

NOx Adsorber Desulfation Techniques for Heavy-Duty On-Highway Diesel Engines

Christopher Laroo, Charles Schenk, Brian Olson, Paul Way, and Joseph McDonald
U.S. EPA – Office of Transportation and Air Quality

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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 (CDPF) and NOx adsorber catalysts arranged in a dual-path configuration, was evaluated with the goal of developing desulfation strategies for in-use NOx adsorber desulfation. NOx adsorber desulfation was accomplished by providing reductant via a secondary exhaust fuel injection system and exhaust flow via an exhaust bypass valve. An alternating restriction of the exhaust flow between the two flow paths allowed reductant injection and adsorber desulfation to occur under very low space velocity conditions. An exhaust bypass valve connecting the dual path configuration upstream of the catalyzed diesel particulate filters allowed controlled addition of exhaust into the desulfating pathway for desulfation method development. Exotherms from the oxidation of reductant on the CDPF, and subsequent convective heat transfer from the CDPF to the NOx adsorbers generated adsorber catalyst temperatures in excess of 750°C. The control of space velocity through the desulfating pathway minimized cooling, allowing the temperature to be held in the target desulfation temperature range for prolonged periods of time. Sulfur release in the form of hydrogen sulfide and sulfur dioxide was measured using a chemical ionization mass spectrometer.

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 NOx, 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 covers the third phase of the continuing program under way at the U.S. EPA – National Vehicle and Fuel Emissions Laboratory (U.S. EPA-NVFEL) to evaluate advanced exhaust emission control systems for heavy-duty on-highway diesel engines. The results of the first and second testing phases have been previously reported.^{2,3} The basis of this work revolves around the use of a dual path exhaust system incorporating CDPFs in series with NOx adsorber catalysts. NOx adsorber catalysts have

been shown to achieve high NOx conversion efficiencies over wide temperature windows in lean burn applications.²⁻⁴ It has been shown that NOx adsorber reduction capacity decreases over time; and this has led to a number of studies that have investigated the mechanisms of deactivation. The main mechanisms responsible for this deactivation are the catalyst's susceptibility to thermal degradation due to precious metal and base metal migration (sintering), and sulfur poisoning.⁵⁻¹⁰

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. Knowledge of the degradation mechanisms has led to the development of on-vehicle techniques for desulfation of NOx adsorber systems. These techniques generally involve elevation of the NOx adsorber temperature, in the presence of reductant, to achieve desulfation.

Many methods have been developed to heat the NOx adsorber catalysts in engine dynamometer settings.¹¹⁻¹⁹ Hirota *et al.* demonstrated desulfation using a dual flow path exhaust purification device where the NOx adsorbent was coated onto a diesel particulate filter (DPF) formed from a metallic substrate. Here, while exhaust was being bypassed from the desulfating pathway, the combination DPF/NOx adsorber was resistively heated by electric current.¹⁵ Masseidvaag *et al.* initiated desulfation using an electrically heated catalyst located between a hydrocarbon trap and combination DPF/NOx adsorber.¹⁶ Yamashita *et al.* performed desulfation using an electric heater in a single flow path exhaust system incorporating an uncatalyzed exhaust bypass. Here, electricity was supplied to a heater upstream of the adsorber to heat the exhaust gas flowing to the NOx adsorber. When the adsorber reached the desired desulfation temperature, exhaust flow was switched to the uncatalyzed exhaust bypass and a hydrocarbon reducing agent was then applied to the desulfating pathway to initiate desulfation.¹⁷ Asik *et al.* used separate rich and lean exhaust gases generated in the engine through in cylinder control to generate an exothermic chemical reaction on the NOx

adsorber.^{11,18} While all of these methods are viable options for on-vehicle desulfation, questions arise as to the feasibility of these techniques in a production setting. The use of electrically heated catalysts to achieve desulfation temperatures is hampered by logistics and cost. Generation of an exothermic chemical reaction on the surface of the NO_x adsorber can cause local temperature extremes leading to an overall reduction in the catalyst's performance due to sintering and base metal migration.

The primary focus of this paper will be an investigation and development of the parameters required to desulfate NO_x adsorber catalysts while attempting to minimize degradation due to high temperatures. All desulfation testing was performed using the previously developed dual flow path exhaust emission control system.^{2,3} Additional phases of this project not covered in this particular paper will be published in subsequent papers. The additional work will include:

1. Investigation of 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 desulfation testing was a modified 5.9 liter displacement Cummins ISB. The engine modifications are identical to those of phase 2 of this program and have been previously described.³ The major engine specifications are summarized in Table 1.

EXHAUST SYSTEM DESCRIPTION

The dual path NO_x adsorber system, specifications of the CDPFs and NO_x adsorbers used with the system, and regeneration/NO_x reduction control strategies used for this testing are similar to the ones previously used and have been previously described in detail.^{2,3} The entire system was built using readily obtainable components. CDPF and NO_x adsorber volumes were not optimized to approximate engine displacement and were oversized for this application. 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.²

Modifications were made to the previously described system for the purpose of sulfur removal from the catalyst. Figure 1 is a functional schematic of the exhaust emission control system tested with the Cummins ISB engine. Modifications to the previously described system include the addition of an exhaust

Table 1: Summary of major engine specifications.³

Engine:	1999 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 HPCR
Engine Management:	Bosch/ETAS
EGR System:	High pressure loop, intake venturi w/ throttled bypass
Bore X Stroke:	102 mm X 120 mm
Cylinder Displacement:	5.88 L
Compression Ratio:	16.3:1

