

**DEMONSTRATION OF A NEW  
EMISSION CONTROL SYSTEM FOR STATIONARY  
DIESEL AND NAURAL GAS FIRED ENGINES**

**Final Report**

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California Air Resources Board**

**by  
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**NON-CONFIDENTIAL****ICAT FINAL REPORT EXECUTIVE SUMMARY**

**Date of Report:** March 31, 2004  
**Contract Number:** ICAT-00-3  
**Title:** **Demonstration of a New Emission Control System for Stationary Diesel and Natural Gas Engines**  
**Principal Investigator:** Brian W. Nelson, Ph.D.  
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**Project Description:**

Diesel engines are used extensively today as power sources for small- and medium-size applications. They will continue to be used extensively in the future because of their durability, low cost and high efficiency. The environmental benefits of using modern diesel engines for power generation include low carbon dioxide and hydrocarbon emissions. Unfortunately, diesel engines produce large amounts of nitrogen oxides (NOx) and particulate matter.

A new technology, Selective NOx Recirculation (SNR), was developed by Sorbent Technologies Corporation specifically for controlling diesel NOx emissions. It is the result of seven years of R&D. Originally, the technology was developed for controlling pollution from sources other than diesel engines. These applications were for larger installations, and ones that do not require constant, unmanned operation. The goal of this project was to improve and adapt the new technology to operate on stationary diesel engine exhaust gases.

This project successfully demonstrated SNR as an easily-retrofitable, cost-effective NOx-control technology for stationary heavy-duty diesel engines. The technology utilizes a special carbon-based sulfur-tolerant, high-capacity, NOx-selective sorbent material to adsorb the pollutants out of the exhaust gas stream, and then directs a concentrated NOx desorption stream to a NOx decomposition system that converts the pollutant into nitrogen and oxygen.

With SNR, the exhaust NOx is adsorbed at low-temperatures so the unit can be straightforwardly retrofitted at the very end of the diesel exhaust train. A catalytic particulate trap installed somewhere upstream of the NOx filter protects the adsorbent filter while significantly reducing the diesel particulate emissions. This simple, innovative scheme uses no consumables and little energy from outside. It can be applied generically to any new or retrofitted NOx-emission source and is capable of 80% NOx reductions.

The work in this project was performed by Sorbent Technologies Corporation, the technology developer, and The Pennsylvania State University's Energy Institute, as a subcontractor. Testing of the new technology was conducted at Sorbent Technologies' laboratory in Twinsburg, Ohio, at Pennsylvania State University's Diesel Combustion & Emission Laboratory, and at a field demonstration site at Hans Hilleby Farm in Woodland, California.

## Summary of Findings:

The objectives of the ICAT program were met. Based on data from experiments conducted during the project, a system for reducing the NO<sub>x</sub> emissions from diesel-fired and natural gas-fired engines by up to 80% has been designed. Specifically:

- The carbon-based NO<sub>x</sub> filtration material was shown to be capable of being made into monolithic cartridges for space-efficient utilization with high NO<sub>x</sub> removal efficiency, reasonable pressure drops, and reasonable structural strength.
- These NO<sub>x</sub> filter cartridges were shown to effectively adsorb NO<sub>x</sub> from actual diesel exhaust gases when the gas temperature is below about 130°F and desorb the NO<sub>x</sub> when the material temperature is elevated to above 230°F. This phenomenon occurs no matter which chemical form the NO<sub>x</sub> is in when it is adsorbed, NO or NO<sub>2</sub>.
- Components of the NO<sub>x</sub> filtration system were miniaturized to the extent that they can be packaged on a small skid for easy installation.
- Electric resistance (Joule) heating of the sorbent beds was found to be an effective method for directly heating the solid sorbent material when it is formed into a monolithic cartridge. The cartridges were found to effectively act as an electric resistor, converting electrical energy into heat energy. However, the cartridges with the chemical composition most effective in physical tests had a electrical resistance that was much lower than that of other cartridges. The potential for optimizing the electrical properties of the adsorbent cartridges should be examined further.
- Commercial ejector pumps were found to be effective at removing the NO<sub>x</sub> from the sorbent cartridges. Ejector pumps, which operate on the principle of aspiration using a high-velocity stream of compressed air, were able to draw up to a -6.5 psi vacuum on the sorber chamber. Leakage of air through the valves that closed off the chamber was the limiting factor in the amount of vacuum that could be applied. However, the vacuum that was achieved was found to be sufficient to regenerate the sorbent cartridges.
- Consistently greater than 80% NO<sub>x</sub> decomposition could be achieved under certain conditions. However, the decomposition process may need to be optimized in each individual application.

## Conclusions:

The SNR technology was successfully demonstrated as an integrated system at a commercial scale for stationary diesel engines. Up to 80% NO<sub>x</sub> removal and decomposition and 95% particulate removal was achieved. The next step in commercializing the technology is to build several prototype systems and run them in different applications for certification and commercial demonstration.

**Publications:** No publications have yet been made, owing to the potential patentability of the discoveries made during the project.

**Commercialization Keywords:** smog; ozone; NO<sub>x</sub>; particulate emissions, diesel engines; stationary sources

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## I. BACKGROUND

Diesel engines and natural gas-fired internal combustion (IC) engines are used extensively today for generating power in numerous applications. They will continue to be used extensively in the future because of their durability, cost, and efficiency advantages.

Diesel engines are often classed into one of two categories, mobile diesel units and stationary diesel units. Although diesel engines come in a wide range of sizes, stationary units tend to be significantly larger in size than mobile units. Generally:

- Large, medium, and small stationary diesel engines often employed to produce distributed electrical power, both in base and stand-by modes.
- Large stationary diesel engines are commonly used to drill for and to pump petroleum and natural gas through pipelines and to supply rotary power at industrial plants.
- Smaller mobile diesel engines power trucks, buses, automobiles, and off-the-road vehicles, such as construction equipment, aerospace ground equipment, and forklifts, and larger units can power ships and tankers.

Internal combustion (IC) engines can also be fueled by natural gas, instead of diesel fuel or gasoline. Natural-gas internal combustion engines also come in a variety of sizes. Small engines tend to be run fuel-rich and, as such, their emissions can be controlled adequately with two-stage catalytic converters. Large engines, however, are generally operated as fuel-lean units, and they present the same control problems relating to NO<sub>x</sub> emissions, as diesel engines.

While significant attention is being given today to reducing pollutants from mobile vehicles with diesel engines, much less attention is being given to stationary diesel engines. However, in most cases, they are significant polluters. With over 1,500 large, stationary diesel engines in continuous service in California alone and more than 10,000 in intermittent operation, this is an air pollution control problem that needs to be solved.

The current project was designed to demonstrate a new technology that can reduce the amount of exhaust pollution from these sources. Although already proven in two specialized applications, jet engine test cells (JETCs) and aerospace ground equipment (AGE), the technology has not yet been proven in larger-use applications, as with stationary diesels and natural-gas-fired engines. To assure the greatest possibility of success, a two-step demonstration effort was conducted: a pilot-scale program to develop the system components and then a first commercial-scale prototype trial on an actual diesel-fired engine in the field.

The opportunity presented by this project for a completely novel, inexpensive, robust, sulfur-tolerant NO<sub>x</sub> and particulate control technology for diesel engines that does not require tight integration with the engine. Placed, literally, at the end-of-the-pipe and with very high NO<sub>x</sub> capacity, it can sit there passively, adsorbing the transient operation and highly-varying emissions of the engine.

Called "Selective NOx Recirculation" or "SNR," this new technology has four basic steps:

1. **PM Removal.** Particulate is filtered from the hot gas by a commercial diesel particulate filter (DPF).
2. **NOx Adsorption.** The gas is cooled and its NOx is physically adsorbed onto a special carbon-based sorbent material in the passive NOx trap.
3. **NOx Desorption.** After an extended period, when the trap becomes largely saturated, it is quickly desorbed into a concentrated NOx stream.
4. **NOx Destruction.** The desorbed NOx is sent back to the air intake of the engine, where much of it is "destroyed," converted to nitrogen and oxygen or water by the engine itself.

Such a process injects no consumables, such as urea or diesel fuel, but instead uses the equilibrium forces of the combustion itself to "destroy" the recirculated NOx. It can be implemented as a two-trap system, with one trap on-line when the other one desorbs, or in a one-trap architecture, where the exhaust bypasses the system while desorbing.

(Note that SNR is a very different process from exhaust gas recirculation, EGR, where from 5% to 25% of the total engine exhaust is continuously cooled and recirculated back to the engine. With EGR the NOx generation is reduced perhaps 10 to 25% (with a significant fuel penalty) because of a lowered oxygen content. With SNR, on the other hand, it is only the nearly-pure NOx-component of the exhaust that is recirculated to the engine, usually less than 0.1% of the total exhaust stream, or less than one one-hundredth that of EGR, and then it only recirculates periodically.)

Each of the four steps described above has been shown to work independently. So what kind of net NOx removal rate might be expected with such a passive lean NOx trap system in a 1-trap application? A per-cycle average NOx adsorption efficiency might be 90%. Arranged properly, 90% of this might be "destroyed." And the desorption/destruction step might take up about 5% of the duty cycle, allowing 5% of the exhaust to bypass. Together, such a system would reduce 77% of the NOx getting to it:

$$(100\% - 5\% \text{ NOx bypass}) * (90\% \text{ NOx adsorption}) * (90\% \text{ NOx destruction}) = 0.77.$$

This would be enough to allow a late model diesel engine that emits 1.0 g/bhp-hr without aftertreatment to meet the new California stationary-engine standards.

## II. PROJECT OBJECTIVES

This project's objective was to demonstrate for the first time the use of a new NO<sub>x</sub>-control technology for controlling emissions in stationary diesel-engine and natural gas-fired IC engine applications at a central California site.

The specific goals of the project were to:

- examine the fundamental chemical reaction dynamics of the material to optimize the systems,
- evaluate options for the design of system components,
- show the feasibility of the technology as an integrated process in a pilot-scale system, and
- design and demonstrate an initial prototype system for controlling NO<sub>x</sub> and particle emissions from a diesel engine operating in the field

### III. RESEARCH EFFORT

#### 1. Pilot-Scale System Design, Construction and Testing

##### A. NOx Sorber Design

The pilot-scale stationary diesel NOx filter was designed so that the exhaust stream to be cleansed of NOx passed horizontally through a vertical, rectangular bed of sorbent. See Figure 1 below. Exhaust gases before entering the filter bed first pass through a triangular open space in front of the bed. Gases are delivered to this space through a tuyere box that distributes the gases evenly across the bed face. Cleaned gases exit the system through a similar tuyere arrangement.

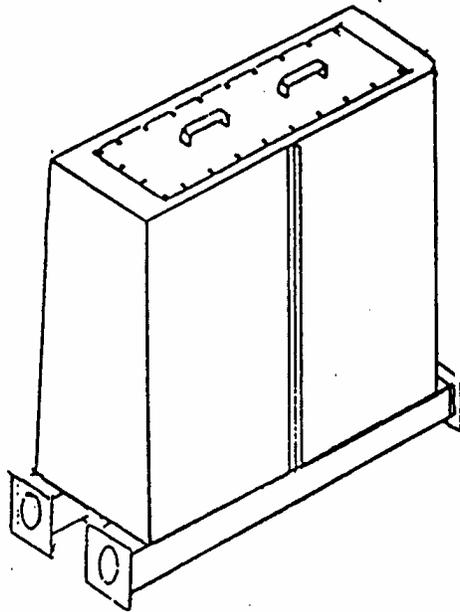


Figure 1 – Drawing of Filter Bed Chamber

Exhaust-gas flow rates of 100 to 400 ACFM were expected to be seen in standard diesel-engine tests to be performed at Penn State. To determine how pressure drop across the filter system and the distribution of gases across the filter-bed face are affected by gas flow rate within this gas-flow range, a series of tests were performed with a mock-up system. Velocity scans across the back of the filter bed were taken continuously during a typical test run, and average values at nine equally-spaced locations were recorded. Also monitored were the gas flows into and out from the tuyere boxes. Observations made during the runs included the following:

- (1) The pressure drop across the filter system increased with increased gas flow rate, as one would expect. Typically, the pressure drops with the tuyeres having 0.375-inch diameter holes were 3.5 inches W.G. at 120 ACFM and 9.6 inches W.G. at 210 ACFM. When the tuyere hole size was increased to 0.5-inch diameter, the pressure drops decreased significantly. It was 3.1 inches W.G. at 190 ACFM and 8.2 inches W.G. at 290 ACFM.
- (2) Over the gas-flow range studied, the 9-inch sorbent bed itself presented minimal pressure drop (less than 0.2 inches W.G.). The tuyere gas-distribution system appeared to present the largest portion of the overall pressure drop.

- (3) Although the tuyere arrangement in the filter system distributed gases evenly into the chamber in front of the filter bed when no filter bed was in place, the introduction of the bed resulted in a redistribution of gases across the bed.
- (4) How the exhaust gases were introduced to the filter system and were taken away from the system affected the distribution of gases across the bed, but did not affect the overall pressure drop across the system. Of the three gas introduction and removal schemes studied, introduction of gases simultaneously at both ends of the tuyere boxes and removing gases in a similar manner gave the best distribution of gases. Adding gases at one end and removing gases at the same end gave the poorest results. With this flow design, gases tended to short circuit through one end of the filter.
- (5) Introducing gas at one side of the tuyere box and removing gas solely at the opposite side provided decent distribution of gases except at the top of the bed nearest the entry site and at the bottom of the bed, in general. Distribution of gas was improved in increasing the tuyere hole size from 0.375-inch diameter to 0.5-inch diameter.
- (6) In nearly all cases, gases tended to flow through the bed in larger quantities in the upper and middle regions of the bed in preference to lower regions. The differences were less significant when the tuyere hole size was 0.50 inches in diameter.
- (7) Increasing the gas flow rate improves the distribution of gases across the filter bed face and results in a more even flow of gases through the filter. For gas flow rates above 350 ACFM, fairly uniform flows occur from the top to the bottom of the filter. The system pressure drop with tuyeres having 0.5-inch diameter holes for 350 ACFM was 9.6 inches W.G.

A photograph of one filter bed chamber, after fabrication and testing, is shown in Figure 2 below.



Figure 2 – Photograph of one of the Pilot-scale NO<sub>x</sub> Sorption Chambers (with the lid removed).

## B. NOx Sorption Bed Chemistry

Isotherm Tests - A series of isotherm tests were run on the sorbent material, to obtain parametric values for equipment design. These data were combined with data from a chemical kinetics study to determine the effects of operating temperature, exhaust gas flowrate, sorbent volume and gas composition on NOx removal rate and breakthrough time. In the isotherm tests, sorbent equilibrium saturations were determined at three temperatures within the design process range: 26°C, 42°C, and 55°C. The isotherm graphs that were determined for each of these temperatures are shown in Figure 3 on the next page.

According to conventional Freundlich isotherm physisorption models, the general equation for predicting the effects of temperature and concentration on sorbent saturation is:

$$X = A \cdot \text{Exp} \left( - \frac{E_a}{RT} \right) \cdot p^{(1/n)}$$

where:

- X = saturation concentration of pollutant on solid surface [g NOx/g C]
- A = pre-exponential factor [g NOx/g C·ppm NOx]
- E<sub>a</sub> = sorption Activation Energy [kcal/mole]
- R = Ideal gas constant = 1.987 cal/mole·K
- T = reactor temperature [K]
- p = concentration of pollutant in gas [ppm]
- n = reaction factor [unitless]

For the NOx sorbent, the equation parameters were found to be:

$$\begin{aligned} A &= 0.0004262 \text{ g NOx/g C} \cdot \text{ppm NOx} \\ E_a &= 2.31 \text{ kcal/mole} \\ n &= 2.90 \end{aligned}$$

A graph of the resulting equation as to sorbent loading and exit NOx concentration at various temperatures is also shown in Figure 3.

Kinetic Tests - A laboratory test system was fabricated to study the kinetics of the NOx sorption and desorption. The system was used to determine fundamental reaction parameters.

Two series of sorption kinetics tests were conducted in the laboratory. The goal of the first series was to determine the relationships between bed temperature, gas residence time in the sorbent bed, NO concentration, and NOx removal rates. The results from these tests were combined with results from the equilibrium tests for aid in the design of the prototype sorber. The data from the kinetics tests were analyzed and a graph of the results follows. Both residence time and gas temperature have a significant influence on the removal rate of NOx; the inlet concentration of NO turned out to be much less important.

