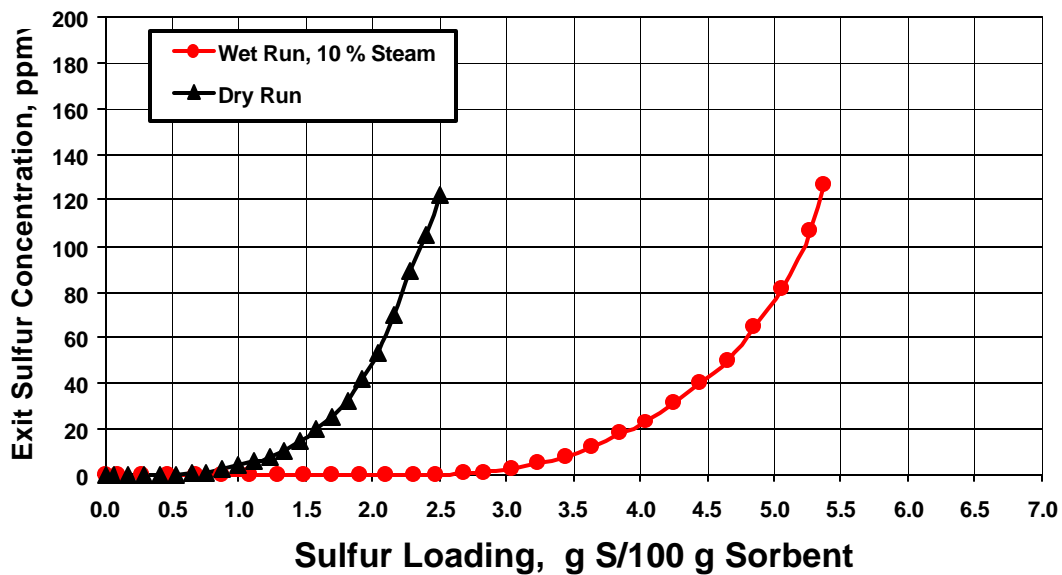


Figure 5. Effect of Steam on Sorbent Performance.

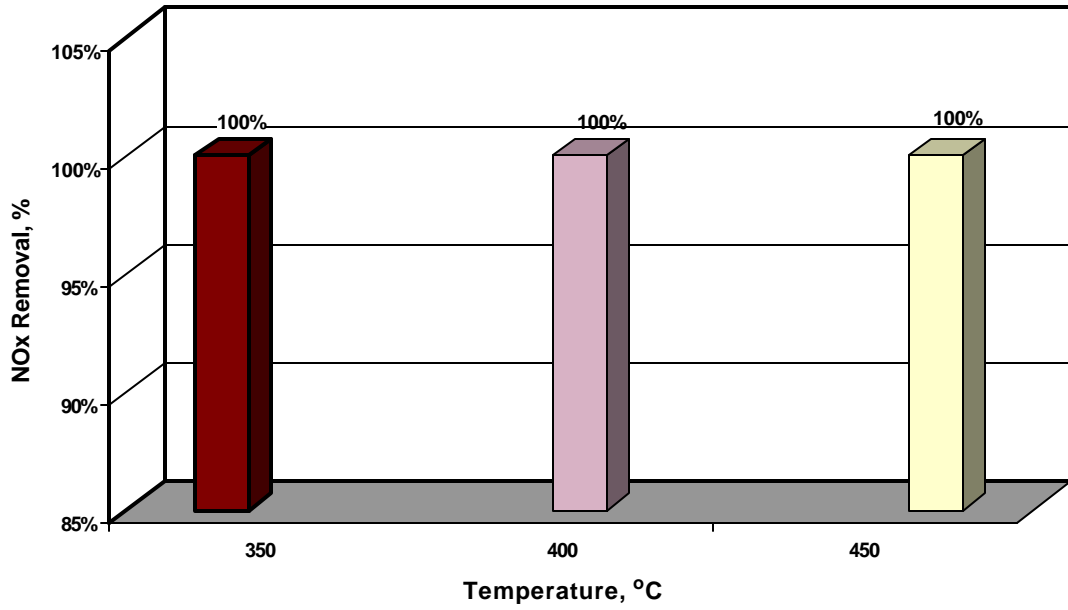


Figure 6. Effect of Temperature on NO<sub>x</sub> Removal Efficiency of ICCI-Cu-10