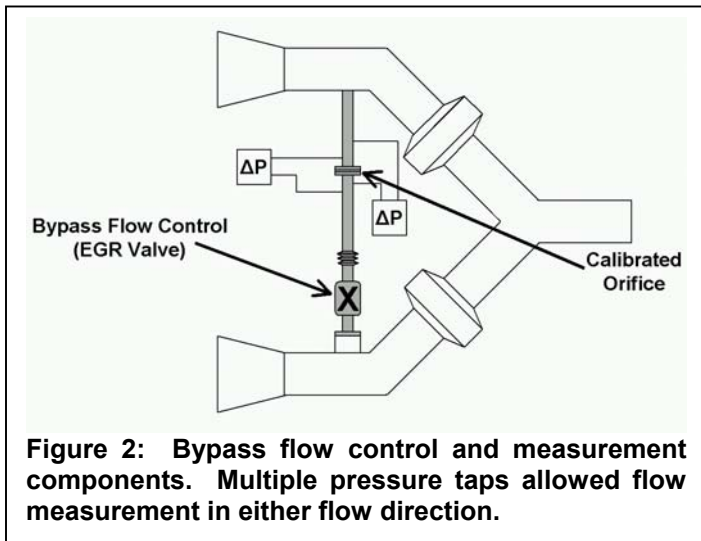
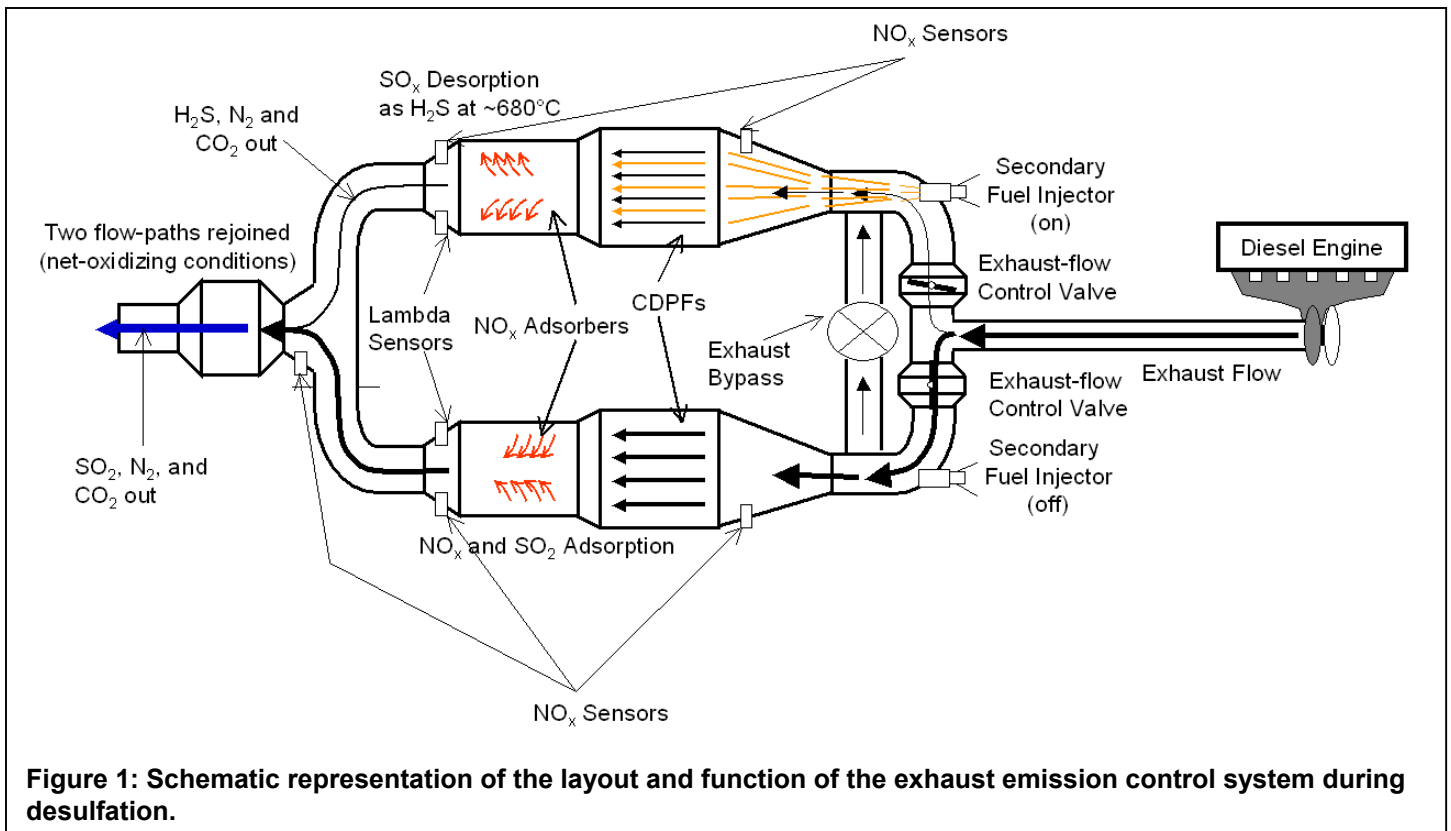
bypass pathway located downstream of the secondary fuel injectors and upstream of the CDPFs. The bypass was constructed of one inch inner diameter stainless steel tubing. The flow through the bypass path was controlled using a Lucas EGR valve. Bypass flow was measured by determining the pressure difference across a calibrated orifice. Figure 2 is a schematic of the bypass flow control and measurement components. Thermocouples were inserted into the NO_x adsorbers at a point perpendicular to the flow path and at the mid-bed point of the substrate. These thermocouples were used to monitor catalyst bed temperatures. The CDPF substrate surface temperatures were also monitored using two multiple-junction thermocouple probes that contained three separate sets of junctions and thermocouple wires within each probe. Figure 3 shows the relative position of the thermocouples and measurement junctions. The thermocouple probes were each inserted into separate cells in the substrate. One probe was inserted at the centerline of the CDPF and the other was inserted at a position 5.25 inches radially from the centerline. The temperature measurement points of the junctions were located 2, 4, and 9 inches from the back of the catalyst at the center position and 1, 6, and 11 inches from the back of the catalyst at the radial position.

TEST CYCLES

All desulfation testing was done at mode 3 of the supplemental emissions test (SET), at 1947 rpm and 328 lb-ft of torque. The nominal engine-out exhaust temperature at this mode was 450°C.

TEST FUEL

The fuel used to poison the NO_x adsorbers used for desulfation testing was Phillips Chemical Company Lot 0EPULD01. This fuel was specified by the U.S. Department of Energy's (U.S. DOE) Diesel Emission Control – Sulfur Effects (DECSE) program to have similar properties to today's on-highway diesel fuel with the exception of very low sulfur content.^{19,20} The fuel properties are shown in Table 2. A very low sulfur fuel was chosen to minimize the impact of sulfur poisoning on NO_x adsorber performance in phases 1 and 2 of the



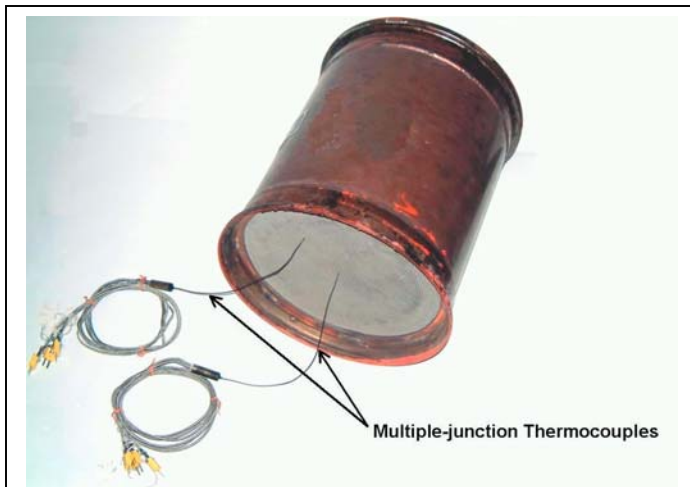
on going testing program at EPA.^{2,3} The catalysts used during phases 1 and 2 accumulated hundreds of hours of aging on this low sulfur fuel. These catalysts were subsequently used for the desulfation testing.

The fuel used during desulfation testing was Phillips Chemical Company Lot 1HPULD01. This fuel was similar to that specified by the U.S. DOE DECSE program. It was formulated to have properties similar to today's on-highway fuel with the exception of zero sulfur content.^{19,20} The fuel properties are shown in Table 3. Fuel sulfur content was measured using x-ray fluorescence spectroscopy (XRF), which had a 0.7 ppm limit of detection (LOD) for sulfur. XRF indicated a fuel sulfur concentration that was below the LOD for the

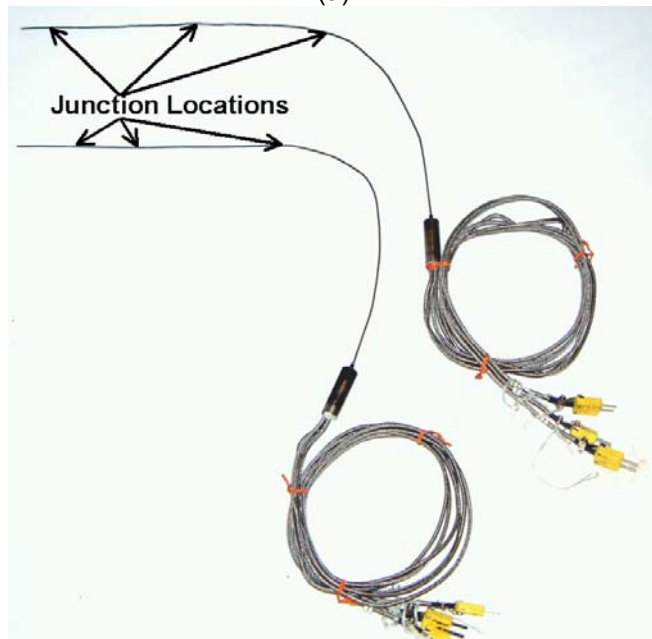
instrument. This "zero" sulfur fuel was used in order to ensure that further poisoning of the NOx adsorbers did not occur during desulfation testing. Engine-out SO₂ concentration was calculated for SET mode 3 using fuel sulfur concentration, fuel flow rate, and intake air flow rate. Although trace amounts of sulfur were present in the fuel, it accounted for less than 28 ppb SO₂ engine-out (assuming 0.7 ppm fuel sulfur as a worst case) at mode 3 and its contribution to adsorber poisoning, as well as that from engine oil consumption, can be considered negligible for the testing done here.