The second set of kinetics tests examined two particular parameters. The first parameter was the effect of high humidity levels on the NO removal rate. Humidity was found to suppress the percentage of NO removed at lower temperatures (25-50°C) by about 5%. The second parameter examined was the

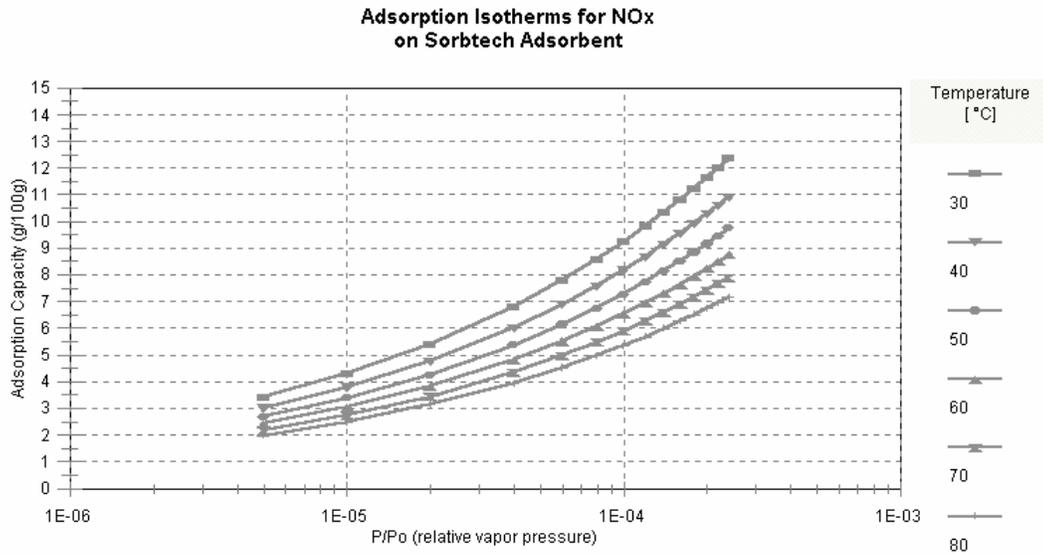


Figure 3 – Graph of Summary of the Results from the NO<sub>x</sub> Sorption Equilibrium Isotherm Tests

adsorption of NO<sub>2</sub> as opposed to adsorption of NO. As expected, NO<sub>2</sub> was found to adsorb more quickly and more effectively, with an increase in removal efficiency of 5-40%, depending on the conditions. The effectiveness of NO<sub>2</sub> desorption still needs to be investigated. A graph summarizing the data is given in Figure 4.

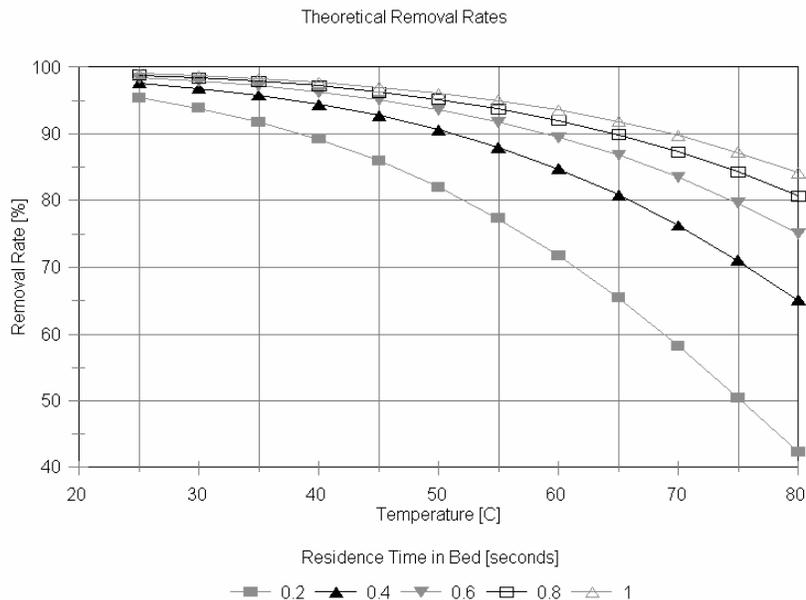


Figure 4 – Graph of the Curves Generated from the NO<sub>x</sub> Sorption Kinetic Tests for 25°C to 80°C. Note: for good NO<sub>x</sub> adsorption (>90%), the reactor temperature must be less than 50°C.

### C. Desorption Heating Strategies

Four methods of heating the saturated sorbent beds were identified. They include the use of:

- 1) microwave generators,
- 2) uncooled exhaust gases,
- 3) resistance-heating elements, and
- 4) internal-resistance joule heating.

Microwave Heating. A simple experiment was performed to evaluate the potential of microwave heating as a method to drive off moisture and NO<sub>x</sub> from saturated sorbent and to regenerate the sorbent for further use. The experiment consisted of placing a beaker with a 64.83g sample of carbon sorbent saturated with NO<sub>x</sub> into a conventional microwave oven. The sample was earlier saturated with NO<sub>x</sub> by exposing it to an actual diesel-engine exhaust gas. The power was then turned on.

At 15-second intervals, the NO<sub>x</sub> level above the bed and the temperature at the center of the bed were measured. Also measured was the weight of the sample. The data collected are provided in Table 1. After the heating cycle, the sample was effective in capturing NO<sub>x</sub> again.

The results of this experiment showed that microwave heating can be an effective approach for releasing moisture and NO<sub>x</sub>, and thereby for regenerating sorbent beds in place. Upon heating, moisture is released initially and then NO<sub>x</sub>. It should be noted, however, that tiny sparks occur during heating and heating does not appear to be uniform. Consequently, it is probable that microwave heating for sorbent-bed treatment of larger beds in a commercial system will not be feasible.

TABLE 1. MICROWAVE HEATING RESULTS

<u>Time (sec)</u>	<u>Sample Wt. (g)</u>	<u>Accumulated wt Loss (g)</u>	<u>Sample Temp (°C)</u>	<u>Comments</u>
Start	64.83	---	24.6	---
15	64.70	0.13	47.0	No NO <sub>x</sub>
25	64.34	0.49	73.5	No NO <sub>x</sub> , H <sub>2</sub> O Released
35	62.14	2.69	77.0	Faint VOC odor
45	60.70	4.13	78.0	---
60	59.26	5.57	84.6	H <sub>2</sub> O Released
75	58.09	6.74	89.0	---
90	56.76	8.07	96.0	---
105	55.62	9.21	96.2	Heavy H <sub>2</sub> O Release
120	55.36	9.47	96.4	1st NO <sub>x</sub> Detected
135	54.66	10.17	96.5	---
150	53.79	11.04	105.6	---
165	53.01	11.82	127.8	NO <sub>x</sub> Release Off-Scale

Uncooled Exhaust Gases. The use of uncooled exhaust gases for the heating the sorbent bed was also explored. A test apparatus was designed for heating a 0.5 L bed of saturated sorbent. The tests that were conducted highlighted the low thermal conductivity of the sorbent material and the difficulty in ensuring a uniform gas flow through the bed. The tests were inconclusive as to the feasibility of direct heating for regeneration, so a larger test unit, which was used to evaluate both exhaust gas heating and resistance heating, was designed. Data from a representative test on this system is shown in Figure 5 below.

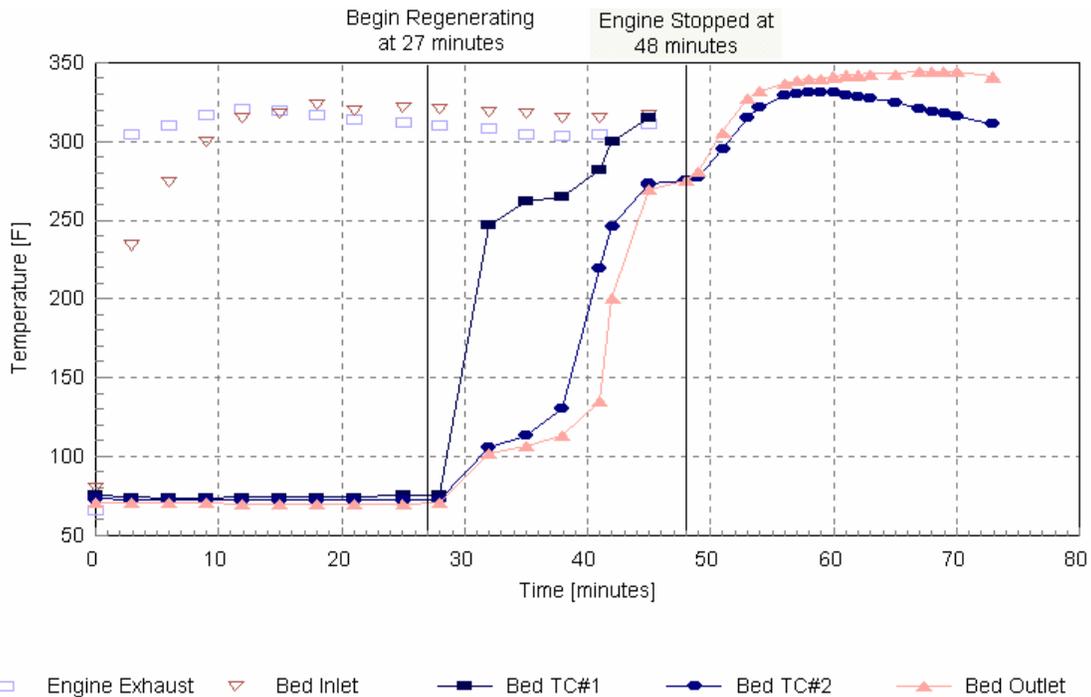
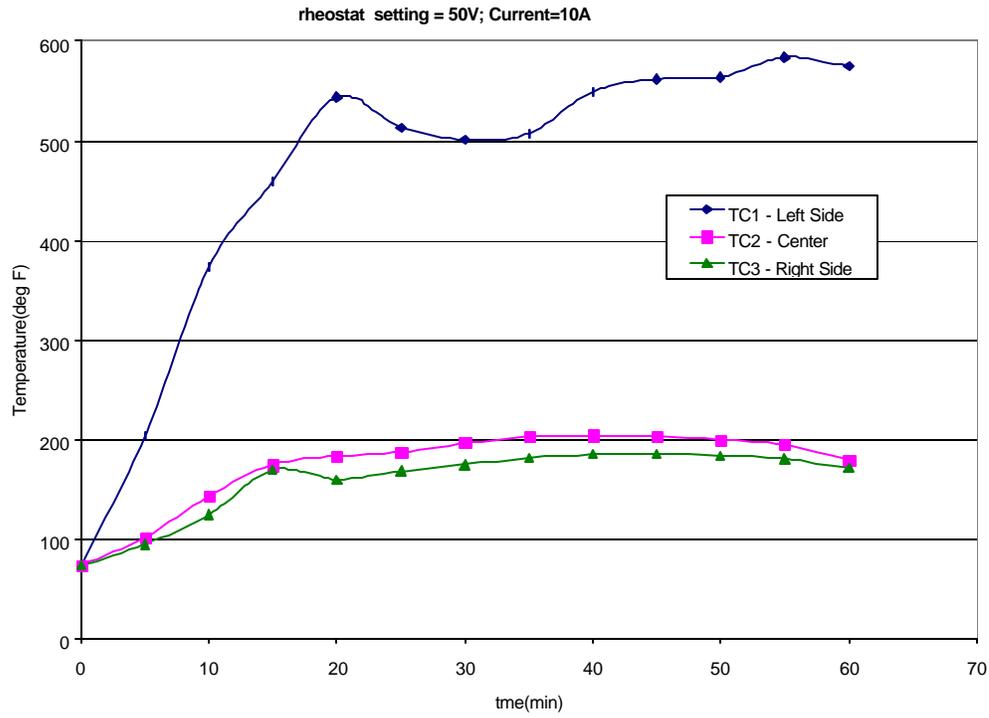


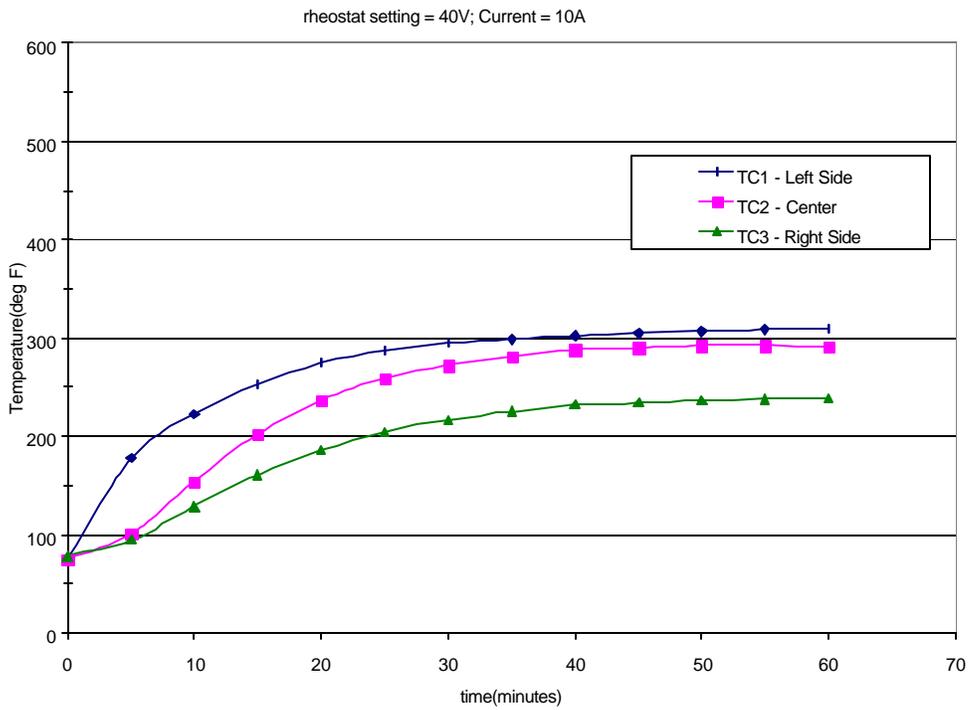
Figure 5 – Graphs of Test Results from Exhaust Gas Heating Test No. 2. Q = 320 scfm

Resistance Heating Elements – The use of embedded resistance heating elements was tested and found to be impractical due to the very low thermal conductivity of the granular activated carbon. All attempts to heat beds of carbon in this manner resulted in excessive “hot spots” developing around the heating elements.

Internal Resistance Joule Heating - Experiments were carried out to determine the effectiveness of internal electrical resistance (joule) heating for heating the sorbent bed to the desorption target temperature. Beds of loose sorbent were created in wood and plastic frames that were 18 inches long, 18 inches wide, and 4 inches thick. The carbon-based sorbent material was vibrated and compressed between metal plates to increase the contact area between particles. Electrodes were then attached to the top and bottom metal plates, and an electric current was applied. The test was repeated with a number of different levels of electric current and voltage. The temperature of the sorbent bed was recorded as a function of heating time. Figures 6 and 7 show plots of bed temperature at three points for voltage/ampere combinations that heated the beds in reasonable amounts of time.



Figures 6 – Graph of Test Results from Joule Heating Test No. 4, with Loose Sorbent.



Figures 7 – Graph of Test Results from Joule Heating Test No. 5, with Loose Sorbent

## Joule Heating of Carbon Monoliths

The NO<sub>x</sub> filter material is a special type of activated carbon, which is a modestly electrically-conductive material. By simply by running an electric current through the material, from one end of a cartridge to the other, the material acts as a natural resistor and converts some of the electrical energy into heat energy. This can be very energy efficient for heating the cartridge because there are no intermediate heat transfer steps and, if the cartridges are symmetrical and uniform in composition, the cartridge can heat up at a uniform rate. Also, this process does not involve any moving parts, does not put any mechanical stress on the cartridge, and utilizes a resource - electricity - that is readily available at a stationary diesel-engine site.

Sorbent Technologies has been working with KX Industries LP, the largest fabricator of monolith carbon cartridges for the filtration industry, on developing a monolithic version of its NO<sub>x</sub> carbon in a sorbent cartridge. During this program, KX Industries fabricated three sets of carbon cartridges for the company, using the Sorbent Technologies-NO<sub>x</sub> adsorption material as a base. These cartridges contained different binder materials and sorbent ground to different particle sizes. Individual cartridges from each batch were then tested in Sorbent Technologies' laboratory to determine temperature tolerance, physical strength, and the ability of the monoliths to be heated using joule heating.

A graph of the results is shown in Figure 8. It should be noted that the first set of cartridges (cylinder 1) had a much greater electric resistivity than the second set of cartridges (cylinder 2). For this reason the voltage across the cartridge was set to a larger value (55 VAC for cyl. 1 and 25 VAC for cyl. 2). This allowed for a greater amount of electrical energy to be inputted to the cartridge in a given time, while keeping the electrical current at a reasonable level.

Both sets of cartridges were successfully heated using electrical-resistance heating within a reasonable time frame. Although the first set of cartridges performed better electrically, it was decided that the second cartridge formula was preferred, based on its adsorption and pressure drop characteristics.

