

# Aging of NOx Absorber Catalysts with Iterations of Sulfur Loading and Desulfation

Jim Parks, Aaron Watson\*, Bill Epling, and Michele Sanders  
EmeraChem LLC

Copyright © 2004 Society of Automotive Engineers, Inc.

## ABSTRACT

NOx absorber catalysts are capable of achieving high NOx reduction in exhaust from lean-burn engines. The temperature range of operation of the NOx absorber catalyst corresponds well to the exhaust temperature range of diesel engines, and the NOx reduction can be accomplished using diesel fuel. These facts make NOx absorber catalysts promising candidates for NOx emission control for diesel engine vehicles. Sulfur masking of NOx sorption sites can lead to degradation of NOx absorber catalyst performance, but engine operation with ultra-low sulfur diesel fuels and improvements in catalyst formulations that allow reversal of sulfur masking effects have shown that degradation from sulfur masking can be minimized. Catalyst improvements to reverse sulfur effects include the capability of the catalyst to "desulfate" by releasing sulfur in a net-reducing atmosphere at elevated temperatures. The study presented here involves engine testing of NOx absorber catalysts with repetitive sulfur loading and desulfation cycles to accelerate aging of the catalysts. Results from the study allow predictions of catalyst durability in terms of vehicle mileage and characterization of catalyst degradation mechanisms.

## INTRODUCTION

NOx absorber catalyst formulations specific to diesel engine applications have been developed. Catalyst capabilities enable reduction of NOx over a broad temperature range well matched to diesel engine exhaust.<sup>1,3</sup> The catalyst is a candidate for NOx emission control in upcoming emission regulations for light-, medium-, and heavy-duty on-road trucks. A critical requirement of the catalyst to meet upcoming regulations is useful life or durability. The strictest regulation is the US 2007/10 heavy-duty on-road truck regulation, which calls for 435,000 miles of durability. To project catalyst durability, NOx absorber catalysts have been aged in diesel exhaust under accelerated conditions.

Previous studies have shown the capability of NOx absorber catalysts to desulfate at catalyst temperatures between 450° and 550°C. The relatively low temperature for desulfation is beneficial to the durability of the catalyst in the actual application by minimizing thermal degradation effects associated with the necessary desulfation process. During previous aging studies with repetitive sulfur loading and desulfation cycles, the thermal degradation associated with desulfation was determined to be the primary degradation mechanism.<sup>4</sup>

NOx absorber catalysts with relatively low desulfation temperatures were aged in engine exhaust. An accelerated aging test was performed by operating the catalyst with 1,000 cycles of sulfur loading and desulfation. High sulfur fuel was used to accelerate sulfur loading and ultra low sulfur fuel was used during desulfation; this combination of fuel allows rapid aging while simulating operation with future fuels (<15-ppm S). A target desulfation temperature of 500°C was used. The results of the aging test are reported here. Catalyst performance for NOx reduction will be analyzed over time, and projections of catalyst durability in miles will be given.

## EXPERIMENT DESIGN

The engine test platform has been described in previous publications and will be reviewed here.<sup>4</sup> A 3.9-liter, 4-cylinder turbo-assisted diesel engine (Cummins 4B3.9T-G4) was used for catalyst testing. The engine has a 6.9 g/bhp-hr NOx emission rating. The engine was connected to a generator as part of a 50 kW generator-set package. A resistive load bank was used to control engine load; all tests were done at steady-state at an engine speed of 1800 rpm.

Two fuels were used for testing: (1) an ultra-low sulfur ("ULS") fuel with <3 ppm sulfur (Chevron-Phillips) and (2) a 150-ppm sulfur fuel (Chevron-Phillips) that was the same chemistry as the ULS fuel but doped to a target level of 150-ppm sulfur with the same sulfur components used in the DECSE program.<sup>5</sup> The engine

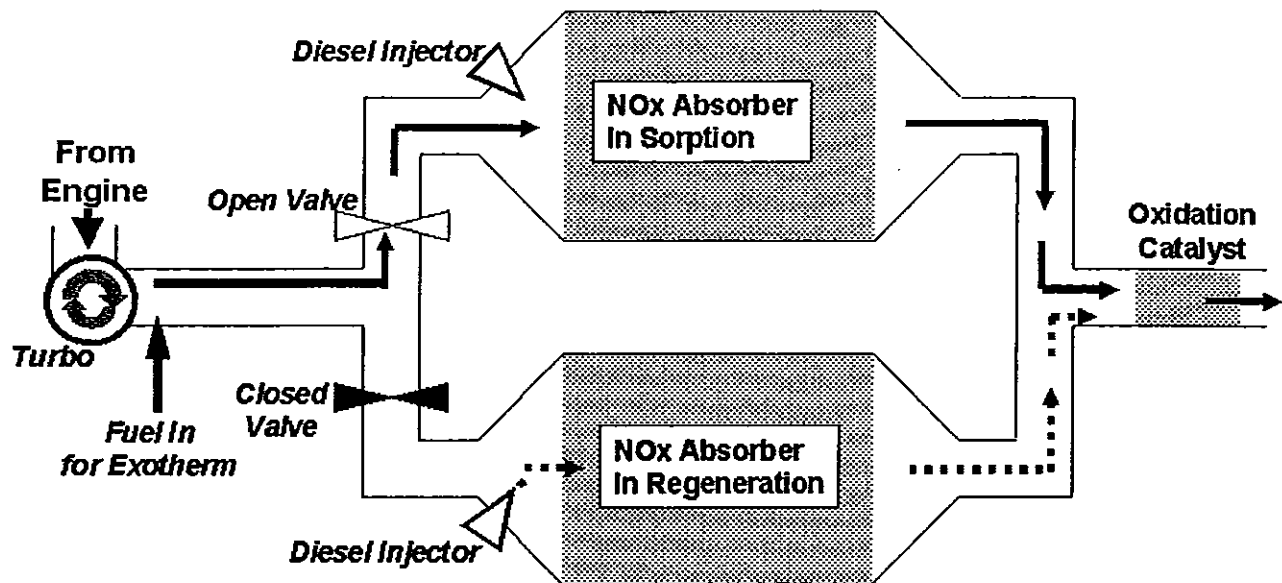


Figure 1. The two-chamber system used for testing. Valves controlled exhaust flow.

was operated with both fuels over the course of testing, but only ULS diesel was used for in-exhaust injections for catalyst regeneration and thermal control.

