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TECHNICAL REPORT

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Project Title: **NOVEL TECHNOLOGIES FOR SO<sub>2</sub>/NO<sub>x</sub> REMOVAL FROM FLUE GAS**

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ABSTRACT

The goal of this project is to develop a cost-effective low temperature deNO<sub>x</sub> process. NO<sub>x</sub> removal at temperatures between 120°C-150°C was investigated using the approaches of 1) selective reduction of NO<sub>x</sub> by alcohol or acetone 2) adsorption of NO<sub>x</sub> with an effective sorbent. The chief problem encountered in low temperature reduction of NO was catalyst deactivation due to coke formation. In this quarter, a possible solution explored was increasing the loading of precious metals (Pd and Ag) on oxide supports, as precious metals are known to be effective in the oxidation of hydrocarbons at low temperatures. However, no improvement was observed. Another solution was the replacement of NO by NO<sub>2</sub> in the feed for the carbon-based catalyst tested, as NO<sub>2</sub> was observed to slow down the deactivation rate over Cu-ZrO<sub>2</sub> catalyst. However, rapid reduction of NO<sub>2</sub> to NO by the carbon support occurred, making this approach impractical. As part of this approach, search for better NO oxidation catalysts continued this quarter. It was found that on different carbon catalysts at 30°C and a W/F of 0.01g.min/cc, NO conversion to NO<sub>2</sub> between 82-90% can be achieved. This activity, however, decreased with increasing temperature. SO<sub>2</sub> also poisoned the oxidation activity of the activated carbon. Au dispersed on lanthanum oxide was another catalyst tested and had an NO conversion to NO<sub>2</sub> of 17% at 250 °C. The catalytic performance of this catalyst could be improved by increasing its surface area. Finally, the adsorption capacity of NO<sub>x</sub> of a carbon sample provided by ISGS and an inorganic sorbent were tested. The capacity of the inorganic sorbent was found to be much higher.

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## EXECUTIVE SUMMARY

Recent strict environmental regulations require the development of more efficient SO<sub>x</sub>/NO<sub>x</sub> processes to make Illinois coal competitive as a source of cheap energy. The objective of this project is to develop a cost-effective deNO<sub>x</sub> process that can be integrated into the low temperature (RTI-Waterloo) deSO<sub>x</sub>/deNO<sub>x</sub> process that is designed for retrofit applications. One approach is to search for a low temperature catalyst that uses environmentally benign reductants to remove NO<sub>x</sub>. Another approach is to search for a practical NO oxidation catalyst and an effective sorbent for NO<sub>x</sub>. The second approach could result in a process that can be easily integrated into the commercial STEAG process.

In the previous quarter, it was found that the obstacle to low temperature reduction over Cu-ZrO<sub>2</sub> was catalyst deactivation due to coke built up. It was also found that using NO<sub>2</sub> instead of NO slowed the coking and retarded the deactivation. Previously, we have also found that very low loadings of Pd promotor (0.2 wt.%) improved the catalytic performance of Cu-ZrO<sub>2</sub>, and a 2 wt.% Ag/Al<sub>2</sub>O<sub>3</sub> appeared to be one of the better catalysts in the selective reduction of NO by alcohols. Since precious metals are well known to be effective in the low temperature oxidation of hydrocarbons and, thus, might alleviate the coking problems, two catalysts containing precious metals of relatively high loadings were studied. Both a 33 wt.% Cu-ZrO<sub>2</sub> catalyst impregnated with 2.5 wt.% Pd and a 10 wt.% Ag/Al<sub>2</sub>O<sub>3</sub> were found to be ineffective in the 150-200°C region in the selective reduction of NO<sub>x</sub> by 2-propanol. The Pd promoted catalyst deactivated with time on stream, and the Ag catalyst was inactive in the selective reduction of NO to N<sub>2</sub>.

Of all the supported precious metal catalysts, supported Pt catalysts are the only ones known to be effective in the selective reduction of NO at temperatures as low as 150°C in the presence of H<sub>2</sub>O and SO<sub>2</sub> (G. Zhang, T. Yamaguchi, H. Kawakami and T. Suzuki, Appl. Catal. 2, 1992) L15). One major problem with this catalyst is that N<sub>2</sub>O was formed together with N<sub>2</sub>. To solve this problem, Ag/Al<sub>2</sub>O<sub>3</sub> was tested for the selective reduction of N<sub>2</sub>O by CO. N<sub>2</sub>O decomposition on Ag was found to be very effective and it was hoped that CO would react with the oxygen deposited on the Ag after N<sub>2</sub>O decomposition. Then, a mixed bed of Pt/Al<sub>2</sub>O<sub>3</sub> and Ag/Al<sub>2</sub>O<sub>3</sub> would be able to convert NO to N<sub>2</sub> at low temperatures. However, it was found that the Ag/Al<sub>2</sub>O<sub>3</sub> catalyst was unable to promote the reduction of N<sub>2</sub>O by CO.

As stated earlier, NO<sub>2</sub> was effective in slowing down the rate of coke formation on Cu-ZrO<sub>2</sub> catalyst. We tested NO replacement with NO<sub>2</sub> in the feed for carbon supported Cu catalysts. NO<sub>2</sub> was found to be ineffective for carbon based catalysts because the carbon support rapidly reduced the NO<sub>2</sub> to NO.

Parallel to the above effort, was the search for an effective NO oxidation catalysts. Among the catalysts studied last quarter, Co/Al<sub>2</sub>O<sub>3</sub> was the most active NO oxidation catalyst at 150°C in the presence of H<sub>2</sub>O and SO<sub>2</sub>. Although the activity appeared to be sustained at 20 hours on stream, it was only half of that after 3 hours. Although with improvement, this

catalyst might be developed into a practical one, it was decided to explore other types of catalysts.

Active carbon fibers (supplied by Professor Mochida) and activated carbon (calgon) showed 90% and 82% NO conversions to NO<sub>2</sub> at 30°C and a W/F of 0.01 g.min/cc. However, the conversions dropped to around 50% at 75°C and to negligible levels at 120°C. This is probably due to the reduction of NO<sub>2</sub> formed by carbon. Several methods (heat treatment, H<sub>2</sub> reduction, acid treatment, addition of Fe<sub>2</sub>O<sub>3</sub> or CoO) to modify the carbon surface did not improve the high temperature performance of the carbon catalysts. 0.1% SO<sub>2</sub> in the feed stream completely suppressed the NO<sub>2</sub> production at 75°C.

