CROSS-FLOW, FILTER-SORBENT CATALYST FOR PARTICULATE, SO₂ AND NOₓ CONTROL

Technical Progress Report:

Fourth Quarterly

4 QTR 1990

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Master

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# Table of Contents

List of Figures iii
List of Tables iv

Summary of Test Results - Fourth Quarter Progress 1

1.0 Introduction 2
   1.1 Background 2
   1.2 Description of Single-Unit, Three Pollutant Control Device 2
   1.3 Research and Development Activity 5

2.0 Task Description Summary 6

3.0 Objectives for Fourth Quarter Activity 7

4.0 Approach 7
   4.1 NOx Reduction Test Approach 7
   4.2 Sorbent-Catalysts Used for NOx Reduction Tests 10

5.0 Results 11
   5.1 NOx Reduction on Fresh Sorbents 11
   5.2 NOx Reduction on Partially Sulfated Sorbents 11
   5.3 NOx Reduction Summary 16
   5.4 Effect of Sulfation at Lower Temperature on Sorbent-Catalyst Sulfation Performance 16

6.0 Plans for Next Quarter 18
   6.1 System Evaluation and Design 18
   6.2 Sorbent Studies 18

7.0 References 18
List of Figures

<table>
<thead>
<tr>
<th>Figure No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic of a Ceramic Cross-Flow Filter-Sorbent Catalyst</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Close-Up of Filter-Sorbent-Catalyst Wall and Gas Flow Scheme</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>Schematic of Packed-Bed Microreactor System</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>NO\textsubscript{x} Reduction on Fresh Sorbents</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>NO\textsubscript{x} Reduction on Cu-7Al-O</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>NO\textsubscript{x} Reduction on CeO2</td>
<td>14</td>
</tr>
<tr>
<td>7</td>
<td>NO\textsubscript{x} Reduction on Cu-Ce-O</td>
<td>15</td>
</tr>
</tbody>
</table>
# List of Tables

<table>
<thead>
<tr>
<th>Table No.</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Summary of Tasks</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>Program Schedule and Milestone Plan</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Physical Properties of Sorbent-Catalysts Tested</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>DeNO(_x) Summary</td>
<td>17</td>
</tr>
</tbody>
</table>
Summary of Test Results: Fourth Quarter Progress

NO\textsubscript{x} Reduction on Sorbent-Catalysts

The NO\textsubscript{x} reduction activity of three sorbent-catalyst materials was tested over a temperature range from 200 to 500°C. We were primarily interested in the sorbent-catalyst NO\textsubscript{x} reduction performance at 400°C because this appears to be a minimum temperature for acceptable sulfur capture with these sorbents. The tradeoff between sulfur capture and NO\textsubscript{x} reduction performance for these sorbent-catalysts is clear: sulfation improves with higher temperatures (e.g., 400-600°C) while NO\textsubscript{x} reduction improves at lower temperatures (e.g., 200-300°C).

NO\textsubscript{x} reduction tests were performed on three sorbent-catalyst materials:

1. Cu-7Al-O;
2. Cu-Ce-O; and
3. CeO\textsubscript{2}.

The first two materials showed good to excellent performance in sulfur capture tests. Ceria was tested to establish baseline data and to determine whether the addition of small amounts of ceria to the Cu-Al-O sorbent (for improved NO\textsubscript{x} reduction efficiency at 400°C) was warranted.

Both Cu-7Al-O and Cu-Ce-O showed high NO\textsubscript{x} reduction efficiency (>90%) at 200°C. However, both sorbents showed a decrease in NO\textsubscript{x} reduction efficiency with increasing temperature. At 400°C, the conversion of NO over the Cu-7Al-O catalyst decreased to 60%. Over Cu-Ce-O, the conversion of NO at 400°C was only 20%. The decrease in NO conversion with increasing temperature was due to ammonia oxidation on the sorbent-catalysts at higher temperature.

NO\textsubscript{x} reduction on ceria (Ce-5) was 90% at 400°C. With ceria, NO\textsubscript{x} reduction goes through a maximum of 95% at 380°C. Unfortunately, ceria alone is not an effective sulfur capture sorbent at these temperatures; at 400°C the sulfation conversion of CeO\textsubscript{2} was only 7% prior to SO\textsubscript{2} breakthrough. Good sulfur capture with this sorbent was achieved at 600°C. At this temperature, however, NO conversion is less than 60% due to ammonia oxidation.

