

# **Diesel Emission Control – Sulfur Effects (DECSE) Program**

## **Phase II Summary Report: NO<sub>x</sub> Adsorber Catalysts October 2000**

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The test program and subsequent data analysis represent a collaborative effort of a technical work group consisting of representatives from the U.S. Department of Energy, its national laboratories, the Engine Manufacturers Association, and the Manufacturers of Emission Controls Association. The work group prepared this report using methods believed to be consistent with accepted practice. All results and observations are based on information available using technologies that were state-of-the-art at the time. To the extent that additional information becomes available, or factors upon which analyses are based change, the findings could subsequently be affected.

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## ACRONYMS

BSFC – brake specific fuel consumption  
BOI – beginning of injection  
CE – conversion efficiency  
CO – carbon monoxide  
cpsi – cells per square inch  
DECSE – Diesel Emission Control-Sulfur Effects  
DOC – diesel oxidation catalyst  
DPF – diesel particulate filter  
EGR – exhaust gas recirculation  
EMA – Engine Manufacturers Association  
EO – engine-out  
FEP – fuel economy penalty  
FEV – FEV Engine Technology  
H<sub>2</sub> – hydrogen  
HC – hydrocarbon(s)  
HSDI – high-speed, direct injection  
MECA – Manufacturers of Emission Controls Association  
N<sub>2</sub> – nitrogen  
NO<sub>x</sub> – oxides of nitrogen  
NREL – National Renewable Energy Laboratory  
NVH – noise-vibration harshness  
OEM – original equipment manufacturer  
ORNL – Oak Ridge National Laboratory  
OTT – Office of Transportation Technologies  
Pd - palladium  
PM – particulate matter  
Pt - platinum  
ppm – parts per million  
Rh - rhodium  
R&D – research and development  
SO<sub>2</sub> – sulfur dioxide  
SO<sub>3</sub> – sulfur trioxide  
TWC – three-way catalyst

# Executive Summary

## *ES.1 Background and Objectives*

The Diesel Emission Control–Sulfur Effects (DECSE) program is a joint government/industry effort to determine the impact of diesel-fuel sulfur levels on emission control systems that could be used to lower emissions of oxides of nitrogen (NO<sub>x</sub>) and particulate matter (PM) for future light-duty and heavy-duty vehicle applications. The program is designed to enhance the knowledge base for engines, diesel fuels, and emission control technologies in a systems approach to (1) guide the industry in developing lower-emitting applications of its products, and (2) provide part of the technical basis for government decisions on regulating the content of sulfur in diesel fuel.

Phase I of the program included objectives focused on evaluating the effects of varying the level of sulfur content in the fuel on the emission-reduction performance of NO<sub>x</sub> adsorber catalysts, diesel particulate filters, lean NO<sub>x</sub> catalysts, and diesel oxidation catalysts. It also investigated measuring and comparing the effects of as many as 250 hours of aging on selected devices for multiple levels of fuel sulfur content. The devices tested include commercially available technologies as well as state-of-the-art technologies under development.

The engine management system and its calibration are critical to the operation of the NO<sub>x</sub> adsorber. In Phase I testing, the initial calibration of the engine management system did not achieve the desired level of NO<sub>x</sub> conversion performance across the range of operating temperatures. A revised calibration improved the conversion efficiency, but additional testing was required to complete the evaluation of the NO<sub>x</sub> adsorber catalyst performance.

Phase II of the program was developed with the following objectives in mind:

- A. Improve the NO<sub>x</sub> regeneration calibration developed in Phase I, achieving 80+% NO<sub>x</sub> conversion between operating temperatures of 250°C to 500°C.
- B. Develop and demonstrate a desulfurization process to restore NO<sub>x</sub> conversion efficiency lost to sulfur contamination.

NO<sub>x</sub> adsorber devices with the same catalyst formulation as that used in Phase I were evaluated in this follow-on effort. The same catalyst pairs aged and evaluated under the Phase I project were also retested. The 1.9 L high-speed, direct injection (HSDI) engine used represents the state-of-the-art and was selected to provide a representative source of diesel exhaust and various exhaust temperature profiles to challenge the emission control devices. Important characteristics of the exhaust stream are the exhaust flow rate, stream temperature, and concentrations of NO<sub>x</sub>, hydrocarbons, carbon monoxide, and PM.

Participants in the Phase II project include representatives of the U.S. Department of Energy's Offices of Heavy Vehicle Technologies and Advanced Automotive Technologies within the Office of Transportation Technologies, the National Renewable Energy Laboratory (NREL), Oak Ridge

National Laboratory (ORNL), the Engine Manufacturers Association, and the Manufacturers of Emission Controls Association.

This DECSE Phase II NO<sub>x</sub> adsorber report describes the continued evaluation of NO<sub>x</sub> adsorber catalysts and the development of a desulfurization process. FEV Engine Technology (FEV), under subcontract to NREL and MECA, conducted the testing in this project.

### *ES.2 NO<sub>x</sub> Adsorber Catalyst – Principles of Operation*

A NO<sub>x</sub> adsorber catalyst is a flow-through emissions control device that temporarily stores NO<sub>x</sub> emissions during typical diesel engine operation. Before the NO<sub>x</sub> adsorbent becomes fully saturated, engine operating conditions and fueling rates are adjusted to produce a fuel-rich exhaust. Under these rich conditions, the stored NO<sub>x</sub> is released from the adsorbent and simultaneously reduced to N<sub>2</sub> over precious metal adsorber catalyst sites.

An engine management system is critical to the operation of the NO<sub>x</sub> adsorber system. It must determine when the NO<sub>x</sub> adsorbent is approaching saturation and then trigger the change in engine operation that creates the rich condition required to release and reduce the stored NO<sub>x</sub>.

The concern with fuel sulfur is that sulfur dioxide (SO<sub>2</sub>) is formed during combustion and released in the exhaust. In a NO<sub>x</sub> adsorber catalyst, this SO<sub>2</sub> undergoes reactions that are analogous to those of NO<sub>x</sub>. However, SO<sub>2</sub> can generate a stronger adsorbate (sulfur trioxide) compared with NO<sub>2</sub>. As a result, SO<sub>2</sub> is a contaminant for the NO<sub>x</sub> adsorption sites.

### *ES.3 Study Design*

The NO<sub>x</sub> adsorber project was designed to address the following study questions:

- What NO<sub>x</sub> conversion efficiency is possible with an improved lean/rich regeneration calibration?
- Can a practical on-engine desulfurization cycle be developed?
- What effect does the desulfurization process have on the long-term performance of the NO<sub>x</sub> adsorber, and does it vary with fuel sulfur level?

This NO<sub>x</sub> adsorber project was conducted in three parts. The first part involved improving the calibration of the engine management system. The goal was to improve the calibration developed during Phase I, achieving a NO<sub>x</sub> conversion efficiency of at least 80% across engine operating temperatures of 250°C to 500°C when operating with the 3-ppm sulfur base fuel. This goal was to be achieved with no more than a 4% average increase in fuel consumption associated with the calibration strategy developed to release and reduce the stored NO<sub>x</sub>.

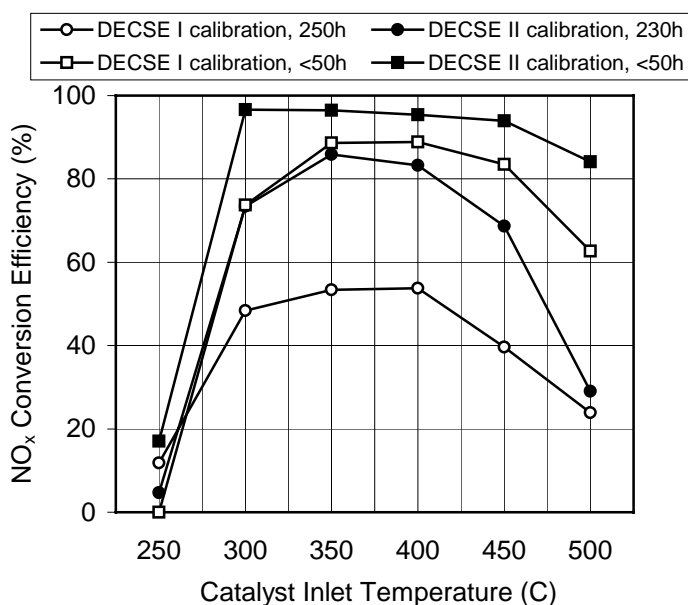
The next part focused on developing a process to desulfurize the NO<sub>x</sub> adsorber catalyst. This process involved controlling the air/fuel ratio and catalyst inlet temperatures to achieve the high temperatures required to release the sulfur from the device. The desulfurization process is run periodically to rid the catalyst of sulfur and restore the NO<sub>x</sub> conversion efficiency of the device. The desulfurization process was demonstrated by running the desulfurization process on the catalysts aged for as long as 250 hours with various sulfur level fuels in the DECSE Phase I project.

The final part of this project was to provide a preliminary assessment of catalyst durability when exposed to repeated aging and desulfurization cycles. Two series of tests were completed during this phase. The first involved a series of aging, performance mapping, desulfurization, and performance mapping cycles; aging was conducted using two different sulfur level fuels. In the second set of tests, multiple consecutive desulfurizations were completed to determine the effect of the high temperature exposure on catalyst durability.

#### ES.4 Findings and Conclusions

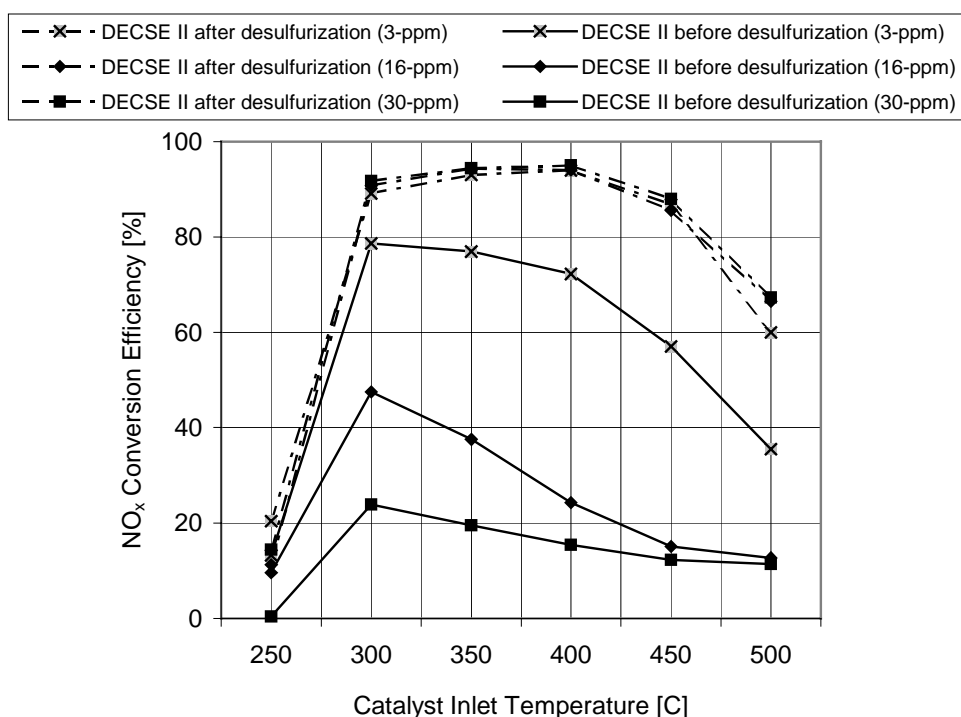
The major findings and conclusions of the Phase II effort are:

- The improved lean/rich engine calibration achieved as a part of this test project resulted in NO<sub>x</sub> conversion efficiencies exceeding 90% over a catalyst inlet operating temperature window of 300°C–450°C (see Figure ES-1). This performance level was achieved while staying within the 4% fuel economy penalty target defined for the regeneration calibration. This calibration was developed using one sulfur level fuel (3-ppm).



**Figure ES-1. Summary of conversion efficiencies using DECSE I and II calibrations. The data presented are averaged results for catalyst pairs tested at the same time.**

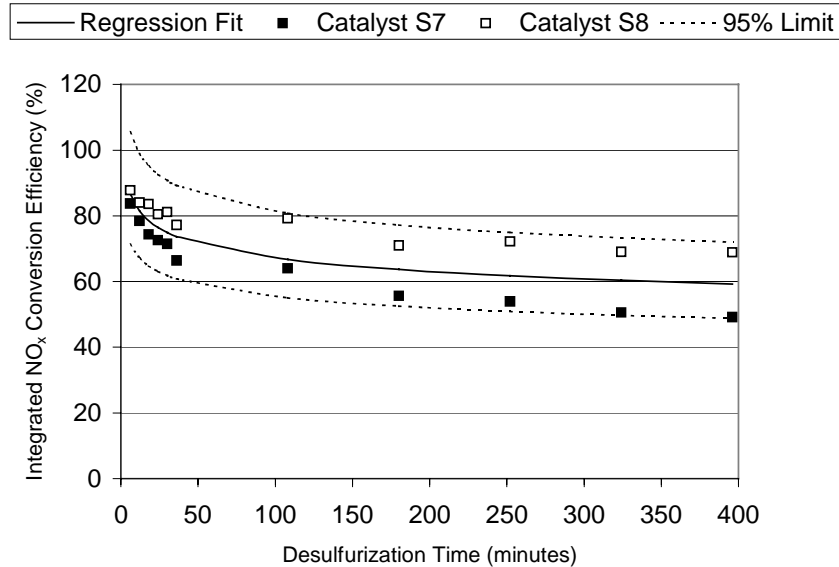
- The desulfurization procedure developed showed that six catalysts, which had been exposed to fuel sulfur levels of 3-, 16-, and 30-ppm for as long as 250 hours, could be recovered to greater than 85% NO<sub>x</sub> conversion efficiency over a catalyst inlet operating temperature window of 300°C–450°C after a single desulfurization event (see Figure ES-2). This performance level was achieved while staying within the 4% fuel economy penalty target defined for the regeneration calibration.



**Figure ES-2. Comparison of NO<sub>x</sub> conversion efficiency before and after desulfurization for catalyst aged as long as 250 hours with 3-, 16-, and 30-ppm sulfur level fuels. The data presented are averaged results for catalyst pairs tested at the same time.**

- The desulfurization procedure developed has the potential to meet in-service engine operating conditions and acceptable driveability conditions.
- Although aging with 78-ppm sulfur fuel reduced NO<sub>x</sub> conversion efficiency more than aging with 3-ppm sulfur fuel as a result of sulfur contamination, the desulfurization events restored the conversion efficiency to nearly the same level of performance. However, exposing the catalyst repeatedly to the desulfurization procedure developed in this program caused a continued decline in the catalyst's desulfurized performance (see Figure ES-3). Additional work will be necessary to identify the cause of this performance decline.
- The rate of sulfur contamination during aging with 78-ppm sulfur fuel increased with repeated aging/desulfurization cycles (from 10% per ten hours to 18% per ten hours). This was not observed with the 3-ppm fuel, where the rate of decline during aging was fairly constant at approximately 2% per ten hours.





**Figure ES-3. Regression model (with 95% confidence interval) of post-desulfurization NO<sub>x</sub> conversion efficiency versus total desulfurization time. Data for catalyst pair aged on 78-ppm sulfur level fuel.**

#### ES.5 Future Work

A limited number of PM measurements were conducted during desulfurization tests, and post-test analyses of the catalysts were included in this project. The PM test results and results of the post-test analyses were not available for inclusion in this report. In addition, further analyses of catalyst inlet temperature data may be required to investigate differences in catalyst performance. This report will be updated to include the additional data and findings from these tests and analyses, as soon as the data are available.