## Joule Heating of KX Carbon Filters In Test Stand

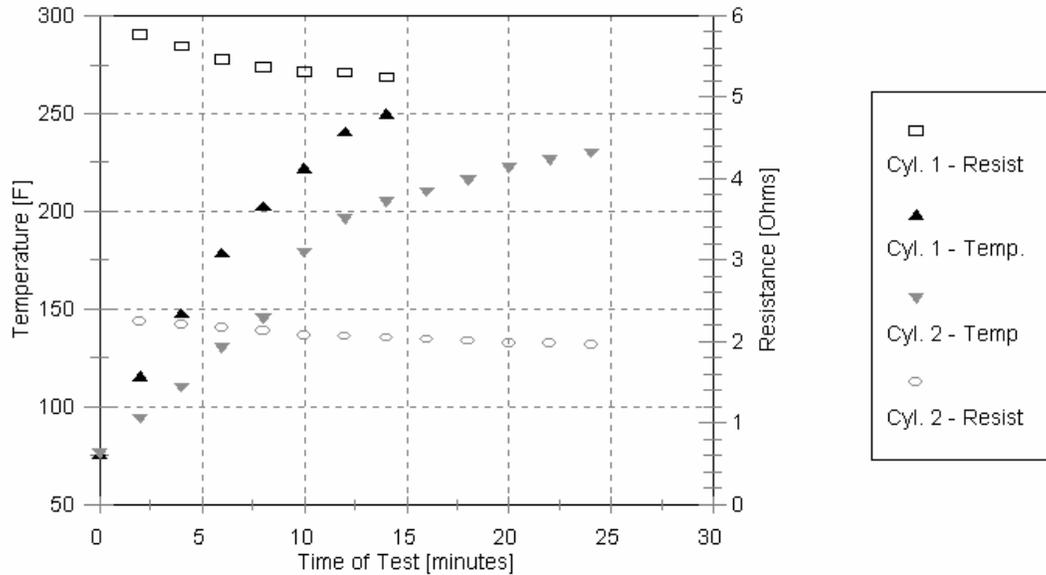


Figure 8. Graph of the Results from Heating the Cylindrical Carbon Cartridges Using Electrical Resistance

### Conclusions

Three of the four methods of sorbent bed heating were successful at raising the bed temperature enough to initiate regeneration. Using industrial heating elements was found to cause very dis-uniform heating due to the low thermal conductivity of the carbon material. Of the three methods that did work, the use of microwaves was found to cause some incidences of sparking and the forming of “hot spots” in the beds. The use of un-cooled exhaust gas provided for a uniform heat up, but some of the adsorbed NOx was released and lost in the heating gas. Finally, the internal electrical resistance heating seemed to produce a uniform temperature increase, as long as the electrical voltage was kept to a low level. It was decided to further test the un-cooled exhaust gas method in the pilot-scale system and the internal electrical resistance method in the prototype system, where monolithic sorbent cartridges were used.

Due to the low inherent resistivity of the cartridges, high voltages (above 200 VAC) have been required to produce the necessary energy flow. This could present a safety concern in a commercial application. Investigations into increasing the electrical resistance of the carbon monolith structures should be considered in any later work.

#### D. Ejector Pumps for Vacuum Desorption

A tiny, inexpensive ejector pump can be used to create the vacuum needed for NO<sub>x</sub> trap desorption. See a photograph of two such ejector pumps below. Either of these pumps, for example, is capable of quickly pulling a -21 in.Hg vacuum while consuming less than 4 scfm of compressed air. The capabilities of ejector pumps could keep bypassed NO<sub>x</sub> during the desorption/destruction step of single-trap systems very low, perhaps to 5% of the time off-line. And it should be noted that these pumps are specifically designed for generating vacuums while tolerating high in-leakage, as was the case with the high-temperature valves used in the Pilot-scale and Prototype systems.



Figure 9. Photograph of Aspirating Vacuum Pumps that Were Used in the Pilot-scale Test System

Two ejector pumps were purchased for each of these systems. They were sized to each handle the full design NO<sub>x</sub> recirculation flow, but were installed to run in parallel. This arrangement allowed for greater flexibility in operation to accommodate higher flows if necessary. During the testing, only one test run was carried out with both pumps operating.

## E. Investigation into the Effects of High NO<sub>2</sub> to NO Ratio

### Task Objectives

In diesel exhaust applications, a catalyzed diesel particulate filter (CDPF), such as a Johnson-Matthey CRT™ or Engelhard DPX™, is likely to be used as the particulate control device. With these devices, an average of 30% to 50% of the NO<sub>x</sub> exiting the CDPF is in the form of NO<sub>2</sub>. While the sorbent used in the passive lean NO<sub>x</sub> trap absorbs NO well, it was not clear that it would remove NO<sub>2</sub> or be as easy to strip off during trap regeneration. During this task, laboratory experiments were conducted and technical literature was reviewed to determine the differences in reactivity between NO and NO<sub>2</sub> in the SNR system.

### Results

Three sets of tests were conducted to examine the three chemical processes that the NO<sub>x</sub> undergo: adsorption onto the carbon, desorption from the carbon, and decomposition in the combustor. Graphs summarizing the results from the three sets of tests are discussed below. In addition, information was gathered from published literature on the proposed chemical pathways for NO and NO<sub>2</sub> adsorption and desorption onto activated carbon. This information does not seem to give a clear explanation of the recent laboratory results. Information about the theoretical behavior of NO<sub>x</sub> in combustion flames was also gathered and was analyzed to determine if more efficient decomposition can be achieved.

To evaluate the relative NO<sub>x</sub> adsorption, a series of fixed-bed adsorption runs were performed in the laboratory using granular adsorbent, at NO and NO<sub>2</sub> levels of 100 ppm and 500 ppm and at a variety of temperatures. The results from these tests are shown graphically in Figure 10.

NO<sub>2</sub> was adsorbed by the sorbent to an even greater degree than NO was. For example, 80% NO<sub>2</sub> removal was achieved at 60 minutes with adsorption temperatures up to 60°C. At this temperature only about 40% NO removal was achieved; it broke through much quicker. Between 100 ppm and 500 ppm, the concentration of the NO<sub>x</sub> in the inlet gas made little difference with either species.

To evaluate relative NO<sub>x</sub> desorption, two series of laboratory tests were then run. In each series of tests, a bed of adsorbent was cycled through sorption and then desorption, up to five times. In one series of tests the sorbent was exposed to NO-laden air (1000 ppm NO) and in the other the bed was exposed to NO<sub>2</sub>-laden air (1000 ppm NO<sub>2</sub>). Results from these tests are summarized in Figure 11.

In the NO tests, the bed absorbed 2.0 weight percent NO in the first cycle before the adsorption effectiveness fell below 85%. The bed then desorbed 90% of the adsorbed gas when subjected to 300 °C for 20 minutes. During subsequent cycles, the bed again absorbed approximately 2 weight percent NO and desorbed effectively all of it during regeneration. See Figure 2. In the NO<sub>2</sub> tests, the bed initially absorbed 3.8 weight percent NO<sub>2</sub> (molarly equivalent to 2.5 weight percent NO), but then only desorbed 65% (1.7 wt.%) of the gas. During subsequent cycles, the bed absorbed approximately 1.7 weight percent NO, and effectively desorbed all of it during regeneration. This is also shown in Figure 11.

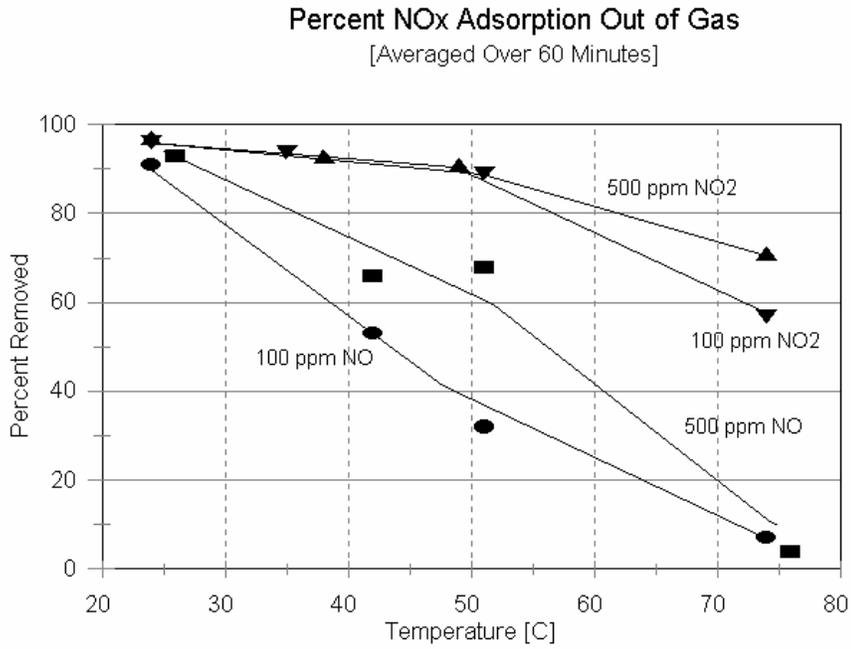


Figure 10. Comparison of NO and NO<sub>2</sub> Adsorption by the Carbon Cartridge

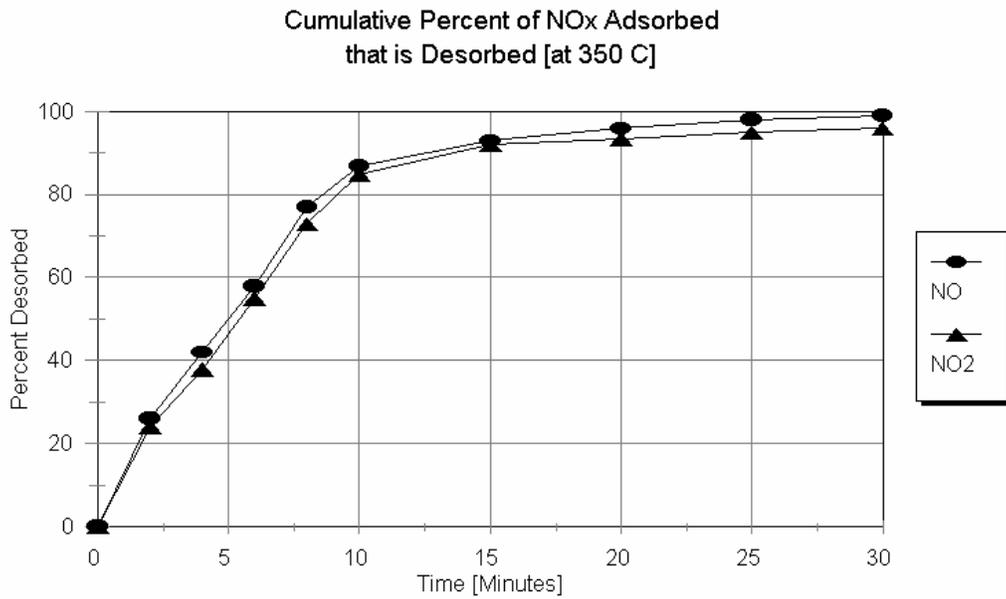


Figure 11. Comparison of NO and NO<sub>2</sub> Desorption by the Carbon Cartridge

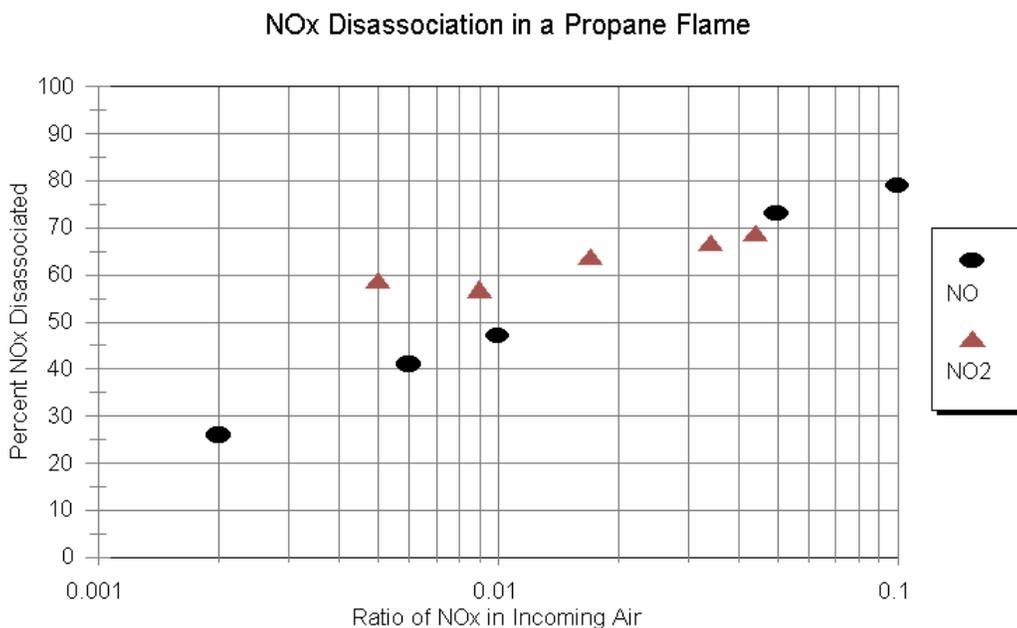


Figure 12. Comparison of NO and NO<sub>2</sub> Decomposition by a Propane Burner

To evaluate relative NOx decomposition, a series of full-scale experiments were performed in which various levels of NO and NO<sub>2</sub> in air were injected into a propane-fueled combustor. The results are shown in Figure 12.

As discovered earlier, the decomposition fraction for NO during combustion increases with increased NO concentration. The results for NO<sub>2</sub> appear to be similar, although decomposition below 1 mol% appears to be slightly higher. Overall, however, we did not find any statistically-significant difference between the two forms of NOx.

### Conclusions

NO<sub>2</sub> initially adsorbs even better than NO on the sorbent material and, after the first desorption cycle, adsorbs and desorbs essentially equivalently. NO and NO<sub>2</sub> both decompose to essentially the same extent during subsequent combustion. Consequently, the increased NO<sub>2</sub> output of a CDPF should not have any detrimental impact on the NOx adsorber for this technology. This is consistent with the gas-phase chemical reactions involved in NOx adsorption and decomposition. NO is thought to oxidize to NO<sub>2</sub> before it is adsorbed onto solid surfaces, and NO<sub>2</sub> is thought to reduce to NO for it decomposes into atomic N<sub>2</sub>.

## F. Pilot-Scale Diesel Engine Trials

### System Design

In this task, the various system components were designed, acquired, built, and individually pre-tested. Next, they were assembled into a full pilot-scale system and the system was tested on a commercial Cummins diesel engine installed on a fully-instrumented dynamometer test-stand at the Diesel Combustion and Emissions Laboratory (DCEL) at Penn State University.

The individual components of the pilot-scale system included:

- a Johnson-Mathey diesel particulate filter (DPF) attached to the engine
- a Gas-to-Gas Heat Exchanger for cooling the exhaust gas to adsorption temperatures
- a Demister Chamber to remove liquid water from the cooled gas
- two NO<sub>x</sub> Sorber Bed Chambers in Parallel [only one operating for sorption at any time]
- a By-Pass Line for allowing hot exhaust gas to enter the sorbers during bed regeneration
- a Vacuum Pump System for drawing off the recycle-gas with concentrated NO<sub>x</sub>, and
- a Recycle Line to return the NO<sub>x</sub> to the inlet to the engine for decomposition

A drawing showing the components of this system is shown in Figure 13 below. The system consisted of two parallel sorption streams, each capable of treating 400 scfm of gas, so that when one bed was saturated, the gas flow was diverted to the other bed while the first bed was regenerated. The sorbent beds consisted of loose granular sorbent material contained between two stainless steel screens.

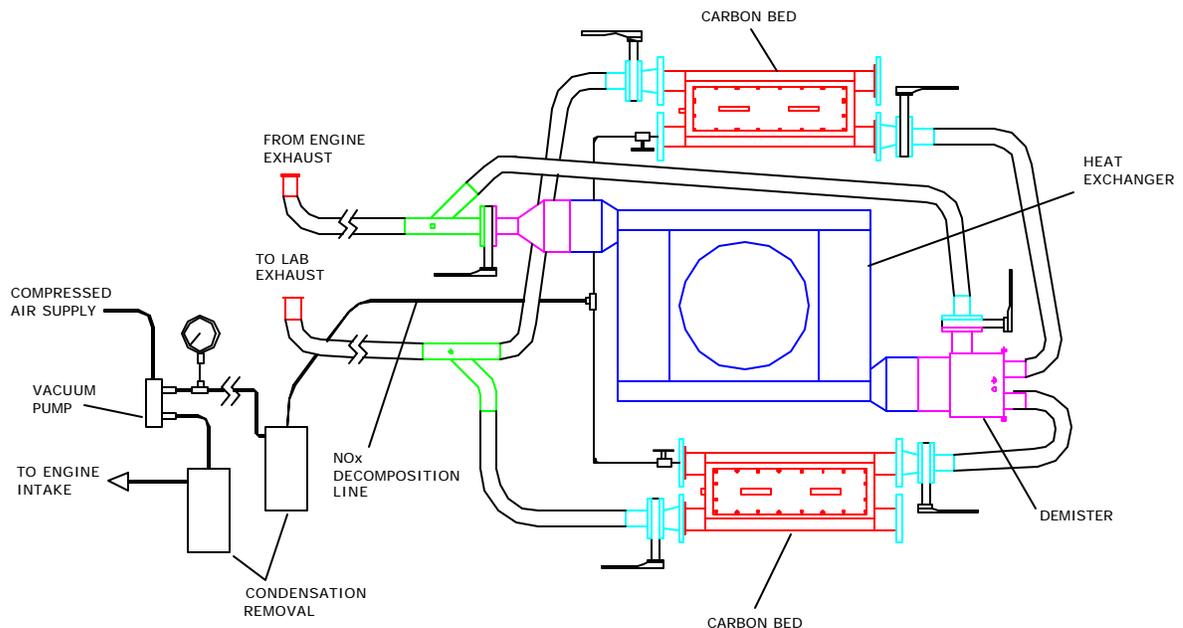


Figure 13. Diagram of Stationary Pilot-scale NO<sub>x</sub> Control System

During regeneration, the sorbent beds were heated using un-cooled, bypassed engine exhaust gas. This method of heat was effective if the engine was operating at a load level greater than about 30%. With this method, however, some of the adsorbed NO<sub>x</sub> was released into the exhaust gas stream during the heating-up phase, before the bed was fully up to regeneration temperature. This resulted in about a 20% NO<sub>x</sub> “slip” during a typical run. A photograph of the system during a test is shown in Figure 14.

