

# Durability of NO<sub>x</sub> Absorbers: Effects of Repetitive Sulfur Loading and Desulfation

Jim Parks, Aaron Watson, Greg Campbell, Bill Epling  
EmeraChem LLC

Copyright © 2002 Society of Automotive Engineers, Inc.

## ABSTRACT

NO<sub>x</sub> absorber catalysts can obtain NO<sub>x</sub> reduction efficiencies greater than 90% in lean exhaust. Since upcoming U.S. EPA emission regulations for diesel engines will require high NO<sub>x</sub> reduction efficiencies, NO<sub>x</sub> absorber catalysts are under consideration for use in compliance. However, durability issues in diesel engine exhaust need to be addressed. Specifically, sulfur is a known masking agent in NO<sub>x</sub> absorber catalysis. One method of controlling sulfur masking is by removal of sulfur compounds from the catalyst in a reducing environment; this process is referred to as desulfation and typically occurs at elevated catalyst temperatures. Over the catalyst lifetime, many (100-1,000) sulfur loading and desulfation cycles may occur, and recovery during desulfation must be sufficient to meet the regulation. Here the effect of multiple repetitive sulfur loading and desulfation cycles on catalyst performance will be studied. The durability testing was performed with an accelerated rate of sulfur masking (150-ppm sulfur fuel). Projections of NO<sub>x</sub> performance over time will be made to predict catalyst lifetime.

## INTRODUCTION

NO<sub>x</sub> absorber catalysts can obtain high (>90%) NO<sub>x</sub> reduction efficiencies in lean exhaust over a broad range of temperatures.<sup>1,2</sup> The capability of the NO<sub>x</sub> absorber to perform the NO<sub>x</sub> reduction with a diesel fuel-based reductant coupled with the broad range of operation makes NO<sub>x</sub> absorber catalysts well suited for diesel engine applications. However, sulfur in diesel fuel is a known masking agent for NO<sub>x</sub> absorbers, and over time sulfur accumulation directly on NO<sub>x</sub> sorption sites degrades NO<sub>x</sub> reduction performance. Sulfur masking is only one type of catalyst degradation mechanism, and other degradation mechanisms need consideration for long-term durability.

Upcoming regulations require high NO<sub>x</sub> reduction efficiencies and strict durability requirements. Specifically, the 2007/10 U. S. EPA regulation target of 0.2 g/bhp-hr NO<sub>x</sub> for heavy-duty on-road trucks will

require NO<sub>x</sub> reductions of >80% from modern diesel engine NO<sub>x</sub> emission levels, and NO<sub>x</sub> reduction must be maintained over a 435,000 mile durability requirement. Although lower sulfur fuel is being required in 2006 to assist compliance for the 2007/10 emission regulations, the 435,000-mile durability requirement is strict and will challenge the long-term performance of any catalyst.

Due to the direct competition of sulfur with NO<sub>x</sub> storage sites and thereby NO<sub>x</sub> reduction, efforts regarding the durability of NO<sub>x</sub> absorbers have focused on the sulfur masking issue. One method for controlling the negative effects of sulfur involves removing the sulfur from the catalyst in a process called "desulfation".<sup>3,4,5,6,7,8</sup> During desulfation, the sulfur is removed from the NO<sub>x</sub> storage site and the site is reactivated for NO<sub>x</sub> storage and release. Desulfation typically occurs at elevated catalyst temperatures; thus, thermal degradation may occur during desulfation. For long-term (435,000 mile) success, desulfation must be repeatable over multiple iterations. Here the process of desulfation is examined over multiple iterations in an accelerated aging test with 150-ppm sulfur fuel on a diesel engine test platform. Performance and post-aging analysis are used to project durability of the NO<sub>x</sub> absorber catalyst.

## EXPERIMENT DESIGN

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 NO<sub>x</sub> 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>9</sup> The engine