LABORATORY

The engine was tested at Heavy-Duty Engine (HDE) Site 2 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 per 40 CFR § 86 Subpart N.¹ Gaseous analyses were performed using a gas-analysis bench made up of loose analyzers and has been previously described.³ Modal measurement of sulfur released in the form of sulfur dioxide (SO₂) and hydrogen sulfide (H₂S) was performed using a V&F AS-2000 chemical ionization mass spectrometer utilizing internal high speed switching. Sulfur release was measured in between the NOx adsorbers and downstream of the second adsorber substrate in one pathway of the dual path system. High speed sample switching allowed measurements to take place in the exhaust at two points with a total cycle time of 1.5 seconds with a T₉₀ of less than 50 ms. Mass spectrometer accuracy and interference with regards to the measurement of SO₂



(a)



(b)

Figure 3: Locations of the thermocouple probes as inserted into the CDPF (a), and relative positions of the thermocouple junctions along the length of each probe (b). As installed, the thermocouple probes exited the CDPF “can” through fittings in the entrance-cone of the CDPF.

and H₂S in diesel exhaust has been described elsewhere.²¹

DESULFATION STRATEGY

Initial Desulfation Testing

Initial development performed using the dual path system was done without the use of the exhaust bypass valve. The desulfation routine was automated using a time-based schedule and the general procedure was as follows:

1. While the engine operated at SET mode 3, fuel was injected into the bypassed flow path of the exhaust system creating a fuel rich environment ($\lambda < 1$).

Table 2: Summary of low sulfur fuel properties.

Test Method	Results
Net Heat of Combustion, ASTM D3338-92 (MJ/kg)	43.19
Density @ 15.5°C (g/cm ³)	0.8258
Cetane Number	43.4
Cetane Index	53.5
Olefins, FIA D1319-93 (% Vol.)	3.3
Aromatics, D1319-93 (% Vol.)	24.2
Sulfur, ASTM D2622 (ppm mass)	3
Carbon, ASTM D3343-95 (% mass)	0.8638
Distillation Properties, ASTM D86	
IBP (°C):	191
10 % (°C):	213
50 % (°C):	258
90 % (°C):	312
End Point (°C):	346
Residue Diesel (mL):	0
Recovery:	100%

Table 3: Summary of zero sulfur fuel properties.

Test Method	Results
Net Heat of Combustion, ASTM D3338-92 (MJ/kg)	43.06
Density @ 15.5°C (g/cm ³)	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%

2. The bypass flow path was then opened to full exhaust flow for a predetermined time. Oxidation of the hydrocarbon reductant over the CDPF and NOx adsorbers generated an exotherm causing an elevation in NOx adsorber temperature. The amount of fuel injected during the first event and the

amount of time that the desulfating flow path is exposed to full exhaust flow determined the temperature rise of the adsorber. If the adsorber reached the preset desulfation temperature, exhaust flow to the flow path was closed off.

3. If the rear NO_x adsorber catalyst did not reach the desired desulfation temperature, the process was repeated and the generated exotherm, in conjunction with convective heat transfer, brought both adsorber substrates to the target temperature.
4. Fuel was then injected into the flow path to maintain the desired lambda value ($\lambda < 1$) causing sulfur release. The low mass flow through the pathway (caused by exhaust brake slip and reductant injection) allowed the adsorbers to stay at the desulfation temperatures for an extended period.

Refined Desulfation Testing

Further desulfation development performed using the dual path system was done with the use of an exhaust bypass valve to study the impact of exhaust flow. The test controller was automated to allow target lambda and exhaust bypass flows to be met. The desulfation pathway lambda and exhaust bypass flow were optimized to allow exotherms to occur on the surface of the CDPF while minimizing exotherms on the NO_x adsorber.²² The general procedure worked as follows:

1. Target lambda, bypass flow, NO_x adsorber temperature, and CDPF maximum temperature set points were inputted into the desulfation controller.
2. While the engine operated at mode 3 of the SET, fuel was injected into the bypassed flow path of the exhaust system to meet the target exhaust lambda value. Bypass exhaust was modulated into the desulfating pathway at a low flow rate.
3. The combination of bypassed exhaust and injected fuel created exotherms from the oxidation of hydrocarbons on the surface of the CDPF causing an elevation in CDPF temperature.
4. When the CDPF reached a predetermined temperature, the desulfation pathway was opened to full exhaust flow. Heat was transferred convectively from the CDPF to the NO_x adsorber. When the CDPF cooled to a preset lower temperature limit, the desulfating pathway was switched back to bypass mode. This process was repeated until the NO_x adsorbers reached the desired desulfation temperature.
5. When the desulfation temperature was reached, the bypass flow was lowered further and reductant was injected to maintain a desired lambda value ($\lambda < 1$) causing sulfur release. Low mass flow through the flow path allowed the adsorbers to stay at desulfation temperatures for an extended period.

Parametric testing was performed to determine the optimum parameters for heating the NO_x adsorbers in preparation for desulfation. The goal was to reach desulfation temperature in the shortest amount of time,

while keeping the adsorber temperature rise rate at a moderate level.

RESULTS

INITIAL TECHNIQUE

The original heating/desulfation technique used an event timer table similar to that used in previous FTP tests.^{2,3} This table commanded fueling rates, fueling durations and the flow control valves for the two exhaust pathways. For heating and desulfation, this table was set up to provide fuel rich ($\lambda < 0.6$) conditions at low exhaust flows (from exhaust brake slip). Since the CDPF was lightly catalyzed and there was little oxygen present to oxidize all of the injected fuel, accumulation of fuel would occur on the adsorber substrates during the rich, low-flow condition. After about 85 seconds, the heating pathway would be exposed to full exhaust flow. The accumulated fuel would then be oxidized producing a very rapid exotherm. This exotherm was primarily isolated on the front NO_x adsorber substrate. The process was then repeated a second time to heat up the rear NO_x adsorber substrate (two 9.5" diameter X 6" long substrates were used). The NO_x adsorber and CDPF temperatures can be seen in Figure 4. The front adsorber bed temperature increased rapidly after the first exposure to full exhaust flow at 90 seconds, while the rear adsorber showed a small rise in temperature. The exhaust flow was reduced again from 115 seconds to 250 seconds while remaining rich as indicated by Desulfation Lambda. When the pathway was opened to full exhaust flow the second time, the rear adsorber substrate saw a rapid increase in temperature, while a small increase was evident on the front adsorber. The NO_x adsorbers reached their target temperature of 680°C in about 270 seconds. The temperature reached by the adsorber substrates for these tests was calculated as the average of the front and rear NO_x adsorber substrate temperatures.

Under these hot, rich conditions, sulfur was released in the form of H₂S. The mass spectrometer used to monitor H₂S was also capable of measuring SO₂. The mass spectrometer LOD for SO₂ was 18 ppb. Throughout testing, sulfur release in the form of SO₂ was not evident. H₂S measured downstream of the adsorbers, NO_x adsorber temperature, and exhaust lambda as a function of time can be seen in Figure 4. The sulfur release for this adsorber formulation started at about 700°C and progressed until the timer table stopped the reductant injection. The DOC downstream of the adsorbers is operated in a lean environment that oxidizes the H₂S to SO₂.

The repeatability of this process and its efficiency at removing sulfur from the adsorbers was then investigated to develop a method to determine the overall effectiveness of the desulfation. Using the above technique, measurements of desulfation parameters were taken for five separate, consecutive desulfation events with sufficient equilibration time between events.