A two-chamber catalyst system (Figure 1) with exhaust brake valves to control flow between the two chambers was used. Exhaust flow alternated between the two chambers with NOx sorption occurring in the chamber exposed to exhaust and NOx release and reduction ("regeneration") occurring in the opposing chamber. NOx absorber catalysts were housed in each chamber. Regeneration of the NOx absorber catalyst was performed by isolating the catalyst from the main exhaust flow with an exhaust brake valve and, subsequently, injecting ULS diesel fuel into the catalyst chamber upstream of the catalyst. A typical flow rate for the diesel injection was 20 g/min for 12-30 seconds. An air-assisted diesel injector was used to assist in atomization of the diesel liquid. The flow of air and exhaust (leaked past the exhaust brake valve) was low (~50 slpm) compared with the exhaust flow from the engine (typically 3400 slpm). Once the diesel was injected into the catalyst chamber, the diesel fog traversed through the catalyst cells where the rich diesel mixture is partially combusted to supply a net-reducing atmosphere suitable for catalyst regeneration. A small oxidation catalyst (space velocity ~200,000/hr) was placed downstream of the convergence of exhaust from both catalyst chambers to assist with the oxidation of CO remaining from the catalyst regeneration process.

In addition to the diesel fuel injected into the exhaust system for catalyst regeneration, diesel fuel was also injected into the exhaust stream to assist in thermal control of the catalyst for the desulfation process. The fuel injected for thermal control was injected into the turbo-outlet manifold to allow for sufficient mixing in the exhaust prior to the catalyst. The amount of fuel injected was controlled via feedback from a thermocouple sensor inserted into the catalyst monolith.

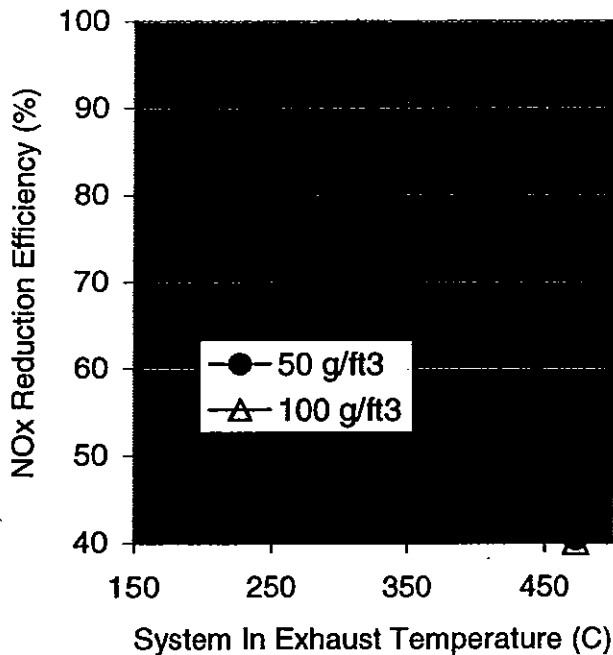
NOx reduction efficiencies were measured by sequentially monitoring the NOx exhaust emissions before ("engine out") and after ("system out") the catalyst system. NOx was measured with a chemiluminescent NOx analyzer (California Analytical Instruments) after the H<sub>2</sub>O was removed from the exhaust sample with a chiller. The same analyzer system sampled exhaust from engine out and system out locations; a valve switched between sampling locations. During the desulfation process, exhaust samples were not collected to avoid hydrocarbon exposure in the analyzers from the supplementary fuel injected into the engine out exhaust stream for thermal control.

## CATALYSTS

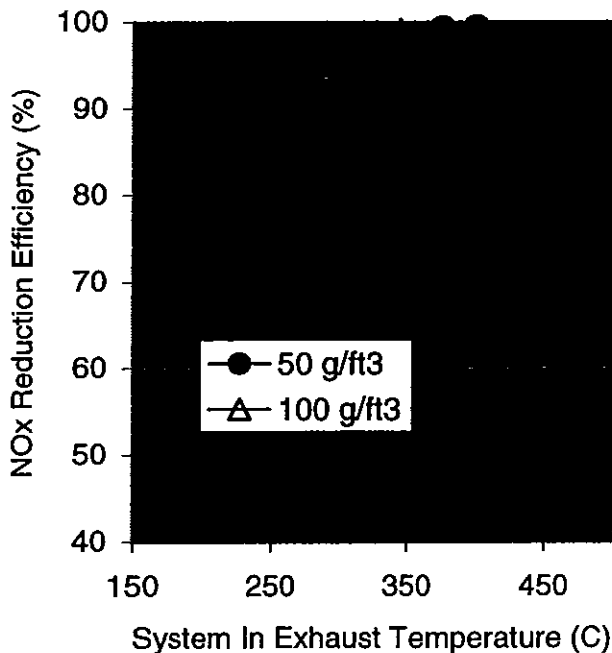
Catalysts tested on the engine were applied to a ceramic monolith with 300 cells per square inch (NGK Insulators, Ltd.). 9.9-liters of NOx absorber catalyst (nominally 21,000/hr space velocity) were housed in each chamber.