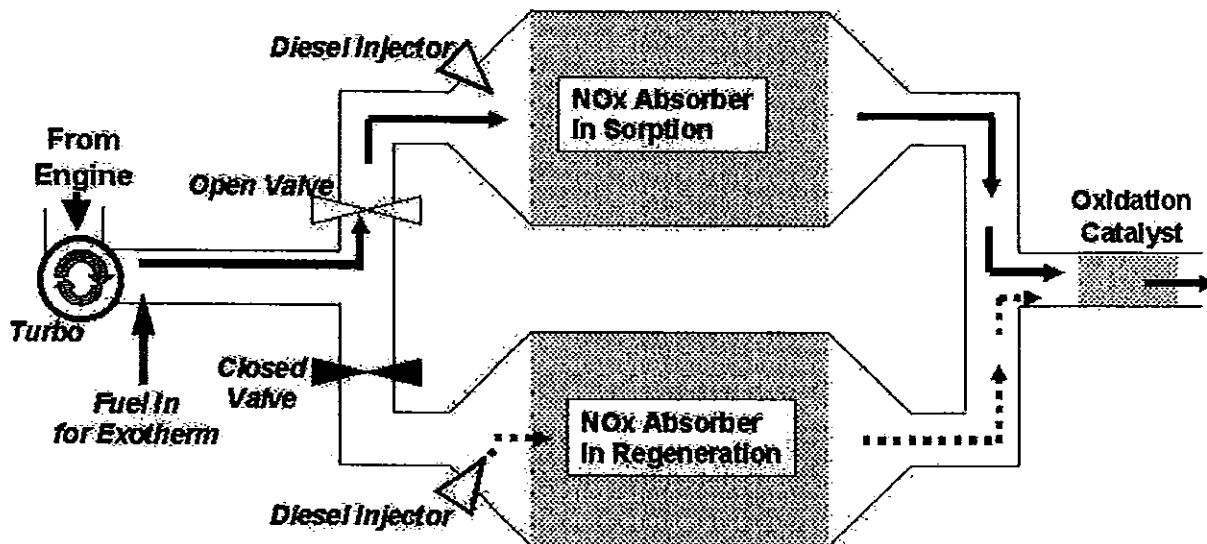


Figure 1. The two-chamber system used for testing. Valves controlled exhaust flow.

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 NO<sub>x</sub> sorption occurring on the chamber exposed to exhaust and NO<sub>x</sub> release and reduction ("regeneration") occurring on the opposing chamber. 9.9-liters of NO<sub>x</sub> absorber catalyst (nominally 20,000/hr space velocity) were housed in each chamber; the catalyst was applied to a ceramic monolith with 300 cells per square inch (NGK Insulators, Ltd.). Regeneration of the NO<sub>x</sub> 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 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.

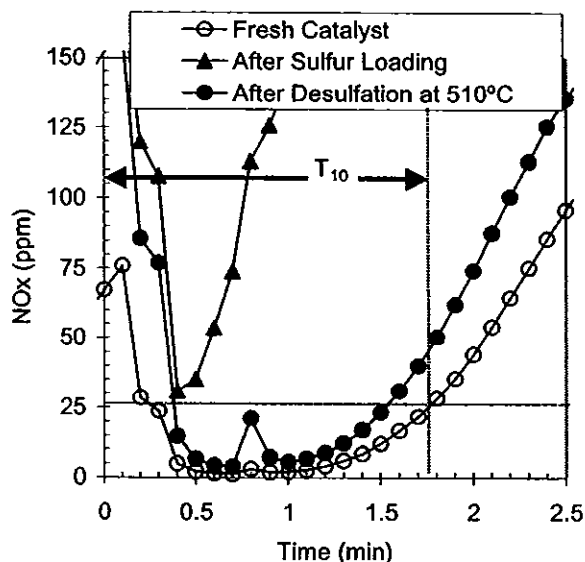
NO<sub>x</sub> reduction efficiencies were measured by sequentially monitoring the NO<sub>x</sub> exhaust emissions before ("engine out") and after ("system out") the catalyst system. NO<sub>x</sub> was measured with a chemiluminescent NO<sub>x</sub> analyzer (California Analytical Instruments) after 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.

## DESULFATION

Under normal operation of a NO<sub>x</sub> absorber catalyst, the catalyst cycles between lean (O<sub>2</sub>-rich) and rich (O<sub>2</sub>-depleted) exhaust gas atmospheres. During lean operation, the catalyst sorbs NO<sub>x</sub> ("sorption"), and during rich operation, the catalyst releases NO<sub>x</sub> and reduces the NO<sub>x</sub> to N<sub>2</sub> ("regeneration"). The same process occurs for the catalyst with sulfur oxides; however, due to the higher stability of sulfate-sorbate species, a higher catalyst temperature (relative to NO<sub>x</sub> operation) is required for release of sulfur compounds from the catalyst. The sulfur compounds are typically released as both SO<sub>2</sub> and H<sub>2</sub>S.