In addition to carbon based catalysts, inorganic catalysts such as Al<sub>2</sub>O<sub>3</sub> supported CuO and MnO were tested. These were not active at 150°C for NO oxidation in the presence of H<sub>2</sub>O and SO<sub>2</sub>. Au/La<sub>2</sub>O<sub>3</sub> was also tested in the presence of 2% H<sub>2</sub>O. 17% NO was converted to NO<sub>2</sub> at 250°C. There is, however, room for improvement for this catalyst as it had a surface area of only 7.4 m<sup>2</sup>/g.

Besides the need for an efficient NO oxidation catalyst, the second approach also required the development of an efficient sorbent for NO<sub>2</sub>. A carbon sample supplied by Tony Lizzio of ISGS proved to be ineffective because the carbon reacted with the NO<sub>2</sub> and converted it to NO at 120°C. An inorganic material prepared at Northwestern was found to be quite effective in the sorption of NO<sub>2</sub>. Addition of 5% CO<sub>2</sub> to the feed did not affect the sorption properties of the inorganic material. The promising results obtained with these initial experiments suggested a new revenue to pursue in the future.

In the coming quarter, the focus of the research will be on screening for better NO oxidation catalysts. Au/La<sub>2</sub>O<sub>3</sub> will be supported on large surface area supports like Al<sub>2</sub>O<sub>3</sub> to increase the effective area of the active catalytic components. In addition to Au/La<sub>2</sub>O<sub>3</sub>, other oxides such as Cu, Co and Ce will be coprecipitated with Au and tested for NO oxidation. Carbon catalysts, prepared from different types of Illinois Basin coal will also be tested for their NO oxidation activities. All catalysts prepared for NO oxidation will also be used for test in the selective reduction of NO by hydrocarbons.

## OBJECTIVES

The goal of this research is to develop a cost-effective low temperature deNO<sub>x</sub> process that could easily be integrated into the novel RTI-Waterloo SO<sub>x</sub>/NO<sub>x</sub> process. It involves either the development of a cost-effective low temperature catalyst that promotes the selective reduction of NO by alcohols or the development of an efficient NO<sub>x</sub> sorbent. In the previous quarter, it was found that the obstacle towards achieving low temperature catalytic NO reduction was excess coking of the catalyst at low temperatures. The deactivation was slowed by NO<sub>2</sub> in the gas phase. Thus screening for active NO oxidation catalyst was made, and it was found that, Co/Al<sub>2</sub>O<sub>3</sub> was promising. Thus, the objectives for this quarter are to: 1) find solution to the problem of coking of the NO reduction catalysts, 2) search for better NO oxidation catalyst, and 3) find an efficient NO<sub>x</sub> sorbent.

## INTRODUCTION AND BACKGROUND

Illinois has the largest reserve of coal. However, the high sulfur content of its coal reduces its attractiveness as a source of cheap energy. Recent stringent environmental regulations require the development of a more effective SO<sub>x</sub>/NO<sub>x</sub> process in order to maintain the competitiveness of Illinois coal. This project is to investigate a low temperature deNO<sub>x</sub> process which can easily be integrated into novel RTI-Waterloo process. It was also found that the process under investigation could be integrated with the existing commercial STEAG process with only minor modifications to the existing processes.

The RTI-Waterloo process involves SO<sub>2</sub> removal as concentrated sulfuric acid over modified carbon material. The SO<sub>2</sub>-free gas is then slightly reheated with incoming flue gas, blended with ammonia and passed over another bed of different modified carbon to remove the NO<sub>x</sub>. The removal of SO<sub>2</sub> before NO<sub>x</sub> is important as the high sulfur level of the flue gas probably would poison most deNO<sub>x</sub> catalyst. The process of SO<sub>2</sub> removal, however, lowers the temperature of the flue gas to around 150°C, which is substantially lower than the operational temperature (350-400°C) of practical SCR (selective catalytic reduction) catalysts. Although a modified carbon catalyst used in the second bed works at low temperature, its activity is low. Furthermore, the reductant used in the process is NH<sub>3</sub>, which itself is environmentally harmful. Thus, the goal of this research will be met if the modified carbon catalyst for the NH<sub>3</sub> reduction of NO can be replaced by a catalyst bed that promotes the selective reduction of NO by hydrocarbons. Alternatively, this goal can also be met if an efficient NO<sub>x</sub> sorbent is developed. An economic analysis of this sorption process, as presented in the last quarterly report, showed it to be competitive with the reduction process.

The commercial STEAG flue gas cleanup process uses char to remove SO<sub>x</sub>, fine particulates, and trace elements such as mercury from the flue gas. If NO<sub>x</sub> is to be removed, the flue gas is reheated after the char bed, and passed over a separate SCR catalyst bed. Thus, an efficient NO<sub>x</sub> adsorption process can also integrate into the STEAG process.

The significant observations made in the previous quarter was that coking of the catalysts was the major obstacle towards achieving low temperature reduction of NO over both the inorganic Cu-ZrO<sub>2</sub> catalyst and the carbon based catalysts. It was also observed that replacing NO in the feed with NO<sub>2</sub> alleviated, though not eliminated, the coking problem. Thus, a considerable effort was expended on screening for efficient NO oxidation catalyst. A Co/Al<sub>2</sub>O<sub>3</sub> catalyst was found to have a relatively stable activity after 20 hours on stream in a flow of 1000 ppm NO, 10% H<sub>2</sub>O, 4% O<sub>2</sub> and 0.2% SO<sub>2</sub>. However, this activity was only half of the maximum activity recorded around 3 hours after the start of the reaction. It appeared that with improvement this may be a viable catalyst. Thus, the objectives this quarter were focused on solving the coking problem, looking for better NO oxidation catalyst and analyzing the necessary components in a sorbent for efficient absorption of NO<sub>2</sub>.

## EXPERIMENTAL PROCEDURES

### Catalyst Preparation

**Pd-Cu-ZrO<sub>2</sub> catalyst:** 33 wt.% Cu-ZrO<sub>2</sub> catalyst was first prepared by co-precipitation of the nitrate salts of Cu and Zr with urea using the method of Amenomiya et al. [1]. After calcination to 350°C, 2.5 wt.% Pd was impregnated onto the catalyst with tetraaminopalladium (II) nitrate precursor. The catalyst was then reheated to 350°C to decompose the palladium precursor.

**Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>:** 10 wt.% Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnating  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Aldrich Chemicals) with AgNO<sub>3</sub> solution. The impregnated solid was reduced in H<sub>2</sub> at 300°C.

**CuO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and MnO<sub>2</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts** were prepared by simple impregnation method. Metal nitrates (Cu and Mn) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> pellets were purchased from Johnson Matthey.

