Diesel Emission Control – Sulfur Effects (DECSE) Program

Phase I Interim Data Report No. 2: NO_x Adsorber Catalysts
October, 1999

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The test program and subsequent data analysis represents a collaborative effort of a technical work group consisting of representatives from the U.S. Department of Energy, National Laboratories, Engine Manufacturers Association, and 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 of this effort. To the extent that additional information becomes available, or factors upon which analyses are based change, the findings could subsequently be affected.

DECSE Interim Data Report
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List of Acronyms

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_2 – hydrogen
HC – hydrocarbon(s)
HSDI – high-speed, direct injection
MECA – Manufacturers of Emission Controls Association
N_2 – nitrogen
NO_x – 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
PM – particulate matter
ppm – parts per million
R&D – research and development
SO_2 – sulfur dioxide
SO_3 – sulfur trioxide
TWC – three-way catalyst

Section 1
Executive Summary

ES.1 Introduction

The Diesel Emission Control–Sulfur Effects (DECSE) program is a joint government/industry program to determine the impact of diesel fuel sulfur levels on emission control systems whose use could lower emissions of nitrogen oxides (NO_x) and particulate matter (PM) from on-highway trucks in the 2002-2004 model years. The program is designed to enhance the collective knowledge base on engines, diesel fuels, and emission control technologies in a systems approach to (1) guide industry in developing lower emitting applications of their products, and (2) provide a portion of the technical basis for government decisions on regulating the content of sulfur in diesel fuel.

Phase 1 of the program was developed with the following objectives in mind:

(A) Evaluate the effects of varying the level of sulfur content in the fuel on the emission reduction performance of four emission control technologies; and

(B) Measure and compare the effects of up to 250 hours of aging on selected devices for multiple levels of fuel sulfur content.

Four emission control technologies are being tested in Phase 1 of the program: (1) NO_x adsorber catalysts; (2) diesel particulate filters (DPF); (3) lean-NO_x catalysts; and (4) diesel oxidation catalysts (DOC). The devices being tested include commercially available technologies as well as state-of-the-art technologies that are under development. The sulfur contents in the test fuels are 3, 16 (NO_x adsorber catalysts only), 30, 150 and 350 parts per million (ppm). The 3-ppm sulfur content fuel represents a diesel fuel that is essentially "sulfur-free". The engines in the DECSE program represent currently available models, and they were 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 exhaust flow rate, stream temperature, and concentrations of NO_x, hydrocarbons (HC), carbon monoxide (CO), and particulate matter (PM).

Participants in the program include representatives from the U.S. Department of Energy's Office of Heavy Vehicle Technologies within the Office of Transportation Technologies (OTT), the National Renewable Energy laboratory (NREL), Oak Ridge National Laboratory (ORNL), the Engine Manufacturers Association (EMA), and the Manufacturers of Emission Controls Association (MECA).

This is the second DECSE Interim Report. The first DECSE Interim Report, published September 1, 1999, reported on the status of the test programs being conducted on three other technologies: lean-NO_x catalysts, diesel particulate filters, and diesel oxidation catalysts. Additional Interim Reports will follow as data become available.

ES.2 NO_x Adsorber Catalyst

A NO_x adsorber catalyst is a flow-through emissions control device that temporarily stores NO_x emissions during typical diesel engine operation. Before the NO_x 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_x is released from the adsorbent and simultaneously reduced to N_2 over precious metal adsorber catalyst sites.

An engine management system is critical to the operation of a NO_x adsorber system. The engine management system must determine when the NO_x adsorbent is approaching saturation and then trigger the change in engine operation that creates the rich condition required for release and reduction of the stored NO_x.

The concern with fuel sulfur is that SO_2 is formed during combustion and released in the exhaust. In a NO_x adsorber catalyst, this SO_2 undergoes reactions that are analogous to those of NO_x. However, SO_2 can generate a stronger adsorbate (SO_3) when compared with NO_2. As a result, SO_2 is a poison for the NO_x adsorption sites.

The test program began with the calibration of the engine management system. The goal was to achieve, when operating with the base fuel (3-ppm sulfur), a NO_x conversion efficiency of at least 80% across engine operating temperatures of 250°C to 500°C with no more than a 4% average increase in fuel consumption associated with the rich calibration strategy developed for release and reduction of the stored NO_x. To determine the effects of sulfur, including aging effects, emission evaluations were performed approximately every 50 hours using fuels containing 3-, 16-, and 30-ppm sulfur. Each evaluation measured NO_x conversion efficiency between 150°C and 550°C in 50°C increments at 3,000 rpm. Testing continued for 250 hours, or until the NO_x conversion efficiency dropped to less than half of the average efficiency established in the initial evaluation with 3-ppm sulfur fuel.

Although the initial engine calibration resulted in lower adsorber catalyst conversion efficiency than anticipated, the DECSE NO_x adsorber technical committee decided that data on the effects of sulfur could nonetheless be investigated in the temperature regions where the engine calibration resulted in higher conversion efficiencies. Therefore, testing proceeded with the initial, less than optimal calibration.

The interim conclusions are:

- The effect of fuel sulfur content on NO_x adsorber conversion efficiency is shown in Figure ES-1. The figure illustrates the effect of fuel sulfur on relative NO_x conversion efficiencies at 400° and 450°C after 150 hours of testing. Compared to 3-ppm sulfur fuel at 150 hours, both 16- and 30-ppm sulfur fuels resulted in significant performance declines.

- Although testing with 3-ppm sulfur fuel showed an initial decline in adsorber catalyst conversion efficiency, the performance subsequently appeared to stabilize, out to the 250-hour period. Further aging would be required to determine adverse affects of 3-ppm sulfur fuel beyond this point.

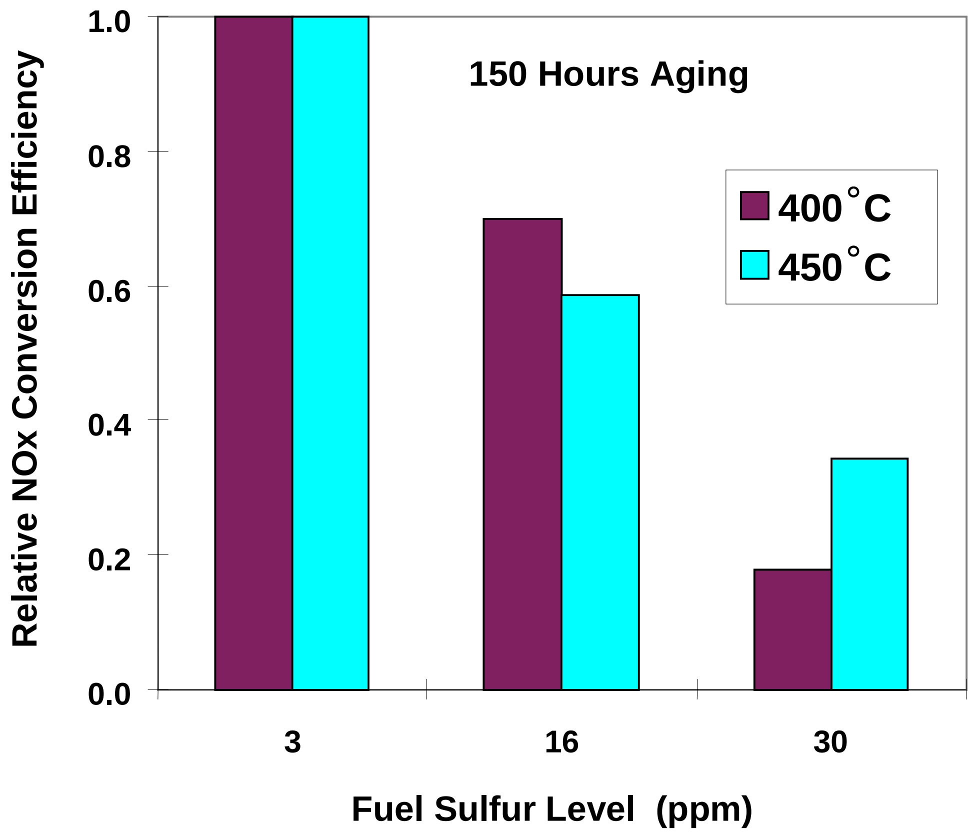

Figure ES-1. Effect of increasing fuel sulfur level on relative NO_x conversion efficiency for 150-hour aged NO_x adsorber catalyst evaluated at 400°and 450 °C

- Fresh NO_x adsorbers are capable of providing high NO_x conversion levels (e.g., more than 80%) across a broad range of operating temperatures when coupled with an optimized engine rich regeneration calibration, while maintaining a fuel economy penalty of less than 4%.

The initial calibration of the engine management system did not achieve the desired level of NO_x conversion performance across the range of operating temperatures. Maximum efficiency was achieved at 450°C and was lower than the desired level, both below and above this temperature, as shown in Figure ES-2. The revised calibration, established after aging tests were completed, produced improved conversion efficiency.