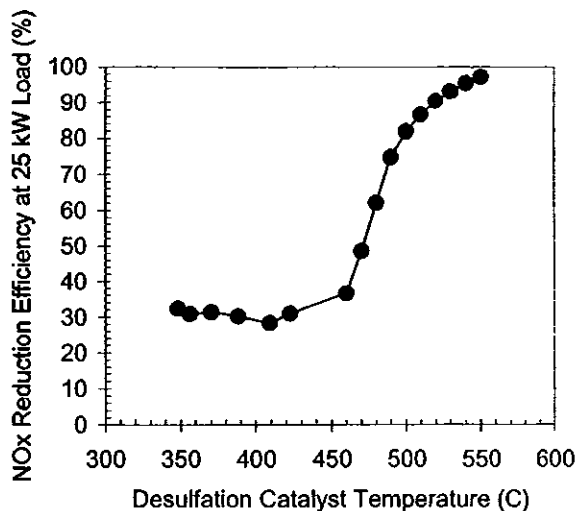
Figure 2 shows the NO<sub>x</sub> sorption profile obtained on the engine test platform before and after sulfur masking has occurred. The NO<sub>x</sub> profile data was obtained at a medium load (25 kW) and catalyst temperature (350°C). The NO<sub>x</sub> catalyst sorbed NO<sub>x</sub> at >90% sorption efficiencies originally for approximately 1.7 minutes; here the time at which the catalyst can operate with >90% NO<sub>x</sub> sorption efficiency will be referred to as T<sub>10</sub>. Then, after exposure to sulfur by operation with 150-ppm sulfur fuel for 30 hours, the

catalyst's ability to absorb NO<sub>x</sub> efficiently was lost due to sulfur masking of active NO<sub>x</sub> sites. After desulfation at a catalyst temperature of 510°C, the catalyst regained nearly all of the capability to sorb NO<sub>x</sub> efficiently ( $T_{10}$ =1.6 min.). Here the catalyst temperature of 510°C was obtained by operating at a higher load (50 kW) plus adding diesel fuel to the exhaust during the sorption cycle to raise and control the catalyst temperature via exotherm production.



**Figure 2.** NO<sub>x</sub> sorption profiles before and after sulfur loading and desulfation.  $T_{10}$  (shown for the "Fresh Catalyst") is the period for which NO<sub>x</sub> levels are less than 10% of the engine out NO<sub>x</sub> level (~250 ppm).

The amount of NO<sub>x</sub> capacity recovered during desulfation is a function of the catalyst temperature during desulfation. Figure 3 shows the NO<sub>x</sub> reduction efficiency obtained after desulfation at sequentially higher desulfation temperatures. The experiment was conducted by first loading the catalyst with a large quantity of sulfur by operation at constant load (25 kW) with 150-ppm S fuel for 26 hours. During the operation with 150-ppm S fuel the NO<sub>x</sub> reduction efficiency of the catalyst dropped from an original (fresh catalyst) level of 98.7% to a sulfur-masked level of 32.6% for a sorption cycle period of 2.5 min. No recovery in NO<sub>x</sub> performance was observed for desulfation temperatures lower than 450°C, but as desulfation at higher catalyst temperatures occurred, NO<sub>x</sub> performance was recovered at temperatures higher than 450°C. The majority of NO<sub>x</sub> capacity recovery occurred in the temperature range of 450 to 500°C; however, more NO<sub>x</sub> capacity was recovered in the temperature range of 500 to 550°C. After desulfation at 550°C, the NO<sub>x</sub> reduction efficiency was 97.3% for a 2.5-min sorption cycle; thus, close to all of the NO<sub>x</sub> performance was recovered.



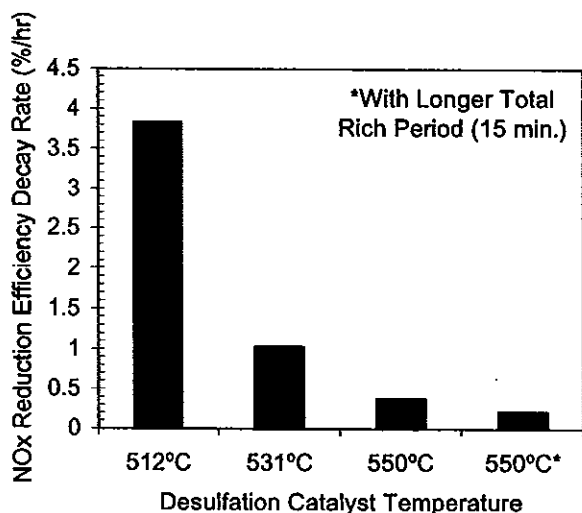
**Figure 3.** NO<sub>x</sub> performance recovery during desulfation occurs between 450°C and 550°C.