**Au/La<sub>2</sub>O<sub>3</sub>:** Au/La<sub>2</sub>O<sub>3</sub> catalyst was prepared by the co-precipitation of hydrogen tetrachloroaurate (III) hydrate (Aldrich Chemical) with La (NO<sub>3</sub>)<sub>3</sub> (Alfa Products). 1 M Na<sub>2</sub>CO<sub>3</sub> solution was the precipitating agent as in the methods of Haruta et al. [2]. The precipitate was suction filtered and washed many times. Then it was calcined in flowing air and controlled heating to 350°C.

Activated carbon (Calgon), activated carbon-supported catalysts, and active carbon fibers (Osaka) kindly supplied by Professor Mochida were studied for NO oxidation to NO<sub>2</sub>. H<sub>2</sub> reduction and heat treatment of activated carbon were carried out at 800°C with 50 cc/min of H<sub>2</sub> and N<sub>2</sub>, respectively. 10 ml of concentrated HNO<sub>3</sub> per gram of activated carbon were used for HNO<sub>3</sub> treatment. The treatment was at the boiling point of HNO<sub>3</sub> solution and last for 3 hours followed by washing and drying.

### Catalytic Tests

Details of the procedure for catalytic tests for the selective reduction of NO by alcohols had been described in previous quarterly reports [3]. Briefly, at Northwestern, the catalysts were tested in a fused silica U-tube reactor. The flow rate and composition of the feed gases were controlled by mass flow meters. The typical composition of the feed was 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>7</sub>OH, 2% H<sub>2</sub>O, 4% O<sub>2</sub>, and the balance He. Before testing, the NO reduction catalyst was pretreated at 300 or 350°C in a flowing mixture of 1% O<sub>2</sub>, 1000 ppm C<sub>3</sub>H<sub>6</sub>, and the balance helium to remove nitrogen-containing species left over from catalyst preparation. When N<sub>2</sub> was no longer detected in the reactor effluent, the reactor temperature was lowered to the desired value and the NO containing reaction mixture was introduced.

The terms used to present the data are defined below:

$$\% \text{ NO Conversion to N}_2 = 200 * \text{N}_2 / \text{NO}_{\text{in}}$$

$$\% \text{ NO competitiveness} = 200 * \text{N}_2 / (2 \text{ O}_2 \text{ consumed} + \text{NO consumed})$$

$$\% \text{ Reductant conversion} = (\text{R}_{\text{n,in}} - \text{R}_{\text{n,out}}) / \text{R}_{\text{n,in}}$$

NO oxidation and sorption experiments were all performed with the catalyst or sorbent in a U-tube reactor with the flow rate of the feed gases controlled by mass flow meters. The effluent from the reactor was analyzed with a Mattson Galaxy series 5000 FTIR

The RTI NO<sub>x</sub> reaction system had been described in the earlier report [3]. 0.1% NO, 0.1% SO<sub>2</sub>, 4% O<sub>2</sub>, and 10% H<sub>2</sub>O with a total flow of 400 cc/min were used for NO oxidation over 4 g carbon catalysts. NO<sub>x</sub> analyzer with NO<sub>x</sub> mode and NO mode was used to determine both the inlet and outlet concentrations of NO<sub>2</sub> and NO. The oxidation conversion was calculated as:

$$\% \text{ NO oxidation to NO}_2 = (\text{NO}_{\text{x,out}} - \text{NO}_{\text{out}}) / \text{NO}_{\text{x,out}} \times 100$$

## RESULTS AND DISCUSSION

### Selective Reduction of NO over Pd-Cu-ZrO<sub>2</sub> and Ag/α-Al<sub>2</sub>O<sub>3</sub> Catalysts

1000 ppm 2-propanol was used to reduce 1000 ppm NO in the presence of 4% O<sub>2</sub> and 2% water over a 2.5 wt.% Pd,-33 wt.% Cu-ZrO<sub>2</sub> at 200°C. The deactivation rate appeared to be very severe for this Pd modified Cu-ZrO<sub>2</sub>. After 2 hours on stream, the activity was only 60% of the initial activity. Ag/α-Al<sub>2</sub>O<sub>3</sub> was chosen because this catalyst promotes the synthesis of ethylene oxide from ethylene at relatively low temperatures without apparent problems of coking (4). Under identical reaction conditions used in the Pd-Cu-ZrO<sub>2</sub> experiment, no N<sub>2</sub> production was observed with the Ag/α-AL<sub>2</sub>O<sub>3</sub> catalyst.

### Selective Reduction of N<sub>2</sub>O over Ag/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

N<sub>2</sub>O readily decomposed on Ag surface into N<sub>2</sub> and oxygen adsorbed on Ag (5). It was possible that the adsorbed oxygen could be removed rapidly by CO at low temperatures, even in the presence of gas phase oxygen. However, in a feed of 1000 ppm N<sub>2</sub>O, 4% O<sub>2</sub>, 2% H<sub>2</sub>O and 1.1% CO, no N<sub>2</sub> production was observed at any temperatures. Combustion of CO to CO<sub>2</sub> was the only reaction observed.

### NO<sub>x</sub> Reduction with Acetone Over Cu supported on Carbon

Since NO<sub>2</sub> was found in the previous quarter to be able to slow down the deactivation process over a Cu-ZrO<sub>2</sub> catalyst, tests were conducted this quarter to see whether this also holds true for carbon-based catalysts. Since it is known that the efficiency of carbon reduction of NO<sub>2</sub> to NO increased with rise in temperatures (6), the comparative studies of NO and NO<sub>2</sub> were conducted at 120°C, which is 30°C lower than the usual 150°C used in reactions over a carbon-supported Cu catalyst. The NO conversion at this temperature after 5 hours on stream was only 20% as compared with the 35% observed at 150°C. The deactivation rate at this temperature was also faster. Replacement of NO with NO<sub>2</sub> in the feed did not improve the catalytic performance. This was attributed to the fact that NO<sub>2</sub> reacted with carbon to form NO and CO<sub>2</sub>, as can be seen by the evolution of a larger amount of CO<sub>2</sub> than the carbon in the hydrocarbon feed.

NO reduction over carbon-supported Cu catalysts synthesized by ISGS was examined. The activity was very low. The surface area of the carbon material synthesized by ISGS was ~100 m<sup>2</sup>/g. This low surface area could be the cause of the low NO<sub>x</sub> reduction activity. However, the Cu was loaded on the carbon using a different method. Thus, either the nature of the carbon support or the method of introducing Cu may be important in determining the catalytic performance of the carbon-supported Cu catalysts.

NO reduction over Cu-Ag/AC was studied in the presence of 0.1% SO<sub>2</sub> at 150°C because we have shown in the last quarter that SO<sub>2</sub> promotes NO oxidation over Co/Al<sub>2</sub>O<sub>3</sub> and because NO<sub>2</sub> may be a possible intermediate during NO reduction. The results with and without SO<sub>2</sub> are compared in Figure 1. The NO reduction activity decreased much more rapidly in the presence of SO<sub>2</sub> and was negligible after 2 1/2 hours on stream. The increased deactivation rate may be due to the formation of sulfates on the carbon supported catalysts.