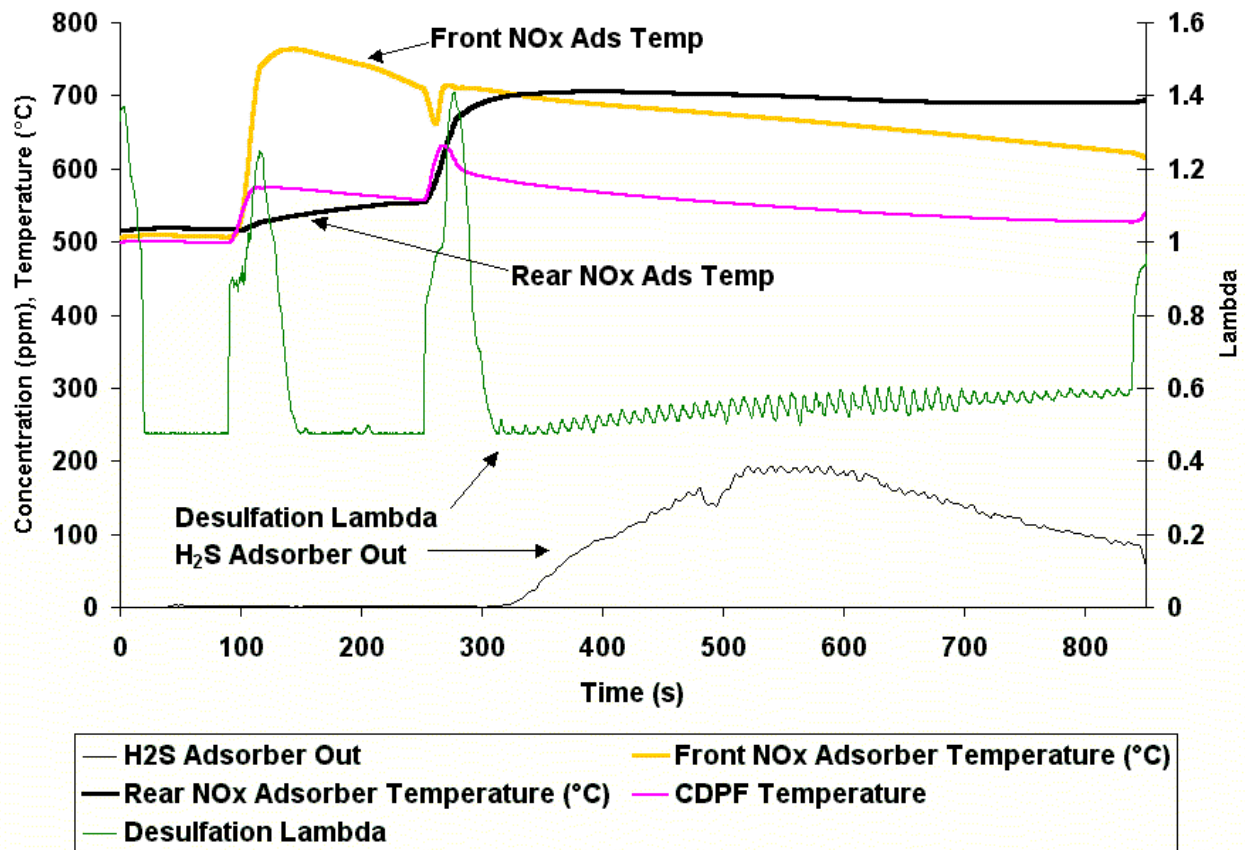


Figure 4. Desulfation using initial heating technique.

The second of these events is shown in Figure 4. The measured parameters, shown in Table 4, include time to start of release, t_R , average NOx adsorber temperature at start of release, T_R , magnitude of peak release, M_R , time to peak release, t_{MR} , time to end of release, t_{EOR} , and temperature at end of release, T_{EOR} . Sulfur release data, from which M_R was taken, was averaged over 10 seconds. The start of release is defined as the point at which release reaches 20% of M_R during positive rate of release, while the end of release is defined as the point at which release again reaches 20% of M_R during negative rate of release. Using these definitions, measurement of sulfur removal at the start and end of release was determined well within the mass spectrometer measurement error of $\pm 1\%$ of reading value, down to 1 ppm.²¹ Approximations of the rate of release approaching ($\Delta M/\Delta t_+$) and receding from ($\Delta M/\Delta t_-$) the peak release were also included as parameters. The approaching and receding rates were approximated by $(t_{MR} - t_R)/(0.8 \cdot M_R)$ and $(t_{EOR} - t_{MR})/(-0.8 \cdot M_R)$, respectively. All five events were performed over the same CDPF and NOx adsorbers without re-poisoning the adsorbers between events. Since the amount of sulfur available for removal decreased after each event, this data allows the impact of sulfur load on the desulfation parameters listed in Table 4 to be determined.

For these five events, release of H_2S began at an average time of 354 seconds with a deviation of approximately 1%, at an average T_R of 702°C. The deviation in T_R is significantly less than the accuracy of the thermocouples used to measure this value. The general characteristics of sulfur removal suggested by $\Delta M/\Delta t_+$ and $\Delta M/\Delta t_-$ are a rapid increase in the amount of sulfur removed, from the start of release to the peak release, followed by a decrease in sulfur removal over a much longer time-scale. The average duration of release was 508 seconds with a deviation on the order of 1%. For each consecutive desulfation event, M_R decreased by 20-54% while t_{MR} increased by 2-5%, when compared to the previous event. It should be noted that although the parameters in Table 4 are dependant on NOx adsorber washcoat formulation, the above data may still be used to determine the qualitative dependence of these parameters on sulfur load for any washcoat with generally similar characteristics to those that have been used here. An understanding of these desulfation parameters will allow a profile of the heating and sulfur release to be established for a specific adsorber formulation, which can then be used to optimize the desulfation.

The drawback to this method of heating/desulfation is that the local NOx adsorber surface temperatures seen during this exotherm must be well in excess of the measured mid-bed temperatures in order to drive such a

Table 4: Measurements made during five desulfation events using the initial heating technique described in the Results section.^a

Event	t_R (s)	T_R (°C)	M_R (ppm)	t_{MR} (s)	t_{EoR} (s)	T_{EoR} (°C)	$\frac{\Delta M}{\Delta t} +$ (ppm/min)	$\frac{\Delta M}{\Delta t} -$ (ppm/min)
1	358.3	701.0	416.7	519.5	852.9	645.0	124	-60
2	349.6	701.6	190.7	543.5	863.4	625.9	47	-29
3	347.9	701.8	152.2	552.2	858.4	633.8	36	-24
4	352.5	701.3	109.0	583.2	859.4	631.5	23	-19
5	348.7	701.6	77.2	594.2	861.0	628.9	15	-14
σ (% of mean)	1.1	0.04	63	4.8	0.4	1.0	79.9	55.8

^aThe columns show, from left to right, attempt number, time to start of release, average NOx adsorber temperature at start of release, magnitude of peak release, time to peak release, time to end of release, and temperature at end of release. The last two columns present an approximation of the rate of release approaching and receding from peak release, respectively. The measured sulfur release was in the form of H₂S.

rapid increase in the adsorber substrate temperatures. Such high temperatures will damage known NOx adsorber washcoat formulations.^{10,23,24} Since the local temperatures cannot be measured directly, the temperature change rate (TCR) has been adopted as an indicator of local surface temperatures and the general harshness of an exotherm with respect to the catalyst washcoat. Figure 5 shows the TCR in °C/sample for the CDPF and the two adsorber substrates. Samples in this test program occurred at 0.27 second intervals. The chart shows a maximum CDPF temperature rate in excess of 3°C/sample. The front adsorber substrate had an even higher maximum rate of 5°C/sample.

The relationship between TCR and catalyst durability has not been firmly established and is washcoat and substrate dependent. The TCRs that resulted from the heating algorithm described above were damaging to the adsorber washcoat, as was evident by a loss in NOx reduction capacity. The CDPF has a simpler washcoat formulation that is designed to be tolerant of the exotherms that occur when accumulated PM rapidly oxidizes. It was thought that the CDPF would be less likely to be damaged by fuel-induced exotherms than the NOx adsorbers. Considering these factors, another heating algorithm was investigated.

REFINED HEATING TECHNIQUE

The refined heating algorithm attempted to minimize the adsorber exotherm by oxidizing most of the fuel on a highly catalyzed DPF. The lambda values were also kept at 0.8 or higher to minimize fuel slippage through the CDPF.

In addition to very high TCRs, the previous timer table method suffered from repeatability issues. The exotherm behavior of the catalysts is dependent on their conditioning prior to the start of the test. Although substrate temperature repeatability at the start and end of the sulfur release was shown in five consecutive tests, the maximum temperatures and lambda values varied from day to day with the same timer table. To address this, the controller was modified in three ways. The first

modification was the addition of a routine that monitored the catalyst temperatures. This routine looked at preset maximum temperatures for the CDPF, shutting off the fuel and opening the desulfating pathway to full flow when the CDPF temperature reached the set maximum, allowing for convective heat transfer to the NOx adsorbers. The adsorber temperatures were also monitored to determine when they had reached the desired temperature. When this happened the controller transitioned from the heating phase to the desulfation phase. During this phase the exhaust flow was lowered to minimize the exotherm caused by the fuel injected to maintain $\lambda < 1$. The elevated temperature and the lambda conditions were then held in these desulfation-promoting conditions.

The other two modifications were the addition of closed loop lambda control based on feedback from an oxygen sensor and closed loop control of the exhaust bypass flow based on feedback from a sharp edged orifice. The hardware changes are described in the Exhaust System Description.

