NO$_x$ Adsorber Aging on a Heavy-Duty On-Highway Diesel Engine – Part One

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ABSTRACT

A 5.9-liter medium-heavy-duty diesel engine, equipped with a diesel exhaust emission control system consisting of catalyzed diesel particulate filters and NO$_x$ adsorber catalysts arranged in a dual flow path configuration was evaluated with the goal of studying the thermal aging characteristics of a number of NO$_x$ adsorber formulations. These adsorbers were tested with near zero sulfur fuel and low sulfur engine oil to minimize the impact of sulfur poisoning on the test results. Testing was performed at a high temperature engine operating mode to provide accelerated but not abusive aging. The test duration ranged from 100 to 250 hours depending on the severity of the aging at the 100 hour mark. The initial "zero" sulfur testing screened the NO$_x$ adsorber formulations for future testing and established a thermal aging baseline.

INTRODUCTION

The U.S. Environmental Protection Agency (U.S. EPA) has promulgated heavy-duty on-highway engine emission standards of 0.20 g/hp-hr NO$_x$, 0.01 g/hp-hr PM, and 0.14 g/hp-hr NMHC over the Heavy-Duty Diesel Engine Federal Test Procedure (HDDE FTP) and the Supplemental Emission Test (SET).[1] This paper summarizes recent results of an ongoing U.S. EPA program to evaluate advanced exhaust emission control systems for heavy-duty on-highway diesel engines. This paper covers the fourth phase of the continuing program under way at the U.S. EPA National Vehicle and Fuel Emissions Laboratory (NVFEL). The results of the first, second, and third testing phases have been previously reported.[1,2,3] The results of phases 1 and 2 have shown that NO$_x$ adsorbers can achieve NO$_x$ reductions efficiencies greater than ninety percent after a modest accumulation of hours.[1,2]

Current adsorber formulations have been shown to lose NO$_x$ reduction performance over time.[4-6] This loss in performance is caused by a number of factors, but is primarily due to high temperature thermal aging and poisoning due to sulfur exposure. Exposure to high temperatures causes sintering of the washcoat and carrier.[6,7] The resulting loss in reactive surface area reduces the NO$_x$ storage and reduction capacity. Sulfates formed in the exhaust have a higher binding affinity for alkali/alkali-earth/rare-earth metals than nitrates, requiring temperatures that are much higher than those present in typical diesel exhaust to be desorbed. This can lead to a gradual decrease in NO$_x$ adsorber storage capacity due to base metal site occupation by sulfate. Elevation of NO$_x$ adsorbers to higher temperatures to remove the sulfur can also lead to sintering.[4,5,8-14]

A number of recent studies have investigated NO$_x$ adsorber thermal aging in light-duty diesel and gasoline direct inject applications using both engine and synthetic gas reactor aging.[5,6,15-17] Little or no work has been published addressing high temperature thermal durability of NO$_x$ adsorbers in on-road heavy-duty diesel applications.[18,19]

The primary focus of this paper will be an investigation into NO$_x$ adsorber catalysts susceptibility to thermal aging at high exhaust temperatures (high speed and load) in on-road heavy-duty diesel applications. Decreases in adsorber NO$_x$ reduction efficiency due to sulfur poisoning was kept at a minimum. All testing was performed using the previously developed dual flow path exhaust emission control system.[1,2] Additional phases of this project not covered in this particular paper will be published in subsequent papers. The additional work will include:

1. Further investigation of issues related to the thermal durability of NO$_x$ adsorber catalysts;
2. Further investigation into the optimization of desulfation parameters;
3. Investigation of systems integration and systems control issues, particularly with respect to system size and catalyst volume.

TEST PROCEDURES

ENGINE DESCRIPTION

The engine used for thermal aging was a 5.9-liter displacement Cummins ISB. The engine was identical to the engine used in phase 1 of this program and has

Table 1. Summary of major engine specifications.[3]

Engine:	2000 Cummins ISB
Engine Configuration:	6-cylinder, turbocharged-aftercooled, DI diesel with 4-valves/cylinder
Rated Power:	194 kW (260 bhp) @ 2500 rpm
Peak Torque:	895 N-m (660 ft-lb) @ 1600 rpm
Fuel System:	Bosch VP44 (Electronic Rotary)
Bore X Stroke:	102 mm X 120 mm
Engine Management:	Stock
Cylinder Displacement:	5.88 L
Compression Ratio:	16.3:1

been previously described.[1] The major engine specifications are summarized in Table 1.

EXHAUST SYSTEM DESCRIPTION

The dual path NO_x adsorber system, specifications of the CDPFs, and regeneration/NO_x reduction control strategies used for this testing are similar to the ones previously used and have been previously described.[1,2] Four different NO_x adsorber formulations were tested from three different manufacturers. The entire system was built using readily obtainable components. CDPF and NO_x adsorber volumes were not optimized. All control system components, including exhaust brakes, exhaust fuel injectors, wide-range linear UEGO sensors, and zirconia-NO_x sensors remained the same as the final configuration tested in the first phase of this work. Figure 1 is a functional schematic of the exhaust emission control system tested with the Cummins ISB engine. [2]

TEST CYCLES

All thermal aging tests were done at AVL mode 8, 2313 rpm and 567 lb-ft of torque. The engine out exhaust temperature at this mode was 510°C. A 13-mode supplemental emissions test (SET) was run after every 25 hour aging interval at AVL mode 8 to address the effects of thermal aging at different speed and load settings.