### NO Oxidation to NO<sub>2</sub> over Inorganic Metal Oxides

In contrast to literature results that reported high activity for NO oxidation over 10% CuO and 10% MnO<sub>2</sub> supported on alumina catalysts (7), we found negligible NO oxidation activities for these catalysts in the presence of SO<sub>2</sub> and H<sub>2</sub>O.

Catalysts containing Au well dispersed in metal oxides are known to be excellent for CO oxidation (2). Since there may be similarities between the mechanism of low temperature CO oxidation and NO oxidation, Au dispersed in metal oxides was studied. The choice of the metal oxide is such that it should not form stable nitrates under the low temperature reaction conditions. We have observed in our studies of  $ZrO_2$  that stable nitrate can be formed even at room temperature. Au/ $La_2O_3$ , the first of a series of Au-based catalyst that we planned to investigate, was tested for NO oxidation activities in a feed of 1000 ppm NO, 4%  $O_2$  and 2%  $H_2O$ . The conversion was 17% at 250°C. However, this catalyst had a very small surface area of 7.4  $m^2/g$ . Thus, supporting this catalyst on a large surface area support may effect large improvement in its performance.

#### NO oxidation over Active Carbon Fibers and Activated Carbon

Both the ACT (activated carbon fibers supplied by Professor Mochida) and activated carbon showed high NO oxidation activities of 90% and 82% conversion (Table I) at 30°C with 400 ppm NO, 4%  $O_2$ , and balance He. The  $NO_x$  concentration at the reactor exit versus time on stream is shown in Fig. 2 for activated carbon at 30°C and in Fig. 3 for active carbon fibers at 75°C. Initially no  $NO_2$  was detected and the concentration of NO increased with time. This suggested that  $NO_2$  adsorption on carbon surface was stronger than that of NO. The NO concentration was at its maximum when the breakthrough of  $NO_2$  occurred.

The activity, however, decreased with increase in temperature similar to that reported by Mochida et al. (8). Conversion of NO decreased to 51% and 42% on active carbon fibers and activated carbon, respectively, at 75°C. Negligible oxidation was observed at 120°C. This decrease in oxidation activity was probably due to the reduction of the  $NO_2$  formed by the carbon to form NO and  $CO_2$ . Since  $H_2O$  suppression of NO oxidation on carbon was more severe at lower temperatures (8), it would be advantageous if the operational temperature can be raised. Thus, efforts were expended in modifying the surface of the activated carbon.

Three different pretreatment were attempted to improve the performance of the carbon catalysts at high temperatures. These included heat treatment at 800°C in  $N_2$ , reduction with  $H_2$  at 800°C, and oxidation using  $HNO_3$ . The thermal treatment in  $N_2$  was undertaken because Mochida et al. (8) reported improved NO oxidation activities over activated carbon fibers in the presence of  $H_2O$ . Such a heat treatment has been proposed to remove the oxygen functional groups on the carbon surface through liberation of  $CO$ , thus increasing the hydrophobic nature of the carbon. More extensive removal of the oxygen functional group could be achieved through reduction of the carbon surface by reduction with  $H_2$  at high temperatures (9). The treatment with  $HNO_3$  was to oxidize the carbon surface. However, as is shown in Tables 2 and 3, all the pretreatments proved to be detrimental to the catalytic performances of the activated carbon and the active carbon fibers.

The effect of  $SO_2$  on the NO oxidation activity over heat-treated activated carbon was studied by adding 0.1%  $SO_2$  to the inlet gas. The results are also shown in Table 3. The NO



oxidation activity was negligible in the presence of  $\text{SO}_2$  at both  $120^\circ\text{C}$  and  $75^\circ\text{C}$ . This result is similar to that reported in the literature (10-12). The competitive adsorption between NO and  $\text{SO}_2$  on carbon surfaces may be the cause for the detrimental effect of  $\text{SO}_2$ .

The combined effect of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  on the NO oxidation activity of the activated carbon was tested. As reported in the last quarterly report,  $\text{SO}_2$  greatly promotes the NO oxidation reaction in the presence of  $\text{H}_2\text{O}$  over  $\text{Co/Al}_2\text{O}_3$ . However, the NO oxidation activity was negligible over the activated carbon in the presence of  $\text{SO}_2$  and  $\text{H}_2\text{O}$  at  $120^\circ\text{C}$ .

#### NO Oxidation Over Activated Carbon-Supported Catalysts

Metal oxides were added to carbon catalysts to increase the NO oxidation activity. 5% CoO and 1%  $\text{Fe}_2\text{O}_3$  supported on activated carbons were tested. Table 4 compared the NO oxidation activity of the metal oxide supported activated carbon with the ones without the metal oxides. Adding the metal oxide to the carbon lowered the oxidation activities. However, it was found out later, from the literature reports (13-14) that adding CuOH or FeOOH was very effective in increasing NO concentration in carbon micropores, and addition of CuO was totally ineffective. Since increasing the local concentration of NO in the micropores should be beneficial to NO oxidation activities, it should be worthwhile to try this approach again.

#### $\text{NO}_2$ Sorption

The adsorption capacity for  $\text{NO}_2$  at  $120^\circ\text{C}$  on a carbon sample supplied by A. Lizzio of ISGS was measured. The sample had a low capacity because  $\text{NO}_2$  was rapidly converted to NO over the carbon sample.

Figure 4 showed the adsorption capacities of an inorganic material (NU1). It can be seen that the adsorption capacity was far superior to that of the carbon sample. Furthermore, the presence of 5%  $\text{CO}_2$  did not affect the sorption capacity of the inorganic material.

### CONCLUSIONS AND RECOMMENDATIONS

Significant effort this quarter was expended in search of a good NO oxidation catalyst. Both active carbon fibers and activated carbon are very active for NO oxidation to  $\text{NO}_2$ . However, the activity decreased with temperature until it was negligible at  $120^\circ\text{C}$ . No improvement of NO oxidation activities at  $120^\circ\text{C}$  was observed with modifications of the surface of activated carbon by oxidative or reductive treatments. Addition of  $\text{SO}_2$  to the feed stream, suppressed the NO oxidation activity at temperatures as low as  $75^\circ\text{C}$ . Future work on the carbon catalysts is to modify the carbon with  $\text{Cu}(\text{OH})_2$  and FeOOH as this method of catalyst preparation was reported to dramatically increase NO adsorption in the micropore through the process of micropore filling (13,14). Increase in the concentration of NO in the pores should promote oxidation of NO to  $\text{NO}_2$ .