Beyond this project, further study is needed to investigate the frequency of desulfurization and to more accurately characterize thermal degradation associated with this high temperature cycle. In addition, more detailed studies are needed to address the long-term operation of a NO<sub>x</sub> adsorber catalyst, including engine and catalyst durability. There is also a need for more information on other exhaust constituents, such as smoke levels during regeneration, and on which trade-offs are required to reduce them or keep them low. Specific technical questions yet to be addressed include the following:

- Does the optimum regeneration calibration and desulfurization process change with catalyst aging?
- Whether or not developing a regeneration calibration for different sulfur level fuels would impact performance of a NO<sub>x</sub> adsorber catalyst is not clear, and should be investigated in future work.
- Which mechanisms cause the decline in catalyst performance with desulfurization, and what are the corrective measures?

- Does transient operation require different regeneration and desulfurization calibrations than steady state operation?
- Can multiple short duration desulfurization events be developed to be as effective as a single longer duration event?

# Section 1

## Introduction

### 1.1 Program Overview

Phase I of the Diesel Emission Control—Sulfur Effects (DECSE) program included objectives focused on evaluating the effects of varying the level of sulfur content in the fuel on the emission-reduction performance of oxides of nitrogen ( $\text{NO}_x$ ) adsorber catalysts. In Phase I testing, the initial calibration of the engine management system did not achieve the desired level of  $\text{NO}_x$  conversion performance across the range of operating temperatures. Phase II was developed to improve the  $\text{NO}_x$  regeneration calibration developed during Phase I, achieving 80+%  $\text{NO}_x$  conversion at operating temperatures of 250°C–500°C, and to develop and demonstrate a desulfurization process to restore  $\text{NO}_x$  conversion efficiency lost to sulfur contamination. Engine testing for both projects was conducted by FEV.

The DECSE II  $\text{NO}_x$  adsorber experiments provide data to address the following study questions:

- What  $\text{NO}_x$  conversion efficiency is possible with an improved lean/rich regeneration calibration?
- Can a practical on-engine desulfurization cycle be developed?
- What effect does the desulfurization process have on the long-term performance of the  $\text{NO}_x$  adsorber, and does it vary with fuel sulfur level?

### 1.2 Principle of Operation

A  $\text{NO}_x$  adsorber catalyst is a flow-through emissions control device that has the potential to significantly lower  $\text{NO}_x$ , hydrocarbon (HC), and carbon monoxide (CO) emissions from diesel engine exhaust. Because a  $\text{NO}_x$  adsorber contains high levels of precious metals, it may also be effective in oxidizing the soluble organic fraction of diesel particulate matter (PM).

The  $\text{NO}_x$  adsorber catalyst consists of two principal components: a  $\text{NO}_x$  adsorbent and a three-way catalyst (TWC). The  $\text{NO}_x$  adsorbent is typically an alkali or alkaline earth carbonate that can chemically interact with the  $\text{NO}_2$  and  $\text{O}_2$ , typically in diesel engine exhaust, to form an alkali or alkaline earth nitrate. Precious metals in the TWC are responsible for oxidizing NO to  $\text{NO}_2$ , which facilitates the adsorption process. Periodically,  $\text{NO}_x$  stored by the adsorbent is released and reduced to  $\text{N}_2$ . This process requires a fuel-rich exhaust gas composition and a TWC. These catalysts are typically based on combinations of platinum, palladium, and rhodium, and they can use the reductants (CO,  $\text{H}_2$ , and HC) in rich engine exhaust to reduce  $\text{NO}_x$  selectively to  $\text{N}_2$ . Three-way catalysts have been used for more than 20 years to reduce  $\text{NO}_x$  in the exhaust of stoichiometric gasoline engines.

An engine management system is critical to the operation of a  $\text{NO}_x$  adsorber catalyst system. It is programmed to trigger the change in engine operation that results in generating the rich condition required to release and reduce the stored  $\text{NO}_x$ . The duration and “richness” (defined by the air/fuel ratio) of the rich pulse are also critical. If it is too long and/or too rich, HC and CO can break

through the adsorber. This results in poor control of these pollutants, as well as unnecessary fuel economy penalties.

Combustion in the engine of sulfur compounds in diesel fuel causes sulfur dioxide ( $\text{SO}_2$ ) to form. In a  $\text{NO}_x$  adsorber, this  $\text{SO}_2$  undergoes reactions that are analogous to those of  $\text{NO}_x$ , and alkali and alkaline earth sulfates are formed. Unlike their corresponding nitrates, these sulfates are extremely stable. It has been shown repeatedly in the literature (see, for example, SAE papers numbered 1999-01-1285 and 982594) that the decomposition of these sulfates requires a combination of rich conditions and temperatures exceeding  $600^\circ\text{C}$ . As a result,  $\text{SO}_2$  in the exhaust is a poison for  $\text{NO}_x$  adsorption sites without a properly developed desulfurization cycle.

## Section 2

### Technical Approach

#### 2.1 Test Program Description

The DECSE II NO<sub>x</sub> adsorber project was conducted in three parts. The first involved improving the calibration of the engine management system for NO<sub>x</sub> regeneration, as described below in Tasks 2 and 3. The second focused on developing and demonstrating a process to desulfurize the NO<sub>x</sub> adsorber catalyst. Tasks 4 and 5 address this phase. The final part, presented as Task 6 below, was to provide a preliminary assessment of catalyst durability when exposed to repeated aging and desulfurization cycles.

Each equivalently formulated NO<sub>x</sub> adsorber device was thermally stabilized with 10 hours of degreening (break-in) in engine exhaust at 400°C and aged using the NO<sub>x</sub> regeneration calibration. Next, efforts were made to improve the NO<sub>x</sub> regeneration calibration strategy, by examining the influence of post-injection, exhaust gas recirculation (EGR)/throttling, and lean/rich modulation. The goal was to achieve an 80+% NO<sub>x</sub> conversion efficiency over an operating temperature range of 250°C–500°C.

Development of the desulfurization process was then begun. This involved controlling the air/fuel ratio and catalyst inlet temperature to achieve the high temperatures required to release sulfur from the device. This process was demonstrated on a catalyst poisoned with high-sulfur-level fuel, and on catalyst pairs aged on 3-, 16-, and 30-ppm sulfur fuel in Phase I. The catalyst performance was mapped following desulfurization to determine the recovery in NO<sub>x</sub> conversion. Mapping involved measuring the NO<sub>x</sub> conversion at catalyst inlet temperature of 250°C–500°C in 50°C increments.

All testing was conducted at an engine speed of 3000 rpm. The original intent of the program focused on heavy-duty applications; therefore, this light-duty engine was operated at the highest volume flow levels that could reasonably be maintained for extended periods with this prototype engine. Catalyst demonstration tests were conducted in pairs throughout this project to increase confidence in the data and results.

To investigate the influence of exhaust gas temperature at the catalyst inlet, the engine torque levels that corresponded to catalyst inlet temperatures of 250°C–500°C in 50°C increments were determined. These load levels at each operating point, considering the placement of the NO<sub>x</sub> adsorber catalysts in the exhaust system and test cell boundary conditions, are shown in Table 2.1-1.

**Table 2.1-1. DECSE II Engine Load Test Points**

Catalyst Inlet Temperature [ °C ]	Brake Mean Effective Pressure [ bar ]
250	4.4
300	6.3
350	8.5
400	10.8
450	12.2
500	13.8

The DECSE program supplied several test fuels with various sulfur levels to this project. Most tests were completed using 3-ppm sulfur fuel. A fuel with a higher sulfur level was used to evaluate the influence of sulfur level on the ability to demonstrate successive desulfurizations. Table 2.1-2 shows the sulfur level fuels used in various tasks.

**Table 2.1-2. Test Summary: NO<sub>x</sub> Absorber Catalyst Performance**

Test Purpose	Catalyst	Fuel Sulfur Level (ppm)	Comments
Task 1: Degreening, initial aging	S3, S4, S5, S6, S7, S8	3	S3 & S4 aged 75 hours, all others aged 10 hours
Task 2: Improve calibration to maximize NO <sub>x</sub> conversion	S4	3	
Task 3: Performance mapping	S4, S5, S6 3a, 3b, 16a, 16b, 30a, 30b	3	
Task 4: Develop desulfurization process	S4 (process dev.)  S3 (process check)	3, 380  3, 150	3-ppm used for desulfurization 380-ppm used for contamination; 3-ppm used for desulfurization 150-ppm used for contamination
Task 5: Desulfurization demo/ performance map	3a, 3b, 16a, 16b, 30a, 30b	3	Phase 1 catalysts desulfurized from current state, no additional contamination
Task 6a: Periodic re-evaluation (10 hour aging, map, desulfurization, map: complete 5 cycles)	S5, S6 S7, S8	3 78, 3	S5, S6 all testing with 3-ppm; S7, S8 aging with 78-ppm, desulfurization with 3-ppm
Task 6b: Characterize performance trends (multiple desulfurizations, map: complete 5 cycles)	S7, S8	3	12 desulfurizations were completed between each performance mapping

Notes:

- 3a, 3b, 16a, 16b, 30a, 30b are catalysts from Phase I project, aged with 3-, 16-, and 30-ppm, respectively. S3 and S4 were also used in Phase I (< 50 h accumulated run time).
- S5, S6, S7, S8 were new catalysts at the start of this project
- During desulfurization development and testing, a warm-up catalyst was installed between the engine and the NO<sub>x</sub> adsorber catalyst to achieve the inlet temperatures required to conduct the desulfurizations.

### Task 1: Age Catalysts

The first task to prepare the catalysts for testing involved accumulating run time on catalysts S3 and S4. Although catalyst pair S3 and S4 had been operated during the final stages of DECSE I, it was decided that they should be aged for 75 hours using the final NO<sub>x</sub> regeneration calibration from DECSE I. The engine was operated at 3000 rpm and at six defined catalyst inlet temperatures of 250°C–500°C at 20-minute intervals.

### Task 2: Develop NO<sub>x</sub> Storage and Regeneration Calibration

DECSE I demonstrated that the NO<sub>x</sub> emissions produced by the test engine can be reduced using the catalysts supplied for evaluation, but not to the desired levels or complete temperature range. The objective of Task 2 of DECSE II was to improve the NO<sub>x</sub> regeneration strategy to increase the range of catalyst inlet temperatures over which 80+% NO<sub>x</sub> is converted. Input from the catalyst manufacturer indicated that the performance of the evaluation catalyst may not achieve the 80% conversion target at 250°C; therefore, testing was initiated at a catalyst inlet temperature of 300°C using spare catalyst S4 from the DECSE I program. At the beginning of Task 2, approximately 100 hours of operating time had been accumulated on catalyst S4.

To increase the NO<sub>x</sub> conversion efficiency over the desired temperature range, several parameters (divided principally into two groups) were screened on line. The first focused on engine performance and in-cylinder development of the appropriate exhaust conditions for NO<sub>x</sub> adsorber operation. The second group included variations in the lean/rich modulation to account for the characteristics of the specific NO<sub>x</sub> adsorber being tested. The investigations examined the influences of post-injection, EGR/throttling, and the lean/rich modulation.

During the testing related to engine performance, the HC and CO emissions upstream and downstream of the NO<sub>x</sub> adsorber catalyst, at each catalyst inlet temperature, were of particular interest. Clearly, excessive levels of unburned HCs do not enhance (and could actually impede) the conversion process. Therefore, levels of approximately 0.5% were established as rough target maximums for unburned HCs. The typical unburned HC level for the engine-out rich mode was lower than 0.1% in the final calibration.

The use of post-injection to create the species required for regeneration was scrutinized, especially relative to the production of HC emissions. Unfortunately, a complete investigation of the influence of post-injection was not possible within the scope of this project. In this project, improved conversion efficiencies, relative to a non-optimized post-injection event, were obtained for most of the catalyst inlet temperatures without post-injection. Also, reducing or eliminating post-injection reduced fuel consumption providing more flexibility for improving lean/rich cycle timing.

During the improvement process, the CO emissions upstream and downstream of the catalyst were used to indicate the ability of the exhaust gas stream to reduce desorbed nitrates to N<sub>2</sub>. The following investigations were based on the search for an improved calibration for an appropriate level of CO output. The conflicting goals were to generate sufficient CO upstream of the catalyst for the highest conversion possible and to reduce the breakthrough of CO downstream. This simplified approach facilitated the relatively rapid development of improved conditions for NO<sub>x</sub> regeneration over the temperature window established for this project (250°C–500°C).

The next series of tests to improve the NO<sub>x</sub> regeneration strategy focused more on the characteristics of the catalyst than on engine parameters. The lean and rich operating times at each catalyst inlet temperature point were varied. In general, a simultaneous decrease in lean and rich duration resulted in an improved conversion ratio. Again the goal was to maximize the NO<sub>x</sub> conversion while minimizing the additional fuel needed for desorbing and reducing NO<sub>x</sub> in the rich mode. Adjusting the lean/rich duration ratio allowed a reasonable strategy to be identified to achieve the highest possible conversion but with a limited fuel penalty.

A single catalyst (S4) was installed into one leg of the split exhaust system; a butterfly valve was installed in the other leg to simulate the flow restriction represented by the catalyst. In this approach, the investigation to improve the NO<sub>x</sub> regeneration capability was conducted using only one catalyst.

### **Task 3: Catalyst Performance Tests**

The performance of each catalyst pair aged and evaluated during DECSE I was mapped using the NO<sub>x</sub> regeneration calibration developed under Task 2. These catalysts had been aged for a various number of hours with fuels of various sulfur levels (see Table 2.1-3). The purpose of this task was to establish the baseline performance of each pair using the DECSE II calibration.

**Table 2.1-3. Total Aging Hours on the Catalyst Pairs at the Completion of DECSE I**

Catalyst Pair	Total DECSE I Aging Hours
3a, 3b	250
16a, 16b	200
30a, 30b	150

**Task 4: Develop a Desulfurization Procedure**

Task 4 required the completion of two subtasks: (1) develop a desulfurization procedure according to the requirements recommended by the catalyst manufacturer, particularly regarding the sulfur release temperature; and (2) demonstrate this procedure by desulfurizing a catalyst that had been poisoned to a specific level of NO<sub>x</sub> conversion performance.

The primary conditions controlling the desulfurization process included the relative air/fuel ratio and the catalyst inlet temperature. On the basis of information received from the catalyst supplier, 700°C was targeted as the temperature for release. During the course of the project, several discussions indicated that, at temperatures higher than 800°C, the performance of these catalysts would begin to decline more rapidly. Therefore, the ideal catalyst inlet temperature for desulfurization would be 700°C–800°C. Several researchers have already reported on the desulfurization of NO<sub>x</sub> adsorbers for gasoline applications, and it is clear that richer gas mixtures facilitate more rapid desulfurization, whereas leaner (though still rich) mixtures cause slower desulfurization. Relative air/fuel ratios from 0.7 to 1.0 have been reported as effective for sulfur release. As a compromise, and to avoid development beyond the scope of this work, an air/fuel ratio value of 0.9 was selected.

The scope of work required only that a desulfurization event, rather than a detailed investigation at each operating point for NO<sub>x</sub> conversion, be established for a single operating point. The desulfurization event was developed at an engine load level corresponding to a catalyst inlet temperature of 400°C. This point represented the middle region of the temperature window, considering fuel economy penalty, turbine outlet temperature, and maximum rich-mode CO level.

Defining the target operating point and desired desulfurization conditions was only part of the challenge in removing stored sulfur from the NO<sub>x</sub> trap. Achieving those conditions using only the engine hardware was another important part of the challenge. The front face of the NO<sub>x</sub> adsorber catalysts was about 1.5 m downstream of the turbocharger outlet in this test cell configuration, and there was a significant temperature drop over this exhaust length. Creating engine-out temperature levels high enough to ensure a temperature at or above 700°C at the NO<sub>x</sub> adsorber inlet would apparently be difficult. This is primarily because of the turbine inlet temperature limit for this turbocharger. Although higher temperature turbochargers are conceivable (considering cooled housings and alternative turbine materials), an alternative approach to developing the high temperature required at the NO<sub>x</sub> adsorber inlet was selected.