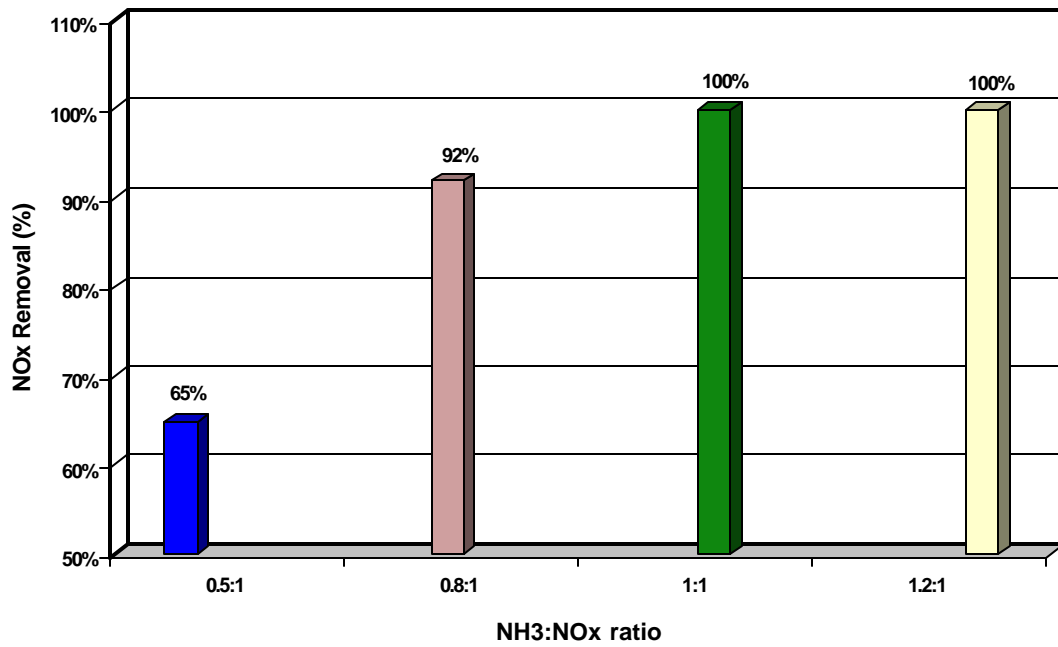


Figure 7. Effect of NH<sub>3</sub>/NO<sub>x</sub> ratio on NO<sub>x</sub> Removal

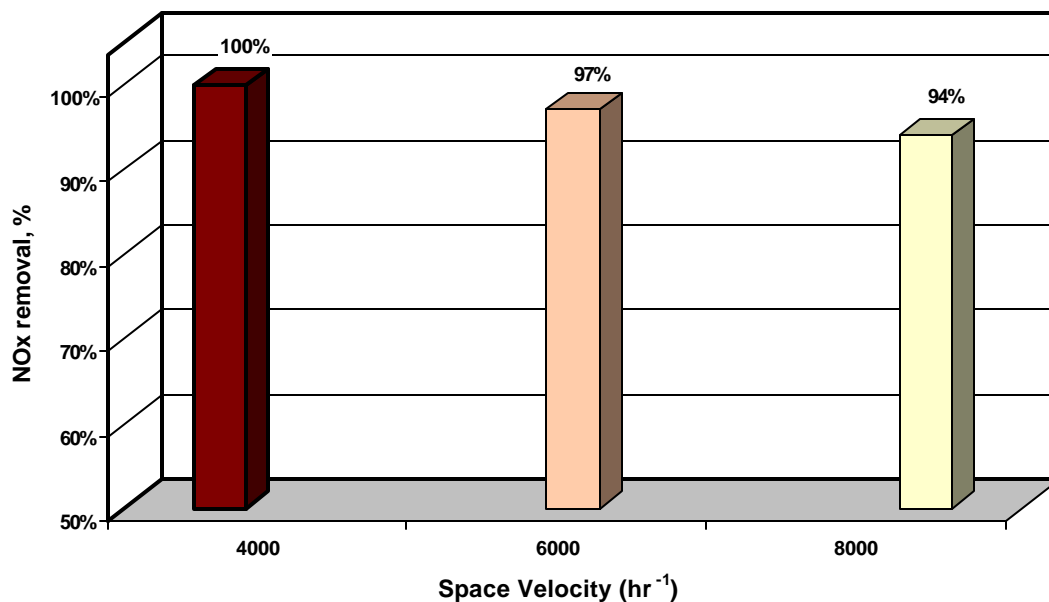


Figure 8. Effect of Space Velocity on NO<sub>x</sub> Removal Efficiency of ICCL-Cu-10