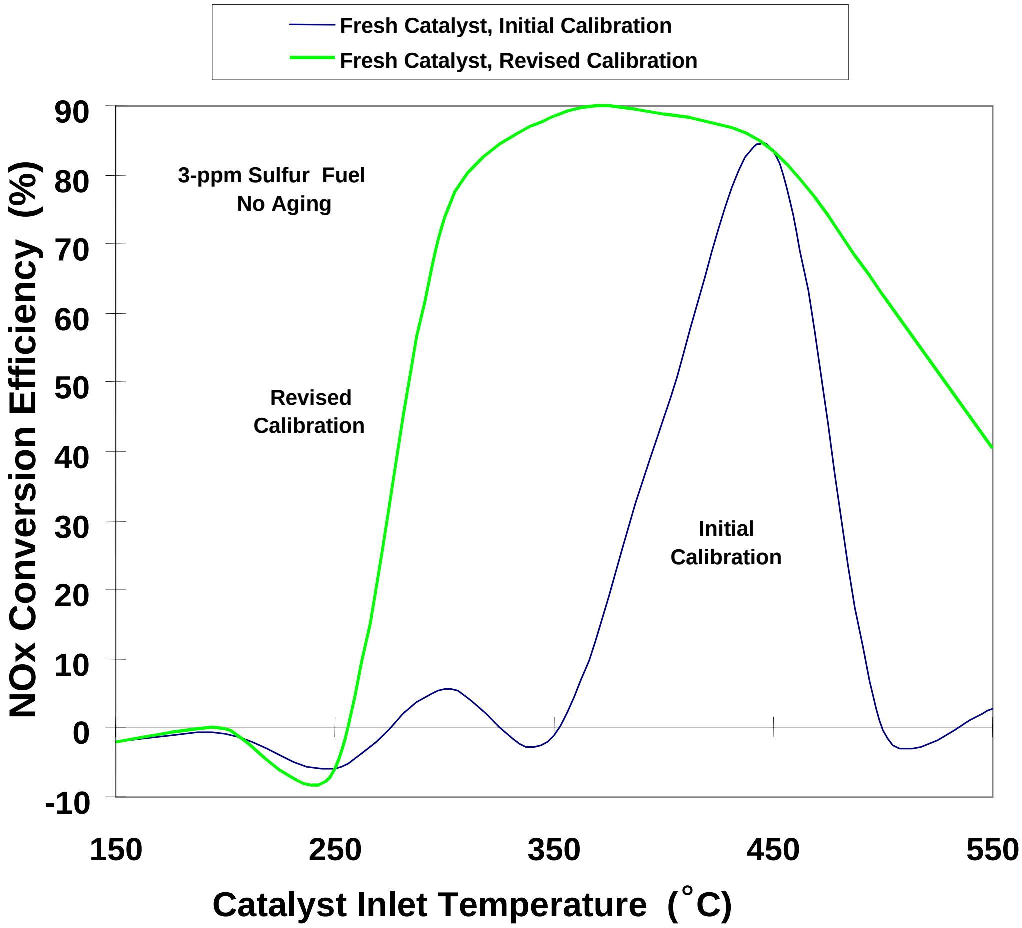

Figure ES-2. NO_x conversion efficiency with initial and revised engine calibration strategies and identical rich/lean timing

ES.3 Future Work

The investigations performed to date have highlighted the importance of developing a proper NO_x regeneration strategy including both an optimized lean/rich modulation cycle and rich engine calibration. Subsequent studies are planned to determine the potential conversion efficiencies that can be achieved with an optimized regeneration strategy on the adsorber catalysts that have been aged with 3-ppm and 16-ppm sulfur fuel. This will further illustrate the effects of different fuel sulfur levels on NO_x adsorption technology. Strategies for adsorber catalyst desulfurization and their effectiveness at different fuel sulfur levels will also be investigated.

Assuming that a high-temperature engine cycle can be developed to desulfurize the NO_x adsorber, it becomes a matter of trading off frequency of desulfurization, fuel sulfur concentration, and fuel economy penalty; the lower the sulfur level the less frequent desulfurization will be required.

Section 2

Description of Technologies and Tests

2.1 NO_x Adsorber Catalyst

2.1.1 Program Overview

The results of the DECSE test program demonstrate the potential of NO_x adsorber catalyst technology across the range of diesel engine operation with a fuel economy penalty less than 4%. That penalty is consistent with that used for the lean-NO_x catalysts also being evaluated in the DECSE test program. The results show how fresh adsorber catalyst performance is affected by sulfur level and how limited aging up to 250 hours affects the performance deterioration rate for three different sulfur levels.

2.1.2 Principle of Operation

A NO_x adsorber catalyst is a flow-through emissions control device that has the potential to lower significantly NO_x, HC, and CO emissions from diesel engine exhaust. Because a NO_x adsorber contains high levels of precious metals, it may also be effective in oxidizing the soluble organic fraction of diesel PM.

A NO_x adsorber catalyst is a temporary storage device for NO_x. During typical diesel engine operation, NO_x in the lean exhaust gas is stored as an alkalai or alkaline earth nitrate in the device. Before the NO_x 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_x is released from the adsorbent and simultaneously reduced to N_2 over downstream precious metal sites on the adsorber catalyst.

A NO_x adsorber catalyst consists of two principal components: a NO_x adsorbent and a three-way catalyst (TWC). The NO_x adsorbent is typically an alkali or alkaline earth carbonate. These carbonates are capable of chemically interacting with the NO_2 and O_2 in typical diesel engine exhaust to form an alkali or alkaline earth nitrate. Precious metals in the TWC are responsible for the oxidation of NO to NO_2, which facilitates the adsorption process. Periodically, NO_x stored by the adsorbent is released and reduced to N_2. This process requires a fuel-rich exhaust gas composition and a TWC. These catalysts are typically based on combinations of platinum (Pt), palladium (Pd), and rhodium (Rh), and they are capable of using the reductants (CO, H_2, and HC) in rich engine exhaust to reduce NO_x selectively to N_2. TWCs have been used for more than 20 years to perform NO_x reduction in the exhaust of stoichiometric gasoline engines.

An engine management system is critical to the operation of a NO_x adsorber catalyst system. The engine management system is programmed to trigger the change in engine operation that results in generation of the rich condition required for release and reduction of the stored NO_x. The duration and "richness" (defined by the air-to-fuel ratio) of the rich pulse is 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 results in the formation of SO_2. In a NO_x adsorber, this SO_2 undergoes reactions that are analogous to those of 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 (SAE paper numbers 1999-01-1285 and 982594) that the decomposition of these sulfates requires a combination of rich conditions and temperatures exceeding 600°C. As a result, SO_2 in the exhaust is a poison for NO_x adsorption sites without a properly developed desulfurization cycle.

The DECSE experiments are providing data to address the following study questions:

What is the effect of fuel sulfur level on:

- NO_x reduction efficiency
- Rate of deactivation of adsorber catalyst
- Production of sulfate?

2.1.3 Overview of Test Program

Each equivalently formulated NO_x adsorber device was first thermally stabilized with 10 hours of degreening (break-in) in engine exhaust at 400°C. Next, the required rich and lean engine operating times were determined, and the NO_x conversion was mapped over the full temperature range (150°C to 550°C, in 50°C increments). Aging of the devices then began. The aging process was interrupted at 50-hour intervals to measure the device performance and to document the extent of deterioration. The experimental matrix is shown in Table 2.1-1.

Table 2.1-1. Tests to Determine Impact of Fuel Sulfur Level on NO_x Adsorber Performance

Test Purpose	**Fuel Sulfur Level** (ppm)		
	3	**16**	**30**
Degreening	Degreen samples for 10 hours at 400°C while running lean		
Determine rich/lean times to maximize NO_x conversion	3a, 3b 4% maximum fuel penalty		
Performance mapping	3a, 3b	16a, 16b	30a, 30b
	150°–550°C, in 50°C increments		
Aging hours	3a, 3b	16a, 16b	30a, 30b
	Cycle: 150°C–550°C, in 50°C increments, for 20 minutes at each temperature at 3,000 rpm with rich/lean times set for 4% fuel consumption penalty at each point		
Periodic re-evaluation (50, 100, 150, 200, and 250 hours)	Map performance to determine change from fresh conversion efficiency at 50-hour intervals		

2.1.4 Experimental System

Engine. Given the uniqueness of the required engine operating system, coupled with the time constraints for testing, the DECSE NO_x adsorber technical committee required that the test laboratory have immediate access to a previously developed engine management system that would allow rich/lean operation for a specific engine design. The engine proposed by the single bidder, FEV Engine Technology, is a modern, 1.9-liter, 4-cylinder, high-speed, direct-injection (HSDI) engine rated at 81 kW at 4,200 rpm. This engine uses a common-rail injection system. Through a combination of inlet throttling, exhaust gas recirculation (EGR), and fuel-injection modifications, the engine allows rich/lean operation without affecting driveability. Although the engine management system is not completely refined, it is representative of a system with production potential. Before agreeing to its use, the DECSE technical committee reviewed and accepted the performance and emissions data supplied for the proposed engine.