TEST FUEL

The fuel used during the thermal aging tests was Phillips Chemical Company Lot 1HPULD01. This fuel was identical to that specified by the U.S. Department of Energy's Diesel Emission Control – Sulfur Effects (DECSE) program to have similar properties to today's on-highway fuel with the exception of "zero" sulfur content.[19] The fuel properties are shown in Table 2. Fuel sulfur content was measured using x-ray fluorescence spectroscopy (XRF), which had a 0.7 ppm limit of detection (LOD) for sulfur. Lab results indicated a fuel sulfur concentration of less than 0.7 ppm by weight, which was below the LOD for the instrument. "Zero" sulfur fuel was used in order to ensure that poisoning of the NO_x adsorbers did not occur during the thermal aging tests. Engine out SO_2 concentration was calculated for AVL mode 8 using fuel sulfur concentration, fuel flow rate, and intake air flow rate.[20] A fuel sulfur concentration of 0.7 ppm (XRF LOD) was chosen for the calculation to provide a worse case engine out SO_2 concentration. Although trace amounts of sulfur could be present in the fuel, it accounted for less than 35 ppb SO_2 engine out (assuming a maximum fuel sulfur concentration of 0.7 ppm) at mode 8 and its
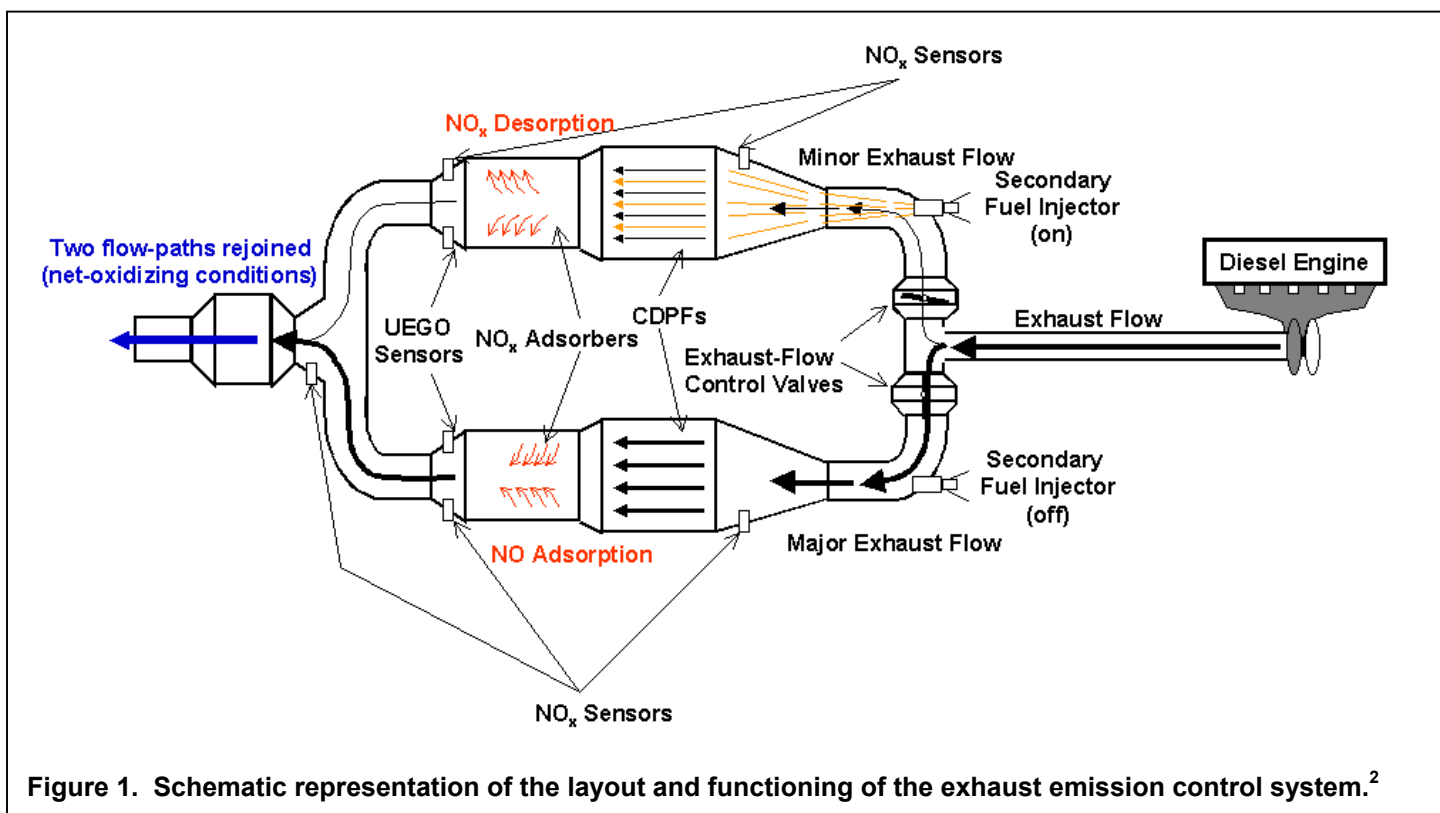
Figure 1. Schematic representation of the layout and functioning of the exhaust emission control system.[2]

Table 2. Summary of "zero" sulfur fuel properties.[3]

Test Method	Results
Net Heat of Combustion, ASTM D3338-92 (MJ/kg)	43.06
Density @ 15.5°C (g/cm³)	0.8348
Cetane Number	44.8
Cetane Index	50.6
Olefins, FIA D1319-93 (% Vol.)	3.2
Aromatics, D1319-93 (% Vol.)	24.5
Sulfur, ASTM D2622 (ppm mass)	< 0.7
Carbon, ASTM D3343-95 (% mass)	0.8659
Distillation Properties, ASTM D86	
IBP (°C):	181
10 % (°C):	205
50 % (°C):	259
90 % (°C):	318
End Point (°C):	351
Residue Diesel (mL):	0
Recovery:	100%

contribution to adsorber poisoning can be considered negligible for the testing done here.

TEST OIL

Low sulfur engine lube oil was used for all thermal aging tests. The lube oil formulation contained 750 ppm S by weight and was measured using XRF. This formulation was used in order to minimize the effect of sulfur poisoning of the NO_x adsorbers from lube oil consumption during the thermal aging tests.

LABORATORY

The engine was tested at Heavy-Duty Engine Site 1 at the U.S. EPA NVFEL facility in Ann Arbor, MI. The test site is equipped with a 600 bhp DC dynamometer and a Horiba full-flow CVS and particulate measurement system. Dilute gaseous regulated emissions were measured using a Horiba MEXA 7200D analyzer bench as per 40 CFR § 86 Subpart N. Some of the recent changes to the Subpart N procedures for measurement of NO_x and PM emissions from post-2007 heavy-duty on-highway diesel engines were also implemented during this testing.[21]

THERMAL DEGRADATION TESTING STRATEGY

Four different catalyst formulations from three different manufacturers were tested to evaluate their thermal aging characteristics under high speed and high load conditions. The catalysts were tested from 100 to 250 hours at AVL mode 8. This mode was chosen for its high temperature, allowing moderate acceleration of the aging process. Testing time depended on the observed rate of thermal aging. Reductant injection for NO_x adsorber regeneration during mode 8 aging was optimized at the beginning of the test and remained the same throughout.

The extent of thermal aging was measured as a loss in NO_x reduction efficiency as measured from the ZrO_2 NO_x/O_2 sensors located in the exhaust emission control system described in Figure 1. The amount of reductant injected into the regenerating flow path at each of the 13 SET modes was optimized at each of the 25 hour intervals during the aging test. This ensured that the highest NO_x reduction efficiency possible was achieved at each of the modes, at each of the intervals.

RESULTS

TEST 1 & 2

The first test incorporated adsorbers from different manufacturers in each flow path. They were referred to as adsorber A and adsorber B. The test was repeated with fresh adsorbers in test 2 to verify the results of test 1. Both adsorbers were supplied on 400 cpsi (4 mil wall thickness) substrates, but they differed in that adsorber A had a volume of 10.5 L and adsorber B had a volume of 13.9 L.

The adsorber regeneration time and fuel quantities were set at the beginning of the aging test. This calibration was used for the duration of the aging. Figures 2 and 3 show the NO_x reduction performance as the adsorbers aged. This NO_x data was taken with ZrO_2 NO_x/O_2 sensors and the outlet sensor values were confirmed by using chemiluminescent detection. The sensors allowed the performance of the individual flow paths to be monitored simultaneously. Only the adsorbing performance of the individual flow paths was shown in the figure due to the exhaust mass flow changes during regeneration. The performance was normalized to the highest value obtained over each test.

These figures show that in the absence of sulfur, the NO_x reduction performance degrades over time if the regeneration calibration is not modified to compensate. To some degree this is normal 'degreening'. Degreening is the term used to describe the initial sintering of a catalyst, after which the performance typically stabilizes. The degreening process can be avoided by pre-aging the catalyst at high temperatures (600-800°C) for a few hours before testing. In this case the adsorbers were completely fresh and unaged. At 100 hours both adsorbers still showed some downward performance slope.