The result of the Au/La<sub>2</sub>O<sub>3</sub> was inconclusive. Although the NO oxidation activity was low, the surface area of the catalyst used was also very low. Future work will focus on supporting Au/mixed oxide catalysts on large surface area supports such as Al<sub>2</sub>O<sub>3</sub>. Improvement of the Co/Al<sub>2</sub>O<sub>3</sub> catalyst, found to be promising in the previous quarter, will be attempted. A solution of hydrogen tetrachloroaurate (III) hydrate and Co(NO<sub>3</sub>)<sub>2</sub> will be impregnated on Al<sub>2</sub>O<sub>3</sub>. Simultaneous precipitation of the two components will be achieved by passing a stream of NH<sub>4</sub>OH over the impregnated catalyst. Co-precipitation of Pt-Co onto Al<sub>2</sub>O<sub>3</sub> will also be attempted. Since Au/Co<sub>3</sub>O<sub>4</sub> was recently discovered to have unusual activities in activating hydrocarbon at low temperatures (15), the Au-Co-Al<sub>2</sub>O<sub>3</sub> catalyst will also be tested in the selective reduction of NO with alcohols.

The sorption of NO<sub>x</sub> over inorganic material was very promising. In the next quarter further research to improve the sorption capacity will be attempted if time permits, but the focus will be on improving the NO oxidation catalyst.

#### DISCLAIMER STATEMENT

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Table 1 NO oxidation to NO<sub>2</sub> over Active Carbon Fibers(ACF) and Activated Carbons(A.C.).

carbon./Temp.	30°C	75°C	120°C
ACF	90%	51%	negligible
A.C.	82%	42%	negligible

a: Activities were obtained after 40 h on stream.

b: Reaction conditions: 400 ppm NO, 4% O<sub>2</sub>, and balance He; 400 cc/min over 4.0 g of catalysts.

Table 2 NO oxidation to NO<sub>2</sub> over Activated Carbons(A.C.).

A.C./Temp.	120°C	75°C
fresh	negligible	42%
heat treatment	negligible	35%
H <sub>2</sub> reduction	negligible	31%
HNO <sub>3</sub> oxidation	negligible	28%

a: Activities at 120°C were obtained after 24 h on stream and the activities at 75°C were obtained after 24 h at 120°C and 40 h at 75°C.

b: Reaction conditions: 400 ppm NO, 4% O<sub>2</sub>, and balance He; 400 cc/min over 4.0 g of catalysts.

Table 3 NO oxidation to NO<sub>2</sub> over Activated Carbons(A.C.).

A.C./Temp.	120°C	75°C
heat treatment	negligible	35%
with 0.1%SO <sub>2</sub>	negligible	negligible
with 0.1%SO <sub>2</sub> +10%H <sub>2</sub> O	negligible	N/A

a: Activities at 120°C were obtained after 24 h on stream and the activities at 75°C were obtained after 24 h at 120°C and 40 h at 75°C.

b: Reaction conditions: 400 ppm NO, 4% O<sub>2</sub>, and balance He; 400 cc/min over 4.0 g of catalysts.

Table 4 NO oxidation to NO<sub>2</sub> over activated carbons(A.C.) activated carbon supported catalysts.

Catalyst./Temp.	120°C	75°C
fresh A.C.	negligible	42%
1%Fe <sub>2</sub> O <sub>3</sub> /A.C.	negligible	26%
5%CoO/A.C.	negligible	24%

a: Activities at 120°C were obtained after 24 h on stream and the activities at 75°C were obtained after 24 h at 120°C and 40 h at 75°C.

b: Reaction conditions: 400 ppm NO, 4%O<sub>2</sub>, and balance He; 400 cc/min over 4.0 g of catalysts.

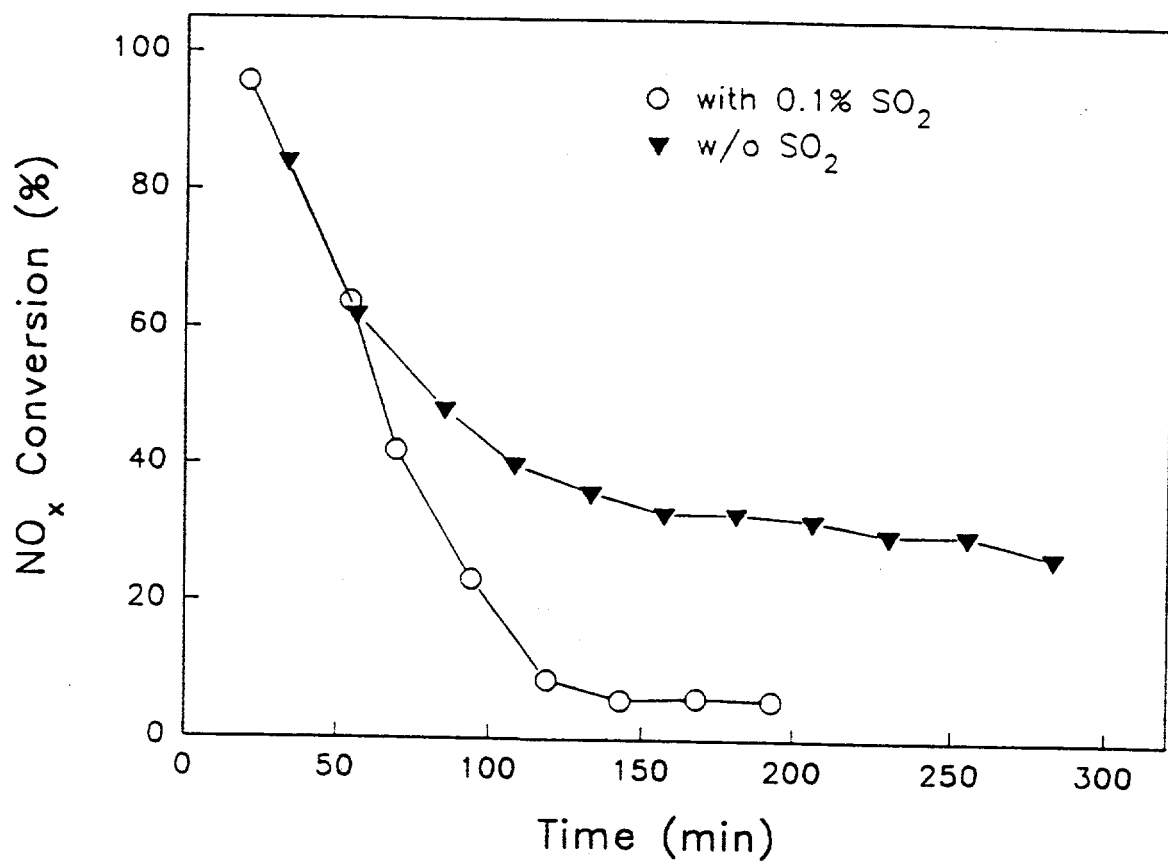


Figure 1. The effect of SO<sub>2</sub> on NO reduction with acetone over a Cu supported carbon catalyst at 150 °C; 0.1% NO, 0.13% acetone, 4% O<sub>2</sub>, and \*% H<sub>2</sub>O; 3000 h<sup>-1</sup>.