The approach for generating the high temperature required at the NO<sub>x</sub> adsorber inlet was to use a warm-up catalyst close-coupled to the turbocharger outlet. This catalyst would provide complete or partial oxidation of unburned HCs, thereby developing a large exotherm over the catalyst. This exotherm would be transferred through the exhaust system to the NO<sub>x</sub> adsorber inlet, providing the necessary temperature conditions to release sulfur from the NO<sub>x</sub> trap.



Task 4 included developing the post-injection strategy required to introduce a sufficient level of unburned HCs into the exhaust stream for processing at the warm-up catalyst. The next part of this task was to demonstrate, using this post-injection strategy, that the warm-up catalyst would provide enough of an exotherm to raise the NO<sub>x</sub> adsorber temperature to the target level of 700°C. Finally, with the post-injection strategy providing a temperature level near the target temperature, fine-tuning the post-injection strategy, EGR, and intake air throttling completed the final adjustment of the temperature and relative air/fuel ratio.

As discussed earlier, the second part of Task 4 involved applying the procedure to a sulfur-poisoned catalyst. To meet this requirement, a single catalyst was installed and its performance measured using fuel with 3-ppm sulfur level at the 400°C catalyst inlet temperature operating point. The catalyst then received an accelerated poisoning using fuel with a much higher sulfur level (Amoco Premier, 380-ppm sulfur). This catalyst was operated using the NO<sub>x</sub> regeneration calibration developed under Task 2 until the absolute NO<sub>x</sub> conversion efficiency at the 400°C point dropped to approximately 25% of the initial value. The NO<sub>x</sub> conversion efficiency was measured with only the NO<sub>x</sub> adsorber catalysts installed (no warm-up catalyst).

Then the desulfurization strategy was applied initially for three minutes. Additional tests were run with desulfurization event lengths varying from one to seven minutes. The catalyst was poisoned to a target level of 60% (approximately 25% below the original NO<sub>x</sub> conversion performance at 400°C) between each desulfurization run.

Installing catalyst S3 to demonstrate the efficacy of the desulfurization procedure completed Task 4. The NO<sub>x</sub> conversion efficiency was first measured at the 400°C point. Catalyst S3 was then poisoned using 150-ppm sulfur level DECSE fuel to achieve a conversion efficiency that was reduced by approximately 25%. A six-minute desulfurization event was selected for all subsequent desulfurization testing under this project. This strategy was applied to the poisoned catalyst S3 and the catalyst was subsequently mapped to demonstrate the extent to which NO<sub>x</sub> conversion efficiency can be recovered.

#### **Task 5: Desulfurization of Catalyst**

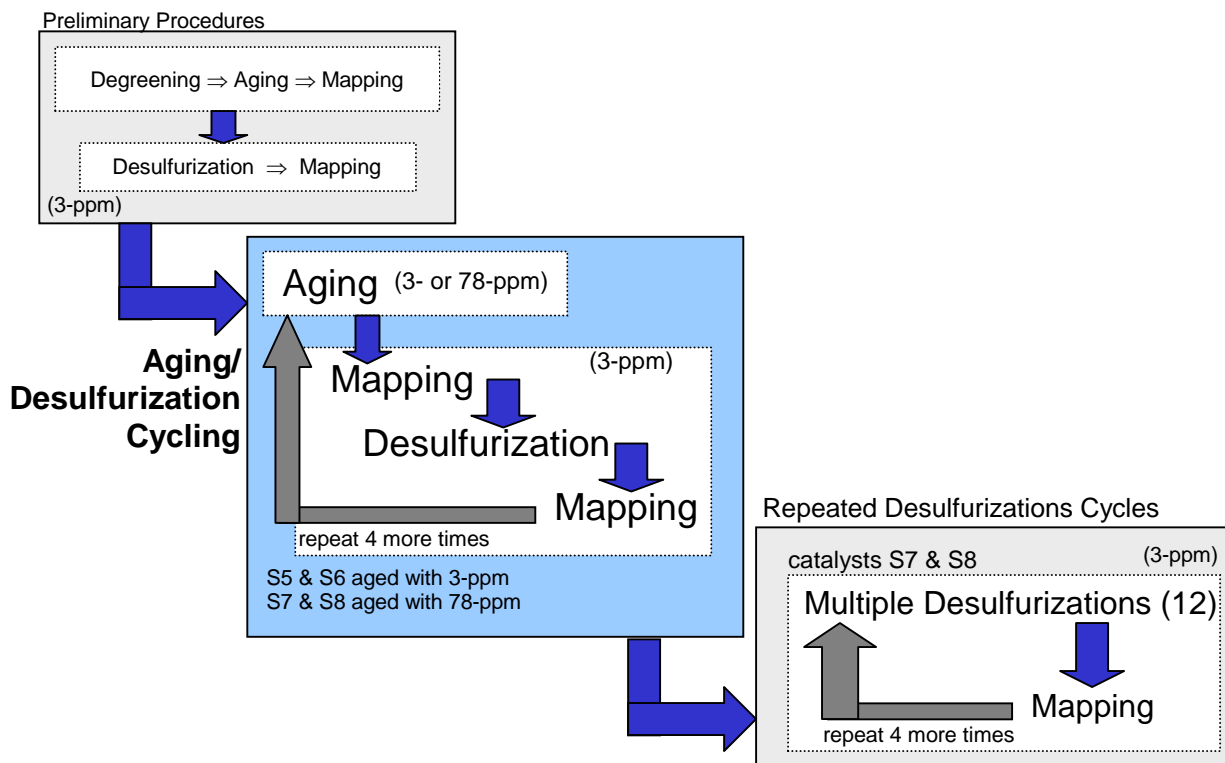
Having been previously mapped for their current NO<sub>x</sub> conversion capability during Task 3, catalyst pairs 3a and 3b, 16a and 16b, and 30a and 30b were subjected to the six-minute desulfurization process developed under Task 4. The warm-up catalyst was then removed so the pair could be mapped with respect to NO<sub>x</sub> conversion efficiency over the designated catalyst inlet temperature window. Each test was conducted using the DECSE-supplied 3-ppm sulfur level fuel.

#### **Task 6: Desulfurization Tests, New Sulfur Levels, and New Catalysts**

The tests conducted under the preceding tasks were designed to demonstrate that the NO<sub>x</sub> adsorber catalyst could indeed be returned to a high level of performance with respect to NO<sub>x</sub> conversion efficiency after exposure to sulfur. The purpose of this task was to provide a preliminary assessment of catalyst durability with exposure to repeated cycles of aging and desulfurization.

The task was split into two parts. In the first, aging was conducted using a 3-ppm sulfur level fuel; in the second a 78-ppm sulfur level fuel was used. Catalyst pair S5 and S6 was used for Part I, and a new catalyst pair (S7 and S8) was used to conduct Part II. Each pair of catalysts underwent the test procedures depicted in Figure 2.1-1.

The catalysts were initially degreened for 10 hours by operating the engine in the conventional lean mode at a constant catalyst inlet temperature of 400°C. After degreening, each catalyst pair was aged for 10 hours while operating the engine using the NO<sub>x</sub> regeneration strategy developed under Task 2. Each step was conducted using a fuel with a 3-ppm sulfur level. After the initial aging, the catalysts were mapped for NO<sub>x</sub> conversion performance over the catalyst inlet temperature range of 250°C–500°C in 50°C increments. Then the warm-up catalyst was installed, the desulfurization process applied, and the NO<sub>x</sub> conversion mapped.



**Figure 2.1-1. Task 6 testing sequence**

Each catalyst pair (S5 and S6; S7 and S8) was subjected to this initial process. The cycle was then reinitiated starting with a 10-hour aging. Aging was conducted using 3-ppm sulfur level fuel for catalysts S5 and S6 and 78-ppm sulfur level fuel for catalysts S7 and S8. Subsequently, the catalysts were mapped, desulfurized, and mapped again. This aging, mapping, desulfurizing, and mapping cycle was then repeated four more times (see Figure 2.1-1).

The original Task 6 scope of work was extended to include several additional tests (final box in Figure 2.1-1). Testing of catalyst pair S7 and S8 continued with multiple consecutive desulfurizations followed by NO<sub>x</sub> conversion mapping. Specifically, 12 consecutive desulfurizations were completed, followed by NO<sub>x</sub> conversion mapping until five mappings had been obtained. This test was designed to expose the NO<sub>x</sub> adsorbers to additional time at high temperature to extend the data collected under this project relative to catalyst performance and durability.

A 1.9-L HSDI diesel engine incorporating a common rail fuel injection system, identical to that used in the DECSE I project, was used for the testing under this project. The basic engine data are shown in the following list:

- The engine was operated using Shell Rotella T lubricating oil and diesel fuels of varying sulfur levels. It was installed into a test cell and equipped with sufficient instrumentation to interrogate the emissions control system and engine operating behavior. Figure 2.2-1 depicts the engine setup and the applied instrumentation.



Several sets of catalysts were delivered for testing under this project. Warm-up catalysts were obtained from the catalyst manufacturer to develop the desulfurization strategy. Four NO<sub>x</sub> adsorber catalyst pairs from the previous DECSE project and two additional new pairs were used to conduct this project. Although the specific formulation applied to these catalysts is proprietary to the supplier, general technical data on these catalysts are provided in Table 2.2-1. The NO<sub>x</sub> adsorber catalyst naming convention and device use in this project have been outlined in Table 2.2-2.

**Table 2.2-1. Technical Information on Catalysts Tested**

<b>NO<sub>x</sub> Adsorber Catalyst</b>	<b>Warm-Up Catalyst</b>
2.5 L volume	2.5 L volume
400 cpsi	400 cpsi
6.5 ml wall thickness ceramic substrates	6.5 ml wall thickness ceramic substrates
5.66 in. by 6 in. round geometry	5.66 in. by 6 in. round geometry
1998 experimental formulation at 164 g/ft <sup>3</sup> Pt:Pd:Rh at 10:3.9:1 ratio	Commercial diesel lean-NO <sub>x</sub> formulation at 70g/ft <sup>3</sup> , Pt only

**Table 2.2-2. NO<sub>x</sub> Adsorber Catalyst Summary**

<b>Catalyst Name</b>	<b>Utilization</b>
3a and 3b	DECSE I: Aged 250 hours with 3-ppm sulfur level fuel DECSE II: Demonstration of desulfurization procedure under Tasks 3 and 5
16a and 16b	DECSE I: Aged 200 hours with 16-ppm sulfur level fuel DECSE II: Demonstration of desulfurization procedure under Tasks 3 and 5
30a and 30b	DECSE I: Aged 150 hours with 30-ppm sulfur level fuel DECSE II: Demonstration of desulfurization procedure under Tasks 3 and 5
S3 and S4	DECSE I: Development of NO <sub>x</sub> regeneration calibration DECSE II: S4 used to develop the NO <sub>x</sub> regeneration strategy under Task 2; S4 and S3 used to develop desulfurization strategy under Task 4
S5 and S6	DECSE II: Utilized to complete Task 6 Part I
S7 and S8	DECSE II: Utilized to complete Task 6 Part II

A test cell automation system was used to perform several functions during the testing process. It controlled the eddy current dynamometer used to absorb engine power. It also performed the critical role of low-speed data acquisition. Signals from various pieces of pressure, temperature, and flow measurement equipment were fed into the system and sampled at a rate of 10 Hz for storage during testing. System digital inputs and outputs were also used to control various features of the test setup, including exhaust system pressure, intercooler outlet temperature, engine coolant temperature, and several pieces of measurement equipment (e.g., smoke meter emission bench).

The emissions data were sampled using a Horiba MEXA 7000 system. The exhaust sample is routed from one of three sampling locations (upstream both catalysts or downstream one or the other catalyst) via a completely heated sample line with filter. The heated sample continues to a hot flame ionization detector while a dry portion is routed to additional analyzers for NO<sub>x</sub>, CO<sub>2</sub>, CO, and O<sub>2</sub>.

## 2.3 Data Handling and Analyses Methodology

The primary data reported during this project include (1) NO<sub>x</sub> conversion efficiency and (2) fuel economy penalty during the lean/rich modulation cycle. Procedures for handling these data are described in Section 2.3.1. These methods were used to generate data to demonstrate the performance of the improved engine calibration and desulfurization processes, and to conduct a formal statistical evaluation of the performance of the NO<sub>x</sub> adsorber catalysts under repeated aging and desulfurization cycles. The statistical analysis approach used in this evaluation is described in Section 2.3.2.

### 2.3.1 Data Handling Procedures

For the purposes of this project the NO<sub>x</sub> conversion efficiency (CE) of the NO<sub>x</sub> adsorber was defined and calculated as follows:

The NO<sub>x</sub> concentration upstream of the NO<sub>x</sub> adsorber, sampled at a rate of 10 Hz, was averaged over seven cycles of the lean/rich modulation to obtain the average NO<sub>x</sub> level upstream of the catalyst. The same calculation was completed based on the NO<sub>x</sub> concentration signal downstream of one or both NO<sub>x</sub> adsorber catalysts, depending on the hardware installed. A percentage difference defined as the NO<sub>x</sub> conversion efficiency was calculated at each operating condition, as defined by the catalyst inlet temperature, based on these average values as follows:

$$NO_x \text{ Conversion Efficiency} [\%] = \frac{\text{Average } NO_x \text{ Upstream} - \text{Average } NO_x \text{ Downstream}}{\text{Average } NO_x \text{ Upstream}} \times 100 \quad (1)$$

The fuel economy penalty (FEP) was similarly calculated as a percent difference between the brake specific fuel consumption (BSFC) in g/kWh averaged during seven cycles of the lean/rich modulation and the BSFC measured only in the lean mode at the same operating point. The following equation was used to determine the FEP:

$$FEP [\%] = \frac{\text{Average } BSFC_{\text{lean/rich modulation}} - \text{Average } BSFC_{\text{lean mode}}}{\text{Average } BSFC_{\text{lean mode}}} \times 100 \quad (2)$$

### 2.3.2 Statistical Analysis Methodology

Statistical analyses were performed to characterize the performance of the NO<sub>x</sub> adsorber catalyst during repeated cycles in which the catalysts were aged for 10 hours with 3-ppm or 78-ppm sulfur fuel, then desulfurized for six minutes with 3-ppm sulfur fuel. The primary objectives for the statistical analysis were as follows:

1. Determine whether there are significant trends in the post-desulfurization NO<sub>x</sub> CE over time, and investigate how operating temperature and fuel sulfur level affect performance. If there are significant trends in post-desulfurization NO<sub>x</sub> CE over time, characterize these trends and determine whether performance stabilizes.

2. Determine whether there are changes in the NO<sub>x</sub> CE caused by aging, and whether the changes are affected by fuel sulfur level, operating temperatures, or number of aging/desulfurization cycles (test cycles).

### Data Collected

Initially, the study design consisted of a series of six, 10-hour aging and six-minute desulfurization cycles conducted on two pairs of catalysts. Catalysts S5 and S6 were aged with 3-ppm sulfur fuel and the catalysts S7 and S8 with 78-ppm sulfur fuel. A mapping of NO<sub>x</sub> CE versus temperature followed each aging and desulfurization cycle. Data consisted of NO<sub>x</sub> CE at operating temperatures of 250°C–500°C following each aging or desulfurization cycle. The first aging cycle for catalysts S7 and S8 was conducted with 3-ppm sulfur fuel instead of 78-ppm sulfur fuel. Therefore, data from the first test cycle were not used in this statistical analysis.