An early test of the refined heating controller is shown in Figure 6. The controller action can be seen in the cycling of CDPF 6" Radial Temperature. As the CDPF heats up, the controller opens up the pathway to full flow, convectively transferring the heat to the NOx adsorbers. By choosing the appropriate CDPF temperature target, sintering of the adsorber washcoat can be minimized. H₂S release can also be seen in Figure 6. H₂S is shown desorbing from the first adsorber substrate along with the total H₂S desorbed from both substrates. From this data it appears that about two-thirds of the sulfur is coming off of the front substrate. This would be expected since the front substrate should capture more sulfur than the rear.²⁵ The data also dispels the concern that sulfur released from the front substrate gets re-adsorbed on the rear substrate. This may still be happening to some degree, but the data indicates a net sulfur release from the second substrate. The release shown here is smaller in magnitude than in Figure 4 due to the frequent desulfations that had occurred prior to this data set.

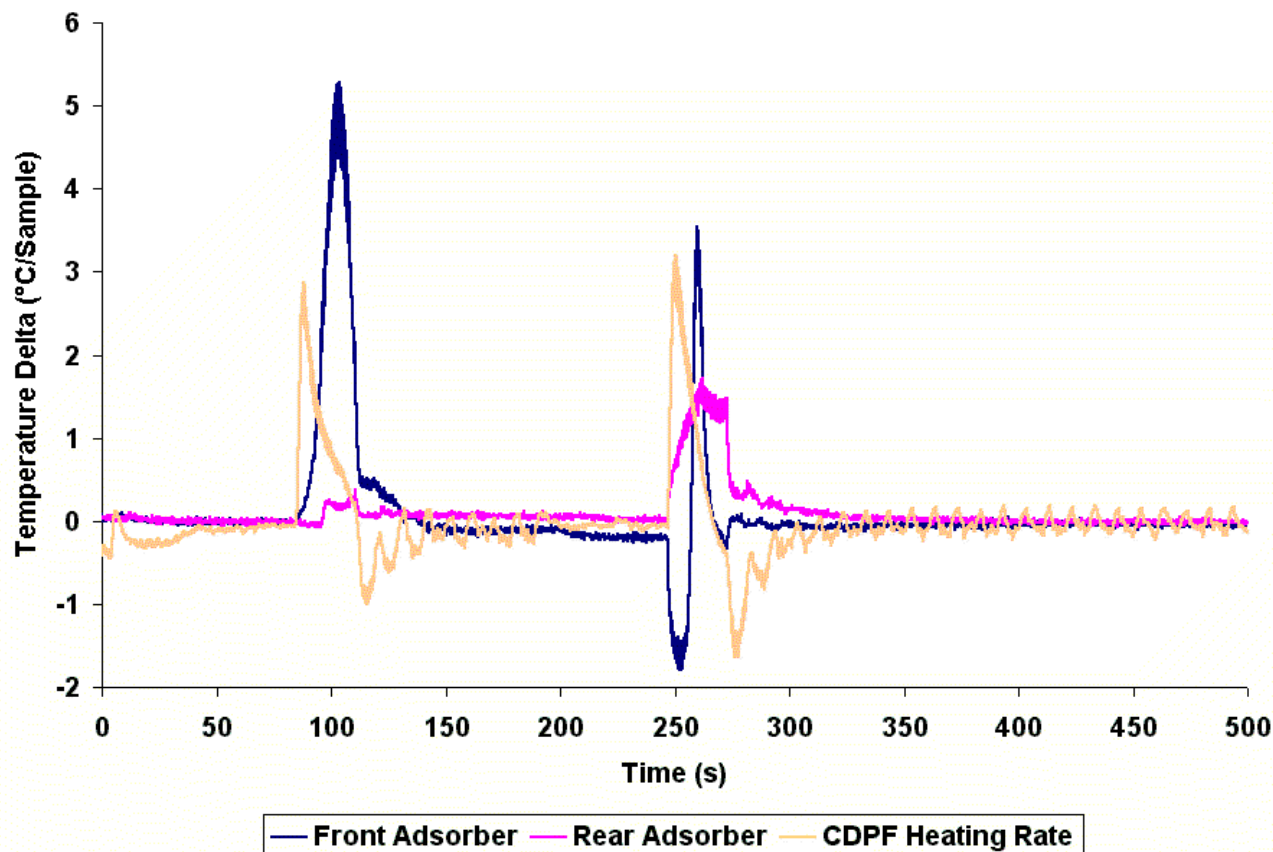


Figure 5. NO_x adsorber and CDPF TCR using initial heating technique.

The benefits of the refined method are evident in Figure 7. The maximum TCRs for all of the catalysts are substantially lower than those of the initial heating technique. The CDPF TCR was about 30% less at 2.2°C/sample and the adsorber TCRs were reduced by more than 80% to less than 1°C/sample. The low adsorber TCR indicates that the exotherm has been substantially moved to the CDPF. The exotherm on the CDPF is controlled by higher lambdas during heating and temperature modulation by the controller. The combination of these parameters minimizes fuel slippage to the adsorbers and lowers the CDPF exotherm when exposed to full flow.

DESULFATION PARAMETRIC STUDY

After refining the desulfation heating technique it was decided to run a parametric study to determine which variables affected NO_x adsorber temperature rise. A (2⁴) Two-Level Factorial Design of Experiments was employed to determine which variables had a significant effect on temperature rise over the CDPF and NO_x adsorbers.

The variables studied were Exhaust Bypass Flow, Exhaust Lambda, CDPF Hysteresis, and the CDPF Maximum Temperature. Exhaust Bypass Flow was the amount of exhaust flowing into the desulfating flow path of the system via the bypass pathway. Exhaust Lambda

was measured downstream of the rear NO_x adsorber. CDPF Hysteresis is defined as the temperature difference between the maximum CDPF temperature that initiated convective heat transfer to the NO_x adsorbers and the minimum CDPF temperature that triggers the end of the heat transfer event. CDPF Maximum Temperature set point was used to trigger convective heat transfer from the CDPF to the NO_x adsorber.

There were six response variables that are thought to characterize the heating of the NO_x adsorbers. The responses that were investigated were the TCR of the front NO_x adsorber substrate, TCR Front Adsorber (°C/Sample); the TCR of the rear adsorber substrate, TCR Rear Adsorber (°C/Sample); the average difference in the NO_x adsorber substrate temperatures over the test cycle, Average Adsorber Temperature Difference (°C); TCR of the CDPF to the maximum temperature set point, TCR to CDPF Maximum Temperature (°C/Sample); the time it took the average NO_x adsorber temperature to reach the desired level, Time to Average Adsorber Temperature (s); and the final adsorber temperature difference, Front/Rear Final Adsorber Temperature Difference (°C).

A test matrix of 16 tests was generated and each test was run twice for a total of 32 tests. Table 5 shows the results of the test matrix. The effects of the four main