## PARAMETER OPTIMIZATION AND DEGREENING

Prior to long-term aging with multiple iterations of sulfur loading and desulfation, experiments were conducted to optimize desulfation parameters for a given sulfur loading and desulfation aging cycle. The catalyst system was tested under accelerated-aging conditions; 150-ppm sulfur fuel was used for the engine. A simple load cycle consisting of a sulfur loading mode and a desulfation mode was used. The sulfur loading mode consisted of three (3) hours of operation at a medium load (25 kW) and catalyst temperature (~340°C). The desulfation mode immediately followed the sulfur loading mode and consisted of one (1) hour of operation at a high load (50 kW) and high catalyst temperature. During the desulfation mode, the catalyst inlet exhaust temperature was ~430°C, and therefore, ULS diesel fuel was injected into the exhaust stream to raise the catalyst temperature to the target desulfation temperature. Here the target catalyst temperature used for desulfation was varied to optimize NO<sub>x</sub> performance recovery; temperatures of 510, 530, and 550°C were studied with 6 minutes of rich operation over the one-hour desulfation period. In addition, the period of fuel injection for regeneration was increased to a total rich period of 15 minutes for the 550°C desulfation temperature to optimize further the total sulfur release during desulfation. The air-to-fuel ratio of the fuel injection for regeneration was constant for all tests. The sulfur loading and desulfation modes were repeated to form the test cycle.

Repetition of test cycles for periods from 15 to 60 hours were performed to determine the optimal desulfation parameters for the 150-ppm S aging. Figure 4 shows the degradation rate over time for the different desulfation temperatures with a 6-min. rich period and the additional 550°C temperature data with a 15-min.

rich period for increased total sulfur release during desulfation. Desulfation at 510°C was not suitable to maintain high NO<sub>x</sub> reduction efficiencies due to a kinetic rate of sulfur release that was less than the rate of sulfur addition. The 150-ppm S fuel used for the engine during the desulfation event hindered the ability of the catalyst to remove sufficient sulfur during desulfation at 510°C, since sulfur was added to the catalyst at high rates during the sorption cycle of the desulfation event. To compensate for the additional sulfur added to the catalyst, catalyst temperatures were increased to 530°C and 550°C, and the NO<sub>x</sub> reduction efficiency loss over time decreased as a higher rate of sulfur release occurred. In addition, a longer rich period during desulfation at 550°C resulted in lower degradation rates by allowing more time for sulfur release to occur. Although a lower desulfation temperature is preferred to minimize thermal degradation, the 550°C desulfation temperature with the 15-min. rich period was determined to be optimal for 150-ppm S fuel aging under the given test cycle.



**Figure 4.** Degradation from sulfur accumulation decreased with increasing desulfation temperature and total time in reducing conditions for desulfation.

Over the course of the parameter optimization for desulfation, the catalyst was exposed to large amounts of sulfur and high temperatures. Thus, the catalyst was degreened during the optimization process.

### MULTIPLE SULFUR LOADING-DESULFATION AGING

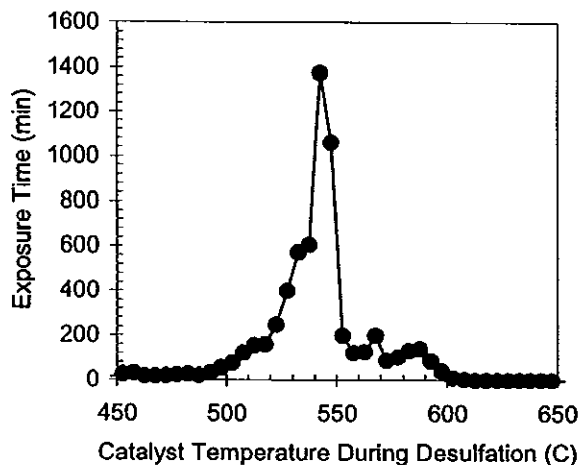
After optimizing the desulfation process parameters for the given test cycle conditions, the catalyst was aged for 416 hours over the following test cycle: (A) three hours of sulfur loading at an engine load of 25 kW (~340°C catalyst temperature), (B) one hour of desulfation at an engine load of 50 kW with

supplementary fuel injection to obtain a catalyst temperature of ~550°C (the target desulfation temperature), and (C) repeat A and B. During sulfur loading (A), sorption periods of 1.0 to 2.5 minutes were used; analysis focused on the 2.5-min. sorption period data, which gave the largest dynamic range of performance for measurement of T<sub>10</sub>. During desulfation (B), a 1.0-min. sorption period was used, and the extended total rich period of 15 min. was used to obtain sulfur balance. The catalyst system was tested under accelerated sulfur-aging conditions; 150-ppm sulfur fuel was used for the engine throughout the aging test.