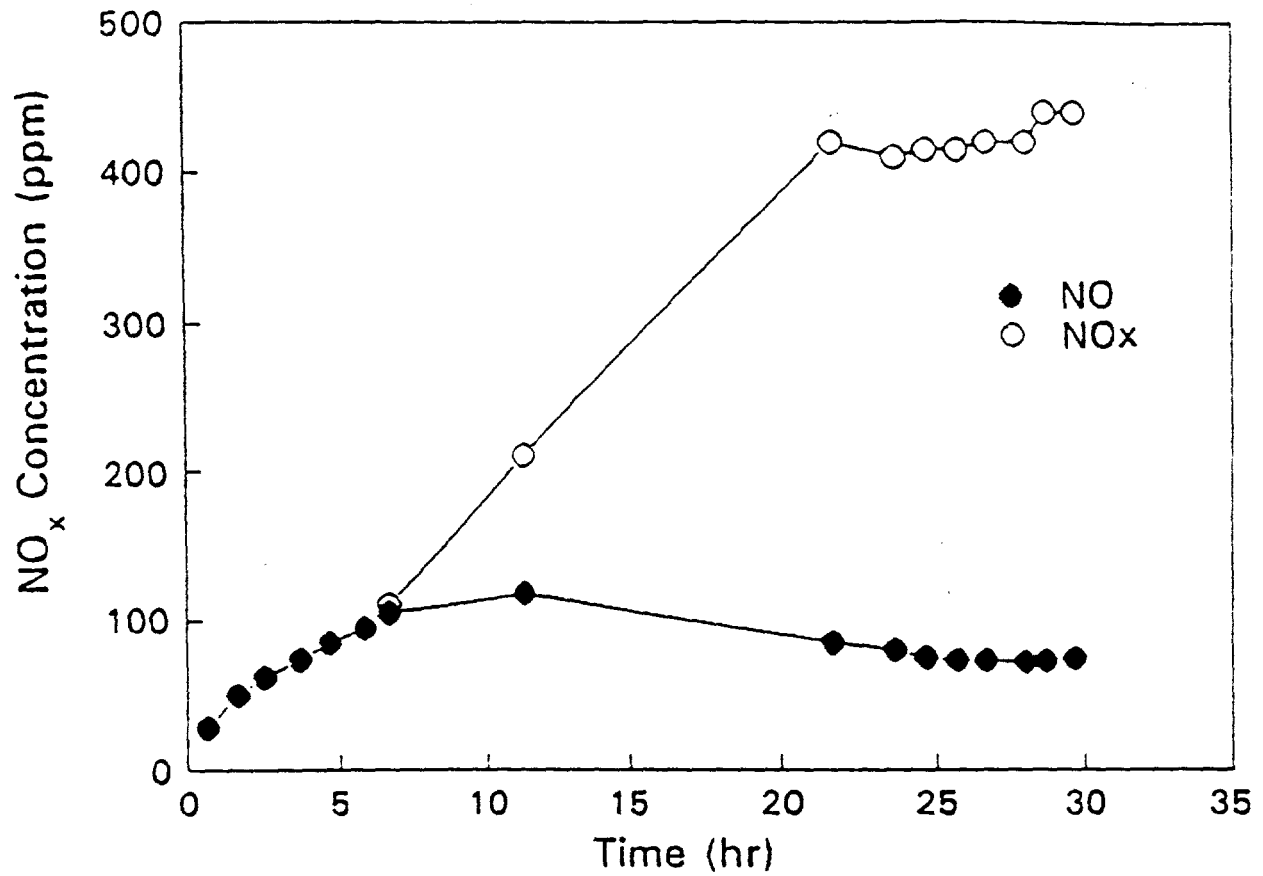


Figure 2. NO and NO<sub>x</sub> concentrations as function of time during NO oxidation over activated carbon at 30 °C; 400 ppm NO, 4% O<sub>2</sub>, and balance He: 400cc/min over 4.0 g of catalysts.