Two different platinum group metal (PGM) loadings were tested. A PGM loading of 50 g/ft<sup>3</sup> was tested in one reactor (reactor "R1"), and a PGM loading of 100 g/ft<sup>3</sup> was tested in the other reactor (reactor "R2"). Operation of the system and analysis of the data were conducted in a manner to separate the performance of the 50 and 100 g/ft<sup>3</sup> catalyst loadings.

The primary difference in the performance of the different precious metal loadings occurred in the low temperature region for fresh catalysts. Figures 2 and 3 show the NOx reduction efficiency for both catalysts operated with 2.5- and 1.0-minute sorption cycles, respectively. Here engine load was varied to change catalyst temperature; thus, NOx levels into the catalyst increased with increasing temperature.



**Figure 2.** NOx reduction efficiency obtained with a 2.5-minute sorption cycle as a function of temperature. PGM loadings of 50 and 100 g/ft<sup>3</sup> are shown.



**Figure 3.** NOx reduction efficiency obtained with a 1.0-minute sorption cycle as a function of temperature. PGM loadings of 50 and 100 g/ft<sup>3</sup> are shown.

The different sorption cycle periods tested allowed comparison of the catalysts for cases with different integrated inlet NOx mass, and thereby, different saturation levels. For the 2.5-minute sorption cycle, the integrated inlet NOx mass resulted in saturation of the catalyst capacity in the low and high temperature zones. The 100 g/ft<sup>3</sup> PGM loading performs

better at low temperatures, but performance at temperatures above 300°C is not dependent on PGM loading. For the 1.0-minute sorption cycle, the integrated inlet NOx mass was not sufficient for saturation of the catalyst capacity; thus, the catalyst performance for 50 and 100 g/ft<sup>3</sup> PGM loadings is comparable. Note that the scales for Figs. 2 and 3 are the same.

## ACCELERATED AGING TEST PROTOCOL

Aging of the catalysts was performed with a protocol designed to accelerate degradation effects by exposing the catalysts to high temperatures and high sulfur levels for extended time frames. During the high temperature and sulfur exposure, the NOx performance of the catalyst was monitored at a medium temperature (350°C) in order to track performance degradation of the catalyst as a function of aging.

Prior to the aging test, a degreening procedure was performed which consisted of 10 hours of exposure to a catalyst temperature of 500°C. In addition to this thermal degreening, a sulfur degreening step was performed that consisted of saturation with sulfur by operating the engine with 150-ppm S fuel; the catalyst was desulfated at 500°C after sulfur saturation.

The aging protocol consisted of a sulfur loading and desulfation step. During the sulfur loading step, the catalyst performance was monitored, and the catalyst was exposed to sulfur. The desulfation portion of the test lasted approximately one hour and included exposure at relatively high catalyst temperatures. Lean-rich cycling was continued during the desulfation step; a total of 6.3 minutes of rich exposure occurred for every 63 minutes of the desulfation step. Conditions and duration for the sulfur loading and desulfation steps are as follows:

### Sulfur Loading Step (A)

Engine Load: 25 kW  
 Catalyst Temperature: 350°C  
 Engine Fuel: 150-ppm S Fuel  
 Fuel for Catalyst Regeneration: ULS Fuel  
 Catalyst Cycle Times: 1.0-, 2.5-min.  
 Duration: 36 minutes

### Desulfation Step (B)

Engine Load: 40-50 kW  
 Catalyst Temperature: 500°C (controlled)  
 Engine Fuel: ULS Fuel  
 Fuel for Catalyst Regeneration: ULS Fuel  
 Fuel for Thermal Management: ULS Fuel  
 Catalyst Cycle Time: 1.5-min.  
 Duration: 63 minutes (Total Rich Time=6.3 min.)

Steps A and B above were repeated in an A-B-A-B-A-B-etc. sequence to form the aging protocol. Aging time is generally reported in terms of hours of desulfation since degradation is expected to be primarily due to the thermal exposure during desulfation. In order to project catalyst performance as a function of vehicle mileage, the aging time in hours was converted to vehicle

miles by assuming that one desulfation would be required for every 1,000 miles of vehicle operation. All mileage data is projected from this estimate.

During the desulfation step, the catalyst temperature was controlled by introducing diesel fuel into the exhaust stream, which subsequently heats the catalyst with the exotherm produced by fuel combustion over the catalyst. A thermocouple mounted in the catalyst monitored catalyst temperature and provided a signal to the control computer, which adjusted the exotherm fuel rate to maintain the correct catalyst temperature via a feedback loop.