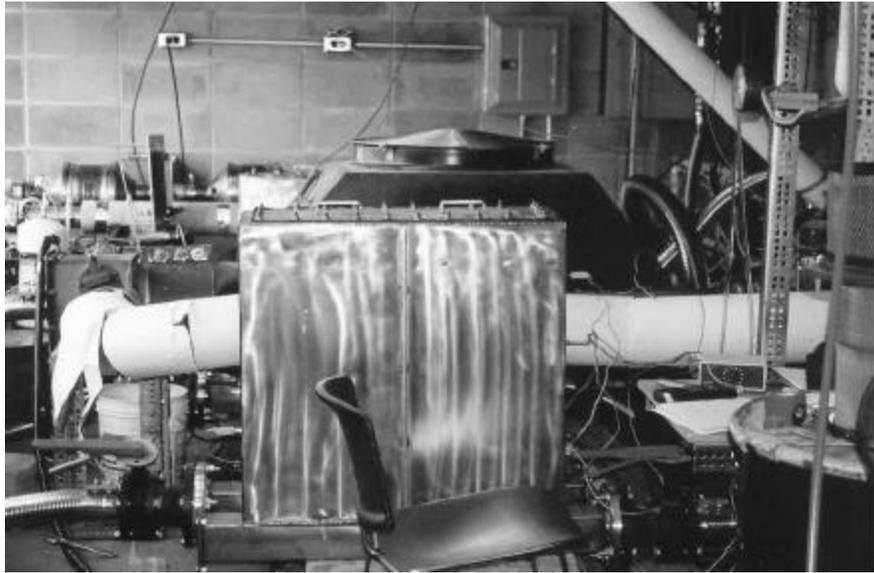


Figure 14. The Pilot-scale Test System Installed at the DCEL,  
During a Test Run

### System Testing

The sorbent beds were able to consistently adsorb between 1.5 – 2 % of their mass of NO<sub>x</sub> before requiring regeneration, defined as the marginal NO<sub>x</sub> removal efficiency falling below 80%. For a few tests, however, channels developed in the loose material, resulting in premature NO<sub>x</sub> breakthrough.

Graphs of representative test runs are shown in Figures 15 and 16 below. During Test B4 the engine was cycled through 5 run modes after idling, corresponding to 17%, 36%, 60%, 38%, and 70% of maximum power. The instantaneous NO<sub>x</sub> adsorption efficiency started at 95% and gradually decreases over 200 minutes to 80%. After the 200 minutes the NO<sub>x</sub> loading was approximately 3.5 lbs. of NO<sub>x</sub> per 100 lbs. of sorbent. At this point, the sorbent bed was taken off stream and regenerated. Once the bed was returned to service, the adsorption efficiency was again greater than 95%.

During Test B7 the engine was repeatedly cycled through a number of run modes, going from a 60% power level up to 100% power. Due to the increased temperature of the exhaust gas, the NO<sub>x</sub> adsorption efficiency was less than for the previous example. However, the average efficiency between regenerations was still greater than 85%. The other four long-term tests of this system showed similar results.

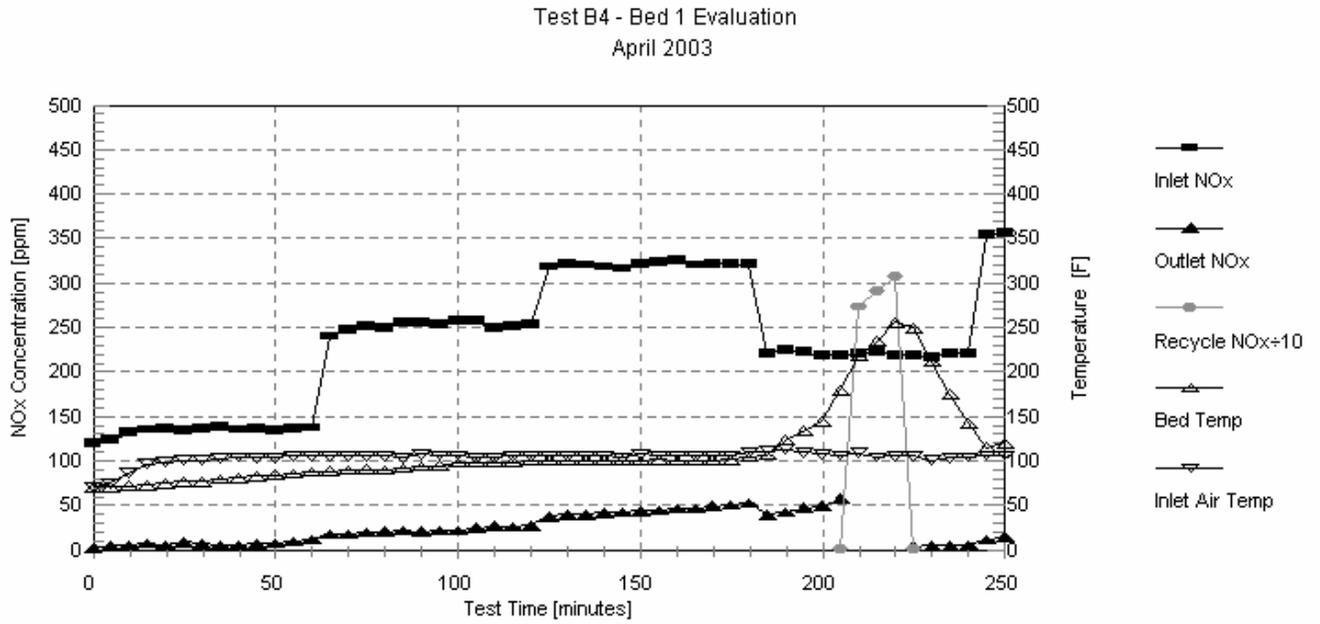


Figure 15. Representative Data from the Stationary Demonstration NOx Control System Test B4  
Bed regenerated between 200 minute and 250 minute marks.

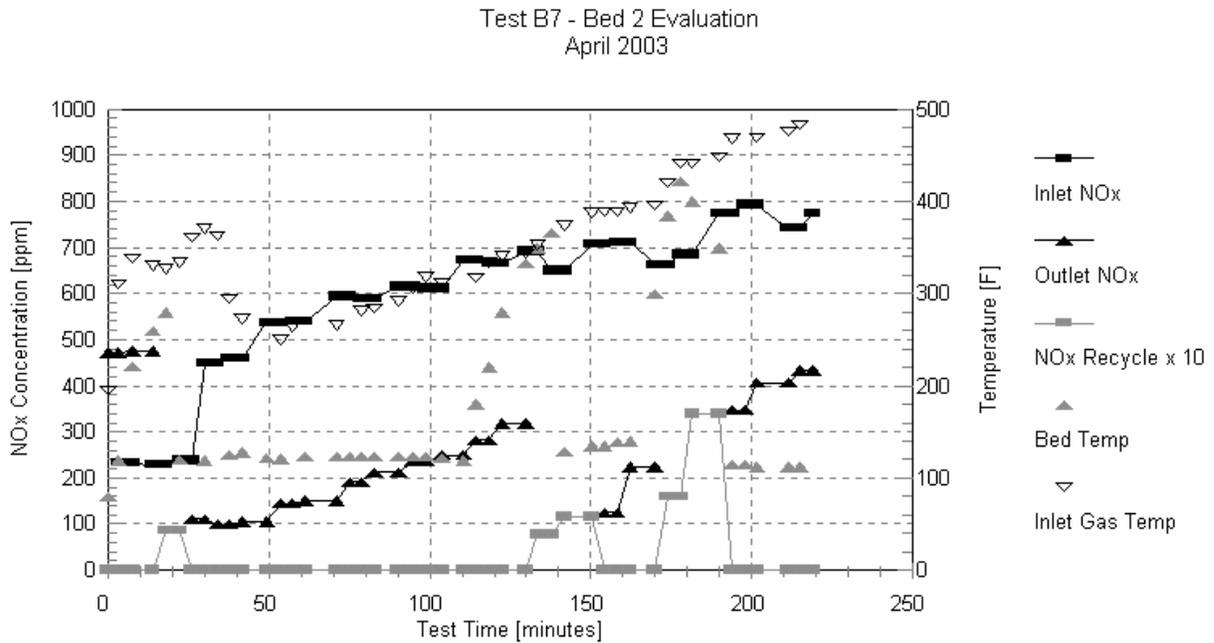


Figure 16. Representative Data from the Stationary Demonstration NOx Control System Test B7.  
The bed was regenerated between the 20 and 40 minute marks, between 130 and 150 minute marks, and between the 170 and 190 minute marks.

## Results

Overall, the pilot-scale system performed well and acceptably proved the viability of the overall concept. Consequently, the project moved ahead to the prototype system design. Results from these tests are summed up as follows:

- Mechanically, the system performed to specifications. However, valves used to isolate the beds during regeneration were found to leak more than was desired.
- NO<sub>x</sub> adsorption performance by the full-size beds paralleled performance found in the laboratory and small pilot-scale beds.
- During regeneration, the carbon beds heated up non-uniformly, with the temperatures at the front of the beds rising faster than at the rear.
- The Cummins engine decomposed the desorbed NO<sub>x</sub> more effectively than was anticipated (averaging 50% NO<sub>x</sub> decomposition compared to an expected 30% decomposition based on data from the laboratory engine tests).

## 2. Prototype Construction and Laboratory Testing

### A. NOx Destruction in Small Auxiliary Engines

In the early-to-mid 1990s, Sorbent Technologies Corporation in the U.S. and Daimler-Benz AG in Germany independently discovered that if nitrogen oxides (NOx) are added to the intake air of an internal combustion engine, the chemical equilibrium forces of NO formation in the combustion process can act to decompose a significant fraction of the added NOx.

This discovery was significant because it pointed to a revolutionary method of NOx-control for internal combustion engines, particularly for diesels, which have few good technology options.<sup>1</sup> If the regular NOx emissions from an engine could be separated from the exhaust stream and then returned to the air intake, the engine could act as its own NOx “destructor.” Daimler-Benz called the process “Selective NOx Recirculation,”<sup>2</sup> or “SNR” and has obtained three U.S. patents related to the concept.<sup>3,4</sup>

Daimler-Benz and a consortium of European researchers recently carried out a two-pronged research program to investigate and attempt to exploit the SNR concept. In the second prong of the research, they injected NOx into three different types of internal combustion (IC) engines and examined the actual NOx decomposition rates that could be achieved. In a gasoline engine, which initiates combustion by spark ignition (SI), they observed high NOx decomposition rates, generally from 70% to 80%. However, there are other, well-established NOx-control technologies that work well on gasoline engines, like three-way catalysts. With diesel-fueled engines, on the other hand, which initialize combustion by compression ignition (CI), the investigators observed only 10% to 50% NOx decomposition. Daimler-Benz' conclusions on the new Selective NOx Recirculation technique were:

"Summarising it can be concluded that the SNR technique is an appropriate aftertreatment device for NOx removal in the case of a diesel engine. ... [However, f]or this newly developed aftertreatment device, the characteristics of the adsorbent materials are very important. For example, the weakness of current [barium-based] materials against sulfur poisoning and thermal deactivation must be overcome."<sup>2</sup>

In this work, they discovered that in IC engines the NOx decomposition efficiency does not depend on whether the added NOx is in the form of NO or NO<sub>2</sub>. On diesel engines, they achieved NOx destructions of from about 10% to 40% with a naturally-aspirated indirect-injection engine (IDI) and from 20% to 50% with a turbocharged direct-injection engine (DI).

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- 1 Lloyd, A. and T. Cackette, “Diesel Engines Environmental Impact and Control,” *Critical Review, Jl. Air & Waste Management Assoc.*, 51:809 (2001).
  - 2 Krutzsch, B., G. Wenninger, M. Weibel, P. Stapf, A. Funk, D. Webster, E. Chaize, B. Kasemo, J. Martens, & A. Kiennemann., "Reduction of NOx in Lean Exhaust by Selective NOx-Recirculation (SNR Technique) Part I: System and Decomposition Process," SAE Paper 982592, Oct. 1998.
  - 3 Boegner, W., K. Haak, B. Krutzsch, & G. Wonninger, U.S. Patent No. 5,457,958, Method and Apparatus for Reducing Nitrogen Oxides in the Exhaust Gas of an Internal Combustion Engine, (1995).
  - 4 Krutzsch, B., A. Seibold, L. Walz, W. Boegner, M. Heinau, M. Hartweg, & B. Konrad, U.S. Patent No. 5,851,501, Process for Absorbing and Desorbing Nitrogen Oxides in Exhaust Gases, (1998).

Daimler-Benz noted a trend of increased NO<sub>x</sub> decomposition rate with increasing engine load in all three of the engine types tested. This, they hypothesized, could be due to higher combustion temperatures at the higher loads, enhancing the reaction rates. With gasoline engines there was also a weak trend towards higher decomposition rates with decreasing engine speeds, which allow longer residence-times for reaction in the cylinders.

For the gasoline engine they also noted a strong effect of the air/fuel ratio on NO<sub>x</sub> decomposition. Under rich to stoichiometric conditions, high decomposition rates of 60% to 90% were achieved, but under gasoline lean-burn conditions rates of only about 20% were obtained.

Daimler-Benz only examined the sensitivity of the NO<sub>x</sub> decomposition rate to “recirculated” NO<sub>x</sub> concentration into the engine over a range of from 1000 to 5000 ppm. They concluded:

“[For diesel engines, NO<sub>x</sub> c]onversion efficiency was found to be almost independent of the concentration of NO<sub>x</sub> in the intake air. This result was obtained for both engine types, IDI and DI. ... [For gasoline SI engines, t]he concentration of NO<sub>x</sub> in the intake air is also of minor influence.”<sup>2</sup>

### Combustion Chemistry

The European-Community-funded team also attempted to numerically model the combustion chemistry of the decomposition of added NO<sub>x</sub> in the gasoline engine case.<sup>2</sup>

In this work, various simplifying assumptions were made. The in-cylinder gas mixture was assumed to be homogeneous and quiescent, reducing the model to a zero-order homogeneous reactor. Thus the chemical effects were studied independently of any local flow-induced effects. Pure heptane was used as the representative gasoline component.

Thermodynamic properties and reaction rates were obtained from CHEMKIN libraries, using detailed reaction mechanisms for both fuel decomposition and NO reactions. Then by applying the consumption of energy and conservation of species mass, the resulting chemical specie levels were calculated as a function of the degrees of crank angle, with spark ignition occurring at 10 degrees of top dead center. The assumption of spatial homogeneity during an ideal combustion process cannot account for heat losses and so the peak temperatures and thermal NO concentrations were over-predicted. However, the model was still able to describe relative changes in the NO concentration caused by the NO added to the intake air.

During the ignition delay phase, the fuel decomposition process was initiated and smaller hydrocarbons and radicals were formed. Simultaneously, the 2000 ppm NO fed to the intake air was oxidized to NO<sub>2</sub> primarily through the reaction path of  $\text{NO} + \text{HNO}_2 \rightleftharpoons \text{NO}_2 + \text{OH}$ . This NO<sub>2</sub> was then completely decomposed when ignition occurred at 10 degrees and combustion-derived NO was formed.

In the base case, the total NO production was dominated by thermal NO<sub>x</sub> reactions, primarily  $\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$  and  $\text{N}_2 + \text{O} \rightleftharpoons \text{N} + \text{NO}$ . NO contributions from non-thermal reactions were small.

With the addition of 2000 ppm NO to the intake air, the net amount of NO formation from the thermal NO mechanisms was lower than that produced in the base case ( $\text{NO}_{\text{th}}$ ). Moreover, a more detailed analysis of the NO<sub>x</sub> reactions indicated that much of the added NO was reduced by non-thermal prompt-NO<sub>x</sub> pathways ( $\text{NO} + \text{NO}_2 - \text{NO}_{\text{th}}$ ). The major prompt-NO reduction reaction was  $\text{HCCO} + \text{NO} \rightleftharpoons \text{HCNO} + \text{CO}$ . The net effect was the decomposition of about 90% of the inlet NO through both interrelated NO pathways. This indicates that the NO<sub>x</sub> level in the outlet from a reciprocating engine will

be determined by the physical conditions in the cylinder – temperature, pressure, residence time, -- much more than by the inlet NO<sub>x</sub> concentration.

### Task Objectives

In this task, Sorbent Technologies' researchers examined and quantified the effectiveness of using internal combustion engines to convert NO<sub>x</sub> introduced into the inlet stream into nitrogen and oxygen. Five different engine types were examined:

- 1) diesel fuel-powered compression-ignition (CI) engine
- 2) methane (natural gas)-fueled spark-ignition (SI) engine
- 3) gasoline-fueled spark-ignition (SI) engine
- 4) propane-fueled spark-ignition (SI) engine, and
- 5) diesel fuel powered spark-ignition (SI) engine

### Task Activities

The compression-ignition engine used for these tests was manufactured by Yanmar and was set up on a dynamometer test stand at the Diesel Combustion and Emissions Laboratory at the Pennsylvania State University. The intake manifold and exhaust line were modified to accommodate NO<sub>x</sub> injection and gas sampling. This engine model is shown in Figure 18.

The natural-gas fired engine used for this Task was a 21-h.p. Caterpillar engine mounted with a backup electric generator for semi-continuous operation. The unit was rented for the test program and connected to a variable electric power load for testing. A picture of the unit prior to running a test is shown in Figure 19.

A 6-h.p. multi-fuel engine/generator was utilized to examine the performance of both propane-fired spark-ignition combustion and gasoline-fired SI combustion in decomposing NO<sub>x</sub>. The generator set was installed in the test facilities at Sorbent Technologies' laboratory and was also connected to a variable electrical load for testing. This unit is shown in Figure 20 below.