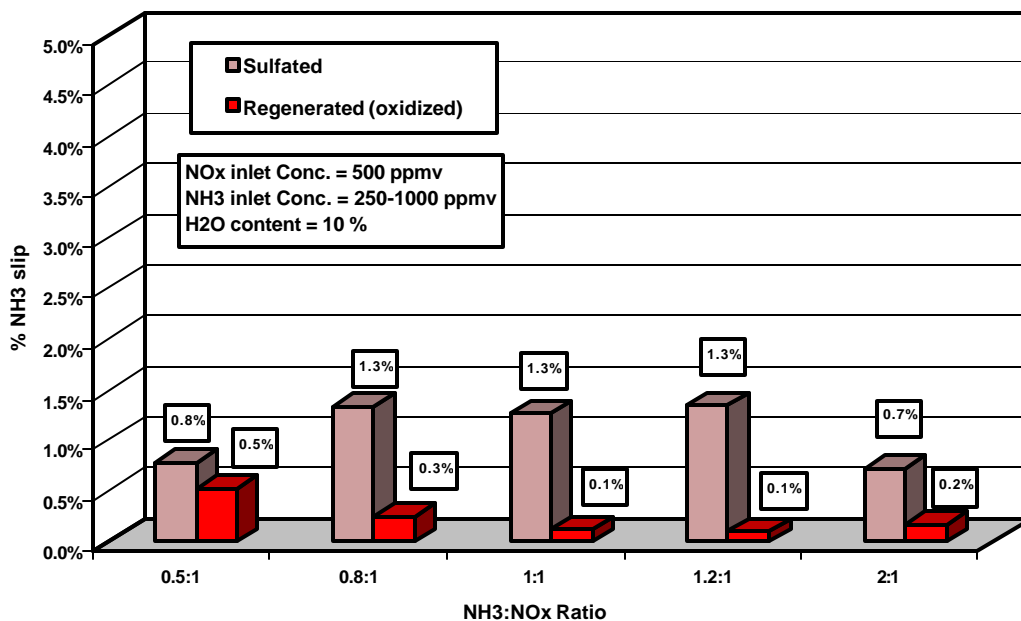


Figure 9. Effect of NH<sub>3</sub>/NO<sub>x</sub> Ratio on NH<sub>3</sub> Slip

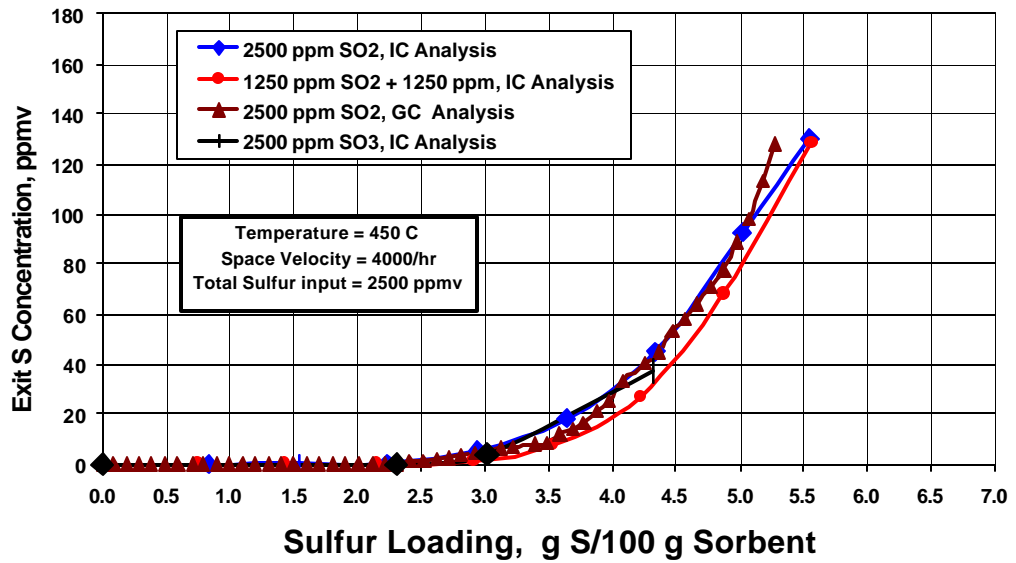


Figure 10. Results of the SO<sub>3</sub> Removal with ICCI-Cu-10