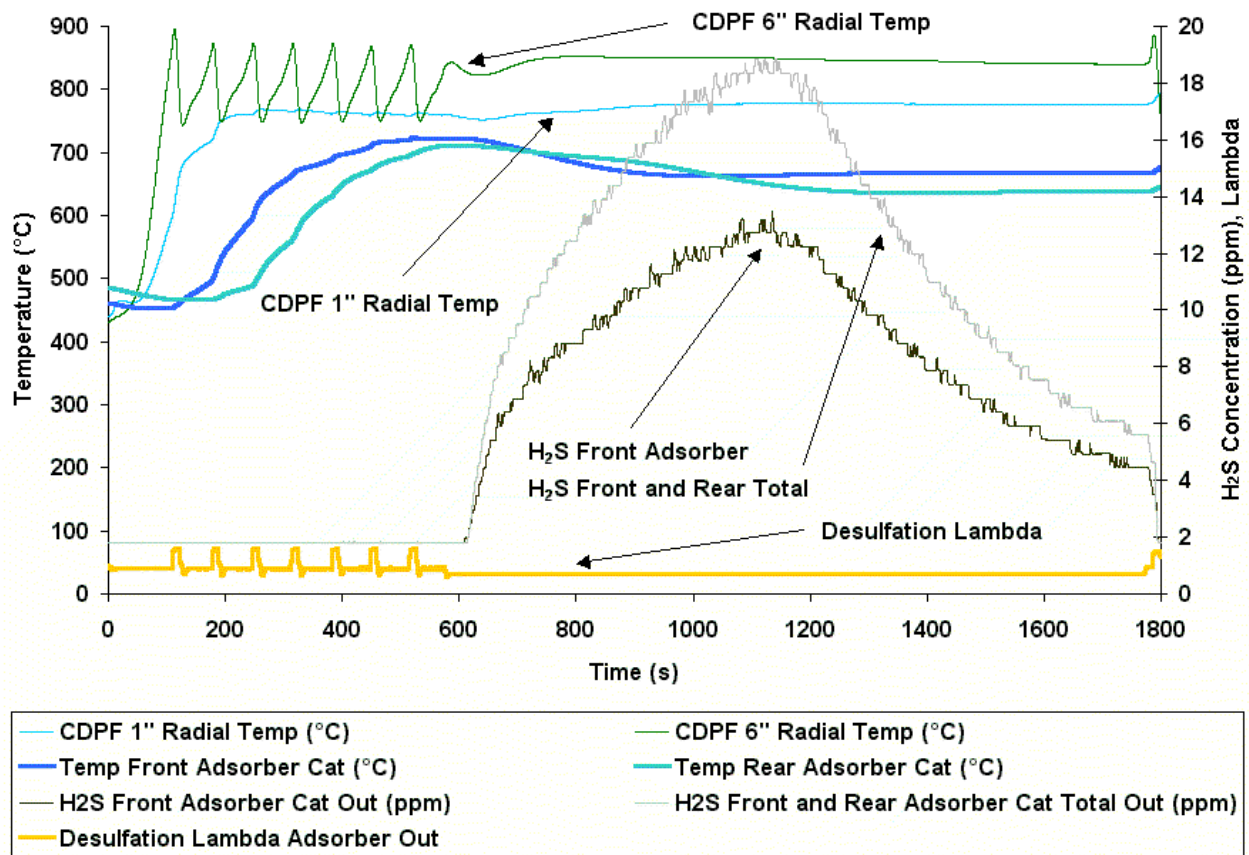


Figure 6. Desulfation using refined heating technique.

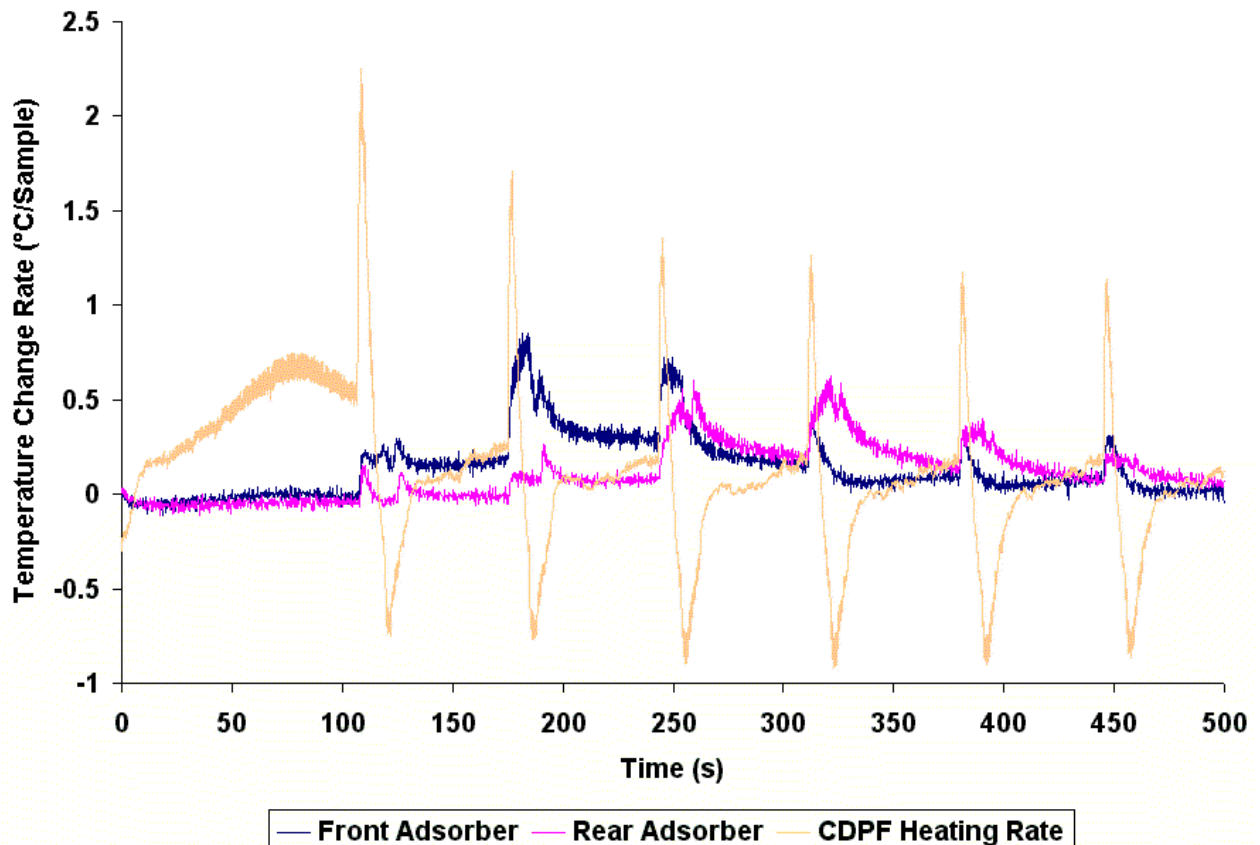


Figure 7. NO_x adsorber and CDPF TCR using refined heating technique.

Table 5: Results of desulfation parametric study test matrix.

	TCR Front Adsorber (°C/sample)	TCR Rear Adsorber (°C/sample)	Average Adsorber Temperature Difference (°C)	TCR to CDPF Maximum Temperature (°C/sample)	Time to Average Adsorber Temperature (s)	Front/Rear Adsorber Final Temperature Difference (°C)
Exhaust Bypass Flow Effects (X1)	0.4	0.4	30.8	-1.1	-152	-34
Lambda Effects (X2)	-0.4	0.3	-22.9	0.1	40	-8
Effect of CDPF Hysteresis (X3)	0.5	0.1	-11.2	0.3	22	-28
Effect of CDPF Max Temperature (X4)	-0.7	-0.1	12.6	0.1	-16	39
Effect of X1X2	-0.4	0.3	-10.7	0.4	33	8
Effect of X1X3	0.3	0	-0.8	0	30	-4
Effect of X1X4	0.1	-0.1	7.4	-0.1	-24	30
Effect of X2X3	-0.1	0.1	18.8	-0.3	12	-39
Effect of X2X4	0.4	0	-1.5	0.1	-18	33
Effect of X3X4	-0.4	0	4.1	0.2	-16	-3
95% Conf Interval	0.4	0.2	14.4	0.3	49	26

variables were calculated, as well as the first order interactions. To test for significance the effects were compared to the 95% confidence interval of the mean for each response variable.

Table 5 shows that the exhaust bypass flow is significant in five of the six response variables. Exhaust lambda shows a weaker significance in three of the six response variables. The CDPF hysteresis and CDPF maximum temperature variables show a much weaker significance than the bypass flow and lambda. The confounded effects, which show significance, are believed to be artifacts of the multiple tests because they do not show significance when each set of runs is looked at separately.

Subsequent analysis of the CDPF temperature profiles, in which different numbers of heating cycles had accrued, might explain the significance of the confounded effects noted during multiple tests. Figures 8, 9, 10, and 11 show the CDPF temperature profiles for the same CDPF after 1, 22, 33, and 105 heating cycles.

CDPF heating parameters remained the same for the cycle numbers show here. As the CDPF is subjected to additional heating cycles, the time it takes for the CDPF to reach its target temperature increases. In addition, as the number of heating cycles increases, the exotherm starts taking place further from the front and outer portion of the CDPF. This is evident in Figures 8, 9, 10, and 11. During heating cycle 1, the exotherm initially occurs at the Radial 6" and Center 4" positions. This gradually shifts to Radial 1" and Center 2" as the cycles progress from 1 to 33. By cycle 105, the time to CDPF

target temperature had increased from 150 seconds at cycle 1 to 425 seconds with the exotherm occurring primarily at the Center 4" position. At cycle 140 (not shown), the CDPF oxidation function has become so degraded that the exotherm no longer occurs on its surface and was observed to take place directly on the surface of the NOx adsorber. It is evident from this data, that this particular CDPF formulation loses its oxidation function over multiple heating cycles. This is most likely due to sintering of the precious metal in the CDPF's washcoat. From these results it was decided that a more robust CDPF formulation must be procured before further testing can be conducted on optimization of the heating/desulfation process.