Fuel and Oil. Under contract to NREL, Phillips Chemical supplied fuel to FEV. FEV blended 50% (by mass) of each of the 3-ppm and 30-ppm fuels to create an additional test fuel, nominally 16-ppm fuel. Shell Rotella T 15W40 engine oil was used. Oil and fuel samples were routinely collected and submitted for analysis.

Adsorber catalyst. The NO_x adsorbers supplied to the DECSE program by a catalyst manufacturer contain a precious metal formulation incorporating Pt, Pd, and Rh, and NO_x adsorbent materials supported on a single 14.4 cm-diameter by 15.2 cm-long, 400-cpsi ceramic substrate for a total volume of 2.5 liters each. Each of the substrates is housed in a stainless steel shell measuring approximately 15.2 cm in diameter by almost 66.04 cm in length, including two 15.2 cm-long by 7.6 cm in diameter inlet and outlet pipes. Pairs of adsorber catalysts (denoted a/b) were tested in parallel. The samples used are identified as 3a, 3b, 16a, 16b, 30a, 30b, S3, and S4, to track at which fuel sulfur levels (3, 16, 30) the tests were performed. (Adsorber catalysts S3 and S4 were spare adsorber catalysts used for calibration revision.)

2.1.5 Special Requirements

Engine Management System. The technical committee determined the acceptability of the rich/lean engine management system by evaluating the NO_x conversion achieved over the adsorber catalyst's temperature window during the initial calibration work. Peak conversion was expected to be greater than 80%, and the temperature window was expected to show at least 30% conversion at the extremes of 150°C and 500°C when operated with 3-ppm sulfur fuel. Results obtained after the calibration are summarized in Sections 3.1 and 4.1.

Although the adsorber evaluations were performed on an engine dynamometer, the regeneration cycle was developed within a constraint and understanding that driveability should not be compromised. The minimal torque fluctuations observed indicate that rich/lean modulation strategies would not significantly impact driveability. In fact, with increasing engine load (where NO_x is highest and the calibration perhaps more aggressive), torque fluctuations decreased to less than 5%. Most likely, however, the calibration would need to be fine-tuned for each application to account for specific torsional and noise-vibration harshness (NVH) characteristics.

Device Desulfurization. No attempts were made in Phase 1 to desulfurize the adsorber catalyst because diesel exhaust gas temperatures do not reach the high level necessary to remove sulfur from the adsorber catalyst during normal operation. An R&D effort on desulfurization was outside the scope of Phase 1, but will be investigated in Phase 2 of the program.

Systems Flushing Between Tests. To avoid contamination, the engine and test cell fuel systems were flushed when fuels were changed. Fuel filters were changed at the same time. Also, because of possible fuel dilution, engine oil and filters were changed.

2.1.6 Test Procedure

Device Set-Up. FEV configured the engine exhaust flow so that two NO_x adsorber catalysts could be tested simultaneously, increasing the statistical confidence level in the results.

Conditions were adjusted to maintain equal flow through the NO_x adsorber catalysts. Maximum back-pressure at the engine was 1.5" of mercury unless FEV obtained advanced approval from the DECSE technical committee for a variation.

Test Sequence. Testing followed a five-step sequence:

- Degreening
- Rich and lean timing engine control calibration
- Adsorber catalyst sample performance mapping
- Device aging
- Periodic measurement at a single temperature during aging.

All testing was conducted at 3,000 rpm, providing operation at a maximum space velocity of 50,000 hours^{-1}. Steps in the sequence are described below (see also Table 2.1-1).

Degreening. Each set of adsorber catalysts was first thermally stabilized with a substitute, low-sulfur (3 ppm) base fuel to expedite work. Degreening was conducted at 400°C adsorber catalyst inlet temperature and 3,000 rpm for 10 hours. The engine control system was set to operate lean only (normal diesel operation).

Rich/Lean Time Optimization. The rich/lean engine management system was calibrated with the times for rich and lean operation meant to maximize NO_x conversion, except that the fuel consumption penalty did not exceed 4% at any test point. This determination was carried out using the base fuel. The same rich/lean time settings found with the base fuel were used for tests with the other two sulfur levels. Conversion calculations were based on the average of the last 7 of a 15-cycle series.

The 4% fuel consumption penalty was selected to provide a basis of comparison with the lean-NO_x catalyst technologies also being evaluated in the DECSE program.

Sample Performance Mapping. Adsorber catalyst performance maps were developed for each of the three sulfur levels. The maps show NO_x conversion between 150°C and 550°C in 50°C increments using the 4% fuel penalty settings at 3,000 rpm.

Device Aging. Next, the devices were aged for a nominal 250-hour period, starting with the 3-ppm base fuel. The technical committee selected the 250-hour period after considering previous work that showed major degradation of NO_x adsorber catalyst conversion efficiency in less than 100 hours when sulfur levels are greater than 100 ppm. This finding indicated that 250 hours was sufficient to define the effect of sulfur on NO_x adsorber technology.

The aging cycle was composed of steady-state rich/lean operation for 20 minutes at each temperature in the following sequence:

150°C– 250°C– 350°C– 450°C– 550°C– 450°C– 350°C– 250°C– 150°C– repeat

Periodic Measurement During Aging. NO_x conversion efficiency was measured for each set of samples at 50-hour intervals during the aging tests to track the performance of the samples. Measurements were conducted using the same test procedure as that used for mapping. A device was defined to have failed when the measurements showed that the NO_x conversion average over the temperature range had dropped by 50% or more from the fresh value.

Section 3

Interim Results

3.1 NO_x Adsorber Catalyst

3.1.1 Development of Engine Calibration

An important aspect of utilizing NO_x adsorber catalyst technology is to define engine operating conditions that allow for the conversion of the stored NO_x to nitrogen at an appropriate frequency – that is before a sufficient number of the adsorption sites are occupied to result in significant breakthrough of NO_x. This is accomplished by defining a lean-to-rich modulation strategy while paying close attention to the resultant exhaust temperatures and NO_x, HC, and CO concentrations. In order to obtain the appropriate conditions for the release and subsequent conversion of the NO_x emissions to nitrogen, strategies such as altering engine fuel injection timing and rate, throttling, and EGR can be employed. A goal of this test program was to define a lean/rich modulation that resulted in no more than a 4 % fuel economy penalty and no more than a 10 % variation in load.

FEV initiated the lean/rich optimization process considering these boundary conditions. Different timings for both the lean and rich periods were investigated, from 30 to 100 seconds for the lean period and from 2 to 5 seconds for the rich period. In order to demonstrate the possible reductions afforded by NO_x adsorbers, a lean/rich timing cycle of 30 seconds of lean operation followed by 5 seconds of rich operation was studied. Figure 3.1-1 shows the results of using such a timing strategy at an exhaust gas temperature of 450°C. As indicated, very high NO_x conversions can be achieved – in excess of 95% for both adsorber catalysts tested. However, employing this strategy also resulted in a fuel economy penalty of 6.8%, outside of the program's target of 4%.

After studying optional timings, the cycle timing strategy shown in Table 3.1-1 was selected. This strategy met both the fuel economy and load fluctuation constraints outlined above.

Table 3.1-1. Cycle-Timing Strategy

Temperature Point [°C]	**150**	**200**	**250**	**300**	**350**	**400**	**450**	**500**	**550**
Lean Timing	60	60	60	60	60	60	60	70	80
Rich Timing	2	2.5	3	3.5	4	4	4	4	4

This strategy resulted in a peak NO_x reduction of almost 80% and a bimodal conversion with very little reduction at 350°C as shown in Figure 3.1-2. One shortcoming in the engine rich regeneration strategy is that the rich engine calibration was not optimized for all temperature conditions. This became apparent only after aging had already begun. Although it was recognized that further optimization of a timing strategy could be performed to exhibit higher NO_x conversion efficiencies, the technical committee agreed that the objective of the program could be investigated with the initial calibration. Plans were made for further optimization of the engine rich calibration at the end of the program.