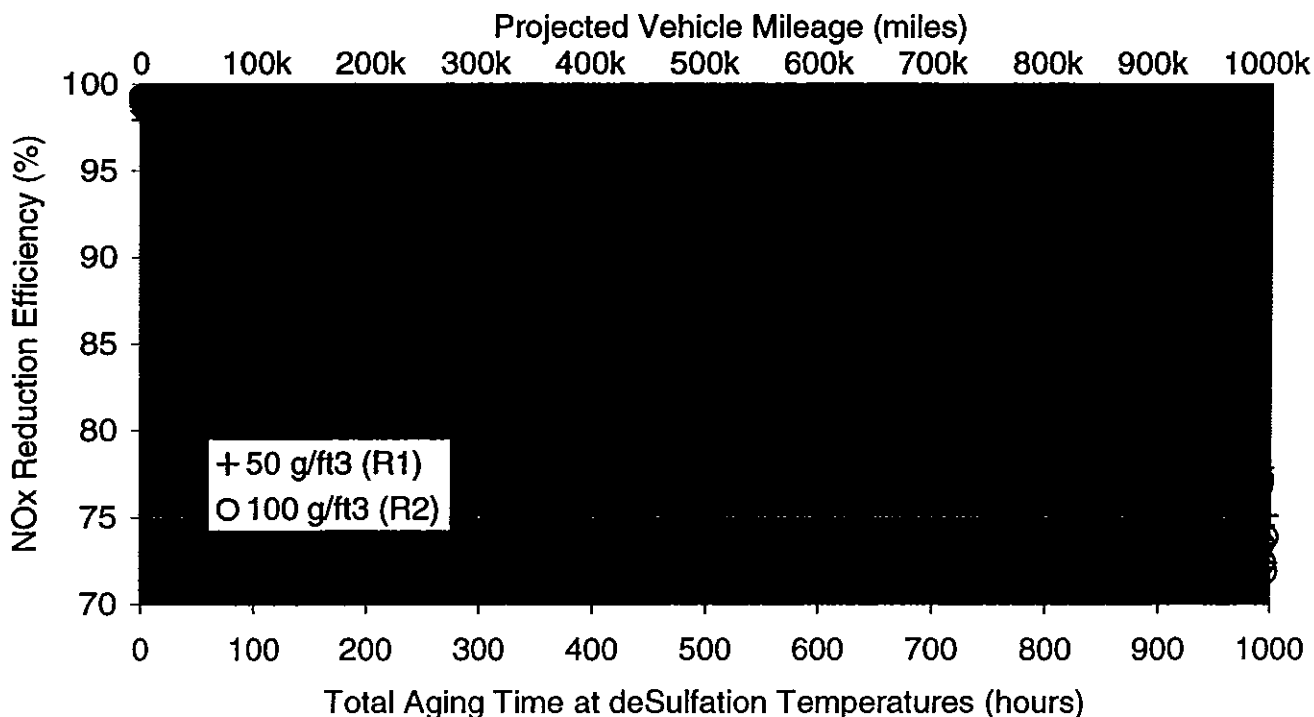
## RESULTS

The NO<sub>x</sub> performance monitored at 25 kW engine load (A) during sulfur loading provided a basis for comparing NO<sub>x</sub> performance over the course of the aging. For a sorption cycle time of 1.0 minutes, NO<sub>x</sub> reduction efficiencies remained above 90% for the first 500 hours of high temperature aging, which corresponds with 500,000 miles of projected life. During the last 500 hours of high temperature aging, the performance declined but remained above 70%. **Figure 4** shows the NO<sub>x</sub> reduction efficiency during sulfur loading for a 1.0-min cycle; the results are shown for mileage projected based on one desulfation every 1,000 miles.

Throughout the test, the catalyst maintained the ability to trap NO<sub>x</sub> at efficiencies greater than 90% during the sorption cycle. **Figure 5** shows the NO<sub>x</sub> trapping capacity at >90% efficiency over the course of catalyst aging. A compilation of results from the 1.0- and 2.5-min sorption cycles is shown. The capacities of the 50 and

100 g/ft<sup>3</sup> PGM samples were similar over the course of aging at the medium load tested (25 kW). The profile of the catalyst capacities shows capacity loss occurring during the initial phases of the test and capacity stabilizing after the initial losses occurred. The same trend is observed in the surface area analysis presented in the following section.

An examination of the NO<sub>x</sub> reduction efficiency and NO<sub>x</sub> capacity data over the last 500 hours of high temperature aging shows that some changes in the catalyst are still occurring after the initial loss in capacity that occurred in the first 500 hours of aging. The NO<sub>x</sub> reduction efficiency also shows an increase in the deviation of the data with aging time. These effects may be linked to unintentional changes in the catalyst operating conditions. The catalyst temperature during desulfation is shown in **Figure 6**. During aging, the average catalyst temperature during desulfation increases and the variation in catalyst temperature increases as well. The effect may be a result of the changing catalyst efficiency coupled with the method of thermal control of the catalyst. The catalyst is part of the feedback loop to control temperature as described in the previous section, and changes in the catalyst oxidation efficiency will alter the heat release from fuel combustion along the catalyst. Thus, the nature of the feedback process is changed. The change in the thermal control loop resulted in the higher catalyst temperatures observed during desulfation in the last half of the aging test. Histograms of the temperatures shown in **Fig. 6** are shown in **Figure 7** and show the increase in overall catalyst temperature during the last half of the aging test.



**Figure 4.** NO<sub>x</sub> reduction efficiency obtained with a 1.0-minute sorption cycle as a function of temperature.