Discussions with the catalyst manufacturer have indicated that a more robust CDPF formulation has been developed and will be made available to the EPA for future testing. Once the new formulation has been procured, a more detailed test plan will be run in which the CDPF maximum temperature and CDPF hysteresis will be held constant while sweeping the lambda and exhaust bypass flow. This data will help to determine the optimum settings for heating the exhaust emission control system to the desired desulfation temperature and will be discussed in a future paper.

CONCLUSION

The initial and refined heating techniques developed here have shown that exotherms from reductant injection can be controlled to occur in different sections of the exhaust emission control system for the purpose of initiating desulfation. Temperature change rate (TCR)

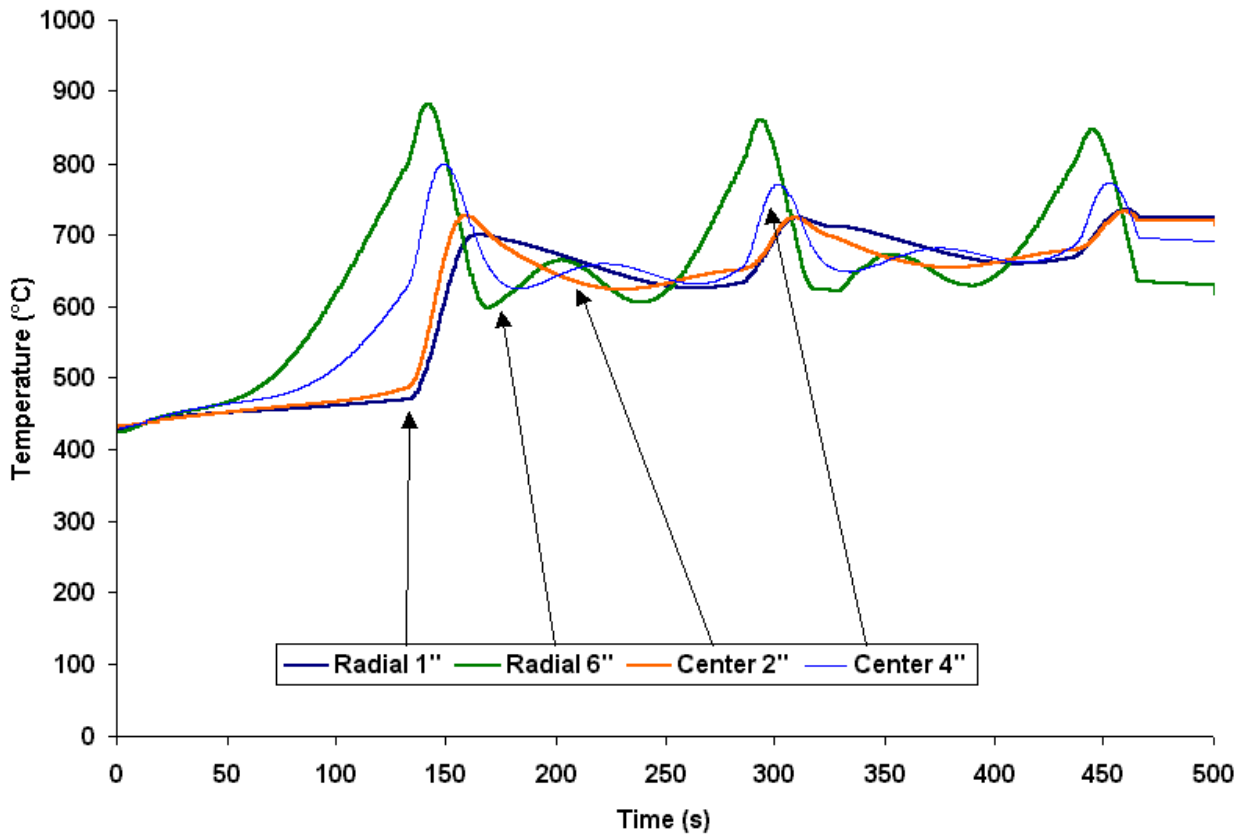


Figure 8. CDPF temperature profile after 1 heating cycle.

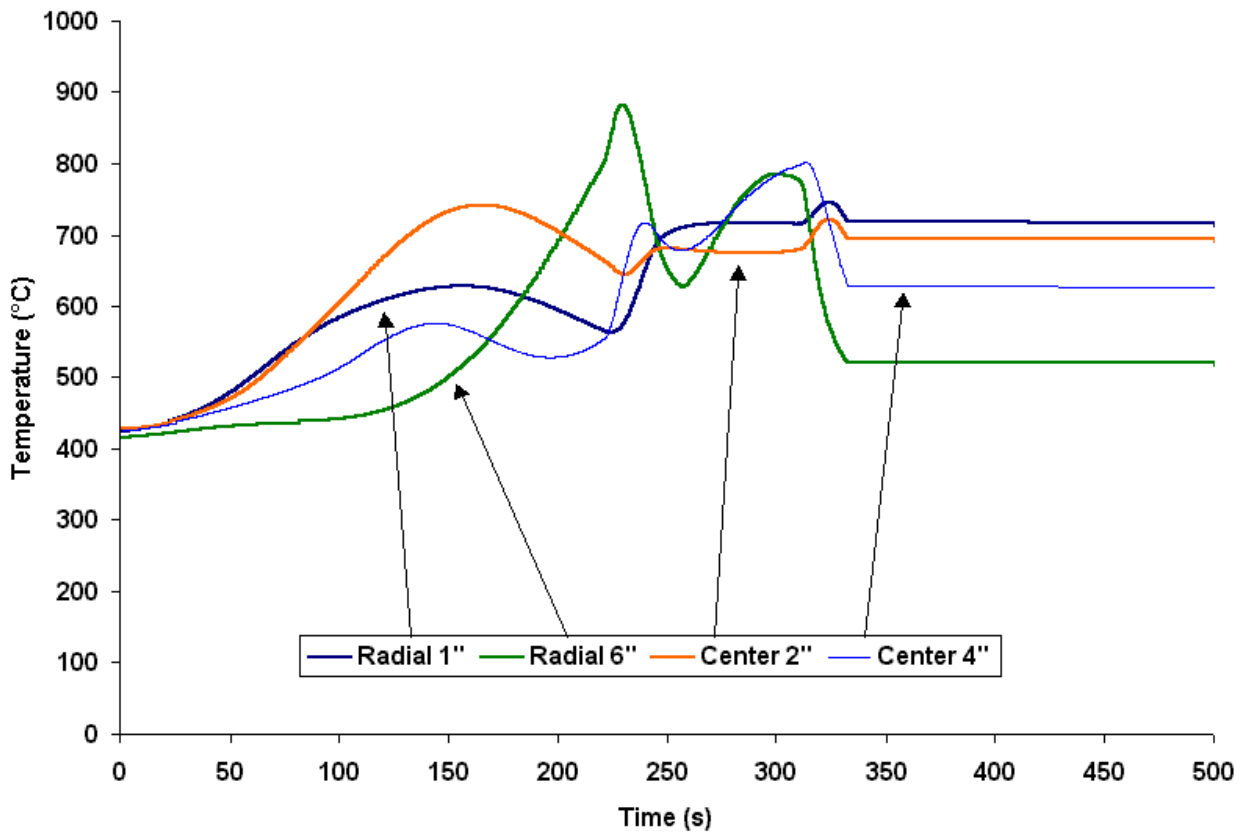


Figure 9. CDPF temperature profile after 22 heating cycles.