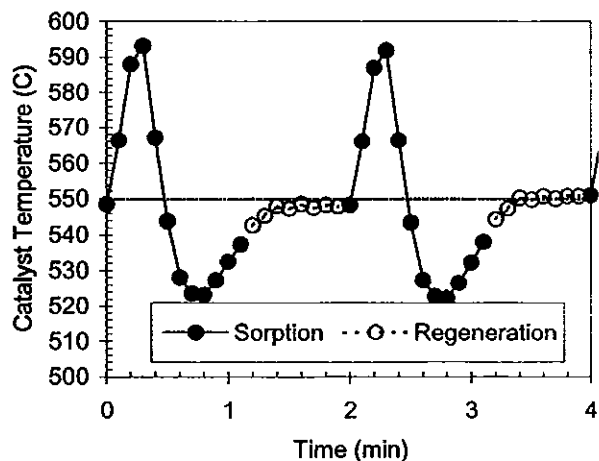
During the 416 hours of aging, three instances of variation from the test cycle occurred. All three instances involved malfunction of the fuel injection system for thermal control during desulfation, which resulted in instances of actual catalyst temperatures being less than the target desulfation temperature. A total of four sulfur loading-desulfation cycles had average catalyst temperatures less than 500°C due to the fuel system malfunction, but the catalyst recovered from each occurrence even though a sulfur balance was not obtained when the proper desulfation temperature was not reached.

Overall the catalyst temperature during desulfation was close to the target of 550°C. Figure 5 shows a histogram of all catalyst temperatures during desulfation over the aging test. The highest exposure occurred at 542.5°C +/- 2.5°C, but significant exposure occurred at catalyst temperatures as high as 600°C. The 600°C catalyst temperatures resulted from control difficulties associated with the cyclic operation of the catalyst. Figure 6 shows the catalyst temperatures during desulfation over the sorption-regeneration cycle. A large temperature rise occurs during the first part of the sorption cycle due to an exotherm created when the O<sub>2</sub>-rich exhaust interacts with fuel vapor remaining from the previous regeneration period. A drop in catalyst temperature occurs immediately after the uncontrolled exotherm as the feedback control mechanism reduces fuel injection to attempt to reduce the thermal excursion magnitude. Feedback regains control the catalyst temperature just prior to the regeneration process where the catalyst temperature stays close to the target of 550°C. Ideally, the catalyst temperature will not vary from the 550°C target temperature since lower temperatures may result in insufficient desulfation and higher temperatures may cause more thermal degradation; however, precise temperature control will be difficult in transient operation.

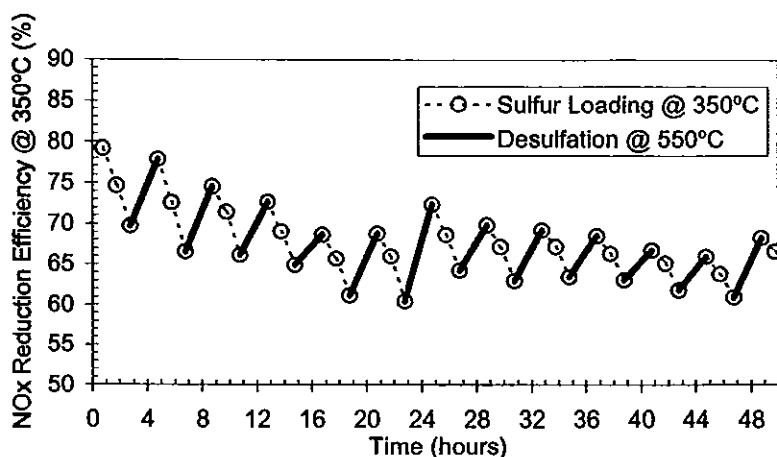
Figure 7 shows the NO<sub>x</sub> reduction efficiency at 25 kW engine load during the first 50 hours of aging. During the sulfur loading part of the cycle, the NO<sub>x</sub> reduction efficiencies decreased 5-10% as sulfur masking occurred, but NO<sub>x</sub> reduction efficiency recovered during desulfation. Thus, the effects of sulfur masking and desulfation could be observed in the performance data.



**Figure 5.** Histogram of catalyst temperatures during desulfation. Although the target temperature was 550 °C, significant exposure occurred at temperatures up to 600°C.