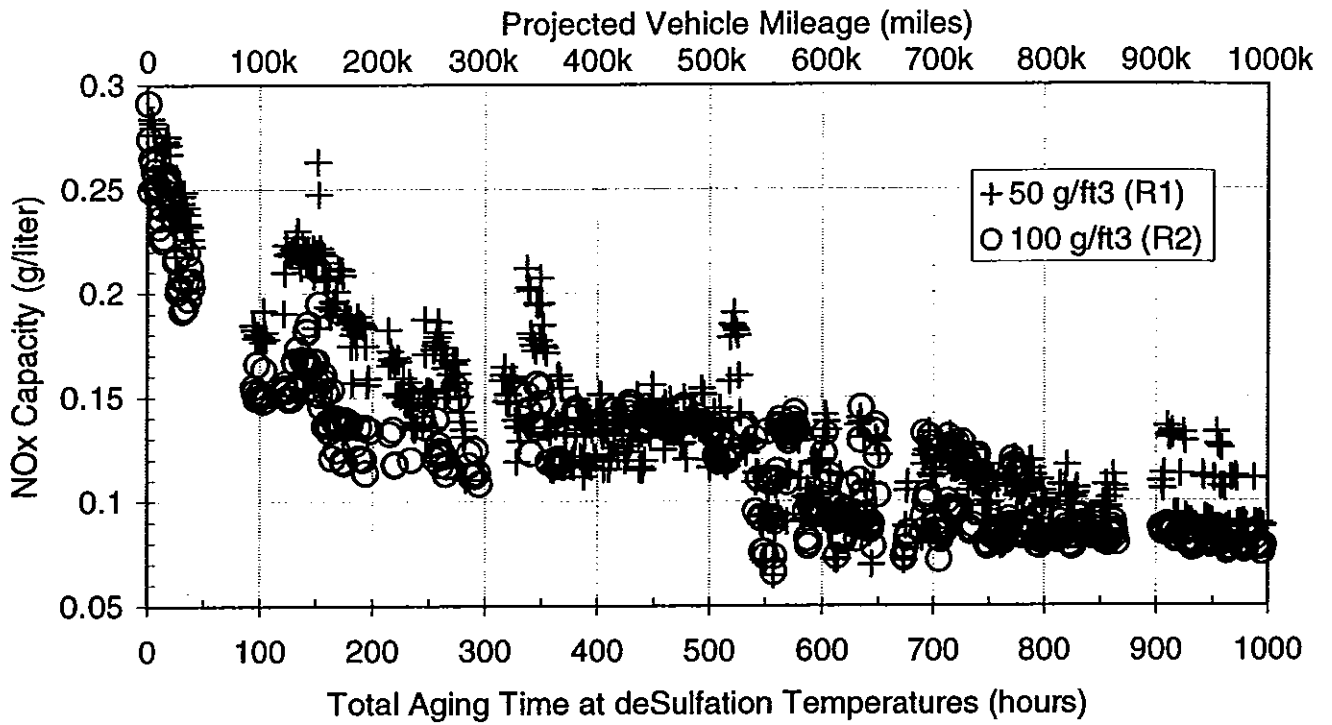


Figure 5. NOx capacity at the baseline condition (catalyst temperature of 350°C) as a function of aging time.

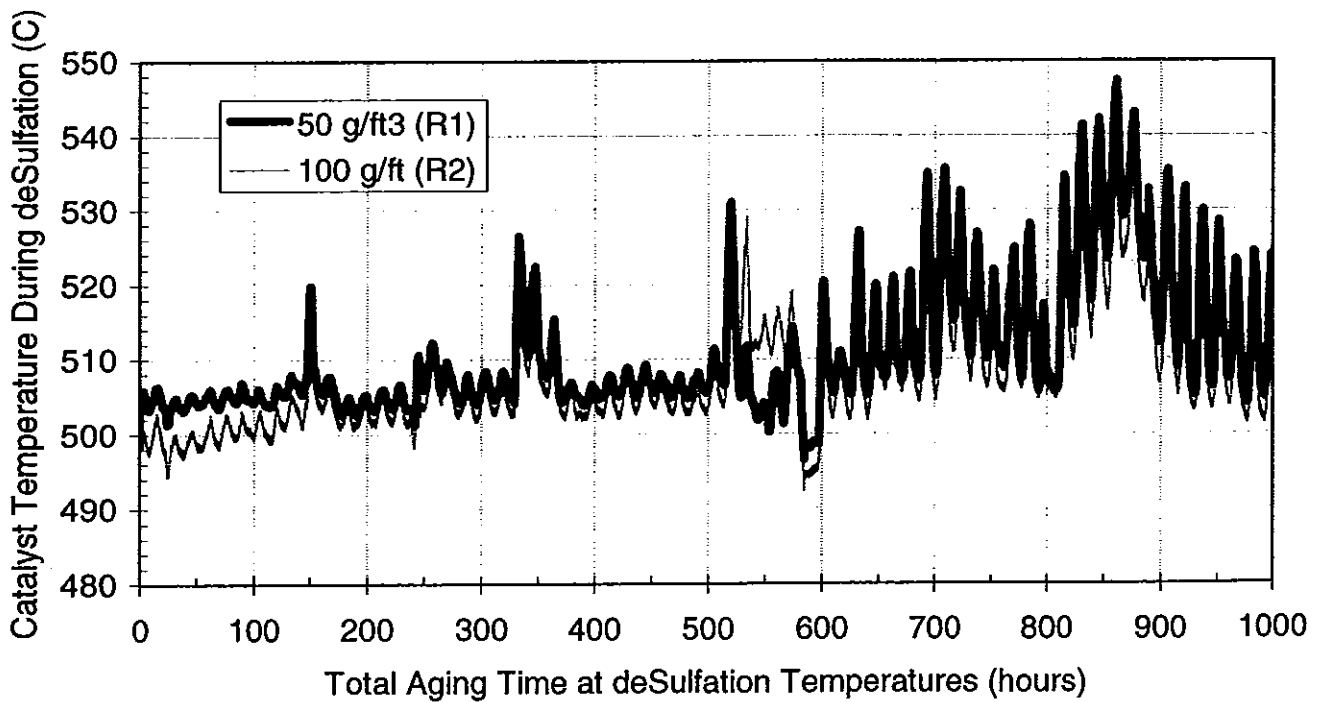
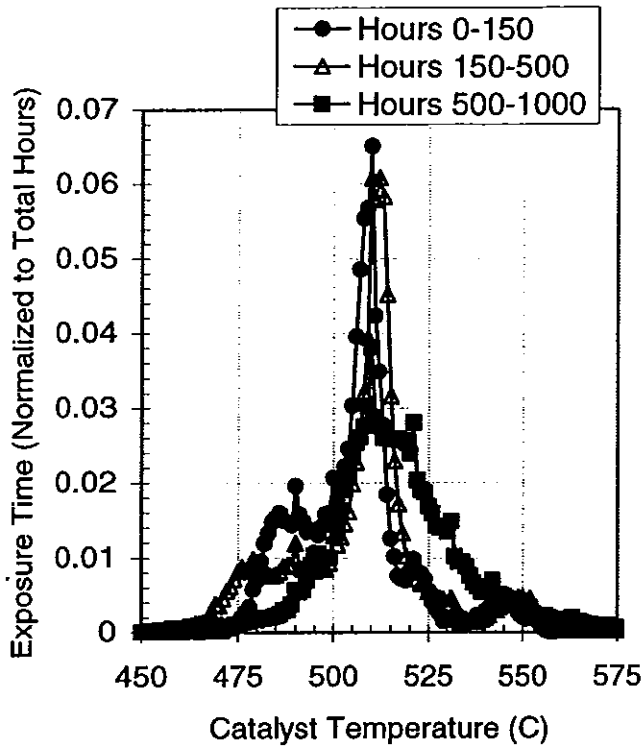