Figure 18. Diesel Fuel-Fired Compression-Ignition Engine Used in NO<sub>x</sub> Decomposition Tests



Figure 19. 21-h.p. 2-Cylinder Natural Gas-Fired Spark-Ignition Generator Engine Used in NO<sub>x</sub> Decomposition Tests

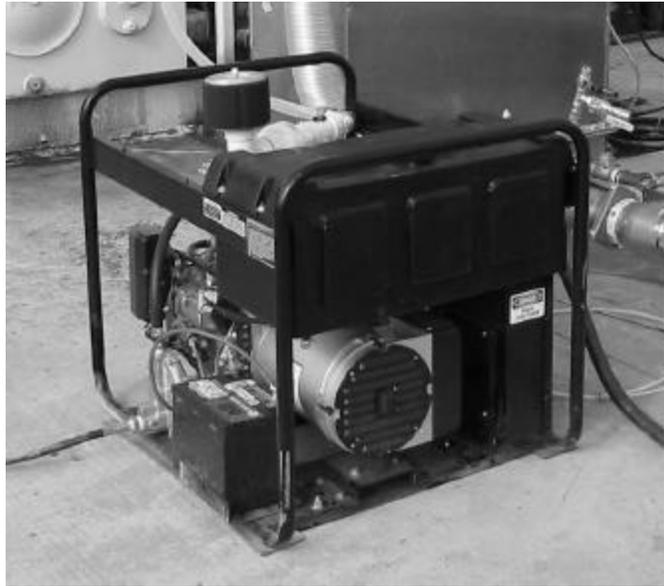


Figure 20. 6-h.p. Propane and Gasoline-Fired Spark-Ignition Generator Engine Used in NO<sub>x</sub> Decomposition Tests

The last engine tested was a prototype designed for U.S. military applications. This experimental engine operates on diesel fuel, but uses spark ignition. Diesel fuel is less dangerous than gasoline to transport and store and the military wishes that in future military operations it can use only diesel fuel in combat areas. Engines with spark ignition weigh roughly half of comparable compression-ignition

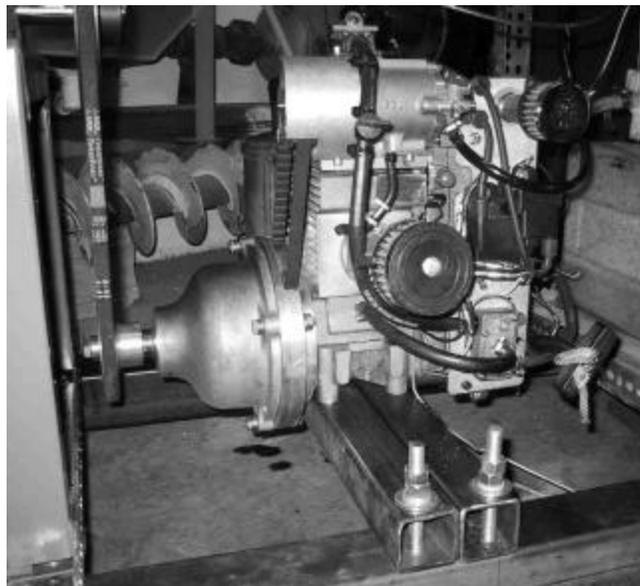


Figure 21. Prototype 2SI 2-Stroke Diesel Fuel-Fired Spark-Ignition Engine Used in NO<sub>x</sub> Decomposition Tests

engines and so are preferred for mobile combat situations. This prototype engine combines both advantages. For this technology, though, the advantage will be that this type of engine uses the fuel that is already available on the truck in a combustion mechanism that decomposes NO<sub>x</sub> more readily. A photograph of this engine is shown in Figure 21.

The researchers obtained engines of the types listed above, and quantities of the various fuels. Then, after instrumenting and characterizing the engines, each one was run through a series of tests to determine the percentage of NO<sub>x</sub> that could be decomposed at different inlet concentrations and different engine operating conditions.

## Results

All of the engines exhibited some degree of NO<sub>x</sub> decomposition. The compression ignition engine showed a marked increase in conversion rate with increase in inlet NO<sub>x</sub> concentration. With the spark ignition engines, this phenomenon was not apparent. Results from the five test series are shown in Figures 22 through 25, with the decomposition efficiency (fraction of NO<sub>x</sub> converted to N<sub>2</sub> and O<sub>2</sub>) graphed as a function of the NO<sub>x</sub> concentration (1=100%=1,000,000ppm) in the combustion inlet air.

The compression-ignition engine (Figure 22) showed a strong positive exponential correlation between NO<sub>x</sub> decomposition and inlet NO<sub>x</sub> concentration, as Sorbent Technologies has found in the past. The highest decomposition rates came close to 100% and occurred at the highest NO<sub>x</sub> concentrations test of 5% by volume. Load rate seemed to have only a minor effect on performance.

The natural gas-fired spark-ignition tests and the propane-fired spark-ignition tests showed no correlation between inlet NO<sub>x</sub> concentration and NO<sub>x</sub> decomposition efficiency. Figure 23 shows the results from the natural-gas tests and Figure 24 shows the results from the propane tests. The natural gas-fired tests also indicated that there was no effect of load level on the decomposition efficiency, although the propane-fired tests showed a strong influence of inlet oxygen content on the NO<sub>x</sub> decomposition efficiency.

The NO<sub>x</sub> decomposition in both of the liquid fuel-fired spark-ignition engines showed small, but definite, correlations with inlet NO<sub>x</sub> concentration. They also showed an effect of inlet oxygen content on engine NO<sub>x</sub> decomposition. Figure 25 summarizes the results from the gasoline-fired spark-ignition tests and Figure 26 summarizes the results from the diesel fuel-fired tests.

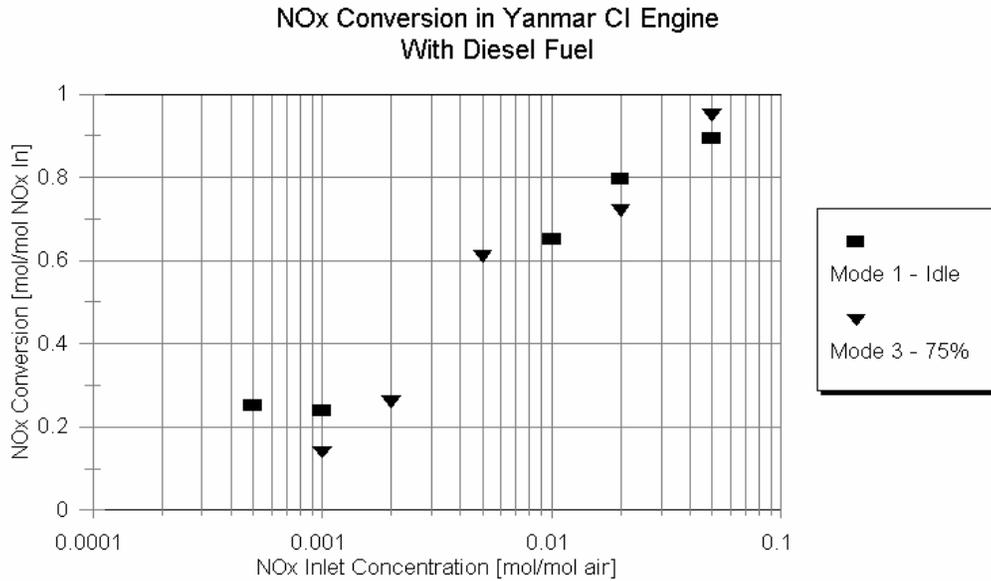


Figure 22. Graph of NO Conversion to N<sub>2</sub> in 4-h.p. Compression-Ignition Engine Using Standard Diesel Fuel – Showing a distinct relationship between inlet NO<sub>x</sub> concentration and conversion efficiency.

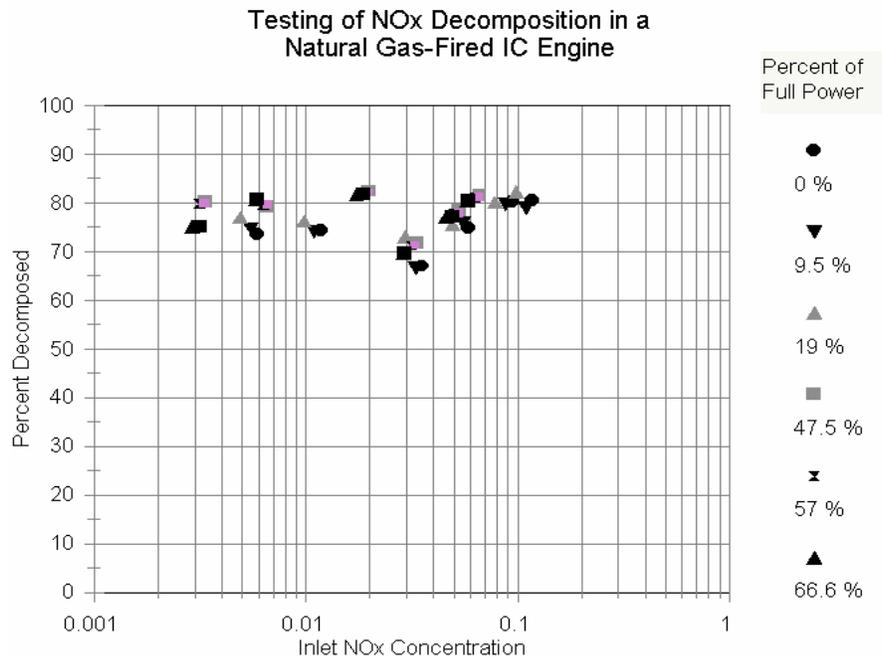


Figure 23. Graph of NO Conversion to N<sub>2</sub> in 21-h.p. Spark-Ignition Generator Engine Using Pipeline Natural Gas – Showing no relationship between inlet NO<sub>x</sub> concentration and conversion efficiency.

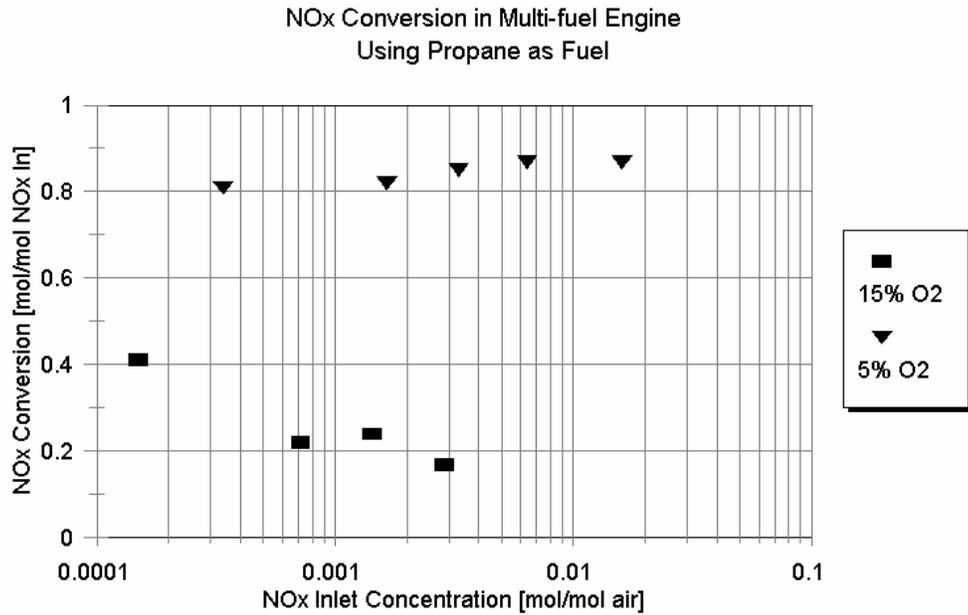


Figure 24. Graph of NO Conversion to N<sub>2</sub> in 6-h.p. Spark-Ignition Electric Generator Engine with Propane as Fuel – Showing no distinct relationship between inlet NOx concentration and conversion efficiency.

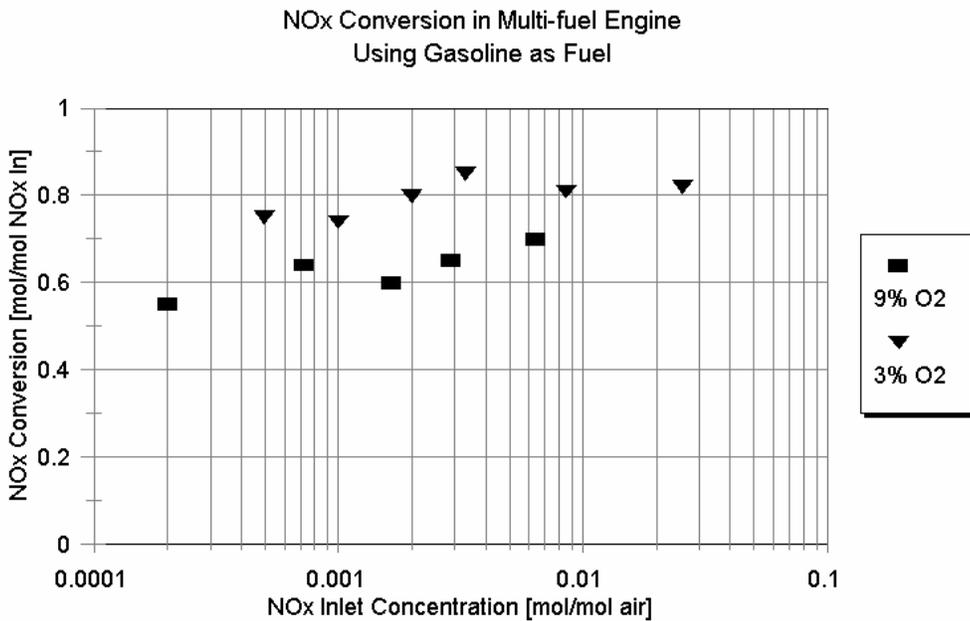


Figure 25. Graph of NO Conversion to N<sub>2</sub> in 6-h.p. Spark-Ignition Engine Using Standard Unleaded Gasoline – Showing only a slight relationship between inlet NOx concentration and conversion efficiency.

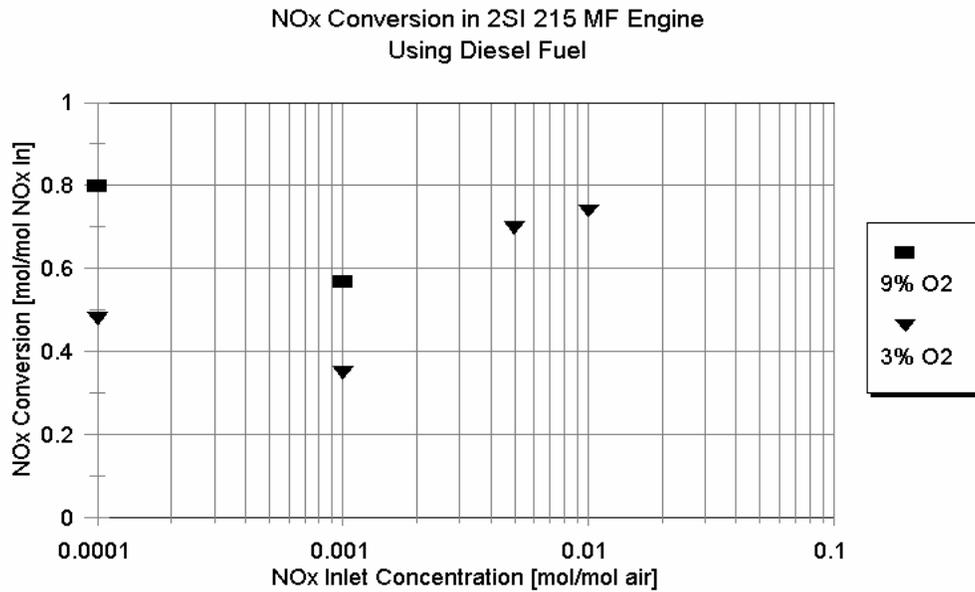


Figure 26. Graph of NO Conversion to N<sub>2</sub> in 10-h.p. Prototype Diesel-Fuel Spark-Ignition Engine Using Standard Diesel Fuel.

### Conclusions

For the application examined in this project, the only practical fuel for NO<sub>x</sub> decomposition is diesel fuel. A small, diesel-powered compression-ignition auxiliary power unit (APU) engine will be effective in converting the NO<sub>x</sub> to N<sub>2</sub> if the inlet concentration of NO<sub>x</sub> to the engine is greater than about 0.3%. This holds true over a range of engine power levels. If the NO<sub>x</sub> concentration in the gas stream to the engine is less than this amount, a spark-ignition engine design will be required; such as the prototype 2SI engine, which shows promise in this application.

In future work, the design of diesel-fueled spark-ignition engines should be further developed, for both this application and for effective powering of APUs. For other application, such as standby electrical generation, compression-ignition engines utilizing other fuels may be practical. In these cases, NO<sub>x</sub> decomposition efficiencies greater than 80% can be easily achieved.