**Figure 6.** Profile of catalyst temperatures during desulfation. The sorption and regeneration periods were 1 minute. The target temperature was 550 °C.



**Figure 7.** NOx reduction efficiency as a function of time during aging with 150-ppm S fuel. Desulfation every four hours recovered NOx performance lost due to sulfur masking.

As multiple sulfur loading and desulfation cycles occurred, the NOx performance was monitored and analyzed over time. The time into the sorption period when system out NOx levels increased above 10% of engine out NOx levels ( $T_{10}$ ) was analyzed for the 2.5-min. sorption cycle to indicate NOx performance. NOx capacity was measured by integrating the mass of NOx (as NO<sub>2</sub>) reduction over the  $T_{10}$  period. Figure 8 shows NOx capacity and  $T_{10}$  obtained 45 minutes after desulfation as a function of time; the data has been smoothed by averaging data over a 24-hour time frame to compensate for variations in performance due to ambient temperature changes (the test system was located outside). The data shows NOx performance declining in the initial 200 hours of operation then stabilizing for the last 200 hours of operation. During the last 200 hours of operation the performance was stable with a  $T_{10}$  of 0.6 minutes. Since exhaust data was

accumulated every 0.1 minutes,  $T_{10}$  was stable within the 0.1-min resolution of data acquisition.

In reference to timeframes necessary for compliance over 435,000 miles of operation, Figure 9 shows the same data shown in Fig. 8; however, time is shown on a log scale. An average speed of 45-55 miles per hour corresponds approximately with 8,000-9,700 hours of operation over 435,000 miles. Projections of the stable NOx performance indicate that the NOx absorber is capable of maintaining high NOx reduction efficiencies after exposure to total sulfur levels associated with engine operation with 15-ppm sulfur fuel over 435,000 miles. Here a linear relationship between durability and sulfur exposure is assumed. It is important to note that the present study can not determine the effects of degradation mechanisms other than sulfur masking since sulfur exposure was the only accelerated parameter in the study.

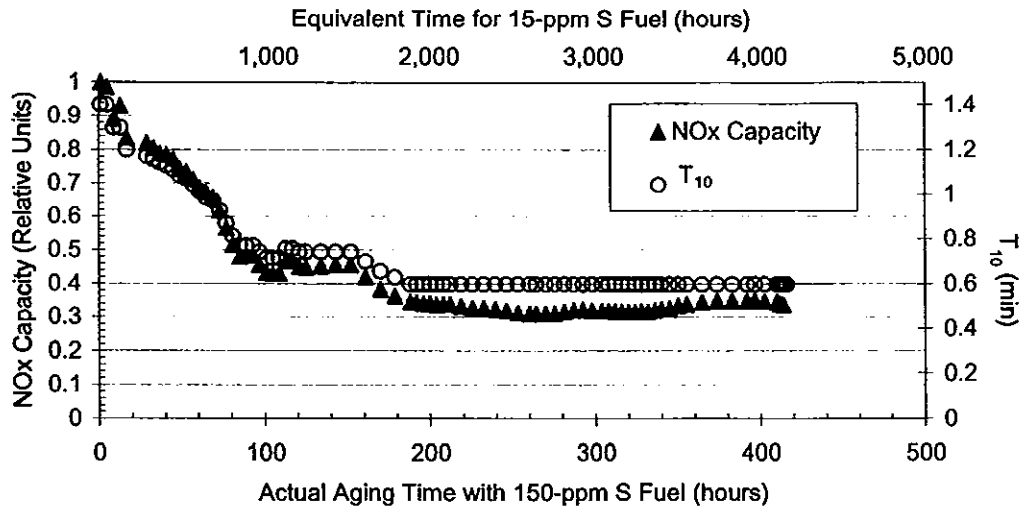


Figure 8. NOx capacity relative to the capacity at the beginning of aging ( degreened catalyst) and T<sub>10</sub> as a function of time during aging with 150-ppm S fuel.