Closer investigation of the NO_x sensor signals reveals that the NO_x reduction performance of the two adsorber formulations was affected differently by the aging. Figure 4 shows the NO_x sensor output for both adsorbers over two complete regeneration cycles; new and after aging 100 hours. Adsorber A was
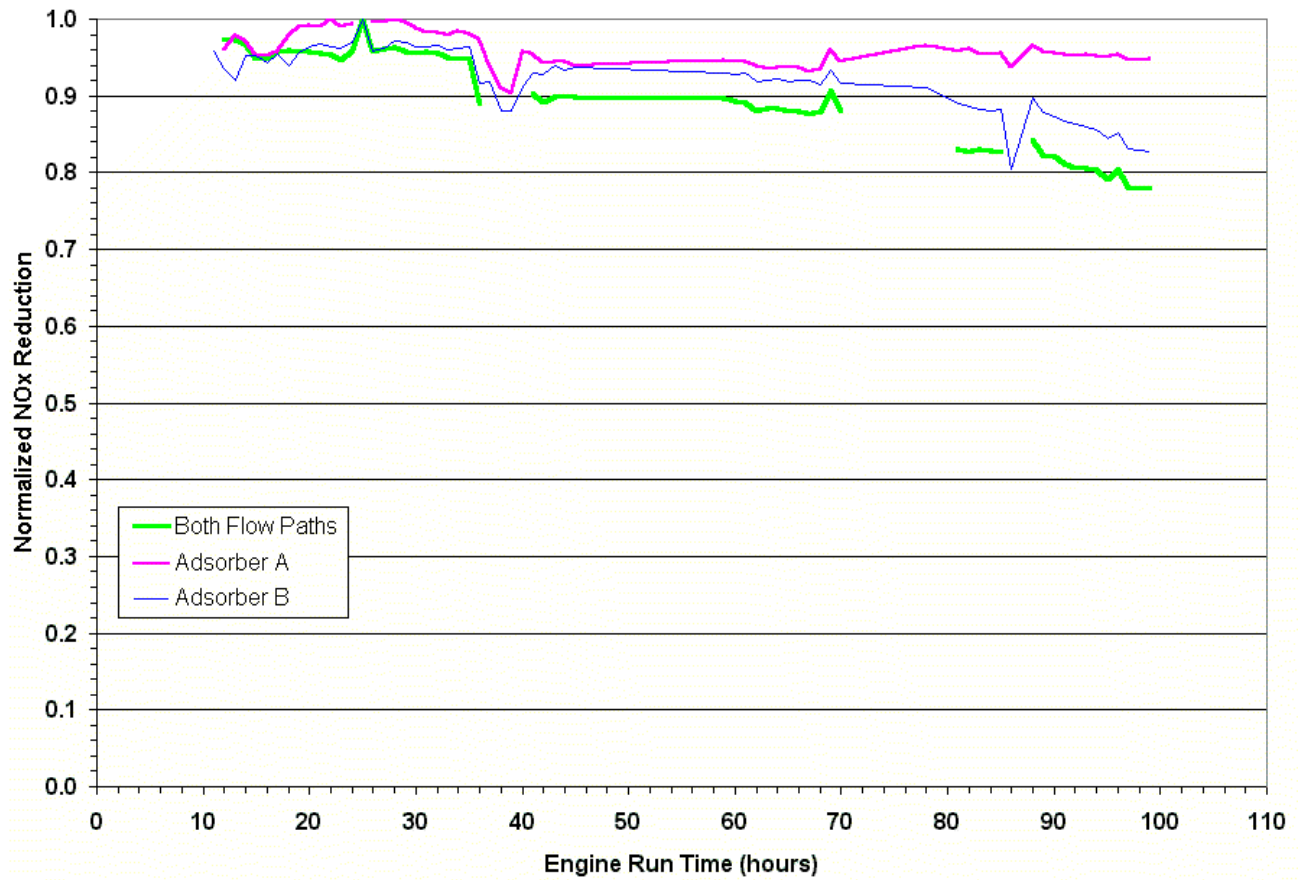
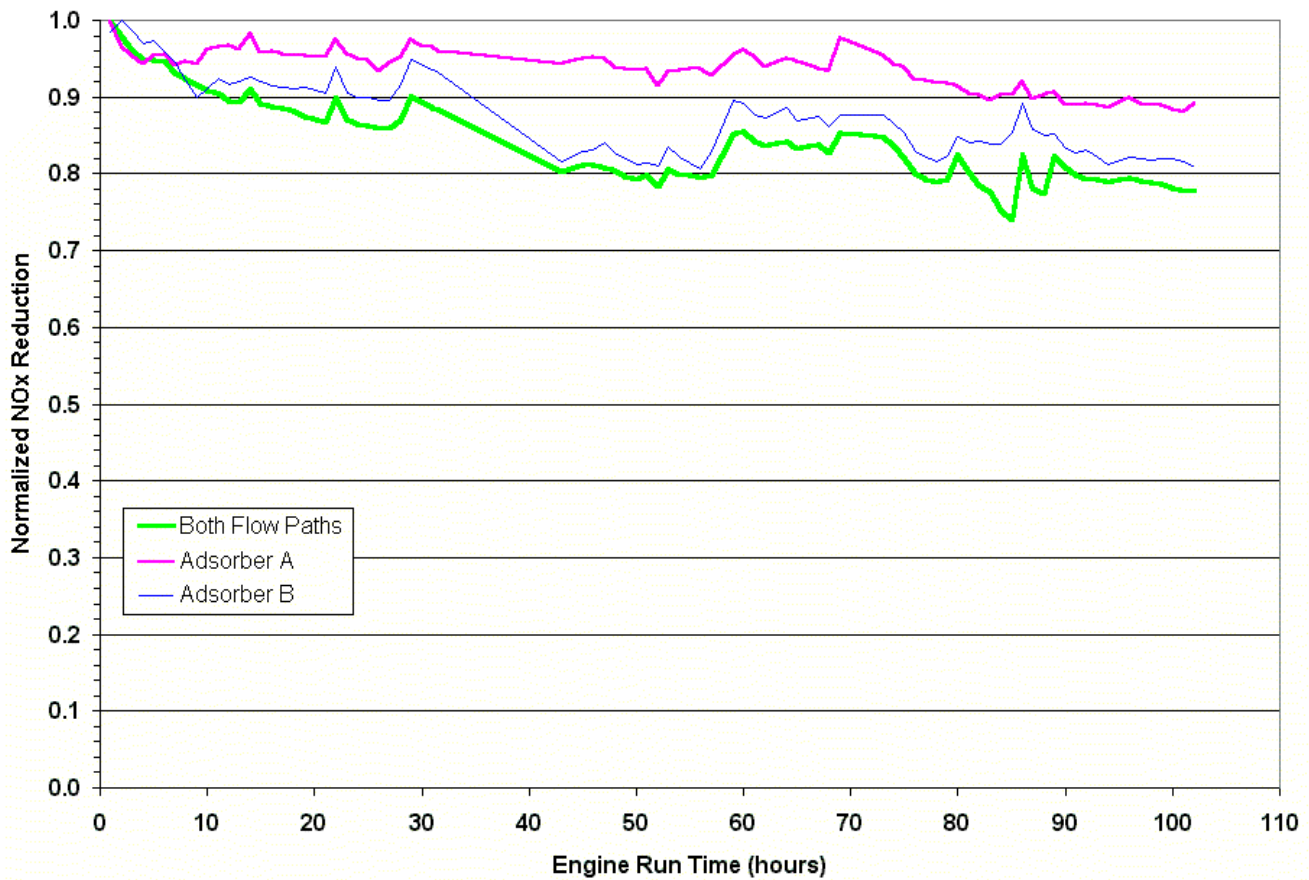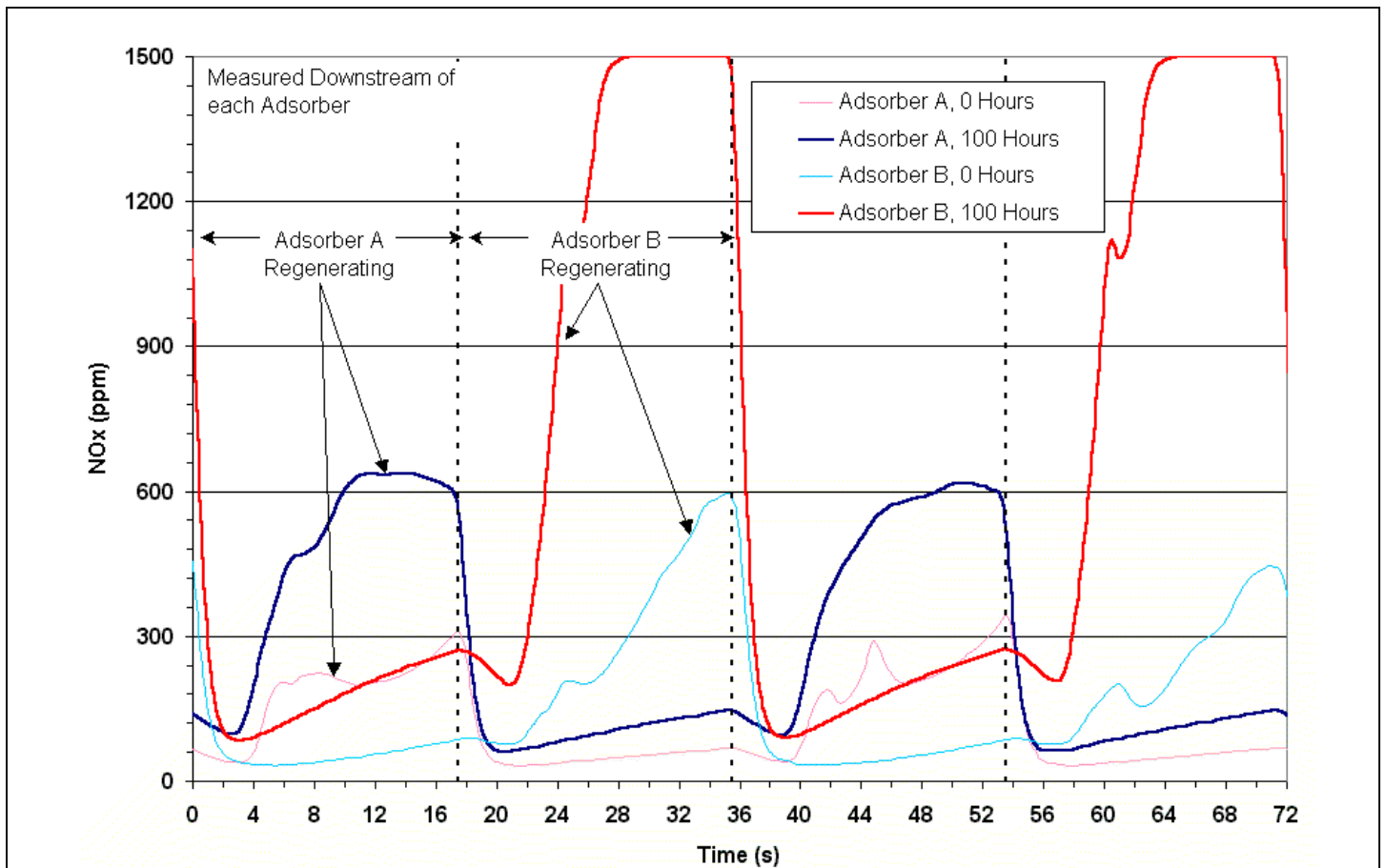**Figure 2. Test 1 NO$_x$ reduction performance as a function of aging.**