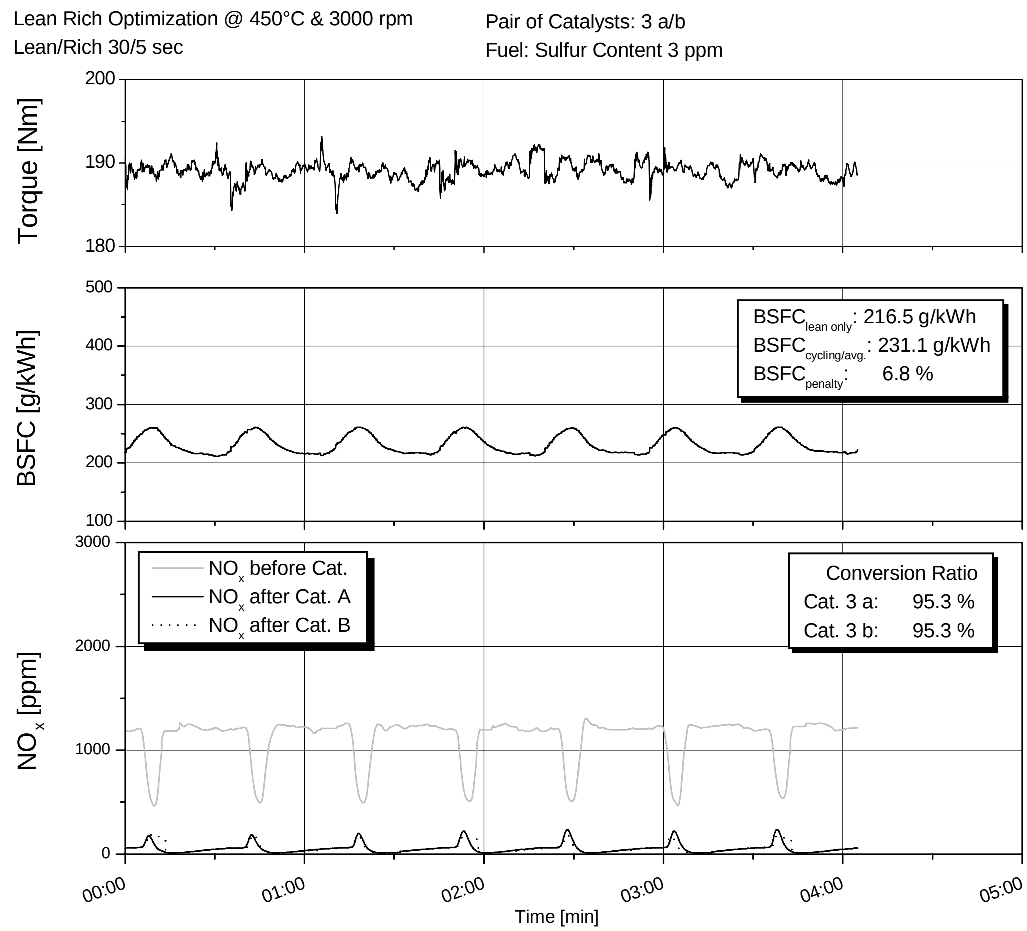

Figure 3.1-1. Engine torque, fuel consumption, and NO_x at 450°C for 30/5s lean/rich sequence with 3-ppm sulfur fuel

With this first engine calibration and the inherent conversion mechanisms associated with NO_x adsorption technology, it is challenging to interpret the effect of fuel sulfur on the adsorbers in the low temperature regions for the three fuels tested, as will later be discussed. Also, the ability to adjust the lean/rich modulations for changes, associated with normal adsorber aging, in an adsorber's adsorption, desorption, and subsequent conversions, was not investigated as a part of Phase 1. A discussion of how lean/rich modulations can be modified to insure high conversion efficiencies as normal adsorber catalyst aging occurs is contained in Section 3.1.3.

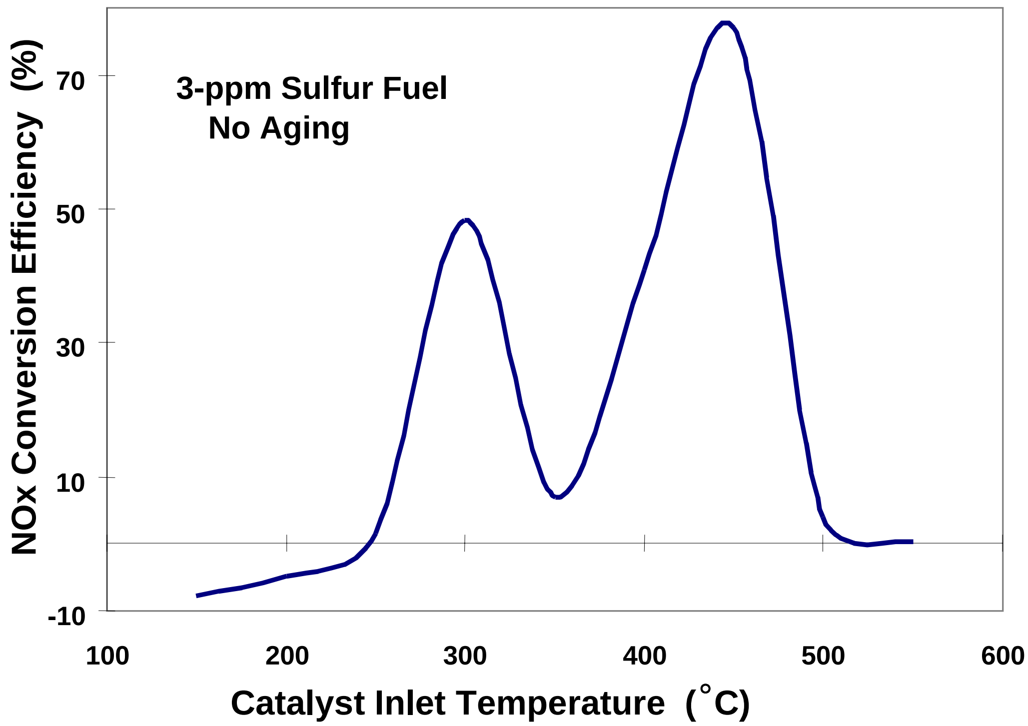

Figure 3.1-2. NO_x conversion efficiency using the initial calibration on a zero-hour aged adsorber catalyst pair using 3-ppm sulfur fuel

Toward the end of Phase 1, after the aging studies had been completed, further adjustments to the engine rich calibration were performed to see if a more robust calibration could be developed. The results of the revised calibration are compared with the old calibration for a fresh adsorber catalyst pair in Figure 3.1-3. These results were achieved without exceeding the 4% fuel consumption penalty maximum.

As can be seen, the new strategy provided more reductants that significantly improved conversion efficiency over a broad temperature range, highlighting the importance of engine calibration. Conversions of more than 80% were achieved between the temperatures of approximately 300° and 450°C, indicating that the dip associated with the initial strategy at 350°C, as well as the relatively low conversions at low and high temperatures, was a result of an improper initial calibration. The improved performance of the adsorber catalyst can be attributed to improved engine calibration, which resulted in an increased level of reductants while leaving engine-out NO_x unchanged.

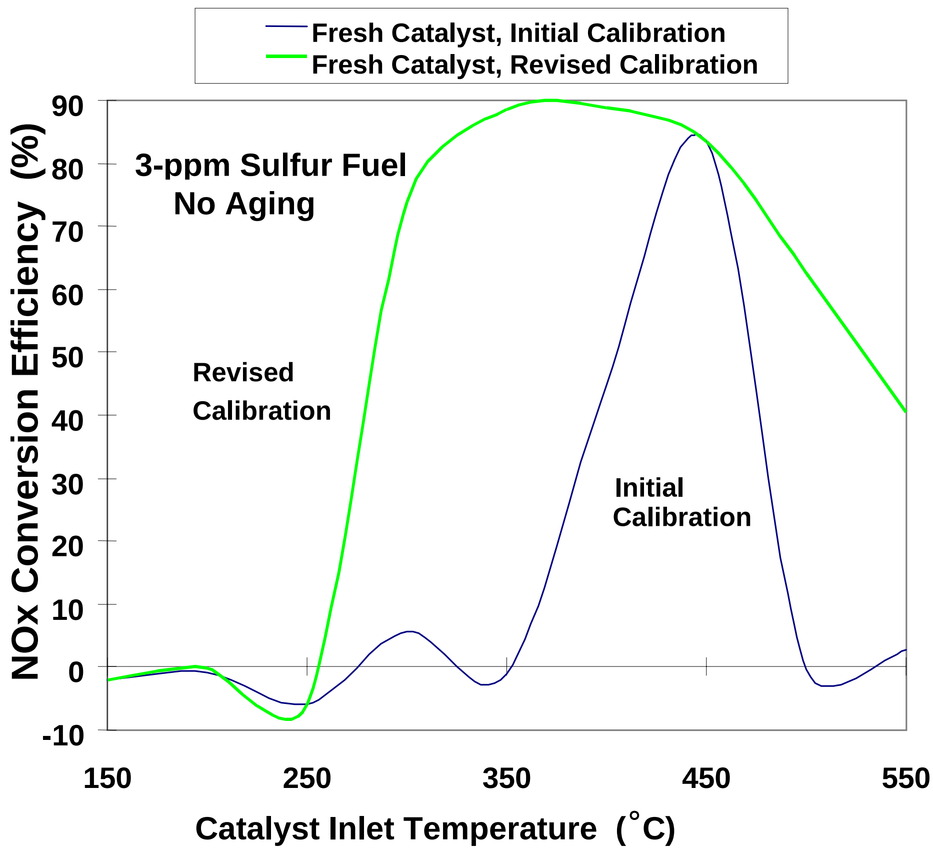

Figure 3.1-3. NO_x conversion efficiency for spare adsorber catalyst pair with 3-ppm sulfur fuel, with initial and revised engine calibration strategy and identical rich/lean timing

3.1.2 Investigation of Sulfur Effects

Using the initial, unoptimized calibration, the effects of three fuel sulfur levels (3-ppm, 16-ppm, and 30-ppm) on NO_x adsorber technology were investigated. During the evaluations, oil and fuel samples were analyzed. Engine oil consumption was measured over the duration of testing to ensure that it was stable and within the range expected for the engine design. No abnormal conditions were found, with average oil consumption well within the rate expected. The results of the sample analysis will be reported in the DECSE final report.