Because of trends observed in post-desulfurization NO<sub>x</sub> CE during the first six aging/desulfurization cycles, additional desulfurizations were performed on catalysts S7 and S8 to further characterize the trends and determine whether the catalysts stabilized. They were performed in five groups of 12 consecutive desulfurizations. NO<sub>x</sub> CE mappings at temperatures of 250°C–500°C were performed after each group of desulfurizations. The purpose of these tests was to characterize the trends over a longer period and, in particular, determine whether performance stabilized.

### Statistical Analysis Approach

The statistical analysis approach was based on a general linear model that simultaneously considers the effects of desulfurization time and operating temperature on the NO<sub>x</sub> CE (Objective 1, as described above), as well as the change in NO<sub>x</sub> CE caused by aging (Objective 2). Interactions of desulfurization time, operating temperature, and aging fuel sulfur level were also evaluated. Initially, Objectives 1 and 2 were addressed using data from the six aging/desulfurization cycles. Additional analyses related to Objective 1 were performed using the supplemental data from the five groups of 12 consecutive desulfurizations on catalysts S7 and S8.

Statistical analyses were performed using the PROC MIXED (mixed model analysis of variance [ANOVA]) procedure in the Statistical Analysis System (SAS<sup>®</sup>) software package. A “mixed” model means that some factors, such as aging time and fuel sulfur level, have fixed additive effects on NO<sub>x</sub> CE and others (e.g., differences among catalysts, measurement error) have random effects. All references to statistical significance are at the p=0.05 level unless otherwise specified.

To investigate how the post-desulfurization NO<sub>x</sub> CE depends on desulfurization time (or number of aging/desulfurization cycles), aging fuel sulfur level, and operating temperature, we started with the following three-way ANOVA model:

$$Y = \mu + S + t + T + S*t + S*T + T*t + S*T*t + C_R + E, \quad (3)$$

where:

Y = the post-desulfurization NO<sub>x</sub> CE

$\mu$	=	a constant
S, t, and T	=	the (fixed) effects of fuel sulfur level, desulfurization time, and operating temperature, respectively
S*t	=	the interaction of fuel sulfur level and time
S*T	=	the interaction of fuel sulfur level and temperature
t*T	=	the interaction of time and temperature
S*T*t	=	the interaction of fuel sulfur level, temperature, and time
$C_R$	=	the (random) effect of differences in catalysts
E	=	the (random) effect of measurement and testing errors

(NOTE: This is a symbolic representation of the ANOVA model. For simplicity, the coefficients of the various factors and interactions are not shown.)

The model did not assume that the estimates of variance components for measurement/testing error and catalyst-to-catalyst differences were the same for each type of fuel tested.

When the fuel sulfur level and several of the interaction terms involving fuel sulfur level were found to be statistically significant, performing the analysis separately for data obtained with each fuel was more practical. In this case, the analysis involved fitting the following two-way ANOVA independently to data for each sulfur fuel:

$$Y = \mu + T + t + T*t + C_R + E \quad . \quad (4)$$

The notations in this equation have the same meaning as those defined in equation (3).

If any interaction terms involving time, temperature, and fuel sulfur level were found to be statistically significant, post-hoc statistical tests were performed to further characterize these interactions. For example, if time-temperature interaction was significant, the post-hoc analysis determined at which times the post-desulfurization  $\text{NO}_x$  CE differed significantly among temperatures, as well as at which temperature levels the post-desulfurization  $\text{NO}_x$  CE differed significantly among times. However, if an estimated interaction term was not statistically significant, it was removed from the ANOVA model before the conversion efficiencies were predicted.

A similar approach was used to evaluate the changes in  $\text{NO}_x$  CE caused by aging or desulfurization. For the aging effects, the dependent variable in the statistical model was calculated as the  $\text{NO}_x$  CE following 10 hours of aging minus the  $\text{NO}_x$  CE following the previous desulfurization cycle. To evaluate the changes in  $\text{NO}_x$  CE caused by desulfurization, the dependent variable was calculated as the  $\text{NO}_x$  CE following desulfurization minus the  $\text{NO}_x$  CE following the previous aging cycle. In addition to the ANOVA approach, a simple linear regression model was fit to the changes in  $\text{NO}_x$

CE to characterize any trends with respect to desulfurization time or, equivalently, number of test cycles.

To evaluate the longer term effects of repeated desulfurization cycles, a generalized regression model was fit to post-desulfurization NO<sub>x</sub> CE data from catalysts S7 and S8 (78-ppm sulfur fuel). The form of this regression model was

$$\ln(Y) = \mu + \beta \ln(t) + C_R + E, \quad (5)$$

where:

$\ln(Y)$  = the natural logarithm of the temperature-integrated NO<sub>x</sub> CE

$\mu$  and  $\beta$  = constants

$\ln(t)$  = the natural logarithm of total desulfurization time (minutes)

$C_R$  and  $E$  = the random effects of catalysts and measurement error, respectively

The regression and ANOVA models were used to (1) determine whether various effects were statistically significant (different from zero), (2) determine predicted values (estimated average values), and (3) characterize the uncertainty in the predicted values using 95% confidence intervals.



## Section 3

### Results and Discussion

The DECSE II NO<sub>x</sub> adsorber project was conducted in three main parts, each addressing one of the project study questions outlined in Section 1. The first part of the DECSE II NO<sub>x</sub> adsorber test project set out to improve the calibration of the engine management system. The goal was to improve the calibration developed in DECSE I, achieving a NO<sub>x</sub> conversion efficiency of at least 80% across engine operating temperatures of 250°C–500°C when operating with the 3-ppm sulfur base fuel. The second part was to develop a process to desulfurize the NO<sub>x</sub> adsorber catalyst. The desulfurization process is run periodically to rid the catalyst of sulfur and restore the NO<sub>x</sub> conversion efficiency of the device. The final part was to provide a preliminary assessment of catalyst durability when exposed to repeated aging and desulfurization cycles. The results that follow are presented in three sections, each focused on addressing one study question of this project.

#### *3.1 Development of Improved Engine Calibration*

Using the final NO<sub>x</sub> regeneration calibration developed during the DECSE I program (referred to as the DECSE I calibration), catalysts S3 and S4 were aged for 75 hours. All other catalysts (S5, S6, S7, and S8) were degreened for 10 hours and then aged for 10 hours using the NO<sub>x</sub> regeneration strategy developed in this test program.

Developing an improved NO<sub>x</sub> regeneration calibration to demonstrate maximum NO<sub>x</sub> conversion efficiency while limiting the fuel economy penalty to 4% was a critical objective of the test program. To evaluate the relative effectiveness of the various engine calibrations used for the rich portion of the lean/rich modulation, the NO<sub>x</sub> conversion efficiency of catalyst S4 was measured at a catalyst inlet temperature of 400°C. The final DECSE I calibration was used as a starting point. From here, post-fuel injection, EGR, and various lean/rich modulations were investigated.

The final rich engine calibration and regeneration strategy selected for the remainder of this program, as run at 400°C, used:

- no post-combustion fuel injection
- an EGR rate of 14%–39%
- a lean/rich modulation of 25s/2.2s

This resulted in a fuel economy penalty of 3.98% and a NO<sub>x</sub> conversion efficiency of approximately 83% for catalyst S4 at an inlet temperature of 400°C. At this point in the test program catalyst S4 had accumulated 230 hours of operation on fuel containing 3-ppm sulfur.

This strategy was modified for the entire engine operating temperature window (see Table 3.1-1). In the table, this intermediate DECSE II calibration is compared to the DECSE I regeneration strategy.

**Table 3.1-1. DECSE II NO<sub>x</sub> Regeneration Intermediate Calibration Parameters**

Parameter	Unit	250°C DECSE I		250°C DECSE II		300°C DECSE I		300°C DECSE II		350°C DECSE I		350°C DECSE II	
		Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich
Fresh Air	mg / stroke	700	230	700	260	709	209	700	386	762	362	722	470
Beginning of Main Injection	°CA	7.38	10.3	6.1	5.0	12.6	10.4	7.99	7.99	13.5	10.5	12.86	13.5
Quantity of Main Injection	mm <sup>3</sup>	20.00	18.50	15.04	21.09	25.80	32.00	20.50	33.89	31.60	31.30	26.87	48.95
Beginning of Post Injection	°CA	0	-40	na	na	0	-70	na	na	0	-71	na	na
Quantity of Post Injection	mm <sup>3</sup>	0	6.00	na	na	0	3.00	na	na	0	3.00	na	na
Lean/Rich Duration	sec.	60	3	30	1.5	60	3.5	30	3	60	4	20	2
EGR	%	0	67	0	74	10	73	11	51	10	57	15	54

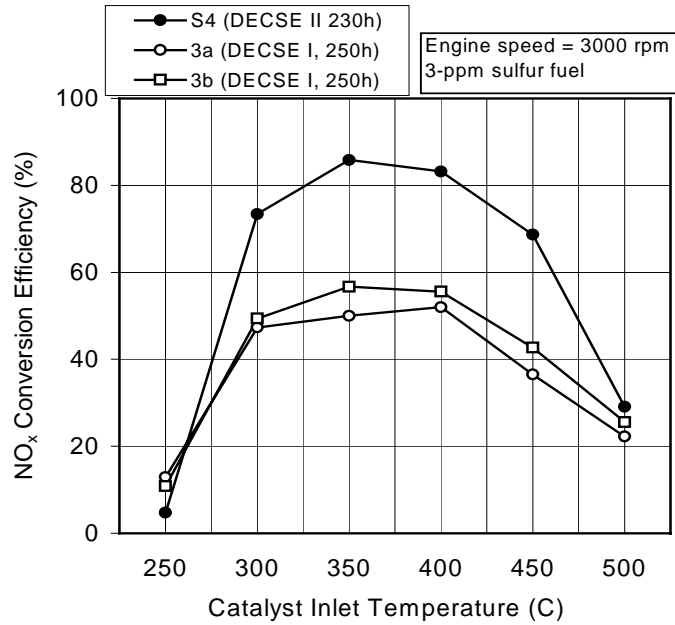
Parameter	Unit	400°C DECSE I		400°C DECSE II		450°C DECSE I		450°C DECSE II		500°C DECSE I		500°C DECSE II	
		Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich
Fresh Air	mg / stroke	835	600	771	570	850	600	830	570	850	650	850	680
Beginning of Main Injection	°CA	13.5	10.5	13.5	17.0	13.5	10.5	13.5	20	13.5	10.5	13.50	10.5
Quantity of Main Injection	mm <sup>3</sup>	38.60	37.20	32.80	58.14	44.30	43.20	37.98	66.15	51.20	46.00	47.19	68.93
Beginning of Pilot Injection	°CA	0	-70	na	na	0	-70	na	na	0	-78	na	na
Quantity of Post Injection	mm <sup>3</sup>	0	30.00	na	na	0	24.00	na	na	0	18.00	na	na
Lean/Rich duration	sec.	60	4	25	2.2	60	4	30	2.2	70	4	70	4
EGR	%	7	33	14	39	0	29	2	32	0	24	0	20

Using the calibration from Table 3.1-1, NO<sub>x</sub> conversion performance of catalyst S4 over the entire temperature window was mapped (see Figure 3.1-1). Also shown are results found in DECSE I for catalysts 3a and 3b, which had also accumulated a comparable number of operating hours (250 compared to catalyst S4, which had accumulated 230) using 3-ppm sulfur fuel.

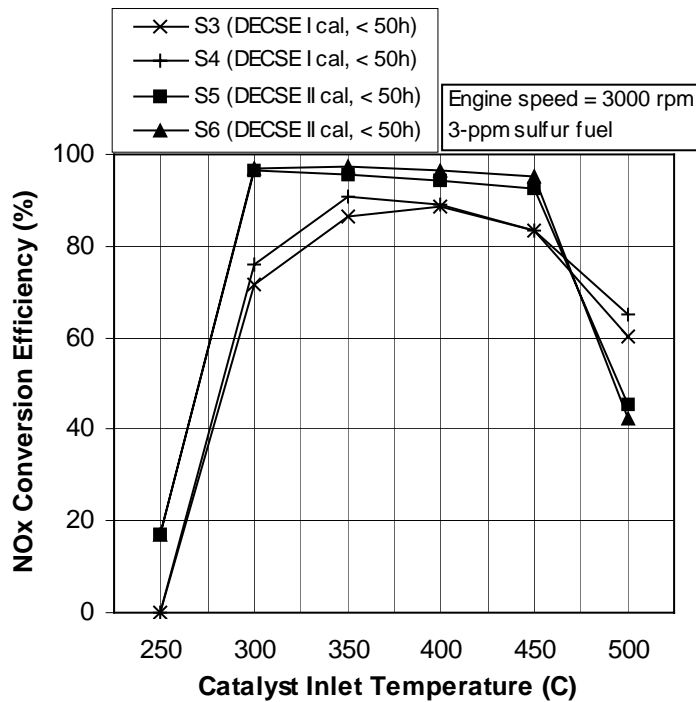
The NO<sub>x</sub> conversion performance of catalyst S4 using the newly developed NO<sub>x</sub> regeneration strategy is significantly superior to that of catalysts 3a and 3b using the final DECSE I NO<sub>x</sub> regeneration strategy. Catalysts S4, 3a, and 3b have accumulated a similar number of operating hours using 3-ppm sulfur fuel.

The NO<sub>x</sub> regeneration strategy significantly improved the NO<sub>x</sub> conversion efficiencies, especially in the mid-range of the investigated temperature window. The results indicated that the performance of a catalyst with many operating hours could be improved; however, there was no indication of how catalysts with relatively few hours would perform. To determine this, a new pair of catalysts, S5 and S6, were degreened, aged for 10 hours, and tested.

The results of the mapping of catalyst pair S5 and S6 are shown in Figure 3.1-2. For comparison, DECSE I results for similarly aged catalysts S3 and S4 (<50 hours) are also shown. Compared with the previous results found for catalysts S3 and S4, the newer calibration operated with catalysts S5 and S6 resulted in higher conversion efficiencies over a wide temperature range.

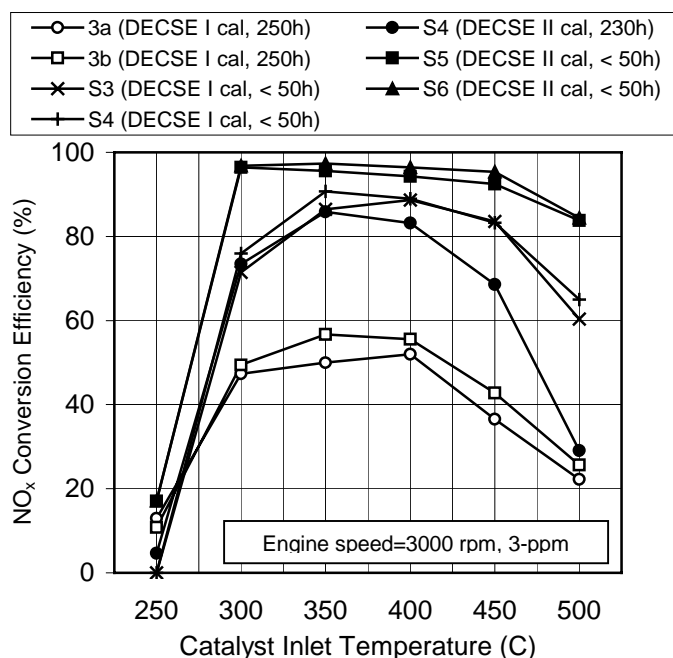


**Figure 3.1-1. Comparison of catalysts with similar operating hours using the final calibration from DECSE I and the calibration developed under Task 2 of this project**



**Figure 3.1-2. Comparison of NO<sub>x</sub> regeneration strategies with catalysts having similar engine hours (<50 hours)**

At this point, only the calibration for the catalyst inlet temperature point of 500°C failed to meet expectations regarding conversion efficiency. After reviewing the data obtained at 500°C with catalysts S5 and S6, we decided that additional conversion was possible with further modifications to the NO<sub>x</sub> regeneration strategy because the catalyst exhibited highly effective lean mode NO<sub>x</sub> storage capability. Additional investigations were conducted to improve the conversion behavior at 500°C. This work resulted in very good NO<sub>x</sub> conversion efficiencies as a function of catalyst inlet temperature at an engine speed of 3000 rpm. A summary of the final conversion efficiencies compared to previous testing is shown in Figure 3.1-3, where conversions in excess of 90% at operating temperatures of 300°C–450°C and in excess of 80% at 500°C were found.