### **3. Prototype Design and Construction**

#### **A. Component Design**

The objective of this task was the design and construction a commercial-scale prototype stationary emissions control system capable of handling approx. 6,000 ACFM of exhaust gas. This unit consisted of the following:

- monolithic NO<sub>x</sub> sorbent columns in a sorber chamber
- a electric-resistance desorption heating system
- a commercial particulate collection system
- a dedicated NO<sub>x</sub> decomposition system
- valves and piping
- data acquisition and monitoring instrumentation

#### **Monolithic NO<sub>x</sub> Sorbent Columns**

The most space-efficient and durable method for utilizing the sorbent materials in an exhaust gas application is to form the individual sorbent particles into a monolithic cylindrical shape, using a non-reactive binder to hold the particles together. This type of filter is commonly used in home water purification applications.

For this program, Sorbent Technologies and KX Industries LP, the largest fabricator of monolith carbon cartridges in the U.S., fabricated three sets of carbon cartridges using Sorbent Technologies' special NO<sub>x</sub> adsorption material as a base. These cartridges contained different binder materials and sorbent ground to different particle sizes. Individual cartridges from each batch were then tested in Sorbent Technologies' laboratory to evaluate a number of design parameters. These included: the pressure drop exhaust gas experiences going through the cartridges at different flow rates, cartridge density, temperature tolerance, physical strength, and the ability to be heated using Joule heating. One set of cartridges had too high a density and too great of a pressure drop to work effectively in this application. The other two compositions were tested for electrical heating. A photograph of one of the cylinders, fitted with end caps and electrical leads, is shown in Figure 27 below.

The monolith material was primarily activated carbon, which is an electrically conductive material. Simply by running an electric current through the material, from one end of the cartridge to the other, the material acts as a natural resistor and converts some of the electrical energy into heat energy. Such "Joule heating" is a very energy-efficient way of heating the cartridge, because there are no intermediate heat-transfer steps and, if the cartridges are symmetrical and uniform in composition, the cartridge mass will heat up at a uniform rate. In addition, this method does not involve any moving parts, does not put mechanical stress on the cartridge, and utilizes a resource, electricity, which is readily available on a diesel-powered vehicle. For these reasons, this was expected to be the preferred method for adding heat to the cartridges for regeneration/desorption.

A graph of Joule-heating results is shown in Figure 28. It should be noted that the first set of cartridges (cylinder 1) had a much greater electric resistivity than the second set of cartridges (cylinder 2). For this reason the voltage across the cartridge was set to a larger value (55 VAC for cyl. 1 and 25 VAC for cyl. 2). This allowed for a greater amount of electrical energy to be inputted to the cartridge per unit of time, while keeping the electrical current at a reasonable level.

Both sets of cartridges successfully heated using electrical resistance heating within a reasonable time frame. Though the first set of cartridges performed better electrically, it was decided that the second cartridge formula was preferred, based on adsorption and pressure drop information.



Figure 27. NOx Adsorbent Cartridge (One of Eight Mounted in Sorber).

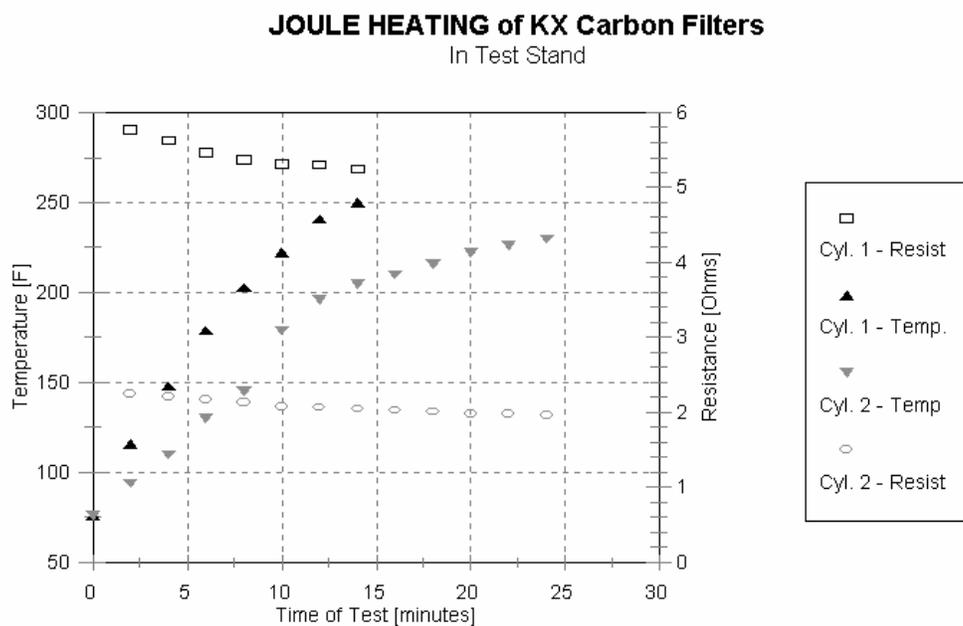


Figure 28. Graph of the Sample Results from the Electric Resistance (Joule) Heating Tests

### Desorption Heating System

The Joule heating experiments went well, so this method was used to heat the carbon-monolith sorbent beds for regeneration and NO<sub>x</sub> removal in the prototype system. Copper plates were fused to the top and bottom of each of the eight individual cartridges and then soldered to electric leads. The plates and cartridge ends were then coated with epoxy to electrically insulate them and fitted into a protective cap. The electric leads were run through the exhaust hole and connected together so that the cartridges were wired in series. This allowed for the highest resistance and therefore the greatest voltage for a given current.

The sorbent cartridges were heated using electricity generated by the auxiliary engine, therefore there was no interference or energy drain from the main diesel engine. The voltage used was 240 volts AC with a current ranging from 20 amps at the beginning of a regeneration cycle to 15 amps when the cartridges were up to temperature. The regeneration heating, along with the rest of the regeneration process, was designed to be automatically controlled by electrical relays.

### Particulate Collection System

It was decided that the Prototype System would utilize an existing, continuously-regenerating commercially-available particulate control system in front of the NO<sub>x</sub> control filter. The particulate filter system that was chosen for this demonstration was supplied by Engine Control Systems (a division of Lubrizol Corp.). It was a UniCat dual K18 Combifilter model and was manufactured in Sweden and Canada. A picture of the system, as it was installed is shown in Figure 29.



Figure 29. The UniCat dual K18 Pre-Filters Used on the Prototype Control System.

## NOx Decomposition System

An auxiliary NOx conversion engine was added to the schematic plan after extensive examination of the NOx conversion technology. The NOx can be converted into N<sub>2</sub> and O<sub>2</sub> effectively in a compression-ignition IC engine, however this reaction requires specific conditions in the engine to achieve greater than 80% conversion efficient. It was felt that maintaining these conditions in the main engine for the duration of the regeneration will effect operation too much for this technology to be “transparent”.

The advantages of using a separate conversion engine are:

- 1) the engine conditions can be optimized for conversion,
- 2) the conversion engine can be 30 to 100 times smaller than the operating engine, and
- 3) the operating engine would not see a periodic high-NOx high-moisture inlet stream, which could cause corrosion problems.

## Valves and Piping

All exhaust gas pipes and fittings in the system were commercial-grade steel piping, obtained from exhaust gas system vendors. The pipes were either four or five inches in diameter, depending on where they were in the system. The regeneration NOx pipes were ¼ inch stainless steel and ¼ inch Teflon. The exhaust gas valves were compressed-air-actuated butterfly valves and fitted the 4-inch pipes. No significant corrosion was observed in any part of the system during testing.

## Data Acquisition and Monitoring Instrumentation

The system was instrumented for both process control and for experimental monitoring. For process control, several electronic feedback loops were developed to initiate different steps in the process and for safety protocol. The parameters that were measured and recorded are given in Table 2 below.

**TABLE 2. SENSORS USED ON THE PROTOTYPE SYSTEM**

<u>Parameter</u>	<u>Number of Sensors</u>	<u>Sensor Type</u>
Temperature	10	Thermocouples
Pressure (4 points)	4	Pressure Transducers
Pressure Drop (2)	2	Pressure Transducers
NOx Levels	3	Solid Surface NOx Sensor
Gas Flow	1	Orifice Plate/Transducers
Engine On/Off	1	Voltage Sensor
Regeneration Current	1	Ammeter

For evaluating the effectiveness of the new technology, all data was recorded on a continuous basis by two data acquisition computers. These computers were able to record data continuously for up to nine days, although a researcher was constantly monitoring the system while it was running and the data was downloaded every evening for security.

## B. System Design

The commercial-scale stationary prototype was designed, built, and installed on the exhaust from an approximately 600 HP stationary diesel power generator at Hans Hilleby Farms outside of Woodland, California and evaluated for long-term operation. A schematic design of the system is shown in Figure 30. Several photographs of the system as it was built are shown in Figures 31, 32 and 33.

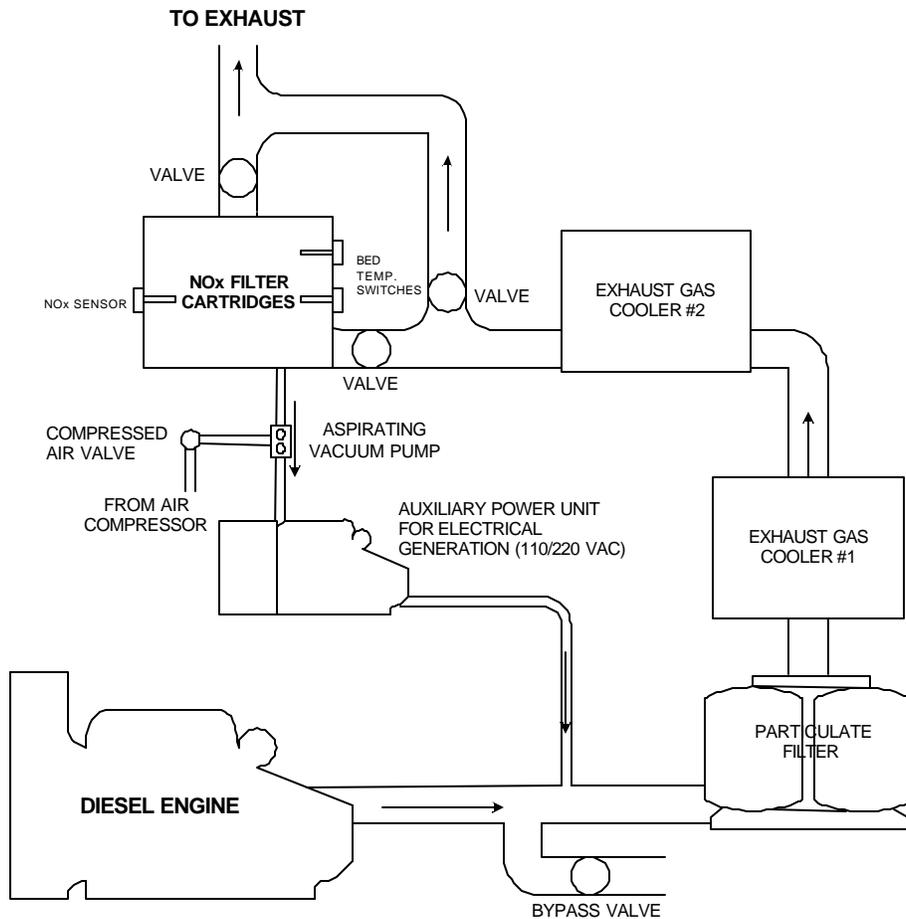


Figure 30. Schematic Diagram of Prototype Test System



Figure 31. Stationary Demonstration NOx Control System Install on a 600 h.p. Diesel Engine in Woodland, California



Figure 32. Stationary Demonstration Sorber and Auxiliary Engine/Generator (for NOx Conversion).



Figure 33. Stationary Demonstration Sorber with System Control Box.

### **3. Large Stationary Diesel-Engine Trials**

#### **A. Testing at Hans Hilleby Farms**

The key Prototype Diesel-Engine Trials were conducted at the Hans Hilleby Farm, located at 37188 County Road 28, just outside Woodland, California. The system was installed on a 600 HP turbo-charged diesel engine that supplied power to a hydraulic oil compression system. The pressurized oil supplies energy to run compressing and baling equipment for processing hay, oats and alfalfa. Some of the important engine operating parameters were:

- during regular process operation, the engine cycles between 60% load and idle at an average of 10 cycles per minute. The cycles are highly variable and based on the operation of the grain processing operation.
- the engine operates during one shift (6 – 10 hours) per day, with some days off, based on demand.
- the engine is located outside of all structures, on a poured-concrete slab without cover.
- the average ambient temperature during the day during testing, spring and summer, was 95°F.
- no work stoppages or changes in operating schedules were incurred to accommodate the installation or operation of the new exhaust gas treatment system.

The test program ran intermittently from April to September 2003. The exhaust gas treatment system was run whenever the host diesel engine was operated. A total of 30 days of testing were completed. During these tests, a researcher was always present to monitor the equipment and take extra data, although for most tests the equipment operated automatically without the need for an operator. Periodically during the testing period, when the equipment was not in operation, the NO<sub>x</sub> sorber chamber was opened and the sorption cartridges were checked for physical integrity and electrical conductivity.

Figures 34, through 37 shown examples of the temperature and NO<sub>x</sub> concentration data recorded for these tests. It should be noted that, although the exhaust gas coolers operated more effectively than originally planned, the ambient temperature during most tests was higher than planned and therefore the bed temperatures were also higher than the original design. This decreased the NO<sub>x</sub> storage capacity of the sorbent materials and necessitated more frequent regenerations than originally anticipated.

Overall the components of the prototype system performed well. NO<sub>x</sub> removal from the exhaust gas stream averaged about 80% for the tests where the bed temperature was below the regeneration threshold. NO<sub>x</sub> conversion efficiency in the auxiliary engine was consistently above 80% on a mass averaged basis. The exhaust gas from the conversion engine was returned to the beginning of the treatment system.

Due to the periodic nature of operating the facility that produced the exhaust gas, the treatment system was cooled down and heated up frequently. The sorbent cartridges and other system components held up under this type of operation well with little or no decrease in performance during start-up. It is anticipated that this will be the typical type of operation that a system like this will see.

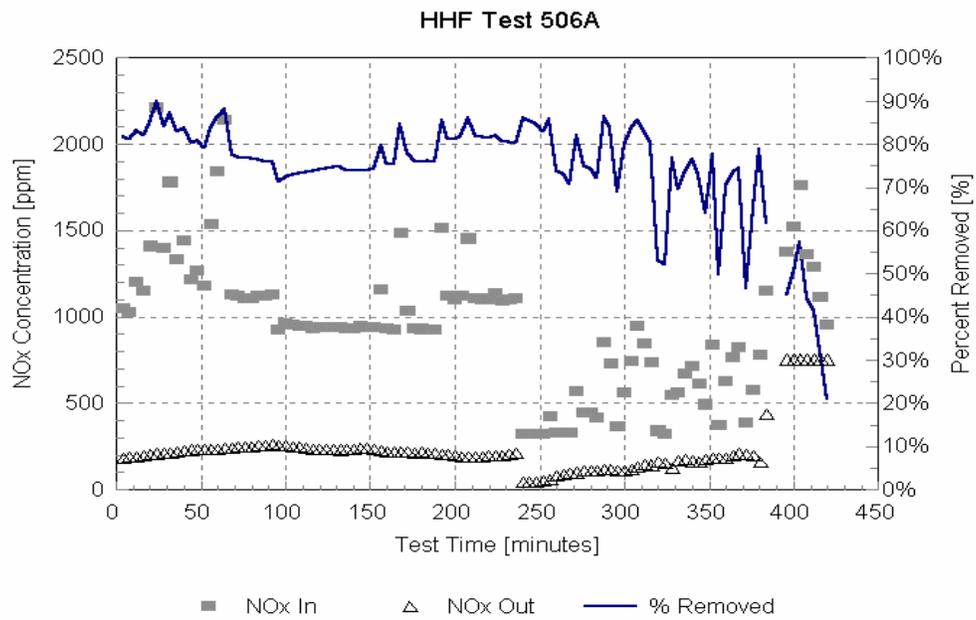


Figure 34. Graph of NOx Into and Out of the Sorber and Removal Efficiency for Test 506 of Prototype System at Hans Hilleby Farm

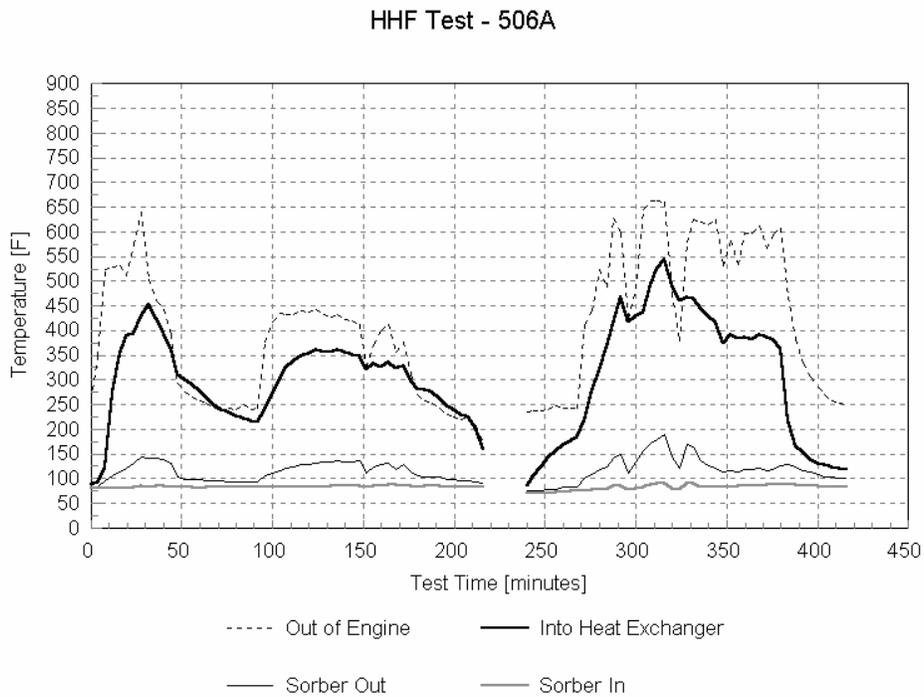


Figure 35. Graph of Temperature Profiles for Test 506 of Prototype System at Hans Hilleby Farm