Figures 3.1-4, 3.1-5, and 3.1-6 show average adsorber performance for adsorbers aged with 3-, 16-, and 30-ppm sulfur fuel at 0, 100, 150, and 250 hours of aging, along with the fresh adsorber catalyst (zero hours) performance.

To best understand the results generated during testing, the data found at temperatures of 300°, 400°, and 450°C can be used.

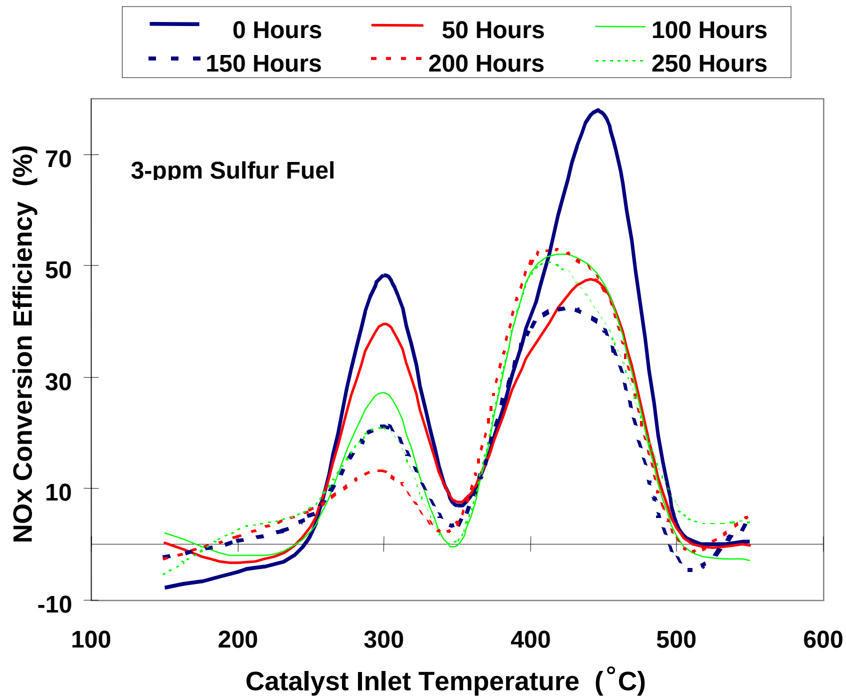

Figure 3.1-4. Effect of aging on NO_x conversion efficiency with 3-ppm sulfur fuel for the analysis temperature range from 150° to 550°C

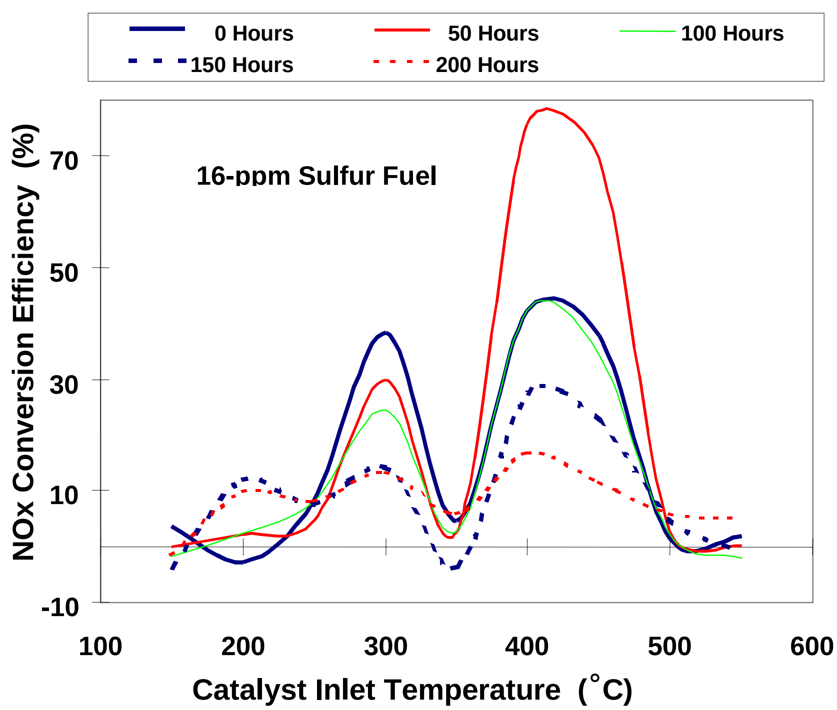

Figure 3.1-5. Effect of aging on NO_x conversion efficiency with 16-ppm sulfur fuel for the analysis temperature range from 150° to 550°C

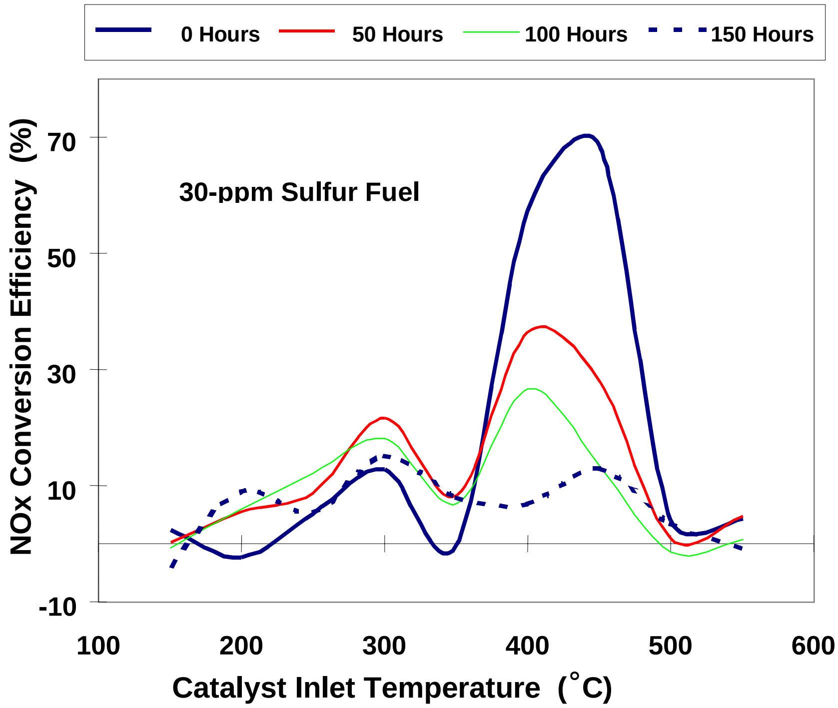

Figure 3.1-6. Effect of aging on NO_x conversion efficiency with 30-ppm sulfur fuel for the analysis temperature range from 150° to 550°C

Figure 3.1-7 illustrates the results at 300°C. As shown, the average performance of both the adsorber catalysts aged with 3- and 16-ppm fuels appeared to degrade with continued exposure, with the average performance of the adsorber catalysts exposed to 3-ppm fuel appeared to improve slightly in the last 50 hours of testing. On the other hand, the initial conversion efficiency of the adsorber catalysts tested with 30-ppm sulfur fuel was less than 20% and remained relatively constant throughout the aging cycle. The low conversions and inconsistent results at 300°C make the interpretation of sulfur effects challenging at this temperature point (see the discussion in Section 3.1-3).

In order to better understand the effects of sulfur on the performance capability of NO_x adsorber technology at lower temperatures, e.g., 300°C, a different rich engine calibration strategy for adsorber NO_x regeneration (accounting for space velocities, anticipated aging, and higher NO_x conversion efficiencies) would need to be investigated. Nonetheless, data obtained at 400° and 450°C (where conversion efficiency sensitivities to space velocities and light-off issues are much reduced) can be used to evaluate the effects of different sulfur levels on NO_x adsorber technology.