**Figure 3.1-3. Comparison of NO<sub>x</sub> conversion efficiency results from regeneration calibrations from DECSE I and II**

The final NO<sub>x</sub> regeneration calibration carried forward throughout the remainder of the test program is listed in Table 3.1-2. These parameters were modified at both the 350°C point for the lean mode duration, and at the 500°C point for the lean mode duration, beginning of injection (BOI), and EGR level.

Typical exhaust, catalyst and engine parameters measured during the catalyst monitoring efforts are shown in Table 3.1-3. Since the engine-out exhaust is split 50/50 to the two catalyst samples, the tailpipe emissions data reflects the concentration-calculated output from each catalyst separately (i.e., half of the mass emissions are coming out of each sample). The NO<sub>x</sub> adsorber data corresponds to the top two curves in Figure 3.1-3. The engine-out NO<sub>x</sub> levels vary between 4.9 and 9.1 g/kW-hr (3.6 to 6.8 g/bhp-hr), with NO<sub>x</sub> efficiencies of the adsorber over 93% efficient between 300°C and 450°C and over 80% efficient above 250°C. In addition to the high efficiency for NO<sub>x</sub>, the adsorber is also very efficient for CO (>90%) and even moderately efficient (33% on average) for HC. Oxygen is consumed in the oxidation of the CO and HC, and the carbon dioxide increases as a

result. Catalyst inlet and outlet temperatures and pressures are included in the table. The overall exothermic process results in the outlet temperature being 3°C to 40°C higher than the inlet temperature. EGR varies from 8% to 15%. The large Lambda values show the overall lean engine operation and the power and torque readings show the engine is operating across much of its full capacity/operating range.

The next task was to operate each of the three catalyst pairs from the DECSE I program using the calibration from Table 3.1-2. The catalyst pair aged for 250 hours under DECSE I with 3-ppm fuel sulfur maintained strong performance using the DECSE II calibration. These results are shown in Figure 3.1-4. Compared to the final DECSE I calibration, the NO<sub>x</sub> conversion efficiencies were improved by 20% or more between 300°C and 450°C. The catalysts exhibited the highest conversion efficiency at 300°C by reaching approximately 80% absolute conversion.

**Table 3.1-2. DECSE II NO<sub>x</sub> Regeneration Calibration Final Parameters**

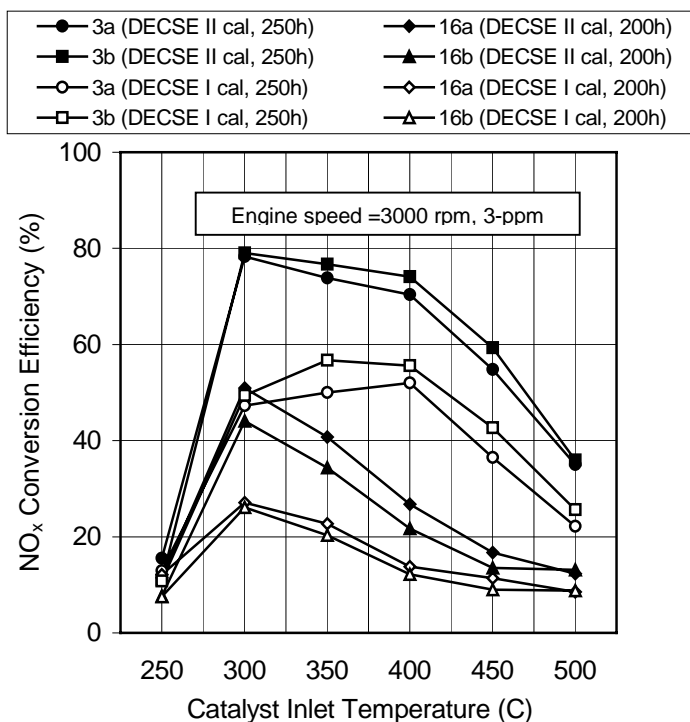
Parameter	Unit	250°C DECSE I		250°C DECSE II		300°C DECSE I		300°C DECSE II		350°C DECSE I		350°C DECSE II	
		Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich
Fresh Air	mg / stroke	700	230	700	260	709	209	700	386	762	362	722	470
Beginning of Main Injection	°CA	7.38	10.3	6.1	5.0	12.6	10.4	7.99	7.99	13.5	10.5	12.86	13.5
Quantity of Main Injection	mm <sup>3</sup>	20.00	18.50	15.04	21.09	25.80	32.00	20.50	33.89	31.60	31.30	26.87	48.95
Beginning of Post Injection	°CA	0	-40	na	na	0	-70	na	na	0	-71	na	na
Quantity of Post Injection	mm <sup>3</sup>	0	6.00	na	na	0	3.00	na	na	0	3.00	na	na
Lean/Rich Duration	sec.	60	3	30	1.5	60	3.5	30	3	60	4	30	2
EGR	%	0	67	0	74	10	73	11	51	10	57	15	54
Parameter	Unit	400°C DECSE I		400°C DECSE II		450°C DECSE I		450°C DECSE II		500°C DECSE I		500°C DECSE II	
		Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich	Lean	Rich
Fresh Air	mg / stroke	835	600	771	570	850	600	830	570	850	650	850	595
Beginning of Main Injection	°CA	13.5	10.5	13.5	17.0	13.5	10.5	13.5	20	13.5	10.5	13.50	18
Quantity of Main Injection	mm <sup>3</sup>	38.60	37.20	32.80	58.14	44.30	43.20	37.98	66.15	51.20	46.00	47.19	68.93
Beginning of Pilot Injection	°CA	0	-70	na	na	0	-70	na	na	0	-78	na	na
Quantity of Post Injection	mm <sup>3</sup>	0	30.00	na	na	0	24.00	na	na	0	18.00	na	na
Lean/Rich duration	sec.	60	4	25	2.2	60	4	30	2.2	70	4	35	3
EGR	%	7	33	14	39	0	29	2	32	0	24	0	30

The catalyst pair aged with 16-ppm fuel sulfur under DECSE I exhibited similar characteristics when operated with the DECSE II calibration (see Figure 3.1-4). The maximum conversion efficiency occurred at 300°C, although the absolute level was reduced by approximately 25% compared to catalysts 3a and 3b. Also, the increase in performance comparing the two NO<sub>x</sub> regeneration calibrations is less significant for the catalyst aged at the higher sulfur level.

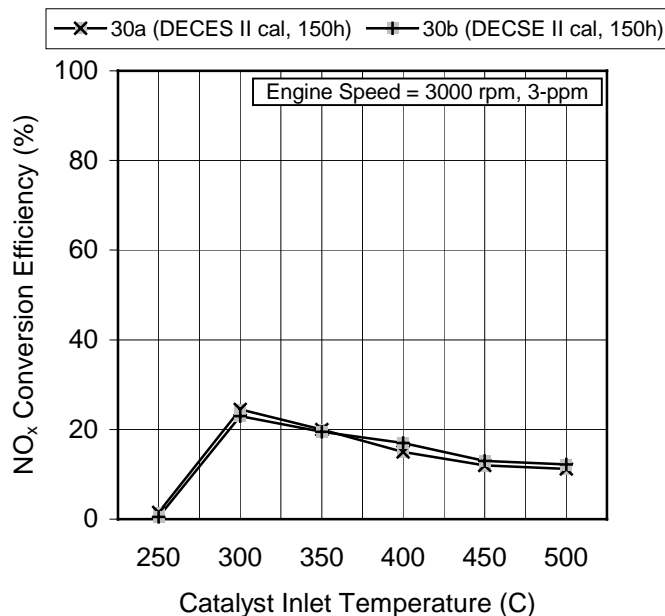
**Table 3.1-3. Exhaust, Catalyst and Engine Parameter Data Integrated over Seven Lean/Rich Cycles**

Nominal Exhaust Temp. (°C)	Data Source*	NO <sub>x</sub> (g/kW·hr)	CO (g/kW·hr)	HC (g/kW·hr)	CO <sub>2</sub> (g/kW·hr)	O <sub>2</sub> (g/kW·hr)	Catalyst Temperature (°C)	Catalyst Pressure (bar [abs])	EGR (%)	BMEP (bar)	Lambda	BSFC (g/kW·hr)	Power (kW)	Torque (N·m)
250	engine-out	4.95	9.63	0.388	986	1784	262 (inlet)	1.04 (inlet)	13.7	4.4	2.81	283	21.2	68
	tailpipe	2.02	0.29	0.106	502	884	265 (outlet)	1.02 (outlet)						
	efficiency	18.1	93.8	46.4	-2.1	0.51								
300	engine-out	4.86	26.71	0.833	877	1010	321 (inlet)	1.04 (inlet)	14.5	6.4	2.08	263	30.9	98
	tailpipe	0.08	1.36	0.237	466	499	343 (outlet)	1.02 (outlet)						
	efficiency	96.6	90.1	44.4	-4.9	2.04								
350	engine-out	7.68	31.28	0.342	825	668	360 (inlet)	1.05 (inlet)	13.3	8.5	1.75	247	41.2	131
	tailpipe	0.14	0.28	0.099	441	320	394 (outlet)	1.02 (outlet)						
	efficiency	96.5	98.2	42.3	-6.8	4.13								
400	engine-out	8.17	21.97	0.241	801	492	411 (inlet)	1.05 (inlet)	13.4	10.6	1.56	237	51.4	164
	tailpipe	0.19	0.22	0.075	419	240	448 (outlet)	1.03 (outlet)						
	efficiency	95.4	98.0	38.9	-4.5	2.52								
450	engine-out	9.08	18.96	0.204	795	424	447 (inlet)	1.06 (inlet)	9.5	12.1	1.49	234	58.6	187
	tailpipe	0.29	0.31	0.106	416	202	485 (outlet)	1.03 (outlet)						
	efficiency	93.7	96.7	-2.2	-4.6	4.52								
500	engine-out	8.96	23.05	0.361	791	311	497 (inlet)	1.06 (inlet)	7.9	13.5	1.35	235	65.4	208
	tailpipe	0.68	0.80	0.122	411	150	537 (outlet)	1.03 (outlet)						
	efficiency	84.6	93.1	32.5	-4.3	3.38								
<p>* Tailpipe emissions are the concentrations from each catalyst. Thus, they represent 50% of engine-out levels.</p> <p>Other Notes:</p> <ol style="list-style-type: none"> <li>1. Data are derived from monitoring of catalysts S5 and S6 after engine management calibration optimization on 3-ppm sulfur fuel.</li> <li>2. Data correspond to the top two curves for NO<sub>x</sub> efficiency in Figure 3.1-3, averaging up to 266 0.1-second data points for S5 and S6 results at each temperature.</li> </ol>														

Unfortunately, catalysts 30a and 30b were not operated using the final DECSE I calibration during the former project; therefore, results are only included in Figure 3.1-5 for the DECSE II calibration. Even with the new calibration, they depict a catalyst that is essentially completely poisoned by sulfur, reaching peak conversion efficiencies of only about 20%.



**Figure 3.1-4. Comparison of NO<sub>x</sub> conversion efficiency results for catalysts 3a and 3b and 16a and 16b using DECSE I and II regeneration calibration**



**Figure 3.1-5. Comparison of NO<sub>x</sub> conversion efficiency results for catalysts 30a and 30b using DECSE II regeneration calibration**

### 3.2 *Development of a Desulfurization Process*

The results of developing the desulfurization procedure will be separated into two sections. First described is the process of demonstrating the exotherm over the warm-up catalyst to achieve the high catalyst inlet temperatures necessary to release sulfur. Tests corresponding to these results were conducted with only the warm-up catalyst installed using “dummies” to replace the NO<sub>x</sub> adsorbers. The second part, which relates to developing the desulfurization procedure, concerns identifying the time required to complete the desulfurization event under constant engine operating conditions.

The desulfurization development was targeted toward a single NO<sub>x</sub> adsorber catalyst inlet temperature to limit the effort required. The desulfurization events were developed for a single engine speed and load operating point so the catalyst inlet temperature would be 400°C.

The initial tests conducted under this program to identify a suitable desulfurization strategy included evaluating various EGR levels and post-injection quantities intended for oxidation over the “warm-up” catalyst.

To develop the desulfurization procedure, EGR was reduced in three stages, conducting post-injection quantity variations at each level. Using an EGR rate of 28.3%, a catalyst inlet temperature of 700°C is achieved 90–180 seconds after initiating the desulfurization, depending on the post-injection quantity. Although this is relatively slow compared with the overall time frame anticipated for desulfurization, further decreasing the EGR rate during desulfurization can reduce the time.

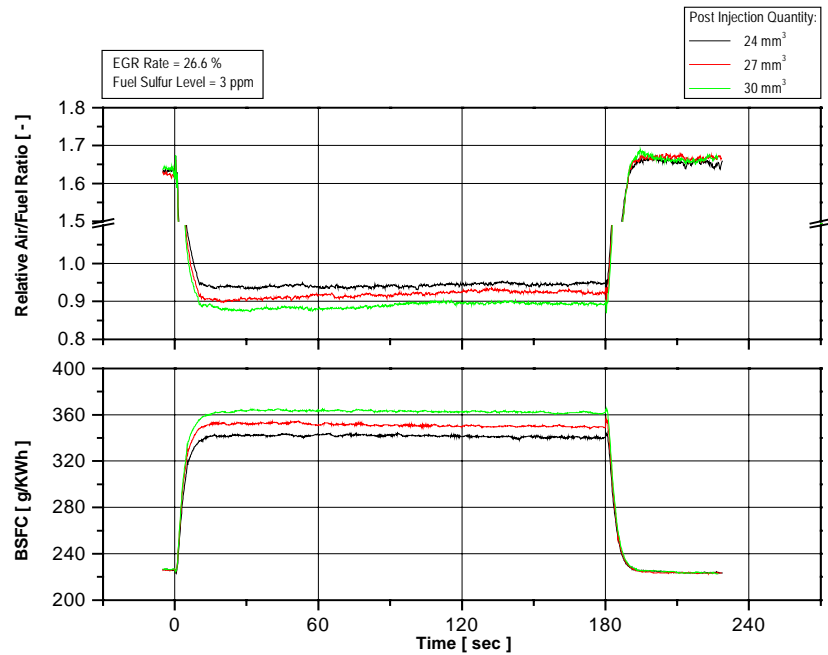
The EGR rate selected was the lowest tested, about 26.6%. Although lower EGR rates may further reduce the time to reach temperature, they would also increase the relative air/fuel efficiency requiring a higher post-injection quantity. Figure 3.2-1 shows that to achieve the desired relative air/fuel efficiency, a post-injection quantity of 30 mm<sup>3</sup>/stroke is necessary, so this value was selected for the desulfurization strategy.

The desulfurization procedure, developed for the 400°C catalyst inlet temperature operating point, considered basic issues with respect to driveability and operator acceptance. Clearly, large torque output variations are not acceptable when the engine management system initiates the desulfurization. Therefore, the strategy was developed to limit the variation in torque output at the beginning, during, and at the end of the desulfurization.