Figure 3. Test 2 NO$_x$ reduction performance as a function of aging.

Figure 4. Adsorber NO$_x$ emission over two regeneration cycles.

regenerating for the first 18 seconds of the chart and shows a doubling of NO$_x$ slippage during regeneration after 100 hours. Note that although the regeneration NO$_x$ concentration is high, the mass flow rate through the regenerating flow path was a small fraction (< 5%) of the overall exhaust flow and therefore the NO$_x$ mass slippage was low. Adsorber B had a much larger NO$_x$ slippage (18-36 seconds) when new and a much larger increase in slippage with aging, more than doubling its new performance and saturating the sensor. The large increases in NO$_x$ slippage during regeneration indicate a loss in NO$_x$ reduction capability and a decrease in three-way performance due to sintering. A loss in oxidation performance was indicated by a 34% increase in HC emission at 100 hours.

While adsorber A was regenerating, adsorber B was adsorbing (0-18 seconds). Figure 4 shows that the NO$_x$ slippage increased steadily as the adsorbent capacity for NO$_x$ was consumed. At 100 hours, the minimum NO$_x$ slippage and the slope had both increased, spanning 85 ppm to 270 ppm NO$_x$, up from 33 ppm to 90 ppm when new. This indicates adsorber B lost considerable NO$_x$ storage capacity due to loss of adsorbent surface area, probably from sintering of the base metal function. Sintering of the three-way function could also be responsible for the decrease in NO$_x$ storage capacity. A loss of precious metal surface area could cause a decrease in reductant oxidation leading to a decrease in the effectiveness of NO$_x$ adsorber regenerations.

Adsorber A showed a similar though less pronounced trend, increasing both the minimum NO$_x$ slippage and the slope at 100 hours.

TEST 3

Since adsorber A had relatively little deterioration during 100 hours of aging in both of the previous tests, it was decided to age these adsorbers another 125 hours to see if their performance would stabilize. The results are shown in Figure 5. Since the plots of the individual flow path performances were calculated to be just the adsorbing performance excluding the regeneration slippage, it can be seen from the plot that the adsorption capacity seems to have stabilized after 190 hours. The overall NO$_x$ reduction plot (trace labeled "Both Flow Paths") included the regeneration slippage and adsorbing performance of both flow paths. It also appears here that the overall adsorber performance had stabilized after 190 hours.