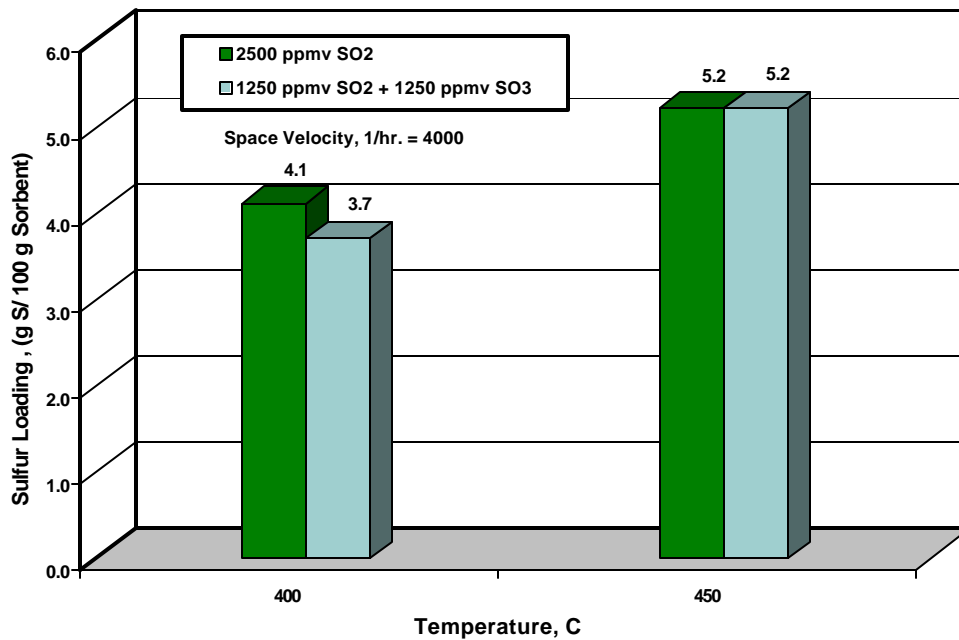


Figure 11. Effect of Temperature on SO<sub>3</sub> removal

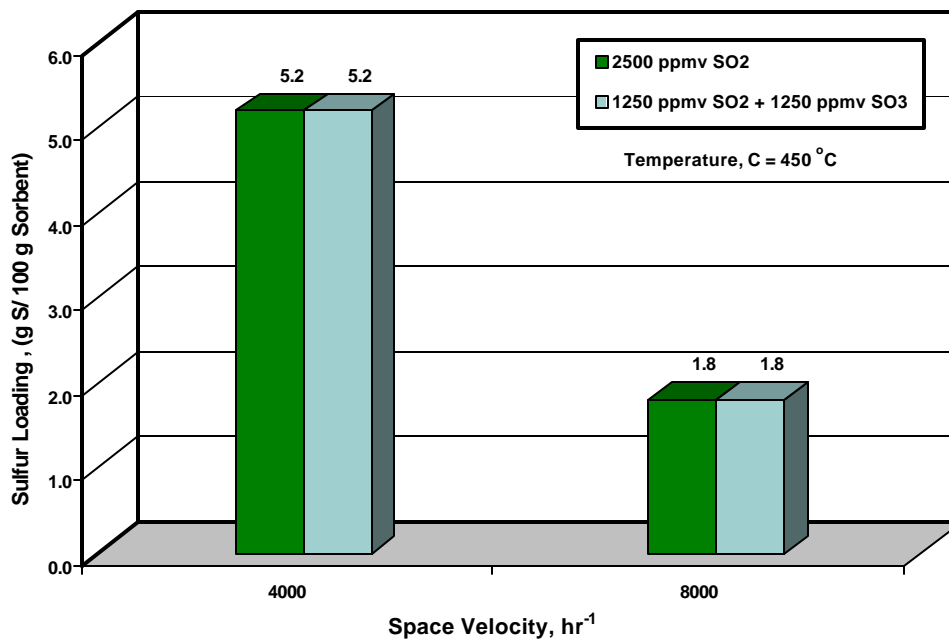


Figure 12. Effect of Space Velocity on SO<sub>3</sub> Removal