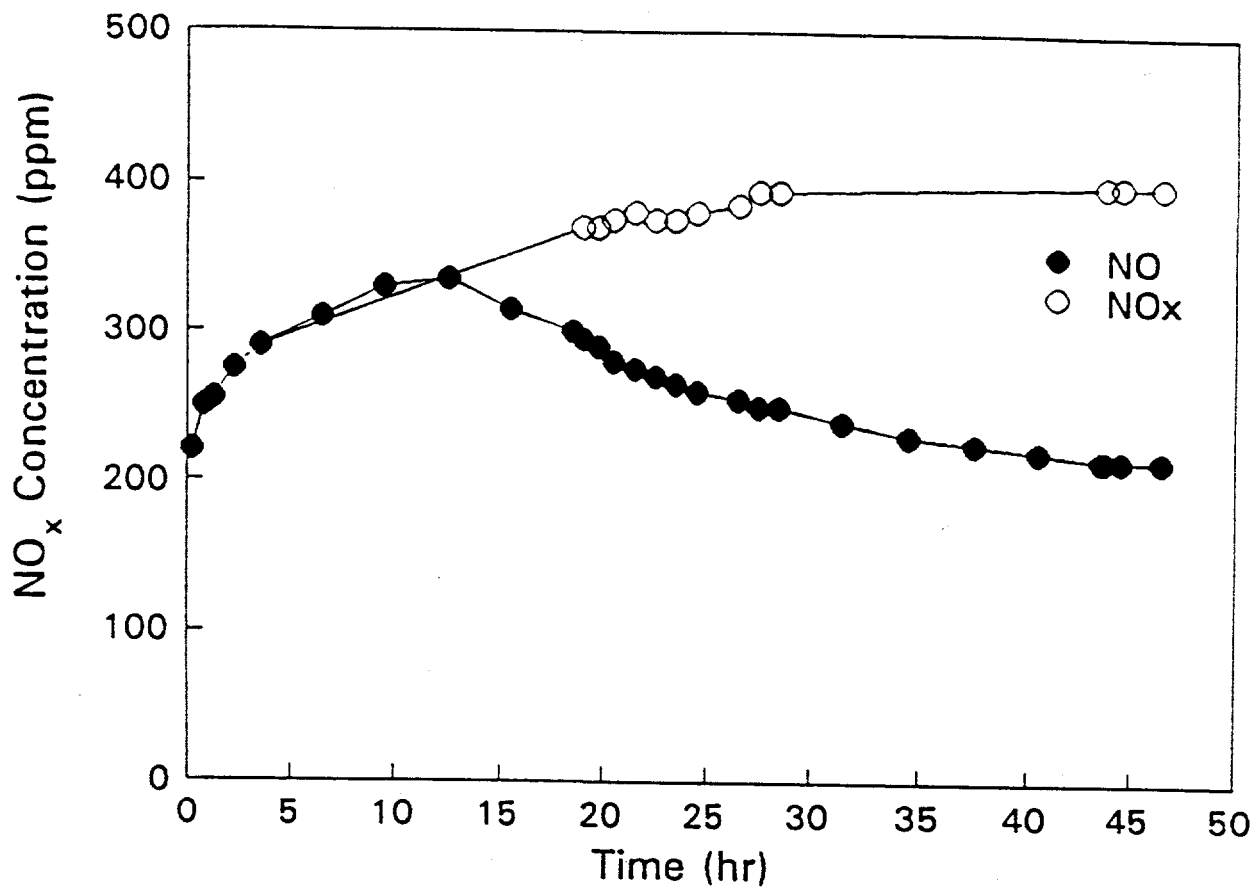


Figure 3. NO and NO<sub>x</sub> concentrations as function of time during NO oxidation over active carbon fibers at 75 °C; 400 ppm NO, 4% O<sub>2</sub>, and balance He; 400cc/min over 4.0 g of catalysts.



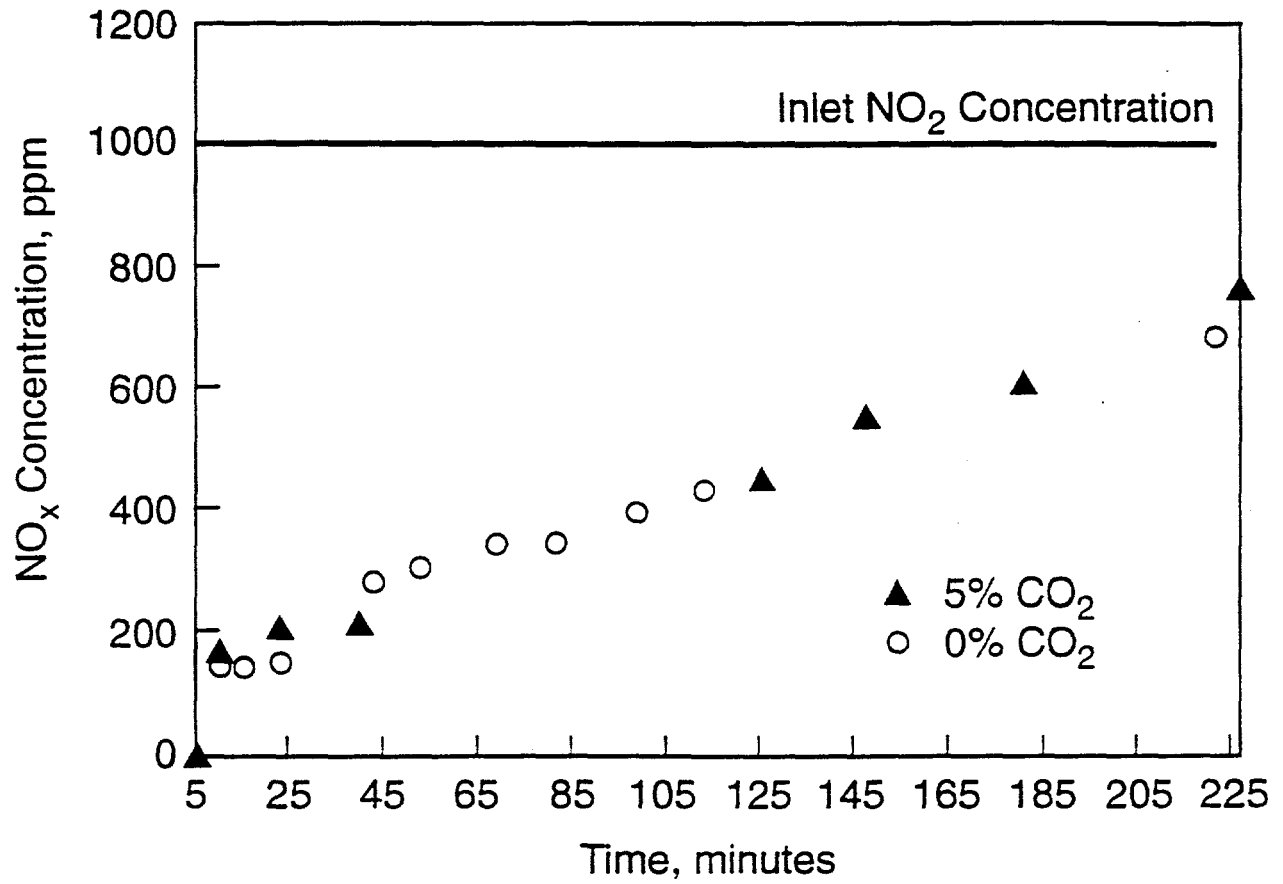


Figure 4. NO and NO<sub>2</sub> breakthrough curves for an inorganic sorbent. 1000 ppm NO<sub>2</sub>, 5% O<sub>2</sub>, 2% CO<sub>2</sub>, flow rate= 100cc/min, 120°C.

**PROJECT MANAGEMENT REPORT**  
December 1, 1994 through February 28, 1995

Project Title: **NOVEL TECHNOLOGIES FOR SO<sub>x</sub>/NO<sub>x</sub> REMOVAL FROM FLUE GAS**

DOE Grant Number: DE-FC22-92PC92521 (year 3)  
ICCI Project Number: 94-1/2.1A-2P  
Principal Investigator: Harold Kung, Northwestern University  
Other Investigators: Mayfair Kung, Northwestern University  
James J. Spivey, Research Triangle Institute  
Ben W. Jang, Research Triangle Institute  
Project Manager: Frank I. Honea, ICCI

**COMMENTS**

In the first quarter of this research project, the investigators began to recognize the potential importance of NO<sub>2</sub> in NO removal. As was stated in the last quarterly report, the idea of removing NO in the form of NO<sub>2</sub> was being formulated. In addition to reducing NO<sub>2</sub> into N<sub>2</sub>, the idea of removing NO<sub>2</sub> by adsorption was seriously considered during this quarter. A meeting was held at Northwestern University that included researchers from RTI and Northwestern, and Dr. Anthony Lizzio from the Illinois State Geological Survey, who has substantial experience in the preparation of adsorbent carbon material from Illinois coal. A process to formulated in concept that could be used directly in the commercial STEAG process. Subsequently, the concept was presented to representatives from STEAG, who found it both technically interesting and commercially possible. They then provided strong encouragement for this group to proceed with exploring and development of the concept into a process. As a result, some of the research effort in this quarter was spent to gather some pivotal data to confirm the technical feasibility of the concept. We were very pleased that the results were very positive. Therefore, we expect to spend more effort this quarter developing the technical basis for the conceptual process, following up on these preliminary results.