Partial sulfation of the sorbent-catalysts resulted in significantly improved NO\textsubscript{x} reduction activity at 400°C.
1.0 Introduction

1.1 Background

Emission control systems for small-scale combustors must be designed to provide highly effective removal of three criteria pollutants (particulate matter, SO\textsubscript{2} and NO\textsubscript{x}) under a set of operational constraints that are unique to the small-scale application. In residential homes, commercial buildings, and light industrial facilities, the availability of space is limited and there may be no trained, on-site technicians. In this environment, any piece of installed equipment must be safe, reliable, quiet, small, easy to access and maintain, and should produce no waste by-products that cannot be handled by local waste handling systems.

In addition to satisfying these operational requirements, the emission control systems must clean the flue gas down to emission levels that are comparable to those produced by existing (fuel-oil) combustors. Reduction or elimination of respirable particulates, odors, and acid mists will be critical because the stacks of these combustors will be low and located in densely populated areas. The deposition of acid-coated particulates will be particularly noticeable in residential areas because these acid smuts eat away the paint on cars and houses.

For high reliability, safety, compactness and cost effectiveness, the emission control system should have few moving parts, involve a minimum of extra flows or treatment process, have high area to volume ratios and produce no additional waste products. It would be desirable to have particulate matter, SO\textsubscript{2} and NO\textsubscript{x} controlled by one device that could be easily serviced on a monthly, quarterly or seasonal basis.

These requirements make dry, regenerative clean-up processes particularly attractive. This report describes a new concept for integrated pollutant control: a cross-flow filter comprised of layered, gas permeable membranes that act as a particulate filter, an SO\textsubscript{2} sorbent, and a NO\textsubscript{x} reduction catalyst.

1.2 Description of Single-Unit, Three Pollutant Control Device

The device described in this section will simultaneously remove particulates, SO\textsubscript{2} and NO\textsubscript{x} from the combustion gases of coal combustors. The device is configured as a cross-flow filter, as shown in Figure 1.\textsuperscript{1} The gas flows from the inlet passages to orthogonally oriented discharge channels via thin, multilayered porous walls. As shown in Figure 1, flue gas enters from both the front and back of the device. With the left wall of the filter sealed, gas discharges from the right side of the device. The key to combined physical (fly ash) and chemical (SO\textsubscript{2}/NO\textsubscript{x}) cleaning is to utilize chemically active sorbent-catalysts (e.g., metal oxides) in the layered walls of the filter. A cross-flow filter wall with layered construction is shown in Figure 2. (This concept is currently under evaluation at MIT; a patent application has been filed.)\textsuperscript{2} This arrangement avoids use of pellet beds that plug in the presence of soot and fly ash and require larger reactor volumes because of low surface/volume ratios.
Figure 1. Schematic of a Ceramic Cross-Flow Filter-Sorbent Catalyst
Figure 2. Close-Up of Filter-Sorbent-Catalyst Wall and Gas Flow Scheme
The top (tight-pore) layer serves as a barrier filter blocking passage of fly ash particles. As the gas flows through the porous walls, particulate impurities are trapped on the walls of the inlet passage. The second layer of the porous walls carry at least one active sorbent-catalyst material to absorb SO\textsubscript{2} into the porous wall. Once the metal oxide is bound with sulfur-oxides (e.g., CuSO\textsubscript{4}), it becomes a catalyst for NO\textsubscript{x} reduction. Thus, with the addition of NH\textsubscript{3} into the flue gas stream, the sorbent layer could also serve as a NO\textsubscript{x} reduction catalyst. However, in order to effect NO\textsubscript{x} reduction throughout the absorption time, a second metal oxide serving as a selective NO\textsubscript{x} reduction catalyst, e.g., CeO\textsubscript{2}, will be added in the (second) sorbent layer. If it becomes necessary, a third layer, containing (and protecting) the deNO\textsubscript{x} catalyst phase can be provided.

This configuration offers a compact filter (10 times higher surface-to-volume ratio than a typical baghouse), a low-attrition sorbent-catalyst (no moving or fluidized solid bed), low pressure drop (through a few mm-thick macroporous membrane), and a very simple flow scheme.

We estimate that better than 90% removal efficiency of SO\textsubscript{2} and NO\textsubscript{x} is achievable with the use of mixed metal oxides (CuO, CeO\textsubscript{2}, or Fe\textsubscript{3}O\textsubscript{4}) in the device. Also, high sulfur capacity is possible by increasing the metal oxide content of the active SO\textsubscript{2} sorbent phase. Aluminum oxide, Al\textsubscript{2}O\textsubscript{3}, is planned to be used as a dispersant and/or catalyst support in the active sorbent-catalyst layer(s). The composite is expected to keep its bifunctional characteristics throughout its operation and not deactivate or lose its structural integrity in the presence of fly ash and trace metals.