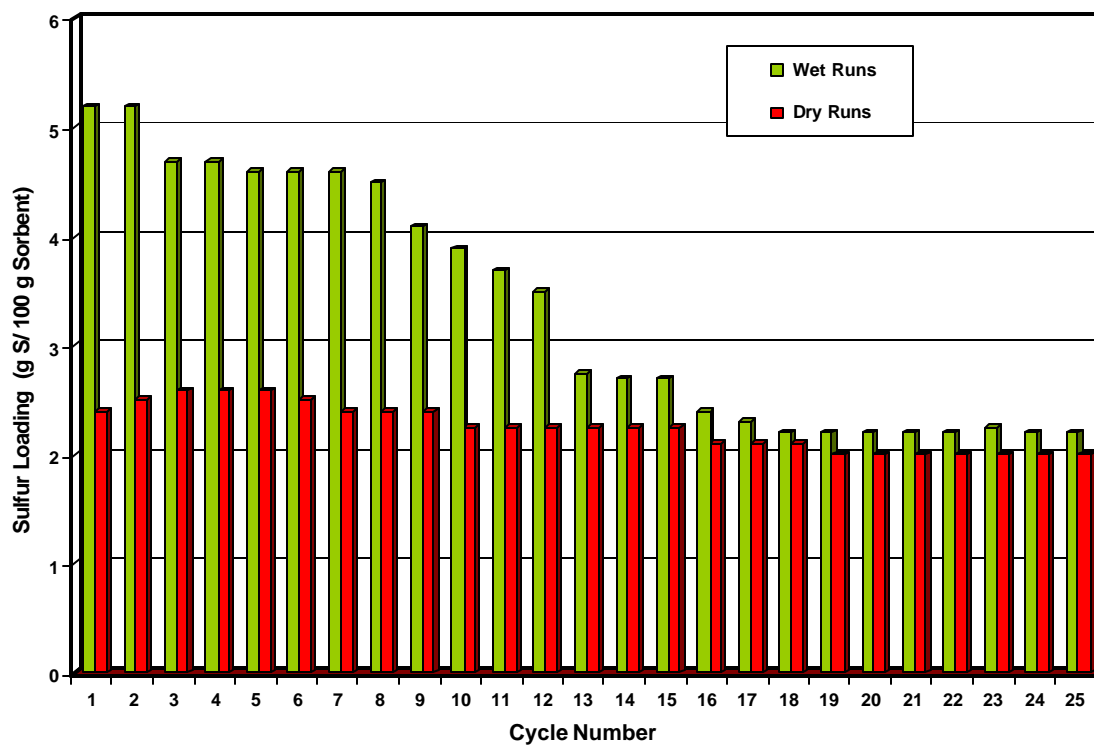


Figure 13. Comparison of the Effective Sulfur Capacities in Durability Studies

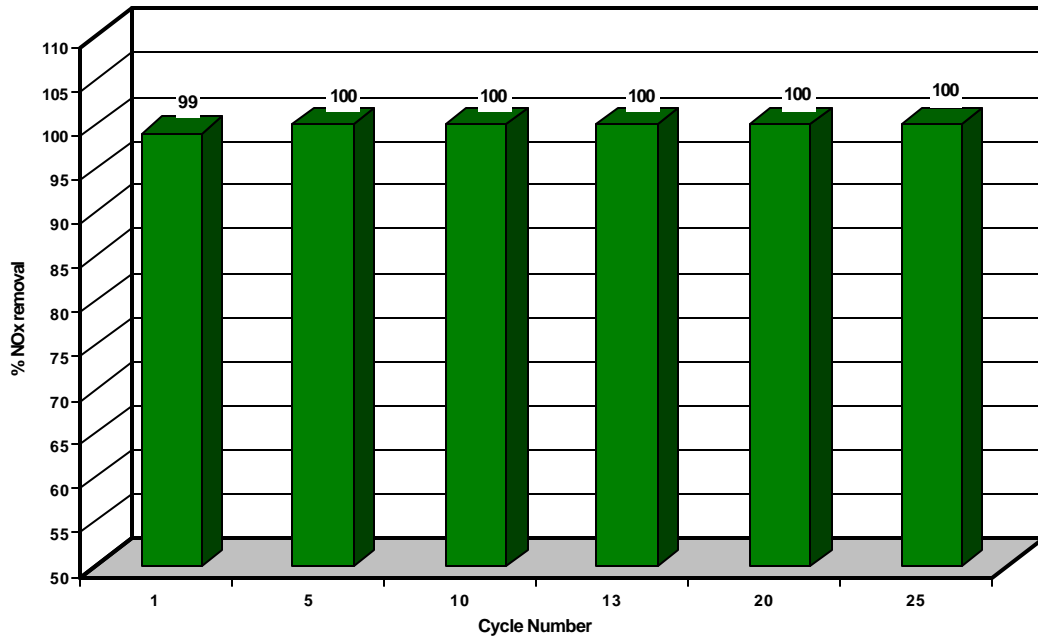


Figure 14. NOx Removal in the Cyclic Process