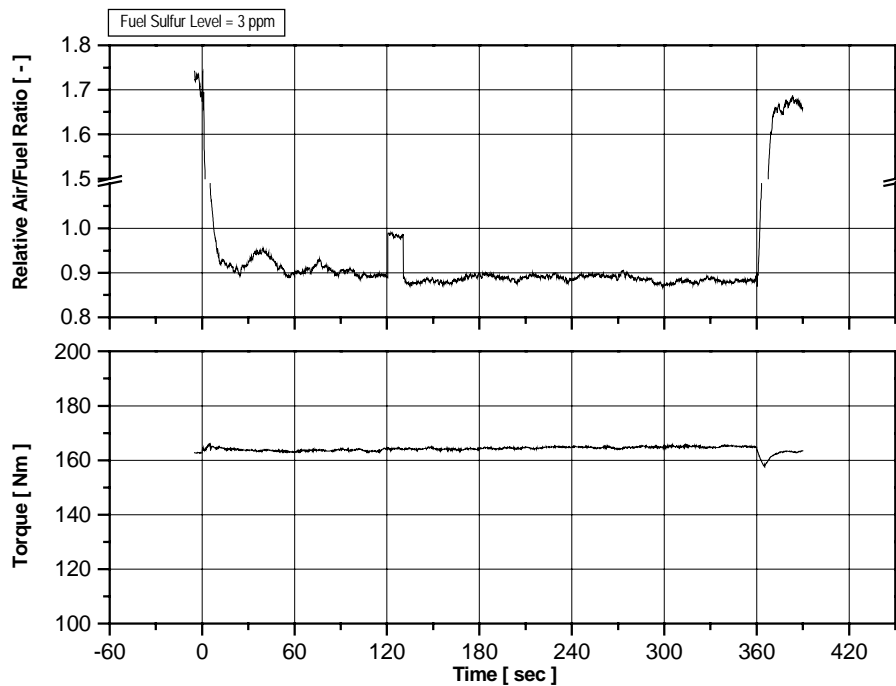
Figure 3.2-2 depicts the results of a typical desulfurization obtained during the desulfurization of catalysts 3a and 3b under Task 5. Although the procedure developed is far from optimized, the figure indicates that the torque variation can be limited to about 1% of the actual torque level. With further development and refinement, the torque fluctuations during these transitions could be even lower.

In the testing, the warm-up catalyst was installed directly on the turbine outlet in a close-coupled configuration. However, because the project required two catalysts to be tested in parallel, the NO<sub>x</sub> adsorber catalysts were installed downstream in a split leg configuration. The resulting distance from the outlet of the warm-up catalyst to the inlet of the NO<sub>x</sub> adsorber was approximately 1.5 meters. This resulted in a large temperature drop between the two and required high outlet temperatures from the warm-up catalyst.





**Figure 3.2-1. The influence of post-injection quantity on the desulfurization process for an EGR rate of 26.6%**



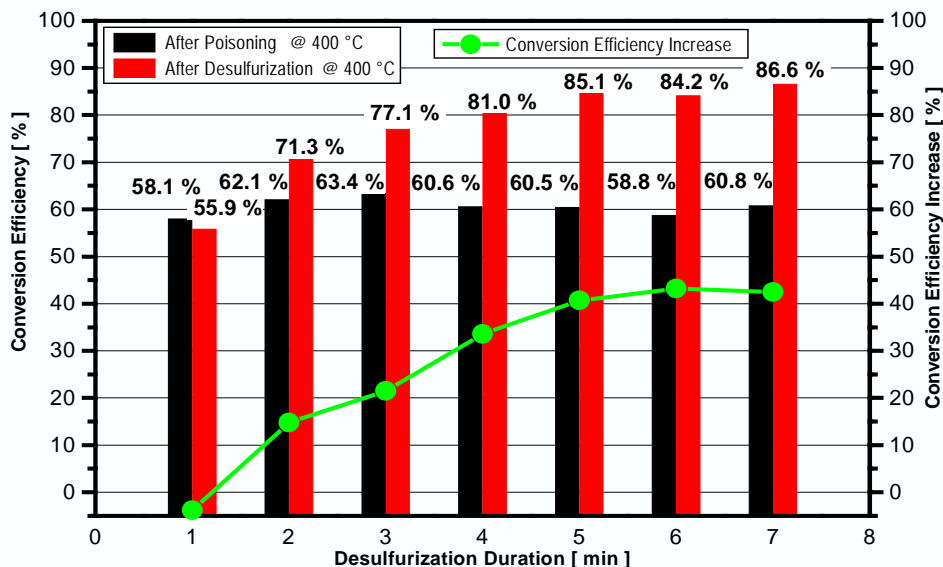
**Figure 3.2-2. Typical torque variation during desulfurization**

With the conditions for sulfur regeneration defined, we had to determine what desulfurization event duration was required to return the  $\text{NO}_x$  adsorber catalysts to a previously high level of  $\text{NO}_x$

conversion efficiency following a defined contamination event. Catalyst S4 was used to confirm the correct period of time.

Catalyst S4 was installed and mapped to measure the NO<sub>x</sub> conversion efficiency at a catalyst inlet temperature of 400°C. A NO<sub>x</sub> conversion efficiency of 80% was found. A drop in conversion efficiency of 25% was selected as the contamination level for desulfurization testing. The catalyst was then systematically poisoned through operation on a high sulfur level fuel. In this case, commercially available fuel with 380-ppm sulfur level was used for contamination until performance dropped to an absolute NO<sub>x</sub> conversion efficiency of 60%. As testing progressed toward defining the length of the desulfurization event, an attempt was made to always poison the catalyst as near to the 60% absolute conversion efficiency as possible.

Figure 3.2-3 shows the influence of the various desulfurization event lengths operated during these tests. The DECSE 3-ppm sulfur level fuel was used to map NO<sub>x</sub> conversion efficiency before and after desulfurization. Each contamination event lasted approximately two hours using the 380-ppm sulfur fuel.



**Figure 3.2-3. The influence of desulfurization duration on NO<sub>x</sub> conversion efficiency recovery for catalyst S4**

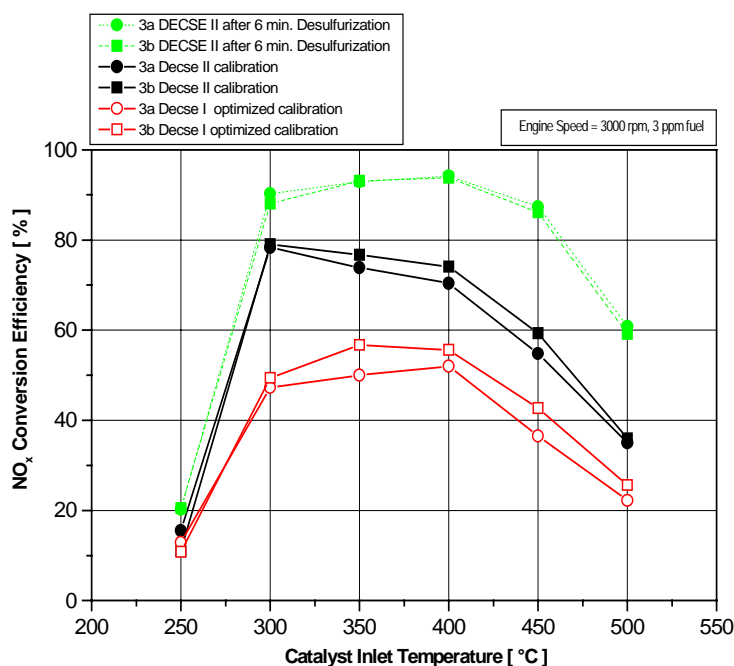
As shown, increasing the length of the desulfurization event tended to increase the absolute NO<sub>x</sub> conversion efficiency. The point of diminishing return with respect to NO<sub>x</sub> conversion efficiency occurred around the 5- or 6-minute length. Clearly seven minutes appeared to be no more effective. The event length selected for the DECSE II desulfurization strategy, therefore, was six minutes.

With the established conditions for desulfurization demonstrated on the test catalyst (S4), the effect of desulfurization was investigated on catalyst S3 using only fuel provided by DECSE. First, the performance of catalyst S3 at 400°C was measured, then S3 was poisoned using the DECSE fuel with a sulfur level of 150 ppm. The catalyst was poisoned with the same approach used while

working with catalyst S4 until the initial conversion efficiency at a catalyst inlet temperature of 400°C was reduced by 25%.

After contamination with the higher sulfur level fuel, the catalyst performance was mapped again over the entire temperature window. The desulfurization procedure was then applied, followed by mapping. The initial conversion efficiency recorded for catalyst S3 at a catalyst inlet temperature of 400°C was 86%. Its performance was reduced to a conversion efficiency of 58% by sulfur contamination. After completing the desulfurization and subsequent mapping, the catalyst exhibited a NO<sub>x</sub> conversion efficiency of 87% at 400°C. This is clearly a positive confirmation of the ability of the desulfurization strategy developed to restore NO<sub>x</sub> conversion ability to a poisoned catalyst.

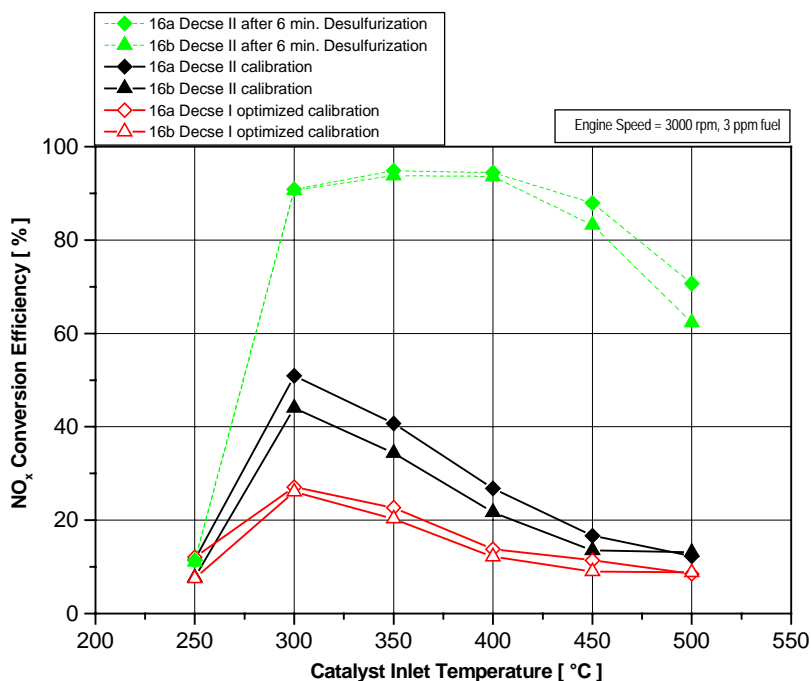
The effectiveness of this desulfurization strategy was further investigated using the catalysts aged during the DECSE I program. Each catalyst pair was installed into the exhaust system, and NO<sub>x</sub> conversion efficiencies were mapped. The results of remapping the catalyst performance after desulfurization are shown in Figures 3.2-4–3.2-7.



**Figure 3.2-4. Comparison of NO<sub>x</sub> conversion efficiency for catalysts 3a and 3b using the DECSE I and DECSE II calibrations before desulfurization and the DECSE II calibration after desulfurization**

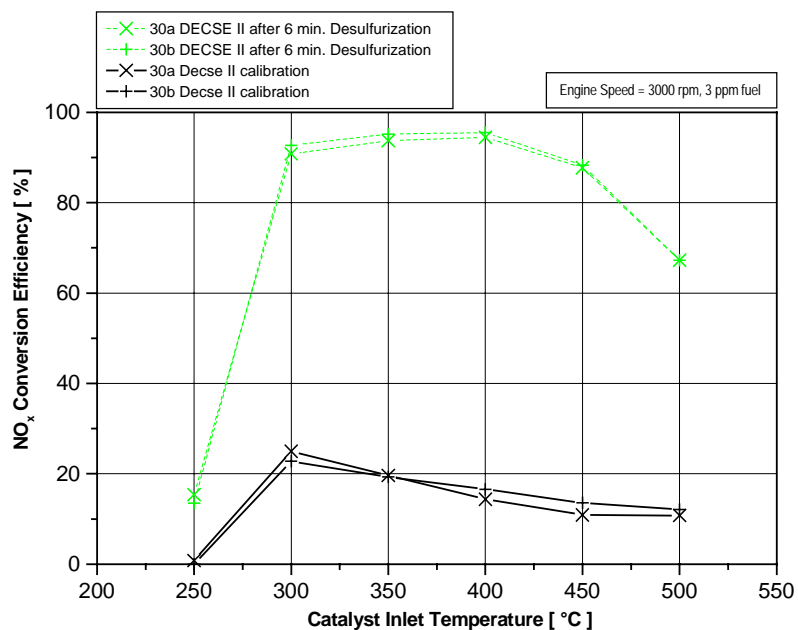
Figure 3.2-4 shows the results for catalysts 3a and 3b. Clearly, the desulfurization procedure successfully returned the catalyst performance to levels typical of nonpoisoned catalyst. This catalyst pair achieved approximately 80% NO<sub>x</sub> conversion from a low temperature of 300°C to an upper limit of 450°C. Even at 500°C this catalyst pair, which by this time had been aged for 250 hours under the DECSE I work and accumulated additional time during the mapping events under Task 3, still exhibited 60% NO<sub>x</sub> conversion. The desulfurization was particularly effective in restoring activity in the middle and high temperature range.

The desulfurization procedure is equally effective at removing sulfur from catalysts aged with higher sulfur level fuels. Figures 3.2-5 and 3.2-6 show the NO<sub>x</sub> conversion efficiency performance of catalyst pairs 16a and 16b and 30a and 30b. The results indicate that each catalyst was restored to levels of nonpoisoned catalyst. Figure 3.2-7 demonstrates that, although these catalysts were aged using different fuel sulfur levels and different amount of aging, the desulfurization procedure effectively released stored sulfur compounds and restored the potential for NO<sub>x</sub> conversion on all catalysts.

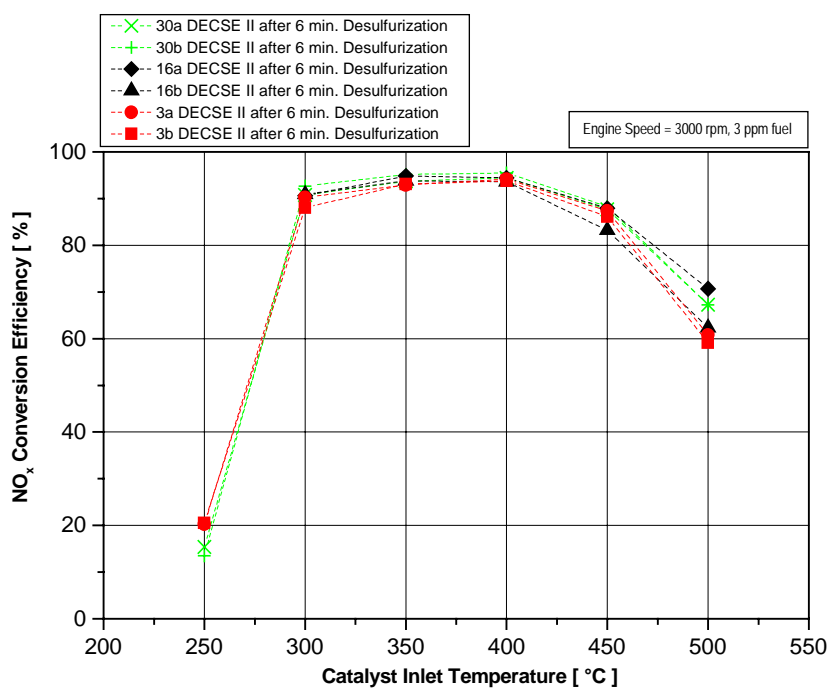


**Figure 3.2-5. Comparison of NO<sub>x</sub> conversion efficiency for catalysts 16a and 16b using the DECSE I and DECSE II calibrations before desulfurization and the DECSE II calibration after desulfurization**

The results obtained under this task indicate that sulfur can be driven from the NO<sub>x</sub> adsorber, and conversion efficiency can be regained from aged catalysts. The tests under the next task were designed to determine whether exposure to repeated desulfurization events would limit the recovery in conversion efficiency.