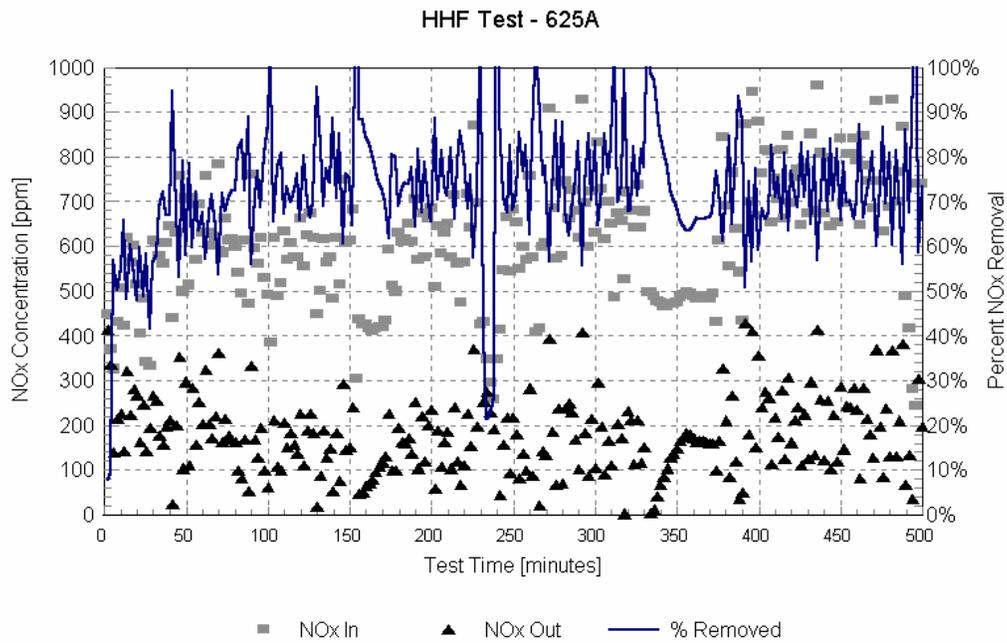


Figure 36. Graph of NOx Into and Out of the Sorber and Removal Efficiency for Test 625 of Prototype System at Hans Hilleby Farm

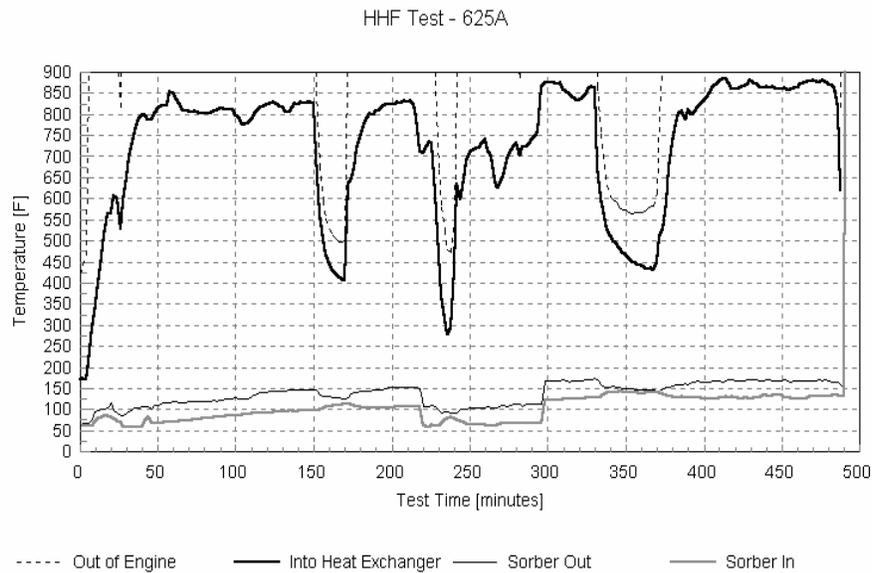


Figure 37. Graph of Temperature Profiles for Test 625 of Prototype System at Hans Hilleby Farm

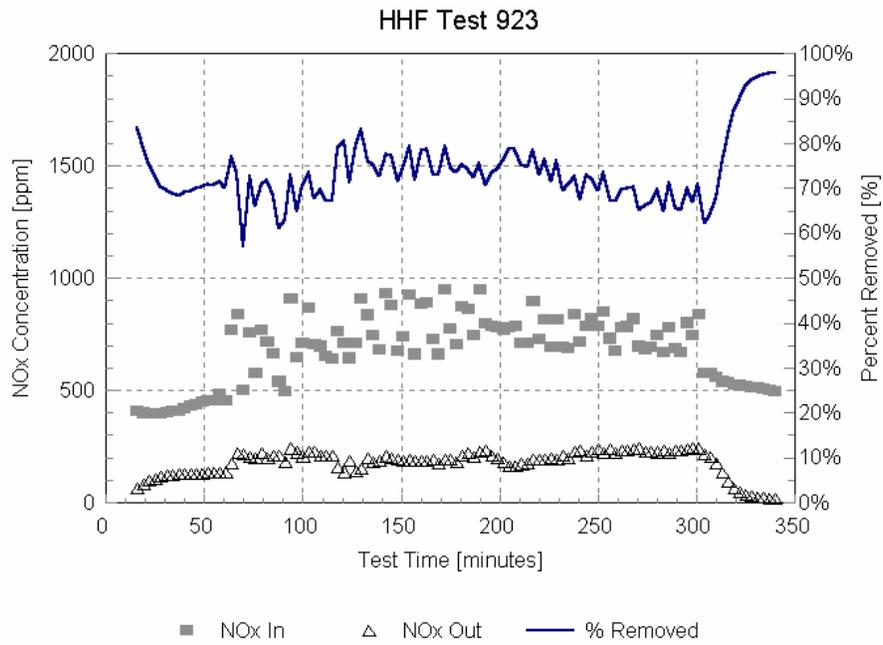


Figure 38. Graph of NOx Into and Out of the Sorber and Removal Efficiency for Test 923 of Prototype System at Hans Hilleby Farm

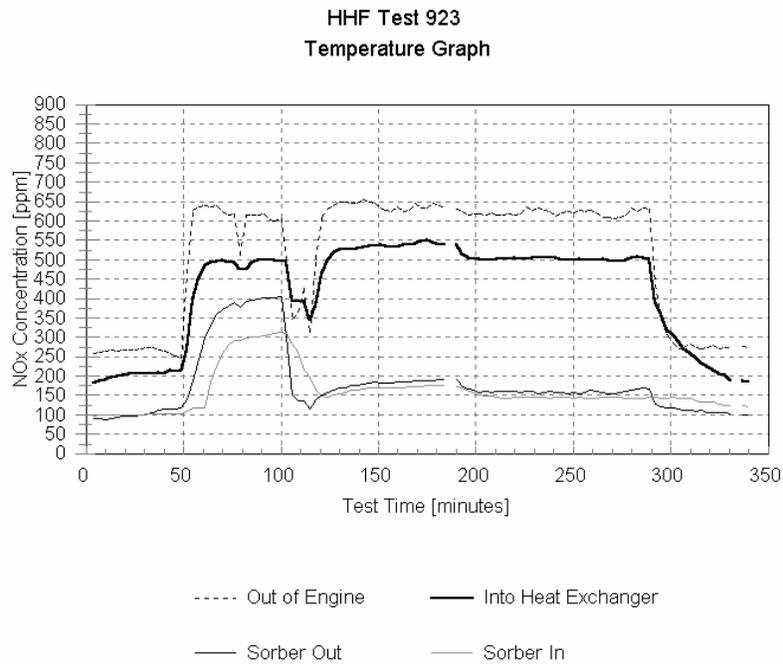


Figure 39. Graph of Temperature Profiles for Test 923 of Prototype System at Hans Hilleby Farm

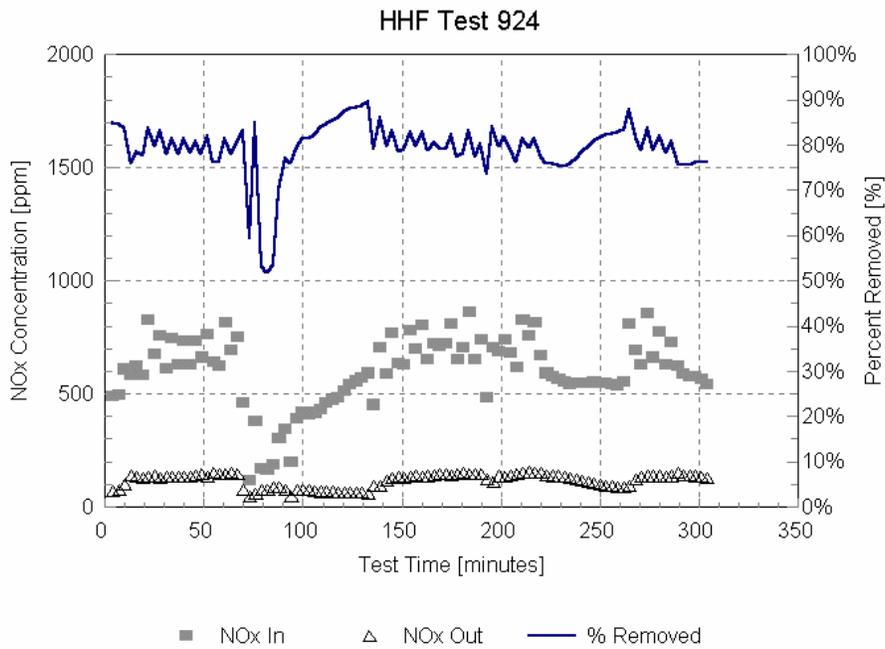


Figure 40. Graph of NOx Into and Out of the Sorber and Removal Efficiency for Test 924 of Prototype System at Hans Hilleby Farm

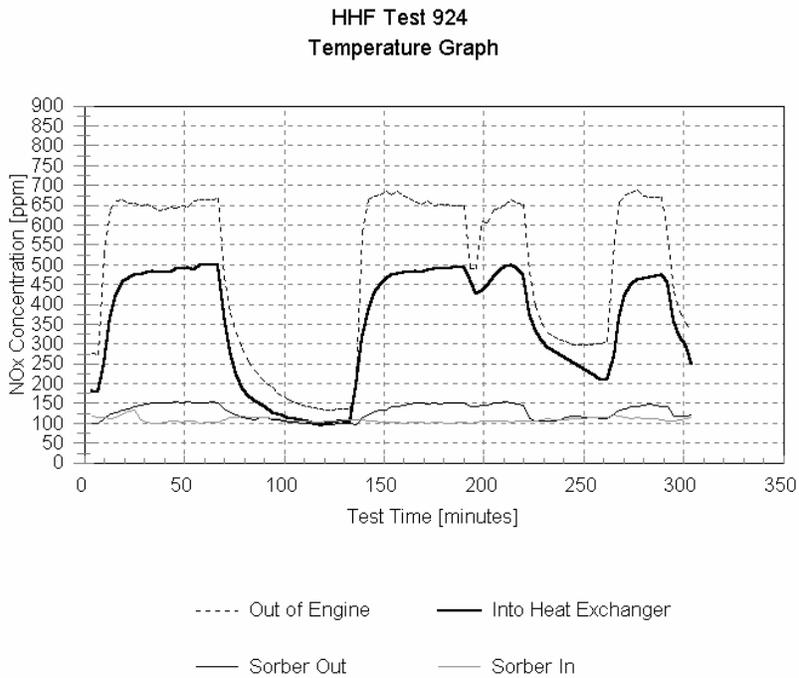


Figure 41. Graph of Temperature Profiles for Test 924 of Prototype System at Hans Hilleby Farm

Test 506A represents a typical run when the diesel engine was being used for a moderate, steady load. The engine only cycled between 10 different load levels over the eight-hour period. The NO<sub>x</sub> adsorption efficiency stayed relatively steady at about 80% removal until the sorbent cartridges began to reach saturation at 4% by weight NO<sub>x</sub> on the carbon. By the end of the day, the cartridges were ready to be regenerated. Note that the break in the graph between minutes 210 and 240 was when the engine was shut down for lunch.

Test 625A was more representative of the typical operation of this facility. The engine was operated at near-maximum power over the whole eight-hour period, with constant, random up and down cycles. This resulted in a larger exhaust gas flow, much hotter exhaust gases, and a scatter of the NO<sub>x</sub> concentration data. Since the NO<sub>x</sub> removal efficiency is based on subtracting the NO<sub>x</sub> in concentration from the NO<sub>x</sub> out concentration, and these values were changing from second to second, the efficiency seems to be jumping over a wide range. However, the average removal efficiency and the total mass removal was still approximately 75% over the course of the test.

Tests 923 and 924 are typical examples of the variability of the engine run cycle during low ambient air operation (outside temperature around 75°F). Note that when the engine is idling, at the beginning and end of the day of test 923 and between 100 and 140 minutes during test 924, the NO<sub>x</sub> removal improves to 90%.

The overall average NO<sub>x</sub> inlet concentration, for all of the tests, was 625 ppm. The overall average NO<sub>x</sub> concentration out of the system, for all of the tests, was 140 ppm. And the average percent NO<sub>x</sub> removed, on a mass basis, for all of the tests, was approximately 75%.

## B. Unburnt Hydrocarbon, Carbon Monoxide and Particulate Removal Tests

An examination of the removal of unburned hydrocarbons (UHC), carbon monoxide, and particulates from the pilot-scale system was also undertaken. This work was run in parallel with the NO<sub>x</sub> removal tests. The pilot-scale program was extended to gain more information on NO<sub>x</sub> removal from diesel engine exhaust gases and to accommodate the UHC, carbon monoxide, and particulate removal evaluation.

### Particulate Removal

To examine the effectiveness of both the Diesel Particulate Filter (DPF) and the NO<sub>x</sub> sorber for the removal of diesel particulates in the PM<sub>10</sub> and PM<sub>1</sub> size ranges, samples of exhaust gases was taken at three points along the treatment stream. The first sample was taken before the gas enters the system, i.e. before the DPF. The second sample point after the DPF and before the NO<sub>x</sub> sorber, and the third sample point after the NO<sub>x</sub> sorber. Gas samples were drawn isokinetically for 15 to 20 minutes from the exhaust pipe, and run through impactors, which collected the particles out of the gas stream in different size ranges. The amount of particulates in each of the three size ranges was measured, so that a particle size distribution at each point could be determined. Two samples were drawn from each sample for each test series over the test program. Chemical analyses of the particulate was not run, since the chemical composition of diesel exhaust particles has already been well characterized, but each sample has been archived so chemical analyses can be carried out in the future.

## Carbon Monoxide Removal

To examine the effectiveness of both the Diesel Particulate Filter (DPF) and the NOx sorber for the removal of carbon monoxide, the level of carbon monoxide in the exhaust gas was monitored periodically at the three locations described above. This testing was done continually during the NOx removal test program, so that the effects of different engine operating conditions on the CO removal rate could be determined. The CO concentrations was measured using an electro-chemical detection device with an automatic sampling system.

## Unburned Hydrocarbon Removal

To examine the effectiveness of both the Diesel Particulate Filter (DPF) and the NOx sorber for the removal of unburned hydrocarbons (UHC), products of incomplete combustion, and volatile organic compounds, the levels of these organics in the exhaust gas was monitored periodically at the three locations described in the particulate tests above. This testing was also done continually, so that the effects of different engine operating conditions on the organic removal rate could be determined. The organic compound concentration was measured using an electrochemical detection device with an automatic sampling system.

## Results

The Unicat Diesel Particulate Filter performed well during the test program; removing approximately 90% of the mass of the particulates. The removal rate for particles in the PM5 range was slightly less, but still effective. The NOx filter did not seem to remove appreciatively more of the particle matter. But the NOx filter did not add to the amount of particulate pollution either. The following graphs summarize the particulate data collected during the experiments.