Fly ash particles trapped by the cross flow structure can be periodically removed by a back-flushing procedure. Pulse-jet backflushing is a well established technique for high pressure applications of the cross-flow filter. This technique may have to be modified for small-scale applications. Modifications may include frequency of backflush, duration and pressure of each pulse, and pressure source for the pulsation. The modifications may be necessary to make the system as simple as possible for small-scale use. The active composition for SO\textsubscript{2} absorption can be renewed by a regeneration procedure that produces either elemental sulfur or concentrated gaseous sulfur species which can be converted to elemental sulfur by well established processes.

The single unit, particle filter, SO\textsubscript{2} sorbent, NO\textsubscript{x} reduction catalyst is an ideal device for small-scale applications. It is modular in configuration, compact, without any moving parts, quiet, producing no toxic materials or new solid wastes to be disposed of and requiring little auxiliary power.

1.3 Research and Development Activity

In October 1989, the team of Arthur D. Little, Massachusetts Institute of Technology, and GTE began a three-year, USDOE/PETC (Pittsburgh Energy Technology Center) funded program to research and develop the filter-sorbent-catalyst. The research priorities of this effort are listed below:

- Sorbent-catalyst material development
- Which metal oxide materials provide best combined performance for \( \text{SO}_2 \) removal, \( \text{NO}_x \) reduction, and sorbent regeneration?
- Under what regeneration conditions is the production of elemental sulfur maximized?

**Active Filter selection**
- What ceramic filter design (thickness, porosity, size, active-phase layering) leads to acceptable pressure drop, particulate matter capture, and structural integrity at expected operating conditions?
- What backflushing scheme is required?

**System design**
- How will these systems be incorporated into furnaces?
- What will be the device size, seals, cost, and operating constraints?

### 2.0 Task Description Summary

The objective of this program is to successfully carry out the experiment and design tasks described herein that will lead to the development a single-unit, cross flow filter-sorbent-catalyst. We plan to carry out this research and design work in two stages.

The first stage of the work will be fundamental in nature: we will investigate the \( \text{SO}_2 \) removal and \( \text{NO}_x \) reduction characteristics of different sorbent-catalyst compositions (in bulk, granular form), and we will conduct exploratory tests of cross-flow filters under conditions similar to those found in the combustion gases of small-scale combustors. After a year of these fundamental studies, we will conduct a preliminary evaluation of the component performance and will design two or three prototype configurations.

In the subsequent stage of the program, we will investigate the pollutant control characteristics of prototype filter-sorbent-catalyst devices. The \( \text{SO}_2 \) removal and \( \text{NO}_x \) reduction efficiency of a 'unit-element' prototype will be investigated. This 'unit element' will be a slot reactor comprised of two flat porous walls, or 'slabs' of filter-sorbent-catalyst material separated by a 0.5 centimeter gap. The particulate collection efficiency and back-flushing requirements of a multi-element version of this device will be tested.

Concurrent with these efforts will be the investigation of a sorbent regeneration scheme that has the potential to produce elemental sulfur in a one step process. Final evaluation of component performance and the design of these emissions control devices for residential, commercial, and small industrial applications will be conducted at the conclusion of the project.

Table 1 summarizes the tasks to be performed in this program. A milestone chart is shown in Table 2. A complete description of each task can be found in March Technical Progress report (First Quarterly Report).³

Arthur D Little
Table 1. Summary of Tasks

<table>
<thead>
<tr>
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</tr>
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<td>Particulate Tests</td>
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3.0 Objectives for Fourth Quarter Activity

The objectives for the July-September 1990 period were to:

1. Screen mixed metal-oxide sorbent-catalysts for their NOₓ reduction efficiency.

2. Investigate the effect of sulfation reaction temperature on SO₂ capture efficiency for promising sorbent-catalysts.

4.0 Approach

4.1 NOₓ Reduction Test Approach

The microreactor test facility used for NOₓ screening is the same as that used for SO₂ removal screening.

The reactor consists of a quartz tube of 1.5 cm I.D., vertically mounted inside an electric furnace equipped with a temperature controller. The sorbent-catalyst granules are supported on a fritted quartz disc in the middle in the reactor tube. A K-type thermocouple moving inside a quartz thermowell (0.3 cm I.D.) concentric to the reactor is used to monitor the axial bed temperature. The reactor pressure is slightly above atmospheric. Premixed gas streams of typical flue gas compositions flow through the reactor in the upward (sulfation-NOₓ reduction) or downward (regeneration) direction. The reactor system is shown schematically in Figure 3.