**Figure 3.2-6. Comparison of NO<sub>x</sub> conversion efficiency for catalysts 30a and 30b using the DECSE I and DECSE II calibrations before desulfurization and the DECSE II calibration after desulfurization**



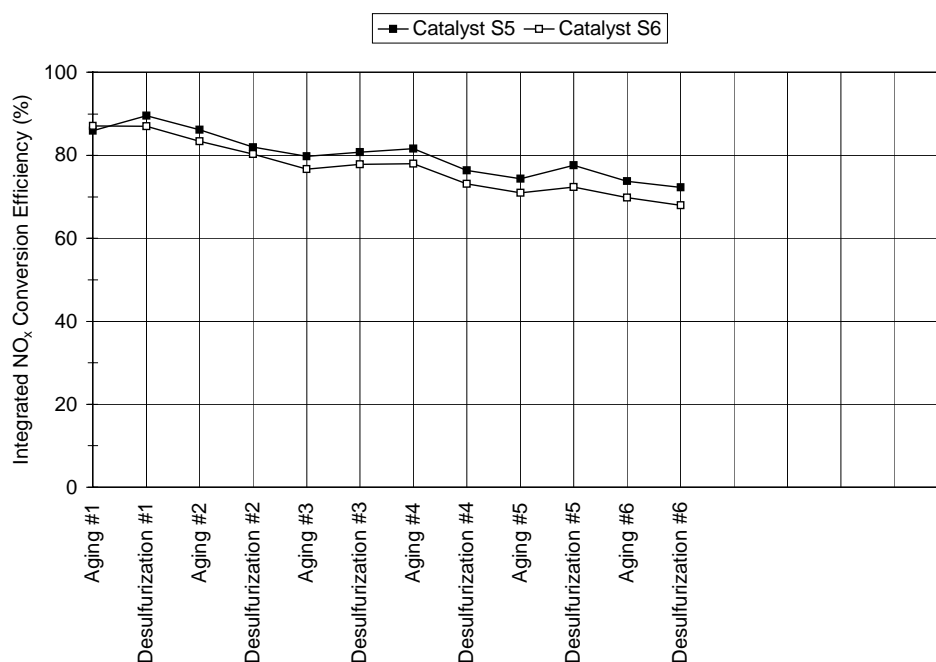
**Figure 3.2-7. Comparison of NO<sub>x</sub> conversion efficiency for catalysts 3a and 3b, 16a and 16b, and 30a and 30b using the DECSE II calibration after desulfurization**

### 3.3 Evaluation of the Desulfurization Process

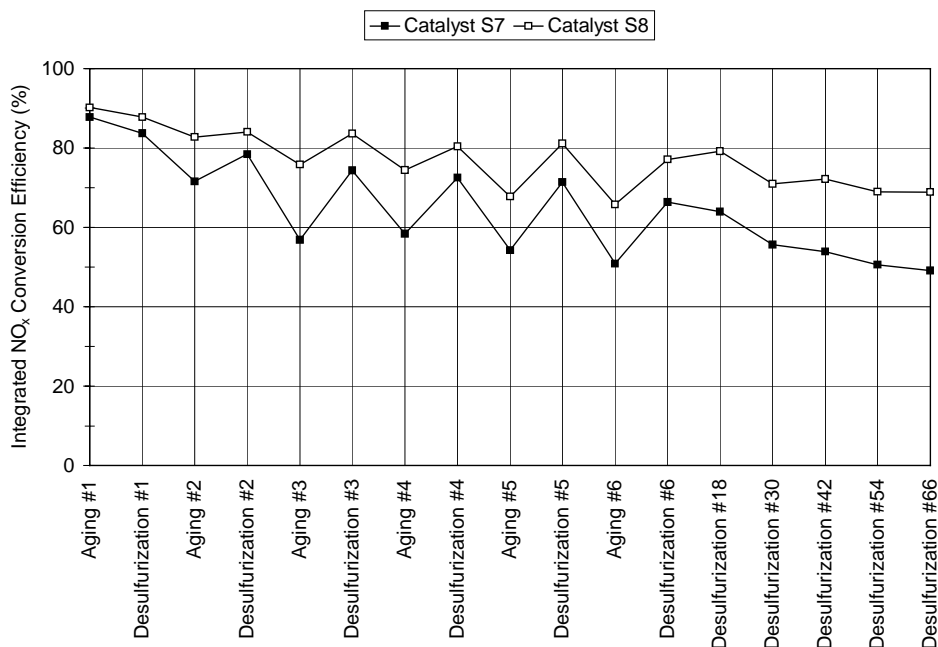
This section presents results that characterize the performance of a NO<sub>x</sub> adsorber catalyst under repeated cycles of aging (10 hours with 3-ppm or 78-ppm sulfur fuel) followed by desulfurization (six minutes). The following section presents the results of statistical analyses that investigated how operating temperature, fuel sulfur level, and number of test cycles (or total desulfurization time) affect catalyst performance under repeated aging/desulfurization cycles.

#### Statistical Evaluation of the Effects of Fuel Sulfur Level, Catalyst Aging, and Desulfurization Time on NO<sub>x</sub> Conversion Efficiency of a NO<sub>x</sub> Adsorber Catalyst

The data obtained in this program consist of mappings of NO<sub>x</sub> CE at temperatures of 250°C–500°C in increments of 50°C. Separate mappings were performed after each 10-hour aging period, using 3-ppm or 78-ppm sulfur fuel, and after the subsequent six-minute desulfurization event. Initially, six aging/desulfurization cycles were performed on a pair of degreened (50 hours with 3-ppm sulfur fuel) catalysts for each type of aging fuel (3-ppm or 78-ppm sulfur). Because of declining trends in post-desulfurization NO<sub>x</sub> CE observed during the first six cycles, additional testing was performed on the 78-ppm aged catalysts (S7 and S8) to evaluate this effect further. NO<sub>x</sub> CE mappings were performed after five additional test cycles, each consisting of 12 consecutive six-minute desulfurizations. Thus, 66 desulfurizations were performed on catalysts S7 and S8. Figures 3.3-1a and 3.3-1b display the temperature-integrated NO<sub>x</sub> CE (%) at each stage of testing.



**Figure 3.3-1a. Integrated NO<sub>x</sub> conversion efficiency for catalysts S5 and S6 (aged with 3-ppm sulfur fuel) following aging and desulfurization events**

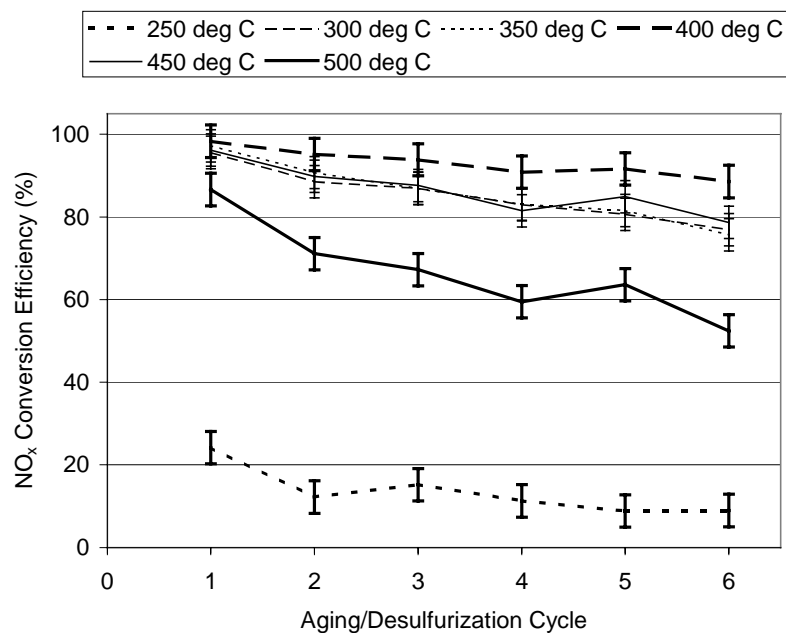


**Figure 3.3-1b. Integrated NO<sub>x</sub> conversion efficiency for catalysts S7 and S8 (aged with 78-ppm sulfur fuel) following aging and desulfurization events**

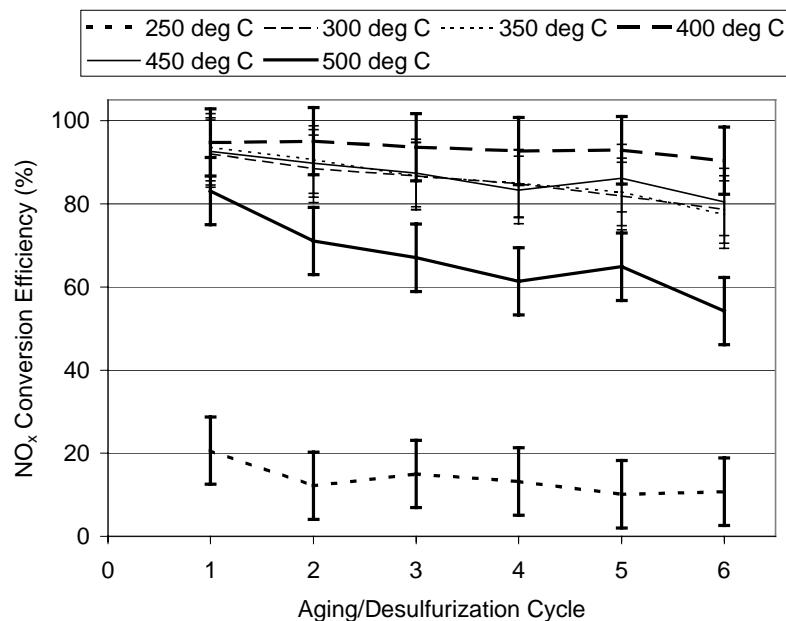
Using the methods described in Section 2.3.2, the statistical analysis addressed two primary objectives. The first objective is as follows:

*Objective 1: Determine whether there are significant trends in the post-desulfurization NO<sub>x</sub> conversion efficiency (CE) over time, and investigate how operating temperature and fuel sulfur level affect performance. If there are significant trends in post-desulfurization NO<sub>x</sub> CE over time, characterize these trends and determine if performance stabilizes.*

For this objective, three separate analyses were performed on the post-desulfurization NO<sub>x</sub> CE data. First, the mixed-model ANOVA (equation 4) was performed to determine whether the effects of desulfurization time (or number of test cycles), operating temperature, and sulfur level used during aging are statistically significant and to evaluate their interactions. This analysis determined that there are statistically significant ( $p < 0.01$ ) effects of cycling and operating temperature on the post-desulfurization NO<sub>x</sub> CE. The interaction of these two factors is also statistically significant. This means that the effects of operating temperature may be different among test cycles; or conversely, the effects of cycling may be different among operating temperatures. These effects can be seen in Figures 3.3-2a and 3.3-2b, which display the estimated average NO<sub>x</sub> CE for all combinations of test cycle and operating temperature for the 3-ppm and 78-ppm aged catalysts, respectively. The error bars represent 95% confidence intervals on the estimated NO<sub>x</sub> CE.



**Figure 3.3-2a. Predicted post-desulfurization NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) at selected operating temperatures versus aging/desulfurization test cycle for catalysts aged with 3-ppm sulfur fuel**



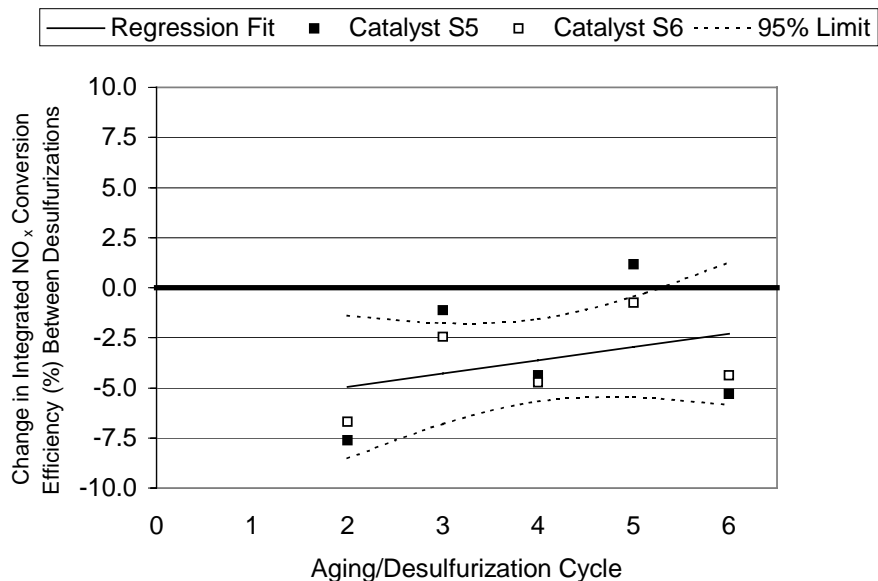
**Figure 3.3-2b. Predicted post-desulfurization NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) at selected operating temperatures versus aging/desulfurization test cycle for catalysts aged with 78-ppm sulfur fuel**



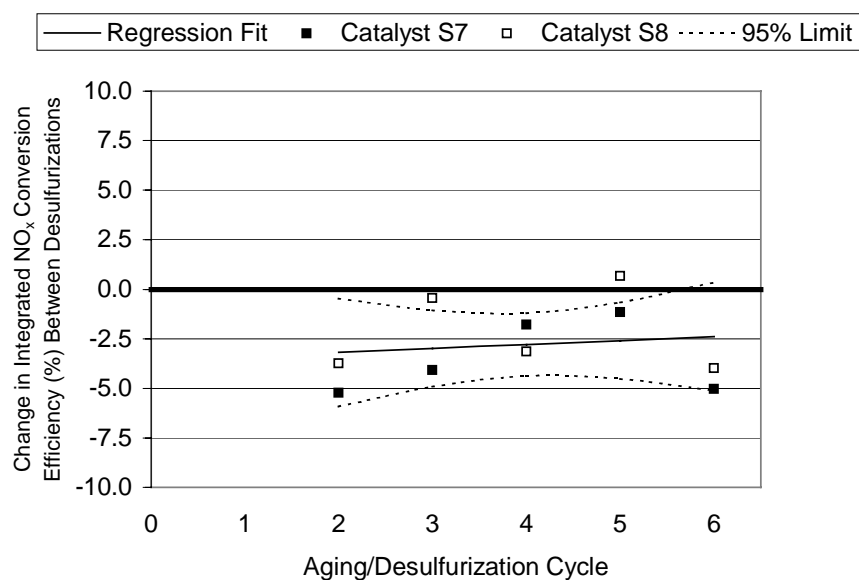
The results of this analysis suggest that the sulfur level of the aging fuel does not affect the performance of the catalyst immediately after desulfurization. This is demonstrated by the similarity of the results presented in Figure 3.3-2a and 3.3-2b. The statistical analysis did find a small, but statistically significant, interaction effect between aging fuel sulfur level and test cycle, but this interaction effect was not significant when the 250°C data were excluded from the model. Nevertheless, the predicted NO<sub>x</sub> CE values shown in Figures 3.3-2a and 3.3-2b include this small interaction term.