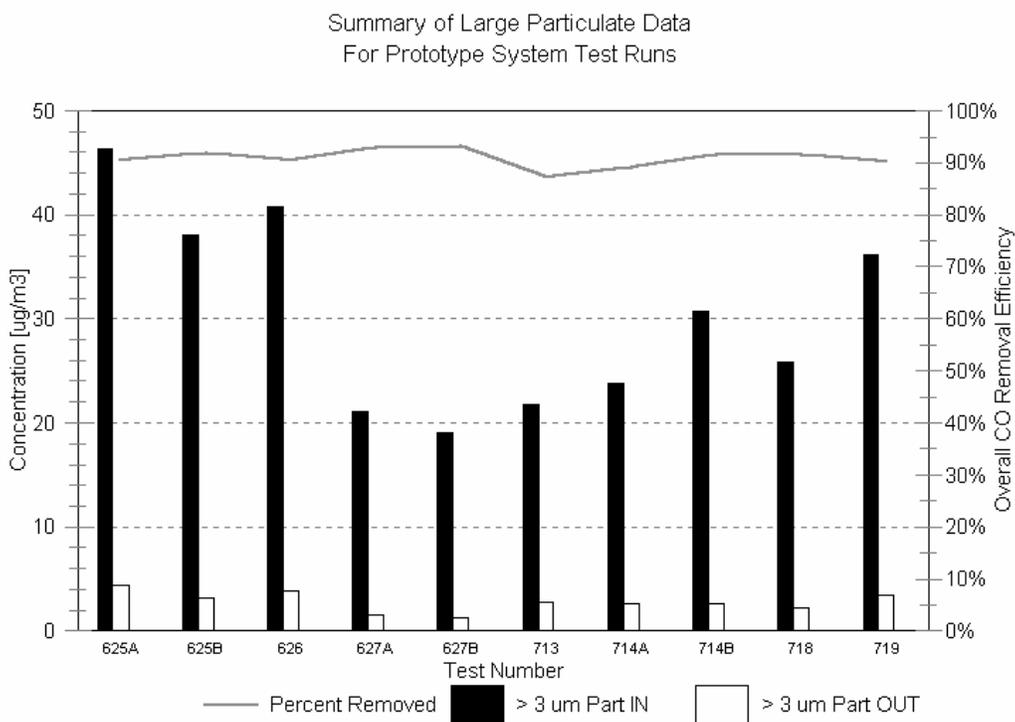


Figure 42.

Summary of Small Particulate Data  
For Prototype System Test Runs

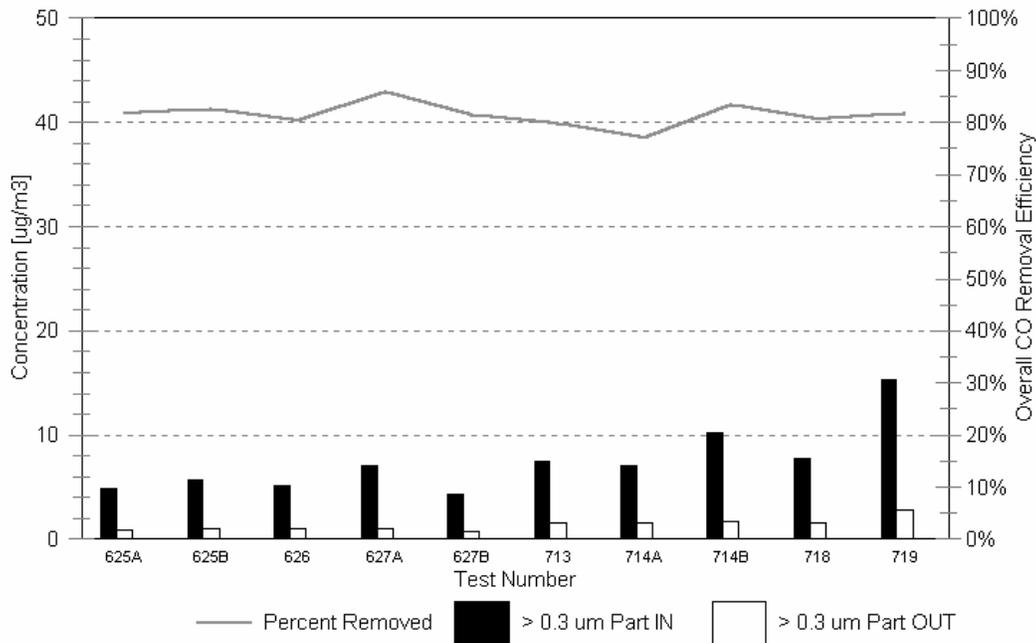


Figure 43.

The Unicat DPF also was effective in removing a majority of the CO and unburned hydrocarbons from the exhaust gas stream. To some extent, this was a surprise, since particulate filters are not generally considered to be good candidates for cleaning up these gases. The average removal rates were 65% and 75% for CO and UHC respectively. The NOx filter also was effective for removal of these gases. On average, 50% of the remaining CO was removed or reacted with the NOx filter, and 35% of the remaining UHC were removed.

Figures 44 and 45 summarize the data from each of the tests where CO and UHC removals were examined. The actual temporal concentrations of these gases varied by factors of up to 50 over the course of a given day, depending on engine load, engine speed and ambient conditions. The values in the graphs are mass-weighted averages.

### Conclusions

As expected, the system was very effective at removing particulates and UHC from the exhaust gas. The commercial DPF was the main contributor to this removal, with the NOx filter “polishing” the gas afterwards. On average, greater than 99% removal of the particulates and greater than 95% removal of the organic pollutants were achieved. The removal of carbon monoxide was not effective. Whereas the DPF removed, on average, 60% of the CO from the gas, the NOx filter seemed to saturate very quickly with CO, and remove only about 40% of what was remaining in the exhaust gas. This resulted in an average overall removal of carbon monoxide of about 75%.

Summary of Average CO Concentrations  
For Prototype System Test Runs

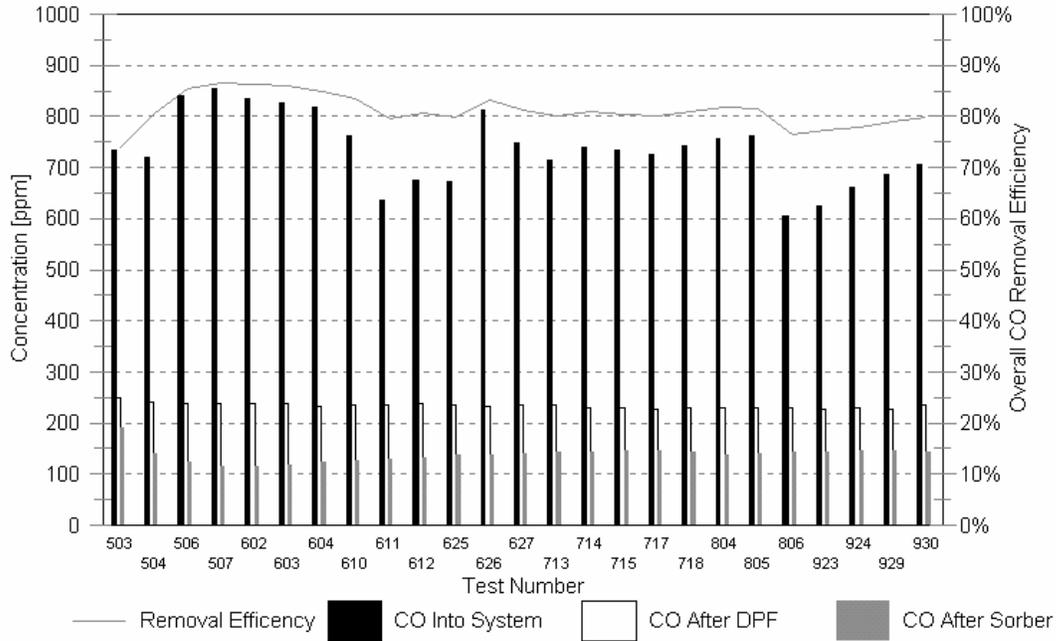


Figure 44.

Summary of Average UHC Concentrations  
For Prototype System Test Runs

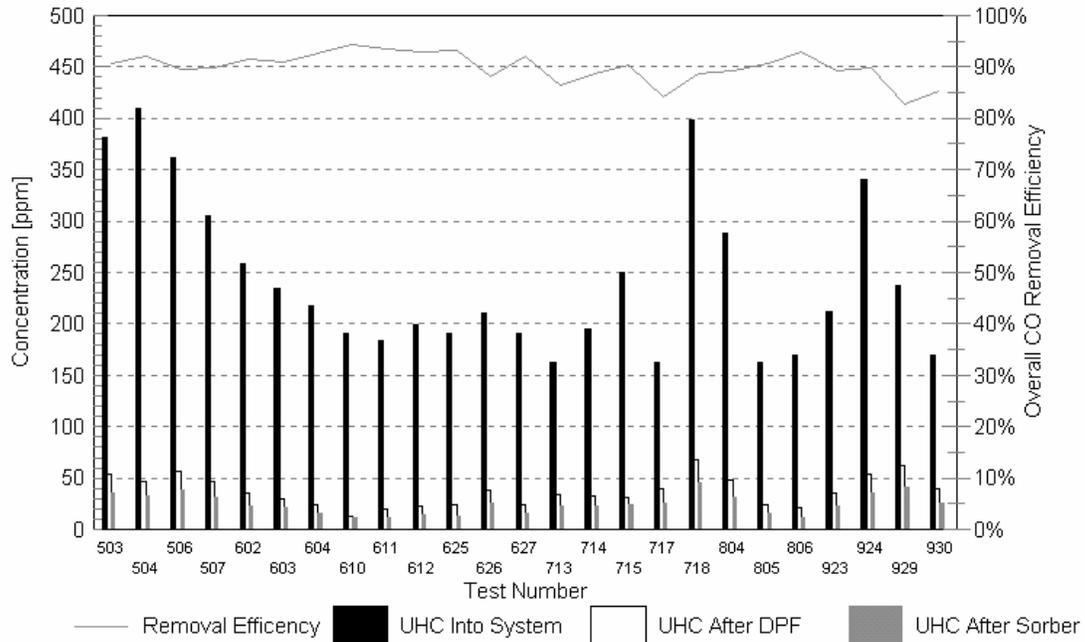


Figure 45.

## C. Discussion

The following conclusions were drawn from these large-scale Prototype Diesel-Engine Trials:

- The new technology can be used to effectively remove NO<sub>x</sub> and fine particles from the exhaust gas of an actual working large-size stationary diesel engine.
- The technology works effectively in applications where there are frequent and irregular variations in the engine load and operating speed.
- If the ambient temperature of operation is higher than 90°F, larger sorbent cartridges are needed to balance the approximately 40% decrease in sorbent capacity.
- Exhaust gas cooling to adsorption temperatures can be accomplished effectively using a single air-to-air intercooler; although a more effective method of removing water droplets from the gas after cooling needs to be designed.
- The binder used to create the sorption cartridges is a key element in engineering these systems and a binder more tolerant of high-temperatures would make the technology applicable to a wide range of stationary diesel engines.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

##### A. Cost Estimate for a Commercial NOx Removal System

###### Initial Costs

It is proposed that the Selective NOx Recirculation System be installed at the end of the exhaust pipe, after the particulate control device. The major pieces of equipment that make up the system will be: an exhaust gas cooler, the sorber housing with valves, pump and by-pass line, the diesel-fired auxiliary engine, and a solid-state electronic controller. The total cost of the system, installed as a retrofit on an existing engine with a 450 h.p. engine is expected to be less than \$8,000. The system would use some of the existing resources of the engine: compressed air (to run the recirculation pump during regeneration), and diesel fuel (approximately equal to 1 to 2% of the total fuel used by the engine, for running the auxiliary engine during regeneration). The electricity needed for heating the cartridges for regeneration/desorption can be supplied by a generator hooked up to the auxiliary engine, which will be operating during cartridge regeneration anyway. A nominal amount of electricity will be needed from the engine's battery to run the NOx sensors and the electronic control system.

The following components are anticipated to be included in the final SNR design:

Component	Size (Approximate)	Source
Exhaust Gas Cooler	7 cu.ft.	Commercially available
Sorber w/valves and by-pass	18 cu.ft.	Sorbent Technologies
Auxiliary Engine/Generator	9 cu.ft.	Commercially available
Recirculation Pump	nominal	Commercially available
Electric Resistance Heater	nominal	With Sorber
Controller w/ NOx Sensors	nominal	Commercially available
Adsorption Cartridges	--	Sorbent Technologies

###### Periodic Costs

In such a system, the adsorption cartridges will be the only component that will need to be replaced periodically. Sorbent Technologies and KX Industries can supply these replacement cartridges, through established retail, diesel engine-service outlets.

At the present time, Sorbent Technologies has cycled the sorbent material through up to 200 adsorption/desorption cycles without seeing any appreciable performance decay. It is anticipated that up to 500 cycles will be achievable before the cylinders will need to be replaced. However, for cost analysis purposes, a conservative useful life of 200 cycles will be used. If an engine is operated 250 days per year and approximately 8 hours per day, with an average duty cycle the NOx-sorption cartridges would be 75% saturated at the end of the 8 hour period. This would mean that a regeneration could occur at the end of the daily use, with some spare capacity for extraordinary circumstances. The cartridges would thus be replaced every 0.8 years (200cycles per replacement/250 cycles per year). During each replacement, all of the carbon cylinders would be replaced. The full-scale prototype sorber contained 8 cartridges, although a system for engines larger than 500 h.p. may require a sorber unit with 10 cartridges to accommodate the extra flow.

The cost of each NO<sub>x</sub>-sorption cylinder is anticipated to be about \$25.00 retail, with perhaps some cost for installation. Therefore the annual cartridge replacement cost would be:

$$10 \text{ cartridges/replacement} \times \$25.00/\text{cartridge} \div 0.8 \text{ replacements/year} = \underline{\$312.50/\text{year}}$$

The only other operating cost will be the diesel fuel needed for operating the 5 h.p. auxiliary power engine during the NO<sub>x</sub> conversion phase of regeneration. This process takes a little under an hour and uses approximately ½ gallon of fuel. If regeneration occurs 250 times per year and diesel fuel costs approximately \$2.00 per gallon, then the fuel penalty will be about \$250 / year.

The total annual operating cost will then be:

$$\$312.50 \text{ (cartridges)} + \$250.00 \text{ (fuel)} = \underline{\$562.50 / \text{year}}$$

## B. Conclusions

The following conclusions were drawn from the various efforts undertaken during this project:

- The NO<sub>x</sub> filter material can be effectively extruded into cylindrical filter cartridges which have reasonable pressure drop characteristics and reasonable structural strength. The binder materials as they were tested, however, lost their structural strength at temperature above 350°F, which can be reached during regeneration; so higher-temperature binders need to be examined.
- The NO<sub>x</sub> filter cartridges effectively adsorb NO<sub>x</sub> from actual diesel exhaust gases when the gas temperature is below about 130°F and desorb the NO<sub>x</sub> when the material temperature is above 230°F. This phenomenon occurs whether the chemical form the NO<sub>x</sub> is NO or NO<sub>2</sub>.
- Components of the NO<sub>x</sub> filtration system can be miniaturized to the extent that they can be packaged on a small skid for easy installation.
- Electric-resistance (Joule) heating of the sorbent itself is the most effective method for directly heating the solid sorbent material when it is formed into a monolithic cartridge.
- Consistently greater than 80% NO<sub>x</sub> decomposition can be achieved in spark-ignition IC engines over a large range of inlet NO<sub>x</sub> concentrations and engine operating conditions. Greater than 80% NO<sub>x</sub> conversion will also occur in compression-ignition IC engines if the inlet NO<sub>x</sub> concentration is greater than about 2.0%.
- Particulate and Unburnt Hydrocarbons were removed from the exhaust gas stream by the treatment system at a rate of consistently greater than 90 percent.

## Component Performance

- Commercial ejector pumps were found effective at removing the NO<sub>x</sub> from the sorbent cartridges. Ejector pumps, which operate on the principle of aspiration using a high-velocity stream of compressed air, were able to draw up to a -6.5 psi vacuum on the sorber chamber. Leakage of air through the valves that closed off the chamber was the limiting factor in the amount of vacuum that could be applied. However, the vacuum that was achieved is sufficient to regenerate the sorbent cartridges.

- Electric resistance (joule) heating was effective at heating the sorbent cartridges. The cartridges were found to effectively act as an electric resistor, converting electrical energy into heat energy. However, the cartridges with the chemical composition most effective in physical tests had a electrical resistance that was much lower than other cartridges. The potential for optimizing the electrical properties of the adsorbent cartridges should be examined further.
- Spark ignition internal combustion engines were effective at decomposing the NO<sub>x</sub>. All of the five types of IC engines that were tested achieved some degree of decomposition. A newly-designed diesel-fuel-fired spark-ignition engine successfully decomposed the NO<sub>x</sub> introduced into it and looks to be the best candidate for inclusion in a commercial system.
- Electrically-actuated butterfly valves are the most practical type of valve for use in the exhaust gas pipe. The materials of construction for these valves has to be able to withstand temperatures up to 300°F, while maintaining their seals. The valves will not seal completely, however, the amount of gas leakage through these valves should be within tolerable limits.
- An electronic control system can be built to operate the cartridge regeneration/NO<sub>x</sub> decomposition process without a need for input from either the main diesel engine or the vehicle operator. This control system will use standard, readily-available components and be relatively inexpensive.

The overall conclusion of the work performed in this program is that it is possible to build and operate a sorbent-based NO<sub>x</sub> control system for heavy-duty diesel fuel engines that will remove and decompose 70% or more of the NO<sub>x</sub> generated by the diesel engine. This system may be light enough in weight and small enough in size to be economical for commercial applications.

### C. Recommendations

The success of this research project is a significant step toward the commercialization of the new NO<sub>x</sub> control technology. Sorbent Technologies will be continuing this process of developing this technology in an effort to address the needs of regions that are experiencing poor air quality. Presently, the company is looking for partners to join it in this effort.

The next step in developing and commercializing the SNR technology is to build several next-generation systems, utilizing the information obtained in this project, install them on diesel-powered engines, and further demonstrate that they will remove and decompose the NO<sub>x</sub> from the engines' exhaust gas streams. Several components of the system (specifically the cartridge binders, the exhaust gas coolers, and the system electronic controllers) need to be developed further, as a parallel effort to such a commercial demonstration.