Figure 6. Catalyst temperatures during desulfation as a function of aging time.



**Figure 7.** Histogram of catalyst temperatures during desulfation. Changes in thermal control caused higher catalyst temperatures during the last 500 hours of exposure at desulfation temperatures. Data for the 50 g/ft<sup>3</sup> catalyst is shown.

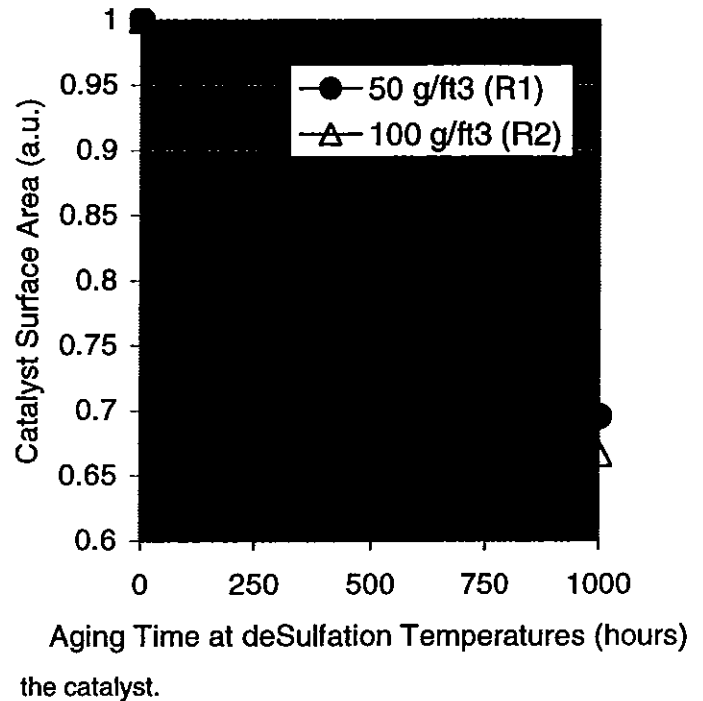
## POST-AGING ANALYSIS

During the course of aging, the aging protocol was interrupted briefly at certain times in order to obtain catalyst samples for materials analysis and to monitor catalyst performance. Breakpoints occurred after 150, 500, and 1000 hours of desulfation, which correspond with mileage projections of 150,000, 500,000, and 1,000,000 miles, respectively. In addition, catalyst samples and performance from a degreened state (0 hours of desulfation and 0 miles) were used as reference points. In this section, results from surface area analysis of catalyst samples at breakpoints in the aging will be presented and discussed. In addition, catalyst performance at the breakpoint will be presented.

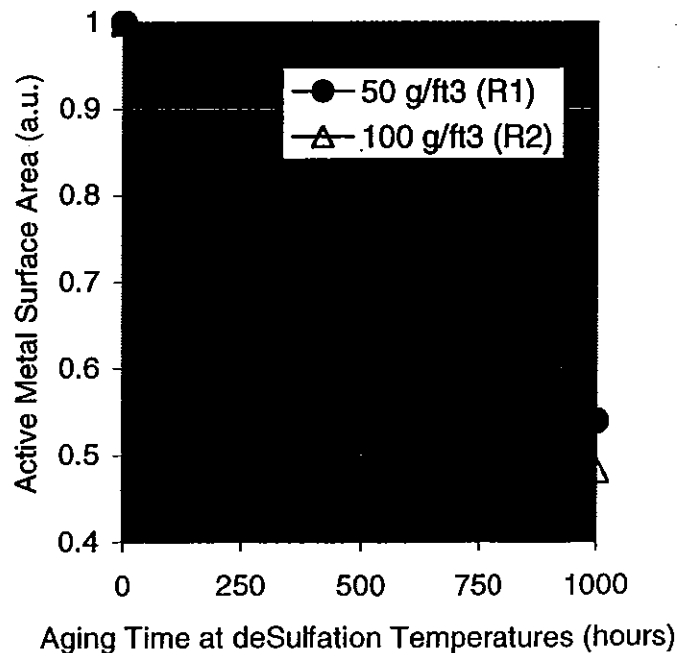
### Surface Area Analysis

The surface areas of the catalysts were measured with standard physisorption techniques. **Figure 8** shows the surface areas for both the 50 and 100 g/ft<sup>3</sup> PGM catalysts as a function of time at desulfation temperatures. The results are normalized to the surface areas after degreening. The profile of surface area over time is consistent with typical surface

area loss during thermal aging of catalyst materials. The surface area decreases initially with aging exposure, but over time the surface area stabilizes as equilibrium at the aging conditions is achieved. The surface area results are qualitatively consistent with the NO<sub>x</sub> capacity data shown in **Fig. 5**; surface area loss and subsequent stabilization leads to a loss and subsequent stabilization of the NO<sub>x</sub> storage site concentration (NO<sub>x</sub> capacity) of