A chemiluminescent NOₓ analyzer is used to monitor the composition change of the flue-gas flow passing through the reactor tube packed with sorbent powders. The feed gas contains 600 ppm NOₓ, 600 ppm NH₃, 3% O₂ and N₂ balance. The gas flow rate corresponds to a space velocity of 2,000 hr⁻¹. With the present chemiluminescent NOₓ analysis,

Arthur D. Little
Table 2
Program Schedule and Milestone Plan

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</tr>
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<tr>
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<td>2</td>
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<td>Lab Shakedown</td>
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</tr>
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<td></td>
<td>Sorbent Preparation and Characterization</td>
<td>2.1 2.1</td>
</tr>
<tr>
<td>2.2</td>
<td>SO2, NOx, Test</td>
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</tr>
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<td>Screening Tests</td>
<td>2.2 2.2</td>
</tr>
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<td>2.2 2.2</td>
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<tr>
<td>2.3</td>
<td>Particulate Test</td>
<td>2.4 2.4</td>
</tr>
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<td>Regeneration Studies</td>
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<tr>
<td>3</td>
<td>Unit Element Prototype Tests</td>
<td>3.1 3.1</td>
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<td>Management and Reports</td>
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Milestones

- **Test Plan Complete**
- **Topical Report Particulate/ SO2/ NOx Control**
- **Revised Test Plan for Prototype Development**
- **Topical Report: Regeneration Studies**
- **Program Review/Tech. Feasibility/ Preliminary Design Guidelines**
- **Technical Feasibility Evaluation Complete**
- **Design Complete**
- **Draft Report**
- **Final Report**

Oct 89  Dec 89  Oct 90  Dec 90  Oct 91  Aug 92
Figure 3. Schematic of Packed-Bed Microreactor System
analyzer, the concentration of NO component and \((\text{NO}_x + \text{NH}_3)\) mixture can be determined precisely. However, no direct information about concentrations of other single nitrogen oxides (except NO) is available. The conversion of NO can be obtained by monitoring the NO concentration change in the flue gas flow passing through the reactor tube. In addition, selectivities and conversions of NO reduction by ammonia can be reconfirmed by monitoring the concentration change of the \((\text{NO}_x + \text{NH}_3)\) mixture.

4.2 Sorbent-Catalysts Used for NO\(_x\) Reduction Tests

NO\(_x\) reduction tests were performed on three sorbent-catalyst materials:

1. Cu-7Al-O;
2. Cu-Ce-O; and
3. CeO\(_2\).

The first two materials showed good to excellent performance in sulfur capture tests. Ceria was tested to establish baseline data and to determine whether the addition of small amounts of ceria to the Cu-Al-O sorbent (for improved NO\(_x\) reduction efficiency at 400°C) was warranted.

The mixed metal oxide sorbents tested in this program are prepared according to the well established amorphous-citrate technique. This involves rapid dehydration (under vacuum, at 70°C) of an aqueous solution containing the metal salts and citric acid in desired proportions, followed by pyrolysis and further calcination of the resulting amorphous solid foam at relatively low temperatures (500-650°C). Citric acid is added in a 1 to 1 mole ratio to the metal salts included in the solution. For most sorbents, the nitrate form of metal salts has been used. Homogeneous, highly dispersed mixed oxides or oxide solid solutions are formed. These materials can be made with larger average pore size than is generally the case in coprecipitated mixed oxides. This is an important feature in gas-solid reactions where a higher molecular volume product (e.g., sulfate) can cause pore mouth blocking. Also, for the application intended here, large pores are needed to allow free gas flow (low pressure drop).

The surface areas of the sorbent catalysts used for these DeNO\(_x\) tests are shown in Table 3.

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<tr>
<th>Sorbent-Catalyst</th>
<th>Surface Area (m(^2)/g)</th>
<th>Pore Volume (cc/g)</th>
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<td>Cu-7Al-O (B2)</td>
<td>373</td>
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<td>Cu-Ce-O (B2)</td>
<td>24</td>
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<td>CeO(_2) (B5)</td>
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5.0 Results

5.1 NO\textsubscript{x} Reduction on Fresh Sorbents

The \( \text{NO}_x \) reduction efficiency of the three fresh, bulk, mixed metal-oxide sorbents (Cu-7Al-O, Cu-Ce-O, and CeO\textsubscript{2}) is shown in Figure 4.