TEST 4

An adsorber designed for passenger car applications was provided by another supplier and designated adsorber C. The catalyst volume was also 13.9 L (400 cpsi, 4 mil wall thickness). This formulation appeared to be a low temperature barium only formulation that one would expect in a passenger car application where low temperature performance is critical. Figure 6 shows the
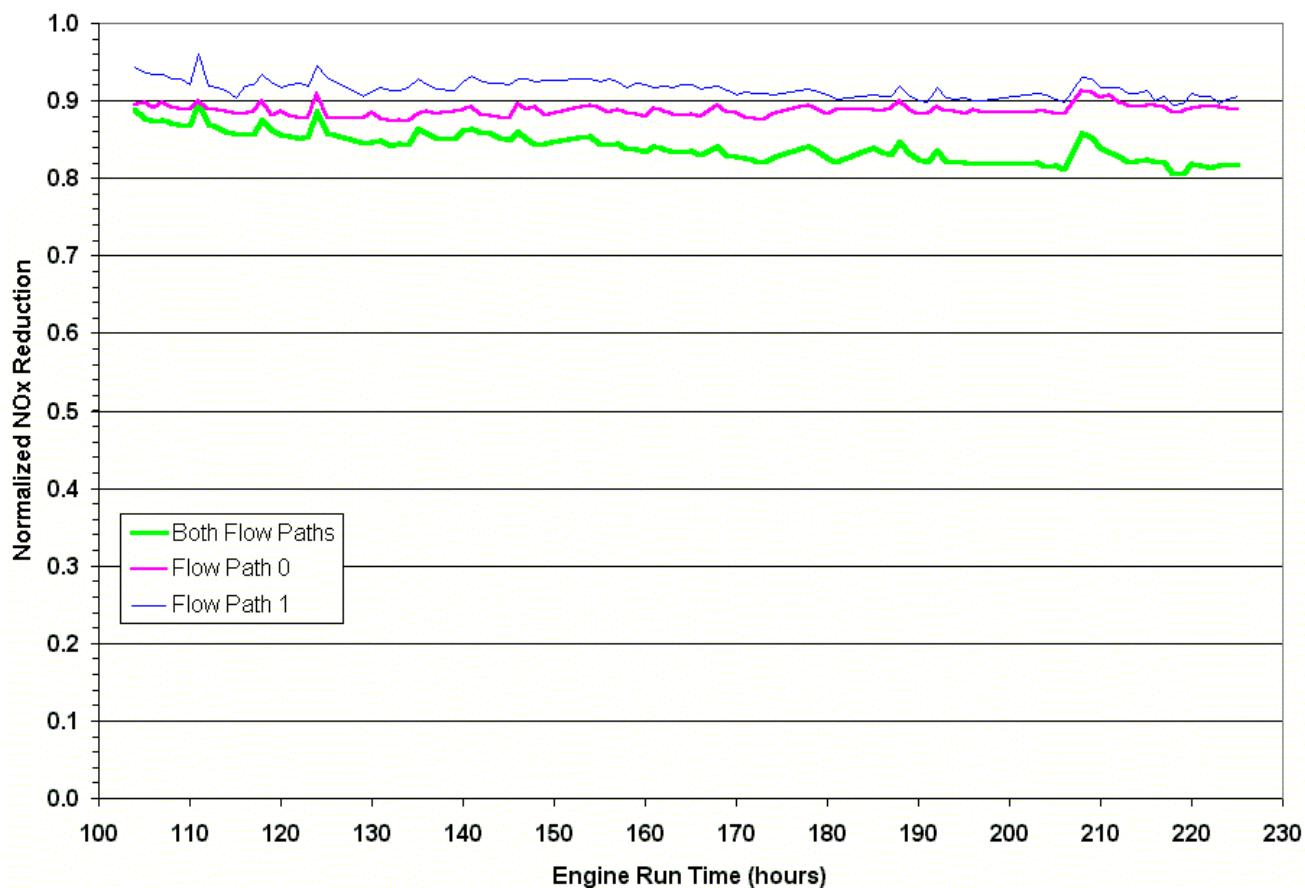
Figure 5. Adsorber A aging out to 225 hours.

performance of this adsorber over twelve modes of the Supplemental Emission Test (SET). Performance of this adsorber dropped quickly above 425°C and below 325°C when new. After aging 211 hours, the performance across the temperature range had decreased significantly. This adsorber was not well suited to a HD engine, which requires high NO_x reduction efficiencies up to approximately 550°C.

The performance of adsorber C dropped steadily with time and did not seem to stabilize (Figure 7). Aging was performed out to 211 hours due largely to some uncertainty caused by test facility and engine issues. From the NO_x sensor outputs, the performance losses seemed to be caused by a combination of NO_x capacity losses and increased slippage during regeneration.

TEST 5

A newer formulation from the supplier of adsorber B, designated adsorber D, was aged to evaluate improvements. Adsorber D was similar to adsorber B in that the washcoat was applied to a 400 cpsi (4 mil wall thickness, 13.9 L) substrate (actually two 6.95 L substrates). The aging performance is shown in Figure 8. It was difficult to compare this plot with those from tests 1 and 2 because there were different adsorber formulations in each flow path for those tests. To get a better idea of the relative performance of the devices, Figure 9 shows the NO_x sensor output for adsorber B

and adsorber D at 100 hours. Adsorber D at 100 hours had markedly lower NO_x slippage than the older adsorber B. Adsorber D performance was much better both while adsorbing and regenerating indicating significant improvements in the washcoat stabilization.

Adsorber D was a much better formulation for HD applications than adsorber C. The temperature window for this adsorber extends out to about 490°C at 75 hours (for NO_x reduction > 90%) and was still above 450°C at 150 hours (Figure 10). The relatively small decrease in high temperature performance with aging was reflected in the SET composite emissions for adsorber D (Figure 11). The SET composite weights the high temperature modes more heavily. The small loss in high temperature performance was compensated for with more frequent regenerations, keeping the SET composite relatively stable. The change in regeneration frequency was noticeable as an increase in regeneration fuel economy impact.