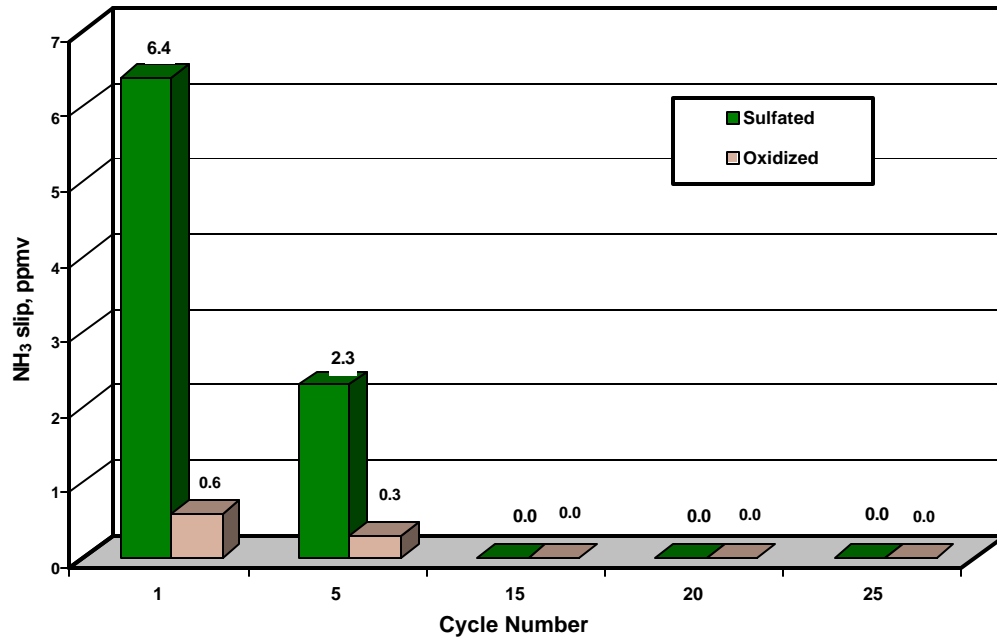
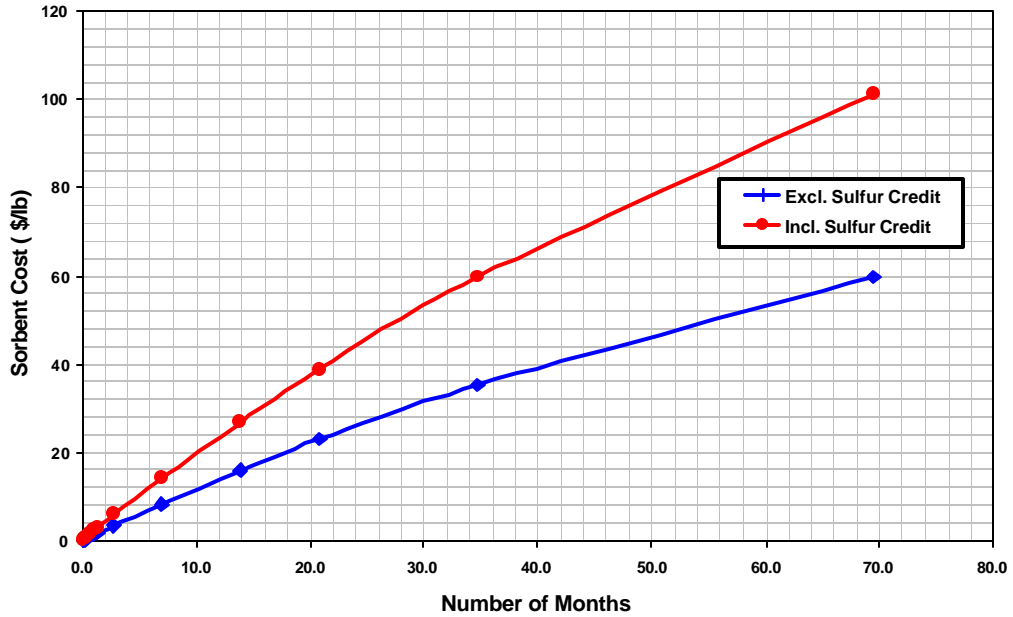


Figure 15. NH<sub>3</sub> Slip Analysis in Cyclic Process



**Figure 16. Cost Analysis and Comparison**

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