Both Cu-7Al-O and Cu-Ce-O showed high \( \text{NO}_x \) reduction efficiency (>90%) at 200°C. However, both sorbents showed a decrease in \( \text{NO}_x \) reduction efficiency with increasing temperature. At 400°C, the conversion of NO over the Cu-7Al-O catalyst decreased to 60%. Over Cu-Ce-O, the conversion of NO at 400°C was only 20%. The decrease in NO conversion with increasing temperature was due to ammonia oxidation on the sorbent-catalysts at higher temperature.

To test the effect of ammonia oxidation on overall NO conversion, we passed 600 ppm NH\textsubscript{3} - 3% O\textsubscript{2} - N\textsubscript{2} balance flue gas through the reactor tube packed with Cu-Ce-O. At 300°C, about 14% of the ammonia was converted to NO. Oxidation of ammonia increases with increasing reaction temperature. The conversion of ammonia to NO was 37% at 400°C and 55% at 473°C, respectively.

\( \text{NO}_x \) reduction on ceria (Ce-5) was 90% at 400°C. With ceria, \( \text{NO}_x \) reduction goes through a maximum of 95% at 380°C. Unfortunately, ceria alone is not an effective sulfur capture sorbent at these temperatures; at 400°C the sulfation conversion of CeO\textsubscript{2} was only 7% prior to SO\textsubscript{2} breakthrough. Good sulfur capture with this sorbent was achieved at 600°C. At this temperature, however, NO conversion is less than 60% due to ammonia oxidation.

5.2 NO\textsubscript{x} Reduction on Partially Sulfated Sorbents

Over the course of emission control system use, the sorbent-catalysts will become sulfated. We were interested in investigating the change in \( \text{NO}_x \) reduction performance that occurs as these sorbent catalysts become partially sulfated.

The effect of partial sorbent sulfation on the \( \text{NO}_x \) reduction efficiency of the three sorbents tested is shown in Figures 5, 6, and 7. For all three sorbent-catalysts, some degree of sulfation improved \( \text{NO}_x \) reduction efficiency at temperatures above 300°C.

The effect of partial sulfation on the deNO\textsubscript{x} activity of Cu-7Al-O is shown in Figure 5. For this material, sulfation of the sorbent-catalyst significantly improved \( \text{NO}_x \) reduction activity at higher temperatures (e.g., 400°C). Three degrees of sulfation are shown: fresh (0% sulfation) sulfated at 300°C (20% sulfation), and sulfated at 375°C (30% sulfation). At 20% sulfation of Cu-7Al-O, \( \text{NO}_x \) conversion was between 85 and 95% in this temperature regime. The \( \text{NO}_x \) conversion over the fresh sorbent catalyst, by comparison, decreased from 80% to 60% as temperatures increased from 300 to 400°C.

Similarly, sulfation of the Cu-Ce sorbent has a significant effect on its own catalytic properties for \( \text{NO}_x \) reduction. The results are shown in Figure 6. For this test, the Cu-Ce (B2) sorbent had been previously sulfated at 400°C for 32 minutes in 1500 ppm SO\textsubscript{2}-3% O\textsubscript{2}-N\textsubscript{2} balance flow (about 20 percent sulfation conversion of the sorbent). The
FIGURE 5

NO\textsubscript{x} REDUCTION ON Cu-7Al-O

SULFATED AT 375 °C

SULFATED AT 300 °C

FRESH

600 ppm NO
600 ppm NH\textsubscript{3}
3% O\textsubscript{2}
N\textsubscript{2} BALANCE
S.V.: 2000 h\textsuperscript{-1}

NO CONVERSION

REACTION TEMPERATURE (°C)
FIGURE 6

NOx REDUCTION ON Cu-Ce-O

600 ppm NO
600 ppm NH3
3% O2
BALANCE N2
S.V.: 2000 h⁻¹
FIGURE 7

NOx REDUCTION ON CeO2

CeO2 SULFATED AT 400°C

600 ppm NO
600 ppm NH3
3% O2
N2 BALANCE
S.V.: 2000 h⁻¹
active temperatures for selective NO\textsubscript{x} reduction by ammonia shifted to higher temperatures as compared to the activity of fresh (unsulfated) sorbent. The obtained NO\textsubscript{x} conversion was 84% at 300°C and 62% at 400°C, respectively. A comparison of the NO\textsubscript{x} reduction effectiveness of partially sulfated versus fresh sorbent shows that the sulfated sorbent has superior performance.