CONCLUSION

The purpose of this test was to provide baseline performance data for future investigations. The data provides a look at the state of adsorber technology in 2001, with a glimpse of improvements that will be made in the future. It was clear that there were vast differences in the performances of the formulations over these short tests. Adsorber suppliers were early on in
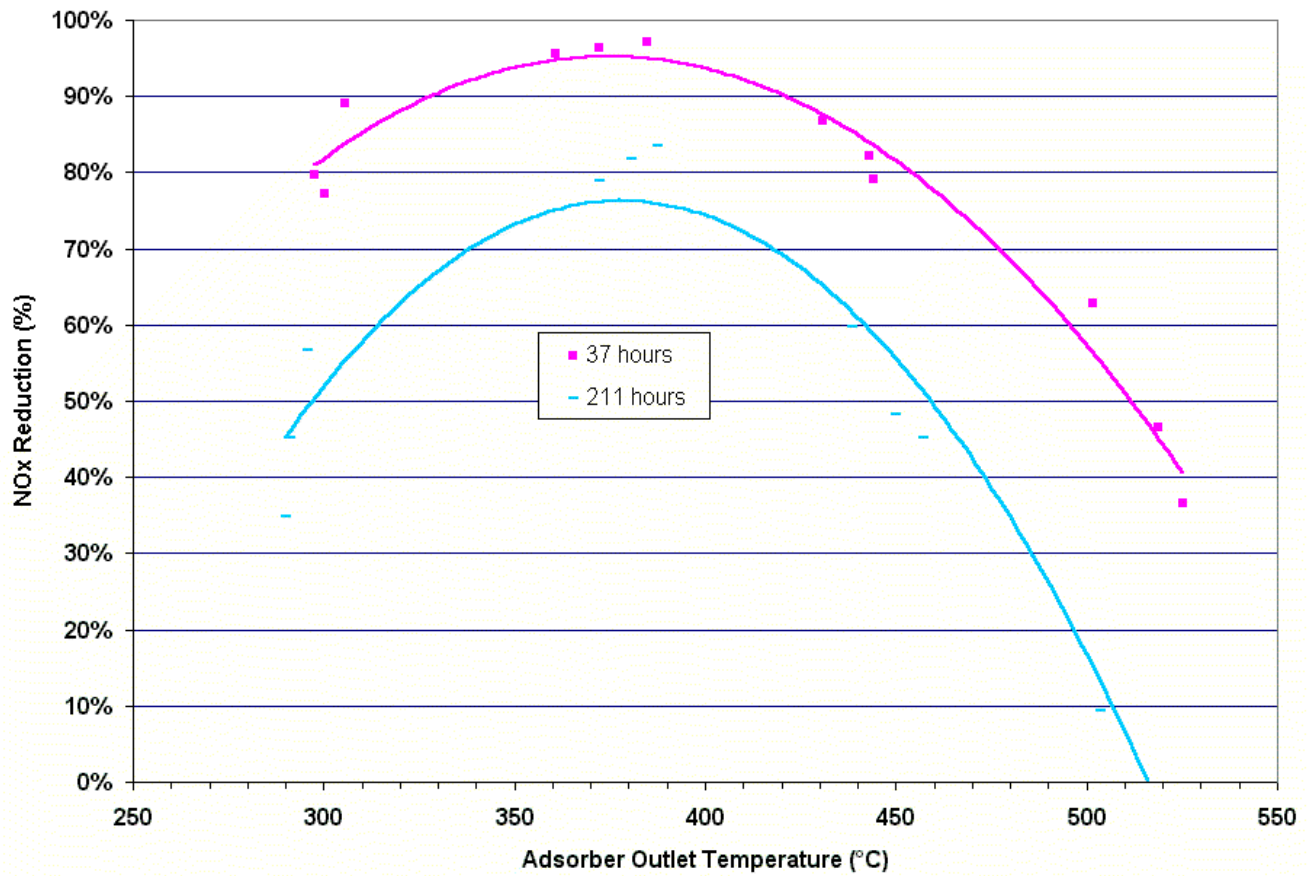
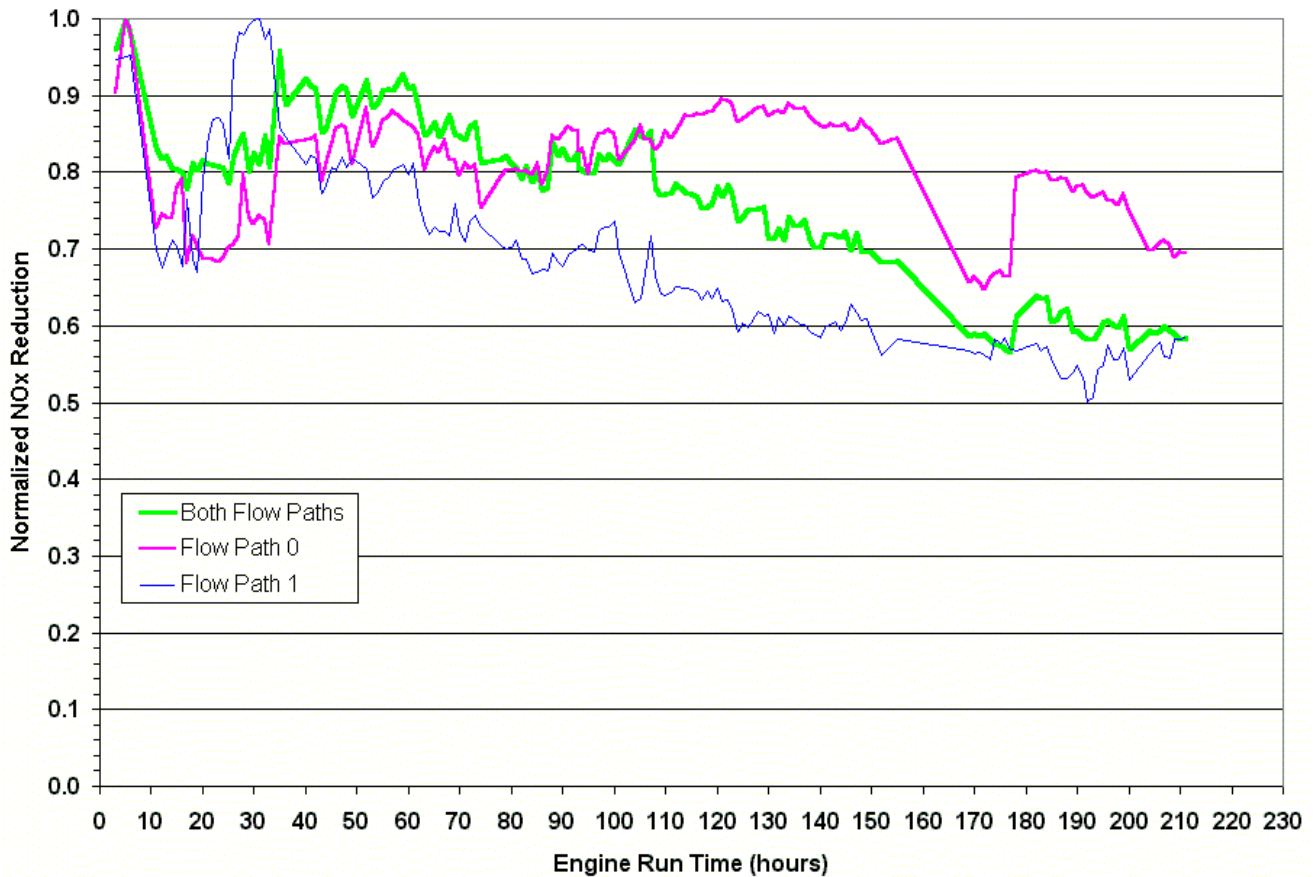**Figure 6. Performance of adsorber C over 12 modes of the SET.**