**Figure 8.** Surface area of catalysts as a function of aging time.



**Figure 9.** Active metal surface area of catalysts as a function of aging time.

An attempt was made to characterize the active metal surface area (PGM surface area) for both PGM loadings with standard chemisorption techniques; however, complications in the analysis occurred. Results were possibly altered due to diesel-based residue on the catalyst samples after aging; diesel contamination was observed in significant quantities upon post-aging inspection.

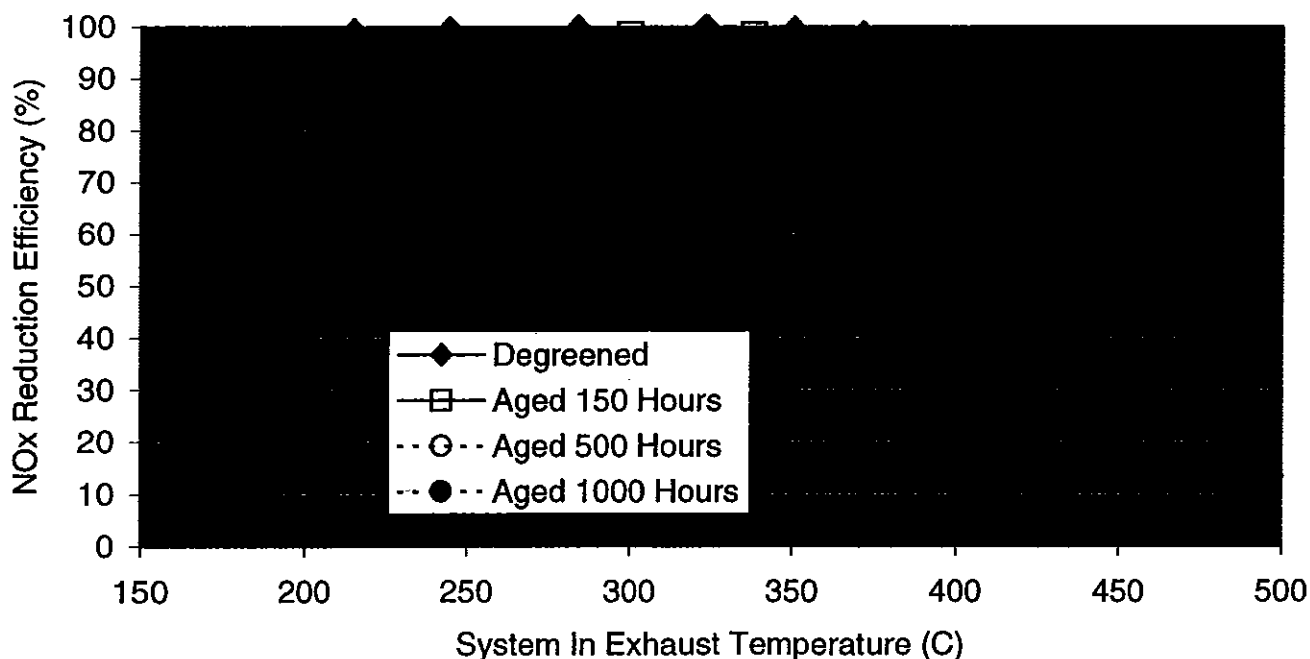
Active metal (PGM) surface area was measured by analyzing the PGM particle size of electron micrographs. Dispersion and active metal surface area were calculated from the physical measurements based on spherical geometries. **Figure 9** shows the active metal surface area as a function of aging time for both PGM loadings; the results are normalized to the active metal surface area of the degreened catalyst sample for each PGM loading. The same trends evident in total catalyst surface area occur for the active metal surface area. An initial loss of active metal surface occurs, but stabilization follows. The trend is indicative of normal thermal degradation observed in catalysis.