A second analysis approach was used to further investigate how the NO<sub>x</sub> adsorber catalyst performed following desulfurization. This time the “change” in NO<sub>x</sub> CE between consecutive desulfurizations was analyzed using a generalized regression approach to determine whether there are trends over time. The analysis was performed at each operating temperature as well as for temperature-integrated NO<sub>x</sub> CE. The results of the latter analyses are presented in Figures 3.3-3a and 3.3-3b, which display the integrated NO<sub>x</sub> CE for each catalyst, the predicted change in NO<sub>x</sub> CE (regression fit), and the 95% confidence limits on the predicted change.

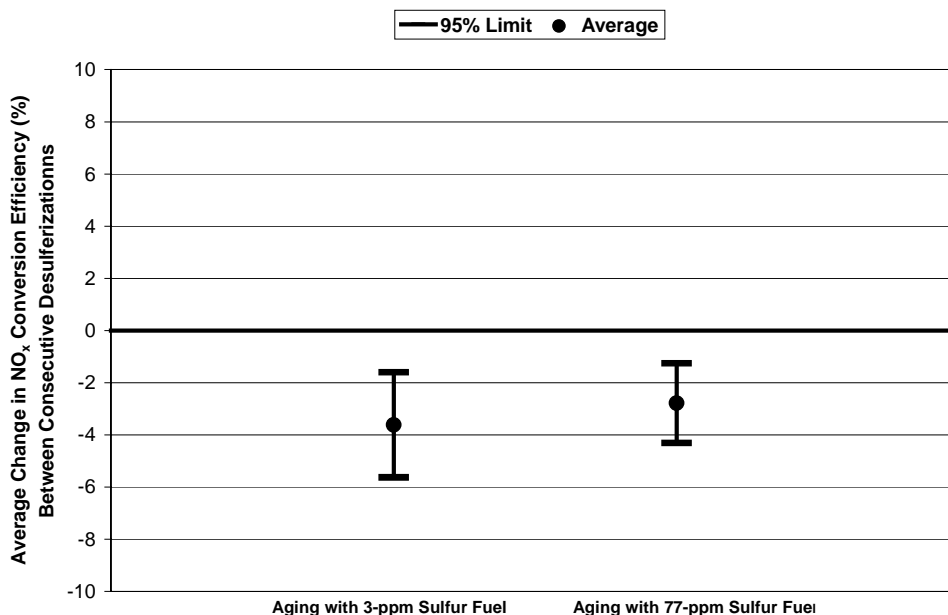
Although there appear to be some slight trends, the slopes of the regression lines were not significantly different from zero. Thus, the change caused by desulfurization is best characterized by the average change in NO<sub>x</sub> CE. These averages, along with 95% confidence limits, are shown in Figure 3.3-4. The overlapping confidence limits suggest that the difference in the average changes (–3.6% for 3-ppm aged catalysts and –2.8% for 78-ppm aged catalysts) is not statistically significant. Also, the fact that these intervals do not contain the value zero implies that the average change is significantly different from zero. These findings support the conclusion that the post-desulfurization NO<sub>x</sub> CE declines linearly during the first six desulfurization events.



**Figure 3.3-3a. Predicted change in post-desulfurization NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) versus aging/desulfurization test cycle with 3-ppm sulfur aging fuel**



**Figure 3.3-3b. Predicted change in post-desulfurization NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) versus aging/desulfurization test cycle with 78-ppm sulfur aging fuel**



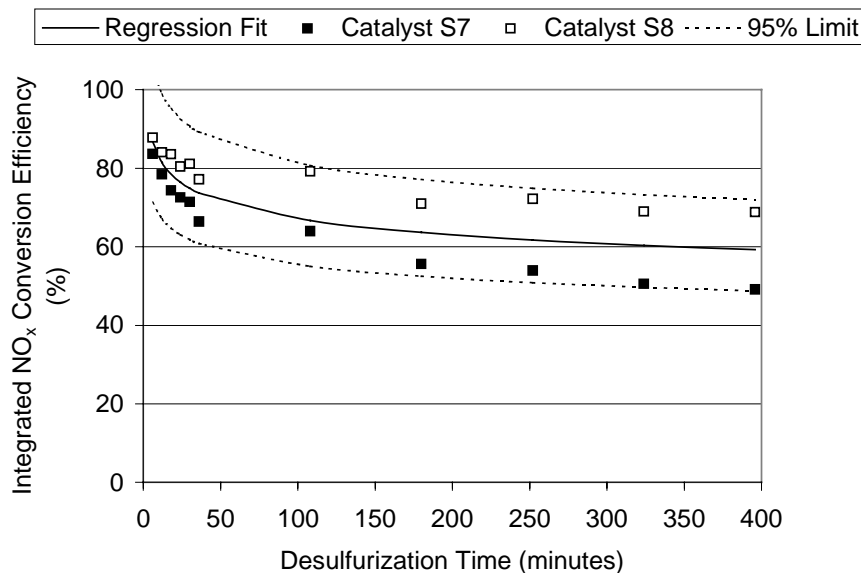
**Figure 3.3-4. Average change in post-desulfurization NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) for catalysts aged with 3-ppm and 78-ppm sulfur fuel**

The final analysis related to Objective 1 involved characterizing the long-term performance of NO<sub>x</sub> adsorber catalysts that undergo repeated desulfurizations. Having demonstrated that desulfurization

returns the catalyst to the same level of performance regardless of the level of sulfur poisoning, it was decided that five additional evaluations would be performed, each following a series of 12 consecutive six-minute desulfurizations. The analysis consists of selecting a regression model that best characterizes the long-term average performance of the NO<sub>x</sub> adsorber catalyst. One hypothesis was that the linear decline observed during the first six desulfurization events would continue. Another is that performance would stabilize over time. The data and the fitted regression model are shown in Figure 3.3-5. The fitted regression equation is

$$\ln(\text{NO}_x \text{ CE}) [\%] = 4.62 - 0.091 \cdot \ln(\text{desulfurization time}). \quad (6)$$

The statistical uncertainty in the estimated slope (0.091), based on a 95% confidence interval, is approximately  $\pm 0.02$ . Thus, the estimated slope is significantly different from zero. This model demonstrates that NO<sub>x</sub> CE continues to decline during the first 396 minutes (66 desulfurization events), but not in a linear manner. However, it does not demonstrate that performance has either stabilized or will continue to decline.



**Figure 3.3-5. Regression model (with 95% confidence interval) of post-desulfurization NO<sub>x</sub> conversion efficiency versus total desulfurization time**

The second objective for the statistical analysis is as follows:

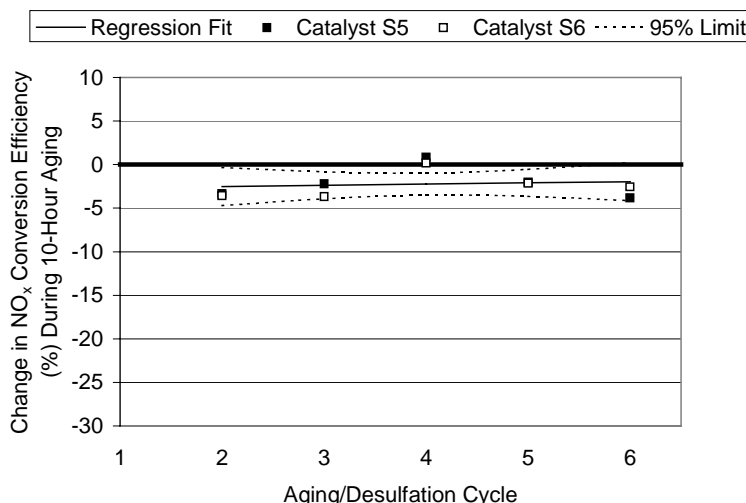
*Objective 2: Determine whether there are changes in the NO<sub>x</sub> CE due to aging, and whether the changes are affected by fuel sulfur level, operating temperatures, or number of aging/desulfurization cycles (test cycles).*

The mixed-model ANOVA (equation 3) was applied to changes in the NO<sub>x</sub> CE observed during each aging cycle. Statistical analysis demonstrated that sulfur level of the aging fuel and all the interaction terms involving fuel sulfur level were found to be statistically significant ( $p < 0.01$ ). Therefore, separate analyses (using equation 4) were performed with data from catalysts aged with 3-

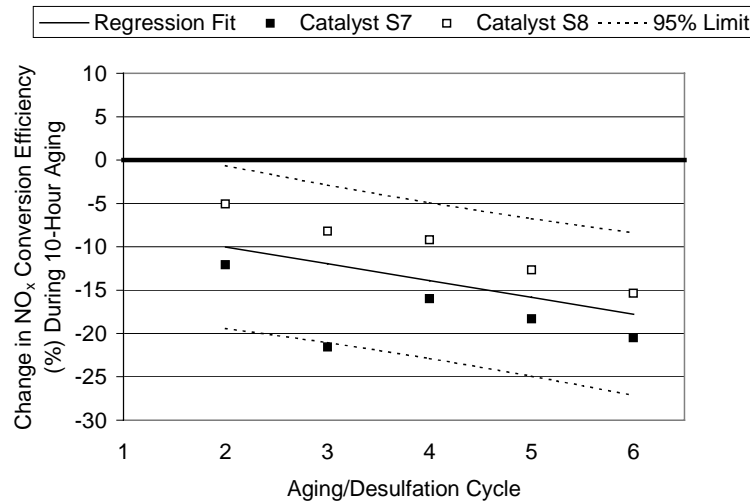
ppm and 78-ppm sulfur fuels. Linear regression was then used to further characterize the relationship between the change in temperature-integrated NO<sub>x</sub> CE during aging and the cumulative number of aging/desulfurization cycles. The primary findings from these analyses follow:

- (1) The average decline in NO<sub>x</sub> CE for a catalyst exposed to 10 hours of aging with 3-ppm sulfur fuel is 2.2% ( $\pm 1.1\%$ ), which is significantly different from zero.
- (2) This rate of decline in NO<sub>x</sub> CE for a catalyst exposed to 10 hours of aging with 3-ppm sulfur fuel remained constant following the first five desulfurization events.
- (3) The rate of decline in NO<sub>x</sub> CE for a catalyst exposed to 10 hours of aging with 78-ppm sulfur fuel increased from 10.0% to 17.8% during the first five desulfurization events.

The findings are illustrated in Figures 3.3-6a and 3.3-6b. Each figure contains the observed changes in temperature integrated NO<sub>x</sub> CE during consecutive aging cycles, the regression fit, and 95% confidence intervals for the predicted change in NO<sub>x</sub> CE caused by aging as a function of the number of aging/desulfurization cycles. The estimated slope for the regression with 3-ppm aged catalysts was not significantly different from zero. On the other hand, the slope for 78-ppm aged catalysts was statistically significant ( $p < 0.01$ ).



**Figure 3.3-6a. Predicted change in NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) during 10 hours of aging with 3-ppm sulfur fuel versus number of aging/desulfurization cycles**



**Figure 3.3-6b. Predicted change in NO<sub>x</sub> conversion efficiency (with 95% confidence intervals) during 10 hours of aging with 78-ppm sulfur fuel versus number of aging/desulfurization cycles**

### Impact of Statistical Modeling Assumptions

The statistical models used in these analyses are based on assumptions that the random effects of catalysts and measurement/testing are distributed independently according to normal distributions. Although it is not possible to prove that these assumptions have been met, several steps were taken to assess the feasibility of the assumptions and demonstrate the robustness of the conclusions.

Because only two catalysts were used with each fuel type, the statistical assumptions concerning the distribution of catalyst effects could not be tested. Theoretically, these assumptions could impact the statistical test of the effect of sulfur in aging fuel on the catalyst post-desulfurization performance. However, based on the data collected in this study, the conclusion that there is no statistically significant effect of fuel sulfur level on post-desulfurization performance would hold up under any reasonable assumptions. This is because the results from catalysts S7 and S8, used with 78-ppm fuel during aging, consistently spanned the results from catalysts S5 and S6, used with 3-ppm fuel. (See Figures 3.3-1a and 3.3-1b.) Also, the analyses of aging effects and changes in post-desulfurization performance, which are based on consecutive differences in NO<sub>x</sub> conversion efficiency, are not sensitive to the assumptions on distribution of catalyst effects. This is because these effects are mathematically eliminated in the calculation of the dependent variable. On the other hand, the distribution assumptions on catalyst-to-catalyst differences do impact the width of the confidence intervals on the predicted NO<sub>x</sub> conversion efficiency as a function of desulfurization time (Figure 3.3-5).

Although the distribution of errors due to measurement and testing appear to follow a normal distribution (the distributions are symmetric and bell-shaped), the exact form of the distributions is not important because ANOVA is fairly robust as long as the sample sizes are adequate. On the other hand, the assumption of independent errors is important to evaluate, especially considering the way in which the data were collected. Each evaluation was performed by measuring NO<sub>x</sub>

conversion efficiency as temperatures were increased from 250°C to 500°C. Because it was not practical to randomize the order of testing, the errors may be correlated. Similarly, there may be correlation between measurements made in consecutive test cycles. Initially it was assumed that all of the errors were independent. Next, separate analyses were performed using an autoregressive model, which assumes that the correlation among measurements is related to the difference in temperatures or test cycles. Comparison of these models (using the log likelihood criterion) for the analysis of post-desulfurization performance suggests that the correlation among measurements at consecutive temperatures is statistically significant. However, the statistical conclusions concerning all of the fixed effects (temperature, test cycle, fuel sulfur level) remain unchanged. There was no evidence of lack of independence of errors for the analyses of aging effects on integrated NO<sub>x</sub> conversion efficiency or the changes in post-desulfurization integrated NO<sub>x</sub> conversion efficiency.

## Section 4

### Findings and Conclusions

The investigations performed in this project demonstrated the ability to develop a NO<sub>x</sub> regeneration strategy including both an improved lean/rich modulation cycle and rich engine calibration, which resulted in a high NO<sub>x</sub> conversion efficiency over a range of operating temperatures. A high-temperature cycle was developed to desulfurize the NO<sub>x</sub> absorber catalyst. The effectiveness of the desulfurization process was demonstrated on catalysts aged using two different sulfur level fuels. The major findings of this project are as follows:

- The improved lean/rich engine calibration achieved as a part of this test project resulted in NO<sub>x</sub> conversion efficiencies exceeding 90% over a catalyst inlet operating temperature window of 300°C–450°C. This performance level was achieved while staying within the 4% fuel economy penalty target defined for the regeneration calibration.
- The desulfurization procedure developed showed that six catalysts, which had been exposed to fuel sulfur levels of 3-, 16-, and 30-ppm for as long as 250 hours, could be recovered to greater than 85% NO<sub>x</sub> conversion efficiency over a catalyst inlet operating temperature window of 300°C–450°C, after a single desulfurization event. This performance level was achieved while staying within the 4% fuel economy penalty target defined for the regeneration calibration.
- The desulfurization procedure developed has the potential to meet in-service engine operating conditions and provide acceptable driveability conditions.
- Although aging with 78-ppm sulfur fuel reduced NO<sub>x</sub> conversion efficiency more than aging with 3-ppm sulfur fuel as a result of sulfur contamination, the desulfurization events restored the conversion efficiency to nearly the same level of performance. However, repeatedly exposing the catalyst to the desulfurization procedure developed in this program caused a continued decline in the catalyst's desulfurized performance. Additional work will be necessary to identify the cause of this performance decline.
- The rate of sulfur contamination during aging with 78-ppm sulfur fuel increased with repeated aging/desulfurization cycles (from 10% per ten hours to 18% per ten hours). This was not observed with the 3-ppm fuel, where the rate of decline during aging was fairly constant at approximately 2% per ten hours.