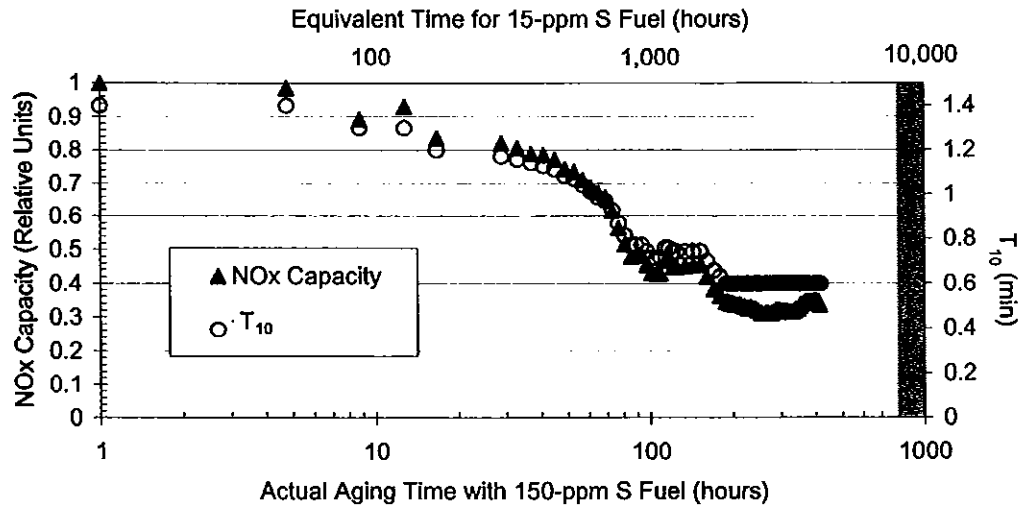


Figure 9. The same data shown in Fig. 8 plotted on a logarithmic scale to show performance over time relative to timeframes associated with 435,000 mile durability requirements. The shaded region represents equivalent time for 15-ppm S fuel required for 435,000 miles of operation based on a linear relationship between durability and sulfur exposure.

## POST-AGING ANALYSIS

### NOx Performance

After the catalysts were aged, the catalysts were tested for performance and surface properties. Figure 10 shows NOx reduction efficiency as a function of temperature before and after the 416 hours of 150-ppm S fuel aging; the data was obtained with a constant sorption cycle period of 1.0 minutes for all data points. Engine load was varied to obtain the different temperatures; engine out NOx levels increased with temperature (and engine load). A loss in NOx reduction

efficiency occurred at all temperatures from degradation during the aging process. However, NOx reduction efficiencies greater than 90% were obtained by decreasing the sorption cycle period. Figure 11 shows the NOx reduction efficiency at 25 kW load (~340°C catalyst temperature) after aging as a function of the sorption cycle period. At a sorption period less than the T<sub>10</sub> for the aged catalyst (0.6 minutes), the NOx reduction efficiency is greater than 90%.

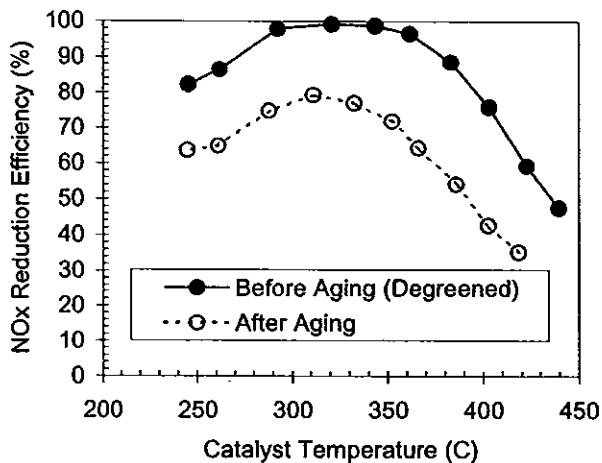


Figure 10. NOx reduction efficiency as a function of catalyst temperature before and after aging with 150-ppm S fuel.

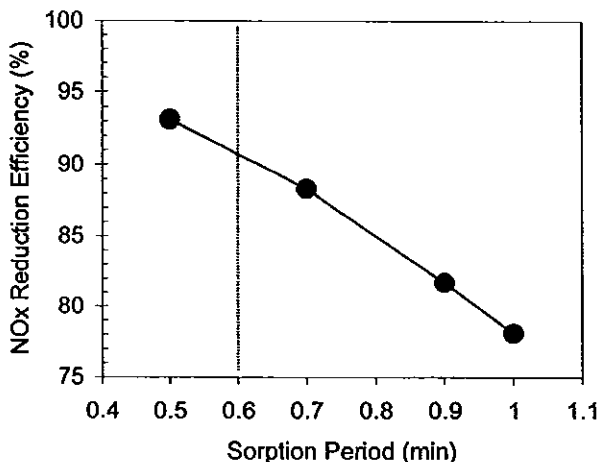


Figure 11. NOx reduction efficiency as a function of sorption period after aging with 150-ppm S fuel. The NOx reduction efficiency is greater than 90% for a sorption period less than  $T_{10}$  (0.6 minutes).