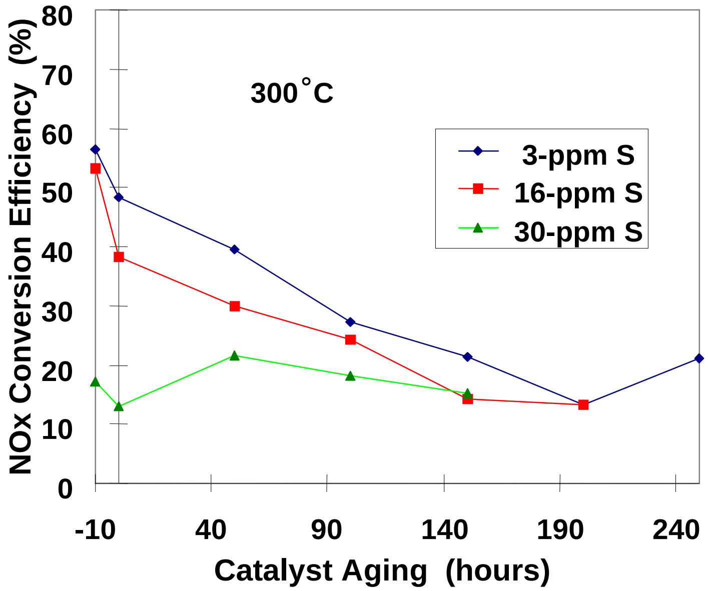

Figure 3.1-7. Effect of fuel sulfur level on NO_x conversion efficiency versus aging up to 250 hours at the 300°C analysis temperature

Results from tests conducted at 400° and 450°C, shown in Figures 3.1-8 and 3.1-9, further demonstrate the detrimental effects of fuel sulfur on the performance of NO_x adsorbers. Although there is significant variation in conversion efficiencies during the first 50 hours of testing (generally between 40% to 80%), NO_x conversion efficiencies with 3-ppm sulfur fuel remain relatively constant through 250 hours of aging. On the other hand, adsorbers aged with 16- and 30-ppm sulfur fuel showed a continued and rapid decline in performance. With 16-ppm fuel, testing was abandoned at 200 hours of aging when the conversion efficiency dropped below 20% at all temperatures. This occurred more rapidly (at 150 hours) with the 30-ppm sulfur fuel.

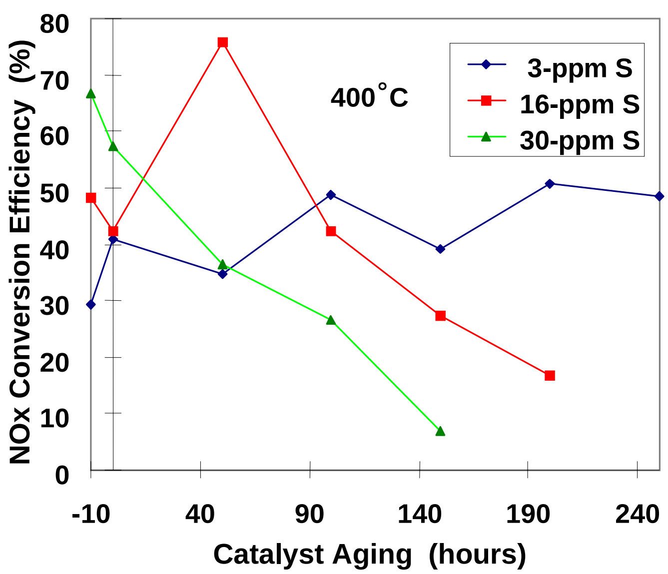

Figure 3.1-8. Effect of fuel sulfur level on NO_x conversion efficiency for aging up to 250 hours at the 400°C analysis temperature

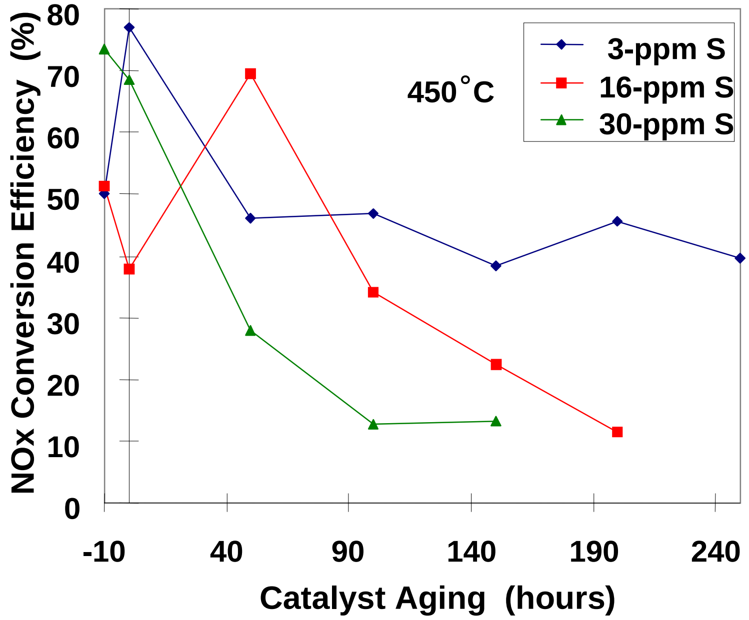

Figure 3.1-9. Effect of fuel sulfur level on NO_x conversion efficiency for aging up to 250 hours at the 450°C analysis temperature

The integrated results are shown in Figure 3.1-10, summarizing data from Figures 3.1-4, 3.1-5, and 3.1-6, over the analysis temperatures of 150° to 550°C. Recognize that the integrated conversion efficiencies are significantly affected by the lowest conversion efficiencies (especially at low temperatures), which resulted from the initial engine rich calibration strategy. There is a clear effect of both age and fuel sulfur level on the decay of NO_x conversion efficiency. The degree of NO_x conversion efficiency degradation increases with increasing fuel sulfur level.

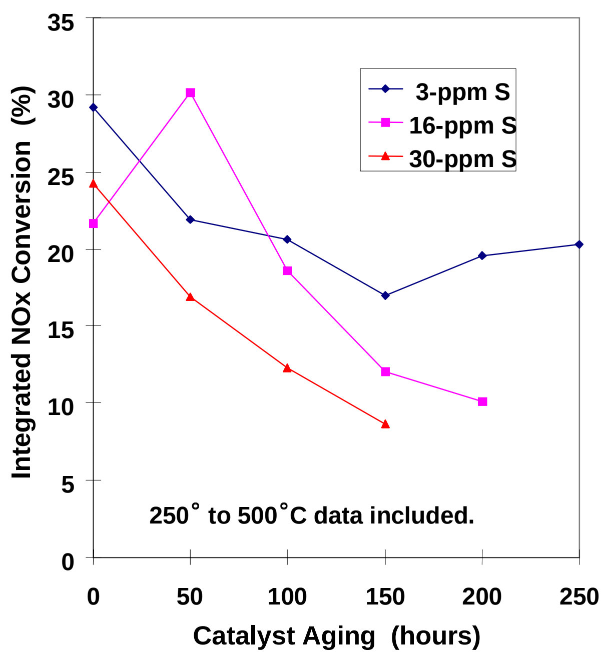

Figure 3.1-10. Integrated NO_x conversion from 250° to 500 °C as a function of age and fuel sulfur level

To further verify the adverse effects of fuel sulfur on the conversion efficiency of NO_x adsorber catalysts, the adsorber pair aged for 250 hours with 3-ppm sulfur fuel and the adsorber pair aged for 200 hours with 16-ppm fuel were retested using the revised calibration shown in Figure 3.1-3.

Figure 3.1-11 compares the average conversion efficiency of adsorber catalysts aged on 3- and 16-ppm fuel. These data show that the average conversion efficiency of the adsorber catalysts aged on 16-ppm fuel was severely degraded compared to the average conversion efficiency of the adsorber catalysts aged on 3-ppm fuel.

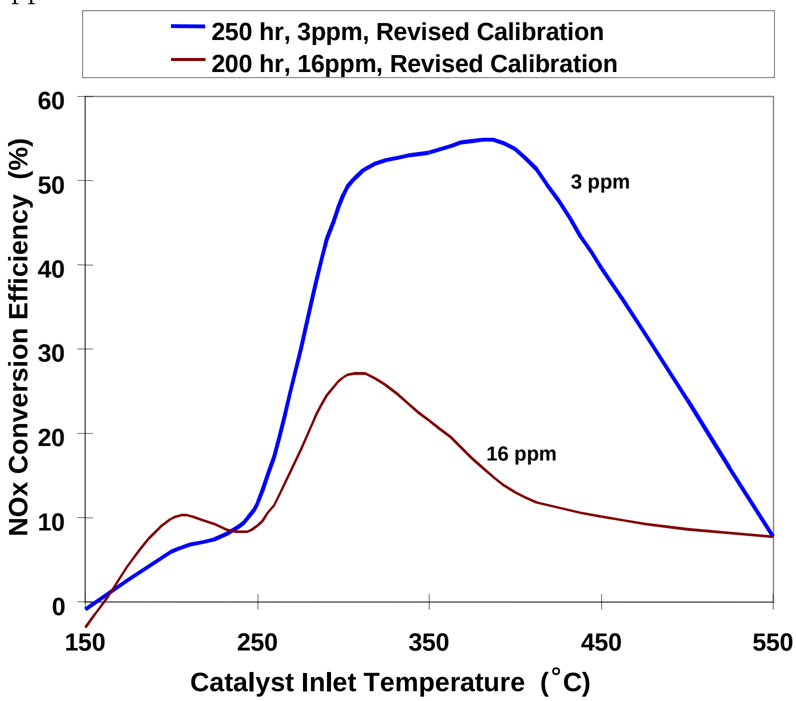

Figure 3.1-11. Effect of fuel sulfur level on NO_x conversion efficiency on 3-ppm sulfur adsorber catalysts (250 hours of aging) and 16-ppm sulfur adsorber catalysts (200 hours of aging) with revised engine management calibration