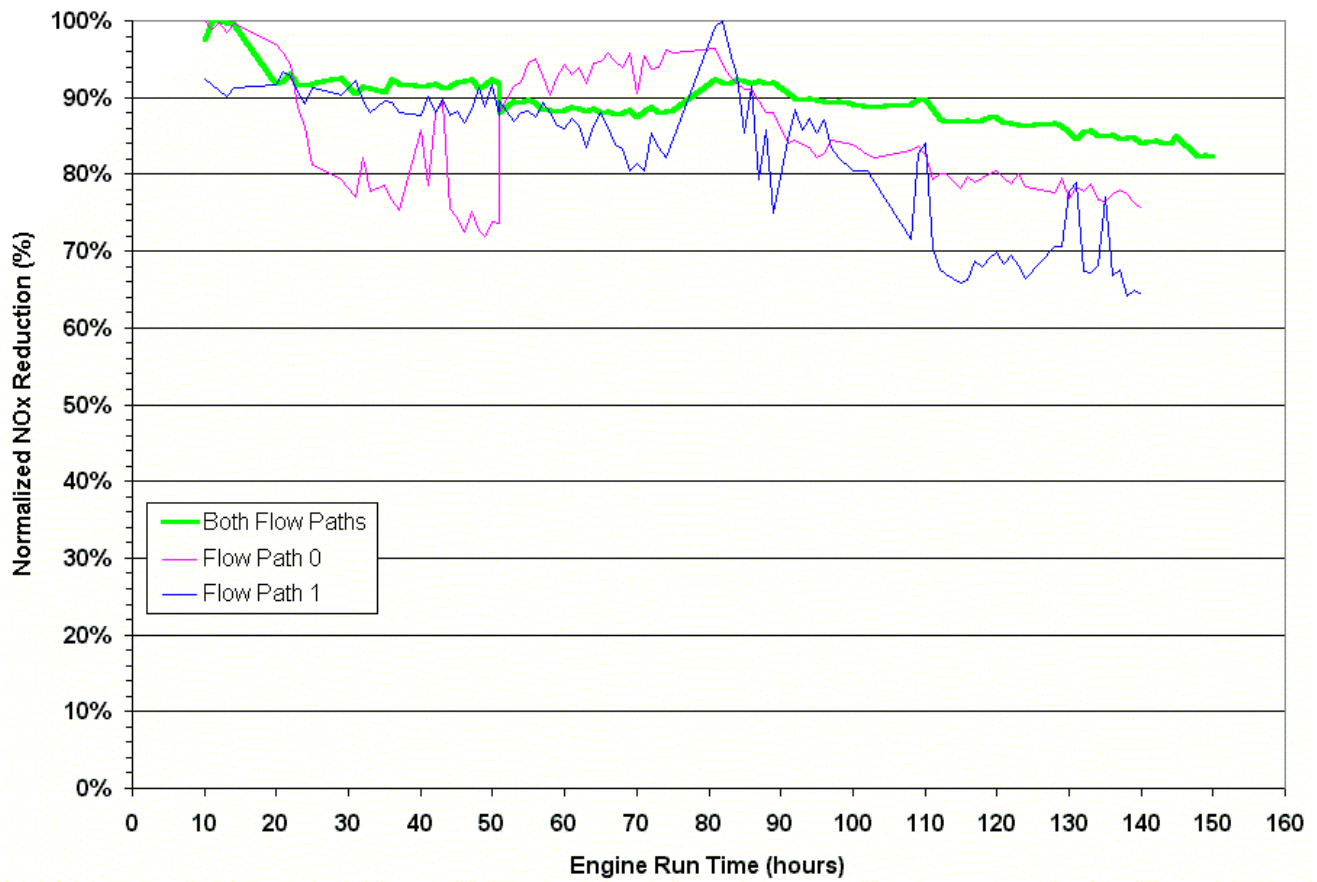**Figure 7. Adsorber C aging out to 211 hours.**

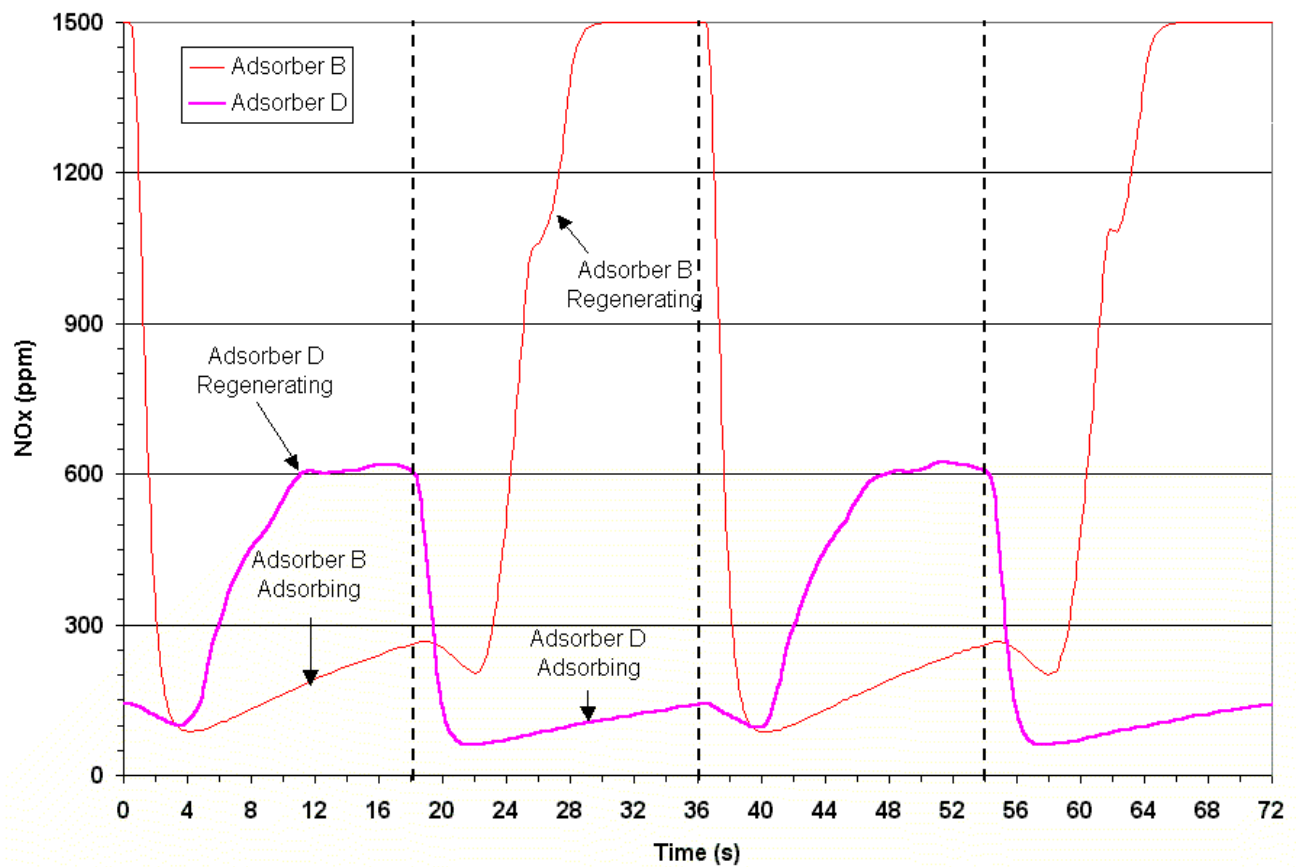**Figure 8. Adsorber D aging out to 150 hours.**