### Surface Area Analysis

Both total and active metal surface areas were measured from core samples of the catalyst before and after aging. 25% of the total surface area was lost during aging, and 44% of the active metal surface area was lost. Thus, thermal degradation represents a significant portion of the performance degradation observed in the study. In addition, the profile of performance as a function of time is indicative of thermal degradation; performance degraded until equilibrium of the catalyst occurred at the exposure temperatures in the aging cycle.

### Elemental Analysis

Analysis of sulfur levels on the catalyst after aging showed molar sulfur levels that were 1-7% of the sorbate component levels. Based on the relatively low sulfur levels, nearly complete desulfation occurred throughout the aging test. Thus, degradation directly from sulfur masking was negligible during the test; indirect degradation occurred from treating sulfur masking via desulfation due to the temperature excursions required for desulfation.

Phosphorous and zinc were detected on the upstream face of the catalyst but were not detected on catalyst samples from downstream. Combustion of oil is the likely source of these elements. The effects of these lube agents may have contributed slightly to degradation, but thermal degradation is considered to be the primary mechanism.

### CONCLUSIONS

- NOx absorber catalysts can be desulfated in the diesel exhaust temperature range. The kinetics of sulfur release increases with higher catalyst temperature.
- After multiple sulfur loading and desulfation cycles, the NOx absorber catalyst performance degraded to a stable condition and maintained the capability of obtaining >90% NOx reduction efficiency.
  - Catalyst sintering experienced during the desulfation process was a primary degradation mechanism.
  - Sulfur levels on the catalyst after aging were relatively low indicating near complete desulfation occurred throughout the test.
  - The total sulfur exposure during the aging study was on the order of sulfur quantities from high mileage operation with 15-ppm sulfur fuel.
  - Although the catalyst lost capacity for NOx during aging, the catalyst maintained the ability to obtain high NOx reduction efficiencies (>90%).

## ACKNOWLEDGMENTS

The authors would like to thank Jason Chen of Cummins Inc. for advice and Michele Sanders of EmeraChem for surface area analysis.

## REFERENCES

1. J. E. Parks II, G. J. Wagner, W. S. Epling, M. W. Sanders, and L. E. Campbell, "NOx Sorbate Catalyst System with Sulfur Catalyst Protection for the Aftertreatment of No. 2 Diesel Exhaust", SAE Technical Paper Series 1999-01-3557 (1999).
2. Brian H. West and C. Scott Sluder, "NOx Adsorber Performance in A Light-Duty Diesel Vehicle", SAE Technical Paper Series 2000-01-2912 (2000).
3. J. E. Parks II, J. A. Watson, W. S. Epling, G. J. Wagner, M. W. Sanders, and L. E. Campbell, "Sulfur-Resistant NOx Sorbate Catalyst for Increasing Longevity in Diesel Exhaust", SAE Technical Paper Series 2000-10-1012 (2000).
4. Sh. Hodjati, F. Semelle, N. Moral, C. Bert, and M. Rigaud, "Impact of Sulphur on the NOx Trap Catalyst Activity – Poisoning and Regeneration Behaviour", SAE Technical Paper Series 2000-01-1874 (2000).
5. M. Guyon, P. Blanche, C. Bert, L. Philippe, and I. Messaoudi, "NOx-Trap System Development and Characterization for Diesel Engines Emission Control", SAE Technical Paper Series 2000-01-2910 (2000).
6. Michel Molinier, "NOx Adsorber Desulfurization Under Conditions Compatible With Diesel Applications", SAE Technical Paper Series 2001-01-0508 (2001).
7. Sam Geckler, Dean Tomazic, Volker Scholz, Margaret V. Whalen, Dale McKinnon, John Orban, Robert A. Gorse, Owen Bailey, and James C. Hoelzer, "Development of a Desulfurization Strategy for a NOx Adsorber Catalyst System", SAE Technical Paper Series 2001-01-0510 (2001).
8. Jim Parks, Aaron Watson, Greg Campbell, Greg Wagner, Mike Cunningham, Neal Currier, Tom Gallant, and George Muntean, "Sulfur Control for NOx Sorbate Catalysts: Sulfur Sorbate Catalysts and Desulfation", SAE Technical Paper Series 2001-01-2001 (2001).
9. Diesel Emission Control – Sulfur Effects (DECSE) Program, "Phase I Interim Data Report No. 2: NOx Adsorber Catalysts", U. S. Department of Energy (1999).

## CONTACT

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