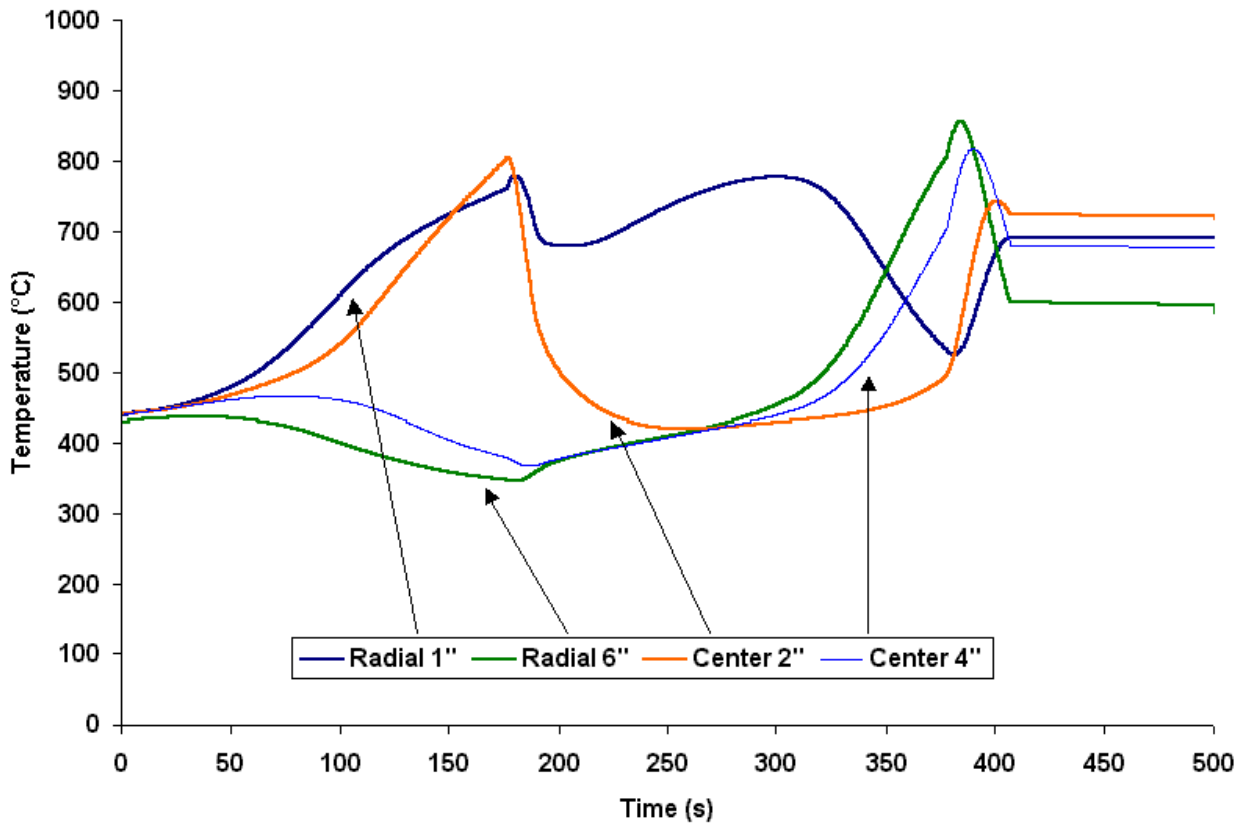


Figure 10. CDPF temperature profile after 33 heating cycles.

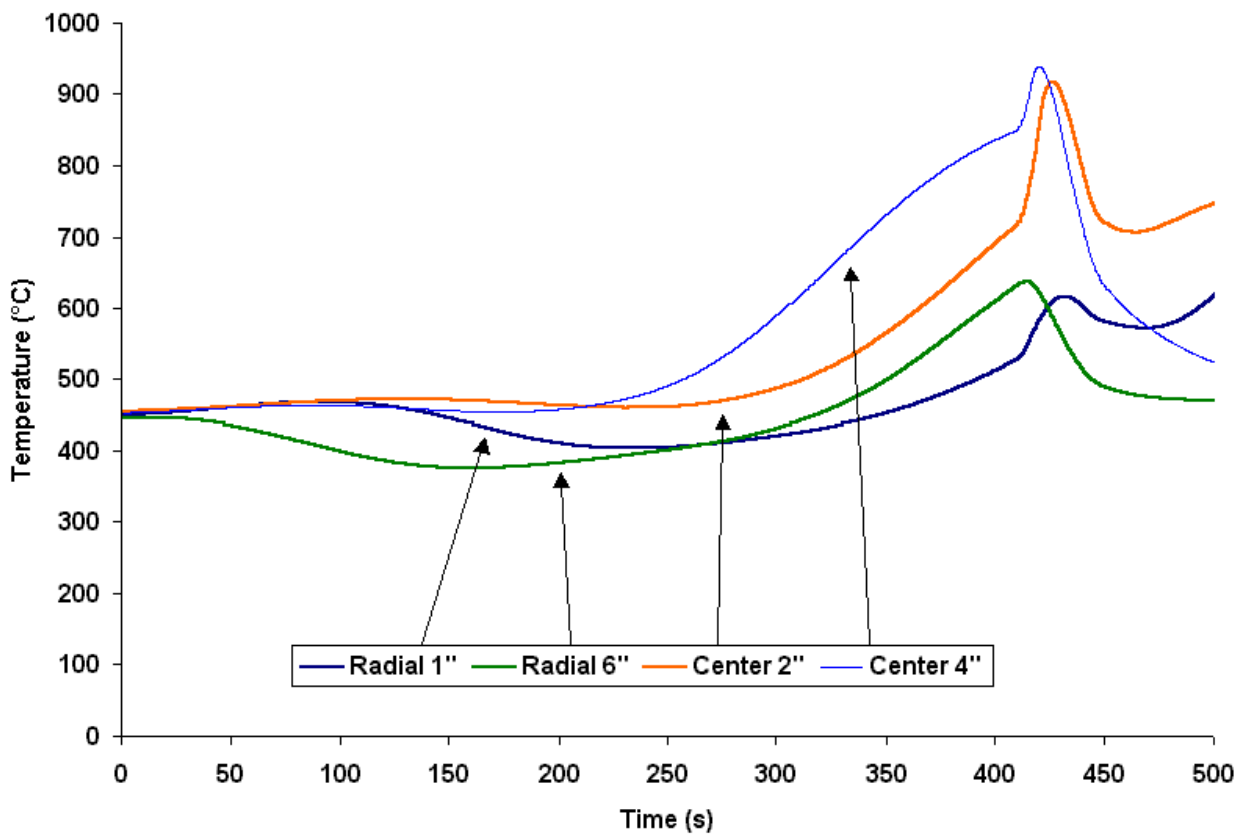


Figure 11. CDPF temperature profile after 105 heating cycles.

was used as a measure of exotherm intensity on the substrates.

Exotherms created using the initial technique occurred directly on the surface of the NO_x adsorber. The resulting TCR was too extreme and was damaging to the adsorbers washcoat. Using the refined technique, exotherms occurred on the CDPF and heat was convectively transferred to the adsorber. This resulted in a decrease in the adsorber TCR and lead to an increase in adsorber durability, minimizing thermal degradation.

The dual-pathway arrangement allowed independent control of the exhaust flow and lambda, which we have shown to be the key parameters controlling the heat released by the oxidation of diesel fuel on the surface of the CDPF. The tests have shown that desulfation temperatures can be repeatably reached using this controlled oxidation.

Sulfur was released in these tests as H₂S. Since the system has a cleanup DOC operating continuously in a lean oxidizing environment, the H₂S should be oxidized to SO₂. This remains to be verified. Dual sampling of the H₂S has revealed a net sulfur release on the front and rear adsorbers rather than a simple transfer of sulfur from the front adsorber to the rear.

Analysis of the CDPF temperature profiles after numerous heating cycles using the refined heating technique determined that degradation of the CDPF oxidation function had occurred. The CDPF used for this testing was not intended for use by the manufacturer in applications over 700°C. Platinum washcoats, which have been used for decades, can address temperatures greater than 850°C. With this in mind, it is the authors belief that reductant oxidation over the CDPF with convective heat transfer to the NO_x adsorber is a promising method for desulfation.

The next stage of this testing will investigate the impact of exhaust flow, lambda, and temperature on the desulfation process as well as evaluating a more robust CDPF formulation. Since tracking the sulfur content of the adsorbers on an engine is difficult, other measures will be investigated to indicate the relative impact of these parameters. The proposed measures are the time to start and end of sulfur release and the temperatures at these times. Data presented herein suggests that these measures remain consistent with repeated desulfations regardless of the quantity of sulfur stored on the adsorbers.

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