Figure 9. Adsorber B and adsorber D NO$_x$ emission over two regeneration cycles at 100 hours.
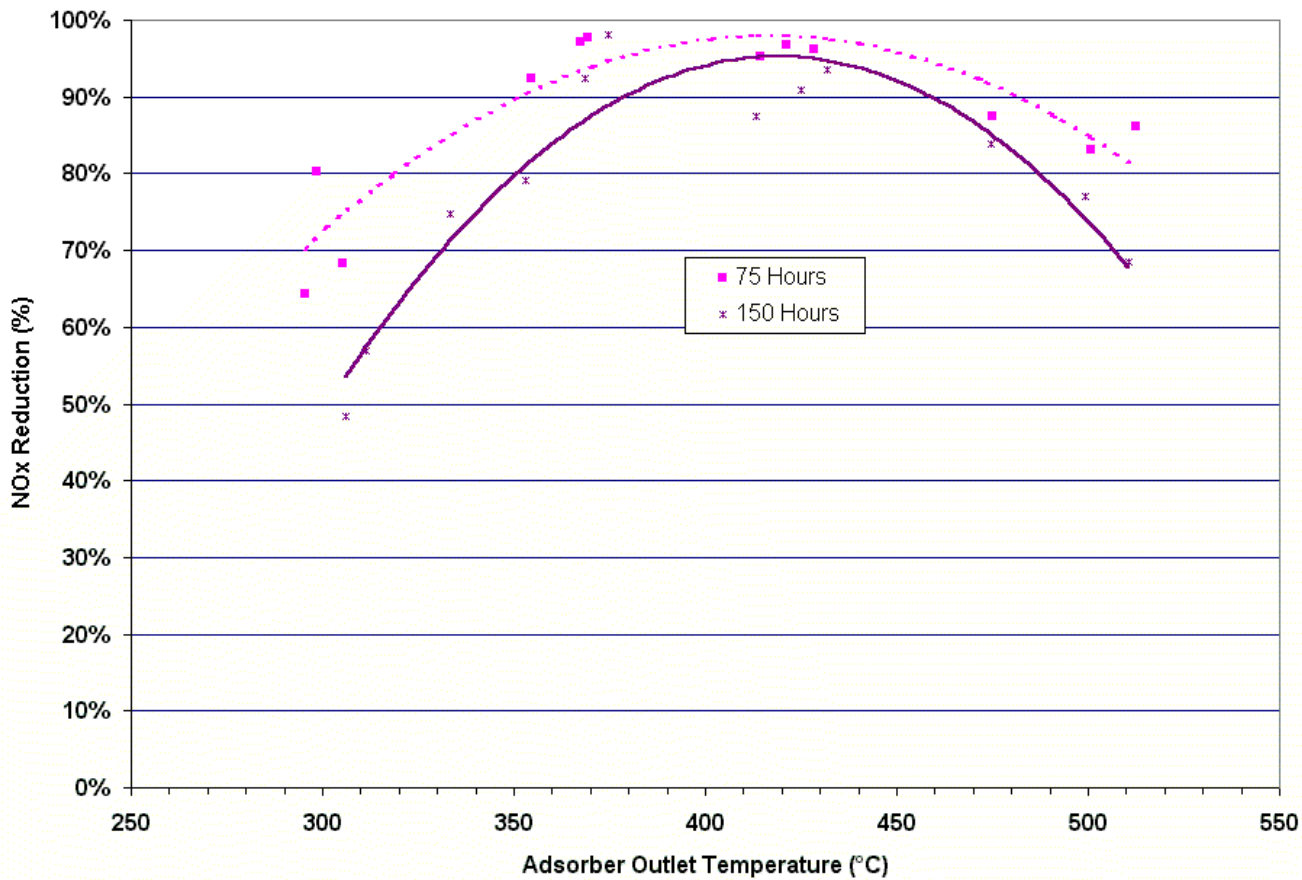
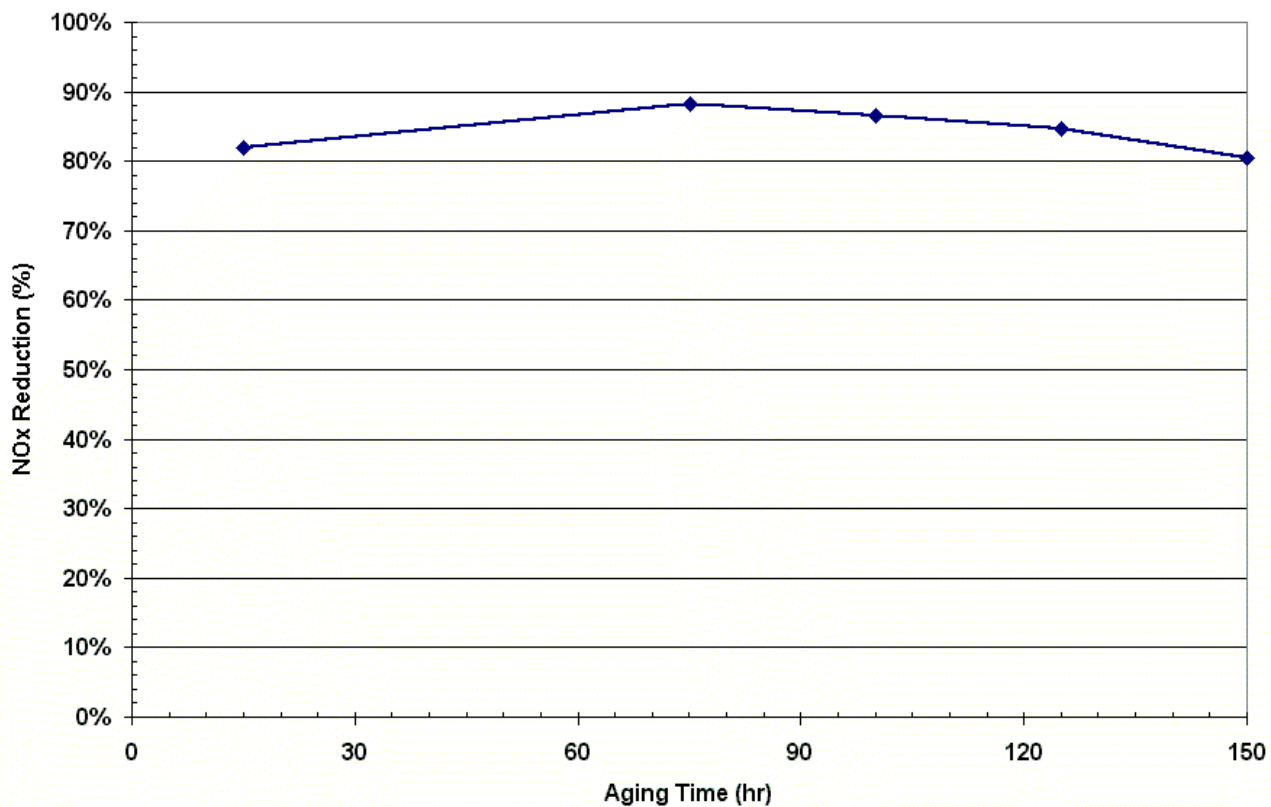**Figure 10. Adsorber D temperature window after 75 and 150 hours of aging.**

Figure 11. SET composite emissions for adsorber D after 150 hours of aging.

their development and rapid improvements were being made. Adsorber D provided the first illustration of the rapid improvements being made to NO_x adsorber formulations. While only a year newer than adsorber B, adsorber D had significantly better aging performance as evidenced by its NO_x adsorbing and regeneration performance after 100 hours. In support of the U.S. EPA's continuing effort to monitor NO_x adsorber progress, new formulations will continue to be evaluated.

The data also provides a thermal aging baseline with minimal sulfur exposure. All of adsorbers appeared to be still degreening after 100 hours of moderately accelerated aging. Adsorber A was the exception, with its performance stabilizing after about 190 hours. This formulation will be used in future testing to evaluate the impact of periodic high temperature (600-700°C) excursions required for desulfation. Initially these desulfations will be performed in the absence of sulfur to evaluate the effect of temperature only. Later, 15 ppm sulfur fuel will be used to look at the cumulative impact of temperature and sulfur on aging performance.

ACKNOWLEDGMENTS

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