A concern exists that even low levels of sulfur (e.g., 3 ppm) will eventually degrade NO_x adsorber performance, but it is possible (theoretically) that an adsorber catalyst desulfurization strategy can be developed. This strategy would be used to remove the sulfur compounds from the NO_x storage sites, thereby regaining adsorber catalyst performance. The investigation and development of such a cycle is planned for Phase 2 of the DECSE program. This work will investigate the operating parameters and conditions required to desulfurize NO_x adsorbers, the effect of sulfur levels on the degree to which the adsorber catalysts can be desulfurized, and the impact of desulfurizing procedures on fuel economy as a function of fuel sulfur level. It is anticipated that the investigation will provide valuable information on the level of sulfur in diesel fuel that will be required to make NO_x adsorber technology commercially viable. The work carried out in this part of the DECSE program demonstrates the benefit of very low levels of sulfur in diesel fuel on NO_x adsorber catalyst technology and also demonstrates the NO_x reduction potential of the technology. Additional aging of the 3-ppm adsorber catalyst pair would also demonstrate whether or not the decline in performance found over a 250 hour period had indeed stabilized, or if degradation with continued exposure to sulfur could be expected.

3.1.3 *Discussion of Limitations of the Initial Engine Calibration Used in the Test Program*

Although the effects of different fuel sulfur levels on NO_x adsorber catalyst technology could be demonstrated using the initial engine calibration strategy developed as a part of this test program (as outlined in Section 3.1.2), the strategy was not optimized to show the potential NO_x reductions that can be achieved using NO_x adsorber catalyst technology. The shortcomings of the calibration can be seen in Figure 3.1-3 (on page 13) that compares the resulting NO_x conversion efficiencies on a pair of spare adsorber catalysts for both the initial calibration and the revised calibration.

As indicated in the figure, the new strategy significantly improved conversion efficiency over a broad temperature range, highlighting the importance of engine calibration. Conversions of more than 80% were achieved between the temperatures of approximately 300° and 450°C, indicating that the dip associated with the initial strategy at 350°C, as well as the relatively low conversions at low and high temperatures, was a result of an improper initial calibration. Analysis of the data indicated that engine-out NO_x emissions were the same for both calibrations, supporting the conclusion that improved performance of the adsorber can be attributed to improved engine calibration and not a change in lean engine-out NO_x emissions. The revised calibration resulted in increases in exhaust CO and HC, and the CO:HC ratio during the rich operating period, without changing lean-period NO_x. The CO and (to a lesser extent) the HC act as reductants for the stored NO_x when it is released from the adsorber catalyst during the rich period.

An examination of the data generated on the initial engine calibration as part of Phase 1 shows a high variability in NO_x conversion efficiencies for fresh catalysts at 300°C for the four sets of catalyst pairs tested, as shown in Table 3.1-2.

Table 3.1-2. Fresh Conversion Efficiencies at 300°C

Catalyst Pair	Fresh* Conversion Efficiency
Pair Tested on 3-ppm Sulfur Fuel	56%
Pair Tested on 16-ppm Sulfur Fuel	53%
Pair Tested on 30-ppm Sulfur Fuel	17%
Spare Pair Tested on 3-ppm Sulfur Fuel	5.7%

*"Fresh" indicates the degreened catalyst-pair average during the mapping test at less than 10 hours of aging.

As shown above, the rich engine calibration used for NO_x regeneration in the testing resulted in low and inconsistent performance for the adsorber catalysts at 300°C. This suggests that more attention to the engine rich calibration strategy at this test point may have resulted in improved adsorber catalyst performance. These low conversions also make the interpretation of the sulfur effects challenging at this temperature. At low temperatures, an adsorber catalyst's light-off (ability to convert NO_x at low temperatures) and storage issues are more pronounced, making it difficult to factor in variations in these parameters, potentially contributing to test-to-test and adsorber sample-to-sample performance variability.

Another aspect of the test program that would adversely affect the adsorber catalysts' abilities to convert NO_x at low temperatures is the fact that during the test program, an engine speed of 3,000rpm was maintained for all testing. These engine speeds result in higher than normally expected catalyst space velocities (a function of exhaust flow) at low engine operating temperatures. Although space velocities are not as critical to catalyst performance at higher temperatures, they can significantly hamper the ability of the catalyst to convert NO to NO_2 at low temperatures where the reactions are mass-transfer limited, again adversely affecting the adsorber catalysts' conversion efficiencies. In practice, low exhaust gas temperatures are associated with lower engine speeds, hence lower catalyst space velocities. Therefore, higher conversion efficiencies would be anticipated in these low temperature regions than were found in this test program. Furthermore, changes in adsorber catalyst performance due to normal adsorber catalyst aging would be more pronounced at 300°C (especially in combination with high space velocities) than at higher temperatures.

In order to better highlight the performance capability of NO_x adsorber catalyst technology at lower temperatures, e.g., 300°C, a different rich engine calibration strategy for adsorber NO_x regeneration (accounting for space velocities, anticipated aging, and higher NO_x conversion efficiencies), perhaps more similar to the calibration used to generate the results in Figure 3.1-3, as well as different lean/rich modulations could be investigated. For example, consider the lean/rich modulation schedule outlined in Table 3.1-1 (on page 10). As shown at low temperatures where the rates of desorption are slowest, the time the engine was operated rich for adsorber catalyst regeneration ranged from 2 to 3 seconds. Increasing this to a 4-second interval, as was the case for the higher temperatures, may have resulted in more complete desorption, thereby increasing catalyst conversion efficiencies. It is also possible that the additional fuel economy penalty associated with this change could have been offset by decreasing the rich running time at higher temperatures where the rate of desorption is inherently more rapid without significantly affecting conversion efficiencies at the higher temperatures.

Another method available to increase low temperature conversion efficiencies (in practice) would be to include a light-off catalyst. This was not investigated as a part of Phase 1 of the test program.

Although not a part of Phase 1, the investigation of engine rich calibration and lean/rich modulation strategies developed for an adsorber catalyst that had already been thermally aged may have produced data showing significantly improved adsorber catalyst performance at all temperatures. Aging the catalyst over the test cycles used as a part of Phase 1 may have caused some precious metal sintering and loss in catalyst surface area due to the exhaust gas temperatures generated. Any sintering of the precious metals and loss in the catalyst surface area would have affected the ability of the catalyst to both store and convert NO_x emissions. Shortening the lean running time with a corresponding decrease in the time the engine is run rich (to preserve the fuel economy penalty target of 4% of the lean/rich modulation schedule shown in Table 3.1-1) could possibly have accounted for any loss in performance due to anticipated thermal aging.

3.1.4 Analysis of NO_x Conversion Efficiency versus Adsorber Catalyst Age and Fuel Sulfur Level

The statistical significance of the change in NO_x conversion efficiency (CE) was tested using a statistical model that assumes the log of NO_x emissions (ppm) has a linear relationship with adsorber catalyst age. Thus, if X=adsorber catalyst emissions and Y=engine-out emissions, then

$$\mathrm{CE(age)} = 1 - X/Y = 1 - \exp(\ln X - \ln Y), \text{ and } \ln X - \ln Y = \text{intercept} + \text{slope} \times \text{age} + \text{error.}$$

Separate regression models were run for each combination of fuel type and adsorber catalyst temperature. However, data from different temperatures (for the same fuel type) were analyzed together in order to obtain a more reliable estimate of the error standard deviations. The difference between adsorber catalysts a and b was treated as a random effect.

There are significant age effects at two of the three temperatures with 3- and 30-ppm sulfur fuel. A positive slope for ln(X/Y) indicates a downward trend in CE versus age. The intercept and slope results are included in Table 3.1-2. The lack of statistical significance with 16-ppm fuel is due to the inflated error estimate caused by the unusual results at age 0 and 50 hours. Similar analyses were performed with several subsets of data (e.g., without zero-hour data) and with different transformations applied to the data. Each analysis approach produced slightly different results (i.e., different slopes were statistically significant). However, the same general conclusions were reached each time: NO_x conversion efficiency decreases with age, and the degradation rate is greater with the higher sulfur fuels.

Table 3.1-3 also contains, for each combination of fuel sulfur level and inlet temperature, the predicted conversion efficiency at ages zero and 150 hours, and the age at which the predicted conversion efficiency would be 50% of the initial (age zero) level. In some cases, the latter value does not exist because the predicted conversion efficiency increases with age (although the increase is not statistically significant).