### Catalyst Performance Analysis

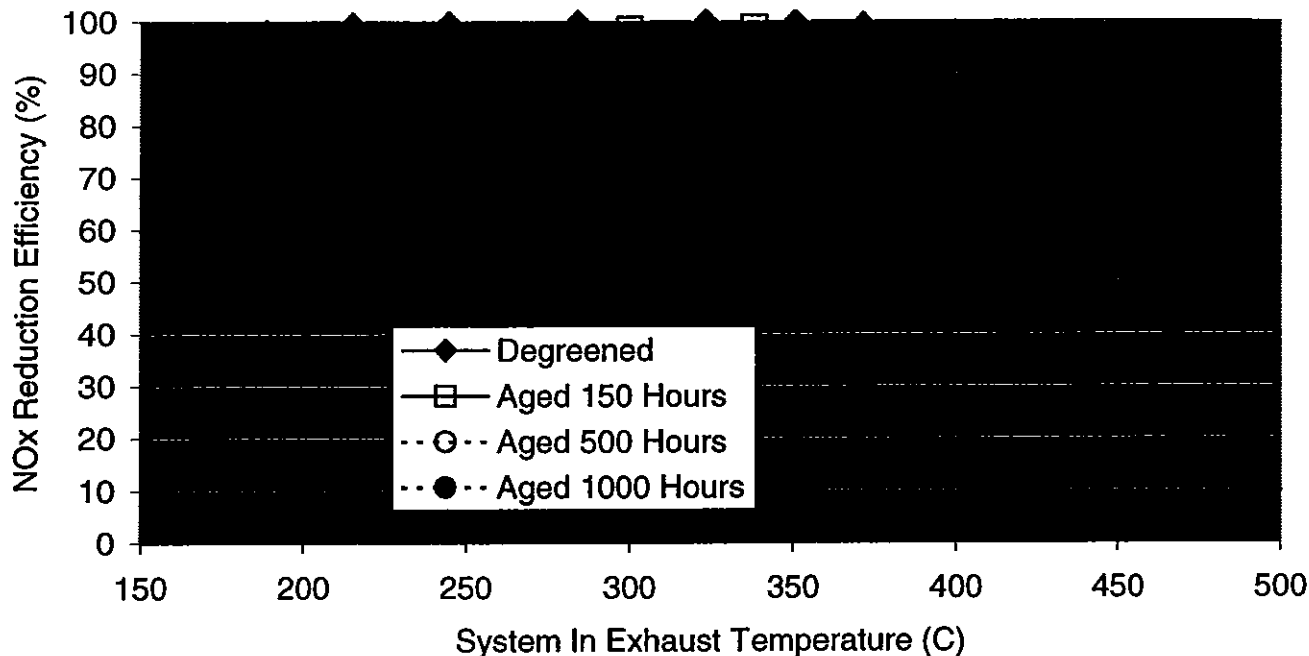
Catalyst performance during aging was monitored at the breakpoints by performing a load (temperature) sweep of performance with a 1.0-min

cycle. **Figures 10 and 11** show the overall NOx reduction efficiency for the 50 and 100 g/ft<sup>3</sup> PGM loadings, respectively. In general, the functionality of the catalyst is maintained throughout aging, and high NOx reduction efficiencies are achieved. However, performance loss does occur with aging. In particular, the NOx reduction efficiency at high temperatures (>350°C) decreases as the capacity of the catalyst decreases with aging time. The capacity loss is similar to the baseline capacity loss shown in **Fig. 5**.

In addition to the loss in trapping capacity, a loss in the efficiency of NOx reduction to N<sub>2</sub> during the regeneration process occurred as well. However, unlike the loss in storage capacity, the loss in NOx reduction efficiency during regeneration occurred primarily during the last 500 hours of aging at desulfation conditions. The cause of reduction efficiency loss is unknown. Since the time frame of the reduction loss opposes the changes occurring due to thermal degradation of catalyst surface area, non-thermal degradation processes are suspected such as masking or poisoning by lubricant and other agents.



**Figure 10.** NOx reduction efficiency as a function of temperature at different points of catalyst aging. Results are shown for the 50 g/ft<sup>3</sup> PGM catalyst.



**Figure 11.** NOx reduction efficiency as a function of temperature at different points of catalyst aging. Results are shown for the 100 g/ft<sup>3</sup> PGM catalyst.

## CONCLUSIONS

- After aging with repetitive sulfur loading and desulfation iterations, NOx absorber catalysts are capable of achieving high NOx reduction efficiencies over a broad range of temperatures.
- Degradation during aging occurs through different mechanisms:
  - Thermal aging causes a loss of catalyst surface area, which results in NOx capacity loss. Since surface areas stabilize over time under constant aging conditions, the NOx capacity stabilizes as well.
  - In the last 500 hours of aging at desulfation conditions, a loss of the efficiency of NOx reduction to N<sub>2</sub> during regeneration was observed which caused degradation in NOx performance.
- Projections of data obtained during the rapid aging protocol in terms of vehicle mileage show:
  - For light-duty vehicles (150,000 mile useful life), NOx absorber catalysts show durable performance with high NOx reduction efficiencies over temperatures representative of certification cycles.
  - For heavy-duty vehicles (435,000 mile useful life), NOx absorber catalysts are capable of maintaining performance over sulfur and desulfation cycles equivalent to heavy-duty mileage requirements. However, obtaining high NOx reduction efficiencies at high exhaust temperatures (>400°C) is difficult; so, steady-state certification cycles (Supplemental Emission Test) requiring high NOx reduction at high engine load will be challenging.
- Degradation due to masking from lubricant agents and other poisons need to be defined.

## ACKNOWLEDGMENTS

The authors would like to thank Cummins Inc. for support of this project.

## REFERENCES

1. R. Mital, J. Li, S. C. Huang, B. J. Stroia, R. C. Yu, J. A. Anderson, K. Howden, "Diesel Exhaust Emissions Control for Light Duty Vehicles", SAE 2003-01-0041 (2003).
2. Charles Schenk and Christopher Laroo, "NOx Adsorber Aging on a Heavy-Duty On-Highway Diesel Engine – Part One", SAE 2003-01-0042 (2003).
3. C. Scott Sluder and Brian H. West, "Effects of Regeneration Conditions on NOx Adsorber Performance", SAE 2002-01-2876 (2002).

4. Jim Parks, Aaron Watson, Greg Campbell, Bill Epling, "Durability of NOx Absorbers: Effects of Repetitive Sulfur Loading and Desulfation", SAE 2002-01-2880 (2002).
5. Diesel Emission Control – Sulfur Effects (DECSE) Program, "Phase I Interim Data Report No. 2: NOx Adsorber Catalysts", U. S. Department of Energy (1999).

Jim Parks  
EmeraChem  
2375 Cherahala Blvd.  
Knoxville, TN 37932  
jparks@emerachem.com

\*Currently at Oak Ridge Y12 Plant, P. O. Box 2009, Oak Ridge, TN 37831

## **CONTACT**