The research expenditure was within expectation. There were no major unexpected delays. We expect the research to progress within expectation in the coming quarter.

**CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER**

**NOVEL TECHNOLOGIES FOR SO<sub>x</sub>/NO<sub>x</sub> REMOVAL FROM FLUE GAS**

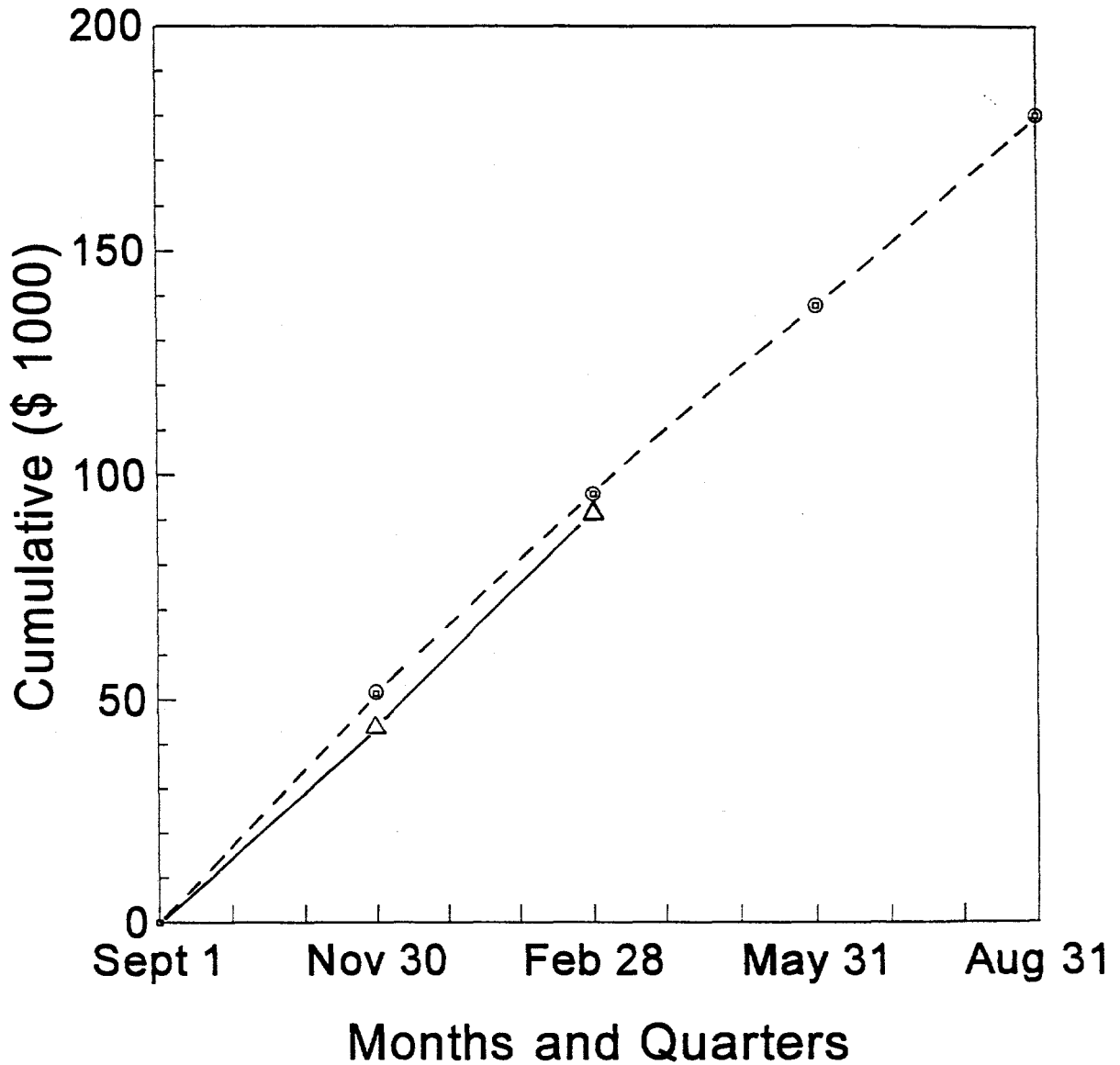
Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1994 to Nov. 30, 1994	Projected	10,739	2,013	1,500	625	0	19,997	16,567	51,441
	Estimated	11,000	2,062	500	0	0	15,000	13,567	42,129
Sept. 1, 1994 to Feb. 28, 1995	Projected	21,478	4,027	3,000	1,250	0	39,994	26,009	95,758
	Estimated	20,000	3,800	600	0	0	42,000	24,400	90,800
Sept. 1, 1994 to May 31, 1995	Projected	32,217	6,040	4,500	1,875	0	59,991	33,076	137,699
	Estimated								
Sept. 1, 1994 to Aug. 31, 1995	Projected	42,956	8,054	6,000	2,500	0	79,989	40,142	179,641
	Estimated								

\*Cumulative by Quarter

# COSTS BY QUARTER

## Novel Technologies for SO<sub>x</sub>/NO<sub>x</sub> Removal from Flue Gas

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--- ⊙ --- = Projected Expenditure    - - - - -  
 —△— = Estimated Actual Expenditures    ————  
 Total Illinois Clean Coal Institute Award \$179,641.00

## SCHEDULE OF PROJECT MILESTONES

### NOVEL TECHNOLOGIES FOR SO<sub>2</sub>/NO<sub>x</sub> REMOVAL FROM FLUE GAS

Begin Sept. 1 1994	MONTH												
	S	O	N	D	J	F	M	A	M	J	J	A	
A	_____									X			
B	_____										X		
C	_____											X	
D	_____			■									
E	_____											X	
F		_____■			_____■			_____X				_____X	
G		_____■			_____■			_____X				_____X	

#### Milestones:

- A: Synthesis and modification of catalysts completed.
- B: Initial tests of new catalysts completed.
- C: Long term stability and deactivation tests completed.
- D: Test of carbon-supported catalysts completed.
- E: Evaluation of feasibility of two-bed catalytic system completed.
- F: Technical reports prepared and submitted.
- G: Project management reports prepared and submitted.