Predicted conversion efficiencies at ages zero and 150 hours were averaged across the three temperatures to determine the "integrated" percent change in conversion efficiency. These values range from 20% loss in conversion efficiency with 3-ppm sulfur fuel to 87% loss with 30-ppm sulfur fuel. If the average were to be taken over only the 400° and 450°C data, the result would be 11, 47 and 100% degradation for the 3-, 16-, and 30-ppm sulfur data sets, respectively. Once again, NO_x conversion efficiency decreases with age and the degradation rate is greater with the higher sulfur fuels.

Table 3.1-3. Results of Statistical Evaluations of NO_x Conversion Changes as a Function of Age and Fuel Sulfur Level

Fuel Sulfur Level (ppm)	**Temperature** (°C)	**Predicted CE(0)**	**Predicted CE(150)**	**150-Hour Decay** (%)	**Age at 50% Change** (hours)	**Intercept**	**Slope**
3	300	44.4	26.0		177	**4.019**	**0.0019**
3	400	38.4	45.3		.	**4.121**	-0.0008
3	450	66.0	47.4		234	**3.527**	**0.0029**
Average		49.6	39.6	**20**	206	3.89	0.0013
16	300	36.8	17.2		142	**4.147**	0.0018
16	400	62.7	35.0		165	**3.620**	0.0037
16	450	56.7	27.9		148	**3.788**	0.0034
Average		52.0	26.7	**49**	152	3.89	0.0030
30	300	16.6	17.8		.	**4.424**	-0.0001
30	400	54.9	4.5		95	**3.809**	**0.0050**
30	450	60.3	-5.2		87	**3.681**	**0.0065**
Average		43.9	5.7	**87**	91	3.89	0.0038

Bold intercept and slope numbers indicate statistical significance at the 95% confidence level.

Predicted CE(age) = 100 - exp {intercept + slope x age }

Age at 50% decay = Solution to predicted CE(age) = 0.5 x predicted CE(0)

3.1.5 Preliminary Emissions Summary for the NO_x Adsorber Catalyst

Smoke testing was performed as a part of the test program to insure that the calibration employed in the timing modulation cycle did not result in the excessive production of smoke. Smoke (Bosch Number) was measured downstream of the adsorber catalyst. The smoke reading showed no obvious sensitivity to adsorber catalyst aging, or to the fuel sulfur level from 3 to 16 to 30 ppm.

The engine produces extremely elevated levels of CO and HC during the rich operating periods, increasing the rich/lean average CO concentration by a factor of 5.5, and the HC by a factor of 11, relative to the lean-only average concentrations in the exhaust. The CO and, to a lesser extent, the HC, act as reductants to reduce the NO_x from the adsorber. Both CO and HC may also be oxidized to CO_2 across the oxidation catalyst.

The CO conversion across the fresh adsorber catalysts is typically 80% to 95%, whereas the HC conversion is generally in the range of 60% to 80%. There is significantly more variability in the HC conversion than in CO conversion. Neither the CO or HC conversion shows a strong response to the fuel sulfur level, but both tend to degrade with catalyst aging. The aging effect is larger with 16- and 30-ppm sulfur fuel than it is for 3-ppm sulfur fuel. The changes in CO and HC conversion are much lower than the NO_x responses to age or to fuel sulfur level. In general, the CO and HC conversion efficiencies remain above 60%, even at the highest sulfur level and the highest aging levels evaluated.

Section 4

Interim Conclusions

4.1 NO_x Adsorber Catalyst Interim Conclusions

The test program's interim results (illustrated in Figure 4.1-1) indicate that:

- Figure 4.1-1 illustrates the effect of fuel sulfur on relative NO_x conversion efficiencies at 400° and 450°C after 150 hours of testing. Compared to 3-ppm sulfur fuel at 150 hours, both 16- and 30-ppm sulfur fuels resulted in significant performance declines.

- Although testing with 3-ppm sulfur fuel showed an initial decline in adsorber catalyst performance, the performance subsequently appeared to stabilize, out to the 250-hour period. Further aging would be required to determine adverse affects of 3-ppm sulfur fuel beyond this point.

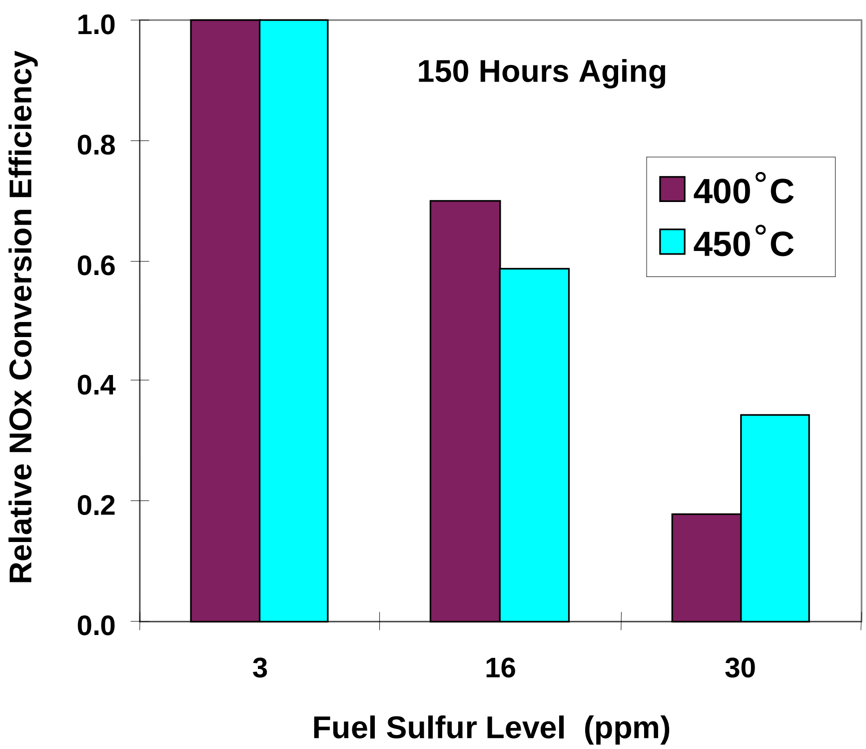

Figure 4.1-1. Effect of increasing fuel sulfur level on relative NO_x conversion efficiency for 150-hour aged NO_x adsorber catalyst evaluated at 400°and 450 °C

- Fresh NO_x adsorbers are capable of providing high NO_x conversion levels (e.g., more than 80%) across a broad range of operating temperatures when coupled with an optimized engine rich regeneration calibration, while maintaining a fuel economy penalty of less than 4%.

The initial calibration of the engine management system did not achieve the desired level of NO_x conversion performance across the range of operating temperatures. Maximum efficiency was achieved at 450°C and was lower than the desired level, both below and above this temperature, as shown in Figure ES-2. The revised calibration, established after aging tests were completed, produced improved conversion efficiency.

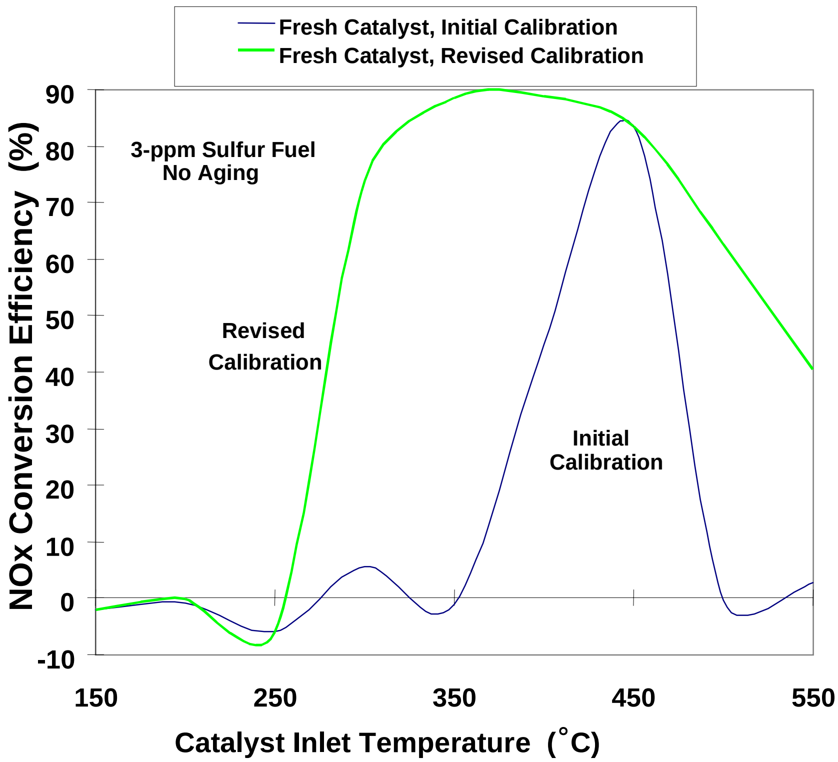

Figure 4.1-2. NO_x conversion efficiency with initial and revised engine calibration strategies and identical rich/lean timing