The same trend of improved NO\textsubscript{x} reduction performance on sulfated sorbent-catalysts held true for CeO\textsubscript{2}, as shown on Figure 7. For partially sulfated CeO\textsubscript{2} (7% conversion), the overall NO\textsubscript{x} reduction performance improved as compared to the fresh sorbent, but the temperature at which maximum NO\textsubscript{x} reduction occurred did not shift upward as much as with the other two sorbent-catalysts.

5.3 NO\textsubscript{x} Reduction Summary

The NO\textsubscript{x} reduction activity of three sorbent-catalyst materials was tested over a temperature range from 200 to 500°C. We were primarily interested in the sorbent-catalyst deNO\textsubscript{x} performance at 400°C because this appears to be a minimum temperature for acceptable sulfur capture with these sorbents: The tradeoff between sulfur capture and NO\textsubscript{x} reduction performance for these sorbent-catalysts is clear: sulfation improves with higher temperatures (e.g., 400-600°C) while NO\textsubscript{x} reduction improves at lower temperatures (e.g., 200-300°C).

Table 4 summarizes the deNO\textsubscript{x} performance of the three sorbent-catalysts tested, both in their fresh and partially-sulfated states. The data showed that at low temperature (i.e., 200°C), both Cu-7Al-O and Cu-Ce-O could catalyze the reduction of 90% of the NO\textsubscript{x} introduced to the system. At 400°C, CeO\textsubscript{2} and partially sulfated Cu-7Al-O and partially sulfated Cu-Ce-O could provide 90% NO\textsubscript{x} reduction, while the fresh materials could provide only 60% NO\textsubscript{x} reduction. We found no sorbent catalysts that could achieve 60%-90% NO\textsubscript{x} reduction at 600°C.

5.4 Effect of Sulfation at Lower Temperature on Sorbent-Catalyst Sulfation Performance

One objective of this quarter's activity was to investigate the effect of sulfation reaction temperature on the SO\textsubscript{2} capture efficiency of our most promising candidate sorbent-catalyst: Cu-7Al-O. We are interested in investigating SO\textsubscript{2} absorption at lower temperatures (300-350°C) because we found that catalytic activities for NO\textsubscript{x} reduction improved at lower temperatures (200-350°C).

We found, however, that a reaction temperature of 400°C may be the lowest acceptable temperature to obtain complete sulfation of Cu-Al sorbents. At 300 and 350°C, this sorbent showed a sulfation conversion of 0.2 and 0.3, respectively. (Sulfation conversion was measured as \(\frac{t}{t^*}\) at 150 ppm breakthrough, where \(t^*\) is the calculated time it would take for all the sorbent material in the test reactor to sulfate completely and \(t\) is the actual time for SO\textsubscript{2} emissions from the reactor to equal 10% of the incoming SO\textsubscript{2} concentration.) Nearly complete sulfation conversion was obtained at 400°C, as previously reported. At 400°C, NO\textsubscript{x} conversion over the Cu-7Al-O sorbent was 60%. The conclusion, therefore, is that there is no opportunity to operate this sorbent-catalyst at a temperature more conducive to high levels of NO\textsubscript{x} reduction.
<table>
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<tr>
<th>TEMPERATURE</th>
<th>60% REMOVAL</th>
<th>&gt; 90% REMOVAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>Cu-7Al Cu-Ce</td>
<td>Cu-7Al (23% SULFATED) Ce</td>
</tr>
<tr>
<td>400°C</td>
<td></td>
<td>Cu-7Al (20% SULFATED) Ce</td>
</tr>
<tr>
<td>600°C</td>
<td></td>
<td>NONE</td>
</tr>
</tbody>
</table>
Last month we also reported that ceria sorbent-catalysts were very effective NO\textsubscript{x} reduction catalysts at 400°C. We had found previously, however, that ceria was not an effective sulfur sorbent at this temperature. This month, we examined ceria sorbents prepared in two different ways to determine whether improved sulfur conversion (at 400°C) could be obtained with this sorbent. It appears that the ceria sorbents are effective sulfur sorbents at higher temperatures (600°C) only.

6.0 Plans for Next Quarter

6.1 System Evaluation and Design

We will conduct a preliminary system evaluation and design for residential, commercial, and light industrial applications.

6.2 Sorbent Studies

We will summarize experiments with binary and ternary sorbents to investigate the effect of sorbent and NO\textsubscript{x} reduction.

7.0 References


